COMPREHENSIVE COORDINATION CHEMISTRY

The Synthesis, Reactions, Properties & Applications of Coordination Compounds

Editor-in-Chief: Sir Geoffrey Wilkinson, FRS

Executive Editors: Robert D. Gillard & Jon A. McCleverty



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COMPREHENSIVE COORDINATION CHEMISTRY

The Synthesis, Reactions, Properties & Applications of Coordination Compounds

Volume 4

Middle Transition Elements

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Preface

Since the appearance of water on the Earth, aqua complex ions of metals must have existed. The subsequent appearance of life depended on, and may even have resulted from, interaction of metal ions with organic molecules. Attempts to use consciously and to understand the metal-binding properties of what are now recognized as electron-donating molecules or anions (ligands) date from the development of analytical procedures for metals by Berzelius and his contempories. Typically, by 1897, Ostwald could point out, in his 'Scientific Foundations of Analytical Chemistry', the high stability of cyanomercurate(II) species and that 'notwithstanding the extremely poisonous character of its constituents, it exerts no appreciable poison effect'. By the late 19th century there were numerous examples of the complexing of metal ions, and the synthesis of the great variety of metal complexes that could be isolated and crystallized was being rapidly developed by chemists such as S. M. Jørgensen in Copenhagen. Attempts to understand the 'residual affinity' of metal ions for other molecules and anions culminated in the theories of Alfred Werner, although it is salutary to remember that his views were by no means universally accepted until the mid 1920s. The progress in studies of metal complex chemistry was rapid, perhaps partly because of the utility and economic importance of metal chemistry, but also because of the intrinsic interest of many of the compounds and the intellectual challenge of the structural problems to be solved.

If we define a coordination compound as the product of association of a Brönsted base with a Lewis acid, then there is an infinite variety of complexing systems. In this treatise we have made an arbitrary distinction between coordination compounds and organometallic compounds that have metal–carbon bonds. This division roughly corresponds to the distinction — which most but not all chemists would acknowledge as a real one — between the cobalt(III) ions $[Co(NH_3)_6]^{3+}$ and $[Co(\eta^5\text{-}C_5H_5)_2]^+$. Any species where the number of metal–carbon bonds is at least half the coordination number of the metal is deemed to be 'organometallic' and is outside the scope of our coverage; such compounds have been treated in detail in the companion work, 'Comprehensive Organometallic Chemistry'. It is a measure of the arbitrariness and overlap between the two areas that several chapters in the present work are by authors who also contributed to the organometallic volumes.

We have attempted to give a contemporary overview of the whole field which we hope will provide not only a convenient source of information but also ideas for further advances on the solid research base that has come from so much dedicated effort in laboratories all over the world.

The first volume describes general aspects of the field from history, through nomenclature, to a discussion of the current position of mechanistic and related studies. The binding of ligands according to donor atoms is then considered (Volume 2) and the coordination chemistry of the elements is treated (Volumes 3, 4 and 5) in the common order based on the Periodic Table. The sequence of treatment of complexes of particular ligands for each metal follows the order given in the discussion of parent ligands. Volume 6 considers the applications and importance of coordination chemistry in several areas (from industrial catalysis to photography, from geochemistry to medicine). Volume 7 contains cumulative indexes which will render the mass of information in these volumes even more accessible to users.

The chapters have been written by industrial and academic research workers from many countries, all actively engaged in the relevant areas, and we are exceedingly grateful for the arduous efforts that have made this treatise possible. They have our most sincere thanks and appreciation.

We wish to pay tribute to the memories of Professor Martin Nelson and Dr Tony Stephenson who died after completion of their manuscripts, and we wish to convey our deepest sympathies to their families. We are grateful to their collaborators for finalizing their contributions for publication.

Because of ill health and other factors beyond the editors' control, the manuscripts for the chapters on Phosphorus Ligands and Technetium were not available in time for publication. However, it is anticipated that the material for these chapters will appear in the journal *Polyhedron* in due course as Polyhedron Reports.

We should also like to acknowledge the way in which the staff at the publisher, particularly

Dr Colin Drayton and his dedicated editorial team, have supported the editors and authors in our endeavour to produce a work which correctly portrays the relevance and achievements of modern coordination chemistry.

We hope that users of these volumes will find them as full of novel information and as great a stimulus to new work as we believe them to be.

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Manganese

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41.1 INTRODUCTION

In preparing a review of the coordination chemistry complementary to that by Treichel[1] in the companion volumes on organometallic chemistry, we have been fortunate in the way in which manganese chemistry is so readily divided between the two. Probably as much as for any other metal, the organometallic chemistry of manganese, *i.e.* compounds with Mn—C bonds, is the chemistry of the lower oxidation states (I, 0 and −I); and the chemistry of manganese(II) and the higher oxidation states (III to VII) is that of classical coordination chemistry with the donor atoms nitrogen, oxygen and the halogens. Compounds with other Group V and Group VI donors have been prepared, but their known chemistry is not yet extensive. There are, of course, overlaps between the two areas, and the elegant work by Wilkinson and co-workers on the manganese(II), (III) and (IV) alkyls immediately comes to mind (see Section 41.3.2.2); similarly, many of the classical ligands of coordination chemistry, such as heterocyclic nitrogen ligands, and the phosphines and arsines, are widely used in organometallic chemistry. But this division into lower oxidation state/organometallic and higher oxidation state/coordination chemistry is as neat a division as one could hope for in chemistry.

Manganese has been a metal much neglected by the coordination chemist. Interest has recently been aroused, however, by the recognition of its biological role, especially in photosynthesis.[2]

This neglect is reflected in the treatment manganese has received, for example, in the Chemical Society's 'Annual Reports', and it is only within the last decade that significant volumes on the chemistry of manganese have appeared within the Gmelin system.[3] We often searched reviews on the chemistry of particular ligand systems in vain, or for just one or two references to manganese. In this regard it is pleasing to see the new series of annual reviews of the particular metals in *Coordination Chemistry Reviews*, which give adequate coverage to manganese.[4–6]

Available reviews are, of course, of diverse quality: they range from good comprehensive, critical reviews to simple compilations of published material, some of which do not even have the virtue of being comprehensive. But, since none of the recent reviews covers large areas, we note them in the sections for the various ligands.

Reasons for the neglect of manganese coordination chemistry undoubtedly relate to the dominance of the Mn^{II} state, its half-filled d^5 configuration, and all that follows from this, especially the lack of any reliable guide to the structure of the coordination polyhedron from anything other than X-ray methods. The great majority of Mn^{II} compounds are high spin, and, in the ^6S ground state, *d–d* transitions are forbidden by both the LaPorte and the spin state selection rules. Thus the *d–d* electronic spectra are of very low intensity and are of little use in determining metal stereochemistry; the compounds are colourless or very pale coloured. Thus in the period when transition metal coordination chemists believed in the *d–d* spectra as a reliable guide to structure, manganese could elicit but little interest.

Manganese(II) compounds are quite labile; the metal shows distinct class (a) character;[7] and its 'ionic radius' (defined by the M—H_2O distances in Table 1) is large compared with the other first row transition metals. These lead to distinct parallels with magnesium(II) rather than the latter, although there are also significant parallels with octahedral high spin nickel(II).

Many, but by no means all, manganese(II) compounds also are sensitive to oxidation by oxygen and their preparation is often complicated by the marked tendency for aqueous manganese solutions, under ambient conditions, to deposit the ubiquitous, highly insoluble manganese dioxide. Both add complications to manganese(II) chemistry and have undoubtedly made it less attractive to some workers. This sensitivity to oxygen and especially the products of the reactions are a major reason for the increasing interest in manganese chemistry. The last decade has seen significant developments: both manganese(III) and manganese(IV) have been properly characterized in a number of systems, and it appears that the +4 oxidation state is more accessible to manganese than, for example, iron. However, a great deal more needs to be done, and done properly, before we can pretend to have a reasonably balanced view of the relative accessibilities and stabilities of Mn^{III} and Mn^{IV}. Much has been, and is being, published on the reaction of manganese(II) species with O_2, the possibility of the existence of Mn—O_2 species and their structure and properties, and the nature of the final oxidized products. But there is very little light yet shed in this area.

The higher oxidation states V, VI and VII are all known, and are largely represented in the chemistry of the oxo ligand manganates. The highest oxidation state VII corresponds to the total number of 3*d* and 4*s* electrons—a feature of the earlier transition metals Sc to Cr. Manganese is, except for a few unstable oxoferrates, the last of this series, and although potassium permanganate is one of the best known manganese compounds, and is widely used, yet the chemistry of manganese and oxo ligands is by no means as extensive as that of chromium and vanadium.

In other aspects, especially in the dominance of the +2 oxidation state, manganese shows parallels with the later transition metals. It is the first transition metal for which +2 is the common oxidation state.

Table 1 M^{II}—OH_2 Bond Distances in the Hexaaquo Cations

Metal:	*Mg*	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Zn*	*Cd*
M—OH_2 (Å)	[a] 2.09	2.19	2.17	2.11	2.09	2.22	2.13	2.30
	2.10	2.20	2.14	2.09	2.08	2.10	2.12	2.30
	2.05	2.15	2.10	2.08	2.04	1.96	2.08	2.24
	[b]	2.20	2.12	2.08	2.04	2.43	2.08	2.29
						1.94		

[a] In the Tutton salts there are three independent pairs of *trans* ligands: H. Montgomery, R. V. Chastain and E. C. Lingafelter, *Acta Crystallogr.*, 1966, **20**, 731; C. S. G. Phillips and R. J. P. Williams, 'Inorganic Chemistry', Oxford, 1966, vol. 2, p. 249.
[b] Aqueous solutions (X-ray data): H. Ohtaki, *Rev. Inorg. Chem.*, 1982, **4**, 103.

Thus, in its broad features, manganese chemistry reflects its position in the middle of the transition series.

As any scientific classification creates problems of definition, so our present classification based on oxidation state leads to difficulty in the placing of material. This is particularly, but not exclusively, true of *nitrosyls*.

It is common to classify M—NO moieties into compounds of: (a) the monoanion NO^-, characterized by lower energy NO stretching frequencies and a bent ($\sim 120°$) M—N—O bond; and (b) the nitronium cation NO^+, characterized by higher energy NO stretching frequencies and a short, linear M—N—O bond. Thus, for example, the compound $[Mn(NO)_3PPh_3]$, with three linear M—NO bonds, becomes a compound of Mn^{-III} and this we believe to be a chemical nonsense or at best a useless formalism. Further, we note also that a recent X-ray structural determination[8] of a compound of type (b) above shows significant bending in the M—N—O bond, and the authors suggest that such bonding may be more widespread in type (b) compounds.

Accordingly, we adopt the convention, in agreement with IUPAC nomenclature recommendations, that NO be regarded as a neutral ligand, and deal with the above trinitrosyl as a compound of manganese(0). This also means, for example, that the anions $[Mn(CN)_5NO]^{n-}$ ($n = 2, 3$) become here compounds of manganese(III) and (II), although they are often classified elsewhere under manganese(II) and (I), respectively.

The nature of the data: Since we have attempted to be critical in our assessment of the published data, it is as well that we note the bases used for much of this critical assessment.

Mixing any ligand (L), especially ligands containing one (or many) nitrogen or oxygen donor atom(s), with MnX_2 (X = a monoanion) in a suitable solvent system will lead to the separation of crystalline species (or a number of them) MnX_2L_n; deprotonation of the ligand, if possible, may give further compounds. Such information is, of itself, often of little interest, even though the products be 'new' compounds. Yet this is often the only established, meaningful fact in what may be quite long papers.

Sadly, many papers are published in which not even such a simple basic fact has been established. Despite published (in 1978) analytical figures, we find it hard to believe that a black residue, obtained by heating manganese(II) with an oxygen donor ligand in an aqueous alkaline solution in open vessels, is a manganese(II) compound; we think it more likely to have been MnO_2, perhaps admixed with some carbonaceous material. Powders, even of the expected colour, are suspect unless X-ray diffraction shows them to be a discrete crystalline species, or recrysallization can be achieved to give a product with say an IR spectrum identical with the original. Ideally all solids should generally be characterized by their X-ray diffraction patterns and IR spectra.

But having characterized a crystalline product, what then? What are the authors trying to achieve beyond preparing a new compound? If it is to show what compounds can form, then many papers fail to explore a proper range of reaction conditions; if it is to show how the ligand is bound to the metal, then there is currently but one reliable physical method for this job—X-ray diffraction. Sometimes this may simply mean demonstrating isomorphism with the compound of another metal of known structure (especially if supplemented with IR data). But practice shows that such isomorphism often does not happen, and then full X-ray analyses are the only reliable answer. It may be fun—perhaps quite absorbing fun—to play with the so-called 'sporting methods', such as vibrational spectra, electronic spectra and magnetism. But, especially in manganese chemistry where electronic spectra are of but little use for indicating structure, we have taken little note of structural assignments based on these 'sporting methods', although we may have noticed the work for other reasons, such as an intrinsic interest in the reported compounds.

Whilst *electronic spectra* do not have the structural use they have (with discretion) with nickel(II), it is at least possible to make some useful deduction from the colour of the products. We can, for example, conclude with some confidence that a black substance described as a manganese(II) compound with oxygen donors was not; that a white substance described as Mn^{IV} or Mn^{V} was not; and that a green compound, having the same intense colour as some related Mn^{III} species, was probably not manganese(II), despite the apparent stoichiometry (Section 41.3.3.2). Yet each of these has appeared in the recent literature.

It is arguable that the study of *magnetic moments* of coordination compounds has been as much a hindrance to the elucidation of stereochemistry as it has been of use. The earlier confidence that it would be possible to correlate 'stereochemistry of an atom with its effective magnetic moment'[9] has not been confirmed, although some impressive work has come out of magnetic studies. What is not arguable is that the chemistry of manganese would be no less further advanced if no paper had been wasted on arguments about structure of solid polymeric materials from magnetic moments.

Manganese with its great variety of oxidation states, each with varying numbers of unpaired 3*d* electrons, is magnetically interesting but not simple. The theoretical 'spin only' magnetic moments for oxidation states* +2, +3 and +4 are in Table 2, and for comparison some experimentally determined moments of some representative compounds are in Table 3.

Monomeric species, with no exchange interaction between adjacent metal atoms, typically exhibit moments close to the 'spin only' values. Most known compounds of manganese(II) and (III) are high spin, with the cyano compounds best known among the few low spin species. But these moments give no information about stereochemistry of the metal atom, and their purpose can be only to give information about the spin state and perhaps to help to confirm oxidation state.

In practice, measured moments range between 0 and 6.5 BM, and those differing significantly from 'spin only' values often are called 'anomalous', in the sense of a deviation from a norm. Such nomenclature, however, is probably in all cases fatuous—the deviation from the norm often itself being the norm.

Table 2 Theoretical Magnetic Moments (in BM) for Mn^{II}, Mn^{III} and Mn^{IV} Compounds (Based on 'Spin Only' Formula)

Oxidation State	*Spin State*			
	Spin Free	*Intermediate Spin*	*Spin Paired*	
			Oh Field	*Td Field*
Mn^{II}	5.92	3.87	1.73	1.73
Mn^{III}	4.90	—	2.83	0
Mn^{IV}	3.87	—	3.87*	1.73

* In an *Oh* field spin pairing will not occur.

Table 3 Experimental Room Temperature Magnetic Moments (in BM) of some Mn^{II}, Mn^{III} and Mn^{IV} Compounds

(a) Magnetically Dilute Species[a]

Oxidation State	*Compound*	*Spin State*	*Stereochemistry*	μ_{eff}
Mn^{II}	$[Mn(py)_6]Br_2$	Spin free	Oh	6.00
Mn^{II}	$(pyH)_2[MnCl_4]$	Spin free	Td	5.95
Mn^{II}	$K_4[Mn(CN)_6]$	Spin paired	Oh	1.80
Mn^{III}	$[Mn(acac)_3]$	Spin free	Oh	4.95
Mn^{III}	$K_3[Mn(CN)_6]$	Spin paired	Oh	3.18
Mn^{IV}	$K_2[MnF_6]$	Spin free	Oh	3.90
Mn^{IV}	$K_2[Mn(CN)_6]$	Spin free	Oh	3.94

(b) Magnetically Interactive Species

Oxidation State	*Compound*	*Stereochemistry*	μ_{eff}	*Ref.*
Mn^{II}	[Mn(salen)]	Five-coord. Dimeric?	5.24	[b]
Mn^{II}	[Mn(pc)]	Square planar	4.34	[c]
Mn^{III}	$[Mn_3O(OAc)_6(py)_3]py$	Trimeric	3.98	[d]
Mn^{III}	[(py)(pc)MnOMn(pc)(py)]	Octahedral O-bridged	2.07	[e]
Mn^{III}	[Mn(salen)(OAc)]	?	4.68	[f]
Mn^{IV}	[MnO(pc)]	?	3.75	[g]

Ligand abbreviations: acac = acetylacetone; OAc = acetate; pc = phthalocyanine; py = pyridine; salen = *N*,*N*′-ethylenebis(salicylaldimine)

References:

[a] B. N. Figgis and J. Lewis in 'Modern Coordination Chemistry', ed. J. Lewis and R. C. Wilkins, Interscience, New York, 1960, p. 406–7.
[b] C. J. Boreham and B. Chiswell, *Inorg. Chim. Acta*, 1977, **24**, 77.
[c] C. G. Barraclough, R. L. Martin and S. Mitra, *J. Chem. Phys.*, 1970, **53**, 1638.
[d] A. R. E. Baikie, M. B. Hursthouse, D. B. New and P. Thornton, *J. Chem. Soc., Chem. Commun.*, 1978, 62.
[e] A. Yamamoto, L. K. Phillips and M. Calvin, *Inorg. Chem.*, 1968, **7**, 847.
[f] A. Earnshaw, E. A. King and L. F. Larkworthy, *J. Chem. Soc.(A)*, 1968, 1048.
[g] A. B. P. Lever, *J. Chem Soc.*, 1965, 1821.

* States lower than Mn^{II} are usually stabilized by strong field ligands giving rise to spin-paired systems; whereas the magnetic properties of Mn^{V}, Mn^{VI} and Mn^{VII} have not been widely studied.

Where magnetic moments are lower than the 'spin only' values, and full experimental evidence of antiferromagnetism is obtained, the results are often interpreted in terms of structures for which the best basis appears to be nothing more than the author's previous experience. The only proper procedure is to interpret the magnetic data *after* the structure is known and not *vice versa.*

The use of magnetic data as primary evidence for any structure is precluded by the variety of structural types—oligomeric and dimeric—which are known to give antiferromagnetism. In addition, manganese compounds exhibiting antiferromagnetism are now known to have metal atoms in different oxidation states and there is the further possibility of different spin states.

Yet another complication of which not sufficient heed is often taken is the presence of the ubiquitous, insoluble and paramagnetic MnO_2. It must be suspected as a by-product of the preparation of almost any compound of oxidation state greater than + 1, and so many products that are reported as dark powders, or even grey powders, probably possess appreciable amounts of MnO_2, thus invalidating the reported magnetic data, and possibly even the reported stoichiometry.

Although *nuclear magnetic resonance* studies have been of great use in elucidating the structures in solutions of the compounds of many of the metals, the paramagnetic nature of many manganese compounds, and in particular high spin Mn^{II}, has limited the applicability of this technique. Nevertheless, the very difficulty associated with obtaining Mn^{II} NMR spectra has been turned to advantage by using Mn^{II} as a magnetic relaxation probe in the study of biomechanisms and biomacromolecules.[10]

Although a drawback to NMR studies, the five unpaired electrons of high spin Mn^{II} compounds give rise to excellent *electron spin resonance* spectra. An early review[11] noted the effect upon ESR spectra of changing ligands about the Mn^{II} ion while retaining high symmetry, whereas a recent review summarizes the work that has been done upon compounds with a low-symmetry environment about the metal.[12] ESR studies have been applied in a most interesting manner to ligand speciation studies of manganese in aqueous environmental samples.[13] Although also paramagnetic, high spin d^4 Mn^{III} compounds appear to have short spin–lattice relaxation times and generally do not give good ESR spectra. Little work has been undertaken on the ESR of the higher oxidation states of manganese, although Mn^{IV} compounds are known to yield spectra.[11]

There is another basic lesson which many authors publishing in this area of chemistry have failed to heed; when labile compounds are dissolved in any solvent, information about the properties of the solution (*e.g.* a conductance measurement) gives no direct information about the solid compound. For some metal compounds, it may be possible to show (*e.g.* from electronic spectra) that the coordination sphere remains unchanged from the crystalline solid to the solution, but this appears not to be possible for manganese.

For these sorts of reasons we have found it necessary to neglect a significant portion of the published work, especially on ligand systems that offer the metal a choice of donor atoms.

The story of the coordination chemistry of manganese is very incomplete; it is only at an early stage of development compared with most of the other transition metals; and there is an obvious need for X-ray structural techniques to be used much more routinely in those studies of manganese chemistry that rely on the isolation and characterization of solid compounds for their purpose.

Finally a general point—we do not usually distinguish between 'binary compounds', 'salts' and 'complexes'. All give interesting examples of metal coordination polyhedra and the terms are arbitrary distinctions, derived from the history of chemistry as our understanding has developed. They have little meaning now beyond their use as jargon words by inorganic chemists. Whilst we (meaning coordination chemists) all understand what they mean and how to use them, they impose a barrier to communication with non-specialists and inhibit the learning process. Unfortunately, also, they are tendentious words, leading almost inevitably to the belief that the 'simple' chemistry of a metal ion can be understood by a study of only the binary compounds and salts, and that a study of the 'complexes' is a higher-order, more esoteric branch of knowledge. For these reasons, we have attempted to show in much of the following how the coordination chemistry of one metal can be described without the use of the tendentious word 'complex'.

41.2 MANGANESE(I) AND LOWER OXIDATION STATES

41.2.1 Introduction

This area of coordination chemistry gives the greatest overlap with the area generally classified as organometallic chemistry and reviewed by Treichel in the companion volume.

We attempt in Table 4 to give an overview of the range of oxidation states covered by the organometallic chemistry of manganese, and thus the bulk of the lower oxidation state chemistry

Table 4 The Oxidation States of the Organometallic Chemistry of Manganese

Oxidation State	*Examples*
Mn^{-I}	$Na[Mn(CO)_5]$
Mn^{0}	$[Mn_2(CO)_{10}]$, $[Mn_2(CO)_{10-n}L_n]$
Mn^{I}	$[Mn(CO)_5X]$, $[Mn_2(CO)_8X_2]$, $[Mn(CO)_{6-n}L_n]^+$, $[Mn(\eta\text{-}C_5Me_5)_2]^-$, $[Mn(\eta\text{-}C_5H_5)(\eta\text{-arene})]$, $[Mn(\eta\text{-arene})_2]^+$, $[Mn(\eta\text{-}C_5H_5)(CO)_3]$, $[Mn(CNR)_6]^+$
Mn^{II}	$(MnR_2)_n$, $[Mn(\eta\text{-}C_5R_5)_2]$, $[Mn(CNR)_6]^{2+}$
Mn^{III}	$[Mn(\eta\text{-}C_5Me_5)_2]^+$
Mn^{IV}	$[MnR_4P_2]$

See also the borane and carborane-manganese carbonyl compounds: R. N. Grimes, in 'Comprehensive Organometallic Chemistry', ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 1, p. 459.

of manganese. It is important to note, however, that in this area the oxidation state formalism is probably less clear cut and less useful than elsewhere.

Apart from the organometallic chemistry, there is but little manganese chemistry left for us to review and most of this is of the cyanides and nitrosyls, most of which could have reasonably been embraced within organometallic. Previous assignments of lower metal oxidation states to species such as [Mn(phthalocyanine)]$^-$ and [Mn(bipy)$_3$]^0 now are known to be incorrect and these species are treated under manganese(II). Furthermore, present indications are that [$Mn^{II}N_4$] macrocyclic systems, in general, cannot be reduced to Mn^I species, unlike those of the later transition metals, especially cobalt, nickel and copper. Although reduced species can and have been obtained, these, when properly studied, turn out to be not Mn^I or Mn^0 species, but rather Mn^{II} species of radical anion ligands (see Section 41.3.10).

As discussed previously, nitrosyls are classified according to oxidation state on the convention that NO is a neutral ligand.

41.2.2 Manganese(−I)

The only compound to be noted here is the recently described[14] cyano nitrosyl $K_3[Mn(CN)_2(NO)_2]$. This green compound has been made by the reduction of the dimeric species $K_4[Mn_2(CN)_4(NO)_4]$ with potassium in liquid ammonia. The IR spectrum suggests a tetrahedral structure similar to the isoelectronic $[Fe(CN)_2(NO)_2]^{2-}$.

41.2.3 Manganese(0)

The interpretation[15] of the observed paramagnetism of some yellow products of the reduction of $[Mn(CN)_6]^{4-}$ with K in liquid NH_3 as evidence for Mn^0 species is by no means unequivocal.

The only other Mn^0 species which come within our sphere of interest are nitrosyls, primarily derived from the carbonyl nitrosyls of Table 5. Of these, the two Mn^0 species have already been reviewed by Treichel,[1], as have the various series of currently known compounds of which these are respectively, the parents: series such as $[MnL(NO)_3]$, $[Mn(CO)_3L(NO)]$ and $[Mn(CO)_2L_2NO]$ *etc.*

Attempts[14] to prepare monocyano derivatives of $[Mn(CO)_4NO]$ and $[Mn(CO)(NO)_3]$ by treating with KCN in liquid NH_3 gave instead; for the former $K_2[Mn(CN)_3(CO)_3]$ and $K_3[Mn(CN)_4(CO)_2]$, and for the latter $K_4[Mn_2(CN)_4(NO)_4]$.

$K_4[Mn_2(CN)_4(NO)_4]$ has been isolated in *cis* and *trans* forms.[14] Evidence for a dimeric structure with Mn—Mn bonds derives from the diamagnetism of the compounds, the IR spectra and *cis–trans* conversions. Yellow crystals of the *cis* are obtained from the reaction in liquid

Table 5 The Primary Carbonyl Nitrosyls of Manganese

Compound	*Isoelectronic Series*	*Ref.*
$[Mn(CO)_4(NO)]$	$[Fe(CO)_5]$	1
$K[Mn(CO)_2(NO)_2]$	$[Fe(CO)_3NO]^-$, $[Co(CO)_4]^-$	a
$[Mn(CO)(NO)_3]$	$[Cr(NO)_4]$, $[Fe(CO)_2(NO)_2]$, $[Co(CO)_3(NO)]$, $[Ni(CO)_4]$	1

[a] R. E. Stevens, T. J. Yanta and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1981, **103**, 4981.

NH_3 {ν_{NO} = 1664 and 1737 cm^{-1} (solid), and 1680, 1685 and 1731, 1734.5 cm^{-1} (ethanol solution)} and these can be converted to bluish needles of the *trans* by heating in ethanol in a sealed tube at 100 °C for several days {ν_{NO} = 1709, 1750 cm^{-1}}.

More recently Behrens and co-workers[16] were able to prepare the series of monocyano nitrosyl carbonyls by reactions such as equation (1). The Mn^0 compounds obtained in this work are listed in Table 6. $Na[Mn(CN)(CO)_3(NO)]$ dissolves readily in polar solvents such as water, ethanol, acetone or THF, but the solutions, even in the absence of light and air, are unstable. Crystalline salts, which are air stable, were obtained by adding such a solution to an excess of the appropriate cation. The related isonitrile species were prepared by alkylation of the cyano anions with R_3O^+.

$$[Mn(CO)(NO)_3] + NaN(SiMe_3)_2 \xrightarrow[20°C]{C_6H_6} Na[Mn(CN)(NO)_3] + O(SiMe_3)_2 \quad (1)$$

The compound $K_4[Mn(CN)_4NO]$ has recently been prepared[17] as a dark green, highly pyrophoric solid by the reduction of $K_3[Mn(CN)_5NO]$ with K in liquid NH_3. {ν_{NO} = 1370 cm^{-1}, *cf.* ν_{NO} for $K_3[Mn(CN)_5NO]$ = 1730 cm^{-1}}.

41.2.4 Manganese(I)

The white hexacyanomanganese(I) cation was first recognized by Manchot and Gall,[18] although a white crystalline solid, previously reported by Grube and Brause,[19], was undoubtedly the potassium salt. Manchot and Gall then reported[20] both the potassium and sodium salts, obtained by reduction of the appropriate Mn^{II} species in aqueous alkaline solution with Al powder, but a variety of other preparative methods now are available.[21,22]

Both $Na_5[Mn(CN)_6]$ and $K_5[Mn(CN)_6]$ are robust in dry air, but are soon oxidized in moist air, the more soluble Na^+ salt decomposing at the faster rate. They are also decomposed in a dry CO_2 atmosphere.

Aqueous solutions are yellow and are strongly reducing: the potential for the reaction $Mn^I \rightarrow Mn^{II} + e^-$ in aqueous 1.5 M NaOH is −1.06 V at 25 °C.

The Mn^I species are reoxidized by water at an appreciable rate, so that all studies of $[Mn(CN)_6]^{5-}$ in aqueous solutions (containing excess CN^-) refer to solutions also containing Mn^{II} species.

It has been shown polarographically[23] that the process $[Mn(CN)_6]^{5-} \rightleftarrows [Mn(CN)_6]^{4-}$ is reversible, and there is no evidence for disproportionation to Mn^{II} and Mn^0.

Decomposition of the yellow solutions in aqueous CN^- has been followed by monitoring[23] the fading of the intense single broad band at 365 nm. The data were interpreted as evidence for $[Mn(CN)_5OH]^{5-}$ and $[Mn_2(CN)_{10}O]^{10-}$ in these aqueous solutions, and the involvement of these species in the oxidation of Mn^I to Mn^{II}.

Closely related to the hexacyano species are the various isonitrile cations $[Mn(CNR)_6]^+$ and $[Mn(CNAr)_6]^+$, but these are covered in Treichel's review.[1]

Two manganese(I) cyanocarbonyls are known. *cis*-$K_3[Mn(CN)_4(CO)_2]$ has been prepared[14] from $Mn_2(CO)_{10}$ or $[Mn(CO)_4NO]$ with KCN in liquid NH_3. The *cis* configuration was assigned to the colourless crystalline compound on the basis of the IR spectrum. *fac*-$K_2[Mn(CN)_3(CO)_3]$ is also a product of the reaction of KCN in liquid NH_3 on $[Mn(CO)_4NO]$, but is best prepared from $[Mn(CO)_5Cl]$ and an ethanol solution of KCN at 120 °C under pressure. Again the isomeric structure is assigned[14] from the IR spectra.

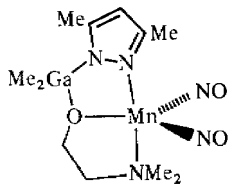
A range of dinitrosyl compounds of manganese(I) is known and most of them have been included in Treichel's review.[1] An interesting recent addition to the list is the compound (1), prepared[24] from

Table 6 Monocyano Nitrosyls[16]

Compound	*Physical form*	ν_{NO} (cm^{-1}) *(KBr disc)*
$Na[Mn(CN)(CO)_3NO]$	Red-brown, amorphous solid	1665
$[Ph_4As][Mn(CN)(CO)_3NO]$	Red needles	1687
[PPN][$Mn(CN)(CO)_3NO$][a]	Red needles	1675
$[Mn(CNMe)(CO)_3NO]$	Red, microcrystalline	1720
$[Mn(CNEt)(CO)_3NO]$	Red oil	1720
$Na[Mn(CN)(NO)_3]$	Grey-green, amorphous solid	1773, 1660
$[Mn(CNMe)(NO)_3]$	Green oil	1795, 1692
$[Mn(CNEt)(NO)_3]$	Green oil	1790, 1682

[a] PPN = bis(triphenylphosphine)immonium.

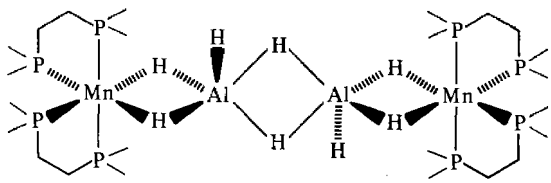
$[MnBr(NO)_2\{P(OMe)_3\}_2]$, $AgPF_6$ and Na^+L^- in THF. The dark red crystals had $\nu_{NO} = 1709$, 1643 cm^{-1} (cyclohexane).



(1)

Another class of compounds which formally comes within the guidelines for this review is the series of dicarbonyl cations $[Mn(CO)_2L_4]^+$, $[Mn(CO)_2L_2(L—L)]^+$ and $[Mn(CO)_2(L—L)_2]^+$ —both *cis* and *trans* isomers. But, since these have been reviewed by Treichel,[1] as have the monocarbonyl compounds, we simply note that several recent papers add significantly to the list of known compounds.[25–27]

An interesting new area of manganese(I) chemistry is opened up by the recent report[28] of the first transition metal compound of the tetrahydroalane(III) anion: $[Mn(AlH_4)(dmpe)_2]$ {where dmpe = 1,2-bis(dimethylphosphino)ethane}. This yellow, diamagnetic compound was prepared from $[MnBr_2(dmpe)_2]$ and excess $LiAlH_4$ in toluene. It appears to be monomeric in solution, with a bidentate AlH_4^- moiety, but an X-ray structure determination of the solid shows that two alane moieties bridge to form the dimer (**2**).



(2)

41.3 MANGANESE(II)

41.3.1 Introduction

This is the dominant oxidation state of manganese. It is the stable oxidation state of hexaaquomanganese, and of almost all of the manganese 'salts' that one finds in reagent bottles in the laboratory. Although many, but not all, manganese(II) species can be oxidized readily, and the chemistry of manganese(III) and manganese(IV) is receiving increasing attention, these oxidized species find use as oxidizing agents. On the other hand, reduction to manganese(I) is unusual, except for carbon ligands, and is apparently impossible for species with exclusively O,N or halogen donors, as evidenced by the scarcity of material in Section 41.2.

Manganese is the first transition metal for which +2 is the 'common' oxidation state—a feature of the remaining first row transition metals from iron to zinc. By comparison with its two neighbours to left and right—chromium and iron—manganese(II) is more stable than expected. This is commonly ascribed to the stable half-filled *d* electron shell of the high spin compounds.

The oxidation state diagrams in Figure 1 give a perspective on the relative stability of manganese(II) for OH_2, OH^- and O^{2-} ligands.

In many of its features, the chemistry of manganese(II) spans that of the alkaline earth metals {especially magnesium(II)} and that of the later first row transition metals. There are also parallels with cadmium(II) rather than zinc(II). These are all related to the more significantly ionic bonding for manganese and to the size of the metal 'ion'.

Manganese(II) is quite distinctly a *class (a) metal*.[7] This is manifest, for example, in the preference for O donor rather than N donor ligands, so that amino acid compounds become simply those of substituted carboxylates, and there is currently little evidence for the N bonding of peptides that leads to the interesting chemistry of the peptide compounds of the later transition metals. Of P and As ligands but little is known, although recent work suggests the possibility that this may become

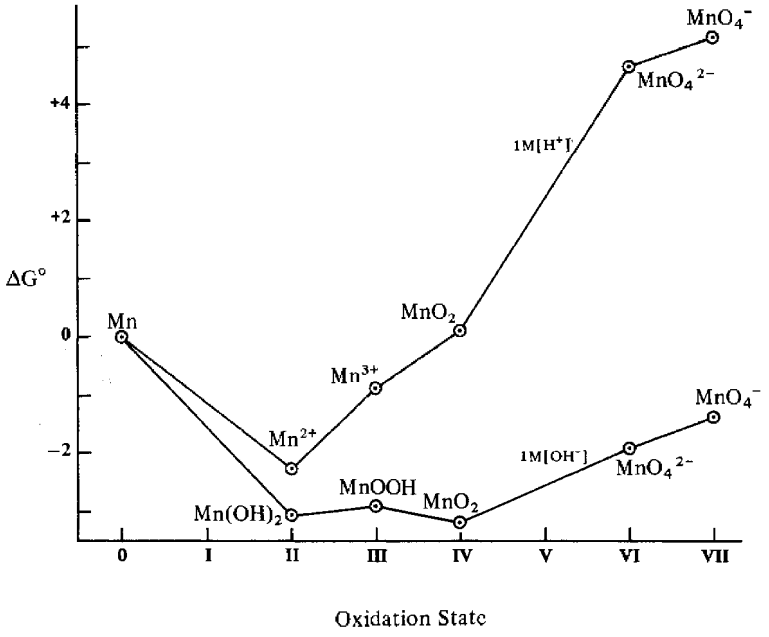


Figure 1 Oxidation state diagrams for manganese

one of the more important areas of Mn^{II} chemistry (see Section 41.3.4). Of S ligands, as well, there is yet little known (Section 41.3.6), although this does give an impression of difficulty in obtaining pure compounds because of lability and low stability. The state of manganese–sulfur chemistry is summed up in the statement that one recent paper adds enormously to this area.

The marked lability of manganese(II) species is undoubtedly one of the reasons for the neglect of manganese chemistry. This lability, often coupled with low stability of species (see Irving–Williams Series)[29] ensures that there is little correlation between solutions and solids, and adds an uncertainty to this area of chemistry that is largely absent from the chemistry of inert compounds.

The *spin state* of most manganese(II) compounds is high spin d^5 with a ^6S ground state—the few known exceptions are noted in the text (see also Table 7).

The *coordination geometries* are quite variable; and, in keeping with the lack of LFSE for the high spin d^5 configuration, ligand steric and electronic effects appear to play a major role in defining these geometries. We have already noted (Table 1) that manganese(II) is larger (whether defined by ionic or covalent radii, or more simply by comparative metal–ligand distances, as in Table 1) than other

Table 7 Coordination Polyhedra and Spin States for Manganese(II)

Coordination Number	*Donor Atoms*
(a) High Spin Polyhedra (μ_{eff} = 5.8–6.2 BM; $S = \frac{5}{2}$)	
8[a]	$[O_8][N_8][N_4O_4]$
7[a]	$[N_7][N_5O_2][N_2O_5]$
6 (Octahedral)	$[N_6][N_xO_{6-x}][O_6][P_4Cl_2][P_4Br_2][P_2I_4]$ $[S_6][S_4N_2][S_4Cl_2][F_6][Cl_6][Br_6][I_6]$ $[X_xO_{6-x}][X_xN_{6-x}]$ and [X, O, N] (X = Cl, Br)
6 (Trigonal Prismatic)	$[O_6][N_6]$
5[a]	$[C_3N_2][N_5][N_2O_3][O_5]$ $[N_4X][N_3X_2][N_2X_3][N_2OX_2]$ (X = Cl, Br)
4 (Tetrahedral)	$[C_4][N_4][C_3N][C_2N_2][C_3P][C_2P_2][S_4]$ $[N_2O_2][O_4][X_4][X_3N]$ (X = Cl, Br, I)
4 (Planar)	$[N_4][O_4]$
3 (Planar)	$[C_3][N_3][N_2O][O_3][X_3]$ (X = Cl, Br)
2 (Linear)	$[X_2][H_2]$ (X = Cl, Br)
(b) Intermediate Spin Polyhedra ($\mu_{eff} \sim 4$ BM; $S = \frac{3}{2}$)	
4 (Planar)	$[N_4]$
(c) Low Spin Polyhedra (μ_{eff} = 1.8–2.2 BM; $S = \frac{1}{2}$)	
6 (Octahedral)	$[C_6][C_5N][C_2P_4][Cl_2P_4][N_3O_3]$[b]

[a] We do not distinguish the various ideal polyhedra. Constraints within the molecules usually ensure that some 'intermediate' shape is adopted.
[b] The tris(ethylnitrosolato)manganese(II) anion (P. Gouzerh, Y. Jeannin, C. Rocchiccioli-Deltcheff and F. Valentini, *J. Coord. Chem.*, 1979, **6**, 221) has been described as a low spin species; but the details given are unique in manganese chemistry, and need further confirmation.

first row (+2) transition metals, and, in some ways, more akin to what are regarded as ionic metals, such as magnesium, calcium and cadmium. There are also indications that Mn^{II} is more plastic than the later transition metals. (This view derives from presently available X-ray structural data, although more comparative data are needed for confirmation.) By more plastic we mean that metal–ligand bond distances appear to be quite variable, and change more in response to ligand steric effects. We associate this 'plasticity' with the greater ionic component in the bonds.

Coordination number six appears, from the limited available data, the most common (Table 7). Lower coordination numbers are known but appear to be fairly rare: three is represented by some silylamides (Section 41.3.3.1) and in a dehydrated zeolite (Section 41.3.5.2.i); four-planar is known only for macrocyclic $[N_4]$ systems and as $[MnO_4]$ in a few unusual crystalline compounds; and four-tetrahedral is well characterized but still apparently less common than for Zn, Co and possibly even Ni. Coordination number five is also known, but few examples are yet characterized. On the other hand, higher coordination numbers seven and eight are less unusual here — hardly surprising in view of the larger size of Mn^{II}. Examples include seven coordinate $[Mn(edta)H_2O]^-$ (Section 41.3.9), $[Mn(py_3tren)]^{2+}$ (Section 41.3.3.6) and an $[MnO_7]$ species (Section 41.3.5.3.iii), and eight coordinate $[Mn(O_4)_2]^{2+}$ species (Section 41.3.5.4).

As noted in Section 41.1, the *electronic spectra* of Mn^{II} compounds have not been particularly useful in the elucidation of structure. Although there is some justification for the claim[30] that tetrahedral compounds are yellow to yellow-green in colour and have molar extinction coefficients of up to 100 times more intense than those for the pale pink or colourless octahedral compounds, yet these distinctions are not, in may cases, clear cut enough to lead to unambiguous stereochemical assignments.

It is true that tetrahedral[31] $[MnCl_4]^{2-}$, $[MnBr_4]^{2-}$ and $[MnI_4]^{2-}$ all have pale yellow or yellow-green colours, as do the isothiocyanato[32] and isocyanato[33] $[MnX_4]^{2-}$ species. It also appears to be true that these anionic species have *d–d* solution spectra (molecular structures appear to be unchanged in the solvents used, including CH_3CN) with molar extinction coefficients of the order of 1 to 15 — values which are indeed some 100 times more intense than those for the peaks in the spectrum[34] of the pale pink octahedral $[Mn(H_2O)_6]^{2+}$. Nevertheless, it does not follow that all pale yellow or green compounds of Mn^{II} are tetrahedral; the octahedral $[Mn(acac)_2(H_2O)_2]$ is yellow,[35] and the compounds $K_4[Mn(NCS)_6]\cdot 3H_2O$ and $Cs_4[Mn(NCS)_6]$ are described as red[36] and yellowish-green,[37] respectively. Furthermore [Mn(salen)] (salen = dianion of *N,N'*-bis(salicylaldehydo)ethylenediamine), which is yellow to orange (depending on crystal size),[38] is more likely to be planar than tetrahedral, although a five-coordinate dimer structure[39] is most likely for the solid; and in acetonitrile solution its *d–d* spectrum has molar extinction coefficients of between one and two.

Thus, whilst there may be some use for electronic spectra in confirming structure of Mn^{II} compounds,[40] it is not likely to be great. Many more spectra of known species will need to be accumulated for assessment, and a major difficulty with these labile systems will be to ensure that we know structure in solution first before we start trying to assign spectra.

41.3.2 Carbon Donor Ligands, Including Cyanides

41.3.2.1 Cyanides

Preparation of a pure binary cyanide $Mn(CN)_2$, which would of course involve bridging cyano groups in a polymeric structure, has not yet been achieved, nor has the preparation of any hydrates, but the crystalline solids $Mn(CN)_2\cdot L$ (L = DMSO, DMF and DMA) have been described recently.[41]

However, many mixed ligand species containing cyanide have been described, and the anionic hexacyano species $[Mn(CN)_6]^{4-}$ has been known[42] since at least 1869. It is a low spin species (Table 3); has been isolated in a range of salts $M^I_4[Mn(CN)_6]$ and $M^{II}_2[Mn(CN)_6]$ and their hydrates; yet it is not very robust in aqueous solution. As well as being subject to oxidation in the air, its aqueous solutions soon lose CN^-; unless such aqueous solutions contain an excess CN^- concentration of at least 1.5 M, green compounds of empirical formulae $M^IMn(CN)_3$ or $M^{II}Mn_2(CN)_6$ are precipitated. The half-life of exchange of labelled CN^- with $[Mn(CN)_6]^{4-}$ at pH 11.8 is only approximately five minutes.[43]

Recent work on aqueous cyanide solutions of $K_4[Mn(CN)_6]\cdot 3H_2O$ indicate that $[Mn(CN)_n(H_2O)_{6-n}]^{(n-2)-}$ with n = 1–5 and the binuclear species $[Mn(CN)_5—CN—Mn(CN)_5]^{7-}$ are present. On the addition of NaOH, the hydroxo species $[Mn(CN)_5OH]^{4-}$ is most likely formed, as are dimeric species with oxo or hydroxo ligands.[44]

$K_4[Mn(CN)_6]\cdot 3H_2O$ is usually a blue-violet material, although the more soluble $Na_4[Mn-$

$(CN)_6]\cdot 12H_2O$ has the expected yellow colour; both dissolve in aqueous cyanide to give yellow solutions. They are made[45] by treating manganese(II) acetate or carbonate with an excess of KCN or NaCN under rigorous exclusion of oxygen. The blue colour of the potassium salt suggests the presence of some Mn^{III} or Mn^{IV} in the solid and an interoxidation-state electron-transfer band.

An X-ray structural analysis[46] of $Na_4[Mn(CN)_6]\cdot 12H_2O$ shows the expected octahedral MnC_6 anion, with Mn—C = 1.95(3) Å.

The magnetic moment of the potassium salt at 300 K is 2.18 BM, corresponding to the presence of one unpaired electron with some orbital contribution.[47]

The acid species $H_4[Mn(CN)_6]$, or perhaps more properly $[Mn(CNH)_4(CN)_2]$, has been prepared[48] from $Pb_2[Mn(CN)_6]$ and H_2S.

The dark green insoluble products such as '$K\,Mn(CN)_3$' obtained from aqueous solutions of $K_4[Mn(CN)_6]$ (*q.v.*) are apparently more properly formulated as, *e.g.* $K_2Mn^{II}[Mn^{II}(CN)_6]$. The X-ray powder photograph can be indexed on a simple cubic cell of $a = 8.89$ Å; the IR spectrum shows a single 'bridging' ν_{CN} of 2062 cm^{-1}; and the magnetic moment of 4.53 BM all are consistent with a structure related to Prussian blue (see iron cyanides), consisting[49] essentially of equal numbers of low spin $[Mn^{II}C_6]$ and high spin $[Mn^{II}N_6]$ octahedra.

Another product formulated[50] as $K_{1.52}Mn(CN)_{3.72}$ has been made by fusing $K_3[Mn(CN)_6]$ and KCN at 650 °C. Available data suggest that it is merely an impure form of '$K\,Mn(CN)_3$'.

Interestingly, the action of NOCl on a suspension of green '$K\,Mn(CN)_3$' in sulfolane gives[51] a tan product of approximate composition $K_{0.5}Mn(CN)_3$. It appears to be identical with the product made by mixing[52] aqueous solutions of manganese(II) acetate and $K_3[Mn(CN)_6]$. Available physicochemical data on both products—$\nu_{CN} \approx 2150\,cm^{-1}$, $\mu_{eff} = 4.2$ BM per Mn, and a cubic unit cell of $a = 10.63$ Å—suggest again a Prussian blue type structure $KMn^{II}[Mn^{III}(CN)_6]$.

It is intriguing to note that the colours of green '$KMn(CN)_3$' and tan '$K_{0.5}Mn(CN)_3$' are the reverse of what one might expect from parallels in the iron Prussian blue system; '$KFe(CN)_3$' or $K_2Fe^{II}[Fe^{II}(CN)_6]$ is colourless, whereas '$K_{0.5}Fe(CN)_3$' or $KFe^{II}[Fe^{III}(CN)_6]$ is deep blue because of an interoxidation-state electron-transfer band. Clearly, further detailed study of these manganese systems is required, and the final explanation will probably need to take account of the availability of the Mn^{IV} state—note especially the tendency, under some conditions, for $[Mn^{III}(CN)_6]^{3-}$ to disproportionate to Mn^{II} and Mn^{IV}.

Species such as $Mn^{II}[M(CN)_6]\cdot 8H_2O$ (M = Fe, Ru, Os) and $Mn^{II}_3[M(CN)_6]\cdot nH_2O$ (M = Cr, Co) have been reviewed by Ludi and Gudel.[53] X-Ray structural analyses show that the former have *fac*-$[MnN_3O_3]$ octahedra from bridging cyanides and both terminal and bridging aquo groups, whereas the latter have[54] $[MnN_4O_2]$ octahedra.

A brown product, formulated[55] as $K_3Mn(CN)_5$, has been prepared by reducing $K_3[Mn(CN)_6]$ in hydrogen at 420 °C. The magnetic moment is 4.4 BM, and there appear to be bridging and terminal cyanides; but the exact formulation, including metal oxidation state, is not established from available data.

$[Mn(CN)_5NO]^{3-}$ is best prepared[56] as the purple, crystalline, diamagnetic potassium salt $K_3[Mn(CN)_5NO]\cdot 2H_2O$ by adding hydroxylamine to an aqueous solution of a manganese(II) 'salt' and an excess of KCN. Yields from the reaction[57] of NO with aqueous solutions of $[Mn(CN)_6]^{4-}$ are usually poor. Treatment of the potassium salt with a non-oxidizing acid gives[58] carmine-red $H_3[Mn(CN)_5NO]$.

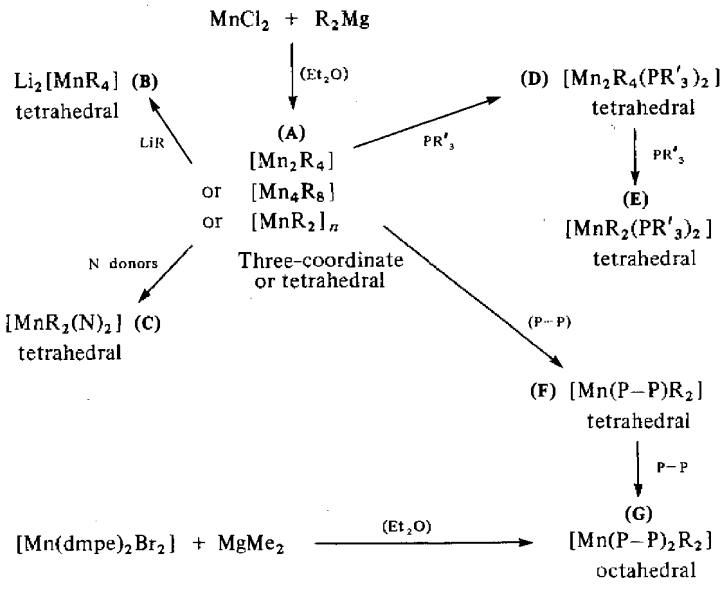
An X-ray structural analysis[59] of the potassium salt shows an almost linear Mn—NO with Mn—N = 1.66 Å and N—O = 1.21 Å. The vibrational spectrum[57] gives $\nu_{NO} = 1706\,cm^{-1}$; and the electronic spectrum shows three bands at 18 500, 28 600 and 45 900 cm^{-1} with molar extinction coefficients of 24, 114 and 16 000. Photolysis (UV) of anaerobic aqueous solutions leads[60] to $[Mn(CN)_6]^{4-}$ and NO, whereas, in the presence of oxygen, $[Mn(CN)_5(NO_2)]^{3-}$ is formed.[61]

Br_2 or HNO_3 oxidizes the nitrosyl anion to $[Mn(CN)_5NO]^{2-}$, and the standard reduction potential[56] for this reversible process is 0.6 V. Methylation[62] with methyl fluorosulfonate gives $[Mn(CNMe)_5NO](SO_3F)_2$.

41.3.2.2 Alkyls and aryls

Although normally classified within organometallic chemistry, the recently defined alkyls are a significant part of manganese(II) chemistry and we include them here.

The compounds described in four recent papers from Wilkinson's group[28,63–65] are summarized in Scheme 1. Comments on the various types of product follow the order of this scheme:

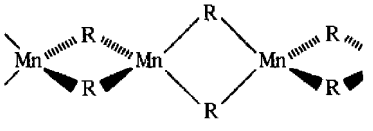


Scheme 1

(*A*) Only three binary alkyls MnR_2 have been isolated in pure form,[63] and are described as yellow to red crystals. X-Ray structural determinations of all three are known. They involved bridging alkyls and range from a dimer with pseudo three-coordinate Mn^{II} (**3**; R = CH_2CMe_2Ph); through a linear tetramer with two terminal three-coordinate metals and two central tetrahedra (R = CH_2CMe_3); to a long-chain polymer with mostly tetrahedral metals (**4**; R = CH_2SiMe_3). The low magnetic moments indicate antiferromagnetism.



(3)



(4)

(*B*) Tetraalkylmanganate(II) species[63] are light sensitive. Colours range from yellow-orange to red. The known manganate with a bulky alkyl $Li_2[Mn(CH_2SiMe_3)_4]$ is orange-brown and behaves as a simple high spin tetrahedral $[MnR_4]^{2-}$ species, but the chemical and physical properties of the known tetramethylmanganates(II) are complicated by the small Li^+ cations.[63] Only when Li^+ is solvated, as in $[Li(TMEDA)_2][Mn(Me)_4]$ {TMEDA = 1,2-bis(dimethylamino)ethane}, do the solids appear to contain the simple high spin, tetrahedral $[MnR_4]^{2-}$ species.

(*C*) Solids isolated from the reaction with nitrogen donor ligands were $[MnR_2(N—N)]$ (where N—N is a chelating diamine: TMEDA or *N,N'*-dimethylpiperazine) and $[MnR_2py_2]$ (py = pyridine). All but one were described[63] as colourless solids and all apparently are high spin tetrahedral manganese(II) species. A related oxygen donor compound $[Mn(CH_2Ph)_2(dioxane)_2]$ also has been described.[66]

(*D*) Addition of unidentate phosphines to the alkyls gives a series of orange coloured dimers $[Mn_2R_4(PMe_3)_2]$. The X-ray structural determinations of three of them[64] show that they are dimers with essentially tetrahedral $[MnC_3P]$ polyhedra, although there is also an interesting close contact between one hydrogen atom on each of the bridging methylene groups and the manganese atom. The solid compounds are antiferromagnetic.

A related aryl compound $Mn(Ph)_2P(cyclo\text{-}C_6H_{11})_3$ has been described,[67] but its structure is unknown.

(*E*) When an excess of phosphine is added to solutions of the dimers, paler coloured bis-phosphine monomers are formed[65] (reaction 2). These tetrahedral monomers are high spin and are

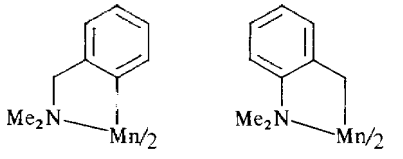
thermally unstable. Indeed most of the solids isolated were found to lose phosphine readily, reverting to the dimers. However, $[Mn(CH_2CMe_2Ph)_2(PMe_3)_2]$ is indefinitely stable at room temperature in the absence of air, and the X-ray structure of the colourless crystals shows[65] the expected (distorted) tetrahedral geometry.

$$Mn_2R_4P_2 + 2P \rightleftharpoons 2[MnR_2P_2] \quad (2)$$

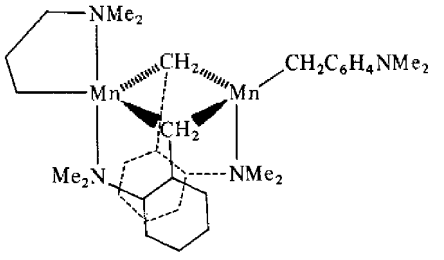
(*F*) With chelating phosphines, on the other hand, more robust $[MnC_2P_2]$ tetrahedra are obtained. Four solids $[MnR_2(dmpe)]$ were described[65] {dmpe = 1,2-bis(dimethylphosphine)ethane, and R = CH_2Ph, CH_2CMe_3, CH_2CMe_2Ph and CH_2SiMe_3} as yellow or colourless solids, containing high spin, tetrahedral monomers, which are thermally stable but air sensitive.

(*G*) Some of these alkyls can add two molecules of chelating phosphines to give red, low spin ($S = \frac{1}{2}$), octahedral $[MnC_2P_4]$ species. The first described[65] was the product of the chelating dialkyl *o*-xylyl—$[Mn\{o\text{-}C_6H_4(CH_2)_2\}(dmpe)_2]$—in which the M—C bonds (2.11 Å) are shorter than in the tetrahedral species (2.15 Å); the other is the dimethyl[28] species $[Mn(CH_3)_2(dmpe)_2]$.

The only other well-characterized alkyl or aryl compounds of manganese(II) appear to be two interesting isomeric species[68] (**5**) and (**6**). The aryl compound (**5**) has been isolated in a complex form $MnL_2 \cdot 2LiI \cdot 2THF$ (L = $C_6H_4CH_2NMe_2$) as pale-yellow air-sensitive crystals (μ_{eff} = 5.7 BM) of unknown molecular structure, and as the yellow-green $[MnL_2]$ (μ_{eff} = 5.5 BM) which is apparently a 'tetrahedral' monomer. On the other hand the bis-benzyl compound (**6**) parallels the alkyl-bridged dimers found for the above phosphines, and gives the only known example of a five-coordinate manganese(II) alkyl; its crystal structure shows a dimeric alkyl-bridged molecule (**7**) in which one metal atom is five-coordinate and the other four-coordinate. The expected antiferromagnetism is reflected in a room temperature magnetic moment of 2.6 BM.



(5) (6)



(7)

41.3.2.3 Fulminates and other carbon ligands

Several mixed ligand fulminates have been described. These include a poorly characterized ammine compound which was obtained[69] by reacting $Hg(CNO)_2$ with manganese amalgam in anhydrous methanol, which had been saturated with NH_3; and there are two reasonably robust yellow compounds $Mn(CNO)_2(N—N)_2$ (N—N = 2,2′-bipyridyl and 1,10-phenanthroline).[70] Various formulations have been suggested for these latter, but there appears to be no good evidence to suggest that they are not simply octahedral *cis*-$[Mn(CNO)_2(N—N)_2]$ species. On heating, they do not explode, but deflagrate vigorously.

An interesting acetylide is the rose-coloured $[Mn(C_2H)_2(NH_3)_4]$.[71] It dissolves in liquid NH_3 in the presence of KC_2H, apparently forming $K_2[Mn(C_2H)_4]$.

Also possibly involving Mn—C bonds is the compound[72] of the tricyanomethanide ion $Mn\{C(CN)_3\}_2\{(Me_2N)_3PO\}_2$. This colourless compound is not isomorphous with the octahedral Ni^{II} species, but also probably has an octahedral polymeric structure with bridging anions.

41.3.3 Nitrogen Ligands

41.3.3.1 Unidentate ligands

(i) Ammonia and amido

Manganese(II) amines[73,74] are distinctly less stable and robust than those of the later transition metals.

In aqueous solutions, buffered with NH_4^+, the species $[Mn(NH_3)_n(OH_2)_{6-n}]^{2+}$, for $n = 1$–4, have been identified and the stability constants have been measured; for example, in 0.4 M NH_4Cl at 25 °C, $\log K_1 = 0.90$, $\log K_2 = 0.67$, $\log K_3 = -0.40$, and $\log K_4 = 0.30$. Apparently, only at high NH_3 concentrations, (> 2 M) is the hexaammine present in any significant concentration.

The known solid ammines are summarized in Table 8. Preparations with maximum n were generally made either by reacting solid MnX_2 with gaseous NH_3, or reacting MnX_2 or a hydrate with liquid NH_3. All lost NH_3 at rates depending on X, and the storage conditions. The species for n less than maximum value were characterized generally as steps in the thermal decomposition of the higher species.

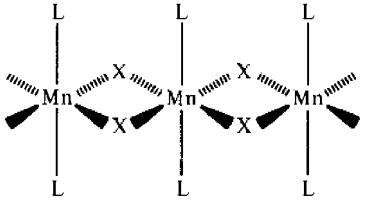
Composition does not necessarily, of course, reflect coordinate number at the metal. This is especially so for the species for which $n > 6$; there is no evidence for $[MnN_7]$ or $[MnN_8]$ polyhedra except where special ligand steric effects promote higher coordinate numbers.

However, most of the species $MnX_2 \cdot 6NH_3$ are white powders, and probably contain the cation $[Mn(NH_3)_6]^{2+}$ (as do those for $n > 7$), and this is proved by X-ray powder diffraction for X = Cl, Br, I, ClO_4, SO_3F and BF_4, which have cubic crystal structures belonging to the CaF_2 type.

These compounds are sensitive to air, especially to moist air, generally turning brown, owing to oxidation and displacement of at least some of the NH_3. Sensitivity is anion dependent, with, for example, decreasing sensitivity from F^- to I^- amongst the halides.

The species $MnX_2 \cdot 4NH_3$ are surprisingly unusual: $MnCl_2 \cdot 4NH_3$ exists only under supercritical conditions, the thiocyanate needs further confirmation and the $[SiF_6]^{2-}$ species appears to be almost an exception; and in none of these cases are we certain of an $[MnX_2N_4]$ structure.

The diammines, on the other hand are well characterized and almost certainly have a linear polymeric structure as in (**8**) for (L = NH_3). The monoammines also are undoubtedly representatives of a well-characterized polymeric structural type, like the monopyridine compounds (*q.v.*).



(8)

Table 8 The Composition of Known Manganese(II) Ammines[73] $MnX_2(NH_3)_n$

X^-	$n NH_3$[a]									*Comments*
F										b
Cl	12	11	10	8	7	6	4	2	1	c
Br			10			6		2	1	
I						6		2		
ClO_4						6		2		
BF_4						6		2		
CN						6		2		d
NCS							4			
SO_3F						6				
$\frac{1}{2}SO_4$						6				
$\frac{1}{2}CrO_4$						6				
$\frac{1}{2}SiF_6$	12						4			e

[a] A few unusual species, listed in Gmelin,[73] but for which we think the evidence unsatisfactory, are omitted.
[b] At least two papers report the reaction of $MnF_2 + NH_3$, but products appear ill-defined and soon revert to MnF_2.
[c] Under normal conditions, the species for which $n = 6$, 2 and 1 only are observed. The other species (including $n = 4$) exist only under supercritical conditions.
[d] The species $Mn(CN)_2 \cdot 2NH_3$ seems suspect; colour was described as yellow-green and $\mu_{eff} = 6.3$ BM. In air it turns brown, losing HCN.
[e] Ref. 74.

Amido species of Mn^{II} are known. The binary compound $Mn(NH_2)_2$ is obtained[75] as an impure light yellow product from KNH_2 and $Mn(SCN)_2$ in liquid NH_3, but is stable only in the absence of air and water and below room temperature. The compounds $M_2[Mn(NH_2)_4]$ (M = Na, K, Rb, Cs), however, are relatively robust in the absence of water. The yellow crystalline compounds were obtained[76] by dissolving Mn in a liquid NH_3 solution of the alkali metal. An X-ray analysis of the K^+ salt confirms[77] the expected tetrahedral $[MnN_4]$ anion, with Mn—N = 2.12(4) Å.

(*ii*) *Aliphatic and aromatic amines and substituted amides*

Available data[78] on the products from the reaction of MnX_2 species with amines are both limited and often of poor quality. For the primary amines, data refer to the reaction of solid MnX_2 with gaseous RNH_2; but for most of the other amines, products were obtained from ethanol solutions. In the latter case, initial products often contained ethanol, $MnX_2 \cdot A_n \cdot (EtOH)_m$ (A = amine), but this was lost either on storage over $CaCl_2$ or on heating. It is not known whether the ethanol is bonded to the Mn or simply solvent of crystallization.

The poor quality of much of the data is evident both from the dark colours of many of the products, and from the lack of any meaningful structural data; of course, all pure species $MnX_2 \cdot A_n$ should be white or perhaps a very pale colour.

Most, but not quite all, of the high spin species $MnX_2 \cdot A_n$ are unstable to oxidation in the air and especially in moist air.

Observed stoichiometries for the compounds with the primary amines (Table 9) are for integral values of n in $(MnX_2 \cdot A_n)$ of 6, 4, 2 and 1 (the two non-integral values, assigned to nitrates, need further confirmation).

For $n = 6$, known compounds are confined to methylamine and ethylamine; these are probably $[MnA_6]X_2$ species. Tetrakis species are better defined here than for NH_3 and probably have $[MnX_2A_4]$ monomeric structures; but the most common stoichiometry is MnX_2A_2. These latter species probably have the linear polymer structure of (**8**).

Very little is known of compounds with the more sterically-demanding secondary amines. Two white aziridine (C_2H_5N) species $MnCl_2A_4$ and MnI_2A_5 have been described, but all other products (with piperidine, dialkylamines and substituted anilines) are described as 1:1 species $MnX_2 \cdot A$. (Unfortunately, all of the latter were described as brown or other dark colours and are therefore suspect.)

Tertiary amine compounds also are generally poorly defined. One attempt to obtain compounds of R_3N (R = Me, Et) from ethanol gave products which were not properly characterized, but which were formulated as containing R_3N and OR^- ligands. However, a white unstable solid $(MnCl_2 \cdot Et_3N)$ was obtained, which probably has a similar layer structure to $(MnCl_2 \cdot py)_n$. Trioctylamine can be used to extract Mn^{II} from aqueous acid solution into organic solvents, but the nature of the species involved is unknown.

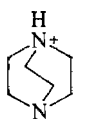
The only available X-ray structural data refer to a compound of hexamethylenetetraamine $\{(CH_2)_6N_4\}$. A crystalline bis species has been shown[79] to have an all *trans*-$[MnCl_2N_2O_2]$ structure with long Mn—N bonds of 2.40 Å. The related cationic ligand (**9**) forms[80] the bis species $[MnX_3(LH)_2]X$ (X = Cl, Br); whereas ligand (**10**) does not bond to Mn; although Co, Ni and Cu form the species $[MnX_3(LH)]$ (X = Cl, Br, I), manganese forms[81] instead $(LH)_2[MnX_4]$.

Amido species of the secondary amine $NH(SiMe_3)_2$ have been studied in some depth.

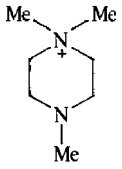
Table 9 The Composition of Known Manganese(II) Amine Compounds $MnX_2(Am)_n$ (Am = RNH_2 or $ArNH_2$)

	n							
	RNH₂			*ArNH₂*				
X	*Me*	*Et*	*Bz*	*C₆H₅*	*2-MeC₆H₄*	*3-MeC₆H₄*	*4-MeC₆H₄*	*Others*[a]
Cl	6	4	2	2	2, 1	2	2	2
Br	6	4		2	2	4, 2	2	2
I	6	(6)[b], 4		4, 2				
NCS							4, 2	
NO_3				2	$\frac{3}{2}$	2	$\frac{2}{4}$	2
$\frac{1}{2}SO_4$								2
$\frac{1}{2}CrO_4$	6	6						
$\frac{1}{2}Cr_2O_7$				4				

[a] 3-ClC_6H_4, 4-ClC_6H_4, 3-BrC_6H_4, 4-BrC_6H_4, 3,4-diMeC_6H_3, and α- and β-naphthylamines.
[b] Obtained only at low temperature.

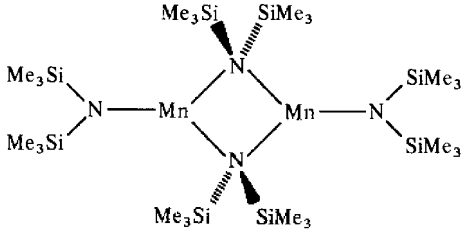


(9)



(10)

$Mn[N(SiMe_3)_2]_2$ was first made by Bürger and Wannagat[82] from MnI_2 and $NaN(SiMe_3)_2$ in THF, but Bradley and co-workers[83] have now shown that a reaction of $MnCl_2$ and the Li salt in THF gives pink $[Mn\{N(SiMe_3)_2\}_2(THF)]$, which is quite robust; it can be distilled without losing THF and is a paramagnetic (μ_{eff} = 5.91 BM) monomer.[84] At 120 °C, in a stream of argon, the THF is lost and recrystallization of the residue from pentane gives pink plates[83] of the dimer (**11**). An X-ray structure of this dimer shows Mn—N = 1.994 Å (terminal) and 2.184 Å (bridging), with a metal–metal distance of 2.841 Å. The magnetic moment of 3.34 BM (at 296 K) shows the expected antiferromagnetism.



(11)

More recently Horvath *et al.*[85] have improved the synthesis of $[Mn(NR_2)_2(THF)]$ and have shown that another series of yellow tetrahedral compounds $[Mn(NR_2)_2L_2]$ (where L = THF, py or Bu^t–CN) can be formed. All are thermally robust, but show exteme oxygen sensitivity. There is also an intriguing benzene species of unknown structure $[Mn\{N(SiMe_3)_2\}_2(C_6H_6)_2]$, and a series of mixed ligand species MnXY (where X = Cl, NO_3 and Bu; and Y = $N(SiMe_3)_2$ or OR).

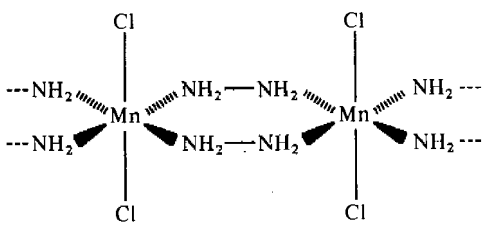
Attempts to prepare compounds of NEt_2^- gave instead compounds of a reaction product of the amide (Section 41.3.3.2).

(*iii*) *Hydrazine and hydroxylamine*

Three types of compound of hydrazine and MnX_2 species have been characterized:[86] $MnX_2(N_2H_4)_n$ for n = 1, 2 and 3. Within these classes, they are of varying robustness—some are stable in air, others not.

The white n = 1 compounds are known only for MnF_2 and MnC_2O_4, and they are the stable species at ambient conditions for both. They can be prepared either by direct reaction or by loss of N_2H_4 from the bis species. The structure is unknown, but is undoubtedly polymeric and probably consists of both bridging hydrazine and anions. A similar compound has been described for 1,2-dimethylhydrazine, and with 4-nitrophenylhydrazine.

The bis compounds $MnX_2(N_2H_4)_2$ are the most common and have been characterized for X = F, Cl, Br, NCS, HCOO and OAc, and X_2 = oxalate and picramate. Crystalline hydrates of these also have been defined, as have hydrates for X = I and NO_3, but whether they have significantly different molecular structures from the anhydrous species is unknown. A full X-ray structural analysis of $MnCl_2(N_2H_4)_2$ characterizes the bis species as linear polymers based on double N_2H_4 bridges (**12**) (Mn—N = 2.27 Å and Mn—Cl = 2.57 Å). Bis compounds have also been described with phenylhydrazine and MnX_2 (for X = Cl, Br, I). Structures could be polymeric based either on bridging hydrazine as in (**12**), or on bridging halide as in (**8**).



(12)

Table 10 The Known Manganese(II) Pyridine Compounds $MnX_2 \cdot npy$

n	*Cl*	*Br*	*I*	*X* *NCZ*[a]	*NO_3*	*ClO_4/BF_4*	*Other*
6		√		√			√[b]
4	√	√	√	√		√	√[c]
3	√	√					
2	√	√	√	√	√		√[d]
1	√	√	√				√[e]
other	($n = \frac{2}{3}$)	($n = \frac{2}{3}$)	($n = \frac{2}{3}$)			($n = 8$)	

[a] Z = O, S or Se.
[b] X = $\frac{1}{2}SnBr_6$.
[c] X = $CF_3CO_2^-$, $CCl_3CO_2^-$, $SbCl_6$, $\frac{1}{2}HgCl_4$, $\frac{1}{2}Cr_2O_7$, ReO_4.
[d] At least ten others have been described.
[e] X = $Me_3CCO_2^-$, $\frac{1}{2}C_2O_4$.

A tetrakis compound of 4-nitrophenylhydrazine and $MnCl_2$ may be an example of a monomeric $[MnCl_2N_4]$ chromophore.

A few compounds of hydroxylamine and MnX_2 have been described,[87] but it is uncertain that any of them contain Mn—N bonds (see Section 41.3.9).

(*iv*) *Pyridines and quinolines*

Almost all of the known compounds[88] appear to be high spin six-coordinate species; they are generally colourless and sensitive to air, turning brown with loss of a nitrogen ligand.

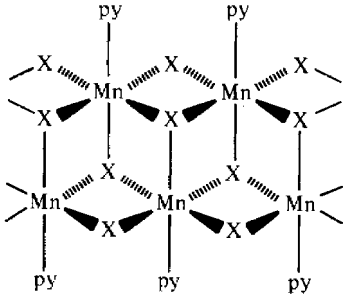
The solid pyridine compounds are summarized in Table 10. Unlike the amines, tetrakis compounds are quite common, and hexakis species are less usual. This is probably related to the steric requirements of the α-hydrogens of pyridine. The room-temperature-stable combination of MnX_2 and py is usually a bis species.

In aqueous solution, potentiometric measurements have been interpreted in terms of only four species $[Mnpy_n(H_2O)_{(6-n)}]^{2+}$ ($n = 1$ to 4), with log K_n determined as 1.86, 1.59, 0.9 and 0.6, respectively. Perhaps the $n = 5$ and 6 species are formed at higher concentrations of pyridine, but, even in the solid state, there is yet no certainty that the compounds $MnX_2 \cdot 6py$ actually contain $[Mnpy_6]^{2+}$. It is virtually certain that the compound $Mn(ClO_4)_2 \cdot 8py$ is not eight-coordinate.

The *tetrakis* compounds, which are quite common here, probably all (because of the steric requirements of py) have a *trans*-$[MnX_2N_4]$ octahedral structure. X-Ray proof of this, however, is available only for $[Mn(NCS)_2py_4]$ and $MnSbCl_6 \cdot 4py$, and is obtained by comparison of the powder patterns with the octahedral Ni species.

Bis compounds are usually the final product of the other species when left at room temperature. They appear generally to have the polymeric structure (**8**) and show some antiferromagnetism, except where the bridging ligands, such as $[Ni(CN)_4]^{2-}$ and $[C_2O_4]^{2-}$, cause sufficient separation of metal centres. A full X-ray analysis of $MnCl_2py_2$ shows the polymeric structure with Mn—Cl = 2.56, 2.57 Å and Mn—N = 2.24 Å.

Monopyridine compounds result from thermal degradation of the bis species. They appear to have the polymeric structure (**13**) ($MnCl_2py$ is isomorphous with $NiBr_2py$). Further thermal degradation sometimes leads to a well-characterized phase $\{Mn_3X_6 \cdot 2py\}_n$.



(13)

Pentakispyridine compounds are known only in $Mn(ClO_4)_2 \cdot 5py \cdot 3H_2O$ which is of unknown structure, and there is an isoquinoline compound $MnCl_2 \cdot 5L$.

Tris compounds have been proposed only in $[py_2H][MnBr_3py_3]$ (which could be instead $[MnBr_2py_4] \cdot pyHBr$) and $[R_4N][MnBrCl_2py_3]$ (R = Me, Et) and a 4-picoline analogue, but even their formulation as discrete species needs X-ray confirmation.

Substituted pyridines (β or γ) generally give compounds of the same type as pyridine, although no hexakis compounds have yet been described. We especially notice, however, the compound $Mn(NCS)_2(3\text{-Br-py})_2$, which is 'freely soluble in the common organic solvents', unlike the other bis species. A tetrahedral $[MnN_4]$ has been proposed, although small oligomers, such as a five-coordinate dimer, are also possible.

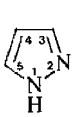
2-Substituted pyridines, including quinoline, have more stringent steric requirements, and generally form only 1:2 and 1:1 species. Those so far described appear to be polymers, with structures such as (**8**) and (**13**), yet it is here especially that we might expect to encounter tetrahedral $[MnX_2L_2]$ species or five-coordinate dimers as in the biquinolyl compounds (Section 41.3.3.2).

A series of compounds formulated as $[RH]_2[MnCl_4py_4]$ are more likely to be six-coordinate, with free pyridine in the crystal lattice, if indeed they are discrete compounds and not mixtures.

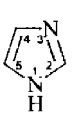
(*v*) *Pyrazoles, imidazoles, triazoles, etc.*

The compounds of these ligands,[89] especially those of imidazole, have been more effectively studied than those of the more classical ligands, *i.e.* pyridine and ammonia. The biological role of imidazole moieties as donors has given impetus to these studies in the 1970s, and the compounds are generally more robust in the air and at ambient temperature, although some are still unstable, especially with respect to oxidation in moist air. Structural data are more complete; more full X-ray determinations are available, and nearly maximum use has been made of X-ray powder data, especially by Reedijk and co-workers,[90] for comparison with other species of known structure.

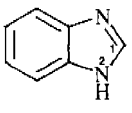
Table 11 gives the stoichiometries of the compounds $MnX_2 \cdot nL$. These were generally obtained as crystalline species from anhydrous ethanol, although a few of the species of lower *n* values were made by thermal decomposition. All are high spin, with some polymers showing antiferromagnetism, and most are, as expected, colourless; a few are pale pink, and there are some yellows, fawns and browns, but the detail is unimportant. A common feature seems to be bonding through the unsaturated nitrogen (=N–), and not through the NH nitrogen.



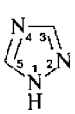
(14)



(15)



(16)



(17)

The compounds for $n = 6$ appear generally to contain $[MnN_6]^{2+}$ octahedra; proof comes from comparative X-ray data in some cases and in others reasonable evidence is available from ESR data. The one observed compound of higher *n*, that is $Mn(ClO_4)_2 \cdot 7(5\text{-Me-pyrazole})$, is isomorphous with an Ni species, known to be $[NiL_6](ClO_4)_2 \cdot L$, and thus belongs to this class. Where there are ring substituents adjacent to the bonding N, steric crowding destabilizes the $[MnN_6]^{2+}$ octahedra and species of lower *n* are obtained. In Table 11 there are two possible exceptions: $Mn(NCS)_2 \cdot 6(3,5\text{-diMe-pyrazole})$ and $Mn(NO_3)_2 \cdot 6(2\text{-Me-imidazole})$. The former appears from available data to have the structure $[Mn(NCS)_2L_4] \cdot 2L$, and there is only doubtful IR evidence that all the imidazoles are bonded in the latter. Note that in this latter case, both ClO_4 and BF_4 form only 1:4 species.

There are many $n = 4$ species here, most of which appear to have a *trans* octahedral $[MnX_2L_4]$ structure. Indications of this come from one available X-ray structure[91] {$[MnBr_2(5\text{-Me-pyrazole})_4]$, which has *trans* bromines at 2.73 Å and Mn—N of 2.25 Å}, from the ESR data and perhaps also from some of the IR data. Two crystalline forms of $Mn(NCS)_2(5\text{-Me-pyr})_4$, both of which are isomorphous with Ni species, have been interpreted as examples of *cis* and *trans* isomers, but the data do not absolutely require the acceptance of the view that one is a *cis* isomer.

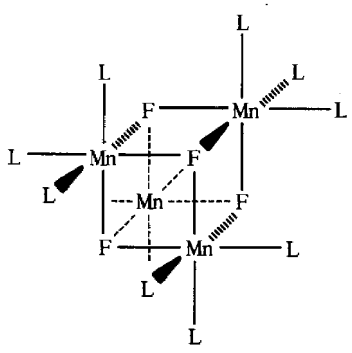
The $n = 3$ species are of some interest in providing one of the few known examples of five-coordinate Mn^{II}. Fourteen of these species have been described (Table 11); some have been assigned (undefined) polymeric structures; but structure is known certainly only for $[MnCl_2(2\text{-Me-imid})_3]$. This is a five-coordinate monomer,[92] with 'intermediate' structure and bond distances Mn—Cl of 2.392 and 2.525 Å, and Mn—N of 2.19, 2.20 and 2.25 Å.

Table 11 Known Compounds $MnX_2 \cdot nL$ for the Pyrazoles, Imidazoles and Triazoles

					n for X =				
L	*F*	*Cl*	*Br*	*I*	*NCS*	NO_3	ClO_4	BF_4	$\frac{1}{2}SO_4$
Pyrazole[a]		4, 2[b]	4, 2	4	4[c]	4[d]	6	6	
5-Me	[e]	4[f]	4[b]	4[f]	4[f]	4[f]	7[f,g]		4[h]
3,5-diMe	2	2	3, 2		6	3, 2			
Imidazole[a]		6, 4, 2, 1	6, 4, 2, 1	6, 4, 2	6, 4, 2	6	6[f]		
1-Me		6, 3, 2, 1	6, 4, 2	6, 4	4, 3	6, 3	6[f]	6	
2-Me		3[b], 2, 1	2			6	4		
4-Me		4, 3	6, 4	6	6, 3	6	6		
1,2-diMe		2[i]	2[i]	2[i]	4[f]	3			
1-Et	[e]	4[f], 3	6, 4[f], 3	6	4	6, 3	6		
1-Pr	[e]	6, 2	6, 2	6	4, 2	6[f], 3	6		
1-Bu		4	4	6	4[f]	6[f]	6		
1-Vinyl		4, $\frac{3}{2}$	4, 2	6	4, 3	6	6, 4		
Benzimidazole[a]					2				
1-Vinyl		2							
2-Me		2	2		2	2			2
2-Bz		2	2	2	2				2
1,2,4-Triazole[a]					2				1[b]
4-Me					$\frac{5}{2}$[b]				

[a] Substituent positions are given in diagrams (**14**) to (**17**).
[b] Full X-ray structural analyses available—see text.
[c] Isomorphous with Fe, Co, Cu and Zn analogues.
[d] Isomorphous with Cu analogue.
[e] Tetrameric $[Mn_4F_4]$ species formed—see text.
[f] Isomorphous with Ni analogue (and usually others) thus identifying *Oh* or *D4h* symmetry.
[g] The structure is $[MnL_6](ClO_4) \cdot L$.
[h] Explosive above 200°C.
[i] See text for X-ray powder data.

Within this class are a series of compounds $MnF(BF_4) \cdot 3L$ (where L = 5-Me-pyrazole, 1-Et- and 1-Pr-imidazole). They resulted from attempts to prepare $Mn(BF_4)_2$ compounds, and all appear to have the tetrameric 'cubane' structure[93] of (**18**).

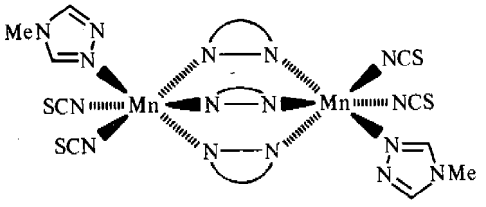


(**18**)

The $n = 2$ compounds appear to be generally antiferromagnetic polymers of structural type (**8**). One full X-ray study is available[94] on $MnCl_2(pyrazole)_2$, which gives Mn—Cl = 2.593 Å and Mn—N = 2.201 Å. There are, however, some interesting exceptions with the sterically hindered ligands. For 3,5-dimethylpyrazole, the F, Cl and NCS species are antiferromagnetic (especially the F), but the Br species which is not isomorphous with the Cl, is isomorphous with the Ni, Co and Zn species, and there are suggestions that it has a tetrahedral monomeric structure. Similarly, for $MnCl_2(1,2\text{-di-Me-imid})_2$, the magnetic moment is invariant between 100 and 300 K, and the compound also appears to be a tetrahedral monomer, whilst the alcohol solubility of the Me- and Bz-substituted benzimidazoles may point to tetrahedral monomers or five-coordinate dimers.

But few $n = 1$ compounds have been described. They probably have a polymeric chain structure like (**13**). There is also a series of tetrahedra $[R_4N][MnX_3L]$ (where X = Cl, Br and L = 1-Me, 1-Et, 1-Pr, 1-vinyl and 4-Me-imidazole).

The few known triazole (**17**) compounds are of different type. $MnSO_4$ forms a mono species under conditions where Ni forms a tris, and this has a monomeric structure[95] $[Mn(SO_4)(H_2O)L]$. On the other hand $Mn(NCS)_2$ forms a polymeric $Mn(NCS)_2 \cdot 2L$ species, in which the polymerization occurs through the triazole ligand (N-2 and N-4) bridging *trans* $Mn(NCS)_2$ units.[96] The other known triazole compound is $Mn_2(NCS)_4$(4-Me-triazole)$_5$ which has[97] the dimeric structure (**19**)



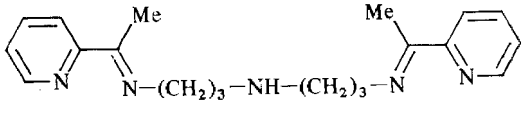
(19)

Another unusual species is the compound of Mn^{II} and the imidazoyl anion $[Mn_3(imid\text{-}H)_6 \cdot 2\,imid]$, made from manganese carbonyl. The colourless crystals are air sensitive, and have[98] a polymeric structure with alternating $[MnN_6]$ octrahedra and $[MnN_4]$ tetrahedra, bridged by the imidazole ligands. Each octahedral Mn is surrounded by four tetrahedral Mn's and each tetrahedron is surrounded by two other tetrahedra and two octahedra.

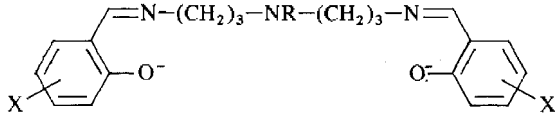
(*vi*) *Other neutral nitrogen ligands*

Very little work appears to have been done on manganese nitrile compounds, although several authors have described[99] $[Mn(RCN)_6]^{2+}$ and $[Mn(ArCN)_6]^{2+}$ species.

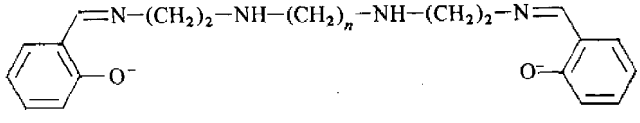
Nitrosyl compounds of manganese(II), in addition to the cyano nitrosyls (Section 41.3.2.2) and porphyrin species (Section 41.3.10.1), are represented by the compounds $[Mn(L)NO](ClO_4)_2$ (L = **20**) and [Mn(L′)NO] (L′ = **21**). The former was prepared by simply treating the compound with the pentaamine ligand with NO, and an X-ray structure analysis[100] shows an octahedral $[MnN_6]^{2+}$ species with Mn—N(O) of 1.58 Å and the other Mn—N distances ranging between 1.91 and 2.12 Å. The Mn^{II} compounds of the salicylaldiminate ligands (**21**) reacted reversibly[101] in solution with NO, many lost NO when attempts were made to isolate them, and even though crystalline, purple-red, diamagnetic solids were obtained, they were thermally unstable, reverting to yellow $[Mn^{II}(L')]$ and NO. The solutions, however, reacted with O_2 to give $[Mn^{III}(L')(NO_2)]$ species. Interestingly, the compounds of the sexadentate ligands (**22**) (n = 2, 3) also react[102] with NO to give red nitrosyl compounds in solution ($CHCl_3$) and these then react with O_2 to give green $[Mn^{III}(L'')(NO_2)]$, which *may* be seven-coordinate species.



(20)



(21)



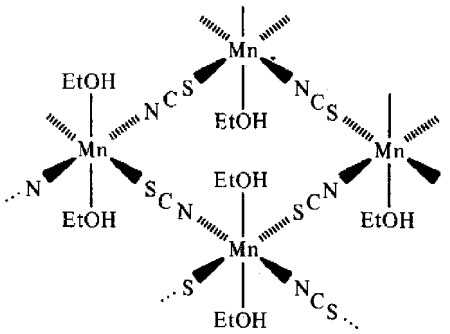
(22)

Thiazyltrifluoride (NSF_3) is an interesting new ligand which forms colourless $[Mn(AsF_6)_2(NSF_3)_4]$. The X-ray analysis[103] shows Mn—N bonds of 2.19 Å and *trans* F atoms (from AsF_6^-) at 2.19 Å.

(*vii*) *Unidentate anions (including thiocyanate and azide)*

The *nitrite* anion appears to bond to Mn^{II} through its O atoms exclusively, and is treated in Section 41.3.5.

Thiocyanato, but not *cyanato* and *selenocyanato* species have been studied in some depth.[104] All three apparently prefer N-bonding to Mn^{II}, although there is at least one example of Mn—NCS—Mn bridging; polymeric $Mn(NCS)_2(EtOH)_2$ has[105] the layer structure represented in (**23**). In golden-yellow $HgMn(SCN)_4$, the bridging is Mn—NCS—Hg like the Fe, Co and Zn analogues. There is also some evidence for Mn—$\overset{|}{N}$—Mn bridging in some compounds of the substituted pyridines, but this needs X-ray confirmation.



(**23**)

The binary thiocyanate has been known[104] as the hydrate $Mn(NCS)_2 \cdot 3H_2O$ since 1842, and $Mn(NCS)_2$ can be obtained by heating this to 170 °C, or by heating the ethanol compound (**23**) to 110 °C. The selenocyanate has only been obtained as a THF or dioxane species, decomposing when attempts are made to remove these other ligands.

All three (NCO, NCS, NCSe) form a range of anionic species, and the known solids are summarized in Table 12. Some studies of solutions are available, but much remains to be learnt of the detailed structures adopted by Mn^{II} in these solutions. Both tetrahedral and octahedral species seem well characterized in the solid state, but it would be reassuring to have some X-ray confirma-

Table 12 Anionic Species with Cyanate, Thiocyanate and Selenocyanate

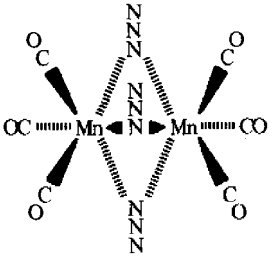
Anion	*Number of Salts*[a]	*Confirmed Structures*[b]	*First Reported*	*Ref.*
$[Mn(NCO)_4]^{2-}$	1	1	1964	33
$[Mn(NCS)_4]^{2-}$	10	—	1905	106
$[Mn(NCS)_4(AA)]^{2-}$[e]	2	—	1981	107
$Mn(NCS)_5^{3-}$[c]	2	—	1905	106
$[Mn(NCS)_6]^{4-}$	8	2[d]	1900	36, 37
$[Mn(NCSe)_4]^{2-}$	1	—	1965	108
$[Mn(NCSe)_6]^{4-}$	3	—	1965	108

[a] This refers to the numbers of solid compounds described with appropriate stoichiometry.
[b] The test adopted here is a demonstrated isomorphism with other metal compounds of known structure— through X-ray powder photography.
[c] These may be five-coordinate, but appear not to have been studied since the original work.
[d] $K_4[Mn(NCS)_6] \cdot 4H_2O$ is an isotype of the rhombohedral $K_4[Ni(NCS)_6] \cdot 4H_2O$ and $K_3[Cr(NCS)_6] \cdot 4H_2O$, and the quinolinium salt has been shown to be isomorphous with the Fe and Ni species.
[e] AA = bipy or phen.

tion of the tetrahedron. There are also two solids which may be examples of five-coordinate $[Mn(NCS)_5]^{3-}$ species. The recently reported yellow anions $[Mn(NCS)_4(AA)]^{2-}$ (where AA = bipy or phen) were prepared readily from aqueous ethanol. Related to these probably are the compounds[109] of the hexamethylenetetraamine monocation, $(C_6H_{13}N_4)_2Mn(NCS)_4$. The manganese compound is isomorphous with the Fe, Co and Ni analogues and the structure may well be an $[Mn(NCS)_4(N)_2]$ octahedron (*cf.* Section 41.3.3.1.2).

Both the binary *azide* $Mn(N_3)_2$, which, of course, detonates readily, and the tetrakis anion $[Mn(N_3)_4]^{2-}$ are known.[110] The latter has been isolated as the NEt_4^+ salt from various non-aqueous solvents and the *n*-cetyltrimethylammonium salt precipitates from aqueous solutions of the former. Products obtained have been described as light grey; the evidence for a monomeric tetrahedron is so far only IR; the compounds are light sensitive, turning brown. They are insensitive to shock, but do detonate in a flame.

Azido compounds with other ligands also have been studied. As with thiocyanate, so there is some evidence that azido can bridge through the one terminal N atom in at least some substituted pyridine compounds, a form of bridging that is well characterized[111] in the Mn^{II} tricarbonyl anion (**24**).



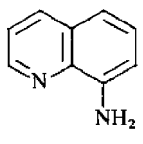
(24)

41.3.3.2 Bidentate ligands

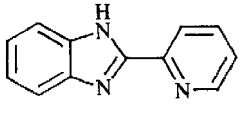
With higher multidentates, but beginning with the bidentates, Mn^{II} compounds with nitrogen ligands become rather more robust. The 1,2-diaminoethane species $[Mnen_3]^{2+}$ is still quite sensitive to air; aqueous solutions are oxidized and the solids $[Mnen_3]X_2$ turn brown at varying rates; but $[Mnbipy_3]^{2+}$ and $[Mnphen_3]^{2+}$ are not at all easily oxidized.

Stability constants in water are generally quite low: log K_n's for $Mn(en)_n^{2+}$ are 2.8, 2.1 and 0.9, respectively (with log β_3 rising to 10.1 in DMSO); and for phen they are 4.0, 3.5 and 3.0.

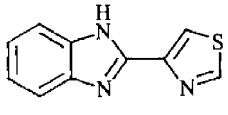
Table 13 lists the solid compounds $MnX_2 \cdot nL$, all of which are high spin. There are also significant reports of compounds with diamines, such as *m* and *p*-phenylenediamines, which are incapable of chelating. These compounds,[112] thus, can be treated simply as variations on the unidentate theme.



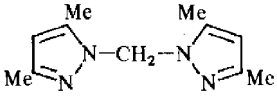
(25)



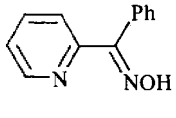
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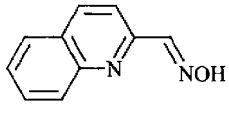
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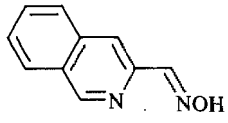
(28)



(29)



(30)



(31)

Except perhaps for the special case of the $n = 4$ species, the values of n seem invariably to define the number of bidentate ligands bonded to Mn: tris compounds are octahedral cations (one salt, the ethylxanthate, has been shown[123] to be isomorphous with the octahedral Fe, Co and Ni salts); bis

Table 13 The Numbers of Known Compounds $MnX_2 \cdot nL$ for the Bidentate Nitrogen Ligands

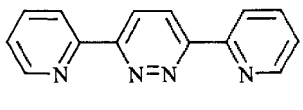
Ligand	*Number of Compounds*[a] $n = 1$	$n = 2$	$n = 3$	$n = 4$	*Ref.*
$NH_2CH_2CH_2NH_2$		1	6		112, 113
$NH_2(CH_2)_3NH_2$		1	1		113
$NH_2(o\text{-}C_6H_4)NH_2$	6	3	1	1	112, 113
$NH_2(2\text{-}C_6H_4\text{-}2\text{-}C_6H_4)NH_2$		4	3		112
$NH_2NHCONHNH_2$		1	1		114
$2\text{-}pyCH_2NH_2^b$	1	4	2		115, 116
$2\text{-}pyCH_2NHCH_3^b$		2			116
$6\text{-}Me\text{-}2\text{-}pyCH_2NH_2^b$		2			116
$2\text{-}pyNHNH_2$		1	1		113
$8\text{-}quinNH_2$ (**25**)	1	4	1	1	113, 117
(**26**)	2	5			118
(**27**)			1		119
(**28**)		1			120
(**29**)		1			121
(**30**)		8			122
(**31**)		8			122
bipy	8	9	8		123
phen	8	14	7	5	123
(**32**)		1			124
(**33**)	1				125
(**34**)	1				126
$2,9\text{-}Me_2\text{-}phen$ (**35**)	1	3			113
(**36**) and (**37**)		5			127
(**38**)[b]		4			128
(**39**) R = H		1		1	129
(**39**) R = Me			1		129

[a] The totals here include solvates and species known to be, for example, $[Mn(N{-}N)_2(H_2O)_2]X_2$.
[b] These products were described as brown and are suspect.

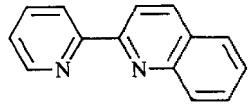
compounds are octahedral[130,131] $[MnX_2(N{-}N)_2]$ or $[Mn(N{-}N)_2(H_2O)_2]^{2+}$, *etc.* species; and, whilst the mono compounds in the solid state appear generally to be $\{MnX_2(N{-}N)\}_x$ polymers with bridging anions,[132] they dissolve to give $[Mn(N{-}N)(solvent)_4]^{2+}$ cations. Several anions $[MnX_4(N{-}N)]^{2-}$ also are known,[107] but have not been significantly explored.

The bis-chelate compounds of bipyridyl and phenanthroline appear to be invariably *cis* isomers[130,131,133] as a result of the steric effect of their α-hydrogens;[133] although, with the larger Mn—N distances, *trans* isomers may be available here.[133] Full X-ray structural analyses of $[Mn(NCX)_2bipy_2]$ (X = O, S) are available,[130,131] with the most reliable data giving[131] Mn—N(bipy) of 2.17–2.31 Å and Mn—N(CS) = 2.145 Å. The structure[124] of the closely related *cis*-$[Mn(NO_3)_2L_2]$ (where L = **32**) shows a significant feature of these Mn compounds: it is eight-coordinate, with both nitrates bidentate (Mn—O = 2.30–2.47 Å (average = 2.42) and Mn—N = 2.29–2.33 Å). Such eight-coordinate structures may be a common feature of the compounds with the oxyanions, including carboxylates.

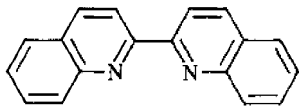
With substituents in the α-positions, the steric requirements of bipy and phen become more demanding, and ligands (**33**) and (**34**) give five-coordinate species.[125,126] The pyridyl-quinolyl ligand (**33**) gives a monomeric $[MnBr_2(H_2O)(N{-}N)]$, whilst the biquinolyl ligand (**34**) gives a dimeric $[(N{-}N)ClMn{-}Cl_2{-}MnCl(N{-}N)]$, no other compounds of these ligands appear to have been reported. With the bis-chelate compounds[113] of 2,9-dimethyl-1,10-phenanthroline (**35**), it will be interesting to see if the larger Mn^{II} will allow octahedral $[MnX_2(N{-}N)_2]$ species, or whether they will be five-coordinate $[MnX(N{-}N)_2]X$.



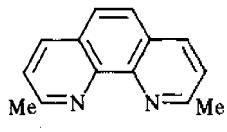
(32)



(33)



(34)

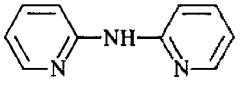


(35)

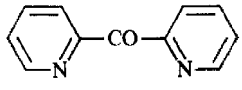
Table 14 Compounds with Bipyridyl Anions

Compound	*Colour*	*Magnetic moment*(BM) *293* K	*80* K
$[Mnbipy_3]$	Black-brown needles	4.09	3.81
$[Mnbipy_3]\cdot 2THF$	Brown needles	4.1	3.8
$Li[Mnbipy_3]\cdot THF$	Deep red crystals	3.6	
$Na_4[Mnbipy_3]\cdot 3THF\cdot 5dioxane$	Black-violet crystals	5.99	

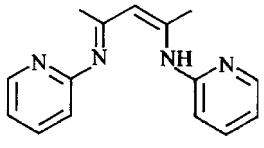
The $n = 4$ compounds (Table 13) have been known[113,134] for phenanthroline since 1933. Analogous Sr and Ba species, but which are not isomorphous with the Mn species, now are known[135] to be $[Mphen_2(H_2O)_4]^{2+}\cdot 2phen\cdot nH_2O$ species, and Drew *et al.*[136] have reported another example of a non-bonded phenanthroline. Attempts to obtain suitable crystals of Mn $phen_4X_2$ species for X-ray analysis have not been successful,[135] so the question of structure of the Mn species is still open. Eight-coordination is, however, established in the 1,8-naphthyridine (**39** for R = H) compound $[Mn(N{-}N)_4](ClO_4)_2$, which is isomorphous[129] with the Fe, Co, Ni, Cu and Pd species; it also occurs again in the $[Mn(NO_3)_2(N{-}N)_2]$ species; but, for the dimethyl ligand (**39** for R = Me), steric effects reduce the coordination number to six.



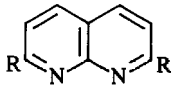
(36)



(37)



(38)

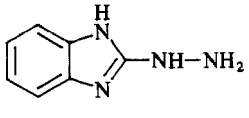


(39)

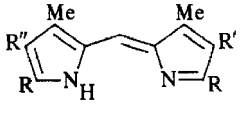
The $[Mnbipy_3]^{2+}$ cation undergoes at one-electron oxidation at ~ 1.4 V (*v* saturated calomel), and a number of reduction steps.[123,137]

Chemical reductions[123] in THF solutions have produced several crystalline reduced species (Table 14). The best available explanation of these species defines them as Mn^{II} compounds of radical anion ligands, either $bipy^-$ (for the first three) or $bipy^{2-}$ for the Na salt. The magnetism of the compounds containing $bipy^-$ is an interesting theoretical problem.

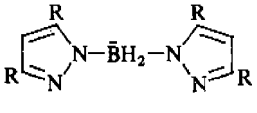
A range of other anionic bidentate ligand compounds also has been described (Table 15), including several $[Mn(N{-}N)_2]^0$ tetrahedra, but these are generally very sensitive to air and the studies so far have been of limited scope. We have real reservations about the dipyrromethane compound: there is little in the report, except stoichiometry, to distinguish it from the tris-Mn^{III} species.



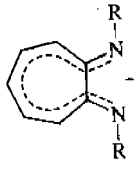
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(41)



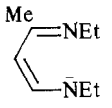
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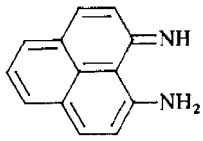
(43)

Table 15 Compounds with Anionic Bidentate Ligands

Ligand	*Mn compound*	*Colour*	*Probable structure*	*Ref.*
(40)	$Mn(L—H)_2(H_2O)_2$			138
(26)	$Mn(L—H)_2L$	Yellow	$[MnN_6]$	118
(41)	$Mn(L—H)_2$?	Dark green	$Mn^{III}—O—Mn^{III}$?	139
(42) R = H, Me	$[MnL_2]$	White	Tetrahedral $[MnN_4]$	140
(43)	$[MnL_2]$		Tetrahedral $[MnN_4]$	141
(44)	$[MnL_2]$			142
(45)	$MnL_2 \cdot 2H_2O$	Dark violet		143



(44)



(45)

41.3.3.3 Terdentate ligands

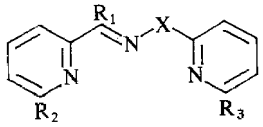
(*i*) *Linear ligands*

The study of the Mn^{II} compounds of the terdentate ligands has generally occurred as an addendum to the study of the compounds of the other metals, the one significant exception being a recent paper by Chiswell and Litster.[144]

Stability constants in aqueous solution are available for dien (bis(2-aminoethyl)amine),[145] bis(2-pyridylmethyl)amine[146] and terpy (2,2′2″-terpyridyl).[147] The determined log K_1's and log K_2's are, respectively: 4.0 and 2.8; 3.5 and 2.6; and 4.4 (K_2 not measured for terpy).

Both 2:1 and 1:1 solid $MnX_2 \cdot nL$ species have been well characterized. The 2:1 species are unexceptionable bis-ligand $[MnN_6]X_2$ octahedra: those with dien are white, and those with the unsaturated heterocyclic ligands related to terpy[144] are generally yellow. Electrochemical studies of the bis-terpy species, and analogues with related ligands,[147] have revealed a series of reduced species, which undoubtedly relate to the Mn^{II}-radical-anion species observed with bipyridyl (previous section).

Monoanions of the ligands (**46** for X = NH), formed by loss of the hydrazone proton, produce neutral molecules $[Mn(N_3)_2]^0$: four of these species have been described, and despite an earlier report to the contrary,[148] they are all high spin.[144]



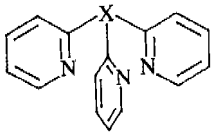
(46)

In the 1:1 compounds $MnLX_2$, five-coordinate monomeric $[MnX_2N_3]$ structures appear to be dominant. Such structures were first seen concurrently in the compounds of pentamethyl-dien (X = Cl, Br),[149] terpy (X = Cl)[150] and paphy (**46** for X = NH, $R_1 = R_2 = R_3 = H$).[151] No full X-ray studies of Mn compounds are available, but powder patterns relate them to known Co and Zn species. Octahedral dimers $[Mn_2X_4L_2]$, and possibly polymers, probably exist also, as postulated by Madden and Nelson[152] for the chloro compound of bis(2-pyridylethyl)amine, but none are yet proven. The most complete study of the $[MnX_2L]$ species[144] produced 58 compounds with X = Cl, Br, I or NCS and L being one of 20 variations on the theme (**46**) or related ligands using quinolyl, benzthiazyl or oxime moieties. They had colours ranging from yellow, through orange, to brown; were all high spin; and X-ray powder patterns of fourteen of them (X = Cl or NCS) showed ten to be isomorphous with the almost certainly five-coordinate Co^{II} analogues, but not with the octahedral Ni^{II} dimers.

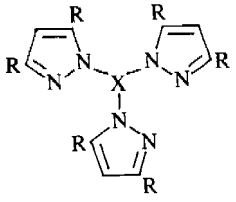
(ii) Tripod ligands

But few compounds of this class have been described. A high spin compound $[MnL_2](ClO_4)_2$ has been described[153] for L = (**47**, X = C—OH) and a compound $[MnCl_2L]$ has been described[154] for L = (**47**, X = N). The latter was thought to be tetrahedral, but seems more likely to be a five-coordinate monomer.

The other ligands studied have been the monoanions (**48**), where R = H or Me, X = GaMe,[155] BH or B-pyrazoyl.[140] These ligands form colourless, high spin $[MnN_6]^0$ octahedral species.



(47)



(48)

41.3.3.4 Quadridentate ligands

(i) Linear ligands

The classical linear tetraamine, triethylenetetraamine (trien), gives a 1:1 species in aqueous solution[156] with a log *K* of only ~5. Such aqueous solutions are very oxygen sensitive. The solid compounds prepared from this ligand and the other linear quadridentates are in Table 16.

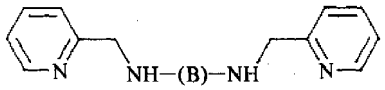
The most common type $MnX_2 \cdot L$, which are yellow, orange or light green in colour, probably are largely octahedral $[MnX_2N_4]$ species. The sterically hindered 3,22,3-tet species[157] were isomorphous with their Fe^{II} analogues, but not with those of the later transition metals, for which five-coordinate [MX(3,22,3-tet)]X structures have been demonstrated: perhaps the larger Mn^{II} and Fe^{II} atoms allow $[MnX_2(3,22,3\text{-tet})]$ octahedral coordination. Also pertinent here is the compound of ligand (**56**): ring closure with formaldehyde to give macrocyclic species (Section 41.3.10) was achieved[162] for the other later transition metals but not for the (larger) Mn^{II}.

The cream or yellow $[Mn_2L_3]X_4$ species are of a type well characterized for such linear quadridentates: they probably have a structure in which each ligand acts as a bridging group between two metals, being bidentate to each, and thus giving two connected $[MnN_6]$ octahedra.

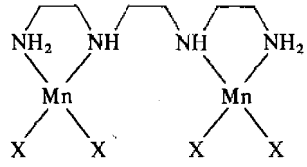
Table 16 Compounds Reported with the Linear Quadridentate Nitrogen Ligands

Ligand	*Compound—defined by X* $MnX_2 \cdot L$	$[Mn_2L_3]X_4$	MnX_2L_2	*Ref.*
trien	Br, ClO_4	Br, BPh_4	Br	156
3,22,3-tet[a]	Cl, Br			157
(**49**), B = $(CH_2)_2$	Cl, ClO_4	ClO_4		158
(**49**), B = $(CH_2)_3$[b,c]	Cl, Br, I, NO_2, NCS, ClO_4	BPh_4		158, 159
(**49**), B = $CH(CH_3)CH_2$	Cl, ClO_4	ClO_4		158
(**51**), B = $(CH_2)_2$	Cl, ClO_4		ClO_4, BPh_4	158
(**51**), B = $(CH_2)_3$	ClO_4	ClO_4, BPh_4		158
(**51**), B = *o*-C_6H_4	ClO_4		ClO_4	158
(**52**), B = $(CH_2)_2$	ClO_4		ClO_4	158
(**52**), B = $(CH_2)_3$	Cl	ClO_4		158
(**53**), $R^1 = R^2 = R^3 = H$	Cl		ClO_4, BPh_4	158
(**53**), $R^1 = R^2$ = Me, $R^3 = H$	Cl, Br, NCS		ClO_4	144, 158
(**53**), $R^1 = R^3 = H$, R^2 = Me			ClO_4	158
(**53**), $R^1 + R^2 = (C_4H_8)$, $R^3 = H$	Cl		ClO_4, BPh_4	158
(**53**), $R^1 = R^3 = H$, $R^2 = Bu^t$	Cl			144
(**53**), $R^1 = R^2 = R^3$ = Me	Cl, Br, NCS			144
(**55**)	ClO_4			160
(**56**), R = H	Cl			161
(**56**), R = Me	Cl, NCS			161

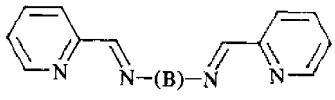
[a] 3,22,3-tet = bis-*N*,*N'*-(3-aminopropyl)piperazine.
[b] This ligand also forms a compound $Mn_2L(N_3)_4$ which is probably of structural type (**50**), but with further polymerization on the azide anion.
[c] A compound $MnLClPF_6$ also has been described.



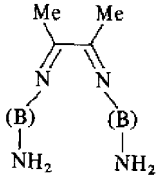
(49)



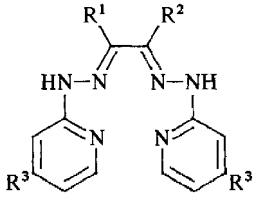
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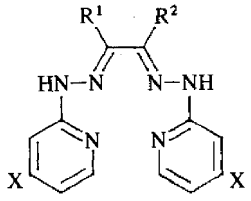
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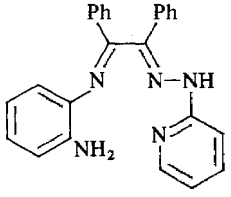
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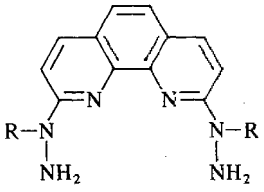
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(54)



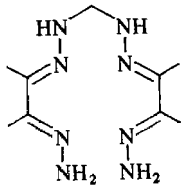
(55)



(56)

But of more interest are the species MnL_2X_2, which are possibly eight-coordinate. They tend to form with the more rigid, planar ligands (but *cf.* trien), and they are all ligands which show cumulative ring strain (C-strain),[163] especially when bound to the larger Mn^{II}. Thus, they are eminently suitable for two of them to fit comfortably, mutually perpendicular, around a manganese(II) atom. As with the tetrakis-bidentates (Section 41.3.3.2) X-ray studies await the collection of suitable crystals.

Ligands (**53**) to (**57**) are capable of losing two protons, to give $[Mn(quad\text{-}2H)]^0$ molecular species, and those of ligands (**53**) to (**55**) have been studied.[160,164] Attempts to prepare them by reaction (3), generally gave mostly MnO_2; but thirteen compounds of the dianions of ligands (**53**), (**54**) and (**55**) have been prepared by irradiating solutions of the ligand and $Mn_2(CO)_{10}$ in THF under N_2. They are generally deep violet to red in colour, the colours arising from ligand based charge transfer transitions, and generally appear to be monomers, rather than dimers with two N—C—N bridges as demonstrated for the Ni^{II} analogues.[165] A few examples of the dimers were found,[164] although, with the larger Mn,[II] they might have been expected to be more common. Perhaps the compound of ligand (**55**),[160] with magnetic moment between 4.8 and 5.4 BM, is a pure dimer of structural type related to the Ni dimer.[165]



(57)

$$Mn(quad)X_2 + 2OR^- \longrightarrow [Mn(quad\text{-}2H)] + 2ROH \quad (3)$$

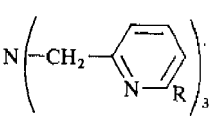
The monomeric Mn^{II} compounds derived from ligands (**53**) and (**54**) appear closely related to [Mn(phthalocyanine)] (Section 41.3.10.2) in their magnetic properties, and some, with temperature independent magnetic moments of near 4.0 BM, appear to be examples of pure $S = \frac{3}{2}$ species.

The reactions of these neutral species with O_2 in pyridine have been studied in depth (see Section 41.3.9.3 for a discussion of the oxygenation of Mn^{II} compounds of multidentate ligands).

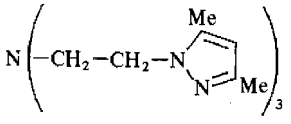
(*ii*) *Tripod ligands*

Me_6tren{tris(2-dimethylaminoethyl)amine} forms[166] five-coordinate species [MnX(Me_6tren)]X, which were among the first five-coordinate Mn^{II} species identified. More recent work has shown that the unsubstituted tren molecule also forms five-coordinate Mn^{II} species:[167] the solid compounds [MnX(tren)]BPh_4 were isolated for X = N_3, Cl, Br, CN, NCS and NCO; and the X-ray structures of the last two have shown a basically [$MnXN_4$]Y structure, although specific H bonding holds the cations in pairs in the solid state. Mn—N(H_2) distances were near 2.2 Å, Mn—N(apical), nearer 2.4 Å and Mn—N(CX) were near 2.1 Å.

Related ligands (**58**, R = H, Me)[146] and (**59**)[168] also have been studied. For the ligand (**58**, R = H), the data in aqueous solution have been interpreted as evidence for an $[MnN_4(H_2O)_3]^{2+}$ seven-coordinate structure.[146]



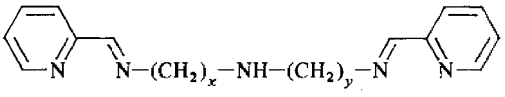
(58)



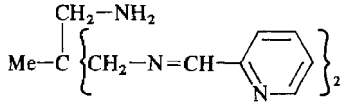
(59)

41.3.3.5 Quinquedentate ligands

The linear aliphatic ligand $(NH_2CH_2CH_2NHCH_2CH_2)_2NH$ forms[169] a 1:1 species in water with log K_1 of 7.0–7.5. Irreversible oxidation occurs in the air, but attempts to isolate Mn^{III} species or solid Mn^{II} species were unsuccessful. Except for several reports of single compounds, with no meaningful structural information, data on compounds of linear quinquedentates are restricted to a report from Coleman and Taylor.[170] They prepared nine compounds of the ligands (**60**) $MnX_2L \cdot nROH$ (X = Cl, Br, I or NCS; R = H, Me or Pr). All were high spin, with colours ranging from yellow to orange; the compounds were soluble in water, methanol, acetone and DMF; and all were said to show no observable reactivity with O_2 or NO, neither in the solid state nor in solution (DMF).



(60)



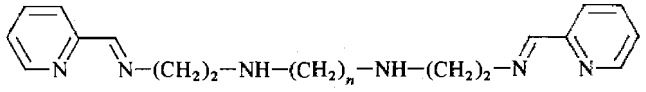
(61)

Early attempts[171] to prepare an Mn^{II} compound of the ligand (**61**) (see Section 41.3.3.6), gave instead white crystals of a compound $MnCl_2 \cdot L$, where L is a partially hydrolysed form (**61**), having lost one pyridylaldimine residue.

41.3.3.6 Sexadentate and septadentate ligands

(*i*) *Linear ligands*

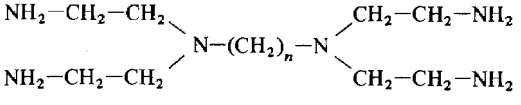
The only report[102] of linear N_6 ligands gave three compounds [MnL]X_2 (X = NCS or I) of the ligands (**62**) (for n = 2 or 3). The bright yellow crystals of the high spin Mn^{II} compounds were stable in air for at least several weeks and do not react with O_2 or NO, neither in the solid nor in solution.



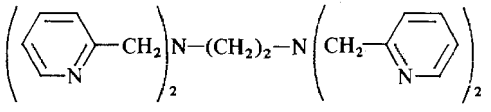
(62)

(ii) Bifurcated ligands

Data are available on the ligands (**63**) (for $n = 2$ or 3) and (**64**). Ligand (**63** for $n = 2$) forms a 1:1 species in water with log K_1 of 9.3 and the solution data have been interpreted[169] as evidence for a seven-coordinate polyhedron $[Mn(N_6)H_2O]^{2+}$, comparable with that proven for $[Mnedta(H_2O)]^{2-}$ (Section 41.3.9.5). Given the steric constraints of this amine ligand, it may be possible to obtain [MnLX]X species here.



(63)



(64)

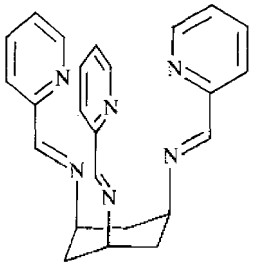
By contrast, the ligand (**63** for $n = 3$) has a log K_1 of only 5.3 and it readily forms binuclear species $Mn_2(N_6)^{4+}_{aq.}$ in water.

The pyridyl ligand (**64**), however, has a log K of 10.27 and the solid compound $[MnL](ClO_4)_2 \cdot H_2O$ has been isolated as yellowish needles.[146] Available data were interpreted as indicating an $[MnN_6]$ octahedral structure, with the water molecule not bonded to the metal.

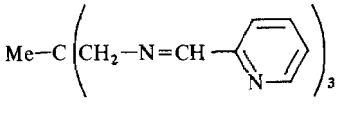
(iii) Tripod ligands

The ligand $Et—C(CH_2NHCH_2CH_2NH_2)_3$ has a log K_1 of 8.2 in water: no solid derivatives have been reported.[169]

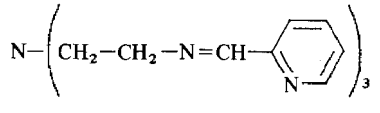
But the more interesting tripod ligands (**65**) to (**67**) are those which induce trigonal prismatic six-coordination and seven-coordination on Mn^{II}. Ligands (**65**) and (**66**) present their donor atoms at positions for trigonal prismatic rather than octahedral coordination, and, whereas the Mn^{II} d^5 high spin metal atom, in its yellow compounds, is largely content to accept the ligand's geometry, the later transition metals induce ligand distortions to approach octahedral geometry.[172]



(65)



(66)



(67)

The closely related ligand (**67**) is potentially septadentate, and although full details are not published, it seems that the Mn^{II} compound is indeed seven-coordinate, with an Mn—N (apical) distance of 2.79 Å.[173]

41.3.3.7 Uses of manganese nitrogen compounds

The following lists some of the more significant uses of the compounds noted in Section 41.3.3.

Manganese(II) nitrogen species, and especially $Mntrien^{2+}_{aq.}$, show strong catalytic activity towards the decomposition of H_2O_2 (only iron compounds seem more effective), and are used to accelerate the photopolymerization of vinyl monomers, in the presence of CCl_4.[156]

Some of the tetrakis compounds of substituted pyridines $[MnX_2L_4]$, especially where X = NCS, form clathrates with hydrocarbons, such as xylenes, cumenes, mesitylene, *etc.*; and specific compounds have been used to separate isomers of these hydrocarbons.[88]

Various nitrogen compounds have found use in corrosion inhibition, as fire-proofing agents for epoxy resins and flame retardants for polyurethane foams. For these and other uses, the reader is referred to the indices of *Chemical Abstracts*. One recent report[174] tells of the use of Mn^{II} chelates of phenanthroline and bipyridyl as contraceptive and antivenereal agents. The antibacterial and antifungal properties of these compounds have long been known.[175]

41.3.4 Phosphorus, Arsenic, Antimony and Bismuth Ligands

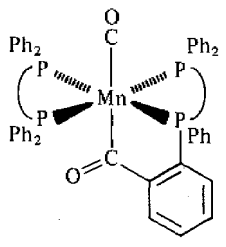
Although many tertiary phosphine, and to a lesser extent arsine, compounds of Mn^{I} have been known for many years, the corresponding complexes of Mn^{II} are relatively rare. The preference of Mn^{II} for oxygen, nitrogen and halogen donors has meant that few compounds with the heavier Group V donor atoms have been isolated. However, recent work demonstrates that, given anhydrous conditions, simple Mn^{II} salts will interact with tertiary phosphines to give compounds with a Mn^{II}—P bond.

Although the compounds $[Mn(PPh_3)_4]X_2$ (X = halogen), $[MnX_2(EPh_3)_2]$ (X = halogen; E = P or As),[176] and $[MnX_2(diars)_2]$ (X = halogen; diars = *o*-phenylenebisdimethylarsine)[177] were reported some years ago, work since then has indicated that in these original preparations, the actual ligands were phosphine or arsine oxides, *i.e.* that the Group V donor had oxidized in solution by reaction with oxygen.[178,179,180]

The lack of early success in obtaining tertiary phosphine and arsine compounds by direct interaction of the relevant ligands with Mn^{II} halides, led to the use of preparative methods incorporating oxidation of suitable Mn^{I} carbonyl compounds. Thus $[MnBr_2(CO)_2(diars)]$ was obtained by bromine oxidation of $[MnBr(CO)_3diars]$,[181] while $[Mn(CO)_2(dppe)_2]^{2+}$ (dppe = 1,2-diphenylphosphinoethane) was prepared by oxidation of $[Mn(CO)_2(dppe)_2]^{+}$ with nitric acid.[182] Such Mn^{II} carbonyl compounds were shown by infrared studies to possess *trans*-carbonyl structures and this fact was used to explain why the Mn^{I} compounds $[Mn(CO)_3TP]^{+}$ and $[Mn(CO)_2QP]^{+}$ {TP = bis(*o*-diphenylphosphinophenyl)phosphine; QP = tris(*o*-diphenylphosphinophenyl)phosphine}, in which the carbonyls must be in the *cis* configuration, could not be oxidized to give stable Mn^{II} compounds.[183]

A further example of the preparation of stable Mn^{II} phosphine and arsine compounds is shown by the oxidation with $NOPF_6$ in benzene of *trans*-$[MnBr(CO)_3L_2]$ (L = PMe_2Ph or $AsMe_2Ph$) and *cis*-$[MnBr(CO)_3L_2]$ (L_2 = dppe or L = $AsMe_2Ph$) to yield *fac*-$[MnBr(CO)_3L_2]^{+}$.[184]

Nevertheless, the complexity of the interaction of dppe with $Mn_2(CO)_{10}$ is a warning to those who postulate invariant ligand integrity in reactions. Although this reaction was originally claimed to yield three products, *viz.* $[Mn(CO)_2(dppe)_2][Mn(CO)_5]$, $Mn(CO)_3dppe$ and $Mn(CO)(dppe)_2$, an X-ray crystal study has shown that the last of these three compounds should be formulated as a Mn^{I} compound with a carbonyl-insertion reaction occurring between one of the phenyl rings on one of the phosphorus atoms and the manganese atom to yield a terdentate ligand (**68**).[185]



(68)

The early work on bidentate phosphine compounds of manganese was reviewed in 1972.[186] More recent preparations of the compounds $[MnX_2(diars)_2]$, and preparations of similar compounds with the ligand *o*-phenylene(dimethylarsine) (dimethylstibine), have indicated that if care is taken in

Table 17 Bond Lengths for $[MnCl_2(diphos)_2]^{n+}$ Compounds

Compound $[MnCl_2(diphos)_2]^{n+}$	*Bond Lengths* (Å) *Mn—Cl*	*Mn—P*
Mn^{II}, $n = 0$	2.502	2.625
Mn^{III}, $n = 1$	2.239	2.345
Mn^{IV}, $n = 2$	2.195	2.428

excluding water from the reactions, these compounds, and not the arsine oxides, can be prepared;[187] however, compounds of the two tertiary stibines, $Me_2Sb(CH_2)_3SbMe_2$ and $C_6H_4(SbMe_2\text{-}o)_2$ could not be obtained under similar conditions.

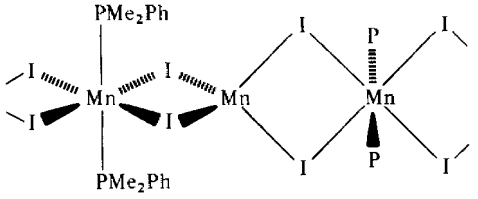
Other workers[180] have reported that the tertiary diphosphine, *o*-phenylenebis(dimethylphosphine) (diphos) reacts with anhydrous manganese(II) halides to yield yellow octahedral compounds of type $[MnX_2(diphos)_2]$ (X = Cl or Br), in which the halogens have a *trans* configuration. Unlike the corresponding diarsine compounds,[187] these diphosphine compounds are readily oxidized to octahedral orange Mn^{III} and then orange-brown Mn^{IV} species by the reactions: $[MnX_2(diphos)_2] + Ph_3CPF_6 \rightarrow [MnX_2(diphos)_2]^+$; $[MnCl_2(diphos)_2]^+ + HNO_3 \rightarrow [MnCl_2(diphos)_2]^{2+}$. The X-ray structures of all three chloro compounds have been reported[188] and are of particular interest as this work allows a rare direct comparison of changes in metal–ligand bond lengths with changes in metal oxidation state (Table 17). The reduction in Mn—Cl bond length with increase in positive charge on the metal is clearly observable, as is the decrease in Mn—P bond length in going from Mn^{II} to Mn^{III}. The unexpected increase in Mn—P bond length when Mn^{III} is oxidized to Mn^{IV} is found to be due to the closer chlorines in the latter compound 'pushing away' the phosphine methyl groups.

Trans-bromo structures are also found in the similar ditertiary phosphine bidentate complex $[MnBr_2(dmpe)_2]$ (dmpe = 1,2-bis(dimethylphosphino)ethane);[28] the Mn—P bond length in this compound (2.655 Å) being comparable with that found in $[MnCl_2(diphos)_2]$ (2.625 Å). The reaction of $[MnBr_2(dmpe)]$ with $LiAlH_4$ yields a Mn^I compound of stoichiometry $Mn(AlH_4)(dmpe)_2$ (Section 41.2.4).

The reactions of anhydrous manganese(II) halides with unidentate tertiary phosphines, R_3P, have been reinvestigated, and it has been shown that polymeric compounds, of formulation $MnX_2(PR_3)$ (X = halogen or thiocyanate), can be isolated from tetrahydrofuran solutions.[189] These compounds, isolated for a large range of phosphines, but excluding triphenylphosphine,[190] undergo reversible oxygenation in both the solid state and in solution yielding deep red, blue, purple or green compounds of type $MnX_2(PR_3)O_2$. A typical example is $MnBr_2(PBu^n_3)$ for which a dioxygen binding isotherm similar to that shown by myoglobin is claimed.[189] There appears to be no dioxygen bond breakage during these oxygenation reactions.[191]

Equilibrium data for the oxygen absorption have been deduced, and it is claimed that, for example, $[MnI_2(PBu^n_3)]$ will reversibly absorb and desorb completely one mole of dioxygen per mole of complex for more than 400 times, if the reaction is carried out in solution at −20 °C. In the solid state only the thiocyanato compounds of formulation $[Mn(NCS)_2(PR_3)]$ (where R = alkyl) reversibly bind oxygen.[192]

It has been shown[193] that the X-ray structure of the compound $MnI_2(PMe_2Ph)$ is polymeric with alternating octahedral and tetrahedral Mn^{II} entities (**69**). However, full details of the structure are as yet unknown. Binding of dioxygen in the solid state must be, one assumes, into the lattice structure of the crystalline compound. Thus crystal structures are most important in ascertaining how the gas molecules fit into the lattice.

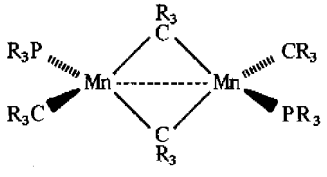


(69)

These oxygenation reactions have been hailed as being of great importance[4] but the findings have been challenged by other workers,[194] who had not been able to isolate other than Mn^{II} tetrahydrofuran complexes from supposedly identical reaction procedures.[195]

Claims[192,196] with no details supplied yet, that many of the compounds of type $[MnX_2(PR_3)]$ reversibly bind not only dioxygen, but carbon monoxide, carbon dioxide, nitric oxide, sulfur dioxide and ethylene as well as dihydrogen, would appear to indicate that these polymeric complexes are a most versatile form of molecular sieve if the reactions proceed in the solid state. What may be the nature of binding of such a diverse group of molecules to the metal compounds is difficult to conceive. A further unresolved problem of the work lies in the results which indicate that reversible oxygenation occurs for many compounds both in solution as well as in the solid state. It is obvious that the mechanisms for oxygenation must be entirely different in these two situations even if in both cases each molecule of the compound can bind one dioxygen molecule.

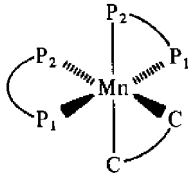
The stabilization of Mn^{II}–alkyl and Mn^{II}–aryl bonds by use of tertiary phosphines has been shown by the ability of $[Ph_2MnP(cyclohexyl)_3]$ to undergo various insertion reactions, *e.g.* CO insertion to give $[(PhCOO)_2MnP(cyclohexyl)_3]$.[67] Further work[64] of great interest has shown that Mn^{II} dialkyls yield orange or yellow dimeric compounds of general type $[Mn_2R_4(PR_3)_2]$ (R = CH_2SiMe_3, CH_2CMe_3 and CH_2Ph) (**70**) when interacted with a number of unidentate tertiary phosphines. The X-ray structures of three compounds of this type have been shown to possess two asymmetrically bridging alkyl groups, with an additional terminal alkyl and one phosphine per manganese atom. In the presence of excess tertiary phosphine in light petroleum, the orange solutions of these dimeric compounds fade to a pale yellow colour. ESR spectra showed that monomers form due to a cleavage reaction (4).



(70)

$$[Mn_2(CH_2CMe_2Ph)_4(PMe_3)_2] + 2PMe_3 \rightleftharpoons 2[Mn(CH_2CMe_2Ph)_2(PMe_3)_2] \quad (4)$$

The X-ray crystal structure of this colourless monomer shows that it has a severely distorted tetrahedral geometry; the compound is high spin with a magnetic moment of 5.9 BM. Monomeric compounds of this type readily lose phosphine to re-form the dimer, but they can be stabilized by use of the bidentate phosphine, 1,2-bis(dimethylphosphino)ethane (dmpe) to replace the two unidentate phosphine moieties. On the other hand, if the two unidentate alkyl moieties are replaced by the bidentate ligand *o*-xylylene (o-$(CH_2)_2C_6H_4$), a low spin octahedral compound $Mn[o$-$(CH_2)_2C_6H_4](dmpe)_2$ (**71**) can be prepared. The metal–ligand bonds in this low spin compound are all noticeably shorter than those in the tetrahedral high spin monomer (Table 18).



(71)

Table 18 Mn—Ligand Bond Lengths (Å) for High Spin $[Mn(CH_2CMe_2Ph)_2(PMe_3)_2]$ (A) and Low Spin $[Mn(o$-$\{CH_2\}_2C_6H_4)(dmpe)_2]$ (B)

Mn—L Bond	*Compound A*	*Compound B*
Mn—C	2.149	2.110 and 2.104
Mn—P	2.633	2.230 (Mn—P_1)*
		2.297 (Mn—P_2)

* see (71).

Other work[197] in the area of Mn^{II} alkyls has led to the disproportionation of Mn^{III} to yield Mn^{II} and Mn^{IV} species in the reaction (5).

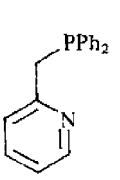
$$[Mn(acac)_3] + dmpe + MeLi \xrightarrow[-78°C]{EtOEt} [MnMe_2(dmpe)_2] + [MnMe_4(dmpe)] \quad (5)$$

Phosphide compounds of manganese(II) have also been isolated. The tetra(diphenylphosphide)-manganate(II) ion has been prepared by the reaction sequence (6),[198] while in liquid ammonia at −75 °C '$[(Mn(NCS)_2(NH_3)_4]$' is claimed to react with $KPPh_2$ to yield either colourless $Mn(PH_2)_2 \cdot 3NH_3$ or $K_2[Mn(PH_2)_4] \cdot 2NH_3$.[199]

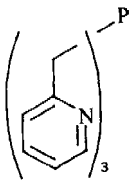
$$MnX_2 + KPPh_2 \cdot 2dioxane \xrightarrow{THF} KMn(PPh_2)_3 \xrightarrow{recryst.} K_2[Mn(PPh_2)_4] + Mn(PPh_2)_2 \quad (6)$$

(X = halide)

The Mn^{II} to phosphorus or arsenic bond can also be stabilized by use of hybrid multidentate ligands containing one or more nitrogen donors. Two early examples of compounds in which both nitrogen and phosphorus were bound to the Mn^{II} are:
(i) $[Mn(N—P)_3]Br_2$, (N—P = **72**);[200] (ii) the apparently five-coordinate $[Mn(N_3—P)Cl]Cl$, (N_3—P = **73**).[201]

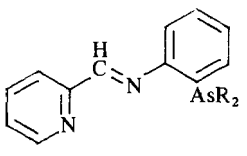


(72)



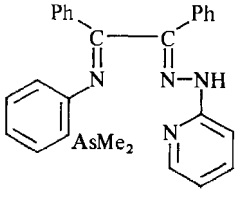
(73)

The linear terdentate hybrid ligands (**74**) with the donor set N—N—As, also yield compounds of the types $[MnX_2(N—N—As)]$ (X = Cl, Br or I), $[Mn(N—N—As)_2](ClO_4)_2$ and $[Mn(NCS)_2$-(N—N—As)], in which all three donor atoms appear to be bonded.[202] Similarly, all four donors of the quadridentate N—N—N—As ligand (**75**) appear to be coordinated in the compound [Mn-(N—N—N—As)], as in which both an imine proton and an arsenic methyl group are lost upon reaction of the ligand with $Mn_2(CO)_{10}$.[160]

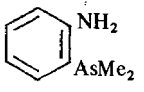


R = Me or Et

(74)



(75)



(76)

The simple bidentate N—As ligand (**76**) yields the compounds $[MnBr_2(N—As)]$ and $[Mn$-$(N—As)_2](ClO_4)_2$ in which both donors are bound.[203]

41.3.5 Oxygen Ligands

Although the lowest limiting oxidation state for all oxygen ligands, Mn^{II} is also, on balance, the most stable. This comment is certainly true for neutral, and especially acid aqueous solutions, and, although alkaline solutions are oxidized by O_2, this is at least partially because of very low solubilities of the higher oxides, especially MnO_2.

Despite the importance of this area of Mn^{II} chemistry, we still have much to learn about basic structural preferences: the variety of polyhedra adopted; their relative importance, distortions of

them and the energy costs of such distortions. Available data, however, do suggest that non-directional, ionic bonding predominates in the Mn—L bond, even though covalency is not negligible.

A consequence of the predominantly ionic bonding is that effects on the ligands of Mn—L bonding, and therefore the energy profiles of the ligand vibrations, are not very different from the effects of H-bonding and 'non-bonded' interactions in crystalline solids. Thus attempts to define stereochemistries by vibrational methods are unreliable, a view that is strongly reinforced by the variety and complexity observed, for example, in the carboxylate compounds (Section 41.3.5.2.ii). We make no further apology for giving prominence in the following to the X-ray structural data.

41.3.5.1 Unidentate ligands

(*i*) *Water, hydroxide and oxide*

There is little doubt that the basic species formed when almost any compound MnX_2 is dissolved in water[204,205] is $[Mn(H_2O)_6]^{2+}$. It is seen in various crystalline solids, and the solution data give no real hint that we need to suspect the other coordination polyhedra, either higher or lower, are present in the aqueous solutions. So, $[Mn(H_2O)_6]^{2+}$ it is—mainly on the basis[205] of the optical spectra and correlation with the crystalline solids. In this respect, we note that XAFS studies on aqueous solutions derive an Mn—OH_2 distance of 2.18 Å, in good agreement with the observed distances in solids (Table 1).

The rate of exchange of bonded water with bulk solvent gives evidence that the process is *associative*, that is, it occurs through a seven-coordinate intermediate.[205] The two reported determinations give (averaged) kinetic parameters of: $k_1 = 2.15 \times 10^7\,s^{-1}$; $\Delta H^* = 7.8$ kcal mole^{-1}; $\Delta S^* = 1.2$ cal mole^{-1} K^{-1}; and $\Delta V^* = -5.4$ ml mole^{-1}. It is the negative ΔV^* which implies the associative mechanism. In the competition between a longer Mn—OH_2 bond favouring dissociation, and the greater space, made available by the longer bonds, favouring association, it appears that the latter wins. We can only notice the result and correlate it with the greater tendency shown by Mn^{II} to form seven-coordinate polyhedra.

All aqueous solutions of MnX_2 are, of course, further complicated by the formation of $[MnX_n(H_2O)_{6-n}]^{(2-n)+}$ species, and a perusal of the reported stability constants for these[206] indicates that they are formed to much the same extent as for the other first row transition metals. They are, however, less evident because of the lack of colour in the solutions. Such species also are encountered in X-ray structural analyses of Mn^{II} compounds. The species with $n > 2$ are formed in water in significant concentrations only in the presence of an excess of anion.

The 'hydrolysis' of Mn^{2+}_{aq} parallels that of its nearest neighbours Cr^{2+} and Fe^{2+}; at pH as low as 3.5, proton transfer to solvent, forming $[Mn(OH)(H_2O)_5]^+$ occurs, and the limiting value at low pH for K_h has been measured (25 °C) as 5×10^{-5} mole l^{-1}. At higher pH, polymerization (apparently dimerization) occurs,[207] leading eventually to the precipitation of solid, polymeric $Mn(OH)_2$.

$Mn(OH)_2$ is a well-characterized, stoichiometric, crystalline compound with the hexagonal $Mg(OH)_2$ structure. Although preparations of it require careful exclusion of O_2, the pure, isolated solid has good stability in the air; it occurs naturally (pyrochroite); and finds use as an industrial catalyst. It is weakly amphoteric, and can be recrystallized from hot, concentrated alkali solutions. This, of course, implies the formation of hydroxo and/or oxomanganates(II), and, indeed, solid, yellow $Na_2[Mn(OH)_4]$ has been desscribed,[208] as have $Ba_2Mn(OH)_6$ and $Sr_2Mn(OH)_6$.

Little is known of the 'basic salts':[209] Mn(OH)Cl has been decribed in two crystalline forms, which are said to have layer structures related to $Mg(OH)_2$; and the compounds $Mn_2(OH)_3X$ (X = Cl, Br, I) also are known, with the chloro compound again in two different crystalline forms, one of which occurs in the mineral kempite, isotypic with δ-$Cu_2(OH)_3Cl$. Crystalline phases containing both OH^- and oxyanion ligands are covered in Section 41.3.5.2.

Manganese(II) oxide exists in only one modification under normal conditions, and this has the simple rock salt cubic structure.[210,211] In addition, Mn^{II} occurs in some of the other binary oxides, and in a wide range of mixed oxides (Table 19). Most of these have been studied mainly for their magnetic and electrical properties, but we are here interested in any light they can shed on the structural preferences of Mn^{II}. Table 19 summarizes available data, referring largely to species for which three-dimensional refinements give bond length data, and confirm structures implied by symmetry and unit cell data. The area of interest shades imperceptibly into the compounds of the oxyanions, which we have separated into Tables 22–25.

The data show that Mn^{II}, unlike Mn^{IV} and some of the other metals, is not particularly fussy about

Table 19 Manganese(II) Coordination Polyhedra in Oxides and Hydroxides[a]

Phase	*Mn^{II} Polyhedra*		*Comments*
MnO	$[MnO_6]$ Octahedra	2.223 Å	Cubic, rock-salt structure
Mn_3O_4 α	$[MnO_4]$ Tetrahedra	2.07 Å	Hausmannite, $(MnO \cdot Mn_2O_3)$
Mn_5O_8	$[MnO_6]$ Trigonal Prism	3×2.13 Å 3×2.30 Å	$(2MnO \cdot 3MnO_2)$ $Cd_2Mn_3O_8$ type
MnM_2O_4	$[MnO_4]$ Tetrahedra	~2.03 Å [Cr]	Normal, cubic spinels M = Al, Ti, V, Cr
$MnMO_3$	$[MnO_6]$ Octahedra	2.10–2.26 Å	M = Ge, Sn, Ti
Mn_2MO_4 α-Ge	$[MnO_6]$ Octahedra	Two sites	Normal temperature and pressure, olivine type
β-Ge	$[MnO_6]$ Octahedra		High temperature and pressure, isotype with Co
δ-Ge	$[MnO_7]$	6(2.15–2.33) + 2.73 Å	High temperature and pressure
α-Ti	$[MnO_4]$ Tetrahedra	2×1.93; 2×1.95 Å	$Mn^{II}(Mn^{II}M^{IV})O_4$ spinel
	$[MnO_6]$ Octahedra	2.08–2.50 Å	
Sn	$[MnO_4]$ Tetrahedra		$Mn^{II}(Mn^{II}M^{IV})O_4$ spinel
	$[MnO_6]$ Octahedra		
$Mn_2V_2O_7$	$[MnO_6]$ Octahedra	2.13–2.30 Å	
$MnMO_4$	$[MnO_6]$ Octahedra	2.09–2.25 Å	M = Mo, W, U
MnM_2O_6	$[MnO_6]$ Octahedra	2.01–2.36 Å	M = Nb, Ta
$Mn_4Nb_2O_9$	$[MnO_6]$ Octahedra	1.99–2.23 Å	
$BaMn_2O_3$	$[MnO_5]$ Trigonal bipyramid	2.07–2.20 Å	
$Na_{14}(MnO_4)_2O$	$[MnO_4]$ Tetrahedra	2.09 Å	
$Mn_2Mo_3O_8$	$[MnO_4]$ Tetrahedra		Mg, Fe, Co, Ni, Zn and Cd isostructural
	$[MnO_6]$ Octahedra		
$Mn_2(Sb, Fe)O_3$	$[MnO_6]$ Octahedra	2.11–2.31 Å	
$Mn_8O_{10}Cl_3$	$[MnO_8]$ Cube	2.32 Å	Also $[Mn^{II}Cl_6]$ and Mn^{III} octahedra
$A_2Mn_3B_2O_2$	$[MnO_4]$ Planar	2.08–2.18 Å	(A = Sr, Ba; B = As, Sb, Bi)
Mn_2TaO_3	$[MnO_6]$ Trigonal prism	2.36 Å	Is this Ta^{II} or a lower (average) oxidation state for Mn?
$Mn_3A_2Ge_3O_{12}$	$[MnO_6]$ Octahedra		Garnet structure (A = Al, V)
	$[MnO_8]$ Dodecahedra		
$Mn(OH)_2$	$[MnO_6]$ Octahedra	2.207 Å	Isotype of $Ca(OH)_2$
$MnSn(OH)_6$	$[MnO_6]$ Octahedra	2.17 Å	
$Mn_2K(CrO_4)_2OH \cdot H_2O$	$[MnO_6]$ Octahedra		Isotype of $Cu_2Na(SO_4)_2 \cdot OH \cdot H_2O$

[a] Data for this table were obtained from the Gmelin volumes or from 'Structure Reports'.

its neighbours — neither their number, nor their arrangement. Certainly, $[MnO_6]$ octahedra are predominant, deriving from the occupation of the octahedral holes of close-packed oxygens. But often these octahedra are quite distorted, with Mn—O distances ranging from 1.99 to 2.50 Å and individual angular distortions of at least 15°. And four-planar, four-tetrahedral, five-, six- trigonal prismatic, seven- and eight- (both cubic and dodecahedral) coordinate polyhedra are observed; and most of these now have parallels in the more discrete coordination polyhedra upon which coordination chemists have largely concentrated to date.

(*ii*) *Monohydric alcohols, alkoxides and phenoxides*

Solutions of MnX_2 in the alcohols give $[Mn(ROH)_6]^{2+}$ species,[212] and these cations have been isolated as crystalline solids for R = Me, Et. In more concentrated solutions, the species $[MnX_n(ROH)_{6-n}]^{(2-n)+}$ have been detected by EPR and ^1H NMR spectra. The alcohol ligands are easily replaced by water.

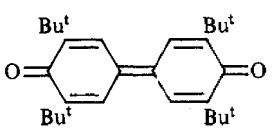
A number of other crystalline solids of type $MnX_2 \cdot n$ROH also have been isolated for primary alcohols, methyl to pentyl, (but not a secondary or tertiary alcohol) and $n = 1$ to 4, but not necessarily an integer. Many appear to be variations on MnX_2 polymeric systems, with ROH donors, as are the only two of known structure: $Mn_2Cl_4 \cdot 3EtOH$ consists of polymeric chains of alternating *cis*-$[MnCl_4(EtOH)_2]$ and $[MnCl_5(EtOH)]$ octahedra;[213] whilst $Mn_5Cl_{10} \cdot 14EtOH$ has three different Mn octahedra making up chains[214] of *trans*-$[MnCl_2(EtOH)_4]$, *cis*-$[MnCl_4(EtOH)_2]$ and *mer*-$[MnCl_3(EtOH)_3]$ (Mn—O distances range from 2.16 to 2.21 Å in the two structures).

Mn^{II} alkoxides and phenoxides have been studied only quite recently. Druce[215] reported two $Mn(OR)_2$ species in 1937, and the pale pink, insoluble $Mn(OMe)_2$ was described[216] in 1966, but the only reasonably complete study is that reported[217] by Horvath *et al.* in 1979. They prepared a total of eighteen solid alkoxides and six phenoxides by reaction (7). These ranged from amorphous polymers and gelatinous fibres to crystalline species. The pale coloured polymers were assigned octahedral $[MnO_6]$ structures, but some of the more crystalline species were more reactive, soluble in common organic solvents, and were thought to be monomers or 'loosely associated'. Wilkinson and co-workers, however, have shown[218] that $Mn(OBu^t)_2$ is trimeric in freezing benzene, and drew parallels with the three- and four-coordinate oligomeric alkyls (Section 41.3.2.2). It seems likely that few, if any, of these alkoxides or phenoxides will turn out to be two-coordinate monomers.[217] In a number of cases, Horvath *et al.* observed compounds $Mn(OR)_2 \cdot n$L (where L = py or THF) and characterized two yellow phenoxides $[Mn(OR)_2(THF)_2]$. All of these alkoxides were extremely air-sensitive, especially when wet, and, with traces of O_2, all the pale coloured products darken to brown or black materials. Several are pyrophoric, and the ethoxide reacts explosively with excess O_2. The solid 2,6-di-*t*-butylphenoxide reacts with controlled amounts of O_2 to give a green intermediate, which may be a compound of dioxygen, and recalls the interesting phosphine work of McAuliffe and co-workers (Section 41.3.4). Further reaction with O_2 gives a black material, from which the purple quinone (**77**) can be isolated in 76% yield.[217]

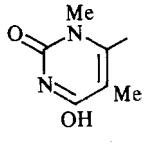
$Mn\{Al(OPr^i)_4\}_2$ is a light brown viscous liquid, which can be distilled *in vacuo* and is monomeric in boiling benzene.[219]

Within the phenoxide class, there is a compound with a four-coplanar $[MnO_4]$ polyhedron: in $[Mn\{Pt(NH_3)_2(L^-)_2\}_2]Cl_2 \cdot 10H_2O$ {where L^- is the anion of 1-Me-thymine (**78**)} the thymines are N-bonded to Pt and each Pt moiety is bidentate to a central Mn^{II}, so that the latter is bonded to four phenoxides in a planar array.[220]

$$Mn\{N(SiMe_3)_2\}_2 + ROH \longrightarrow Mn(OR)_2 + 2HN(SiMe_3)_2 \qquad (7)$$



(77)



(78)

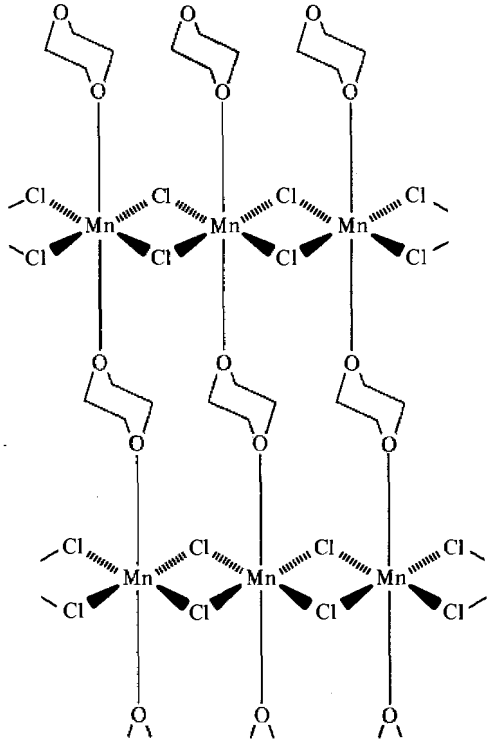
(iii) Ethers

It is clear, from the behaviour of various MnX_2 species in diethyl ether,[221] that the ether molecules bind to the metal, although no significant crystalline solid compounds have been isolated and characterized, at least partially because of the volatility of the ether.

Two other commonly used solvent ethers (THF and dioxane), both of which have less significant steric problems, form somewhat more robust species.

For the solid compounds $MnX_2 \cdot 2THF$ (X = Cl, Br, I, NCS) the data,[221,222] at least for the halides, are consistent with an expected chain polymeric structure of type (**8**). The same proposed *trans*-$[MnX_4O_2]$ polyhedron is observed[223] in the crystal structure of $[Mn\{Ti^{III}(Cp)_2Cl_2\}_2(THF)_2]$, in which the *trans* THF oxygens are at 2.227(3) Å. The hexakis species $[Mn(THF)_6][SbCl_6]_2$ seems to be the only known compound with an all-ether $[MnO_6]^{2+}$ polyhedron.[224] A previously described perchlorate[221] is probably $[Mn(THF)_4(H_2O)_2](ClO_4)_2$.

Although capable of bidentate function to one metal, steric and conformational preferences generally seem to dictate that dioxane[221] acts either as a unidentate ligand or that it bridges two different metals, as in (**79**). The compound $MnCl_2 \cdot$ dioxane, for which (**79**) is the proposed structure, is not affected by six hours in vacuum at 100 °C! Other known $MnX_2 \cdot n$ dioxane species include those defined by $n = 1$, for X = ClO_4, NCS and NCSe, and $n = 2$ for X = Br and I, and some mixed aquo–ether compounds.[221]



(79)

(iv) Carbonyl ligands

The most commonly described class is that of the octahedral compounds $[ML_6]X_2$, which are summarized in Table 20. All appear to be simple octahedral cationic species, although only the pyrone and 4-butyllactam compounds have been shown to be isomorphous with a reliably octahedral Ni^{II} analogue. Robustness varies from the aldehydes, which rapidly turn brown, even if kept below 0 °C, to the lactam, which is 'stable to air and light, and moderately stable to heat'; but all are rapidly attacked by water.

In parallel with some of the nitrogen ligand compounds, a few of these carbonyl ligands give crystalline species $MnX_2 \cdot nL$, where $n > 6$. These include X = NCS, $n = 8$ and X = Br or I, $n = 10$ for urea;[225] and X = $SbCl_6$, $n = 7$ for 4-chlorobenzaldehyde.[226]

Table 20 Carbonyl Ligand Compounds $[MnL_6]X_2$

Ligand Class	*Specific Ligands*	X^-	*Ref.*
Aldehydes	Acet-, propion- and benz-aldehyde	$FeCl_4$, $InCl_4$	a
	2-Cl, 4-Cl and 4-Me-benzaldehyde	$SbCl_6$	226
Ketones	Acetone, chloroacetone, methylethylketone and acetophenone	$FeCl_4$, $InCl_4$	a
	2,6-Dimethyl-4-pyrone	ClO_4, BF_4	b
Esters	Methyl formate	$FeCl_4$, $InCl_4$	c
	Ethyl acetate	$SbCl_6$	c
Amides	Dimethylformamide, acrylamide	ClO_4	d, 231
Lactams	6-Capro and 4-butyl-lactam	ClO_4	e, f
Ureas	Urea, *t*-butyl-, dimethyl- and diethyl-urea	Br, I, ClO_4, NO_3	225, g, h

[a] W. L. Driessen and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 977; 1971, **90**, 87 and 258.
[b] A. De Jager, J. J. De Vrieze and J. Reedijk, *Inorg. Chim. Acta*, 1976, **20**, 59.
[c] W. L. Driessen, W. L. Groeneveld and F. W. van der Way, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 353.
[d] W. Schneider, *Helv. Chim. Acta*, 1963, **46**, 1842.
[e] S. K. Madan and H. H. Denk, *J. Inorg. Nucl. Chem.*, 1965, **27**, 1049.
[f] S. K. Madan and J. A. Sturr, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1669.
[g] A. Kircheiss, U. Pretsch and U. Borth, *Z. Chem.*, 1980, **20**, 349.
[h] B. C. Stonestreet, W. E. Bull and R. J. Williams, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1895.

Compounds $MnX_2 \cdot 4L$ are described only for amides and ureas:

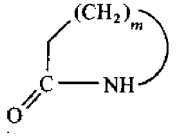
dimethylacetamide (X = NCS, ClO_4)[227,228] with the former being isomorphous with the Ni^{II} analogue and octahedral;

the lactams (**80**) (m = 5, 7 and 11; X = NCS)[229] — similar compounds are formed by Ni, Cu and Zn, but Co and Cd form $[ML_6][M(NCS)_4]$;

formamide (X = Cl),[230] and acrylamide ($X = NO_3$);[231]

urea (X = NCS, Cl, Br)[225,232] — an unrefined X-ray structure[233] proves the *trans*-octahedral structure for X = NCS;

dimethyl- and diethyl-ureas (X = NCS).[225]



(**80**)

Only three $MnX_2 \cdot 3L$ compounds have been described[234–236]: $[MnBr_2(dimethylurea)_3]$ has a five-coordinate structure[234] with Mn—O at 2.04 and 2.18 Å; and $[MnCl_2(propionamide)_3]$ and $[MnCl_2(4\text{-butyllactam})_3]$ probably have a similar structure. A more exhaustive study of these ligand systems will probably produce more such five-coordinate species.

Well-defined crystalline compounds $MnX_2 \cdot nL$ for n = 2, 1 and < 1 also are described.[227,230,232,237] Most are apparently polymers of types (**8**) and (**13**), although tetrahedral $[MnX_2L_2]$ species may eventually be identified. A different polymer, with *cis* unidentate ethylacetates, at 2.17 and 2.24 Å, has been identified[238] in $[Mn(PO_2Cl_2)_2(ethylacetate)_2]$.

(*v*) *Ligands with NO, PO, AsO, SO and SeO groups*

With possible minor exceptions in the case of RNO_2, all of these ligands provide a single oxygen donor atom and all form similar compounds. The numbers of known compounds for the different ligand types are summarized in Table 21, both as an indication of areas of concentration of effort and an entry to the literature. Unfortunately, this contains very little basic structural data (Table 21) — only two full X-ray analyses and a few correlations of powder data.

After early problems in preparing some of these species, the use of special solvent systems, including ethyrlorthoformate as a dehydrating agent, and the $SbCl_6^-$ anion, has allowed significant extension of the class. The NO species are covered in a recent Gmelin volume[239] and the PO species were reviewed in 1971.[240]

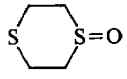
The compounds $MnX_2 \cdot nL$, for n = 6, are found quite commonly in the pyridine-*N*-oxides and sulfoxides, but only one PO group compound is known. This is generally ascribed to steric (bulk

Table 21 The Numbers of Known Compounds $MnX_2 \cdot nL$ for the N, P, As, S and Se Oxide Ligands

Ligand Class	*Number[a] of Compounds for n =* 6	5	4	3	2	1	0.5	*Ref.*
R_3NO			1		2			239
pyO	3			(2)	3	3(1)		239
X-pyO[b]	13(1)	3(2)	2(1)	1	15	6	2	239, c
RNO_2	2		1	1	1			d, e
R_3PO		1(1)	7		6			240, 243, 244, 246, f
$R_2(R'O)PO$			(1)					g
$R(R'O)_2PO$	1		2(1)	(1)		(1)		h, i
$(RO)_3PO$		1	(2)					i
$R(NR'_2)_2PO$			2		1			j
$(NR_2)_3PO$			3		12		2	k, l
R_3AsO		1	5		6			243, f
R_2SO	10		2	3(2)	2	1		m–r
SO_2					1			s, t
R_2SeO				1	1			u

[a] The numbers in parentheses refer to hydrates.
[b] This includes quinoline, *etc.*, species.
[c] A. N. Speca, L. S. Gelfand, F. J. Iaconianni, L. L. Pytlewski, C. M. Mikulski and N. M. Karayannis, *Inorg. Chim. Acta*, 1979, **33**, 195.
[d] W. L. Driessen, L. M. Van Geldrop and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 1271.
[e] C. Dragulescu, E. Petrovici and I. Lupu, *Monatsch. Chem.*, 1974, **105**, 1176.
[f] G. A. Rodley, D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 1965, 1499.
[g] C. M. Mikulski, J. Unruh, L. L. Pytlewski and N. M. Karayannis, *Transition Met. Chem.*, 1979, **4**, 98.
[h] N. M. Karayannis, C. M. Mikulski, L. S. Gelfand and L. L. Pytlewski, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1513.
[i] N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta*, 1974, **8**, 91.
[j] M. W. G. De Bolster and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 1153.
[k] M. W. G. De Bolster and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 477.
[l] M. W. G. De Bolster, I. K. Kortram and W. L. Groeneveld, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1843.
[m] G. V. Tsintsadze, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1971, **16**, 614.
[n] A. H. M. Fleur and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 317.
[o] W. D. Harrison, J. B. Gill and D. C. Goodall, *J. Chem. Soc., Dalton Trans.*, 1979, 847.
[p] W. F. Currier and J. H. Weber, *Inorg. Chem.*, 1967, **6**, 1539.
[q] P. W. N. M. Van Leeuwen and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1967, **86**, 721.
[r] F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, 1960, **82**, 2986.
[s] C. D. Desjardins and J. Passmore, *J. Fluorine Chem.*, 1975, **6**, 379.
[t] P. W. Dean, *J. Fluorine Chem.*, 1975, **5**, 499.
[u] R. Paetzold and P. Vordank, *Z. Anorg. Allg. Chem.*, 1966, **347**, 294.

or B-strain) effects and the argument probably is valid. But arguments, that 2,6-dimethylpyridine-oxide forms only a tetrakis compound for steric reasons, are confounded by the hexakis compound formed by the 2,4,6-trimethyl analogue. These hexakis compounds generally are pale yellow, are assumed to be $[MnL_6]X_2$ octahedra, and such a structure is proven for ligand (**81**).[241] They tend not to be very robust; the pyO species generally are sensitive to air, light and heat, apparently more so than the compounds for $n < 6$.



(81)

Whether steric bulk or crystal-packing effects are more important, many of the ligands, and especially the PO and AsO species, do form pentakis and tetrakis compounds several of which are hydrates.

The $n = 5$ compounds may be five-coordinate or may contain an anion in the sixth coordination site. The former is known[242] for $[Mn(Me_3AsO)_5](ClO_4)_2$. It absorbs H_2O in the air, forming octahedral $[Mn(Me_3AsO)_5H_2O](ClO_4)_2$.

In the $n = 4$ series, there are fixed points in the known structures[244,245] of the square pyramidal cations $[MnI(Ph_3PO)_4]^+$ and $[MnClO_4(Ph_2MeAsO)_4]^+$, and there has been a tendency to relate most of the other compounds to these. However, other compounds of the group may turn out to be tetrahedral $[MnO_4]X_2$ species*, and some, especially the hydrates, may be octahedral.

* Some of the correlations with Co and Ni structures, assigning tetrahedra, were made before the variety of five-coordinate structures was recognized, and must be considered doubtful.

The $n = 3$ species, on simplest interpretation, may be five-coordinate monomers $[MnX_2L_3]$ or ionic $[MnL_6][MnX_4]$ species. There has been a tendency to believe more in the latter than the former. There are also some hydrates, such as $Mn(ClO_4)_2 \cdot DMSO \cdot 4H_2O$, for which it is impossible to make even a reasonable guess about structures.

A wider variety of structural assignments is available for the $n = 2$ species: possible structures include tetrahedral monomers, five-coordinate anion-bridged dimers; other oligomers; and polymers, such as (**8**). Many tetrahedral monomers have been postulated, but none have yet been confirmed. The only fixed point in the sea of data is the structure of $[MnCl(NCS)(Ph_3PO)_2]$ which is a five-coordinate dimer,[246] with chlorine bridges.

The compounds for $n = 1$ or 0.5 undoubtedly have polymeric (layer) structures, of which (**13**) is an example. There is also an example of a 'cubane' tetramer like (**18**) in this class, $MnF(BF_4) \cdot$(2,6-diMepyO)$\cdot$MeOH, which resulted[239] from the reaction of 2,6-dimethylpyridine *N*-oxide with $Mn(BF_4)_2$.

(*vi*) *Dioxygen*

Reversibly formed Mn^{II} compounds with O_2 are persistent in the literature.[247] However, whilst it is clear that they do have a limited existence, no firm detail of the bonding in any of them is available through X-ray analyses. Attempts to obtain crystalline species have been thwarted by reactions of the $[MnO_2]$ moiety, giving other Mn^{III} and/or Mn^{IV} species.

Equally strong claims have been made for an $[Mn^{IV}—O_2^{2-}]\eta_2$ formulation in porphyrins, and an $[Mn^{III}—O_2^{-}]\eta_1$, superoxo formulation in phthalocyanines. Probably both can exist for the more electrovalently versatile manganese; but eventual hard proof, through X-ray work would seem at this stage to require some elegant chemical and physical experimentation, or perhaps just further exploration. (We think that the reversible combination of O_2 with the solid phosphine compounds (Section 41.3.4) is likely to have its final explanation given more in terms of clathrate formation, especially in view of the wide range of other gases reported to bind reversibly.)

It is somewhat surprising that Mn compounds with O_2 moieties appear to have such limited existence; 'peroxo' compounds of the higher oxidation states are an important feature of the earlier transition metals (and we shall notice a few, poorly characterized, examples for Mn in Section 41.5.3); and the metals which follow manganese — Fe and Co — have an extensive and important chemistry of reversible combination with the oxygen molecule. It is perhaps pertinent to recall that some Mn^{II} species are very efficient catalysts for the decomposition of hydrogen peroxide (Section 41.3.3.7).

41.3.5.2 Oxyanions

In this section we deal with the oxyanions of the non-metals, which usually have well-defined polyhedra, in contrast to the mixed oxides of Section 41.3.5.1(i). Such distinction is, of course, not always sharp.

(*i*) *Borates, carbonates and silicates*

A variety of crystalline borates of Mn^{II} has been characterized, and structural data are available for many[248] (Table 22). These show that the dominant Mn polyhedron is the octahedron, although two exceptions have been identified, derived from distortion of tetrahedra: in $LiMnBO_3$, the Mn atoms are displaced towards a fifth oxygen and are at the centres of $[MnO_5]$ polyhedra; and in MnB_4O_7, the MnO_4 tetrahedra have four other oxygens along normals to the faces, making an effectively $[MnO_8]$ polyhedron.

The octahedron also is adopted in the known carbonates[249] (Table 22). $MnCO_3$, although thermodynamically unstable in O_2 or air, decomposes only slowly, and the pink, almost white, compound occurs naturally as the mineral rhodochrosite. Only one crystalline form is known which has the calcite structure; and both $CaMn(CO_3)_2$ and $BaMn(CO_3)_2$ have the dolomite structure. The carbonate mineral sidorenkite ($Na_3MnCO_3PO_4$) has a bidentate carbonate group, which is somewhat unusual in inorganic structures.

However, there is distinctly more complexity in the range of known compounds, and in the observed coordination polyhedra, in the crystalline silicates.[250] There are only two basic silicates: Mn_2SiO_4, which occurs naturally (tephroite); and $MnSiO_3$ the metasilicate, which also occurs

Table 22 The Coordination Polyhedra of Crystalline Mn^{II} Borates and Carbonates

Compound	*Coordination Polyhedra with (av.) Bond Lengths* (Å)	*Comments*
MnB_4O_7	$[MnO_n]$ n = 4–8 (2.442–3.188)	Distorted tetrahedra with four other oxygens on normal to faces.
MnB_2O_4		Isomorphous with Fe and Mg.
MnB_2O_5	$[MnO_6]$	Isomorphous with known Co.
$Mn_3(BO_3)_2$	(i) $[MnO_6]$ (2.184) (ii) $[MnO_6]$ (2.214)	Jimboite.
$MnB_6O_{10}\cdot 8H_2O$		Isomorphous with Fe and Co.
$MnB_4O_7\cdot 9H_2O$	$[MnO_6]$ 2.15–2.22	
$MnB_2O_4\cdot 3H_2O$	$[MnO_6]$	Sussexite—chains of edge-linked octahedra.
$LiMnBO_3$	(i) $[MnO_5]$ 2.135 (ii) $[MnO_5]$ 2.156	H.c.p. oxygens; Mn in tetrahedral holes, but displaced towards fifth oxygen.
$Mn_3(OH)_2\{B(OH)_4\}PO_4$	(i) $[MnO_6]$ 2.204 (ii) $[MnO_6]$ 2.203	Very distorted, edge-sharing a bidentate BO_3 unit; Mn—O up to 2.41 Å (Seamanite).
Pinakiolites	$[MnO_6]$	A family of Mn^{II}/Mn^{III} borate minerals.
$CaMnB_2O_5\cdot H_2O$	(i)–(iii) $[MnO_6]$ 2.21	Roweite.
$MnCO_3$	$[MnO_6]$ 2.196	Calcite structure.
$CaMn(CO_3)_2$	$[MnO_6]$	Dolomite structure.
$Na_3MnCO_3PO_4$	$[MnO_6]$ 2.092–2.350	Sidorenkite—bidentate CO_3.

Table 23 Structural Data for Crystalline Mn^{II} Silicates

Compound	*Phase, Mineral*	*Mn Polyhedra and Bond Lengths (av. in* Å*)*
$MnSiO_3$	I (Rhodonite)	(i)–(iii) $[MnO_6]$ 2.219; 2.242; 2.223 (iv) $[MnO_7]$ 6 × ~2.2; 1 × 2.778 (v) $[MnO_7]$ 3 × 2.743; 4 × 2.139
	II (Pyroxmanganite)	(i)–(iv) $[MnO_6]$ 2.2 (v) $[MnO_7]$ 3 × 2.743; 4 × 2.141 (vi) $[MnO_7]$ 6 × 2.2; 1 × 2.796 (vii) $[MnO_7]$ 3 × 2.696; 4 × 2.144
	IV Garnet-type, tetragonal	(i) $[MnO_8]$ dodecahedral (ii) $[MnO_6]$
	β-form	$[MnO_6]$
Mn_2SiO_4	Tephroite	$[MnO_6]$
Mn^{II}/Mn^{IV} mineral	Långbanite	(i) $[MnO_6]$ 2 × 2.25; 4 × 2.34 (ii) $[MnO_5]$ TBP 2 × 2.23; 1.92; 1.96; 2.07 (iii) $[MnO_8]$ distorted rhombohedron 2 × 2.22; 6 × 2.46
Mn^{II}/Mn^{III} mineral	Braunite	(i) $[MnO_8]$ 2.33
$Mn_5(OH, F)_2(SiO_4)_2$	Allegheneyite	$[MnO_6]$(× 3) 2.221; 2.199; 2.215
$Mn_7(OH)_2(SiO_4)_3$	Leucophoenicite	$[MnO_6]$(× 4) 2.203; 2.258; 2.217; 2.206
$Na_2Mn_2Si_2O_7$		(i) $[MnO_4]$ 2.00–2.10 (ii) $[MnO_5]$ 2.03–2.42
$Na_2Mn(SiO_3)_2$		$[MnO_6]$ (× 2) 2.10; 2.33
$Na_5(Mn, Na)_3MnSi_6O_{18}$		$[(Mn_2Na)O_6]$ (× 3) 2.39; 2.27; 2.40[b] $[MnO_6]$ 1.96–2.24
$(Li, Na)Mn_4Si_5O_{14}OH$	Nambulite	$[MnO_6]$ (× 3) 2.233; 2.242; 2.188 $[MnO_7]$ 3 × 2.752; 4 × 2.145
$K_2Mn_5Si_{12}O_{30}\cdot H_2O$		$[MnO_6]$ (these polyhedra share an edge) $[MnO_4]$
$CaMnSi_2O_6$	Johannsenite	$[MnO_6]$ 2.17
$(Ca, Mn)_3Si_3O_9$	Bustamite	$[MnO_6]$ (× 2) 2.245; 2.203
$CaMn_4OH(Si_5O_{14}OH)\cdot H_2O$		$[MnO_6]$ (× 3) 2.204; 2.199; 2.205
$Ca_2Mn_7(OH)_2Si_{10}O_{28}\cdot 5H_2O$	Inesite	$[MnO_6]$ (× 4) $[MnO_6]$ 2.113–2.460; 2.133–2.513
$CaMn_2(BeSiO_4)_3$		
$Zn_2Mn(OH)_2SiO_4$	Hodgkinsonite	$[MnO_6]$ 2.222
$K_2Zn_4Mn_2(SiO_4)_2Si_2O_7$		$[MnO_5]$ (× 2) SP 1.91–2.22
$Na_2InOH\{SiO_3(OH)\}_2$		$[MnO_6]$ TP (× 2) 2.15–2.53
$PbMn(Si_2O_7)_3$		$[MnO_6]$ 2.26
$13MnO\cdot Sb_2O_5\cdot 2Al_2O_3\cdot 2SiO_2$	Catoptrite	$[MnO_6]$ (× 3) 2.22; 2.24; 2.19
$Mn_4(BeSiO_4)_3S$	Kelvite	$[MnO_3S]$ 2.082

[a] Unless otherwise stated $[MnO_6]$ polyhedra are octahedral, albeit often somewhat distorted; and $[MnO_4]$ polyhedra are tetrahedral. The more 'flexible' $[MnO_7]$ polyhedra are not defined, and the $[MnO_5]$ polyhedra only when they are very close to the extremes of trigonal bipyramid (TBP) or square pyramid (SP). TP = trigonal prism. Quoted bond lengths are usually averages, but hyphens, in some cases, indicate the range.

[b] Mn^{II} and Na^{I} share these sites, so the (averaged) distances observed experimentally probably overestimate the size of the hole in which the Mn^{II} is located.

naturally in several forms (Table 23). Both were described by Gorgeu in 1883. The former is known as a single phase, and is the end member of the olivine group of silicates. Its structure is simply based on hexagonal close packing of oxygens, with Mn^{II} in half the octahedral holes, and Si^{IV} in one-eighth of the tetrahedral holes. By contrast, the metasilicate has been characterised in five distinct phases, some of which are known only in minerals and appear to require the presence of small amounts of other metals for stability of the phase.

Available structural details for these silicates, and for the wide range of other known species containing Mn^{II} and silicate, are summarized in Table 23. Coordination numbers four (tetrahedral), five (both square pyramid and trigonal bipyramid and 'in-between' structures), six (mainly octahedral and distorted, but including one trigonal prism), seven (of various shapes) and eight (dodecahedra and distorted rhombohedra) all are defined; and there is evidence for three-coplanar in a zeolite: the hydrated form is five-coordinate (3×2.28 Å and 2×2.05 Å) but, on dehydration of this Mn-exchanged zeolite, the solid contains planar three-coordinate Mn^{II} with Mn—O = 2.11 Å.[251]

(*ii*) *Monocarboxylates*

(Monocarboxylates with other, different, functional groups, such as salicylate and picolinate, are discussed in other sections.)

This is one of the few areas of Mn^{II} chemistry for which a significant amount of structural data is available. Yet, the only pattern to emerge is one of variety of structure, mainly polymeric, and the absence of any hard evidence for a dimeric tetra-bridged species of the copper(II) acetate structure. There is a distinct impression, when first following through the literature, of encountering with almost each new structure some unexpected, novel feature, and the data certainly underline the sheer futility of attempting to define structure of crystalline solids by other than X-ray methods.

Two groups have been most prolific; Kennard's group[252] have been looking mainly at the structures of herbicide carboxylates, and Ciunik and Glowiak[253] the amino acid compounds, generally $MnX_2(AA)_2 \cdot nH_2O$. These latter all are bonded in zwitterion form, so that they are generally examples of substituted Mn^{II} carboxylate hydrates. The rest of the literature is accessible through the latest publications of these groups[252,253] and Gmelin.[254]

The majority of the Mn^{II} carboxylates and their hydrates are robust in the air, but some, for example $Mn(Bu^tCOO)_2$, react readily forming red-brown trinuclear Mn^{III} species. It is with the same carboxylate, that so-far-unsubstantiated claims have been made for dinuclear species,[255] such as $[Mn_2(Bu^tCOO)_4py_2] \cdot 2Bu^tCOOH$. Both formate and acetate have given compounds $M_2Mn(RCOO)_4 \cdot nH_2O$ (M = Na, K, NH_4).[254] Although structures are yet unknown, it is tempting to draw parallels with the tetrakis-nitrito and nitrato-manganate^{II} species (Section 41.3.5.2.iii).

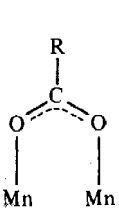
Table 24 contains data on approximately half the known structures, and a similar story emerges from the amino acid structures.[253] Monomers are known and there is the first example of a transition metal compound $[M(RCOO)(H_2O)_5]RCOO$; but most structures involve carboxylate bridging of three basic types (**82**)–(**84**), although one structure has *cis*-unidentate carboxylates and chooses to polymerize on a single bridging water molecule. The Mn polyhedron in the tetrahydrate for R = (**89**) is the only one to depart from the pattern of $[MnO_6]$ octahedra. It has *trans*-H_2O molecules at relatively normal distances of 2.28 and 2.31(2) Å, and in the plane normal to these are three

Table 24 Representative Structures of Carboxylate Compounds $Mn(RCO_2^-)_2 \cdot nH_2O$[252]

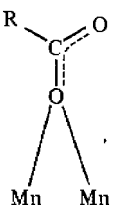
R	*n*	*Mn Polyhedra*	*Bridge Type*	*Comments (Mn—O Bond Lengths in Å)*
H	2	*t*-$[MnO_2(H_2O)_4]$ $[MnO_6]$	(**82**)	Polymer (linear) (2.14–2.22)
Me	4	*c*-$[MnO_4(H_2O)_2]$ $[MnO_6]$	(**82**), (**84**)	Polymer (chain) (2.15–2.26) (2.16–2.23)
Et	2	*t*-$[MnO_4(H_2O)_2]$	(**82**), (**84**), (**85**)	Polymer (chain) (2.125–2.369)
(**87**)	2	*t*-$[MnO_4(H_2O)_2]$	(**82**)	Polymer (two-dimensional) (2.15–2.22)
(**88**)	2	*t*-$[MnO_4(H_2O)_2]$	(**82**)	
(**89**)I	4[a]	*t*-$[MnO_2(H_2O)_4]$		Monomer
II	5	$[MnO(H_2O)_5]^+$		An unusual $[MnX(H_2O)_5]X$ species
III	4	*t*-$[MnO_3(H_2O)_2]$	(**83**)	Dimer (see text) (2.28–2.46)
(**90**)	4	*c*-$[MnO_2(H_2O)_4]$	(**86**)	Polymer (chain) (2.11–2.29)
(**91**)	5	*c*-$[MnO_2(H_2O)_4]$	(**85**)	Polymer (linear)
(**92**)	4	*t*-$[MnO_2(H_2O)_4]$		Monomer (2.19–2.22)

[a] Full formula is $[Mn(RCO_2)_2(H_2O)_4] \cdot 2RCO_2H$

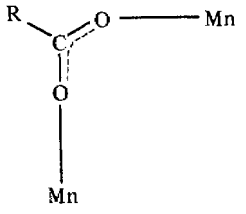
carboxylate oxygens (at 2.35–2.46(2) Å and O—Mn—O angles of 80 and 85°), an ether O (at 2.96 Å) and a ring Cl (at 3.07 Å). It is pertinent to add that, in at least one case, the phenoxy ether oxygen bonds more closely to Cu^{II} but not at all to Mn^{II}.



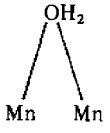
(82)



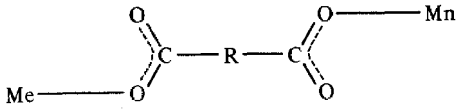
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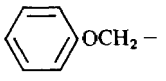
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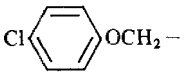
(85)



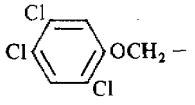
(86)



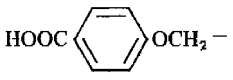
(87)



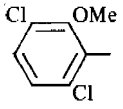
(88)



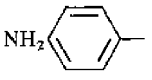
(89)



(90)



(91)



(92)

(*iii*) *Nitrites and nitrates*

Known details of the *nitrites* are largely confined to three papers.[256,257] Anhydrous $Mn(NO_2)_2$ is stable below 40 °C, and the pale yellow compounds $M_2[Mn(NO_2)_4]$, including the Cs salt and the yellow $Cs_3Mn(NO_2)_5$ require storage under mother liquor at 0 °C. The tetrakisnitrito species appears to have an $[MnO_8]$ polyhedron with all bidentate nitrites and is closely paralleled by other larger M^{II} species, *i.e.* those of Ca, Sr, Ba, Zn, Cd and Hg. A few mixed ligand compounds, with various neutral ligands, have been described but none give acceptable evidence for an N-bonded nitro.

Anhydrous manganese(II) *nitrate* is readily obtainable as pale red crystals, and like the hydrates, is hygroscopic.[258] Hydrated $Mn(NO_3)_2$, apparently largely as the tetrahydrate, is used commercially to colour porcelain and as an intermediate in the preparation of specific forms of MnO_2.

There are four well-characterized hydrates $Mn(NO_3)_2 \cdot nH_2O$ $n = 6$, 4, 2 and 1. The former appears to be another $[Mn(H_2O)_6]X_2$ species, but X-ray structural analyses of the others give examples of the modes of bonding of nitrate. $Mn(NO_3)_2 \cdot 4H_2O$, isostructural[259] with Zn and Ni, is a monomeric *cis*-$[Mn(NO_3)_2(H_2O)_4]$ octahedral species, with unidentate nitrates (Mn—O = 2.13–2.19 Å); the dihydrate is isostructural with Zn,[260] and has *trans*-$[MnO_4(H_2O)_2]$ octahedra (Mn—O = 2.05–2.14 Å), with nitrates bridging as in (**82**); and the monohydrate has both $[MnO_6]$ and $[MnO_8]$ polyhedra:[261] the former are *cis*-$[MnO_4(H_2O)_2]$ octahedra (Mn—O = 2.20 Å) and the latter are approximately dodecahedral, with four bidentate nitrates (Mn—O = 2.31–2.37 Å). The same eight-coordinate polyhedra are found in the compounds $M_2[Mn(NO_3)_4]$ (M = Na, K,

Ph_3MeAs and Ph_4As)[262]—the crystal structure of the latter showing two crystallographically distinct nitrates, one of which has Mn—O distances of 2.25 and 2.29 Å and the other 2.29 and 2.40 Å.

Nitrate groups also are found in various mixed ligand species with the other neutral ligands, and one of the few species to have been explored crystallographically is $[Mn(NO_3)_2(N{-}N)_2]$,[124] which also has bidentate nitrato groups (Section 41.3.3.2).

(*iv*) *Oxyanions of P and As*

The oxyanions of phosphorus and arsenic take up the major portion of a recent large volume of *Gmelin* (**C9**), which includes more than 100 compounds, hydrates and phases containing phosphate groups.[263] To pursue the detail of the latter is an exercise in phosphorus chemistry, so we concentrate on a survey of the available data on the Mn^{II} coordination polyhedra.

Mn^{II} phosphates find significant use in industry, including $MnHPO_4 \cdot 3H_2O$ for the preparation of luminescent materials, and $Mn(H_2PO_4)_2 \cdot 2.5H_2O$ in fertilizers and especially for manganese phosphate coatings on metals to improve wear resistance. The pyrophosphate $Mn_2P_2O_7$ is a useful calibrant for magnetic measurements.

There appears to be but one reference[179] to a *phosphinite* $Mn(Ph_2PO)_2$, although *phosphinates* are receiving attention: the compounds $Mn(R_2PO_2)_2$ (R = Bu^n, Bu^t, pentyl and octyl) are polymeric[264] and probably octahedral; and structural data are available on five compounds $Mn(R_2PO_2)_2 \cdot L$, showing close parallels with the carboxylates,[132,265] including zwitterion species.[266] PO_2 bridging like (**82**) and (**84**) occurs in these.

Only one *phosphonate*, the rather insoluble $MnHPO_3 \cdot H_2O$, appears to have been described, and there are six known polyphosphonates, ranging up to $Mn_2H_{17}P_7O_{21} \cdot 4H_2O$. A *fluorophosphate* $Mn(PO_3F) \cdot nH_2O$ and several *chlorophosphates* $Mn(Cl_2PO_2)_2 \cdot nL$ also are characterized.[238,267]

The remainder of the P oxyanion compounds, hydrates and phases are *phosphates* of various types, including pyro- and meta-phosphates, and polymers. Of the > 100 described species, including such mixed ligand species as Mn_2ClPO_4 and $Mn_5(OH)_4(PO_4)_2$, X-ray analyses are available on twenty-two and all but one $\{\beta'\text{-}Mn_3(PO_4)_2\}$ have $[MnO_6]$ octahedra with Mn—O generally averaging between 2.18 and 2.24 Å. This predominance of the octahedron probably derives in significant part from the general compatibility of Mn in octahedral holes and P in tetrahedral holes of close-packed oxygen. This 'compatibility', however, is seldom perfect for most of the polyhedra are distorted: in one case[268] bond length variations of 2.08–2.59 Å occur in the one octahedron and angular distortions of 10° are seen. Such distortion reaches a peak among known structures in $\beta'\text{-}Mn_3(PO_4)_2$, the nine independent atoms of which all have five nearest neighbours (range = 2.03–2.36 Å; average = 2.13–2.19 Å) and distinctly longer bonds to a sixth oxygen, that may be as close as 2.39 Å in the more regular octahedra to > 3.0 Å in the least.[269]

Table 25 Mn^{II} Arsenate Species with Non-octahedral Coordination Polyhedra

Compound Mineral	*Coordination Polyhedra*	*Bond Lengths* (Å) *Average*	*Range*
$Mn_2(OH)AsO_4$	$[MnO_5]$ (× 4)	2.129	2.065–2.223(6)
Sarkinite	$[MnO_6]$ Octahedron (× 4)	2.212	2.149–2.344
$Mn_2(OH)AsO_4$	$[MnO_5]$ (× 4)	2.12	
Eveite	$[MnO_6]$ Octahedron (× 4)	2.19	
$Mn^{II}Mn^0_2Sr_2As_2O_2^a$	$[MnO_4]$ Square plane	2.078	
$Mn^{II}Mn^0_2Ba_2As_2O_2$	$[MnO_4]$ Square plane	2.124	
$(Mn, Mg, Cu)_5(OH, Cl)(AsO_3)_3$	$[MnO_8]$ Cube	2.42	
Magnussonite (cubic)	$[MnO_6]$ Octahedron	2.19	
	$[MnO_6]$ Trigonal prism	2.24	
	$[MnO_4]$ Square plane	2.10	
$Mn_{26}[As_6(OH)_4O_{14}](As_6O_{18})_2CO_3$	$[MnO_6]$ Octahedron (× 4)	2.217	
Armagite	$[MnO_6]$ Trigonal prism	2.237	
$Mn_4[AsSi_3O_{12}(OH)]$	$[MnO_6]$ Octahedron (× 3)	2.222	2.099–2.366
Tiragalloite	$[MnO_{5+2}]$	2.198 (× 5), 2.625, 2.974	2.102–2.366
$Mn_{10}Sb_2As_2Si_2O_{24}$	$[MnO_8]$ Cube	2.42	
Parwelite	$[MnO_6]$ Octahedron	2.21	2.17–2.24
	$[MnO_5]$	2.09 and 2.12	
	$[MnO_4]$ Tetrahedron	2.07	

[a] Related Sb and Bi compounds have the same structure.

The arsenate polyhedra, on the other hand, show distinctly more variability; of the > 60 species described,[270] many of which are minerals, structural analyses are available for one-third and, of these, one-third appear to have non-octahedral Mn polyhedra (Table 25). (The proviso results from a report[268] that the earlier analysis, describing arsenoclasite as containing $[MnO_4]$, $[MnO_5]$ and $[MnO_6]$ polyhedra, was in error, and that there are only $[MnO_6]$ polyhedra—albeit distorted.)

One other interesting feature occurs in mixed Mn, Zn species: where there is a choice of octahedral and tetrahedral holes, Mn occupies the former and Zn the latter. Undoubtedly the size difference is the major, if not only, cause.

(*v*) *Oxyanions of S, Se and Te*

Robust manganese(II) *sulfinates* and *sulfonates* undoubtedly can exist, but there is very little detail on them in the literature. Lindner and co-workers[271] claimed evidence for both O,O- and S-bonded forms of $PhSO_2^-$, but the latter seems very unlikely.

The binary *sulfite* $MnSO_3$ and five distinct hydrates have been defined,[272-274] and the structures of the two different forms of the trihydrate are available. They show *fac*-$[MnO_3(H_2O)_3]$ and *cis*-$[MnO_4(H_2O)_2]$ octahedra. Various compounds $M_2Mn(SO_3)_2$, $K_2Mn_2(SO_3)_3$ and $Na_2Mn_4(SO_3)_5$ were described by Berklund in 1879 and Gorgeu in 1883.[272] They are unlikely to represent discrete $[Mn(SO_3)_2]^{2-}$ anions.

The *sulfate* $MnSO_4$ and its hydrates (7, 5, 4, 2 and 1) represent the stable oxidation state under ambient conditions. Compounds are colourless in finely-divided form and pale pink or rose coloured when crystalline. All appear to be examples of high spin octahedral Mn^{II}. Aqueous solutions have been much studied, to define the physical parameters, because of their importance in Mn production from its ores. Stability constants for 1:1, 1:2 and 1:3 species have been defined but detail (structurally) of the labile Mn polyhedra is unclear. Examples of unidentate and bridging sulfato are seen in the known crystal structures, but not bidentate or terdentate to the same metal atom. (However, bidentate function may occur in some of the mixed-ligand compounds described earlier.)

In all, some 80 compounds, phases and hydrates are listed in a 1976 volume of *Gmelin* (**C6**), including a few thiosulfates and polythionates. Of these, structural data are available only on *ca.* 10%, but they refer to at least one third of the types, and all show $[MnO_6]$ octahedra, often containing water molecules as well as oxygens of the sulfates. The octahedra $[MnO_x(H_2O)_{6-x}]$ are described for $x = 6$, 5, (*c*- and *t*-) 4 and 2, and the mineral mooreite $\{Mg_7Zn_4Mn_2(SO_4)_2(OH)_{26}\cdot 8H_2O\}$[275] has $[Mn(OH)_2(H_2O)_4]$ octahedra (and, incidentally, $[Zn(OH)_4]$ tetrahedra as well).

Species like $K_2Mn(SO_4)_2$ and $K_2Mn_2(SO_4)_3$ are known,[272] but they are unlikely to represent discrete 'complex' Mn anions. The 'complexity' of the solids will be defined primarily by close packing of the sulfates, with charge neutralization achieved by Mn^{2+} and other cations in appropriate 'holes'.

Of the 20 known *selenite* and *selenate* species,[272] structures are now available on more than one-third, and all show $[MnO_6]$ octahedra.[276] Manganese(II) selenite ($MnSeO_3$) has the perovskite ($CaTiO_3$) structure, with each $[MnO_6]$ octahedron provided by three SeO_3 groups (Mn—O = 2.235 Å); the monohydrate has $[MnO_5(H_2O)]$ octahedra (Mn—O = 2.14–2.31 Å); and the dihydrate has *cis*-$[MnO_4(H_2O)_2]$ octahedra (2.14–2.29 Å). This system also gives an example of an unexpected redox reaction: hot solutions of Mn^{II} and H_2SeO_3, and various other reaction routes, give orange-red crystals of $Mn(SeO_3)_2$, which is apparently another Mn^{IV}compound, like MnO_2, stabilized by its insolubility. There is an interesting structural parallel with the insoluble, white iodate $Mn(IO_3)_2$. $MnSe_2O_5$, $MnSeO_4$ and their hydrates also are known, as well as species like $Na_2Mn(SeO_4)_2$.

Fewer *tellurites* and *tellurates* are known:[272] $MnTeO_3$ is isostructural with the Se analogue, and tellurates are represented by species like Mn_3TeO_6—no $MnTeO_4$ species appear to have been described.

(*vi*) *Oxyanions of the halogens*

Very few binary compounds of this class have been described, but ClO_4^- is widely used as a counter ion for the preparation of many of the cationic species of the other neutral ligands, despite the instability that gives some risk of explosion! For many years, it was regarded as the standard for 'non-coordination'—especially in aqueous solution—and both the chlorate and perchlorate crystallized from aqueous solution as $[Mn(H_2O)_6]X_2$. However, the anhydrous $Mn(ClO_4)_2$ can be

Table 26 Isopoly- and Heteropolyanion Compounds of Manganese

Compound Type and Structural Data	*Gmelin ref.*
Isopolyvanadates	*C3*, 162
Tetravanadomanganates(IV)	*C3*, 164
11-Vanadomanganate(IV)	*C3*, 165
13-Vanadomanganate(IV)	*C3*, 166
12-Niobomanganate(IV); $[MnO_6]$ (1.87 Å)	*C3*, 173, 174
6-Molybdomanganate(II)	*C3*, 209
9-Molybdomanganate(IV); $[MnO_6]$ (1.90 Å)[a]	*C3*, 210
12-Molybdomanganate(IV)	*C3*, 211
Mn^{II} 11-molybdogermanate	*C3*, 212
Mn^{II} 12-molybdosilicate	*C8*, 331
Triheteropoly-molybdomanganosilicates of Mn^{II} and Mn^{III}	*C8*, 331
Mn^{II} 11-molybdophosphate	*C9*, 208
Mn^{II} 12-molybdophosphate; isomorphous Mg, Ca	*C9*, 209
Triheteropoly-molybdomanganophosphates of Mn^{II} and Mn^{III}	*C9*, 209
11-Tungstomanganate(III)	*C3*, 223
5-Tungstomanganate(IV)	*C3*, 224
6-Tungstomanganate(IV); $[MnO_6]$ (1.94 Å)[b]	
12-Tungstomanganate(IV)	*C3*, 225
Heteropoly species $[MMnW_{11}O_{40}]^{n-}$ (M = Zn, Ga, Ge) of Mn^{II} and Mn^{III}	*C3*, 225
Mn^{II} 12-tungstosilicates	*C8*, 332
Triheteropoly-tungstomanganosilicates of Mn^{II} and Mn^{III}	*C8*, 332
Tungstomanganophosphates ($PMnW_{11}$ and P_2MW_{17}) of Mn^{II} and Mn^{III}	*C9*, 210
Tungstomanganoarsenates of Mn^{II} and Mn^{III}	*C9*, 363

[a] R. Allmann and H. d'Amour, *Z. Kristallogr.*, 1975, **141**, 342; T. J. R. Weakley, *J. Less-Common Metals*, 1977, **54**, 289.
[b] V. S. Sergienko, V. N. Malčanov, M. A. Porai-Košic and E. A. Torčenkova, *Koord. Khim.*, 1979, **5**, 936.

prepared,[277] and both the di- and tetra-hydrates have been defined. Beginning with $Mn(ClO_4)_2$, other anhydrous metal perchlorates,[277] and some copper(II) and nickel(II) compounds,[278] perchlorato coordination has been increasingly recognized in the literature, and one of the first to be defined crystallographically was the arsine oxide species[245] $[MnClO_4(Ph_3AsO)_4]ClO_4$. Other perchlorato species have been noticed in the various sections on neutral ligands.

Two anhydrous iodates also are known[279] and both were first reported by Rammelsberg in the 19th century. The insoluble $Mn(IO_3)_2$ precipitates from aqueous mixture of Mn^{II} and IO_3^-. It is relatively robust in the short-term, but on long keeping releases I_2. The periodate $Mn_3(IO_5)_2$, however, is stable only below 15°C.

(*vii*) *Isopoly- and heteropolyanions of V, Nb, Mo and W*

Anions of this type containing Mn (II, III and IV) are listed in Table 26. Most of these have been isolated as crystalline solids.

There is a tendency for stability of the higher oxidation states (III and IV), but a number of Mn^{II} species are defined,[280,281] the most robust of which appear to be the triheteropolyanion tungstomanganophosphates $[PMnW_{11}O_{39}(OH_2)]^{5-}$ and $[P_2MnW_{17}O_{61}(OH_2)]^{8-}$. Both are readily oxidized to Mn^{III}. The Mn atoms are high spin and magnetically dilute; and the anions are yellow-brown because of a metal–ligand charge-transfer band in the near UV. A cation exchange resin, in the H^+ form, completely removes Mn^{II}.

41.3.5.3 Bidentate ligands

(*i*) *Diethers, diols and diphenols*

The *ether* compounds have been little studied: only the 1,2-dimethoxyethane species $MnLX_2$ (X = Cl, Br), $[MnL_2(H_2O)_2](ClO_4)_2$ and $[MnL_3][SbCl_6]_2$ appear to have been described,[221] and all may contain ether chelates. Dioxane, on the other hand, acts as a bridging group in quite robust polymers (Section 41.3.5.1.iii).

Diol compounds are known, both of the neutral aliphatic ligands and in their deprotonated (alkoxide) form,[212] but generally have been studied for their reaction with O_2 and other oxidizing

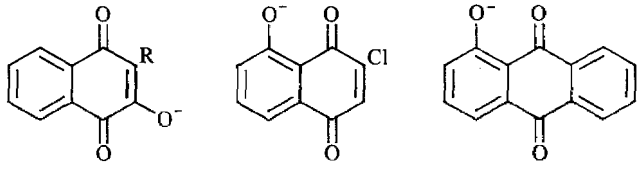
agents, to form Mn^{III} and Mn^{IV} species. Ethane-1,2-diol species $[MnX_2L_2]$ (X = Cl, Br, NO_3, $\frac{1}{2}SO_4$) are characterized by an X-ray analysis of the chloro compound, showing an $[MnCl_2O_4]$ octahedron. The alkoxide Mn(L-2H) was studied for its catalytic activity, but not characterized structurally. Various polyols, such as mannitol, inositol, *etc.*, appear also to act as diols, forming similar chelate compounds.[282] These have been studied mainly for their reaction with O_2 to give Mn^{III} and Mn^{IV} species, and little is known of the structures they adopt.

Catechol, with its more readily ionized protons (and other *o-diphenols*), in aqueous alkaline solution forms soluble, colourless anionic species. Stability constants for the 1:1 and 2:1 species have been measured ($\log K_1 = 7.5$, $\log K_2 = 5.7$) and the 3:1 species forms at pH > 11. In 0.3 M NaOH, the latter is readily oxidized by ferricyanide to Mn^{III}. Some crystalline species have been described, but need further characterization and most seem to be very air sensitive.[212,282] Again the interest in these compounds has been directed mainly towards their oxidation to Mn^{III} and Mn^{IV} species.

(*ii*) *Diketones and related ligands*

Significant data are available only on the α- and β-diketones and structurally related ligands.[283] A single tris-chelate cationic species of dimethylphthalate appears to be the sole representative of the γ-diketone type.

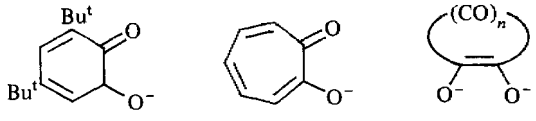
Neutral *α-diketones* are represented only in two crystalline quinone species $MnBr_2 \cdot L$ of unknown structure, but there is a litle more detail available on the anions of hydroxyquinones (**93**)–(**97**), the related tropolone (**98**) and the dianions of the cyclic carbonyls (**99**) for $n = 2$, 3 and 4. The latter give polymeric hydrates based on $[MnO_6]$ octahedra.[284] The hydroxyquinonate anions (**93**)–(**97**) have all given crystalline species $Mn(O, O)_2$, one of which (**97**) has been shown to be tetrameric.[285] This compound was prepared from $Mn_2(CO)_{10}$ and the hydroxyquinone in toluene; reaction in pyridine gave $[Mn(O,O)_2py_2] \cdot 2py$. The anion (**94**) has also been reported to give a solid $MnCl(O,O) \cdot 4EtOH$.



(**93**) R = H
(**94**) R = Me

(**95**)

(**96**)



(**97**)

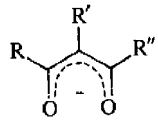
(**98**)

(**99**)

The tropolone compound $Mn(O,O)_2$, where (O,O) = (**98**), was prepared from the ligand and $Mn(OAc)_2$ in aqueous methanol, and, after drying, was sublimed. Undoubtedly, it is polymeric, but the details are unknown.

Acetylacetonate is usually considered the reference ligand for the *β-diketonates* and it has been comprehensively studied. Neutral ligand compounds are known: acacH acts as a unidentate ligand on an $(MnBr_2)_n$ linear polymer, like (**8**), and it chelates in $[Mn(acacH)_3][InCl_4]_2$.[286] A related ligand diamidomalonate has been proven to chelate in $[Mn(NO_3)_2L_2]$, which has bidentate amide and unidentate nitrates.[289]

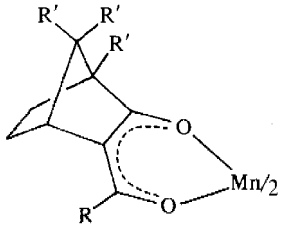
But most of the chemistry of acetylacetone and related ligands concerns their behaviour as monoanions, bonding essentially in the keto-enol form (**100**). The types of ligands of this general



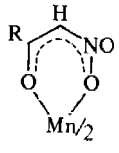
(**100**)

Table 27 Mn^{II} Compounds with β-Diketonate Type Ligands

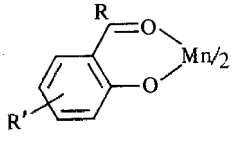
Ligand Class	*R*	*R′*	*R″*	*Diagram*	*Compound Type*	*Ref.*
Dialdehyde	H	var.	H	(**100**)	$\{Mn(O,O)_2\}_n$	283
Ketoaldehyde	H	H, Me	—	(**101**)	$\{Mn(O,O)_2\}_n$	283
Diketone (i)	var.	H	var.	(**100**)	$\{Mn(O,O)_2\}_n$; $\{Mn(O,O)_2L\}_2$;	283
					$[Mn(O,O)_2L_2]$; $[Mn(O,O)_3]^-$;	291
					$\{Mn(O,O)_2X\}^-$; $\{Mn(O,O)X\}_n$	292
(ii)	CF_3	Me	—	(**101**)	$\{Mn(O,O)_2\}_n$; $\{Mn(O,O)_2L'\}_2$	283
(iii)	Me	var.	Me	(**100**)	$Na[Mn(O,O)_3]$	283
Ketoesters (i)	H	Me	OMe	(**100**)	$\{Mn(O,O)_2\}_n$	283
(ii)	var.	var.	OR	(**100**)	$\{Mn(O,O)_2\}_n$; $[Mn(O,O)_2L'_2]$	283
Nitroketones	Ph	—	—	(**102**)	$\{Mn(O,O)_2\}_n$; $[Mn(O,O)_2L'_2]$	283
Phenolaldehydes	H	var.	—	(**103**)	$\{Mn(O,O)_2\}_n$; $[Mn(O,O)_2L'_2]$	283, 39
Phenolketones	var.	var.	—	(**104**)	Compounds not isolated	283
Hydroxyquinones				(**105**)	$[Mn(O,O)_2(H_2O)_2]$	283



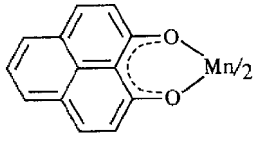
(101)



(102)



(103) R = H
(104) R = Me



(105)

class, for which Mn^{II} compounds have been described, are summarized in Table 27, together with the structural types of the Mn compounds.

The binary compounds $Mn(O,O)_2$ are probably mostly, if not all, octahedral polymers[39] like the known Ni^{II} and Co^{II} species, but the detail is unknown beyond a report that $Mn(acac)_2$ is trimeric in benzene. However, for most of the other structural forms, X-ray analyses are available of proof of type: $[Mn(acac)_2(H_2O)_2]$, $[Mn(dbm)_2(THF)_2]\cdot 2THF$ {dbm = (**100**) for R = R″ = Ph; R′ = H},[288] $[Mn(acac)_2phen]$, $[Mn_2(acac)_4(allylNH_2)_2]$ and $NH_4[Mn(O,O)_3]$ {(O,O) = (**100**) for R = CF_3; R′ = H; R″ = furyl}.[289] All show Mn octahedra and there is no compelling evidence in any of the literature for alternative polyhedra in related compounds.

Most are pale-yellow crystalline products and are robust in the air. $Mn(acac)_2$ and its hydrate are sensitive to oxidation, as are many of the others, when wet (that is in equilibrium with a solution) but are reasonably robust when dried. Yet other compounds are distinctly less O_2 sensitive. The dihydrate $[Mn(acac)_2(H_2O)_2]$ readily loses water, and the anhydrous species can be sublimed at low pressures.[290] $Mn(acac)_2$ has been used as a catalyst for a variety of chemical reactions, including polymerizations.

(*iii*) *Dicarboxylates and hydroxycarboxylates*

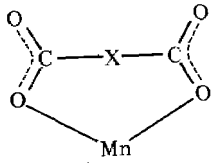
The dicarboxylates have been separated from the compounds of Section 41.3.5.2(ii) because of the possibility of the formation of chelate rings (**106**). Such chelation, however, is by no means universal in these compounds. The 1:1, 1:2 and 1:3 species, which have been shown to exist in aqueous

Table 28 Mn^{II} Oxalato Compounds[a]

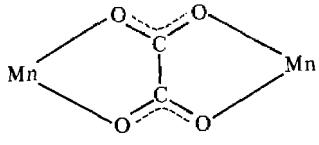
Compound	*Structural Detail*	*Ref.*
MnC_2O_4		
$MnC_2O_4 \cdot 3H_2O$		
$MnC_2O_4 \cdot 2H_2O$ (α)	*trans*-$[MnO_4(H_2O)_2]$, type (**107**) bridging	[b]
(γ)		
$M_2Mn(C_2O_4)_2$ (Li, K)		
$M_2Mn(C_2O_4)_2 \cdot 2H_2O$ (K, NH_4)	K: *trans*-$[MnO_4(H_2O)_2]$, (**106**) and (**109**)	[c]
$Cs_2Mn_2(C_2O_4)_3 \cdot 3H_2O$	$[MnO_5(H_2O)]$, (**107**) and (**108**)	[d]
$[Cr(urea)_6]_2Mn_2(C_2O_4)_5 \cdot 12H_2O$		
$K_2Mn(C_2O_4)(NO_2)_2 \cdot H_2O$		
$K_2Mn(C_2O_4)S_2O_3 \cdot 2H_2O$		
$Mn_2(C_2O_4)_2WO_3 \cdot 7H_2O$		

[a] *Gmelin* (ref. 3), 1980, **D2**, 85.
[b] R. Deyrieux, C. Berro and A. Péneloux, *Bull. Soc. Chim. Fr.*, 1973, 25.
[c] H. Siems and J. Lohn, *Z. Anorg. Allg. Chem.*, 1972, **393**, 97.
[d] H. Schulz, *Acta Crystallogr., Sect. B*, 1974, **30**, 1318.

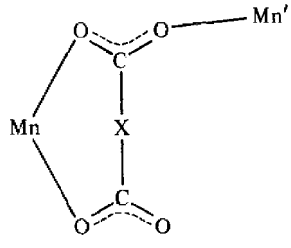
solutions and which, for oxalate, have log K's of approximately 4.5, 2 and 1.5 respectively, probably all have chelated ligands.[293] Certainly the 1:2 and 1:3 species can be oxidized to the chelated Mn^{III} species. However, most of the solid compounds (see Table 28 for the oxalate species, which have been most studied) are polymers, with the dicarboxylates currently known to bridge in the forms (**107**)–(**110**).



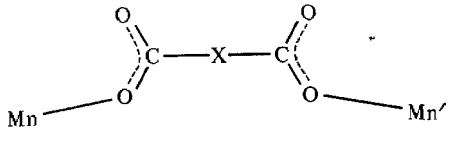
(**106**)



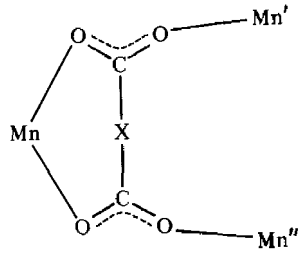
(**107**)



(**108**)



(**109**)

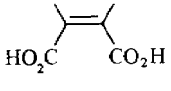


(**110**)

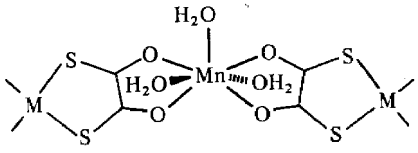
Malonate and the dianions of the other aliphatic dicarboxylic acids $HO_2C(CH_2)_nCO_2H$ (n = 1–8) have been isolated as crystalline hydrates, and some of these have been dehydrated.[293] X-Ray structural analyses have been reported for the malonate dihydrate,[294] which has *trans* H_2Os and bridging malonates of type (**110**), and for the succinate tetrahydrate and adipate dihydrate:[295] the succinate reputedly has a *trans*-$[MnO_2(H_2O)_4]$ polyhedron with bridging dicarboxylate, presumably as in (**109**). The monoanion of maleic acid (**111**) is only unidentate in crystalline $[Mn(H\text{-maleate})_2(H_2O)_4]$;[296] but the equivalent compound of phthalic acid is a bis-chelated octahedral $[Mn(O,O)_2(H_2O)_2]$ species.[297] Clearly other interactions in the solids, as well as the bonding interactions with Mn^{II}, define structure in the carboxylate compounds.

All of these species are relatively robust in the air, even in solution; but, especially when the pH is raised, they can be readily oxidized to Mn^{III}.

Another interesting structural variation has recently been reported[298] as occurring in some mixed metal compounds of dithiooxalate, *i.e.* $MMn(S_2C_2O_2)_2 \cdot 7.5\,H_2O$ (for M = Ni and Cu). These have the linear polymer structure (**112**), with seven-coordinate Mn^{II}.



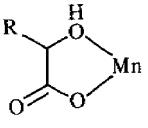
(111)



(112)

The *hydroxycarboxylates* are known in a range of crystalline binary Mn^{II} hydrates,[299–303] but the only ternary compounds are a $5NO_2$-salicylate, which is probably $Na_2[MnL_2(H_2O)_2]$, and the Na and K tartrates $M_2MnC_4H_2O_6 \cdot 6H_2O$.[299] Both the aliphatic and aromatic (only salicylates) hydroxycarboxylates form 1:1 and 1:2 species in aqueous solution, which are of relatively low stability, and much of the interest to date has been in their oxidations to Mn^{III} and Mn^{IV}—such oxidations being readily achieved in alkaline solutions, especially as the number of hydroxy groups on the ligand is increased.

Table 29 contains the known structural details.[300–303] All are octahedral [MnO_6] species and a common feature is the chelate ring (**113**). Several of the compounds are *cis*-$[Mn(O,O)_2(H_2O)_2]$ monomers, but the more complex acids {(**113**) for R containing OH and/or CO_2H groups} form polymers. For example, citrate in $Mn_3(C_6H_5O_7)_2 \cdot 9H_2O$ acts as a terdentate ligand to one Mn and bridges to two others: there are $[Mn(H_2O)_6]^{2+}$ and $[MnO_5(H_2O)]$ polyhedra.



(113)

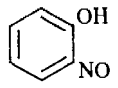
(*iv*) *Other ligands*

A range of bidentate O donor ligands, based on nitrogen oxides, have been reacted with Mn^{II}. Although several compounds of ligands (**114**) and (**115**) in their monoanion form have been described,[304] they are not fully characterized as Mn^{II} species, and the reported dark colours suggest the oxidation may have occurred during the preparations. Compounds of the other potentially anionic bidentates (**116**)–(**119**) are somewhat better characterized, although (**116**) appears to have been detected so far in only neutral unidentate function.[305] One compound of ligand (**117**) has been shown to be a *trans*-$[Mn(O,O)_2(H_2O)_2]$ octahedral species,[306] and the ligands (**118**) and (**119**) form rather insoluble $Mn(L—H)_2$ species, which are probably polymeric with [MnO_6] octahedra.[307,308]

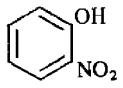
The orange tris-chelated compounds of 2,2′-bipyridyl-*N*,*N*′-dioxide (**120**) are very sensitive to light and to oxygen: the most robust, the $[PtCl_4]^{2-}$ salt, has been described as being stable in the light for one hour. Like the $[Mn(terpyO_3)_2]^{2+}$ cations, they can be oxidized in CH_3CN to Mn^{III} and to Mn^{IV} (Section 41.3.5.4). Also described, have been $[Mn(bipyO_2)_2(NCS)_2]$ and $Mn(bipyO_2)Cl_2$, which appear to be somewhat more robust.[309]

Table 29 The Mn^{II} α-Hydroxycarboxylates of Known Structure

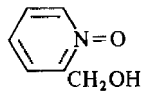
Compound	*Coordination Polyhedra*	*Ref.*
$Mn(glycollate)_2 \cdot 2H_2O$	*cis*-$[Mn(O,O)_2(H_2O)_2]$ monomers	301
$Mn(L\text{-lactate})_2 \cdot 2H_2O$	*cis*-$[Mn(O,O)_2(H_2O)_2]$ monomers	301
$Mn(malate) \cdot 3H_2O$	*cis*-$[Mn(O,O)O_2(H_2O)_2]$ polymer	302
$Mn_3(citrate)_2 \cdot 9H_2O$	$[Mn(H_2O)_6]^{2+}$ and $[Mn(O,O,O)O_2(H_2O)]$ polymer	300
$Mn(D\text{-gluconate})_2 \cdot 2H_2O$	*cis*-$[Mn(O,O)O_2(H_2O)_2]$ polymer	300
$Mn(H\text{-salicylate})_2 \cdot 2H_2O$	[MnO_6]	303



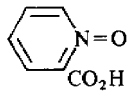
(114)



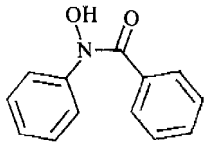
(115)



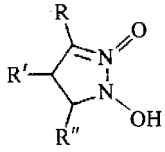
(116)



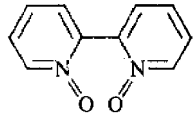
(117)



(118)



(119)



(120)

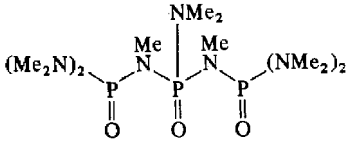
A few tris-bidentate di-sulfoxides also are known,[310] and a bidentate phosphate ester[311] and amide[312].

Two compounds of sulfoacetic acid ($HO_3SCH_2CO_2H$) were described by Hahn and Wolf in 1925, but there appears to have been no detailed study since on this ligand, or any other alkylsulfonic acid with Mn^{II}.

41.3.5.4 Multidentate ligands

For the cyclic, or crown, ethers, see Section 41.3.10.4. There appears to have been no systematic study of multidentate all-oxygen ligand compounds of Mn.

Two well-defined *neutral terdentates* terpyridyl-*N*,*N*′,*N*″-trioxide and the phosphoramide (**121**) both form MnX_2L and $[MnL_2]X_2$ species. For terpyridyltrioxide, the bright orange crystalline compounds $MnCl_2(terpyO_3)\cdot 3H_2O$ and $[Mn(terpyO_3)_2](ClO_4)_2\cdot 2H_2O$ are light sensitive, but the latter forms stable solutions in CH_3CN. Oxidation to both Mn^{III} and Mn^{IV} has been achieved electrochemically in reversible one-electron steps at half-wave potentials $E_{1/2} = 1.06$ and 1.77 V (versus SCE).[314] The phosphoramide (**121**) also forms 1:1 and 1:2 crystalline solids.[315]

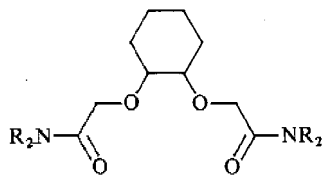


(121)

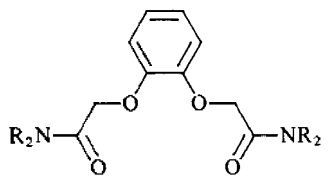
Anionic terdentates are certainly represented in a crystalline citrate (Section 41.3.5.3(iii)), and probably in some compounds of glycerol $\{CH_2(OH)CH(OH)CH_2OH\}$ and higher polyols which have been studied mainly for their oxidations to Mn^{III} and Mn^{IV} species.[316]

Quadridentate ligands appear to be represented solely by the ligands (**122**) and (**123**), which form eight-coordinate bis-chelate $[MnL_2]^{2+}$ cationic species.[317] The related $[Mn(N_4)_2]^{2+}$ compounds (Section 41.3.3.4(i)) have not yet been structurally characterized.

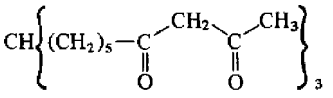
And there is a recent example of a *sexadentate* tris(β-diketone) ligand (**124**). Perhaps not surprisingly the trianion of this ligand gives a very robust Mn^{III} neutral molecule, which can be reduced to Mn^{II}; and this latter species also is kinetically stable to ligand exchange.[318]



(122)



(123)



(124)

Table 30 The Coordination Polyhedra of the Binary, Ternary and Quaternary Mn^{II} Sulfides

Tetrahedra	*Bond Lengths* (Å)[a]	*Octahedra*	*Bond Lengths* (Å)
β-MnS (Zinc blende)		α-MnS	2.612
γ-MnS (Wurtzite)		MnS_2	2.59
$Cs_2Mn_3S_4$	2.41–2.54	Ga_2MnS_4 ($MgGa_2S_4$ type)	
$BaMnS_2$	2.38–2.47	$Mn_{11}La_{32.66}S_{60}$	2.38–2.86
Ba_2MnS_3	2.39–2.42	MnM_3AlS_7	2.62
$BaMnS_4Sn$	2.38–2.51	MnM_3GaS_7	
Al_2MnS_4(I) ($ZnIn_2S_4$ type)		Mn_2SnS_4	2.60–2.62
Al_2MnS_4(II) (Cubic spinel)		Mn_2GeS_4	2.52–2.75
$Ga_{2.17}Mn_{0.75}S_4$	2.36	$Mn_{0.25}NbS_2$	
$MnYb_2S_4$		$La_6MnSi_2S_{14}$	2.64–2.67
Cu_2MnS_4Sn		$MnAg_4S_6Sb_2$	2.60–2.63
$MnCr_2S_4$	2.39	$MnIn_2S_4$ (35% Inverse spinel)	
$MnIn_2S_4$		MnV_2S_4 (Fe_3S_4 type)	

[a] Bond length data usually refer to the observed range. Where single values appear, these are averaged values. For phases without bond length data, inclusion in the table relies on X-ray powder data showing isomorphism with known species.

41.3.6 Sulfur Ligands

Manganese sulfur chemistry has been much neglected. Most detail is known of the simple solids, *i.e.* the bi-, ter- and quaternary sulfides, which so far have been generally neglected by the coordination chemist; something is understood of the 1,1-dithiolates, such as the dithiocarbamates, and of the 1,2-dithiolates or dithiolenes; but only now are results being reported of a systematic study of the thiol compounds. All Mn^{II} compounds are high spin d^5 species, with moments significantly below 5.9 BM being observed only where structures allow antiferromagnetism.

41.3.6.1 Sulfides and thiolates

Structural data are available (Table 30) for a range of binary, ternary and quaternary *sulfides* of manganese, almost invariably Mn^{II}, and these set the scene for the structures to be expected in the compounds with the more discrete polyhedra.[319] Indeed, the structural pattern is established in the simple binary compound MnS. Whereas, the stable modification of this (α-MnS) is green and has the cubic rock salt structure with $[MnS_6]$ octahedra, the well-known flesh-coloured precipitates of the qualitative analysis system are metastable β- and γ-modifications, which have $[MnS_4]$ tetrahedra with respectively the zinc blende or diamond (cubic) and wurtzite (hexagonal) structures. And so, in the rest of the known solids, there are almost equal numbers of four-coordinate tetrahedra and six-coordinate octahedra with no other polyhedra having been detected.

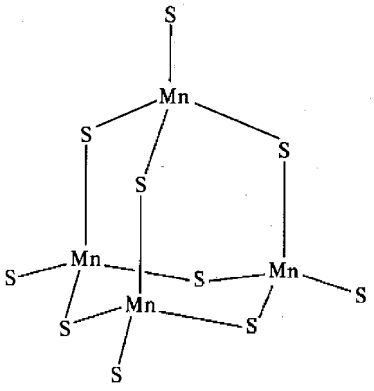
Although this same structural pattern is found in the discrete polyhedra formed by the *thiols*, there is a marked difference in redox properties; although there are no binary sulfides of higher oxidation state and very few ternary sulfides, yet many of the thiol species are very easily oxidized to stable Mn^{III} species. Hence, anaerobic conditions are usually required for the preparation of the Mn^{II} thiol species.[320]

The only monothiol studied, thiophenolate (PhS^-), forms pink tetrahedral $[Mn(SPh)_4]^{2-}$, isolated as $[NR_4]^+$ and $[PPh_4]^+$ salts,[320,321] and a red-orange, tetrameric anion $[Mn_4(SPh)_{10}]^{2-}$, which has the adamantane-like structure (**125**)[320] (which is, of course, a small fragment of the zinc blende or diamond structure of β-MnS). Each of these species has parallels in the other transition metals.

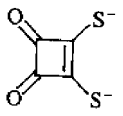
The anion $[Mn(SPh)_4]^{2-}$ was first prepared[321] from the manganese compound of dithiosquarate {dts (**126**)} and $[Mn(SPh)_2dts]^{2-}$ also was isolated. It probably represents another example of a tetrahedral $[MnS_4]$ species with a bidentate dithiol.

The original study[322] described the pink solids $K_2Mn(dts)_2 \cdot 2H_2O$, $[Ph_4P]_2Mn(dts)_2$ and $[Ph_4P]_2Mn(dts)_2 \cdot 2EtOH$. Perhaps they also are examples of bis-bidentate dithiolates, but the structural detail is unknown.

However, a dithiolate chelate compound has certainly been identified for 1,2-dithioethane[320] {$^-S(CH_2)_2S^- = edt$}: yellow-brown $[Me_4N]_2[Mn(edt)_2] \cdot CH_3CN$ and orange-yellow $[Ph_4P]_2[Mn(edt)_2]$ have been characterized; and an X-ray analysis of the former proves the bis-bidentate tetrahedral structure, with Mn—S = 2.43 Å (average) and an interchelate angle S—Mn—S of 91.5°. This anion is particularly sensitive to oxidation by O_2, giving green Mn^{III} species (Section 41.4.4).



(125)



(126)

A related chelate compound—the first to be reported[323], and the most stable towards air (pink crystals were prepared by slow evaporation of solvent in the air)—is $[Mn\{SP(Ph)_2NP(Ph)_2S\}_2]$. This also is tetrahedral, with Mn—S distances of 2.426–2.457 Å and interchelate S—Mn—S angles of 106 and 112°.

41.3.6.2 Dithiolenes

Manganese(II) is but poorly represented in the chemistry of the dithiolenes.[324,325] Only one red-brown paramagnetic compound, $[PPh_4]_2[Mn(mnt)_2]$ {mnt = $(CN)_2C_2S_2^{2-}$}, appears to have been described. In addition, several unstable nitrosyls, such as $[NEt_4]_2[Mn(mnt)_2NO]$, are known.[326] They are described as being extremely unstable in air, decomposing rapidly in solution, but more slowly in the solid state.

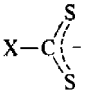
41.3.6.3 Thiocarbonyls

This section appears to be represented so far by but one ligand and that by but one fully-characterized compound: *trans*-$[MnCl_2tu_4]$ (where tu = thiourea) is isomorphous with the Ni^{II} analogue.[327]

Dithio-β-diketonates have not yet been described for Mn. Under conditions which give $[M(SacSac)_2]$ species for M = Co, Ni, Cu, the only Mn^{II} products {and Fe^{II}} obtained[328] were the dithiolylium salts of $[MnCl_4]^{2-}$.

41.3.6.4 1,1-Dithiolates

Data are available on the dithiocarbamates {(**127**) for X = R_2N—abbreviated as R_2dtc}, xanthates {(**127**) for X = RO—abbreviated as Rxanth},[329,330] dithiophosphinates ($R_2PS_2^-$ for R = Me, Ph and CF_3)[331] and dithiocacodylate ($Me_2AsS_2^-$),[332] but mostly refer to the CS_2 ligands.



(127)

Generally, preparation of the Mn^{II} species requires anaerobic conditions—$Mn(Et_2dtc)_2$ is pyrophoric, although some of the other compounds are reasonably robust. On mixing aqueous solutions of $MnCl_2$ and the Na or K salt of the ligand, yellow MnL_2 compounds precipitate. The dithiocarbamates are rather insoluble, but the ethylxanthate has significant water solubility (0.1 $g\,l^{-1}$ at 25°C). One structural determination,[333] that of $Mn(Et_2dtc)_2$, shows a linear polymer with $[MnS_6]$ octahedra (Mn—S = 2.51–2.78 Å), no chelation but bridging of type (**84**). A recent study has explored the

antiferromagnetism of this compound.[334] A related compound (1,2-bis-dithiocarbamato-ethane) is the fungicide 'maneb'.

Through an electrochemical study of the Mn^{III} compounds, the anionic species $[Mn(R_2dtc)_3]^-$ have been characterized,[335] but not isolated. Reversible reduction to Mn^{II}, as in equation (8), is followed by dissociation (9) to MnL_2 and L^-; and reoxidation to Mn^{III} then is irreversible. Such tris aniono species, which appear to contain three chelating ligands, are apparently more stable in the xanthate series and $[MEt_4][Mn(Etxanth)_3]$ has been isolated as well as $[Mn(Etxanth)_2phen]$ and two forms of $[Mn(Etxanth)_2bipy]$. This difference has been ascribed to the insolubility of the bis-dithiocarbamates. However, the electrochemical study[335] shows that the dissociation (9) occurs in solution, and there is an alternative explanation: the small chelate ring for the RCS_2^- ligands confers significant instability on the larger Mn—S polyhedra of Mn^{II}, but this instability is reduced and the 'bite' of the chelate ring increased as Mn—S distances are reduced in Mn^{III} and Mn^{IV}.

$$[Mn^{II}(R_2NCS_2)_3]^- \underset{+e}{\overset{-e}{\rightleftharpoons}} [Mn^{III}(R_2NCS_2)_3]^0 \underset{+e}{\overset{-e}{\rightleftharpoons}} [Mn^{IV}(R_2NCS_2)_3]^+ \quad (8)$$

$$[Mn(R_2NCS_2)_3]^- \rightleftharpoons Mn(R_2NCS_2)_2 + R_2NCS_2^- \quad (9)$$

The enhanced stability of the tris-chelate species in the higher oxidation states is thus explained.

41.3.7 Halides

The artificiality of attempting to separate the compounds of the metals into 'salts' and 'complexes' becomes perhaps most apparent with the halides. As with the other transition metals, Mn^{II} forms, for example, at least the crystalline chlorides $MnCl_2$, M^IMnCl_3, $M^IMn_2Cl_5$, $M^IMn_4Cl_9$, $M^I_2MnCl_4$, $M^I_3MnCl_5$ and $M^I_4MnCl_6$ and other ternary and quaternary phases. As well, many of these, when crystallized from water, form hydrates; and, equally, there are 'solvates' formed from the other solvents including traditional 'ligands' like pyridine.

In almost all of the series of binary and ternary compounds known, there are examples of the dominant structural theme in the crystalline halide compounds—the $[MnCl_6]$ octahedron. These octahedra are derived, according to the point of view, from Mn^{2+} (and the other M^+) fitting into appropriate 'holes' in close-packed halide lattices, or from face-, edge- or corner-sharing of interconnected octahedra, forming polymers. In the hydrates and the other solvates, other octahedra, containing molecules of solvent, occur.

In the above list, there are also examples of discrete $[MnCl_4]^{2-}$ tetrahedra, especially in the $M^I_2MnCl_4$ and $M^I_3MnCl_5$ series, and especially when M^I is large. There are no known examples of tetrahedral fluoro species, but they are quite significant in the bromides and iodides. In describing such solids, it is perhaps not illogical to talk of Mn^{II} 'complexes'. However, the problem of definition of a 'complex' is well illustrated by the ternary hydrate $(NH_4)_2MnCl_4 \cdot 2H_2O$. Its structure is derived (Figure 2) from that of NH_4Cl, simply by replacing two adjacent NH_4^+ ions by a *trans*-$Mn(H_2O)_2$ unit; and a continuous series of solid solutions are known in the range $6NH_4Cl \cdot MnCl_2 \cdot 2H_2O$ to $2NH_4Cl \cdot MnCl_2 \cdot 2H_2O$. Which is the complex? Surely the ternary hydrate is at least as much a complex of NH_4Cl as it is a complex of manganese(II). Any attempt to separate, for example, $MnCl_2$ from ternary phases like $KMnCl_3$, by classifying one as a 'salt' and the other as a 'complex', is not only illogical but also denies their close relationship.

Accordingly we have tried a novel (to the coordination chemist) classification: taking firstly the solid compounds which contain linked octahedra; treating the tetrahedral $[MnX_4]^{2-}$ species as a separate problem; and then addressing the problem of the polyhedra formed in the fluid phases in another separate section. On current knowledge, these are the only coordination polyhedra to be considered for Mn^{II} halo compounds: four-planar is unknown, and five-coordinate species have been detected only in a few examples of $[MnX_2L_3]$ and $[Mn_2(\mu\text{-}X)_2X_2L_4]$, which have been discussed in the sections on the appropriate unidentate ligands.

The basic data are available in the Gmelin volumes **C4** and **C5**, with earlier reviews in Colton and Canterford's book,[336] and by Kemmitt;[210] and more recent data are in the annual reviews,[4–6] and from *Structure Reports*.

41.3.7.1 Crystalline halides with octahedral coordination

(*i*) *Fluorides*

All known crystalline Mn^{II} fluoro compounds have octahedral coordination for the metal. A feature of these fluorides is the lack of crystalline hydrates: only $MnF_2 \cdot 4H_2O$ (isostructural with Zn) appears to have been characterized.

The pink binary compound MnF_2, known since the time of Berzelius, is reasonably stable chemically and barely soluble in most common solvents. It is the most thoroughly studied of any manganese fluoro compound, being of interest for both its spectroscopic and magnetic properties: it was the compound in which the exciton and exciton–magnon structure of electronic transitions in antiferromagnetic insulators was first discovered and identified. The cubic perovskite $RbMnF_3$ also has been much studied because its magnetic behaviour is very close to that of the ideal isotropic Heissenberg antiferromagnet.

MnF_2, in its normal crystalline form (at least four others are known), has a tetragonally distorted rutile (TiO_2) structure, with Mn—F (average) = 2.11 Å. Similar bond lengths are found in the known structures of the ternary and quaternary phases (Table 31), many of which also can exist in different structural forms at different temperature and pressure. In only one known case, that of $Ba_2[MnF_6]$ at high pressure, is there evidence for a discrete $[MnF_6]^{4-}$ octahedron. (However, it may well be possible to define conditions for the separation from solution of compounds $[ML_6]^{4+}[MnF_6]^{4-}$, using suitably sized inert cations.) The normal form of Ba_2MnF_6 is best represented as $Ba_{2n}F_{2n}(MnF_4)_n$, with chains of corner sharing $[MnF_6]$ octahedra — a common feature of the M_2MnF_4 species.

Probably one of the major driving forces for the formation of such 'polymers', rather than discrete $[MnF_6]^{4-}$ anions, is the electroneutrality concept, which leads one to expect that highly charged ions will be unstable.

(*ii*) *Chlorides*

The structural variation observed here is greater than for the other halides; there is almost as much variety in the crystalline hydrates as in the (often hygroscopic) anhydrous compounds; and undoubtedly further variants will be found as the systems are further explored.

$MnCl_2$ is certainly the stable manganese chloride, as $MnCl_3$ is unstable above − 40°C, and claims for $MnCl_4$ have never been substantiated. Recent reports[85,189] describe reactive forms of the anhydrous material useful for preparing various compounds of $MnCl_2$ (and the other halides). However, in the normal form, crystalline $MnCl_2$ has the hexagonal layer-type structure defined first for $CdCl_2$. The pink solid is hygroscopic, very soluble in water and forms hydrates $MnCl_2 \cdot nH_2O$ (for n = 1, 2, 4 and 6). It also, of course, forms compounds $MnCl_2 \cdot nL$, often called complexes, with an enormous range of other ligands (L): those for unidentate ligands and n = 1 have structures like (**13**); the great majority of the n = 2 compounds appear to be chain polymers like (**8**); and $MnCl_2 \cdot 4H_2O$, like many other of the n = 4 species, is an octahedral monomer *cis*-$[MnCl_2(H_2O)_4]$. The hexahydrate, which is almost certainly $[Mn(H_2O)_6]Cl_2$, is stable only below − 2°C. For some

Table 31 Manganese(II) Ternary and Quaternary Fluorides with $[MnF_6]$ Octahedra

Phase	*Comment*
M^IMnF_3	Na, K, Rb, Cs, NH_4, Tl — usually cubic perovskites (Mn—F = 2.11–2.13 Å)
$MgMn_2F_6$ and Mg_2MnF_6	Both have MnF_2 structure
$M^IMn_3F_7$	Na only — no structural detail
$M^I_3Mn_2F_7$	M = K, Rb — tetragonal M_3 = NaCd or NaCa — cubic
$M^I_2MnF_4$	M = K, Rb, Cs — tetragonal (Mn—F = 2.09–2.11 Å) M_2 = Ba — orthorhombic, Mn—F = 2.037–2.151 Å (av. 2.098 Å)
$M^{III}MnF_5$	M = Al, Ga, Cr
Ba_2MnF_6	Normally $Ba_{2n}F_{2n}(MnF_4)_n$, but high pressure form has the $K_2[GeF_6]$ structure
$LiMn[GaF_6]$	Cation ordered version of $Na_2[SiF_6]$ (Mn—F = 2.121 Å)
$Na_2MnM^{III}F_7$	M = Fe, V (Mn—F = 2.08 Å)

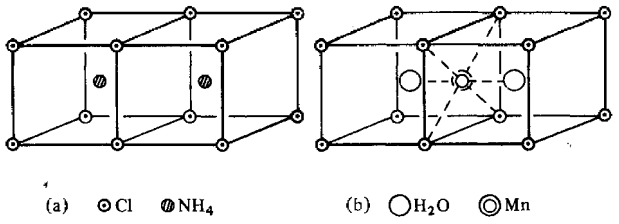


Figure 2 The relationship of $MnCl_2 \cdot 2NH_4Cl \cdot 2H_2O$ to the structure of NH_4Cl: (a) two adjacent cubic cells of NH_4Cl; (b) replacement of $2NH_4^+$ by $Mn(H_2O)_2^{2+}$

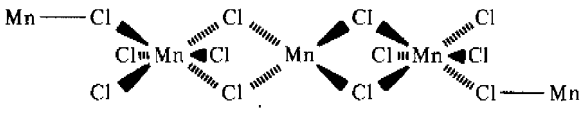
of the other unidentate ligands, we have also noticed compounds $MnCl_2 \cdot nL$ for $n < 1$. These have structures shading from the double chains of (**13**) into the fully layer structures of $MnCl_2$.

Mixing $MnCl_2$ and MCl (M = alkali metal cation, NH_4^+, *etc.*) in a melt of appropriate composition gives on cooling the ternary compounds $MMnCl_3$. Most of these pink or red solids are very hygroscopic and their preparation from water usually gives hydrates of them. At different stoichiometries, compounds of the series M_2MnCl_4 and sometimes also M_3MnCl_5 and M_4MnCl_6 can be

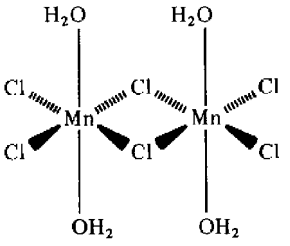
Table 32 Structural Variety in the Ternary Mn^{II} Chlorides and Their Hydrates

Phase	*Structural Data*	*Examples*	*Ref.*
Na_6MnCl_8	C.c.p. Cl^-, with Mn and Na in ordered octahedral sites		
$(NH_4)_6MnCl_8 \cdot 2H_2O$	See Figure 2		
MMn_2Cl_5		Na, pyH	
$CsMn_4Cl_9$	Tetragonal, with ~ c.c.p. Cl^-—$[MnCl_6]$ octahedra share five edges and one corner		
$Na_2Mn_3Cl_8$	Both c.c.p. and hexagonal stacking of Cl^-, Mn in $\frac{3}{4}$ of octahedral sites		
$MMnCl_3$ (*a*)	Hexagonal ($P6_3/m$) infinite chains of face-sharing octahedra $[MnCl_6]$	NMe_4, NEt_4	
(*b*)	Hexagonal ($P6_3/mmc$)—variation of (*a*)	Rb, Cs^{II}, $MeNH_3$	
(*c*)	Rhombohedral ($R\bar{3}$)—Ilmenite ($FeTiO_3$) structure—trigonal distortion of h.c.p. Cl^-	Na	
(*d*)	Rhombohedral ($R\bar{3}m$) Mn_3Cl_{12} trimers of face-shared octahedra, interconnected in spirals by corner-sharing (**128**)	Cs^I	
(*e*)	Tetragonal (P_4mm)—distorted perovskite, see (*f*)	K	
(*f*)	Cubic-perovskite $[MnCl_6]$—formed by three-dimensional corner-sharing	NH_4, Cs^{III}	
(*g*)	Monoclinic ($P2_1/c$)—infinite chains of face-sharing octahedra, like (*a*)	Me_2NH_2	
$MMnCl_3 \cdot H_2O$	Edge-sharing linear polymer $[MnCl_5O]$	pyH, quinH	337
$MMnCl_3 \cdot 2H_2O$ (*a*)	Orthorhombic (*Pcca*). Corner sharing *cis*-$[MnCl_4O_2]$	α-Rb, Cs	
(*b*)	Orthorhombic (*Cmca*). Corner sharing *cis*-$[MnCl_4O_2]$	Me_2NH_2	338
(*c*)	Monoclinic. Corner sharing *cis*-$[MnCl_4O_2]$	$MeNH_3$	338
(*d*)	Triclinic. Dimers, as in (**129**) *trans*-$[MnCl_4O_2]$	β-Rb, Cs Pr^iNH_3	339
$M_3Mn_2Cl_7$ (*a*)	Hexagonal. Face-sharing, infinite chains of $[MnCl_6]$ *and* discrete $[MnCl_4]^{2-}$ tetrahedra	Me_3NH	
(*b*)	Tetragonal (*I*4/*mm*). Double perovskite layers, with each $[MnCl_6]$ sharing five corners	K, Rb	340
M_2MnCl_4 (*a*)	Cubic inverse spinel $[MnCl_6]$	Li	341
(*b*)	Tetragonal (*I*4/*mm*). Perovskite layers of K_2NiF_4 type, each $[MnCl_6]$ sharing four corners in plane	Rb, α-Cs	
(*c*)	Orthorhombic (*Pbam*). Edge-sharing chains of $[MnCl_6]$	Na	
(*d*)	Complex of phases based on K_2NiF_4 perovskite layer structure—variations depend on RNH_3 groups	RNH_3	342
(*e*)	Orthorhombic (*Pnma*) $[MnCl_4]^{2-}$ *tetrahedra*	NMe_4, β-Cs	
(*f*)	Cubic $P2_13$ $[MnCl_4]^{2-}$ *tetrahedra*	$[Ph_3MeAs]$	
(*g*)	Triclinic $[MnCl_4]^{2-}$ *tetrahedra*	NEt_4, pyH	
$M_2MnCl_4 \cdot 2H_2O$ (*a*)	Tetragonal (*I*4/*mmm*) *trans*-$[MnCl_4O_2]$ (Figure 2)	NH_4, K	
(*b*)	Triclinic. Linear chains of *trans*-$[MnCl_4O_2]$—edge-sharing	Rb, Cs	
M_3MnCl_5	$M_2[MnCl_4] \cdot MCl$, with *tetrahedra*	Cs, $dienH_3$	343
$[Cr(NH_3)_6][MnCl_5H_2O]$	Octahedral		344

prepared, as well as hydrates of them, but especially of the former. In addition, a variety of more complex species, including the NH_4Cl complex of solid solutions (Figure 2), have been identified structurally (Table 32). The use of larger quaternary ammonium, phosphonium and arsonium cations to precipitate appropriate ternary compounds from organic solvents, like the alcohols and acetone, has further extended the range of known types.



(128)



(129)

In the great bulk of the known solids,[345] from $MnCl_2$ to $M_4\,MnCl_6$, and including M_2MnCl_4, the dominant coordination polyhedron for Mn is the octahedron: $[MnCl_6]$ units are formed by face-, corner- or edge-sharing of bridging chlorides in the anhydrous species (Table 32). Many of the compounds listed also undergo phase changes at different temperature and pressure, but the manganese retains octahedral coordination.

The only example of a discrete hexachloromanganese(II) anion appears to be in $K_4[MnCl_6]$, although others may be obtainable with appropriately sized 4+ cations, based, for example, on Pt^{IV}. The few examples of M_2MnCl_5 are examples of the only other structural theme, that of the tetrahedral $[MnCl_4]^{2-}$. Despite apparent stoichiometry, few of the known M_2MnCl_4 solid compounds contain this tetrahedral anion: although they give tetrahedra in melts,[346] most of the solids have layer type structures related to K_2NiF_4, containing corner-sharing $[MnCl_6]$ octahedra. Only one example of mixed coordination polyhedra for Mn^{II}–chloro species is known, the recently described $(Me_3NH)_3Mn_2Cl_7$, which contains both $[MnCl_6]$ in chains of face-sharing octahedra and discrete $[MnCl_4]^{2-}$ tetrahedra. As expected, the tetrahedra are most common in the compounds of the larger cations (Cs for the alkali metals). Measured bond lengths in the $MnCl_6$ octahedra range from 2.46 to 2.63 Å, but they are generally near 2.53–2.55 Å for bridging Cl and 2.50 Å for terminal Cl.

In the various 'hydrates', the water molecules usually are in the Mn coordination sphere. They make up the octahedra without the embarassment of high negative charges, and thus there are more examples here of monomers or small oligomers, like the dimers of (**129**). Other neutral ligands can replace the water, but very little work seems to have been attempted in this area for Mn. One recent report[347] postulated both $[MnCl_4L_2]^{2-}$ and $[MnCl_4L_4]^{2-}$ species for N donor ligands, but, whilst the former are quite acceptable, the latter are most unlikely to occur and cannot be accepted without full X-ray evidence.

Much of the interest in these compounds has been in their physical properties such as spectra, which have been reviewed recently in the Gmelin volumes,[348] and magnetism. Of particular interest for magnetic studies have been the compounds, such as $[NMe_4]MnCl_3$, which have one-dimensional magnetic coupling in the chains of face-sharing $MnCl_6$ octahedra.

(*iii*) *Bromides and iodides*

The bromo, and especially the iodo compounds of Mn^{II} are somewhat less robust than the chlorides, so that the variety of observed compounds and the structural patterns are less rich[349] (Tables 33 and 34).

Where compounds have been studied (and the structural data are less complete), there are close parallels between the chloro and bromo species, with one significant variation: there is a noticeable tendency for the bromides to form $[MnX_4]^{2-}$ tetrahedra more readily. Thus, $Rb_2[MnBr_4]$ is tetrahedral, whereas the chloro compound (Table 32) is known only as an octahedral polymer; and there is no octahedral polymer form of Cs_2MnBr_4 as there is for the chloro analogue. Similarly, in the various onium salts, discrete $[MnBr_4]^{2-}$ tetrahedra are more common. One intriguing compound in

Table 33 Structural Detail for the Mn^{II} Bromo Compounds

Compound	*Coordination Polyhedra*	*Comment*
$MnBr_2$	$[MnBr_6]$	CdI_2 layer structure
$MnBr_2 \cdot 2H_2O$	*cis*-$[MnBr_4O_2]$	Monomer
$MnBr_2 \cdot 2H_2O$	*trans*-$[MnBr_4O_2]$	Chains—edge sharing, as in (**8**)
$MMnBr_3$ (K, Tl)	$[MnBr_6]$	Double chains—edge sharing (NH_4CdCl_3 type)
(Rb, Cs, NMe_4)	$[MnBr_6]$	Face-sharing chains[5] of $CsNiCl_3$ type
$MMnBr_3 \cdot 2H_2O$ (Cs)	*cis*-$[MnBr_4O_2]$	Corner-sharing chains, as in $CsNiCl_3 \cdot 2H_2O$
(Me_3NH)		$P2_1/m$
M_2MnBr_4 (Rb, RNH_3)	$[MnBr_6]$	Tetragonal, K_2NiF_4 layer structure[350]
(Cs, pyH, NMe_4)	$[MnBr_4]^{2-}$	*Pnma*. Discrete tetrahedra
(Ph_3MeAs)	$[MnBr_4]^{2-}$	Cubic. Discrete tetrahedra
Cs_3MnBr_5	$[MnBr_4]^{2-}$	Isomorphous with chloride
K_4MnBr_6	$[MnBr_6]$	

this series is $[Et_2OH]MnBr_3$, which is described as a light yellow solid. Perhaps it is an example of an $[Mn_2Br_6]$ dimer of tetrahedra. $K_4[MnBr_6]$ is an example of a discrete octahedron, and there is a recent report[351] of the preparation of $[Me_2NH_2]_4MnBr_6$.

Both $MnBr_2$ and MnI_2 have the CdI_2 layer structure, rather than the $CdCl_2$ variant of the chloride, but all form similar 'hydrates' of similar properties, with the tetrahydrates being the normally stable form. The compounds with the other neutral ligands appear generally to parallel the chloro species; but a recent report[193] of the structure of $MnI_2 \cdot PMe_2Ph$ raises an interesting structural variant: $[MnI_4P_2]$ octahedra alternate with MnI_4 tetrahedra, as in (**69**).

Ternary iodo compounds are formed only with large cations: the onium salts appear to be invariably examples of $[MnI_4]^{2-}$ tetrahedra, although both $CsMnI_3$ and $TlMnI_3$ give examples of $[MnI_6]$ polymers (Table 34).

41.3.7.2 Tetrahedral $[MnX_4]^{2-}$ and $[MnX_3L]^-$ species

Tetrahedral $[MnX_4]^{2-}$ species were identified by Nyholm and co-workers[352] in the first unequivocal demonstration of tetrahedra in transition metal compounds. More recent structural studies[317,328,343,345,349,350] have confirmed the existence and range of such tetrahedra some of which are listed in Tables 32–34. They are known for Cl, Br and I, but not for F. Cotton and Goodgame[31] first studied the electronic spectra, details of which have been summarized.[348]

There are also descriptions in the literature[349] of mixed ligand species $[MnBr_2Cl_2]^{2-}$, $[MnCl_2I_2]^{2-}$ and $[MnBr_2I_2]^{2-}$, but the data do not appear to prove the existence of such definite species rather than mixtures.

The conditions under which tetrahedra form are becoming clearer, although some of the identifications rely on spectra and a doubt must remain. (How different will be the spectra of $[MnCl_5]^{3-}$, if and when identified, from that of $[MnCl_4]^{2-}$?) The structural data (Tables 32–34) show that, of the binary and ternary compounds, few of the chloro species, more of the bromo species, and most of the iodo species have $[MnX_4]^{2-}$ tetrahedra in the solids. This progression needs no further explanation than size of halide (see especially the Cs and Rb species M_2MnX_4). In melts, however, M_2MnCl_4 compounds give tetrahedra.[345,346,349] Even in aqueous solution, and in other solvents (Section 41.3.7.3), in the presence of an excess of X^-, such tetrahedra have been detected, and it is assumed that $[MnX_3 \text{ solvent}]^-$ tetrahedra also are present. Such latter species are yet poorly

Table 34 Structural Detail for the Mn^{II} Iodo Compounds

Compound	*Coordination Polyhedra*	*Comment*
MnI_2	$[MnI_6]$	CdI_2 layer structure
$MMnI_3$ (Cs)	$[MnI_6]$	Hexagonal, related to $CsNiCl_3$, chains of face-sharing octahedra[5]
(Tl)	$[MnI_6]$	Edge-sharing double chains, like bromide
M_2MnI_4 (various)	$[MnI_4]^{2-}$	No X-ray data, but all known compounds appear to contain discrete tetrahedra
$MnI_2 \cdot PhMe_2P$	$[MnI_4]$ and $[MnI_4P_2]$	Octahedra and tetrahedra alternate in the chains[193]

characterized for Mn^{II}: among the few crystalline species are $[NR_4][MnX_3L]$ (R = alkyl; X = Cl, Br; and L = a unidentate imidazole N ligand).[39] In another pertinent example, whereas Co, Ni and Cu form compounds $[MnX_3L]$ {X = Cl, Br, I; and L = (**10**)}, Mn forms $L_2[MnX_4]$ species.[81]

41.3.7.3 Halo compounds of Mn^{II} in the fluid phases

In the gas phase, all MnX_2 compounds are linear symmetrical molecules with zero dipole moment.[346,353] In addition, dimers $[Mn_2(\mu\text{-}X_2)X_2]$ have been detected for at least the chloride and bromide.[353] Parallels with the alkyl (**3**) and amido (**11**) species are evident.

Liquid (melt) phases of the ternary compounds, or of MnX_2 in MX melts[346] give only octahedra for the fluorides, but tetrahedra for Cl, Br and I.

In water, all MnX_2 species dissolve to give $[Mn(H_2O)_6]^{2+}$, although at higher concentrations $[MnX_n(H_2O)_{6-n}]^{-(n-2)}$ species occur.[346,354] For F^-, K_1 is only of the order of five to ten. With excess halide, such species assume greater importance, and there is reasonable evidence for $[MnX_3H_2O]^-$ and $[MnX_4]^{2-}$ for X = Cl, Br. However, without the spin-allowed transitions found in the electronic spectra of the other transition metals, it is less easy to detect the various halo species for Mn^{II}.

In non-aqueous solutions, such as in $MeNO_2$ and CH_3CN, the tetrahedral anions $[MnX_4]^{2-}$ (X = Cl, Br, I) appear to maintain their integrity sufficiently, despite their lability, to allow meaningful measurement of some of the physical properties of these tetrahedra.

41.3.7.4 Fluoro anions of the nonmetals as ligands

Fluoro anions of the nonmetals, such as BF_4^-, PF_6^- and SiF_6^{2-} are usually used, instead of the explosive ClO_4^-, especially in non-aqueous solvents, when a counterion is required that does not compete too effectively for a place in the metal coordination sphere. However, since the acceptance of the reality of ClO_4^- coordination,[277,278] it has become to be recognized that these fluoro anions also can bond: BF_4^- is as good a ligand as ClO_4^-, although more subject to side reactions and therefore leading to unexpected products like the tetrameric species (**18**); PF_6^- is less good than ClO_4^-, and was originally used,[278] by contrast, to demonstrate perchlorate coordination; but direct bonding of AsF_6^- and SbF_6^- have now been demonstrated, both in the binary compounds MnX_2[335] and in the compound $[Mn(AsF_6)_2(NSF_3)_4]$.[103]

41.3.8 Hydrogen and Hydride Ligands

This is but a fringe area of Mn^{II} chemistry, although some detail of each class is known.

41.3.8.1 Hydrogen

The classification 'Mn hydrides' is persistent in the literature. The earlier view that H_2 'only dissolved' in metallic Mn, and formed no well-defined hydrides, was probably too simplistic, although Mn—H species are unlikely to be of great interest to the preparative chemist.

MnH_2 has been trapped in Ar or N matrices at 4 K, and spectroscopic measurements[356] suggest a bent molecule with H—Mn—H of $117 \pm 30°$; other authors[357] think that the results of some mathematical calculations in favour of a linear molecule should take precedence.

MnHI·1.5 THF has been described as resulting from the reaction of MnI_2 with $AlEt_3$ in THF, whereas related reactions usually produce binary MnAl derivatives.

The role of Mn^{II} hydrides in organometallic chemistry was reviewed[359] in 1973. But, most of the recent papers on Mn hydrides refer to the effect on the magnetism of intermetallic phases when H_2 is absorbed. In a few cases, stoichiometry has been determined—examples are Mn_2ErH_4, $Mn_2ErH_{4.6}$,[360] Mn_2ScH_4,[361] and Mn_2ZrH_3.[362] A neutron diffraction analysis of the latter shows 12 hydrogen (or deuterium) nearest neighbours for Mn, at 1.74–1.77 Å. Although no pattern is yet emergent, it seems not improbable that the oxidation state formalism will have but little use in this area of chemistry.

41.3.8.2 Hydride ligands

Both $Mn(BH_4)_2$ and $Mn(AlH_4)_2$ have been described,[363] but little is known of them and their reactions. Nöth[364] also described the species $Li_nMn(BH_4)_nX_2 \cdot mEt_2O$ ($n = 1, 2, 3$ and X = Cl, I) and $LiMn_2BH_4I_4$ as yellow or orange oils, obtained by reacting ether solutions of $LiBH_4$ and MnX_2 in various ratios and then evaporating to dryness.

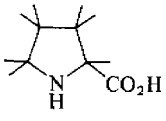
The Mn^{II} compounds of the boranes and carboranes were covered in the companion volume[365] and they include at least one example of a low spin Mn^{II} carborane.[366]

41.3.9 Mixed Donor Atom Ligands

Macrocyclic systems are discussed in Section 41.3.10.5.

41.3.9.1 'Ambiguous' N—O and bidentate N—O ligands

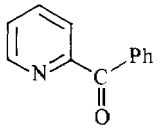
This is an area of chemistry in which most that has been attempted has been at a very superficial level. It is very easy in particular to synthesize Schiff base N—O donor set hybrid ligands and to make Mn^{II} compounds from them. It is not easy, unless one uses X-ray techniques, to unambiguously assign which ligand donor atoms are bound. Furthermore, the marked tendency of oxygen donors to form bridges, (such behaviour is very common for carboxylic acid residues, see Section 41.3.5.2.ii)often complicates the ligand binding pattern immensely. Thus in $[Mn(pro)(H_2O)_4]^{2+}$ {pro = D,L-proline (**130**)} one might simplistically expect a monomeric octahedral ion with both N and O donors of the proline coordinated. In fact X-ray analysis indicates that the N atoms do not bind to the Mn^{II}, but that the carboxylic acid groups bind both O atoms to adjacent Mn atoms to give a continuous polymer and an MnO_6 chromophore.[253]



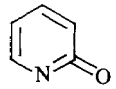
(130)

This section is constructed to deal firstly with the group of ligands which possess potential N and O donors which cannot both bind to the one Mn atom. The coverage will then extend, with increasing ligand denticity, to deal with ligands that can potentially bind more than one type of donor atom to the one Mn atom.

The major analytical technique that has been used to assign ligand binding atoms has been IR spectroscopy. Large numbers of workers have based their claims for or against the binding of specific donors on the change (or lack of change) of such 'parameters' as amine stretching frequencies, pyridine breathing modes or carbonyl stretching frequencies, upon binding of the free ligand to the metal. Thus 2-benzoylpyridine (**131**) in $[MnCl_2L_2(H_2O)_2]$ is postulated on IR data to be bound only by the pyridine nitrogen with the carbonyl group, whose IR stretching frequencies are virtually unchanged upon complexation, unbound.[367] On the other hand, $MnCl_2(tp)$ (tp = 2-pyridone, **132**) appears to be isomorphous with the corresponding Cu^{II} compound, which has been shown to possess a four-coordinate dichloro-bridged structure with unidentate oxygen bonding of tp. Again, in this case, the IR carbonyl stretching frequencies are unchanged upon complexation.[368]



(131)



(132)

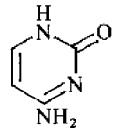
To demonstrate the difficulty of using IR evidence, Table 35 lists the CO stretching vibrations for cytosine {cy = (**133**)} and some cytosine compounds.[369] It is known that the structure of $CuCl_2(cy)_2$

Table 35 IR Carbonyl Stretching Vibrations for Cytosine and Some Cytosine Metal Compounds

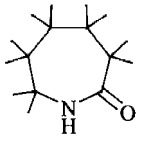
Compound	*C=O stretching frequencies* (cm^{-1})
Cytosine (cy)	1703, 1662, 1615
$MnCl_2(cy)_2$	1676, 1658, 1601
$CuCl_2(cy)_2$	1676, 1656, 1621
$MnBr_2(cy)_2$	1676, 1656, 1621, 1593
$CuBr_2(cy)_2$	1683, 1660, 1630

is effectively planar with a $CuCl_2N_2$ chromophore, however the IR evidence would indicate that the carbonyl groups are bound in all cases.

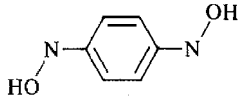
Some ligands, which possess both potential N and O donors, but whose structure forbids chelation of both donors, are listed in Table 36 along with proposed bonding evidence. Although structures are in most cases unproven and may well be polymeric, many workers appear to favour the O-bonded system rather than the N-bonded. Such bonding is proposed for probably the simplest of these 'ambiguous' ligands, *viz.* hydroxylamine;[379] however the somewhat similar ligand, cyanoacetic acid is claimed to form N and O-bonded polymers with Mn^{II}.[380] The claim[381] that in $MnCl_2(biuret)_2$ the ligand (**148**) binds only O atoms to the metal would appear to support the contention that Mn^{II} prefers O donors. However, as this is the preferred method of binding of biuret to other transition metal ions, when the ligand is not acting as an anionic group, such support is questionable.



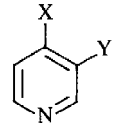
(133)



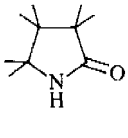
(134)



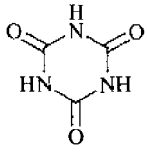
(135)



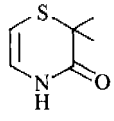
(136) X = CO_2H, Y = H
(137) X = H, Y = CO_2H
(138) X = H, Y = CHO
(139) X = H, Y = $C(O)NEt_2$



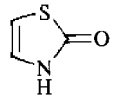
(140)



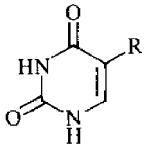
(141)



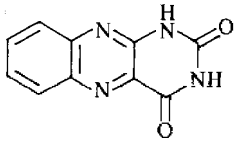
(142)



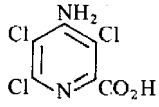
(143)



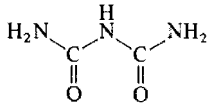
(144) R = H
(145) R = Me



(146)



(147)



(148)

Possibly the clearest indication of the preference of Mn^{II} for O rather than N donors is seen in the compounds formed by the amino acids. The early work of Berezina and Pozigun[382] indicated that $MnX_2(aa)_n$, $MnSO_4(gly)_n$ and $Mn(NO_3)_2(gly)_n$ (where X = Cl or Br; aa = either glycine (gly) or α-alanine (α-ala); and n = 2, 4 or 6) could be prepared. IR evidence was used to show that the amino acids coordinated as zwitterions through only the O donor, except in the two cases, $MnCl_2(\alpha\text{-ala})_n$ and $Mn(NO_3)_2(gly)_n$, in which both the N and the O were bonded. A series of Polish papers[383] has shown that there is no X-ray evidence that, while the amino acid residue does not lose a proton, the N atom bonds. There are two types of amino acid compounds formed: (a) octahedral chain polymers in which the carboxylic acid group acts as a bridge between two adjacent Mn^{II} atoms, *e.g.*

Table 36 Some 'Ambiguous' Ligands and Their Proposed Bonding to Mn^{II}

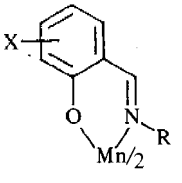
Ligand and Structure	*Bonding and Evidence*	*Ref.*
DL-Proline (**130**)	O-bonded polymer; X-ray	253
Cytosine (**133**)	N-bonded; IR	369
ε-Caprolactam (**134**)	O-bonded; IR	229
p-Quinonedioxime (**135**)	O-bonded; IR	370
Isonicotinic acid (**136**)	O- and N-bonded polymer; IR	371
Nicotinic acid (**137**)	O- and N-bonded polymer; IR	372
Nicotinic aldehyde (**138**)	N-bonded; IR	372
N,N-Diethylnicotine amide (**139**)	O-heterocyclic N-bonded bridging Mn atoms; X-ray	373
2-Pyrrolidinone (**140**)	O-bonded; IR	236
Cyanuric acid (**141**)	O-bonded; IR	374
Tetrahydra-1,4-thiaza-3-one (**142**)	O-bonded; IR	375
Thiazolidine-2-thione (**143**)	O-bonded; IR	375
Uracil (**144**)	O-bonded; IR	376
Thymine (**145**)	O-bonded; IR	376
Flavoquinone (**146**)	O-bonded; NMR	377
4-Amino-3,5,6-trichloropicolinate (**147**)	O- and N-bonded polymer; X-ray	

$[MnCl_2(gly)(H_2O)_2]_n$ and $[Mn(gly)_2(H_2O)_2]_nBr_2$, and (b) monomeric octahedral compounds in which the amino acids bind only through one of the O atoms, *e.g.* $[MnCl_2(gly)_2(H_2O)_2]$.

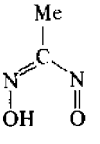
Stability constant measurements have been undertaken to show that in basic solution mixed amino acid ligands with two amino acid moieties present, *i.e.* NH_2—C(R)—C=N—C(R′)—COOH), yield complexes with log K values of the order of 6 to 7;[384] such compounds appear to bind the amine nitrogen.[385]

Berezina *et al.*[386] claim, using IR evidence, that the anionic glycine residues in $Mn(gly)_2 \cdot 2H_2O$ chelate as N—O bidentates. If this is the case, glycine is here paralleling what is believed to be the behaviour of the bidentate salicylaldimines (**149**), and the behaviour of the interesting low spin $[Mn^{II}L_3]^-$ ion {HL = ethylnitrosolic acid (**150**)}, which has been shown by X-ray work to be octahedral with binding of the N of the nitroso group and the oxime O atom.

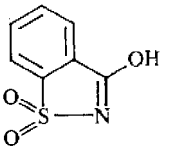
However, there are always exceptions to any rule; in the compound $[MnL_2(H_2O)_2]$ {HL = (**151**)}, X-ray structural analysis[388] has shown the Mn atom to be bonded to the nitrogen atoms of two *trans* ligands.



(149)

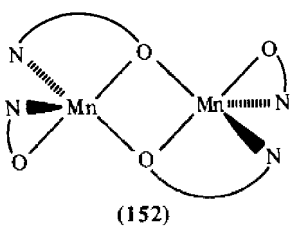


(150)



(151)

The bis-bidentate salicylaldiminato compounds (**149**) of Mn^{II} have not been studied systematically.[173,389] Since Tsumaki[390] reported the red-gold benzyl compound (**149**) (R = $CH_2C_6H_5$ and X = H) in 1938, a number of yellow or orange solid compounds of empirical formula $MnL_2(H_2O)_x$ for various values of R and X in (**149**), have been prepared[39,391–393] (see Table 37). Many of these compounds appear to be polymeric[392] or at least dimeric,[39,393] but one of the few certain pieces of structural data is that reported on the orange compound (**149**) (R = Me, X = H), which has been shown to be isomorphous with its Zn analogue.[395] This Mn compound thus has the dimeric structure (**152**), with two five-coordinate Mn atoms. The compound does not exhibit antiferromagnetic coupling,[393] although other compounds of type (**149**) with different values for R and X appear to have low magnetic moments and their structures have been postulated as dimeric on the basis of temperature dependent magnetic studies.[39]



(152)

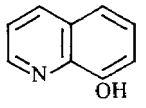
Table 37 Mn^{II} Compounds of Formulation (**149**)

R	*X*	*Ref.*
Ph—	H	394
o-Me—Ph—	H	394
m-Me—Ph—	H	394
p-Me—Ph—	H	394
Ph—CH_2—	H	390
p-NH_2SO_2—Ph—	H	391
Ph—	5-SO_3H	391
p-NH_2SO_2—Ph—	5-SO_3H	391
Ph—	3-CO_2H	392
p-NH_2SO_2—Ph—	3-CO_2H	392
Me—	H	292
Me—	Fused Ph ring	39
o-Me—Ph—	Fused Ph ring	39

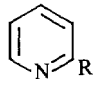
Undoubtedly, a whole series of Mn^{II} compounds of type (**149**) are readily obtainable, and should be of comparable air stability to the analogous Co^{II} species. One attempt to prepare the compound (**149**) for R = Pr^i and X = H, by mixing $Mn(NO_3)_2$ in water with salicylaldehyde and excess amine in ethanol, gave yellow crystals of formulation $[MnL_2]\cdot Pr^iNH_3NO_3$. Identical reactions for Co, Ni, Cu and Zn nitrates yielded only the corresponding compounds of type (**149**).[396] The stability constants of some of the bis-bidentate salicylaldiminato compounds of Mn^{II} have been found to be of the order expected in the Irving–Williams series.[394] Undoubtedly much more work is required in the area of synthesis and structural analysis before a clear picture of this system can be obtained and the relevance of magnetic data properly assessed.

The possible bidentate ligands with a chelating N—O donor set constitutes a virtually infinite set and a large number of this set has been thrust upon an unsuspecting Mn^{II} atom, often with very few conclusive results. Thus the Mn^{II} and Mn^{III} compounds of 8-hydroxyquinoline (**153**) and its substituted derivatives attract some 16 pages in Gmelin.[397] For Mn^{II} both deprotonated MnL_2 and protonated, *e.g.* $[MnCl_2(HL)_2]$, ligand compounds are described, but there are no X-ray structures. It appears likely that both the N and the O atoms are bound in the MnL_2 compound, as the structure of the Mn^{III} compound, $[MnL_3]$, has been published.[398]

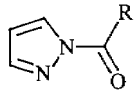
A number of N—O bidentate ligands developed from α-substituted pyridines (**154**) have been reacted with $MnCl_2$ to yield $MnCl_2L_2$ (see Table 38). It is claimed that these compounds bond *via* the pyridine N atom and the O atom. Other workers[403] have looked at similar ligands such as (**155**) and claimed, from IR studies, that both the N and the O atoms are bound in compounds of types of $MnCl_2L$ and $[MnL_2(H_2O)_2]_n$.



(**153**)

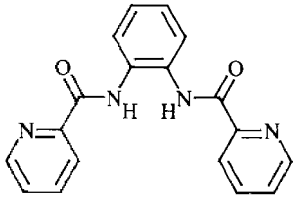


(**154**)

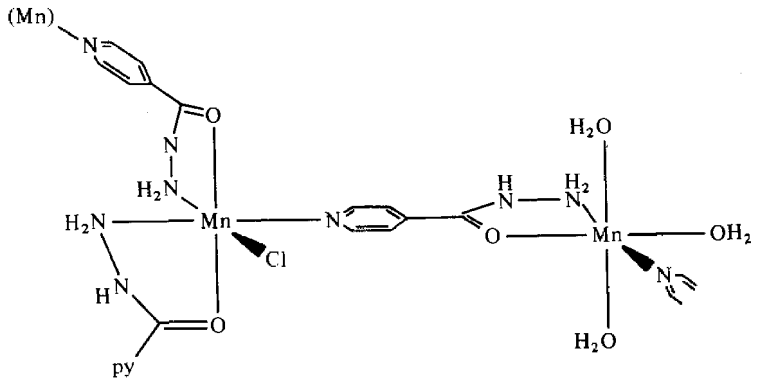


(**155**) R = NH_2 or Me

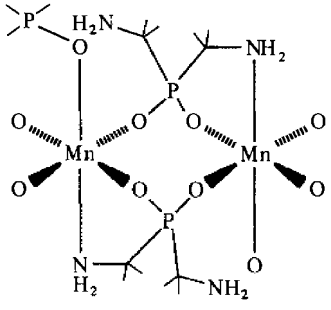
A development of the ligands derived from α-substituted pyridines is the potentially quadridentate ligand (**156**). It is suggested that the anhydrous cream-white $[MnCl_2L]$ compound is polymeric with each N—O pair of the ligand binding to a different Mn^{II} atom.[404] This tendency to polymerization is ably demonstrated in the X-ray structure (**157**) of the compound $[Mn_2ClL_3(H_2O)_3]Cl_3\cdot L_{0.5}$ (L = isonicotinyl hydrazide)[405], and in the possible structure[406] of di(bis[*N*-phenylaminomethyl]phosphinato)manganese(II) (**158**).



(**156**)



(157)



(158)

41.3.9.2 Mixed N—O donor atom terdentate ligands

Mn^{II} compounds of several types of terdentate Schiff base ligands are known.[173] Of interest for supposed biological reasons are ligands of donor set O—N—O derived from condensation of α-amino acids with salicylaldehyde,[407] pyruvic acid,[408] pyridoval[409] and substituted salicylaldehydes.[410] Although X-ray analysis[411] indicates that the compound $[Mn^{II}(pyridoxal\text{-}valine)_2]$ is octahedral, the structures of most of these compounds have not been fully elucidated. Claims of monomeric, dimeric and polymeric molecules are based mainly upon analytical results and upon room temperature magnetic susceptibility measurements. Nothing of special biological interest has come from this work.

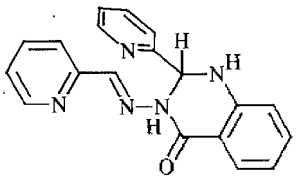
The Mn^{II} compounds, derived from the terdentate O—N—O or S—N—O donor set Schiff base ligands obtained from the condensation of both substituted[412] and unsubstituted[412,413] *o*-hydroxyaniline, anthranilic acid[412] or *o*-aminobenzenethiol[413] with various salicylaldehyde residues, have the

Table 38 $MnCl_2L_2$ Compounds from Ligands of Type (**154**)

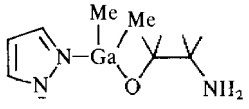
R	*Structure Proposed*	*Ref.*
—C(=O)—NH—NH_2	Octahedral Mn^{II} with $Cl_2N_2O_2$ chromophore from X-ray structure	399
—CH_2—C(=O)—NH_2	Bidentate N—O ligands from IR spectra	400
—C(Ph)=N—OH	Bidentate N—O ligands from IR spectra	121
—C(=O)—NH—N—C(Me)(Me)	Bidentate N—O ligands from IR spectra; tetrahedral?	401
—C(=O)—Ph	Bidentate N—O ligands from IR spectra; polymeric?	402

stoichiometry MnL (where H_2L = the ligand). Temperature dependent magnetic data[412] support the polymeric nature of these compounds but their ready oxidation[412,414] suggests that such results may be due to the presence of higher oxidation state manganese.

The preference of Mn^{II} for oxygen donor atoms is evidenced by the fact that with (**159**) Mn^{II} coordinates by a N—N—O donor set to yield the distorted trigonal bipyramidal compound $[MnCl_2L]$.[415] Comparison of the X-ray structure of this compound with the corresponding Cu^{II} compound shows that the latter compound uses an N—N—N donor set with both pyridine nitrogens coordinating.[416] Nevertheless, this preference is not always exhibited. In $[MnL_2](ClO_4)_2$, tris(2-pyridyl)methanol (**47**; X = COH) is claimed to possess an N—N—N donor set rather than the possible N—O—N set.[153] How the ligand would coordinate upon removal of the methanol proton is of interest; certainly the N—O—N donor set appears to be present in the white air-sensitive compound $[MnL_2]$ obtained when the sodium salt of (**160**) is reacted with $MnCl_2$.[24] Nevertheless, one must be impressed with the predilection of Mn^{II} for oxygen donors when one finds that the structure of $[MnL(H_2O)_2]$ (where L = iminodiacetic acid) is octahedral with an MnO_6 chromophore.[417]



(159)



(160)

41.3.9.3 Mixed N—O donor atom quadridentate ligands

The most comprehensively studied Mn^{II} Schiff base compounds are those of the quadridentate hybrid O—N—N—O donor set ligands of structure (**161**); the ligand salenH_2 {(**161**) where Y = H and X = $(CH_2)_2$} being the object of a number of different studies.[389,418] The orange-yellow, crystalline, air-stable compound [Mn(salen)(en)] was isolated in 1933 and shown to rapidly oxidize in solution.[419] The compound [Mn(salen)] has been prepared by the four main methods used to prepare metal compounds of ligands derived from the interaction of salicylaldehydes and primary amines,[420] these are:

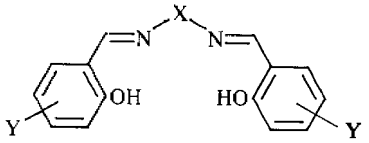
(i) Preparation and isolation of the ligand and subsequent reaction with the metal salt (often the acetate);

(ii) Preparation and isolation of the bis(salicylaldehydato)metal(II) compound and subsequent reaction with the amine;

(iii) Reaction of the stoichiometric amounts of salicylaldehyde, amine and metal salt;

(iv) Interaction of a metal carbonyl with the prepared ligand in non-aqueous solvent under a nitrogen atmosphere (for cases in which the metal compound may be air sensitive).[421]

The magnetic properties of [Mn(salen)] have been the subject of a number of studies,[38,39,422] all of which have indicated the presence of antiferromagnetic interactions. As [Mn(salen)] has an X-ray powder pattern similar to $[Cu(salen)]_2$, a dimeric compound with mutual sharing of one of the oxygen atoms of each ligand,[423] its magnetism has been analysed in terms of such a structure.



(161)

The reaction of [Mn(salen)] with oxygen has been the subject of much study since the early claim that the product was $[Mn^{III}(salen)(OH)]$.[419] The topic has been reviewed,[424] but the nature of the product is still uncertain and the field badly requires definitive work, not least because the oxidation of Mn^{II} species is rapidly assuming great biological importance. Some results of oxygenation

Table 39 Oxygenation Reactions of [Mn(salen)]

Solvent and Temperature of Oxygenation	*Postulated Compounds Obtained*	μ_{eff} *per Mn atom*	*Ref.*
(i) Pyridine, 20°C	$[Mn^{III}(salen)O_{1/2}]_n$	1.92	39
(ii) DMF, 25°C	$[Mn^{III}(salen)]_2O \cdot H_2O$	1.97	39
(iii) DMSO, 25°C	$[Mn^{III}(salen)]_2O_2$	1.96	425
(iv) Pyridine, 25°C	$[Mn^{IV}(salen)O]_n$	1.99	425
(v) Pyridine, −15°C	[Mn(salen)(OH)]	2.01	426
(vi) Pyridine, 115°C	[Mn(salen)OH] + MnO_2		426

experiments of [Mn(salen)] are summarized in Table 39. Such reactions are not reversible. Oxygenation of Mn^{II} compounds of quadridentate N ligands has been noted in Section 41.3.3.4(i).

It is also claimed that nitric oxide reacts in DMSO with [Mn(salen)] to yield $[Mn^{III}(salen)O]_2O_2$.[427] This is surprising, as an ethanolic solution of manganese(II) acetate and salenH_2 is claimed to react with NO to yield $[Mn^{III}(salen)(OAc)]$.[38] On the other hand, it has been claimed that $[Mn^{III}(salen)CO]ClO_4$, a dimer with bridging carbonyls, can be isolated from the interaction of $[Mn(salen)(H_2O)_2]$ with oxygen in 50/50 MeOH/EtOH in the presence of ClO_4^- and NaOH.[428]

Much work has been published on the Mn^{II} compounds of (**161**) with X = $(CH_2)_2$ and Y = various substituents; a summary is provided in Table 40a. The remainder of Table 40 demonstrates the large number of compounds of general structure MnL (L = **161**) that have been prepared; structures of such components are not known, excepting that in which X = *meso*-2,3-butane, Y = H, which has been shown[426] to be isomorphous with the corresponding Co^{II} compound whose structure is square planar.[432]

The oxygenation reactions of many of these MnL compounds have been studied. $MnL \cdot H_2O$ (X = $(CH_2)_3$; Y = H) in refluxing pyridine reacts irreversibly with O_2 to yield a dimeric Mn^{III}

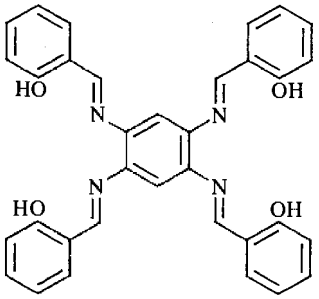
Table 40 Mn^{II} Compounds Prepared from Quadridentate Ligands of Structure (**161**)

	Ligand X	Y	*Mn^{II} Compound Formulation*	μ_{eff} (BM *at R.T.*)	*Ref.*
(a)	$(CH_2)_2$	H	MnL	5.25	426
	$(CH_2)_2$	H	MnL	5.27	39
	$(CH_2)_2$	H	MnL	5.29	422
	$(CH_2)_2$	H	MnL	5.24	38
	$(CH_2)_2$	H	MnL	5.28	392
	$(CH_2)_2$	3-CO_2H	MnL	5.88	392
	$(CH_2)_2$	5-Cl	MnL·EtOH	5.89	39
	$(CH_2)_2$	5-Br	MnL·EtOH	5.96	39
	$(CH_2)_2$	5-SO_3	MnL	4.74	391
	$(CH_2)_2$	5-SO_3	MnL	4.74	429
	$(CH_2)_2$	3-MeO	$MnL \cdot H_2O$	5.92	425
	$(CH_2)_2$	3-NO_2	$MnL \cdot H_2O$	5.96	39
	$(CH_2)_2$	Fused-Ph	$MnL \cdot 2H_2O$	5.37	391
(b)	*o*-Ph	H	MnL	5.29	432
	o-Ph	3-CO_2H	MnL	5.47	392
	o-Ph	5-Cl	MnL	5.86	39
	o-Ph	5-Br	MnL	5.68	39
	o-Ph	Fused-Ph	MnL	5.38	391
(c)	*meso*-2,3-Butane	H	MnL	5.92	426
	1,2-Diphenylethane	H	MnL	5.97	426
	meso-1,2-Diphenylethane	H	MnL	5.83	426
	Tetramethyl-1,2-ethane	H	MnL	5.98	426
(d)	$(CH_2)_3$	H	$MnL \cdot H_2O$	5.93	430
	$(CH_2)_3$	5-Cl	MnL·EtOH	5.99	39
	$(CH_2)_4$	H	MnL	5.74	431
	$(CH_2)_5$	H	MnL	5.63	431
	$(CH_2)_6$	H	MnL	5.64	431
	$(CH_2)_6$	5-Cl	MnL	5.63	431
	$(CH_2)_7$	H	MnL	5.76	431
	$(CH_2)_7$	5-Cl	MnL	5.88	431
	$(CH_2)_8$	H	MnL	5.63	431
	$(CH_2)_8$	5-Cl	MnL	5.76	431
	$(CH_2)_{10}$	H	MnL	5.71	431

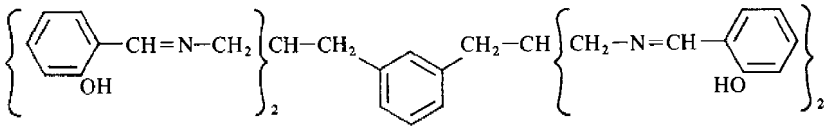
compound,[433] which can also be obtained by heating the Mn^{II} compound in the solid state in air at 80°C;[430] however in benzene at room temperature the oxygenation reaction yields $[MnL(O)\cdot\frac{1}{2}C_6H_6]$.[430] All the compounds of Table 40(c) react with O_2 in (i) boiling pyridine to yield [MnLOH] + MnO_2; (ii) pyridine at −15°C to yield [MnLOH]. These apparently Mn^{III} compounds do not reversibly lose oxygen.[426]

The preparation and oxygenation of a series of MnL compounds with L = (**161**) and X of varying aliphatic chain lengths from $(CH_2)_4$ up to $(CH_2)_{10}$ has been reported[431] {see Table 40(d)}. The compounds with X = $(CH_2)_5$ to $(CH_2)_{10}$ react with O_2 in DMSO to yield insoluble red-brown powdery materials of formulation [MnL(O)], excepting where X = $(CH_2)_8$ in which case $[MnL(O)_{1/2}]$ is obtained. The magnetic moments of the compounds [MnL(O)] fall in the range 3.2 to 3.7 BM, and it is claimed that Mn^{IV} μ-dioxo-bridging dimers are present. Oxygenation is not reversible. As noted above definitive (and hard) work is required in this area.

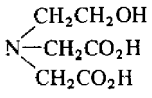
A 'double-sided' version of (**161**) has been produced in the ligand (**162**), which has shown to yield a Mn^{II} compound of formulation $Mn_2L\cdot H_2O$;[434] this compound being similar to the $Mn_2L\cdot 3H_2O$ compound obtained from (**163**).



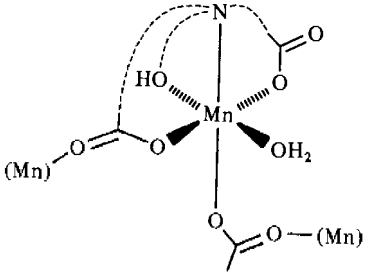
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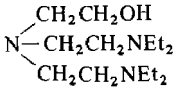
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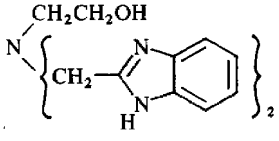
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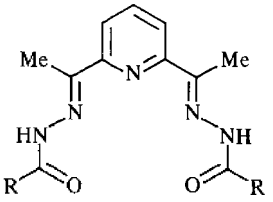
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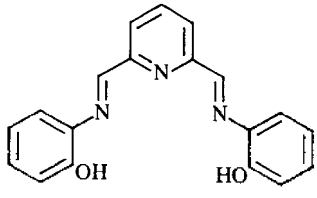
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(167)



(168)



(169)

Quadridentate hybrid ligands of the tripod variety appear to favour polymerization, although such behaviour is not shown by the sexadentate edta. The ligand (**164**) loses two protons to yield the compound $[MnL(H_2O)]_n \cdot nH_2O$ (**165**),[435] while it is suggested that the ligand (**166**) dimerizes through the oxygen atoms in $[Mn_2L_2]^{2+}$.[436] However, the somewhat similar ligand (**167**) has been shown by X-ray analysis of the compound $[MnL(NCS)_2]$ to form a monomer with a distorted octahedral Mn^{II} atom.[437]

41.3.9.4 Mixed N—O donor atom quinquedentate ligands

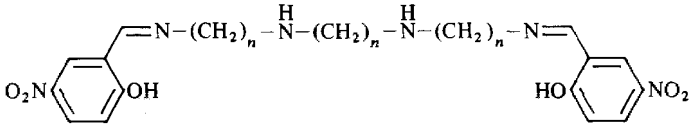
Structure (**161**) can be expanded to yield quinquedentates by the inclusion of a donor atom in the X chain to yield for example $X = (CH_2)_n—Z—(CH_2)_n$ (where $n = 2$ and Z = NH or S; $n = 3$ and Z = O). Such ligands react with manganese(II) acetate to yield yellow $[MnL \cdot nH_2O]$ (where $n = 0.5$ or 1),[438] whose structures may well be polymeric as in the [CuL] compound (L = **161** in which $X = (CH_2)_2—NH—(CH_2)_2$ and Y = H).[439] These Mn^{II} compounds react with dioxygen irreversibly to yield probably Mn^{III} compounds. Various mechanisms of the interaction are fully discussed in a review.[424]

A most interesting quinquedentate is ligand (**168**) (R = 2′-pyridyl), which has been shown to yield the compounds $[Mn(LH_2)Cl_2] \cdot 5H_2O$ and $[MnL(H_2O)_2] \cdot 7H_2O$. In both compounds X-ray structural work proves that the ligand binds through two N and two O atoms of the ligand with the two pyridine residues at either end of the ligand chain non-bonding; the ligand forming a pentagonal plane about the metal with the two chlorine atoms in the former compound, and two water molecules in the latter, occupying positions six and seven of the coordination sphere above and below the ligand plane.[440] A similar seven-coordinate structure has been found in (**168**) in which $R = NH_2$.[441]

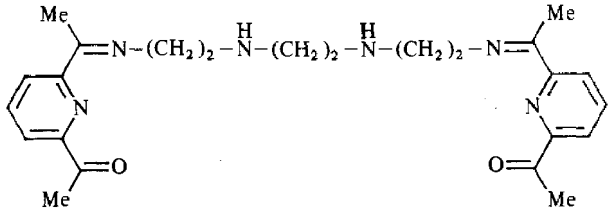
The preference of Mn^{II} for O donors (although it is very doubtful if both terminal pyridines could bind in a planar situation due to steric interaction), and the lack of preference of Mn^{II} for any particular stereochemical shape, are both clearly shown in these results. It is of interest that other workers believe that for the similar ligand (**169**), in the neutral compound $[MnL(H_2O)_2]$ the ligand binds *via* two N and two O atoms, with the octahedral coordination being completed by the two water molecules.[442]

41.3.9.5 Mixed N—O donor atom sexa- and octadentate ligands

Long-chain sexa- and octadentates are very often derived from Schiff base condensations. Some recent examples are shown in ligands (**170**)[443] and (**171**);[444] in both cases it is believed that the six and eight potential donor atoms respectively are bound in the Mn^{II} compounds.



(170)



(171)

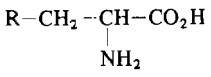
The edta compound of Mn^{II} has played on important role in expanding the coordination chemist's vision of the occurrence of higher coordination numbers. Hoard *et al.*[445] demonstrated that the large size of the Mn^{II} ion pushed back the sexadentate ligand and allowed a water molecule to coordinate, thereby producing a seven-coordinate ion, $[Mn(edta)H_2O)]^-$. On the other hand, the tetramethyl-

substituted 'edta' appears to be octahedral and possess at least some non-bonded oxygen donors in $[MnCl_2L]$.[446] Bi- and tri-nuclear edta compounds of Mn^{II} have been prepared. In the compound $Mn_2edta \cdot 9H_2O$ a seven-coordinate bridging structure is proposed,[447] whereas in $Mn_3(edta)_2 \cdot 10H_2O$ each of the edta residues retains a proton and adjacent seven-coordinate $[MnedtaH_2O]$ units are bridged by an $[Mn(H_2O)_4]$ unit bound to carboxyl oxygens of the edta residues.[448]

41.3.9.6 Mixed N—S donor atom ligands

As might be expected by reference to Section 41.3.6 on sulfur compounds of Mn^{II}, little work of real consequence has been done in this area.

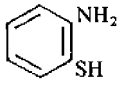
A review[449] of the early 1970's details the manganese compounds of sulfur-containing amino acids, and quotes evidence that cysteine (**172**; R = SH) and penicillamine bind *via* both the N and S donor atoms at higher pH values; however, analysis of the papers quoted yielded little evidence for S binding. On the other hand, there is sound evidence that when the thiol group is methylated, as in *S*-methylcysteine and methionine (**172**; R = SMe and CH_2SMe respectively), the S does not coordinate, either in solution[450] or in the solid state.[451]



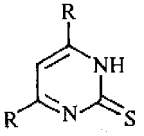
(172)

Work up to 1974 on N—S chelating agents is comprehensively covered by Ali and Livingstone;[452] although one has to delve deeply into this review to find the few references to Mn.

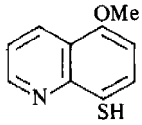
Table 41 lists some of the bidentate N—S ligands that are claimed to bind both donor atoms to Mn^{II}. Evidence for such binding is usually based upon doubtful IR interpretations coupled with compound stoichiometries; even the X-ray isomorphism of the compound of ligand (**174**) to a similar Co^{II} compound is somewhat doubtful.



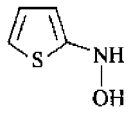
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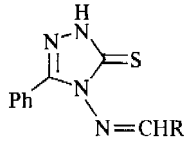
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(175)



(176)



R = Ph or Furanyl

(177)

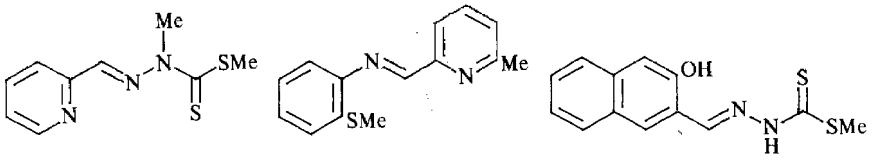
Long-chain terdentate ligands of donor sequence N—N—S (**178**), (**179**) and (**180**) have been shown to yield compounds of formulation $MnLX_2$ (X = halogen); such compounds have been claimed to be six-coordinate polymeric,[459] five-coordinate monomeric[460] and tetrahedral[461] respectively, with both N and S bonding. However, there is little evidence to justify any of these claims.

When the field is expanded to cover ligands of even higher denticity, the proof of binding of both N and S is indeed difficult. (**181**) is claimed to possess an N_4S chromophore in $[Mn(L)I]ClO_4$,[462] while (**182**) is proposed as a quinquedentate in $[Mn^{II}L]$, but not to form a compound with Mn^{III}.[463]

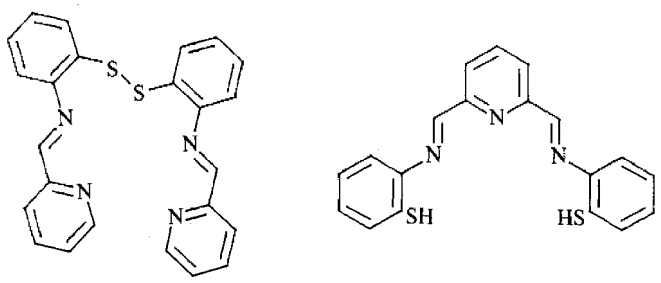
Table 41 Some Mn^{II} Compounds in which Bidentate N—S Ligands are Claimed to Bind both Donor Atoms

Ligand	*Compound Stoichiometry*	*N—S Binding Evidence*	*Ref.*
(**173**)	MnL_2	IR	453
(**174**) (R = H)	$Mn(HL)_2Cl_2$	X-Ray isomorphism	454
(**174**) (R = Me)	$Mn(HL)_2Cl_2$ (and Br_2)	IR and ESR	455
(**175**)	$MnL_2 \cdot 2HL$	IR	456
(**176**)	$Mn(HL)_2Cl_2$	IR	457
(**177**)	MnL_2Cl_2 (and Br_2)	IR	458

Note: Except for (**177**), HL = protonated and L = deprotonated form of the ligand.



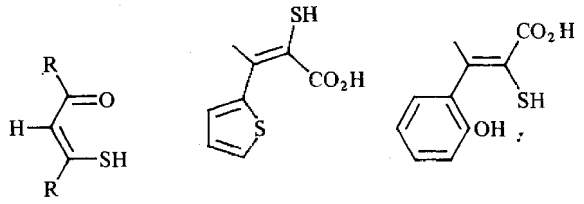
(178) (179) (180)



(181) (182)

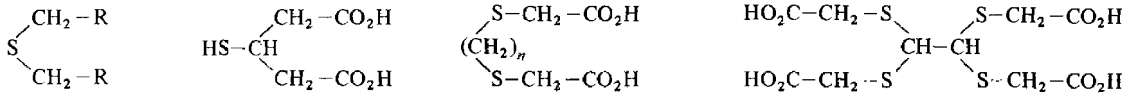
41.3.9.7 Mixed O—S donor atom ligands

There is sound evidence that bidentate O—S ligands can bind both donors to Mn^{II}. Ligand (**183**) has been shown to yield the compound $[Mn^{II}(L)_2(py)_2]$,[464] in which proton loss and both O and S binding appear certain. Ligands such as (**184**) may well bind both O and S to Mn^{II},[465] although it appears doubtful if (**185**) does.[466]



(183) (184) (185)

There is a small literature on multidentate O—S ligands possessing thioether sulfur atoms and carboxylic acid or hydroxy groups. Table 42 lists some of these compounds, together with their proposed stereochemistries and structures. In all compounds listed, binding of both all the sulfur atoms and all the carboxylic acid or hydroxy groups is proposed.



(186) (187) (188) (189)

Table 42 Some Mn^{II} Compounds of Multidentate O—S Ligands in Which Both O and S Donors are Bound

Ligand	*Compound Stoichiometry*	*Stereochemistry*	*Ref.*
(**186**) (R = CH_2OH)	$Mn(L)Cl_2$	Five-coordinate	467
(**186**) (R = CO_2H)	$Mn(L\text{-}2H)\cdot H_2O$	*Oh* polymer	468
(**187**)	$Mn(L\text{-}2H)\cdot 2H_2O$	*Oh* polymer	469
(**187**)	$M^IMn(L\text{-}3H)\cdot nH_2O$[a]		469
(**188**) (n = 2)	$Mn(L\text{-}2H)$	*Oh* polymer	470
(**188**) (n = 4)	$Mn(L\text{-}2H)\cdot 2H_2O$	*Oh* polymer	471
(**189**)	$Mn_2(L\text{-}4H)\cdot 12H_2O$	*Oh* dimer	472

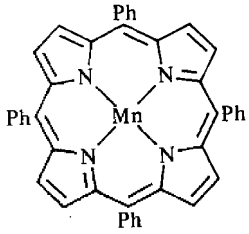
[a] M^I = Li, Na or K and n = 3, 2 or 2 respectively.

41.3.10 Macrocyclic Ligands

41.3.10.1 Porphyrin ligands

Since the first report of a manganese porphyrin in 1904,[473] there has been a great deal of research involving such compounds largely because of their unusual properties and their possible relevance to biological systems such as green-plant photosynthesis.[474–477] For example, it is believed that a manganese porphyrin may function as the oxidant for the natural photosynthetic oxidation of water to molecular oxygen. This latter aspect has provided a motivation for a number of redox and photochemical studies.[478–481] The manganese porphyrins were reviewed in detail by Boucher in 1972.[482] Porphyrin complexes in the +2 to +5 oxidation states all exist although the +3 state is most stable.

Mn^{II} porphyrins may be obtained by direct reduction of the corresponding Mn^{III} porphyrin; for example, the tetraphenyl porphyrin (**190**), [Mn(TPP)], may be obtained by reduction of $[Mn^{III}Cl(TPP)]$ with $Cr(acac)_2$ in toluene[190] to yield the purple product [Mn(TPP)]·2(toluene).[483]



(190)

A number of other reductants have also been used to reduce Mn^{III} porphyrins in solution.[482] With dithionite,[480] the reaction is stoichiometric for a one-electron reduction above pH 8 but below this pH the $[Mn^{II}(TPP)]$ product undergoes demetallation. Related reduction can be induced by irradiation of a Mn^{III} porphyrin with visible light although, in the absence of an added electron donor, the quantum yields are low.[484]

Mn^{III} porphyrins may also be electrochemically reduced in a single electron step to yield the corresponding Mn^{II} porphyrin in both aqueous and non-aqueous media.[485] The potentials at which these reductions occur are sensitive to the nature of the solvent, counter ion present and pK_a of any bound ligands, as well as to the basicity of the porphyrin ring involved.[482–484] Similar factors also cause variation in the visible spectra of the respective compounds.[482]

In contrast to [Mn(phthalocyanine)] (see later) and [Fe(TPP)] which adopt intermediate-spin configurations, [Mn(TPP)] appears to be fully high-spin.[483] Treatment of this compound with a heterocyclic base such as 1-methylimidazole (1-MeImH), 2-methylimidazole (2-MeImH) or pyridine (py) leads only to 1:1 adducts being obtained; there appears to be no tendency for six-coordinate species to form even when the bases are present in large excess.[482–486] All the solid adducts have magnetic properties which correspond to high-spin d^5 configurations (with magnetic moments of 6.2–6.6 BM).

X-Ray analyses of [Mn(TPP)] and the THF solvate of [Mn(TPP)(1-MeImH)] have been performed.[483,487,488] The X-ray data for the former compound suggests[487] that the Mn^{II} ion, with its relatively large radius, is positioned out of the N_4-plane of the macrocycle. This result is in accordance with earlier theoretical predictions.[489] The five-coordinate [Mn(TPP)(1-MeImH)] also has the Mn^{II} displaced from the porphyrin plane; in this case, the Mn^{II} lies 0.56 Å above the plane towards the 1-methylimidazole ligand. Calculations of the charge and spin distribution in the related Mn^{II} porphyrin containing a coordinated water in the axial position indicate that the Mn^{II} is strongly bound and that about 30% of the unpaired spin population ($S = 5/2$) is delocalized away from the Mn^{II} on to the attached ligands.[490]

The Mn^{II}(TPP) complexes of imidazole (ImH) and the imidazolate ion (Im) have also been isolated; both are high spin and five-coordinate.[491] The increased field strength of imidazolate over imidazole is insufficient to cause spin pairing (which was proposed to be a prerequisite for six-coordination to occur).

In part, because the Mn^{II} ion is not held in the donor plane of the porphyrin, demetallation of such complexes in acid becomes facile as shown in one study (where loss of metal was found to be

10^6 times faster than for the analogous Mn^{III} species).[492] Other studies involving the kinetics of exchange of zinc or cobalt for Mn^{II} in a porphyrin compound in ammoniacal medium have been reported.[493]

Mn^{II}-substituted haemoglobin undergoes irreversible oxidation to the corresponding Mn^{III} compound on exposure to oxygen[494] and the five-coordinate imidazole adducts mentioned previously also undergo similar oxidation in solution. For [Mn(TPP)], oxidation is very rapid although it is apparent that coordination of an axial base decreases the ease of oxidation. This effect is illustrated by the behaviour of the five-coordinate Mn^{II} species incorporating the 'picket fence' porphyrin[495] in the presence of a slight excess of the axial ligand. For this system the rate of oxidation to the Mn^{III} species is very slow (hours). At low temperatures (−78 to −90°C) a number of Mn^{II} porphyrins have been observed to react reversibly with oxygen in solvents such as toluene or toluene/THF.[483,484,496-498] Examples of such behaviour are illustrated by equations (10) and (11).

$$[Mn(TPP)] + O_2 \rightleftharpoons [Mn(TPP)O_2] \tag{10}$$

$$[Mn(TPP)py] + O_2 \rightleftharpoons [Mn(TPP)O_2] + py \tag{11}$$

A comparison of the affinities of the compounds of type [M(TPP)py] (M = Mn, Fe, Co) for molecular oxygen (under one atmosphere pressure) in toluene at −79°C gives $Co^{II} < Fe^{II} < Mn^{II}$. This order also corresponds to the ease of oxidation of the base-free metalloporphyrins from $M^{II} \rightarrow M^{III}$.[497,498]

Optical and ESR measurements were initially used to study the reversible coordination of dioxygen by the above Mn^{II}(TPP) compound. The oxygenated product differs from the corresponding Co^{II} and Fe^{II} porphyrin adducts since it is of intermediate spin and contains three unpaired electrons ($S = 3/2$) rather than being low spin (as are the Fe^{II} and Co^{II} analogues). The ESR results suggested a bonding scheme in which the three unpaired electrons are localized on the manganese thus corresponding to a 'Mn^{IV}–peroxo' valency formalism. However subsequent IR studies suggest that the negative charge on the O_2 in [Mn(TPP)O_2] lies between those of the superoxo (O_2^-) and peroxo (O_2^{2-}) ions.[499] The studies[497,498] indicate that O_2 does not add to [Mn(TPP)py] but rather, adduct formation results in loss of the pyridine ligand to yield five-coordinate [Mn(TPP)O_2] as the product. The equilibrium constants for replacement of a metal-bound pyridine moiety by O_2 in [Mn(TPP)Py] and in the related compounds of a series of *p*-substituted tetraphenylporphyrins at −78°C are all less than unity.[496] Thus a high concentration of the coordinating base will not favour oxygen-adduct formation; this provides a rationale for the reported inability of Mn^{II} haemoglobin (with its high 'local' concentration of imidazole in the region of the metal ion) to reversibly bind molecular oxygen.[494]

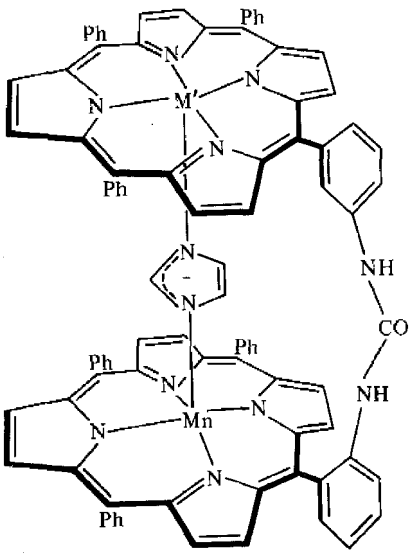
The visible, ESR and IR studies mentioned previously are in accordance with the symmetric sideways coordination of dioxygen in [Mn(TPP)O_2] and such a coordination geometry is also consistent with the results of MO calculations.[500] The mode of bonding of the dioxygen thus appears to differ from that in the corresponding Fe^{II} and Co^{II} porphyrin adducts which contain the oxygen bound in an end-on fashion. Recent IR studies of the dioxygen adduct of octaethylporphyrinatomanganese(II), [Mn(OEP)O_2], prepared by matrix condensation techniques, indicate that the $\nu(O_2)$ stretch for this compound, as well as for the corresponding TPP and phthalocyanine complexes, all fall in the range 922–983 cm^{-1}.[501]

Deuterium NMR spectroscopy has been used to define the electronic structure of compounds generated by reaction of the superoxide ion with a Mn^{II} porphyrin.[502] The position of a deuterated-pyrrole signal together with a solution magnetic moment of 5.0 BM were interpreted as indicating the presence of a superoxomanganese(II) porphyrin system with spin coupling between the superoxide ligand and the manganese ion. This system has been proposed to be an excellent model for what has been postulated to be (formal) superoxide coupling to low-spin iron(III) in the oxyhaemoglobin molecule. Although the superoxide ion is not a usual substrate for haemoproteins, it is significant as an important resonance configuration for oxygenated haemoglobin and cytochrome P-450.

In contrast to its behaviour towards O_2, manganese-substituted haemoglobin binds NO reversibly at room temperature. Moreover, the Mn^{II} + NO system is isoelectronic with Fe^{II} + CO and has been argued to be a close model for the binding of CO to haemoglobin.[503] Examples of nitrosyl adduct formation by simple Mn porphyrins have also been reported.[504]

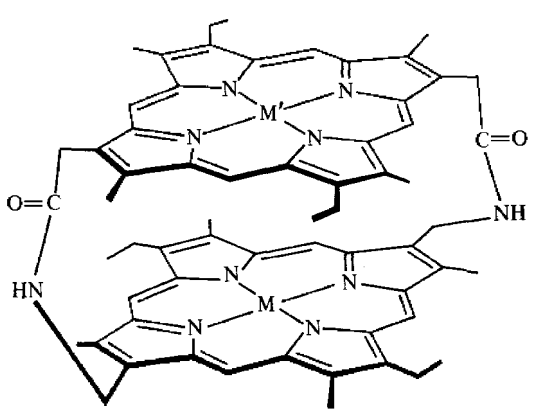
A number of dimetallic 'face to face' dimeric porphyrins containing Mn^{II} have been synthesized.[505] For example, urea-linked TPP dimers (**191**) have been obtained containing imidazolate ligands

bridging between Mn^{II}/Mn^{II} and Mn^{II}/Co^{II} centres. The study of such dimeric species is timely because of the growing number of bi- and tetra-nuclear metalloproteins (haemocyanin, copper oxidases, haemerythrin, superoxide dismutase and cytochrome oxidase) which have been found to exhibit interaction betwen heteronuclear metal sites. In particular, the imidazolate-bridged compound has been proposed to be a spin model for cytochrome oxidase even though it contains Mn^{II}/Co^{II} rather than Fe^{III}/Cu^{II} as occurs in the natural system. However, in each system there is an $S = 5/2$ metalloporphyrin interacting with an $S = 1/2$ centre. From the measured small value of $-J (= 5\,cm^{-1})$ for the antiferromagnetic coupling in the synthetic dimer it was concluded unlikely that histidine acts as a bridging ligand to Cu_B at the haem a_3 site of cytochrome oxidase.



(191)

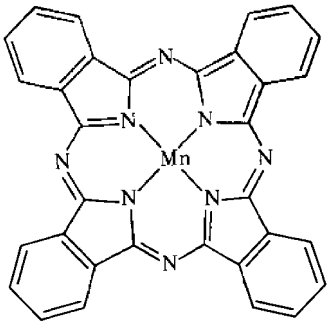
A related series of mixed-metal 'face to face' porphyrin dimers (**192**) has been studied by Collman *et al.*[506] A motivation for obtaining these species has been their potential use as redox catalysts for such reactions as the four-electron reduction of O_2 to H_2O *via* H_2O_2. It was hoped that the orientation of two cofacial metalloporphyrins in a manner which permits the concerted interaction of both metals with dioxygen may promote the above redox reaction. Such a result was obtained for the Co^{II}/Co^{II} dimer which is an effective catalyst for the reduction of dioxygen electrochemically.[507] However for most of the mixed-metal dimers, including a Co^{II}/Mn^{II} species, the second metal was found to be catalytically inert with the redox behaviour of the dimer being similar to that of the monomeric cobalt porphyrin. However the nature of the second metal ion has some influence on the potential at which the cobalt centre is reduced.



(192)

41.3.10.2 Phthalocyanine ligands

Much of the early interest in manganese porphyrins had its origins in prior work,[508,509] involving manganese phthalocyanine {**193**; [MnPc]}. Phthalocyanines (including those of manganese) were reviewed by Lever in 1962.[510] Since then, the general metal-ion chemistry of Pc and its derivatives has been discussed in numerous books and articles; two more recent reviews are by Boucher[511] and Berezin.[512]



(193)

Self condensation of phthalonitrile or *o*-cyanobenzamide in the presence of manganese metal gives a product which, on sublimation, yields pure [MnPc].[510] Alternatively this product may be obtained by the reaction of phthalonitrile with manganese acetate. Although similarities exist, the chemistry of manganese phthalocyanine species show many differences to that of the corresponding porphyrins.[6,510]

[MnPc] (β-polymorphic form) is unusual in that it provides an example of an intermediate spin state with $S = 3/2$ for the d^5 configuration. This compound also provides a rare example of a ferromagnetic molecular crystal ($J = +7.6\,cm^{-1}$). [MnPc] has been the subject of both X-ray[513,514] and neutron diffraction[515] studies. The coordination environment of the Mn ion is square planar and the overall molecule is isostructural with a range of other divalent phthalocyanines. Stacking of the planar [MnPc] molecules occurs in the lattice such that two pyrrole nitrogen atoms from each molecule lie exactly above or below the manganese belonging to adjacent molecules. The distance between manganese and the axial nitrogen atoms is 3.4 Å. The Mn^{II} atoms are aligned in linear arrays parallel to the *b* axis of the molecule such that [MnPc] may be considered to contain magnetic linear chains along the *b* axis of the crystal. The magnetic properties of [MnPc] are consistent with the presence of ferromagnetic intrachain exchange together with weak antiferromagnetic interchain interaction; the Curie temperature is 8.6 K.[516–518]

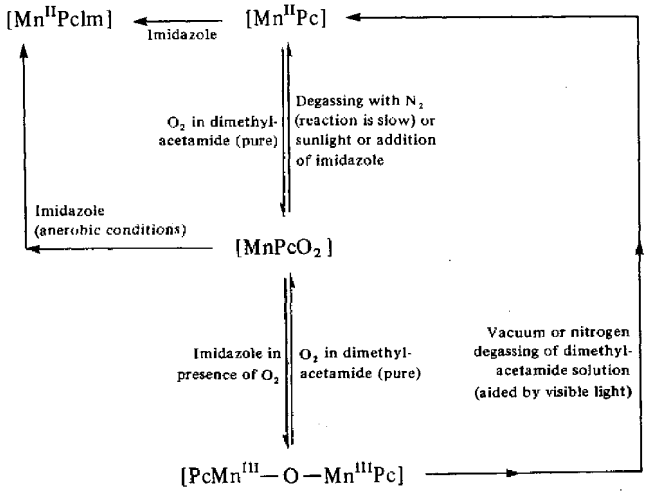
The X-ray and neutron diffraction data mentioned previously have been used in conjunction with the technique of polarized neutron diffraction (at 4.2 K) to deduce spin-density distributions in [MnPc].[519,520] In further investigations[514] it proved possible to determine individual 3*d* and 4*s* orbital populations on the manganese ion together with an estimate of 24% for the *d*-orbital electron density delocalized in the macrocyclic ring. From these studies it appears that the charge on the manganese is approximately +1; this charge appears to be achieved primarily by the loss of a 3*d* electron rather than a 4*s* electron.

Largely because of the possible involvement of manganese in the photosynthetic production of oxygen, the energetics of manganese phthalocyanine redox processes have been of considerable interest. Lever *et al.*[521] have used a number of electrochemical and other techniques to effect and characterize the oxidation of Mn^{II}(Pc) to Mn^{III}(Pc) species, ligand oxidation of Mn^{III}(Pc) and two successive one-electron reductions of Mn^{II}(Pc). The electrochemical studies were carried out using pyridine, dimethylsulfoxide or dimethylacetamide as solvent and perchlorate, chloride or bromide as the supporting electrolyte anion. Heterogeneous rate constants were obtained for several of these couples in the presence of perchlorate anion. Each of the couples showed near ideal behaviour with the exception of the chloride and bromide systems at higher scan rates. No evidence for the formation of Mn^{I} species was obtained.

[MnPc] reacts with a number of monodentate bases to yield low spin ($S = \frac{1}{2}$) adducts of type [$MnPcL_2$] (L = pyridine, imidazole, triethylamine *etc.*).[522,523] In the solid state [$MnPc(py)_2$] loses its two pyridines to yield [MnPc] on heating the adduct *in vacuo* at 100°C.[523]

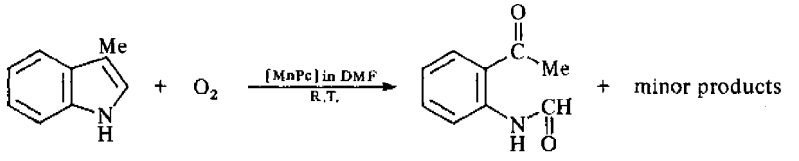
Despite earlier reports to the contrary [MnPc] does not react with oxygen in pyridine provided

the pyridine is rigorously dried and purified. If the latter condition is not met then reaction does occur with the end-product of the oxidation being a dinuclear Mn^{III} species of type $[(MnPcpy)_2O]$.[508,522–524] Nevertheless, reaction does occur in pure *N,N*-dimethylacetamide to yield a solution of the oxygen adduct. Reversal of the oxygenation occurs over many days on degassing the solution. The deoxygenation occurs more rapidly upon exposure to bright white light or upon addition of an electron donor to the solution in an evacuated flask. For the first reaction type the released molecular oxygen was detected using mass spectrometry. In contrast, when the adduct is reconverted to [MnPc] with electron donors such as imidazole, triethylamine, catechol *etc.*, no oxygen apears to be released. In this case the adduct seems to be mimicing oxidase activity of the type proposed by Uchida *et al.*[525] (see later). Further, addition of certain electron donors, such as imidazole, to the adduct in the presence of oxygen results in formation of a dinuclear species of type $[PcMn^{III}—O—Mn^{III}Pc]$; the latter may be reconverted to the oxygen adduct by reaction with oxygen in *N,N*-dimethylacetamide. The oxygen adduct has been isolated and has $S = \frac{1}{2}$. From the results of physical measurements,[522,526,527] the adduct was proposed to contain a bound superoxide and to be of type $[Mn^{III}PcO_2]$. The various reactions involving this compound are summarized in Scheme 2 (modified from reference 522 using, where appropriate, imidazole as the electron donor).



Scheme 2

[MnPc] has been demonstrated to show high catalytic activity for the oxidation of 3-methylindole (equation 12) and thus mimics the action of tryptophan-2,3-dioxygenase.[525] The major product of the catalyzed oxygenation is 2-formamidoacetophenone, with 2-aminoacetophenone and the 2-isonitrile derivative as minor products. The model studies indicate that the substrate specificity for the oxygenation of indole derivatives is different to that of singlet oxygen or radical autoxidation. In other studies, the [MnPc] catalyzed autoxidation of phenols has been investigated[528] together with other catalytic redox reactions involving a number of different substrate types.[511]



(12)

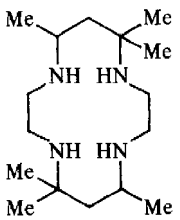
41.3.10.3 Other nitrogen donor macrocycles

In contrast to the large number of studies concerned with porphyrins and phthalocyanines, other macrocyclic ligand compounds of Mn^{II} have received somewhat less attention.[173,529,530] In part, this appears to reflect the fact that many compounds of this type tend to be of only moderate thermodynamic stability and in some instances are air and/or moisture sensitive. In addition, Mn^{II} has been shown to be ineffective as a template metal for certain cyclization reactions which occur in the presence of other ions.[159,162,531,532] This effect may be a consequence of the relatively large size of the Mn^{II} ion not enabling it to fit in the cavity of the target macrocycle. Alternatively, the often low affinity of Mn^{II} for the macrocycle precursors may contribute to the absence of a template effect for particular systems.

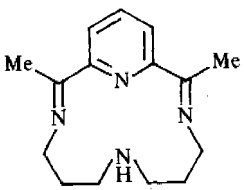
The *meso* form of the saturated tetradentate macrocycle (**194**) has been used to synthesize the

colourless compounds [MnX_2(**194**)] (X = CF_3SO_3, CH_3CO_2).[533] The synthetic procedure used to obtain these species is more demanding than often required for other first row transition metal complexes since these compounds are both oxygen and water sensitive. Further, the macrocycle appears to exhibit only low affinity for Mn^{II}. The compounds were obtained by reaction of (**194**) with $Mn(SO_3CF_3)_2 \cdot CH_3CN$ or $Mn(CH_3CO_2)_2$ in hot degassed acetonitrile under anhydrous conditions. Both compounds are high spin and the solid state ESR spectra indicate that the manganese ion is experiencing a relatively small tetragonal distortion in each case.

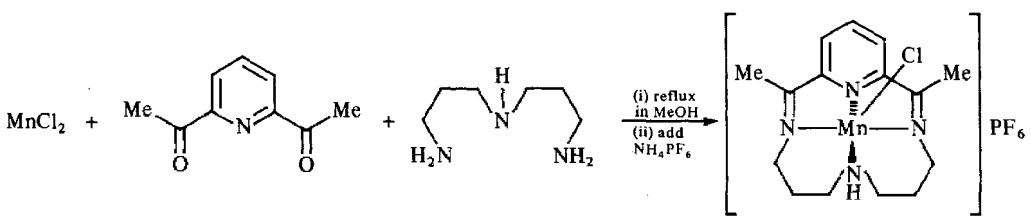
Using a template procedure involving condensation of 2,6-diacetylpyridine and the appropriate triamine in the presence of Mn^{II}, compounds of type [Mn(NCS)$_2$(**195**)] and [MnCl(**195**)]PF_6 have[534] been isolated. The synthesis of [MnCl(**195**)]PF_6 is illustrated by equation (13). Both compounds are high spin with magnetic moments of 5.94 BM; they appear to contain either five or six coordinated Mn^{II}. It is of interest that attempts to chemically oxidize these compounds to Mn^{III} species using $NOPF_6$ or H_2O_2 in acetonitrile in the presence of excess Cl^- ion were unsuccessful even though the Mn^{II} compounds of the fully-saturated (14-membered) macrocycle (**194**) readily oxidize under similar conditions. This difference in redox behaviour is undoubetedly related to the presence in (**195**) of a conjugated fragment containing three nitrogen donors. However it is inappropriate to speculate further about this since larger ring (N_5-donor) macrocycles incorporating this moiety do undergo oxidation to Mn^{III} species.



(194)



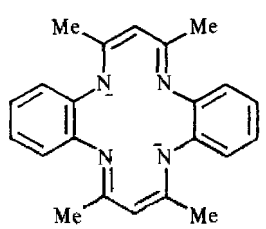
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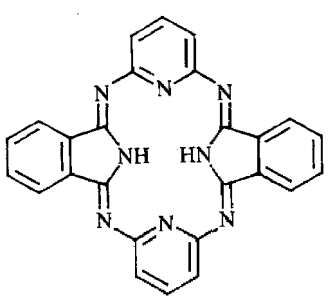
(13)

Mn^{II} compounds of the rigid dianionic macrocycle (**196**) of type [Mn(**196**)(amine)] (where amine = triethylamine or tri-*n*-propylamine) have been synthesized directly by reaction of the preformed macrocyle with $Mn(SO_3CF_3)_2$ in acetonitrile followed by addition of the amine.[535] These high spin compounds were assigned square pyramidal structures with the metal ion displaced from the plane of the macrocycle towards the axial ligand. Such a structure has been confirmed for [Mn(**196**)NEt_3] by X-ray diffraction.[536] This compound has the Mn^{II} ion 0.73 Å out of the N_4-macrocyclic plane. The hole size in (**196**) is smaller than in the porphyrins; the five-coordinate geometry appears to be a direct consequence of the Mn^{II} ion being too large to fit completely in the macrocyclic cavity. The coordinated macrocycle adopts a saddle shape reflecting steric interactions between the methyl groups and the aromatic rings.

A detailed resonance Raman study of these Mn^{II} species has been undertaken.[537,538] Relative to the spectrum of the free ligand, the vibrations observed to undergo large shifts on incorporation of the metal ion were those associated with the 'porphyrin-like' six-membered chelate rings.



(196)

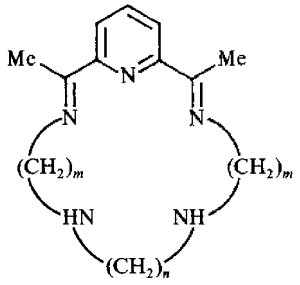


(197)

Descriptions of the synthesis of the tetraaza macrocycle (**197**) by a non-template procedure from *o*-phthalonitrile and 2,6-diaminopyridine as well as the synthesis of its Mn^{II} compound have been published.[539] The manganese species is very insoluble; it is high spin with a magnetic moment of 5.80 BM and obeys the Curie law between 85 and 300 K.

Manganese compounds of a number of N_5-donor macrocycles have been investigated. For example, following earlier work involving iron complexes of (**198**),[540,541] Alexander *et al.*[542] synthesized a range of high spin ($S = 5/2$) complexes of type $[MnX_2(\mathbf{198})]\cdot nH_2O$ (X = Cl, ClO_4, $n = 0$, 1 or 6). For example, orange $[MnCl_2(\mathbf{198})]\cdot 6H_2O$ was obtained by condensation of 2,6-diacetylpyridine with triethylenetetramine in methanol in the presence of manganese chloride. This product is isomorphous with the corresponding magnesium compound which was postulated to contain a $[Mg(\mathbf{198})(H_2O)_2]^{2+}$ moiety.[543] The single-crystal ESR spectrum of the Mn^{II} compound exhibits an unusual angular dependence of the ESR transitions.[544] This and the other compounds in the series were assigned seven-coordinate structures. For $[Mn(ClO_4)_2(\mathbf{198})]$, infrared evidence suggests that the perchlorate groups are coordinated in the solid.

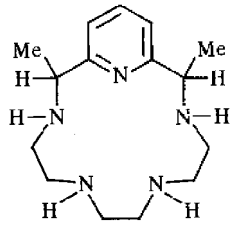
The macrocycle in $[MnCl_2(\mathbf{198})]\cdot H_2O$ can be reduced using a nickel–aluminium alloy under basic conditions.[545] Addition of cold concentrated nitric acid then leads to isolation of the reduced macrocycle (**201**) as its tetrahydrogennitrate salt.



(**198**) $n = m = 2$

(**199**) $m = 2$, $n = 3$

(**200**) $m = 3$, $n = 2$



(**201**)

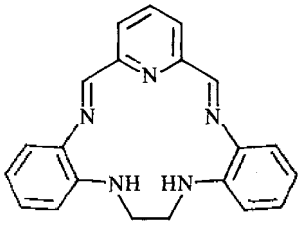
Using a related *in situ* procedure to that just described, Drew *et al.*[546] showed that Mn^{II} acts as a template for the synthesis of compounds of all three macrocycles (**198**)–(**200**) containing 15-, 16- and 17-membered great rings respectively. The products are of type $M_nX_2L\cdot xH_2O$ and $MnXL(ClO_4)\cdot xH_2O$ (X = Cl, NCS or BPh_4; $x = 0$, 0.5, 2 or 6). As before, all the compounds are high spin with $S = 5/2$ ground states. The compounds of the 15- and 16-membered macrocycles have been assigned pentagonal bipyramid structures in which the macrocycle coordinates in the equatorial plane with the negatively charged monoanions or water molecules occupying the axial positions. These species are all mononuclear with the exception of those of type $[\{Mn(NCS)L\}_n][ClO_4]_n$ which were assigned NCS-bridged, polymeric structures in the solid state. The latter complexes exhibit Curie–Weiss behaviour with Weiss constants of -13 K in each case; this behaviour has been interpreted in terms of weak antiferromagnetic exchange. The 17-membered ring appears to yield metal compounds which have a somewhat different structure to those of (**198**) and (**199**). This was confirmed for $[Mn(NCS)_2(\mathbf{200})]$ by an X-ray diffraction study which shows that, while the coordination sphere is best considered as a distorted pentagonal bipyramid with the thiocyanate groups in axial sites, the macrocycle is distorted from planarity. The pyridine nitrogen is 0.92 Å out of the plane containing the other four ring nitrogens and the metal ion. The remaining compounds containing the 17-membered ring, $[MnCl(\mathbf{200})][ClO_4]$ and $[MnCl(\mathbf{200})]Cl\cdot 0.5H_2O$, appear to be six-coordinate and have been proposed to have pentagonal pyramidal structures with the vacant (axial) site being partially shielded by the folded macrocycle. In separate work, Dabrowiak *et al.*[534] also prepared manganese compounds of the 16- and 17-membered rings; these were used as precursors for the corresponding Mn^{III} compounds (see later).

A crystal structure of the 1:1 adduct of 1,10-phenanthroline and the seven coordinate species, $[Mn(\mathbf{199})(H_2O)_2](ClO_4)_2$, indicates that the phenanthroline molecule is not coordinated to the manganese but is sandwiched between $[Mn(\mathbf{199})(H_2O)_2]^{2+}$ units in a lamellar structure.[136] The phenanthroline nitrogens are hydrogen bound to water molecules in adjacent complex ions; the structure also appears to be held together by π donor/π acceptor and dispersion forces.

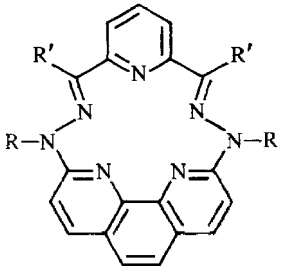
Compounds of type $[MX_2(\mathbf{202})]$ ($X = ClO_4$, NO_3) have also been reported.[547] Like the closely related dimethylated species, these compounds have been assigned distorted pentagonal bipyramidal structures and for the compound with $X = ClO_4$, an X-ray structure determination confirms this geometry.

Mn^{II} complexes of type $[MnClL]^+$ (where L = (**203**) with R = Me or $CH_2CH_2CH_2OH$; R′ = Me and R = Me; R = H) and $[MnX_2L]\cdot nH_2O$ (where L = (**203**) with R = Me, R′ = H or R = Me, R′ = Me) have been synthesized by Lewis and co-workers using a template procedure.[548–551] For example, to prepare the complex of (**203**; R = H, R′ = Me),[549] 2,6-diformylpyridine and 2,9-di(1-methylhydrazino)-1,10-phenanthroline monohydrochloride were condensed in a methanol/water mixture containing manganese chloride. X-Ray structure determinations of each of the species $[MnClL](BF_4)$ (L = (**203**) with R = CH_3 or CH_2CH_2OH),[549,550] indicate that they have similar coordination geometries: the Mn^{II} ion is six-coordinate (pentagonal pyramidal) and is bound by five macrocyclic nitrogens in a plane and by an axial chloro group. The metal ion is displaced from the N_5-plane towards the chloro ligand in each compound. For the metal compound containing the peripheral hydroxyethyl substituents, these groups are not coordinated. They lie on the same side of the macrocycle as the axial chloro ligand. The compounds of type $[MnX_2L]\cdot nH_2O$ have been assigned pentagonal bipyramidal coordination geometries.

The electrochemistry of a number of such six-coordinate compounds $[MnXL]^+$ and seven-coordinate compounds $[MX_2L]$ (with L = (**203**), R,R′ = Me and X = halide, water, triphenylphosphine oxide, imidazole, 1-methylimidazole or pyridine) has been investigated.[551] The redox behaviour of these compounds was of interest because it was considered that the potentially π-acceptor macrocycle (**203**; R = R′ = Me) may promote the formation of Mn^0 or Mn^I species or may yield a metal-stabilized ligand radical with the manganese remaining in its divalent state. For a number of macrocyclic ligand systems, it has been demonstrated that the redox behaviour can be quite dependent on axial ligation; it was also of interest to study whether this was the case for the present systems.



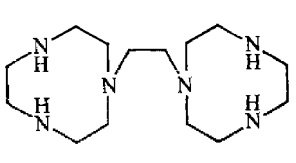
(202)



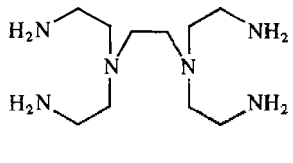
(203)

Cyclic voltammetry on the above compounds in acetonitrile gave a reversible one-electron reduction wave near −1.4 V (versus $Ag/AgNO_3$) in each case. Thus the reduction potential showed little variation with change of axial ligand. This suggests that the redox behaviour is confined to the coordinated macrocycle since, as just mentioned, axial ligand type would be expected to markedly influence redox behaviour directly involving the metal centre. Quantitative reduction using controlled potential electrolysis led to isolation of the corresponding one-electron reduction products. These were shown by ESR studies to be Mn^{II} ligand-radical species; it was postulated that the additional electron in these species resides in the diimine pyridine portion of the ligand. No evidence for metal-ion reduction was obtained even when π-acceptor axial ligands such as CO or phosphines were added to the solution in the electrochemical cell.

Few stability constants for manganese compounds of cyclic ligands have been reported. A log K value of 15.0 (I = 1.0 M, KNO_3; 25°C) for the 1:1 compound of the dicyclic ligand (**204**) and Mn^{II} has been reported.[552] The log value for the corresponding compound of the related non-cyclic ligand (**205**) is 9.3.[553] The large difference in these values illustrates well the operation of the 'macrocyclic effect'[544] in the bicyclic system.



(204)

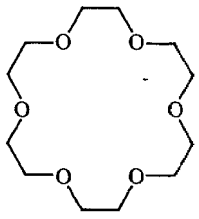


(205)

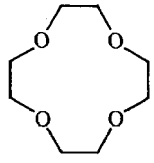
41.3.10.4 Oxygen donor macrocycles

Mn^{II} compounds incorporating crown ether macrocycles have been reported. The coordination chemistry of crown ethers has been mainly concerned with the compounds of non-transition ions.[555] This is due, in part, to the generally weaker affinity of such ligands for transition metals. X-Ray studies indicate that a number of transition metal compounds containing crowns (which were isolated from aqueous solution) have the crowns H-bound to coordinated water molecules rather than being bound directly to the metal ion. Such an arrangement occurs in $[Mn(H_2O)_6](ClO_4)_2 \cdot L$,[556] $[Mn(NO_3)(H_2O)_5](NO_3) \cdot L \cdot H_2O$[557] and $[Mn_2Cl_2(H_2O)_8]Cl_2 \cdot L$ (where L = (**206**); 18-crown-6).[558] In contrast, it has proved possible to isolate yellow-orange $[MnL_2](Br_3)_2$ (L = (**207**); 12-crown-4) in which the macrocycles bind directly to the Mn^{II} ion; the synthesis was performed in methanol under anhydrous conditions.[559] The X-ray analysis of this compound indicates that the cation consists of two 12-crown-4 macrocycles bound in 'sandwich' fashion to the Mn^{II} ion. The Mn^{II} is located on a crystallographic mirror plane which requires that the O_4-donor set of each crown ligand be coplanar. The overall coordination geometry is square antiprismatic. It is evident from the mean length (2.31 Å) of the Mn—O bonds that the ether ligands are weakly bound.

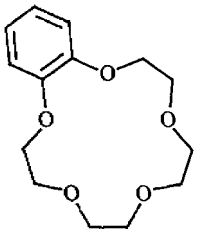
Other Mn^{II} compounds of polyethers have been reported. For example, a mono-crown species of composition $[MnL(MeNO_2)](SbCl_6)_2$ (where L = **206**) has been isolated after addition of 18-crown-6 in CH_2Cl_2 to $[Mn(MeNO_2)_6](SbCl_6)_2$ in $MeNO_2$.[508] The product rapidly decomposes in the presence of water. From infrared studies it was concluded that the $MeNO_2$ molecule is bound to the Mn^{II} and that at least one of the ether oxygens is not coordinated. Compounds of composition $(MnBr_2)_2L \cdot 3/2acetone \cdot H_2O$ (L = (**208**) benzo-15-crown-5) and $(MnX_2)_2L \cdot 8H_2O$ (L = **206**; X = Cl, Br) have also been isolated from non-aqueous reaction solutions.[561] Comparative infrared studies have also been used to investigate the nature of these species; however, it has not been possible to assign their structures with certainty.



(206)



(207)

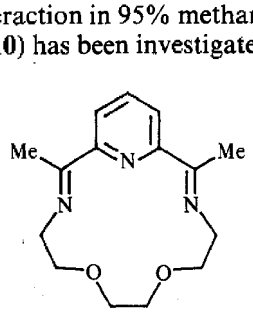


(208)

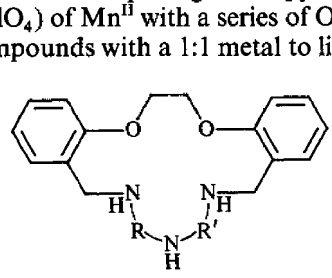
41.3.10.5 Mixed donor macrocycles

Studies in which 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine were condensed in the presence of a stoichiometric amount of Mn^{II} led to isolation of orange $[Mn(NCS)_2(\mathbf{209})]$.[562] As found for the Mn^{II} compounds of the related N_5-ligand system, an X-ray study indicates that this high-spin species is seven-coordinate with the macrocycle occupying the pentagonal plane and the axial positions being filled by isothiocyanate groups. The five donor atoms of the macrocycle are almost coplanar although the structure is slightly distorted from true pentagonal bipyramidal geometry.

The interaction in 95% methanol (I = 0.1, Et_4NClO_4) of Mn^{II} with a series of O_2N_3-macrocycles of type (**210**) has been investigated.[563] In all cases compounds with a 1:1 metal to ligand stoichiome-



(209)



(210) R = $-(CH_2)_2-$, R′ = $-(CH_2)_2-$

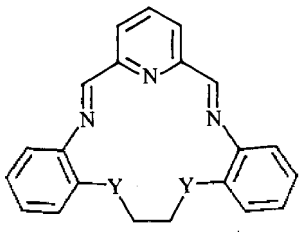
R = $-(CH_2)_2-$, R′ = $-(CH_2)_3-$

R = $-(CH_2)_3-$, R′ = $-(CH_2)_3-$

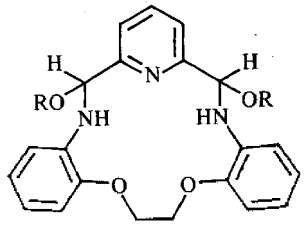
R = $-CH_2CH(CH_3)-$, R′ = $-CH_2CH(CH_3)-$

try were observed. As expected from the position of Mn^{II} in the Irving–Williams stability order, these compounds are all less stable (with log K values in the range 3.5–4.0) than the corresponding complexes of Co^{II}, Ni^{II}, Cu^{II} or Zn^{II}.

Pentagonal bipyramidal compounds of type $[MnX_2L]$ (where L = (**211**) with Y = O or S; X = ClO_4, NO_3) have been synthesized[547] using *in situ* procedures. In other studies it was observed that reaction of $MnCl_2$ with the appropriate ligand precursors in ethanol yielded initially a bright orange-yellow product of composition $MnCl_2L \cdot 2H_2O$ (L = (**211**) with Y = O.[564] If this product was removed from the reaction solution, needles of the free macrocycle (**212**) crystallized. In this product ethanol has added across each of the imine bonds of (**211**) with Y = O. Additions of this type have been documented in other imine-containing complexes,[565] a driving force for these reactions may be the relief of strain in the highly conjugated diimine precursor. If (**212**) is returned to the reaction filtrate and the solution warmed then red-brown $[MnCl_2(\mathbf{212})]$ crystallizes. In a further experiment the condensation was performed in the absence of the Mn^{II} and (**212**) was still isolated indicating that its formation is not controlled by a metal-template reaction.

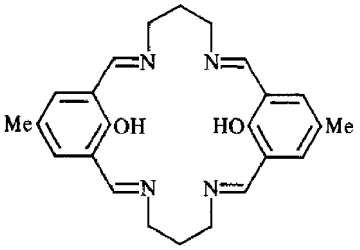


(211) Y = O, S



(212)

Reaction of 5-methylisophthalaldehyde with 1,3-diaminopropane in the presence of manganese(II) chloride and manganese(II) acetate in methanol yields a dimetallic complex of type $Mn_2Cl_2L \cdot 2H_2O$ (where LH_2 = **213**)[566] in which the dianionic form of the macrocycle acts as a novel binucleating species. The proposed structure is one in which each metal ion is surrounded by an O_2N_2-donor set in an approximately planar arrangement with a chloro group occupying an axial position on each Mn^{II}; the coordination geometry of each Mn^{II} is approximately square pyramidal. A stereochemistry of this type has been confirmed for the analogous dicopper(II) species by X-ray diffraction.[567] The study of metal–metal interactions in the dimetallic compounds of (**213**) is simplified by the fact that both metal ions are in identical environments. However, in contrast to the compounds of this ligand with some other metal ions,[566,568,569] $Mn_2Cl_2L \cdot 2H_2O$ (where LH_2 = **213**) exhibits little evidence of antiferromagnetic interaction between adjacent Mn^{II} ions — the compound shows Curie–Weiss behaviour with a Weiss constant of $-7°$.[566] In other studies, the anhydrous compound Mn_2Cl_2L has been demonstrated to contain a slight ferromagnetic exchange interaction with $J = +0.2\,cm^{-1}$.[568]



(213)

Magnetic and electrochemical studies involving mixed metal compounds of deprotonated (**213**) have also been reported.[570,571] These compounds include Cu^{II}/Mn^{II} and Cu^{I}/Mn^{II} species.

For the $[Cu^{II}Cu^{II}L]^{2+}$ compound mentioned previously, two sequential reductions corresponding to conversion of this species to $[Cu^{II}Cu^{I}L]^{+}$ and then to $[Cu^{I}Cu^{I}L]$ were observed at -0.93 and $-1.32\,V$, respectively, relative to Fe/Fe^{+} in dimethylformamide. In contrast, for $[Cu^{II}Mn^{II}L]^{2+}$ the Cu^{II}/Cu^{I} wave occurs at $-1.0\,V$; a wave at $+0.150\,V$ corresponds to the Mn^{III}/Mn^{II} couple. It is

perhaps surprising that substitution of Fe^{II}, Co^{II}, Ni^{II} or Zn^{II} for the Mn^{II} in the above heteronuclear compound does not alter (within experimental error) the value of the Cu^{II}/Cu^{I} couple. This difference between the redox behaviour of the dicopper(II) species and $[Cu^{II}M^{II}L]^{2+}$ (M = Mn, Fe, Co, Ni or Zn) has been postulated to reflect the fact that only the $[Cu^{I}Cu^{II}L]^{+}$ species can exist to any extent as a resonance-stabilized delocalized ion.

The Cu^{I} in a series of $[Cu^{I}M^{II}L]^{+}$ compounds (including $[Cu^{I}Mn^{II}L]^{+}$) has been demonstrated[570] to have an axial affinity for some or all of the bases: carbon monoxide, ethylene, tris(*o*-methoxyphenyl)phosphine and 4-ethylpyridine. In all cases the binding constants for adduct formation are low; for example, for $[Cu^{I}Mn^{II}L]^{+}$ and CO or 4-ethylpyridine the values are $0.9\,M^{-1}$ and $22.5\,M^{-1}$, respectively. In contrast to the constant Cu^{II}/Cu^{I} reduction potentials mentioned above for the $[Cu^{II}M^{II}L]^{2+}$ species, the binding constants for the attachment of axial ligands to the Cu^{I} in the respective $[Cu^{I}M^{II}L]^{+}$ compounds show a slight dependence on the nature of M^{II}. Thus the binding studies indicate that communication occurs between adjacent metal ions. While the nature of these effects are as yet little understood, studies in this general area show potential for providing a fuller understanding of a number of metal-containing biological systems in which communication between adjacent metal ions has been demonstrated to occur.

41.4 MANGANESE(III)

Oxidation of Mn^{II} to Mn^{III} has long been known to occur, but details of the, sometimes complex, products are only now emerging. Whereas, in many systems, simple one-electron oxidation gives well-defined Mn^{III} species, yet in others the products may be mixtures of oxidation states, and there are examples of direct oxidation to Mn^{IV} without any detectable Mn^{III} intermediate (Section 41.5). Accordingly, many compounds which are called Mn^{III} in the literature, especially the various products of the 'oxygenation' of Mn^{II} salicylaldiminates (Section 41.3.9.3), must be assigned to the 'not proven' category at this stage.

There are few cationic compounds with neutral ligands: the known chemistry largely refers to compounds of the anionic ligands and generally the more electronegative donors O and F. However, there is an extensive chemistry with the macrocyclic $[N_4]$ ligands; $[Mn^{III}S_6]$ species are well characterized with the dithiolates, which can satisfy both charge and coordination shell requirements; and there is a recent report of $[MnI_3(PR_3)_2]$ (Section 41.4.2) which opens the possibility of new vistas. Compounds of the oxygen ligands have found good use as oxidizing agents in hydrocarbon chemistry, as has MnF_3 as a fluorinating agent.

Figure 1 indicates, and the observations for the various ligand systems (*q.v.*) add further detail, that Mn^{III} is often subject to disproportionation (14), a reaction which, in aqueous solutions, is often driven by precipitation of MnO_2 (equation 15).

$$2Mn^{III} \rightleftharpoons Mn^{II} + Mn^{IV} \tag{14}$$

$$Mn \rightleftharpoons MnO_2\downarrow + nH^{+} \tag{15}$$

Table 43 Coordination Polyhedra[a] and Spin States for Manganese(III)

Coordination Number	*Donor Atoms*
(a) High Spin Polyhedra (μ_{eff} = 4.8–5.3 BM)	
7	$[N_2O_5]$, $[N_5X_2]$[b]
6 (Octahedral)	$[N_6]$, $[N_xO_{6-x}]$, $[O_6]$
	$[S_6]$, $[S_4O_2]$
	$[F_6]$, $[F_4O_2]$
	$[Cl_6]$, $[Cl_3N_3]$, $[Cl_3O_3]$, $[Cl_2O_4]$, $[Br_3O_3]$
5	$[N_4X]$[b], $[O_5]$, $[S_5]$, $[Cl_5]$, $[I_3P_2]$[c]
4 (Tetrahedral)	$[O_4]$
(Planar)	$[O_4]$[d]
(b) Low Spin Polyhedra (μ_{eff} = 3.1–3.2 BM)	
6 (Octahedral)	$[C_6]$, $[N_6]$, $[C_5N][P_4Cl_2]$

[a] In most cases, the polyhedra are included only if X-ray proof of structure is available.
[b] Macrocyclic ligands.
[c] Spin state not yet reported.
[d] This refers to the basic chloride in Table 46.

Mn^{III} is formally d^4, and therefore the high spin configuration in an octahedral field is one of those, like the d^9 of Cu^{II}, which the Jahn–Teller theorem predicts should distort. Such distortions are indeed observed in the great majority of, but not all, known structures; and they often serve to identify the Mn^{III} polyhedra in mixed oxidation state compounds. There are few examples of other spin states (Table 43): $[Mn(CN)_6]^{3-}$ is an example of a low spin ($S = 1$) compound, and there are other examples in the macrocyclic compounds (Section 41.4.8).

Magnetic measurements, although useful for confirmation of spin state, have little diagnostic value, and ESR signals are usually not observed, reputedly because of fast spin relaxation.

Although again of little proven diagnostic value, except within limited classes like the solid halides,[348] the electronic spectra of these d^4 systems have spin allowed d–d transitions; and accordingly the compounds have more colour than those of Mn^{II}.

Except where specific ligand steric effects add kinetic stability, the compounds of Mn^{III}, including the low spin $[Mn(CN)_6]^{3-}$, are quite labile.

41.4.1 Carbon Ligands

The literature of Mn^{III} and Mn^{IV} *cyano* compounds[21,22,573] is somewhat confused by claims for non-existent species, which have since been disproved. Hence, we list in Table 44 only the known species for which acceptable proof has been published.

$K_3[Mn(CN)_6]$, which was one of the few examples of low spin Mn^{III}, was first prepared in 1837. Standard methods of preparation have been described; but, in some hands at least, these may lead to contamination of products with $[Mn_2O(CN)_{10}]^{6-}$. Hence, much of the early work on the physical properties of $[Mn(CN)_6]^{3-}$ is in doubt. There is but one form of the compound $K_3[Mn(CN)_6]$, —red, monoclinic crystals—in which measured Mn—C distances are 1.94, 1.99 and 2.00(×2) Å, giving the same average value of 1.98 Å as for the cubic $Cs_2Li[Mn(CN)_6]$. Magnetic measurements ($\mu_{eff} = 3.50$ BM at room temperature) indicate a low spin t_{2g}^4 configuration. The undiluted K^+ salt showed no ESR signal between 12 and 290 K.

Exchange of CN^- with $[Mn(CN)_6]^{3-}$ in water is very fast, and there are indications[22] of an 'associative' mechanism involving $[Mn(CN)_6H_2O]^{3-}$. Aqueous perchloric acid solutions often precipitate $Mn(CN)_3 \cdot nH_2O$,[574] which is another example of disproportionation of Mn^{III}, being formulated as $Mn^{II}[Mn^{IV}(CN)_6] \cdot nH_2O$ (Section 41.5.1).

A major contaminant of many of the earlier preparations of $K_3[Mn(CN)_6]$,[575] and often described as a different form of this, was a golden brown dimeric oxo-bridged species $[(CN)_5Mn—O—Mn(CN)_5]^{6-}$. It is also formed when $KMnO_4$ is reacted with KCN, and an X-ray analysis of the crystalline compound $K_7[Mn_2O(CN)_{10}] \cdot CN$ showed a linear Mn—O—Mn bridge, with Mn—O = 1.72 Å and Mn—CN = 1.97–2.06 Å. It is almost diamagnetic because of antiferromagnetism.

Various metal cations form precipitates with $[Mn(CN)_6]^{3-}$ in neutral or acid solution. One of them, $Fe_3[Mn(CN)_6]_2$ undergoes an interesting reaction: on heating, rearrangement occurs to $[Fe(CN)_6]^{4-}$.

With our formalism, accepting NO as a neutral ligand, $[Mn(CN)_5NO]^{2-}$ becomes an Mn^{III} compound, although it is not very comfortable here, especially when placed against $[Mn(CN)_5(NO_2)]^{3-}$, which it forms when irradiated (UV) in the presence of O_2. The nitrosyl is yellow, has a magnetic moment of 1.73 BM and a ν_{NO} of 1885 cm^{-1}.

Mn^{III} alkyls appear to be particularly prone to disproportionation.[197] Attempts to prepare them from $[Mn(acac)_3]$ and Li alkyls in the presence of phosphines give transient colour changes at low temperatures which appear to be the Mn^{III} species, but only Mn^{II} and Mn^{IV} alkyls (*q.v.*) have been isolated from the solutions. An interesting report,[576] which has not yet been confirmed, describes

Table 44 The Mn^{III} and Mn^{IV} Cyano Compounds

Compound	*Oxidation State*	*Structure*	*Colour*
$M_3[Mn(CN)_6]$	III	$[Mn(CN)_6]^{3-}$ octahedral	Red
$Mn(CN)_3 \cdot nH_2O$	II/IV	$Mn^{II}[Mn^{IV}(CN)_6] \cdot nH_2O$	Green
$K_7Mn_2O(CN)_{11}$	III	$[(CN)_5MnOMn(CN)_5]^{6-}$	Golden-brown
$M_2[Mn(CN)_5NO]$	?	$[Mn(CN)_5NO]^{2-}$ octahedral	Yellow
$M_3[Mn(CN)_5NO_2]$	III		
$M_2[Mn(CN)_6]$	IV	$[Mn(CN)_6]^{2-}$ octahedral	Yellow

Mn^{III} monoalkyls $[MnR(N_2O_2)H_2O]$ {where (N_2O_2) is a Schiff base ligand (**161**)}, which is analogous to the well-characterized Co^{III} species. Six compounds were described, all with magnetic moments near 5.0 BM.

41.4.2 Nitrogen and Phosphorus Ligands

The known chemistry of Mn^{III} with nitrogen ligands, other than the macrocycles (Section 41.4.8), is still quite limited {but see also the mixed N, O ligands, Section 41.4.7}. Perhaps the tendency for Mn^{III} to disproportionate, in many ligand systems, is responsible for the failure to obtain $[Mn\{N(SiMe_3)_2\}_3]$, when these species have been obtained[84] for all other metals Sc^{III} to Fe^{III}.

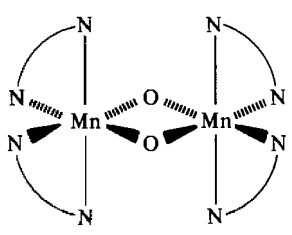
Most of the data for this section come[78,210,572] from the reactions of $MnCl_3$ with uni-, bi- and ter-dentate ligands (Table 45). The green monopyridine compound (**214**) is not at all robust, but reacts further to give a more stable, brown tris compound $[MnCl_3py_3]$ (**215**). Compounds of the latter class generally are sensitive to moisture (although the NEt_3 compound is distinctly less so), but the py compound is stable up to 100°C under N_2. No physical measurements were reported, but the related terpy compound (**219**) is a typical, high spin, octahedral species.

The air stable red compounds (**215**) formed with the bidentate ligands, appear to be dimers, with magnetic moments reduced by antiferromagnetism; but the aquo species (**217**) are almost certainly $[MnCl_3(H_2O)(N_2)]$ octahedra. A structural analysis of the related, but more versatile, nitrato species $[Mn(NO_3)_3bipy]$ shows a seven-coordinate polyhedron with two bidentate nitrates and one bipy nitrogen almost co-planar (Mn—O = 2.11–2.40; Mn—N = 2.09 Å), and axial N (2.00 Å) and unidentate NO_3 (Mn—O = 1.90 Å). ESR spectra have been observed for the compounds (**215**), but they are very broad single lines (600 Øe).

Table 45 Solid $MnX_3 \cdot L_N$ Compounds for Nitrogen Ligands

Class		*Ligand and Comments*	μ_{eff} (BM)
(**214**) MnX_3N	($X = Cl^-$)	py, quin: green crystals from cold ether	
	($X = \frac{1}{2}SO_4^{2-}$)	py: chocolate-brown from hot py	
(**215**) MnX_3N_2	($X = Cl^-$)	bipy, phen: red or red-brown	3.9
(**216**)	($X = NO_3^-$)	bipy, phen: red crystals	5.0
(**217**) $[MnX_3N_2(H_2O)]$	($X = F^-$)	phen: orange-brown	4.9
	($X = Cl^-$)	bipy, phen: red-brown	5.0
(**218**) $[MnCl_3N_3]$		$N = NH_3$, RNH_2 (R = Me, Et, Pr, Bu): brown R_2NH (R = Me, Et): brown R_3N (R = Et, Bz): Et, brown; Bz, green py, quin: brown	
(**219**)		N_3 = terpy: brown	4.9
(**220**) $[(Mn^{III}O_2—Mn^{IV})(N_2)_4]X_3$		N_2 = bipy, phen ($X = ClO_4$, PF_6, $\frac{1}{2}S_2O_8^{2-}$): green	2.1–2.8
(**221**) $[Mn(N_2)_3](ClO_4)_3$		N_2 = en: green	4.9

Various reactions of excess phenanthroline or bipyridyl with Mn^{II} or Mn^{III} species in the air, or with $KMnO_4$ solutions, produce the compounds (**220**), which have the dimeric, dioxo-bridged, Mn^{III}/Mn^{IV} structure (**222**). These green compounds, isolated with various X^-, are stable in moist air at room temperature and in the daylight for several days, but decompose somewhat faster in solution. The Mn^{III} and the Mn^{IV} octahedra are well defined in the X-ray structural analysis of $[Mn_2O_2bipy_4](ClO_4)_3 \cdot 3H_2O$, with the Mn^{III} having the longer bond lengths and the expected tetragonal distortion.[577] Magnetic moments are low because of antiferromagnetism and ESR spectra showing hyperfine coupling to both Mn^{III} and Mn^{IV} have been obtained.



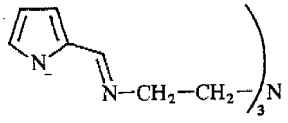
(**222**)

The green dimeric 3+ species can be oxidized to the 4+ Mn^{IV} species (Section 41.5.2), but, although there is good electrochemical evidence (in CH_3CN solution) for the quasi-reversible step (a) in reaction (16), the Mn^{III} dimer (2+) is unstable. Equally protonation of the dioxo-bridge atoms leads to increased instability; green solutions of the Mn^{III}/Mn^{IV} anion turn red on the addition of H^+; the process is immediately reversible; but reversibility decreases with time as the dimer decomposes to Mn^{II}.

$$[(N,N)_2Mn^{III}O_2Mn^{III}(N,N)_2]^{2+} \underset{(a)}{\rightleftharpoons} [(N,N)_2Mn^{III}O_2Mn^{IV}(N,N)_2]^{3+} \underset{(b)}{\rightleftharpoons} [(N,N)_2Mn^{IV}O_2Mn^{IV}(N,N)_2]^{4+} \quad (16)$$

Dihydroxy-bridged species with other N ligands have been postulated for some biguanide compounds, but the details here need to be confirmed by X-ray structural studies. However, both dihydroxy- and dimethoxy-bridged dimers are known for Mn^{III} compounds of salicylaldiminate ligands (Section 41.4.7).

The only reference to a tris-bidentate species is the compound (**221**), which is reported[578] to be a green crystalline compound with $\mu_{eff} = 4.85$ BM and $g = 2.08$. Many other $[MnN_6]$ compounds should therefore be accessible. One interesting recent example is the Mn^{III} compound of the ligand (**223**). This molecule lies on a crystallographic three-fold axis; is nearly octahedral $[MnN_6]$, but with a significant twist towards the eclipsed, trigonal prism, with Mn—N (pyrrole) 2.054 and (azomethine) 2.148(2) Å; and is the first example of Mn^{III} or any d^4 system, with a crossover from the high spin $S = 2$ state to the low spin $S = 1$ state at 40–50 K.[579]



(223)

The low spin configuration was earlier found in the deep-coloured, tris chelated amino-troponiminates $[Mn(L_N)_3]$ (for L_N = **43**). Black $[Mn(L_N)_3]$, prepared from $Mn_2(CO)_{10}$ and L_NH, had a magnetic moment of 3.12 BM; whereas the brown-black $[Mn(acac)_2(L_N)]$ and black $[Mn(acac)(L_N)_2]$ both were high spin species with $\mu_{eff} = 4.9$ BM (in $CHCl_3$).[141] An X-ray structural analysis of the latter showed a tetragonal distortion of the $[MnN_2O_4]$ octahedron.[580]

Phosphorus ligand compounds of Mn^{III}, except for alkyl and hydride species (Section 41.4.6), are confined to a report of $[MnCl_2(diphos)_2]Cl$ (see Section 41.3.4 and Table 17); and now the unexpected, dark-green, phosphine-iodo compound[581] $[MnI_3(PMe_3)_2]$, which has a trigonal bipyramidal five-coordinate structure, with axial phosphines (at Mn—P = 2.43–2.44 Å). Undoubtedly the latter compound is but the 'tip of the iceberg', and we can expect to see a considerable further development of this area of Mn^{III} chemistry; although it is pertinent to recall that the phosphine alkyls of Mn^{III} disproportionate.

41.4.3 Oxygen Ligands

Many compounds, with a range of ligands, have been isolated as crystalline solids. They are almost invariably good oxidizing agents; and, as such, are used in organic (hydrocarbon) chemistry, especially the acetate, but also now the sulfate and diphosphonate.[4–6]

41.4.3.1 Water, hydroxide and oxide

$[Mn(H_2O)_6]^{3+}$ is perfectly well characterized in the red crystalline alum $CsMn(SO_4)_2 \cdot 12H_2O$, but we have significant doubts about the current orthodoxy that it also is a significant component of green aqueous acid solutions.[572,582,583]

Mn^{III} in water was well reviewed[583] in 1968, and nothing published since appears to add significantly to the basic data. Interpretations were given in terms of $Mn^{3+}_{aq.}$, with hydrolysis to $MnOH^{2+}_{aq}$; which translates, not unreasonably to $[Mn(H_2O)_6]^{3+}$ and $[Mn(OH)(H_2O)_5]^{2+}$. The aqueous solutions are described as green and rather unstable. All data referring to $[Mn(H_2O)_6]^{3+}$ were obtained by extrapolating to some ideal, either of time or concentration. But, even so, the extinction coefficient obtained for the visible spectrum of this species is ten times that obtained for it in

$CsMn(SO_4)_2 \cdot 12H_2O$. Thus it seems not improbable that the solution data, even in concentrated acid solutions may refer instead to $[Mn(OH)(H_2O)_5]^{2+}$ or the dimer $[(H_2O)_4Mn(OH)_2Mn(H_2O)_4]^{4+}$; with the second species required by the analyses of the various kinetic data[583] being a further 'hydrolysed' (proton-transfer) species.

Complications which militate against the observance of pure $[Mn(H_2O)_6]^{3+}$ in aqueous solution are its oxidizing properties, the usual electroneutrality-driven 'hydrolysis' (or, more exactly, proton transfer to solvent) and the disproportionation reactions (14) and (15). The instability of the cation is shown in the behaviour of the alums $MMn(SO_4)_2 \cdot 12H_2O$ (M = K, Rb, Cs, NH_4): all four were isolated by Christensen in 1901, as red crystalline compounds, but only the Cs compound is stable at normal room temperatures and even this one begins to blacken and decompose at 33°C. No other solids containing the cation appear to have been described.

The aqueous solutions of Mn^{III} are stabilized by the presence of Mn^{II} and H^+. They become cloudy on standing, and at a rate which is accelerated by decreasing $[H^+]$ or $[Mn^{II}]$, or by increasing $[Mn^{III}]$. The cloudiness results, of course, from the formation of oxo/hydroxo polymers; but the detail of these and the kinetics of their formation are not understood, except by extrapolation from the behaviour of the other metal compounds.

At least for the solid state, we are on firmer ground, and the structural data[211] for most of the Mn^{III} oxo and hydroxo compounds are in Table 46. $Mn(OH)_3$ has not been detected, instead MnO(OH), in two major crystalline forms, is the species first formed when $Mn(OH)_2$ is oxidized in contact with alkaline solutions. Several other crystalline solids are known to contain OH^- (Table 46). However, we can only speculate that the green crystalline Na, Ba and Sr hydroxomanganates(III), described by Scholder and Kyri[584] in 1952, may contain the $[Mn(OH)_6]^{3-}$ anion, although the authors postulated $[Mn(OH)_5]^{2-}$ and $[Mn(OH)_7]^{4-}$ as well.

The coordination polyhedra are generally $[MnO_6]$ octahedra, with the sorts of distortion (Table 46) required by, but not certainly attributable to, the Jahn–Teller theorem. Such distortion is as often rhombic (2 + 2 + 2) as tetragonal (4 + 2). Bond distances average between 2.0 and 2.1 Å, and

Table 46 Structural Data for the Mn^{III} Oxo and Hydroxo Compounds

Compounds	*Polyhedra*	*Bond Distances* (Å)[a]
Mn_2O_3	$[MnO_6]$ (*i*)	1.963 (× 2); 1.996 (× 2); 2.050 (× 2) (2.00)
	(*ii*)	1.960 (× 2); 1.998 (× 2); 2.047 (× 2) (2.00)
	(*iii*)–(*v*)	1.88–1.92; 1.96–2.01; 2.19–2.31 (2.05)
MnO(OH)[b] (α)	$[MnO_3(OH)_3]$	1.896 (× 2); 1.968 (× 2); 2.178, 2.340 (2.04)
(β)	$[MnO_3(OH)_3]$	1.868, 1.878; 1.965, 1.981; 2.199, 2.333 (2.04)
$MMnO_2$ (α-Na)	$[MnO_6]$	1.92 (× 2); 1.92 (× 2); 2.40 (× 2) (2.08)
(β-Na)	$[MnO_6]$	1.91 (× 2); 1.95 (× 2); 2.41 (× 2) (2.09)
Li	$[MnO_6]$	1.89 (× 2); 1.96 (× 2); 2.29 (× 2) (2.05)
$Na_4Mn_2O_5$[c]	$[MnO_5]$	1.953 (× 2); 1.941 (× 2); 2.068 (S.P.)
$K_6Mn_2O_6$[d]	$[MnO_4]$	1.85–1.95 (tetrahedral dimer)
$MnPbO_2(OH)$	$[MnO_6]$	(2.05 and 2.07)
$CaMn_2O_4$	$[MnO_6]$	1.90–1.96 (× 4); 2.29, 2.46
$ZnMn_2O_4$	$[MnO_6]$	1.93 (× 2); 1.93 (× 2); 2.22 (× 2) (2.03)
$CdMn_2O_4$	$[MnO_6]$	1.88 (× 2); 1.88 (× 2); 2.24 (× 2) (2.00)
$LaMnO_3$	$[MnO_6]$	1.905 (× 2); 1.959 (× 2); 2.187 (× 2) (2.02)
$LuMnO_3$	$[MnO_5]$	Trigonal bipyramidal
$DyMn_2O_5$	$[MnO_5]$	1.911 (× 2); 1.926 (× 2); 2.020 (S.P.)
$Bi_2Mn_4^{III,IV}O_{10}$	$[MnO_5]$	1.91–2.10 (× 4); 2.94 (S.P.)
$Cs_3Mn_3V_5O_{16}$[e]	$[MnO_6]$ (*i*)	1.916 (× 2); 1.976 (× 2); 2.147 (× 2) (2.01)
	(*ii*)	1.903, 1.923; 1.945, 1.964; 2.196, 2.217 (2.04)
$Na_4Mn_4Ti_5O_{18}$	$[MnO_6]$	1.94 (× 2); 1.97 (× 2); 2.03, 2.27 (2.02)
	$[MnO_5]$	1.95 (× 2); 1.99 (× 2); 2.17 (S.P.)
$Mn(OH)SO_4 \cdot 2H_2O$[f]	*t*-$[MnO_2(OH)_2(H_2O)_2]$ (*i*)	1.90 (× 2); 1.91 (× 2); 2.24 (× 2) (2.02)
	(*ii*)	1.90 (× 2); 1.91 (× 2); 2.20 (× 2) (2.00)
$Mn_3(OH)_2(PO_4)_2 \cdot 4H_2O$[g]	$[MnO_6]$	(2.02)
$Mn_8O_{10}Cl_3$	$[MnCl_2O_4]$	1.87 (× 2); 1.91 (× 2); (Cl) 2.83, 2.84
	$[MnCl_2O_4]$	1.84 (× 2); 1.92 (× 2); (Cl) 2.84 (× 2)
	$[MnO_6]$	2.01 (× 4); 2.03 (× 2)

[a] Bond distances for the octahedra are listed in *trans* pairs to feature the distortions. The figure in parentheses is the average.
[b] The shorter distances refer to O^{2-}.
[c] Ref. 585.
[d] Ref. 586.
[e] Ref. 587.
[f] Ref. 588.
[g] The mineral bermanite—ref. 263.

thus are intermediate between those for Mn^{II} and Mn^{IV}. These distances, and the distortions, often serve to identify the +3 oxidation state in the solids. Similar octahedra are observed in silicate minerals,[250] such as braunite and henritermierite, and borate minerals,[248] such as the pinakiolites and gaudefroyite. One apparent exception to the rule of distortion is the $[Mn^{III}O_6]$ octahedron in $Mn_8O_{10}Cl_3$, which has bond lengths of 2.01 and 2.03 Å; but the $[MnCl_2O_4]$ octahedra, with Mn—Cl of 2.84 Å, are so distorted as to closely approach a planar $[MnO_4]$ geometry.

Five-coordinate and four-coordinate (tetrahedral) structures also are known. The five-coordinate polyhedra usually are square pyramidal with a distinctly longer axial bond; and, in one case, this is so long (2.94 Å) as again to suggest planar $[MnO_4]$ coordination.

The tetrahedron is known so far only in the dimeric oxoanion $[Mn_2O_6]^{6-}$, which was made by heating MnO and K_2O together at 610°C for ten days.[586]

41.4.3.2 Oxyanions

Nitrato compounds appear to be confined[258] to the thermally unstable $Mn(NO_3)_2$, $NO_2[Mn(NO_3)_4]$ and $[Mn(NO_3)_3L]$ (where L = bipy or phen). The latter are dichroic (red/green), and an X-ray analysis of the bipy compound[589] shows a (5 + 2) seven-coordinate structure, with axial (unidentate) nitrate (1.90 Å) and N (1.99 Å), and equatorial N (2.09 Å) and two bidentate nitrates (Mn—O = 2.11, 2.40 and 2.20, 2.24 Å).

Phosphato compounds,[590] however, are more significant: stable crystalline solids have been known since 1844 (Table 47); aqueous solutions of diphosphatomanganese(II) species have been used analytically; and $NH_4MnP_2O_7$ is a violet pigment ('manganese violet'). Even so, reported studies on the solids are quite limited—in many cases nothing has been reported since the original preparations, more than 60 years ago. X-Ray structural analyses of the red-violet compounds $MnH_3P_2O_6 \cdot 2H_2O$[590] and $Mn(PO_3)_3$[591] both show the expected, distorted $[MnO_6]$ octahedra.

The phosphate system is dominated by the insoluble green-grey $MnPO_4 \cdot H_2O$. However, violet solutions, which appear to contain mainly $[Mn(PO_4)_2]^{3-}$, can be obtained by dissolving Mn^{III} acetate in concentrated H_3PO_4. Phosphonato compounds have been studied in Ac_2O, and evidence reported for the 1:1, 2:3, 1:2 and 1:3 species with Mn^{III}; but only the 1:3 species could be detected in MeOH.

But the most intensively studied system, the most stable and that used as an oxidometric reagent, has been that of diphosphate ($P_2O_7^{4-}$) and Mn^{III} in aqueous solutions. The violet solutions, prepared by oxidizing Mn^{II} with $KMnO_4$ or HNO_3, are most robust at pH 4–6 and can be stored unchanged for at least one month. There is no agreement in the literature about the nature of the molecular anions present but at, and below, pH 4, $[Mn(H_2P_2O_7)_3]^{3-}$ appears to predominate; and, above pH 4, $HP_2O_7^{3-}$ species probably becomes more significant.

The *sulfate* $Mn_2(SO_4)_3$ can be prepared from Mn_2O_3 in hot, concentrated H_2SO_4 as dark-green needles, which are thermally stable but very hygroscopic.[592] From 70% H_2SO_4, red $[H^+(H_2O)_n]Mn(SO_4)_2$ can be obtained and the compounds $MMn(SO_4)_2$ (M = NH_4, K, Rb) have been described. (Unstable, hydrated 'alum' forms were noted in the previous section.) Sulfato compounds are formed in solution, are somewhat more robust than the aquo/oxo species, but details are still not clear. The blue colour described for $Al_4Mn_2(SO_4)_9$ by Étard in 1878/79 (and there are other compounds with other M^{III} sulfates)[592] suggest that it is worthy of further study.

Table 47 Crystalline Phosphato and Arsenato Compounds of Mn^{III}

Compound	*Comments*
$MnH_3P_2O_6 \cdot 2H_2O$	Red-violet—$[MnO_4(H_2O)_2]$ octahedra[590]
$MMn(HPO_4)_2 \cdot nH_2O$	(M = Li, Na, K, NH_4) Red crystals—water soluble
$MnPO_4 \cdot H_2O$	Grey-green, insoluble
$Mn(PO_3)_3$	Red-violet—$[MnO_6]$ octahedra[591]
$NaMn(PO_3)_4$	From Mn_2O_3, HPO_3 and $NaPO_3$ at 1000°C
$Mn_4(P_2O_7)_3 \cdot nH_2O$	Violet
$MMnP_2O_7$	(M = K, NH_4) Red or violet
$MMnP_2O_7 \cdot nH_2O$	(M = Na, K, NH_4) Red or violet
$MnAsO_4 \cdot H_2O$	Brown-violet. X-Ray pattern related to PO_4 analogue
$Mn(H_2AsO_4)_3 \cdot 3H_2O$	Dark violet
$Mn^{II}_2Mn^{III}(OH)_4AsO_4$	The mineral Flinkite—$[MnO_6]$ octahedra

Selinites, on the other hand, have attracted recent interest: compounds $MMn(SeO_3)_2 \cdot nH_2O$ (M = H, NH_4, K, Rb, Cs) have been described[593] and X-ray analyses[594] of $Mn_2(SeO_3)_3 \cdot 3H_2O$ and $MnH(SeO_3)(Se_2O_5)$ reveal distorted $[MnO_6]$ octahedra.

Iodates of Mn^{III} are perhaps represented in the yellow to brown-yellow solids $M_2Mn(IO_3)_5$.

There is also a range of isopoly- and heteropoly-anion compounds which we have summarized in Table 26.

41.4.3.3 Carboxylates

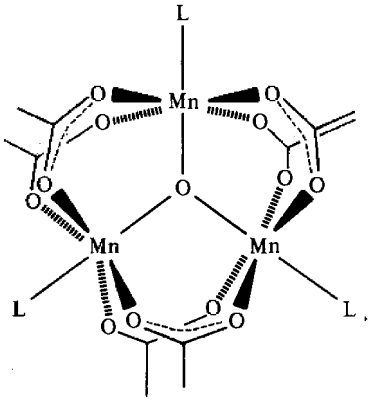
There are two basic classes here: (a) the compounds of the monocarboxylates, such as acetate, which turn out to have a rather complex chemistry; and (b) the bidentate carboxylates, such as oxalate, malonate and salicylate which are straightforward bidentate anionic chelates.

Contrary to the assumptions in most of the literature,[254] it is now becoming clear that the monocarboxylates of Mn^{III} are 'basic' species, that is, they are compounds with oxo, as well as carboxylato, ligands. For acetate, neither the cinnamon brown 'dihydrate' first reported by Christensen in 1901, nor the 'anhydrous' species made from $Mn(NO_3)_2 \cdot 6H_2O$ and acetic anhydride by Späth in 1912, are examples of simple binary acetates. Rather, they are variants on a trinuclear structural theme $[Mn_3O(OOCR)_6L_3]^+$, with the planar structure (**224**), in which each Mn atom is bridged to its neighbours by two carboxylate bridges. This is proven for the product from acetic anhydride,[595] but is yet only an assumption for the 'dihydrate', for which the story may be more complex: similar reaction conditions to those used for its preparation, but with 50% more $KMnO_4$, produce a red-black mixed Mn^{III}/Mn^{IV} species,[596] described below.

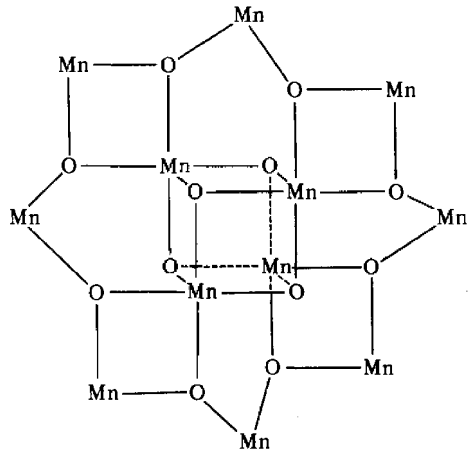
Known variants of the structural theme (**224**) are: $[Mn_3O(OAc)_7HOAc]$ — the so-called anhydrous acetate[595] — in which L is an oxygen from an acetate which links the trimers into linear polymers, or, in one case, HOAc; $K_2\{Mn^{II}(H_2O)_2[Mn_3^{III}O(HCO_2)_9]_2\}$, in which L is an oxygen from a formate which links the Mn^{II} atoms to the trimer; and $[Mn_3O(OAc)_6L_3]\ ClO_4$ for L = py or β-pic[598] — the py compound is isomorphous with the Cr, Fe, Ru, Rh and Ir analogues.

A minor variation on this theme is seen in the neutral compounds $[Mn_3O(OAc)_6L_3]$ where L = py[599] or 3Cl-py.[600] In these, one of the Mn atoms is Mn^{II}, which is distinguished experimentally in the X-ray analysis of the 3Cl-py compound,[600] but not in that of the py compound.[599]

A further variation on this theme is seen in a mixed Mn^{III}/Mn^{IV} acetate, prepared[596] as red-black crystals as for '$Mn(OAc)_3 \cdot 2H_2O$', but using more $KMnO_4$. The compound is a dodecanuclear species $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4] \cdot 2HOAc \cdot 4H_2O$, in which the central $Mn_{12}O_{12}$ unit has the structure (**225**). There is a central cubane-like (Mn_4O_4) cluster of Mn^{IV} atoms, each linked *via* further triply-bridging oxides to two Mn^{III} atoms. The Mn atoms are then further linked by single or double acetate bridges of type (**82**) and water molecules complete the octahedra for half the Mn^{III} atoms. Bond lengths and distortions of the Mn^{III} polyhedra here, and in the other acetate compounds, serve to distinguish the different oxidation states.



(224)



(225)

Undoubtedly further variations will be identified as these carboxylates are further explored.

Oxalate forms red $[MnOx_3]^{3-}$ and green (*cis*) or yellow *trans*-$[MnOx_2(H_2O)_2]^-$, which have been known since 1936.[293,572] Usually, preparations of the bis species give the *cis* isomer, but it is the *trans* isomer which predominates in aqueous solution. The compounds are all rather unstable and are particularly sensitive to light. However, the malonates, known since 1922, are rather more robust and especially towards light. X-Ray structural analyses are available on tris[601] and *trans* bis[602] species, with all showing 2 + 2 + 2 distortions of the Mn^{III} octahedra.

Hydroxycarboxylate compounds of Mn^{III} are known for salicylates and various aliphatic acids.[299] Some crystalline solids have been isolated, including bis-chelate species of the salicylates $M[Mn(X\text{-}sal)_2L_2]$ ($L = H_2O$, py); but the only tris-chelate compound isolated is the black $Cs_3[Mn\{(CF_2)_2C(O)COO\}_3]$. Various red or green crystalline solids also are known with tartrate ligands and they are reasonably robust, but no structural data are available.

Much of the known detail on the hydroxycarboxylate ligands refers to the redox properties of aqueous alkaline solutions; and especially to electrochemical studies on the oxidation of the Mn^{II} species of glyceric, tartaric, gluconic, glucaric and citric acids to Mn^{III} and Mn^{IV}.[299,603] For each ligand, two Mn^{III} species were detected, and they appear to be a monomeric tris-chelate species and a dimeric oxo/hydroxo-bridged bis-chelate species.

41.4.3.4 Alcohol and phenol ligands

Orange-red Mn^{III} compounds of the polyhydroxy ligands, including the polyhydroxycarboxylates noted in the previous section, are formed either by bubbling air through the Mn^{II} compounds in aqueous alkaline solution or by dissolving 'manganese(III) acetate' in the liquid polyhydroxy alcohol.[212,603,604] Such solutions are relatively robust, but in acid solutions the Mn^{III} compounds appear only as intermediates in the oxidation of the alcohol to the ketone. Stability (robustness) of the Mn^{III} compounds increases with the number of alcohol groups, so that, for example, the sorbitol compounds[604] are more robust than those of glycerol.

Catechol and other diphenols have been known since 1926 to form Mn^{III} species, and they have recently been receiving closer attention.[282,603] In aqueous alkaline solution, tris-chelate species apparently are formed. However, these systems have the added complication of ligand oxidation to the semiquinone, which forms more (thermodynamically) stable species than the diphenol (see also Section 41.5.3.4): there is evidence for a tris-semiquinone Mn^{III} molecule, which is a four electron oxidizing agent according to equation (17).[603] Another semiquinone compound of Mn^{III} [Mn(salen)(DBSQ)] (DBSQ = 3,5-di-*tert*-butyl-*o*-benzosemiquinonate) has been described.[605]

$$[Mn^{III}(\text{semiquinone})_3] + 4e^- \rightleftharpoons [Mn^{II}(\text{diolate})_3]^{4-} \qquad (17)$$

41.4.3.5 Acetylacetonate and related ligands

A range of Mn^{III} compounds of acetylacetonate[283] is well established; they are used for preparing other Mn^{III} species; and have been studied as catalysts, especially for vinyl polymerizations.

Brown $[Mn(acac)_3]$, somewhat less robust than its Cr, Fe and Co analogues, has been prepared by a variety of routes, including the action of $KMnO_4$ on the ligand, reaction of the metal with the ligand in the presence of O_2, various oxidations of Mn^{II} species or reaction of the ligand with other Mn^{III} compounds. Details of a convenient preparation, from $KMnO_4$ and acacH, have appeared recently.[606]

The molecular species can be recrystallized from a variety of hydrocarbon and halocarbon solvents, and it has been identified in three crystalline forms, of which X-ray structural analyses are available on the β- and γ-forms.[607] Despite a misleading report in 1964, the $[MnO_6]$ octahedra are distorted: there is a 'compressed' (2 + 4) distortion for the β-form (Mn—O = 1.93–2.02 Å) and an 'elongated' (4 + 2) distortion for the γ-form {Mn—O = 1.94(×4) and 2.11(×2)}.

Similar green or brown tris-chelated compounds are described[283] for many of the usual range of available β-diketonates, the most stable compound being that formed with the sexadentate ligand (**124**).[318]

Solutions of $[Mn(acac)_3]$ react with HX to give brown $Mn(acac)_2X$ species (X = Cl, Br, I), and other compounds of this type (X = N_3, NCS, RCOO)[608] have been made by direct reactions. These compounds also are used for the preparation of other Mn^{III} compounds, especially of the por-

phyrins. X-Ray data on the azido and thiocyanato compounds show planar $Mn(acac)_2$ units (Mn—O = 1.91 Å) linked into linear polymers by bridging of the anion (for azide, Mn—N = 2.245 Å; and for thiocyanate, Mn—N = 2.189 and Mn—S = 2.880 Å).

In water, the cationic species $[Mn(acac)_2(H_2O)_2]^+$ form and several salts of this have been isolated, while with pyridine and other neutral unidentate ligands $[Mn(acac)_2XL]$ have been produced.[609]

Other mixed ligand systems studied include the troponeiminates (**43**) and 8-hydroxyquinoline; in both cases $[MnL_2L']$ and $[MnLL'_2]$ have been characterized. [Mn(acac)(salen)] represents a non-planar form of the salen ligand, related to the well-characterized Co^{III} compounds.[610]

In the tris-tropolonato compound (L = **98**), the two independent molecules show either a 4 + 2 or a 2 + 2 + 2 distortion of the $[MnO_6]$ octahedra.[611]

41.4.3.6 Other oxygen ligands

Several *ether* compounds of $MnCl_3$ have been described,[221] but most are thermally unstable well below normal temperatures.

Of neutral *carbonyl* ligands, only purple $[Mn(urea)_6](ClO_4)_3$ appears to have been described. All Mn—O bond lengths are constrained to equality by the space group, but an analysis of the 'temperature factors' showed that there was scope for distortion of the octahedron and this was suggested to be dynamic.[612]

Related red $[MnL_6]X_3$ compounds with *pyridine* N-*oxides* have been reported,[613] but no structural data are yet available. These unidentate pyridine-*N*-oxides also form[613–615] red or green compounds $[MnCl_3L_3]$, which are probably octahedral, and green compounds $MnCl_3L_2$, which may well prove to be five-coordinate monomers. Blue $MnCl_3(Ph_3PO)_2$ and $MnCl_3(Ph_3AsO)_2$ also are known; and there is a bromo species $[MnBr_3(quinO)_3]$. Most of these tris- and bis-ligand compounds of MnX_3 are quite robust in dry air at normal temperatures, but are instantly decomposed by water and slowly decompose in moist air.

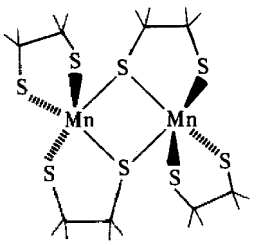
The tris-ligand cation of bipy-*N*-oxide (**120**),[613] and the bis-ligand cation of terpy-*N*-oxide[314] can be prepared by electrochemical oxidation of the Mn^{II} species in CH_3CN, and the robust dark-red crystalline perchlorates have been isolated.

41.4.4 Sulfur Ligands

No binary Mn^{III} *sulfide* is known and this oxidation state is known[319] only in several ternary sulfide phase: perhaps in cubic spinel species, such as $ZnMn_2S_4$, and probably (magnetic evidence) in several Nb and Ta ternary phases, formulated as $Mn_{0.33}NbS_2$, $Mn_{0.33}TaS_2$ and $Mn_{0.5}NbS_2$. Bond lengths for the first two are reported as 2.52 and 2.49 Å.

On the other hand, oxidation of the thiol compounds to Mn^{III} occurs so readily that Mn^{II} compounds have to be prepared anaerobically.

For simple *thiols*, only one species has been isolated and characterized to date. The dianion of 1,2-dithioethane (edt) in methanol solution with Mn^{II} forms $[Mn(edt)_2]^{2-}$ and reacts rapidly with O_2 to give green solutions, from which dark green crystalline $[Et_4N]_2[Mn_2(edt)_4]$ and the $[Ph_4P]$ salt were obtained.[320] X-Ray analysis of the former showed the dimeric structure (**226**) with asymmetric bridges Mn—S = 2.346 and 2.632(2) Å. The other three S atoms have shorter distances (2.316–2.323 Å), and the overall five-coordinate structure is reasonably close to the square pyramidal extreme with four short bonds and one long (axial) bond. The magnetic moment (3.96 BM) suggests some antiferromagnetic coupling.



(226)

Table 48 Bond Length Data for the Mn^{III} Dithiocarbamate Compounds $[Mn(R_2dtc)_3]$

R_2	*Mn—S bond lengths*			*Ref.*
Et_2	2.373(9)	2.428(7)	2.541(7)	a
	2.383(8)	2.431(7)	2.557(7)	
$O(CH_2CH_2)_2$	2.385(3)	2.447(3)	2.529(3)	b
	2.385(3)	2.486(3)	2.534(3)	
$O(CH_2CH_2)_2$	2.344(1)	2.433(1)	2.527(1)	c
	2.365(1)	2.483(1)	2.584(1)	

[a] P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 1883.
[b] CH_2Cl_2 solvate: R. J. Butcher and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1975, 2517.
[c] $CHCl_3$ solvate: R. J. Butcher and E. Sinn, *J. Am. Chem. Soc.*, 1976, **98**, 5159.

In solutions in donor solvents (DMF, DMSO and MeCN), dissociation equilibria occur, with the formation of presumably $[Mn(edt)_2(solvent)_2]^-$ monomers. Magnetic moments in these solutions (5.0–5.1 BM) are close to the spin-only value for high spin d^4, and the electronic spectra have been characterized.[320]

Dithiocarbamates of Mn^{III} have long been known because of the ease of oxidation from Mn^{II}: Marcel Delepine first described some of the dark violet $[Mn(R_2dtc)_3]$ compounds in 1907. They result[329,330,616] from the reaction, in open vessels, of aqueous Mn^{II} with the Na or K salt of the ligand; are reasonably robust under ambient conditions, but sensitive to light and moisture; and they have magnetic moments near 5 BM. The Se analogues also are known and have similar properties.[617]

Three X-ray analyses structurally characterize the compounds as tris-bidentate with four-membered chelate rings (Table 48); and show that the $[MnS_6]$ octahedra are distorted, not only trigonally by the chelate rings, but also by the (2 + 2 + 2) variation of the 'tetragonal' distortion observed in most Mn^{III} octahedra.

An electrochemical study has shown reversible reduction to Mn^{II} and oxidation to Mn^{IV} species; and a ^1H NMR study shows that isomerization, of the compounds of unsymmetrical ligands such as MePhdtc, is slow on the NMR time scale at $-60°C$ and occurs *via* a trigonal twist mechanism rather than a dissociative one.

Bis-dithiocarbamato compounds, such as $Mn(R_2dtc)_2Cl$, appear to be available, but not studied; and there is a recent report[618] of a nitrosyl $[Mn(R_2dtc)_2Cl(NO)]$.

41.4.5 Halides

The coordination chemistry of Mn^{III} with the halides[210,336,572] is distinctly more limited than that of Mn^{II}; the former are good halogenating agents for hydrocarbon compounds and the only binary compound able to exist at normal temperatures is MnF_3. Black solids, stable only below $-40°C$, probably represent $MnCl_3$, but the bromo and iodo compounds have never been observed.

There is more of a tendency here for the stoichiometry of the ternary compounds and their hydrates to reflect the coordination polyhedra. For example, there are a number of examples of $M_3[MnF_6]$ compounds, and those of formulae $MMnF_4 \cdot 2H_2O$ generally appear to be of structural type $M[MnF_4(H_2O)_2]$, with *trans* octahedra. However, the series M_2MnF_5, $M_2MnF_5 \cdot H_2O$, $MMnF_4$ and $MMnF_4 \cdot H_2O$ all are examples in which octahedra are formed by bridging of fluorides; although discrete $[MnCl_5]^{2-}$ five-coordinate polyhedra exist in the series M_2MnCl_5 and there are some unstable examples of $[MnCl_6]^{3-}$.

All of these coordination polyhedra are quite labile, and the structures of the Mn^{III} polyhedra in any solution depend only on the nature of the solvent and not the starting material. Stability constants K_1 to K_3, for aqueous fluoro species in perchlorate media, have recently been reported.[619]

MnF_3 is a red-purple crystalline solid which is readily soluble in water. It is antiferromagnetic only at low temperature. Also known are a mixed oxidation state fluoride, Mn_2F_5, and a hydrate which is said to be isostructural with $NiSnCl_6 \cdot 6H_2O$. Perhaps the latter represents an example of disproportionation, and may be $[Mn^{II}(H_2O)_6][Mn^{IV}F_6]$.

MnF_3 is structurally related to the other fluorides TiF_3 to CoF_3, but with the significant 2 + 2 + 2 distortion expected for the high spin d^4 configuration (Table 49). The $M_3[MnF_6]$ series of ternary compounds generally have tetragonally distorted fluoroperovskite structures, in which there are two sites for M, and hence mixed cation species such as $K_2Na[MnF_6]$ are readily prepared. Large tervalent cations, however, like $[M(NH_3)_6]^{3+}$ (M = Cr, Co, Rh) give cubic crystals which contain discrete $[MnF_6]^{3-}$ octahedra with experimentally equal Mn—F bonds, although the data can be interpreted in terms of a dynamic (or random) disorder.

Table 49 Bond Length Data for $[Mn^{III}F_6]$ Octahedra

Compound	*Bond Lengths* (Å)[a]				
MnF_3	1.79		1.91	2.09	(1.93)
K_2NaMnF_6		1.86[b]		2.06	(1.93)
$[Cr(NH_3)_6][MnF_6]$			1.922[c]		(1.92)
$[NH_4]_2MnF_5$		1.84[b]		2.09	(1.92)
$K_2MnF_5 \cdot H_2O$	1.821		1.842	2.072	(1.91)
$Rb_2MnF_5 \cdot H_2O$	1.835		1.860	2.089	(1.93)[d]
$Cs_2MnF_5 \cdot H_2O$	1.835		1.868	2.127	(1.94)[d]
$RbMnF_4 \cdot H_2O$	1.83		1.85	2.157	(1.94)[e]

[a] These are generally given in *trans* pairs, with averaged values in parentheses. Data are from Gmelin (C4) unless otherwise stated.
[b] Four equal bonds.
[c] All bonds equal in the cubic space group.
[d] Ref. 621.
[e] Ref. 622.

The violet M_2MnF_5 compounds and their monohydrates, for which a new, convenient method of preparation recently has been given,[620] all have chains of corner-sharing $[MnF_6]$ octahedra with *trans* bridging fluorides[621] (Table 49). The water molecules of the hydrates are accommodated between the chains.

$CsMnF_4$ has a layer structure with corner-sharing $[MnF_6]$ octahedra, and there are at least two different hydrates here: $RbMnF_4 \cdot H_2O$ has chains of alternating $[MnF_6]$ and *trans*-$[MnF_4(H_2O)_2]$ octahedra, whereas both Cs and $NMe_4[MnF_4(H_2O)_2]$ have discrete *trans*-diaquo octahedra.[622]

There is even less variety in the known chemistry of the chloro compounds because of their lower redox stability.[623] Although $MnCl_3$ is stable only below $-40°C$, apparently decomposing through a disproportionation reaction,[623] the oxidation state is stabilized with other ligands. Thus $MnCl_3$ is more robust in donor solvents, undoubtedly as species like $[MnCl_3L_3]$, and compounds of this type are well established for both N and O donors (Sections 41.4.2 and 41.4.3.6). There is also a series of pyridine-*N*-oxide compounds (Section 41.4.3.6) $MnCl_3L_2$ which may well be five-coordinate.

Certainly five-coordination is well established in the series of green compounds M_2MnCl_5 (M = alkyl ammonium, 2M = $bipyH_2$, $phenH_2$),[624] through an X-ray analysis of the bipyridylium salt.[625] Several purple or red-brown monohydrates (M = K, Rb and NH_4) also are known.[624] There is an interesting recent report[4] that Mn^{III} in a mixture of acetic acid and acetyl chloride, also containing MOAc, gives crystalline $M_2[MnCl_5]$ (M = Na, K, NH_4).

The brown hexachloro anion also is well established, but not very robust. It is isolated from solution[624,626] with large tervalent cations, such as $[Coen_3]^{3+}$, $[Copn_3]^{3+}$ and $[Rhpn_3]^{3+}$. The solids are instantly decomposed by water or on keeping at room temperature.

Of *bromo* compounds, there are yet only one or two compounds $[MnBr_3L_3]$ (Section 41.4.3.6), so the advent of a well-proven *iodo* compound $[MnI_3(PR_3)_2]$[581] was unexpected. It would be most surprising if the latter were to remain the sole representative of Mn^{III} iodo compounds: we can surely expect interesting further developments here.

Table 50 Mn^{III} Compounds[a] of Bidentate N—O Ligands of Type (**227**)

Compound Stoichiometry	*R*	*X*	*Magnetic Moment (BM at R.T.)*	*Ref.*
MnL_2OAc	Alkyl[b]	H	4.9–5.1	628
MnL_3	[c]	H	4.8–5.0	629
MnL_2OAc	Pr^n, Pr^i	H	4.9–5.0	629
MnL_2X[d]	Pr^n	H	4.9–5.0	629
MnL_3	*o*-Me—C_6H_4	H	4.97	630
MnL_3	C_6H_5	5-Br	5.03	630
MnL_3	*p*-Cl—C_6H_4	5-Br	4.84	630
MnL_3	C_6H_5	H	5.06	631
MnL_2OAc	*m*-NO_2—C_6H_4	H	4.95	631
MnL_2OAc	*p*-NO_2—C_6H_4	H	4.98	631
MnL_2OH[e]	—CH_2—C_6H_5	H	—	419
MnL_3	—CH_2—C_6H_5	H	—	632

[a] All compounds, excepting e which is dark brown, are described as being green to dark green in colour.
[b] CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11} or *n*-C_6H_{13}.
[c] R = H, *n*-C_3H_7, cyclohexyl, —CH_2—C_6H_5, C_6H_5 or *p*-Br—C_6H_4.
[d] X = Cl or Br.
[e] See footnote a above.

41.4.6 Hydrogen and Hydride Ligands

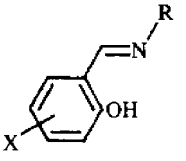
There is very little information available: MnH_3 has possibly been observed[356] in Ar and N_2 matrices at 4 K; $MnH_3(dmpe)_2$ appears to result from the reaction of H_2 with $MnH(C_2H_4)(dmpe)_2$ under pressure;[28,627] and there is a report of the preparation of $Mn(BH_4)_3$, but no confirmatory detail.[363]

41.4.7 Mixed Donor Atom Ligands

The chemistry in this section is almost exclusively that of Schiff base ligands; this reflects the predominance of the aldehyde/carbonyl condensation reaction with primary amines in the preparation of mixed donor atom ligands.

41.4.7.1 Mixed N—O donor atom bidentate ligands

Salicylaldehyde has been condensed with many primary amines to yield bidentate N—O ligands. Such ligands react with Mn^{III} acetate dihydrate to give compounds of stoichiometries $Mn(L)_3$ or $Mn(L)_2(X)$ (where HL = (**227**); X = Cl, Br, OH or OAc); examples are listed in Table 50.



(227)

Reliable structural information on most of these compounds is not available, although there is mass spectral evidence that the compounds listed against reference 629 are polymeric when X = OAc, but monomeric when X = Cl or Br. There has been an X-ray structural determination undertaken on the compound $Mn(L)_3$ for reference 632; bond lengths are listed in Table 51 (compound 1) and the structure has been shown to be a *trans* array of the three ligands around a pseudotetragonally distorted Mn atom.

Such distortion, which is predicted by the Jahn–Teller theorem, has also been found in the structures of the $Mn(L)_3$ compounds derived from non-Schiff base N—O bidentate ligands, such as the octahedral tris(8-hydroxyquinolato)manganese(III)·CH_3OH (or $0.5C_6H_{13}OH$) and the octahedral tris(α-picolinato)manganese(III) compounds (see compounds 2 and 3 respectively in Table 51).

41.4.7.2 Mixed N—O donor atom terdentate ligands

Once again the Schiff base ligand type predominates. The most common stoichiometry of compounds formed by the interaction of such ligands with Mn^{III} acetate, is that of Mn(L)(OAc) (L = dianionic Schiff base terdentate), obtained at higher pH values. Such compounds have been obtained from ligands (**228**) (n = 2 and X = H, 5-Br, 5-NO_2, 3-OMe or 3,5-diBr;[635] n = 3 and X = H),[636] (**229**) (R = Me and R′ = 2- or 4-pyridyl;[637] R = H, Me, Et or Pr and R′ = Ph[638]), and (**230**) (R = H, 5-Cl or 5-Br[639]). X-Ray structural analysis[636] of the compound Mn(L)(OAc) (where L = (**228**); X = H and n = 3) shows that it is a dimer with octahedral Mn^{III} atoms (**232**); bond

Table 51 Bond Lengths for $[Mn(N—O)_3]$ Compounds of Mn^{III}

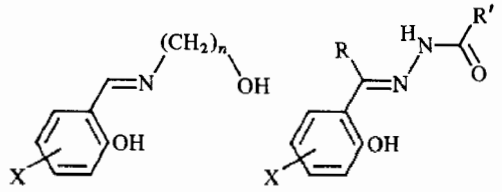
	Bond Lengths (Å)			
	Axial Donors	*Equatorial Donors*		
N—O Ligand	*Mn—N*	*Mn—N*	*Mn—O*	*Ref.*
(**227**) R = Bz; X = H	2.251, 2.271	2.082	1.882, 1.896, 1.917	632
(**153**)	2.231, 2.265	2.056	1.912, 1.913, 1.920	633
(**154**) R = CO_2H	2.217, 2.254	2.059	1.891, 1.908, 1.942	634

lengths are, for the terdentate, Mn—O: 1.849 to 1.951 Å and Mn—N: 2.006 Å, and for the axial acetates, Mn—O: 2.2084 to 2.251 Å.

In the presence of anions other than acetate, compounds of similar stoichiometry, Mn(L)(X) (where X = Cl or Br;[638] OH[639] and OMe[640]) have been prepared. The compound in which X = OMe was obtained by hydrolysis of the potential quadridentate ligand (**231**) in an alkaline solution of $MnCl_2$, to yield (**233**) in which the terdentate ligand is (**229**) (where R = H and R′ = *o*-$NH_2C_6H_4$). Structure (**233**) indicates the marked tendency for these ligands to form polymers with Mn^{III} in the solid state.

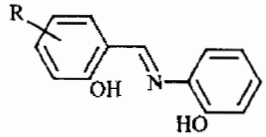
Nevertheless, the monomeric Mn^{III} anionic compound $[Mn(L)_2]^{1-}$ (where L = *N*-salicylideneglycinato ligand) has been shown to exist in $[Mn^{II}(H_2O)_6][Mn^{III}(L)_2]\cdot 2H_2O$; the crystal structure[641] has a distorted octahedral Mn^{III} with two planar ligands with bond lengths: Mn—O 2.236 and 2.046, Mn—N, 2.065 Å for one ligand, and Mn—O, 1.934 and 1.861, Mn—N, 1.981 Å for the other ligand.

The compounds $[Mn(L)_2](NCS)$ (where L = (**234**); $n = 1$ or 2) are also claimed[642] not to be polymeric.

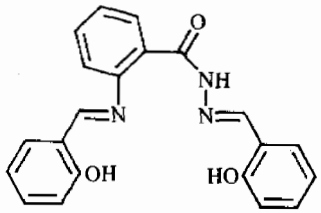


(228)

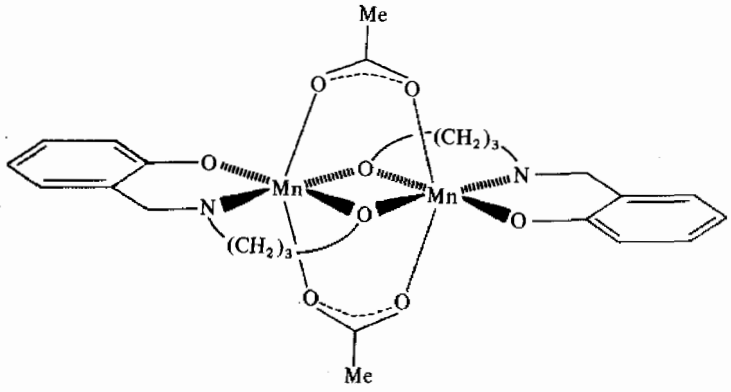
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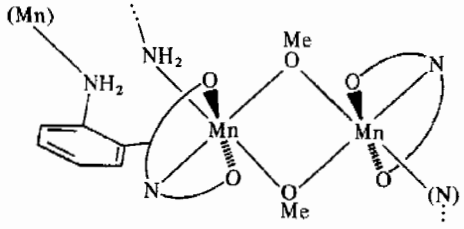
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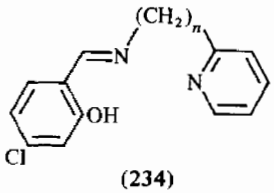
(231)



(232)



(233)



(234)

41.4.7.3 Mixed N—O donor atom quadridentate ligands

Once again Schiff base ligands predominate, and such work up to 1980 has been extensively reviewed by Connors *et al.*[173] Many of the compounds claimed to be Mn^{III} species have been

Table 52 Mn^{III} Compounds[a] of Formula Mn(L)(Z) in which L = (**161**) and Z = Monoanionic Ligand

L = (**161**) X	Y	Z	μ_{eff} (BM *at r.t.*)	*Ref.*
$(CH_2)_2$	H	OAc	4.68	38
$(CH_2)_2$	H	OH	4.90	38
$(CH_2)_2$	H	OH	—	419
$(CH_2)_2$	H	Me[b]	4.98	646
$(CH_2)_2$	H	Ph[b]		646
$(CH_2)_2$	H	Cl	4.85	647
$(CH_2)_2$	H	Br	4.96	647
$(CH_2)_2$	H	I	4.98	647
$(CH_2)_2$	H	Br	4.75	629
$(CH_2)_2$	H	I	4.80	629
$(CH_2)_2$	5-Br	OAc	4.92	649
$(CH_2)_2$	H	Cl	4.84	653
$(CH_2)_2$	4-Me	Cl	4.86	653
$(CH_2)_2$	4-Bu^s	Cl	4.30	653
$(CH_2)_2$	4-OMe	Cl	4.74	653
$(CH_2)_2$	4-Br	Cl	4.54	653
o-C_6H_4	H	Me[b]	4.98	646
o-C_6H_4	H	Ph[b]		646
o-C_6H_4	H	OAc	5.16	648
o-C_6H_4	4-Me	OAc	4.92	648
o-C_6H_4	4-OH	OH	4.81	648
o-C_6H_4	5-Br	OAc	5.03	648
o-C_6H_4	5-Cl	OH	5.40	648
4-NO_2-*o*-C_6H_3	H	OH	5.06	648
CH_2—CH(OH)—CH_2	H	Cl	4.80	650
CH_2—CH(OH)—CH_2	H	Br	4.84	650
CH_2—CH(OH)—CH_2	H	I	4.76	650
CH_2—$CH(CH_3)$	4-Bu^s	Cl	5.00	651
CH_2—$CH(CH_3)$	H	Cl	5.02	652
CH_2—$CH(CH_3)$	H	NO_2	4.94	652

[a] All compounds are brown in colour.
[b] These compounds analyse as monohydrates; they may well be alcoholates.

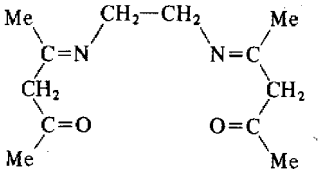
obtained by oxygenation reactions with Mn^{II} compounds of ligands of type (**161**). This is an area of research which has generated much information, but little definitive result. The literature has been extensively reviewed by Coleman and Taylor.[424]

Products of such oxygenation reactions are nearly always brown powders, and usually analyse as $Mn^{III}(L)(\frac{1}{2}X)$ or $Mn^{IV}(L)(X)$ (where L = (**161**) and X = O or OH).[425,643,426] Polymeric structures are suspected in most cases, and indeed black crystals of the compound Mn(saltn)OH·4py (where saltn = (**161**) with X = $(CH_2)_3$ and Y = H), obtained by the oxygenation of the corresponding Mn^{II} compound in pyridine solution, have been treated to X-ray structural analysis,[433] and the structure shown to be dimeric with two five-coordinate Mn^{III} atoms, each bridged by two hydroxy groups; the pyridine moieties are not bound directly to the metal.

Many compounds of formulation Mn(L)(Z) (where L = (**161**) and Z = a monoanion) have been prepared (see Table 52). Structural evidence upon such compounds is not abundant, but [Mn(salen)-(OAc)] has been shown[644] to possess approximately planar Mn(salen) units linked in a polymeric chain by singly bridging acetate ions. The very similar compound, in which the benzene rings of salen are replaced by naphthalene rings, also possesses the same polymeric structure.[645]

Other similar types of Mn^{III} compounds, in which Z is a non-charged ligand, *e.g.* $[Mn(L)H_2O]$ (see entry in Table 52 against reference 651), have been isolated, while compounds of type [Mn(salen)-(bident)] (where bident = acac or salicylaldehyde monoanions) and $[Mn(salen)(bident)]ClO_4$ (where bident = en or bipy), which were first reported[419] in 1933, have been studied more recently.[654]

Boucher *et al.*[655] have studied the Schiff base compounds of formulation [Mn(L)(X)] (where L = (**235**) and X = monoanionic ligand); X-ray structural analysis of the compound in which X = Cl shows that it has a distorted square pyramidal structure with a non-planar ligand arrangement.[656]



(235)

41.4.7.4 Mixed N—O donor atom quinque- and sexadentate ligands

The Schiff base quinquedentate ligands (**161**), in which X = $(CH_2)_3$—NH—$(CH_2)_3$ and Y = 5-NO_2 or 3-MeO, form Mn^{III} compounds of the type Mn(L)(OH) when the corresponding Mn^{II} compound is oxygenated (see Section 41.3.9.4), whereas in similar compounds, in which Y is not an electron-withdrawing group, the ligand undergoes reaction when the Mn^{II} compound is oxygenated.[657]

An X-ray structural analysis of the compound [Mn(L)(NCS)] (where L = (**161**), X = $(CH_2)_3$—NH—$(CH_2)_3$ and Y is a fused C_6H_4 ring) shows an octahedral Mn^{III} atom, with the NCS group and the central N atom of the quinquedentate ligand occupying the apical positions.[658]

Coleman *et al.*[438] have described the preparation and cyclic voltammetry of a series of compounds [Mn(L)(NCS)] (where L = (**161**); X = $(CH_2)_n$—NH—$(CH_2)_m$ (n = 2 or 3 and m = 2, 3 or 4), $(CH_2)_2$—S—$(CH_2)_2$ and $(CH_2)_3$—O—$(CH_2)_3$; Y = H, 3-NO_2, 5-NO_2 and 5-OMe). Similar compounds, in which X = $(CH_2)_2$—P(Ph)—$(CH_2)_2$, have been described.[659]

In a series of interesting papers,[443] it has been shown that the Mn^{II} compounds from both quinque- and sexadentate ligands based on (**161**), in which X = $(CH_2)_n$—NH—$(CH_2)_m$ (n = 2 or 3, and m = 2 or 3) and $(CH_2)_n$—NH—$(CH_2)_m$—NH—$(CH_2)_p$, (n = 2 or 3, m = 2 or 3 and p = 2 or 3) respectively, will react with oxygen and nitric oxide. However, replacement of the salicylaldehyde group in (**161**) by a 2-pyridyl residue renders the Mn^{II} compounds inactive to such reactions.

The interesting potential septadentate tripod ligand, obtained by the condensation of 5-chlorosalicylaldehyde with tris(2-aminoethane)amine, has been shown to yield an almost undistorted octahedral Mn^{III} compound, MnN_3O_3, with the apical N atom of the ligand unbound.[660]

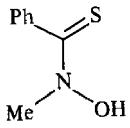
Early work on the dark red compound of Mn^{III} with edta suggested that its structure was $K[Mn(edta)H_2O]\cdot 1.5H_2O$.[661] However, X-ray work shows the compound to possess an octahedral structure with a sexadentate edta residue. Axial bond length distortion is observed, with two *trans* O atoms being 2.050 and 2.022 Å from the Mn atom, while the two equatorial Mn—O bonds are 1.907 and 1.889 Å and the two Mn—O bonds are 2.211 and 2.237 Å.[662] A very similar structural result was found in the case where edta was replaced by *trans*-1,2-diaminocyclohexane tetraacetic acid in $K[Mn(L)]\cdot H_2O$.[663]

Mechanisms of reduction by hydrazine, hydroxylamine and substituted benzene-1,2-diols of Mn^{III} compounds containing edta-type moieties have been studied.[664]

41.4.7.5 Mixed O—S and N—O—S donor atom ligands

A few interesting Mn^{III} compounds of O—S bidentates have been prepared. The interaction of Mn^{III} acetate with (**183**) (R = Ph) leads to ligand oxidation, but when R = Bu^t the tris-ligand Mn^{III} compound was obtained.[665]

A similar compound, $[Mn(L)_3]$ (HL = **236**), has been shown to possess an octahedral stereochemistry with marked tetragonal distortion; the bond lengths for the MnO_3S_3 chromophore are: Mn—$O_{(eq)}$ = 1.958 and 1.941; Mn—$O_{(ax)}$ = 2.132; Mn—$S_{(eq)}$ = 2.324 and 2.354; Mn—$S_{(ax)}$ = 2.584 Å.[666]



(236)

The sexadentate ligand (**161**) (where X = $(CH_2)_2$—S—$(CH_2)_2$—S—$(CH_2)_2$ and Y = H) has been claimed[463] to bind all three pairs of N, O and S atoms to yield a Mn^{III} compound; no Mn^{II} compound could be obtained (see Section 41.3.9.6).

41.4.8 Macrocyclic Ligands

41.4.8.1 Porphyrin ligands

Mn^{III} porphyrins have been extensively studied[482] with compounds containing the metal in this oxidation state being especially stable. Mn^{III} derivatives of partially reduced[482,667] porphyrins (such as the chlorins) have also been synthesized.

A number of physical studies have been performed on Mn^{III} porphyrins in an attempt to understand their electronic structure. The visible spectra of such compounds have been of particular interest. For most metal porphyrins the visible spectrum is insensitive to the nature of the coordinated metal and this has been interpreted as indicating little interaction between the metal and the porphyrin π-orbitals in such compounds. However this is not the case for Mn^{III} porphyrins which exhibit metal-dependent charge transfer absorptions. This dependence appears to reflect significant π orbital–Mn^{III} interaction. Resonance Raman and linear dichroism spectral studies are also consistent with this conclusion.[667]

X-Ray structures of several Mn^{III} porphyrin compounds have been determined. Five-coordinate square pyramidal structures occur for [MnCl(TPP)],[668] $[MnN_3(TPP)]$[669] and [MnCN(TPP)][670] while *trans* pseudooctahedral geometries are found in $[MnN_3(TPP)(CH_3OH)]$,[668,671] and [MnCl(TPP)(py)].[672] For all these compounds the average inplane Mn—N bond lengths are near constant at 2.02 ± 0.1 Å. The manganese is displaced from the N_4-donor plane in each case with the displacement tending to be greatest for the five-coordinate species (0.23–0.27 Å). As expected from the smaller size of Mn^{III} the displacements in the latter compounds are less than that found in the related (high-spin) five-coordinate Mn^{II} compound, [Mn(TPP)(1-methylimidazole)]. In this case the Mn^{II} is positioned 0.56 Å above the donor plane.[483,488] Using spectrophotometric measurements the binding constant for formation of the latter 1:1 adduct with 1-methylimidazole was found to be 24.7 M^{-1} at 21°C.[673]

$[Mn(TPP)(CH_3OH)_2]^+$ as its perchlorate salt exists as two near identical independent ions in the solid state. The Mn^{III} is tetragonally coordinated with long Mn—O bonds in the axial positions.[673] The metal lies in the N_4-donor plane in each case.

The structure of the Mn^{III} compound $[Mn(TPP)imidazolate]_n$ consists of a linear polymer with imidazolate bridges between adjacent $[Mn^{III}(TPP)]^+$ moieties.[491] A curious feature of the structure is a short–short/long–long alternation of the Mn—N(Im) bond distances along the chain. This has been suggested to reflect alternating (predominantly) low- and high-spin Mn^{III} atoms in the chain. Before the synthesis of this compound all previously reported six-coordinated Mn^{III} porphyrins were high spin.[491] The unusual magnetic properties of the polymeric complex appear to reflect the enhanced ligand field strength of the deprotonated imidazole moiety. In accordance with this, the bis(imidazolate) compound $[Bu_4N][Mn(Im)_2(TPP)]$ is completely low spin.

Kinetic and equilibrium studies of the interaction of imidazole with a Mn^{III} porphyrin in aqueous solution have been reported.[675] Imidazole bonds to the Mn^{III} porphyrin in a step-wise fashion to yield initially an imidazole-bridged dimeric species followed by a monomeric bis(imidazole)–Mn^{III} porphyrin adduct.

Comparative variable-temperature magnetic susceptibility studies have been undertaken for [MnCl(TPP)] and [MnCl(TPP)(py)][676,677] and accurate estimates (-2.3 and $-3.0\ cm^{-1}$ respectively) of the zero-field splitting of the ground state of Mn^{III} in these compounds obtained. As expected the magnetic moments of both compounds at room temperature are close to the spin-only value for $S = 2$.

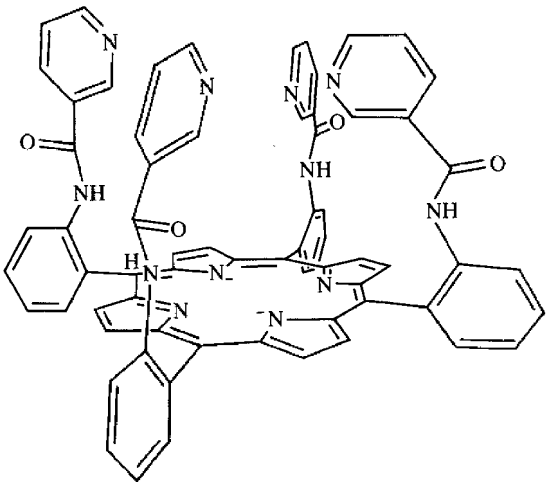
The reduction of Mn^{III} porphyrins [to Mn^{II} species] has been treated in Section 41.3.10.1.

Mn^{III} porphyrins may be electrochemically oxidized in non-aqueous media to yield Mn^{III} cation radicals and dications as the probable products.[485] The redox potentials depend on the nature of the solvent, counter ion present, pK_a of any axially-bound ligands as well as on the basicity of the porphyrin ring involved. Water-soluble Mn^{III} porphyrins are oxidized by a range of oxidants in aqueous alkaline solution to the corresponding Mn^{IV} porphyrins which appear to exist as μ-oxo dimers;[480] using hypochlorite as oxidant, a second oxidation step also occurs. In this case the product has been postulated to be a Mn^{V} oxo porphyrin. The Mn^{IV} and Mn^{V} porphyrins show only limited stability in water and revert to the stable Mn^{III} porphyrin upon standing in the dark for several

hours. Although in alkaline (or neutral) solution the initial oxidation product is a Mn^{IV} porphyrin, in acid the first electron may be removed from the π system of the porphyrin ring.

In other studies, reaction of [MnX(TPP)] ($X = N_3^-$ or OCN^-) with iodosylbenzene in hydrocarbon or halocarbon solvents yielded products formulated as μ-oxo dimers, $[Mn^{IV}X(TPP)]_2O$.[678] $[Mn^{IV}N_3(TPP)]_2O$ has been characterized by X-ray diffraction (see Section 41.5.7.1). Infrared evidence supports[678,679] the formulation of the dimers as being metal-centred oxidized products rather than containing porphyrin cation radicals; the possibility of ligand-centred *versus* metal-centred oxidation in higher-valent metallo porphyrins has been discussed by several authors.[680–682]

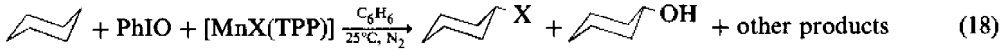
Meso-$\alpha,\alpha,\alpha,\alpha$-tetrakis(*o*-nicotinamidophenyl)porphyrin (**237**) is able to bind two metals in square planar environments which are orientated in planes coaxial with each other.[683] A number of studies using this ligand were instigated in attempts to obtain models for cytochrome *c* oxidase. However the coordination chemistry of this system is less straightforward than originally appeared, especially when involving substitution-labile metals such as Fe^{II}, Fe^{III} or Cu^{II}.[684] When an inert metal such as Ru^{II} is reacted with (**237**), coordination of the four pyridyl groups occurs to the ruthenium; ruthenium did not insert into the prophyrin under the conditions used. Once coordinated, the Ru^{II} appears to lock the nicotinic 'pickets' into place and hence inhibit the ligand isomerization reported to occur in the presence of more labile metal ions.[684] From this starting product, a mixed Ru^{II}/Mn^{III} product has been prepared. From cyclic voltammetric and spectrophotometric data, it was concluded that the proximity (~ 5 Å) of the two metal centres does not result in a major electronic perturbation of either metal in this case.



(237)

One motivation for the characterization of the above compounds has been to more fully understand the involvement of such higher valent manganese porphyrin complexes in model systems which imitate the catalytic activity of monooxygenase cytochrome P-450 and related enzymes. The catalytic cycle of cytochrome P-450 appears to involve the binding and reduction of molecular oxygen at a haem centre followed by the ultimate formation of a reactive iron oxo complex which is responsible for oxidation of the substrate. For example, cytochrome P-450 is able to catalyse alkane hydroxylation with great selectivity.

In model studies by Groves *et al.*,[685] an iron porphyrin was shown to catalyse the insertion of oxygen from iodosylbenzene into such hydrocarbons as cyclohexane; the enzyme can also cause the transfer of oxygen from iodosylbenzene.[686] It has been suggested[687] that the model reaction may proceed by oxygen atom transfer to yield an oxo–metal compound which then removes an aliphatic hydrogen atom followed by capture of the resulting carbon radical. Manganese porphyrin complexes, in the presence of a variety of reduced oxygen sources, have been demonstrated to act as a catalyst for the oxidation of alkanes, alkenes, alcohols, ethers, amines, phosphines and sulfides.[687–692] Equation (18) gives a typical reaction sequence.[692]



$$+ \text{PhIO} + [\text{MnX(TPP)}] \xrightarrow[25°C,\ N_2]{C_6H_6} \text{X} + \text{OH} + \text{other products} \qquad (18)$$

$$X = Cl, Br, I, N_3$$

In the majority of these reactions, higher valent (Mn^{IV} or Mn^{V}) compounds have been implicated in the respective reactions (*vide supra*). As mentioned previously, two μ-oxo Mn^{IV} porphyrin species have been characterized from the reaction of iodosylbenzene with Mn^{III} compounds of the type [MnX(TPP)].[678,690] These latter compounds are capable of oxidizing alkanes in good yield at room temperature, apparently *via* the intermediacy of alkyl free radicals.[693]

Within this general context, the formation of an acylperoxymanganese(III) species and its decomposition to an oxomanganese(V) species which undergoes oxygen atom transfer to alkenes has been investigated.[694]

Anchoring [MnOAc(TPP)] to a rigid polymer support considerably enhances the rate of cyclohexene epoxidation using sodium hypochlorite as the oxygen source.[695] This enhancement may be the result of site isolation restricting the formation of (less reactive) μ-oxo dimers during the formation of the higher-valent manganese species.

In the natural system, cytochrome P-450 catalyses reductive dioxygen activation to give the reactive iron oxo compound which is involved in the oxidation of the organic substrate. Such reductive dioxygen activation has been modelled by Tabushi *et al.*[696,697] using a $NaBH_4/Mn^{III}(TPP)/O_2$ redox system. In the presence of the reductant, $[Mn^{III}(TPP)]^+$ is converted to $[Mn^{II}(TPP)]$ which activates dioxygen to yield the strongly oxidizing species.

In a related reaction [MnCl(TPP)] has been reported to catalyse the specific oxidation of certain alkenes to ketones by molecular oxygen in the presence of $[NBu_4][BH_4]$;[688] the product ketones were then further reduced to alcohols under the conditions used. Related reactions involving $NaBH_4$ have been shown to convert ethylene to ethanol, propylene to acetone and *i*-propyl alcohol, and cholesterol to 3β,5α-dihydroxycholestane.[698] In these systems, molecular oxygen plus a reducing agent can be considered to be a substitute for the single oxygen donors such as iodosylbenzene. Colloidal platinum/H_2 will also effect the $[Mn^{III}(TPP)]^+$ to $[Mn^{II}(TPP)]$ reduction.[699] The relative reactivities of alkenes using the $H_2/[Mn^{III}(TPP)]^+/O_2$ system have been shown to closely resemble those for the $[Mn^{III}(TPP)]^+/C_6H_5IO$ system. A related biphasic system involving ascorbate as the reducing species has been reported.[700]

In an extension of the above studies involving oxygen atom transfer, Breslow and Gellman[701] have carried out a related amidation involving tosylamidation of cyclohexane to yield *N*-cyclohexyltoluene-*p*-sulfonamide in the presence of [MnCl(TPP)]; equation (19).

$$C_6H_{12} + PhI{=}NSO_2C_6H_4Me\text{-}p + [MnCl(TPP)] \xrightarrow[25°C,\ argon]{CH_2Cl_2} C_6H_{11}NHSO_2C_6H_5Me\text{-}p + \text{other products} \quad (19)$$

There appears to be considerable promise for other related metal-porphyrin catalysed nitrogen insertions for obtaining amides and amines. In this context, Groves and Takahashi[702] have reported the activation and transfer of nitrogen from a nitridomanganese(V) porphyrin complex, the reaction investigated being the aza analogue of epoxidation.

41.4.8.2 Phthalocyanine ligands

A number of Mn^{III} compounds of type [MnXPc] (where X is a singly charged monodentate ligand) have been prepared from [MnPc].[703,704] For example, reaction of [MnPc] with $SOCl_2$ or $SOBr_2$ yields [MnClPc] and [MnBrPc], respectively.[704] All these compounds exhibit high-spin d^4 magnetic moments of about 4.9 BM.

Reaction of [MnPc] with oxygen in pyridine which has not been rigorously purified yields the μ-oxo dimer, [pyPcMn^{III}—O—Mn^{III}Pcpy].[522–524] This purple compound has been studied by X-ray diffraction.[524] The structure contains two near flat and parallel MnPc systems joined by an oxygen atom which is midway between the manganese atoms. Each manganese has a pyridine bound opposite to the oxygen atom.

As discussed in Section 4.3.10.2, the dinuclear species reacts with oxygen in dimethylacetamide quantitatively to form the adduct $[MnPcO_2]$ which is formulated as containing Mn^{III} and a superoxo ion.[522] The dinuclear species is unstable in dimethylacetamide (or dimethylformamide) *in vacuo* to yield a mixture of mononuclear M^{II} and M^{III} compounds which in white light are cleanly photoreduced to [MnPc].[705]

The electrochemistry of the dinuclear compound has also been investigated; this compound undergoes a one-electron oxidation (+0.35 V *vs.* SCE) in pyridine to yield a species which is presumably mixed valent. It also undergoes a four-electron reduction (at −0.9 V) to yield two

molecules of a species formulated as $Mn^{II}(Pc^{3-})$. An investigation of the reduction process indicates that an ECE mechanism takes place in this latter case. The presence of a Mn—O—Mn moiety in the dimeric species appears to shift the redox behaviour of the metal centres to potentials that are 700 mV more negative. As such, a Mn^{IV} state appears accessible for this system. The electrochemical generation of Mn^{III} phthalocyanine from [MnPc] under different conditions has already been discussed in Section 41.3.10.2. Related photochemically induced redox transitions have also been reported.[705] A study of the electrochemistry of mononuclear $[Mn^{III}OHPc]$ has also been performed.[706] This high-spin hydroxy species is readily prepared by treatment of the binuclear compound with water; the Mn—O—Mn bridge is quite susceptible to cleavage by nucleophiles. The voltametry of the hydroxy species is typical of $[Mn^{III}XPc]$ compounds with X being strongly bound. The cyclic voltammogram of the hydroxy compound in pyridine gives potentials for the Mn^{III}/Mn^{II} couple and for two successive one-electron reductions which are, as expected, virtually the same as those obtained for $Mn^{II}Pc$ species under related conditions.[521]

An artificial 'haemoglobin' has been synthesized in which Mn^{III} tetrasulfonated-phthalocyanine (TsPc) was used to replace the haem group.[707] On the basis of spectroscopic data, the product has been formulated as $[Mn^{IV}OPc]$·globin. Electrophoresis and molecular weight determinations indicate that the compound is dimeric. The compound does not reversibly bind oxygen and cannot act as a physiological carrier of oxygen. However, [MnOPc]·globin does have an affinity for additional ligands such as CN^-, CO, NO and imidazole.

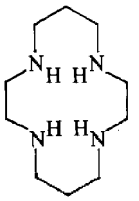
In the solid, the dioxygen adduct of $[Mn^{II}(TsPc)]$ is best formulated as $[Mn^{III}(TsPc)O_2^-]$.[708] In solution, the ESR spectrum as a function of pH suggests that intramolecular electron transfer may occur between $[Mn^{II}(TsPc)O_2]$ and $[Mn^{III}(TsPc)O_2^-]$. The superoxide is only stable within the approximate pH range 11.5 to 13.5. Reaction of $[Mn(TsPc)O_2]$ with hydrazine hydrate has been reported to produce [Mn(TsPc)].[709]

41.4.8.3 Other nitrogen donor ligands

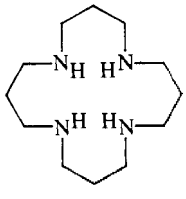
Largely because a manganese porphyrin containing the metal in a high oxidation state appears to be involved in the photosynthetic process,[710] a number of studies involving nitrogen donor synthetic macrocycles have been carried out in order to examine the oxidation states accessible to this ion as a function of macrocycle structure. Mn^{III} compounds of such macrocyclic ligands have been generated both chemically and electrochemically, and for a number of systems of this type, Mn^{III} appears to be the preferred oxidation state.

Mn^{III} species of cyclam (**238**) of type $[MnX_2(\mathbf{238})]^+$ (X = Cl, Br, NCS or N_3) have been prepared.[711] All compounds are high spin and appear stable indefinitely in the solid state. From spectral evidence the compounds were assigned *trans* octahedral structures. The species $[MnCl_2(\mathbf{238})]^+$ was obtained by reaction of (**238**) with manganese(II) chloride in methanol; oxidation was then effected by bubbling air through the solution for six hours. The product precipitated as its chloride salt on addition of concentrated hydrochloric acid to the reaction solution. The other compounds in the series were obtained from $[MnCl_2(\mathbf{238})]Cl$ by exchange reactions involving the chloro ligands.

In other studies, Mn^{III} compounds of cyclam (**238**) and the related 15-membered ring (**239**) have been reported.[712] The compounds are of types $[MnX_2(\mathbf{238})]Y$ (X = Cl, Y = BF_4; X = Br, Y = Br_3, PF_6) and $[MnBr_2(\mathbf{239})]Y$ (Y = Br_3, PF_6) and were synthesized by reaction of anhydrous Mn^{II} chloride or bromide with the appropriate macrocycle in refluxing methanol (under nitrogen) following by oxidation to the Mn^{III} products using chlorine or bromine. The BF_4^- and PF_6^- salts were obtained by metathesis reactions involving the initial product from each preparation. Once again, the compounds have been assigned six-coordinate, high spin (d^4) structures in which the macrocycles coordinate to the Mn^{III} in a planar fashion.



(238)



(239)

Mn^{III} species of the *meso* form of the fully saturated N_4-macrocycle (**194**) may be prepared by oxidation, using a range of oxidants (such as chlorine, bromine, oxygen, nitrosonium salts and hydrogen peroxide), of the corresponding Mn^{II} species (see Section 41.3.10.3).[533] However the most efficient route involves oxidation of the product formed from Mn^{II} acetate and the macrocycle with $NOBF_4$ or $NOPF_6$ followed by addition of HX to give products of type $[MnX_2(\mathbf{194})]Y_2$ (where X = Cl, Br; Y = BF_4, PF_6^-). These Mn^{III} species display magnetic moments and electronic spectra which are consistent with high spin, tetragonally distorted d^4 systems. They are more stable to pH variation than are the Mn^{II} analogues. These Mn^{III} compounds are more readily reduced than a number of Mn^{III} porphyrins.

Corresponding complexes of the *racemic* form of (**194**) have also been obtained.[713] The *racemic* macrocycle was initially resolved as its nickel species and, after removal of the nickel, the optically-active macrocycle was used to prepare Mn^{III} compounds by a similar procedure to that given above for compounds of the *meso* ligand.

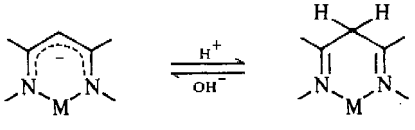
Two high spin Mn^{III} compounds of the pyridine-containing 15-membered macrocycle (**198**) of type $[MnX_2(\mathbf{198})]PF_6$ (X = Cl, Br) have been isolated after oxidation of the corresponding Mn^{II} complexes in acetonitrile with $NOPF_6$.[534] These compounds have been assigned pentagonal bipyramidal coordination geometries in which the macrocycle coordinates in a planar manner; reports of such a geometry for Mn^{III} are rare. Both compounds are high spin with magnetic moments of 4.94 BM. The analogous 16- and 17-membered N_5 ligands appear not to stabilize Mn^{III} and it has been suggested that these ligands may fold to yield octahedral Mn^{II} species in which the nitrogens of the macrocycle occupy one axial and four equatorial positions. The remaining axial position is filled by a halide ion. It is perhaps significant in this context that attempts to oxidize the octahedral Mn^{II} species of the N_4 macrocycle (**195**) to the corresponding Mn^{III} compounds were unsuccessful.

High spin Mn^{III} products of the dianionic N_4 macrocycle (**196**) of type [MnX(**196**)] where X is Cl, Br, SCN and N_3 have been prepared.[535] The chloro and bromo derivatives crystallize with a molecule of acetonitrile while the thiocyanate and azide derivatives were obtained unsolvated. In the former compounds, the acetonitrile may be weakly coordinated to the manganese ion. An X-ray structure determination of [MnNCS(**196**)] indicates that it has a square pyramidal coordination geometry with the NCS^- group N-bonded and coordinated in the axial position. As in other structures of this ring system, the macrocycle has a pronounced saddle shape. The Mn^{III} ion is displaced 0.356 Å from the N_4-donor plane.[714] The overall structure is similar to that of the Mn^{II} species, [Mn(**196**)NEt_3], discussed previously.[536]

The azide compound exhibits a slightly reduced magnetic moment (μ_{eff} = 4.78 BM);[535] this suggests the presence of antiferromagnetic coupled Mn^{III} ions (*via* an N_3^- bridge) in this compound.

Except for the azide derivative, the various Mn^{III} compounds gave similar electrochemical behaviour.[715] Each compound showed two one-electron oxidation steps, the first being reversible and the second somewhat irreversible. Evidence suggests that these oxidations essentially involve the coordinated macrocycle. Each compound exhibits a one-electron reduction wave which has been assigned to the conversion of Mn^{III} to Mn^{II}. It is evident that, relative to the saturated macrocycle (**194**),[533] the dianionic ligand (**196**) stabilizes Mn^{III} over Mn^{II}. No evidence for the generation of Mn^{IV} species was obtained during these studies.

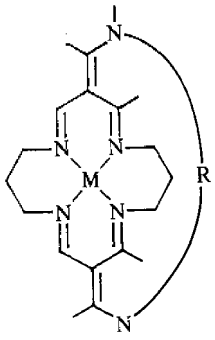
All the above Mn^{III} compounds of (**196**) are stable as solids under dry nitrogen although they slowly decompose in air.[535] They also decompose in aqueous base but in acid undergo reversible protonation. The protonation site is probably the alkenic carbon of the β-diketone fragment; equation (20). Ni^{II} complexes of related macrocyclic ligands have been reported to undergo similar protonation reactions.[716,717]



(20)

In situ condensation of 2,6-diaminopyridine and acetylacetone has been proposed to yield compounds of type [MXL] (where LH_2 is the N_6-cyclic ligand formed by condensation of two molecules of each of the above precursors;[718] M = Cr, Mn, Fe or Co; and X is a range of mono anions). The structure of the Mn^{III} species (and, indeed of all of the compounds) was proposed to be square pyramidal; the pyridine nitrogens of the organic ligand were assumed not to bind to the Mn^{III}. However non-coordination of these donors would appear to induce considerable strain into the macrocyclic system and hence, in the absence of full X-ray structural data, the assigned structure should be considered tentative.

Reaction of tris(2,4-pentanedionato)manganese(III) with either of the macrobicyclic ligands of type (**240**) in acetonitrile leads to isolation of compounds of type $[MnClL](PF_6)_2$ in each case.[719] These compounds are five-coordinate and high spin. Both display slow but efficient catalase activity; both react smoothly with hydrogen peroxide in acetonitrile but the rate of oxygen evolution is much slower than for an effective catalase model compound based on Fe^{III} studied previously.[720] The manganese species gave no evidence that they exhibit peroxidase activity since, in the presence of phenolic substrates, no oxygenation activity was detected.[719]



(**240**) R = $(CH_2)_6$
R = *m*-xylylene

Electrochemical reduction of the Mn^{III} species leads to isolation of the corresponding high spin Mn^{II} compounds. The latter react irreversibly with dioxygen to regenerate the deprotonated forms of the respective Mn^{III} compounds.

41.5 MANGANESE(IV)

Manganese(IV) chemistry is dominated by the insoluble MnO_2, which forms so readily in aqueous solutions; and indeed the great bulk of Mn^{IV} chemistry involves compounds in which the metal's coordination partners are O-donor ligands. As well, in recent years, the range of known coordination partners for Mn^{IV} has been significantly extended: we now know of reasonably robust tetraalkyls $[MnC_4P_2]$, there are $[Mn^{IV}S_6]$, $[Mn^{IV}Cl_6]$ and $[Mn^{IV}F_6]$ compounds and some compounds with nitrogen ligands including porphyrins.

Except in the few cases where there is antiferromagnetic coupling between adjacent metal atoms, the compounds are high spin d^3 ($S = \frac{3}{2}$) species and the great majority of them are octahedral.

Some at least of the observable Mn^{IV} chemistry derives from the disproportionation of the Mn^{III} species, rather than from direct oxidation of the latter.

Many of the Mn^{IV} species are redox unstable and have significant existence because they react slowly. The ubiquitous MnO_2 is one example; and there is another in the insoluble $Mn(SeO_3)_2$, which precipitates from a solution of Mn^{II} and H_2SeO_3 in water.

One of the more interesting developments in Mn chemistry has been the recent demonstration of a thermal equilibrium between oxidation states II and IV in an $[MnO_4N_2]$ system, details of which may well offer the key to an understanding of the role of Mn in O_2 production in the photosynthetic system. Undoubtedly the continuing search for an understanding of this system will produce further advances in our understanding of Mn chemistry.

41.5.1 Carbon Ligands

Cyano compounds of Mn^{IV} are properly characterized only for the hexacyano anion $[Mn(CN)_6]^{2-}$: it has been isolated, as the yellow K^+ salt,[51] from the oxidation of the Mn^{III} anion in DMF with NOCl. It is immediately decomposed by deaerated water, with the separation of MnO_2. Magnetic measurements ($\mu_{eff} = 3.94$ BM) show it to be a high spin d^3 species. Perhaps surprising, in view of the reactivity of this anion, it has now been shown[574] that $Mn(CN)_3 \cdot nH_2O$, which precipitates from aqueous acid solutions of $[Mn(CN)_6]^{3-}$, has a cubic, Prussian blue type structure and should be formulated as $Mn^{II}[Mn^{IV}(CN)_6] \cdot nH_2O$. Impure samples of analogous compounds, in which Zn^{II} and Cd^{II} replace the Mn^{II}, also have been obtained.

'$K_4Mn(CN)_8$' does not exist. It is one of those chimeras that seem to persist through acquiring textbook status before being debunked: products, which were described as such, were mixtures containing Mn^{III}—O—Mn^{III} species.

The relatively robust, tetrahedral, green, volatile MnR_4 (R = norbornyl) was reported in 1972 from the reaction of LiR and $MnCl_2$ in petroleum,[721] and the oxidation mechanism leading to the Mn^{IV} species in still apparently unexplained.[63] Related, but less thermally robust green compounds of 2-methyl-2-phenylpropyl and trimethylsilylmethyl were described by Wilkinson and co-workers[63] as arising when traces of O_2 were admitted to a solution of the Mn^{II} alkyl, and were identified particularly by their ESR spectra as $S = \frac{3}{2}$ species.

More recently octahedral [$MnMe_4$dmpe] has been isolated from a reaction that involves disproportionation of the Mn^{III} species.[576] The reaction of [$Mn(acac)_3$] with dmpe and MeLi in diethylether at −78°C gives a clear yellow solution, from which yellow crystals of the Mn^{IV} compound {and then the orange [$MnMe_2(dmpe)_2$]} were obtained. In another similar reaction [$MnMe_4(PMe_3)_2$] also was obtained. Such reactions would appear to offer a route to the exploration of an extensive chemistry of Mn^{IV} alkyls.

Yellow [$MnMe_4$dmpe] is a high spin compound (μ_{eff} = 3.87 BM in solution) and an X-ray analysis of its structure[576] shows Mn—P = 2.50 Å and Mn—C = 2.07 Å (*trans* to P) and 2.12 Å (*trans* to C).

41.5.2 Nitrogen and Phosphorus Ligands

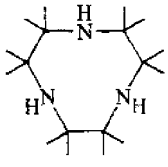
Knowledge of nitrogen ligands, apart from the macrocyclic, and especially the porphyrin ligands, (Section 41.5.7) is confined to just a few compounds, which also have other ligands in their coordination sphere.[572]

Black [$MnCl_4$bipy] (with μ_{eff} = 3.82 BM) is one of the compounds formed in the reactions of $KMnO_4$ and bipy with concentrated aqueous HCl. It loses Cl_2 at room temperature.

Still reactive, but nonetheless well characterized are the μ-dioxo dimers noticed in Section 41.4.2. The reaction of bipy or phen and $KMnO_4$ in concentrated HCl produces green μ-dioxo species (**222**), which contain both Mn^{III} and Mn^{IV}. The latter has, of course, the shorter bond lengths (Mn—O = 1.784 and Mn—N = 2.02–2.08 Å, compared to 1.85 and 2.13–2.23 for Mn^{III}). Oxidation to the red, fully Mn^{IV} dimer, according to equation (16), occurs in CH_3CN at $E_{1/2}$ = 1.33 V (*vs.* SCE), for both bipy and phen; and the phenanthroline species has been isolated as [$Mn_2O_2(phen)_4$]-$(ClO_4)_4 \cdot H_2O$. Its magnetic moment is 1.86 BM at room temperature, reducing to 1.36 BM at 94 K. ESR data confirm the equivalency of the two Mn atoms and the absence of any significant electron pairing between them in solution (for bipy, g = 2.03 and A = 83 G).

Again, as for Mn^{III} (Section 41.4.2), there are some biguanide compounds,[722] which have been described as Mn^{IV} μ-dioxo species of similar type to the above; but there is a need for further characterization, especially, if possible, by X-ray techniques.

An even more interesting vista is opened up by a recent report of a tetranuclear [$Mn_4^{IV}O_6$] compound with the terdentate ligand (**241**).[723] The reaction of aqueous solutions of the amine and $MnCl_2$ in water with O_2 produces a black solution, and the addition of NaBr, and adjustment to pH 8, gives needle-like crystals of $[Mn_4O_6L_4]Br_{3.5}OH_{0.5} \cdot 6H_2O$.



(241)

An X-ray analysis shows the Mn_4O_6, adamantane-like nucleus (*cf.* the S analogue in Section 41.3.6.1) with each Mn atom also bonding to the terdentate amine ligand, giving [MnO_3N_3] octahedra {average bond lengths: Mn—O = 1.79 Å and Mn—N = 2.08(1) Å; and O—Mn—O = 128.7(8)°}. The magnetic moment of 3.96 BM per Mn suggests very little, if any, antiferromagnetism.

It would be surprising if this is not the first of many such cluster compounds to be detected, and they may form a class like the basically trinuclear carboxylates (Section 41.4.3.3).

Phosphine ligand compounds of Mn^{IV} are confined to the phosphine alkyls of Section 41.5.1, and $[MnCl_2(diphos)_2]Cl_2$ of Table 17 (Section 41.3.4). There are no authenicated arsine compounds.

41.5.3 Oxygen Ligands

41.5.3.1 Water, hydroxide and oxide

There is no evidence for the significant existence of an Mn^{IV} aquo species in water, nor for the binary hydroxide $Mn(OH)_4$, nor indeed for a definite oxide hydrate: the aqueous chemistry of Mn^{IV} is dominated by the insoluble MnO_2.[211,572]

Yet the $[Mn(OH)_6]^{2-}$ octahedron is found in the yellow-green to orange mineral jouravskite[724] $Ca_3Mn(OH)_6 \cdot CO_3 \cdot SO_4 \cdot 12H_2O$, in which the Mn—OH distance has been measured at 1.87 Å; and in despujolsite[725] $Ca_3Mn(SO_4)_2 \cdot (OH)_6 \cdot 3H_2O$ (Mn—O = 1.92 Å).

MnO_2 exists in an almost bewildering array of different structural types.[4–6,210,572,726] Most of them are non-stoichiometric, and contain more or less H_2O, OH^- and/or other metal atoms. It has been suggested that such phases, in the range of MnO_n (n = 1.7–2.0), whether synthetic or natural, should be designated by the German language name 'Braunstein'.[725] Of the known phases, only the β-modification (pyrolusite) corresponds in oxidation state and chemical purity to 'MnO_2'. The different modifications find widespread use in quite diverse areas of industry: from the Leclanché dry cells; through [O] sources in welding rods, safety matches, explosives and fireworks; as additives in glasses and cements; as ion-exchangers in water; to a wide range of applications as a catalyst, especially in oxidizing reactions.

Known forms of MnO_2 and the great bulk of other binary and ternary oxides[211] all contain octahedrally coordinated Mn^{IV}, with Mn—O distances averaging near 1.9 Å (Table 53), paralleling the situation in all known compounds of the chelating oxygen ligands.

However, there is at least one example of an $[MnO_4]^{4-}$ tetrahedron: Ba_3MnO_5 has the Cs_3CoCl_5 structure[572] and thus contains discrete tetrahedra. Such tetraoxomanganate tetrahedra dominate the chemistry of the higher oxidation states V to VII, and have been observed in the dimeric Mn^{III} compound $K_6[Mn_2O_6]$ (Section 41.4.3.1). It is not unlikely that, as the solid state structural chemistry of Mn^{IV} is further elucidated, more of these tetrahedra will be found and they may be significant in aqueous alkaline solutions. There are probably other examples in the solids reported by Scholder and co-workers.

Bridging oxide ligands are beginning to be detected in various oligomeric/cluster compounds: $[Mn_3O]$ (Section 41.4.3.3), $[Mn_2O_2]$ and $[Mn_4O_6]$ (Section 41.5.2) units are now known.

Table 53 Some of the Binary and Ternary Oxides of Mn^{IV}

Compound	*Comments*		*Bond Lengths* (Å) *Av.*	*Range*
MnO_2 (β-form)	Tetragonal rutile type	$[MnO_6]$	(1.88)	
Ramsdellite		$[MnO_6]$	(1.89)	1.86–1.92
Mn_3O_8	$(Mn^{II}_2Mn^{IV}_3O_8)$	$[MnO_6]$		1.85–1.92
$M^{II}_2Mn_3O_8$	M = Cu, Co, Cd	$[MnO_6]$		1.81–2.00
Li_2MnO_3 α	NaCl structure type	$[MnO_6]$		
β	$NaFeO_2$ superstructure of NaCl	$[MnO_6]$		
$BaMnO_3$	$CsNiF_3$ structure	$[MnO_6]$		1.88–1.91
$NiMnO_3$	Ilmenite structure	$[MnO_6]$		
Mg_2MnO_4	Cubic spinel			
M_2MnO_4	(M = Ca, Sr, Ba) Tetragonal K_2NiF_4 layer structure	$[MnO_6]$		
$CaMn_3O_7$				
$Ca_3Mn_2O_7$	$Sr_3Ti_2O_7$ type			
$Ca_4Mn_3O_{10}$	Isostructural with $Ca_4Ti_3O_{10}$	$[MnO_6]$		
$ZnMn_3O_7 \cdot 3H_2O$	Chalcophanite	$[MnO_6]$		
Mg_6MnO_8		$[MnO_6]$	(1.93)	
Sr_2CrMnO_6	Disordered perovskite	$[MnO_6]$	(1.94)	1.85–1.96
			(1.91)	
$CaCu_3Mn_4O_{12}$	Perovskite-like structure	$[MnO_6]$	(1.92)	
Ba_3MnO_5	Isotype of Cs_3CoCl_5—tetrahedral	$[MnO_4]^{4-}$		

41.5.3.2 Peroxo

There are arguments in the literature that the products of reversible oxygenation of Mn^{II} porphyrins should be regarded as Mn^{IV}–peroxo (η_2) species (Section 41.3.5.1.vi); and, although yet unproven, this does seem to fit with the emerging pattern of Mn chemistry.

Unlike its neighbour Cr, which also forms high oxidation state tetraoxo species, Mn does not form robust compounds containing peroxo ligands. The reaction of alkali tetraoxomanganate(VI) or Mn^{II} species with H_2O_2 in cooled, concentrated alkaline solutions gives slightly soluble red-brown to brown crystalline products, which are probably peroxomanganate(IV) species.

The product was dependent on concentration of alkali, and Scholder and Kolb[727] claimed the preparations of pure $M_2H_2[Mn(O_2)_3O]$ (M = Na, K), and of mixtures containing the compounds $M_3H[Mn(O_2)_4]$ (M = Na, K), $K_3H[Mn(O_2)_3O]$ and $K_4[Mn(O_2)_4]$. Undoubtedly, they were peroxo compounds, but confirmation of their structures must await X-ray data. They are unlikely to find much use: when dry they detonate above 0°C.

$K_2H_2[Mn(O_2)_3O]$ gives a red-brown aqueous solution, from which O_2 is slowly evolved, with precipitation of MnO_2.

41.5.3.3 Oxyanions

In these compounds the $[MnO_6]$ octahedron is clearly becoming unstable: the known compounds are not generally robust, but there are several interesting exceptions. There are yet no indications of any coordination polyhedron other than the octahedron.

Oxalate forms the only known carboxylato species—the green $K_4[Mn_2O_2(Ox)_4]\cdot nH_2O$ and apparently another orange coloured compound of unknown type.[572,728] The green dimer can be kept for *ca.* one week at −6°C, in the dark; but useful physical measurements have been made and its decomposition studied.[728]

Mn^{IV} phosphato species are formed[729] in solution only at very high $[H_3PO_4]$, by the reaction of $KMnO_4$. Such brown-red solutions, on standing or upon dilution, deposit the insoluble Mn^{III} species $MnPO_4\cdot H_2O$. Black plates, formulated as $[NH_4]_2Mn(PO_4)_2\cdot H_2O$, and the flesh-pink coloured solid obtained from concentrated aqueous H_3AsO_4 and formulated as $Mn(H_2AsO_4)_4$, may be examples of Mn^{IV} species; but further characterization is needed.

With the group VI oxyanions, sulfates and tellurates are probably represented in some of the reported data, but the major interest is in the insoluble selenite $Mn(SeO_3)_2$. $Mn(SO_4)_2$ may be represented[592] in the unstable black solid that can be prepared from $MnSO_4$ and $KMnO_4$ in 55% H_2SO_4. It dissolves in cold 40–70% H_2SO_4, forming a brown solution, which probably contains Mn^{IV} sulfato species. And some tellurates have been described as $Na_7H_7Mn(TeO_6)_3\cdot 3H_2O$ and $K_6H_8Mn(TeO_6)_3\cdot 5H_2O$, but not firmly characterized.

Thus the ready preparation of $Mn(SeO_3)_2$ stands in contrast: it can be made[730] as orange-red crystals in high yields by reacting aqueous Mn^{II} and H_2SeO_3 on the water bath; MnO_2 and SeO_2 in boiling water, or in a sealed flask at 250–300°C; Se and MnO_2 in aqueous H_2SO_4; or $KMnO_4$ and SeO_2 in water. The reaction (21) is reversible. Clearly, $Mn(SeO_3)_2$ represents a significant energy minimum for the Mn/Se/O system, and it is interesting to note that $Mn^{II}(IO_3)_2$ is an energy minimum in the Mn/I/O system.

$$MnSeO_4 + SeO_2 \underset{400°C}{\overset{200°C}{\rightleftharpoons}} Mn(SeO_3)_2 \qquad (21)$$

Iodato compounds of Mn^{IV} are known, having been first described by Berg in 1899; but do not appear to have been obtained free from Mn^{III} materials.[279] Amber or brown solutions can be obtained by dissolving MnO_2 in iodic acid and adding some periodate. Such solutions are robust in sealed quartz tubes, but in glass deposit red $K_2Mn(IO_3)_6$. A recent[731] study of the solid products has detected a range of solid solutions from $K_2Mn(IO_3)_6$ to $K_3H_2Mn(IO_3)_9$; and salts with other cations are known.

Periodate oxidizes Mn to $[MnO_4]^-$, but, with the proper choice of conditions, Mn^{IV} compounds (unstable now to oxidation rather than reduction) can be isolated. Red $Na_7H_4Mn(IO_6)_3\cdot 17H_2O$ and $K_7H_4(IO_6)_3\cdot 8H_2O$ have been described, and an X-ray analysis of the former showed a tris-bidentate $[Mn^{IV}O_6]$ species with Mn—O = 1.90 Å. The red, insoluble compounds $NaMnIO_6$ and $KMnIO_6$ are isostructural[732] with $NaNiIO_6$.

Another octahedral oxyanion $[Mn^{IV}O_6]$ species has been characterized[733] in one of the products

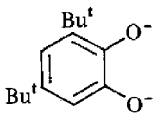
of evaporation of an aqueous solution of $HMnO_4$: violet $(H_3O)_2[Mn(MnO_4)_6]\cdot 5H_2O$ is unstable above $-4°C$.

And there is a range of heteropoly- and isopoly-anion compounds of Mn^{IV} with V, Nb, Ta, Mo and W (Table 26), most of which appear to be $[MnO_6]$ species.

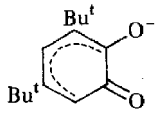
41.5.3.4 Di- and polyhydroxy ligands, including catechol

A range of polyhydroxy and polyhydroxy-carboxylate manganese compounds has been shown to be oxidizable to Mn^{IV}, and one of them, the tris-chelate of the dianion of sorbitol, has been isolated[734] as a red-brown hygroscopic solid $(NMe_4)_2[Mn(C_6H_{12}O_6)_3\cdot 6H_2O$. Such compounds have been known[316] since Schottländer reported some yellow glycerate species $Na_2[MnL_3]$ and $Sr[MnL_3]$ in 1870; but they have only recently been studied in some detail.[734] Although X-ray data are not available, the sorbitolate compound appears to be another example, like the periodate (Section 41.5.3.3) of a tris-chelated Mn^{IV} anion, using two adjacent hydroxy groups of the sorbitol.

More detail is available on the chelated Mn^{IV} compounds of the anion of one of the catechols —3,5-di-*ter*-butylcatecholate (**242**). The Mn compounds of this dianion, in the presence of an excess of the ligand, can be oxidized to the Mn^{III} (Section 41.4.3.4) and Mn^{IV} species.[282] X-Ray analyses of the tris-chelated Mn^{IV} anion $[MnL_3]^{2-}$ give Mn—O bond lengths[735,736] between 1.89 and 1.92 Å. There are conflicting reports about the possibility of this anion supporting reversible binding of O_2.[282,737] The final explanation of the observed phenomena[282,737] will probably involve ligand oxidation to the semiquinone form (**243**).



(242)



(243)

The latter is almost certainly involved in an interesting thermal equilibrium (22), which has been observed in both pyridine and toluene solutions. When $[Mn_4^{II}L_8]$ (L = **243**) (Section 41.3.5.3.ii) was treated with py, purple crystals $[Mn^{IV}L_2py_2]\cdot 2py$ (L = **242**) were obtained. An X-ray analysis[738] proved the Mn^{IV}/catecholate formulation {Mn—O = 1.854(2) and Mn—N = 2.018(3) Å}, and a spectrophotometric study of the equilibrium (22) showed that the Mn^{IV} form prevails at low temperature in the solutions. There seems to be a real possibility that some such redox changes may offer an explanation of the role of Mn in biological photosynthetic water oxidation.

$$\underset{\text{Green}}{[Mn^{II}(\mathbf{243})_2py_2]} \rightleftharpoons \underset{\text{Purple}}{[Mn^{IV}(\mathbf{242})_2py_2]} \qquad (22)$$

41.5.3.5 Other ligands

Electrochemical studies[314,613] have shown that the $[Mn(bipyO_2)_3]^{2+}$ and $[Mn(terpyO_3)_2]^{2+}$ cations can be oxidized to the Mn^{IV} species in CH_3CN. The spectra of the Mn^{IV} cations were measured, but they are rather unstable and were not isolated.

There have also been some reports in the literature of Mn^{IV} compounds of acetylacetonate, but they have not yet been fully substantiated.

41.5.4 Sulfur Ligands

No binary or ternary phases containing Mn^{IV} sulfides appear to have been described; but well characterized, although reactive and somewhat difficult to handle, compounds are known with both 1,1- and 1,2-dithiolates.

As noticed in equation (8), the tris-*dialkyldithiocarbamato*-manganese(III) compounds $[Mn(R_2dtc)_3]$ are readily oxidized to the monocations[329,330] (oxidation potentials for the 16 compounds studied varied between 0.25 and 0.53 V). Such oxidations have been achieved chemically by

adding BF_3 to CH_2Cl_2 solutions of $[Mn(R_2dtc)_3]$ in the air, whence oxidized $[Mn(R_2dtc)_3]BF_4$ species were obtained; and, alternatively, by mixing benzene solutions of the Mn^{III} compound with acetone solutions of $[Mn(H_2O)_6]X_2$ ($X = ClO_4$, BF_4), whence either the ClO_4^- or BF_4^- salts were obtained. (The oxidizing agent in each case appears to have been O_2.)

The dark purple compounds $[Mn(R_2dtc)_3]X$ have magnetic moments typical of high spin d^3 systems (3.70–4.25 BM), and give EPR signals with isotropic g values and small hyperfine interaction. Confirmation of the $[Mn^{IV}S_6]$ structure of these compounds is given by an X-ray analysis of the piperidine compound $[Mn\{S_2CN(CH_2)_5\}_3]ClO_4 \cdot CHCl_3$: the tris bidentate species has Mn—S distances between 2.325 and 2.353 Å, averaging at 2.33 Å.

Tris-dithiolenemanganese compounds are known[324,325] only in the Mn^{IV} oxidation state, just as the bis compounds are only known as Mn^{II} (Section 41.3.6.2). Green crystals of $M_2[Mn(mnt)_3]$ ($M = PPh_4^+$ and $AsPh_4^+$) were prepared from $Mn(OAc)_3$, and black crystals of $[NR_4]_2[Mn(S_2C_6Cl_4)_3]$, giving magenta solutions, were prepared either from Mn^{II} in the air, or from $KMnO_4$. All have magnetic moments near 4 BM which is typical of high spin d^3 systems. Electrochemical studies have shown that they can be reduced in two one-electron steps and oxidized in two one-electron steps, but none of the reduced or oxidized species have been isolated. Identity of X-ray powder patterns with the Fe analogue suggests that $[AsPh_4]_2[Mn(mnt)_3]$ has the same octahedral structure defined for the Fe compound.

A recent report[739] describes several mixed ligand compounds $[Mn(R_2dtc)_2X_2]$ (X = Cl, Br).

41.5.5 Halides

The only binary halide known is the fluoride MnF_4; and, although ternary compounds are well established for both F^- and Cl^-, the latter are particularly unstable at normal temperatures and all are, to varying degrees, sensitive to water.[210,336,572]

MnF_4, known since 1928, has now been obtained in single crystals,[740] which have a trigonal unit cell, but the structure has not yet been reported. The ultramarine blue solid is very hygroscopic, loses F_2 slowly at normal temperatures and hydrolyses instantly in contact with water.

Three classes of ternary fluorides are known (Table 54). Red $O_2^+[Mn_2F_9]^-$ is the only representative of this class;[741] but all of the alkali metal species $MMnF_5$ are known. The former is polymeric, with double chains of linked $[MnF_6]$ octahedra, and, although structural analyses are not available, it seems certain that the brick-red $MMnF_5$ spp. also contain chains of $[MnF_6]$ octahedra. Magnetic moments, except for the O_2^+ species, are near 3.8 BM. They were first prepared by Hoppe and co-workers by fluorinating $MMnF_3$ at 450–510°C in a flow system, but details have now been given[742] of a wet method using 48% HF. This method also gave an interesting pyridine compound formulated as $MnF_4 \cdot py \cdot H_2O$, which is described as quite robust at normal temperatures, although having a faint odour of pyridine. Undoubtedly a wide range of N-donor compounds of similar type will be obtainable.

The third class of ternary fluorides is the simplest one—the compounds $M_2[MnF_6]$. All are yellow or orange-yellow with magnetic moments near 3.8 BM, as expected for octahedral Mn^{IV}. They crystallize in various forms: the alkali metal salts, being known in two hexagonal forms (one having the $Na_2[SiF_6]$ structure), a trigonal and a cubic form (the latter having the $K_2[PtCl_6]$ structure). The salts $M[MnF_6]$, for M = Mg, Ca, Cd, Hg have the $Li[SbF_6]$ structure; and, for M = Sr and Ba, the $Ba[GeF_6]$ structure. Mn—F bond lengths for six different measurements range between 1.72 and 1.75 Å, and average at 1.735 Å. These yellow, hygroscopic compounds are prepared by the action of F_2 on a mixture of MF and MnF_n or by reduction of $[MnO_4]^-$ in HF. Recently, $(NF_4)_2[MnF_6]$

Table 54 The Ternary Halide Compounds of Manganese(IV)

Compound Type	*Comments*	*Ref.*
$O_2^+Mn_2F_9^-$	Ruby-red needles or plates $\mu_{eff} = 5.63$ BM $[MnF_6]$ octahedra linked in double chains	741
$MMnF_5$	$M = O_2^+$. Red	740
	Li, Na, K, Rb, Cs. Brick-red $[MnF_6]$ octahedra, but details unknown	742
$M_2[MnF_6]$	M = Li–Cs, NO, NF_4; 2M = Mg–Ca Yellow or orange-yellow $[MnF_6]^{2-}$ octahedra	572, 743
$M_2[MnCl_6]$	M = K, Rb, Cs, NH_4, NR_4. Dark red, unstable solids. $K_2[PtCl_6]$ structure	623
$[MnCl_4bipy]$	Black crystals	572

has been proposed[743] as 'an outstanding solid oxidizer, with good thermal stability and a high active fluorine content'. It is, however, shock sensitive, especially in the presence of fuels, and reacts violently with water.

The chloro analogues are much less robust.[623] $MnCl_4$ is not known in crystalline form, although $[MnCl_4bipy]$ has been prepared (Section 41.5.2) and characterized. Like the hexachloromanganate(IV) species, however, it loses Cl_2 at normal temperatures. The very dark red, unstable solid $K_2[MnCl_6]$ was first prepared by the reduction of $Ca(MnO_4)_2$ with 40% HCl, followed by the addition of KCl; but it has also been made from 'Mn^{III} acetate' and potassium acetate in a large excess of acetyl chloride. Other salts of Rb, Cs, NH_4 and NMe_4 have been made, and all have face-centred cubic lattices of the K_2PtCl_6 type. The Mn—Cl distance in the potassium salt is 2.28 Å.

41.5.6 Mixed Donor Atom Ligands

Compounds of Mn^{IV} with the various multidentate ligands with different donor atoms have been postulated, especially as products of the 'oxygenation' of the Mn^{II} salicylaldiminato ligands (Section 41.3.9.3). But there is no unequivocal proof of this oxidation state in these compounds. It would be surprising if Mn^{IV} species do not form, even if they turn out to be oxidatively unstable. But we currently know nothing of consequence about the detail.

41.5.7 Macrocyclic Ligands

41.5.7.1 Porphyrin ligands

Higher-valent manganese porphyrins have been of interest since they have been shown to be important intermediates in the activation of hydrocarbons under mild conditions (Section 41.4.8). Their use as sensitizers for the photooxidation of water to oxygen has also provided a motivation,[479] although the involvement of a manganese porphyrin in the natural system has not been fully documented.

M^{IV} porphyrins may be generated by treatment of the corresponding Mn^{III} porphyrin with a strong oxidant, such as hypochlorite (Section 41.4.8.1). The local environment affects the ease of such oxidation and also the nature of the oxidation products.[480] In alkaline solution, such oxidation is facile and yields both Mn^{IV} and Mn^{V} porphyrins. The oxidation is similar, but less efficient, when it occurs in membranes or positively charged micelles. However, in both negatively charged micelles and microemulsions the oxidation is very inefficient: under these conditions no Mn^{V} was observed. In contrast to their redox behaviour, such changes in environment have little effect upon the spectroscopic and chemical properties of Mn^{III} porphyrin species.

Radiochemical (γ-irradiation) one-electron oxidation of [MnCl(TPP)] has also been demonstrated in tetrachloroethane at 77 K.[744] ESR and optical spectroscopy indicate that oxidation occurs at the metal centre to yield a Mn^{IV} compound.

The Mn^{IV} porphyrins tend to be of limited stability in water at neutral pH but are stable under strongly alkaline conditions.[479,482] In acid, rapid decomposition to Mn^{II} species occurs *via* a complex redox mechanism.[479] The reduction is catalyzed by redox catalysts, such as RuO_2 in acid, to yield O_2 in low yield as one product. This latter observation documents (in part) a route for the catalytic oxidation of water.

Hill and coworkers[745] have reported a range of Mn^{IV} porphyrin species, including the monomeric species $[Mn(OCH_3)_2(TPP)]$,[746] $[Mn\{PhI(OAc)O\}_2(TPP)]$[745] and $[MnX_2(TPP)]$ (X = N_3, NCO)[747] as well as the two types of dimeric species mentioned previously in Section 41.4.8.1, $[\{MnX(TPP)\}_2O]$[678] (X = N_3 and OCN) and $[\{MnX(OIPh)(TPP)\}_2O]$.[690] $[Mn(OCH_3)_2(TPP)]$ is obtained by oxidation of [Mn(OAc)(TPP)] in basic methanol using sodium hypochlorite or iodosylbenzene.[746] X-Ray diffraction indicates that this molecule is pseudooctahedral with the methoxy groups coordinated above and below the N_4-donor plane of the macrocycle. The compound has a high spin d^3 Mn^{IV} ground state with a magnetic moment of 3.9 BM. X-Ray studies of a number of the other monomeric species indicate related pseudooctahedral coordination geometries for these compounds. The X-ray structure of $[MnN_3(TPP)]_2O$ indicates an oxygen-bridged dimeric structure in which each manganese ion achieves a six-coordinate geometry.[678] The ground state of this compound is best described as containing two antiferromagnetically coupled Mn^{IV} (d^3) ions.

41.5.7.2 *Phthalocyanine ligands*

As noted in Section 41.4.8.2, there are suggestions in the literature of Mn^{IV} phthalocyanine species, such as [MnOPc]; but they appear much less accessible than for the porphyrins; and have yet to be fully characterized.

41.6 MANGANESE(V), (VI) AND (VII)

The coordination chemistry of these higher oxidation states is dominated by, but not completely confined to, the tetraoxomanganates.

41.6.1 Tetraoxomanganates

The tetraoxomanganate ion can be isolated, although it appears to be but of minor importance, for Mn^{IV} (in Ba_3MnO_5, Table 53), Mn^{III} (in $K_6[Mn_2O_6]$, Table 46) and even for Mn^{II} (in $Na_{14}(MnO_4)_2O$, Table 19); and it seems not unlikely that further examples will be found, especially for Mn^{IV}.

At the other end of the oxidation scale, purple tetraoxomanganate(VII) is, of course, the permanganate that one learns about so soon after the first introduction to chemistry; green MnO_4^{2-}, which is stable in alkaline solutions, has been 'known' since Glauber described a green melt obtained by heating pyrolusite (MnO_2) with saltpetre (KNO_3) in 1659; but MnO_4^{3-}, although noticed in the older literature as hypomanganate, was not recognized as such until the work of Lux in 1946.

Thus the tetrahedral $[MnO_4]^{n-}$ unit is remarkable in being the only coordination polyhedron that has been detected throughout the whole range of oxidation states Mn^{II} to Mn^{VII}.

It has not proven possible (at least not yet) to study the full range of these redox changes in any solution, but at least for the last three of the series (Mn^{V} to Mn^{VII}) there is considerable detail available on their relative stabilities.[211]

Tetraoxomanganate(V), first characterized by Lux, has been isolated in a range of solid compounds. Relatively pure salts $M_3[MnO_4]$, for M = Li, Na, K, Rb and Cs, have been described,[572,748,749] as well as $Ba_3[MnO_4]_2$, $Ba_5(MnO_4)_3OH$ and halo-apatite species such as Sr and $Ba_5(MnO_4)_3Cl$. Although a complete X-ray analysis is not available, there is no doubt about the existence of the $[MnO_4]^{3-}$ tetrahedron, through comparative powder data with $[VO_4]^{3-}$ and $[PO_4]^{3-}$ species; and mixed crystals $Li_3(PO_4/MnO_4)$ and $Sr_5(PO_4/MnO_4)_3Cl$ have been studied. Preparations rely on the reduction of $[MnO_4]^{-}$ in concentrated aqueous alkali, or oxidation of Mn^{II} or MnO_2 in an alkaline melt. The blue solids are very moisture sensitive; magnetic moments are near 2.8 BM, as expected for a d^2 system; and details of their spectra have been studied, especially in Li_3PO_4 and $Sr_5(PO_4)_3Cl$ matrices. The study involving the latter reports[750] a 'dynamic Jahn–Teller effect' in an excited state of $[MnO_4]^{3-}$.

The relative stabilities of Mn^{V} and Mn^{VI} in nitrite, nitrate, hydroxide, oxide and peroxide melts have recently been studied in some detail.[750] In $NaNO_2$ and $NaNO_2/Na_2O_2$ melts, $[MnO_4]^{3-}$ is favoured over $[MnO_4]^{2-}$, whereas in KNO_2 or KNO_3 melts it is the Mn^{VI} species which is favoured.[751] In aqueous alkaline solutions of blue Mn^{V}, the concentration of OH^- must be at least 8 M to prevent disproportionation to $[MnO_4]^{2-}$ and MnO_2.

Green tetraoxomanganate(VI), however, is robust in aqueous alkaline solutions only slightly above 1 M in $[OH^-]$: lower $[OH^-]$ leads to rapid disproportionation to MnO_2 and MnO_4^- (Figure 1). This anion has been isolated in a number of crystalline solids, especially the alkali metal salts $M_2[MnO_4]$ (M = Li → Cs), and an X-ray analysis of the K salt has proven the tetrahedral $[MnO_4]^{2-}$ unit, with Mn—O distances between 1.647 and 1.669 (average = 1.659 Å).

The green manganate(VI) ion is a d^1 system, and measured magnetic moments are near 1.8 BM.

Rapid exchange reactions between MnO_4^- and MnO_4^{2-} have been studied, and cation effects were interpreted in terms of an outer-sphere bridged activated complex.

Permanganate $[MnO_4]^-$ is relatively robust for a strong oxidizing agent. The potassium salt is widely used industrially for bleaching; as an antiseptic, preservative and astringent; as an oxidizer in water and air treatment; and for oxidizing hydrocarbon compounds: world production in the early 1970s was estimated at near 40 000 tonnes. It is as an oxidizing agent, rather than for its coordination chemistry, that it is best known chemically, being the source of a five electron oxidation in acid solution (reduced to Mn^{II}) or three electron oxidation in alkaline solution, where reduction stops at Mn^{IV} because of precipitation of MnO_2. Aqueous solutions are unstable, as any

student of its analytical applications will know; and indeed MnO_4^- is a good example of a kinetically stabilized compound.

A range of salts of the anion has been described and it is known as a ligand — one notable example being $(H_3O)_2[Mn^{IV}(MnO_4)_6]\cdot nH_2O$, which is one of the products of dehydration of $HMnO_4$ in water. An X-ray analysis of the potassium and calcium salts has given Mn—O at 1.63 Å — somewhat shorter, as expected, than in the manganate(VI) species.

One area of MnO_4^- oxidations that has not been greatly explored, and which may lead to new Mn compounds in lower oxidation states, is reaction in non-aqueous solvents. A recent description[752] of the salt of the $[(Ph_3P)_2N]^+$ cation, which is rather soluble in a number of dipolar aprotic solvents, gives at least one starting material for such work; and the use of crown ethers and cryptates, to 'solubilize' $MMnO_4$ species, gives another.

41.6.2 Other Oxo and Oxohalo Species

The compounds for which reasonable evidence is available of their existence are listed in Table 55. Other than the tetraoxomanganates, the compounds are rather unstable, are also very strong oxidizing agents and are liable to detonation, especially in contact with a fuel.

41.6.3 Porphyrin Ligands

Reactions of hypochlorite with Mn^{III} porphyrins (Section 41.4.8.1) under alkaline conditions appear to produce, as well as the Mn^{IV} species (Section 41.5.7.1), some Mn^V species, such as $[Mn(N_4)ClO]$; but these have a very limited existence.[687]

However, quite robust crystalline Mn^V nitrido compounds are produced when these oxidations are carried out in the presence of NH_3.[757]

These red compounds contain a Mn—N triple bond, are diamagnetic, five-coordinate and show considerable chemical stability. Thus while the isoelectronic oxochromium(IV) or oxomolybdenum(IV) porphyrins behave, respectively, as weak oxidants and reductants, the corresponding manganese(V)nitrido species exhibits enhanced redox stability. [MnN(TPP)] and related porphyrin species were also independently prepared by the reaction of iodosylbenzene with $[Mn^{III}X(porphyrin)]$ (X = Cl, Br, OAc) in dichloromethane in the presence of excess ammonia.[758]

Table 55 Compounds of Manganese(V), (VI) and (VII)

Compound	*Comments*
MnO_4^{3-}	Blue anion — characterized in crystalline compounds, in concentrated alkali solutions and in melts.
MnO_4^{2-}	Green anion — stable in aqueous solutions with $[OH^-] > 1M$; crystalline salts.
MnO_4^-	Purple anion — reasonably robust in water and in crystalline salts.
Mn_2O_7	Very unstable red/green liquid. Liable to detonation but IR and UV spectra recently obtained on matrix-isolated samples.[753]
$HMnO_4$	Permanganic acid or hydroxotrioxomanganate(VII). Also as a dihydrate. Both crystalline;[754] strong oxidizing agents, with parallels to $HClO_4$.
MnO_3F	Highly volatile (Wohler 1828).[572] Microwave data give *Td* with Mn—O = 1.586(5) and Mn—F = 1.724(5) Å. Dark green crystals at −78°C. Very moisture sensitive and decomposes explosively.
$MnOCl_3$	Green liquid from $KMnO_4$ reduced in HSO_3Cl.[755] Decomposes to $MnCl_3$ above 0°C and to $[MnO_4]^{3-}$ in aqueous alkali.
MnO_2Cl_2	Least stable of oxochlorides — decomposing at −30°C. Brown solutions in CCl_4.[755]
MnO_3Cl	Green in CCl_4 solution. Detonates in air above 0°C. Slowly hydrolysed to MnO_4^- and Cl^- in water.[755]
$MnO_3\cdot SO_3Cl(?)$	This species may exist in solution, but decomposes, during isolation attempts, to $MnO\cdot SO_3Cl$.[756]
Mn^V porphyrins	See Section 41.6.3

X-ray structural analyses[758,759] show square pyramidal structures with the metal 0.4 Å out of the $[N_4]$ donor atom plane and short, axial Mn≡N distances of 1.51 Å.

One of the structural analyses refers to a porphodimethene macrocycle,[759] which survived (12% yield) the reductive methylation of the analogous nitrido(octaethyl-porphyrin)manganese(V) species, illustrating the redox stability of such formally Mn^V compounds.

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42

Technetium

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43

Rhenium

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43.1 INTRODUCTION

The coordination chemistry of rhenium, the last of the stable elements to be discovered (in 1925), has in the last 25 years undergone a tremendous growth. This element now occupies an important place in contemporary inorganic chemistry. Entry into its chemistry is usually afforded by access to the commercially available (but relatively expensive) perrhenate salts NH_4ReO_4 and $KReO_4$, although rhenium metal is sometimes used as the starting material.

In surveying the coordination chemistry of rhenium we have been greatly assisted by the availability of the superb review entitled 'Recent Advances in the Chemistry of Rhenium' that was written by George Rouschias and published in 1974.[1] This comprehensive review covers all aspects of

rhenium chemistry and can usefully be consulted and used in conjunction with the present review. Other useful reference sources are an early review by Fergusson[2] on the coordination chemistry of rhenium dating from 1966, and two monographs on rhenium chemistry published around this same time.[3,4] Additionally, we have made use of the more recent editions of *Annual Reports (Section A)* and the *Specialist Periodical Reports*, published by the Royal Society of Chemistry, in surveying material for use in this review.*

Rhenium occupies a very important place in the development of the chemistry of complexes containing metal–metal double, triple and quadruple bonds. This chemistry involves coordination complexes that contain pairs or trinuclear clusters of rhenium atoms and has been surveyed in a recent monograph entitled 'Multiple Bonds Between Metal Atoms'.[5] This source, which covers the literature up to early 1981, has also been invaluable in preparing the present review and can be consulted for a more complete and detailed coverage of these classes of complexes.

Since the organometallic chemistry of rhenium is surveyed in the companion series *Comprehensive Organometallic Chemistry*,[6] every effort has been made to minimize overlap with these topics, although an occasional reference is made in the present review to certain alkyl, aryl, carbonyl and isocyanide complexes that may be covered more fully in the excellent review by Boag and Kaesz.[6]

Salts of the perrhenate anion (including perrhenic acid) are not only the single most important group of starting materials for the synthesis of other rhenium compounds but are also of importance in catalysis and other commercial processes. Although they are formally coordination complexes of Re^{VII} and they appear quite extensively in the chemical literature (*e.g.* see *Chemical Abstracts*), much of the interest in them is outside the confines of the topic of coordination chemistry as it is commonly accepted. Accordingly, an effort has been made here to keep the coverage of their chemistry to a minimum.

Oxidation states ranging from Re^{VII} to Re^{0} will be the subject of this review. Of these, Re^{VI}, Re^{I} and Re^{0} are rare, while Re^{II} is encountered mainly in triply bonded dirhenium complexes, *i.e.* those possessing the Re_2^{4+} core. Examples of mononuclear complexes that possess these oxidation states, together with their stereochemical properties, are presented in Table 1, while some properties of coordination complexes containing multiply bonded pairs or trinuclear clusters of rhenium atoms are given in Table 2. Several systematic studies have been carried out that correlate Re 4*f* binding energies (as measured by the ESCA technique) of complexes ranging from those of Re^{VII} to Re^{I} with metal oxidation state.[7–11] These results can be useful in helping to identify complexes of unknown structure.

Table 1 Oxidation States and Typical Stereochemistries of Mononuclear Coordination Complexes of Rhenium[a]

Oxidation state	*Coordination number*	*Geometry*	*Examples*
Re^{I}, d^6	6	Octahedron	$ReCl(N_2)(PMe_2Ph)_4$, $K_5Re(CN)_6$
		Trigonal bipyramid	$ReCl(dppe)_2$
Re^{II}, d^5	6	Octahedron	$[ReCl(N_2)(PMe_2Ph)_4]^+$
Re^{III}, d^4	7	Pentagonal bipyramid	$K_4Re(CN)_7 \cdot 2H_2O$
	6	Octahedron	*mer*-$ReCl_3(PMe_2Ph)_3$, $[Re(acac)_2Cl_2]^-$
	5	Trigonal bipyramid	$Re(SAr)_3(NCMe)(PPh_3)$
Re^{IV}, d^3	6	Octahedron	$ReCl_2(acac)_2$, K_2ReCl_6
	8	?	$ReH_5(PR_3)_3$
Re^{V}, d^2	6	Octahedron	$[ReF_6]^-$, $ReOCl_3(PEt_2Ph)_2$, $[ReO_2(en)_2]^+$
	5	Square pyramid	$[ReOBr_4]^-$, $[ReO(SPh)_4]^-$
Re^{VI}, d^1	8	Square antiprism?	$[ReF_8]^{2-}$
	7	Pentagonal bipyramid?	$[ReF_7]^-$
	6	Octahedron	$[ReN(NCS)_5]^{2-}$, $ReOCl_4(H_2O)$
		Trigonal prism	$Re(S_2C_2Ph_2)_3$
	5	Square pyramid	$[ReNCl_4]^-$
	4	Tetrahedron	$[ReO_4]^{2-}$
Re^{VII}, d^0	9	Tricapped trigonal prism	$[ReH_9]^{2-}$
	8	?	$[ReF_8]^-$
	7	?	$[ReOF_6]^-$
	6	Octahedron	$ReO_3Cl(bipy)$, $[ReO_3Cl_3]^{2-}$
		Trigonal prism	$[Re(NHSC_6H_4)_3]^+$
	5	Square pyramid	$Re(NPPh_3)(SPh)_4$
	4	Tetrahedron	$[ReO_4]^-$

[a] There are no well-documented mononuclear non-organometallic complexes of Re^{0} known as of this time.

* Several important papers (references 574–639) dealing with the coordination chemistry of rhenium were published after the submission of the original manuscript. The chapter has been updated by inclusion of paragraphs discussing these recent developments at appropriate points throughout the text.

Table 2 Some Properties of Multiply Bonded Dirhenium and Trirhenium Complexes Possessing the Re_2L_8 and Re_3L_{12} Units

Oxidation state	*Metal core*	*Electronic configuration*[a]	*Metal–metal bond order*	*Example*
Re^{II}	Re_2^{4+}	$\sigma^2\pi^4\delta^2\delta^{*2}$	3	$Re_2Cl_4(PR_3)_4$
	Re_3^{6+}		1.5?	$[Re_3Cl_6(py)_3]_n$
$Re^{II,III}$	Re_2^{5+}	$\sigma^2\pi^4\delta^2\delta^{*1}$	3.5	$Re_2Cl_5(PR_3)_3$
Re^{III}	Re_2^{6+}	$\sigma^2\pi^4\delta^2$	4	$[Re_2Cl_8]^{2-}$
	Re_2^{6+}	$\sigma^2\pi^2\delta^2\delta^{*2}$	2	$Re_2Cl_6(dppm)_2$
	Re_3^{9+}		2	$[Re_3Cl_{12}]^{3-}$
Re^{IV}	Re_2^{8+}	$\sigma^2\pi^4$	3	$[Re_2Cl_9]^-$

[a] Given for the dirhenium cores only. For a description of the Re—Re bonding in Re_3^{9+} and Re_3^{6+} see B. E. Bursten, F. A. Cotton, J. C. Green, E. A. Seddon and G. G. Stanley, *J. Am. Chem. Soc.*, 1980, **102**, 955 and references therein.

In the systematic treatment of the coordination chemistry of rhenium, we shall start with the lowest oxidation state and proceed, in order, to the next highest. Compounds will be considered, within each oxidation state, in order of increasing nuclearity (*i.e.* mono-, di- and tri-nuclear); we define nuclearity in terms of the number of metal atoms held together by metal–metal bonds. Some complexes where an ambiguity in assigning the metal oxidation state may exist (*e.g.* nitrosyls) are discussed in a separate section. In the case of hydrides we have arbitrarily given the hydride ligand a charge of -1 (*i.e.* H^-) and assign the metal oxidation state accordingly; for example, $Re_2H_6(PMe_2Ph)_5$ is treated as a hydride complex of rhenium(III).

43.2 RHENIUM(0) COMPLEXES

This is, as expected, the rarest oxidation state as far as non-organometallic complexes of rhenium are concerned. The dirhenium phosphite complex $Re_2[P(OMe)_3]_{10}$ has been prepared[12,13] in low yield by several methods, *viz.* the potassium–potassium iodide reduction of $ReOCl_3(py)_2$ or an $ReCl_4$–pyridine complex, followed by treatment with trimethyl phosphite. This yellow complex displays a $^{31}P\{^1H\}$ NMR spectrum that appears as a first order AB_4 pattern, and is isoelectronic with $Re_2(CO)_{10}$. It reacts with H_2 upon photolysis in THF solution to produce hydridorhenium(III) and other species.[13] The related triphenyl phosphite derivative $Re_2[P(OPh)_3]_{10}$ has been described[14] as a product of the reaction between $ReH_3(PPh_3)_4$ and $P(OPh)_3$.

A report describing the isolation of $K_6Re(CN)_6$ could not be substantiated in a later investigation of this system.[15]

43.3 RHENIUM(I) COMPLEXES

The most important complexes of rhenium(I) are those containing the dinitrogen ligand, in which the rhenium atom is also complexed by phosphine ligands.

43.3.1 Cyanide, Alkyl Isocyanide and Aryl Isocyanide Complexes

Through a careful reexamination of several literature reports, the existence of salts of the rhenium(I) $[Re(CN)_6]^{5-}$ anion has been confirmed.[15] It can be prepared by the reduction (using BH_4^- or K/Hg as reducing agents) of mixtures of $[ReCl_6]^{2-}$ and CN^-.[15–17] The potassium salt is isomorphous with its manganese and technetium analogues.[16] Other methods, including the reaction of Re_3Cl_9 with aqueous KCN solution and the reaction of K_2ReCl_6 with KCN under N_2(g), are also believed to give $K_5Re(CN)_6$.[15]

The pentacyanonitrosylrhenate(3−) ion, $[Re(CN)_5(NO)]^{3-}$, can be prepared by the reaction of hydroxylamine hydrochloride, $KReO_4$ and KCN in alkaline solution.[15] This preparative procedure had previously (and presumably incorrectly) been described as affording $K_3[Re(CN)_7(NO)]\cdot 4H_2O$.[18] The diamagnetic, red crystalline trihydrate $K_3[Re(CN)_5(NO)]\cdot 3H_2O$ is formally a derivative of rhenium(I), with coordination from NO^+. Its vibrational spectrum (Raman and IR), with ν(NO) at $\sim 1650\,cm^{-1}$, has been assigned in terms of C_{4v} symmetry.[15]

While non-carbonyl-containing isocyanide complexes of rhenium(I) are discussed elsewhere,[6] some recent developments are worthy of note here. The multiply bonded dirhenium(III) complexes $Re_2(O_2CMe)_4Cl_2$ and $(Bu^n_4N)_2Re_2Cl_8$ are reductively cleaved by alkyl and aryl isocyanides under reflux conditions to give salts of the homoleptic $[Re(CNR)_6]^+$ (R = CMe_3 or C_6H_{11}) and $[Re(CNAr)_6]^+$ (Ar = phenyl, *p*-tolyl, 2,6-dimethylphenyl or 2,4,6-trimethylphenyl) cations.[19–21] Similar forcing reaction conditions can also be used in the formation of the same cations by reaction of the isocyanides with K_2ReX_6 (X = Br or I) and Re_3X_9 (X = Cl, Br or I).[22] Milder conditions (reaction in acetone at room temperature) lead to the conversion of K_2ReI_6 to $Re(CNAr)_5I$ (Ar = phenyl or 2,6-dimethylphenyl), complexes that react reversibly with I_2 to give the rhenium(I) derivatives $Re(CNAr)_5I_3$ that contain coordinated triiodide.[22] While $[Re(CNR)_6]^+$ is inert to substitution by monodentate tertiary phosphines, routes to species of the type $[Re(CNR)_4(PR_3)_2]^+$ are provided by (a) the reductive cleavage of the triply bonded complexes $Re_2Cl_4(PR_3)_4$ (PR_3 = PEt_3 or PPr^n_3) by RNC ligands or (b) the reductive elimination of H_2 from the polyhydride complexes $ReH_7(PR_3)_2$ (PR_3 = PPh_3 or $PEtPh_2$) or $ReH_5(PPh_3)_2(NH_2C_6H_{11})$.[19] These rhenium(I) species exhibit electrochemically reversible one-electron oxidations ($E_{1/2}$ = +0.6 to +0.8 V *vs.* SCE for the RNC complexes and +1.05 to +1.20 V *vs.* SCE for the ArNC complexes),[19,21] and can be oxidized by the halogens to give $[Re(CNR)_6X]^{2+}$ and $[Re(CNAr)_6X]^{2+}$ (X = Cl or Br).[19,21]

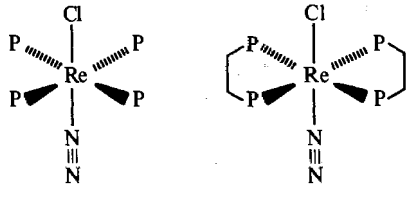
The reduction of $ReCl_4(THF)_2$ by Na/Hg in the presence of *t*-butyl isocyanide is a high yield route to $ReCl(CNBu^t)_5$.[23] The trimethylphosphine derivatives of this, $ReCl(CNBu^t)_2(PMe_3)_3$ and $ReCl(CNBu^t)_3(PMe_3)_2$, are prepared by the reaction of Bu^tNC with $ReCl(PMe_3)_5$ (see Section 43.3.3). Both have been shown by X-ray crystallography to have octahedral structures and are protonated by fluoroboric acid to give $[ReCl(CNBu^t)(CNHBu^t)(PMe_3)_3]BF_4$ and $[ReCl(CNBu^t)_2(CNHBu^t)(PMe_3)_2]BF_4$, respectively, in which the $CNHBu^t$ ligands are believed to be *trans* to the Re—Cl bonds.

The X-ray crystal structure of *trans*-$ReCl(CNBu^t)(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) as its tetrahydrofuran solvate has been reported,[574] and the Re—C≡N—C unit found to be close to linear. The preparation of *cis*- and *trans*-$[ReCl(CNMe)\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}p\text{-}CF_3)_2\}_2]$ has also been described.[575] They are prepared by reacting $ReCl\{(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}p\text{-}CF_3)_2\}_2$ with MeNC in THF at room temperature and reflux, respectively. The complexes *trans*-$[ReL_2(dppe)_2]BF_4$ (where L = CO or RNC, with R = Me, Bu^t, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, *p*-ClC_6H_4 or 2,6-$Cl_2C_6H_3$) have been prepared from the reaction of *trans*-$ReCl(N_2)(dppe)_2$ with L in THF in the presence of $TlBF_4$.[576]

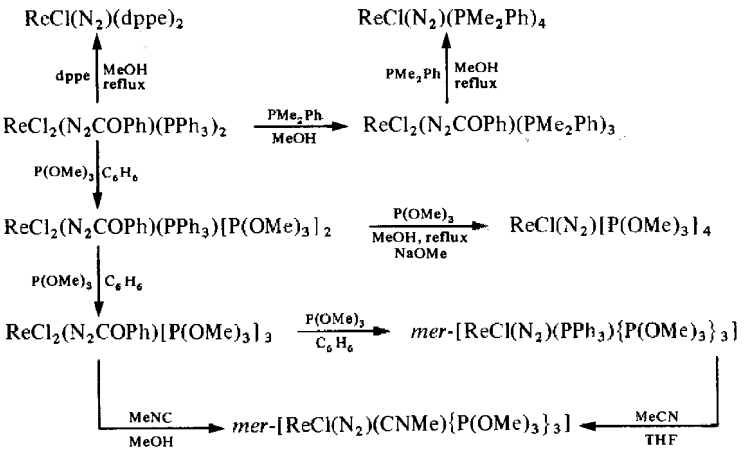
43.3.2 Mixed Dinitrogen–Phosphine Ligand Complexes

43.3.2.1 Mononuclear derivatives

The chelated benzoyldiazenido complex of rhenium(V), $ReCl_2(N_2COPh)(PPh_3)_2$, is the key compound for the preparation of a series of rhenium(I)–dinitrogen complexes.[11,24–26] It reacts with monodentate and bidentate phosphine donors to form yellow complexes of the types $ReCl(N_2)(PR_3)_4$, (PR_3 = PMe_2Ph, $PMePh_2$, Me_2NPF_2 or $PHPh_2$) and $ReCl(N_2)[Ph_2P(CH_2)_2PPh_2]_2$. Of these, the complexes $ReCl(N_2)(PMe_2Ph)_4$ (**1**) and $ReCl(N_2)(dppe)_2$ (**2**; dppe = 1,2-bis(diphenylphosphino)ethane) are by far the most important, the structure of (**1**) having been established by X-ray crystallography which demonstrated the presence of a terminally bound dinitrogen ligand.[27] Analogous derivatives with arsine ligands such as arphos (1-diphenylphosphino-2-diphenylarsinoethane) and the mixed phosphine–phosphite species $ReCl(N_2)L_2(PPh_3)_2$ (L = PF_3, PH_2Ph or $P(OCH_2)_3OMe$) and the tetrakisphosphito derivatives $ReCl(N_2)[P(OMe)_3]_4$ and $ReCl(N_2)(dmope)_2$ (dmope = $(MeO)_2PCH_2CH_2P(OMe)_2$) have also been prepared by this same general procedure, or variations thereof (Scheme 1).[24,25,28,29]

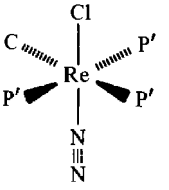


(1) P = PMe_2Ph (2) P⌒P = dppe



Scheme 1 Routes to some dinitrogen complexes of rhenium(I)

If the benzoylazo complex $ReCl_2(N_2COPh)(PPh_3)_2$ is first converted into the related organodiazenido derivatives $ReCl_2(N_2COPh)(PMe_2Ph)_3$, $ReCl_2(N_2COPh)[P(OMe)_3]_3$ or $ReCl_2(N_2COPh)(PPh_3)[P(OEt)_3]_2$,[25,29,30] then the latter Re^{III} species can be used as precursors to the mixed phosphine–phosphite complex $ReCl(N_2)(PMe_2Ph)_2[P(OMe_3)_2]_2$ and the methyl isocyanide complexes *mer*-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3]$ (**3**) and $ReCl(N_2)(CNMe)(PPh_3)[P(OEt_3)]_2$ (see Scheme 1). The structure of (**3**) shows it to be analogous to that of (**1**).[30] A listing of a selection of the more important dinitrogen complexes of rhenium(I) together with several of their of properties is given in Table 3. Other characterization studies have included ^{15}N NMR, X-ray photoelectron (ESCA) and low frequency vibrational spectroscopic measurements.[24,31–33]



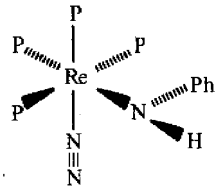
(**3**) P′ = $P(OMe)_3$; C = CNMe

An alternative route to a dinitrogen complex of rhenium(I) involves the Na/Hg reduction of THF solutions of the phenylimido complexes of Re^V, $Re(NPh)Cl_3(PPh_3)_2$ or $Re(NPh)Cl_3(PMe_3)_2$, under a nitrogen atmosphere in the presence of excess PMe_3.[34] This gives $Re(NHPh)(N_2)(PMe_3)_4$ (**4**), which has been shown by X-ray crystallography to have a structure containing a *cis* disposition of N_2 and NHPh ligands. The Na/Hg reduction of $ReCl_4(THF)_2$ in THF solutions of PEt_2Ph under

Table 3 Some Properties of Representative Dinitrogen Complexes of Rhenium(I)

Complex	*Color*	*ν(NN)*[a] (cm^{-1})	*Structural details*[b]	*Ref.*
$ReCl(N_2)(PMe_2Ph)_4$ (**1**)	Yellow	1925 ($CHCl_3$)	*r*(Re—N) = 1.97(2), *r*(N—N) = 1.06(3)[c]	25, 27
$ReCl(N_2)(dppe)_2$ (**2**)	Yellow	1980 ($CHCl_3$)		25
$ReCl(N_2)[P(OMe)_3]_4$	White	2103 (CH_2Cl_2)		29
$ReCl(N_2)(PMe_2Ph)_2[P(OMe)_3]_2$	Yellow	2000 (C_6H_6)		25
$ReCl(N_2)(CNMe)[P(OMe)_3]_3$ (**3**)	Yellow	2030 (N.S.)[d]	*r*(Re—N) = 1.98(1), *r*(N—N) = 1.04(2)	30
$Re(NHPh)(N_2)(PMe_3)_4$ (**4**)	Yellow	2000 (Nujol)	*r*(Re—N) = 1.955(13), *r*(N—N) = 1.10(2)	34
$ReH(N_2)(PEt_2Ph)_4$	Yellow	1945 (Nujol)	*r*(Re—N) = 2.055(5), *r*(N—N) = 1.018(8)	35
$ReH(N_2)(dppe)_2$	Yellow	2006 (Nujol)		36
$ReCl(N_2)(py)(PMe_2Ph)_3$	Orange	1905 (Nujol)		25
$Re(S_2CNEt_2)(N_2)(PMe_2Ph)_3$	Red	1945 (Nujol)		26
$Re(N_2)(PMe_2Ph)_3[PMe_2(C_6H_4)]$		2000 (Nujol)	*r*(Re—N) = 1.960(10), *r*(N—N) = 1.117(13)	38

[a] Medium given in parentheses; N.S. = not specified.
[b] Bond distances in Å.
[c] Disorder problem precluded a precise determination of this distance.
[d] ν(C≡N) of MeNC at 2140 cm^{-1}.



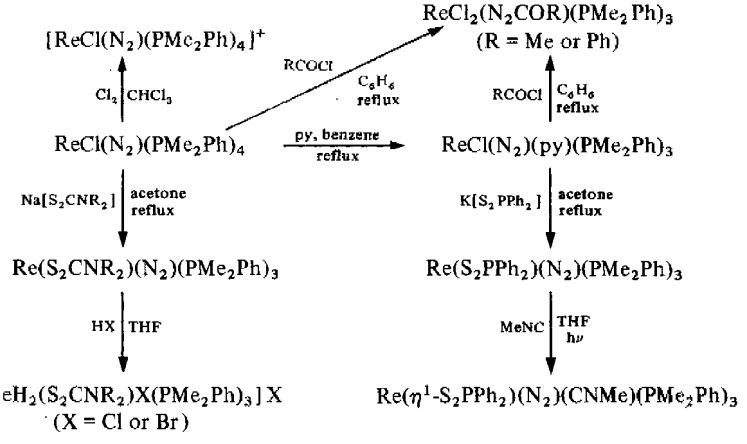
(4) P = PMe_3

an N_2(g) atmosphere gives a separable mixture of $ReH(N_2)(PEt_2Ph)_4$ and $ReCl(N_2)(PEt_2Ph)_4$.[35] The identity of the hydride derivative (for which ν(Re—H) = 1945 cm^{-1}) has been confirmed crystallographically (Table 3).

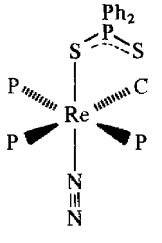
The hydrido species $ReH(N_2)(dppe)_2$ results from the reaction of $(Et_4N)_2ReH_9$ with dppe in propan-2-ol under an N_2 atmosphere.[36] An alternative preparation of this complex involves the reaction of N_2 with photogenerated coordinatively unsaturated $ReH(dppe)_2$.[37] This reaction can be reversed through the photo induced loss of N_2. Reaction of this complex with MeX (X = Br or I) gives $ReX(N_2)(dppe)_2$, while displacement of the N_2 ligand occurs upon its reaction with C_2H_4 and CO.[36] The properties of the hydride and phenylimido complexes resemble those of the other derivatives (Table 3).

An interesting and unusual route to a dinitrogen complex of rhenium(I) occurs upon reacting photogenerated $ReH_5(PMe_2Ph)_2$ and *t*-butylethylene in benzene under N_2. This yields the arene complex $(C_6H_6)Re(PMe_2Ph)(CH_2CH_2CMe_3)$ together with the *ortho*-metallated dinitrogen containing product *fac*-$Re(N_2)(PMe_2Ph)_3(PMe_2C_6H_4)$ (Table 3).[38]

Although the coordinated N_2 ligand in the Re^I derivatives has not yet been protonated or alkylated,[24] these complexes exhibit, nonetheless, an interesting reaction chemistry. The reactions of $ReCl(N_2)(PMe_2Ph)_4$ with pyridine ligands and bidentate monoanionic sulfur ligands proceed as shown in Scheme 2,[24–26] to give species in which the Re—N_2 unit is retained and which possess properties similar to those for the complexes listed in Table 3. Treatment of the dithiophosphinato complex $Re(\eta^2\text{-}S_2PPh_2)(N_2)(PMe_2Ph)_3$ with MeNC in THF under argon and tungsten filament light (Scheme 2) gave *mer*-$[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)_3$ (**5**) as yellow crystals [ν(CN) = 2100 cm^{-1}, $\nu(N_2)$ = 1980 cm^{-1}].[39] Its crystal structure shows Re—N and N—N bond lengths [1.83(1) and 1.13(1) Å, respectively] somewhat shorter and longer, respectively, than those of (**3**), a result which is in accord with differences in the values of the $\nu(N_2)$ modes [2030 cm^{-1} for (**3**) *versus* 1980 cm^{-1} for (**5**)].



Scheme 2 Some reactions of dinitrogen complexes of rhenium(I)



(5) P = PMe_2Ph; C = CNMe

Cationic complexes may be obtained *via* abstraction of Cl^- from $ReCl(N_2)(dppe)_2$ by $TlBF_4$ (equation 1) in the presence of CH_3CN or PhCN.[29] An interesting by-product in the reaction with benzonitrile is the non-dinitrogen containing product $[Re(NCPh)_2(dppe)_2]BF_4$ which was isolated in low yield as orange plates. Hydrido complexes of Re^{III} result upon protonation of $ReH(N_2)(dppe)_2$[36] and $Re(S_2CNR)(N_2)(PMe_2Ph)_3$[26] with acids such as HBF_4, HCl and HBr in non-aqueous media (Scheme 2). When $Re(NHPh)(N_2)(PMe_3)_4$ is treated with HBF_4/THF, the BF_4^- salt of $[Re(N_2)(PMe_3)_5]^+$ can be isolated.[35] This cation has also been isolated as its chloride salt upon reacting $ReCl(PMe_3)_5$ with N_2 in methanol ($\nu(N_2) = 2030\,cm^{-1}$ (Nujol)).[35] The N_2 ligand in $Re(NHPh)(N_2)(PMe_3)_4$ is lost upon reaction of this complex with I_2/benzene and CO_2/toluene; the complexes $[Re(NHPh)I(PMe_3)_4]I$ and $Re(NHPh)(\eta^2\text{-}CO_2)(PMe_3)_3$ are formed, respectively.[35]

The lability of the N_2 ligand towards alkyl and aryl isocyanides has been demonstrated by equation (2) which occurs readily with both alkyl and aryl isocyanides.[40] The resulting complexes are 'electron rich', the alkyl isocyanide derivatives $ReCl(CNR)(dppe)_2$ (R = Me or Bu^t) undergoing electrophilic attack upon treatment with HBF_4 to form the carbyne complexes *trans*-$[ReCl(CNHR)(dppe)_2]BF_4$.[41] Other noteworthy features of the series of complexes $ReCl(CNR)(dppe)_2$ and $ReCl(CNAr)(dppe)_2$, are the low value of $\nu(CN)$, the presence of a 'bent' M—CNR coordination mode, and their ease of oxidation (as measured by cyclic voltammetry) to the corresponding rhenium(II) monocations.[40]

$$ReCl(N_2)(dppe)_2 + TlBF_4 \xrightarrow{RCN} [Re(N_2)(NCR)(dppe)_2]BF_4 + TlCl \quad (1)$$

$$trans\text{-}ReCl(N_2)(dppe)_2 + RNC \longrightarrow trans\text{-}ReCl(CNR)(dppe)_2 + N_2 \quad (2)$$

Many of the dinitrogen complexes of Re^I have been found to undergo a reversible one-electron oxidation to the corresponding 17-electron Re^{II} cations ($E_{1/2}$ between +0.05 and −0.26 V *vs.* SCE in CH_2Cl_2/MeOH solution with $(Bu^n_4N)BF_4$ as supporting electrolyte).[11,24] Such an oxidation can be accomplished chemically using $Cl_2/CHCl_3$ (Scheme 2) and other oxidants to give paramagnetic purple or green salts of $[ReCl(N_2)(PMe_2Ph)_4]^+$ or $[ReCl(N_2)(dppe)_2]^+$. Other important reactions that lead to the oxidation of the metal center involve the formation of rhenium(III) acyl- and aroyl-diazenido complexes $[ReCl_2(N_2COR)(PMe_2Ph)_3]$ (R = Me or Ph) by the treatment of $ReCl(N_2)(py)(PMe_2Ph)_3$ or $ReCl(N_2)(PMe_2Ph)_4$ with RCOCl (Scheme 2).[24,42] On the basis of ^{15}N NMR spectroscopy,[43] the diazenido ligands in these complexes are suggested to be 'singly-bent', *i.e.* $M{=}{=}{=}N{\equiv}{\equiv}{\equiv}N\diagdown R$. The formation of $ReCl_2(N_2COR)(PMe_2Ph)_3$ by this procedure is especially noteworthy since it represents essentially the reverse of the original preparation of the N_2 complexes starting with $ReCl_2(N_2COPh)(PMe_2Ph)_3$. Attempts to acylate or aroylate $ReCl(N_2)(dppe)_2$ have not yet been successful.[24]

A wider range or complexes of the type $ReCl(N_2)(R_2PCH_2CH_2PR_2)_2$ have now been prepared by the reaction of rhenium(V) complex $ReCl_2(N_2COPh)(PPh_3)_2$ with the appropriate diphosphine ligand (R = Et, C_6H_{11}, Ph, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, *p*-ClC_6H_4 or *p*-$CF_3C_6H_4$).[575] The relationship between $E^{ox}_{1/2}$ (determined by cyclic voltammetry) and $\nu(N_2)$ for these complexes and others of this type has been examined.[575] The ^{15}N and ^{31}P NMR spectra of *trans*-$ReCl(N_2)(R_2PCH_2CH_2PR_2)_2$ (R = Ph or *m*-MeC_6H_4) and *trans*-$ReCl(N_2)(PMe_2Ph)_4$ are part of an extensive study of the NMR spectra of complexes that contain terminal dinitrogen ligands.[577] The treatment of *trans*-$ReCl(N_2)(dppe)_2$ with $PhC{\equiv}CCH_3$ in refluxing benzene or THF gives the η^2-phenylallene complex $ReCl(\eta^2\text{-}H_2C{-}C{=}CHPh)(dppe)_2$,[578] while terminal alkynes $HC{\equiv}CR$ (R = Et, Ph or CO_2Et) react to give the vinylidene complexes *trans*-$ReCl(C{=}CHR)(dppe)_2$.[579]

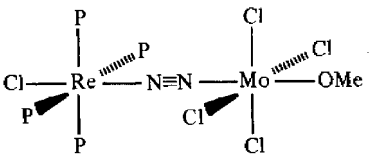
43.3.2.2 Mixed metal dinuclear and trinuclear derivatives

The complex $ReCl(N_2)(PMe_2Ph)_4$ (1) shows a remarkably strong tendency to react with other transition metal centers *via* its terminally bound dinitrogen ligand to give dinitrogen-bridged di- and tri-nuclear complexes.[24] A listing of these complexes, together with the preparative routes employed and certain of their properties, is given in Table 4. Two of these complexes, *viz.* (**6**) and (**7**) in Table 4, have been fully characterized structurally by X-ray crystallography, and shown to possess N—N bonds longer than those in the mononuclear complexes containing terminally bound dinitrogen (Table 3). Solution studies that have monitored the formation of adducts between $ReCl(N_2)(PMe_2Ph)_4$ and other Lewis bases (including several other Re^I—N_2 complexes) and the Lewis acids AlR_3 (R = Me, Ph or Cl), have demonstrated that this particular Re^I complex ranks high in

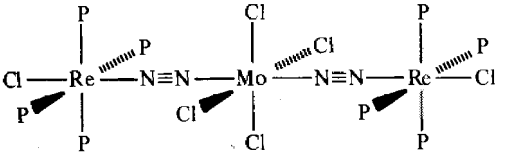
Table 4 Di- and Tri-nuclear Dinitrogen-bridged Complexes of Rhenium(I) with Transition Metals

Complex[a]	*Color*	*Preparation*[c]	$\nu(NN)$[d] (cm^{-1})	*Structural details*[e]	*Ref.*
$TiCl_4[(N_2)Re']_2$	Blue	(1) + $TiCl_4$ in CH_2Cl_2 or benzene	1800 (CH_2Cl_2)		44
$TiCl_4(THF)[(N_2)Re']$	Red	(1) + $TiCl_4$ in THF	1726 (CH_2Cl_2)		44
$Ti_2OCl_6(Et_2O)[(N_2)Re']$	Red-brown	(1) + $TiCl_4$ in C_6H_6/Et_2O	1635 (CH_2Cl_2)		44
$CrCl_3(THF)_2[(N_2)Re']$	Dark violet	(1) + $CrCl_3(THF)_3$ in CH_2Cl_2	1875 (CH_2Cl_2)		45
$MoCl_4(OMe)[(N_2)Re']$ (6)	Purple	(1) + $MoCl_4(THF)_2$ in CH_2Cl_2/MeOH	1660 (Nujol)	r(Re—N) = 1.82(2), r(Mo—N) = 1.90(1), r(N—N) = 1.18(3)	46, 47
$MoCl_4[(N_2)Re']_2$ (7)[b]	Green	(1) + $MoCl_4(PPh_3)_2$ in CH_2Cl_2	1800 (Nujol)	r(Re—N) = 1.75(4), r(Mo—N) = 1.99(4), r(N—N) = 1.28(5)	48

[a] $[(N_2)Re']$ is used as the abbreviation for $(N_2)ReCl(PMe_2Ph)_4$.
[b] Tungsten analogue prepared similarly (ref. 48).
[c] All preparations carried out at room temperature.
[d] Medium given in parentheses.
[e] Bond distance in Å.



(6) P = PMe_2Ph



(7) P = PMe_2Ph

$$ReCl(N_2)(PMe_2Ph)_4 + ReOCl_2X(PPh_3)_2 \rightleftharpoons ReOCl_2X(PPh_3)[(N_2)ReCl(PMe_2Ph)_4] + PPh_3 \quad (3)$$

X = Cl or OMe

the order of base strength; 1:1 adducts of $AlMe_3$ with $ReCl(N_2)(PMe_2Ph)_4$, $ReCl(N_2)(dppe)_2$ and $ReCl(N_2)(py)(PMe_2Ph)_3$ have been isolated.[49] Apparently, the greater the transfer of electron density from the metal into the π^* dinitrogen orbitals (*i.e.* the lower $\nu(N_2)$ is) the more basic the terminal nitrogen atom is. In the case of the interaction of $ReCl(N_2)(PMe_2Ph)_4$ with $ReOCl_3(PPh_3)_2$ and $ReOCl_2(OMe)(PPh_3)_2$,[36] an equilibrium (equation 3) is established in $CHCl_3$ with K_{eq} values of 0.28 ± 0.03 and 0.004 ± 0.002, respectively, at 27°C.

Following the establishment of the structure of (**7**), a detailed study of the bonding in this molecule has been conducted through a combined electronic, IR, Raman and resonance Raman spectral investigation.[51] The Raman-active $\nu(N_2)$ mode is found close to 1800 cm^{-1}, while ν(Re—N) is at ~680 cm^{-1}. The bonding in this complex can approximately be described in terms of Re=N=N=Mo.[51]

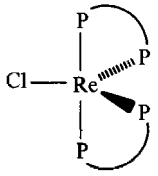
Dinitrogen-bridged complexes of *trans*-$ReCl(N_2)(PMe_2Ph)_4$ with $NbCl_5$ and $TaCl_5$ (1:1 adducts) and $ZrCl_4$ (2:1 adduct like $TiCl_4$) have been isolated.[579] The ^{15}N NMR spectra of these and other complexes of this type as well as dinitrogen complexes of rhenium(I) with the main group acceptor $AlMe_3$ have been studied.[580] Fenske–Hall MO calculations have been carried out on the molecule $[\{MoCl_4(OH)\}(\mu\text{-}N_2)\{ReCl(PH_3)_4\}]$.[581]

43.3.3 Other Phosphine Complexes

The sodium amalgam reduction under N_2 of $ReCl_4(THF)_2$ in THF containing an excess of PMe_3 affords the yellow chloride $ReCl(PMe_3)_5$ and the white hydride $ReH(PMe_3)_5$.[35] Both complexes are quite air stable and fairly reactive. The hydride can be hydrogenated to the trihydride $ReH_3(PMe_3)_4$, whereas the chloride $ReCl(PMe_3)_5$ can be methylated (using LiMe) to $ReMe(PMe_3)_5$. $ReCl(PMe_3)_5$ reacts directly with N_2 (in methanol) and CO (in diethyl ether) to form $[Re(N_2)(PMe_3)_5]Cl$ (see Section 43.3.2.1) and $ReCl(CO)_2(PMe_3)_3$, respectively.[35]

Although the Na/Hg reduction of $Re(NPh)Cl_3(PMe_3)_2$ in THF under N_2(g) in the presence of PMe_3 leads to $Re(NHPh)(N_2)(PMe_3)_4$ (see Section 43.3.2.1), a prolonged reaction time gives this complex as a minor product and the η^2-dimethylphosphinomethyl derivative $Re(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4$ as the major one.

Irradiation of $ReH_3(dppe)_2$ with 366 nm light leads to the reductive elimination of H_2 and the formation of $HRe(dppe)_2$ or a solvated derivative thereof.[37] This photoproduct reacts with, among other things, N_2 and CO_2, to form the complexes $ReH(N_2)(dppe)_2$ (see Section 43.3.2.1) and the formate $Re(O_2CH)(dppe)_2$. The $ReH(dppe)_2$ intermediate can also be trapped by CO, C_2H_4 and C_2H_2, and can undergo reversible intramolecular insertion into the C—H bonds of the phenyl groups of the dppe ligands.[37] Related chemistry can also be developed from $ReCl(N_2)(dppe)_2$ (and to a certain extent also from $ReCl(N_2)(PMe_2Ph)_4$) which upon irradiation in methanol generates $ReCl(dppe)_2$ (**8**).[52] Under these conditions, the reactive photogenerated $ReCl(dppe)_2$ reacts with the solvent to yield $ReCl(CO)(dppe)_2$ and $ReClH_2(dppe)_2$. The X-ray crystal structure of (**8**) has recently been reported[53] and found to be that of a trigonal bipyramid.

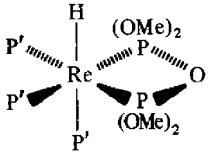


(8) P—P = dppe

The complex $[ReCl\{p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}p\text{-}CF_3)_2\}_2]$ is obtained in moderate yield from the reaction of $ReCl(N_2)(PMe_2Ph)_4$ with the diphosphine in refluxing toluene.[575]

43.3.4 Phosphite Complexes

Using the same synthetic procedures that produce the Re^0 derivative $Re_2[P(OMe)_3]_{10}$ (Section 43.2),[12,13] the monohydrido complex $HRe[P(OMe)_3]_5$ is often formed in low yield and is also generated, along with other products, upon photolyzing $Re_2[P(OMe)_3]_{10}$ in the presence of H_2. It has been characterized by ^1H NMR spectroscopy (C_7D_8, $\delta - 9.5$ as a quintet of doublets with $J(P—H)_{trans} = 12$ Hz and $J(P—H)_{cis} = 24$ Hz) and mass spectroscopy, but has otherwise been little studied. When solutions of $ReCl_5$ in THF are reacted with trimethyl phosphite for one day, the resulting solution stripped to dryness, treated with fresh $P(OMe)_3$, and then reduced with K/Hg, the complex $[(MeO)_3P]_5Re—O—P(OMe)_2$ can be isolated in low yield.[13] It is formally a derivative of Re^I and may be formed by loss of a CH_3 radical from the putative 19-electron intermediate $Re[P(OMe)_3]_6$. It reacts with MeI to give $[Re\{P(OMe)_3\}_6]^+I^-$. An additional hydridorhenium(I) phosphite complex that has been isolated, albeit in low yield, from the K/Hg reduction of higher valent rhenium species in the presence of $P(OMe)_3$ ligand, is $HRe[P(OMe)_3]_3[(MeO)_2P—O—P(OMe)_2]$ (**9**) containing the novel tetramethyl diphosphite ligand. This stereochemically rigid molecule (^1H NMR spectrum in C_7D_8 shows the Re—H resonance as a multiplet at $\delta - 8.8$) is believed to contain a four-membered MPOP ring.



(9) P' = $P(OMe)_3$

The triphenyl phosphite complex $ReCl[P(OPh)_3]_5$ is obtained as white crystals in high yield by the reaction of $P(OPh)_3$ with $ReCl_2(N_2COPh)(PPh_3)_2$ in benzene.[29] This reaction clearly proceeds in a fashion different from that found with $P(OMe)_3$, *viz.* the formation of $ReCl(N_2)[P(OMe)_3]_4$.

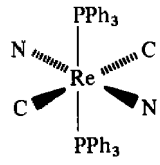
43.4 RHENIUM(II) COMPLEXES

The most extensive group of complexes that are known to have this oxidation state are the mixed halide–phosphine derivatives of the triply bonded Re_2^{4+} core, a moiety that possesses the electron-rich $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration (Table 2).[5]

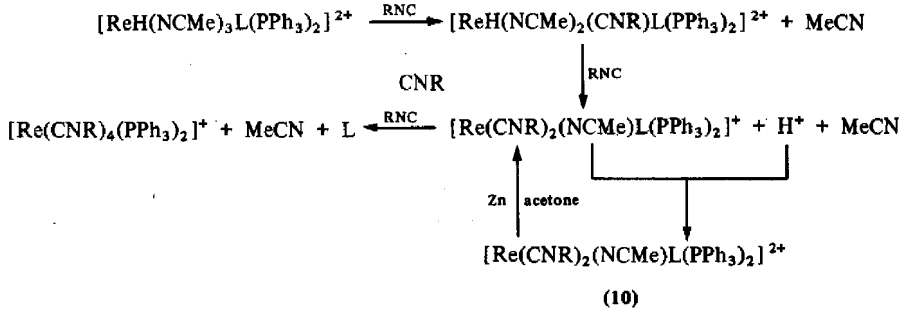
43.4.1 Mononuclear Complexes

43.4.1.1 Cyanide, alkyl isocyanides and aryl isocyanides

Early reports of cyano complexes of rhenium(II) of the types $[Re(CN)_6]^{4-}$ and $[Re(CN)_5]^{3-}$ could not be confirmed in a reinvestigation of the reactions that were said to lead to these products.[15] The only species definitively identified was the $[Re(CN)_7]^{4-}$ anion. Accordingly, the claim[54] that '$Ag_4[Re(CN)_6]$' can be methylated to give $[Re(CNMe)_6]^{2+}$ cannot now be supported. Indeed, solutions containing the authentic $[Re(CNR)_6]^{2+}$, $[Re(CNR)_4(PR_3)_2]^{2+}$ and $[Re(CNAr)_6]^{2+}$ cations (R = alkyl, Ar = aryl) can be generated electrochemically,[19,21] and do not appear to have properties that are in accord with those reported[54] for '$[Re(CNMe)_6]^{2+}$'. The rhenium(I) complexes $ReCl(CNR)(dppe)_2$ and $ReCl(CNAr)(dppe)_2$ also undergo a reversible electrochemical one-electron transfer to generate the corresponding monocations, but these latter species have not otherwise been characterized.[40] However, a series of quite stable, paramagnetic, mixed-ligand complexes of the type $[Re(CNR)_2(NCMe)L(PPh_3)_2](BF_4)_2$ (R = Pr^i or Bu^t, L = MeCN or py) have been prepared, and the crystal structure of $[Re(CNBu^t)_2(NCMe)_2(PPh_3)_2](BF_4)_2$ (**10**) has shown that it possesses the all-*trans* geometry.[55] Through an investigation of the reactions between RNC (R = Pr^i or Bu^t) and a range of monohydridorhenium(III) species $[ReH(NCMe)_3L(PPh_3)_2](BF_4)_2$ (L = MeCN, py, $C_6H_{11}NH_2$ or Bu^tNH_2), it was demonstrated that the sequence of reactions which involve the formation of (**10**) and other complexes of this type is as shown in Scheme 3. Note that these complexes are easily converted into their 18-electron rhenium(I) congeners, and are also formed



(10) C = CNR; N = NCMe



Scheme 3

from them upon treatment with acid and other mild oxidants.[55] Some properties of (**10**) and other mononuclear rhenium(II) species are given in Table 5.

Recent attempts[22] to repeat the preparations of compounds that have been formulated[6] as the rhenium(II) derivatives $Re_3I_6(CNCy)_3$ and $Re_3I_6(CNCy)_6$ (Cy = cyclohexyl) were unsuccessful. The reactions of K_2ReI_6 and Re_3I_9 with cyclohexyl isocyanide and other isocyanides give well-defined complexes of Re^I and Re^{III} only. Also, the existence of *trans*-$ReBr_2(CNCy)_4$ has not yet been confirmed, despite attempts to do so.[22]

43.4.1.2 Phosphines and arsines

Such complexes occur exclusively as derivatives of the rhenium(II) halides. The neutral, presumably octahedral, complexes $ReX_2(diars)_2$ and $ReX_2(qas)$ (X = Cl, Br or I; diars = *o*-phenylene(bisdimethylarsine); qas = tris(*o*-diphenylarsinophenyl)arsine) are formed by reduction of the corresponding cationic rhenium(III) species.[2] The species $ReX_2(tas)$ (X = Cl, Br or I; tas = bis(*o*-diphenylarsinophenyl)phenylarsine) are prepared similarly but may be five-coordinate.[2] The complex $ReCl_2(PMe_2Ph)_4$ and some of its properties have been described (including its ESCA spectrum and electrochemical properties),[11] but details of its preparation have not.

The paramagnetic complexes *trans*-$[ReCl(N_2)(dppe)_2]X$ (X = Cl^-, Br_3^-, I_3^-, ClO_4^-, BF_4^-, PF_6^-, $FeCl_4^-$ or $CuCl_2^-$) and *trans*-$[ReCl(N_2)(PMe_2Ph)_4]FeCl_4$ are prepared by oxidation of the rhenium(I) analogues using oxidizing transition metal salts such as $AgNO_3$, $FeCl_3$ or $CuCl_2$ in ethanol or, alternatively, a stoichiometric amount of halogen in chloroform.[25] These complexes, which exist in green or purple forms, can be oxidized further with concomitant loss of N_2. Typical properties are given in Table 5, where it can be seen that these complexes resemble other isoelectronic rhenium(II) complexes, including the carbonyl derivatives *trans*-$ReCl_2(CO)_2(PR_3)_2$.[6,56]

43.4.2 Dinuclear Complexes Containing the Re_2^{4+} and Re_2^{5+} Cores

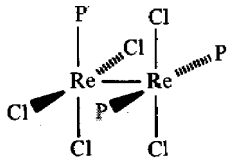
43.4.2.1 Monodentate phosphines

The most important complexes that possess these cores are those of stoichiometry $Re_2X_4(PR_3)_4$ (X = Cl, Br or I; PR_3 = PMe_3, PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph or PEt_2Ph).[5,56] They are best prepared by the reaction between monodentate tertiary phosphines and the salts $(Bu^n_4N)_2Re_2X_8$ (X = Cl, Br or I).[57–61] These reactions proceed in a stepwise fashion, first to give the unreduced substitution product $Re_2X_6(PR_3)_2$, and then $Re_2X_5(PR_3)_3$ (**11**), followed by $Re_2Cl_4(PR_3)_4$ (**12**). While most reactions with phosphines have been found to terminate at the stage $Re_2Cl_4(PR_3)_4$, in the case of PPh_3 the reaction does not proceed beyond $Re_2Cl_6(PPh_3)_2$. This may be due in part to the insolubility of the resulting

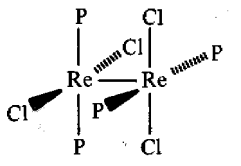
Table 5 Properties of Representative Mononuclear Rhenium(II) Species

Complex	*Color*	$E_{1/2}$ (V *vs* SCE)[b]	*ν(NN), ν(CN), or ν(CO)* (cm^{-1})[c]	μ_{eff} (BM)	*Electronic absorption spectra (nm)*[c]	*Ref.*
$[Re(CN\text{-}p\text{-}tol)_6]^{2+}$[a]	Dark blue	+1.06[d]	2130 (CH_2Cl_2)	N.M.	654, 596 (CH_2Cl_2)	21
trans-$[Re(CNBu^t)_2(NCMe)_2(PPh_3)_2](BF_4)_2$	Purple	+0.24[d]	2126 (Nujol)	1.2[e]	565 (CH_2Cl_2)	55
trans-$[ReCl(N_2)(dppe)_2]ClO_4$	Purple	+0.12[f]	2055 ($CHCl_3$)	g	590 (solid)	25
trans-$[ReCl_2(CO)_2(PPr^n_3)_2$	Green	—	1906 (C_6H_6)	2.1	650 (solid)	6

[a] Generated electrochemically.
[b] Value for the Re^{I} and Re^{II} couple.
[c] Medium given in parentheses.
[d] Measured in 0.2 M $(Bu^n_4N)PF_6$–CH_2Cl_2.
[e] Evans' method in dichloromethane.
[f] Measured in $(Bu^n_4N)BF_4$–CH_2Cl_2/MeOH.
[g] ESR active; $g = 1.64$ and 2.00 in $CHCl_3$ glass at 80K.



(11) P = PR_3



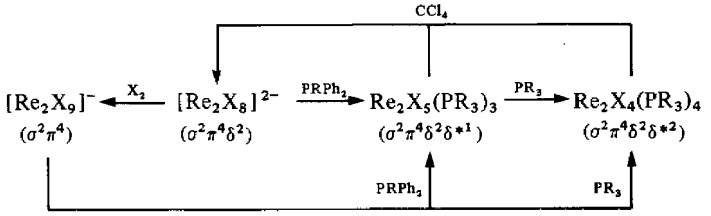
(12) P = PR_3

dirhenium(III) product in the reaction medium, although steric and/or electronic factors also dictate the course of this reaction.[56] The diphenylalkylphosphines $PRPh_2$, where R = Me or Et, give the 'mixed-valent' species $Re_2X_5(PRPh_2)_3$.[57] The extent of reduction (*i.e.* to Re_2^{5+} or Re_2^{4+}) is apparently dependent to a large extent upon the basicity of the phosphine. Thus, the addition of $NaBH_4$ to a reaction mixture containing $(Bu^n_4N)_2Re_2Cl_8$ and $PEtPh_2$ leads to further reduction to $Re_2Cl_4(PEtPh_2)_4$.[62]

While other methods have been used to form $Re_2X_4(PR_3)_4$ and $Re_2X_5(PR_3)_3$, (for example, the reductive cleavage by PR_3 of the Re_3X_9 clusters (X = Cl, Br or I) under reflux conditions[56]), these procedures are less convenient than the ones which utilize $(Bu^n_4N)_2Re_2X_8$. Those reactions between $(Bu^n_4N)_2Re_2X_8$ (X = Cl or Br) and phosphines that lead directly to the dirhenium(II) complexes $Re_2X_4(PR_3)_4$ are difficult to control so that they stop at the intermediate stage of reduction corresponding to $Re_2X_5(PR_3)_3$. However, quite simple methods exist for reoxidizing $Re_2X_4(PR_3)_4$ back to $Re_2X_5(PR_3)_3$.[56]

The X-ray crystal structures of two complexes of the type $Re_2Cl_4(PR_3)_4$ (**12**) (PR_3 = PEt_3 or PMe_2Ph), together with spectroscopic and magnetic studies on the paramagnetic $Re_2X_5(PR_3)_3$ (**11**) compound, have demonstrated that these two groups of complexes possess non-ligand bridged M_2L_8 eclipsed rotational geometries.

Relativistic Xα-SW calculations[5,63] on the hypothetical molecule $Re_2Cl_4(PH_3)_4$ and its monocation have shown that the two electrons in excess of those necessary to ensure a quadruple bond ($\sigma^2\pi^4\delta^2$ configuration) reside in the Re—Re δ^* orbital. The spectroscopic properties, redox behavior and general reaction chemistry of complexes of types (**11**) and (**12**) all serve to support this picture of the electronic structure.[5] Thus, they can be oxidized (both chemically and electrochemically) back to complexes of Re^{III} containing the Re_2^{6+} core. Refluxing CCl_4, oxidizes $Re_2Cl_4(PEt_3)_4$ to $[Et_3P\text{-}Cl]_2Re_2Cl_8$, while with the bromide analogue a mixture of $Re_2Cl_4Br_2(PEt_3)_2$ and $[Et_3PCl]_2Re_2Cl_4Br_4$ is produced.[57] Note that the salt $(Bu^n_4N)Re_2Cl_9$, which like other $[Re_2X_9]^-$-containing species can be formed by halogen (Cl_2 or Br_2) oxidation of $(Bu^n_4N)_2Re_2X_8$,[5] reacts with the phosphines PPh_3, $PEtPh_2$ and PEt_3 to give $Re_2Cl_6(PPh_3)_2$, $Re_2Cl_5(PEtPh_2)_3$ and $Re_2Cl_4(PEt_3)_4$, respectively.[64] The preceding redox results are summarized in Scheme 4.



Scheme 4 Chemical redox behavior of the Re_2^{n+} core

Although oxygen-free solutions of $Re_2X_4(PR_3)_4$ are quite stable, the presence of small amounts of oxygen can lead to the formation of species containing the Re_2^{5+} core.[63,65] In the case of the reaction between $Re_2Cl_4(PR_3)_4$ and O_2, it is believed that the $[Re_2Cl_4(PR_3)_4]^+$ cation is the dirhenium species that is formed initially, and that it is then converted into $Re_2Cl_5(PR_3)_3$ by scavenging chloride ion. This conclusion is supported by cyclic voltammetric studies[5,65] on solutions of $Re_2X_4(PR_3)_4$ (X = Cl, Br or I) in 0.2 M $(Bu^n_4N)PF_6$–CH_2Cl_2 which reveal that these complexes possess two one-electron oxidations that approach electrochemical reversibility. The first oxidation occurs at quite negative potentials (*e.g.* $E_{1/2} = -0.30$ V *vs.* SCE for $Re_2Cl_4(PMe_2Ph)_4$), thereby explaining the ease of oxidation to the monocation. In the presence of chloride ion, a series of coupled electrochemical–chemical reactions are possible for the chloro complexes as shown in Scheme 5. The difference between pathways *A* and *B* is the potential used for the oxidation of $Re_2Cl_4(PR_3)_4$ (*i.e.* +1.0 V in *A* and +0.5 V in *B*). It is also important to realize that either potential is sufficient to oxidize the first chemical product $Re_2Cl_5(PR_3)_3$ to its monocation $[Re_2Cl_5(PR_3)_3]^+$.

Note that both $Re_2Cl_5(PR_3)_3$ and $Re_2Cl_6(PR_3)_2$ have their own well-developed redox chemistry.[65] The former exhibits a one-electron oxidation in the neighborhood of +0.40 V *vs.* SCE and a one-electron reduction at $\simeq -0.7$ V *vs.* SCE. For the complexes $Re_2Cl_6(PR_3)_2$, a well-defined one-electron reduction to $[Re_2Cl_6(PR_3)_2]^-$ occurs very close to −0.05 V *vs.* SCE. In all instances, the species which may be generated electrochemically (*viz.* $[Re_2Cl_4(PR_3)_4]^+$, $[Re_2Cl_4(PR_3)_4]^{2+}$, $[Re_2Cl_5(PR_3)_3]^+$, $[Re_2Cl_5(PR_3)_3]^-$ or $[Re_2Cl_6(PR_3)_2]^-$) can be prepared chemically using $NO^+PF_6^-$ as the oxidant or cobaltocene as the reductant. By this mean the dirhenium cations can be isolated as their PF_6^- salts and the anions as their $[(\eta^5\text{-}C_5H_5)_2Co]^+$ salts.[65–67] These studies have included the isolation of the three complexes $Re_2Cl_4(PMe_2Ph)_4$, $[Re_2Cl_4(PMe_2Ph)_4]PF_6$ and $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$, and their X-ray structural characterization.[66] This has provided a series of three complexes possessing M—M bonds of order 4, 3.5 and 3 with identical sets of monodentate ligands. The Re—Re bond lengths change from 2.241(1) to 2.218(1) to 2.215(2) Å as the bond order increases from 3 to 3.5 to 4. All three complexes have the same basic eclipsed structure that characterizes all compounds of the type $Re_2X_4(PR_3)_4$ (**12**). The expected shortening of the bond occurs on going from $Re_2Cl_4(PMe_2Ph)_4$ to $[Re_2Cl_4(PMe_2Ph)_4]^+$, but there is no change between $[Re_2Cl_4(PMe_2Ph)_4]^+$ and $[Re_2Cl_4(PMe_2Ph)_4]^{2+}$. Any decrease expected on the basis of an increase in Re—Re bond order (from 3.5 to 4) is nullified by a second effect which apparently results in a lessening of the σ and/or π bonding. The latter change results from orbital contraction effects which accompany the increase in charge (*i.e.* from Re_2^{5+} to Re_2^{6+}).

(A) EECC Process

$$[Re_2Cl_4(PR_3)_4]^0 \xrightarrow{-e^-} [Re_2Cl_4(PR_3)_4]^+ \qquad E$$

$$[Re_2Cl_4(PR_3)_4]^+ \xrightarrow{-e^-} [Re_2Cl_4(PR_3)_4]^{2+} \qquad E$$

$$[Re_2Cl_4(PR_3)_4]^{2+} \xrightarrow{Cl^-} [Re_2Cl_5(PR_3)_3]^+ + PR_3 \qquad C_1$$

$$[Re_2Cl_5(PR_3)_3]^+ \xrightarrow{Cl^-} [Re_2Cl_6(PR_3)_2]^0 + PR_3 \qquad C_2$$

(B) ECEC Process

$$[Re_2Cl_4(PR_3)_4]^0 \xrightarrow{-e^-} [Re_2Cl_4(PR_3)_4]^+ \qquad E$$

$$[Re_2Cl_4(PR_3)_4]^+ \xrightarrow{Cl^-} [Re_2Cl_5(PR_3)_3]^0 + PR_3 \qquad C_1$$

$$[Re_2Cl_5(PR_3)_3] \xrightarrow{-e^-} [Re_2Cl_5(PR_3)_3]^+ \qquad E$$

$$[Re_2Cl_5(PR_3)_3]^+ \xrightarrow{Cl^-} [Re_2Cl_6(PR_3)_2]^0 + PR_3 \qquad C_2$$

Scheme 5 Coupled electrochemical–chemical processes for Re_2^{n+} species

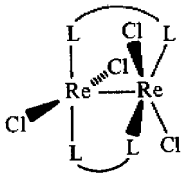
The use of cobaltocene has also been applied to the reduction of the dirhenium(III) carboxylates $Re_2(O_2CR)_4Cl_2$, where R = Pr, CMe_3 or Ph, to give the paramagnetc salts $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(O_2CR)_4Cl_2]$ which are derivatives of the Re_2^{5+} core.[67] These same anions have also been generated electrochemically.[68]

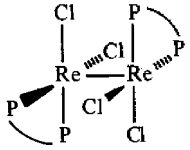
In addition to the rich redox chemistry that characterizes multiply bonded dirhenium complexes containing Re—Re bond orders of 4, 3.5 and 3, there are instances where facile Re—Re bond cleavage is encountered. Perhaps the best examples are those which involve reactions with π-acceptor ligands such as CO and RNC. Under such circumstances, the species $[Re_2Cl_4(PR_3)_4]^{n+}$, where $n = 0$, 1 or 2, react to form mononuclear complexes such as $ReCl_2(CO)_2(PR_3)_2$, $ReCl(CO)_3(PR_3)_2$ and $[Re(CNR)_4(PR_3)_2]^+$, the actual product isolated depending upon the starting material and choice of reaction conditions.[19,69] This is a reaction course that is encountered with many multiple bonded species containing M—M triple and quadruple bonds.[5]

43.4.2.2 Bidentate phosphines and arsines

Starting from $(Bu^n_4N)_2Re_2X_8$ (X = Cl, Br or I) or $Re_2X_4(PR_3)_4$, the dirhenium(II) complexes $Re_2X_4(LL)_2$ can be prepared[61,70] with the ligands LL = 1,2-bis(diphenylphosphino)ethane (dppe) or 1-diphenylphosphino-2-diphenylarsinoethane (arphos). The method that involves displacement of the PR_3 ligands from $Re_2Cl_4(PR_3)_4$ is the preferred synthetic procedure.[70] The spectroscopic properties of $Re_2X_4(LL)_2$ are in accord with these molecules possessing a structure in which the ligands

LL bridge the two metal centers. Because of the conformational demands of the resulting six-membered Re—Re—P—C—C—P and Re—Re—P—C—C—As rings, the rotational conformation about the Re—Re bond is expected to be staggered, a result which has been confirmed[71] by an X-ray crystal structure determination on the compound $Re_2Cl_4(dppe)_2$ (**13**). The mean torsional (rotational) angle is 39°, reflecting the absence of any inherent electronic barrier to rotation in a compound possessing the $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration. An example of a triply bonded $Re_2X_4(LL)_2$ complex has been encountered in which the two ligands LL each chelate to a single metal atom and the conformation is eclipsed; this occurs for LL = $Ph_2P(CH_2)_3PPh$ (**14**).[72] This complex is prepared in modest yield upon refluxing an acetonitrile solution containing $(Bu^n_4N)_2Re_2Cl_8$ and the bidentate phosphine ligand.



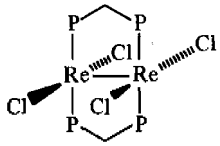


(13) L—L = dppe or arphos (14) P—P = $Ph_2P(CH_2)_3PPh_2$

Like the complexes $Re_2X_4(PR_3)_4$, the staggered species $Re_2X_4(LL)_2$, where LL = dppe or arphos and X = Cl, Br or I, exhibit two accessible one-electron oxidations.[73] These occur at $\simeq +0.25$ V and $\simeq +1.0$ V *vs.* SCE for solutions of these complexes in 0.2 M $(Bu^n_4N)PF_6$–CH_2Cl_2. The first process has been accomplished chemically using $NO^+PF_6^-$ as the oxidant to give paramagnetic, ESR-active $[Re_2Cl_4(LL)_2]PF_6$.

The chemistry of the dirhenium(II) complexes changes somewhat when the dppm ligand ($Ph_2PCH_2PPh_2$) is used. Although this bidentate phosphine can chelate, it shows a propensity for bridging two metal atoms. The complex $Re_2Cl_4(dppm)_2$ can be prepared by displacing the PPr^n_3 ligands in $Re_2Cl_4(PPr^n_3)_4$, although the use of $Re_2Cl_4(PEt_3)_4$ gives the mixed phosphine complex $Re_2Cl_4(PEt_3)_2(dppm)$.[70] Related procedures have been used to prepare $Re_2Cl_4(dppa)_2$ and $Re_2Cl_4(PMePh_2)_2(dppa)$ (dppa = bis(diphenylphosphino)amine).[74]

The bis-dppm complex can also be prepared, somewhat more conveniently, from the reaction between dppm and $Re_2Cl_6(PBu^n_3)_2$ in methanol, whereas the 'mixed-valent' species $Re_2Cl_5(dppm)_2$ results when diethyl ether is used as the reaction solvent.[74] While the structure of $Re_2Cl_4(dppm)_2$ (**15**) has not yet been determined crystallographically, there is little doubt that it contains two bridging dppm ligands in a *trans* disposition to each other. It exhibits, as expected, two one-electron oxidations ($E_{1/2} = +0.27$ V and $+0.80$ V *vs.* SCE).[74] When the electrolysis of dichloromethane solutions of $Re_2Cl_4(dppm)_2$ containing an excess of Cl^- is carried out at $+0.60$ V, the paramagnetic complex $Re_2Cl_5(dppm)_2$ is first formed, and this is in turn converted to $Re_2Cl_6(dppm)_2$, a complex that contains a Re—Re double bond (see Section 43.5.2.4). This conversion of $Re_2Cl_4(dppm)_2$ to higher oxidation state dirhenium species is represented in Scheme 6.



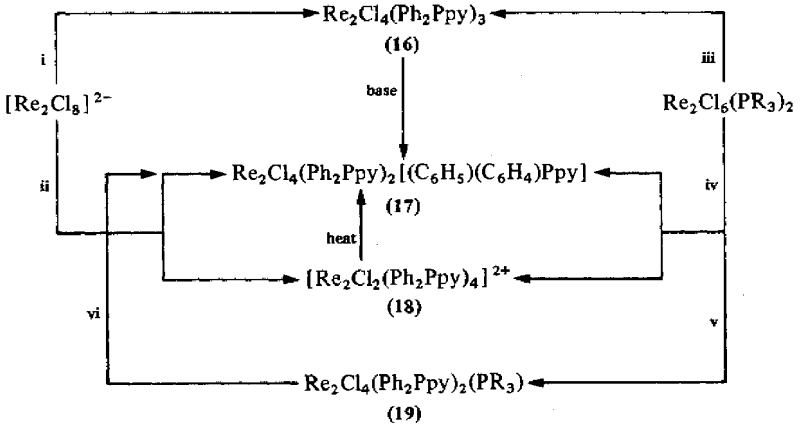
(15) P⌒P = dppm

$$Re_2Cl_4(dppm)_2 \xrightarrow{-e^-,\ +Cl^-} Re_2Cl_5(dppm)_2 \xrightarrow{-e^-,\ +Cl^-} Re_2Cl_6(dppm)_2$$

Configuration	$\sigma^2\pi^4\delta^2\delta^{*2}$	$\sigma^2\pi^4\delta^2\delta^{*1}$	$\sigma^2\pi^2\delta^2\delta^{*2}$
Bond order	3	3.5	2

Scheme 6 Coupled electrochemical–chemical reactions involving $Re_2Cl_4(dppm)_2$

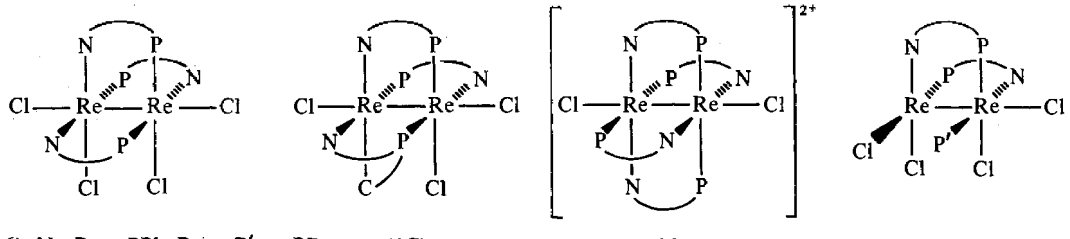
In the reactions between 2-(diphenylphosphino)pyridine (Ph_2Ppy) and the dirhenium(III) complexes $(Bu^n_4N)_2Re_2Cl_8$ and $Re_2Cl_6(PR_3)_2$ (R = Et or Bu^n), reduction takes place and several dark red-purple dirhenium(II) complexes can be isolated (Scheme 7).[75,76] The most noteworthy reaction is that between $(Bu^n_4N)_2Re_2Cl_8$ (or $Re_2Cl_6(PR_3)_2$) and Ph_2Ppy in methanol which first affords $Re_2Cl_4(Ph_2Ppy)_3$ (**16**); this complex in turn eliminates HCl in the presence of base to give the *ortho*-metallated complex $Re_2Cl_3(Ph_2Ppy)_2[Ph(C_6H_4)Ppy]$ (**17**). This complex has been subjected to an X-ray structure determination. Another product from this same reaction is the dirhenium(II) salt $[Re_2Cl_2(Ph_2Ppy)_4]Cl_2$, which contains four bridging Ph_2Ppy ligands. It can be metathesized with KPF_6 to give the salt $[Re_2Cl_2(Ph_2Ppy)_4](PF_6)_2$ (**18**), whose structure has been determned by X-ray crystallography. When acetone is used as the reaction solvent, $Re_2Cl_6(PR_3)_2$ reacts with Ph_2Ppy to give $Re_2Cl_4(Ph_2Ppy)_2(PR_3)$ (**19**) which can be converted into (**17**) upon reaction with one or two equivalents of Ph_2Ppy.[76]



i, MeOH, reflux, M:L = 1:⩽5; ii, MeOH, reflux, M:L = 1:⩾6;
iii, MeOH, reflux, M:L = 1:⩽3; iv, MeOH, reflux, M:L = 1:⩾4;
v, acetone, reflux, M:L = 1:6; vi, MeOH, reflux, M:L = 1:2.

Note: M represents the stoichiometry of the metal complex, L that of the Ph_2Ppy liqand

Scheme 7 Dirhenium(II) complexes of Ph_2Ppy

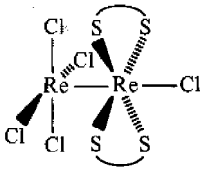


(16) N—P = PPh_2Ppy; P′ = PR_3 (17) (18) (19)

X-Ray crystal structures have now been carried out on the triply bonded complexes $Re_2Cl_4(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$) and α-$Re_2Cl_4(Me_2PCH_2CH_2PMe_2)_2$.[582] Studies have been made of the reactions between $Re_2Cl_4(dppm)_2$ and both CO and nitrile ligands; the metal–metal bonded complexes $Re_2(\mu\text{-Cl})(\mu\text{-dppm})_2Cl_3(CO)$,[583] $Re_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Cl_3(CO)$[583] and $[Re_2(\mu\text{-dppm})_2Cl_3(NCR)_2]X$ (X = Cl^- or PF_6^-; R = Me, Et, Ph or 4-PhC_6H_4)[584] have been isolated and characterized. The Re—Re bond is also retained in the reactions of $Re_2Cl_4(dppm)_2$ with isocyanide ligands from which 1:1 and 1:2 complexes have been isolated, *viz.* $Re_2Cl_4(dppm)_2(CNR)$ (R = Me, Bu^t or xylyl) and $[Re_2Cl_3(dppm)_2(CNBu^t)_2]PF_6$.[585] As a by-product of the reaction between $Re_2Cl_4(dppm)_2$ and two equivalents of Bu^tNC, the novel paramagnetic μ-iminyl dirhenium(II,III) complex $[Re_2(\mu\text{-Cl})(\mu\text{-C=NHBu}^t)(\mu\text{-dppm})_2Cl_2(CNBu^t)_2]PF_6$ has been isolated.[586] The chemical oxidation of $[Re_2Cl_3(dppm)_2(NCR)_2]PF_6$ to $[Re_2Cl_3(dppm)_2(NCR)_2](PF_6)_2$ can be accomplished using $NOPF_6$,[587] and this same reagent converts $Re_2Cl_4(dppm)_2(CNR)$ to its monocation.[585] The complexes $[Re_2X_3(LL)_2L']^{n+}$ (n = 1 or 2; X = Cl or Br; LL = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2CH_2AsPh_2$; L′ = nitrile or isocyanide ligand) have also been prepared and characterized.[588]

43.4.2.3 Sulfur ligands

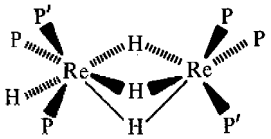
There are two compounds which fall into this category, *viz.* $Re_2Cl_5(DTH)_2$ and $[ReBr_2(DTH)]_n$ (DTH = 2,5-dithiahexane). Both are prepared by reaction of the appropriate $(Bu^n_4N)_2Re_2X_8$ salt with DTH in refluxing acetonitrile.[5] The structure of the bromide complex is unknown, although *n* is probably 2. In the case of $Re_2Cl_5(DTH)_2$ (**20**), this paramagnetic air-stable complex can be isolated as beautiful red-black dichroic crystals and its X-ray crystal structure shows that it possesses a staggered rotational conformation in which the two rhenium atoms are in quite dissimilar environments.[77] Formally, at least, it can be considered as the 'zwitterion' $Cl(DTH)_2Re^{II}Re^{III}Cl_4$.



(20) S—S = DTH

43.4.2.4 Hydrides

The reaction of two equivalents of the phosphite ligand $P(OCH_2)_3CEt$ (abbreviated P′) with the dirhenium(IV) hydride $Re_2H_8(PMe_2Ph)_4$ in benzene produces cleanly the complex $Re_2H_4(PMe_2Ph)_4P'_2$ (**21**), the unusual unsymmetric structure of which has been established by an X-ray crystal structure determination.[78] The two metal atoms have different coordination numbers and different formal oxidation states. Protonation of this complex with excess $HBF_4 \cdot Et_2O$ in benzene at room temperature gives the dirhenium(III) hydride $[Re_2H_5(PMe_2Ph)_4P'_2]BF_4$. Consistent with the fact that (**21**) has no symmetry, four Re—H resonances are seen in the ^1H NMR spectra at $-48°C$; by $+57°C$ these have coalesced to a single broad resonance implying that hydride migration to all four environments occurs.[79]



(21) P = PMe_2Ph; P′ = $P(OCH_2)_3CEt$

43.4.3 Trinuclear Complexes

The trinuclear rhenium(III) cluster halides Re_3X_9 (X = Cl or Br) react with many Lewis bases to form adducts of the type $Re_3X_9L_n$, where $n = 2$ or 3.[5] However, in the case of reactions with pyridine and related tertiary amines, reduction to the dark green-black trinuclear rhenium(II) complexes $[Re_3X_6L_3]_n$ occurs quite readily.[79,80] The three-electron reduction of the Re_3^{9+} cluster unit to give Re_3^{6+} is in accord with current ideas[81] concerning the electronic structures of these species. These reactions proceed *via* the unreduced adducts $Re_3X_9L_3$, but whether reduction does or does not occur depends upon the nature of X and L. The more basic amines (pK_a values > 4.9), *i.e.* pyridine, 3- and 4-methylpyridine, isoquinoline, 2-methylquinoline and benzimidazole, reduce Re_3Cl_9 to $[Re_3Cl_6L_3]_n$, while the relatively weak bases pyrazine, 2,6-dimethylpyrazine and 3-chloropyridine (pK_a values < 3) give the dark red-purple unreduced adducts $Re_3Cl_9L_3$. In the case of 2-methylpyridine, 2-vinylpyridine, 2,6-lutidine and quinoline, materials of 'intermediate' composition, approximating to $[Re_3Cl_7L_2]_n$, are produced. These phases correspond to a two-electron reduction of the Re_3^{9+} core.[5] A similar situation to that described above pertains to Re_3Br_9, but in this instance the more readily reducible bromide cluster is also reduced (to $[Re_3Br_6L_3]_n$) by the weak base 3-chloropyridine.[80] Based upon a consideration of the electronic absorption and ESCA spectral properties of the complexes $[Re_3X_6L_3]_n$, and their conversion to the rhenium(III) salts $(amineH)_2Re_3X_{11}$, it has been suggested[5] that they possess a halogen-bridged 'polymer of trimers' structure.

A variation in the nature of the reaction products that are formed by the amine reductions of Re_3Cl_9 is encountered in the case of acridine. The dark green salt $(AcrH)_2Re_3Cl_8$ is produced rather

than the adduct $[Re_3Cl_6(Acr)_3]_n$,[82] a noteworthy result since this complex contains the only known chloroanion of rhenium(II).

The reactions of Re_3X_9 (X = Cl or Br) with 2,2′-bipyridyl, 1,10-phenanthroline and 2,2′,2″-terpyridyl in acetone produce dark purple insoluble solids whose properties are in accord with the stoichiometry $(amineH)_xRe_3Cl_9(amine)_y$, in which the formal oxidation state of the rhenium is $+(3-x)$. The degree of reduction depends upon the reaction conditions that are used.[5]

43.5 RHENIUM(III) COMPLEXES

Most complexes of this oxidation state are derivatives of the rhenium(III) halides. They are classified according to the other ligands (if any) that are present. For example, $ReCl_3(PR_3)_3$ will be found under 'phosphine complexes' rather than 'halide complexes'. Mononuclear complexes of rhenium(III) are mostly of the types $[ReX_2L_4]^+$ and ReX_3L_3, but rarely $[ReX_4L_2]^-$. Additionally, two very important classes of complexes exist that are derivatives of the quadruply bonded dinuclear $[Re_2X_8]^{2-}$ and doubly bonded trinuclear $[Re_3X_{12}]^{3-}$ anions (X = Cl, Br or I).[1]

43.5.1 Mononuclear Complexes

43.5.1.1 Cyanide, alkyl isocyanides and aryl isocyanides

The best characterized cyanide complex of rhenium(III) is $K_4Re(CN)_7 \cdot 2H_2O$. It can be prepared as pale-yellow crystals through a variety of reactions between KCN and K_2ReX_6 (X = Cl or I), Re_3Cl_9 or $KReO_4$ in both aqueous and non-aqueous media.[15] The mixed salt $NaK_3Re(CN)_7 \cdot 3H_2O$ can be formed when NaCN is used in place of KCN. The $[Re(CN)_7]^{4-}$ anion is now known to be the product, often admixed with other well-defined higher oxidation state cyano rhenium species, in reactions that have previously been described as giving $[Re(CN)_6]^{4-}$, $[Re(CN)_5]^{3-}$, $[Re(CN)_6]^{3-}$, $[Re(CN)_6]^-$ and $[Re(CN)_8]^{3-}$. Indeed, there remains to be definitive structural proof that any of these latter anions have been isolated in a pure state, although there is no good reason to believe that such species cannot be prepared. For example, the X-ray powder pattern of the complex purported to be '$K_3Re(CN)_8 \cdot H_2O$'[83] resembles closely that of $K_4Re(CN)_7 \cdot 2H_2O$. The X-ray crystal structure of $K_4Re(CN)_7 \cdot 2H_2O$ shows[84] that this complex contains a pentagonal bipyramidal anion, with $r(Re—C_{ax}) = 2.077(3)$ Å and $r(Re—C_{eq}) = 2.095(5)$ Å, and is isostructural with $K_4V(CN)_7 \cdot 2H_2O$. This structural result confirms the conclusions based upon vibrational spectroscopic studies[15,85] that this geometry holds for $[Re(CN)_7]^{4-}$ in aqueous solution, as well as solid $K_4Re(CN)_7 \cdot 2H_2O$. The diamagnetism of this potassium salt is in accord with the presence of a low-spin d^4 configuration.

The following characterized isocyanide complexes of rhenium(III) are described elsewhere: $ReCl_3(CNMe)(PPh_3)_2$, $ReCl_3(CNMe)(dppe)$, $ReCl_3(CNMe)_3(PPh_3)$, $[ReCl_2(CNMe)_4(PPh_3)]^+$, $ReBr_3(CNMe)_4$ and $ReBr_3(CN\text{-}p\text{-}tol)_4$.[6] A recent attempt to isolate $ReBr_3(CN\text{-}p\text{-}tol)_3$, through the reaction of K_2ReBr_6 with *p*-tolNC in ethanol,[6] gave a material with the appropriate microanalytical data, color and IR spectroscopic properties, but it is by no means certain that this is the correct structural formulation.[22] The reaction between K_2ReI_6 and Bu^tNC in ethanol at room temperature gives golden-brown crystals of $[Re(CNBu^t)_5I_2]I_3$.[22] The related seven-coordinate chloride and bromide derivatives, $[Re(CNBu^t)_5X_2]PF_6$ (X = Cl or Br), are formed by the non-reductive cleavage of quadruply bonded $(Bu^n_4N)_2Re_2X_8$ upon their reaction with Bu^tNC in methanol.[19] The mixed isocyanide–halide–phosphine complexes of rhenium(III), $[Re(CNBu^t)_4(PEtPh_2)Cl_2]PF_6$ and $[Re(CNBu^t)_3(dppe)Cl_2]PF_6$, are likewise prepared by isocyanide cleavage of $Re_2Cl_6(PEtPh_2)_2$ or dimeric $Re_2Cl_6(dppe)_2$ (the latter containing $Re(\mu\text{-}Cl)_2Re$ bridges but no Re—Re bond).[19] These complexes show IR active $\nu(C{\equiv}N)$ modes (at $\sim 2200\,cm^{-1}$) that are in accord with them being derivatives of Re^{III}. The halogen (Cl_2, Br_2 or I_2) oxidation of $[Re(CNBu^t)_6]PF_6$ and $[Re(CNPh)_6]PF_6$ in chlorocarbon or acetone solvents in the presence of KPF_6, gives the salts $[Re(CNBu^t)_6X](PF_6)_2$ (X = Cl, Br or I) and $[Re(CNPh)_6X](PF_6)_2$ (X = Cl or Br).[19,21] Cyclic voltammetric studies have demonstrated that these complexes are quite easily reduced back to the parent rhenium(I) cations, the ease of reduction being I > Br > Cl and PhNC > Bu^tNC.[19,21]

When the reactions between various aryl isocyanides ArNC and $(Bu^n_4N)_2Re_2Cl_8$ are carrried out in methanol at room temperature, then rhenium(III)-containing complexes of the types $[Re(CNAr)_6]^+[ReCl_4(CNAr)_2]^-$ and $ReCl_3(CNAr)_3$ can be isolated.[21] These compounds display well-defined electrochemistry (cyclic voltammetry) in 0.2 M $(Bu^n_4N)PF_6$–CH_2Cl_2, the mononuclear Re^{III}

species displaying the redox processes

$$Re^{IV} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Re^{III} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Re^{II}$$

Characterization of the salts $[Re(CNAr)_6]^+[ReCl_4(CNAr)_2]^-$ has shown that freshly prepared samples contain the *trans* anion, but that CH_2Cl_2 solutions slowly isomerize to the corresponding *cis* isomer. The ^1H NMR spectra of these same salts reveal substantial Knight shifts associated with the paramagnetic d^4 $[ReCl_4(CNAr)_2]^-$ anions.[21] The properties of $[ReCl_4(CNAr)_2]^-$ resemble those for the nitrile analogues $[ReCl_4(NCR)_2]^-$ described in Section 43.5.1.5.

43.5.1.2 Amines, N-heterocycles and amido ligands

There are few simple complexes that contain two or more of these ligands bound to a single Re^{III} center. There are, on the other hand, a variety of mixed ligand complexes where one of these ligands is present.[1] Red-brown crystalline $ReCl_3(py)_3$ is prepared by the reaction between $ReCl_3$(benzil)(PPh_3) and pyridine, while with $ReCl_3(NCMe)(PPh_3)_2$ as the starting material, orange-brown $ReCl_3(py)_2(PPh_3)$ is produced.[86] A similar reaction between $ReCl_3(NCMe)(PPh_3)_2$ and 2,2′-bipyridyl in mixed dichloromethane–benzene solvent gives green crystalline $ReCl_3$-(bipy)(PPh_3).[86] The dark green complex $ReBr_3(NH_2$-*p*-tol$)_3$ is apparently the product from the reaction of *p*-toluidine with K_2ReBr_6.[22]

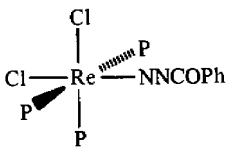
The rhenium(I) complex $Re(NHPh)(N_2)(PMe_3)_4$, which is prepared by the Na/Hg reduction of $Re(NPh)Cl_3(PMe_3)_2$ under an N_2(g) atmosphere,[34] reacts with I_2 to give $[Re(NHPh)I(PMe_3)_4]I$.[35] This constitutes a quite rare example of an amido complex of Re^{III} (see also Section 43.5.1.8).

Deprotonation of the rhenium(V) alkylimido (*i.e.* nitrene) complexes *trans*-$ReCl_3(NMe)(PRPh_2)_2$ and *trans*-$ReCl_3(NMe)(PMe_2Ph)_2$, using pyridine and PMe_2Ph/NEt_3 mixtures, respectively, gives the methyleneamido complexes of rhenium(III), $ReCl_2(N{=}CH_2)(py)(PRPh_2)_2$ (R = Me, Et or Ph) and $ReCl_2(N{=}CH_2)(PMe_2Ph)_3$.[1]

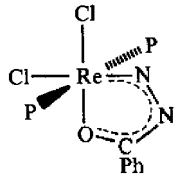
New methods for obtaining 2,2′-bipyridyl complexes of the types *fac*-$Re(bipy)(PR_3)Cl_3$ and *trans, cis*-$[Re(bipy)(PR_3)_2Cl_2]^+$ have been described.[589] The electrochemical and spectroscopic properties of these complexes have been measured.

43.5.1.3 Dinitrogen, diazenido and triazenido ligands

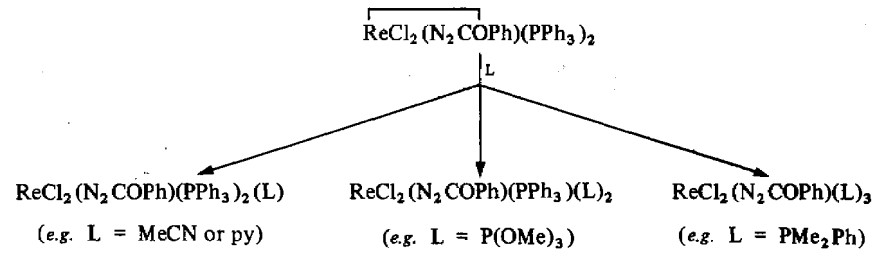
Dinitrogen complexes of rhenium(III) are rare while those of rhenium(I) are comparatively common (Section 43.3.2.1). The mixed hydride–dinitrogen complex $[ReH_2(N_2)(dppe)_2]BF_4$ is mentioned in Section 43.5.1.8. The reactions by which the rhenium(III) acyl- and aroyl-diazenido complexes $ReCl_2(N_2COR)(PMe_2Ph)_3$ (R = Me or Ph) can be formed by treatment of the rhenium(I) complexes $ReCl(N_2)(PMe_2Ph)_4$ and $ReCl(N_2)(py)(PMe_2Ph)_3$ with RCOCl have been described in Section 43.3.2.1 (see Scheme 2). These complexes display a ν(CO) mode at $\sim 1620\,cm^{-1}$ and ν(NN) at $1505\,cm^{-1}$.[42] The complex $ReCl_2(N_2COPh)(PMe_2Ph)_3$ (**22**) has also been prepared by reacting $ReCl_2(N_2COPh)(PPh_3)_2$ (**23**) with excess PMe_2Ph. This is one example of a more general type of reaction where (**23**) reacts with various ligands (MeCN, py, phosphites and other phosphines)[29,87] to give the products that are shown in Scheme 8. Further reaction with some of these same nucleophiles can give dinitrogen complexes of Re^I (see Section 43.3.2.1). An X-ray structure determination on complex (**22**) supports its formulation as a derivative of Re^{III}.[88] On the other hand, the green crystalline triphenylphosphine complex (**23**), which is prepared by the reaction of $ReOCl_3(PPh_3)_2$ with monobenzoylhydrazine and dibenzoylhydrazine in benzene–ethanol in the presence of hydrochloric acid, can be described formally as a derivative of Re^V or Re^{III}. The same is true for other complexes of this type that have been prepared by a similar procedure.[87] However,



(22) P = PMe_2Ph



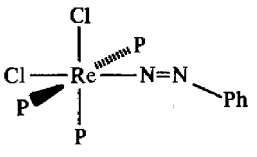
(23) P = PPh_3



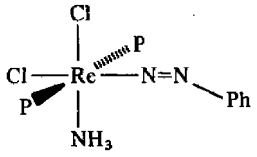
Scheme 8

while ν(CO) and ν(NN) modes have not been assigned in the IR spectra of these complexes, the ESCA spectrum of (**23**) has been interpreted in terms of its formulation as a derivative of Re^{III}.[89] In this event, the conversion of (**23**) to (**22**) constitutes a non-redox ligand substitution process.

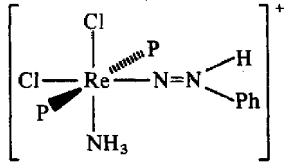
When *mer*-$ReX_3(PMe_2Ph)_3$ (X = Cl, Br or I) is heated with phenylhydrazine in ethanol, a mixture of the phenyldiazenido complexes $ReX_2(N_2Ph)(PMe_2Ph)_3$ (**24**) and $ReCl_2(N_2Ph)(NH_3)(PMe_2Ph)_2$ (**25**) is produced.[88,90] The X-ray crystal structure of (**24**), when X = Cl, has confirmed its identity (r(Re—N) = 1.77(2) Å; r(N—N) = 1.23(2) Å),[91] and (**25**) is believed to have a very similar structure. The NH_3 ligand of (**25**) is easily displaced by CO, PMe_2Ph or PEt_2Ph, but not by MeCN, MeNC, py or PPh_3.[88,90] Reversible protonation of (**25**) can be achieved using HCl or HBr to give the salts $[ReCl_2(NNHPh)(NH_3)(PMe_2Ph)_2]X$. Structural studies on the bromide salt of (**26**) have shown that protonation occurs at the second nitrogen atom.[88,90]



(**24**) P = PMe_2Ph



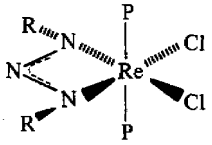
(**25**) P = PMe_2Ph



(**26**) P = PMe_2Ph

The compound $ReOCl_3(PPh_3)_2$ reacts, in the presence of PPh_3, with the lithium salts $Li(RN_3R)$ (R = Ph, *p*-MeC_6H_4, *p*-FC_6H_4 or *p*-ClC_6H_4) in boiling THF to yield the mononuclear, paramagnetic Re^{III} complexes $ReCl_2(RN_3R)(PPh_3)_2$. The reaction is believed to proceed as shown in equation (4).[92] The X-ray crystal structure of the derivative where R = *p*-MeC_6H_4 (**27**) shows the presence of chelating triazenido ligands. These complexes display the distinctive Knight-shifted ^1H NMR spectra that characterize paramagnetic mononuclear Re^{III} species.[92]

$$ReOCl_3(PPh_3)_2 + PPh_3 + Li(RN{=}{=}{=}N{=}{=}{=}NR) \longrightarrow ReCl_2(R_2N_3)(PPh_3)_2 + Ph_3PO + LiCl \quad (4)$$



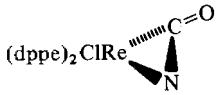
(**27**) P = PPh_3; R = *p*-tol

The syntheses and X-ray crystal structures of the diazenido complexes $Re(SCH_2CH_2SCH_2CH_2CH_2SCH_2CH_2S)(PPh_3)(N_2COPh)$[590] and $(Et_3NH)[Re_2(N_2Ph)_2(SPh)_7]$[591] have been published. The complex $ReCl(N_2Ph)_2(PPh_3)_2$ is formed by the reaction of $ReOCl_3(PPh_3)_2$ with excess phenylhydrazine in methanol,[591] or with Me_3SiN_2Ph in dichloromethane.[592] The bromo analogue can be made in an analogous fashion.[592] They react with excess HX in methanol to give the hydrazido(2−) ligand complex $ReX_2(NNHPh)(N_2)(PPh_3)_2$.[592]

43.5.1.4 Cyanate and thiocyanate

The isocyanate complex $ReCl(MeNCO)(dppe)_2$ (**28**), which has been formulated as a complex of Re^{III}, is prepared by a sequence of reactions that first involves the formation of the orange methyl

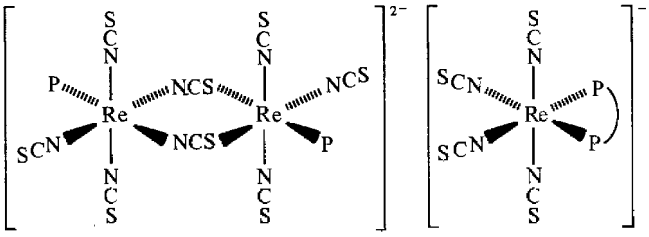
isocyanide complex $ReCl_3(CNMe)(PPh_3)_2$, from the reaction of a mixture of PPh_3 and $ReOCl_3(PPh_3)_2$ with MeNC, followed by its conversion, *via* a ligand-exchange reaction, to paramagnetic $ReCl_3(CNMe)(dppe)$ (μ_{eff} = 1.91 BM), and subsequent hydrolysis–deprotonation.



(28)

Electrochemical studies have shown that in non-aqueous media (MeCN or CH_2Cl_2), the $[Re(NCS)_6]^{2-}$ anion possesses a very accessible and quite reversible one-electron reduction ($E_{1/2}$ between −0.1 and −0.3 V depending upon solvent, *etc.*).[94,95] This result has led to the design of a procedure for the reduction of $(Bu^n_4N)_2Re(NCS)_6$ to pale yellow crystalline $(Bu^n_4N)_3Re(NCS)_6$ using $N_2H_4 \cdot H_2O$ as the reductant.[96] The resulting complex is extremely air sensitive in both the solid state and in solution, reverting to the stable $[Re(NCS)_6]^{2-}$ anion.

In contrast to the instability of $[Re(NCS)_6]^{3-}$, a variety of quite stable mixed ligand complexes are known.[94,97] The reactions of the quadruply bonded dirhenium(III) salt $(Bu^n_4N)_2Re_2(NCS)_8$ with monodentate and bidentate tertiary phosphines (PPr^n_3, PEt_2Ph, PPh_3, dppm and dppe) produce the green complexes $(Bu^n_4N)_2Re_2(NCS)_8L_2$ which contain dimeric thiocyanate-bridged anions (**29**) with magnetically dilute Re^{III} centers.[97] In the case of the dppm and dppe complexes, these phosphine ligands are believed to be bound in a monodentate fashion. These two complexes are unstable in acetonitrile solutions due to rapid intramolecular attack of the unbound 'dangling' tertiary phosphine groups upon the thiocyanate bridges. This leads to the formation of the yellow monomeric anions $[Re(NCS)_4(dppm)]^-$ and $[Re(NCS)_4(dppe)]^-$ (**30**). The orange-brown mononuclear complex $(Bu^n_4N)Re(NCS)_4(PEt_3)_2$ is formed by the reaction of $(Bu^n_4N)_2Re_2(NCS)_8$ with PEt_3, *via* the green intermediate $(Bu^n_4N)_2Re_2(NCS)_8(PEt_3)_2$.[97]



(29)

(30) P—P = dppm or dppe

Upon reacting $(Bu^n_4N)_2Re_2(NCS)_8(PEt_2Ph)_2$ (**29**; P = PEt_2Ph) with the bidentates dppe, bipy and phen, the paramagnetic mononuclear complexes $Re(NCS)_3(PEt_2Ph)$(bidentate) are formed.[97] These complexes display three electrochemically reversible one-electron waves in their cyclic voltammograms (recorded in 0.2 M $(Bu^n_4N)PF_6$–CH_2Cl_2) attributable to the processes

$$[Re]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Re]^0 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Re]^- \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Re]^{2-}$$

([Re] represents the complex).[94] The X-ray crystal structure of the dppe derivative has confirmed that these compounds possess distorted octahedral structures.[94]

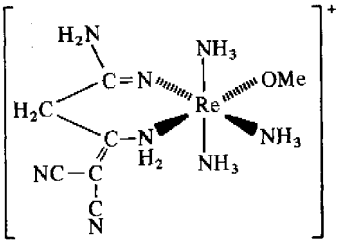
43.5.1.5 Nitriles and amidinates

The most important nitrile compound of Re^{III} is $ReCl_3(NCMe)(PPh_3)_2$, a complex which finds much use as a starting material for the synthesis of other Re^{III} complexes and some derivatives of Re^{IV}.[1] This complex and others of its kind are discussed in Section 43.5.1.6. Other complexes that contain a single nitrile ligand, *e.g.* $[ReOBr_4(NCMe)]^-$ and $[ReBr_4(NO)(NCMe)]^-$, are most conveniently considered in other sections, *i.e.* 'Rhenium(V) Complexes' (Section 43.7) and 'Nitrosyls' (Section 43.10), respectively, for the two examples cited here.

The reduction of $ReCl_4(NCMe)_2$ by NMe_3 in ethanol or by Cd/Hg in acetonitrile generates the paramagnetic $[ReCl_4(NCMe)_2]^-$ anion which can be isolated as its Cs^+, Cd^{2+} or Me_3NH^+ salts.[98]

These compounds, like $ReCl_3(NCMe)(PPh_3)_2$, do not display $\nu(C{\equiv}N)$ modes in their IR spectra (see Section 43.5.1.6). The *cis* stereochemistry of $[ReCl_4(NCMe)_2]^-$ has been confirmed by X-ray crystallography.[1] Reoxidation of the orange anion to *cis*-$ReCl_4(NCMe)_2$ can be accomplished using cold nitric acid, iodine or various oxidizing metal salts. The potential of the $[cis\text{-}ReCl_4(NCMe)_2]^{0,1-}$ couple is -0.33 V *vs.* SCE, as measured by cyclic voltammetry on 0.2 M $(Bu^n_4N)PF_6$–CH_2Cl_2 solutions.[65] The salt $[Me_3NH]ReCl_4(NCMe)_2$ reacts with APh_3 (A = P, As or Sb) to give $ReCl_3(NCMe)(APh_3)_2$.[98] A novel route to the $[ReCl_4(NCMe)_2]^-$ anion involves the photochemical cleavage of the $[Re_2Cl_8]^{2-}$ anion. Ultraviolet irradiation of acetonitrile solutions of $(Bu^n_4N)_2Re_2Cl_8$ affords both tan-coloured $(Bu^n_4N)ReCl_4(NCMe)_2$ and orange $ReCl_3(NCMe)_3$.[99]

A most unusual reaction takes place between $ReOCl_3(PPh_3)_2$ and malononitrile in benzene to give a crystalline red product of stoichiometry $ReCl_3(C_6H_4N_4)(PPh_3)_2$. The yield of this product is increased in the presence of added PPh_3. It has been proposed[98] that this complex contains the 4-(dicyanomethylene)azetid-2-imine ligand $(NC)_2C{=}\overline{CNHC(NH)CH_2}$, formed by intramolecular nucleophilic addition of the enamine amino group to the non-conjugated nitrile group of the malononitrile dimer $(NC)_2C{=}C(NH_2)CH_2CN$ (abbreviated MND). When this complex is heated with pyridine, free MND is formed, while an orange crystalline complex, analyzing as 'Re(OMe)(MND)$(NH_3)_4$Cl', is produced when a methanol solution is treated with gaseous ammonia.[98] This compound is suspected of being the unusual amidine derivative (**31**); it can be isolated as its Cl^- or BPh_4^- salt.



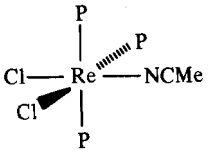
(31)

43.5.1.6 Phosphines, phosphites, arsines and stibines

The most extensive and important group of complexes are those with phosphine ligands. They are usually encountered as derivatives of mononuclear rhenium(III) halides. Compounds of the type ReX_3L_3, where L represents a trialkyl-, dialkylphenyl- or alkyldiphenyl-phosphine, or -arsine, constitute an extensive class of mononuclear rhenium(III) complexes; examples are $ReCl_3(PEt_3)_3$, $ReBr_3(PMePh_2)_3$ and $ReCl_3(AsEt_2Ph)_3$.[1,100] These complexes, which range in color from yellow to dark brown, are paramagnetic, exhibit Knight-shifted ^1H NMR spectra and invariably possess the *mer* octahedral configuration. The X-ray crystal structure of *mer*-$ReCl_3(PMe_2Ph)_3$ has been determined.[101] They are most conveniently prepared by reacting $ReOCl_3(PPh_3)_2$ or $ReCl_3(NCMe)(PPh_3)_2$ with the appropriate phosphine in boiling benzene,[1,100,102] the reaction of *trans*-$ReCl_4(PR_3)_2$ with excess PR_3 in boiling ethanol[1] or, in the case of *mer*-$ReX_3(PMe_2Ph)_3$ (X = Cl or Br), by heating $KReO_4$ in concentrated hydrohalic acid with PMe_2Ph in ethanol.[103] By reacting $ReOCl_3(dppe)$ with PEt_2Ph in boiling benzene, the mixed phosphine complex $ReCl_3(dppe)(PEt_2Ph)$ can be produced.[100] In the reactions involving the reduction of higher valent oxo–rhenium species, the phosphine ligand serves as the reducing agent by facilitating oxygen transfer from the metal through formation of the appropriate phosphine oxide. Spectroscopic studies (*e.g.* electronic absorption, IR and NMR) have been carried out on many of these complexes.[1,100]

When $ReOCl_3(PPh_3)_2$ is reacted with an excess of PPh_3 in refluxing acetonitrile, reduction to Re^{III} again occurs, but in this instance the product is $ReCl_3(NCMe)(PPh_3)_2$ (**32**).[86] This same complex has also been prepared as a relatively minor product in the reaction between β-$ReCl_4$ and PPh_3 in acetonitrile.[104] The mechanism of its formation from $ReOCl_3(PPh_3)_2$ has been looked at in some detail.[86] This complex is a very important starting material for synthesis of many rhenium(III) species,[1,86] including some of the $ReCl_3(PR_3)_3$ complexes described above. Several complexes of the type $ReX_3(NCR)(PPh_3)_2$ have been prepared using other nitrile solvents (R = Pr^n, Bu^t, n-C_7H_{15} or Ph) and $ReOX_3(PPh_3)_2$ (X = Cl or Br) as the starting material.[86] The reactions of $ReX_3(NCMe)(PPh_3)_2$ with the phosphines $PEtPh_2$, PPr^nPh_2 and PBu^nPh_2 result in displacement of the PPh_3 ligands and the formation of $ReBr_3(NCMe)(PEtPh_2)_2$ and $ReX_3(NCMe)(PRPh_2)_2$ (X = Cl or Br;

R = Pr^n or Bu^n) rather than $ReX_3(PRPh_2)_3$.[100] The $AsPh_3$ and $SbPh_3$ analogues $ReCl_3(NCMe)(APh_3)_2$ (A = As or Sb) are prepared by the reaction of $[Me_3NH]ReCl_4(NCMe)_2$ with $AsPh_3$ or $SbPh_3$.[98]



(32) P = PPh_3

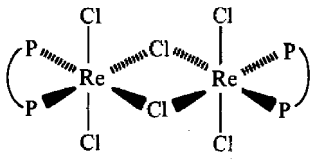
Although complexes of the type $ReX_3(NCR)(PPh_3)_2$ do not exhibit an identifiable $\nu(C{\equiv}N)$ mode in the IR mull spectra, the X-ray crystal structure of $ReCl_3(NCMe)(PPh_3)_2$ (**32**) confirms the presence of normal N-bound acetonitrile, with Re—Cl distances of 2.35 Å (*trans* to Cl) and 2.40 Å (*trans* to MeCN).[105] These complexes exhibit the expected paramagnetism for d^4 Re^{III} complexes.[86] The complex $ReCl_3(NCMe)(PPh_3)_2$ and its analogues are readily oxidized by halocarbons to give Re^{IV} complexes. When solutions of $ReCl_3(NCMe)(PPh_3)_2$ are allowed to undergo oxidation in air, the pale green crystalline complex $ReOCl_3(OPPh_3)(PPh_3)$ is formed; the latter complex in turn reacts with PPh_3 to give $ReOCl_3(PPh_3)_2$ and Ph_3PO.[86]

Studies of the electrochemical behavior of *mer*-$ReCl_3(PMe_2Ph)_3$ in 0.2 M $(Bu^n_4N)PF_6$–CH_2Cl_2 show that it possesses both a reversible one-electron oxidation ($E_{1/2} = +0.67$ V *vs.* SCE) and a one-electron reduction.[65] A later investigation of this system showed that the electrochemical oxidation of $ReCl_3(PMe_2Ph)_3$ in acetonitrile at +0.9 V with $NaClO_4$ as supporting electrolyte could be used to prepare the violet colored rhenium(IV) complex $[ReCl_3(PMe_2Ph)_3]ClO_4$. In the presence of $(Et_4N)Cl$, this electrolysis produced *trans*-$ReCl_4(PMe_2Ph)_2$.[106] When $ReCl_3(PMe_2Ph)_3$ is reduced in acetonitrile, it is believed that the resulting monoanion reacts rapidly with solvent to produce $ReCl_2(PMe_2Ph)_3(NCMe)$, although a pure sample of the latter compound has not been isolated. However, its Re^{III} analogue, *viz.* $[ReCl_2(PMe_2Ph)_3(NCMe)]ClO_4$, is apparently formed upon reacting *mer*-$ReCl_3(PMe_2Ph)_3$ with $AgClO_4$ in acetonitrile.[106]

Complexes of the type *trans*-$ReCl_4(PR_3)_2$ (PR_3 = PEt_3, PPr^n_3, PBu^n_3, $PMePh_2$ or PPh_3) exhibit a very accessible one-electron reduction in the potential range −0.1 to −0.5 V *vs.* SCE (in 0.2 M $(Bu^n_4N)PF_6$–CH_2Cl_2).[65] Solutions containing the yellow Re^{III} monoanions have been generated but pure salts have not yet been isolated.[106]

A variety of well-characterized paramagnetic salts of the cationic species $[ReX_2(diars)_2]^+$ and $[ReX_2(dppe)_2]^+$ (X = Cl, Br or I) have been known for many years.[2] They are believed to possess a *trans* configuration. Their preparations have involved the reaction of $KReO_4$ with dppe in ethanolic hydrochloric acid, or $ReOX_3(dppe)$ with dppe in boiling EtOH, and the reaction of $HReO_4$ with diars in hot EtOH in the presence of hypophosphorous acid and the appropriate HX.[1,2,107] These two general synthetic methods (or variations thereof) are probably the best ones, although these complexes have been prepared by several other less direct routes.[1] More recent developments have included the synthesis of $[ReCl_2(Ph_2P(CH_2)_3PPh_2)_2]Cl$ and $[ReCl_2(Ph_2PCH{=}CHPPh_2)_2]Cl$ by the usual method starting from $KReO_4$,[100] and the preparation of $[ReCl_2(dppa)_2]X$ (X = Cl or PF_6; dppa = bis(diphenylphosphino)amine) from the cleavage of $(Bu^n_4N)_2Re_2Cl_8$.[74] Salts containing the diamagnetic $[ReCl(dppe)_2]^{2+}$ dication can apparently be produced by oxidizing $ReCl(N_2)(dppe)_2$ beyond the stage $[ReCl(N_2)(dppe)_2]^+$, using $AgNO_3$ or $AgClO_4$ as oxidants.[25] Another class of well-defined complexes that contain bidentate phosphines and arsines are the halide-bridged species $Re_2(\mu\text{-}X)_2X_4(LL)_2$ (X = Cl or Br; LL = dppe or arphos). These magnetically dilute compounds are the major products formed when $(Bu^n_4N)_2Re_2X_8$ (X = Cl or Br) is reacted with dppe or arphos in acetonitrile at room temperature.[70,108] An earlier report[2] describing the existence of diamagnetic, 'five-coordinate' $ReCl_3(diars)$ is worth reinvestigating in view of these more recent findings. The X-ray crystal structure of the magenta colored acetonitrile solvate $Re_2(\mu\text{-}Cl)_2Cl_4(dppe)_2 \cdot 2MeCN$ (**33**) has shown that the Re—Re distance is very long (~3.81 Å).[109] When complex (**33**) is refluxed in acetonitrile, the orange-brown monomer $ReCl_3(NCMe)(dppe)$ is formed through cleavage of the Re—Cl—Re bridging bonds.[70] When this reaction is carried out in the presence of an excess of dppe, a yellow insoluble complex of stoichiometry $[ReCl_3(dppe)_{1.5}]_n$ is produced.[70] It is unclear at present whether it is a dppe-bridged polymer, or ionic $[ReCl_2(dppe)_2][ReCl_4(dppe)]$.

Complexes with polydentate phosphine and arsine ligands are known but in most instances their structures are in doubt and they remain inadequately characterized.[2] The reaction between $ReCl_3(NCMe)(PPh_3)_2$ and $(Ph_2PCH_2)_3CMe$ (abbreviated P_3) gives paramagnetic (μ_{eff} = 1.8 BM), green-



(33) P—P = dppe

yellow crystalline *fac*-$ReCl_3(P_3)$.[100] A complex of this same stoichiometry had previously been prepared by the reduction of $ReOCl_3(P_3)$ in aqueous acetone using sodium dithionite.[110] This buff colored complex could be converted to the bromide by reaction with LiBr. Both the chloride and bromide are paramagnetic ($\mu_{eff} \sim 1.7$ BM) and exhibit sharp ^1H NMR spectra. However, the two different samples of $ReCl_3(P_3)$ have quite different melting points (154–6°C[110] *versus* 225–227°C[100]) thereby implying that they are not one and the same. Other less well-defined species are mentioned briefly in Section 43.5.3.3 (see Table 7).

There are a few reports which describe phosphite complexes of rhenium(III) that bear a close analogy to the phosphine derivatives $ReX_3(PR_3)_3$. Thus, the sythesis of *fac*-$ReCl_3[P(OEt)_3]_3$ has been accomplished through the reaction of $ReOCl_3(PPh_3)_2$ with an excess of $P(OEt)_3$. This structural formulation is based upon IR and NMR spectra characterization.[111] A more extensive study has led to the isolation of paramagnetic *mer*-$ReX_3[P(OR)_3]_3$ (X = Cl, Br or I; $P(OR)_3 = P(OEt)_3$ or $P(OCH_2)_3CMe$).[112] The triaryl phosphite complexes $ReI_3[P(OPh)_3]_3$, $ReI_3[P(O\text{-}p\text{-}tol)_3]_3$ and $ReX_3(PPh_3)_2[P(OPh)_3]$ are also known,[1,2] and the suggestion has been made that $ReI_3[P(OPh)_3]_3$ exists in the *mer* configuration.[113]

Phosphido complexes are not at present an important facet of rhenium(III) chemistry. The reaction between $ReOCl_3(PPh_3)_2$ and $PHPh_2$ in hot benzene gives $ReCl_2(PPh_2)(PHPh_2)_3$, but, surprisingly, this complex is said to be diamagnetic.[1] Preliminary details of the isolation of the diamagnetic homoleptic dicyclohexylphosphide complex [Li(DME)]$Re(PCy_2)_4$ have been reported.[114] The $[Re(PCy_2)_4]^-$ anion may be four-coordinate but in good donor solvents (*e.g.* THF or DME) it is believed to equilibrate with a purple paramagnetic adduct.

The complex *trans*-$[ReCl_2(Me_2PCH_2CH_2PMe_2)_2]PF_6$ has been synthesized and its X-ray crystal structure determined.[593] The related ^{186}Re-labeled complex has been made from $[^{186}ReO_4]^-$.[593]

43.5.1.7 Oxygen and sulfur donors

β-Diketone complexes of rhenium(III) are the most extensive and best characterized of those that contain oxygen and sulfur ligands. The tris-acetylacetonate (pentane-2,4-dionate, acac) of rhenium(III), $Re(acac)_3$, was first reported in 1960 as being a product of the reaction of ReO_2 with acetylacetone.[115] Twelve years later more convenient synthetic procedures were reported that involved the reaction between $Re(acac)_2Cl_2$ or $ReCl_2(acac)(PPh_3)_2$ and Na(acac).[116] Other synthetic methods involve the Zn or Zn/Hg reduction of $Re(acac)_2Cl_2$.[117] The complex $Re(hfac)_3$ (hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) has been prepared by reacting $ReCl_2(hfac)(PPh_3)_2$ with Na(hfac).[116] Dark red crystalline $Re(acac)_3$ and $Re(hfac)_3$ are volatile and exhibit well-defined mass spectra.[116] They are paramagnetic ($\mu_{eff} = 1.7$–1.8 BM at 290 K) and exhibit temperature independent paramagnetism. A consideration of the X-ray powder data for these two complexes indicates that they possess the typical tris(β-diketonate)metal structure. $Re(acac)_3$ is extremely susceptible to oxidation thereby making its handling quite difficult.[116] A rhenium(III) complex of salicylaldehyde, $ReCl_3(salH)(PPh_3)_2$, is also known (Section 43.5.1.9).

When the rhenium(V) complexes $ReOX_2(OEt)(PPh_3)_2$ (X = Cl, Br or I) are reacted with acacH in hot benzene, the species $ReOX_2(acac)(PPh_3)_2$ are formed first, and then react further to give paramagnetic, orange-red $ReX_2(acac)(PPh_3)_2$.[118] In the related reactions between $ReOCl_2(OEt)(PEt_2Ph)_2$ and acacH, and of $ReOCl_2(OEt)(PPh_3)_2$ with hfacH and tfacH (tfac = 1,1,1-trifluoropentane-2,4-dionate), the complexes $ReCl_2(acac)(PEt_2Ph)_2$, $ReCl_2(hfac)(PPh_3)_2$ and $ReCl_2(tfac)(PPh_3)_2$, respectively, can be produced.[118] When $ReOCl_2(OEt)(PPh_3)_2$ is refluxed with acacH in the absence of the benzene solvent, it appears that further substitution occurs to give $ReCl(acac)_2(PPh_3)$ (after 16 hours), and that this is followed by oxidation to the Re^{IV} complex $Re(acac)_2Cl_2$ as the reflux time is increased (to 50 hours).[118] An X-ray structure determination on a crystal of $ReCl_2(acac)_2(PPh_3)_2$ has shown[119] that it is the isomer that possesses a *trans* arrangement of phosphine ligands and *cis* disposition of Re—Cl bonds.[119]

The one-electron reduction of *cis*- or *trans*-$Re(acac)_2Cl_2$ to [*trans*-$Re(acac)_2Cl_2]^-$ can be accom-

plished through the reaction of these Re^{IV} complexes with Tl(acac) in ether, Na/MeCN or K/MeCN.[117] The bromide complex $K[Re(acac)_2Br_2]$ has also been prepared using the potassium reduction method. Cation exchange between $K[Re(acac)_2Cl_2]$ and $(Ph_4As)Cl$ in aqueous solution affords blue-green crystals of $(Ph_4As)[Re(acac)_2Cl_2]$,[117] the X-ray crystal structure of which has shown that the anion possesses a *trans* octahedral structure.[120] The major difference between the structure of the anion and *trans*-$Re(acac)_2Cl_2$ is the lengthening of the Re—Cl bond lengths of the former.[120]

When $ReCl_3(NCMe)(PPh_3)_2$ is heated with benzil (PhCOCOPh) in benzene, dark purple $ReCl_3(PhCOCOPh)(PPh_3)$ is formed along with *trans*-$ReCl_4(PPh_3)_2$. The analogous reaction with 9,10-phenanthraquinone (phenquin) gives the blue complex $ReCl_3(phenquin)(PPh_3)$.[86] The benzil complex is paramagnetic ($\mu_{eff} = 1.85$ BM) and reacts with pyridine to give $ReCl_3(py)_3$ and benzil, an important reaction since this is the only route to the tris-pyridine complex (see Section 43.5.1.2).

Coordination complexes of rhenium(III) that contain sulfur ligands are relatively uncommon, although a couple of derivatives with the diethyldicarbamato ligand resemble the related acac complexes. The reaction of $ReCl_3(NCMe)(PPh_3)_2$ with $NaS_2CNEt_2 \cdot 3H_2O$ in acetone leads to the formation of red-brown $Re(S_2CNEt)_3$. The related reaction with $NaS_2CNPh_2 \cdot 2H_2O$ gave dark purple crystalline $Re(S_2CNPh_2)_3(PPh_3)$ in which one of the diphenyldithiocarbamate ligands is believed to be monodentate.[121] The complex $ReCl_2(S_2CNEt_2)(PPh_3)_2$ is best prepared by the reaction of $ReOCl_2(S_2CNEt_2)(PPh_3)_2$ with PPh_3 by prolonged refluxing in ethanol.[121] The seven-coordinate carbonyl-containing rhenium(III) complex $Re(S_2CNEt_2)_3CO$ is produced by the reaction of $ReCl(CO)_5$ with $(Et_2NCS)_2$ and has been structurally characterized by X-ray crystallography.[6] Mixed hydrido–dithiocarbamate complexes of Re^{III} of the types $ReH(S_2CNR_2)X(PMe_2Ph)_3$ and $ReH(S_2CNR_2)_2(PMe_2Ph)_2$ are also known (see Section 43.5.1.8).

Thiourea reacts with $(Bu^n_4N)_2Re_2X_8$ (X = Cl or Br) with the resulting cleavage of the Re—Re quadruple bond and the formation of insoluble complexes formulated as $ReX_3(tu)_3$.[1] Similar products are formed upon reacting thiourea with ReO_4^- in 2 M hydrochloric acid, but all these products remain incompletely characterized.[1] The reactions of K_2ReX_6 (X = Cl, Br or I) with cysteine ($cystH_2$) have been investigated and preliminary details reported describing the isolation of the crystalline, non-ionic, diamagnetic compounds of formula $Re(cystH)_2X$ (X = Cl, Br or I).[122] A well-characterized set of thiol derivatives are the five-coordinate complexes $Re(SAr)_3(NCMe)(PPh_3)$ (Ar = Ph, *p*-tol, C_6F_5 or C_6Cl_5) that are formed by the reaction of $[ReO(SAr)_4]^-$ with excess PPh_3 in refluxing MeCN. The X-ray crystal structure of the derivative where Ar = Ph has shown that the geometry is trigonal bipyramidal.[204]

43.5.1.8 Mononuclear and dinuclear hydrides

Hydride complexes of rhenium, including those of Re^{III}, were the subject of an excellent review by Kaesz and Saillant that covered the literature up to 1971.[123] Included in this, and also in the slightly later review by Rouschias,[1] was coverage of the important complexes $ReH_3(PPh_3)_4$, $ReH_3(dppe)_2$ and $ReH_3(PPh_3)_2(dppe)$, together with $ReH_2X(dppe)_2$ (X = Cl, Br or I) which is formed by the halogenation of $ReH_3(dppe)_2$, plus the acac-containing complexes $ReH_2(acac)(PPh_3)_3$ and $ReHX(acac)(PPh_3)_3$ (X = Cl, Br or I). The complexes $ReH_3(dppe)_2$ and $ReH_3(PPh_3)_2(dppe)$ are prepared by reacting $ReH_5(PPh_3)_3$ with dppe,[124] while $ReH_3(PPh_3)_4$ is formed upon treating $ReO(OEt)I_2(PPh_3)_2$ with $NaBH_4$ in the presence of an excess of PPh_3.[127] The synthesis of the analogous PMe_2Ph derivative $ReH_3(PMe_2Ph)_4$ has been accomplished by the $LiAlH_4$ reduction of a THF solution of *mer*-$ReCl_3(PMe_2Ph)_3$ and PMe_2Ph.[125] An attempt to prepare the tri-*p*-tolylphosphine analogue of $ReH_3(PPh_3)_4$ by a related procedure gave a red product that was formulated as $[ReH_3(P\text{-}p\text{-}tol_3)_2]_2$.[126] This compound, which purportedly has a PPh_3 analogue of this same stoichiometry,[127] is most likely $Re_2H_8(P\text{-}p\text{-}tol_3)_4$, or some closely allied dirhenium polyhydride, and therefore possesses a formal oxidation state higher than Re^{III}. The white PMe_3 complex $ReH_3(PMe_3)_4$ can be prepared by treating $ReH(PMe_3)_5$ or $Re(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4$ with H_2.[35]

The spectroscopic properties of $ReH_3(PR_3)_4$ (PR_3 = PPh_3, PMe_2Ph or PMe_3) and $ReH_3(dppe)_2$ (see Table 6) show that in solution they are fluxional, as evidenced by a high field quintet for the Re—H resonance in the ^1H NMR spectra. The temperature dependence of the ^1H NMR spectra of $ReH_3(dppe)_2$, $ReH_3(dpae)_2$, $ReH_3(PPh_3)_2(dppe)$ and $ReH_3(PPh_3)_2(dpae)$ (dpae = $Ph_2AsCH_2CH_2AsPh_2$) have been studied down to -90°C or so.[136] For $ReH_3(dppe)_2$ and $ReH_3(dpae)_2$, two of the three hydride ligands were equivalent at ~ -50°C, the decoupled spectrum appearing as an AB_2 pattern with $J_{H_A-H_B} \approx 9.5$ Hz. The ^1H NMR spectrum of $ReH_3(PPh_3)_2(dppe)$ consists of a triplet of triplets, as expected for three equivalent protons coupled to two non-equivalent pairs of phosphorus atoms.[136] While the solid-state structures of the complexes with monodentate phos-

Table 6 Some Mononuclear Hydrido Complexes of Rhenium(III) and Their Spectroscopic Properties

Complex	*Color*	*^1H NMR*[a] $\delta(Re—H)$ (p.p.m.)	*^1H NMR*[a] $J_{P—H}$ (Hz)	*IR*[b] $\nu(Re—H)$ (cm^{-1})	*Ref.*
$ReH_3(PPh_3)_4$	Yellow	−7.56q	40.7	1983sh, 1962m (KBr)	125
$ReH_3(PMe_2Ph)_4$	Yellow	−6.74q	20.0	1952m, 1890m, 1784s, 1750sh (KBr)	125
$ReH_3[P(OMe)_3]_4$	N.R.[c]	−8.1q	18	N.R.[c]	13
$ReH_3(PMe_3)_4$	White	−7.85q	20.8	1915w, 1887w, 1785m, 1758s (NM)	35
$ReH_3(dppe)_2$	Yellow	−7.35q	17.8	1860s (NM)	37, 124
$[ReHCl(PMe_3)_5]BF_4$	Orange	−9.7br		2004 (NM)	35
$ReH_2(NHPh)(PMe_3)_4$	Yellow	−8.8qd[d]	21.0[e]	1925w, 1885w (NM)	34
		−7.8q[d]	21.3		
$ReHCl(S_2CNMe_2)(PMe_2Ph)_3$	Yellow	−9.97dt	63 ± 3 55 ± 3	2067w (NM)	26
$ReH(S_2CNMe_2)_2(PMe_2Ph)_2$	Dark red	−8.88t	66	N.O.[f]	26

[a] Measured in C_6D_6 or C_7D_8 at room temperature or thereabouts. Abbreviations are as follows: q = quintet, qd = quintet of doublets, t = triplet, dt = doublets of triplets, br = broad.
[b] Measured as KBr pellet or Nujol mull (NM).
[c] Not reported.
[d] Resonances due to different isomers.
[e] $J_{H—H} = 2.4$ Hz.
[f] Not observed.

phines, $ReH_3(PR_3)_4$, have not been determined by X-ray crystallography, those of $ReH_3(dppe)_2$ and $ReH_3(PPh_3)_2(dppe)$ have and, in both instances, the geometry has been described as a distorted pentagonal bipyramid.[128]

The reaction chemistries of $ReH_3(PR_3)_4$ (PR_3 = PPh_3 or PMe_2Ph) and $ReH_3(dppe)_2$ have to date been explored more thoroughly than those of any other hydrido complexes of rhenium(III). While $ReH_3(PPh_3)_4$ reacts with an excess of HX (X = Cl or Br) in benzene to give the rhenium(IV) salts $(Ph_3PH)ReX_5(PPh_3)$,[129] $ReH_3(dppe)_2$ and $ReH_3(PMe_3)_4$ can be protonated to give the tetrahydrido cationic complexes,[35,124] as shown in equation (5) for $ReH_3(PMe_3)_4$. Upon treatment of $ReH_3(PPh_3)_4$ with $P(OPh)_3$, substitution of up to three of the PPh_3 ligands can occur to give $ReH_3(PPh_3)_2[P(OPh)_3]_2$ and $ReH_3(PPh_3)[P(OPh)_3]_3$.[130] Few other mixed hydride–phosphite complexes of rhenium(III) are known at present. A mixture of $[ReH_2[P(OMe)_3]_5]^+$ and $ReH_2[P(OMe)_3]_3(O_2CCF_3)$ is believed to be produced upon protonating $Re_2[P(OMe)_3]_{10}$ with trifluoroacetic acid, while $ReH_3[P(OMe)_3]_4$ has been characterized by ^1H NMR spectroscopy (Table 6) as one of the products from photolyzing H_2–$Re_2[P(OMe)_3]_{10}$ mixtures in THF.[13]

$$ReH_3(PMe_3)_4 + HBF_4 \xrightarrow[-78°C]{THF} [ReH_4(PMe_3)_4]BF_4 \quad (5)$$

A very important reactivity difference between $ReH_3(dppe)_2$ and $ReH_3(PR_3)_4$ lies in their photochemical properties. While the initial photoproduct of the 366 nm irradiation of $ReH_3(dppe)_2$ is the highly reactive species $ReH(dppe)_2$ (see Section 43.3.3), in the case of $ReH_3(PMe_2Ph)_4$ phosphine loss rather than the elimination of H_2 occurs.[125] Under an H_2 atmosphere the 16-electron species $ReH_3(PMe_2Ph)_3$ smoothly converts to $ReH_7(PMe_2Ph)_2$ *via* the intermediacy of $ReH_5(PMe_2Ph)_3$ (equation 6). The putative 14-electron intermediates $ReH_3(PAr_3)_2$ (Ar = aryl) are other examples of coordinatively and electronically unsaturated hydrido species. They are believed to be formed in reactions of $ReH_7(PAr_3)_2$ that result in the dehydrogenation of alkanes.[131]

$$ReH_3(PMe_2Ph)_4 \xrightarrow[H_2]{h\nu} PMe_2Ph + ReH_5(PMe_2Ph)_3 \xrightarrow[H_2]{h\nu} PMe_2Ph + ReH_7(PMe_2Ph)_2 \quad (6)$$

Protonation of $ReH(N_2)(dppe)_2$ with HBF_4 in benzene gives the cream colored salt $[ReH_2(N_2)(dppe)_2]BF_4$. When HCl is used in place of HBF_4 then $ReHCl_2(dppe)_2$ is formed, presumably *via* the intermediacy of $[ReH_2(N_2(dppe)_2]Cl$.[36] In a similar fashion, treatment of the rhenium(I) complex $ReCl(PMe_3)_5$ with one equivalent of aq. 48% HBF_4 produces the yellow monohydride $[ReHCl(PMe_3)_5]BF_4$ (Table 6).[35] Other dinitrogen complexes of rhenium(I) provide a route, *via* protonation, to hydrido–rhenium(III) species. The complexes *mer*-$Re(S_2CNR_2)(N_2)(PMe_2Ph)_3$ (R = Me or Et) react with an excess of HX (X = Cl or Br) in THF to give $[ReH_2(S_2CNR_2)X(PMe_2Ph)_3]X$, which on treatment with NEt_3 or pyridine give $ReH(S_2CNR_2)X(PMe_2Ph)_3$. The latter species are converted to $ReH(S_2CNR_2)_2(PMe_2Ph)_2$ when reacted with $Na(S_2CNR_2)$ in acetone solution.[26] Spectroscopic properties of representative complexes of these types are given in Table 6.

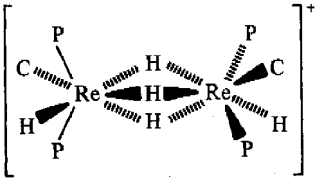
When slurries in acetonitrile of the heptahydride complex $ReH_7(PPh_3)_2$ and the pentahydrides $ReH_5(PPh_3)_2L$ (L = py or $C_6H_{11}NH_2$) are treated with HBF_4, then H_2 is evolved and quantitive yields of the yellow colored salts $[ReH(NCMe)_3(PPh_3)_2L](BF_4)_2$ (L = MeCN, py or $C_6H_{11}NH_2$) are obtained.[132] This constitutes an alternative and quite simple strategy for the preparation of monohydrido–rhenium(III) complexes. These complexes exhibit a reversible one-electron oxidation at ~ 1.0 V *vs.* SCE, as measured by the cyclic voltammetric technique. Bulk electrolysis of CH_2Cl_2 solutions of $[ReH(NCMe_3)_3(PPh_3)_2L]^{2+}$ affords purple $[ReH(NCMe)_3(PPh_3)_2L]^{3+}$, a rare example of a mononuclear hydrido–rhenium(IV) species.[132]

A more complete account is now available[594] describing the protonation reactions of the complexes $ReH_7(PPh_3)_2$, $ReH_5(PPh_3)_2L$ (L = py, $C_6H_{11}NH_2$ or Bu^tNH_2) and $ReH_4I(PPh_3)_3$ with $HBF_4 \cdot Et_2O$ in acetonitrile or propionitrile (for a preliminary report see ref. 132). This procedure affords the seven-coordinate monohydrido complexes $[ReH(NCR)_3(PPh_3)_2L](BF_4)_2$ in good yield.

The very air-sensitive complex $ReH_2(NHPh)(PMe_3)_4$ can be obtained by the Na/Hg reduction of $Re(NPh)Cl_3(PMe_3)_2$ in the presence of excess PMe_3 under an H_2 atmosphere or by the oxidative addition of hydrogen to $Re(NHPh)(N_2)(PMe_3)_4$. This reaction (equation 7) is reversible at room temperature. The ^1H NMR spectrum of this complex has been interpreted in terms of the presence of two isomers (Table 6).[34] When the reduction of $Re(NPh)Cl_3(PMe_3)_2$ is carried out under argon in the presence of excess PMe_3 then the yellow crystalline monohydride $ReH(NHPh)(\eta^1\text{-}CH_2PMe_2)(PMe_3)_4$ is believed to be the reaction product.[34]

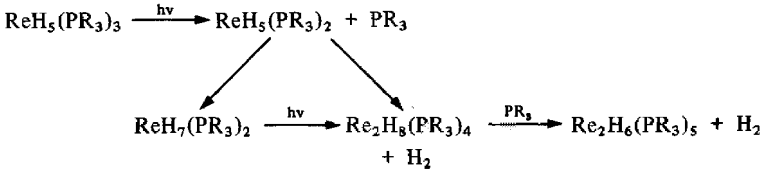
$$Re(NHPh)(N_2)(PMe_3)_4 + H_2 \rightleftharpoons ReH_2(NHPh)(PMe_3)_4 + N_2 \quad (7)$$

The tetrahydrido–dirhenium(II) complex $Re_2H_4(PMe_2Ph)_4P'_2$ (**21**) (P′ = $P(OCH_2)_3CEt$) (see Section 43.4.2.4) can be protonated using $HBF_4 \cdot Et_2O$ in benzene solution to give the dirhenium(III) complex $[Re_2H_5(PMe_2Ph)_4P'_2]BF_4$.[78] An X-ray structure determination (carried out at −160°C) shows it to have the symmetric structure $(Me_2PhP)_2(P')HRe(\mu\text{-}H)_3ReH(P')(PMe_2Ph)_2$ with an Re—Re distance (2.605(2) Å) very similar to that in $Re_2H_4(PMe_2Ph)_4P'_2$ (2.597(1) Å).[78] At −60°C this complex exhibits (in CD_2Cl_2) three hydride resonances in its ^1H NMR spectrum, two of which are due to inequivalent bridging hydride environments (ratio 2:1), and one ^{31}P ABX pattern consistent with the solid-state symmetry. By +16°C the $^{31}P\{^1H\}$ spectrum appears as an A_2X pattern, and the two types of bridging hydride ^1H NMR resonances coalesce but remain distinct from the terminal hydride triplet. The latter triplet pattern arises from coupling of each of the equivalent terminal hydride ligands to the two 'local' PMe_2Ph ligands.[78] The characteristics of the ^1H NMR spectrum of $[Re_2H_5(PMe_2Ph)_4P'_2]^+$ at +16°C are also seen in the related spectrum of $[Re_2H_5(PPh_3)_4(CNBu^t)_2]PF_6$ (**34**) over the temperature range +35 to −70°C. This complex is prepared through the reaction of $[Re_2H_8(PPh_3)_4]PF_6$ with Bu^tNC in dichloromethane,[132,133] and an X-ray crystal structure determination has shown that it possesses a structure very similar to that of the mixed phosphine–phosphite derivative with an Re—Re distance of 2.604(1) Å.[133] The maroon complex (**34**) can be oxidized by $(NO)PF_6$ in acetone to afford the paramagnetic, ESR-active, dark blue compound $[Re_2H_5(PPh_3)_4(CNBu^t)_2](PF_6)_2$.[132,134] In contrast to the lack of reaction between (**34**) and Bu^tNC, its oxidized congener reacts rapidly to give $[Re(CNBu^t)_4(PPh_3)_2]PF_6$ and gaseous H_2, along with significant quantities of (**34**) that are formed by back reduction of the dication without concomitant isocyanide coordination.



(34) P = PPh_3; C = $CNBu^t$

Photolysis of benzene or isooctane solutions of $ReH_5(PR_3)_3$ (PR_3 = PMe_2Ph, $PMePh_2$ or PPh_3) results in the photoextrusion of a PR_3 ligand rather than H_2.[125,135] This leads (as shown in Scheme 9) to the formation of several products, including $Re_2H_6(PR_3)_5$ in the case of PR_3 = PMe_2Ph or $PMePh_2$ (but not PPh_3). A further product obtained in the case of the photolysis of $ReH_5(PPh_3)_3$ is the trihydride $ReH_3(PPh_3)_4$.[125] The structural characterization of $Re_2H_6(PMe_2Ph)_5$ has included an X-ray structure determination, but not all the metal-bound hydrogens have been located.[135] The metal–metal separation is 2.538(4) Å. ^1H NMR spectral evidence is consistent with the structure $(Me_2PhP)_3HRe(\mu\text{-}H)_3ReH_2(PMe_2Ph)_2$, so that this complex could be viewed as a mixed oxidation state species.[135]



Scheme 9 Photochemistry of $ReH_5(PR_3)_3$ (ref. 135)

43.5.1.9 Mixed donor atom ligands

An important recent development has been the isolation of several mixed N—O ligand complexes of Re^{III}. The complex $ReCl_3(NCMe)(PPh_3)_2$ reacts in boiling salicylaldehyde (salH) to produce green $ReCl_3(salH)(PPh_3)_2$ in low yield.[205] In this paramagnetic complex the salH ligand is believed to be bound through its carbonyl oxygen, at least on the basis of its IR spectral properties. The Schiff base rhenium(V) complexes $ReOX_2L(PPh_3)$ [X = Cl or Br; L = *N*-methylsalicylideneiminate, *N*-phenylsalicylideneiminate, ½*N*,*N*′-ethylenebis(salicylideneiminate)] react with an excess of PMe_2Ph to give the red rhenium(III) complexes $ReX_2L(PMe_2Ph)_2$ *via* the intermediacy of $ReOX_2L$-

(PMe_2Ph).[206] These paramagnetic complexes exhibit well-defined Knight-shifted ^1H NMR spectra and are believed to have a *trans* disposition of PMe_2Ph ligands and a *cis* arrangement of Re—X bonds. The complex $ReCl_2$(Ph-sal)$(PMe_2Ph)_2$ is said to isomerize when heated under argon in toluene to give the isomer with the phosphine and halide ligands mutually *cis* to one another.[207] The Schiff base complex $ReCl_2$(Ph-sal)$(PMe_2Ph)_2$ reported previously,[206] has now been structurally characterized by X-ray crystallography.[595] The complex $ReCl_2$(Me-sal)$(PPh_3)_2$ has been prepared by the reaction of *trans*-$ReCl_4(PPh_3)_2$ with the lithium salt of the ligand in refluxing benzene.[207]

The pyrazolylborate complex $ReCl_2(PPh_3)[HB(pz)_3]$ can be prepared in high yield by the reaction of $ReOCl_2[HB(pz)_3]$ with PPh_3 in hot toluene.[572]

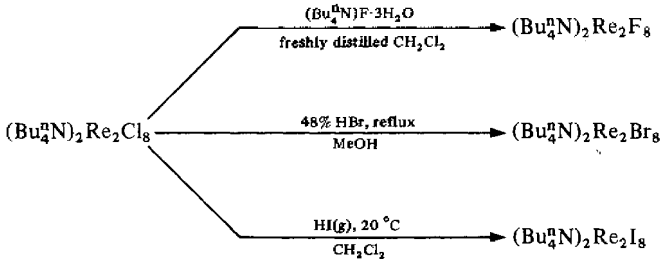
43.5.2 Dinuclear Complexes Containing the Re_2^{6+} Core

Section 43.4.2 dealt with the chemistry of coordination complexes that are derivatives of the triply bonded Re_2^{4+} core, possessing the $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration. The removal of two electrons from this configuration gives rise to complexes that contain the quadruply bonded Re_2^{6+} core. The literature covering the period between the discovery of this class of complexes in 1964 and the latter part of 1981 is surveyed in the text 'Multiple Bonds Between Metal Atoms' by F. A. Cotton and R. A. Walton that was published in 1982.[5] This source (Chapters 2 and 8 in particular) should be consulted for an exhaustive survey of this field. Accordingly, we shall in the present section restrict our coverage to a relatively brief consideration of the literature for the period 1964–81 and a more thorough treatment of the work that has been published since that time. Since salts of the octahalodirhenate(III) anion serve as the most convenient starting point for the synthesis of almost all dirhenium(III) complexes, they will be considered first.

The quadruply bonded dirhenium(III) acetate complex $Re_2Cl_4(O_2CCH_3)_2 \cdot 2H_2O$ reacts with PPh_3 in refluxing ROH (R = Me, Et or Pr^n) to give the red crystalline complexes $Re_2Cl_4(OR)_2(PPh_3)_2$ which have proved to be the $Re^{IV}Re^{II}$ mixed valent species $(RO)_2Cl_2ReReCl_2(PPh_3)_2$.[596] The one-electron oxidation and one-electron reduction of the complex $Re_2(\mu\text{-}Cl)_2(\mu\text{-dppm})_2Cl_4$[74] can be accomplished using $NOPF_6$ and cobaltocene as the oxidant and reductant, respectively, to give paramagnetic ions that possess Re—Re bond orders of 1.5.[587,597]

43.5.2.1 Halides

The tetra-*n*-butylammonium salt $(Bu_4^nN)_2Re_2Cl_8$, because of its relative ease of preparation and favourable solubility properties in many organic solvents, has been the most commonly used starting material in dirhenium(III) chemistry. This blue crystalline material was for many years most conveniently prepared by the hypophosphorous acid reduction of $[ReO_4]^-$ in aqueous hydrochloric acid.[137] However, because of the relatively low yield in which this salt was prepared (40% or less), another more convenient method has been sought and, very recently, discovered.[138,139] The reaction between $(Bu_4N)ReO_4$ and refluxing benzoyl chloride affords a solution which upon the addition of an HCl(g) saturated solution of $(Bu_4^nN)Br$ dissolved in ethanol gives $(Bu_4^nN)_2Re_2Cl_8$ in 90% yield. Both $[ReCl_6]^{2-}$ and $Re_2(O_2CPh)_2Cl_4$ have been isolated as intermediates in this reaction.[138] An alternative starting material for the synthesis of $(Bu_4^nN)_2Re_2Cl_8$ with PhCOCl is $ReOCl_3(PPh_3)_2$, which is itself prepared from perrhenate. This reaction proceeds *via* red *trans*-$ReCl_4(PPh_3)_2$ which can be isolated.[138] Cation exchange reactions can be used to obtain other salts of this anion,[5] while halide exchange reactions can be used to prepare the related fluoride, bromide and iodide anions as shown in Scheme 10.[5,140,141] An alternative route to $(Bu_4^nN)_2Re_2X_8$ (X = Cl, Br or I) involves the treatment of solutions of the benzoate complex $Re_2(O_2CPh)_4Cl_2$ with HX(g) in the presence of $(Bu_4^nN)X$ (equation 8).[61] A variety of other less convenient procedures exist for the preparation of salts of the $[Re_2X_8]^{2-}$ anions (X = Cl or Br) that contain the cesium cation or various organic cations.[5] Of these, the conversion of the trinuclear cluster Re_3Cl_9 to $[Re_2Cl_8]^{2-}$ by reaction with molten $Et_2NH_2^+Cl^-$ is of special note since it proceeds in quite high yield.[142] However, it suffers from one big disadvantage, in that it requires a ready source of Re_3Cl_9, a compound that is itself best prepared from $[Re_2Cl_8]^{2-}$ *via* the quadruply bonded acetate complex $Re_2(O_2CMe)_4Cl_2$.[143] Another recent noteworthy study[144] showed that the dirhenium octahydride complex $Re_2H_8(PPh_3)_4$ (see Section 43.6.1.10), reacts with allyl chloride or bromide to give $(Ph_3PC_3H_5)_2Re_2X_8$ in 70–80% yield (equation 9). When $Re_2H_8(PPh_3)_4$ is treated with HCl(g) in MeOH the mixed salt $(Ph_3PH)_2Re_2Cl_8 \cdot 5(Ph_3PH)ReCl_5(PPh_3)$ is formed.[144]



Scheme 10

$$Re_2(O_2CPh)_4Cl_2 + 8HX + 4(Bu^n_4N)^+ \xrightarrow[\text{reflux}]{ROH} (Bu^n_4N)_2Re_2X_8 + 4Ph_2CO_2H + 4H^+ \quad (8)$$

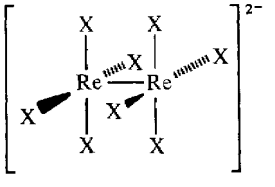
(X = Cl, Br or I)

$$Re_2H_8(PPh_3)_4 + \text{excess } C_3H_5X \xrightarrow{THF} (Ph_3PC_3H_5)_2Re_2X_8 + C_3H_6 + H_2 \quad (9)$$

(X = Cl or Br)

With the exception of $Cs_2Re_2Cl_8 \cdot H_2O$ and $Cs_2Re_2Br_8$, other salts possessing alkali metal cations (K^+ or Rb^+) and the NH_4^+ cation have generally been prepared (admixed with the corresponding salts of $[ReCl_6]^{2-}$) *via* the high pressure reduction of $[ReO_4]^-$ by molecular hydrogen in concentrated hydrochloric acid.[5] These compounds, while being structurally similar to $(Bu^n_4N)_2Re_2X_8$ and possessing the same electronic structure, have such low solubilities in non-aqueous organic solvents that their chemical reactivities have not been explored in any great detail.

Several X-ray crystal structures have been determined for salts containing the $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ anions, all of which were published before 1982.[5,145] The only recent structure determination is that of $[(DMA)_2H]_2Re_2Br_8$ (DMA = dimethylacetamide).[146] While the crystal structures of the fluoride and iodide salts $(Bu^n_4N)_2Re_2X_8$ have not yet been determined, there can be no doubt that they possess the typical $[Re_2X_8]^{2-}$ (**35**) structure, which is characterized by an eclipsed rotational conformation and a very short Re—Re distance (2.22–2.25 Å).[5] Following the isolation of the complex $Re_4I_8(CO)_6$ by the I_2 oxidation of $Re_2I_2(CO)_6(THF)_2$ in heptane, an X-ray crystal structure determination showed that this tetrarhenium complex could be viewed formally as a complex between two $Re(CO)_3^+$ fragments and $[Re_2I_8]^{2-}$, the association occurring *via* bent Re—I—Re bridges that involve six of the iodine atoms of $[Re_2I_8]^{2-}$. However, as a consequence of this structure, the rotational conformation within the central Re_2I_8 unit is staggered rather than eclipsed and, as a result, the Re—Re bond length increases to 2.279(1) Å.[147] In accord with the bonding scheme for such a species,[5] as the conformation shifts from eclipsed to staggered, the δ bonding diminishes (*i.e.* d_{xy}–d'_{xy} overlap) and the metal–metal bond order decreases from four to three.



(35)

The electronic structures of the $[Re_2X_8]^{2-}$ anions have been the subject of much interest. Molecular orbital calculations have established the correctness of the bonding model that pictures the Re—Re bond as being one of order four with the $\sigma^2\pi^4\delta^2$ ground state electronic configuration.[5,148] This has further been supported by electronic absorption spectral studies, including the definitive assignment of the $\delta \rightarrow \delta^*$ transition,[5,148,149] and vibrational spectral measurements (including resonance Raman spectra).[149] The latter have led to the assignment of the ν(Re—Re) frequencies both in the ground and excited states.[5,149]

An appreciation of the bonding in these molecules has led to studies of the emission spectra of $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$,[5] including an investigation of the electron transfer chemistry of the luminescent excited state of the octachlorodirhenate(III) anion, *i.e.* $\{[Re_2Cl_8]^{2-}\}^*$. These experiments have revealed that $\{[Re_2Cl_8]^{2-}\}^*$ functions as a strong oxidant as well as a moderately good reductant in non-aqueous media.[150] In particular, the reaction of the $\delta\delta^*$ singlet $\{[Re_2Cl_8]^{2-}\}^*$ with

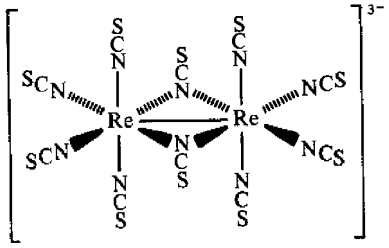
electron acceptors such as TCNE provides a facile route to the powerful inorganic oxidant $[Re_2Cl_8]^-$.[150] In this context it should be noted that the $[Re_2Cl_8]^{2-}$ anion has a quite well-defined electrochemistry. A one-electron reduction occurs close to -0.85 V *vs.* SCE in acetonitrile, but approaches electrochemical reversibility only at high sweep rates.[5] This reduction is chemically irreversible. Cyclic voltammetric measurements have shown[21,150] that the $[Re_2Cl_8]^{2-}/[Re_2Cl_8]^-$ couple occurs at $+1.24$ V *vs.* SCE in MeCN and at $+1.20$ V *vs.* SCE in CH_2Cl_2. The electrochemical properties of $(Bu^n_4N)_2Re_2Br_8$ have not been as extensively studied, although acetonitrile solutions of this complex have been shown by cyclic voltammetry to possess irreversible reductions at -0.70 V and -1.32 V *vs.* SCE.[5] Chemical oxidations and reductions of the $[Re_2X_8]^{2-}$ anions and their derivatives which give rise to dirhenium complexes possessing formal charges either greater or less than $+6$[5] are discussed in those sections that survey the appropriate oxidation states, *i.e.* $[Re_2Cl_9]^-$ is discussed with other Re^{IV} compounds while the complexes $Re_2Cl_4(PR_3)_4$ (and $Re_2Cl_5(PR_3)_3$, *etc.*) are included with Re^{II} species.

Few methods have yet been developed for preparing mixed octahalo anions, although the reaction of $(Bu^n_4N)_2Re_2Cl_8$ with calculated quantities of 48% hydrobromic acid has been used to prepare $[Re_2Cl_6Br_2]^{2-}$, $[Re_2Cl_3Br_5]^{2-}$ and $[Re_2Cl_2Br_6]^{2-}$.[151] Also, the CCl_4 oxidation of $Re_2Br_4(PEt_3)_4$ produces the salt $(Et_3PCl)_2Re_2Cl_4Br_4$, along with a quantity of $Re_2Cl_4Br_2(PEt_3)_2$[57] (see Section 43.4.2.1). The analogous reaction of $Re_2Cl_4(PEt_3)_4$ with CCl_4 gives $(Et_3PCl)_2Re_2Cl_8$,[57] an illustration of the relative ease with which complexes possessing the Re_2^{4+} and Re_2^{5+} cores can be oxidized back to Re_2^{6+}.[5]

43.5.2.2 Thiocyanate and selenocyanate

The reactions of $(Bu^n_4N)_2Re_2Cl_8$ with NaSCN and KSeCN in non-aqueous media give dark red $(Bu^n_4N)_2Re_2(NCS)_8$ and purple $(Bu^n_4N)_2Re_2(NCSe)_8$, respectively.[5] The spectroscopic characterizations of these two complexes accord with them possessing the type of structure depicted by (**35**) with N-bound NCS and NCSe ligands.[5] In the case of $[Re_2(NCS)_8]^{2-}$, cation exchange reactions can be used to give other salts. Polarographic and cyclic voltammetric measurements, in MeCN and CH_2Cl_2 respectively, have shown that $(Bu^n_4N)_2Re_2(NCS)_8$ possesses two accessible one-electron reductions close to -0.1 V and -0.75 V *vs.* SCE.[5,94]

In the reaction between $(Bu^n_4N)_2Re_2Cl_8$ and NaSCN, acidified MeOH is the solvent which is used in the preparation of the aforementioned $(Bu^n_4N)_2Re_2(NCS)_8$, whereas the use of acetone produces red-brown $(Bu^n_4N)_2Re(NCS)_6$ and dark green $(Bu^n_4N)_3Re_2(NCS)_{10}$ (**36**), both of which are oxidation products of $(Bu^n_4N)_2Re_2(NCS)_8$.[152,153] The X-ray crystal structure of paramagnetic (**36**) shows that this symmetric dirhenium complex possesses an edge-shared bioctahedral structure with an Re—Re bond (2.613(1)Å). The structural details imply that the oxidation state description is $(+3.5, +3.5)$ rather than $(+4, +3)$. Note that in the reaction of $(Bu^n_4N)_2Re_2(NCS)_8$ with phosphines, the Re—Re bond is cleaved to a similar bioctahedral structure $[Re_2(\mu\text{-}NCS)_2(NCS)_6(PR_3)_2]^{2-}$ (see Section 43.5.1.4) which, however, does not possess an Re—Re bond, *i.e.* the latter complexes are magnetically dilute $(+3, +3)$ species.



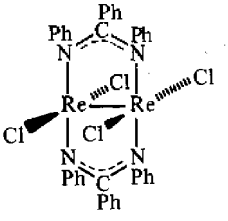
(36)

43.5.2.3 N-Heterocycles and amidine ligands

A poorly characterized, insoluble, gray-black 2,2′-bipyridine complex formulated as $[ReCl_3(bipy)\cdot 3/2H_2O]_n$ (the value of n is unknown) has been obtained from the reaction of $(Bu^n_4N)_2Re_2Cl_8$ with bipy in *n*-butanol. It is paramagnetic ($\mu_{eff} = 1.36$ BM), but its spectral properties give few clues as to its structure.[108]

The reactions of $(Bu^n_4N)_2Re_2Cl_8$ with *N,N′*-diphenylbenzamidine ($PhC(NPh)_2H$), *N,N′*-di-

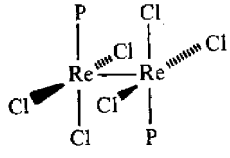
methylbenzamidine ($PhC(NMe)_2H$) and *N,N'*-diphenylacetamidine ($MeC(NPh)_2H$) have been found to produce the amidinato-bridged species $Re_2[(PhN)_2CPh]_2Cl_4$, $Re_2[(PhN)_2CPh]_2Cl_4 \cdot THF$, $Re_2[(PhN)_2CMe]_2Cl_4$ and $Re_2[(MeN)_2CPh]_4Cl_2 \cdot CCl_4$, all of which have been characterized by X-ray crystallography. The first three complexes have a *trans* disposition of amidinate ligands as shown in the case of $Re_2[(PhN)_2CPh]_2Cl_4$ (**37**), whereas $Re_2[(MeN)_2CPh]_4Cl_2 \cdot CCl_4$ has the closely related tetracarboxylato-type structure (*i.e.* $Re_2(O_2CR)_4Cl_2$, see Section 43.5.2.5) with two weakly bound axial chloride ligands. The THF solvate is of special interest since the THF molecule occupies one of the empty coordination sites colinear with the Re—Re bond and the rotational conformation is twisted 6° from the perfect eclipsed one found in the parent.[5] The Re—Re distances in these complexes fall in the narrow range 2.18 to 2.21 Å.[154,155]



(37)

43.5.2.4 Phosphines and arsines

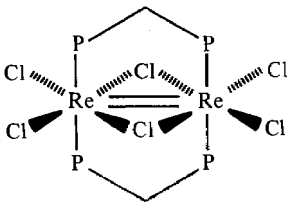
The reaction of the $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ anions with monodentate tertiary phosphines (*e.g.* PEt_3, PPr^n_3, PBu^n_3, PEt_2Ph, $PEtPh_2$ and PPh_3) in methanol gives the green substitution products $Re_2X_6(PR_3)_2$. The X-ray crystal structure of $Re_2Cl_6(PEt_3)_2$ (**38**) has confirmed the close structural relationship of these complexes to the parent anions.[57,156,157] The related reaction of $[Re_2X_8]^{2-}$ with $AsPh_3$ gives $Re_2X_6(AsPh_3)_2$. The phosphine complexes have been found to undergo one-electron reductions to give the monoanions $[Re_2X_6(PR_3)_2]^-$ possessing Re—Re bonds of order 3.5 (see Section 43.4.2.1). The oxidation of the triply bonded dirhenium(II) complex $Re_2Cl_4(PMe_2Ph)_4$ using $(NO)PF_6$ has been shown to give the salts $[Re_2Cl_4(PMe_2Ph)_4]PF_6$ and $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ (Section 43.4.2.1).[66] The latter diamagnetic quadruply bonded dicationic complex is isoelectronic with the neutral derivatives $Re_2X_6(PR_3)_2$. It reacts with Cl^- to give $Re_2Cl_6(PMe_2Ph)_2$ and can be cleaved by CO to give the mononuclear rhenium(I) carbonyl complex $ReCl(CO)_3(PMe_2Ph)_2$.[65,69]



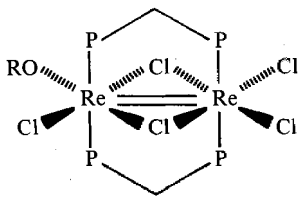
(38) P = PEt_3

While the reactions of $[Re_2X_8]^{2-}$ (X = Cl, Br or I) with dppe or arphos give either the triply bonded dirhenium(II) complexes $Re_2X_4(LL)_2$ (LL = dppe or arphos) (see Section 43.4.2.2) or the dimeric halogen-bridged magnetically dilute rhenium(III) complexes $Re_2(\mu\text{-}X)_2X_4(LL)_2$ (see Section 43.5.1.6), the complex $Re_2Cl_6(dppm)_2$ (**39**) can be prepared by the reaction of $(Bu^n_4N)_2Re_2Cl_8$ with bis(diphenylphosphino)methane in acetonitrile or dichloromethane.[70,74] It can also be generated by the electrochemical oxidation of $Re_2Cl_4(dppm)_2$ or $Re_2Cl_5(dppm)_2$ in the presence of chloride ion (see Section 43.4.2.2). The X-ray crystal structure of purple crystalline (**39**) confirms the structure proposed previously on the basis of ESCA data.[70,74] Furthermore, the structural details, including the Re—Re bond distance of 2.616(1) Å,[74] are in accord with the structure that had been predicted on the basis of this compound possessing a rhenium–rhenium double bond ($\sigma^2\pi^2\delta^2\delta^{*2}$ configuration).[158] The properties of (**39**) are very similar to those of the complexes $Re_2Cl_6(Ph_2Ppy)_2$[76] and $Re_2Cl_6(dppa)_2$ (dppa = bis(diphenylphosphino)amine)[74] that have been prepared by the reactions of $Re_2Cl_6(PBu^n_3)_2$ and $(Bu^n_4N)_2Re_2Cl_8$ with Ph_2Ppy and dppa, respectively. Accordingly, these three complexes are believed to have similar structures and to be members of the class of complexes that contain Re—Re double bonds. Other such derivatives are the alkoxide complexes $Re_2Cl_5(OR)(dppm)_2$ (**40**) (R = Me, Et, Pr^n or Bu^n) that are formed preferentially over

$Re_2Cl_6(dppm)_2$ when $(Bu^n_4N)_2Re_2Cl_8$ is reacted with dppm in the appropriate refluxing ROH solvent.[74]



(39) P⌒P = dppm

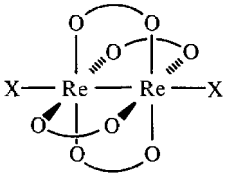


(40)

Electrochemical studies on solutions of (**39**) and (**40**) in 0.2 M $(Bu_4N)PF_6$–CH_2Cl_2 show that these complexes exhibit a well-defined and rich redox behavior. In the case of (**39**) four couples are observed in the potential range + 1.8 to − 1.4 V *vs.* SCE; two correspond to one-electron oxidations and two to one-electron reductions.[74]

43.5.2.5 Sulfates and alkyl and aryl carboxylates

The sulfato-bridged complex $Na_2Re_2(SO_4)_4 \cdot 8H_2O$ has been prepared by the reaction of $(Bu^n_4N)_2Re_2Cl_8$ with sulfate anion and may be reconverted to the chloro anion by reaction with refluxing hydrochloric acid in the presence of $(Bu^n_4N)Cl$. The structure shows the presence of weakly coordinated axial water molecules (r(Re—Re) = 2.214(1) Å, $r(Re—O)_{H_2O}$ = 2.28 Å).[159]



(41) O⌒O = O_2CR; X = Cl, Br, or I

Dirhenium(III) carboxylates of the type $Re_2(O_2CR)_{4-x}X_{2+x}$ (x = 0, 1 or 2) are known for a variety of carboxylate ligands and for X = Cl, Br or I. They constitute derivatives of $[Re_2X_8]^{2-}$ that are formed by the stepwise replacement of up to three pairs of *syn* halide ligands by bridging carboxylate ligands. They possess electronic structures that are closely related to those of the $[Re_2X_8]^{2-}$ anions. Their syntheses, structures and chemical reactivities have been fairly extensively reviewed for the period up to late 1981.[5,154] An example is shown in (**41**).

The conversion of the $[Re_2X_8]^{2-}$ anions (X = Cl, Br or I) into the orange-brown alkyl carboxylate complexes of the type $Re_2(O_2CR)_4X_2$ is most conveniently accomplished by reaction with refluxing mixtures of the appropriate acid and anhydride (if available).[61,142] In the reactions between $[Re_2X_8]^{2-}$ and XCH_2CO_2H (X = Cl or Br) both carboxylate coordination and halide exchange can occur, *e.g.* $[Re_2Cl_8]^{2-} + CH_2BrCO_2H \rightarrow Re_2(O_2CCH_2Br)_4Br_2$.[160] Rather than starting with salts of the $[Re_2Br_8]^{2-}$ and $[Re_2I_8]^{2-}$ anions, it is actually more convenient to react the chloro complexes $Re_2(O_2CR)_4Cl_2$ with liquid HBr or HI (equation 10).[68] In the presence of an excess of HX and the appropriate $(Bu^n_4N)X$ salt, this latter reaction may be used to regenerate $(Bu^n_4N)_2Re_2X_8$.[61] The corresponding aryl carboxylate complexes $Re_2(O_2CAr)_4X_2$ are best prepared from the acetates through exchange reactions (equation 11). While several other procedures have been used to prepare $Re_2(O_2CR)_4X_2$ complexes (X = Cl or Br) (*e.g.* using Re_3Cl_9 or *trans*-$ReOX_3(PPh_3)_2$[5]), none are as convenient or as generally applicable as the methods that employ $[Re_2X_8]^{2-}$.

$$Re_2(O_2CR)_4Cl_2 + 2HX \longrightarrow Re_2(O_2CR)_4X_2 + 2HCl \quad (10)$$

(X = Br or I)

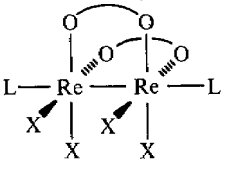
$$Re_2(O_2CCH_3)_4X_2 + 4ArCO_2H \longrightarrow Re_2(O_2CAr)_4X_2 + 4CH_3CO_2H \quad (11)$$

X-Ray structural studies on several complexes of the type $Re_2(O_2CR)_4X_2$ (**41**) (R = alkyl or aryl; X = Cl or Br) have established the now familiar multiply bonded carboxylate-bridged structure containing a very short Re—Re distance (~2.24 Å).[5,145] This structural unit is also present in $[Re_2(O_2CR)_4](ReO_4)_2$,[161] a 'mixed-valent' complex that contains weakly coordinated axial perrhenate anions and which is formed, along with $Re_2(O_2CR)_4Cl_2$ and $[Re_2(O_2CR)_3Cl_2](ReO_4)$ (*vide infra*), from the reaction of Re_3Cl_9 with refluxing carboxylic acids;[162] the perrhenate-containing species arise when oxygen is present. The existence and stability of $[Re_2(O_2CR)_4](ReO_4)_2$ (the derivative with R = Pr^n has been characterized by X-ray crystallography)[161] point out the lability of the axial halide ligands of $Re_2(O_2CR)_4X_2$, a result that accords with the formation of $Re_2(O_2CR)_4(NCS)_2$ and $[Re_2(O_2CR)_4(H_2O)_2]SO_4$ upon the reaction of $Re_2(O_2CR)_4Cl_2$ (R = Pr^n) with AgSCN and Ag_2SO_4, respectively.[5]

Electrochemical measurements of $Re_2(O_2CR)_4X_2$ (R = an alkyl or aryl group and X = Cl, Br or I) have revealed that CH_2Cl_2 solutions of these complexes are fairly easily reduced to the corresponding monoanions $[Re_2(O_2CR)_4X_2]^-$. The voltammetric half-wave potentials fall in the range −0.13 to −0.42 V *vs.* SCE, and show a dependence upon the nature of the halogen (becoming more negative in the order I < Br < Cl) and upon the Taft σ^* parameter for R.[68] The reduced anions can be prepared chemically using cobaltocene as the reducing agent to give $[(\eta^5\text{-}C_5H_5)_2Co]$-$[Re_2(O_2CR)_4X_2]$.[67] ESR spectral measurements and other characterization studies show that these species possess the $\sigma^2\pi^4\delta^2\delta^{*1}$ electronic configuration and, therefore, an Re—Re bond order of 3.5.

An especially important set of reactions of $Re_2(O_2CMe)_4Cl_2$ occurs with gaseous HX (X = Cl, Br or I). When run at temperatures between 300 and 350°C, these reactions afford the trinuclear rhenium(III) halides Re_3X_9 in close to quantitative yield. This is the one procedure that can conveniently be used to prepare all three halides.[143]

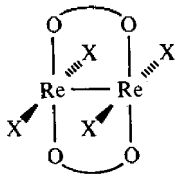
Complexes of stoichiometry $Re_2(O_2CR)_2X_4$ and $Re_2(O_2CR)_3X_3$ represent intermediate degrees of substitution between $[Re_2X_8]^{2-}$ and $Re_2(O_2CR)_4X_2$. Of these two sets of derivatives, the former are the more commonly encountered, the dark blue hydrated acetates $Re_2(O_2CMe)_2X_4\cdot 2H_2O$ (X = Cl or Br) being prepared either from $[Re_2X_8]^{2-}$ or by the high pressure hydrogen reduction of $KReO_4$ or K_2ReX_6 in a mixture of HX and acetic acid.[5,163,164] These hydrated species react with ligands (L) such as py, DMF, DMSO, dimethylacetamide and Ph_3PO to form other adducts of the type $Re_2(O_2CMe)_2X_4L_2$.[5,165] In those instances where the X-ray crystal structures of such molecules have been determined,[5,145] there is a *cis* arrangement of bridging acetate groups (**42**). This is also the case for the formate complex $(NH_4)_2[Re_2(O_2CH)_2Cl_6]$ and its diphenylformamide (DPF) derivative $Re_2(O_2CH)_2Cl_4(DPF)_2$ where a *cisoid* arrangement of carboxylate groups is present.[5] A close similarity in the spectral properties (IR and electronic absorption) of this group of acetate complexes[165] supports the notion that they are structurally very similar. Several mixed halide derivatives of the type $Re_2(O_2CMe)_2Cl_{4-x}Br_xL_2$ (L = DMF, DMSO or dimethylacetamide) were obtained as by-products during the autoclave synthesis of *cis*-$Re_2(O_2CMe)_2Br_4L_2$. Apparently, the presence of chloride in these products arose from impurities adsorbed on the wall of the autoclave from preceding experiments that involved an HCl-containing reaction mixture.[166]



(42) $O\overset{\frown}{O}$ = O_2CR; X = Cl, Br, or I

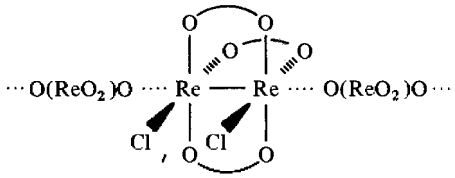
While thermal studies show that the axial ligands L of $Re_2(O_2CMe)_2X_4L_2$ can be lost upon heating, it is clear that this can be a complex process, although in the case of L = H_2O, this gives rise to the anhydrous form of the acetates $Re_2(O_2CMe)_2X_4$.[164,167] These same anhydrous compounds have also been formed through the thermal decomposition of $Re_2(O_2CMe)_4X_2$,[164] and the decomposition of the pivalate complex $Re_2(O_2CCMe_3)_4Cl_2$ *in vacuo* gives green crystalline $Re_2(O_2CCMe_3)_2Cl_4$ or pink $Re_2(O_2CCMe_3)_3Cl_3$ (*vide infra*) depending upon the temperature.[168] X-Ray structural studies on anhydrous $Re_2(O_2CMe)_2X_4$ (X = Cl or Br), $Re_2(O_2CCMe_3)_2Cl_4$ and $Re_2(O_2CPh)_2I_4$ have shown that a *trans* arrangement of carboxylate groups is present (**43**),[5,168,169] thereby demonstrating that a loss of axial ligands is accompanied by a *cis* → *trans* isomerization.

A few examples of the 3:3 carboxylate:halide complexes $Re_2(O_2CR)_3X_3$ have been obtained. One such example is $Re_2(O_2CCMe_3)_3Cl_3$ which is formed during the thermal decomposition of



(43)

$Re_2(O_2CCMe_3)_4Cl_2$ *in vacuo* at 240°C.[168] Violet $Re_2(O_2CMe)_3Cl_3$ has been prepared by dissolving $Re_2(O_2CMe)_2Cl_4$ in cold glacial acetic acid, while the analogous bromide is formed upon treating a chloroform solution of $Re_2(O_2CMe)_2Br_4$ with the stoichiometric quantity of acetic acid.[5,164] The structure of $Re_2(O_2CCMe_3)_3Cl_3$ represents a situation intermediate between that of (**41**) and (**43**), with $[Re_2(O_2CCMe_3)_3Cl_2]^+$ units linked by bridging Cl^- ligands into chains. A similar structure exists for $Re_2(O_2CH)_3Cl_3$, while in the case of $[Re_2(O_2CR)_3Cl_2]ReO_4$, a complex formed upon refluxing Re_3Cl_9 with carboxylic acids in the presence of oxygen,[162,170] perrhenate substitutes for an axial halide as shown by an X-ray crystal structure for the derivative where R = Pr^i (**44**).



(44) $O\overset{\frown}{O} = O_2CR$

A variety of dirhenium(III) carboxylates of the types $Re_2(O_2CMe)_4Br_2$, *trans*-$Re_2(O_2CMe)_2X_4$ (X = Cl or Br), *cis*-$Re_2(O_2CMe)_2X_4L_2$ (L = py, DMSO, *etc.*), $Re_2(O_2CH)_2Cl_4L_2$ (L = DMF or DMSO) and $(NH_4)_2[Re_2(O_2CH)_2Cl_6]$ have been studied by ^{35}Cl or ^{81}Br NQR spectroscopy and the results compared with data for salts of the $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ anions.[171] Also of interest are some screening studies that were carried out on the use of $[Re_2(O_2CEt)_4]SO_4$ and several derivatives of the type $Re_2(O_2CR)_2X_4 \cdot 2H_2O$ as antitumour agents.[172]

Mixed alkyl–carboxylato complexes of dirhenium(III) have been prepared starting from either $Re_2(O_2CMe)_4Cl_2$ or $[Re_2Me_8]^{2-}$. The chemistry of these multiply bonded complexes (*e.g.* $Re_2(O_2CMe)_2R_4$ and $Re_2(O_2CMe)_4Me_2$) is discussed elsewhere (see refs. 5 and 6).

43.5.2.6 Sulfur ligands

The complexes $Re_2X_6(tmtu)_2$ and $Re_2X_6(DTH)_2$ (X = Cl or Br; tmtu = tetramethylthiourea; DTH = 2,5-dithiahexane) are formed upon reacting $(Bu^n_4N)_2Re_2X_8$ with these ligands under mild reaction conditions. These complexes are believed, on the basis of spectroscopic data, to possess structures akin to that of $Re_2Cl_6(PEt_3)_2$ (**38**), although in the case of the DTH derivatives this means that this potentially bidentate ligand may be bonding in a monodentate fashion.[5]

43.5.2.7 Mixed donor atom ligands

Only two such complexes will concern us here. One of them, the doubly bonded dirhenium(II) complex $Re_2Cl_6(Ph_2Ppy)_2$ which contains the mixed P—N bidentate 2-(diphenylphosphino)pyridine ligand, has been described in Section 43.5.2.4. The other complex is $Re_2(hp)_4Cl_2$ (Hhp = 2-hydroxypyridine), which is prepared by the reaction of $(Bu^n_4N)_2Re_2Cl_8$ with the molten ligand and has a structure very similar to that of $Re_2(O_2CR)_4X_2$ (**41**), but with an even shorter Re—Re bond distance (2.206(2) Å *versus* 2.24 Å).[173]

43.5.3 Trinuclear Complexes Containing the Re_3^{9+} Core

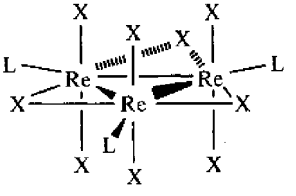
The trinuclear rhenium(III) halides Re_3X_9 (X = Cl, Br or I), and the mixed halides $Re_3X_{9-n}Y_n$ (*e.g.* $Re_3Cl_3Br_6$), contain Re—Re double bonds[174] and are the precursors to an extensive class of coordination complexes that are formed by the addition of up to three ligands to the available

coordination sites on these cluster halides, *i.e.* $Re_3X_9L_n$, where $n = 1$, 2 or 3 (**45**).[5] Many such complexes exist for X = Cl or Br,[5] but for Re_3I_9, only complexes with L = alkyl or aryl isocyanide ligand are known. Note that the reaction of Re_3I_9 with ligands such as tertiary amines or tertiary phosphines leads to the decomposition of the cluster.[175]

The synthetic and structural chemistry of Re_3X_9 has been reviewed and this source[5] can be usefully consulted for coverage of the literature up to late 1981. Note that in addition to the ability of Re_3X_9 to form coordination complexes involving minimum perturbation of the cluster structure, other reactions of note are the reductive cleavage of Re_3X_9 (X = Cl, Br or I) by isocyanide ligands to give $[Re(CNR)_6]^+$ (see Section 43.3.1)[22] and by phosphine ligands to give $Re_2X_4(PR_3)_4$ and $Re_2X_5(PR_3)_3$ (see Section 43.4.2.1).[56] Also, heterocyclic tertiary amines (L) can reduce Re_3X_9 (X = Cl or Br) to give trinuclear clusters of the type $[Re_3X_6L_3]_n$ (Section 43.4.3). The coordination chemistry that has been developed for trirhenium(III) cluster species containing Re—C (alkyl) bonds (*i.e.* $—CH_3$ and $—CH_2SiMe_3$) is discussed elsewhere (see refs. 5 and 6).

43.5.3.1 Cyanide, alkyl isocyanides and aryl isocyanides

The only cyanide-containing complexes known are $(Et_4N)_3[Re_3Cl_9(CN)_3]$ and $(Et_4N)_3[Re_3Cl_3(CN)_9]$ which can be isolated by the reaction between $(Et_4N)CN$ and Re_3Cl_9. In these reactions, no more than six of the Re—Cl bonds of the parent Re_3Cl_9 cluster can be replaced by cyanide.[176] The Re—Cl bonds that remain intact involve the Re—Cl—Re bridging units of (**45**).



(**45**) X = Cl or Br

While the earlier literature on isocyanide ligands has been reviewed recently,[6] subsequent studies have demonstrated the generality of the reactions that occur at room temperature between Re_3X_9 (X = Cl, Br or I) and alkyl or aryl isocyanides that lead to $Re_3X_9(CNR)_3$ (R = Me, $CHMe_2$, CMe_3, C_6H_{11} or *p*-tolyl).[22] The spectroscopic properties of these complexes show that the Re_3X_9 unit is intact. The electrochemical properties of solutions of the chloride and bromide complexes in 0.2 M $(Bu^n_4N)PF_6$–CH_2Cl_2 show a well-behaved one-electron oxidation close to +1.6 V *vs.* SCE and an irreversible reduction at ~ −0.15 V.[22] Note that when the reactions between Re_3X_9 and RNC are carried out in refluxing acetone and alcohol solvents, reductive cleavage of these clusters occurs to give $[Re(CNR)_6]^+$ (Section 43.3.1).

43.5.3.2 Nitrogen ligands

The reactions between Re_3X_9 (X = Cl or Br) and the more basic heterocyclic tertiary amines (L) that result in the reduction of the cluster and the formation of $[Re_3X_9L_3]_n$ (Section 43.4.3) are known to proceed *via* the intermediacy of $Re_3X_9L_3$, since purple $Re_3Cl_9py_3$ can first be isolated by careful control of the reaction conditions.[79] The less basic amines such as pyrazine, 2,6-dimethylpyrazine and 3-chloropyridine give unreduced $Re_3X_9L_3$. Similar 1:3 adducts have also been prepared by the reactions of Re_3Cl_9 with acetonitrile and benzonitrile.[5]

A careful study of the Re_3Cl_9–NH_3(l) system has shown[177] that ammonolysis occurs, and that the purple material that remains upon evaporation of the resulting reaction solution is a mixture of $Re_3Cl_6(NH_2)_3(NH_3)_3$ and NH_4Cl. This work has permitted a meaningful reassessment of earlier studies dealing with the reaction of Re_3X_9 with ammonia, and with primary and secondary amines, and their reinterpretation in terms of solvolysis of the Re—X bonds.[5]

Azide and thiocyanate react with Re_3Cl_9 in a similar fashion to that described for cyanide (Section 43.5.3.1) to give salts of the $[Re_3Cl_9X_3]^{3-}$, $[Re_3Cl_6X_6]^{3-}$, $[Re_3Cl_3X_9]^{3-}$ and $[Re_3Cl_3X_8]^{2-}$ anions (X = N_3 or NCS).[176,178] There is also evidence that $[Re_3(NCS)_{12}]^{3-}$ can be formed from Re_3X_9 (X = Cl or Br) under forcing reaction conditions, further reflecting the fact that the order of Re—Cl bond lability is $Cl_t \gg Cl_b$.[178]

43.5.3.3 Phosphines and arsines

The preparation and structural characterization of $Re_3Cl_9(PEt_2Ph)_3$ was an important early advance in the development of the chemistry of the halides Re_3X_9.[5] An X-ray crystal structure determination established that it possessed structure (**45**) (L = PEt_2Ph) with short Re—Re bonds (2.49 Å) but long Re—P distances (2.70 Å), the latter arising from steric crowding.[179] Other monodentate phosphines ($PMePh_2$, $PEtPh_2$ and PPh_3) and $AsPh_3$ from crystalline purple-red tris adducts with Re_3Cl_9 and Re_3Br_9 that bear a close structural relationship to $Re_3Cl_9(PEt_2Ph)_3$.[5] When the reactions between phosphines PR_3, PR_2Ph or $PRPh_2$ (R = alkyl) and Re_3X_9 (X = Cl, Br or I) are carried out in refluxing acetone or alcohol solvents, the lower valent dirhenium complexes $Re_2X_4(PR_3)_4$, $Re_2X_4(PR_2Ph)_4$ and $Re_2X_5(PRPh_2)_3$ are produced.[57,80,175] The coordination of several phosphole ligands to Re_3Cl_9 has also been investigated. Ethanol solutions of 3-methyl-1-phenylphosphole (mPP) and 3,4-dimethyl-1-phenylphosphole (dPP) react immediately to form diamagnetic $Re_3Cl_9L_3$ (L = mPP and dPP). With bulky phospholes like 1,2,5-triphenylphosphole (TPP), complex formation requires reflux conditions and gives the less stable solvated complexes $Re_3Cl_9L_2 \cdot CH_2Cl_2$.[180]

In contrast to the well-defined adducts with monodentate phosphines and arsines, the reactions of Re_3Cl_9 and Re_3Br_9 with polydentate ligands give products that with few exceptions are not well characterized. An exception is $Re_3Cl_9(dppe)_{1.5}$ which is formed upon mixing acetone or THF solutions of Re_3Cl_9 and dppe. Spectroscopic evidence favors it being an authentic Re_3Cl_9 derivative, containing intermolecular dppe bridges.[181] There is also evidence that small quantities of mononuclear $[ReCl_2(dppe)_2]Cl$ are formed in this reaction.[182] The corresponding reaction between Re_3Cl_9 and *o*-phenylenebisdimethylarsine (diars) in acidified (HCl) ethanol gives red insoluble $Re_3Cl_9(diars)_2$ together with small quantities of $[ReCl_2(diars)_2]Cl$.[182] In the case of tri-, tetra- and hexadentate and phosphine and arsine ligands, the true nature of the resulting products is poorly understood.[5,183] A summary of the reactions that have been carried out together with the proposed stoichiometries of the products is given in Table 7.

43.5.3.4 Oxygen ligands

Most complexes containing oxygen donors are of the type $Re_3X_9L_3$ (X = Cl or Br).[5] These have been prepared with Ph_3PO, Ph_3AsO, DMF, HMPA and sulfoxide ligands and they possess properties that clearly demonstrate their close structural relationship to $Re_3Cl_9(PEt_2Ph)_3$ (**45**).[5] The ligand 1,2,5-triphenylphosphole oxide reacts with Re_3Cl_9 in refluxing dichloromethane to give the solvate $Re_3Cl_9L_2 \cdot CH_2Cl_2$.[186] With the bidentate ligand acetylacetone (acacH), both in-plane coordination and solvolysis of one of the out-of-plane terminal Re—X bonds per rhenium atom occurs to give $Re_3Cl_6(acac)_3$.[178] The rather novel cluster complex $Re_3Br_3(AsO_4)_2(DMSO)_3$ is apparently formed upon reacting an acetone solution of Re_3Br_9 with silver arsenate, followed by extraction of the resulting solid into dimethyl sulfoxide.[184] The structure, on the basis of spectroscopic measurements, has been suggested to involve the capping of the faces of the Re_3 triangle by two tridentate arsenate ligands. This is a further illustration of the lability of the terminal Re—X bonds in the Re_3X_9 clusters.

A recent and quite original approach to the synthesis of Re_3X_9 cluster complexes involves the cocondensation of rhenium atoms, generated from a positive hearth electron-gun furnace, and reactive halocarbons such as 1,2-dibromo- (or dichloro-) ethane. Extraction of the reaction matrix at room temperature with THF gives $Re_3X_9(THF)_3$ (X = Cl or Br) in yields of ~90%.[185] This strategy will likely see further developments in the future.

Table 7 Products from the Reactions of Re_3Cl_9 with Tri-, Tetra- and Hexa-dentate Phosphine and Arsine Ligands

Ligand (abbreviation)	*Product(s)*	*Comments*	*Ref.*
$(Ph_2PCH_2)_3CMe$ (P_3)	$Re_3Cl_9(P_3)$	Red crystals; THF as solvent	5
$(Ph_2PCH_2CH_2)_2PPh$ (Pf—Pf—Pf)	$Re_3Cl_9[(Pf)_3]_2$	Reaction solvent dependent	5
$(Ph_2AsCH_2CH_2)_2PPh$ (Asf—Pf—Asf)	$Re_3Cl_9(Asf—Pf—Asf)_2$	Brown solid; MeCN as solvent	183
$(Ph_2PCH_2CH_2)_3P$ ($P(Pf)_3$)	$Re_3Cl_9[P(Pf)_3]_2$, $\{ReCl_3[P(Pf)_3]\}_n$[a]	Reaction solvent dependent	5
$Ph_2P(CH_2)_2P(Ph)(CH_2)_2P(Ph)(CH_2)_2PPh_2$ (Pf—Pf—Pf—Pf)	$\{ReCl_3[(Pf)_4]\}_n$[a]	Reaction solvent dependent	5
$(Ph_2PCH_2CH_2)_2PCH_2CH_2P(CH_2CH_2PPh_2)_2$ ($P_2(Pf)_4$)	$ReCl_2[P_2(Pf)_4]^+$[a]	2-Methoxyethanol as solvent	5

[a] Product is believed to be a mononuclear rhenium(III) derivative.

The nitrate-containing salt $Cs_3Re_3Cl_9(NO_3)_3$ has been prepared by the addition of $CsNO_3$ to a solution of Re_3Cl_9 in ice-cold nitric acid. This reaction is accompanied by the oxidation of some of the rhenium and the formation of Cs_2ReCl_6.[187]

There also exist several stable derivatives of Re_3X_9 that contain coordinated water molecules. This situation arises with certain complex halides of Re_3X_9 (Section 43.5.3.6) and in the case of the diethyl sulfide complex $Re_3Cl_9(Et_2S)_2(H_2O)$ (Section 43.5.3.5). The aforementioned sections should be consulted for further reference to these complexes.

43.5.3.5 Sulfur and selenium ligands

Few such complexes are known and once again they are of the type $Re_3X_9L_3$ (**45**). The complexes with 1,4-thioxane, $Re_3Cl_9(C_4H_8OS)_3$, and diethyl sulfide, $Re_3Cl_9(Et_2S)_2(H_2O)$, have been described, the former possessing S-bound 1,4-thioxane.[181,182] In acetone solution Re_3Cl_9 reacts with 2,5-dithiahexane (DTH) to give polymeric $Re_3Cl_9(DTH)_{1.5}$, possessing, it is believed, bridging DTH ligands that are in the *trans* rotational conformation.[181] Under more forcing reaction conditions, the polymer structure breaks down and up to three monodentate DTH ligands may coordinate to the Re_3Cl_9 cluster. Both the chloride and bromide clusters Re_3X_9 react with sodium diethyldithiocarbamate (Nadtc) to form $Re_3X_6(dtc)_3$, species that are very similar to the corresponding acac derivative $Re_3Cl_6(acac)_3$ (Section 43.5.3.4). The remaining terminal Re—Cl bonds of the chloride complex $Re_3Cl_6(dtc)_3$ can be replaced upon reaction with silver thiocyanate to yield $Re_3Cl_3(NCS)_3(dtc)_3$.[178]

The only derivative of Re_3X_9 that contains a selenium ligand is one of stoichiometry $Re_3Cl_9L_2 \cdot CH_2Cl_2$ that is formed by the reaction of Re_3Cl_9 with 1,2,5-triphenylphosphole selenide in refluxing dichloromethane.[186]

43.5.3.6 Halides

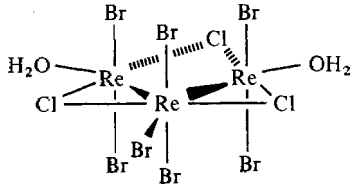
Salts containing the complex halides $[Re_3X_{9+n}]^{n-}$ (X = Cl or Br; n = 1, 2 or 3) constitute the most important group of coordination complexes of the trinuclear halides of rhenium(III). The key example is $Cs_3Re_3Cl_{12}$, because its structural characterization by X-ray crystallography first demonstrated the trinuclear structure of Re_3X_9 and its derivatives (see structure **45**), and its identification played a decisive role in opening up the field of multiple metal–metal bond chemistry.[5] The cesium salt is prepared by mixing Re_3Cl_9 with CsCl in concentrated hydrochloric acid.[188] This simple synthetic procedure can be effectively used to prepare nearly all such complex halides of Re_3Cl_9 and Re_3Br_9.[5] Salts have been prepared with both alkali metal cations and various organic cations (*e.g.* pyH^+ and Ph_4As^+).[5] The success relies in large part upon the quite remarkable stability of such solutions to oxidation to mononuclear rhenium(IV) species. The $[Re_3Cl_{12}]^{3-}$ anion and species like it bear a close structural relationship to Re_3Cl_9; each of the intermolecular Re—Cl bridges of Re_3Cl_9 are cleaved and replaced by a terminally bound chloride ligand.[189,190] The Re—Re distance in $Cs_3Re_3Cl_{12}$ is 2.477(3) Å.

The specific salt of an $[Re_3X_{9+n}]^{n-}$ anion that can be isolated depends primarily upon the choice of cation and of X, although in a few instances crystals have been grown under conditions sufficiently different that different anions can be stabilized by the same cation, *e.g.* $Cs_3Re_3Br_{12}$ and $Cs_2Re_3Br_{11}$.[5,178] Crystal structure determinations on the salts $(Ph_4As)_2Re_3Cl_{11}(H_2O)$, $Cs_3Re_3Br_{12}$ and $Cs_2Re_3Br_{11}$ have confirmed their identity, the first complex containing a coordinated water molecule.[5] These studies have further demonstrated that in cases where one of the rhenium atoms is deficient (*i.e.* $Cs_2Re_3Br_{11}$), the structure distorts in such a way that the two Re—Re bond lengths that are associated with the deficient Re atom are shorter (2.43 Å) than the remaining Re—Re bond (2.49 Å).[191]

An important radiochemical exchange experiment using $H^{36}Cl$ has shown that for $[Re_3Cl_{12}]^{3-}$, the order of substitutional lability is Cl_t (in-plane) > Cl_t(out-of-plane) ≫ Cl_b, a conclusion that is further supported by chloride–pseudohalide exchange reactions using N_3^-, CN^- and NCS^- (see Sections 43.5.3.1 and 43.5.3.2). In addition to these lability studies, there are other reactions that have revealed that the Re_3X_9 clusters are susceptible to oxidative disruption under certain conditions. Thus it has been found that while the quinolinium salt $(quinH)_2Re_3Br_{11}$ can be isolated upon treating a saturated solution of Re_3Br_9 in 48% hydrobromic acid with an excess of quinoline, the salt $(quinH)_2Re_4Br_{14}$ can also be isolated from this reaction medium.[192] Use of pyridine or Et_4N^+ in place of quinoline gives the pyH^+ or Et_4N^+ salts of $[Re_4Br_{14}]^{2-}$. An X-ray crystal structure determination of $(quinH)_2Re_4Br_{14}$ shows that it should be formulated as $(quinH)_2[ReBr_6]$-

$[Re_3Br_9(H_2O)_3]$.[193] The closely related green-brown complex $(Bu^tPCl_3)_2[ReCl_6][Re_3Cl_9]$ has been prepared by a different route, namely, the reaction between $ReCl_5$, PCl_3 and Bu^tCl in CS_2. Its structural formulation is based upon IR, electronic absorption and mass spectral studies.[194]

When solutions of Re_3Br_9 in hydrobromic acid are subject to air oxidation, salts of $[ReBr_6]^{2-}$ and $[ReOBr_4]^-$ can be isolated upon addition of the appropriate cation.[195] In a similar vein, the addition of a hydrobromic acid solution of Re_3Cl_9 to an aqueous solution of CsBr can lead to crystals of Cs_2ReCl_6, Cs_2ReBr_6, $Cs_5Re_4Cl_6Br_{12}$ (believed to be $Cs_2ReBr_6 \cdot Cs_3Re_3Cl_6Br_6$) and $CsRe_3Cl_3Br_7(H_2O)_2$ (**46**) provided one is patient in the work-up procedure.[187] The X-ray crystal structure of complex (**46**) has revealed that the $[Re_3Cl_3]^{6+}$ core is intact and that water molecules occupy two of the three in-plane terminal coordination sites.[196] These oxidations of the Re_3Cl_9 and Re_3Br_9 units in hydrohalic acids presumably arise, at least in part, from oxygen. However, another important reaction that can lead to Re^{IV} is the well-documented disproportionation of Re_3X_9 (equation 12) in the solid state at elevated temperatures or in molten halide media.[31,197]



(46)

$$4Re_3X_9 \longrightarrow 3Re^0 + 9[ReX_6]^{2-} \qquad (12)$$

43.5.4 Hexanuclear Clusters of Rhenium(III)

The ternary sulfide phases $M^I_4[Re_6S_8]S_{4/2}(S_2)_{2/2}$ (M^I = Na or K) have been prepared by the reaction of Re, $KReO_4$ or ReS_2 with a large excess of Na_2CO_3 or K_2CO_3 and sulfur (alternatively a stream of H_2S can be used) at a temperature of 750–800°C.[198,199] X-Ray crystal structure determinations have confirmed the presence of the $[Re_6S_8]$ core in these Re^{III} complexes (Re—Re distance 2.59–2.63 Å) and the presence of intra- and inter-cluster sulfide bridges and bridging disulfide units. These red crystalline complexes have been found to transform to black crystals upon standing in air or various solutions with little loss of crystal integrity but with a change from insulating to semiconducting behavior.[198]

The preparation of similar ternary sulfide phases using barium or strontium carbonates in place of sodium and potassium has led to the isolation of $Ba_2Re_6S_{11}$ and $Sr_2Re_6S_{11}$ when the preparations are carried out at $\approx$ 1400°C in a stream of H_2S.[200] These rhenium(III) complexes are, like their alkali metal analogues, diamagnetic and have a structure containing the $\{[Re_6S_8]S_{6/2}\}^{4-}$ framework, thereby differing from $M^I_4[Re_6Cl_8]S_{4/2}(S_2)_{2/2}$ in the absence of bridging disulfide units.

One of the stimuli for studying these complexes is their close relationship to the well-known Chevrel phases MMo_6Y_8 (Y = S, Se or Te). Accordingly, a noteworthy recent development is the discovery of octahedral rhenium–selenide clusters. The phase $Re_6Se_8Cl_2$ has been prepared by the high temperature reaction ($\sim$ 1300 K) of $ReCl_5$ with mixtures of Re and Se.[201] An X-ray crystal structure has shown the presence of the $[Re_6Se_8]$ core possessing Re—Re distances of 2.63–2.67 Å. The presence of two terminal Re—Cl bonds (*trans* to one another) inhibits interlayer linkages.[201]

The semiconductor-like rhenium telluride phase Re_2Te_5 has been characterized by X-ray crystallography and shown to possess the usual octahedral Re_6 core (r(Re—Re) = 2.67–2.72 Å) within the structure $\{[Re_6Te_8]Te_6\}Te$, in which the $[Re_6Te_8]$ clusters are linked *via* butterfly-like [Te{Te—Te—Te}$_2$] units.[202]

Mixed-metal clusters that contain rhenium, *e.g.* the phase $Mo_{1.5}Re_{4.5}Se_8$, can also be prepared by direct reaction of the elements. They contain the octahedral $(Mo,Re)_6$ cluster.[203]

Preliminary X-ray structural data have been reported[598] for $Re_6(\mu_3\text{-}Se)_4(\mu_3\text{-}Cl)_4Cl_6$. The phases $Re_6X_4X'_{10}$ (X = Se or Te; X′ = Cl or Br) react with various ligands L in DMSO to give materials of stoichiometry $[Re_3X_2X'_5 \cdot L \cdot DMSO]_n$ (L = Et_3N, $Me_2NCH_2CH_2NMe_2$ or bipy).[599] The clusters $M^I_4[Re_6S_8]S_{2/2}(S_2)_{4/2}$ (M^I_4 = Rb_4 or K_2Rb_2) have been synthesized by the reaction of alkali metal carbonates with Re in a stream of H_2S at 800°C. The analogous selenides $M^I_4Re_6Se_{13}$ have also been obtained.[600]

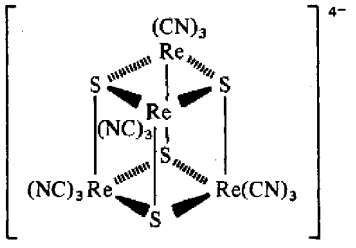
43.6 RHENIUM(IV) COMPLEXES

The most numerous complexes of this oxidation state are halide species of the types ReX_4L_2, $[ReX_5L]^-$ and $[ReX_6]^{2-}$.[1] Also, in contrast to the lower oxidation states, Re^{IV} begins to display the tendency for oxo–rhenium bonding (in this instance in Re—O—Re bridges) that becomes so dominant in the chemistry of the higher oxidation states Re^V, Re^{VI} and Re^{VII}. At the same time, the propensity of rhenium to form multiple metal–metal bonds that was apparent in the chemistry of Re^{II} and Re^{III} begins to diminish in the case of Re^{IV}. One final general point concerns the fact that the Re^{IV} oxidation state, like that of Re^V, is apparently present in many of the complexes that contain multidentate mixed donor ligands which have been used for the spectrophotometric determination of rhenium. These complexes, which are usually generated by the $SnCl_2$ reduction of Re^{VII} in hydrochloric acid, are for the most part of ill-defined structure and often of uncertain oxidation state, although the Re:ligand stoichiometry is usually known. Such poorly characterized systems, recent examples of which include rhenium complexes of *N*-(4-methoxyphenyl)-α-thiopicolinamide and various thiohydrazones,[208,209] will not be discussed further.

43.6.1 Mononuclear Complexes

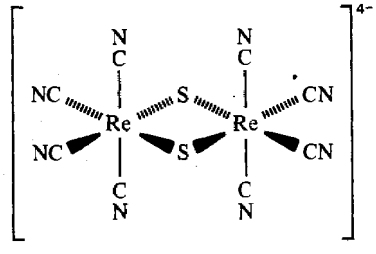
43.6.1.1 Cyanides and alkyl isocyanides

Salts of the $[Re(CN)_{6+n}]^{(n+2)-}$ anions are unknown, and a report that $K_4[ReO_2(CN)_4]$ can be prepared by the reaction of K_2ReCl_6 with an excess of aqueous KCN at room temperature gave, in other hands, a mixture of $K_3[ReO_2(CN)_4]$, $K_5[Re(CN)_6]$ and $K_5[Re_2(CN)_9(OH)_3]\cdot 2H_2O$.[15] The reactions of K_2ReCl_6 with KSCN/KCN or KSeCN/KCN melts at 250 and 320°C respectively give the diamagnetic, red-brown, cubane-like clusters $[Re_4(\mu_3\text{-}S)_4(CN)_{12}]^{4-}$ and $[Re_4(\mu_3\text{-}Se)_4(CN)_{12}]^{4-}$. When KOCN is used in place of KSCN then ReO_2 is formed.[15,210] The sulfide and selenide species have been isolated as their K^+, Cs^+, $(Ph_4P)^+$ and $(Ph_4As)^+$ salts, and the X-ray crystal structures of $(Ph_4P)_4[Re_4L_4(CN)_{12}]\cdot 3H_2O$ (L = S or Se) (**47**) determined.[210] These results contradict an earlier report that $[Re(CN)_6]^-$ can be prepared using this procedure. The IR and Raman spectra of the crystalline salts and their solutions accord quite nicely with the crystal structure data.[15]



(47)

The reaction between $NaReO_4$ and H_2S in an excess of aqueous NaCN solution yields salts of the diamagnetic $[Re_2(\mu_2\text{-}S)_2(CN)_8]^{4-}$ ion.[15] The blue-green Cs^+, $(Ph_4P)^+$ and $(Ph_4As)^+$ salts have been isolated and the X-ray crystal structure of $(Ph_4P)_4[Re_2(\mu_2\text{-}S)_2(CN)_8]\cdot 6H_2O$ (**48**) shows it to be an edge-shared bioctahedron with Re—S—Re bridges.[211] The Re—Re distance of 2.60 Å is substantially shorter than the comparable distance(s) (2.755 Å) present in tetranuclear (**47**), but the extent of Re—Re bonding in these complexes remains unknown.



(48)

The methyl isocyanide complex $(Bu^n_4N)[ReCl_5(CNMe)]$ is prepared in rather low yield in the reaction between $(Bu^n_4N)_2Re_2Cl_8$ and MeNC in ethanol.[212] It is a member of a relatively extensive class of complexes of the type $[ReX_5L]^-$ (X = halide) (Section 43.6.1.9).

43.6.1.2 *Ammonia and* N-*heterocycles*

Complexes of Re^{IV} with ammonia and aliphatic amines are not well defined and the chemistry has been little explored. $ReCl_5$ reacts with NH_4Cl at 195°C to give a material formulated as $[ReCl_4(NH_3)]$ which at higher temperature (250°C and above) decomposes first to $[ReCl_3(NH_2)]$ and then to ReNCl and Re_2NCl.[213]

The pyridine complex *cis*-$ReCl_4(py)_2$ has been obtained by dissolving β-$ReCl_4$ in dry pyridine, a reaction which also gives $(pyH)_2Re_2Cl_8$.[104] It has also been obtained, as has its bromide analogue, by the more traditional method of pyrolyzing $(pyH)_2ReX_6$,[1,2] a procedure that has been used for the synthesis of other compounds of the type $ReCl_4L_2$. The complexes $ReX_4(bipy)$ and $ReX_4(phen)$ (L = Cl or Br) can be prepared by the pyrolysis of $(LH)_2ReX_6$(L = bipy or phen), the reaction of $ReCl_5$ or K_2ReBr_6 with molten bipy, or the reaction of $ReBr(CO)_3(bipy)$ with refluxing dry Br_2.[1,214] A variation of the last of these procedures to include the reaction between $ReCl(CO)_3(bipy)$ and Br_2 gives the mixed halide derivative $ReClBr_3(bipy)$.[214]

The brown or red py, bipy and phen complexes have electronic absorption spectra and magnetic properties that accord with their being magnetically dilute t_{2g}^3 species, and low frequency IR spectra that show ν(Re—X) patterns consistent with *cis* octahedral geometries. This contrasts with the properties of a black complex purported to be $Re(OH)Cl_3(phen)$ that was prepared by the reaction of an aqueous solution of K_2ReCl_6 with an ethanol solution of phen.[215] A magnetic moment of 2.1 BM is not consistent with its formulation as a normal magnetically dilute Re^{IV} complex. However, the presence of a low-spin configuration is a possibility. Previous reports of the isolation of $ReI_4(py)_2$ from the interaction of ReI_4 with pyridine in acetone[2] could not be confirmed in a later reinvestigation of this system.[216] Also, since $ReI_4(bipy)$ and $ReI_4(phen)$ are not formed in the analogous reactions involving 2,2-bipyridyl or 1,10-phenanthroline,[216] a report describing the preparation of $ReI_4(phen)$ by such a procedure[2] is at this time still open to question. However, the treatment of $[ReO_2(py)_4]I \cdot H_2O$ with freshly distilled HI has been reported to give $ReI_4(py)_2$. The magnetic moment of this complex (μ_{eff} = 3.59 BM) supports it being a Re^{IV} derivative.[258]

The mixed phosphine–pyridine complex $ReCl_4(py)(PPh_3)$ is formed as orange crystals by the reaction of *trans*-$ReCl_4(PPh_3)_2$ with boiling pyridine for ten minutes.[217] Salts of the $[ReCl_5(py)]^-$ and pyrazine-bridged $[(ReCl_5)_2pyz]^{2-}$ anions are also known and are discussed in Section 43.6.1.9.

43.6.1.3 *Diazenido and imido ligands*

While rhenium(III) complexes containing diazenido ligands are quite numerous and well characterized (Section 43.5.1.3), those of rhenium(IV) are rare. The benzoyldiazenido complex $ReCl_2(N_2COPh)(PPh_3)_2$ (**23**) reacts with Cl_2 in CCl_4 in two steps. The brown, crystalline, air stable Re^{IV} complex $ReCl_3(N{=}NCOPh)(PPh_3)_2$ is formed first, and this on further treatment with Cl_2 is converted to *trans*-$ReCl_4(PPh_3)_2$ according to equations (13) and (14).[87] This Re^{IV} complex exhibits a ν(N=N) mode at 1580 cm^{-1} in its IR spectrum and has a magnetic moment of 2.85 BM.

$$ReCl_2(N_2COPh)(PPh_3)_2 + \tfrac{1}{2}Cl_2 \longrightarrow ReCl_3(N_2COPh)(PPh_3)_2 \quad (13)$$

$$ReCl_3(N_2COPh)(PPh_3)_2 + Cl_2 \longrightarrow ReCl_4(PPh_3)_2 + PhCOCl + N_2 \quad (14)$$

The one example of an imido complex of rhenium(IV) is $Re(NPh)Cl_2(PMe_3)_3$ which has been prepared by the reduction of $Re(NPh)Cl_3(PMe_3)_2$ in THF using one equivalent of Na/Hg in the presence of an excess of trimethylphosphine. This air sensitive, dark red crystalline complex is paramagnetic with a magnetic moment of 1.66 BM at room temperature, and is further characterized by a broad ESR signal centered at g = 1.74 for a frozen benzene solution.[34] These observations have been interpreted in terms of a low-spin Re^{IV} species with a ligand field of low symmetry.

43.6.1.4 *Cyanate and thiocyanate*

The brown hexacyanato complex $(Ph_4As)_2[Re(CNO)_6]$ has been reported to be the product of reaction K_2ReCl_6 with KOCN in molten dimethylsulfone followed by dissolution of the residue in

water and its rapid precipitation by the addition of $(Ph_4As)Cl$.[218] Its magnetic moment (4.1 BM) is significantly higher than that found for other species of the type $[ReX_6]^{2-}$ (*e.g.* X = thiocyanate) and is not readily explained. The interpretation of the IR spectrum of this salt, based upon a consideration of the ν(CN), ν(CO) and ν(NCO) modes,[218] in terms of O-bound cyanate ligands should be treated with caution in the absence of definitive X-ray structure data. Also, the ease with which $[Re_4(\mu\text{-}S_3)_4(CN)_{12}]^{4-}$ is formed in a K_2ReCl_6/KSCN/KCN melt system by sulfide abstraction from the KSCN (Section 43.6.1.1), raises the question as to whether an analogous reaction course (*i.e.* O abstraction) might occur to some extent in a KOCN/dimethylsulfone melt system. Indeed, the reaction of a KCNO/KCN melt with K_2ReCl_6 is known to give ReO_2.

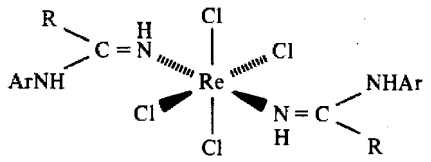
The well-characterized and stable hexakis(isothiocyanato)rhenate(IV) anion is a key species (along with $[ReO(NCS)_5]^{2-}$) in the spectrophotometric determination of rhenium in solutions generated by the reduction of $[ReO_4]^-$ with thiocyanate and tin(II) ion in hydrochloric acid.[219,220] The dark red-brown salts $Cs_2Re(NCS)_6$ and $(Bu^n_4N)_2Re(NCS)_6$ are best prepared by the reaction of K_2ReCl_6 with molten KSCN, followed by cation exchange in aqueous CsCl, and of $(Bu^n_4N)_2Re_2Cl_8$ with NaSCN in acetone, respectively.[152,221] The addition of thallous acetate to an aqueous solution of $Cs_2Re(NCS)_6$,[221] and the mixing of a methanol solution of $(Ph_4As)Cl$ with a THF solution containing $[Re(NCS)_6]^{2-}$,[152] have been used to prepare $Tl_2Re(NCS)_6$ and $(Ph_4As)_2Re(NCS)_6$, respectively. The Sn^{II} reduction of $[ReO_4]^-$ and SCN^- in hydrochloric acid produces red solutions from which the salts $(Ph_4As)_2Re(NCS)_6$ and $(Ph_4As)_2ReO(NCS)_5$ have both been isolated.[220,222] These results throw into doubt the recent notion that $[ReO(SCN)_4]^{2-}$ is present in such solutions.[223] The $[Re(NCS)_6]^{2-}$ anion has been thoroughly characterized spectroscopically,[152,220] and magnetic moment determinations on the Cs^+, Tl^+, $(Bu^n_4N)^+$ and $(Ph_4As)^+$ salts show them to be well-behaved octahedral Re^{IV} species; the room temperature magnetic moments are 3.66, 3.36, 3.50 and 3.38 BM, respectively.[152,221] Electrochemical measurements have shown that the $[Re(NCS)_6]^{2-}$ anion exhibits an irreversible one-electron oxidation above +1.0 V *vs.* SCE (+1.23 V in MeCN and +1.03 V in CH_2Cl_2) and a reversible reduction at ~ −0.2 V *vs.* SCE (−0.11 V in MeCN and −0.28 V in CH_2Cl_2).[94,95] The one-electron reduction is both electrochemically and chemically reversible as demonstrated by the isolation of $(Bu^n_4N)_3Re(NCS)_6$ upon using $N_2H_4 \cdot H_2O$ as reducing agent (Section 43.5.1.4).[96]

A report[2] describing the isolation of the complex $ReO(SCN)_2(py)_3$ through the addition of pyridine to the solution generated by the $SnCl_2$ reduction of $KReO_4$ has not been confirmed. Such a complex would be most unusual for it would contain the hitherto unknown terminal $[Re{=}O]^{2+}$ moiety.

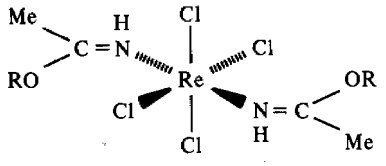
43.6.1.5 Nitriles and amidates

Like other higher valent halides of the transition metals, $ReCl_5$ is reduced by acetonitrile to give the rhenium(IV) complex $ReCl_4(NCMe)_2$.[98] Other nitrile complexes $ReCl_4(NCR)_2$ (R = Pr^n or Ph) can be prepared by this same route or by ligand exchange from $ReCl_4(NCMe)_2$. Later work has shown[224] that this synthetic procedure for $ReCl_4(NCMe)_2$ gives predominantly the crystalline green *cis* isomer together with a small amount of the brown-green *trans* form. A detailed comparison has been made of the spectroscopic properties (IR, electronic absorption and ESCA) of *cis*- and *trans*-$ReCl_4(NCMe)_2$.[224] This complex can also be prepared by the dissolution of β-$ReCl_4$ in boiling acetonitrile.[104] The oxidation of acetonitrile solutions of *fac*-$Re(CO)_3X(NCMe)_2$ (X = Cl or Br) with Cl_2 or Br_2 gives pale green *cis*-$ReCl_4(NCMe)_2$ and brown *cis*-$ReBr_4(NCMe)_2$, respectively in yields exceeding 50%.[225] This method provides a convenient alternative and, furthermore, is applicable to the bromide complex. The acetonitrile complex $[Et_4N][ReCl_5(NCMe)]$ is also known (Section 43.6.1.9).

The reactivity of *cis*-$ReCl_4(NCR)_2$ has been studied in considerable detail.[98] Reduction to $[ReCl_4(NCMe)_2]^-$ takes place quite readily (Section 43.5.1.5), while displacement of the MeCN ligands can be accomplished using APh_3 (A = P, As or Sb) (Section 43.6.1.6). The complexes $ReCl_4(NCR)_2$ react rapidly in the cold with primary aromatic amines ($ArNH_2$) to give the stable, orange amidato complexes $ReCl_4[NH{=}C(R)(NHAr)]_2$ (Ar = *p*-tol, *m*-C_6H_4F and *p*-$C_6H_4(CO_2Et)$ for R = Me; Ar = *p*-$C_6H_4(OMe)$ for R = Ph). These behave as typical Re^{IV} species (*e.g.* μ_{eff} = 3.5 BM) and are believed to possess a *trans* octahedral structure (**49**). The corresponding reactions of $ReCl_4(NCMe)_2$ with methanol and ethanol give the green crystalline complexes $ReCl_4[NH{=}C(Me)OR]_2$ (M = Me or Et) (**50**); in the case of the methanol reaction, $Cs_2[Re(OMe)Cl_5]$ (Section 43.6.1.9) can be isolated from the reaction filtrate upon addition of CsCl.



(49)



(50) R = Me or Et

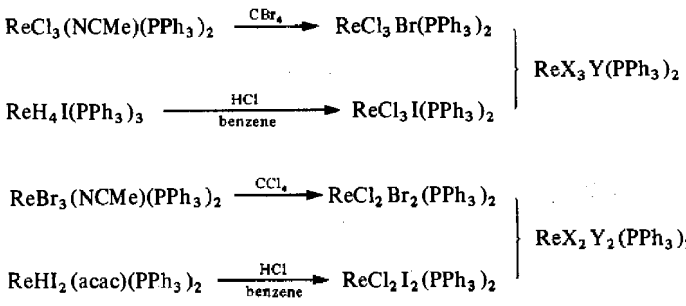
43.6.1.6 Phosphines, arsines and stibines

The complexes *trans*-$ReCl_4L_2$ that are formed with monodentate phosphine, arsine and stibine ligands constitute a very stable and easily prepared class of compounds. This is especially true in the case of *trans*-$ReCl_4(PPh_3)_2$ which can be obtained by what seems to be a myriad of procedures. This is illustrated in Table 8 wherein are listed a selection of the more important methods that are known to produce complexes of the type *trans*-$ReX_4(AR_3)_2$ (X = Cl, Br or I; A = P, As or Sb). Note that in the reaction between *cis*-$ReCl_4(NCMe)_2$ and PPh_3, a short reaction time followed by a rapid quenching of the reaction gives *cis*-$ReCl_4(NCMe)(PPh_3)$.[233] There are numerous other examples where such complexes, especially the dark red-scarlet phosphine derivatives, are formed as reaction by-products; *e.g.* the formation of *trans*-$ReCl_4(PR_3)_2$ in the carbonylation of $Re_2Cl_4(PR_3)_4$ (PR_3 = PPr^n_3 or PMe_2Ph).[69,234] Several mixed halide complexes of the types $ReX_3Y(PPh_3)_2$ and $ReX_2Y_2(PPh_3)_2$ are known, and can be prepared either by the reactions of hydrido–rhenium species with HX[227,235] or the halocarbon oxidation of $ReX_3(NCMe)(PPh_3)_2$ (Scheme 11).[86] Salts of the $[ReX_5(PR_3)]^-$ anions are also known (Section 43.6.1.9).

The vibrational spectrum (a single IR active ν(Re—X) mode),[1] magnetic properties (μ_{eff} = 3.4–3.7 BM),[102] and an X-ray crystal structure determination on *trans*-$ReCl_4(PMe_2Ph)_2$,[101] all

Table 8 Preparative Methods for *trans*-$ReX_4(AR_3)_2$ (A = P, As or Sb)

X	*AR_3*	*Synthetic procedure*	*Comments*	*Ref.*
Cl, Br	PPh_3	$ReOX_3(PPh_3)_2$ + boiling RCO_2H + HCl		217
		$ReX_3(NCMe)(PPh_3)_2$ + halocarbons		86
		$ReCl_5$ + PPh_3 in dry Me_2CO		226
		$ReOCl_3(PPh_3)_2$ + boiling PhCOCl		138
		$ReH_2(acac)(PPh_3)_3$ or $ReHX(acac)(PPh_3)_3$ + HX in benzene		227
I	PPh_3	ReI_4 + PPh_3 in dry Me_2CO		216
Cl, Br	PPh_3	$ReH_3(PPh_3)_4$ + HX		127
Cl	PPh_3	$ReH_7(PPh_3)_2$ + chlorocarbons (CCl_4, $CHCl_3$, CH_2Cl_2 Me_3CCl and C_6H_5Cl)	H_2 and hydrocarbons as by-products	144
Cl, Br	PEt_nPh_{3-n}	Pyrolysis of $[LH]_2ReX_6$	n = 1, 2 or 3 $[LH]^+$ = $[Ph_{3-n}Et_nPH]^+$	228–231
Cl	PR_2Ph	$ReCl_3L_3$ + CCl_4 or Cl_2	R = Me, Et, Pr^n or Bu^n	102
Cl, Br	PPh_3, PEt_2Ph	ReX_3L_3 + X_2		228
Cl	PEt_2Ph	$ReH_7(PEt_2Ph)_2$ + HCl	No evidence for chloro-hydride intermediates	232
Cl	APh_3	$ReCl_4(NCMe)_2$ + APh_3	A = P, As or Sb	98, 104
Cl	APh_3	$ReCl_3(NCMe)(APh_3)_2$ + CCl_4	A = As or Sb	98



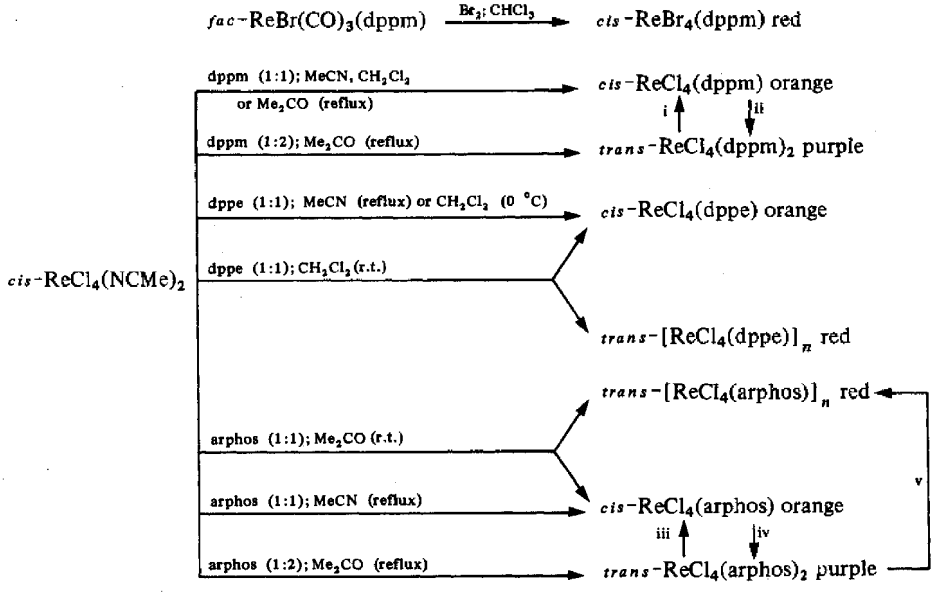
Scheme 11 Mixed halide complexes of the types $ReX_3Y(PPh_3)_2$ and $ReX_2Y_2(PPh_3)_2$

serve to confirm the magnetically dilute *trans*-octahedral structure of this class of complexes. Electrochemical measurements on acetonitrile and dichloromethane solutions of several *trans*-$ReCl_4(PR_3)_2$ complexes show that a reversible one-electron reduction to the monoanion $[trans\text{-}ReCl_4(PR_3)_2]^-$ is very accessible ($E_{1/2}$ in the range -0.1 to -0.5 V *vs.* SCE).[65,106]

A suggestion some years ago that the reaction of $[ReO_4]^-$ with PEt_2Ph and hydrochloric acid in boiling ethanol yields the well-characterized *cis* and *trans* isomers of $ReOCl_3(PEt_2Ph)_2$ together with the violet rhenium(IV) complex *trans*-$Re(OH)Cl_3(PEt_2Ph)_2$,[107] has apparently been confirmed by an X-ray structure determination of the latter complex.[236] The observed Re—O bond length of 1.795(4) Å and the observation of an IR-active ν(O—H) band at 2920 cm^{-1} support this contention.[236] Some degree of double bond character in the Re—O(H) bond may explain the low magnetic moment (1.92 BM),[107] since this could impart a low-spin configuration (one unpaired electron) to this system.

Complexes of the type $ReX_4(LL)$ containing bidentate phosphine and arsine ligands have been prepared by two general methods. The halocarbon oxidation of the rhenium(III) complexes $Re_2(\mu\text{-}X)_2X_4(dppe)_2$ (X = Cl or Br) (Section 43.5.1.6) leads to the halocarbon solvates of *cis*-$ReX_4(dppe)$.[108] The X-ray crystal structure of *cis*-$ReCl_4(dppe)\cdot 3/4\ CCl_4$ has confirmed the nature of these products.[237] Orange-red crystalline *cis*-$ReX_4(dppe)$ can also be prepared upon heating $Re_2(\mu\text{-}X)_2X_4(dppe)_2$ with acetic acid–acetic anhydride mixtures but, depending upon the reaction conditions, contamination by $Re_2(O_2CMe)_4X_2$ or $ReOCl_3(dppeO_2)$ can ensue.[108] Orange *cis*-$ReCl_4(dppe)$ has also been prepared by the Cl_2 oxidation of $ReH_3(dppe)(PPh_3)_2$ in benzene solution.[124]

A second general approach involves the reaction of *cis*-$ReCl_4(NCMe)_2$ with bis(diphenylphosphino)methane (dppm), bis(1,2-diphenylphosphino)ethane (dppe) and 1-diphenylphosphino-2-diphenylarsinoethane (arphos)[233] but, surprisingly, the reaction products are very dependent upon the reaction conditions. These results[233] are summarized in Scheme 12, together with details of the route to *cis*-$ReBr_4(dppm)_2$ *via* the Br_2 oxidation of $ReBr(CO)_3(dppm)$.[214] Complexes of the types *cis*-$ReCl_4(LL)$, *trans*-$ReCl_4(LL)_2$ or polymeric *trans*-$ReCl_4(LL)$ with LL in a *trans*, bridging conformation, can be isolated depending upon the nature of LL, the reaction stoichiometry and the reaction conditions (solvent and temperature).[233] These complexes have been thoroughly characterized on the basis of their far IR, electronic absorption and ESCA spectra, and also their magnetic properties.[214,233] Cyclic voltammetric measurements on CH_2Cl_2 solutions of *cis*-$ReCl_4(LL)$ reveal the existence of a reversible one-electron reduction at ~ -0.05 V *vs.* SCE.[65] The differences in behavior observed with the dppm, dppe and arphos ligands can be rationalized in terms of *trans*-$ReCl_4(LL)_2$



i, refluxing CH_2Cl_2; ii, excess dppm, refluxing acetone; iii, refluxing $CHCl_3$ or DMF; iv, excess arphos, refluxing acetone; v, *cis*-$ReCl_4(NCMe)_2$, refluxing acetone.

Scheme 12

being the thermodynamically favored product for LL = dppm or arphos but not dppe. In the case of *cis*-$ReCl_4$(dppm), the strained chelate ring is unstable in the presence of excess dppm. Although a more stable five-membered ring is present in *cis*-$ReCl_4$(arphos), the formation of a second Re—P bond provides the driving force for its conversion to *trans*-$ReCl_4$(arphos)$_2$. On the other hand, when CH_2Cl_2, $CHCl_3$ or DMF solutions of *trans*-$ReCl_4(LL)_2$ are kept at room temperature for many hours or heated for short periods, the orange complexes *cis*-$ReCl_4$(LL) can be regenerated, provided that excess ligand is not present. The course of these reactions is clearly favored by an increase in entropy upon loss of one of the bidentate ligands.

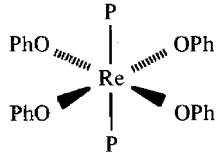
While attempts to prepare the complex $ReCl_4$(dpae) (dpae = 1,2-bis(diphenylarsino)ethane) were unsuccessful,[233] complexes with other bidentate arsines have been isolated. ReX_4(diars) {X = Cl or Br; diars = *o*-phenylenebis(dimethylarsine)} has been prepared by the halogen oxidation of $ReX(CO)_3$(diars),[1] while the complexes $ReCl_4$(dtcb) and $ReCl_4$(dhcp) (dtcb = 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobut-1-ene and dhcp = 1,2-bis(dimethylarsino)-3,3,4,4,5,5-hexafluorocyclopentene) are formed as green solids from the reaction of $ReCl_5$ with dtcb and dhcp in carbon tetrachloride.[238,239] The dtcb complex is also isolable, admixed with yellow $[ReCl_2(dtcb)_2]ClO_4$, from the reaction of dtcb with solutions generated by the H_3PO_2 reduction of the $KReO_4$/HCl/EtOH/H_2O system.[238] The room temperature magnetic moments of $ReCl_4$(dtcb) and $ReCl_4$(dhcp) are 2.97 and 2.55 BM, respectively, and are lower than normally found ($\sim$3.4 BM) for Re^{IV} complexes.[239] Nonetheless, these are authentic mononuclear Re^{IV} species containing *cis* chelating arsine ligands as demonstrated by an X-ray crystal structure determination of $ReCl_4$(dtcb).[238]

43.6.1.7 Oxygen and sulfur ligands

The chemistry of Re^{IV} with oxygen ligands is not especially well developed. The simple aqua anions $[ReCl_5(H_2O)]^-$ are known (Section 43.6.1.9), as are the hydroxo species $[ReX_5(OH)]^{2-}$ and the methoxide $[ReCl_5(OMe)]^{2-}$ (Section 43.6.1.9). Rhenium(IV) is also believed to be incorporated into certain heteropolyacids upon treating $[SiW_{11}O_{39}]^{8-}$ and $[P_2W_{17}O_{61}]^{10-}$ with $[ReCl_6]^{2-}$ under nitrogen.[1]

The $[ReX_5(OH)]^{2-}$ anions exist in equilibrium with the μ-oxo-bridged dirhenium(IV) species $[Re_2OX_{10}]^{4-}$ (Section 43.6.1.8). The latter constitute examples of a class of complex that possess a linear Re^{IV}—O—Re^{IV} unit, and which may contain additional oxygen or sulfur ligands. These complexes include $Re_2OX_6(SEt_2)_4$ and $Re_2OX_6(EtSCH_2CH_2SEt)_2$ (X = Cl or Br),[240] $K_2[Re_2OL_2Cl_6]$ (HL = a dipeptide or tripeptide ligand such as glycylalanine, glycylleucine or glyclglycylglycine),[241] $K_2H_2[Re_2OL_2(SO_4)_4]$ (HL = picolinic acid, nicotinic acid or isonicotinic acid), $K_2[Re_2OL_2(SO_4)_4]$ (L = picolinamide, nicotinamide or isonicotinamide),[242] as well as an assortment of μ-oxo species containing OH^- ligands, *e.g.* $[Re_2O(OH)_6(LL)_2]^{4-}$ (LL = oxalate, citrate, tartrate or gallate)[1] and $K_2[Re_2OL_2(OH)_2(SO_4)_2]$ (HL = picolinic acid or isonicotinic acid),[243] and Re^{IV} complexes that purportedly contain the $[Re_2O_3]$ moiety, *e.g.* $H_2[Re_2O_3L_4]$ (HL = penicillamine).[244] The identities of these complexes require confirmation since they are based mostly upon conductance, spectroscopic and magnetic data. In no instance has an X-ray crystal structure been carried in order to support the formulations of any of these systems.

The complex *trans*-$Re(OPh)_4(PMe_3)_2$ (**51**) is one of the two well-characterized alkoxides of Re^{IV}. It is prepared in low yield by the reaction of $ReOCl_4$ with NaOPh in diethyl ether/THF followed by the addition of PMe_3.[245] The red crystalline complex (**51**) has been shown by X-ray crystallography to possess the *trans* structure that usually characterizes ReX_4L_2 type complexes. The other complex is $Cs_2[ReCl_5(OMe)]$ that is discussed in Section 43.6.1.9.



(51) P = PMe_3

An earlier report that the reaction of $ReOCl_2(OEt)(PPh_3)_2$ with hot acetylacetonate produces dimeric $Re_2Cl_4(acac)_4$, *via* the intermediacy of $ReCl(acac)_2PPh_3$ (Section 43.5.1.7), was later shown to be incorrect; orange $Re_2Cl_4(acac)_4$ is in reality *trans*-$ReCl_2(acac)_2$.[246] This conclusion has been confirmed by an X-ray crystal structure determination.[247] Alternative methods have been developed

to prepare *trans*-$ReCl_2(acac)_2$, *viz.* refluxing $ReOCl_2(acac)(PPh_3)$ in acacH under N_2, or refluxing solutions of $ReCl_2(acac)(PPh_3)_2$ {or $ReCl_2(acac)(PPh_3)(OPPh_3)$} in acacH in air overnight. By work-up of the reaction filtrates, small amounts of red-brown *cis*-$ReCl_2(acac)_2$ can be isolated.[246] The reactions between $ReOX_2(OMe)(PPh_3)_2$ (X = Cl, Br or I) and the β-diketones acacH or dbmH (dbmH = dibenzoylmethane) have been used to prepare $ReX_2(acac)_2$ (X = Br or I) and *cis*-$ReCl_2(dbm)_2$. The acac complexes display characteristic mass spectra, exhibiting an abundant parent ion peak, and they have room temperature magnetic moments of 3.1–3.3 BM. Their IR spectra, dipole moments (in benzene) and X-ray powder patterns support the notion that the bromide complex consists primarily of the *cis* isomer (with a small amount of *trans*), while the iodide is the *trans* isomer.[246]

In an extraction–photometric method for the determination of rhenium, a sulfito complex $[(Me_2CHCH_2CH_2)_2NH_2]_2ReO(SO_3)Cl_2$ is supposedly formed when Re^{IV} is extracted from 3.2 M hydrochloric acid containing SO_3^{2-} with diisoamylamine in ethyl acetate or CCl_4.[248] This formulation should be treated with some scepticism until it can be confirmed. Complexes of Re^{IV} with organic acids have been prepared by the reaction of K_2ReCl_6 with the appropriate acid in a 1:3 or 1:2 molar ratio.[249] These products were claimed to contain the $[Re(C_2O_4)_3]^{2-}$ or $[ReCl_2L_2]^{2-}$ (LH_2 = phthalic, glutaric or aspartic acid) anions but have not been characterized in much detail, although upon hydrolysis they apparently give ReO_2.

There is a report describing the isolation of the violet 1:1 nitromethane complex $ReCl_4(MeNO_2)$ following the dissolution of $ReCl_5$ in $MeNO_2$,[250] but this complex remains otherwise uncharacterized and its existence unsubstantiated. By a similar procedure, namely reaction with $ReCl_5$, the solvents THF, dioxane and 1,4-oxathiane reduce this halide to give *trans*-$ReCl_4L_2$ (L = THF, dioxane or oxathiane), the complex *trans*-$ReCl_4(C_4H_8OS)_2$ containing S-bound thioxane.[251] The related bromide complex *trans*-$ReBr_4(C_4H_8OS)_2$ can be prepared by reacting K_2ReBr_6 with 1,4-oxathiane in HBr.[251] Upon heating *trans*-$ReCl_4(PPh_3)_2$ in air to 200°C, the corresponding triphenylphosphine oxide complex is obtained. This shows a characteristic ν(P=O) mode (at ~1150 cm^{-1}) in its IR spectrum.[229] This behavior contrasts to some extent with the related thermal transformations of *trans*-$ReCl_4(PEtPh_2)_2$ and *trans*-$ReCl_4(PEt_2Ph)_2$ which give $ReCl_4[OP(OEt)Ph_2]_2$ (*via* $ReCl_4(OPEtPh_2)_2$) and $ReCl_4[OPEt_{2-n}(OEt)_nPh]_2$ (n = 0, 1 or 2), respectively.[230,231] The course of these reactions can be followed by IR spectroscopy through monitoring of the ν(P=O) and ν(P—O—Et) vibrations.

The salts $(Et_4N)[ReCl_5L]$ (L = DMSO and DMF) are known, as is the thiourea (tu) derivative $(Et_4N)[ReCl_5(tu)]$ (see Section 43.6.1.9). Thioether (Et_2S, $EtSCH_2CH_2SEt$ and 1,4-oxathiane) and thiol (penicillamine) sulfur ligand complexes of Re^{IV} have already been mentioned in this section, and constitute, along with some dithiocarbamate derivatives, the majority of the complexes of Re^{IV} that are known to contain Re—S bonds. The reaction of $ReCl(CO)_5$ with tetraethylthiuram disulfide gives several products of which two contain Re^{IV}.[252] Both brown $[Re(S_2CNEt_2)_4][ReCl_4(S_2CNEt_2)]$ and red crystalline $ReCl_2(S_2CNEt_2)_2$ can be isolated from a benzene solution of the reactants. These complexes have room temperature magnetic moments of 3.7 and 2.9 BM, respectively. IR spectral measurements on $ReCl_2(S_2CNEt_2)_2$ show two ν(Re—Cl) modes (305s and 278 m cm^{-1}) in accord with a *cis* octahedral stereochemistry. This complex can also be prepared through the reaction of *trans*-$ReCl_4(PPh_3)_2$ with this same thiuram disulfide in benzene, while the related dibenzyl dithiocarbamate analogue $ReCl_2[S_2CN(CH_2Ph)_2]_2$ is obtained by the interaction of $ReCl(CO)_5$ with tetrabenzylthiuram disulfide.[252] The mixed sulfide–cyanide and selenide–cyanide species $[Re_4(\mu_3\text{-}X)_4(CN)_{12}]^{4-}$ (X = S or Se) and $[Re_2(\mu\text{-}S)_2(CN)_8]^{4-}$ are described in Section 43.6.1.1.

43.6.1.8 The mixed oxide–halide anions $[Re_2(\mu\text{-}O)X_{10}]^{n-}$

Salts of these anions (n = 4 or 3) constitute the best characterized of the Re^{IV} complexes that contain a linear Re—O—Re unit.[1,2] Prepared by the reduction of $KReO_4$,[253] the nearly diamagnetic red-brown salt $K_4[Re_2OCl_{10}]$ was shown by X-ray crystallography to possess a structure with a linear Re—O—Re unit (Re—O distances = 1.865(2) Å) which joins to two $[ReOCl_5]$ octahedra.[254] The question as to the nature of the blood-red product that is formed upon treating $[Re_2OCl_{10}]^{4-}$ in dilute hydrochloric acid with H_2O_2 or other oxidants[1,253] has apparently been answered by an X-ray crystal structure determination on a product, $Cs_3Re_2OCl_{10}$, isolated from one such solution.[255] Formally, this mixed-valent complex is derived by a one-electron oxidation of $[Re_2OCl_{10}]^{4-}$ but in view of its symmetrical structure with r(Re—O) = 1.832(3) Å, it must be considered an Re (+3.5, +3.5) species.[255] There is no explanation for the earlier reported magnetic moment of 3.57 BM for this complex, the implication being that this value is probably in error.[253,255] These

complexes contain the type of linear Re—O—Re unit that is believed to be present in the 'parent' oxide–chloride $[ReOCl_2]_n$.[256] Furthermore, these results provide the structural base from which to consider the nature of other derivatives that supposedly contain the Re^{IV}—O—Re^{IV} unit (Section 43.6.1.7).

A report describing the preparation of oxyfluoro species purported to be $M_4Re_2OF_{10}$ (M = K or Cs) has been published.[601] They have been characterized on the basis of spectroscopic, magnetic and conductivity measurements.

43.6.1.9 Complex halides $[ReX_6]^{2-}$, $[ReX_5(OH)]^{2-}$, $[ReCl_5L]^-$ and related species

Stable and easily prepared hexahalorhenate(IV) species $[ReX_6]^{2-}$ are known for X = F, Cl, Br and I. The preferred method for making $[ReX_6]^{2-}$ (X = Cl, Br or I) is by the reduction of $[ReO_4]^-$ in concentrated HX in the presence of a reducing agent such as I^-, Sn^{II} or hypophosphorous acid (which gives yields greater than 90%).[1] $[ReF_6]^{2-}$ can be prepared by reducing ReF_6 with alkali metal iodides in liquid SO_2 or by reacting molten KHF_2 with either a $KReO_4/KI$ mixture or K_2ReBr_6.[257]

The remarkable stability of the $[ReX_6]^{2-}$ anions is demonstrated by their formation as by-products in numerous reactions. For example, treatment of $[ReO_2(py)_4]Br \cdot 2H_2O$ with hot concentrated HBr produces $ReOBr_3(py)_2$ along with $(pyH)_2ReBr_6$.[258] Reaction of $(Bu^n_4N)_2Re_2Cl_8$ with CO(g) in MeCN gives $ReCl(CO)_5$ as the major product, but $[Re(NCMe)_4(CO)_2]_2[ReCl_6]$ is also formed.[259] When $ReH_7(PPh_3)_2$ is reacted with allyl halide (C_3H_5X; X = Cl, Br or I) in an ether solvent the salt $(Ph_3PC_3H_5)_2ReX_6$ is formed in quite good yield.[144] The addition of PCl_3 and Bu^tCl to a solution of rhenium(V) chloride in carbon disulfide, results in a product containing both Re_3Cl_9 and $[ReCl_6]^{2-}$, $(Bu^tPCl_3)_2[Re_3Cl_9]$ $[ReCl_6]$.[194] K_2ReCl_6 is also formed as an 'intermediate' in the preparation of $(Bu^n_4N)_2Re_2Cl_8$ in the method involving the reaction of PhCOCl with $KReO_4$. K_2ReCl_6 does not react further due to its insolubility in the reaction solvent (PhCOCl), and reduces the yield of the desired product, however, use of $(Bu^n_4N)ReO_4$ in place of $KReO_4$ allows the production of the $[Re_2Cl_8]^{2-}$ to proceed with yields up to 95%.[138] A final example is from a spectroscopic study done on the products of the H_2 reduction of $KReO_4$ in HCl solution. These products were determined to be $[ReCl_6]^{2-}$ and $[Re_2Cl_8]^{2-}$, both of which could be precipitated from the solution by addition of NH_4Cl.[260]

The mixed ligand species of the type $[ReX_nX'_{6-n}]^{2-}$ (n = 1–5; X = Cl; X' = Br or I) can be prepared by heating a mixture of K_2ReX_6 and $K_2ReX'_6$ in a quartz tube at high temperature, and then separating the products by ion column chromatography. Apparently the *cis* and *trans* isomers for n = 2, 3 and 4 of the mixed Re—I—Cl complexes cannot be separated.[261–264] Mixed Re—Br—Cl complexes have also been obtained by pouring concentrated solutions of K_2ReCl_6 and K_2ReBr_6 dropwise into ethanol.[265] The mixed ligand complexes have been studied by electronic absorption[261,262,264] and far IR spectroscopy,[263] as well as by X-ray diffraction.[261,263]

The structure of $[ReX_6]^{2-}$ is expected from simple ligand field considerations to be a regular octahedron. Crystals of K_2ReF_6 have been studied[266] by X-ray diffraction and found to be of the K_2GeF_6 type. The Re—F distance is 1.953 Å, and the $[ReF_6]^{2-}$ octahedron is slightly compressed. K_2ReCl_6 and K_2ReBr_6 have regular octahedral structures of the K_2PtCl_6 type; all Cl and Br atoms are crystallographically equivalent. K_2ReI_6, however, is less symmetrical and has three different iodine environments.[1] Structural studies done on $[ReX_6]^{2-}$ salts with cations other than K include recent neutron diffraction measurements on $(NH_4)_2ReCl_6$.[267]

The spectroscopic and magnetic properties of $[ReX_6]^{2-}$ anions have been thoroughly studied; the reviews by Rouschias[1] and Fergusson[2] should be consulted for a detailed discussion of these studies through 1972. Subsequent work in this area has expanded or refined previous measurements, and in many cases has been confirmatory or complimentary. Sharp-line absorbance, luminescence and Raman spectra have been measured for $[ReF_6]^{2-}$ in pure and host crystal environments.[268] $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ have been studied by high resolution IR[269] and sharp-line luminescence spectroscopy[270] and the far IR region of $M^I_2ReCl_6$ (M^I = K, Rb, Cs, Tl, NH_4, *etc.*) has been examined at very high pressures (up to 20 kbar).[271] Accurate values of the Raman-active fundamentals ν_1 (a_{1g}), ν_2 (e_g) and ν_5 (t_{2g}) of $[ReCl_6]^{2-}$ have been reported along with calculations of the parallel and perpendicular bond polarizability derivatives.[272] These results have been discussed in terms of the pre-resonance Raman effect. The resonance Raman spectrum of $(Et_4N)_2ReI_6$ has been measured at 80 K; the a_{1g} vibrational mode was found to be coupled to the electronic transition Γ_8 ($^4A_{2g}$) → Γ_8 ($^2T_{1g}$).[273]

The hexahalorhenate(IV) anions have been the subjects of extensive electronic absorption spectra studies. Their spectra have been recorded in aqueous and non-aqueous solvents, in halide melts, in the solid state and doped into other crystal hosts (*e.g.* K_2PtCl_6 or Cs_2ZrCl_6). The energy level

diagram for Re^{IV} in an octahedral crystal field has been assigned and crystal field parameters have been measured.[1] More recently, the low temperature single crystal absorption spectra of $[ReX_6]^{2-}$ (X = F, Cl or Br) in a variety of Sn host crystals with trigonal symmetry have been recorded using polarized light.[274,275] Ligand field calculations were used to rationalize the type and degree of trigonal field splitting. The electronic transitions of $[ReF_6]^{2-}$ in single crystals of Cs_2ReF_6 and doped into Cs_2GeF_6 have been measured at liquid He temperatures.[276] Crystal field parameters and spin–orbit coupling information have been derived and the vibrational structure has been interpreted on the basis of $K \neq O$ lattice effects and a small distortion in the pure Cs_2ReF_6 crystal. K_2ReCl_6 single crystals have also been studied at liquid He temperatures.[277] The magnetic circular dichroism and absorption spectra of $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ in cubic hosts at liquid He temperatures have been measured and most of the bands have been assigned to allowed or parity forbidden charge transfer transitions.[278] Earlier work had favored a *d–d* interpretation of these bands. Another study has analyzed the charge transfer (ligand-to-metal) spectra of a series of octahedral transition metal complexes including $[ReX_6]^{2-}$ (X = Cl, Br or I) using a simple crystal field model.[279]

Most of the recent investigations of the magnetic properties of $[ReX_6]^{2-}$ have involved ammonium or substituted ammonium salts. K_2ReCl_6 and K_2ReBr_6 are ordered antiferromagnetics at 4.2 K.[1] Antiferromagnetic behavior is also found for the $(MeNH_3)^+$ and $(Me_2NH_2)^+$ salts of $[ReX_6]^{2-}$ (X = Cl or Br).[280,281] Additionally, the synthesis and properties of $(NH_4)_2ReCl_6$ have been the subjects of a recent study,[282] as have those of $(RH)_2ReCl_6$ (R = cyclohexylamine, $PhNEt_2$, $PhNMe_2$ or 2,5-lutidine).[283]

There have been several polarographic studies done on $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ in which a one-electron reduction has been observed.[284,285] The cathodic one-electron reduction of $[ReX_6]^{2-}$ (X = Cl, Br or I) to give $[ReX_6]^{3-}$ is complicated by a secondary process involving the reduction of $[ReX_5(H_2O)]^-$ (*viz.* $[ReX_5(H_2O)]^- + e^- \rightarrow ReX_5(OH)^{3-} + H^+$) which is formed in solution by the hydrolysis of $[ReX_6]^{2-}$.[286,287] Cyclic voltammetric measurements on acetonitrile solutions of $(Bu^n_4N)_2ReX_6$ (X = Cl or Br) have shown that in addition to the one-electron reduction ($E_{1/2} = -1.18$ and -0.90 V *vs.* SCE for X = Cl and Br, respectively), a reversible one-electron oxidation is also observed.[95]

In general, the $[ReX_6]^{2-}$ anions are quite inert to substitution. Aquation of $[ReCl_6]^{2-}$ is especially slow, but is catalyzed by Hg^{II}, Tl^{III}, Cd^{II} and In^{III}.[288] For $[ReBr_6]^{2-}$, aquation is somewhat easier, but is also catalyzed by Tl^{III}. $[ReF_6]^{2-}$ is stable to hydrolysis and can be recrystallized from aqueous solutions.[257] The hydrolysis and the kinetics of metal-ion-catalyzed aquation have been investigated for both $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$.[288,289]

The aqua anion $[ReCl_5(H_2O)]^-$, which can undergo hydrolysis to $[ReCl_5(OH)]^{2-}$, has been structurally characterized by X-ray crystallography in the bis(dithiobisformamidinium) salt $[(NH_2)_2CSSC(NH_2)_2]_2[ReCl_5(H_2O)]Cl_3 \cdot 2H_2O$.[290] This green crystalline substance was obtained as one of several products in a study of the $[ReO_4]^-$/thiourea/HCl system. The Re—O distance in the pseudooctahedral anion is quite short (2.076(10) Å).[290] An alternative means of preparing $[ReCl_5(H_2O)]^-$ is through the reaction of the salt $[(Pr^n_4N)ReCl_5]_n$, which contains the polymeric chlorine-bridged $[(ReCl_5)^-]_n$ anion, with a moist atmosphere.[291] Salts of $[(ReCl_5)^-]_n$ can be prepared by reacting $ReCl_5$ with an equimolar amount of $(R_4N)Cl$ (R = Et or Pr^n) in boiling CH_2Cl_2 for several days. If $ReCl_5$ is reacted with Et_4NCl in a 1:3 mole ratio, then $(Et_4N)_2ReCl_6$ is formed in almost quantitative yield. The air-stable mustard-colored salts $[(R_4N)ReCl_5]_n$ react with many donors (MeCN, DMF, py, DMSO, PPh_3, tu or H_2O) to form the salts $(R_4N)ReCl_5(L)$. Reaction with the bridging ligand pyrazine (pyz) gives $[(R_4N)ReCl_5]_2pyz$.[291] This is the most general synthetic route for salts of $[ReCl_5L]^-$, although other methods are known, such as the treatment of $ReH_3(PPh_3)_4$ with HX to give $(Ph_3PH)[ReX_5(PPh_3)]$ (X = Cl or Br),[129] and the reaction of $(pyH)_2ReX_6$ with pyridine at 190°C which gives $(pyH)[ReX_5(py)]$ (X = Cl or Br).[292] These complexes possess spectroscopic (far IR and electronic absorption) and magnetic properties that are typical of magnetically dilute Re^{IV} species.[291]

Salts of the $[ReX_5(OH)]^{2-}$ anions (X = Cl, Br or I), which are related to $[ReX_5(H_2O)]^-$ through the hydrolysis reaction given in equation (15), have been isolated in a few instances[1,2] and appear to have properties in accord with the expected pseudooctahedral structure. These anions are in equilibrium with the μ-oxo dirhenium(IV) species $[Re_2OX_{10}]^{4-}$ (Section 43.6.1.8). The cream-yellow colored methoxide derivative $Cs_2[ReCl_5(OMe)]$ has been prepared from the reaction of *cis*-$ReCl_4(NCMe)_2$ with hot MeOH saturated with gaseous HCl.[98]

$$[ReX_5(H_2O)]^- \rightleftharpoons [ReX_5(OH)]^{2-} + H^+ \qquad (15)$$

The complexes $[ReCl_4(PhC_2Ph)]_2$ and $ReCl_5(PhC_2Ph)$ have been prepared by the reaction of $ReCl_5$ with diphenylacetylene, and the former converted into the salt $Ph_4P[ReCl_5(PhC_2Ph)]$.[602]

Some interesting radical cation salts of dibenzotetrathiafulvalene (DBTTF) and tetramethyltetrathiafulvalene (TMTTF) with inorganic anions, including $[ReCl_6]^{2-}$, have been prepared which possess metallic conductivity. These compounds, having the general formula $(DBTTF)_8(MCl_6)_3$ (M = Sn, Pt, Re or Te), have identical electrical properties, with their metal–insulator transition occurring in the range 120–150 K.[293,294]

43.6.1.10 Hydrides

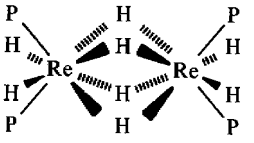
Mononuclear hydride compelxes of Re^{IV} are very rare. The only class of such complexes that has been isolated in the solid state is $ReHX_2(acac)(PPh_3)_2$ (X = Cl, Br or I).[227] The iodide complex is apparently prepared by the reaction of $ReH_2(acac)(PPh_3)_3$ with I_2, whereas the chloride and bromide are formed upon dissolving this same complex in CHX_3. Although the chloride and iodide were shown by magnetic susceptibility measurements to be paramagnetic, their moments are quite different. All three complexes display weak ν(Re—H) modes in their IR spectra.[227] The electrochemical oxidation of the yellow monohydride of rhenium(III) $[ReH(NCMe)_3(PPh_3)_2(py)](BF_4)_2$ generates solutions that contain the violet colored tricationic species $[ReH(NCMe)_3(PPh_3)_2(py)]^{3+}$. Similar behavior characterizes the systems $[ReH(NCMe)_3(PPh_3)_2(NH_2C_6H_{11})](BF_4)_2$ and $[ReH(NCMe)_4(PPh_3)_2](BF_4)_2$, but in none of these cases have salts of the rhenium(IV) trications been isolated.[132]

The most thoroughly studied hydrido complexes of rhenium(IV) are those of the type $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ (PR_3 = PPh_3, $PEtPh_2$, $PMePh_2$, PEt_2Ph or PMe_2Ph) which can be prepared by thermolysis of $ReH_7(PR_3)_2$,[232] the photolysis of $ReH_7(PR_3)_2$ or $ReH_5(PR_3)_3$[125,135] and/or the reaction of mixtures of phosphine and $(Bu^n_4N)_2Re_2Cl_8$ with $NaBH_4$ in methanol or ethanol.[62,144] The triphenylarsine analogue $Re_2H_8(AsPh_3)_4$ has been prepared in low yield (12%) by reacting $ReOCl_3(AsPh_3)_2$ with $LiAlH_4$ in THF at 0°C.[134] The chemistry of these complexes, which had originally been reported as 'agnohydrides' because of the uncertainty as to the number of hydride ligands present,[232] was not explored in any detail until their structure was established through a neutron diffraction analysis of $Re_2H_8(PEt_2Ph)_4$ (**52**).[295] The short Re—Re distance (2.538(4) Å) may indicate some degree of multiple Re—Re bonding in these complexes but this is by no means certain. The terminal H_2P_2 units and the bridging H_4 unit are in a mutually staggered arrangement.[295] In the high field ^{1}H NMR spectra of these complexes, the resonance due to the hydride ligands is seen as a symmetric quintet in the region δ − 5.0 to − 8.1, with J(P—H) ~ 8–9.5 Hz.[125,232,295,296] For the arsine complex $Re_2H_8(AsPh_3)_4$, the ^{1}H NMR spectrum shows a hydride singlet at δ − 6.66.[134] These observations are in keeping with this class of molecules being fluxional at room temperature; details of variable temperature studies have not yet been reported, with the exception of a limited ^{1}H NMR spectral study of $Re_2H_8(PEt_2Ph)_4$ which did not yield a frozen-out spectrum at low temperatures.[295]

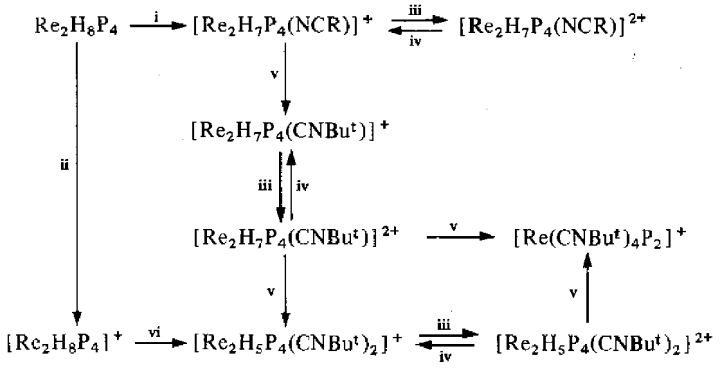
These structural studies have been followed by a consideration of the bonding and the conformational preferences in molecules of the type represented by (**52**).[297] Also, it has been shown that the dinuclear core of $Re_2H_8(PPh_3)_4$ is preserved upon the reactions of this complex with allyl chloride and bromide which give a mixture of $(Ph_3PC_3H_5)_2Re_2X_8$ (X = Cl or Br), H_2 and propene. However, this dimetal unit is disrupted when reacted with allyl iodide since, in this instance, the mononuclear rhenium(IV) complex $(Ph_3PC_3H_5)_2ReI_6$ is formed.[144] Electrochemical measurements by the cyclic voltammetric technique have shown that solutions of $Re_2H_8(PEt_nPh_{3-n})_4$ (n = 0, 1 or 2) and $Re_2H_8(AsPh_3)_4$ in 0.2 M $(Bu^n_4N)PF_6$–CH_2Cl_2 possess two one-electron oxidations, the first of which ($E_{1/2}$ = − 0.16 to − 0.40 *vs.* SCE) is reversible. Solutions of the paramagnetic ESR-active cations $[Re_2H_8L_4]^+$ (L = PEt_nPh_{3-n} or $AsPh_3$) can be generated by controlled potential electrolysis and, in the case of the PPh_3 derivative, the salt $[Re_2H_8(PPh_3)_4]PF_6$ can be prepared using $Ph_3C^+PF_6^-$ (or $C_7H_7^+PF_6^-$) as the oxidant in CH_2Cl_2.[134,296] Interestingly, when a nitrile solvent RCN (R = Me, Et or Ph) is used in place of CH_2Cl_2 in this reaction, hydride abstraction rather than oxidation takes place to give $[Re_2H_7(PPh_3)_4(NCR)]PF_6$. In these complexes the RCN ligands are easily substituted by Bu^{t}NC to give $[Re_2H_7(PPh_3)_4(CNBu^t)]PF_6$, and this complex like its nitrile precursors can be oxidized reversibly in two one-electron steps. The most accessible one-electron oxidation ($E_{1/2}$ = − 0.03 to + 0.19 V *vs.* SCE) can be accomplished chemically using $NOPF_6$.[134]

The paramagnetic, monocationic species $[Re_2H_8(PPh_3)_4]^+$ displays a tremendous enhancement in reactivity compared to its neutral parent $Re_2H_8(PPh_3)_4$, as does $[Re_2H_7(PPh_3)_4(CNBu^t)]^{2+}$ compared to $[Re_2H_7(PPh_3)_4(CNBu^t)]^+$. This aspect of the chemistry of these complexes is shown in Scheme 13, wherein the redox chemistry and substitution chemistry of the dirhenium polyhydrides towards Bu^{t}NC are summarized.[134] Another means of activating the complexes $Re_2H_8(PR_3)_4$ (PR_3 = $PMePh_2$ or PMe_2Ph) involves their interaction with $[Cu(NCMe)_4]PF_6$ according to equation

(16).[307] These novel hexanuclear species display an unprecedented planar rhomboidal metal array consisting of two intact Re_2 units and two Cu^+ cations. These clusters can be considered as 'raft-like' aggregates and therefore represent a geometric analogue of a metal surface.[307]



(52) P = PEt_2Ph



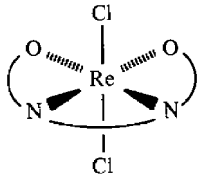
i, $Ph_3C^+PF_6^-$, RCN (R = Me, Et, Ph); ii, $Ph_3C^+PF_6^-$, CH_2Cl_2, 0 °C;
iii, $NO^+PF_6^-$, acetone; iv, Zn, CH_2Cl_2; v, Bu^tNC, CH_2Cl_2, room temperature;
vi, Bu^tNC, CH_2Cl_2, 0 °C. P = PPh_3

Scheme 13 Redox and subsitution chemistry of $Re_2H_8(PPh_3)_4$

$$2Re_2H_8(PR_3)_4 + 2[Cu(NCMe)_4]PF_6 \xrightarrow{THF} [Re_4Cu_2H_{16}L_6](PF_6)_2 + 8MeCN \qquad (16)$$

43.6.1.11 Mixed donor atom ligands

Certain of these complexes have been described in Section 43.6.1.7, *viz.* those with peptide ligands, pyridinecarboxylic acids and derivatives, and penicillamine. The most extensive studies have been carried out on Schiff base complexes in which the Schiff base ligands are either tetradentate and dianionic, or bidentate and monoanionic. The complexes of the former type, *trans*-$ReCl_2(N_2O_2)$, where N_2O_2 represents the dianionic Schiff base ligands derived from sal_2enH_2 = *N,N′*-ethylenebis(salicylideneimine), sal_2propH_2 = *N,N′*-trimethylenebis(salicylideneimine), sal_2phenH_2 = *N,N′-o*-phenylenebis(salicylideneimine) and $acac_2enH_2$ = *N,N′*-ethylenebis(acetylacetimine), are formed by refluxing *trans*-$ReCl_4(PPh_3)_2$ with one equivalent of the Schiff base and two equivalents of NEt_3 in dry toluene under nitrogen.[298] These complexes are paramagnetic and show a single ν(Re—Cl) mode in the IR spectra in accord with the *trans* geometry (**53**). In the absence of NEt_3, the preceding reactions of $ReCl_4(PPh_3)_2$ with sal_2enH_2 and sal_2propH_2, when carried out in dry THF, give $ReCl_4(sal_2enH_2)$ and $ReCl_4(sal_2propH_2)$. The complexes are believed to contain the neutral Schiff base ligand bound only through its N-donor atoms.[298]



(53)

The complex *trans*-$ReCl_4(PPh_3)_2$ is also the starting material for the synthesis of several complexes derived from the bidentate Schiff bases Me-salH = *N*-methylsalicylideneimine and Ph-salH = *N*-phenylsalicylideneimine.[207] In benzene or toluene solvents the Schiff base (LH) or its lithium salt reacts to give $ReCl_4(LH)(PPh_3)$, $ReCl_4(LH)_2$, $ReCl_3(L)(PPh_3)$ or $ReCl_2(L)_2$. The related PMe_2Ph derivatives $ReCl_3(L)(PMe_2Ph)$ can be obtained by refluxing *cis*-$ReCl_2(L)(PMe_2Ph)_2$ in CCl_4 or by heating it in toluene under a stream of CO for a long time. The detailed stereochemistries of these complexes have not been established, although $ReCl_2(L)_2$ probably has a *trans* arrangement of Re—Cl bonds on the basis of a single ν(Re—Cl) mode in the IR spectra.[207] The analogous 8-hydroxyquinoline (oxineH) complexes $ReCl_3(oxine)(PPh_3)$ and $ReCl_2(oxine)_2$ were prepared by procedures similar to those used for their Schiff base analogues.[207] Also, paramagnetic complexes of the type $Re(OH)Cl(L)_2$ (LH = 2- or 8-hydroxyquinoline) have been described but they remain inadequately characterized. They are said to be formed when the appropriate $(LH_2)_2ReCl_6$ salts are heated with excess of LH in acetic acid.[215]

There is a report that describes the isolation of several complexes of Re^{IV} (and of Re^{V}) with thiosemicarbazide and its derivatives. These are obtained by the reactions of $[ReCl_6]^{2-}$, and the so-called α-$ReCl_4$, with thiosemicarbazide and the thiosemicarbazones of acetone, quinolinealdehyde and 5-chlorosalicylaldehyde.[299] While the thiosemicarbazide complex is paramagnetic, in accord with its being an Re^{IV} species, the structural formulation proposed for this complex (and for others of its kind) is based primarily upon IR spectroscopic data and should therefore be regarded as highly speculative.

Neutral complexes $ReX_2(L)_2$, where X = Cl or Br, and LH = 8-quinolinol or 8-quinolinethiol, are formed in the dehydrohalogenation of the corresponding $(LH_2)_2ReX_6$ salts.[603] Several complexes of rhenium(IV) with pyridinecarboxylic acids have also been described.[604] These include $ReCl_2(CO_2\text{-}2\text{-}py)_2$, $ReCl_4(3\text{-}pyCO_2H)_2$ and $ReCl_4(4\text{-}pyCO_2H)_2$.

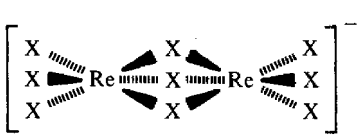
43.6.2 Dinuclear Complexes Containing a Rhenium–Rhenium Bond and Oxide and/or Halide Bridges

The nonahalodirhenate(IV) anions $[Re_2X_9]^-$ (X = Cl or Br) (**54**) possess Re—Re triple bonds ($\sigma^2\pi^4$ configuration) and can be prepared by halogen oxidation of $(Bu^n_4N)_2Re_2X_8$.[300] The salts $(Bu^n_4N)Re_2Cl_9$ (dark green) and $(Bu^n_4N)Re_2Br_9$ (dark red) have been isolated and while they are quite stable in the solid state their solutions are easily reduced to produce either $(Bu^n_4N)_2Re_2X_9$ (an Re (+3.5, +3.5) derivative) or $(Bu^n_4N)_2Re_2X_8$.[300] The paramagnetic, violet $[Re_2Cl_9]^{2-}$ anion has also been prepared by the reactions of β-$ReCl_4$ with $(Ph_4As)Cl$ in MeOH–conc. HCl and with PPh_3 in anhydrous acetone.[5,104] These reactions lead to the salts $(Ph_4As)_2Re_2Cl_9$ and $(DOTP)_2Re_2Cl_9$, respectively, where DOTP represents the 1,1-dimethyl-3-oxobutyltriphenylphosphonium cation which is formed by the acid-catalyzed condensation of acetone followed by a Michael addition of triphenylphosphine. Various salts of $[Re_2Cl_9]^{2-}$ (with $(DOTP)^+$, $(Ph_3PH)^+$, $[(Ph_3PO)_2H]^+$, $(Ph_4As)^+$ and $(Et_4N)^+$) have also been prepared starting from $ReCl_5$, but in several of these instances the yields are rather low.[5,226,301]

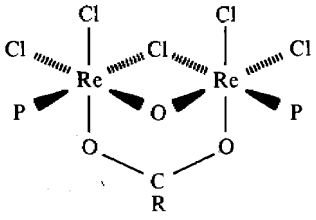
An X-ray crystal structure determination has been carried out on (**54**) for X = Cl. The ESCA spectrum of the complex $(Bu^n_4N)Re_2Cl_9$ shows that the bridging Cl atoms have higher Cl 2*p* binding energies (by ~1.3 eV) than those in the terminal Re—Cl bonds.[302] The complexes $(Bu^n_4N)Re_2Cl_9$ and $(Bu^n_4N)_2Re_2Cl_8$ display identical reactivities towards tertiary phosphines, reactions with PPh_3, $PEtPh_2$ and PEt_3 giving $Re_2Cl_6(PPh_3)_2$, $Re_2Cl_5(PEtPh_2)_3$ and $Re_2Cl_4(PEt_3)_4$, respectively.[64]

Amongst the products that can be isolated when *trans*-$ReOX_3(PPh_3)_2$ (X = Cl or Br) are reacted with carboxylic acids in boiling toluene are dark green $Re_2OX_5(O_2CR)(PPh_3)_2$ (X = Cl or Br) and purple $Re_2OCl_3(O_2CR)_2(PPh_3)_2$.[217] X-Ray crystal structure studies on $Re_2OCl_5(O_2CEt)(PPh_3)_2$ (**55**) and $Re_2OCl_3(O_2CEt)_2(PPh_3)_2$ (**56**) have shown that these complexes possess short Re—Re bonds (2.51–2.52 Å) although it is unclear what these values reflect in terms of actual Re—Re bond orders.[303,304] Complexes of the types (**55**) and (**56**) represent intermediate stages of reduction (Re(+4) and Re(+3.5), respectively) in the conversion of $ReOCl_3(PPh_3)_2$ to $Re_2(O_2CR)_4Cl_2$, the final product of these reactions.

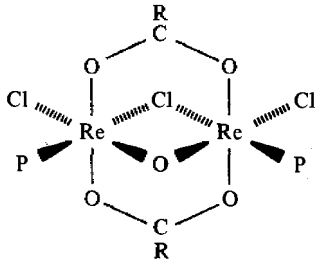
There is one example of a structurally characterized μ-dioxo complex of rhenium(IV). Dissolution of ReO_2 in an oxalic acid–potassium oxalate mixture ($Re:H_2C_2O_4:K_2C_2O_4$ = 1:3:1) gave, amongst other things, three groups of crystals (dark-red, red and green-red).[305] Yields of these products were not reported but an X-ray structure determination on the green-red material showed it to be $K_4[Re_2O_2(C_2O_4)_4]\cdot 3H_2O$, containing an $Re(\mu\text{-}O)_2Re$ unit and an Re—Re distance (2.362(1) Å) which is shorter than that in (**55**) and (**56**) and presumably reflects a considerable degree of Re



(54) X = Cl or Br



(55) P = PPh_3



(56) P = PPh_3

—Re multiple bond character. This result raises the important question as to whether some of the rhenium(IV) complexes that are believed to contain a linear Re—O—Re unit (Section 43.6.1.7) might not in reality have structures related to this oxalate derivative. The suggestion that the Re^{IV} complex with 5,6-diphenyl-2,3-dihydro(asym)triazine-3-thione (HL), that has been used for the spectrophotometric determination of rhenium, might be $Re_2(\mu\text{-}O)_2L_4$, containing bidentate (N and S) coordination from L, is not without precedent. This complex is prepared by the usual $SnCl_2$ reduction of $[ReO_4]^-$ in HCl in the presence of HL.[306]

Other oxide ligand complexes that can be mentioned here are the ternary rare earth rhenates. These include a few phases that contain dirhenium(IV) centers, of which $La_4Re_2O_{10}$ and $La_6Re_4O_{18}$ are of special note since the eclipsed $[Re^{IV}{}_2O_8]$ units that are present can be considered to contain Re—Re bonds of order three.[5,308] The phase $NH_4ReO_{1.5}F_3 \cdot H_2O$ has been shown to possess a structure that contains isolated $[Re_8O_{12}F_{24}]$ units. This material is paramagnetic and is an insulator.[309]

43.7 RHENIUM(V) COMPLEXES

The most prevalent complexes of this oxidation state are those which contain the $[ReO]^{3+}$, $[ReO_2]^+$ and $[Re_2O_3]^{4+}$ moieties, a reflection of the increasing stability of the rhenium–oxygen bond as the oxidation state increases. The tendency of Re^V to form multiple bonds (as in $[Re{=}O]^{3+}$ and $[O{=}Re{=}O]^+$) is also seen in its behavior toward nitrogen, *viz.* the stabilization of the $[Re{\equiv}N]^{2+}$ (nitrido) and $[Re{\equiv}NR]^{3+}$ (nitrene) moieties. With few exceptions, complexes of Re^V have been found to be essentially diamagnetic, *i.e.* to contain a spin-paired d^2 configuration. Because of the dominance of the $[ReO]^{3+}$, $[ReO_2]^+$ and $[Re_2O_3]^{4+}$ units in the chemistry of Re^V, such complexes will be considered first in the chemistry of this oxidation state.

43.7.1 Mononuclear Complexes Containing the $[ReO]^{3+}$ Moiety

43.7.1.1 Cyanides and aryl isocyanides

The species $[ReO(OH)(CN)_4]^{2-}$ is formed upon protonation of $K_3ReO_2(CN_4)$ and then eliminates water to give $[Re_2O_3(CN)_8]^{4-}$.[310] While other methods have been described for generating $[ReO(OH)(CN)_4]^{2-}$, cyano derivatives containing the $[ReO]^{3+}$ unit are rarely encountered. However, another example is the monoanionic species $[ReO(H_2O)(CN)_3F]^-$, which is believed to be formed upon the treatment of $[ReO_2(CN)_4]^{3-}$ with hot, 40% HF.[311] The reaction of *p*-tolyl isocyanide (*p*-tolNC) with $ReO(OEt)I_2(PPh_3)_2$ is reported to give $[ReO(OEt)I(PPh_3)_2(CN\text{-}p\text{-}tol)]I$ or $ReO(OEt)I_2(PPh_3)(CN\text{-}p\text{-}tol)$ depending upon whether hot ethanol or acetone is used as the reaction solvent.[312]

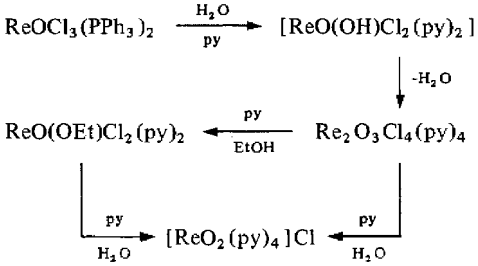
43.7.1.2 Amines and N-heterocycles

There are several reports in the older literature that describe the isolation of $ReOCl_3(py)_2$, $ReOCl_3(en)$ and $ReOX_3(bipy)$ (X = Cl or Br), often *via* the protonation of the corresponding dioxo–rhenium(V) species.[1,2] In more recent years interest in these particular molecules, none of which has been characterized crystallographically, has continued. The thermal decomposition of $(NH_4)_2ReOCl_5$ is said to lead to $(NH_4)[ReOCl_4(NH_3)]$ and $ReOCl_3(NH_3)_2$, whereas the reaction of

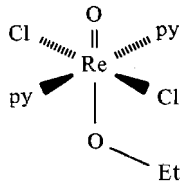
$(NH_4)_2ReOCl_5$ with various nitrogen donors is described as giving $ReOCl_3(L)_2$ (L = py, Et_2NH, 1/2bipy or 1/2phen), $(NH_4)[ReOCl_4(Et_2NH)]$ and $ReOCl_3(DMF)$.[313] Green $ReOCl_3(py)_2$ is formed upon reacting $ReOCl_4$ or $ReOCl_4(POCl_3)$ with pyridine.[314] $ReOCl_3(bipy)$ has been prepared by the reaction of bipy with $ReOCl_4$,[314] and as a brown solid through a similar reaction involving $ReOCl_3(PPh_3)(OPPh_3)$,[86] while green and violet isomers have also been described.[315] The former is isolated both by the H_3PO_2 reduction of a mixture of $HReO_4$ and bipy in HCl/EtOH, and upon heating $(bipyH)_2ReCl_6$ in 6 M hydrochloric acid in a current of air; dark green $ReOBr_3(bipy)$ is prepared by a similar procedure. The violet form is produced, along with $[ReO(OH)(bipy)_2]^{2+}$, when the latter reaction is carried out in more dilute hydrochloric acid (0.4 M). The violet form converts to green $ReOCl_3(bipy)$ when heated in 6 M HCl and has a much higher magnetic moment (2.1 *vs.* 0.4 BM).[315] This high magnetic moment raises the question as to whether Re^{IV} is present, perhaps as an impurity.

The protonation of the ethylenediamine complex $[ReO_2(en)_2]^+$, using the hydrohalic acids, has been described as a means of forming complexes that have been formulated $ReO(OH)X_2(en)$ (green), $[ReO(OH)(en)_2]X_2$ (purple) (X = Cl, Br or I) and $[Re(OH)_2Cl_2(en)]Cl$ (green).[316] These structural formulations are based largely upon the spectroscopic and magnetic properties of the products. In no instance has the result of an X-ray structure determination been reported, although a brief mention was made (in 1978) of the forthcoming publication of the structural details of $[ReO(OH)(en)_2](ClO_4)_2$, for which the Re=O and Re=OH distances are 1.72 and 1.83 Å, respectively.[317] Crystallographic measurements may be necessary in order to distinguish the $ReO(OH)X_2(en)$ formulation from the alternative one of $Re_2O_3X_4(en)_2$. These reactions are also complicated by the fact that in boiling concentrated HX, the complexes Cs_2ReOCl_5, $(enH_2)ReBr_6$ and $ReI_4(en)$ are also formed.[316] While the protonation of $[ReO_2(py)_4]^+$ in cold moderately concentrated HBr and HI is said to give $ReO(OH)X_2(py)_2$ {X = Br (green) or I (light brown)}, complexes which are analogous to $ReO(OH)X_2(en)$, more concentrated hot acid produces $ReOBr_3(py)_2$ and $(pyH)_2ReBr_6$ and $ReI_4(py)_2$, respectively.[258]

The complex $[ReO_2(py)_4]Cl$ is the final product in the reaction of $ReOCl_3(PPh_3)_2$ (or $ReCl_5$) with wet pyridine. Its formation has been postulated to occur *via* the intermediacy of the three complexes shown in Scheme 14.[318] While the hydroxy species has not been structurally characterized, its ethoxide analogue $ReO(OEt)Cl_2(py)_2$ has been shown by X-ray crystallography to have a structure (**57**) with the EtO ligand *trans* to the terminal Re—O bond.[319] Of special note is the shortness of the Re—O bonds (1.896(6) and 1.684(7) Å, an observation that has led to the suggestion that the Re—O bond orders lie somewhere between two and three for Re—O_t, and between one and two for Re—OEt.[319] The reaction of $ReOCl_3(py)_2$ with ethanol has been found to be a route to this same ethoxide complex.[314]



Scheme 14



(57)

43.7.1.3 Thiocyanate and other nitrogen donors

The most important thiocyanate complex of rhenium(V) is the oxopentakis(isothiocyanate) species $[ReO(NCS)_5]^{2-}$. It has been implicated as one of the species that is present (along with $[Re(NCS)_6]^{2-}$) when $[ReO_4]^-$ is reduced with tin(II) ion in acidic thiocyanate solutions.[220] Several well-characterized salts (Et_4N^+, $Bu^n_4N^+$, Ph_4P^+ and Ph_4As^+) have been prepared by ligand exchange reactions involving salts of the $[ReOBr_4(NCMe)]^-$, $[ReOCl_5]^{2-}$ or $[ReOCl_5]^-$ anions.[220,320] The salt $(Ph_4As)_2ReO(NCS)_5$ has also been prepared by the tin(II) chloride reduction of $NaReO_4$ in an acidic NH_4NCS solution.[220] It has been suggested that the samples of the salts $M^I_2ReO(NCS)_5$ ($M^I = Cs^+$, Tl^+ or Me_4N^+), that can be prepared by the reaction of Cs_2ReOCl_5 with KSCN in hot water,[321] are contaminated with $[Re(NCS)_6]^{2-}$ salts and possibly with other complexes as well.[220] The $[ReO(NCS)_5]^{2-}$ salts display characteristic IR and electronic absorption spectral properties, *e.g.* a ν(ReO) mode close to 960 cm^{-1} in their IR spectra, but variations in the magnetic properties reported for the salt $(Ph_4As)_2ReO(NCS)_5$ need to be clarified.[220,320] Other thiocyanate complexes that have been reported include those formulated as being of the types $ReO(SCN)_3(PR_3)_2$ (PR_3 = PPh_3 or PEt_2Ph), $ReOCl(NCS)_2(PPh_3)_2$ and $ReO(OH)(NCS)_2(PPh_3)_2$, some of which remain inadequately characterized especially with regard to the mode of thiocyanate binding.[1,2] Also, a brown solid analyzing as $(Et_4N)_2ReOCl_2(NCS)_3$ has been isolated from the reaction mixture that is obtained upon reacting KSCN with a compound purported to be $ReCl_3(OEt)_2$.[322]

The acetonitrile-containing anion $[ReOBr_4(NCMe)]^-$ is described in Section 43.7.1.6. The only known dialkylamido compound is red, diamagnetic, crystalline $ReO[N(SiMe_3)_2]_3$ (ν(Re=O) at 978 cm^{-1}), It is a unique four-coordinate compound of rhenium(V), that can be prepared by the interaction of $ReOCl_4$ with $LiNMe_2$.[245]

43.7.1.4 Phosphines, phosphites, arsines and stibines

Monodentate tertiary phosphines and arsines form a very large number of six-coordinate complexes of the types $ReOX_3(L)_2$, $ReOX_3(L)(L')$ and $ReO(OR)X_2(L)_2$, where X = halide or NCS; L = a tertiary phosphine, arsine or stibine ligand; L′ = DMSO, Ph_3PO or a phosphite ligand; and R = alkyl group.[1,2] Of these, $ReOCl_3(PPh_3)_2$ is by far the most important compound since it is commonly used as a starting material for the synthesis of many other rhenium complexes. The preparations of $ReOX_3(L)_2$ and $ReO(OR)X_2L_2$ can be quite varied but usually utilize solutions of $[ReO_4]^-$ in alcohol in the presence of an excess of the appropriate hydrohalic acid.[1,2] Alternative procedures include reactions of $[ReOX_5]^{2-}$ (X = Cl or Br) with phosphines,[323] phosphine exchange reactions using $ReOX_3(PPh_3)_2$ (X = Cl or Br)[323], the thermal decomposition of $(Ph_3PH)_2ReOCl_5$ which gives $ReOCl_3(PPh_3)_2$ *via* the intermediacy of $(Ph_3PH)[ReOCl_4(PPh_3)]$,[324] and thiocyanate or halide exchange reactions of $ReOX_3(PR_3)_2$.[107,325] Complexes of the type $ReOX_3(L)_2$ have been prepared for X = Cl, Br, I or NCS, and phosphine and arsine ligands (L) such as PPh_3, PEt_2Ph, PEt_3, $AsPh_3$, $AsMe_2Ph$ and the stibine Ph_3Sb.[1,2] The mixed halide complex $ReOCl_2I(PPh_3)_2$ has also been described; its preparation involves the reaction of $[ReOI_2(PPh_3)_2]^+$ with HCl.[1] In the case of the complexes $ReO(OR)X_2(L)_2$, both alkyl and aryl alkoxy derivatives have been prepared.[1] Further details of these and other synthetic procedures are described by Rouchias.[1] However, note should be taken of the remarkable ease with which rhenium halides partake in 'oxygen abstraction' reactions to afford oxorhenium(V) species; the formation of $ReOCl_3(PPh_3)_2$ in the reaction between PPh_3 and $ReCl_5$ or β-$ReCl_4$ in acetone is an illustration of this tendency.[104,226]

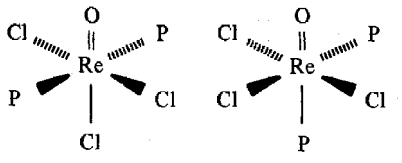
Assignment of the structures of the $ReOX_3L_2$ complexes [*trans* (one form) or *cis* (two forms)] has until recently rested largely upon spectroscopic data (IR, NMR and electronic absorption) and dipole moment measurements.[107,323,325,326] Of special note is the very characteristic ν(ReO) mode that occurs as a sharp intense band in the vicinity of 970 cm^{-1}.[107,326] Thus, $ReOCl_3(PEt_2Ph)_2$ has been shown to exist in *cis* and *trans* forms (blue and green respectively);[107] a third 'isomeric' violet form has been shown to be in actuality the rhenium(IV) complex *trans*-$Re(OH)Cl_3(PEt_2Ph)_2$.[236] The X-ray crystal structure of *trans*-$ReOCl_3(PEt_2Ph)_2$ (**58**) has confirmed this structural assignment, as is also the case for *cis*-$ReOCl_3(PEt_2Ph)_2$ (**59**), although in this particular instance the structure determination is not yet complete.[327,328] Some structural details of these complexes and related species are given in Table 9.

The structural characterization of the alkoxide derivatives *trans*-$ReO(OEt)Cl_2(PPh_3)_2$ and *trans*-$ReO(OR)I_2(PPh_3)_2$ (R = Me or Et) show that these complexes resemble closely the structure of the pyridine complex *trans*-$ReO(OEt)Cl_2(py)_2$ (**57**) (Section 43.7.1.2), with a *trans* O=Re—OR unit

Table 9 Structural Details for Phosphine and Arsine Complexes of the Type $ReOX_3L_2$

Complex	*r(Re—O)*, Å	*r(Re—L_{trans})*,[a] Å	*Comments*	*Ref.*
trans-$ReOCl_3(PEt_2Ph)_2$ (**58**)	1.660(9)	2.445(3) (Cl)	Phosphine ligands *trans* to one another	327, 328
cis-$ReOCl_3(PEt_2Ph)_2$ (**59**)			Structural details not reported	327, 328
$ReOCl_3(PEt_2Ph)(OPEt_2Ph)$	1.672(9)	2.063(9) ($OPEt_2Ph$)		327
$ReOBr_3(PEt_2Ph)(OPEt_2Ph)$	1.663(7)	2.053(7) ($OPEt_2Ph$)		327
$ReOCl_3$(dppe)	1.680(5)	2.429(2) (Cl)	Other *cis* isomer to that shown by (**59**)	327
$ReOBr_3$(dppe)	1.679(8)	2.580(1) (Br)	Other *cis* isomer to that shown by (**59**)	327
$ReOCl_3(PPh_3)$(DMF)	1.664(4)	2.133(4) (O of DMF)		327
trans-$ReOCl_2(OEt)(PPh_3)_2$	1.76(1)	1.89(1) (O of OEt)	Structure similar to that of the py complex (**57**)	329
trans-$ReOI_2(OMe)(PPh_3)_2$	1.698(5)	1.859(5) (O of OMe)	Structure similar to that of the py complex (**57**)	329
trans-$ReOI_2(OEt)(PPh_3)_2$	1.715(9)	1.880(9) (O of OEt)	Structure similar to that of the py complex (**57**)	332
$ReOCl_2(acac)(PPh_3)$	1.69(1)	2.10(1) (O of acac)	*cis*-Re-O (acac) distance is 1.99(1)	

[a] Re—L distance *trans* to the terminal Re—O multiple bond.



(58) P = PEt_2Ph (59) P = PEt_2Ph

and a *trans* arrangement of Re—P bonds.[327,329] This is, in turn, similar to (**58**) but with OR replacing the *trans* chloride ligand. There is some evidence that complexes of the type $ReO(OR)X_2(PPh_3)_2$ isomerize quite rapidly in certain organic solvents.[118]

Cationic species of the type $[ReOX_2(PPh_3)_2]ReO_4$ (X = Cl, Br or I) have been described as being produced when $ReO_2I(PPh_3)_2$ is reacted with oxygen or $ReO(OEt)X_2(PPh_3)_2$ is treated with perrhenic acid in acetone, but their identity requires confirmation. Several well-characterized mixed ligand complexes of the type $ReOX_3(L)(L')$ are also known, where L represents a phosphine ligand and L′ is DMSO, DMF, Ph_3PO, $PhEt_2PO$ or one of several phosphite ligands. The mixed phosphine–phosphine oxide complex $ReOCl_3(PPh_3)(OPPh_3)$ is formed when a current of air is passed through a suspension of $ReCl_3(NCMe)(PPh_3)_2$ in boiling benzene,[86] and probably has a structure similar to that of $ReOX_3(PEt_2Ph)(OPEt_2Ph)$ (X = Cl or Br) (Table 9) in which the phosphine oxide ligand is *trans* to the terminal Re=O bond.[327] The DMSO analogue $ReOX_3(PPh_3)(DMSO)$ (X = Cl or Br) is formed by the interaction of DMSO with $ReOX_3(PPh_3)_2$ or $ReO(OEt)Cl_2(PPh_3)_2$ and concentrated hydrohalic acid.[331] The DMF-containing complex $ReOCl_3(PPh_3)(DMF)$ has also been prepared and possesses a structure where the O-bound DMF ligand is *trans* to the terminal Re =O unit.[327] When *trans*-$ReOX_3(PPh_3)_2$ is treated with $P(OMe)_3$ and phosphites of the type $P[(OCH_2)_3CR]$ (R = Me or Et), the mixed phosphine–phosphite complexes $ReOX_3(PPh_3)$(phosphite) are formed.[112] In the case of the $P(OMe)_3$ complex $ReOCl_3(PPh_3)[P(OMe)_3]$, two isomers can be isolated (blue and green); these are best distinguished on the basis of differences in their low frequency IR spectra (ν(Re—Cl) modes).

Another type of mixed ligand complex is that which contains an anionic ligand, as exemplified by the acetylacetonate derivative $ReOCl_2(acac)(PPh_3)$. This green complex, as well as its bromide and iodide analogues, can be prepared by the reaction of $ReOX_2(OEt)(PPh_3)_2$ with acacH using very short reaction times.[118] $ReOCl_2(acac)(PPh_3)$ can also be prepared by the interaction of $ReOCl_3(PPh_3)(OPPh_3)$ with acacH.[86] The related PEt_2Ph complex $ReOCl_2(acac)(PEt_2Ph)$ has also been prepared.[118] These diamagnetic complexes are characterized by a ν(Re=O) band at $\sim 980\,cm^{-1}$ in their IR spectra, and a structure in which one of the oxygen atoms of the chelating acac ligand is *trans* to the terminal Re=O unit (Table 9).[332]

Several complexes of $[ReO]^{3+}$ that contain bidentate and tridentate phosphine/arsine ligands have been prepared and characterized. Some of these, *viz.* $ReOCl_3$(dppe), $ReOCl_3(Et_2PCH_2CH_2PEt_2)$, $ReOCl_3$(diars) and $ReOX_3$(tas) (X = Cl or Br; tas = bis(*o*-diphenylarsinophenyl)phenylarsine) are described in the older literature which has been summarized by Fergusson.[2] $ReOCl_3$(dppe) and $ReOCl_3(Et_2PCH_2CH_2PEt_2)$ can be prepared by the reaction of the phosphine with $NaReO_4$ in a boiling alcohol–conc. HCl solution.[107] More recent preparations of $ReOX_3$(dppe) (X = Cl, Br or I) have involved the reactions of $[ReO_2(dppe)_2]X$ with HX in ethanol (X = Cl or Br) and of $ReO_2I(PPh_3)$(dppe) with HI.[330,333] The X-ray crystal structures of $ReOX_3$(dppe) (X = Cl or Br) have been determined (Table 9).[327] The pale green dppm complex $ReOCl_3$(dppm) has been obtained by the reaction of *cis*-$ReCl_4(NCMe)_2$ with dppm in hot acetone for a period of 48 hours. This complex apparently forms by oxygen abstraction from the acetookwzwne solvent.[233] The reaction between $KReO_4$, $(Ph_2PCH_2)_3CMe$ (abbreviated P_3) and H_3PO_2 in ethanol–conc. HCl gives blue $ReOCl_3(P_3)$ and upon prolonged reflux (24 hours) a small quantity of a green isomer. Although both complexes possess a ν(Re=O) mode at $\sim 985\,cm^{-1}$, it has been suggested that the green isomer is a seven-coordinate complex containing tridentate P_3 while the blue form is six-coordinate with bidentate coordination from the P_3 ligand.[110] The reaction of either the green or blue form with ethanol gives $ReO(OEt)Cl_2(P_3)$, in which one of the phosphine groups is uncoordinated.[110]

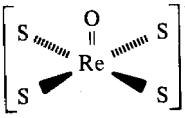
43.7.1.5 Oxygen and sulfur ligands

Mixed phosphine–oxygen donor complexes of $[ReO]^{3+}$ that contain DMSO, DMF, acac, Ph_3PO and $PhEt_2PO$ are described in Section 43.7.1.4. Complexes of the type $ReOX_3(OPR_3)_2$ (X = Cl or

Br; R_3PO = Ph_3PO, Ph_2EtPO, Ph_2HPO, $Ph_2P(O)CH_2CH_2P(O)Ph_2$ or $Ph_2P(O)CH{=}CHP(O)Ph_2$) can be prepared by reaction of the ligand with solutions of K_2ReOX_5 (X = Cl or Br) in acidified (HCl or HBr) acetone.[323] Alternatively, the thermal oxidation of the phosphine derivatives $ReOX_3(PR_3)_2$ in air at temperatures up to 200°C can give these same phosphine oxide species.[323,324]

The reaction between $ReOCl_3(AsPh_3)_2$ and dioxane or 1,4-oxathiane leads to displacement of $AsPh_3$ by the latter ligands; the oxathiane complex presumably contains S-bound ligands.[251] In fact, a range of sulfur donors are capable of stabilizing the Re^V oxidation state containing the $[ReO]^{3+}$ moiety. 1,2-Bis(ethylthio)ethane ($EtSCH_2CH_2SEt$) reacts with K_2ReOCl_5 in hydrochloric acid to give a mixture of diamagnetic blue needles and green plates (ν(Re=O) at 980 and 970 cm^{-1}, respectively) that are believed to be $ReOCl_3(EtSCH_2CH_2SEt)$ and $ReO(OH)Cl_2(EtSCH_2CH_2SEt)$, respectively.[334] Several complexes of Re^V with thiourea (tu) and *N,N'*-ethylenethiourea (entu) have been reported, but the structural formulations are based largely upon microanalytical data and IR spectroscopic and conductiometric measurements, *e.g.* $ReOCl_3(L)_2 \cdot nH_2O$, $[ReOCl(L)_4]Cl \cdot 2H_2O$, $K[ReOCl_4(L)] \cdot 2H_2O$ (L = tu or entu). The formation of these complexes has been investigated by spectrophotometric and potentiometric methods through monitoring the reaction between $[ReOCl_5]^{2-}$ and tu or entu in 6 M HCl.[336,337] While none of the complexes isolated in these studies have been subjected to X-ray crystal structure analyses, closely related species have been prepared by reacting $KReO_4$, with tu in concentrated hydrochloric acid. The structures of two of the resulting complexes, one obtained as blue crystals, the other being green, have been determined.[338,339] These complexes, $[ReOCl_2(tu)_2(H_2O)]Cl$ and $ReOCl_3(tu)(H_2O)$, both possess octahedral structures in which the water molecule is bound *trans* to the oxo O atom. The terminal Re—O distances are 1.654(10) and 1.713(19) Å, respectively, in the cationic and neutral complex, while the corresponding Re—OH_2 distances are 2.231(10) and 2.291(20) Å. These results are of additional significance in view of the application of the Re^{VII}–HCl—Sn^{II}–thiourea system in the analytical chemistry of rhenium. However, while Re^V and Re^{IV} thiourea complexes are said to be formed depending on the $SnCl_2$ concentration, attempts at the structural characterization of any tin-containing species have so far been frustrated.[340,341]

Synthetic procedures for complexes of oxorhenium(V) containing thiol ligands are now well established and several of these derivatives are well characterized structurally. The reaction between $(Ph_4As)ReOBr_4$ and PhSH in acetonitrile in the presence of the base NEt_3 has proved to be a convenient means of preparing $(Ph_4As)ReO(SPh)_4$ (**60**). The crystal structure of this complex as its acetonitrile solvate has shown that the anion possesses a square pyramidal geometry with an Re—O distance of 1.686(9) Å.[342] An alternative route to this anion and others of the type $[ReO(SAr)_4]^-$ (Ar = Ph, *p*-tol, C_6F_5 or C_6Cl_5) involves the reaction of $ReOCl_3(PPh_3)_2$ with excess aryl thiolate anion in refluxing methanol.[204] These species, which have been isolated as their Ph_4P^+ salts, show an intense ν(Re=O) band in the range 990–950 cm^{-1} in their IR spectra.[204] The selenol analogue $(Ph_4As)ReO(SePh)_4$ has also been prepared and characterized.[342]



(60) S = SPh

The analogous ethanedithiol derivative $(Ph_4As)ReO(SCH_2CH_2S)_2$ can be prepared by one of two procedures, namely, the reaction of $NaReO_4$ with ethanedithiol and $NaBH_4$ in THF, or the reaction of $(Bu^n_4N)ReOBr_4$ with a solution of the ethanedithiolate in THF.[343] Similar procedures have been developed for the synthesis of $A_2[ReO(dtox)_2]$ (A = Bu^n_4N or Ph_3MeAs; dtox = 1,2-dithiooxalate), $(Ph_4As)ReO(mnt)_2$(mnt = maleonitriledithiolate) and $(Bu^n_4N)ReO(tdt)_2$ (tdt = 3,4-dimercaptotoluene) using the appropriate $[ReOBr_4]^-$ salt as the synthetic starting material.[343] The mnt derivative has also been prepared by the reaction of $[ReCl_6]^{2-}$ with Na_2mnt and I_2.[344] These orange-brown crystalline compounds exhibit the usual ν(Re=O) modes in the range 990–950 cm^{-1}, and possess low magnetic moments which are field strength dependent.[343] In all instances, they most likely possess a mononuclear square pyramidal geometry. This has been confirmed in the case of the Cs^+ salt of $[ReO(dtox)_2]^-$ by an X-ray crystal structure determination.[345] A rhenium(V) complex containing dithiooxamide (dto) of stoichiometry $ReOCl_3(dto)_2$ is formed upon reacting dto with a solution containing $[ReOCl_5]^{2-}$ in acetic acid–HCl.[346]

The voltammetric behavior of $[ReO(L{-}L)_2]^-$ (L–L = SCH_2CH_2S, tma, dtox, mnt or tdt) has been

examined at Hg and Pt electrodes. A reduction occurs at potentials more negative than −0.9 V (*vs.* SCE) but oxidatively there appears to be little tendency to form Re^{VI} complexes.[343]

An especially interesting complex is the one derived from mercaptothioacetic acid ($HSCH_2COSH$, tmaH), *viz.* $(Bu^n_4N)ReO(tma)_2$. This has been prepared by the reaction of (Bu^n_4N)-$ReOBr_4$ with commercial samples of thioglycolic acid in MeOH following adjustment of the pH to 7.5 with 10 M NaOH. The formation of $[ReO(tma)_2]^-$ reflects the presence of sizeable concentrations of mercaptothioacetic acid in the thioglycolic acid.[343] These observations are important since several studies have been made of the complexation of Re^V (and Re^{VII}) by thioglycolic acid in acidic media, although the resulting complexes are poorly defined.[347,348]

The dialkyl dithiocarbamate complexes $ReOCl_2(Et_2dtc)(PPh_3)$ and $ReOX(R_2dtc)_2$ (X = Cl or Br; R = Me, Et or $\frac{1}{2}(CH_2)_5$) are best prepared by the reaction of $ReOX_3(PPh_3)_2$ in dry acetone with the appropriate tetraalkylthiuram disulfide, or, in the case of the Et_2dtc derivatives, by treatment with thallium diethyldithiocarbamate.[121] The methoxide-containing complex $ReO(OMe)(Et_2dtc)_2$ is formed by the reaction of $Re_2O_3(Et_2dtc)_4$ with dry methanol. Like the other R_2dtc complexes it displays a characteristic $\nu(Re{=}O)$ mode (940 cm^{-1}) in its IR spectrum.[349]

Salts of the $[ReO(SAr)_4]^-$ anions (Ar = mesityl, 2,6-diisopropylphenyl or 2,4,6-triisopropylphenyl) have been isolated as their Et_3PH^+ and Ph_4P^+ salts.[605] Attempts to recrystallize $Re(SC_6H_3(Pr^i)_2)_3(MeCN)(PPh_3)_2$ from CH_2Cl_2–EtOH gave the salt $[Ph_3PSC_6H_3(Pr^i)_2]^+[ReO(SC_6H_3(Pr^i)_2)_4]^-$. The X-ray crystal structure of this complex and $(Ph_4P)[ReO(SC_6H_2Me_3)_4]$ have been determined.[605]

43.7.1.6 Halides

The oxo species that will be considered here are those of the types $[ReOX_5]^{2-}$, $[ReOX_4]^-$ and $[ReOX_4L]^-$, where L represents a monodentate donor and X = Cl, Br and/or I.[1,2] Salts containing the pseudooctahedral $[ReOX_5]^{2-}$ anions (X = Cl or Br) are often easily prepared but can be contaminated with paramagnetic $[ReCl_6]^{2-}$ and diamagnetic $[ReO_4]^-$ due to the disproportionation of Re^V to Re^{VII} and Re^{IV} that can occur in aqueous media (equation 17).[1,350] The $[ReOCl_5]^{2-}$ anion may be obtained by reducing $[ReO_4]^-$ with iodide in concentrated hydrochloric acid, or by dissolving $ReOCl_4$ or $ReCl_5$ in concentrated hydrochloric acid and adding a large cation.[1,331,351] The bromide analogue $[ReOBr_5]^{2-}$ is probably best prepared as its Cs^+ salt by the dissolution of $ReCl_5$ in 48% hydrobromic acid followed by the addition of CsBr, but can also be prepared from the reduction of $ReOBr_4$ in hydrobromic acid.[352,353] Cation exchange can also be used to prepare other salts.[324,354] Only a very brief mention has been made of the $[ReOI_5]^{2-}$ anion and it is not well characterized.[1]

$$3Re^V \longrightarrow 2Re^{IV} + Re^{VII} \qquad (17)$$

Magnetic studies on pure samples of $M^I_2ReOX_5$ salts have shown that these complexes are essentially diamagnetic, so that claims[354] of significant residual paramagnetism can most likely be attributable to $[ReX_6]^{2-}$ contaminants.[351] Potassium, rubidium and cesium salts of $[ReOX_5]^{2-}$ (X = Cl or Br) are seemingly isostructural with those of other closely related transition metal species of the type $[MOX_5]^{2-}$ (M = Cr, Mo, W, Tc).[355,356] A careful study has been made of the electronic absorption spectral properties and vibrational spectra (IR and Raman) of Cs_2ReOX_5 (X = Cl or Br), the latter dealing with the assignment of the Re=O and Re—X stretching and deformation modes.[351,355]

Studies of the equilibria existing in solutions of $[ReOCl_5]^{2-}$ in hydrochloric acid reveal that the Re—Cl bond *trans* to Re=O is labile and that substitution by water can occur to give $[ReOCl_4$-$(H_2O)]^-$,[357,358] which is a derivative of the $[ReOCl_4]^-$ anion. The best procedure for the preparation of salts of $[ReOX_4]^-$ (X = Cl, Br or I) involves the reduction of $[ReO_4]^-$ with zinc in concentrated sulfuric acid with HX present.[359] Reactions of $[ReOX_4]^-$ with monodentate ligands can be used to prepare the six-coordinate anions $[ReOX_4(L)]^-$ (L = H_2O or MeCN).[359,360] The triphenylphosphine derivative $(Ph_3PH)[ReOCl_4(PPh_3)]$ can be obtained by the treatment of $ReOCl_3(PPh_3)_2$ with hydrogen chloride and through the thermolysis of $(Ph_3PH)_2ReOCl_5$,[324,331] while the treatment of $(NH_4)_2ReOCl_5$ with Et_2NH, MeCN and EtOH is said to give complexes of stoichiometry $(NH_4)[ReOCl_4(L)]$.[313] X-Ray structural data have confirmed the octahedral structures of several $[ReOX_4(L)]^-$ salts in which L is weakly bonded *trans* to the Re=O bond. Such data were first reported for $(Ph_4As)[ReOBr_4(NCMe)]$[361] and $(Et_4N)[ReOBr_4(H_2O)]$,[360] and later supplemented by crystallographic data for $(Ph_4As)[ReOCl_4(H_2O)]$[362,573] and the salt $[(NH_2)_2CSSC(NH_2)_2][ReOCl_4$-

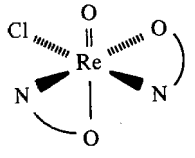
H_2O)]Cl·H_2O.[363] All revealed a very short Re—O distance (1.63–1.73 Å) that accord with its multiple bond character. The crystals of $[(NH_2)_2CSSC(NH_2)_2][ReOCl_4(H_2O)]Cl \cdot H_2O$ were obtained (together with $[ReOCl_2(tu)_2(H_2O)]Cl$ and $ReOCl_3(tu)(H_2O)$ — see Section 43.7.1.5) in a complicated reaction involving the reduction by thiourea (tu) of $KReO_4$ in concentrated HCl. The dithiobisformamidinium cation is an oxidation product of the thiourea.[363]

The complex $(Ph_4P)_2ReOCl_5$ which can be obtained as its bis-CH_2Cl_2 solvate from the reaction of $ReCl_5$ with Ph_4PCl in the presence of water has been characterized by X-ray crystallography.[606]

43.7.1.7 Mixed donor atom ligands and macrocycles

Complexes of $[ReO]^{3+}$ containing Schiff bases constitute the most extensive group of complexes derived from mixed donor atom ligands. Salicylaldehyde (salH), which serves as a precursor to most of the Schiff bases, also forms several well-defined complexes. The compound $ReOCl_2(sal)(PPh_3)_2$ can be prepared by reacting salH (or its lithium salt) with $ReOCl_3(PPh_3)_2$, or with a mixture of $KReO_4$, PPh_3 and excess hydrochloric acid in boiling EtOH.[205] Treatment of this complex with PMe_2Ph leads to the formation of $ReOCl_2(CHOsal)(PMe_2Ph)_2$ through the opening of the chelate ring and the conversion of the monoanionic bidentate sal ligand to a monodentate donor, bound through its phenolic oxygen (in which form it is abbreviated CHOsal). The reaction of salH with $(Ph_4As)ReOCl_4$ in refluxing ethanol gives $(Ph_4As)[ReOCl_3(sal)]$. These three diamagnetic complexes each possess a ν(Re=O) mode in the range 975–960 cm^{-1}, and probably have structures in which the phenolic oxygen in bound *trans* to the terminal Re=O unit.[205] The salt $(Ph_4P)[ReOCl_3(sal)]$ has also been reported and is synthesized by heating neat salicyaldehyde with $(Ph_4P)_2ReCl_6$ or a solution in ethanol with $(Ph_4P)ReOCl_4$.[364]

The bidentate monoanionic Schiff bases *N*-methylsalicylideneiminate (Me-sal) and *N*-phenylsalicylideneiminate (Ph-sal) react with $ReOX_3(PPh_3)_2$ or $ReOX_2(OEt)(PPh_3)_2$ (X = Cl or Br) to afford the six-coordinate species $ReOX_2(L)(PPh_3)$ or $ReOX(L)_2$ (L = Me-sal or Ph-sal), depending upon the reaction stoichiometry.[365] A similar procedure can be used to obtain the analogous complexes derived from 8-hydroxyquinoline (oxineH), *viz.* $ReOX_2(oxine)(PPh_3)$ and $ReOX(oxine)_2$,[365] while the reaction of $(Ph_4As)ReOCl_4$ with a two-fold stoichiometric amount of Schiff base in hot ethanol can be used to prepare $ReOCl(L)_2$ (L = Me-sal, Ph-sal or oxine).[366] The reaction of $ReOX_2(L)(PPh_3)$ with PMe_2Ph has proven to be a simple means of preparing $ReOX_2(L)(PMe_2Ph)$.[206] An X-ray crystal structure determination on $ReOCl(Me\text{-}sal)_2$ (**61**) has shown that the phenolic oxygen of one of the Me-sal ligands is, as expected, *trans* to the short multiply bonded Re=O unit (1.680(4) Å).[367] In the case of $ReOX_2(L)(PPh_3)$, some systems have been isolated as *cis* and *trans* isomers, and the pale green 'intermediate' $ReOCl_3(Me\text{-}salH)(PPh_3)$ has been prepared by the reaction of $ReOCl_3(PPh_3)_2$ with Me-salH in benzene at room temperature.[368]

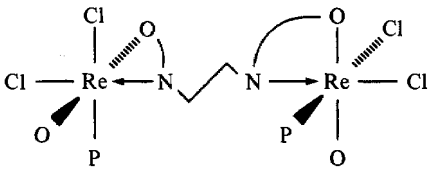


(**61**) $\overset{\frown}{N\ O}$ = Me—sal

When a stoichiometric quantity of the Schiff base Me-salH or Ph-salH, or the bidentate oxineH, is reacted with $(Ph_4As)ReOCl_4$ in anhydrous THF, the salts $(Ph_4As)[ReOCl_4(LH)]$ are produced, whereas these same reactions when carried out in boiling ethanol give $(Ph_4As)[ReOCl_3(L)]$.[366]

Studies involving the tetradentate, dianionic Schiff base ligands derived from sal_2enH_2 = *N*,*N*′-ethylenebis(salicylideneimine), sal_2propH_2 = *N*,*N*′-trimethylenebis(salicylidenamine), sal_2phenH_2 = *N*,*N*′-*o*-phenylenebis(salicylideneimine) and $acac_2enH_2$ = *N*,*N*′-ethylenebis(acetylacetimine) have shown that analogous procedures to those described above can be used to prepare the Schiff-base-bridged species $[ReOX_2(PPh_3)]_2(sal_2en)$ (X = Cl or Br), $[ReOCl_3(PPh_3)]_2(acac_2enH_2)$, $\{[ReOCl_3]_2(sal_2en)\}^{2-}$ and $\{[ReOCl_4]_2(sal_2enH_2\}^{2-}$, as well as the mononuclear complexes $ReOCl(L)$ (L = sal_2en, sal_2prop, sal_2phen or $acac_2en$).[298,365,366,368] The latter mononuclear species have been proposed to contain a structure with the Re—Cl bond *trans* to Re=O,[298] although such a stereochemistry is not found in the case of the X-ray crystal structure of green crystalline $[ReOCl_2(PPh_3)]_2(sal_2en)$ (**62**).[369] In this complex (r(Re=O) = 1.68(1) Å and ν(Re=O) = 969 cm^{-1}) a phenolic oxygen is *trans* to the terminal Re=O bond. The mustard-yellow complex $ReOCl_3$(a-

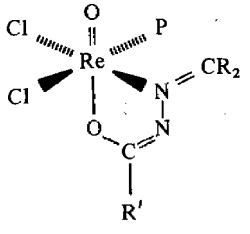
cac_2enH_2) can be isolated upon reacting $ReOCl_3(PPh_3)_2$ with $acac_2enH_2$ in refluxing THF. ^1H NMR spectral data for this complex have been interpreted in terms of a bidentate chelating N-bound $acac_2enH_2$ ligand in the enolized form.[298]



(62)

Several complexes derived from the tridentate Schiff base *N*-(2-hydroxyphenyl)salicylideneimine (HOPh-salH) have been synthesized and the X-ray crystal structures of *trans*-ReOCl(L)(OPh-sal) (L = H_2O or MeOH) and *cis*-ReOCl(PMe_2Ph)(OPh-sal) determined.[607] The structures of the previously prepared Schiff base complexes *trans*-$ReOBr_2$(Ph-sal)(PPh_3),[608] and *cis*- and *trans*-$ReOCl_2$(Me-sal)(PPh_3)[609] have been reported.

Rhenium(V) complexes of vinyl amides RCOCH=C(R′)NH_2 of the type $ReOCl_2$[C(O^-)=CHC(R′)=NH](PPh_3) have been prepared by reacting the amides with $ReOCl_3(PPh_3)_2$ in anhydrous benzene or THF. These complexes, for which R′ = $CH_2CH_2CO_2H$ when R = Ph or C_6H_{13}, or R′ = Me or $CH_2CH_2CO_2Me$ when R = Ph, probably possess the usual octahedral structure with the ligand oxygen donor *trans* to Re=O.[370] When mixtures of ketones and $ReOCl_3(PPh_3)_2$ are treated with acyl- or aryl-hydrazine hydrohalides in refluxing benzene, derivatives of the ketone hydrazone are formed. The reaction of $ReOBr_3(PPh_3)_2$ with benzoylhydrazine hydrobromide and acetone gives an analogous bromide complex.[87] An X-ray crystal structure on the derivative [acetone benzoylhydrazonido(1)-*N*′,*O*]dichlorooxo(triphenylphosphine)rhenium(V) shows that these species have the structure depicted in (**63**).[371]



(63) P = PPh_3

An assortment of other mixed donor ligand complexes of oxo–rhenium(V) are also known but these are not particularly well characterized and, generally speaking, their structures are uncertain. These data include the complexation of Re^V by such ligands as 2-aminobenzenethiol,[372] thiosemicarbazides,[373] 1-methyl-2-mercaptoimidazole[374] and 2-mercaptobenzothiazole.[345] Recently, the pyrazolylborate complex $ReOCl_2[HB(pz)_3]$ has been prepared.[572]

Macrocylic complexes of rhenium are rare. The complex [ReO(OPh)L], where H_2L = octaethylporphine, has been prepared starting from the oxide Re_2O_7 in refluxing phenol. Its spectral properties have been described, including the assignment of ν(Re=O) at 946 cm^{-1}.[375]

43.7.2 Mononuclear Complexes Containing the $[ReO_2]^+$ Moiety

43.7.2.1 Cyanide and aryl isocyanides

One of the most stable and best characterized cyano complexes of rhenium is the $[ReO_2(CN)_4]^{3-}$ anion. It is prepared quite conveniently by the reduction of $[ReO_4]^-$ using hydrazine hydrate in the presence of CN^-.[2] The structure of the potassium salt $K_3ReO_2(CN)_4$ has been determined by both X-ray[376] and neutron diffraction[377] and shown to contain a *trans* dioxo arrangement of Re=O bonds, with r(Re—O) ≃ 1.78 Å. The protonation of $[ReO_2(CN)_4]^{3-}$ leads first to $[ReO(OH)(CN)_4]^{2-}$, which then eliminates water to give $[Re_2O_3(CN)_8]^{4-}$.[310,378] Rates of oxygen exchange between *trans*-$[ReO_2(CN)_4]^{3-}$ and water have been determined in both acidic and basic

media. In acid, a mechanism involving exchange of an oxo ligand that is facilitated by protonation is believed to occur. On the other hand, in basic media exchange occurs only after replacement of an equatorial cyano ligand by a solvent water molecule or hydroxide ion.[379]

An MO treatment of the bonding in diamagnetic $[ReO_2(CN)_4]^{3-}$ has been used to interpret the electronic absorption spectrum of this species,[380] while a detailed analysis of the vibrational spectra of $K_3ReO_2(CN)_4$, $K_3ReO_2(^{13}CN)_4$ and $K_3Re^{18}O^{16}O(CN)_4$ is available.[381] The $\nu(^{16}O{=}Re{=}^{16}O)$ modes are at 775 (IR) and 879 (Raman) cm^{-1}. The electronic absorption and emission spectra of $[ReO_2(CN)_4]^{3-}$ (and the ethylenediamine and pyridine complexes $[ReO_2(en)_2]^+$ and $[ReO_2(py)_4]^+$ — see Section 43.7.2.2) have been investigated.[610]

A *p*-tolyl isocyanide complex of stoichiometry $[ReO_2(PPh_3)_2(CNR)_2]I$ has been reported[312] but remains incompletely characterized. Other isocyanide-containing derivatives are unknown.

43.7.2.2 Amines and N-heterocycles

Diamagnetic species of the types $[ReO_2L_4]^+$ (L = py, picolines, NH_3 or primary amines) and $[ReO_2(LL)_2]^+$ (LL = ethylenediamine (en) and other bidentate primary amines, or bipy) constitute an extensive series of complexes whose preparations and reactivities, including the protonation of the dioxorhenium unit, are thoroughly reported in earlier reviews.[1,2] These species are usually encountered in salts with the following anions: Cl^-, Br^-, I^-, ClO_4^- and ReO_4^-. The most extensively studied systems are the yellow-orange species $[ReO_2(py)_4]^+$ and $[ReO_2(en)_2]^+$, both of which display characteristic $\nu(O{=}Re{=}O)$ vibrations at $\sim 820\,cm^{-1}$ in their IR spectra.[326]

Their syntheses can be accomplished using starting materials like K_2ReCl_6 and $KReO_4$,[382,383] but they can also be formed easily from compounds such as β-$ReCl_4$ and $Re_2O_3Cl_4(py)_4$ (and many others) when oxygen and water are present.[318,384]

The X-ray crystal structure of *trans*-$[ReO_2(en)_2]Cl$ has been the subject of three separate studies, the most recent determination giving $r(Re{-}O) = 1.765(7)$ Å.[317] The results of X-ray structural studies are also available for *trans*-$[ReO_2(en)_2]NO_3$[385] and *trans*-$[ReO_2(py)_4]Cl \cdot 2H_2O$,[317] for which the Re=O bond distances are reported as 1.764(9) Å and 1.764(13) Å, respectively.

Several complexes are also known where more than one type of ligand (including an amine or *N*-heterocycle) is present in the $[ReO_2]^+$ coordination sphere; examples include $[ReO_2(py)_3(PPh_3)]^+$ and $[ReO_2(py)_2(PPh_3)_2]^+$ (see Section 43.7.2.3), and some mixed aqua–fluoride–pyridine derivatives, *e.g.* $[ReO_2py_3]F$, $[ReO_2(py)_2(H_2O)F]$ and $[ReO_2(py)_2(H_2O)_2]F$, that have been described as being formed starting from $[ReO_2(py)_4]F$.[386]

The electronic absorption spectra of various dioxorhenium(V) *trans*-$[ReO_2L_4]^+$ species have been investigated (L = py, 4-Mepy or 4-Bu^{t}py), and these species have been shown to exhibit luminescence in the solid state and in aprotic solvents but not in water.[387]

In addition to spectroscopic studies on $[ReO_2(en)_2]^+$ and $[ReO_2(py)_4]^+$,[610] the reduction of the en complex and its 1,3-diaminopropane analogue with the aquated electron has been found to generate transient d^3 Re^{IV} complexes.[611] Re_2O_7 is reduced by PEt_3 in the presence of pyridine, 4-methylpyridine or 4-phenylpyridine, to give $[ReO_2L_4]ReO_4$ in good yield. The X-ray crystal structure of *trans*-$[ReO_2(4\text{-}Mepy)_4]ReO_4$ has been determined.[612]

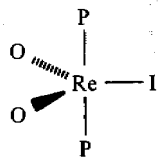
The incorporation of rhenium into zeolites *via* $[ReO_2(en)_2]Cl$ has been found to lead to lower catalytic activity (in the hydrogenation of benzene) than is the case for catalysts obtained by impregnating zeolite NaY with NH_4ReO_4 solution.[388]

43.7.2.3 Phosphines

The six-coordinate complexes $ReO_2I(PEt_2Ph)_3$ and $ReO_2I(dppe)(PPh_3)$ are formed when five-coordinate $ReO_2I(PPh_3)_2$ is reacted with PEt_2Ph or one equivalent of dppe.[330] In a similar fashion, the reaction of $ReO_2I(PPh_3)_2$ with an excess of py can be used to prepare $[ReO_2(py)_3(PPh_3)]X$ (X = I or ClO_4), which in turn reacts with PPh_3 to give $[ReO_2(py)_2(PPh_3)_2]^+$.[330] The treatment of $ReO_2I(PPh_3)_2$ with an excess of dppe gives $[ReO_2(dppe)_2]^+$, which can also be generated directly from ReO_4^- by reaction with HX in ethanol.[330,333]

The complex used to prepare the preceding complexes, *viz.* $ReO_2I(PPh_3)_2$ (**64**), is itself most easily obtained as violet crystals by stirring a suspension of $ReOI_2(OR)(PPh_3)_2$ (R = Me or Et) in wet acetone.[329,330] This reaction is believed to occur as shown in equation (18), and an X-ray crystal structure determination has shown that (**64**) possesses a geometry somewhat intermediate between that of a trigonal bipyramid and a square pyramid, although it resembles the former more closely. This structure is characterized by a *trans* disposition of phosphine ligands, an O—Re—O angle of

139° and Re=O distances of 1.742(11) Å.[329] This is the only structure known to date in which the two oxide ligands in an $[ReO_2]^+$ moiety are not *trans* to one another.



(64) P = PPh_3

$$ReOI_2(OR)(PPh_3)_2 + H_2O \xrightarrow{\text{acetone}} ReO_2I(PPh_3)_2 + ROH + HI \quad (18)$$

The complexes $ReO_2I(PPh_3)_2$ and $ReOI_3(AsPh_3)_2$ are useful synthetic starting materials for the preparation of the 2-butyne complex $ReOI(MeC{\equiv}CMe)_2$.[613] Dirhenium heptaoxide Re_2O_7 reacts with PMe_3 to give *trans*-$[ReO_2(PMe_3)_4]ReO_4$,[614] while when the reduction is carried out using PEt_3 in the presence of pyridine, 4-methylpyridine or 4-phenylpyridine, the mixed valent salts $[ReO_2L_4]$-ReO_4 are obtained.[612]

43.7.2.4 Other ligands

Complexes in which both fluoride and water have been incorporated into the inner coordination sphere are described in Section 43.7.2.2. A DMSO derivative $ReO_2I(DMSO)_2$ has been reported to exist but remains inadequately characterized,[331] as are the thiocyanate-containing species formulated as $[ReO_2(CNS)_4]^{3-}$, for which evidence of solid compounds is doubtful,[2] and $[ReO_2(NCS)_2(PPh_3)_2]^-$, the latter having been isolated as its Na^+, NH_4^+ and Ph_4As^+ salts through the reaction between $ReO(OH)(NCS)_2(PPh_3)_2$ and OH^- in the presence of an excess of SCN^-.[389] The existence of the thiourea-containing cation $[ReO_2(tu)_4]^+$ has been described in the literature before 1963, but its identity remains questionable.[2]

43.7.3 Complexes Containing the μ-Oxo-bridged $[Re_2O_3]^{4+}$ Moiety

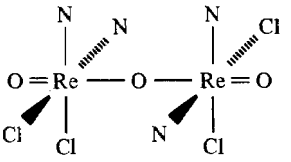
43.7.3.1 Cyanide

The acidification of solutions containing $[ReO_2(CN)_4]^{3-}$ leads to $[Re_2O_3(CN)_8]^{4-}$, a species which has been isolated as its $[Pt(NH_3)_4]_2Re_2O_3(CN)_8$ salt and structurally identified by X-ray crystallography.[310,390] The linear O=Re—O—Re=O unit is characterized by Re—O distances of 1.698(7) and 1.915(1) Å. A detailed analysis has been made of the vibrational spectrum of $[Re_2O_3(CN)_8]^{4-}$ and the ν(Re=O) and ν(Re—O—Re) modes assigned, *viz.* ν(Re=O) (Raman), 1017 cm^{-1}, ν(Re=O) (IR), 1008 cm^{-1}, ν(Re—O—Re) (IR), 720 cm^{-1} and ν(Re—O—Re) (Raman), 205 cm^{-1}.[381] The rates of oxygen exchange of the anion have been determined, the mechanism by which the exchange of terminal oxo ligands occurs being facilitated by association with H^+.[379] The diamagnetic, mixed alkali metal salt $K_3Na[Re_2O_3(CN)_8]\cdot 2H_2O$ has also been prepared and spectroscopically characterized by IR and electronic absorption spectroscopy. Its IR-active ν(Re=O) and ν(Re—O—Re) modes have been assigned to bands at 995 and 725 cm^{-1}, respectively.[378] An MO analysis of the electronic structure of $[Re_2O_3(CN)_8]^{4-}$ is available.[391]

43.7.3.2 Ethylenediamine and N-heterocycles

The neutral ethylenediamine complex $Re_2O_3Cl_4(en)_2$ is formed upon allowing a solution of $[ReO(OH)(en)_2]^{2+}$ in 2 M HCl to stand.[331] The green crystalline material that results has a structure very closely related to that of $[Re_2O_3(CN)_8]^{4-}$ as established by X-ray crystallography.[392] The related pyridine and 2,2′-bipyridyl complexes have been prepared by reacting $ReCl_4$ or $ReCl_5$ with py or bipy in wet acetone, by the reaction of $ReOCl_4$ with bipy in absolute ethanol, and by the reactions of $ReOX_3(PPh_3)_2$ or $ReO(OEt)Cl_2(PPh_3)_2$ with py in wet benzene.[314,318,384] The reaction scheme by which $ReOCl_3(PPh_3)_2$ is converted into $Re_2O_3Cl_4(py)_4$ is shown in Scheme 14. The pattern of Re—O stretching modes of the py complex (**65**) is similar to that of the analogous CN^- and en complexes. However, this complex differs from the CN^- and en derivatives in havings its two sets of equatorial ligands in a staggered arrangement one to the other (in this molecule the twist angle

is 113°).[393] The Re—O distances are as follows: Re=O_t, 1.715(16), 1.764(16); Re—O_b, 1.943(16), 1.903(16) Å.[393]



(65) N = py

43.7.3.3 Dialkyldithiocarbamates

The dialkyldithiocarbamate complexes $Re_2O_3(R_2dtc)_4$ (R = Me, Et or Ph) are best prepared by reacting $ReOCl_3(PPh_3)_2$ or $Re_2O_3Cl_4(py)_4$ with $Na^+R_2dtc^-$ in acetone.[121,349] The best characterized complex is the diethyldithiocarbamate derivative $Re_2O_3(Et_2dtc)_4$, whose X-ray crystal structure has been determined.[394,395] The complex has a structure which closely resembles that of (**65**), but with an angle of twist of 40° away from the fully eclipsed conformation. Its vibrational spectrum exhibits the following characteristic Re—O stretching modes: ν(Re=O) (Raman), 961 cm^{-1}, ν(Re=O) (IR), 955 cm^{-1}, ν(Re—O—Re) (IR), 670 cm^{-1} and ν(Re—O—Re) (Raman), 191 cm^{-1}.[381] An interesting reaction of $Re_2O_3(Et_2dtc)_4$ is its conversion to $ReO(OMe)(Et_2dtc)_2$ when treated with dry methanol. This reaction can be reversed in the presence of trace amounts of water through the formation of $ReO(OH)(Et_2dtc)_2$ which subsequently dimerizes.[349]

The related nitrene(imido)–oxo complex $[Re(NPh)(Et_2dtc)_2]_2O$ is known (Section 43.7.4), and can be prepared by the action of aniline on $Re_2O_3(Et_2dtc)_4$ in refluxing benzene.[121] The oxo–sulfido derivative $Re_2O_2S[(PhCH_2)_2dtc]_2$ can be isolated as brown needles in low yield as one of the products from the reaction between $ReCl(CO)_5$ and tetrabenzylthiuram disulfide in benzene. The IR spectral characteristics of this complex include ν(Re=O) at 895 cm^{-1} and ν(Re—S—Re) at 448 and 435 cm^{-1}.[252]

43.7.3.4 Other ligands

Several oxo-bridged mixed fluoro–hydroxo–oxalato complexes of rhenium(V) that are prepared by boiling freshly precipitated ReO_2 with oxalic acid and 40% HF may actually be derivatives of the $[Re_2O_3]^{4+}$ moiety. They have been formulated as containing the $[Re_2O(C_2O_4)(OH)_6F_2]^{2-}$ anion but remain inadequately characterized.[396]

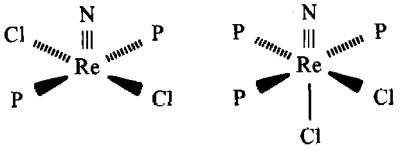
The tin(II) chloride reduction of $[ReO_4]^-$ and 2-aminobenzenethiol (N—S) in hydrochloric acid gives a red-brown complex $ReO(OH)(N—S)_2$ which is air sensitive and converts to green $Re_2O_3(N—S)_4$.[372] The macrocyclic complex $Re_2O_3(L)_2$ (LH_2 = octaethylporphine) has been the subject of a preliminary report but few details are available.[375]

The reaction of $ReOCl_3(PPh_3)_2$ with the tetradentate Schiff base ligands LH_2 (sal_2enH_2, sal_2propH_2, sal_2phenH_2 or $acac_2enH_2$) in the presence of two equivalents of NEt_3 without precautions to exclude air gives $Re_2O_3(L)_2$.[298] These brown or green complexes have IR spectral properties {ν(Re=O) and ν(Re—O—Re)} fully in accord with this formulation and exhibit the parent molecular ion in their mass spectra. When the complex $ReOCl(acac_2en)$ is exposed to O_2 in dichloromethane–benzene solution, the novel compound $[Re_3O_4(acac_2en)_3]ReO_4$ is formed.[397] An X-ray crystal structure shows that the O=Re—O—Re—O—Re=O backbone contains three different Re—O bond lengths. The terminal Re—O bonds are shortest (1.683(5) Å), and *trans* to these are two long bonds (2.076(12) Å), while the two remaining Re—O bonds on either side of the central rhenium atom are intermediate in length (1.785(7) Å).[397]

43.7.4 Nitrides and Imides (Nitrenes)

The stable nitrido complexes $ReNX_2(PR_3)_n$(X = Cl, Br or I; n = 2 or 3) are easily prepared by the reaction of species containing the $[ReO]^{3+}$ moiety with hydrazine hydrochloride in ethanol.[87,398–400] The mechanism of these reactions has been investigated.[399] The X-ray crystal structures of the representative five- and six-coordinate species $ReNCl_2(PPh_3)_2$(**66**) and $ReNCl_2(PEt_2Ph)_3$ (**67**)

have been determined and the Re—N bonds, which are formally of order three, found to be very short (1.603(9) and 1.788(11) Å, respectively).[401,402] A similar structure has also been established for $ReNCl_2(PMe_2Ph)_3$, but the Re—N distance is shorter that in the case of the PEt_2Ph analogue, *viz.* 1.660(8) Å.[403]



(66) P = PPh_3 (67) P = PR_2Ph

The diphosphine analogues $[ReNX(LL)_2]Y$ (X = Cl, Br or I; LL = dppm, dppe or $Ph_2P(CH_2)_3PPh_2$; Y = Cl, Br, I, I_3, ClO_4 or BPh_4) are prepared either by reacting $ReNX_2(PPh_3)_2$ with LL in a suitable solvent or, in the case of $[ReNCl_2(dppe)_2]Cl$, the reaction of $ReOCl_3(dppe)$ with hydrazine hydrochloride in ethanol.[404,405] Another important derivative is the square pyramidal complex $ReN(Et_2dtc)_2$ which can be isolated as lemon-yellow crystals by the interaction of $ReNCl_2(PPh_3)_2$ with $NaEt_2dtc \cdot 3H_2O$ in acetone.[121,406] The cyano species $K_3ReN(CN)_5$ and $K_2ReN(CN)_4 \cdot H_2O$ are also known and are believed to contain six-coordinate rhenium.[407,408]

A fairly detailed study has been made of the ^1H NMR, far IR and electronic absorption spectral properties of the complexes $ReNX_2(PEt_2Ph)_3$ (X = Cl, Br or I).[325] The characteristic $\nu(Re{\equiv}N)$ modes occur close to 1000 cm^{-1} in the IR spectra of these and other nitrido–rhenium(V) complexes.[399,404]

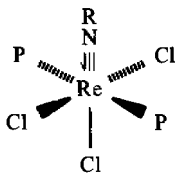
The terminal nitrido ligand is sufficiently basic so as to coordinate to Lewis acids, as in the reaction of $ReNCl_2(PMe_2Ph)_3$ with $MoCl_4(NCMe)_2$ to give the bridged nitrido complex $(PhMe_2P)_3Cl_2ReNMoCl_4(NCMe)$.[1,409] Another illustration of the basicity of $[Re{\equiv}N]^{2+}$ is seen in the reactions of $ReN(R_2dtc)_2(PMe_2Ph)_n$ (R = Me or Et; $n = 0,1$) with the electrophilic reagents $Ph_3C^+BF_4^-$, $[Me_3O]^+BF_4^-$ and 2,4-$(NO_2)_2C_6H_3SCl$ to give the salts $[Re(NR')(R_2dtc)_2(PMe_2Ph)_n]BF_4$ (R′ = Ph_3C or Me) and $Re(NSAr)Cl(Et_2dtc)_2$ (Ar = 2,4-$(NO_2)_2C_6H_3$).[410] These complexes are imido derivatives, other examples of which will be considered below. Substitutional lability of the other ligands bound to the $[Re{\equiv}N]^{2+}$ moiety are another characteristic of these complexes. Thus the phosphine ligands of $ReNX_2(PPh_3)_2$ (X = Cl or Br) can be replaced, completely or partially, by the N-heterocycles py, bipy and phen.[411,412]

A large number of octahedral organoimido (nitrene) complexes of the form $Re(NR)X_3L_2$ (X = halide; R = alkyl, aryl or aroyl) are known which formally contain a rhenium–nitrogen double bond.[1] These complexes are usually prepared by routes which involve the reaction of $ReOCl_3(PR_3)_2$ with aromatic amines (equation 19), 1,2-disubstituted hydrazines, phosphinimines ($Ph_3P{=}NR$), phenyl isocyanate and sulfynilamines (ArNSO) (equation 20), some of the procedures being quite general while others are rather specific.[1,413,417] Interestingly, when $ReOCl_3(PPh_3)_2$ is reacted with mono- or di-aroylhydrazine hydrochlorides in benzene–ethanol, the diazenido species $ReCl_2(N_2COAr)(PPh_3)_2$ is formed. This can be considered either as a derivative of Re^V or Re^{III} (see Section 43.5.1.3 for further details). In the presence of a ketone, the hydrochlorides of both aryl- and aroyl-hydrazines ($R'CONHNH_2$) give oxo–rhenium(V) complexes of the corresponding ketone hydrazine ligands rather than imido complexes (see Section 43.7.1.7).

$$ReOCl_3(PR_3)_2 + ArNH_2 \longrightarrow Re(NAr)Cl_3(PR_3)_2 + H_2O \quad (19)$$

$$ReOCl_3(PPh_3)_2 + ArNSO \longrightarrow Re(NAr)Cl_3(PPh_3)_2 + SO_2 \quad (20)$$

The X-ray crystal structures of the isostructural set of complexes $Re(NR)Cl_3(PEtPh_2)_2$ (R = Me, C_6H_4-*p*-OMe or C_6H_4-*p*-Ac) (**68**) show that the Re—N—C moiety is very close to being linear (*i.e.*



(68) P = PEt_2Ph

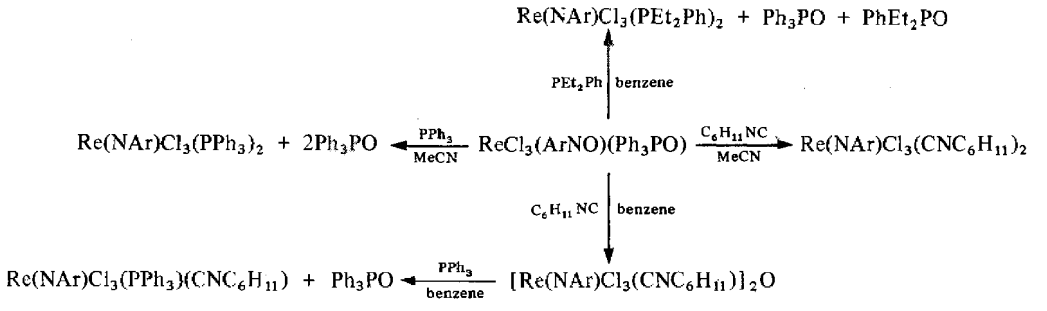
sp hybridization at N) and that the Re—N bond lengths are so similar to those of the corresponding nitrido complexes that the Re—N bonds can be considered as being of order three.[414,415] The structurally characterized complex *trans*-$[Re(NMe)(NH_2Me)_4Cl](ClO_4)_2$ (r(Re—N) = 1.694(11) Å) has been obtained from the reaction between K_2ReCl_6, $MeNH_2$, water and oxygen.[416]

Mixed phosphine–phosphite complexes $Re(NPh)X_3(PPh_3)[P(OMe)_3]$ can be obtained by the reaction of $ReOX_3(PPh_3)[P(OMe)_3]$ with aniline in refluxing benzene,[112] while the mixed pyridine–phosphine species $[Re(NR)Cl_2(PR_3)_2(py)]^+$ are also isolable as is $[Re(NMe)Cl_2(PMe_2Ph)_3]^+Cl^-$.[419] The diethyldithiocarbamate species $Re(NPh)Cl(Et_2dtc)_2$ and $[Re(NPh)(Et_2dtc)_2]_2O$ are formed by the action of tetraethylthiuram disulfide upon $Re(NPh)Cl_3(PPh_3)_2$, and the reaction of aniline on $Re_2O_3(Et_2dtc)_4$ in refluxing benzene, respectively.[121] The μ-oxo bridged complex can also be prepared by the reaction of an acetone solution of sodium diethyldithiocarbamate trihydrate with $Re(NPh)Cl_3(PPh_3)_2$, and is formed from $Re(NPh)Cl(Et_2dtc)_2$ in wet acetone in the presence of Na_2CO_3. This complex exhibits a ν(Re—O—Re) mode at 660 cm^{-1} in its IR spectrum.[121] A detailed study of the imino–dithiocarbamate system has shown that the complexes $Re(NR)(R'_2dtc)_3$ and $Re(NR)(R'_2dtc)_2(OR'')$ (R = Me, Ph or *p*-tol; R′ = Me or Et; R″ = Me or Et) can be prepared by the action of $Tl(R'_2dtc)$, $Me_3SiS_2CNR'_2$ or $NaOR''$ upon $Re(NR)Cl(R'_2dtc)_2$.[417] While IR and ^1H NMR spectral evidence suggests that one of the R'_2dtc ligands is monodentate in $Re(NR)(R'_2dtc)_3$, an X-ray crystal structure determination of *trans*-Re(*N*-*p*-tol)$(Me_2dtc)_2(OEt)$ reveals a bent nitrene unit (Re—N—C ≃ 156°) with an abnormally long Re—N bond (1.745(5) Å). The ethoxy ligand is also bent at the O atom. These observations reflect the 'electron rich' nature of the Re atom in these complexes, and as a consequence the Re—N bond order approaches two.[417]

A compound which is believed to be the arylimido–hydrido complex Re(*N*-*p*-tol)$HCl_2(PPh_3)_2$ is formed upon reacting Re(*N*-*p*-tol)$Cl_3(PPh_3)_2$ with sodium isopropoxide in isopropanol.[418] This compound, as well as its *p*-methoxyphenylimido analogues, can also be obtained by using ZnO/EtOH in place of $NaOPr^i/Pr^iOH$. However, the reaction between Re(*N*-*p*-tol)$Cl_3(PPh_3)_2$ and ZnO (or triethylamine) in EtOH proceeds further in a second step to give Re(*N*-*p*-tol)$HCl(OEt)(PPh_3)_2$, and when C_2D_5OH is used in place of C_2H_5OH, the deuterated species Re(*N*-*p*-tol)$DCl(OC_2D_5)(PPh_3)_2$ is formed. The methoxide derivative Re(*N*-*p*-tol)$HCl(OCH_3)(PPh_3)_2$ and the non-hydrido complex Re(*N*-*p*-tol)$Cl_2(OCH_3)(PPh_3)_2$ have also been prepared by similar procedures to those described above.[418] The conversion of Re(*N*-*p*-tol)$HCl(OEt)(PPh_3)_2$ back to Re(*N*-*p*-tol)$HCl_2(PPh_3)_2$ is achieved by reaction with gaseous HCl in diethyl ether, and when the latter product is in turn treated with gaseous Cl_2 in this same solvent, the starting arylimido complex Re(*N*-*p*-tol)$Cl_3(PPh_3)_2$ is regenerated.[418] An unusual feature of the ^1H NMR spectra of the $Re(NAr)HCl_2(PPh_3)_2$ complexes is the assignment given to the resonance due to the hydridic hydrogens; this is purported to occur as a triplet at around δ3.5 (J(P—H) = 15 Hz). The ν(Re—H) modes in the IR of the hydrido complexes are located at ~2000 cm^{-1}.[418]

Alkyl and arylimido complexes of rhenium(V) undergo a variety of interesting reactions. These include the conversion of the alkylimido complexes $Re(NR)Cl_3(PR_3)_2$ to methyleneamido–rhenium(III) species containing the Re(N=CHR′) moiety upon reaction with bases such as pyridine. The complexes isolated by this method are $Re(N{=}CH_2)Cl_2(PR_3)_2(py)$ (PR_3 = PPh_3, $PEtPh_2$ or $PMePh_2$), $Re(N{=}CH_2)Cl_2(PMe_2Ph)_3$ and Re(N=CHR)$Cl_2(PPh_3)_2$(py) (R = Me or Et).[419] Another instance where reaction occurs at the imido ligand is that between $Re(NAr)Cl_3(PPh_3)_2$ and O_2 in refluxing toluene. In the case of Ar = Ph, *p*-tol or C_6H_4-*p*-OMe, the diamagnetic N-bound arylnitroso complexes $ReCl_3(ArNO)(Ph_3PO)$ are formed.[413,420] Although they are not yet fully characterized structurally, these nitroso complexes have an IR absorption band at ~1350 cm^{-1} which has been assigned to ν(NO) of the N-bound ArNO ligand.[413] The arylnitroso ligand ArNO in these complexes is easily deoxygenated as shown by the reactions given in Scheme 15 for the case where Ar = *p*-tol.[420] In all instances, reaction with phosphines or $C_6H_{11}NC$ gives arylimido species. This includes the formation of a compound that is believed to be a μ-oxo-rhenium(VI) derivative in the case of reaction with $C_6H_{11}NC$ in benzene.

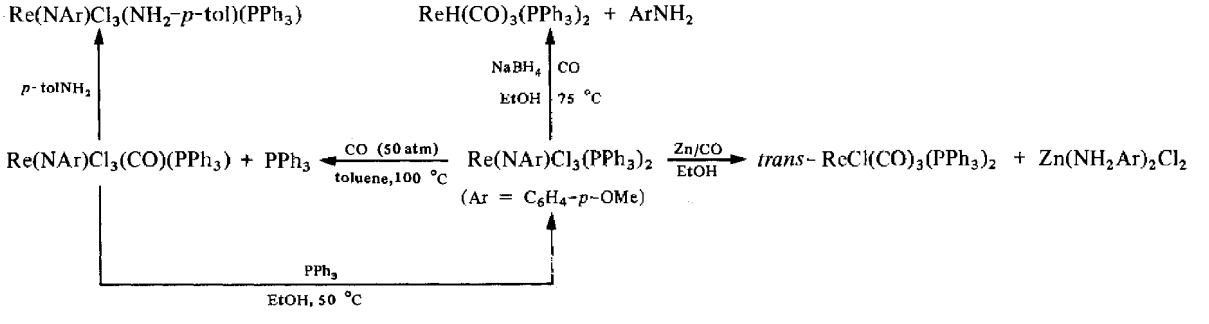
The substitutional lability of $Re(NAr)Cl_3(PPh_3)_2$ has been demonstrated through reactions with CO under various conditions (Scheme 16).[413] However, enhanced reactivity is encountered if $Re(NAr)Cl_3(PPh_3)_2$ (Ar = *p*-tol) is first reacted with elemental sulfur to remove one PPh_3 ligand as Ph_3PS and generate $[Re(NAr)Cl_3(PPh_3)]_n$ (n is probably 2).[420] This latter complex reacts with *p*-nitrotoluene (at 80–90°C) to give the nitroso complex $ReCl_3(ArNO)(Ph_3PO)$ with *p*-toluidine as the by-product, while in benzene or CCl_4 solvents, O_2 reacts with $[Re(NAr)Cl_3(PPh_3)]_n$ to give $ReCl_3(ArNO)(Ph_3PO)$ together with the rhenium(VI) species $Re(NAr)Cl_4(Ph_3PO)$ (see Section 43.8.1).[420] The reactions of $[Re(NAr)Cl_3(PPh_3)]_n$ with various neutral ligands are summarized in Scheme 17. Of special note is the complex $Re(NAr)Cl_2(NHC_6H_{11})(NH_2C_6H_{11})$ which contains



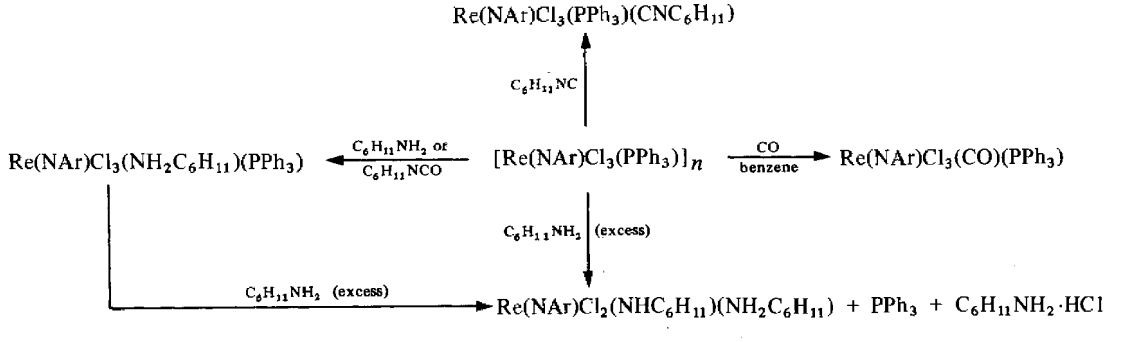
Scheme 15

amine, amido and arylimido ligands. The carbonyl-containing complex $Re(NAr)Cl_3(CO)(PPh_3)$ resembles the related *p*-methoxyphenylimido derivative in Scheme 16. It is of further significance in that it contains a CO ligand bound to a very high oxidation state metal center; the high value of the $\nu(CO)$ mode (at $2040\,cm^{-1}$) reflects this.

The reactions of $Re(NR)Cl_3(PPh_3)_2$ and related complexes with salicylaldehyde[615] and Schiff base ligands[616] produce various complexes in which the organoimido ligand is retained. The X-ray crystal structures of six-coordinate $Re(NC_6H_4\text{-}p\text{-}Me)Cl_2(sal)(PPh_3)$[615] and $Re(NC_6H_4\text{-}p\text{-}Me)Cl_2(R\text{-}sal)(PPh_3)$ (R = Me or Ph)[616] have been reported. The preparation of $Re(NR)Cl_3(PPh_3)_2$ complexes has been accomplished by heating $ReOCl_3(PPh_3)_2$ with the formamidine ligands RNHCHNR (R = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4 or *p*-FC_6H_4) in THF under reflux and, in the case of R = *p*-MeC_6H_4, by heating the triazenido complex $ReCl_2(RN_3R)(PPh_3)_2$ in CCl_4 under reflux.[617] The X-ray crystal structure of $Re(NPh)Cl_3(PPh_3)_2$ as its CH_2Cl_2 solvate has been published,[618] as have details of the preparation and structure of the Lewis acid–base complex $Re(NBCl_3)Cl_2(PMe_2Ph)_3$ which contains a nitrido bridge.[619] Treatment of $ReCl_2(N_2COPh)(PPh_3)_2$ (**23**) with excess benzoylhydrazine in methanol gives $ReCl_2(PPh_3)_2(NNHCOPh)(NHNHCOPh)$ which has been characterized by X-ray crystallography; the latter complex exhibits both linear hydrazido(2−) and end-on hydrazido(1−) ligation.[620] There is a report on a rhenium(V) nitrido complex of phthalocyanine.[621]



Scheme 16



Scheme 17

43.7.5 Other Complexes

43.7.5.1 Oxygen and sulfur ligands

One of the best characterized molecules is $ReCl_5(OPCl_3)$ which is obtained in crystalline form by cooling a saturated solution of $ReCl_5$ in $POCl_3$. Its structure has been solved by X-ray crystallography (r(Re—O) = 2.15(1) Å), and details of its IR spectrum are available.[421] The incorporation of Re^V into heteropolymolybdate and heteropolytungstate anions has been accomplished (*e.g.* $[PRe^VW_{11}O_{40}]^{4-}$),[422] and this oxidation state is also encountered in certain oxo anions, including the phases $Ln_4Re_2O_{11}$ and $Ln_6Re_4O_{18}$ (Ln = lanthanide) which contain edge-sharing $[Re_2O_{10}]$ units. The latter phases are reviewed elsewhere.[1,308]

Several well-characterized sulfur ligand complexes are known including the anionic species $[ReS(SCH_2CH_2S)_2]^-$ which contains a terminal sulfido ligand. It is a close structural analogue of $[ReO(SCH_2CH_2S]_2]^-$ (Section 43.7.1.5) and is prepared by reacting K_2ReCl_6 with an excess of 1,2-ethanedithiol in refluxing methanol in the presence of Et_3N, or in the reactions between $ReCl_4(PPh_3)_2$ or $ReNCl_2(PPh_3)_2$ and ethanedithiol. Cation exchange can be used to prepare the Me_4N^+ and Ph_4P^+ salts, the X-ray crystal structure of the former showing the presence of a square pyramidal anion (r(Re=S) = 2.104(2) Å and r(Re—S) ≃ 2.30 Å).[243] A similar synthetic strategy to that described above, but using the trithiol $MeC(CH_2SH)_3$ in place of $HSCH_2CH_2SH$, gives $[Re\{SCH_2)_3CMe\}_2]^-$. This trigonal prismatic anion has been structurally characterized as its Ph_4P^+ salt. The average Re—S distance is 2.331(5) Å, and the average eclipsed inter-ligand S···S distance is 2.83 Å, indicative of a significant sulfur–sulfur interaction contributing towards the stabilization of this trigonal prismatic geometry.[424]

The Re^{VI} complexes derived from the ligands 2-aminobenzenethiol and 4-chloro-2-aminobenzenethiol $Re(NHSC_6H_4)_3$ and $Re(NHSC_6H_3Cl)_3$ (abbreviated as $Re(abt)_3$ and $Re(abtCl)_3$, respectively), can be reduced by hydrazine to give the deep blue Re^V anions which may be isolated as the salts $Ph_4As[Re(abt)_3]$ and $Ph_4As[Re(abtCl)_3]$ upon the addition of Ph_4AsCl.[425] A similar situation holds in the case of dithiolates of the type $A[Re_2(S_2C_2R_2)_3]$ (A = Et_4N or Ph_4As; R = Ph or H).[2]

Various salts that contain the $[Re(Et_2dt)_4]^+$ cation can be prepared by several routes starting from $ReCl(CO)_5$. These compounds are diamagnetic and the cation evidently possesses an eight-coordinate geometry.[252]

43.7.5.2 Halides

Hexafluororhenates(V) can be formed by reacting ReF_6 with alkali metal iodides in SO_2 or IF_5 solution. ReF_6 is also reduced by NO to give $NOReF_6$ and in HF solution by $N_2H_6F_2$ to $N_2H_6(ReF_6)_2$.[257] A study of the reaction of ReF_6 with $Re_2(CO)_{10}$ in liquid HF has shown that the complexes $Re(CO)_5F\cdot ReF_5$ and $[Re(CO)_6]^+[Re_2F_{11}]^-$ are formed.[426] The metals Cd, Cu and Tl reduce ReF_6 in acetonitrile to yield the acetonitrile solvates $Cd(ReF_6)_2\cdot 5MeCN$, $CuReF_6\cdot 4MeCN$ and $TlReF_6\cdot 2MeCN$.[257] The IR, Raman and electronic spectra of the salts of $[ReF_6]^-$ accord with the octahedral symmetry of the anion,[257,427] while the magnetic properties of some hexafluororhenate(V) salts can be attributed to antiferromagnetic interactions.[257]

Crystals of $CsReF_6$ were grown from a solution containing ReF_5 and CsF dissolved in anhydrous hydrogen fluoride, and an X-ray structure determination carried out.[622]

The reaction of $ReCl_5$ with PCl_5 at 300°C gives the hexachlororhenate(V) salt $[PCl_4]^+[ReCl_6]^-$.[428]

43.7.5.3 Hydrides

Hydrido complexes of rhenium(V) are well known and are in many instances easily prepared and very stable.[123,429] The pentahydrido complexes are usually prepared by treating $ReCl_3(PR_3)_3$ or $ReOCl_3(PR_3)_2$ with $LiAlH_4$ or $NaBH_4$ in tetrahydrofuran, or by reacting the heptahydride $ReH_7(PR_3)_2$ with excess PR_3. The complexes so prepared include $ReH_5(PR_3)_3$ (PR_3 = $P(p\text{-tol})_3$, PPh_3, $PEtPh_2$, $PMePh_2$, PEt_2Ph or PMe_2Ph), $ReH_5(AsEtPh_2)_3$, $ReH_5(PPh_3)(dppe)$ and $ReH_5(dppe)_2$, in which one of the two bidentate phosphines is monodentate.[125,126,232,430,431] The mixed-ligand complexes $ReH_5(PPh_3)_2L$ (L = PEt_2Ph, $AsPh_3$, $C_3H_5NH_2$, $C_3H_5NH_2$, $C_6H_{11}NH_2$, py or $C_5H_{10}NH$) are obtained upon heating $ReH_7(PPh_3)_2$ with excess L in boiling tetrahydrofuran.[144,232] The room temperature ^1H and ^{31}P NMR spectra of the complexes show that on the NMR time scale all five Re—H protons are equivalent as are the phosphorus nuclei; the proton resonance appears as a quartet in the spectrum of the $ReH_5(PR_3)_3$ complexes and as a triplet in the mixed ligand

complexes $ReH_5(PR_3)_2L$.[232] The temperature dependence of the $^1H\{^{31}P\}$ NMR spectrum of $ReH_5(PEtPh_2)_3$ and the ^1H NMR spectrum of $ReH_5(AsEtPh_2)_3$ shows that at low temperature three of the five hydride protons are magnetically inequivalent, the observed intensity ratio being 1:2:1:1.[432] This study, coupled with a partial crystal structure determination of $ReH_5(PPh_3)_3$ (the hydride ligands were not located), has led to the suggestion that the structures of these species approximate to either a dodecahedron, a truncated octahedron or bicapped octahedron.[432]

The complexes $ReH_5(PAr_3)_3$ (Ar = Ph or *p*-tol) react with halogens ($X_2 = Br_2$ or I_2) to give the mixed hydride–halide species $ReH_4X(PAr_3)_3$, while reaction with $SnCl_2$ gives $ReH_4(SnCl_3)(PAr_3)_3$.[235] When $ReH_4I(PPh_3)_3$ is treated with additional I_2 in air, oxidation to $ReO_2I(PPh_3)_2$ occurs.[235] The mixed hydride–halide complexes $ReH_2X_3(PMe_2Ph)_3$ (X = Cl or Br) have been isolated as light yellow solids by reacting $ReX(N_2)(py)(PMe_2Ph)_3$ with HX(g) in THF solution at 0°C.[42] Protonation of the rhenium(III) hydrides $ReH_3(dppe)_2$ and $ReH_3(PPh_3)_2(dppe)_2$ by the addition of various acids gives colorless salts of the $[ReH_4(dppe)_2]^+$ and $[ReH_4(PPh_3)_2(dppe)]^+$ cations.[124] In a similar fashion, the addition of HBF_4 to $ReH_3(PMe_3)_4$ in THF at −78°C gives white, air-stable $[ReH_4(PMe_3)_4]BF_4$. The ^1H NMR spectrum of this complex is temperature dependent showing a quintet ($\delta - 5.40$) at 60°C.[35] The reaction of excess of HX (X = Cl or Br) with *mer*-$Re(S_2CNR_2)(N_2)(PMe_2Ph)_3$ in THF at 20°C gives the salts $[ReH_2X(S_2CNR_2)(PMe_2Ph)_3]X$ according to equation (21). These complexes (R = Me or Et) have ^1H NMR spectra that for the Re—H units display a doublet of triplets ($\delta ca. -4.2$) which reflect the equivalence of the two hydride ligands with splitting arising from one unique and two equivalent phosphorus atoms.[26]

$$mer\text{-}Re(S_2CNR_2)(N_2)(PMe_2Ph)_3 + 2HX \longrightarrow [ReH_2X(S_2CNR_2)(PMe_2Ph)_3X + N_2 \quad (21)$$

The pentahydrido complexes $ReH_5(PR_3)_3$ and $ReH_5(PR_3)_2L$ are quite stable kinetically to further reaction with σ donors, such as phosphines, and π acceptors, such as CO and RNC, since vigorous reaction conditions are necessary to induce further reaction.[296] However, these complexes can be activated by electrochemical oxidation in the potential range +0.10 to +0.40 V *vs.* SCE; an irreversible oxidation is observed within this range, the value of which correlates with the basicity of L ($E_{p,a}$ decreases in the sequence PPh_3 (+0.37 V) > PEt_2Ph (+0.29 V) > py (+0.17 V) > $C_6H_{11}NH_2$ (+0.16 V) > $C_5H_{10}NH$ (+0.11 V). Oxidation is easiest with the complex where the build-up of electron density at the metal is greatest.[296] Interestingly, the reaction of the mild oxidant $[Cu(NCMe)_4]PF_6$ with $ReH_5(PR_3)_3$ (PR_3 = $PMePh_2$ or PMe_2Ph) in THF does not result in a redox reaction but rather in the formation of the novel complex $[(R_3P)_3H_2Re(\mu\text{-}H)_3Cu(\mu\text{-}H)_3ReH_2(PR_3)_3]PF_6$ according to the stoichiometry given in equation (22). The structural formulation is based upon an X-ray structure determination together with ^1H NMR spectral measurements.[307] A redox reaction occurs between $ReH_5(PPh_3)_2L$ (L = $C_6H_{11}NH_2$ or $C_5H_{10}NH$) and allyl chloride leading to expulsion of H_2 and the formation of $(Ph_3PC_3H_5)_2ReCl_6$ and some propene.[144]

$$2ReH_5(PR_3)_3 + [Cu(NCMe)_4]PF_6 \longrightarrow [(ReH_5(PR_3)_3)_2Cu]PR_6 + 4MeCN \quad (22)$$

(PR_3 = $PMePh_2$ or PMe_2Ph)

Photolysis of benzene or isooctane solutions of $ReH_5(PR_3)_3$ (PR_3 = PPh_3, $PMePh_2$ or PMe_2Ph) results in the formation of the reactive 16-electron species $ReH_5(PR_3)_2$ as a result of the photoextrusion of a PR_3 ligand. Several hydrido–phosphine products can be produced following the formation of $ReH_5(PR_3)_2$ as shown in Scheme 9.[125,135] These include $ReH_7(PR_3)_2$ which is formed if the photolysis is carried out under an H_2 atmosphere.[125] The photochemistry of $ReH_5(PMe_2Ph)_3$ has also been investigated by laser and conventional flash photolysis.[433] While the species $ReH_5(PMe_2Ph)_2$ is observed in saturated hydrocarbon solvents, photolysis in benzene gives $(\eta^2\text{-}C_6H_6)ReH_5(PMe_2Ph)_2$. Also, dimerization to give $Re_2H_8(PMe_2Ph)_4$ (see Scheme 9 and refs. 125 and 135) proceeds by the thermal reaction of a phototransient with the ground state saturated species $ReH_5(PMe_2Ph)_3$. The phototransient species $ReH_5(PR_3)_2$ exhibits some interesting organometallic chemistry as demonstrated by its reaction with saturated and unsaturated organics, the former in the presence of a hydrogen acceptor.[38]

43.7.5.4 Miscellaneous ligands

The hexacyanate anion $[Re(OCN)_6]^-$ has been claimed to be the species that is formed upon reacting $ReCl_5$ with KCNO in dimethyl sulfone,[218] while the ammonolysis of $ReCl_5$ in liquid ammonia gives $ReCl_3(NH_2)_2 \cdot 2NH_3$.[352] Halogens oxidize the $[ReX_2(diars)_2]^+$ cations to eight-coordinate $[ReX_4(diars)_2]^+$ (X = Cl or Br).[2]

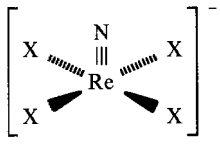
Rhenium pentachloride reacts with diisopropylcarbodiimide in CCl_4 to form the monomeric six-coordinate amidino complex $ReCl_4[Pr^iNC(Cl)NPr^i]$.[623]

43.8 RHENIUM(VI) COMPOUNDS

43.8.1 Nitrides, Imides (Nitrenes) and Amides

The reaction between anhydrous liquid ammonia and $ReOCl_4$ at $-33°C$ affords brown insoluble $[ReO(NH_2)_4]_2$ together with an ammonia-soluble species formulated (tentatively) as $NH_4[ReO(NH_2)_4Cl]$. The IR spectrum of $[ReO(NH_2)_4]_2$ displays a ν(Re—O—Re) mode at 830 cm^{-1}, thereby supporting the presence of a polymeric [—O—Re—O—Re—] chain system.[434]

The nitrido complexes $A[ReNCl_4]$ ($A = Me_4N^+$ or Ph_4As^+) are formed upon reacting $ReNCl_4$ with ACl in $POCl_3$.[435] The Ph_4As^+ salt has also been formed by reacting Ph_4AsCl with the chlorothionitrene complex $Re(NSCl)Cl_4(POCl_3)$ in CH_2Cl_2 solution.[436] The analogous bromide $Ph_4As[ReNBr_4]$ is formed by the thermal decomposition *in vacuo* at 210°C of dark violet crystalline $Ph_4As[Re(NBBr_3)Br_4]$ which is itself prepared by reacting $Ph_4As[ReNCl_4]$ with excess BBr_3.[437] The salts of the $[ReNX_4]^-$ anions possess IR-active ν(ReN) modes between 1085 and 1100 cm^{-1}, as does the salt $Ph_4As[Re(NBBr_3)Br_4]$.[435,437] The X-ray crystal structures of the salts $Ph_4As[ReNX_4]$ (X = Cl or Br) have been determined and show that the $[ReNX_4]^-$ anions possess a distorted square pyramidal geometry (**69**) with very short Re—N distances of 1.62 Å and the Re atom located above the plane of the four X groups.[435,437] The ESR spectrum of $[ReNCl_4]^-$ doped into the $Ph_4As[ReNCl_5]$ host has been reported, and the spectrum of $[ReNCl_4]^-$ in frozen MeCN solution is indicative of the presence of $[ReNCl_4(NCMe)]^-$.[438]



(69) X = Cl or Br

The reaction of $ReNCl_3$ with py, bipy and PPh_3 gives $ReNCl_3(py)_3$, $ReNCl_3(bipy)$ and $ReNCl_3(PPh_3)_2$, respectively, whereas when $Ph_4As[ReNCl_4]$ is treated with py or PPh_3, $Ph_4As[ReNCl_4(L)]$ (L = py or PPh_3) is formed.[439] The admixing of KNCS and $Ph_4As[ReNCl_4]$ in refluxing methanol in the presence of an excess of Ph_4AsNCS gives the salt $(Ph_4As)_2[ReN(NCS)_5]$, which possesses the expected octahedral structure with a short Re—N (nitrido) distance of 1.66 Å.[440] Other nitrido–rhenium(V) complexes include $[ReNCl_3(POCl_3)]_4 \cdot 2POCl_3$, which forms eight membered Re_4N_4 rings with alternating Re≡N· · · ·Re units (r(Re≡N) = 1.68(2) Å) and is prepared upon treating $ReNCl_4$ with excess $POCl_3$.[441] Another example is a compound formulated as $(Ph_4As)_2[Re_2FN_2Cl_7]$, which is proposed to be a μ-fluoro complex with terminal nitrido ligands.[442] It is formally a derivative of Re^{VI} and is prepared by mixing $ReNCl_4$ and Ph_4AsF in acetonitrile. Its structure has not yet been determined by X-ray crystallography, but magnetic susceptibility measurements (over the range 4.8–280 K) indicate that the complex is magnetically dilute (μ_{eff} = 1.66 BM per Re atom), behavior that is similar to that found for $Ph_4P[ReNCl_4]$ (μ_{eff} = 1.67 BM per Re atom).[442]

The *p*-tolylimido complex Re(*N*-*p*-tol)$Cl_4(Ph_3PO)$ is believed to be formed as one of the products in the oxygenation of $[Re(N\text{-}p\text{-tol})Cl_3(PPh_3)]_n$ in CCl_4 or benzene.[420] Its magnetic moment (μ = 1.61 BM) supports this formulation.[420] The *N*-chloroalkylated derivatives $Re(NR)Cl_4(POCl_3)$ (R = CCl_3 or C_2Cl_5) are formed upon reacting $ReCl_5$, dissolved in $POCl_3$, with cyanogen chloride or CCl_3CN in the presence of Cl_2. An X-ray crystal structure determination has shown that for the complex $Re(NC_2Cl_5)Cl_4(POCl_3)$, the Re—N distance is 1.69(1) Å and the Re—N—C angle approaches linearity (169°).[443] When cyanogen is used in place of cyanogen chloride and CCl_3CN in the above reactions, the bis-nitrido complex $(Cl_3PO)Cl_4M(NCCl_2CCl_2N)MCl_4(POCl_3)$ is formed.[444] The treatment of $Re(NR)Cl_4(POCl_3)$ (R = CCl_3 or C_2Cl_5) with Ph_4AsCl gives the salts $Ph_4As[Re(NR)Cl_5]$.[445]

A novel reaction occurs when $ReCl_5$ reacts in $POCl_3$ solution with $(NSCl)_3$ to give the formally rhenium(VI) chlorothionitrene complex $Re(NSCl)Cl_4(POCl_3)$, together with the rhenium(VII) derivative $Re(NSCl)_2Cl_3(POCl_3)$.[436] The chlorothionitrene ligand is related to the arylthionitrene moiety as found in $Re(NSAr)Cl(Et_2dtc)_2$ (Ar = 2,4-$(NO_2)_2C_6H_3$) (Section 43.7.4).

43.8.2 Halides and Oxide Halides

The only complex halides of Re^{VI} that do not contain a terminal Re=O moiety are the fluororhenate(VI) anions $[ReF_7]^-$ and $[ReF_8]^{2-}$ which are prepared by the reaction of ReF_6 with alkali metal fluorides. The action of ReF_6 on $M^I_2ReF_8$ is also a route to M^IReF_7 (M^I = K, Rb or Cs).[257] While $[ReF_8]^{2-}$ has a square antiprismatic geometry, the vibrational spectra of $[ReF_7]^-$ salts is in accord with pentagonal bipyramidal structure (D_{5h} symmetry). The magnetic moments of $M^I_2ReF_8$ salts are apparently higher (1.6–1.7 BM) than those reported for M^IReF_7 (0.6–0.7 BM).[257]

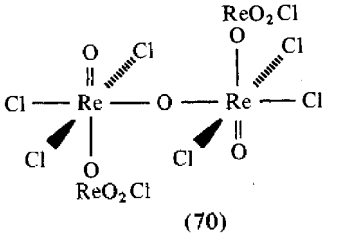
The controlled hydrolysis of M^IReF_7 (M^I = Rb or Cs) in wet acetonitrile is a suitable method for preparing the light green oxidefluorides M^IReOF_5.[446] The $[ReOF_5]^-$ anion has also been generated by the partial hydrolysis of ReF_6 in aqueous HF and characterized by ESR spectroscopy at 77 K.[447] The vibrational spectrum of M^IReOF_5 (M^I = Rb or Cs) has been assigned in terms of C_{4v} symmetry for the anion.[448] The parent oxidefluoride $ReOF_4$ forms a pale blue 1:1 adduct with SbF_5 which has a dimeric structure in which two Re atoms and two Sb atoms are linked through fluorine bridges into distorted eight-membered rings.[449]

The oxidechloride $ReOCl_4$ reacts with stoichiometric amounts of water, MeCN and $POCl_3$, to form the adducts $ReOCl_4(L)$, in which L is *trans* to the Re=O group.[314,434,450] These complexes are paramagnetic ($\mu_{eff} \approx 1.7$ BM) and possess ν(Re=O) modes close to 1020 cm^{-1}.[314,434] The ESR spectra at low temperature of the MeCN and $POCl_3$ adducts have been recorded and analyzed in considerable detail,[451] and comparable spectral data are also available for anhydrous toluene and CCl_4 solutions of $ReOCl_4$ in the presence of Ph_3PO, urea, MECN, acetone, Et_2O, DMG and dioxane.[452] The X-ray crystal structure of the bright red, volatile hydrate $ReOCl_4(H_2O)$ confirms that the strongly bonded oxo group (Re—O = 1.63(2) Å) is *trans* to a weakly bonded H_2O ligand (Re—O = 2.27(2) Å).[450] A gas-phase electron diffraction study has been made of $ReOCl_4$.[625]

The reaction between $ReOX_4$ (X = Cl or Br) and A^+X^- (A = Et_4N, Ph_4P or Ph_4As) in anhydrous $CHCl_3$ or CH_2Cl_2 is a convenient method for preparing $A[ReOX_5]$.[434,453] The action of gaseous HCl upon suspensions of $[ReO_4]^-$ in various aqueous and non-aqueous media has also been used to prepare the salts $(Ph_4As)ReOCl_5$ and $(Ph_4P)ReOCl_5$.[362,454] The $[ReOCl_5]^-$ anion is also generated in the $[ReOCl_5]^{2-}$–H_2SO_4–HCl and $[ReOCl_5]^{2-}$–$H_4P_2O_7$–HCl systems where it has been characterized by ESR and electronic absorption spectroscopy.[455,456] In the pyrophosphoric acid system, the existence of $[ReOCl_4(H_3P_2O_7)]^-$ has also been proposed. A study of the electronic absorption spectrum of the $[ReOBr_5]^{2-}$–H_2SO_4–HBr system indicates that $ReOBr_4$ and $[ReOBr_5]^-$ are formed,[457] a result that has led to the development of a good synthetic procedure for $ReOBr_4$ through the reaction of NH_4ReO_4 with an excess of NaBr in concentrated sulfuric acid.[458] In the case of the analogous $[ReOF_5]^{2-}$–H_2SO_4–HF system, it is believed that $[ReOF_5]^-$ is generated.[457]

The results of various studies on the ESR spectrum of $[ReOCl_5]^-$ are available,[451,455,459] and the magnetic properties and IR and electronic absorption spectra of the paramagnetic salts $A[ReOCl_5]$ (A = Et_4N, Ph_4P or Ph_4As) have been reported.[434,453] The partial hydrolysis of the $[ReOCl_5]^-$ ion gives mauve $[Re_2O_3Cl_8]^{2-}$ which can be isolated as its Et_4N^+ and Ph_4As^+ salts.[453] These complexes, which display ν(Re=O) and ν(Re—O—Re) modes at ~970 and ~740 cm^{-1}, respectively, are essentially diamagnetic, but other than the presence of an O=Re—O—Re=O moiety, it remains unclear as to which of several possible isomers has been isolated.[453] The use of a different method to generate the $[Re_2O_3Cl_8]^{2-}$ anion was reported subsequently, namely, the reaction of $[ReO_4]^-$ with acetyl chloride in acetic acid–HCl.[460] However, the salts that were isolated (tetraphenylphosphonium and 2,3,5-triphenyltetrazolium) did not have the same properties as those that had been prepared *via* $[ReOCl_5]^-$. For example, they are described as possessing a magnetic moment of 1.5 BM and their ν(Re—O—Re) mode is purportedly close to 910 cm^{-1}.[460]

An interesting 'derivative' of $[Re_2O_3Cl_8]^{2-}$ is the complex oxidehalide $Re_2O_3Cl_6(ReO_3Cl)_2$ (**70**) which is formed in the reaction between ReO_3 and $ReCl_5$, and by the UV irradiation of a mixture of $ReOCl_4$, $ReOCl_4(H_2O)$ and ReO_3Cl.[461] The X-ray crystal structure of (**70**) shows that each of the two perrhenyl chloride fragments are weakly bound to the $Re_2O_3Cl_6$ unit *via* an oxygen atom. The short Re=O terminal bonds (Re—O) = 1.69(2) Å) are *cis* to the bridging Re—O—Re unit (Re—O = 1.847(1) Å).[461]

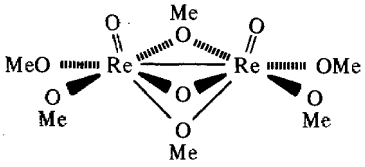


(70)

43.8.3 Oxoanions and Alkoxides

There exist quite a large number of ordered perovskites A_2BReO_6 (A = Ca, Sr or Ba; B = Ca, Sr, Ba, Mg, Mn, Fe, Co *etc.*) and other mixed oxides that contain Re^{VI},[1] but these are not considered to be coordination complexes and, accordingly, they will not be considered here. The interesting violet colored salt $(Me_4N)_2ReO_4$, which contains the paramagnetic $[ReO_4]^{2-}$ anion, can be prepared by the controlled potential one-electron reduction of $[ReO_4]^-$ in acetonitrile (-2.30 V *vs.* SCE).[462,463] In water, the first electron transfer is believed to be followed by the disproportionation of Re^{VI} to Re^{VII} and Re^{IV}, thereby leading to an overall three-electron process at the electrode.[463] In weakly acidic solutions, oxalate and citrate increase the ease of reduction of the $[ReO_4]^-$ anion through the reversible formation of 1:1 complexes.[464] A study has been made of the reaction of $[ReO_4]^-$ with the equated electron in neutral aqueous solution to give $[ReO_4]^{2-}$.[624] The salt $(Me_4N)_2ReO_4$ crystallizes in an antifluorite-like cubic face-centered lattice. The magnetic and spectroscopic properties of this complex have been reported.[462]

The simplest alkoxide of Re^{VI} is $Re(OMe)_6$ which can be prepared by reacting ReF_6 with $Si(OMe)_4$. It is volatile in high vacuum at room temperature and displays the parent ion in its mass spectrum.[465] The alkoxide $ReO(OBu^t)_4$ is formed when $ReOCl_4$ is treated with $LiOBu^t$ in diethylether. This paramagnetic blue crystalline solid is thermally unstable above 0°C, but has been characterized by IR spectroscopy (ν(Re=O) at 992 cm^{-1}).[245] The analogous reaction of $LiOPr^i$ with $ReOCl_4$ can lead to the isolation of green crystalline $\{Li[ReO(OPr^i)_5]\cdot LiCl(THF)\}_2$. This ESR-active complex possesses a ν(Re=O) mode at 987 cm^{-1} in its IR spectrum and a complicated dimeric structure in the crystalline state in which octahedral $[ReO(OPr^i)_5]^-$ anions are present and some of the alkoxide groups are involved in forming bridges to the Li^+ ions in the lattice.[247] When $ReOCl_4$ is dissolved in methanol in the presence of a tertiary amine, orange air-sensitive crystals of the complex $(MeO)_2ORe(\mu\text{-}O)(\mu\text{-}OMe)_2ReO(OMe)_2$ (**71**) are formed. This diamagnetic complex has Re—O stretching frequencies at 982 and 968 cm^{-1} assignable to ν(Re=O) and at 756 cm^{-1} to ν(Re—O—Re).[245] Its X-ray crystal structure shows the presence of a short Re—Re contact (2.559 Å) and Re=O and Re—O—Re distances of ~1.70 and ~1.91 Å, respectively.[245]



(71)

43.8.4 Sulfur and Mixed Sulfur–Nitrogen Ligands

The trigonal prismatic complexes $Re(S_2C_2Ph_2)_3$ and $Re(tdt)_3$, where $S_2C_2Ph_2$ and tdt are the *cis*-1,2-diphenylethene-1,2-dithiolato and toluene-3,4-dithiolato ligands, respectively, can be prepared from the reactions of the appropriate ligands with $ReCl_5$.[2] The X-ray crystal structure of $Re(S_2C_2Ph_2)_3$ reveals it to be a near perfect trigonal prism.[2] Detailed studies have been made of the ESR and electronic spectra and redox properties of these complexes.[2,466,467] Similar complexes to those obtained with these 1,2-dithiolate ligands (1,2-dithiolenes)[468] can be prepared using 2-aminobenzenethiol and 4-chloro-2-aminobenzenethiol. The blue-green complexes $Re(NHSC_6H_4)_3$ and $Re(NHSC_6H_3Cl)_3$ (abbreviated $Re(abt)_3$ and $Re(abtCl)_3$, respectively) were prepared by dissolving the Re^{VII} complexes $Re(NSC_6H_4)(NHSC_6H_4)_2$ and $Re(NSC_6H_3Cl)(NHSC_6H_3Cl)_2$ in aqueous acetone.[425] Both complexes are paramagnetic ($\mu_{eff} \simeq 1.46$ BM) and are found to undergo reversible one-electron oxidation and reduction processes. Thus, this series of complexes resembles the corresponding tri(dithiolene) set in attaining formal oxidation states of V, VI and VII. These complexes are believed to have a trigonal prismatic geometry.[425] An ESR study of trigonal prismatic $Re(abt)_3$ (where $abtH_2$ = 2-aminobenzenethiol) has been carried out to study the effects of concentration and solvent composition on the extent of molecular aggregation.[626]

43.9 RHENIUM(VII) COMPLEXES

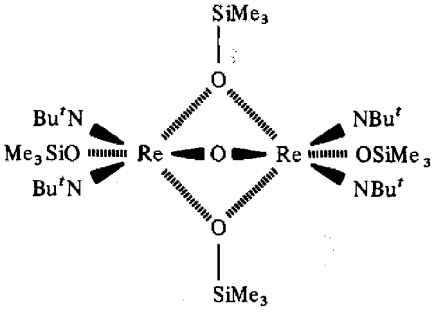
43.9.1 Nitrides, Imides (Nitrenes) and Amides

The only simple nitrido complex is the salt K_2ReO_3N, which is formed in the reaction between Re_2O_7 and KNH_2 in liquid ammonia.[1] The reaction of PPh_3 with $ReNCl_4$ gives the phosphinimato

complex $Re(NPPh_3)Cl_4(PPh_3)$,[439] which is analogous to the compound $Re(NPPh_3)(SPh)_4$. This latter molecule can be isolated, in low yield, following air oxidation of the solution that is generated by the interaction of $ReNCl_2(PPh_3)_2$ with excess phenylthiolate anion in hot acetonitrile.[204] The role of oxygen in this reaction may involve the oxidation of a $[ReN(SPh)_4]^{2-}$ intermediate to the Re^{VII} nitride $ReN(SPh)_4$. The X-ray crystal structure of square pyramidal $Re(NPPh_3)(SPh)_4$ shows that the Re—N—P angle is ~163° and that the Re—N and N—P distances of 1.743(7) and 1.634(9) Å are in accord with considerable Re—N and P—N multiple bonding. The formation of these phosphinimato complexes of Re^{VII} presumably reflects the considerable electrophilic character of the Re^{VII}–nitride moiety.

The tris(*tert*-butylimido) complex $(Me_3SiO)Re(NBu^t)_3$ can be prepared by the reaction of trimethylsilylperrhenate with *tert*-butyl(trimethylsilyl)amine in hexane (equation 23).[469] When a deficiency of amine is used in this reaction, the yellow crystalline complex (**72**) is formed.[470] It can be viewed as the product of the silylation of $[(Me_3SiO)Re(NBu^t)_2O]_2$ by $Me_3SiOReO_3$. The addition of four equivalents of HCl to $Me_3SiORe(NBu^t)_3$ in CH_2Cl_2 produces $Re(NBu^t)_2Cl_3$ in high yield. This monomeric complex is believed to possess a trigonal bipyramidal geometry with the two imido ligands in equatorial positions.[471] The analogous bromide complex is best prepared by reacting $Re(NBu^t)_2Cl_3$ with Me_3SiBr in toluene, and various alkyl, alkylidene and alkylidyne complexes can be generated by addition of the appropriate alkylating agent.[471]

$$Me_3SiOReO_3 + 3Bu^tNH(SiMe_3) \longrightarrow Me_3SiORe(NBu^t)_3 + 3Me_3SiOH \qquad (23)$$



(72)

While the treatment of ReO_3Cl with diisopropylamine gives the volatile, moisture sensitive dialkylamine compound $(Pr^i)_2NReO_3$, the related reaction with $(Me_3Si)_2NLi$ in diethylether produces the red, air-stable, crystalline complex $(Me_3SiO)_2Re[N(SiMe_3)_2](NSiMe_3)_2$, which is believed to be five-coordinate with trimethylsilyl-amide, -imide and -oxide groups.[472] Another imido complex is the bis-chlorothionitrene derivative $Ph_4As[ReCl_4(NSCl)_2]$ which is formed upon reacting $Re(NSCl)_2Cl_3(POCl_3)$ with Ph_4AsCl in CH_2Cl_2.[436] An X-ray crystal structure determination reveals that the two NSCl ligands have a *cis* arrangement with nearly linear Re=N=S units.[436]

Other nitrene-containing compounds are the pair of molecules $ReF_5(NCl)$ and $ReF_5(NF)$ which are formed upon reacting ReF_6 with Me_3SiN_3 at low temperature in the presence of ClF_3. The resulting complex reaction mixture also gives rise to small and variable quantities of $ReNF_4$.[473] X-Ray crystal structure determinations on $ReF_5(NX)$ (X = Cl or F) show that the Re—N bond is short (~1.73 Å), a result which accords with the high frequency of the IR active ν(Re—N) mode (1205 cm^{-1}).[473] The nitride—chloride $ReNCl_4$ has been prepared by the reaction of $ReCl_5$ with NCl_3, and it has been structurally characterized by X-ray crystallography; it possesses a structure similar to that of $WOCl_4$.[474]

The direct fluorination of $ReNCl_4$ between 80°C and 130°C gives the moisture-sensitive material $ReNF_4 \cdot ReF_5(NCl)$, an *N*-chloronitrene adduct,[627] in which the $ReNF_4$ and $ReF_5(NCl)$ molecules are linked by a linear asymmetric fluorine bridge. The black crystalline salt $(Ph_3PCl)[ReCl_4(N_2S_2)]$ is obtained by the reaction of $Re(NSCl)_2Cl_3(POCl_3)$ with PPh_3. An X-ray crystal structure determination reveals the presence of an ReN_2S_2 five-membered ring.[628]

43.9.2 Oxo Species

43.9.2.1 Perrhenates and related species

The aqueous chemistry of rhenium(VII) is dominated by the great stability of the $[ReO_4]^-$ ion.[1] Dirhenium heptoxide (Re_2O_7) is a yellow volatile crystalline compound which dissolves in water to

form a colorless, strongly acidic solution of perrhenic acid. The anhydrous acid can be obtained as pale yellow hygroscopic needles, the crystal structure of which shows the presence of $O_3Re—O—ReO_3(H_2O)_2$ molecules possessing a linear Re—O—Re bridge.[475] In more dilute solutions the acid is completely dissociated to the $[ReO_4]^-$ anion.[1]

A study has been made of the oxygen exchange between $[ReO_4]^-$ and water under acid catalysis,[476] and while molecular $ReO_3(OH)$ has not been isolated, several esters of perrhenic acid have been prepared. These include R_3MOReO_3 (M = Si, Ge or Sn; R = Me, Et or Ph), which can be prepared by the reaction of $AgReO_4$ with R_3MCl, and $Bu^t_3SiOReO_3$, which is formed by treating Re_2O_7 with tri-*t*-butylsilanol.[477–479] The alkoxides $ROReO_3$ (R = Me or Bu^t) are formed through the interaction of ReO_3Cl or $Me_3SiOReO_3$ with the silyl ethers Me_3SiOR in hydrocarbon solvents.[472] An X-ray crystal structure on $Me_3SiOReO_3$ has confirmed its monomeric tetrahedral structure,[480] while the properties of $MeOReO_3$ suggest that it has a polymeric structure with methoxide bridges.[472] NQR studies (Re-185 and Re-187) have been carried out on Me_3MOReO_3.[481] A variety of other derivatives of the type ReO_3X exist, including the cases where X = halide, NO_3 or $N(Pr^i)_2$.[1,472] These compounds react with various ligands to form coordination complexes that are described in Sections 43.9.2.3 and 43.9.2.4.

Perrhenic acid can be extracted into non-aqueous organic solvents by aliphatic amines, tributyl phosphate, phosphine oxides, arsine oxides and amine *N*-oxides.[1,482,483] Most metal cations form very stable perrhenates. This is especially true of the main group elements, the first transition series and the rare earths.[1,308] The X-ray crystal structure of some of the simplest salts have been determined, *e.g.* NH_4ReO_4 and $KReO_4$.[1,484,485] Rhodium(III) perrhenate $Rh(ReO_4)_3 \cdot nH_2O$ has also been described,[486] and is apparently the first of the platinum metal derivatives to be isolated. While the $[ReO_4]^-$ ion is strictly tetrahedral in solution, lower symmetries may be encountered in crystalline salts as monitored by IR and Raman spectroscopy.[1] The electronic structure of the $[ReO_4]^-$ ion has been studied experimentally and theoretically,[1] including a study of the valence level electron structure by X-ray photoelectron spectroscopy.[487]

There is a quite extensive chemistry associated with the so-called mesoperrhenates and orthoperrhenates, which are derivatives of the $[ReO_5]^{3-}$ and $[ReO_6]^{5-}$ anions, and various mixed metal oxides. These phases have been surveyed in some detail in the review by Rouschias.[1] More recent developments have included studies on rhenium–apatites containing the square pyramidal $[ReO_5]^{3-}$ unit,[488–490] hexagonal perovskites with cation vacancies that contain $[ReO_6]^{5-}$,[491] and the double oxides $M_3Re_2O_{10}$ (M = Sr or Ba) and $M_5Re_2O_{12}$ (M = Ca or Sr).[492]

The $[ReO_4]^-$ ion is known to be a weak ligand.[1] Recent examples of this are encountered in the case of [Cu(HL)($OReO_3$)], where H_2L = 2,2′-(1,3-propanediyldiiminobis(2-methyl-3-butanone)dioxine), which has been structurally characterized by X-ray crystallography,[493] the cation $[Co(NH_3)_5(OReO_3)]^{2+}$,[494] and the structurally characterized species $[Re_2(O_2CR)_4](ReO_4)_2$ and $[Re_2(O_2CR)_3Cl_2]ReO_4$ (see Section 43.5.2.5).

The perrhenate anion is present in the organic superconductor materials $(TMTSF)_2ReO_4$, where TMTSF = tetramethyltetraselenafulvalene, and $(BEDT\text{-}TTF)_4(ReO_4)_2$, where BEDT-TTF = bis(ethylenedithiolo)tetrafulvalene,[495,496] and is also an important precursor to Re—Pt reforming catalysts and metathesis catalysts. The latter role has led to studies of the thermal decomposition,[497,498] the laser Raman spectra[499] and the X-ray photoelectron spectra[497,499,500] of catalytically important perrhenates, especially NH_4ReO_4 and $Al(ReO_4)_3$.

43.9.2.2 Other oxygen ligands

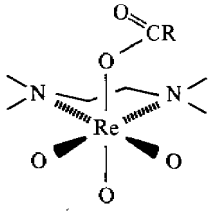
In addition to the structurally characterized species $Re_2O_7(H_2O)_2$ (Section 43.9.2.1), the complex $Re_2O_7(H_2O)_2(dioxane)_2$ can be isolated from solutions of Re_2O_7 in H_2O–dioxane.[1] In the presence of small amounts of water, the compound $Re_2O_6(OH)_2 \cdot 3dioxane$ has been obtained.[501] The crystals contain dimeric centrosymmetric $[O_3Re(\mu\text{-}OH)_2ReO_3]$ units with the octahedral coordination sphere around each rhenium being completed by bridging 1,4-dioxane molecules (one O donor per Re), the latter linking the dimeric units into endless chains. The remaining dioxane molecules are hydrogen bonded to the μ-OH groups.[501]

Evidence has been presented that in 1–10 M H_2SO_4 rhenium(VII) forms 1:1 and 1:2 complexes, the latter being formulated as $[ReO_2(SO_4)_2]^-$.[502,503] The complexation of $[ReO_4]^-$ in concentrated alkali with polyhydroxyl compounds (*e.g.* D-gluconolactone and D-mannitol) is said to occur,[504] while edta (H_4L), when treated with an aqueous Re^{VII} solution, precipitates a complex formulated as $Ba[ReO_3(HL)] \cdot Ba_2L \cdot 4H_2O$ upon the addition of $BaCO_3$.[505]

The addition of $B(OTeF_5)_3$ to ReF_7 produces the complex $ReO_2(OTeF_5)_3$,[506] while $ReCl_5$ reacts

with Cl_2O, in the presence of $POCl_3$, to give dimeric $[ReO_3(O_2PCl_2)(POCl_3)]_2$ in which bridging O_2PCl_2 groups are believed to be present.[507]

Several carboxylate complexes of the type $RCO_2ReO_3(L)$ {R = Me, CF_3, CMe_3 or Ph; L = THF, py or tetramethylethylenediamine(tmed)} have been prepared and characterized.[472] The treatment of Re_2O_7 with the acid anhydrides in THF allows the isolation of colorless crystalline $RCO_2ReO_3(THF)$ (R = Me, CF_3 or CMe_3). The benzoate complex can be prepared by carboxylate exchange in diethyl ether. The complexes with py and tmed are formed by ligand exchange involving the displacement of the THF ligand of $RCO_2ReO_3(THF)$. All these complexes are believed, on the basis of IR and NMR spectroscopic studies, to be six-coordinate. In the case of the tmed complexes (**73**), monodentate RCO_2 groups are present.[472] The same is apparently true in the case of an analogous complex that contains the chelating 2-hydroxypyridine ligand, $MeCO_2ReO_3(Hhp)$, and which is prepared by reacting $MeCO_2ReO_3(THF)$ with Hhp in ether or chlorocarbon solvents.[472]



(73)

Complexes that contain dimethylformamide, *viz.* $ReO_3X(DMF)_2$ (X = F or Cl) and $Et_4N[ReO_3Cl_2(DMF)]$, and other oxygen donors are described in Section 43.9.2.4.

43.9.2.3 Amines and N-heterocycles

The complexes $RCO_2ReO_3(L)$, where L = py, tmed or Hhp, have been described in Section 43.9.2.2. The analogous alkoxide derivatives $ROReO_3(tmed)$ (R = Me or Bu^t) have also been prepared and so have the stable, crystalline diisopropylamido species $(Pr^i)_2NReO_3(py)$ and $[(Pr^i)_2NReO_3]_2tmed$.[472] Reference to the complexes $ReO_3Cl(L)_2$ (L = py, 1/2bipy or 1/2phen) is found in Section 43.9.2.4 along with other halide containing species.

The thermal decomposition of $[ReO_2(py)_4]X\cdot nH_2O$ (X = Br or I) at temperates of 135°C (X = I) or 155°C (X = Br) gives a pale brown solid formulated as $Re_2O_7(py)_2$. This product is described as having ν(Re—O) bands at 970, 910 and 880 cm^{-1}. The material obtained by the pyrolysis of $[ReO_2py_4]Cl\cdot 2H_2O$ is, however, violet and its structural relationship to the pale brown material described above is uncertain at present.[258]

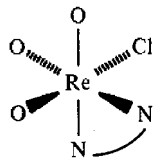
The X-ray crystal structure of the complex $Re_2O_7py_3$[612] has been reported. It is composed of two inequivalent Re atoms, linked by a single μ-O bridge, which exhibit coordination numbers of five and six.[629]

43.9.2.4 Halides

A variety of neutral adducts of the halides ReO_3F and ReO_3Cl are known. Both form 1:2 complexes with DMF, the fluoride being formed by the reaction of Re_2O_7 with HF in DMF,[508] while the solvolysis of $[ReO_3Cl_3]^{2-}$ in DMF first gives $Et_4N[ReO_3Cl_2(DMF)]$, followed by the formation of $ReO_3Cl(DMF)_2$.[509] Other complexes of the type $ReO_3Cl(L)_2$ (L = DMSO, $MeCONMe_2$, $(Me_2N)_2CO$ and $(Me_2N)_3PO$) have also been prepared but are rather unstable.[1] Complexes of ReO_3Cl with 8-hydroxyquinoline (oxineH) have been prepared and have been formulated as $ReO_3Cl(oxineH)_2$ and $ReO_3Cl(oxineH)\cdot noxineH$, in which oxineH is believed to be bound in a monodentate and bidentate fashion, respectively. In DMF solution the complex $ReO_3(oxine)(DMF)$ is formed.[510]

The py and bipy complexes $ReO_3Cl(py)_2$ and $ReO_3Cl(bipy)$ can be obtained quite easily from the direct reaction of ReO_3Cl with the corresponding ligand in CCl_4 solution.[314] An alternative method that has been used for the bipy complex, which is also applicable to its phen analogue, $ReO_3Cl(phen)$, involves the reaction of $HReO_4$ with bipy (or phen) in the presence of concentrated

hydrochloric acid.[9] The IR spectral properties of the py, bipy and phen complex (the ν(Re—O) modes)[9,314] are in accord with the complexes possessing similar structures. The X-ray crystal structure derivative ReO_3Cl(bipy) (**74**) has shown that it has a *fac*-stereochemistry, with Re—O distances of 1.708(9) Å (*trans* to N) and 1.718(15) Å (*trans* to Cl).[511] ReO_3Cl(phen) is believed to be isostructural with this. However, when attempts were made to grow crystals by dissolving it in concentrated hydrochloric acid and allowing the solution to stand in a desiccator over P_2O_5, a resulting yellow crystalline complex was identified as $(phenH_2)[ReO_3Cl_2(H_2O)]Cl$ by X-ray crystallography.[512] The structure solution is not of high precision because of a disorder problem, but the anion clearly possesses a *fac* octahedral geometry.[512]



(74) N—N = bipy

Complex oxide fluorides of Re^{VII}, which can be regarded as derivatives of $ReOF_5$, ReO_2F_3 and ReO_3F, are all known. The only salts that contain $[ReOF_6]^-$ are $NO[ReOF_6]$ and $NO_2[ReOF_6]$ which are produced by the reaction of NOF and NO_2F with $ReOF_5$.[257] The reaction between ReO_2F_3 and MF (M = Na, K, Rb or Cs) in a sealed quartz tube at 200°C has been used to prepare $MReO_2F_4$.[513] On the other hand, two procedures can be used to prepare salts of the $[ReO_3F_3]^{2-}$ anion. The action of IF_5 upon a mixture of $KReO_4$ and KF gives $K_2ReO_3F_3$, a white solid that is hydrolyzed by moist air,[446] while $(Me_4N)_2ReO_3F_3$ is formed by reacting $ReO_3F(DMF)_2$ with Me_4NF in ethanol.[508] The vibrational spectra of $KReO_2F_4$ and $K_2ReO_3F_3$ have been studied and assigned assuming C_{2v} symmetry for each.[448] Studies of the $[ReO_4]^-$—HF—H_2O system have led to suggestions that the $[ReO_4F]^{2-}$, $[ReO_3(OH)F_2]^{2-}$ and $[ReO_2(OH)(HF_2)_3]^-$ ions exist under certain conditions, but none have been isolated.[257]

While the isolation of $CsReO_2Cl_4 \cdot CsCl$ has been reported and its thermal stability investigated,[514] the best known oxide chloride anion of Re^{VII} is $[ReO_3Cl_3]^{2-}$. Various salts have been prepared by the reaction of ReO_3Cl with the chlorides ACl (A = Me_4N^+, Et_4N^+, pyH^+, Me_3NH^+ and $Mepy^+$) in inert solvents,[515] and the important cesium salt $Cs_2ReO_3Cl_3$ by the dissolution of $[ReO_4]^-$ in concentrated hydrochloric acid saturated with hydrogen chloride.[516] The X-ray crystal structure of $Cs_2ReO_3Cl_3$ has confirmed the *fac* octahedral geometry of the anion (similar to that in **74**), with an average Re—O bond length of 1.70(2) Å.[517] This geometry is the same as that deduced on the basis of IR spectral measurements.[515]

A somewhat different mode of coordination is encountered in the complexes $ReO_3Cl \cdot AlCl_3$, $ReO_3Cl \cdot NbCl_5$ and $ReO_3Cl \cdot SbCl_5$, which are believed (from IR spectral evidence) to contain Re =O—M (M = Al, Nb or Sb) bridges, and thereby do not involve any increase in the coordination number about rhenium.[518,519]

The fluoride ion donor properties of $ReOF_5$ have been demonstrated by the preparation of $[ReOF_4]AsF_6$ and $[Re_2O_2F_9]Sb_2F_{11}$ which have been characterized by vibrational spectroscopy and mass spectrometry. The X-ray crystal structure of $[Re_2O_2F_9]Sb_2F_{11}$ consists of discrete monofluorine-bridged dimeric anions and cations.[630] The ^{19}F NMR spectra of solutions obtained by dissolving Re_2O_7 in 60% HF in ethanol have been interpreted in terms of the presence of ReO_3F, $[ReO_2F_4]^-$, $[ReO_2(OEt)F_3]^-$ and $ReO(OEt)F_4$.[631] The five-coordinate anion $[ReO_3Cl_2]^{2-}$ has been isolated as its Ph_4P^+ salt from the reaction of ReO_3Cl with Ph_4PCl in dichloromethane.[632]

43.9.2.5 Thioperrhenates

When H_2S is passed into an aqueous solution of $[ReO_4]^-$, the electronic absorption spectrum changes, signaling the formation of the species $[MO_{4-n}S_n]^-$ (n = 1–4).[1,520] Of the four possible species only $[ReO_3S]^-$ and $[ReS_4]^-$ have been completely characterized structurally in the crystalline state.[1,520] The electronic absorption spectra of all four species have been reported,[520] and a detailed study has been made of the resonance Raman spectrum of $[ReS_4]^-$ as part of a more general investigation of the vibrational spectra of some of these species.[1,520] In this case, particularly informative spectra were obtained for $(Ph_4P)ReS_4$ where the overtones of the ν_1 mode were seen out

to $10\nu_1$.[520] The laser-excited emission spectrum of this same salt reveals a mixture of relaxed and partially relaxed luminescence thought to originate from the vibronic levels of the $^1T_2$ excited state.[521]

Further studies of the resonance Raman spectra of $(Ph_4P)ReS_4$ have been reported.[633]

43.9.3 Thiolate Ligands

Oxidation of the Re^{VI} complexes $Re(NHSC_6H_4)_3$ and $Re(NHSC_6H_3Cl)_3$ (abbreviated $Re(abt)_3$ and $Re(abtCl)_3$, respectively) in THF in the presence of an excess of *p*-toluenesulfonic acid can be accomplished using O_2 and H_2O_2, respectively.[425] This gives the diamagnetic salts $[Re(abt)_3]^+(C_7H_7SO_3)^-$ and $[Re(abtCl)_3]^+(C_7H_7SO_3)^-$. These complexes resemble the corresponding tris(dithiolene) derivatives $Re(S_2C_2R_2)_3$ in attaining a formal oxidation number of VII upon undergoing a one-electron oxidation.[522] When $KReO_4$ is reacted with *o*-aminobenzenethiol, the brown complex $Re(NSC_6H_4)(NHSC_6H_4)_2$, *i.e.* Re(abt-H)$(abt)_2$, containing one doubly deprotonated and two singly deprotonated coordinated amines, is formed. The analogous complex derived from 4-chloro-2-aminobenzenethiol is made by a related procedure.[425] These two complexes can be converted to the Re^{VI} species $Re(abt)_3$ and $Re(abtCl)_3$ (see Section 43.8.4) upon prolonged treatment with acetone.[425]

43.9.4 Halides

Rhenium heptafluoride reacts with nitryl and nitrosyl fluorides to form NO_2ReF_8 and $NOReF_8$.[257] The Raman spectra of the solids and ^{19}F NMR spectra of their HF solutions have been interpreted in terms of D_{4d} symmetry for the $[ReF_8]^-$ anion. The cationic species $[ReF_6]^+$ can be formed by heating ReF_7 with SbF_5 by which means $[ReF_6]^+[SbF_6]^-$ and $[ReF_6]^+[Sb_2F_{11}]^-$ can be formed.[257]

More extensive studies of the ReF_7–SbF_5 system (see ref. 257) have led to the isolation of $[ReF_6]^+[Sb_2F_{11}]^-$ and $[ReF_6]^+[Sb_3F_{16}]^-$ which have been characterized by vibrational spectroscopy.[630]

43.9.5 Hydrides

Hydrido complexes of the types $[ReH_9]^{2-}$, $[ReH_8(L)]^-$ and $ReH_7(L)_2$ (L = a phosphine or arsine ligand) constitute one of the more important groups of polyhydride complex of the transition elements.[123,429] Of these, $[ReH_9]^{2-}$ is historically of most importance since it was the first polyhydride complex to be prepared. It can be isolated as its sodium and potassium salts which can be prepared by the reduction of $[ReO_4]^-$ using Na or K metal.[523,524] The reaction of $[ReH_9]^{2-}$ in 2-propanol with the phosphines PPh_3, PBu^n_3 or PEt_3, and with $AsPh_3$ gives the substitution products $[ReH_8(L)]^-$,[431] while the reactions of $ReCl_4(L)_2$, $ReOCl_3(L)_2$ or $ReO(OR)Cl_2L_2$ with $LiAlH_4$ provide convenient routes to $ReH_7(L)_2$ (L = P-*p*-tol$_3$, PPh_3, $PEtPh_2$, PEt_2Ph, $AsEt_2Ph$ or 1/2dppe).[126,232]

A neutron diffraction study of K_2ReH_9 has shown that the anion possesses a tricapped trigonal prismatic geometry with an average Re—H distance of 1.68(5) Å.[525] The ^1H NMR spectrum of $[ReH_9]^{2-}$ in aqueous solution reveals a single proton signal, and detailed studies have been made of the vibrational spectrum of this anion, including measurements on single crystals of K_2ReH_9.[1,526] On the other hand, structural data on $[ReH_8(L)]^-$ and $ReH_7(L)_2$ are incomplete. The monoanions are characterized by ν(Re—H) modes at 1980, ~1930 and ~1850 cm^{-1} in their IR spectra, and a doublet for the Re—H resonance is found at $\delta \approx -8$ (J(P—H) ≈ 18 Hz) in the NMR spectra denoting dynamic isomerization.[431] SCF-Xα-SW calculations have been carried out on $[ReH_9]^{2-}$ and $[ReH_8(PH_3)]^-$ assuming a close structural relationship between these two species, with the PH_3 ligand in an equatorial position. Fluxionality is also found for solutions of $ReH_7(L)_2$ as studied by ^1H NMR spectroscopy; a triplet is observed in the region between $\delta - 4$ and $\delta - 6$ for phosphine derivatives (J(P—H) ≈ 13–20 Hz) and a singlet at $\delta - 6.0$ for $ReH_7(AsEt_2Ph)_2$.[126,232] The ν(Re—H) modes of these complexes have been located between 1980 and 1870 cm^{-1} in their IR spectra.[126,232] X-Ray crystal structure determinations have located the R_3P—Re—PR_3 unit of $ReH_7(PPh_3)_2$, $ReH_7(PMe_2Ph)_2$ and $ReH_7[P(Pr^i)_2Ph]_2$, the P—Re—P angles being in the range 139 to 147°. However, whether this is in accord with the expected distorted tricapped trigonal prismatic geometry is unclear.[528,529]

The deuterides $ReD_7(PPh_3)_2$, $ReD_7(PEt_2Ph)_2$, and ReD_7(dppe) are easily prepared and undergo acid-catalyzed H–D exchange with ethanol but the mechanism of this exchange is unknown.[232]

Exchange also occurs between $ReH_7(PEt_2Ph)_2$ and deuterobenzene at 100°C, and $ReD_7(PPh_3)_2$ is slowly converted to the hydride by hydrogen gas under ambient conditions.[232] $ReH_7(PPh_3)_2$ also serves as a key starting material for some important organic transformations.[131]

The interaction of $LiAlH_4$ with $Re(NPh)Cl_3(PMe_3)_2$ followed by methanol hydrolysis at low temperatures gives $ReH_6(NHPh)(PMe_3)_2$. The ^1H NMR spectrum of this complex in the hydride region shows a triplet at $\delta -5.73$ with $J(P—H) = 21$ Hz, while the $^{31}P\{^1H\}$ spectrum possesses a singlet at $\delta -30.9$. Accordingly, this complex, like other nine-coordinate rhenium hydrido species, is fluxional.[530]

43.10 NITROSYL COMPLEXES AND OTHERS WHERE AN AMBIGUITY IN OXIDATION STATE ASSIGNMENT MAY EXIST

While this section deals primarily with nitrosyl complexes of rhenium, there are other systems where ambiguity in assigning oxidation states can arise. These include rhenium complexes derived from the 2-aminobenzenethiol ligands, *viz.* $[Re(NHC_6H_3X)_3]^{+,0,-}$ (X = H or Cl), and the dithiolates $[Re(S_2C_2R_2)_3]^{+,0,-}$, species which are described in the appropriate sections dealing with Re^V, Re^{VI} and Re^{VII} oxidation states (see Sections 43.7.5.1, 43.8.4 and 43.9.3). Other examples are the tris(2,2′-bipyridine) and tris(1,10-phenanthroline) complexes $Re(bipy)_3$ and $Re(phen)_3$, which can be prepared by the Na/Hg reduction of $ReCl_4(THF)_2$ in THF in the presence of bipy or phen. These air-sensitive, purple solids have magnetic moments of 4.1 and 4. BM, respectively.[531]

In the case of the nitrosyl derivatives, a quite extensive chemistry has been developed. For convenience, we consider these complexes as a single group to avoid any confusion in the assigning of formal oxidation states. $[Re(NO)X_5]^{2-}$ salts are known for X = F, Cl, Br and I. General methods for preparation of the F,[532] Cl[533] and Br[534] derivatives include the addition of NO gas to hydrated ReO_2 in either aqueous or ethanolic HX solutions and the reaction between so-called $Re(NO)(OH)_3$ and aqueous HX. The iodide salt has been made by the latter method: Cs_2CO_3 or Rb_2CO_3 dissolved in aqueous HI is added to a solution of $Re(NO)(OH)_3$ in warm aqueous HI to produce black crystalline $M^I_2[Re(NO)I_5]$ (M^I = Cs or Rb).[535]

Neutral $Re(NO)X_3(L—L)$ and cationic $[Re(NO)X(L—L)_2]PtCl_6$ (L—L = bipy or phen) can be prepared from $[Re(NO)X_5]^{2-}$ (X = F, Cl, Br or I).[532–535] Reactions of $(Et_4N)_2[Re(NO)X_5]$ with a variety of polar solvents produce $(Et_4N)[Re(NO)X_4L]$ (L = MeOH, EtOH, MeCN, DMSO, *etc.*) which upon heating yield $(Et_4N)[Re(NO)X_4]$.[536] Crystal structures of $(Et_4N)[Re(NO)Cl_4(py)]$[537] and $(Et_4N)[Re(NO)Br_4L]$[538] (L = EtOH or MeCN) have been performed showing the molecules to have a distorted octahedral geometry with the solvent molecules situated *trans* to linear Re—NO units. The reaction of $(Et_4N)_2[Re(NO)X_5]$ with N-donor ligands in EtOH or MeCN also gives salts with the formulation $(Et_4N)[Re(NO)X_4L]$, where L = pyridine, aniline or $PhCH_2NH_2$, while refluxing $[Re(NO)X_5]^{2-}$ in diglyme produces the trisubstituted complexes $Re(NO)X_2L_3$, where L = pyridine or 4-picoline.[539] The reactions of $H_2[Re(NO)X_5]$ (X = Cl or Br) have been studied and include the addition of L = bipy or phen to concentrated HX solutions of $H_2[Re(NO)X_5]$ to give $LH_2[Re(NO)X_5]$,[540] which gives $Re(NO)X_3L$ on heating, and the reaction of $H_2[Re(NO)X_5]$ with pyHX in HX solution which yields $(pyH)_2[Re(NO)X_5]$.[541] Heating the latter complex to 250°C in a CO_2 atmosphere produces $(pyH)[Re(NO)X_4(py)]$; heating to 400°C under CO_2 gives $[Re(NO)X_3(py)_2]$.

Another reaction producing $[Re(NO)X_5]^{2-}$ (X = Cl or Br) as a variety of R_4N^+ salts (R = Me, Et, Bu or Ph) is that of $ReO(OEt)(PPh_3)_2X$ with NO gas in refluxing EtOH in the presence of R_4NX.[542] $Re(NO)X_3(PPh_3)_2$ is also produced in this reaction.

The electronic absorption spectra and far IR spectra of tertiary phosphine complexes of the types $Re(NO)X_3(PR_3)_2$ and $Re(NO)X_2(PR_3)_3$ have been compared,[325] and an IR spectral study made of $[Re(^{14}NO)X_5]^{2-}$ and $[Re(^{15}NO)X_5]^{2-}$.[543] Several polarographic studies[544–546] have been carried out on the $[Re(NO)X_5]^{2-}$ anions and their related substitution products. One study[545] compared $[Re(NO)X_5]^{2-}$ with $[ReX_6]^{2-}$, finding the two species electrochemically similar and implying that Re is 'quadrivalent' in the nitrosyl complex. X-Ray photoelectron spectroscopic (XPS) evidence, in conjunction with electrochemical and dipole moment measurements,[11] also indicates that NO is present in a neutral or negatively charged state in a variety of Re—NO complexes with formal oxidation states ranging from +1 to +4 even though the Re—NO interaction is essentially linear, and thus can be considered formally as a three-electron donor, NO^+. Whether the nitric oxide is present as NO^+ with Re^{II}, or as NO^- with Re^{IV}, or as some intermediate situation has not been determined. In another study focusing on the charge distribution in these complexes, it was concluded, on the basis of electrochemical measurements, that the electron transfer was from the Re, with NO making little contribution to the redox orbital.[547]

A more recent XPS study of $[Re(NO)X_5]^{2-}$ and some related complexes reports evidence for a linear to bent transformation in the bonding mode of coordinated NO when the samples are exposed to X-rays.[548]

$ReH_2(NO)(PPh_3)_3$ has been prepared by refluxing $[Re(NO)X_5]^{2-}$ (X = Cl or Br) and PPh_3 in ethanol followed by slow addition of $NaBH_4$. This hydride complex reacts with X_2 to give $Re(NO)X_3(PPh_3)_2$ (X = Cl, Br or I) and either $ReH_2(NO)(PPh_3)_3$ or $[Re(NO)X_5]^{2-}$ reacts with CO gas to give $Re(NO)(CO)_2(PPh_3)_2$.[549] The crystal structure of $ReH_2(NO)(PPh_3)_3$[550] shows it to have distorted octahedral geometry with two PPh_3 ligands in axial positions and the other PPh_3, the two hydrides, and the NO in equatorial positions. The NO is linked linearly as NO^+.

In the reaction of hydrated ReO_2 with gaseous NO in the absence of HX, the complex $Re(NO)(OH)_3 \cdot H_2O$ is said to be formed.[533] Both this reaction and that of ReO_2 and NO in the presence of HX have $[ReO_4]^-$ as a by-product. $Re(NO)(OH)_3 \cdot H_2O$ and the related $Re(NO)Cl_3 \cdot xH_2O$ have been the subjects of a number of investigations with regard to their synthesis, interconversion and hydrolysis reactions.[551–553] The acid $H[Re(NO)(C_2O_4)(OH)_2(H_2O)]$ is purported to be formed from the reaction of $Re(NO)(OH)_3 \cdot H_2O$ with oxalic acid in aqueous medium, and the K^+, NH_4^+ and Pb^{2+} salts of the acid have been described.[554] The anion of this acid reacts with organic diimines to produce the mixed ligand complexes, $Re(NO)L(C_2O_4)X$ (L = bipy or phen; X = OH or Cl). $Re(NO)(OH)_3 \cdot H_2O$ does not react directly with acetic acid, but when refluxed in a mixture of acetic acid and acetic anhydride, a product proposed to be $[Re_4(NO)_4(O_2CCH_3)_6O(OH)_4]$ has been reported.[555]

Most rhenium nitrosyl complexes have been prepared using NO, NOX or HNO_3 as the nitrosylating agent. Recently, the reductive nitrosylation of $[ReO_4]^-$ with $NH_2OH \cdot HCl$ in the presence of NCS^- or N_3^- in an alkaline medium has been accomplished.[556] The complexes formed in this way include $[Re(NO)X_3(H_2O)]^-$ (X = NCS or N_3) and $[Re(NO)X_2(L)(H_2O)]$ (L = bipy or phen), containing the $[ReNO]^{2+}$ moiety and existing in several isomeric forms.

Another method of introducing a nitrosyl group is by the use of *N*-nitrosoamides. An ethanol solution of $ReCl_4(PPh_3)_2$, *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide, PPh_3 and $NaBH_4$ gives $ReH(NO)_2(PPh_3)_2$. Addition of the same *N*-nitrosoamide to $ReH(CO)_2(PPh_3)_3$ in refluxing benzene yields $Re(NO)(CO)_2(PPh_3)_2$.[557] The reactions of these complexes with X_2 (X = Cl, Br or I) and RX (X = halide; R = H, Me, MeCO and PhCO) have been investigated.

A phase that is said to possess the stoichiometry $Re(NO)Cl_5$ has been prepared by passing NO gas through a CCl_4 solution of $ReCl_5$. Using benzene instead of CCl_4 yields $Re(NO)Cl_4 \cdot C_6H_6$.[558] So-called $Re(NO)Cl_5$ has been reacted with a variety of donor ligands to produce materials analyzing as $Re(NO)Cl_4(NCMe)$, $Re(NO)Cl_4(py)_2$, $Re(NO)Cl(Ph_3PO)(NCMe)$ and $Re(NO)Cl_4(phen)_2$.[558] The X-ray crystal structure of $Re(NO)Cl_4(NCMe)$ shows the molecules to have an octahedral geometry with a *cis* arrangement of the NO and MeCN ligands.[559]

A complex which was first reported to be $[Re(NO)Cl_2(PPh_3)_2]$,[560] made by passing NO gas through a suspension of $[ReCl_2(N_2COPh)(PPh_3)_2]$ in benzene–methanol (1:1), has been reformulated as $[Re(NO)Cl_2(OMe)(PPh_3)_2]$.[561] Reactions of this complex with L (L = CO, NH_3, SO_2, MeCN, PhCN, py, $MeNHNH_2$, $NH_2CH_2CH_2OMe$ or TCNE) result in the substituted products $[Re(NO)Cl_2(PPh_3)_2L]$, while reactions with tertiary phosphines tend to give products in which the PPh_3 ligands are displaced, such as $[Re(NO)Cl_2(PR_3)_3]$. The reaction with PMe_2Ph yields $[Re(NO)Cl_2(PMe_2Ph)_2(PPh_3)]$.[560]

$[Re(NO)Cl_2(OMe)(PPh_3)_2]$ also reacts with $NaBH_4$ and PPh_3 to give a high yield of $ReH_2(NO)(PPh_3)_3$, which in turn is a useful starting material for a variety of rhenium nitrosyl complexes.[561] $ReH_2(NO)(PPh_3)_3$ reacts with HCl in ethanol to form $Re(NO)Cl_2(PPh_3)_3$, while the addition of the latter complex to a CH_2Cl_2 solution saturated with CO gas results in $Re(NO)Cl_2(CO)(PPh_3)_2$. $Re(NO)Cl_2(PPh_3)_3$ also reacts with *p*-tolyl isocyanide in refluxing benzene to yield $Re(NO)Cl_2(CN\text{-}p\text{-}tol)_2(PPh_3)$. The fluoro cation $[Re(NO)F(CO)(PPh_3)_3]^+$ can be prepared by the reaction of $ReH_2(NO)(PPh_3)_3$ with HBF_4 or HPF_6 in the presence of CO. This cation reacts with $X^- = H^-$, OCH_3^- or F^- to give the neutral species $Re(NO)XF(PPh_3)_3$. The crystal structure of the perchlorate salt of this fluoro cation has been determined; the PPh_3 ligands are meridonal and the fluoride is *trans* to the linear Re–NO group.

A thiolato–nitrosyl complex $[Re_2(NO)_2(SPh)_7]^-$ has been made in low yield by reacting $[Re(NO)Cl_2(PPh_3)_2]$ (later reformulated as $[Re(NO)Cl_2(OMe)(PPh_3)_2]$)[560,561] with thiophenol in refluxing methanol in the presence of triethylamine. The crystal structure performed on the $[Ph_4P]^+$ salt of the *p*-tolylthiol derivative shows the complex to consist of two pseudooctahedral rhenium units linked by three bridging thiolato ligands. The Re—Re distance of 2.783(1) Å indicates significant metal–metal interaction.[562]

Thionitrosyl complexes of rhenium have been prepared either by the addition of S_2Cl_2 or SCl_2 to nitride-containing rhenium species or by introduction of NS *via* $NS^+SbF_6^-$. Thus, $ReNCl_2(PRPh_2)_2$ (R = Ph or Pr^n) and S_2Cl_2 give $Re(NS)Cl_3(PRPh_2)_2$; $ReNX_2(PR_3)_3$ (PR_3 = PMe_2Ph, PEt_2Ph or

$PMePh_2$; X = Cl or Br) and half an equivalent of S_2Cl_2 yield $Re(NS)ClX(PR_3)_3$; an excess of either S_2Cl_2 or SCl_2 added to $ReNCl_2(PR_3)_3$ gives $Re(NS)Cl_3(PR_3)_2$; and $[ReNCl(dppe)_2]Cl$ with S_2Cl_2 forms $[Re(NS)Cl(dppe)_2]Cl$.[563] The reaction between $Re(CO)_5Br$ and $NS^+SbF_6^-$ leads to formation of $[Re(CO)_5NS]^{2+}$, a cation which can also be prepared by elimination of F^- from $[Re(CO)_5(NSF)]^+$ using AsF_5.[564,565]

There are very few monomeric rhenium complexes with two nitrosyl ligands. The earliest examples also contained PPh_3, such as $Re(NO)_2X(PPh_3)_2$ (X = Cl, Br or I)[542,566] and $Re(NO)_2X_2(PPh_3)_2$ (X = Cl or Br).[566] More recently, $Re(NO)_2X_3$ (X = Cl or Br) and several related dinitrosyl complexes have been prepared. $Re(NO)_2Cl_3$ is associated by Cl bridges and can be obtained in quantitative yield from the reaction between $ReCl_5$ and CCl_3NO_2.[567] The bromo derivative cannot be made directly from $ReBr_5$, but addition of excess BBr_3 to $Ph_4P[Re(NO)_2Cl_4]$ yields $Ph_4P[Re(NO)_2Br_4]$ which can then be reacted with $AlBr_3$ in CH_2Br_2 to produce $Re(NO)_2Br_3$.[568] The NO ligands are in a *cis* arrangement; $Re(NO)_2Br_3$ is dimeric with Br bridges.

$Re(NO)_2Cl_3$ adds an MeCN molecule when dissolved in this solvent giving $Re(NO)_2Cl_3(NCMe)$. Addition of Ph_4AsCl to the MeCN product in CH_2Cl_2 produces the salt $Ph_4As[Re(NO)_2Cl_4]$.[567] The X-ray crystal structures of the MeCN adduct and the Ph_4As^+ salt have been solved; the NO groups are *cis* to one another in both cases. The reaction of $Ph_4As[Re(NO)_2Cl_4]$ in CH_2Cl_2 in the presence of MeCN and H_2O gives $Ph_4As[Re(NO)Cl_4(OC(NH_2)CH_3)]$.[569]

Other reactions of $Re(NO)_2Cl_3$ include the addition of PPh_3 in CH_2Cl_2 to form the phosphene-iminato complex $[Re(NO)Cl_3(NPPh_3)(OPPh_3)]$[570] and the addition of excess $SbPh_3$ in CH_2Cl_2 to produce $[Re(NO)_2Cl_2(SbPh_3)_2]$.[571]

Further examples of rhenium nitrosyls have been reported. The reactions of $Re(NO)Cl_2(OCH_3)(PPh_3)_2$ with thiophenols which contain methyl or isopropyl groups in their *ortho* positions gives trigonal bipyramidal complexes of the type $ReNO(SR)_4$. The X-ray crystal structure of the complex where R = 2,6-diisopropylphenyl has been determined.[634,635] Thiophenols without ortho substituents give dinuclear $[Re_2(NO)_2(SR)_7]^-$ which contain a triple thiolate bridge.[634,635] The reductive nitrosylation of $[ReO_4]^-$ using an excess of CN^-, OH^- and $NH_4OH \cdot HCl$ has been used to prepare $K_3[Re(NO)(CN)_5] \cdot 2H_2O$.[636] A similar procedure using NCS^- in place of CN^-, followed by acidification and treatment with NO_2^-, is said to provide a route to the dinitrosyls $A[Re(NO)_2(NCS)_3]$ (A = Me_4N, Et_4N, Ph_4P or Ph_4As) and $Re(NO)_2(NCS)_2(LL)$ (LL = bipy or phen).[637] Another interesting example of a thionitrosyl complex has been described. $[Ph_4As]_2[Re(NS)(NSCl)Cl_4]$ has been synthesized from the reaction between S_4N_4, $ReNCl_4$ and Ph_4AsCl in CH_2Cl_2. Its X-ray crystal structure has been solved.[638] The analogous reaction of S_4N_4 with $ReCl_5$ gives $[Ph_4As]Re(NS)Cl_5$.[638]

43.11 MISCELLANEOUS COMPLEXES

A series of polyoxotungstate anions which contain high valent rhenium, *e.g.* $[SiW_{10}Re_2O_{40}]^{2-/3-/4-}$, have been synthesized in the form of $Bu^n_4N^+$ salts.[639] The anions contain rhenium in oxidation states VII, VI and V. Cyclic voltammograms, ESR and electronic absorption spectra have been used to characterize these complexes.

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44.1

Iron(II) and Lower States

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Because of factors beyond the editors' control, the submission of the manuscript for this chapter was delayed. In order to minimize any delay in publishing 'Comprehensive Coordination Chemistry' as a whole, the coverage of iron(II) and lower states appears at the end of this volume, commencing on page 1179.

44.2

Iron(III) and Higher States

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44.2.1 INTRODUCTION

The common oxidation states of iron are +2 and +3. The relative stability of the two oxidation states in acid aqueous solution is defined by the standard electrode potential of +0.77 V for the Fe^{3+}/Fe^{2+} couple.[1a] This potential is such that the hydrated Fe^{II} cation is thermodynamically unstable with respect to atmospheric oxidation (equation 1). The oxidation is even more favourable in basic solution (equation 2). It is apparent, therefore, that the chemistry of iron, including its

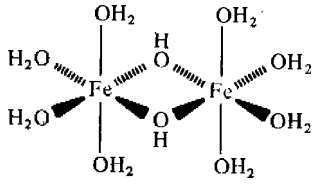
importance in biology, is closely associated with the ready interconversion of these two oxidation states and with the dependence of the redox potential on the ligand environment.

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ \longrightarrow 2Fe^{3+} + H_2O \qquad E^0 = 0.46\,V \tag{1}$$

$$Fe(OH)_2(s) + OH^- \longrightarrow \tfrac{1}{2}Fe_2O_3 \cdot 3H_2O + e^- \qquad E^0 = -0.56\,V \tag{2}$$

The small size (Goldschmidt radius 0.53 Å) and relatively high charge of the Fe^{3+} ion are responsible for its strong tendency to hydrolyze in aqueous solution. Thus, the hexaaqua ion is a Brönsted acid of moderate strength ($pK_a = 3.05$) existing in the undissociated form only below pH ~ 2 (equation 3). At higher pH further proton dissociations lead to the formation of hydroxo- and oxo-bridged di- and poly-nuclear species such as (1) and eventually to precipitation of hydrated iron(III) oxide.[1b] The high charge density of Fe^{3+} is also responsible for its strong affinity for 'hard' or 'class a' donors such as oxygen and F^-. It is for this reason that Fe^{3+}, unlike Fe^{2+}, forms few stable complexes with ligands such as ammonia or simple amines which are also good Brönsted bases in aqueous solution.

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+ \tag{3}$$



(1)

The Fe^{III} ion has a d^5 electron configuration. While it is high spin ($S = \frac{5}{2}$) in most of its complexes there is the possibility of the stabilization of low-spin ($S = \frac{1}{2}$) ground states in strong octahedral fields such as generated by CN^- and many bi- or poly-dentate ligands containing unsaturated nitrogen (Figures 1 and 2). In addition, intermediate spin ($S = \frac{3}{2}$) states may be produced in fields of lower symmetry.

Magnetic susceptibility measurements and ESR and Mössbauer spectra provide convenient means for distinguishing between different possible spin states in most cases. For the common case of high-spin octahedral iron(III) which has an orbitally non-degenerate $^6A_1$ ground state the magnetic moment is given by the high-spin-only value of 5.92 BM which should be temperature independent. Where deviations from this value occur either an antiferromagnetic or, less commonly, a ferromagnetic interaction between adjacent paramagnetic centres of a thermally controlled equilibrium between different spin states is usually indicated. Spin-doublet and spin-quartet ground states are associated with magnetic moments, at ambient temperature, close to 4.0 BM and 2.2 BM, respectively, corresponding to the presence of one and three unpaired electrons (Figure 1).

Because of the orbital singlet nature of high-spin Fe^{III} there are no excited states of the same spin multiplicity and all '*d–d*' transitions are therefore spin forbidden as well as Laporte forbidden. The free-ion ground state ^6S becomes $^6A_1$ in a cubic field while the first excited state ^4G splits into two T states, $^4T_1$ and $^4T_2$, and into a degenerate pair, $^4A_1$ and ^4E (Figure 2). The first four ligand field

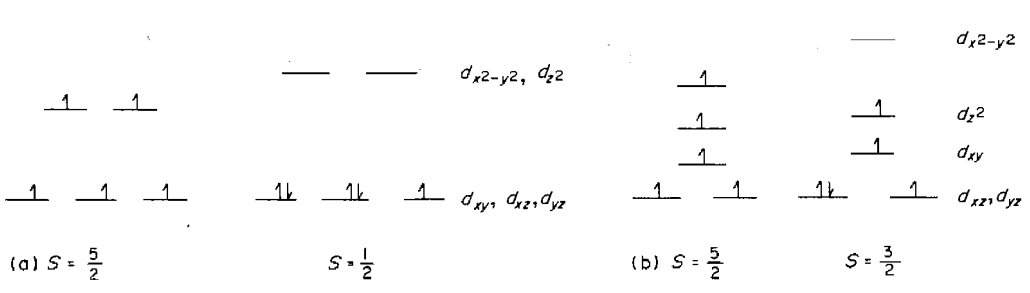


Figure 1 The occupation of the 3*d* orbitals in weak and strong field (a) octahedral and (b) square pyramidal Fe^{III} complexes

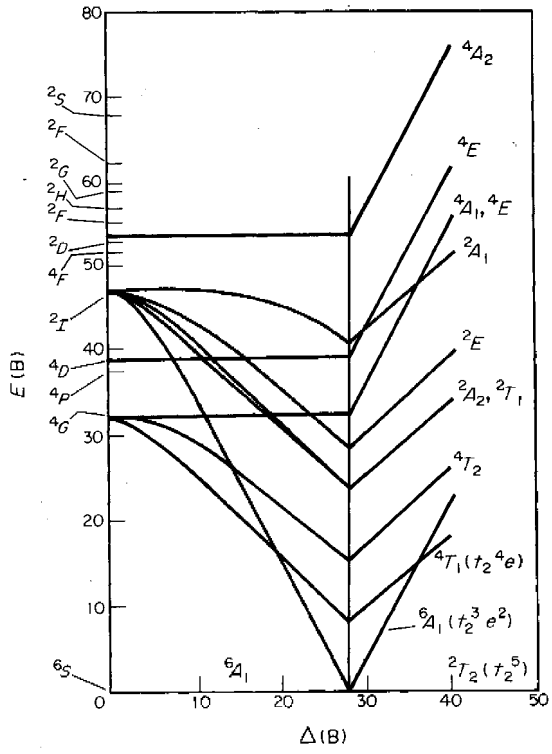


Figure 2 A semiquantitative energy level diagram (Tanabe–Sugano diagram) for the d^5 configuration[2]

transitions for the high-spin d^5 ion are therefore those indicated in equation (4). Since these sextet–quartet transitions are both spin and parity forbidden, intensities seldom exceed $\sim 0.01\ dm^3 mol^{-1} cm^{-1}$; in tetrahedral symmetry a measure of *d–p* mixing occurs and somewhat higher intensities are usually observed. In strong octahedral fields the $^2T_2$ component of the ^2I free-ion excited state becomes sufficiently lowered in energy to become the ground state (Figure 2) corresponding to the spin-paired t_{2g}^5 *d* orbital electron occupation shown in Figure 1.

$$\begin{aligned} {}^6A_1 &\longrightarrow {}^4T_1 \\ {}^6A_1 &\longrightarrow {}^4T_2(G) \\ {}^6A_1 &\longrightarrow {}^4T_1, {}^4E \\ {}^6A_1 &\longrightarrow {}^4T_2(D) \end{aligned} \tag{4}$$

As a result of the spin- and parity-forbidden nature of the ligand field transitions of the high-spin d^5 ion many simple salts and complexes of iron(III) have little or no colour. The hexaaqua ion, for example, has a very pale violet colour while $[FeF_6]^{3-}$ is virtually colourless. Where strong colour in high-spin iron(III) compounds does occur this can usually be assigned to ligand-to-metal charge transfer absorption (or to internal transitions of the coordinated ligand) as in the yellow and red-brown $[FeCl_4]^-$ and $[FeBr_4]^-$ complexes. The analytical applications of the blood red colour of Fe^{3+}/NCS^- complexes are well known.

The commonest coordination number of Fe^{III} is six but a range of other coordination numbers — three, four, five, seven and eight — are also well established. Examples of all of these will be given in the following pages along with discussion of the structural and electronic factors which determine them.

The treatment of the coordination chemistry of iron(III), and higher states, adopted in this review is, as elsewhere in this volume, by means of ligand type. We begin with Main Group IV ligands and follow with ligands of Groups V, VI, VII, mixed donor atom ligands and macrocyclic ligands. Naturally occurring ligands are not considered separately as in other chapters but, instead, are treated together with synthetic ligands of the same donor atom class. Some overlap between sections is inevitable. Iron(III) complexes are considered first followed by complexes of higher oxidation

states. Because of the comparable stabilities of iron(II) and iron(III) no discussion of the coordination chemistry of iron(III) can ignore that of iron(II). However, it is hoped that the unavoidable reference to iron(II), the subject of the preceding chapter, will be illuminating rather than merely repetitive. In preparing this review emphasis has naturally been placed on recent rather than early work while at the same time hopefully giving due place to the latter. The coverage is far from comprehensive since limitations of space dictated ruthless selection of material. Such selection is necessarily subjective and, in this chapter, probably reflects as much on the author's preferences and prejudices as on his good judgement. Valuable early accounts of various aspects of iron(III), (IV) and (VI) chemistry may be found in refs. 3–9. For more recent general treatments see refs. 10–15.

44.2.2 CARBON LIGANDS

Organometallic compounds of iron have been comprehensively covered in the companion work, 'Comprehensive Organometallic Chemistry'.[16] The present review is therefore restricted to Fe^{III} complexes of cyanide.

44.2.2.1 Cyanide Complexes

A comprehensive monograph[17] on cyano complexes of the transition metals, including Fe^{III}, is available. Cyanides and fulminates as ligands are also the subject of Chapter 12 of Volume 1 of this series.[18] The ambidentate nature of the CN^- ion has also been reviewed.[19]

The short C—N distance of 1.16 Å in CN^- is in accordance with the existence of a C≡N triple bond. The highest occupied σ orbital is localized on the carbon atom (Figure 3) and this dictates that the carbon end of the ion is more basic than the nitrogen end.[20] It is thus expected, and observed, that when acting as a monodentate ligand CN^- coordinates *via* the carbon atom, with a linear, or near linear, M—C≡N bond system. CN^- can, of course, act as a bridging ligand between neighbouring metal ions, using both carbon and nitrogen atoms.

The most important cyano complex of Fe^{III} is the red hexacyanoferrate(III) anion, $[Fe(CN)_6]^{3-}$. This is usually prepared, as the potassium salt, by the oxidation of hexacyanoferrate(II), $[Fe(CN)_6]^{4-}$, with chlorine. $[Fe(CN)_6]^{3-}$ has a magnetic moment of 2.25 BM at 300 K in accordance with the presence of one unpaired electron as required for a $^2T_2$ ground state (Figure 1) with appreciable orbital contribution.[21]

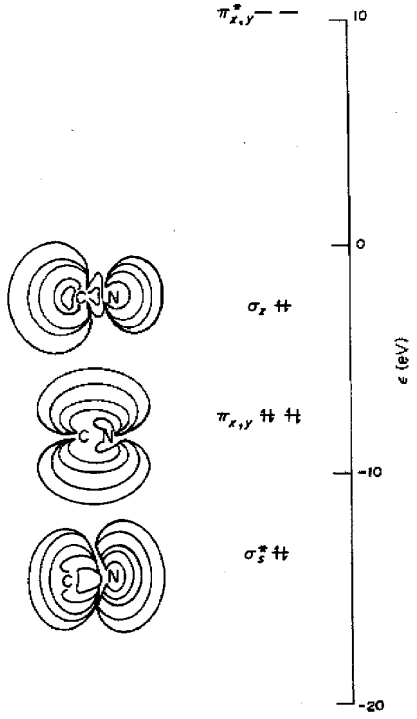


Figure 3 Molecular orbitals of the cyanide ion. Orbital energies calculated by a semiempirical SCF–MO procedure[19]

$K_3[Fe(CN)_6]$ is dimorphic, existing in monoclinic and orthorhombic forms, depending on how the ordered layers are stacked in the crystal lattice. The complex anion has near octahedral symmetry with Fe—C and C—N distances close to 1.95 and 1.14 Å, respectively.[22] Interestingly, the Fe—C bond in $[Fe(CN)_6]^{3-}$ is longer than in $[Fe(CN)_6]^{4-}$ (1.92 Å) despite the smaller size of the Fe^{3+} ion. This is attributed to the π-accepting capacity of the CN^- ion, the π bonding being more pronounced in the lower valence state complex[15,17]. However, the Fe^{III} complex is nonetheless thermodynamically more stable (by about 10^7) than the Fe^{II} complex. This apparent anomaly has been attributed to a very negative entropy of hydration of the highly charged $[Fe(CN)_6]^{4-}$ anion. The same considerations account, of course, for the less positive standard electrode potential ($E^\circ = +0.36$ V) for $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ than observed for the hydrated ions ($E^\circ = +0.77$ V).[17] $[Fe(CN)_6]^{3-}$ is therefore a moderately effective oxidizing agent. In contrast to $[Fe(CN)_6]^{4-}$ the corresponding Fe^{III} complex is poisonous and is generally more reactive in regard to ligand substitution. Several substitution products of the type $[Fe^{III}(CN)_5L]^{n-}$ are known where L = *e.g.* H_2O, NH_3, N_3^-, SCN^-, heterocyclic amine.[23–26] Like the parent $[Fe(CN)_6]^{3-}$ ion, all have magnetic properties and Mössbauer spectra[27] characteristic of low-spin Fe^{III}. In the IR spectra the ν(CN) stretching vibrations occur in the range 2090–2150 cm^{-1}. Further details may be found in Sharpe's monograph[17] and references therein. In the pentacyano complexes a new band in the electronic spectra has been assigned as L → Fe charge transfer in origin with the aid of magnetic circular dichroism measurements.[28]

The bridging capacity of the CN^- ion has been mentioned, this arising from the presence of a non-bonded electron pair on the nitrogen as well as the carbon atom. Many polymeric transition metal cyanides are known, the structures of which may involve chains, sheets or three-dimensional networks. For the case of iron the best known are the Prussian blues and the Turnbull's blues.[29,17,19] The former are obtained by treating a solution of Fe^{III} with $[Fe(CN)_6]^{4-}$ and the latter by treating a solution of Fe^{II} with $[Fe(CN)_6]^{3-}$. IR,[30] magnetic[31] and Mössbauer[32] data have shown that the two substances are essentially the same although variations in composition accompany variations in preparative conditions (Figure 4). These materials are now formulated as iron(III) hexacyanoferrate(II) complexes regardless of the combination of starting materials, the iron(III) component being high-spin. The intense colour is attributed to electron transfer between Fe^{II} and Fe^{III}. Significantly, $K_2Fe[Fe(CN)_6]$, which contains only Fe^{II}, is white. A single crystal X-ray study of $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ (x = 14–16) has revealed[33] that the average distances are Fe^{II}—C = 1.92 Å, C—N = 1.13 Å and Fe^{III}—N = 2.03 Å. A neutron diffraction study has also been carried out.[34] The complexes $Fe[Fe(CN)_5X] \cdot xH_2O$ (X = H_2O, NH_3 or CO) have been prepared.[35] These also contain high-spin Fe^{III}—N and low-spin Fe^{II}—C centres. The structure of the $[PPh_4]^+$ salt of the binuclear complex anion $[Fe_2(CN)_{10}(NH_3)]^{4-}$ formed by reaction of $[Fe(CN)_6]^{3-}$ with $[Fe(CN)_5(NH_3)]^{2-}$ has been described.[36] The polynuclear complex formed by reaction of $[Fe(CN)_6]^{3-}$ with $[Cu(dien)]^{2+}$ contains both linear and non-linear Fe—C≡N—Cu linkages.[37]

The bifunctional capability of the CN^- ion also means that, as well as acting as a bridge between adjacent metal centres, the nitrogen end may act as a base towards H^+ and various Lewis acids. The acid $H_3Fe(CN)_6$ is somewhat unstable and difficult to obtain pure; it is said to be a strong acid in aqueous solution. Not surprisingly, when charge effects are considered, the coordinated CN^- group has poorer basic character in Fe^{III} complexes than in corresponding Fe^{II} complexes.[38] A number of adducts with Lewis acids such as BF_3 have been reported.[20]

An interesting series of dinuclear iron–cyano complexes $[(NC)_5Fe—L—Fe(CN)_5]^{4-,5-,6-}$ in which the metal centres are bridged *via* bifunctional heterocyclic amines such as pyrazine, 4,4′-bipy-

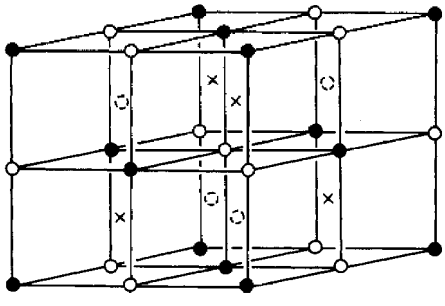


Figure 4 The structure of Prussian blue and related compounds. If none of the cube centre sites are occupied, the structure is that of ferric ferricyanide (both black and white Fe positions occupied by Fe^{III}); if every second cube centre site (marked with a dotted circle) is occupied by K^+, the structure is that of soluble Prussian blue (black = Fe^{II}, white = Fe^{III}); if all the centre sites are occupied by K^+ (crosses as well as dotted circles) the structure is that of dipotassium ferrous ferrocyanide (black and white sites = Fe^{II})

ridine and *trans*-1,2-bis(4-pyridyl)ethylene have been described.[36] Mixed valence species $[Fe^{II}—L—Fe^{III}]^{5-}$ are generated as intermediates in the two-electron redox process (equation 5). However, conproportionation constants for the [II.II] + [III.III] $\rightleftharpoons$ 2[II.III] equilibria corresponded fairly closely to a statistical distribution of the three species, rendering unlikely the isolation of the pure mixed valence complex. An intervalence transfer transition for solutions of the mixed valence species was observed in the near IR at $\sim 8000\,cm^{-1}$, the energy depending only slightly on the nature of the bridging ligand. The intensity of the intervalence band indicated only a small degree ($\sim 1\%$) of electron delocalization. These systems therefore appear to belong to Class II of the Robin–Day classification[40] for which there is only a weak coupling between the metal centres.

$$[Fe^{III}—L—Fe^{III}]^{4-} + 2e^- \rightleftharpoons [Fe^{II}—L—Fe^{II}]^{6-} \quad (5)$$

Other cyano complexes of Fe^{III}, containing only one or two cyano groups, will be considered in later sections which focus principally on the coordination chemistry of the associated ligands.

44.2.3 NITROGEN LIGANDS

The affinity of iron(III) for nitrogen is relatively low except where stability is enhanced by chelation, particularly with multidentate ligands containing anionic oxygen, or in macrocyclic ligands, or where stability is enhanced *via* ligand field stabilization effects accompanying spin pairing.

44.2.3.1 Monodentate Ligands

Addition of ammonia or simple amines to aqueous solutions merely precipitates the hydrous oxide, $Fe_2O_3 \cdot nH_2O$, though under anhydrous conditions the poorly stable hexaammines $[Fe(NH_3)_6]X_3$ (X = *e.g.* Cl, Br) are said to be formed.[41] These of course, are readily decomposed by water. $[Fe(NH_3)_5(NO)]Cl_2$ has been formulated[42] as a complex of Fe^{III} with NO^- rather than of Fe^I with NO^+.

A number of Fe^{III} compounds containing pyridine have been reported. Some of these[43] have salt structures containing the pyridinium cation, $[pyH]^+$, however, together with *e.g.* $[FeCl_4]^-$. Some genuine complexes do appear to exist, however. Reaction of $FeCl_3$ with anhydrous pyridine gives a red complex formulated as *fac*-$Fepy_3Cl_3 \cdot py$ on the basis of IR and ESR spectra.[44] An analogous thiocyanate complex, $Fepy_3(NCS)_3$, has also been prepared from ethanolic solution.[45] Use of pyrazine or pyrimidine in place of pyridine afforded complexes believed to be dimeric or polymeric containing pyrazine or pyrimidine bridges.[43] The green complex $[FeL_2Cl_3]$ (L = 4-cyanopyridine), prepared by reaction of anhydrous $FeCl_3$ with 4-cyanopyridine in trichloromethane, has a trigonal bipyramidal structure in which the three chlorine atoms occupy the equatorial positions and the pyridine nitrogen atoms the axial positions.[46] The magnetic properties (μ_{eff} = 5.56 BM at 296 K, 4.77 BM at 9 K) suggest a measure of intermolecular antiferromagnetic interaction.

The Fe^{III} atom in the complex salt $[Ph_4As]_2[Fe(N_3)_5]$[47] also has a trigonal bipyramidal geometry with the equatorial Fe—N distances slightly shorter than the axial distances.[48] The complex is high-spin with the magnetic moment (6.0 BM) close to the spin-only value. In contrast to the five-coordination found for the azido complex the cyanato and thiocyanato complexes, $[Ph_4As][Fe(NCO)_4]$ and $[Me_4N]_3[Fe(NCS)_6]$, isolated from non-aqueous media, are, respectively, tetrahedral and octahedral.[49,50] IR and electronic spectral data indicate that the bonding atom of the pseudohalide ion is nitrogen in both cases.[49,50]

Among the relatively few examples of three-coordinate transition metal compounds is the Fe^{III} complex of bis(trimethylsilyl)amine, $[Fe\{N(SiMe_3)_2\}_3]$.[51] The structure has been determined.[52] The 'FeN_3' and '$FeNSi_2$' units are planar, the latter making an angle of 49° with each other. The magnetic moment is 5.91 BM at 298 K and the susceptibility obeys the Curie–Weiss law with $\theta = -10°$. A very large quadrupole splitting ($5.12\,mm\,s^{-1}$) was observed in the Mössbauer spectrum.[53]

44.2.3.2 Bidentate Ligands

$[Fe(en)_3]Cl_3$ has been prepared by the slow addition of 1,2-diaminoethane (en) to anhydrous $FeCl_3$ in absolute ethanol. The complex is low-spin having a magnetic moment of 2.45 BM at room

temperature, falling to 2.17 BM at 80 K. The data are in accord with those predicted assuming a spin–orbit coupling constant of $-400\,cm^{-1}$, a delocalization constant of 1.0 and little or no axial distortion. Mössbauer data also indicate low distortion, the quadrupole splitting being much smaller ($1.09\,mm\,s^{-1}$ at 290 K) than observed for $[Fe(phen)_3]^{3+}$ ($1.67\,mm\,s^{-1}$) or $[Fe(terpy)_2]^{3+}$ ($3.09\,mm\,s^{-1}$).[54] The absence of low energy charge transfer absorption allowed a determination of and tentative assignment of the ligand field spectrum in the solid state and evaluation of the ligand field parameters Dq, B and C as 1950, 500 and $2000\,cm^{-1}$, respectively; the value of B corresponds to ~ 50% reduction from the free ion value. Corresponding values of Dq and B for $[Fe(CN)_6]^{3-}$ have been reported as 3500 and $720\,cm^{-1}$, respectively.[55]

Oxidation of the tris complexes of Fe^{II} with the α-diimine ligands such as 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen)[56] affords the corresponding Fe^{III} complexes $[Fe(bipy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$. These blue complexes have low-spin ($S = \frac{1}{2}$) ground states, as conclusively shown by magnetic,[57,58,61] Mössbauer[59] and ESR[60] measurements. The crystal structure of $[Fe(phen)_3][ClO_4]_3 \cdot H_2O$ has been determined.[60] The Fe^{III} ion is octahedrally coordinated by three symmetrically bidentate phen ligands, the Fe—N distance being 1.973(8) Å. The ESR spectrum determined at ~ 85 K showed the principal g values to be along the molecular pseudo C_3 axis ($g_1 = 1.459$) and in plane normal to it ($g_2 = 2.615$, $g_3 = 2.727$). The ESR measurements together with the temperature dependent magnetic susceptibility data were interpreted to yield a splitting of the orbital degeneracy of the $^2T_{2g}$ ground term such that the $^2A_{1g}$ orbital singlet lies lowest, some $800\,cm^{-1}$ below ^2E_g.

Unlike the CN^- ion, replacement of H_2O in the coordination sphere of the hexaaqua Fe^{2+} or Fe^{3+} by bipy or phen raises the standard redox potential (from 0.77 V to 1.12 V in the case of phen). This stabilization of the lower oxidation state is attributed to extensive back-coordination of the t_{2g}^6 electrons into the vacant p_π^* orbitals of the α-diimine ligands. The intense red colour of the Fe^{II} complexes is likewise due to this metal-to-ligand charge transfer. The reversibility of the redox reaction and the easily detectable colour change make these complexes very useful redox indicators.[61,62]

The dicyano complexes $[Fe(bipy)_2(CN)_2]X$ and $[Fe(phen)_2(CN)_2]X$ (X = ClO_4, NO_3) are also low-spin with magnetic properties[63] and Mössbauer spectra[59] (Table 1) comparable with those of the tris complexes. Little or no t_{2g} electron delocalization was apparent in the magnetic results. The stereochemistry of these mixed ligand complexes is presumably *cis*.

Table 1 Mössbauer Parameters for Some Iron(III) Complexes with Nitrogen Donor Ligands

Complex	*T (K)*	*Isomer shift (δ)*[a] ($mm\,s^{-1}$)	*Quadrupole splitting (ΔE_Q)* ($mm\,s^{-1}$)
$[Fe(en)_3]Cl_3$	r.t	0.14	1.09
$[Fe(bipy)_3][ClO_4]_3 \cdot 3H_2O$	300	0.03	1.69
	80	0.06	1.80
$[Fe(phen)_3][ClO_4]_3 \cdot H_2O$	300	0.05	1.62
	80	0.10	1.71
$[Fe(bipy)_2(CN)_2][ClO_4]$	300	−0.02	1.63
$[Fe(terpy)_2][ClO_4]_3$	r.t.	−0.01	3.09
	77	0.07	3.43

[a] Relative to iron foil.

Treatment of Fe^{III} salts in aqueous media with phen gives not the blue tris complex $[Fe(phen)_3]^{3+}$ but brown dinuclear complexes of composition $Fe_2O(phen)_2X_2 \cdot nH_2O$ (X = ClO_4^-, NO_3^-, Cl^-, $\frac{1}{2}SO_4^{2-}$).[64] These binuclear complexes have temperature dependent paramagnetic susceptibilities corresponding to *ca.* 1.9 BM per Fe atom at room temperature and decreasing with decrease in temperature. The results are best interpreted[65] in terms of antiferromagnetic superexchange interaction[81] between high-spin ($S = \frac{5}{2}$) paramagnetic centres linked *via* an oxo bridge as in structure (**2**). Analysis of the magnetic data gave values of the exchange coupling constant J of *ca.* $-100\,cm^{-1}$. In support of the presence of a μ-oxo bridge was the observation of a strong band in the IR at 840–860 cm^{-1} assigned to the Fe—O—Fe stretching vibration, this being a commonly observed feature of such compounds. Mössbauer isomer shifts confirm the assignment of $S = \frac{5}{2}$ spin states to the interacting Fe^{III} ions.[59]

$$[Cl(phen)_2Fe{-}O{-}Fe(phen)_2Cl]^{2+}$$

(2)

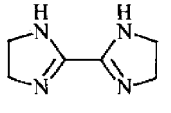
A number of studies of the complex of empirical formula $Fe(phen)Cl_3$ have been made. First prepared by Simon *et al.*[65] it has been formulated as $[Fe(phen)_2Cl_2][FeCl_4]$ on the basis of magnetic,

spectrophotometric, conductimetric and IR data and of the isolation of a perchlorate salt $[Fe(phen)_2Cl_2]ClO_4$.[65–67] On the other hand two modifications prepared by Fitzsimmons and co-workers[59] in glacial acetic acid and in aqueous HCl have been assigned a chloride-bridged structure since neither form displayed the Mössbauer resonance expected for the $[FeCl_4]^-$ anion. More recently, a single crystal X-ray structure determination[68] on the product of reaction of $FeCl_3$ with phen in acetone has revealed the $[Fe(phen)_2Cl_2][FeCl_4]$ structure. The six-coordinate cation has the expected *cis* configuration. The complex is high-spin, the magnetism conforming fairly closely to the Curie law. The high-spin nature of this complex shows that, as with Fe^{II}, coordination of only two phen molecules does not affect spin pairing. Not unexpectedly, the Fe—N distances are significantly longer than in the low-spin complex $[Fe(phen)_3][ClO_4]_3$.[60]

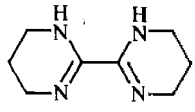
The red complexes $[Fe(phen)_2ox]\cdot 5H_2O$ and $[Fe(phen)_2mal]\cdot 7H_2O$ (ox = oxalate, mal = malonate), as well as related complexes containing 4,7-dimethyl-1,10-phenanthroline and 2,2′-bipyridyl as ligands, originally formulated[69] as containing Fe^{II} in the rare spin-triplet ($S = 1$) ground state, have been reexamined.[70] It was found that when the complexes were prepared under the rigorous exclusion of oxygen the products were violet in colour and showed different magnetic properties, typical of Fe^{II} complexes exhibiting a $^5T_2 \rightleftharpoons {}^1A_1$ spin equilibrium (the oxalate) or having a $^5T_2$ ground state (the malonate). The originally prepared red species are now believed to be $[Fe^{II}(diimine)_3]_2[Fe^{III}(dianion)_3]$ $(dianion)_3 \cdot nH_2O$ by analogy with the properties of complexes such as $[Fe^{II}(diimine)_3]_3[Fe^{III}(dianion)_3]_2 \cdot nH_2O$ obtained directly by reacting solutions of $[Fe^{II}(diimine)_3]^{2+}$ and $[Fe^{III}(dianion)_3]^{3-}$. These mixed valence salts contain low-spin ($S = 0$) cations and high-spin ($S = \frac{5}{2}$) anions thus displaying average magnetic moments per Fe atom of close to 4.0 BM, *i.e.* in the range expected for spin-triplet Fe^{II} systems. A reinvestigation[71] of the complex first thought to be an O_2 adduct of $[Fe(bt)_2(NCS)_2]$ (bt = 2,2′-bi-2-thiazoline) with a spin-triplet ground state[72] has similarly led to its reformulation as $[Fe^{II}(bt)_3]_2[Fe^{III}(NCS)_6](ClO_4)$. Spin-quartet ground states ($S = \frac{3}{2}$) have been proposed[73] for some Fe^{III} complexes of biguanides on the evidence of their magnetic properties ($\mu_{eff} = ca.$ 4.0 BM) and Mössbauer spectra. The structures of the complexes are unknown, however.

Whereas the complexes $[Fe(bipy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ are low spin the tris ligand complexes of other α-diimine ligands with Fe^{III} may not be. Thus, $[Fe(bi)_3][ClO_4]_3$ [bi = 2,2′-bi-2-imidazoline (**3**)] is high spin ($S = \frac{5}{2}$) while $[Fe(bhp)_3][ClO_4]_3$ [bhp = 2,2′-bi-1,2,3,4-tetrahydropyrimidine (**4**)] has a $^2T_2$ ground state but with a thermally accessible $^6A_1$ excited state in the 80–300 K temperature range.[74] The corresponding Fe^{II} complexes of (**3**) and (**4**) also show thermally controlled spin transitions in this temperature range; (**4**) is therefore an example of a ligand which generates spin-cross-over conditions in both iron(II) and iron(III) complexes.[74]

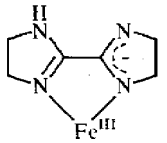
The orange tris ligand complexes of (**3**) and (**4**) with Fe^{III} can be reversibly deprotonated using NaOMe, but not weaker bases such as pyridine, to afford the dark green complexes $[Fe(bi)_2(biH)]^{2+}$ (**5**) and $[Fe(bhp)_2(bhpH)]^{2+}$ (**6**) in which one of the three ligands is monodeprotonated. The latter complex (**6**) has $\mu_{eff} = 1.87$ BM at 93 K rising to 3.70 BM at 353 K indicative of a $^2T_2 \rightleftharpoons {}^6A_1$ spin equilibrium in this complex also, a conclusion supported by Mössbauer spectra. In contrast, the complex $[Fe(bi)_2(biH)][ClO_4]_2$ (**5**) is fully in the high-spin form ($\mu_{eff} = 5.91$ BM) at 293 K though there are indications of the beginnings of a transition to $^2T_2$ below 100 K.[74]



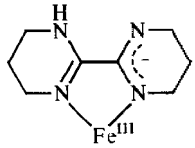
(3)



(4)



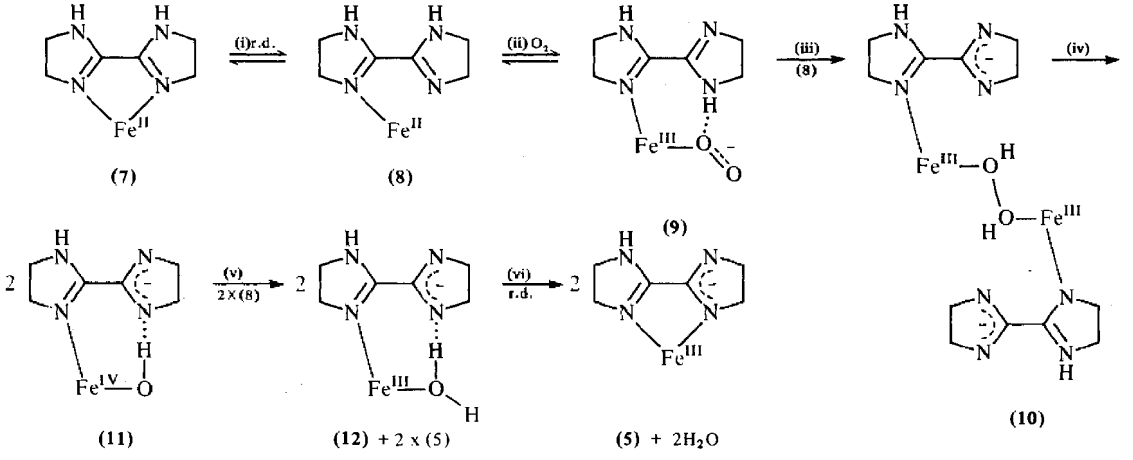
(5)



(6) Only monodeprotonated ligand shown

The green Fe^{III} complex $[Fe(bi)_2(biH)]^{2+}$ (**5**) containing one monodeprotonated ligand can also be prepared by aerial oxidation of the red Fe^{II} complex $[Fe(bi)_3]^{2+}$ (**7**) in dry acetonitrile solution. The stoichiometry of the oxidation (equation 6) was established by measurement of the O_2 consumed (pressure change at constant volume) and of the water produced (GLC) and the kinetics of

the reaction were monitored spectrophotometrically.[75] The reaction occurs in two stages, each essentially first order in complex and independent of $[O_2]$ except where $[O_2]$ is low. An unusual feature of the reaction is that while all the O_2 is consumed in the initial (fast) reaction ($t_{1/2}$ *ca.* 6 m at 30°C in MeCN) only half of the Fe^{III} product is formed during this stage. It follows that the second reaction ($t_{1/2}$ *ca.* 60 m) involves the (slow) decay of some oxygen-containing intermediate to the remainder of the product. The mechanism outlined in Scheme 1 has been proposed.[75] While no direct evidence for the intermediacy of the iron(IV) species (**11**) was found the scheme is consistent with the dissociative kinetics observed during the initial rapid uptake and associated formation of half of the Fe^{III} product (**5**) [steps (i)–(v)], followed by the formation of the remainder to (**5**) *via* the slow step (vi). It is considered that the ligand-to-metal proton transfer does not occur until after the two-electron transfer step (iii) and that the initially formed adduct (**9**) may be stabilized *via* a hydrogen bonding interaction involving the coordinated O_2 and the acidic hydrogen of the ligand. 2-(2′-Pyridyl)imidazole (pyim) forms low-spin tris complexes both of the neutral ligand and of the monodeprotonated anionic ligand.[76]



Scheme 1 r.d. = rate determining step. Only one of three ligands is shown

$$4[Fe^{II}(bi)_3]^{2+} + O_2 \longrightarrow 4[Fe^{III}(bi)_2(biH)]^{2+} + 2H_2O \quad (6)$$

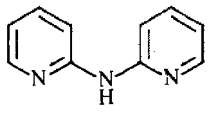
44.2.3.3 Ter- and Poly-dentate Ligands

Rather few well-defined complexes of Fe^{III} with ter- and poly-dentate nitrogen ligands are known other than those of macrocyclic ligands, synthetic and naturally occurring, which are considered in later sections.

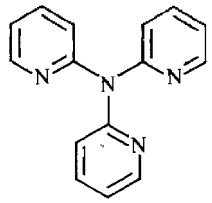
Direct addition of 2,2′,2″-terpyridyl to Fe^{III} salts leads to reduction and formation of the $[Fe^{II}(terpy)_2]^{2+}$ cation. However, oxidation of the Fe^{II} complex gives Fe^{III} complexes the nature of which depends on the particular anion present. For the case of X = halide or NCS the product have the formula $Fe(terpy)X_3$ and may have a high-spin five-coordinate (distorted square pyramidal) structure.[77] For $X = ClO_4$ the low-spin $[Fe(terpy)_2][ClO_4]_3$ is obtained while for $X = NO_3$ the product appears to have a μ-oxo binuclear structure with strong antiferromagnetic coupling[78] similar to the situation in analogous complexes of bipy and phen.

In di-2-pyridylamine (**13**) and tri-2-pyridylamine (**14**) the central aliphatic nitrogen atom is unfavourably positioned for participation in a chelating coordination mode and usually only bidentate (**13**) or tridentate (**14**) behaviour is observed. Three classes of complex with Fe^{III} have been identified.[79] One class comprises salt structures such as $[dipyamH]_2[Cl_3Fe{-}O{-}FeCl_3]$ containing protonated ligand cations and binuclear μ-oxo anions. These complexes show the expected ν(NH) vibration in the IR along with a strong ν(Fe—O—Fe) vibration at 860–890 cm^{-1}. The crystal and molecular structure of the related complex $[pyH]_2[Cl_3Fe{-}O{-}FeCl_3]\cdot py$ containing the pyridinium cation has been determined.[80] Tripyam also forms a series of apparently mononuclear complexes $[Fe(tripyam)X_3]$ (X = halide) while for dipyam a third class of complex, *e.g.* $Fe_2Cl_4O(dipyam)_3\cdot 5H_2O$ of uncertain structure has been obtained.[79]

The tetradentate ligands *N*,*N*′-bis(2-pyridylmethyl)ethylenediamine (pmen) and 2,2′:6′,2″:6″,2‴-tetrapyridyl (tetpy) form μ-oxo binuclear Fe^{III} complexes in which the pairs of $S = \frac{5}{2}$ ions are

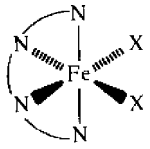


(13)

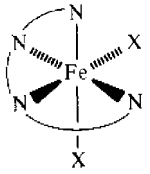


(14)

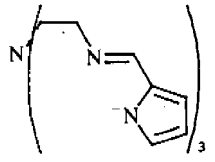
antiferromagnetically coupled with $J = -89\,cm^{-1}$ for $[Fe_2(pmen)_2(H_2O)_2O][SO_4]_2 \cdot H_2O$ and $-83\,cm^{-1}$ for $[Fe_2(tetpy)_2(H_2O)_2O][SO_4]_2 \cdot 5H_2O$.[82,83] The former complex is assigned a *cis* configuration while the latter complex of the less flexible tetpy ligand has the *trans* configuration. Both complexes largely retain the binuclear structure in aqueous solution but differ in stability as pH is increased. This stability difference is attributed to the different stereochemistry of the two quadridentate ligands, *cis*-α for pmen and *trans* for tetpy. The corresponding mononuclear complexes of pmen, *viz.* high-spin $[Fe(pmen)Cl_2]Cl$ and low-spin $[Fe(pmen)(OH_2)(OH)][ClO_4]_2$, have been prepared.[84] An interesting spin-state change ($S = \frac{1}{2}$ to $X = \frac{5}{2}$) accompanies a structural rearrangement from *cis*-α (**15**) to *cis*-β (**16**) geometry when the conjugate dihydroxo base of both salts is formed.



(15) *cis*-α



(16) *cis*-β



(17)

Although the Schiff base {(pyrol)$_3$tren} (**17**) formed by condensation of pyrrole-2-carboxaldehyde with 2,2′,2″-tris(ethylamino)amine is potentially heptadentate the neutral low-spin complex [Fe{(pyrol)$_3$tren}] has a six-coordinate (trigonally distorted octahedral) structure, the distance between the metal atom and the central tertiary aliphatic nitrogen being greater than the van der Waals contact distance.[85]

44.2.4 PHOSPHORUS AND ARSENIC LIGANDS

Unlike the lower oxidation states of iron the affinity of Fe^{III} for phosphorus, arsenic and antimony donor atoms is relatively low. Simple adducts $Fe(PPh_3)Cl_3$ and $Fe(AsPh_3)Cl_3$, presumably of distorted tetrahedral structure, have been prepared by reaction of $Fe_3(CO)_{12}$ with PPh_3 or $AsPh_3$ in $CHCl_3$[86,87] while direct reaction of Fe^{III} salts with the tertiary phosphines and arsines in diethyl ether afforded bis complexes of the type $Fe(PPh_3)_2X_2$ (X = Cl, NCS, NO_3). These were non-electrolytes in nitrobenzene and high-spin with magnetic moments close to 5.9 BM but in the absence of further information the structures must remain uncertain.[88–90]

Complexes with bidentate ligands are better defined.[97] Common reaction products of $FeCl_3$ and, to a lesser extent $FeBr_3$, with bidentate P- and As-containing bidentate ligands, are salt structures of the type *trans*-$[Fe(E—E')Cl_2][FeCl_4]$ containing low-spin cations (E,E′ = P or As).[91–96] Many of these complexes have been studied by Mössbauer spectroscopy[98–100] as well as by more conventional techniques. The complex anion $[FeCl_4]^-$ may be replaced by *e.g.* halide, ClO_4^-, BF_4^- and PF_6^- in many cases.[95,96] Examples of complexes containing tri- and tetra-dentate ligands are the neutral complex [Fe(TAS)(NCS)$_3$] (TAS = methylbis(3-propanedimethylarsine)arsine)[101] and the complex salt $[Fe(TTA)Cl_2][FeCl_4]$ (TTA = tris(3-dimethylarsinopropyl)arsine)[102] in both of which the complexes Fe^{III} ions are low-spin.

Consideration of the $[Fe^{IV}]$ oxidation products of diarsine Fe^{III} complexes is deferred.

44.2.5 OXYGEN-CONTAINING LIGANDS

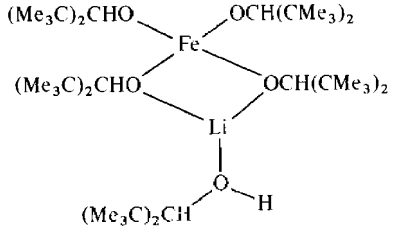
44.2.5.1 Complexes of Neutral Monodentate Ligands

Most simple hydrated Fe^{III} salts of oxyacids such as nitrate and perchlorate are presumed to contain the hexaaqua ion $[Fe(H_2O)_6]^{3+}$ though few crystallographic studies are available.[103,104] The

structure of $Fe(NO_3)_3 \cdot 9H_2O$ comprises two crystallographically distinct $[Fe(H_2O)_6]^{3+}$ octahedra, each possessing crystallographic ($\bar{1}$) symmetry, connected by a complex hydrogen-bonded network involving the nitrate anions and lattice water molecules.[103] The mean Fe^{III}—O distance (1.986(7) Å) is 0.14 Å shorter than the Fe^{II}—O distance in $[Fe(H_2O)_6]^{2+}$ and is, in fact, the shortest Fe^{III}—O distance yet determined for coordinated water molecules. The introduction of other ligands into the coordination sphere results in a lengthening of the Fe^{III}—O distances of the remaining water molecules. Salts of other anions including sulfate and chloride usually contain one or more coordinated anions.[103–107] Thus, for example, $FeCl_3 \cdot 6H_2O$ contains the *trans*-$[Fe(H_2O)_4Cl_2]^+$ cation[105] while $[NH_4]_2FeCl_5 \cdot H_2O$ contains $[Fe(H_2O)_5Cl]^{2+}$.[106] The strong yellow colour of these salts contrasts with the pale violet colour of this hexaaqua cation and is, of course, due to chloride-to-Fe^{III} charge transfer absorption. ESR spectra of $FeCl_3 \cdot 6H_2O$ in $AlCl_3 \cdot 6H_2O$ are consistent with the presence of *trans*-$[Fe(H_2O)_4Cl_2]^+$ ions.[44] $FeCl_3 \cdot 2.5\,H_2O$, however, is made up of a *cis*-$[Fe(H_2O)_4Cl_2]^+$ cation, a $[FeCl_4]^-$ anion and a water of crystallization.[107] X-Ray diffraction studies of concentrated aqueous solutions of $FeCl_3$, $FeCl_3 \cdot 6H_2O$ and $Fe_2(SO_4)_3$ have revealed the presence of a range of species, mononuclear and polynuclear, depending on concentration and pH.[108,109] $[FeCl_4]^-$ may be extracted into ether from hydrochloric acid solutions.

Iron(III) chloride, and other simple salts, react with a range of organic ligands such as alcohols, ethers, aldehydes, ketones, amides, sulfoxides, amine and phosphine oxides, *etc.* The structures of many of these complexes are unknown; some appear to be simple addition compounds while others have salt structures.

The alcoholates $FeCl_3 \cdot 2ROH$ (R = Me, Et, *etc.*) have been isolated from solutions of $FeCl_3$ in benzene containing the appropriate alcohol.[109] When base is present the corresponding alkoxides may be obtained.[110] These have trimeric $[Fe_3(OR)_9]$ structures containing a triangular core of three antiferromagnetically coupled Fe^{III} ions linked by oxo bridges.[111] In contrast, reaction of $FeCl_3$ with $Li[OCH(CMe_3)_2]$ gave the binuclear complex (**18**).[112]



(18)

Ethers generally have poor coordinating capacity for transition metals except where the ether function forms part of a multidentate chelating ligand. They appear to interact best with metal ions having few *d* electrons, and complexes of cyclic ethers appear to be more stable than those of open-chain ethers. A four-coordinate, presumably distorted tetrahedral, high-spin complex $[FeCl_3(THF)]$ (THF = tetrahydrofuran) has been prepared by direct reaction under anhydrous conditions.[113] Molecular weight and other measurements indicate some concentration-dependent association in benzene and 1,2-dichloroethane. A distorted octahedral structure has been assigned to the perchlorate salt of the cationic complex $[Fe(THF)_4(H_2O)_2]^{3+}$, however.[114]

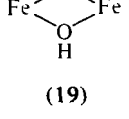
Although amides and sulfoxides have a potential ambidentate character, complexes with first row transition metal ions appear, invariably, to be oxygen bonded. Many six-coordinate Fe^{III} complexes $[FeL_6]X_2$ (L = *e.g.* DMF, DMA, urea, HMPA, DMSO; X = ClO_4^-, NO_3^-, Cl^-) have been prepared and their physical properties (IR, UV/vis, ESR and magnetic) reported in many cases.[115] Complexes of other stoichiometries such as $FeCl_3 \cdot 2DMSO$ and $FeCl_3 \cdot 4DMSO$ have also been reported,[116] the latter having the familiar salt structure $[Fe(DMSO)_4Cl_2][FeCl_4]$. Analogous complexes of the cyclic amides ethyleneurea and propyleneurea may have the same structure.[117] Treatment of metallic iron with DMSO and CCl_4 at above 100°C is said to give a mixture of *cis*- and *trans*-$[Fe(DMSO)_4Cl_2] \cdot X$ (X = Cl^- or $FeCl_4^-$).[118]

A number of hexakis(pyridine *N*-oxide) complexes $[FeL_6]X_3 \cdot nH_2O$ (L = pyridine *N*-oxide or ring-substituted derivative, X = ClO_4^-, NO_3^-) have been prepared.[119–121] As expected for an octahedral field of O-donor ligands the complexes are all high-spin ($\mu_{eff} \simeq 6.0$ BM). The ν(Fe—O) stretching vibration has been observed in the 320–400 cm^{-1} range. ESR measurements suggest considerable distortion from octahedral symmetry in at least some of these complexes.[120] Use of Fe^{III} chloride or bromide led to complexes of the type $[FeL_2Cl_2][FeCl_4]$[120,121] or $[FeL_3Cl_3]$[120] as found also for complexes with other O-donor ligands.

In contrast to the complexes of pyridine *N*-oxides, it appears that not more than four phosphine *N*-oxides can coordinate to one Fe^{III} ion, presumably for steric reasons. With Ph_3PO and Ph_3AsO and analogous ligands, complexes of stoichiometry $FeL_4(ClO_4)_3$ and FeL_2X_3 (X = Cl, Br, NCS, NO_3) are common.[122,123] ESR and vibrational spectra imply that the perchlorate complexes contain planar $[FeL_4]^{3+}$ ions, the arsine oxide exercising the larger ligand field, that the halide complexes have the salt structure *trans*-$[FeL_4X][FeX_4]$, and that the thiocyanate and nitrate are five-coordinate monomers.[123] Perchlorate ion coordination may be involved in some complexes of *n*-alkylphosphine oxides reflecting lower steric effects than in corresponding aromatic phosphine oxides.[124] Bidentate bitertiary phosphine oxides (L—L) in which the phosphorus atoms are linked *via* methylene, ethylene, tetramethylene and hexamethylene groups react with Fe^{III} chloride and nitrate in organic solvents to yield complexes of the types $[Fe(L—L)_2Cl_2][FeCl_4]\cdot nH_2O$, $[Fe(L—L)(ONO_2)_3]$, $[Fe(L—L)(ONO_2)_2][NO_3]$ or $[Fe_2(L—L)_3(ONO_2)_4][NO_3]_2\cdot 2H_2O$. Analytical, spectroscopic (IR, UV/vis, ESR, Mössbauer), magnetic and conductance measurements have been used to assign probable structures, these being five- or six-coordinate depending on the nature of the bis-phosphine.[125]

44.2.5.2 Complexes of Carboxylates and Related Anionic Ligands

An important aspect of the chemistry of iron(III), briefly referred to in the introduction, is the tendency of Fe^{III} to undergo hydrolytic polymerization in aqueous media, leading to di- and poly-nuclear complexes in which the metallic centres are linked by oxygen bridges.[126] Perhaps the simplest of these species is the dihydroxo-bridged dimer di-μ-hydroxo-octaaquadiiron(III) $[(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+}$ postulated to be the dominant species present at low pH on the basis of spectral, magnetic and other physical properties.[127] More recently, confirmation of the nature of this dimer has been obtained from EXAFS studies.[128] The results show that each Fe^{III} is octahedrally coordinated to two bridging OH^- ligands and to four H_2O molecules. The planar ring **(19)** comprises Fe—O(H)—Fe and O—Fe—O angles of 101° and 79°, the Fe—(OH), Fe—(OH_2) and Fe···Fe distances being 1.89, 2.03 and 2.91 Å, respectively. These parameters compare well with those found for the same structural unit occurring in di-μ-hydroxo-bis[2,6-pyridinedicarboxylatoaquairon(III)] and derivatives.[129] All of these doubly bridged di-Fe^{III} systems show magnetic moments below the spin-only value of 5.92 BM expected for high-spin Fe^{III} which further decrease with decrease in temperature. Generally, the susceptibility *vs.* temperature data can be fitted to the spin–spin interaction model based on the exchange Hamiltonian $H = -2J\bar{S}_1\bar{S}_2$ with $\bar{S}_1 = \bar{S}_2 = \frac{5}{2}$, for which the variation of molar susceptibility with temperature is given by equation (7), where $x = \exp(J/kT)$, J = coupling constant and $N\alpha$ is the temperature-independent-paramagnetism term.[130–132] For the doubly bridged dimers the antiferromagnetic coupling is usually relatively weak ($J < -20\,cm^{-1}$) whereas for the single bridged μ-oxo dimers (*vide infra*) J is commonly of the order of -90 to $-100\,cm^{-1}$.

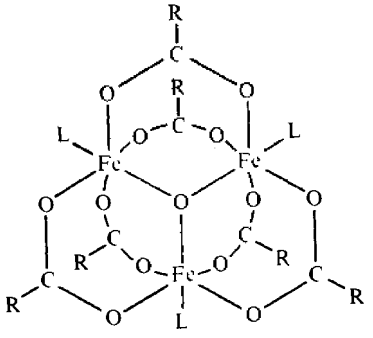


(19)

$$X_A = \frac{N\beta^2 g^2}{kT}\left[\frac{55 + 30x^{10} + 14x^{18} + 5x^{24} + x^{28}}{11 + 9x^{10} + 7x^{18} + 5x^{24} + 3x^{28} + x^{30}}\right] + Na \qquad (7)$$

Fe^{III} forms a number of basic carboxylates of general formula $[Fe_3O(O_2CR)_6L_3]X$ where R = Me, CMe_3, amino acid residue, *etc.*, L = *e.g.* H_2O, MeOH, py, DMF and X = anion.[133–136] X-Ray diffraction studies have shown that these complexes are trinuclear (see structure **20**) containing an O-centred triangular cluster of Fe^{III} atoms, the Fe_3O core being planar[133] or nearly so.[134] These complexes also show weak antiferromagnetic interactions. A variety of models have been considered.[136] The most appropriate appears to be that, consistent with the known structures, based on an equilateral triangular arrangement of Fe^{III} atoms with a small degree of *inter*trimer antiferromagnetic exchange in addition to the (larger, *i.e.* $J \approx -30\,cm^{-1}$) *intra*molecular interaction. The mixed valence complexes $[Fe^{II}Fe^{III}_2O(O_2CMe)_6L_3]$ (L = H_2O or py)[137,138] have been studied by Mössbauer, IR and optical spectroscopy and magnetic susceptibility methods.[139a] Variable-temperature magnetic susceptibility data for the aqua complex are interpreted in terms of a Heisenberg–Dirac–Van Vleck $S_2 = 2$, $S_1 = S_3 = \frac{5}{2}$ spin-exchange model with $J_{12} = J_{23} = -50.0\,cm^{-1}$ and $J_{13} = -14.5\,cm^{-1}$.

An intervalence electron–transfer band, not present in the 'Fe_3^{III}' analogue, was observed in the room temperature electronic spectrum at 13 800 cm^{-1}. Mössbauer spectra indicated distinct Fe^{II} and Fe^{III} sites at 17 K while at 300 K a single absorption was observed. The thermal barrier to electron transfer in the trimer was estimated as about 470 cm^{-1}. Triiron clusters of this type, in the presence of zinc powder, acetic acid, aqueous pyridine and oxygen, are reported[140] to effect the oxidation of saturated hydrocarbons. The exchange interactions in the series of complexes $[Fe_2^{III}M^{II}O(O_2CMe)_6py_3]\cdot py$ (M = Mg, Mn, Co, Ni or Zn) which, M = Ni excepted, are isomorphous with the mixed valence complex referred to above have been measured.[139b]



(20)

Tetranuclear and pentanuclear Fe^{III} clusters can also be prepared.[134,141] The Fe_5 complex is antiferromagnetic while the Fe_4 complex is ferromagnetic with a very asymmetric Mössbauer spectrum.[134]

The complex $K_5[Fe_3O(SO_4)_6(H_2O)_3]$, like the corresponding acetate, also contains a planar Fe_3O core, with, in this case, each pair of Fe atoms additionally bridged by two SO_4^{2-} groups.[142] The magnetic behaviour likewise conforms to that predicted by the triangular cluster model ($H = -2JS_1\cdot S_2 + S_1\cdot S_3 + S_2\cdot S_3$) with $J = -26.0\,cm^{-1}$, $g = 2.00$ and $N\alpha = 0$. The generally similar behaviour to that of the structurally related carboxylates indicates that magnetic exchange originates predominantly from interaction of different Fe^{III} ions *via* their mutual overlap with appropriate filled valence orbitals of the central oxygen atom; superexchange *via* the bridging sulfate ions is considered to be small or negligible.[143]

In addition to the polynuclear carboxylate complexes considered above, a number of mononuclear complexes are also known. Among these are the tris(oxalato) complexes. $K_3[Fe(ox)_3]\cdot 3H_2O$ is readily prepared by H_2O_2 oxidation of the Fe^{II} oxalate in the presence of oxalic acid and excess oxalate ion.[144] The green crystals are photosensitive, the oxalate ligand being oxidized to CO_2 with concomitant reduction of the metal to Fe^{II}. The structure has been determined;[145] the FeO_6 coordination sphere has approximate octahedral symmetry with some trigonal distortion. As expected for a magnetically dilute mononuclear Fe^{III} complex the magnetic moment at 300°C (5.96 BM) is close to the spin-only value.[146]

The tetranitratoferrate anion $[Fe(NO_3)_4]^-$, like the corresponding anionic complexes of Mn^{II}, Co^{II} and Zn^{II}, contains eight-coordinate metal ion involving four almost symmetrical bidentate nitrate groups.[147] The anion has essentially dodecahedral (D_{2d}) symmetry.

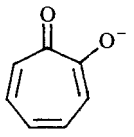
44.2.5.3 Complexes of Diketones and Related Ligands

Fe^{III} readily forms a range of stable, highly coloured complexes with the anions of β-diketones, such as acetylacetone (acacH).[148] The best known of these is the neutral tris complex $[Fe(acac)_3]$ for which a convenient new high yield synthesis has recently been described.[149] A single crystal X-ray structure determination[150] has confirmed the expected near-octahedral arrangement of the six oxygen donor atoms. Considerable distortion from octahedral symmetry is found in the corresponding tris complex of the tropolone anion (**21**), largely because of the smaller bite of the chelating group.[151] These complexes are, of course, high-spin; some magnetic anisotropy of the $^6A_{1g}$ ground state has been detected and interpreted in terms of zero-field splitting.[146] A simple one-electron MO scheme has been used to treat the UV/vis spectra of $[Fe(acac)_3]$ and derivatives containing Me, CF_3 and Ph substituents.[152] The three main absorption bands at 30 000–37 000 cm^{-1}, 24 000–29 000 cm^{-1}

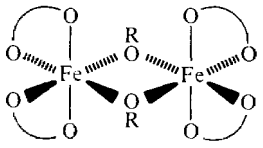
and 20 000–23 000 cm^{-1} were assigned to $\pi \rightarrow \pi^*$, $t_{2g} \rightarrow \pi^*$ and $\pi \rightarrow e_g$ transitions, respectively. [Fe(acac)$_3$] has been reported to have catalytic activity for stereoselective β-epoxidation of cholesterol and analogues with H_2O_2.[153]

The complex [Fe(acac)$_2$Cl] is mononuclear and five-coordinate. The Fe^{III} atom is located slightly above (0.51 Å) the plane of the four acac oxygen atoms (Fe—O, 1.95 Å) with the Cl atom occupying the apical position (Fe—Cl, 2.22 Å) of an overall square pyramid.[154] Magnetic properties and Mössbauer spectra have been measured.[155]

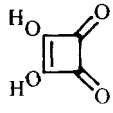
A series of dimeric Fe^{III} complexes [L_2Fe(OR)]$_2$ (where L = acac or the enolate of dipivaloylmethane, R = Me, Et or Pr^i) have been prepared and characterized.[130] These contain the dialkoxy-bridged structures (**22**) as judged by molecular weight, IR and magnetic susceptibility measurements. Values of J in $H = 2J\vec{S}_1 \cdot \vec{S}_2$ ($S_1 = S_2 = \frac{5}{2}$) were determined to be *ca.* $-10\,cm^{-1}$. A similar structural framework occurs in the dinuclear complex formed from Fe^{III} and the dianion of 3,4-dihydroxy-3-cyclobutene, better known as squaric acid (**23**).[156] In this complex the bridging groups are hydroxide rather than alkoxide groups and the superexchange coupling in somewhat smaller ($J = -7.0\,cm^{-1}$).



(21)



(22)



(23)

44.2.5.4 Complexes of Phenols, Catechols, Quinones and Related Systems

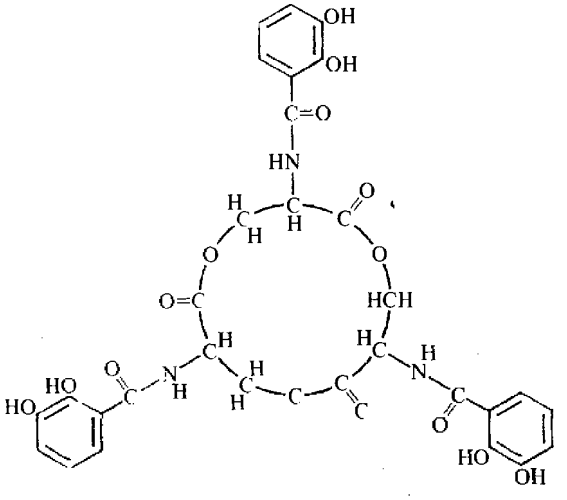
Much of the recent interest in iron complexes of hydroxybenzenes derives from the importance of such compounds in controlled iron transport within bacteria. Since, at physiological pH, iron is largely present as insoluble hydrated iron(III) oxide ($K_{sp} \sim 2 \times 10^{-39}$) it is not readily available. Nature has therefore developed mechanisms for the controlled solubilization, transport and release of the iron as needed by the organism.[157] This mechanism utilizes chelating agents called siderophores.[158] Nearly all the siderophores employ negatively charged oxygen-donor chelating functional groups. The two prinicpal classes are the catecholates and the hydroxamates. (Hydroxamate complexes are considered in the following section.) Fe^{III}–phenolate groups also occur in catechol dioxygenases.[159]

Despite the large amount of recent work devoted to iron(III)–catecholate derivatives rather less is known of the coordination chemistry of Fe^{III} with monophenols. The colour reaction of Fe^{III} with the phenolic group has been employed analytically for a long time but only very recently has a complex of monodentate phenoxide been structurally defined.[160] The red-orange compounds [Et_4N][$Fe(OC_{10}H_{13})_4$] (**24**) and [Ph_4P][$Fe(OC_6H_2Cl_3)_4$] (**25**) of 2,3,5,6-tetramethylphenolate and 2,4,6-trichlorophenolate were obtained from reactions of $FeCl_3$ with the appropriate lithium phenolate in the presence of the quaternary ammonium (or phosphonium) cation in anhydrous ethanol. Both complexes have somewhat distorted FeO_4 coordination geometry, the distortion being most marked in (**25**) where the O—Fe—O bond angles range from 99.3° to 122.9°. The Fe—O distances in both complexes are, at 1.847 Å in (**24**) and 1.866 Å in (**25**), significantly shorter than the average Fe—O distance (2.02 Å) observed in the FeO_6 core of [Fe(catecholate)$_3$]$^{3-}$ complexes. Both (**24**) and (**25**) undergo a reversible one-electron reduction at -1.32 and -0.45 V, respectively (*vs.* SCE in MeCN), reflecting, in the case of the tetramethylphenolato complex particularly, strong stabilization of the +3 oxidation state. Electronic spectra are dominated by three intense charge transfer transitions, the two low energy bands allowing a determination of the tetrahedral ligand-field splitting parameter, Δ_t, of 8000 cm^{-1} (**24**) and 7400 cm^{-1} (**25**), *i.e.* about twice as large as for $[FeCl_4]^-$.

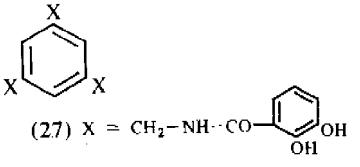
Catechol is a very weak acid and at low pH is a poor ligand forming only a transient complex which undergoes a redox reaction to give Fe^{II} and *o*-quinone as products. At higher pH, however, very stable iron(III) tris(catecholate) complexes are formed which are indefinitely stable in the absence of air.[161] The structure of K_3[Fe(cat)$_3$]·1.5 H_2O has been determined by single crystal X-ray diffraction,[161] in order to probe the coordination occurring in the Fe^{III} complex of the microbial iron transport compound enterobactin (**26**) (the cyclic triester of 2,3-dihydroxy-*N*-benzoyl-l-serine) which is itself a tricatechol.[162,163] The complex anion has approximate D_3 symmetry, the primary distortion being a bending of the catechol rings away from planarity with the O—M—O planes. The

average Fe—O bond lengths are 2.015 Å, somewhat longer than the Cr—O bonds (1.986 Å) in the isostructural Cr^{III} complex.

The high-spin Fe^{III}–enterobactin complex is exceptionally stable thermodynamically having the largest formation constant (*ca.* 10^{52}) known for any Fe^{III} complex.[164] A number of synthetic analogues for enterobactin which contain 1,2-dihydroxyphenyl chelating groups have been investigated.[162,165] One of these, hexadentate 1,3,5-tris(2,3-dihydroxybenzoylaminomethyl)benzene (**27**) has been shown[165] to form a 1:1 $[FeL]^{3-}$ complex with a formation constant of $10^{45.8}$.



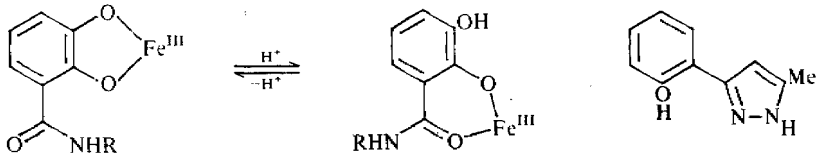
(26)



(27) X = CH_2–NH–CO–

An important biological requirement of iron–enterobactin systems is the release of iron from the highly stable $[Fe(ent)]^{3-}$ complex once inside the cell. The redox potential for $[Fe(ent)_3]^{3-}$ (estimated as *ca.* −750 mV at pH 7) is probably too negative to allow reduction to Fe^{II} by known biological reductants at physiological pH.[168] At lower pH the redox potential may shift towards positive values, however. In one mechanism for the release of iron from enterobactin at low pH it is proposed[166,169] that an internal redox reaction occurs between Fe^{3+} and catechol to generate a blue Fe^{II}–semiquinone species.[167] However, this mechanism in aqueous solution has been challenged by Raymond and co-workers[170] who, using Mössbauer and ESR techniques, found no evidence for reduction to Fe^{II} in the pH range 2–10, though some indication of a quasireversible redox reduction at low pH in methanol was apparent. An earlier mechanism[171] for iron release involves cleavage of the central triester ring of enterobactin by a specific esterase which would raise the redox potential. However, it has since been shown that catechoylamides which lack the triester ring retain the very negative redox couples. An alternative mechanism involves three protonation steps with a concomitant change from a 'catecholate' (**28**) to a 'salicylate' (**29**) mode of bonding which has the effect of dramatically raising the redox potential and bringing it within the range of physiological reductants.[164,170]

In an attempt to model the specific iron-binding site of the human milk protein, lactoferrin, believed to involve two or three tyrosyl residues per iron atom, a range of Fe^{III} phenolate complexes have been prepared.[172] These exemplify the donor sets FeO_6 to $FeO_2N_2O'_2$ where O represents a phenolate oxygen, N an aliphatic or aromatic nitrogen and O′ a carboxylate or methanol oxygen. Electronic and ESR spectra have been reported along with the results of an X-ray structure determination of one member of the series, $[FeL_2(MeOH)_2]NO_3 \cdot MeOH$ where LH is 2-(5-methylpyrazol-3-yl)phenol (**30**). The high-spin six-coordinate complex has an all-*trans* configuration, the Fe—O (phenolate) bond being 1.888 Å.

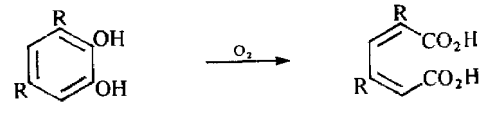


(28) (29) (30)

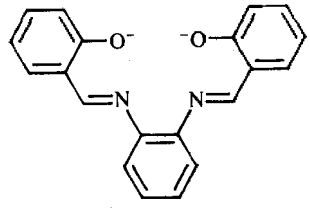
The non-heme iron enzymes catechol 1,2-dioxygenase and protocatechuate 3,4-dioxygenase catalyze the dioxygenation of catechols to *cis,cis*-muconic acids (**31**).[159] Spectroscopic studies suggest the active site to contain a mononuclear high-spin Fe^{III} centre coordinated to at least two tyrosines, this being responsible for the LMCT absorption resulting in the red colour of the enzymes. Substrate binding alters the colour but does not replace the bound tyrosine.[173,174] Kinetic and resonance Raman (RR) studies[175] further suggest that the cathechol substrate may be bound in a monodentate fashion. This coordination mode has recently been confirmed in the model compound [Fe(saloph)(catH)] (saloph = *N,N'*-(1,2-phenylene)bis(salicylidinimato); (**32**).[176] In this mononuclear high-spin complex the metal ion has a square pyramidal geometry in which it is raised 0.55 Å above the mean basal plane and with a rather short (1.828 Å) apical Fe—O (cat) bond. The analogous complex [Fe(salen)(catH)] has also been prepared. This can be deprotonated with strong base to give the anionic complex $[Fe(salen)(cat)]^-$ having markedly different properties[177] and in which the catecholate is chelated in a six-coordinate structure in which the tetradentate salen ligand has rearranged from an equatorial to a *cis-β* configuration in order to accommodate the bidentate catecholate dianion. An interesting observation is that the monodentate catecholate complex reacts readily with O_2 to form the chelated semiquinone while the chelated catecholate is unreactive.[178] While these results may imply a monodentate catecholate interaction between substrate and enzyme it should be noted that other workers found that chelated 3,5-di-*tert*-butylcatechol in [Fe(NTA)-(cat)] (NTA = nitrilotriacetate) does undergo the catechol ring cleavage.[179]

Fe^{III} complexes of semiquinones may also be prepared by reaction of Fe^{II}–Schiff base complexes such as [Fe(salen)] with *o*-quinones.[180,181] The product complexes $[Fe^{III}(salen)(SQ)]$ have Mössbauer spectra characteristic of high-spin Fe^{III} and magnetic moments near 4.86 BM at room temperature and are therefore formulated as high-spin Fe^{III} complexes in which the unpaired electron of the coordinated *o*-semiquinone is antiferromagnetically coupled to the Fe^{III} ion ($-J > 600\,cm^{-1}$) to give complexes with $S = 2$ ground states.[181] The crystal structure of the complex in which SQ = phenanthrenesemiquinone (phenSQ) has been determined.[178] This complex has a similar distorted octahedral geometry to that of $[Fe(salen)(cat)]^-$. The complex $[Fe(phenSQ)_3]\cdot phenQ$ (phenQ = the quinone form of phenSQ) reacts with bipy or phen to give complexes of formulation [Fe(phenSQ)(phenCAT)(bidentate nitrogen base)], which, on the basis of magnetic properties and Mössbauer spectra, are considered to be high-spin Fe^{III} complexes.[182] The mixed valence character of the complexes is indicated by the observation of an intervalence transfer band at 1100 nm in the solid state and in solvents of low dielectric constant. The non-appearance of the intervalence band in high dielectric constant solvents may be due to an intramolecular electron transfer to a $[Fe^{II}(phenSQ)(nitrogen\ base)]$ species.

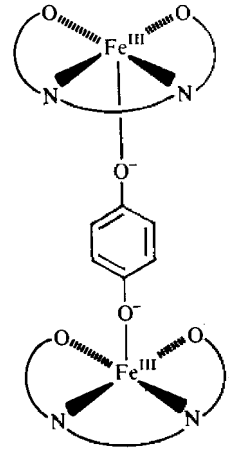
Reaction of $[Fe^{II}salen]$ with *p*-quinones gives, in contrast, the binuclear complexes $[Fe_2(salen)_2Q]$.[180] It was shown by a variety of properties (magnetic measurements and IR, ESR and Mössbauer spectra) that the compounds consist of high-spin Fe^{III} ions bridged by the dianion Q (structure **33**) of the hydroquinone which transmits weak ($-J < 6\,cm^{-1}$) antiferromagnetic interaction.[183] This structure has been confirmed, for the case of Q = the dianion of hydroquinone, by a single crystal structure determination.[176]



(31)



(32)



(33)

The electrochemistry of 8-quinolinol and 2-methyl-8-quinolinol complexes of iron in DMSO has been studied with a view to probing the redox chemistry of iron proteins containing histidine and tyrosine functional groups. Four reversible Fe^{II}/Fe^{III} redox couples occur between $+0.25$ V and -0.30 V (*vs.* SCE) as a function of solution acidity.[184] The methyl-substituted ligand also forms a μ-oxo bridged binuclear complex comprising high-spin five-coordinate Fe^{III} with $J = -80\,cm^{-1}$.[185]

44.2.5.5 Complexes of Hydroxamic Acid, Thiohydroxamic Acid and Derivatives

The second main class of Fe^{III}–specific sequestering agents (siderophores) responsible for the acquisition and assimilation of iron employ hydroxamate ligating groups (**34**).[157,158,186] Two important subclasses are the ferrioxamines and the ferrichromes (Figure 5). Examples are ferrioxamine B, a linear trihydroxamic acid and ferrichrome A, a cyclic hexapeptide carrying three hydroxamate-containing side chains.



(34)

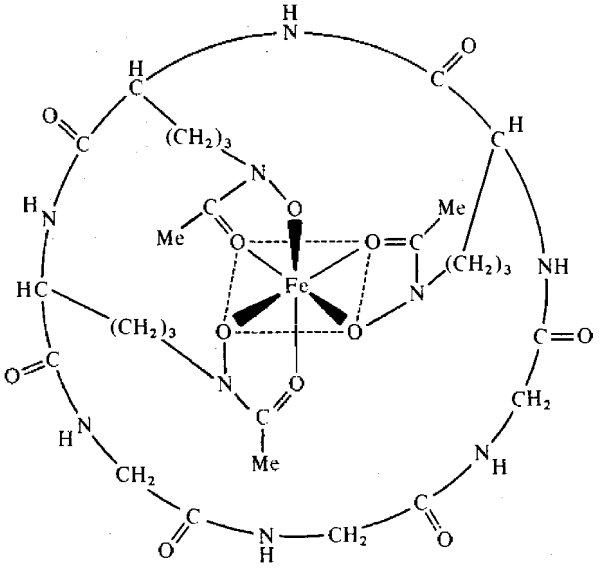
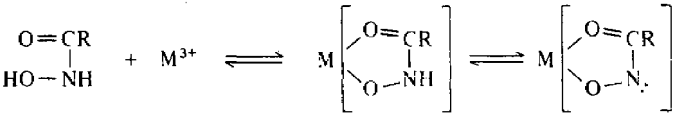


Figure 5 The structure of ferrichrome

The hydroxamic acids (**35**) are rather weak acids ($pK_a \sim 9$) which in acid solution form deeply coloured 1:1 complexes with Fe^{III}, a reaction which has long had analytical application for the hydroxamate functional group. Complexes of hydroxamic acids with a range of metal ions, including Fe^{III}, have been reviewed.[187] Mössbauer spectra are typical of high-spin Fe^{III} complexes.[188] In neutral solution a high-spin, octahedral tris(hydroxamato)iron(III) complex (**36**) is formed, the hydroxamate anion acting as a bidentate ligand. Such complexes are very stable with formation constants (β_3) approaching 10^{30}. In sharp contrast, the stabilities of corresponding Fe^{II} complexes are much lower (β_2 for the bis complex with acetohydroxamic acid $= 3 \times 10^8$) so that reduction of the Fe^{III} provides a mechanism for the release of the iron in the natural situation. The neutral tris complexes of Fe^{III} (**36**) can be further deprotonated in strongly basic media to generate the trianionic hydroximato complex $[FeL_3]^{3-}$ (**37**).



(35) Hydroxamic acid (36) Hydroxamato complex (37) Hydroximato complex

The asymmetry of the hydroxamate ligand leads to the possibility of the isolation of geometrical (and optical) isomers in the tris complexes. However, for high-spin Fe^{III}, expected to be kinetically labile, all structures so far determined have the *cis* configuration. Thus, for example, the most stable crystalline form of tris(benzohydroxamato)iron(III) has the *cis* configuration,[189] as have also ferrichrome A,[190,191] and ferric *N,N',N''*-triacetylfusarinine.[192] However, for the inert Cr^{III} complexes, on the other hand, both the *cis* and *trans* geometrical isomers have been separated and characterized in solution;[193] in addition, the *trans* isomer of tris(benzohydroxamato)chromium(III) has been structurally defined by X-ray diffraction.[194] More recently, the structures of both *cis* and *trans* isomers of the tris(benzohydroximato)chromate(III) anions have been determined.[195] Interestingly, the *cis* and *trans* isomers were obtained by deprotonation of the neutral hydroxamato complexes of opposite geometry.

In view of the kinetic lability of high-spin Fe^{III} it might be expected that the metal ion undergoes ready exchange in hydroxamate complexes. However, as shown by Raymond and co-workers, this is not always the case. For example, tris(hydroxamato)iron(III) complexes have been resolved into their component optical isomers and have been found to be very stable in various non-aqueous solvents.[196] Even slower substitution kinetics may be expected for natural siderophores comprising a single hexadentate ligand. Experiments on the kinetics of iron exchange and iron removal from complexes of ferrioxamine and ferrichrome A using ^{55}Fe and UV/vis spectrophotometric techniques have in fact shown that exchange is extremely slow; half-lives for exchange are > 200 h under certain conditions.[197]

The stabilities of Fe^{II} complexes of hydroxamates are much lower than those of Fe^{III} (β_2 for the bis Fe^{II} complex of acetohydroxamic acid = 3×10^8). It is thought, therefore, that the mechanism of release of iron from hydroxamate siderophores may occur *via* reduction of Fe^{III} to the much more weakly bound Fe^{II} state,[157] as also proposed for the tris(catecholato) siderophores. Cyclic voltammetry has shown that the Fe^{III} hydroxamate complexes undergo reversible or quasi-reversible one-electron reductions under suitable conditions. The observed formal potential E_f is pH dependent, decreasing from -0.388 mV (*vs.* SCE) at pH 7 by 60 mV per pH unit, for the case of tris(acetohydroxamato)iron(III), consistent with progressive deprotonations of the coordinated ligand. Thus, deprotonation stabilizes the Fe^{III} *vs.* the Fe^{II} state.[198,199]

Recently, a potentially new class of siderochrome has been isolated from bacteria such as *Pseudomonas fluorescens* containing thiohydroxamic acids which form very stable Fe^{III} complexes.[200] Both the parent acids and their chelates show antibiotic properties and may be involved in bacterial iron transport. The thiohydroxamate chelates, like their hydroxamate analogues, display high-spin $S = \frac{5}{2}$ properties, though some evidence for a high-spin $\rightleftharpoons$ low-spin equilibrium in one case has been reported.[201] The structure of tris(*N*-methylthioformohydroxamato)iron(III) has been determined.[202] The crystals examined contained a Λ-*cis* arrangement of ligands though the related complex, tris(benzothiohydroxamato)iron(III), could be resolved into the Λ and Δ isomers.[203] Electrochemical studies[199,204] have shown that replacing the carbonyl oxygen (in hydroxamates) by sulfur (as in thiohydroxamates) increases the reduction potential which would make the biological release of iron by reduction easier.

The bis(thiohydroxamate) complex $[FeL_2Cl]$ (L = *N*-methylbenzothiohydroxamate anion) has a five-coordinate (pseudo square pyramidal) structure comprising two *trans* bidentate 'SO' donor groups and a Cl atom.[205,206] It has been shown[205] (by magnetic, Mössbauer and ESR properties) to be high-spin indicating that the overall ligand field is smaller than that occurring in intermediate-spin dithiocarbamate systems ('S_4Cl' donor set).

44.2.6 SULFUR LIGANDS

44.2.6.1 Sulfido and Thiolato Complexes

Few areas of coordination chemistry can have undergone such rapid advances in the last decade as the chemistry of iron–sulfur cluster compounds. The stimulus for the rapid growth in this field has been the goal of modelling the active sites in the non-heme iron proteins involved in photosynthesis, mitochondrial respiration and nitrogen fixation. Following the recognition of the occurrence of the 'FeS_4' coordination unit in mono-, di- and tetra-nuclear proteins which mediate rapid and reversible electron transfer reactions, inorganic chemists have accepted the challenge to prepare synthetic analogues having the same distinctive physical and chemical properties. A remarkable degree of success has been achieved. Many excellent reviews[207] are available and these should be consulted as sources to the detail contained in primary publications.

There are at least five structural types of iron–sulfide–thiolate complex. The best known are

mononuclear tetrahedral $[Fe(SR)_4]^{2-,1-}$, binuclear $[Fe_2S_2(SR)_4]^{3-,2-}$ containing the planar $[Fe_2(\mu_2\text{-}S)_2]$ core, and tetranuclear $[Fe_4S_4(SR)_4]^{3-,2-}$ containing the cubane $[Fe_4(\mu_3\text{-}S)_4]$ core (Figure 6). Recently, two other classes of cluster containing three and six iron atoms have been discovered.[208,209]

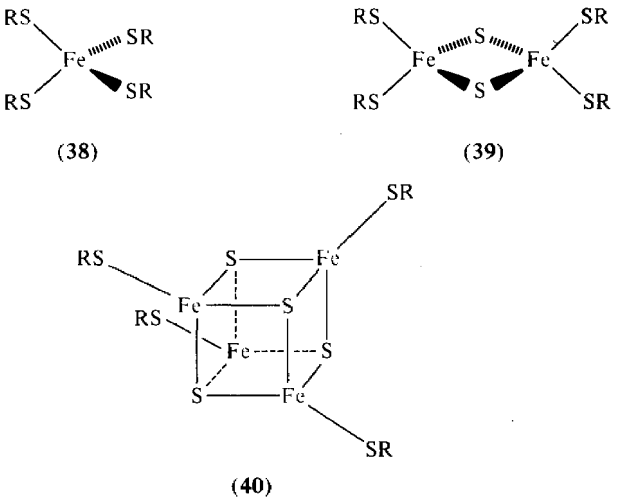


Figure 6 Structural units occurring in iron–thiolate complexes

44.2.6.1.1 Mononuclear 'FeS_4' systems

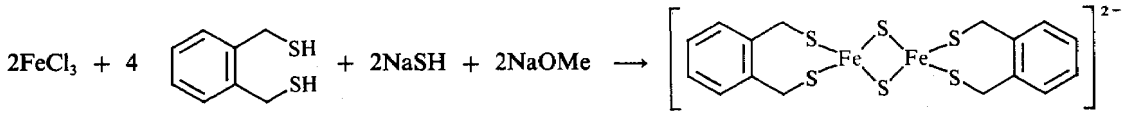
This structural unit occurs in the one-iron proteins, rubredoxins (Rd), obtained from bacteria, in which the active site is $[Fe(S\text{-}Cys)_4]$, where S-Cys is a cysteinyl residue of the protein chain [structure (**38**) of Figure 6]. These proteins have molecular weights typically about 6000. The variety of physical investigations (magnetic susceptibility,[210] ESR,[211] Mössbauer,[212] optical absorption,[207,213] MCD[214]) have demonstrated that the two redox states, Rd_{ox} and Re_{red}, coupled by one-electron transfer at $E^0 \sim -0.4$ to -0.6 V, contain Fe^{III} and Fe^{II}, respectively.[215] The X-ray structure[216] of *Clostridium pasteurianum* Rd_{ox} at 1.2 Å resolution has indicated a distorted tetrahedral 'FeS_4' active site; the Fe—S distances range from 2.24 to 2.33 Å and the S—Fe—S angles from 104° to 114°. Rather few well-characterized synthetic compounds containing the 'FeS_4' coordination unit are known;[217] most contain Fe^{II} and are not oxidizible to Fe^{III}, often because of the tendency of the Fe^{III} complexes to undergo autoredox reactions to Fe^{II} and RSSR. A notable exception is the complex $[NEt_4][Fe(S_2\text{-}o\text{-}xyl)_2]$ (S_2-*o*-xyl = *o*-xylyl-α,α′-dithiolate) prepared by reaction of the dithiol with $[FeCl_4]^{2-}$ followed by aerobic oxidation.[218] Comparison of the structures of the Fe^{III} and Fe^{II} complexes has shown that in both cases the metal atom is in a slightly distorted tetrahedral environment. There is some lengthening (~ 0.09 Å) of the mean Fe—S bond distance on reduction. Both complexes are high-spin ($S = \frac{5}{2}$, $S = 2$). In the 77 K Mössbauer spectra the isomer shifts (δ, *cf.* natural iron) and quadrupole splittings (ΔE_Q) are 0.13 and 0.57 mm s^{-1} (Fe^{III}) and 0.61 and 3.28 mm s^{-1} (Fe^{II}). Cyclic voltammetric measurements in DMF confirmed that the two complexes are related by a quasi-reversible one-electron process at ~ 1.0 V, a somewhat more negative potential than would be expected for the proteins in the same medium.

More recently three other mononuclear $[Fe(SR)_4]^-$ complexes containing monodentate thiolate have been structurally defined. In these SR$^-$ = SPh^-,[219] SEt^-[219] and 2,3,5,6-tetramethylbenzenethiolate.[220] Sterically hindered thiolate ligands appear to stabilize the $[Fe(SR)_4]$ coordination unit and thus provide a means for the preparation by ligand exchange of the previously elusive (non-hindered) monodentate tetrathiolato iron(III) complexes.

44.2.6.1.2 Dinuclear 'Fe–S' systems

A wide variety of synthetic binuclear iron complexes (**39**) bridged by sulfide, disulfide and/or thiolate groups are known. They have proven to be good models for the two-iron ferredoxin proteins, as demonstrated by comparisons of structure and properties. Early attempts to isolate two-iron complexes by direct reaction of a monothiol with $FeCl_3$, NaSH and NaOMe afforded only four-iron products suggesting that a particularly high stability is associated with the tetrameric

cubane structure (**40**) relative to other possible Fe—S reaction products.[221] It was argued that use of a chelating dithiol which is unable to span the ~7 Å distance between thiolate coordination sites in the tetramer might lead to the desired two-iron product. This strategy proved successful for the case where RSH is *o*-xylydithiol (**41**) (equation 8), a crystalline product (**42**) being isolated by the use of a quaternary cation. It was further discovered that related complexes of non-chelating aryl thiols could be readily prepared by ligand exchange. The structures of the *o*-xylyl dimer (**42**) and of the corresponding complex containing *o*-tolylthiol ligands have been determined.[221] Both are centrosymmetric sulfide-bridged dimers containing a planar Fe_2S_2 core with each Fe^{III} atom in an approximately tetrahedral environment. The short Fe···Fe separation suggests some direct metal–metal interaction. Subsequently, improved syntheses for the two-iron complexes were developed.[222] These involved reaction of $FeCl_3$, elemental sulfur and thiolate in the presence of tetraalkylammonium ions in MeOH solution at ambient temperature; in the absence of $[NR_4]^+$ the final reaction products were the four-iron tetranuclear clusters. Analogous selenium compounds were obtained by the use of elemental selenium in place of sulfur.



(41) (42)

A remarkable similarity in properties between the synthetic two-iron complexes and the oxidized forms of the two-iron ferrodoxins has been observed and subsequently placed on a firm structural basis by the X-ray structure determination of Fd_{ox} of *Spirulina platensis*.[223] Optical spectra of $[Fe_2S_2(S\text{-}o\text{-}xyl)_2]^{2-}$ (**42**) and Fd_{ox} are closely similar.[224] Both the synthetic and natural systems have magnetic susceptibilities well below those expected for isolated Fe^{III} ions and which approach zero at low temperature, indicative of strong intramolecular antiferromagnetism. The data lead to coupling constants $J = -148\,cm^{-1}$ for (**42**)[225] which compares with $J = -143$ to $-185\,cm^{-1}$ for various Fd_{ox}.[226] Mössbauer parameters are also in good agreement. The isomer shifts for spinach Fd_{ox} is $0.22\,mm\,s^{-1}$[227] while for the synthetic analogues values of $0.17\,mm\,s^{-1}$ have been observed.[225] The smaller quadrupole splitting ($\sim 0.35\,mm\,s^{-1}$) in the synthetic systems[225] compared to spinach Fd_{ox} ($0.65\,mm\,s^{-1}$)[228] may reflect a lower site symmetry in the latter.

Electrochemical investigation[221] of the synthetic dimers in DMF has revealed two quasi-reversible one-electron reduction waves at -1.25 V and -1.49 V (*vs.* SCE), for the *o*-xylyl system, attributable to the three-member electron transfer series given in equation (9). Since two-iron Fd_{ox} proteins undergo a single one-electron reduction (to give Fd_{red}) it is concluded that Fd_{red} contains the total oxidative level (formally $Fe^{II} + Fe^{III}$) as the synthetic trianion. No protein oxidation level corresponding to the tetraanion (Fe^{II}, Fe^{II}) has yet been detected. The antiferromagnetic coupling present in Fd_{ox} proteins in retained on reduction to Fd_{red} ($J \approx -100\,cm^{-1}$) leading to a spin doublet ground state.[226] Spectroscopic studies[226] (ESR, NMR, optical, Mössbauer) have revealed the occurrence of two (spectroscopically) distinct metal sites having the properties of high-spin tetrahedral Fe^{III} and Fe^{II}, thus characterizing Fd_{red} as a class II mixed valence species, *i.e.* one having a localized Fe^{III}, Fe^{II} oxidation state configuration. Similar properties were found for the one-electron reduction product (generated in solution) of $[FeS_2(S_2o\text{-}xyl)_2]^{2-}$ (**42**) leading to the conclusion that the localized mixed-valence behaviour is not a consequence of the protein structure but is an intrinsic property of any $[Fe_2S_2(SR)_4]^{3-}$ species and, indeed, of any species containing the $[Fe_2S_2]$ core.[229]

$$\underset{[Fe^{II}, Fe^{II}]}{[Fe_2S_2(SR)_4]^{4-}} \rightleftharpoons \underset{[Fe^{II}, Fe^{III}]}{[Fe_2S_2(SR)_4]^{3-}} \rightleftharpoons \underset{[Fe^{III}, Fe^{III}]}{[Fe_2S_2(SR)_4]^{2-}} \quad (9)$$

The exchange of *o*-xylyl dithiolate by aryl thiolate has already been noted. Such exchange (equation 10) is fairly general for one-iron and four-iron systems as well as two-iron and is the basis of the core extrusion method for the identification of active sites in iron–sulfur proteins. This type of reaction can be extended to the replacement of coordinated thiolate by other nucleophiles. For example, reaction of the complexes $[Fe_2S_2(SR)_4]^{2-}$ (and also the four-iron clusters) with benzoyl chloride afford $[Fe_2S_2Cl_4]^{2-}$ (or $[Fe_4S_4Cl_4]^{2-}$).[230] Comparison of the crystal structure of $[NEt_4]_2$-$[Fe_2S_2Cl_4]$ with those of the previously investigated *o*-xylyl dithiolate and *p*-tolyl thiolate complexes demonstrates that the replacement occurs virtually without structural change and reinforces the view that the Fe_2S_2 core in two-iron systems (and the Fe_4S_4 core in four-iron systems) is an integral

substructural unit which can be transferred intact from one ligand environment to another, including those in proteins. Both the two-iron and four-iron dimers and tetramers are also reactive with respect to substitution of core S by Se as demonstrated by ^{1}H NMR spectroscopy in MeCN solution.[231]

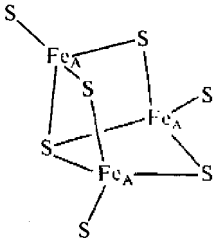
$$[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-} + 4RSH \longrightarrow [Fe_2S_2(SR)_4]^{2-} + 2o\text{-xylSH} \quad (10)$$

44.2.6.1.3 Trinuclear 'Fe–S' systems

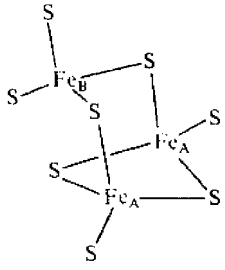
Three-iron clusters have been detected only very recently. An $Fe_3(\mu\text{-}S)_3$ unit from *Azotobacter vinelandii* ferrodoxin I has been identified crystallographically.[208] This protein also contains a [4Fe–3S] cluster. The [3Fe–3S] unit has a near planar cyclic structure (**43**). Each tetrahedral Fe atom has two terminal ligands of which five are cysteinyl side chains while the sixth appears to be an oxygen atom from H_2O or OH^-. The Fe···Fe distances, unlike those in two-iron and four-iron clusters, are long at 4.1 Å. On the other hand, EXAFS measurements on two other proteins, ferrodoxin II from *Desulfovibrio gigas*[232] and beef heart aconitase,[233] both containing isolated three-centre Fe cores, have indicated Fe···Fe distances of ~2.7Å. This closer metal···metal separation is incompatible with a planar [3Fe–3S] ring. Moreover, it has been shown that aconitase contains four labile S atoms, not three.[233] The situation is further confounded by the resonance Raman results of Spiro and collaborators[234] on ferredoxins from *A. vinelandii*. The observed spectra are not compatible with the planar [3Fe–3S] structure obtained in the crystallographic study. Instead, they strongly indicate a [3Fe–4S] structure of type (**44**) or (**45**) derived from the [4Fe–4S] cubane core. Since there is no reason to question the validity of the crystallographic results[208] it must be concluded that the two groups of investigators examined different chemical species. Since the [3Fe–4S] structure appears to occur in all other three-iron proteins so far examined it has been speculated[234] that one S atom was lost during the isolation procedure for the planar [3Fe–3S] specimen, with accompanying structural rearrangement.



(43)

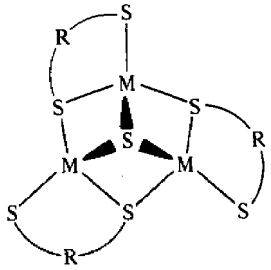


(44)

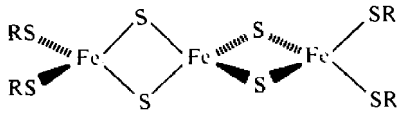


(45)

Structural diversity in trinuclear iron sulfide complexes has been extended by the isolation of a number of synthetic systems having a pyramidal $[Fe_3(\mu_3\text{-}S)]$ central unit (**46**)[235] or a linear arrangement $[FeS_2FeS_2Fe]$ (**47**).[236] The former structure (**46**) occurs in Fe^{II} and Co^{II} complexes of stoichiometry $[M_3S(S_2\text{-}o\text{-xyl})_3\}^{2-}$ and comprises an apical μ_3-S atom bonded to three M atoms arranged in a nearly equilateral triangle.[235] Each M atom is coordinated to one terminal and one bridging sulfur atom of a dithiolate ligand, affording distorted tetrahedral $M^{II}S_4$ units in structures that closely approach overall C_3 symmetry. The reduced, somewhat temperature dependent, magnetic moments (2.28 BM per metal ion at 301 K for M = Fe) and other properties are consistent with the occurrence of magnetic coupling. The Fe^{II} complex shows a quasi-reversible oxidation (at −0.59 V *vs.* SCE).[235]

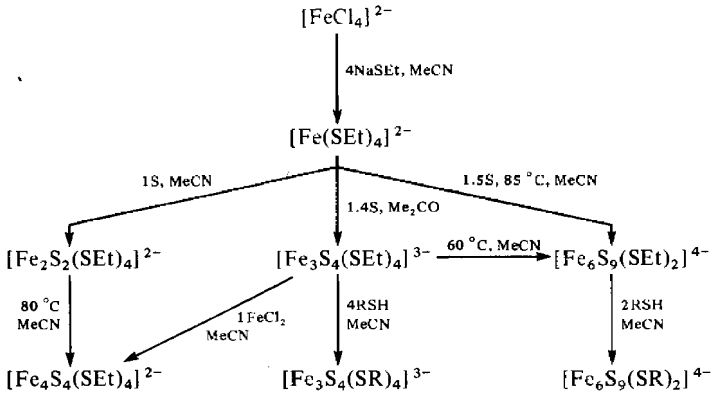


(46)



(47)

The complexes $[Fe_3S_4(SR)_4]^{3-}$ (R = Et or Ph), isolated as the $[NEt_4]^+$ salts, were prepared by reaction of the strongly reducing $[Fe^{II}(SEt)_4]^{2-}$ complex with 1.4 equivalents of sulfur in acetone. The corresponding benzenethiolate was then obtained by ligand exchange. Indeed, the $[Fe(SEt)_4]^{2-}$ complex was found to be a very versatile precursor to a range of Fe—S—SR compounds, affording direct entry to bi-, tri-, tetra- and hexa-nuclear clusters, as outlined in Scheme 2 which also indicates conversion pathways between [3Fe–4S] and higher order clusters.[236]



Scheme 2 Preparation routes to two-, three-, four- and six-iron sulfur–thiolate clusters

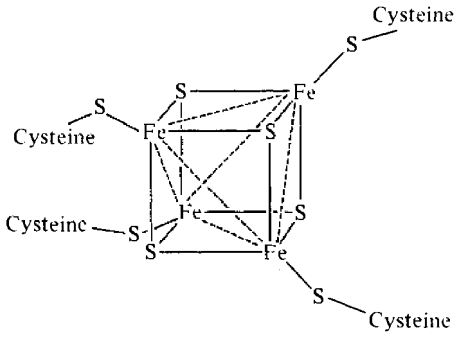
The anion of $[NEt_4]_3[Fe_3S_4(SPh)_4]$ consists of two tetrahedral FeS_4 units linked by a central Fe atom also in tetrahedral sites; the two outer Fe atoms are each coordinated by two thiolate groups (structure **47**). The Fe···Fe separation is 2.714 Å, *i.e.* similar to that deduced from EXAFS experiments for *D. gigas* ferredoxin II. Despite this, the structures of the three-iron cores in the natural and synthetic systems are considered to be quite different as judged by their different ESR spectra ($g \approx 2.01$ in the oxidized form of the protein, $g \approx 4.2$ in $[Fe_3S_4(SEt)_4]^{3-}$) and other properties.

44.2.6.1.4 Tetranuclear 'Fe—S' systems

The four-iron clusters are the most thoroughly studied group of iron–sulfur cluster compounds.[207,237] In nature they occur in the four-iron and eight-iron ferredoxins (Fd) and the so-called high-potential (HP) proteins and many synthetic analogues have been studied. Their structures and properties are naturally rather more complex than those of the systems considered above. The physiological function of the ferredoxins is to transfer electrons and a major challenge of the inorganic chemist has been to develop simpler synthetic systems which reproduce, as far as possible, the distinctive electrochemical and other properties of the active sites of the proteins. As in the case of the one-iron, two-iron and three-iron sulfur compounds already considered, our present understanding of the chemistry of the ferredoxins owes much to the elegant synthetic analogue approach of Holm and co-workers whose publications should be consulted for fuller detail.

The ferredoxin and high-potential proteins contain one or two $[Fe_4S_4(S\text{-}Cys)_4]$ clusters (**48**) each of which acts as a one-electron transfer agent. The same structural unit occurs in many synthetic systems in which a thiolate ion takes the place of the cysteinyl residue of the proteins. The close similarity in the structures of the $[Fe_4S_4(SR)_4]$ units between proteins and synthetic analogues has been demonstrated by X-ray structure determinations[238–244] on members of both classes, as can be seen from an inspection of the structural parameters collected in Table 2. Clearly, the synthetic compounds can be regarded as accurate structural models for the proteins. The basic geometry of this common structural unit is that of a tetrahedron of four iron atoms interpenetrating a second (larger) tetrahedron of four S atoms. Each S^{2-} ion (designated S*) is bonded to three Fe atoms and each Fe atom bears a terminal SR group, cysteinyl residues in the case of the proteins. In all cases the central 'cube' is compressed towards D_{2d} symmetry. An important feature of results of HP_{red} and HP_{ox} is that the structural parameters appear very insensitive to the overall oxidation level. Moreover, there is no evidence for localized Fe^{II}, Fe^{III} states in any of these mixed valence structures. This is in accord with the findings of spectroscopic investigations[245] capable of detecting localized Fe^{II}, Fe^{III} states with lifetimes of 10^{-4} to 10^{-16} seconds. Physical properties have shown that the Fe–S clusters in $[Fe_4S_4(SR)_4]^{2-}$ are isoelectronic with those occurring in the Fd_{ox} and HP_{red} proteins thus

establishing that these forms of the proteins contain, formally, two Fe^{III} and two Fe^{II} ions. Since the magnetic moments of the dianions are well below the values for high- and low-spin Fe^{III} and high-spin Fe^{II}, and since they are further reduced on cooling, it follows that the metal centres are antiferromagnetically coupled giving a resultant singlet ground state.[246]



(48)

Table 2 Average Dimensions (Å or °) in Some $[Fe_4S_4^*(SR)_4]$ Units[a]

	*Fe—S**	*Fe—S*	*Fe···Fe*	*S—Fe—S**	*S*—Fe—S**	*Fe—S*—Fe*
Fd_{ox} from *P. aerogenes*	2.29	2.18	2.85	116	101	77
HP_{red} from *Chromatium*	2.33	2.22	2.82	115	103	74.6
HP_{ox} from *Chromatium*	2.26	2.22	2.71	114	104	73.7
$[Fe_4S_4^*(SPh)_4]^{2-}$	2.286	2.251	2.746	114.4	104.1	73.8
$[Fe_4S_4^*(SCH_2Ph)_4]^{2-}$	2.286	2.263	2.736	115.1	104.3	73.5
$[Fe_4S_4^*(SCH_2CH_2CO_2)_4]^{6-}$	2.287	2.250	2.755	114.6	103.9	74.1
$[Fe_4S_4^*(SCH_2CH_2OH)_4]^{2-}$	2.287	2.256	2.729	114.2	104.3	73.5

[a] Data from ref. 207 and 238–244 in which original sources may be found.

Electrochemical studies[247] have shown that $[Fe_4S_4(SR)_4]^{2-}$ complexes undergo both one-electron reductions and one-electron oxidations (equation 11). Property comparisons with the proteins have allowed the equivalence, in overall oxidation state level, between $[Fe_4S_4(SR)_4]^{3-}$ and Fe_{red} and between $[Fe_4S_4(SR)_4]^{-}$ and HP_{ox}, to be established. The 'super-reduced' species HP_{s-red} and the 'super-oxidized' species do not appear to be active in the natural protein metabolism. However, the $[Fe_4S_4(SR)_4]^{3-}$ complex ($S = \frac{1}{2}$) has been isolated and shown to have similar optical ESR and Mössbauer spectra to those of Fd_{red} proteins.[248] In contrast to the [4Fe-4S] core of the Fd_{red} analogue, $[Fe_4S_4(SPh)_4]^{3-}$, which is distorted from cubic to elongated D_{2d} symmetry, the core of the $[Fe_4S_4(SCH_2Ph)_4]^{3-}$ anion consists six short and six long Fe—S bonds in C_{2v} symmetry.[249] This kind of distortion appears to be exceptional, however, the usual structural effect accompanying $[Fe_4S_4(SR_4)]^{2-}$ to $[Fe_4S_4(SR)_4]^{3-}$ being compressed $D_{2d} \rightarrow$ elongated D_{2d}.

$$\begin{array}{ccccc} [Fe_4S_4(SR)_4]^{3-} & \rightleftharpoons & [Fe_4S_4(SR)_4]^{2-} & \rightleftharpoons & [Fe_4S_4(SR)_4]^{-} \\ Fd_{red} & & Fd_{ox} & & Fd_{s\text{-}ox} \\ HP_{s\text{-}red} & & HP_{red} & & HP_{ox} \end{array} \qquad (11)$$

A point of difference between the natural and synthetic Fe—S compounds lies in the potential values at which oxidation/reduction occurs, these generally being more negative for the analogues ($E_{1/2} \sim -1.05$ to -0.75 V). Discrepancies originally ascribed to effects due to the influence of the polypeptide structure can now be attributed, in part, to differences in solvent medium.[247] However, the polypeptide must still have an attenuating effect on redox potentials, possibly by protecting the active site from solvent. A ^1H NMR study[250] of the redox equilibria of $[Fe_4X_4(SR)_4]^{2-,3-}$ (X = S, R = CH_2Ph or *p*-C_6H_4Me; X = Se, R = CH_2Ph) showed rates *ca.* 10^4 greater than for Fd or HP proteins, the differences being attributed to the steric influence of protein structure.

Preparative methods and reaction sequences leading to $[Fe_2S_4(SR)_4]^{2-}$ complexes, and pathways for interconversion to related clusters have been described and discussed.[236,251,252] The series of complexes $[Fe_4S_4(SC_6H_4\text{-}o\text{-}X)_4]^{2-}$ (X = NH_2, OMe, OH or SMe) have been prepared by ligand substitution from $[Fe_4S_4(SBu^t)_4]^{2-}$ and the structure of the complex in which X = OH has been

solved by X-ray crystallography. This cluster contains three conventional tetrahedral FeS_4 sites and one distorted trigonal bipyramidal FeS_4O site achieved by chelation of one *o*-SC_6H_4OH ligand. The Fe—S bond to the chelated ligand is only 0.035 Å longer than the other three though the Fe—O(H) distance (2.318 Å) reflects a weaker, secondary interaction. Mössbauer spectra displayed separate quadrupole-split doublets for the case of X = OH and SMe but only a single doublet for X = NH_2 suggestive of no secondary bonding in this case.[253] An interesting feature of the Mössbauer results is the high isomer shifts ($\delta > 0.5$ mm s^{-1} at 4.2 K relative to natural Fe) very close to the values found for the P clusters of nitrogenase.[254]

Several other tetranuclear iron–sulfur cluster compounds of general formula $[Fe_4S_4X_4]^{n+,n-}$, in which X is a non-thiolate terminal ligand, have been studied in some detail. These include systems in which X = Cl, η^5-C_5H_5, NO and dithiolene. The structure of the dianion $[Fe_4S_4Cl_4]^{2-}$ has been determined; it exhibits the same cubane-like stereochemistry, distorted from T_d to D_{2d}, found in the corresponding thiolate tetramer dianion, showing that the core structure is rather insensitive to the nature of the terminal ligands.[230] Similar considerations apply to the case of complexes containing the X = η^5-C_5H_5[255,256] or X = $[S_2C_2(CF_3)_2]$[257] terminal ligands. Variations in core dimensions occur, however, according to the overall charge of the core. Thus, the geometry of the parent neutral diamagnetic $[Fe_4S_4(\eta\text{-}C_5H_5)_4]$ complex distorts from tetragonal D_{2d} to orthorhombic D_2 on oxidation (*via* Ag^I, I_2 or Br_2) to the monocation, while, on further oxidation to the dication[258] there is a further distortion of the cube towards a flattened iron tetrahedral structure with four short and two long Fe···Fe distances; this contrasts with the four long and two short bonds in the neutral compounds.[256] Nonetheless, the basic structural features of the core framework remain intact as is nicely illustrated[258,259] by the occurrence of four electrochemically reversible one-electron waves in the cyclic voltammogram (Figure 7) of $[Fe_4S_4(\eta^5\text{-}C_5H_5)_4]^n$ in MeCN corresponding to the couples 3+/2+ through to 0/−1 (equation 12).

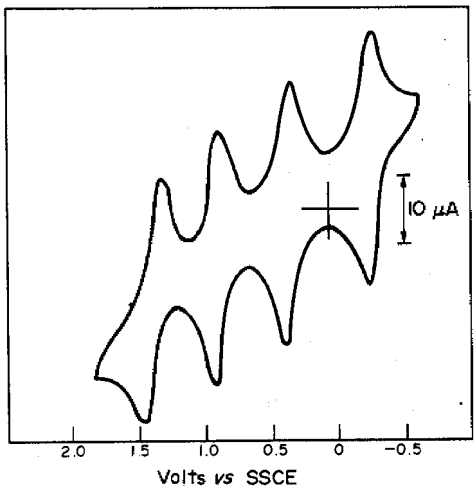


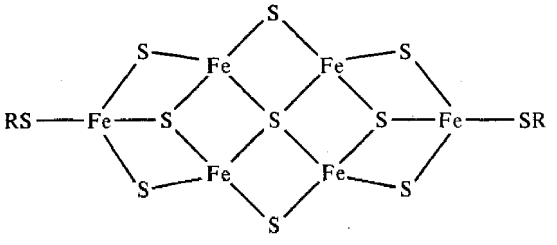
Figure 7 Cyclic voltammogram of $[Fe_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]^{2+}$ in acetonitrile at a platinum bead electrode with a scan rate of 1 V s^{-1}

$$+3 \overset{1.41\,V}{\rightleftharpoons} +2 \overset{0.88\,V}{\rightleftharpoons} +1 \overset{0.33\,V}{\rightleftharpoons} 0 \overset{-0.33\,V}{\rightleftharpoons} -1 \qquad (12)$$

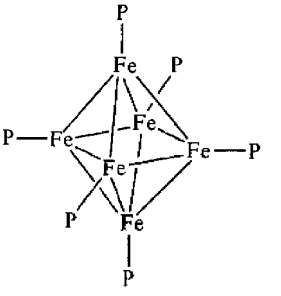
The nitrosyl complex $[Fe_4S_4(NO)_4]$ reveals two reversible 0/−1 and −1/−2 couples in CH_2Cl_2 solution. A structural comparison of the monoanion with the neutral parent again reveals core deformation ($T_d \rightarrow D_{2d}$) on reduction involving changes in Fe···Fe distance within the core. The architectural variations have been rationalized in terms of a cluster bonding model in which the unpaired electron in the monoanion occupies a t_1 level of largely antibonding character.[260] Analogous complexes $[Fe_4S_2(\mu_3\text{-}NCMe_3)_2(NO)_4]^{0,-1}$ in which two of the bridging sulfide ions of the core have been replaced by the electronically equivalent triply bridging *N-tert*-butyl anion, have been described.[261] A different core structure is found in the black Roussin salt $[AsPh_4][Fe_4S_3(NO)_7]$. Here, the anion comprises a trigonal pyramid of four Fe atoms with triply bridging S^{2-} ions and Fe—Fe bonds linking the apical Fe(NO) fragment to each of the three basal $Fe(NO)_2$ moieties.[262]

44.2.6.1.5 Hexanuclear 'Fe–S' systems

The most recent additions to the family of polynuclear iron–sulfur cluster compounds are those having a hexanuclear six-iron core. Two types have been isolated, exemplified by $[Fe_6S_9(SR)_2]^{4-}$ (**49**) (R = Et, Bu^t or SCH_2Ph)[263,256,264] and $[Fe_6S_8(PEt_3)_6]^{2+}$ (**50**).[265] The complexes (**49**) have a delocalized ($4Fe^{III}$, $2Fe^{II}$) mixed valence formulation while paramagnetic (**50**) contains all six metals, formally, in the Fe^{III} oxidation state. Complexes (**49**) were prepared by methods outline in Scheme 2 while (**50**) was prepared by reaction of $Fe(BF_4)_2 \cdot 6H_2O$ and PEt_3 (molar ratio *ca.* 1:3) with H_2S in O_2-free acetone–ethanol at room temperature, followed by a period of air exposure, and, finally, precipitation as the $[BPh_4]^-$ salt.[265] The two complexes have quite different structures. The dication (**50**) is built up of an octahedron of iron atoms with the sulfur atoms triply bridging all octahedral faces; each square pyramidal Fe atom is additionally coordinated by a PEt_3 molecule.[265] The core structure in (**49**) on the other hand contains three different types of bridging sulfur atom, six μ_2-S, two μ_3-S and one μ_4-S. The structure can be regarded as derived from two incomplete $[Fe_4S_4]$ units, each lacking one Fe atom, linked by the common μ_4-S atom.[236,264]



(**49**) The structure of the hexanuclear $[Fe_6S_9(SR)_2]^{3-}$ cluster



(**50**) Each of the eight sulfur atoms triply bridges an octahedral

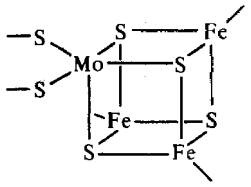
44.2.6.1.6 'Mo–Fe–S' complexes

The isolation by Shah and Brill[266] from nitrogenase enzyme of an iron–molybdenum cofactor (FeMo-co) containing Fe, acid labile S and Mo in the approximate ratio (6–8)Fe:(4–6)S:Mo, believed to be the catalytic site (in a reduced oxidation level) for the reduction of dinitrogen to ammonia, has greatly stimulated attempts to prepare and characterize synthetic compounds containing Mo and Fe together in the same cluster. This goal was given added significance by the recognition from X-ray absorption spectra (XAS) and EXAFS studies[267] of several Fe—Mo proteins that the coordination unit might contain structures such as (**51**) or (**52**), *i.e.* types of cluster very similar to those already well established for Fe—S compounds, and for which synthetic procedures *via* 'spontaneous self-assembly' were available. Application of these synthetic methods, involving the use of $[MoS_4]^{2-}$, known to act as a ligand,[268] as a soluble source of Mo led to the isolation of a series of heteropolynuclear products *via* reactions such as given in equations (13) and (14).[269] Structure determinations[270,271] of crystalline salts of anions (**53**) and (**54**) have confirmed the occurrence in both of the cubane-like $MoFe_3S_4$ unit, one of the proposed structural models for FeMo-co. The two cubane $MoFe_3S_4$ subclusters are linked by different types of bridging unit to afford the so-called 'double cubane' cluster. Other smaller, Fe—Mo—S complexes such as (**55**) and (**56**) have also been prepared.[272,273] The structural similarity of (**52**) to the other proposed model for FeMo-co is obvious. The tungsten analogues of many of these complexes have also been prepared.[274] A significant observation is the occurrence of a spin-quartet ($S = \frac{3}{2}$) type of ESR spectrum in some of the synthetic clusters[273] as also observed in FeMo-co.[275] For a detailed description of the structures, physical properties and reactions of these complexes the review article by Holm,[276] and the references therein, should be consulted.

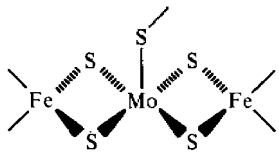
$$2MoS_4^{2-} + 6FeCl_3 + 17RS^- \longrightarrow \underset{(53)}{[Mo_2Fe_6S_8(SR)_9]^{3-}} + 4RSSR + 18Cl^- \quad (13)$$

$$2MoS_4^{2-} + 7FeCl_3 + 20RS^- \longrightarrow \underset{(54)}{[Mo_2Fe_7S_8(SR)_{12}]^{3-}} + 4RSSR + 21Cl^- \quad (14)$$

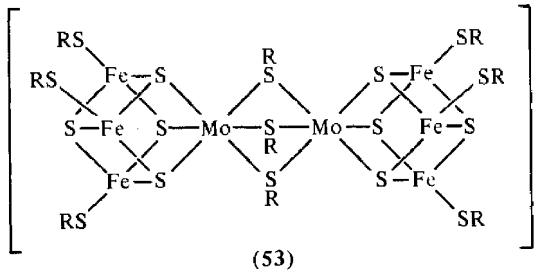
More recently, the preparation of the trianion $[MoFe_4S_4(SEt)_3(cat)_3]^{3-}$ (**57**) (cat = catecholate), which contains a single cubane type $[MoFe_3S_4]$ core, by a cleavage of the Fe^{III}-bridged double cubane $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ (**54**) has been described. The EXAFS spectrum of (**57**) is in qualitative



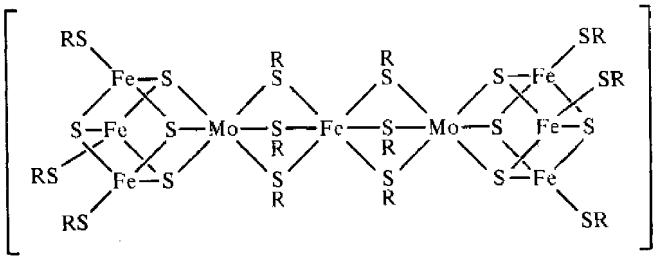
(51)



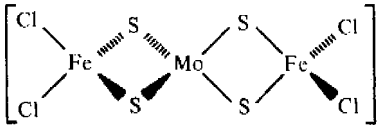
(52)



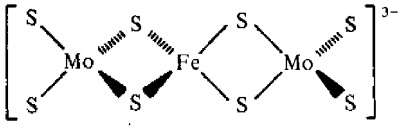
(53)



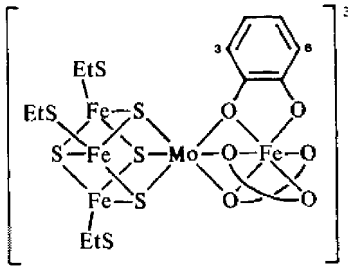
(54)



(55)



(56)

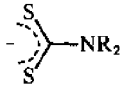


(57)

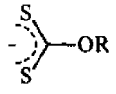
agreement with that of FeMo-co.[277] The electronic properties of single and double $[MoFe_3S_4]$ cubane-type clusters have been compared and contrasted. Oxidized $[MoFe_3S_4]^{3+}$ single cubanes consist of electronically delocalized spin-coupled clusters with $S = \frac{3}{2}$ ground states. In one case, at least, the reduced $[MoFe_3S_4]^{2+}$ cluster has an $S = 2$ ground state. The double cubanes having two Mo—(SR)—Fe bridges exhibit subcluster spin coupling resulting in a singlet ground state while triply bridged double cubanes show weaker subcluster interaction giving an $S = 2$ ground state for each subcluster.[278]

44.2.6.2 Complexes of Dithiocarbamates and Related Ligands

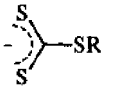
There are a number of negatively charged ligands capable of coordinating *via* two sulfur atoms (or one sulfur and one oxygen atom) to a metal ion with formation of four-, five- or six-membered chelate rings (see structures **58** to **68**). Other modes of coordination, *i.e.* unidentate or bridging, are also known for the same group of ligands. Several reviews are available.[279–286]



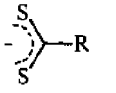
(58) Dithiocarbamate



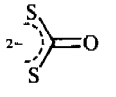
(59) Xanthate



(60) Thioxanthate



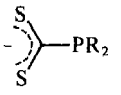
(61) Dithiocarboxylate



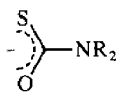
(62) Dithiocarbonate



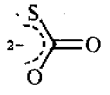
(63) Trithiocarbamate



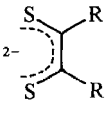
(64) Dithiophosphinate



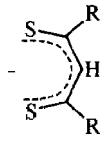
(65) Monothiocarbamate



(66) Monothiocarbonate



(67) Dithiolate

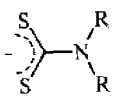


(68) Dithio-β-diketonate

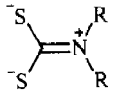
The iron(III) dithiocarbamates are the most extensively studied, largely because of their interesting magnetic properties. Cambi and co-workers[287] first showed that tris(dialkyldithiocarbamato)-iron(III) displayed spin cross-over phenomena between high-spin and low-spin states. As indicated earlier (Figure 1) Fe^{III} in a weak octahedral field has a $^6A_{1g}$ ($t_{2g}^3e_g^2$) ground term and gives rise, in the absence of magnetic interactions with other paramagnetic centres, to magnetic moments close to the spin-only value of 5.92 BM ($S = \frac{5}{2}$). In a strong field, on the other hand, the term $^2T_{2g}$ (t_{2g}^5) lies lowest and in this case room temperature moments are commonly close to about 2.0 BM corresponding to the presence of one unpaired electron in the t_{2g} orbital set, *i.e.* $S = \frac{1}{2}$. The difference between the observed moment and the spin-only value of 1.73 BM arises from small contributions from the non-zero value of the orbital contribution of the angular momentum in the t_{2g}^5 configuration. In practice, deviations from standard high- or low-spin behaviour in magnetically dilute systems can arise whenever the ligand field is comparable in strength with the mean electron-pairing energy appropriate to the Fe^{III} d^5 configuration. In cases where the energy of the high-spin state lies only slightly (from *ca.* 50 to *ca.* 400 cm^{-1}) above that of the low-spin state there will be a thermally controlled population of the two states which will be manifested by a temperature dependent magnetic moment between the limiting values of 5.9 BM at high temperatures and 2.0 BM at low temperatures.

Temperature dependent magnetic susceptibility measurements of several tris-*N*,*N*-dialkyldithiocarbamate complexes have been successfully interpreted in these terms.[288–291] However, only in the case of solutions can a simple Boltzmann distribution between high- and low-spin states be expected.[292] This is because of complicating secondary solid state effects such as vibrations in crystal packing, solvation and, in certain cases, the existence of the complex in more than one crystal modification leading to phase changes on temperature variation. Mössbauer effect studies[293] show only one, averaged, temperature dependent quadrupole-split doublet. The failure to observe separate signals due to the two spin states has been attributed to high-spin $\rightleftharpoons$ low-spin cross-over periods shorter than the Mössbauer timescale (1.5×10^{-7} s). The same applies to NMR shifts. Also, Hall and Hendrickson[294] demonstrated, from ESR measurements, that the spin-flipping rate is of the order of 10^{10} s^{-1}. It should be noted, however, that separate signals for the two spin isomers could be detected in the Mössbauer spectra of some tris(monothio-β-diketonato)iron(III) complexes, indicating slower exchange in the case of this unsymmetrical chelating ligand.[295]

It has been observed that the position of the $^6A_1 \rightleftharpoons {}^2T_2$ equilibrium in dithiocarbamate complexes $[Fe(S_2CNR_2)_3]$ is quite sensitive to the nature of the NR_2 substituent.[290] As is apparent from the collected data in Table 3 the room temperature magnetic moments shift in favour of the $^2T_2$ state as the NR_2 groups change from the cyclic pyrrolidyl group of *N*,*N*-di-*n*-alkyl, to *N*-alkyl, *N*-aryl, to *N*,*N*-di-*sec*-alkyl. It has been suggested that this trend may have a steric origin since the RNR angle is expected to increase in the same order leading in turn, to an increased contribution of resonance form (**70**), compared to (**69**), this having the stronger ligand field. However, other workers[296] have argued that limiting structure (**70**) will have the lower field and that its importance will increase with increase in electron releasing ability of the NR_2 group. In agreement with this argument an increase in μ_{eff} with increase in pK_a of the secondary amine was observed, except for those amino groups having a secondary carbon atom. The exceptional position of these systems in the correlation was explained in terms of non-coplanarity of the CS_2 and NR_2 planes. It was further observed[290] that xanthates $[Fe(S_2COR)_3]$ are almost completely in the low-spin form while dithiophosphinates $[Fe(S_2CPR_2)_3]$ (R = OMe, OEt, OPr^n, OPr^i) are almost completely high-spin in the 90–300 K temperature range. The magnetic properties of diselenocarbamato complexes are very similar to those of corresponding thio compounds but with the position of the spin equilibrium shifted towards the low-spin state in most examples.[297] The thioxanthates, in contrast to xanthates, also appear to be examples of spin equilbrium systems.[298]



(69)



(70)

Table 3 Magnetic Moments in Solid and Solution Phases at 23°C of the Complexes $[Fe(S_2CNR_2)_3]$

	μ_{eff} (BM) as Solid	μ_{eff} (BM) in Solution[a]
NR_2 = pyrrolidyl	5.83	5.82 (B)
NR_2 = piperidyl	4.01	4.16 (C)
NR_2 = morpholyl	5.12	—
R = Me	4.17	4.20 (C)
Et	4.24	4.41 (B, C)
Pr^n	4.48	4.42 (B)
Bu^n	5.32	4.34 (B)
isoamyl	4.30	4.57 (B)
n-hexyl	3.52	4.42 (B)
allyl	4.40	4.34 (B)
R_1, R_2 Me, Ph	2.99	3.33 (C)
Et, Ph	4.70	3.63 (C)
Pr^n, Ph	4.68	3.55 (B)
Am^i, Ph	3.36	3.43 (B)
dibenzyl	4.02	3.60 (B)
di-*sec*-alkyl Pr^i	2.62	2.32 (B)
Bu^i	3.02	2.88 (B, C)
cyclohexyl	2.75	2.63 (C)

[a] B = Benzene, C = Chloroform.

Since it can be predicted that depopulation of the (high-spin) sextet level in favour of the (low-spin) doublet level should be accompanied by a contraction of the $[FeS_6]$ core in spin transition systems, it is to be expected that the position of the spin equilibrium K will depend on pressure. This has been experimentally verified for several tris(dithiocarbamato)iron(III) complexes in chloroform solution at pressures up to 5000 atmospheres at room temperature. On the assumption that the molecular volume contraction ΔV arises entirely as a result of the spin change, equation (15) can be applied to the calculation of the volume change. Values of ΔV of the order of $5\,cm^3\,mol^{-1}$ were obtained for systems with a wide variety of N substituents.[289,290] The values correspond to a contraction of the Fe—S bond length of about 0.1 Å, during the ${}^5A \rightarrow {}^2T$ transition.

$$\Delta V = -RT\left(\frac{\delta \ln K}{\delta P}\right)_T \tag{15}$$

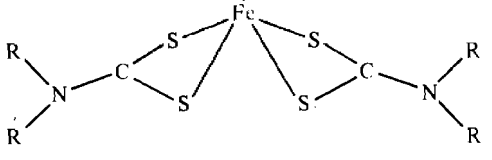
Crystallographic confirmation of this effect has been obtained, first by Hoskins and Kelly[299] and subsequently by Healy and White.[300] In the complex $[Fe(S_2CNBu^n_2)_3]$ which is largely in the high-spin form at room temperature ($\mu_{eff} = 5.32$ BM) the mean Fe—S bond length is 2.42 Å whereas in the xanthate complex $[Fe(S_2COEt)_3]$, largely in the low-spin form ($\mu_{eff} = 2.72$ BM at 296 K), the mean Fe—S distance is 2.32 Å. The same difference of 0.1 Å in mean Fe—S distance was observed between the high-spin ($\mu_{eff} = 5.9$ BM at 300 K) tris(*N*-pyrrolidyldithiocarbamate) and the mainly low-spin ($\mu_{eff} = 3.0$ BM at 300 K) *N*-methyl-*N*-phenyl derivative. In addition, there are certain alterations in the overall symmetry of the coordination polyhedron as a consequence of the spin change. Thus, the high-spin dithiocarbamate with Bu^n as substituent has a structure intermediate between trigonal prismatic and octahedral, whereas in the low-spin xanthate the structure is closer to octahedral.[299] In $[Fe(S_2CNEt_2)_3]$ the Fe—S distance changes from 2.357 Å at 297 K ($\mu_{eff} = 4.3$ BM) to 2.306 Å at 79 K ($\mu = 2.2$ BM) but in this case crystal packing is also different at these two temperatures.[301]

The contraction in Fe—S bond length accompanying the ${}^6A \rightarrow {}^2T$ spin change is also reflected in a change in the Fe—S stretching frequencies. With the aid of ^{54}Fe and ^{57}Fe isotopic substitution the assignment of ν(Fe—S) vibrations in the regions 210–240 cm^{-1} and 300–340 cm^{-1} for high- and low-spin forms, respectively, has been made.[302]

The ${}^6A_1 \rightleftharpoons {}^2T_2$ spin transition in dithiocarbamatoiron(III) complexes is sensitive not only to temperature, pressure and chemical modification but also to the number and nature of solvent

molecules included in the lattice structure.[290,303] With solvents such as benzene and nitrobenzene the equilibrium is shifted towards a low-spin ground state while in solvents such as H_2O, $CHCl_3$ and CH_2Cl_2 capable of hydrogen bonding the equilibrium is shifted towards the high-spin state. Although the symmetry of six-coordinate tris(dithiocarbamato)iron(III) complexes is that of a trigonally distorted octahedron rather than pure octahedral, the distortion would seem to be too small for a component, $^4A_2$ to ^4E, of the split $^4T_1$ ($t_{2g}^4 e_g$) level to become the ground state. However, it was speculated[303] that this might occur in the case of the CH_2Cl_2 solvate of tris(morphoinyldithiocarbamate)iron(III) whose magnetic moment appeared not to fall below values (~4 BM) appropriate to a spin quartet ground state even at very low temperatures. However, a subsequent detailed Mössbauer examination of this system by the same group,[304] and by others,[305] has shown conclusively that only sextet and double states are involved.

Treatment of the tris(dialkyldithiocarbamato)iron(III) complexes in benzene with a controlled amount of concentrated hydrohalic acid affords the black bis(ligand) complexes $[FeX(S_2CNR_2)_2]$ (X = Cl, Br or I).[306] For X = Cl the complexes may also be prepared by irradiation of the tris(ligand) complex in a halogenated solvent. This free radical reaction is believed to proceed *via* excited-state labilization of one ligand followed by attack of solvent.[307] Analogous complexes of pseudohalide ions (X = NCO^-, NCS^- or $NCSe^-$) have been obtained from reaction of the parent tris complex with the appropriate Ag^+ salt.[380] Representative complexes of this class have been shown by X-ray diffraction methods to have square pyramidal structures (**71**) in which the sulfur atoms of the two bidentate ligands comprise the basal plane (Fe—S ~ 2.228–2.30 Å) with the halide ion in the apical position (Fe—Cl ~ 2.26–2.28 Å).[309,310] In the cases examined the metal atom sits ~0.6 Å out of the mean S_4 plane in the direction of the apical halide ion.



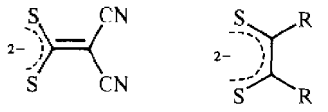
(71)

While for the tris(dithiocarbamate) complexes the symmetry is not sufficiently distorted from cubic to generate a spin-quartet ground state ($S = \frac{3}{2}$), this is no longer true for the square pyramidal bis(complexes) and these exhibit nearly temperature independent magnetic moments close to 3.9 BM corresponding to three unpaired electrons (Figure 1). ESR and magnetic anisotropy data are consistent with a $^4A_2$ ground state.[306,310] Large quadrupole splittings ($\Delta E \approx 2.7\ mm\ s^{-1}$) are consistent with the large electric field gradient at the iron nucleus expected for the C_{2v} point symmetry.[311]

Fe^{III} dithiocarbamates $[Fe(dtc)_3]$ undergo reversible or nearly reversible one-electron oxidations and one-electron reductions in polar organic solvents to generate Fe^{IV} and Fe^{II} species, respectively (equation 16). The bright yellow air-sensitive Fe^{II} complexes appear to be high spin while the Fe^{IV} systems (*vide infra*) have low-spin d^4 configurations.[282b]

$$[Fe^{IV}(dtc)_3]^+ \rightleftharpoons [Fe^{III}(dtc)_3] \rightleftharpoons [Fe^{II}(dtc)_3]^- \qquad (16)$$

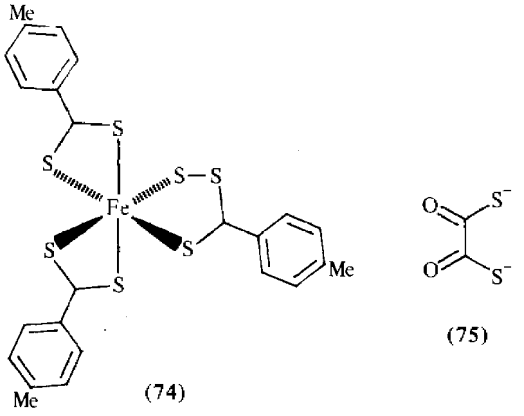
1,1-Dicyanoethylene-2,2-dithiolate (**72**), which like the dithiocarbamates forms four-membered chelate rings, gives tris complexes with Fe^{III} which are high spin ($S = \frac{5}{2}$) with, presumably, six-coordinate structures.[312] The geometrical isomer 1,2-dicyanoethylene-1,2-dithiolate (**73**; R = CN) and related dithiolenes give five-membered chelate rings and form Fe^{III} complexes with a variety of structures and properties. The $[PPh_4]^+$ salt of $[Fe\{S_2C_2(CN)_2\}_3]^{3-}$ is low spin.[313] The bis complexes $[Fe\{S_2C_2(CN)_2\}_2]_2^n$ are dimeric in the solid state and constitute an electron transfer series with $n = 0$, -1 and -2. The structure of $[NBu_4]_2[Fe\{S_2C_2(CN)_2\}_2]_2$ has been determined. Each Fe atom has a square pyramidal geometry in which the basal plane contains four sulfur atoms (of two bidentate dithiolene anions) the apical position being occupied by a bridging sulfur atom of a second monomer unit. The magnetic properties are consistent with antiferromagnetically coupled $S = \frac{1}{2}$ spins.[314] The dimeric bis(dithiolene) complexes are cleaved by various monodentate bases to afford complexes of the type $[Fe(S_2C_2R_2)_2B]^-$. Those complexes in which B is a 'soft' ligand such as PPh_3, $AsPh_3$ RNC or CN^- have doublet ground states, while those where B is *e.g.* amine, phosphine oxide, halide or N_3^-, exhibit quartet ground states.[315]



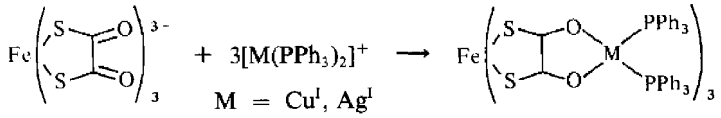
(72) (73)

The low-spin complex [Fe(*p*-tol CS_2)$_2$ (*p*-tol CS_3)] contains two four-membered chelate rings and one five-membered chelate ring (**74**) involving the metal–disulfide linkage. Fe—S distances in the five-membered chelate ring are slightly smaller than in the four-membered ring, while the S···S 'bite' distance is distinctly larger, as in dithiolene complexes.[316]

The dithiooxalate ion (**75**) binds to metal ions *via* the sulfur atoms, and the tris complexes with Fe^{III} may be low- or high-spin depending on the charge distribution within the ligand. Thus when the low-spin (μ_{eff} = 2.30 BM at 300 K) complex $[Ph_4As]_3[Fe(dto)_3]\cdot 3MeNO_2$ (**76**) was treated with the cations $[M(PPh_3)_2]^+$ M = Cu^I or Ag^I (reaction 17), the crystalline high-spin complexes (**77**) were obtained ($\mu_{eff} \simeq$ 5.9 BM).[317] Although the dithiooxalates show some electrochemical activity they are not subject to the same extensive electron delocalization which is a prominent feature of the dithiolenes; they are thus closer in properties to the thioxanthates in this respect.



(74) (75)



(76) (77) (17)

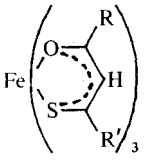
Six-membered chelate rings are found in complexes of dithioacetylacetonate (SacSac). [Fe(Sacac)$_3$] may be obtained in crystalline form by reaction of Fe^{II} salts with acetylacetone and H_2S in acidified alcohol. The 'FeS_6' unit is a slightly distorted octahedron, two of three ligands being related by a two-fold symmetry axis with the third inequivalent ligand subtending a larger S—Fe—S angle. The mean Fe—S distance is 2.25 Å in good agreement with values found in other low-spin dithio chelates, and, as before, the metal–chelate rings are essentially planar. The low-spin nature of this complex inferred from magnetic susceptibility measurements (μ_{eff} = 2.00 BM at 293 K, 1.75 BM at 100 K) is confirmed by the large values of the quadrupole spitting (1.96 mm s^{-1} at 4.2 K) in the Mössbauer spectrum. A rhombic character is apparent from the observation of three g values in the ESR spectrum of the powder (g_1 = 2.14, g_2 = 2.09, g_3 = 2.01).[318]

The spin-pairing effect of sulfur as a donor atom is nicely illustrated by a comparison of the magnetic properties of the series of complexes [Fe(acac)$_3$], [Fe(Sacac)$_3$] and [Fe(SacSac)$_3$]. Thus, while the first has a high-spin ground state and the last is essentially fully low-spin, the asymmetrical 'O,S' ligand Sacac forms both high- and low-spin complexes (**78, 79**) depending on the nature of the ligand substituents. Thus, for R = R^1 = Ph the room temperature moment is 5.50 BM, while for R = CF_3, R^1 = Ph, it is 2.31 BM. A trigonal antiprismatic rather than trigonal prismatic arrangement of the *fac*-O_3S_3 donor set is seen in the values of the twist angles ϕ(52° in **78**, 60° in **79**) of the two parallel triangles defined by the three oxygen and the three sulfur donor atoms.[319]

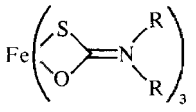
There is a marked difference, for systems of comparable spin state, between the Fe—S bond lengths of four-membered chelate rings and those of six-membered chelate rings. The values of

~2.41 and ~2.32 Å found for high- and low-spin dithiocarbamates and xanthates are significantly larger than the values of 2.36 and 2.25 Å observed for (**78**) and (**79**).[319]

Complexes of the monothiocarbamate anion (R_2mtc) promise to have a coordination chemistry as rich as that of the dithiocarbamates and are the subject of a recent review.[284] The tris bidentate arrangement of ligands found in the six-coordinate dithiocarbamates is also found in the monothiocarbamates. In the complex [Fe(mtcMe$_2$)$_3$] the twist angle ϕ between the triangle formed by the three sulfur atoms and the parallel triangle formed by the three oxygen atoms was found to be 33.2°, *i.e.* intermediate between that ($\phi = 0°$) for a trigonal prismatic arrangement and that ($\phi = 60°$) for an trigonal antiprismatic (pseudooctahedral) arrangement, similar to the situation found in most analogous dithiocarbamato iron(III) complexes.[320] The two complexes (**80**) and (**81**) are also $^6A \rightleftharpoons {}^2T$ spin-equilibrium systems between 6 and 300 K although the former can also be obtained in a crystalline modification that remains high-spin down to 10 K. Mössbauer spectra at low temperatures indicate that the $^6A \rightleftharpoons {}^2T$ interconversion rates are $> \sim 10^7 s^{-1}$. A single ESR signal at $g = 4.3$ probably arises from rhombically distorted high-spin Fe^{III} isomers.[321]



(78) R = R′ = Ph
(79) R = CF_3, R′ = Ph



(80) R = Me
(81) R = Et

44.2.7 HALIDE COMPLEXES

In keeping with the 'hard' or 'class a' nature of the Fe^{3+} ion the most stable complexes are formed with the small non-polarizable F^- ion.[322] Consecutive formation constants for some fluoro and chloro complexes in aqueous solution may be found in ref. 322. Bromo complexes are even less stable than chloro complexes while with the easily oxidizable I^- ion no stable simple iodides have been prepared although a very few complexes containing Fe^{III}—I bonds are known in combination with other ligands. Consistent with the stability order $F^- > Cl^- > Br^-$ is the occurrence of higher coordination number Fe^{III} complexes with F^- than with Br^-. Thus, while F^- readily forms hexacoordinate $[FeF_6]^{3-}$ complex ions and no tetrafluoro complex ions, Cl^- forms both $[FeCl_6]^{3-}$ and $[FeCl_4]^-$ while Br^- apparently does not form a stable hexabromo complex $[FeBr_6]^{3-}$.

The anhydrous binary halides FeX_3 (X = F, Cl or Br) have near regular octahedral coordination as reflected in the absence of resolved splitting in the Mössbauer spectra (isomer shifts 0.49–0.55 mm s^{-1}). The hexahydrate, $FeCl_3 \cdot 6H_2O$, however, has a *trans* octahedral arrangement $[Fe(H_2O)_4Cl_2]Cl \cdot 2H_2O$ and exhibits pronounced quadrupole splitting.[27,323] The dihydrate and heptahydrate of pentafluorodiiron, $Fe_2F_5 \cdot 2H_2O$ and $Fe_2F_5 \cdot 7H_2O$ are Fe^{II}, Fe^{III} mixed valence systems. The structure of the red dihydrate has been determined.[324] It consists of a three-dimensional network with distinct Fe^{II} and Fe^{III} sites. The formally Fe^{III} ions occupy vertex-sharing 'FeF_6' octahedra while the Fe^{II} sites in '$Fe(H_2O)_2F_4$' share the vertex positions of the fluoride equatorial plane. The Fe^{III}—F and Fe^{II}—F distances are 1.941 and 2.060 Å, respectively. The structure is ferromagnetically ordered below 48 K but above this temperature distinct quadrupole-split absorptions for the two sites are apparent showing that this is a class II[40] mixed-valence compound.[325] The yellow heptahydrate, on the other hand, is formulated as $[Fe^{II}(H_2O)_6][Fe^{III}F_5(H_2O)]$ and therefore as a class I mixed-valence system.

A number of tetra-, penta- and hexa-fluoride anions are known, the last mentioned being the most important.[326] The tetra- and penta-fluorides have reduced magnetic moments and are probably polymers with fluoride bridges;[327] the hexafluorides containing the discrete $[FeF_6]^{3-}$ have magnetic moments close to 5.90 BM at room temperature.[328] The complex $K_2[FeF_5(H_2O)]$ also consists of discrete six-coordinate anions with one F^- ion replaced by a water molecule, although the anions are linked into chains by strong hydrogen bonds (O···F, 2.54 Å).[329]

A large number of complexes containing the tetrahedral $[FeCl_4]^-$ anion have been prepared; some have already been mentioned. Several single crystal X-ray structure determinations are available. Among the most accurate are those of $[AsPh_4][FeCl_4]$,[330] $[PCl_4][FeCl_4]$[311] and $[Fe(NCMe)_6][FeCl_4]_2$.[332] Fe—Cl distances (2.182–2.187 Å) agree well among the different structures although there are small departures in Cl—Fe—Cl angle from the tetrahedral value in some cases.

The complex of stoichiometry $(NMeH_3)_2FeBr_5$ should be formulated as $[NMeH_3]_2[FeBr_4]Br$ since it contains the tetrahedral $[FeBr_4]^-$ complex anion; mean Fe—Br distances are 2.32Å while the Br—Fe—Br angles vary up to 4° from the true tetrahedral value.[333] It has also been shown[334] that the complex of formula $(pyH)_3Fe_2Cl_9$ contains only the $[FeCl_4]^-$ ion and not the triply chloride-bridged dinuclear $[Fe_2Cl_9]^{3-}$ anion as first supposed; the complex should thus be formulated as the mixed salt $[pyH]_2[FeCl_4]_2 \cdot [pyH]Cl$.

The complete series of complexes $[NEt_4][FeX_{n-4}Y_n]^-$ (X = Cl, Y = Br, n = 0–4) has been synthesized and the far IR and Mössbauer spectra reported. The vibrational spectra are consistent with the lowering of the molecular symmetry from T_d to C_{3v} and from T_d to C_{2v} (Table 4). The reduction in symmetry is not reflected in the Mössbauer spectra, however, since a narrow unbroadened single peak was observed in all the spectra.[335]

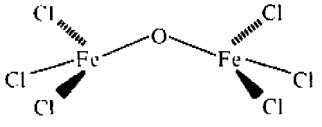
Table 4 IR and Mössbauer data[a] for $[Fe^{III}X_{(4-n)}Y_n]^-$ anions

Anion	*ν(Fe—X)* (cm^{-1})	*δ(X—Fe—X)* (cm^{-1})	*Isomer Shift at 77 K* ($mm\,s^{-1}$)
$[FeCl_4]^-$	388	137	0.282
$[FeCl_3Br]^-$	391, 350, 296	135, 117	0.285
$[FeCl_2Br_2]^-$	385, 348, 296, 266	126, 225, 74	0.321
$[FeClBr_3]^-$	384, 295, 270	120, 73	0.333
$[FeBr_4]^-$	294	98	0.350

[a] Data from ref. 335.
[b] Relative to natural iron.

The hexachloroferrate(III) anion $[FeCl_6]^{3-}$ may be stabilized in the solid state by the use of large cations such as $[Co(NH_3)_6]^{3+}$, $[Co(pn)_3]^{3+}$ (pn = 1,3-diaminopropane) and $[NMeH_3]^+$. Magnetic moments lie in the accepted range for high-spin ($S = \frac{5}{2}$) octahedral configurations as do the Mössbauer spectra also which consist of a single absorption at *ca.* $+0.5\,mm\,s^{-1}$ (*vs.* natural iron).[336] The vibrational spectra[337] and optical spectra[336] have been assigned.

Slow evaporation of aqueous solutions of $FeCl_3 \cdot 6H_2O$ and *e.g.* NH_4Cl or KCl affords salts of the six-coordinate $[FeCl_5(H_2O)]^{2-}$ anion. Single crystal Raman studies have been reported for this ion.[338] Several other complexes, in which one or more of the chlorides of $[FeCl_4]^-$ or $[FeCl_6]^{3-}$ have been replaced by other ligands, have been described and structurally characterized. The μ-oxo dinuclear complex $[pyH]_2[Cl_3Fe—O—FeCl_3] \cdot py$ (**82**) contains distorted tetrahedral '$FeOCl_3$' units bridged by the oxygen atom *via* short Fe—O bonds (1.755 Å), the Fe—O—Fe angle being 155.6°. The Cl—Fe—Cl and Cl—Fe—O angles are in the range 108–111° and the Fe—Cl distances (2.208–2.219 Å) are somewhat lengthened with respect to those in $[FeCl_4]^-$. As expected for the local C_{3v} symmetry about each Fe^{III} atom two IR active Fe—Cl stretching vibrations, *e* and a_1, are observed, at $360\,cm^{-1}$ and $311\,cm^{-1}$. Strong absorption at $860\,cm^{-1}$ is assigned to the Fe—O—Fe antisymmetric stretch. Strong antiferromagnetic coupling occurs between the $S = \frac{5}{2}$ spins. The coupling constant ($J = -92\,cm^{-1}$) is not appreciably different from values reported for other binuclear μ-oxo complexes in which the Fe^{III} ions are in a square pyramidal or octahedral environment. This is the first example of a binuclear Fe^{III} complex containing, apart from the bridge, only monodentate ligands, and the first example of a μ-oxo Fe^{III} complex having tetrahedral coordination.[339]



(82)

The complex $[Fe(4\text{-}CN\text{-}py)_2Cl_3]$ (4-CN-py = 4-cyanopyridine) is a trigonal bipyramid with the three Cl atoms occupying the equatorial sites and the pyridine ring nitrogens the axial positions.[340] This is one of a very few structurally defined trigonal pyramidal Fe^{III} complexes. An earlier example, $[Fe(N_3)_5]^{2-}$, has already been mentioned;[48] the complex $FeCl_3$(diox) (diox = dioxane) may have a similar geometry.[341]

The molecular structure of the dimeric species $[Fe_2Cl_6]$ has been investigated by vapour phase electron diffraction. The two tetrahedral Fe^{III} atoms are bridged by two Cl atoms in a puckered Fe_2Cl_2 ring. As for related dimeric molecules such as $[Al_2Cl_6]$ the terminal Fe—Cl bonds (2.127 Å) are significantly stronger than the bridging Fe—Cl bonds (2.326 Å).[342]

44.2.8 COMPLEXES OF MIXED DONOR ATOM LIGANDS

44.2.8.1 Complexes of Schiff Base Ligands

In this section complexes of acyclic Schiff base ligands only are considered, macrocyclic Schiff base complexes are included in a later section.

Condensation reactions (equation 18) between carbonyl compounds and primary amines have provided one of the most important and widely studied classes of chelating ligand. A particularly important carbonyl precursor for the synthesis of Schiff base ligands is salicyaldehyde first used by Pfeiffer and Tsumaki.[343] A wide variety of ligand types may be obtained *via* the Schiff base condensation reaction which vary in denticity, flexibility, nature of donor atoms (in addition to nitrogen and oxygen) and in electronic properties. Some of the more important classes of ligand derived from salicyaldehyde are shown, in the anionic (deprotonated) form, in Figure 8. Within each class subtle alterations in coordinating characteristics can be achieved by variation in the nature of the R substituents and in the nature and position of the phenyl ring substituents. A wide diversity of coordination geometries and magnetic behaviour has been found.

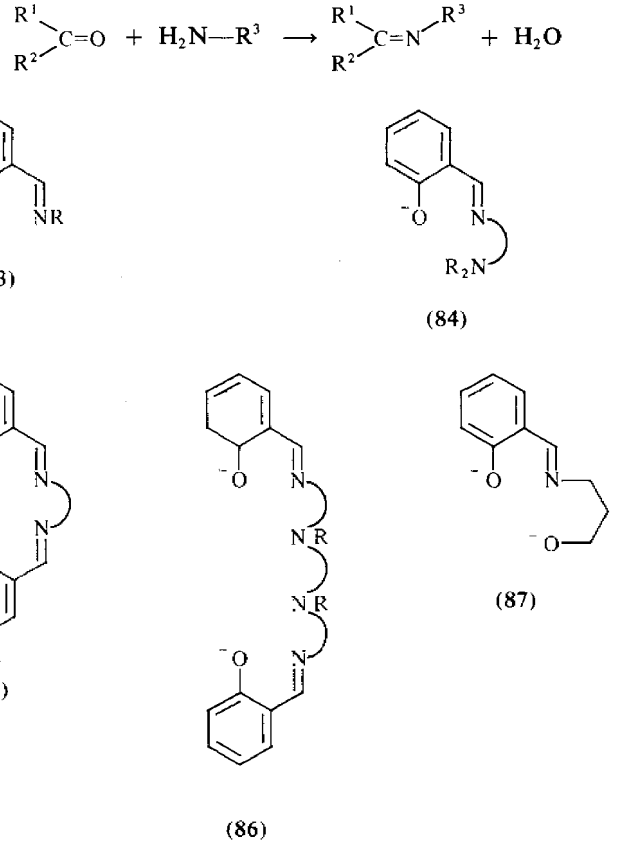


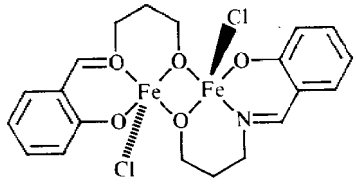
Figure 8 Some important classes of Schiff base ligands derived from salicylaldehyde

The bidentate *N*-substituted salicyaldimines (**83**) form complexes of stoichiometry $[Fe(salNR)_2X]$ (X = Cl or Br) which have high-spin ($S = \frac{5}{2}$) monomeric five-coordinate structures.[344] An X-ray investigation of the R = *n*-propyl, X = Cl derivative indicated a stereochemistry intermediate between trigonal bipyramidal and square pyramidal.[345] The derivative with R = 2-phenylethyl, X = Cl apparently exists in two crystalline modifications, one having a monomeric trigonal bipyramidal structure,[346] the other having a distorted structure intermediate between a trigonal bipyramid and a square pyramid which allows a loose association between adjacent monomer units.[347] This weak association leading to a phase change to a six-coordinate modification is suggested to be responsible for the reduction in magnetic moment, from the normal high-spin value, at temperatures below 140 K.

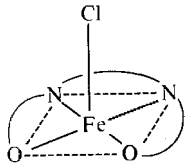
The complex $[Fe(salpa)Cl_2]_2$, where salpa is the tridentate dianionic ligand of type (**87**) formed from the reaction of salicyaldehyde with 3-aminopropanol, also contains five-coordinate Fe^{III} but, this time, in a genuinely dimeric structure (**88**). The iron atoms of the dimer are bridged by the

alkoxide oxygens to form a four-membered ring with Fe—O distances of 1.983 and 1.934 Å and angles of 75.9° and 104.1° at iron and oxygen, respectively. Considering the geometry as (distorted) square pyramidal the basal plane is made up of the donors of the tridentate ligand and the bridging alkoxide oxygen with the chlorine atom in the apical position. The magnetic behaviour accords with the occurrence of antiferromagnetic superexchange interaction mediated by the dialkoxy bridge, μ_{eff} having the reduced value of 4.52 BM at room temperature and falling further to 2.37 BM at liquid nitrogen temperature.

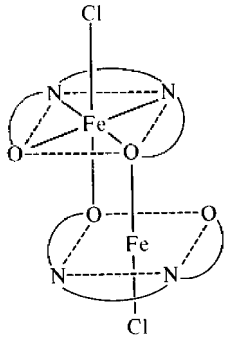
Reaction of $[Fe(salpa)Cl]_2$ with Na_2O_2 afforded the red crystalline complex $[Fe_2(salpa)(salpaH)_2]$·toluene in which salpaH is the monomeric form of the tridentate ligand.[348] In this dinuclear complex each Fe^{III} atom is six-coordinate and linked to the other *via* bridging propoxide groups in, once again, an almost planar four-membered Fe_2O_2 ring. Despite having nearly identical distorted octahedral geometries (with *trans* nitrogen atoms) the iron atoms are nevertheless non-equivalent. One iron atom is coordinated by two doubly deprotonated tridentate salpa ligands, the two propoxide groups which are in *cis* positions providing the bridging atoms for the dimeric unit. The second iron atom is coordinated by the two monodeprotonated salpaH ligands each acting in a bidentate fashion with uncoordinated OH groups. As in the dimeric five-coordinate complex described, the Fe^{III} centres are antiferromagnetically coupled with the coupling constant being in the range -5 to $-10\,cm^{-1}$.



(88)



(89)

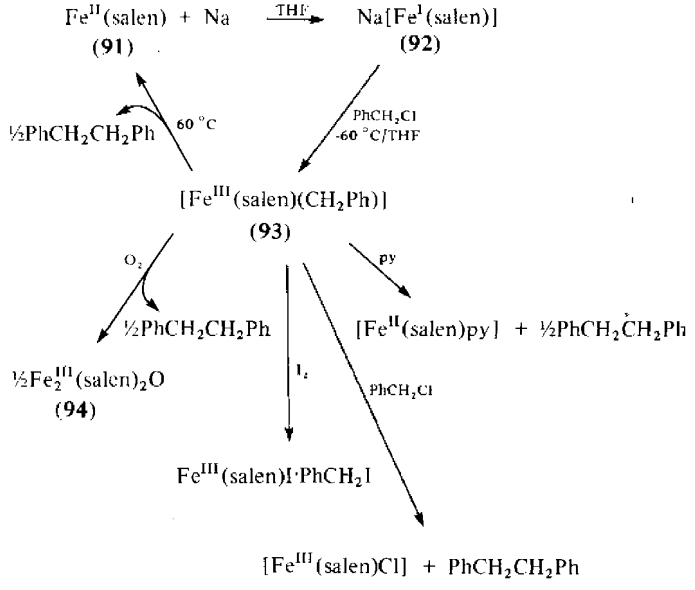


(90)

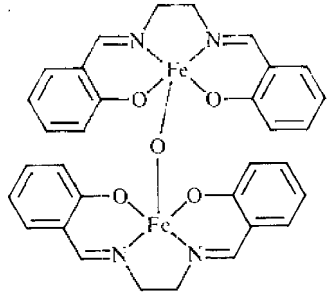
Condensation of two equivalents of salicyaldehyde with a diprimary amine, commonly 1,2-diaminoethane (en), provides a convenient route to tetradentate Schiff base ligands of type (**85**). For the case where the amine is en the product ligand is abbreviated as salen. Different modifications of the complex of formula Fe(salen)Cl may be obtained according to the method of preparation or isolation, one monomeric and one dimeric.[349] The monomeric form (**89**), obtained by recrystallization of the dimeric form from nitromethane and containing a molecule of solvent in the lattice, has a square pyramidal structure with the metal atom sitting ~0.46 Å above the best plane defined by the 'N_4O_2' donor set of the tetradentate ligand, in the direction of the apical Cl atom.[350] In the dimer (**90**), isolated from acetone solution, two molecules of monomer each share one oxygen atom from each salen ligand to give an overall octahedral coordination for each metal ion.[351] The bridging Fe—O bond, *trans* to the Fe—Cl bond, in the dimer is 0.24 Å longer than the mean of the Fe—O bonds in the N_4O_2 planes and may reflect the tendency for the dimer to dissociate into monomers in chloroform solution. The monomeric and dimeric Fe(salen)X (X = Cl or Br) complexes, and various ring substituted derivatives are readily distinguished on the basis of their magnetic properties.[349] The monomers have magnetic moments at room temperature close to the spin-only value of 5.92 BM and obey the Curie–Weiss law with small Weiss constant. The dimers, on the other hand, have subnormal room temperature moments which are further reduced on decrease in temperature. In these cases the magnetic data have been successfully fitted to the theoretical equation describing antiferromagnetic superexchange between pairs of interacting $S = \frac{5}{2}$ spins, yielding coupling constants J of between -6.5 and $-8.0\,cm^{-1}$ in different cases. IR and Mössbauer spectra also provide useful criteria for the recognition of monomeric and dimeric forms of Fe(salen)X complexes. Those compounds known or suspected to be dimeric displayed up to three bands between 800 and 900 cm^{-1}, while in compounds believed to be mononuclear a single band was observed in this region. Similarly Mössbauer isomer shifts and quadrupole splittings both tended to be smaller for the five-coordinate (mononuclear) complexes than for the six-coordinate (dinuclear) complexes.[352]

The preparation and properties of some unusual organometallic Fe^{III} complexes of salen have been described by Floriani and Calderazzo.[353] It was found that the iron(II) complex (**91**) can be reduced to the corresponding monoanion (**92**) by sodium in THF. The extremely air-sensitive

monoanion, believed to be a high-spin Fe^{I} d^7 species, behaves as a strong nucleophile and reacts at $-60°$ with benzyl chloride to give (**93**) (see Scheme 3), a rare example of a compound containing an Fe^{III}—carbon σ bond. This complex has a high-spin ($S = \frac{5}{2}$) configuration as evidenced by the magnetic moment of 5.87 BM at room temperature and presumably has a mononuclear square pyramidal structure similar to that of the mononuclear form of Fe(salen)Cl. The complex (**93**) is both thermally unstable and O_2 sensitive (Scheme 3) leading to reduction to Fe(salen) and oxidation to the μ-oxo complex (**94**), respectively, along with dibenzyl. The Fe—C bond is also cleaved by Lewis bases such as pyridine and cyclohexyl isocyanide and by reaction with benzyl chloride and I_2 (Scheme 3).



Scheme 3 Preparation and reactions of organometallic iron(III) complexes



(**94**)

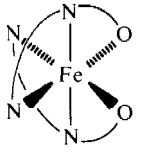
A second series of dinuclear Fe^{III}–salen complexes [Fe(salen)O_2] (**94**) has been extensively investigated[354–357] following Pfeiffer and Tsumaki's first report.[343] These complexes have five-coordinate structures, in contrast to the six-coordinate [Fe(salen)Cl]$_2$ dimers, in which the two approximately square 'FeN_2O_2' moieties are linked by a single oxygen bridge. In two solvate modifications the Fe—O—Fe bridge angle has been shown[354,355] to be 139° and 142°. A much larger antiferromagnetic coupling occurs in the singly-bridged μ-oxo compounds than in the doubly oxygen-bridged [Fe(salen)Cl]$_2$ dimers already discussed, J having values in the range of -87 to $-100\,cm^{-1}$ for various members of the former class. Various possible reasons for the different exchange interactions can be considered. Firstly the Fe—O distances (1.97–1.98 Å) are appreciably shorter in the μ-oxo complex than those (1.92–2.18 Å) in [Fe(salen)Cl]$_2$. This would suggest a measure of multiple bonding in the former, possibly allowing transmission of exchange coupling *via* π as well as σ pathways. There is also a large difference in Fe—O—Fe angle in the two systems. Since a ferromagnetic interaction is predicted when the bridge angle is close to 90° it may be that the relatively small net antiferromagnetism in [Fe(salen)Cl]$_2$ is a result of the small Fe—O—Fe angles ($\sim 95°$) in this case. The products of reaction of [Fe_2(salen)$_2$O] with trichloroacetic, trifluoroacetic, salicylic and

picric acids are dimers of composition $[Fe(salen)X]_2$, where X is the conjugate base of the acid HX, with magnetic properties very similar to those of $[Fe(salen)Cl]_2$. A monomeric compound is formed on reaction with picolinic acid, however.

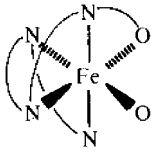
The reduced form of salen, salen-H, in which the two imino groups have been hydrogenated, also forms a dimeric complex $[Fe(salen\text{-}H)Cl]\cdot 2H_2O$ believed[358] to have a similar phenoxy-bridged six-coordinate structure to that of the parent Schiff base complex $[Fe(salen)Cl]_2$. However, this ligand gives a di-μ-hydroxo dimer $[Fe(salen\text{-}H)(OH)]_2\cdot 2H_2O\cdot 2py$ rather than a μ-oxo dimer and, as expected for a 'FeO_2Fe' bridging unit in which the bridge angles are relatively small (102.8° in this case), the superexchange coupling ($J = -10.4\,cm^{-1}$) is relatively weak.[359]

44.2.8.1.1 Spin-crossover iron(III)–Schiff base complexes

Several examples of high-spin ($S = \frac{5}{2}$) $\rightleftharpoons$ low-spin ($S = \frac{1}{2}$) systems have already been encountered in the section dealing with dithiocarbamato and related ligands. Iron(III) complexes of the tridentate and hexadentate Schiff base ligands of types (**84**) and (**86**) constitute new families providing many examples of spin crossover.[360–366] The bis(tridentate) and mono(hexadentate) ligand complexes both contain the metal ion in a distorted octahedral geometry, FeN_4O_2 core, in which the two terminal oxygen atoms occupy *cis* positions and the remaining four nitrogens (two *cis* amines and two *trans* imines) complete the coordination sphere structures (**95**) and (**96**). These complexes may be high-spin or low-spin depending on the nature and position of substituents, counterions, lattice solvent and even geometrical isomerism. In addition, the position of the spin equilbrium and the nature of the transition is significantly influenced by pressure and often by grinding[366] of the solid. Structures of several complexes of this class, in both spin states, are now available.[361–363] It is of particular interest to examine the effects of the spin change on bond lengths and other structural parameters. It has been observed, for example, that the average Fe–ligand bond length is longer by about 0.12 Å in the high-spin complex ($\mu_{eff} = 5.75$ BM at room temperature) $[Fe(X\text{-}salmeen)_2]PF_6$ (X = 5-OMe, salmeen = *N*-methylethylenediaminesalicylaldiminato anion, *i.e.* R = Me in structure **84**) than in the predominantly low-spin complexes where X = 3-OMe ($\mu_{eff} = 3.20$ BM) or X = 5-NO_2 ($\mu_{eff} = 2.58$ BM). However, the bond length difference is not uniform, the Fe—N bonds varying much more (~0.16 Å) than the Fe—O bonds (~0.02 Å).[363] Closely similar effects are also observed for complexes of the hexadentate ligands (**86**).[361] The $^2T \rightleftharpoons {}^6A$ spin equilibria are dependent on the nature of ring substituent X and, for solids, on the nature of the counterion. NO_2 as substituent favours the low-spin form while OMe as substituent favours the high-spin form relative to the parent unsubstituted complex. In solution the position of the spin equilibrium is solvent dependent. The effect of solvent is interpreted largely as arising from a specific hydrogen-bonding interaction of the solvent with the N—H groups of the trien backbone.[360] The $[Fe(X\text{-}sal)_2\ trien]^+$ complexes exhibit a reversible one-electron electrochemical reduction. From the temperature dependence of the half-wave potentials for the reduction it has been possible to determine the electron-transfer entropy change (ΔS_{et}) and to compare with this the entropy change (ΔS_{sc}) associated with the spin equilibrium. It was found that while ΔS_{sc} is almost constant for different systems, ΔS_{et} shows a considerable dependence on the high- and low-spin isomer populations, becoming larger as the low-spin fraction increases.[364] The question as to whether spin crossover occurs before (equation 19) or after (equation 20) electron transfer was approached by measurement of heterogeneous electron transfer rates. Results obtained strongly point to an overall electron transfer mechanism that involves spin conversion of Fe^{III}, prior to electron transfer, *i.e.* equation (19) and not equation (20).[365]



(95)



(96)

$$[Fe^{III}{}_{ls}(t_{2g}{}^5) \overset{SC}{\rightleftharpoons} [Fe^{III}{}_{hs}(t_{2g}{}^3 e_g{}^2)] \overset{e^-}{\rightleftharpoons} [Fe^{II}{}_{hs}(t_{2g}{}^4 e_g{}^2)] \quad (19)$$

$$[Fe^{III}{}_{ls}(t_{2g}{}^5)] \overset{e^-}{\rightleftharpoons} [Fe^{II}{}_{ls}(t_{2g}{}^6)] \overset{SC}{\rightleftharpoons} [Fe^{II}{}_{hs}(t_{2g}{}^4 e_g{}^2)] \quad (20)$$

Both ultrasonic and laser Raman temperature jump techniques have been applied to the measurement of the spin state interconversions (equation 21) in solution.[361–369] On the basis of measurements on a range of complexes it was concluded that intersystem crossing rates are faster in solution than in the solid state, as judged from Mössbauer spectra, and faster for the bis complexes of the tridentate ligands than for those of the hexadentate ligands. Data pertaining to some differently substituted $[Fe(X\text{-salmeen})_2]^+$ complexes are in Table 5.[367]

$$^2T \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^6A \tag{21}$$

Table 5 Equilibrium Constants (K_{eq}), Relaxation Times (τ) and Intersystem Crossing Rate Constants (k_1, k_{-1} in Equation 21) For Some $[Fe(X\text{-salmeen})]^+$ Complexes in Acetone/Methanol Solution[a]

X	$K_{eq}(T)$[b]	τ(s × 10⁹)	$k_1(s^{-1})$	$k_{-1}(s^{-1})$
H	1.31 (20)	9	7.1×10^7	5.4×10^7
3-OMe	2.79 (25)	8	9.2×10^7	3.3×10^7
4-OMe	1.67 (19)	11	5.7×10^7	3.4×10^7
5-OMe	0.72 (−7)	9	4.6×10^7	6.4×10^7
3-NO_2	0.34 (21)	8	3.2×10^7	9.3×10^7
5-NO_2	0.18 (22)	7	2.2×10^7	1.2×10^8

[a] Data from ref. 367. [b] K_{eq} = [hs]/[ls] at temperature T in °C in parenthesis.

A limited number of Fe^{III} complexes with sulfur-containing Schiff base ligands derived from thiosalicylaldehyde have been prepared. Among these is the complex $[\{Fe(tsalen)\}_2O]\cdot py$ obtained from reactions of the Fe^{II} complex Fe(tsalen) with O_2 (tsalen is the sulfur analogue of the tetradentate ligand salen). Like the salen complex the sulfur analogue also contains a μ-oxo linkage and a square pyramidal arrangement for each Fe(tsalen)O unit. The Fe—O—Fe bond angle is 159°, *i.e.* somewhat larger than in corresponding salen complexes but within the range of bond angles found in Fe^{III}—O—Fe^{III} complexes generally. A point of difference between $[\{Fe(salen)\}_2O]$ and $[\{Fe(t\text{-}salen)\}_2O]$ is that while the metal ions in the 'oxygen' ligand complex are in the $S = \frac{5}{2}$ state and strongly coupled, in the 'sulfur' complex the Fe^{III} ions are $S = \frac{1}{2}$ and weakly coupled. Low-spin Fe^{III} also occurs in the bis complexes of the tridentate ligand (tsaleten), the sulfur analogues of ligand type **(84)**.[368–370]

44.2.8.2 Complexes of Aminocarboxylates, Amino Acids and Related Ligands

The polydentate anions of the polyamine-polycarboxylic acids are well known to form stable high coordination number complexes with a wide range of metal ions. Edta is, of course, the best known. In the complexes $Li[Fe(edta)(H_2O)]\cdot 2H_2O$ and $Rb[Fe(edta)(H_2O)]\cdot H_2O$ the hexadentate edta tetraanion and one H_2O molecule provide the seven donor atoms for a pentagonal bipyramidal coordination shell for each Fe^{III} ion.[371] In $[Fe(edtaH)(H_2O)]$ the coordination number of the metal ion is six since one carboxylic acid group of the ligand is protonated and uncoordinated.[372] The complex $Ca[Fe(DCTA)(H_2O)]_2$ contains seven-coordinate Fe^{III} (DCTA = *trans*-1,2-diaminocyclohexane-*N*,*N*′-tetraacetate).[373] The coordination numbers of the central Fe^{III} atom in the chelates of diethylenetriaminepentaacetic acid H_5DTPA and several of its salts are variable, six in the complex of the parent acid, seven in the mono $[NH_4]^+$ salt and eight in the dialkali metal salts.[374]

The dimeric complex $[Fe_2(edta)_2O]^{4-}$ is formed by base hydrolysis of the mononuclear complexes.[375] The X-ray structure of the related complex $[enH_2][Fe_2(Hedta)_2O]\cdot 6H_2O$ has been determined (Hedta = *N*-hydroxyethylenediaminetriacetate). Each Hedta ligand is pentadentate and the two Fe(Hedta) moieties are linked by a near linear (165°) Fe—O—Fe bridge.[376] As found for other μ-oxo bridged di-Fe^{III} complexes already mentioned, these complexes are also antiferromagnetically coupled with $J \approx -95\,cm^{-1}$. The complexes also exhibit a series of ligand field bands of enhanced intensity in the visible region and a number of higher energy absorptions which have been assigned to simultaneous pair electronic excitations arising from coupled LF transitions.[375]

44.2.8.2.1 Hemerythrin and model compounds

An important group of naturally occurring amino acids complexes of iron are the hemerythrins —the oxygen-carrying proteins in a variety of marine worms. Most hemerythrins have molecular

weights of about 108 000 and consist of eight subunits each of which contains a binuclear iron active site. As a result of the application of modern physical methods such as EXAFS, resonance Raman and Mössbauer spectroscopy, as well as crystallographic studies, together with conventional chemical and biochemical studies, a very useful picture of the nature of the active site in hemerythrin has now emerged.[377]

The oxidation states present in the different forms of hemerythrin are indicated in Figure 9. The colourless deoxy form reversibly binds O_2 in the ratio of $2Fe:O_2$ to give the burgundy coloured oxy form. In addition, an oxidized met form containing only Fe^{III} but no O_2 may be obtained as well as a mixed valence semi-met form [Fe^{III}, Fe^{II}]. Assignment of oxidation states originally based on chemical reactions[378] has been amply confirmed by spectroscopic[379–382] measurements. Moreover, the presence of a μ-oxo bridge between the metal centres in the oxy and met forms of the protein became apparent from magnetic studies and from Mössabuer,[380] optical and vibrational spectra. The exchange coupling constants J of $-134\,cm^{-1}$ for met hemerythrin and of $-77\,cm^{-1}$ for oxyhemerythrin[383] are not too different from the range of values of -90 to $-130\,cm^{-1}$ found in synthetic compounds containing μ-oxo linkages. These structural conclusions have been confirmed by various crystallographic studies[384,385] of the met and azidomet forms, the latest of these being carried out at 2.0 Å resolution. In the met form one of the two iron atoms is octahedrally coordinated while the second iron atom is in a highly distorted trigonal bipyramidal environment. In addition to the μ-oxo bridge the metal centres are also linked by the carboxylate groups of glutamate and aspartate groups. Remaining coordination sites are taken by nitrogen atoms from histidine residues of the amino acid side chains (Figure 10). Addition of azide converts the five-coordinate centre in met hemerythrin to octahedral with accompanying minor changes in bond lengths and angles and conformational changes in the protein. Although there is some disagreement between X-ray and EXAFS studies in relation to bond angles and distances, the main geometrical features of the oxy and met forms of the protein appear well established.

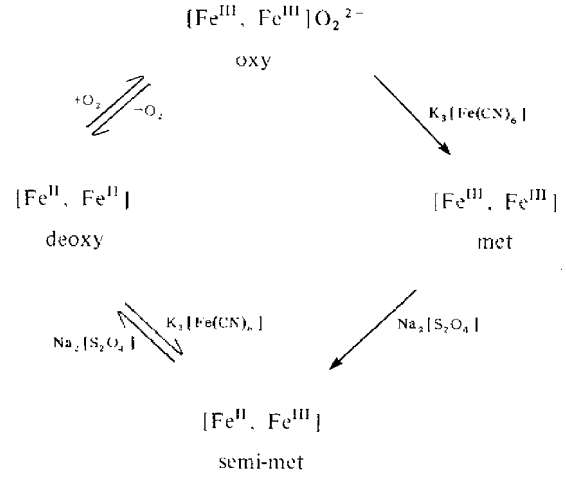


Figure 9 Interconversion of different forms of hemerythrin

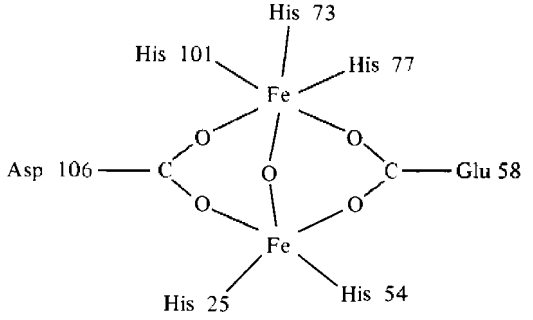


Figure 10 The coordination of the two Fe^{III} ions in met hemerythrin

A (μ-oxo)bis(μ-carboxylato)diiron(III) core in a model for met hemerythrin has been prepared by spontaneous 'self-assembly' in aqueous solutions of iron(III) perchlorate, sodium acetate and sodium tri-1-pyrazolylborate.[386] The resulting binuclear complex was shown to be very similar in structure and properties to that of met hemerythrin. Thus, the two Fe^{III} atoms are linked *via* a μ-oxo

bridge (Fe—O—Fe = 123.5°) and two μ-acetato bridges, the remaining coordination sites being filled by the tridentate pyrazolylborate ligands. Antiferromagnetic behaviour with $J = -122\,cm^{-1}$ compared well with that ($J = -134\,cm^{-1}$) for metaquo hemerythrin.[386]

EXAFS spectra[387] of the deoxy[Fe^{II}, Fe^{II}] form of hemerythrin suggest the absence of the μ-oxo bridge, in agreement with the lack of antiferromagnetic coupling. Analysis of the data suggests that on conversion of oxy- to deoxy-hemerythrin (equation 22) the bound O_2 is replaced by OH^- and the short bond to the bridging oxygen atom is broken, leaving it bound to one iron. Thus, one iron becomes five-coordinate while the other remains six-coordinate.

$$[Fe^{III}—O—Fe^{III}—O_2] + H_2O \rightleftharpoons [Fe^{II}—OH, Fe^{II}—OH] + O_2 \quad (22)$$

Of central interest in the chemistry of hemerythrin is the mode of interaction of O_2 with the binuclear Fe^{III} active site. Several structural models (**97–101** in Figure 11) have been considered, all incorporating a peroxido diiron(III) formalism, as required by the resonance Raman identification of ν(O—O) at 844 cm^{-1}, and its displacement to 796 cm^{-1} on $^{18}O_2$ isotopic substitution.[388] The use of unsymmetrically labelled dioxygen, $^{16}O^{18}O$, has been of service in discriminating between the symmetrically bound O_2 adducts (**97**), (**98**) and (**101**) and the asymmetric models (**9**) and (**100**). For the former a single symmetric O—O stretch would be expected whereas ν(O—O) should be a doublet if either of the unsymmetrical structures (**99**) or (**100**) is the correct one. The RR results obtained strongly favour the unsymmetrical structure (**99**) or (**100**).[389] In fact, structure (**100**) in which the peroxo group is terminally bound to one Fe^{III} centre, taking the place of the azide ligand in metazido hemerythrin, is the preferred structural candidate on present knowledge.

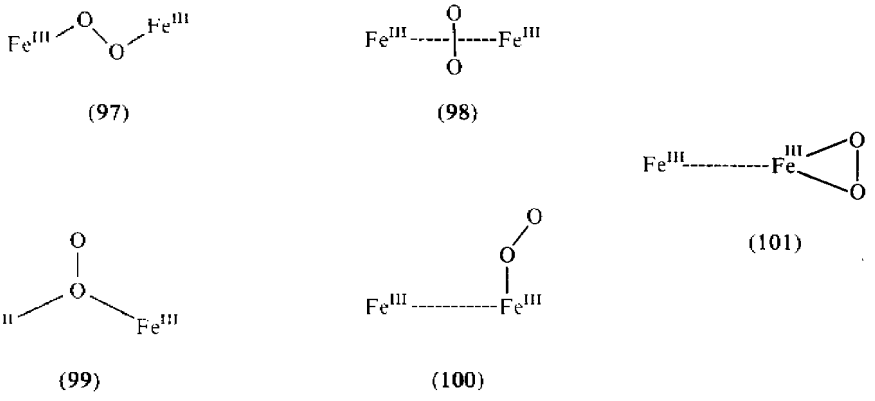


Figure 11 Idealized structural representations for the $Fe_2 \cdot O_2$ active site in hemerythrin

44.2.9 MACROCYCLIC LIGANDS

Complexes of large ring compounds containing a set of suitably positioned donor atoms—macrocyclic ligands—have engaged the attention of chemists for a long time but particularly over the last two decades. A major stimulus for the study of macrocyclic compounds has been the desire to mimic and probe the function of certain metal ions in natural systems where they are known to be ligated to macrocyclic molecules. These include, of course, the well-known porphyrin and corrin rings containing a planar array of four nitrogen atoms. Iron(III) complexes of porphyrins will be considered in a later section. We first consider some iron(III) complexes of synthetic macrocylic ligands.

44.2.9.1 Synthetic Macrocyclic Ligands

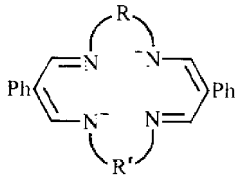
Nearly all iron complexes of synthetic macrocyclic ligands contain nitrogen either as the only ligand atom or as the major donor present. Moreover, most macrocyclic ligands are tetradentate usually presenting a roughly planar 'N_4' donor set to the centrally complexed metal ion. The comprehensive review by Melson[390] of the coordination chemistry of macrocyclic compounds should be consulted for work published up until 1978.

Iron(III) complexes of tetradentate 'N_4' macrocyclic ligands may be five-coordinate (square pyramidal) or six-coordinate (approximately octahedral), and high-spin ($S = \frac{5}{2}$), intermediate spin

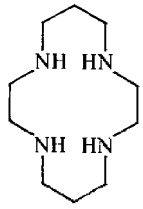
($S = \frac{3}{2}$) or low-spin ($S = \frac{1}{2}$), depending on the nature of the macrocyclic ligand, *i.e.* its size and degree of unsaturation, and on the number of the axial ligands.

Examples of iron(III) complexes displaying all three ground states within the same family of macrocycles are found among complexes of the 14-, 15- and 16-membered ligands (**102**), (**103**) and (**104**).[391] The five-coordinate complexes $[Fe^{III}N_4X]$ have the intermediate ($S = \frac{3}{2}$) spin ground state when the macrocycle is 14- or 15-membered and where X = halide or carboxylate, whereas analogous compounds of the 16-membered macrocycle (**104**) are high spin ($S = \frac{5}{2}$). For the case of X = thiolate, all three spin states were found: *viz.* [14]-SPh, $S = \frac{1}{2}$; [15, 16]-SPh, $S = \frac{3}{2}$; [16]-SCH_2Ph, $S = \frac{5}{2}$. The results demonstrate the effects of ring size and axial ligand on spin state (Table 6).

The spin state of the six-coordinate complexes $[Fe(cyclam)X_2]^+$ [cyclam = 1,4,8,11-tetraazacyclotetradecane (**105**)] is governed by the geometrical configuration of the 14-membered macrocycle, being high-spin for the *cis* complexes and low-spin for the *trans* complexes. However, *trans*-$[Fe(cyclam)Br_2][ClO_4]$ with $\mu_{eff} = 3.90$ BM at 295 K may exist in a high-spin $\rightleftharpoons$ low-spin equilibrium.[392]



(**102**) R = R′ = $(CH_2)_2$
(**103**) R = $(CH_2)_2$, R′ = $(CH_2)_3$
(**104**) R = R′ = $(CH_2)_3$



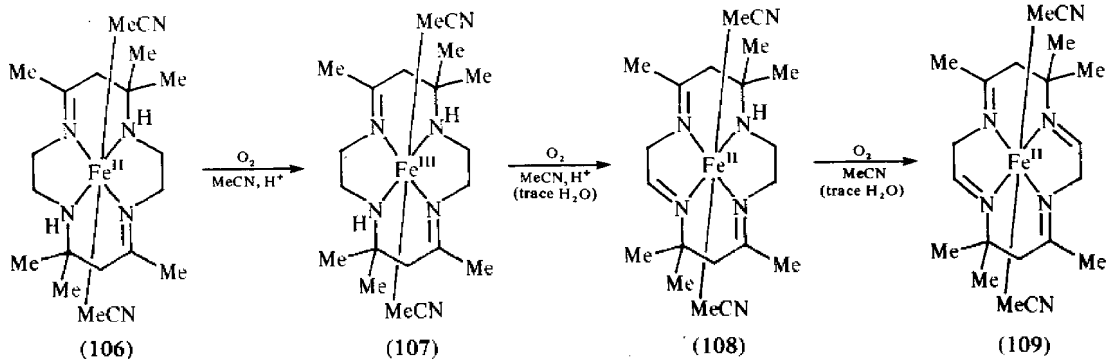
(**105**)

Table 6 Magnetic and Mössbauer Data[a] for Fe^{III} Complexes $[FeN_4SR]$ of Tetradentate Macrocyclic Ligands (**102**)–(**104**)

Complex	*Spin State*	μ_{eff}(BM)	*Isomer*[b] *Shift* δ(mm s^{-1})	*Quadrupole Splitting* ΔE_Q(mm s^{-1})
[Fe(**102**)(SPh)]	$S = \frac{1}{2}$	1.95	0.04	3.60
[Fe(**103**)(SPh)]	$S = \frac{3}{2}$	3.94	—	—
[Fe(**104**)(SPh)]	$S = \frac{1}{2}$	4.17	0.26	1.93
[Fe(**104**)(SCH_2Ph)]	$S = \frac{5}{2}$	5.88	0.35	0.71

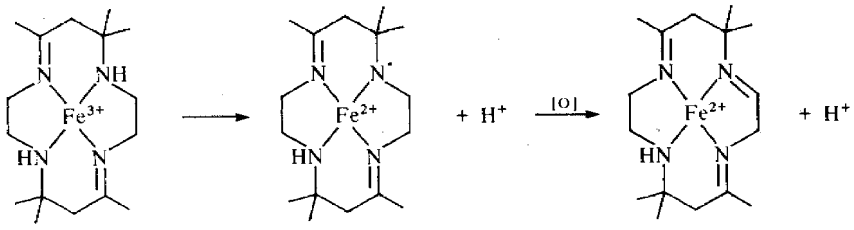
[a] From ref. 391. [b] Relative to iron metal.

Iron has been found to be very effective in promoting the oxidative dehydrogenation of secondary amine groups bound to the metal as part of a macrocyclic ligand generating new macrocyclic complexes having higher degrees of unsaturation.[393–395] One example is the preparation of, successively, the triimine complex (**108**) and the tetraimine complex (**109**) from the diimine complex (**106**) (see Scheme 4). Atmospheric oxygen readily performs the oxidation under the influence of Fe^{III}, while stronger oxidizing agents are generally required in the case of nickel or copper complexes. Although reactant and product complexes contain the metal ion in the +2 oxidation state there seems little doubt that a first step in the oxidative dehydrogenation is an oxidation of Fe^{II} to Fe^{III}, this being followed by an electron transfer, with accompanying deprotonation, from the coordinated secondary amine group to Fe^{III}. Oxidation of the radical so formed then generates the new imine centre (Scheme 5).[393] The intermediate iron(III) complex [Fe([14]4,11-diene-N_4)$(MeCN)_2$][ClO_4]$_3$ (**107**) has been isolated. This, and other derivatives containing coordinated Cl^- or NCS^- in place of MeCN, are low-spin ($\mu_{eff} = 2.15$–2.30 BM).[394]



(**106**) (**107**) (**108**) (**109**)

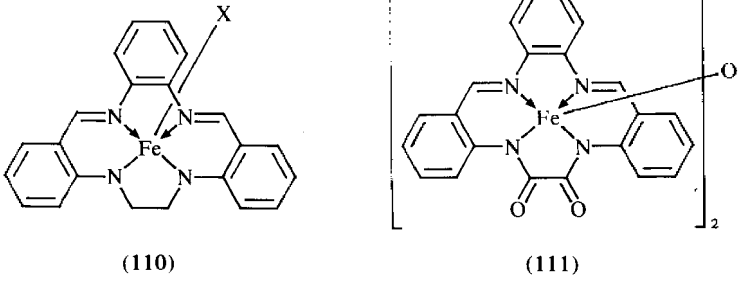
Scheme 4 Proposed pathway for the generation of triimine and tetraimine complexes *via* oxidative dehydrogenation



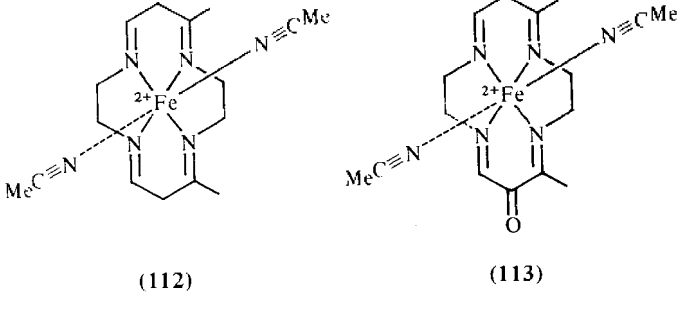
Scheme 5 Proposed radical mechanism for the iron-promoted oxidative dehydrogenation of a coordinated secondary amine group[393]

An interesting Fe^{III}-mediated macrocyclic ligand *oxygenation* has been observed.[396] When the Fe^{III} complex (**110**; X = $MeCO_2$) in DMF was heated for 6 h at 80°C black needles were slowly deposited. X-Ray analysis revealed that the product is the μ-oxo dimer (**111**) in which the —N—CH_2—CH_2—N— bridge of the reactant macrocyclic has been oxidized to the oxamido ligand. It was suggested that this oxidation also proceeds *via* a radical mechanism in which the initial step is elimination of acetic acid and generation of an Fe^{II} radical species.

Ligand oxygenation (**112** → **113**) of Fe^{II} complexes of bis(β-diimine) macrocycles by molecular oxygen has also been observed. Again, an Fe^{III}-mediated radical mechanism has been suggested for this oxidation.[397]



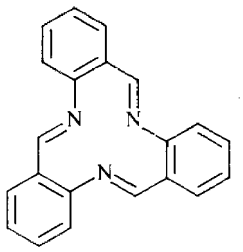
(**110**) (**111**)



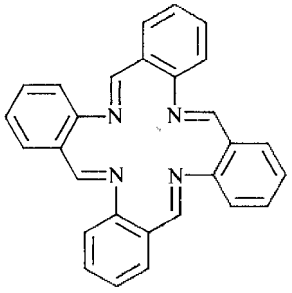
(**112**) (**113**)

Many of the synthetic macrocyclic ligands have been synthesized by metal ion template methods. One of the best examples is provided by the self-condensation reactions of *o*-aminobenzaldehyde.[390,398] In the absence of metal ions, *o*-aminobenzaldehyde gives a variety of polycyclic structures. In the presence of certain metal ions complexes of the tridentate macrocycle (**114**) and/or of the tetradentate macrocycle (TAAB) (**115**) may be obtained. Among those in the latter category are the dinuclear Fe^{III} complexes $[Fe_2(TAAB)_2O]X_4 \cdot 4H_2O$ (X = ClO_4 or NO_3) (**116**) and the mononuclear complexes $[Fe(TAAB)F]X_2 \cdot 2H_2O$. Magnetic and other properties have established μ-oxo structures for the binuclear complexes, with the expected strong antiferromagnetic coupling ($J = -65$ to $-111\ cm^{-1}$). The μ-oxo bridge is cleaved, with difficulty, by acid fluoride to generate the low-spin mononuclear species. An interesting reaction of the μ-oxo dimers is that with methoxide ion giving complexes (**117**) of the new dianionic ligand formed by nucleophilic addition of the OMe^- to two imine bonds.[398]

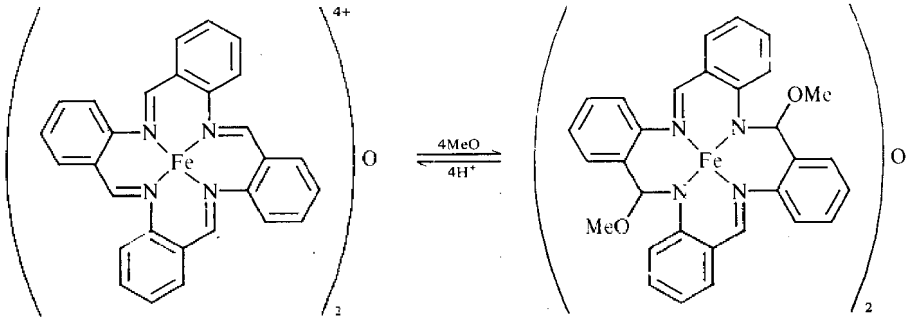
An early demonstration of the template effect in the synthesis of macrocyclic ligands was the metal-ion-controlled cyclic condensation of 2,6-diacetylpyridine with 3,3′-diaminodipropylamine to give complexes of the 14-membered 'N_4' ring (**118**), usually abbreviated (Me_2pyo[14]triene N_4).[399] Effective template ions include Ni^{II}, Co^{II} and Cu^{II}. Well-characterized iron complexes have not been

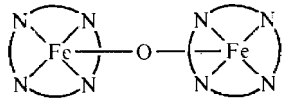


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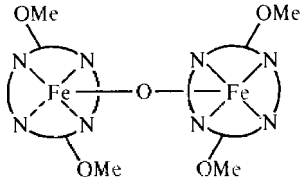


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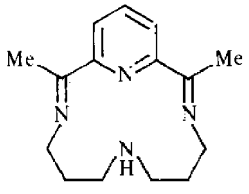


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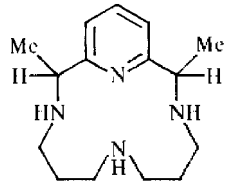


(117)

obtained. However, the two C=N bonds of (**118**) may be hydrogenated to afford the macrocycle (**119**), Me_2pyo[14]ene N_4, which can exist in *meso* and racemic forms. Fe^{III} derivatives of the *meso* ligand have been prepared. These have the formula $[Fe(Me_2pyo[14]ene N_4)X_2]Y$ (X = Cl or Br; Y = ClO_4 or BF_4) and, on the evidence of the magnetic properties and Mössbauer spectra, are assigned low-spin six-coordinate structures. They show excellent catalytic activity for the decomposition of H_2O_2 in aqueous acid solution.[400]



(118)

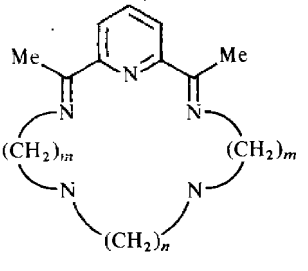


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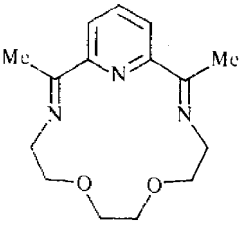
Extension of the metal ion template method to condensations between 2,6-diacetylpyridine with other linear polyamines has proven successful in many cases. Thus, for example, Fe^{III} salts are effective templates for the synthesis of the pentadentate macrocycles (**120**), (**121**) and (**123**) denoted (222-N_5), (232-N_5) and (222-N_3O_2), respectively, but not for the (323-N_5) macrocycle (**122**).[401–403] The template action of the metal ion was evidenced by the fact that in its absence the products of reaction were oils or gums, indicative of an oligomeric or polymeric constitution. Such materials showed IR in bands at $\sim 1700\,cm^{-1}$ and/or $\sim 3300\,cm^{-1}$ indicating the presence of unreacted keto and/or primary amine groups. In contrast, in the presence of an equimolar quantity of Fe^{III} salt, crystalline high-spin complexes of stoichiometry $[Fe(mac)X_2]Y$ (X = *e.g.* Cl, Br, I or NCS; Y = ClO_4, NO_3, BF_4, BPh_4 or PF_6) were obtained from acid solutions. In basic media antiferromagnetically coupled

dinuclear complexes containing μ-oxo bridges are obtained. In both series of complexes, mononuclear or binuclear, the pentadentate macrocyclic ligand maintains an approximately planar array of donor atoms around the central metal ion. Two monodentate ligands above and below this pentagonal plane complete the pentagonal bipyramidal geometry of the complexes. Single crystal structure determinations of $[Fe(222\text{-}N_5)(NCS)_2][ClO_4]$[402,404], $[Fe(232\text{-}N_5)(NCS)_2][ClO_4]$[402] and $[Fe_2(222\text{-}N_5)_2(ClO_4)_2O][ClO_4]_2\cdot H_2O$[404] have been carried out. Cyclic voltammetry has shown that the mononuclear Fe^{III} complexes undergo two one-electron processes in acetonitrile solution. The more positive (reversible) process can be ascribed to the Fe^{III}/Fe^{II} couple, and the more negative reduction (reversible at fast scan speeds) corresponds to the formation of a ligand radical anion, *i.e.* addition of an electron to the lowest antibonding orbital of the conjugated pyridyl–diimino system. The Fe^{III}/Fe^{II} couple occurs in the range $+0.3$ to -0.4 V *vs.* SCE depending somewhat on the nature of the axial ligands as well as on the particular macrocyclic ligand. The values of the couples suggested that the Fe^{II} complexes should have reasonable stability to oxidation. In agreement with this prediction crystalline Fe^{II} complexes of all three macrocycles could be prepared by dithionite reduction.[405] Structural studies and various physical properties have established the retention of the basic pentagonal bipyramidal structure on reduction. Despite the differences in size of Fe^{3+} and Fe^{2+} there is little change in the average Fe—N(macrocycle) bond length on change of oxidation state. What does occur, however, is a movement of the metal closer to the unsaturated (trimethine) segment of the macrocycle on reduction.[406] This is attributed to a measure of metal-to-macrocycle back coordination in the lower oxidation state. The apparent instability of the Fe^{III} complex of the 17-membered 'N_5' macrocycle (**122**) is presumably a consequence of a mismatch in size between metal ion and macrocycle cavity in this case. Mössbauer spectra of several of the high-spin seven-coordinate complexes $[Fe(222\text{-}N_5)X_2]ClO_4$ have been measured over a range of temperatures. The temperature dependent spectra were interpreted in terms of paramagnetic relaxation effects; a correlation between the electric field gradient and the zero-field splitting was demonstrated and shown to change sign as the field strength of the axial ligand X was varied.[407] The complexes are photochemically active[408,409] to a degree dependent on the nature of the axial ligands, leading to reduction of the metal centre and oxidation of the axially coordinated ligand.[409]

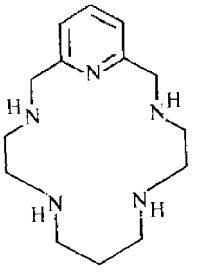
Reaction of the Fe^{II} complexes of $222\text{-}N_5$ and $232\text{-}N_5$ with O_2 leads to formation of the μ-oxo dimers. It is conceivable that an intermediate in the formation of the μ-oxo dimer is a μ-peroxo–di-iron(III) species as proposed for reactions of other Fe^{II} complexes with O_2. Evidence for the stabilization of the μ-peroxo species in aqueous solution has been adduced by Kimura *et al.*[410] for the case of the Fe^{II} complex of the related saturated macrocycle (**124**). This yellow Fe^{II} complex absorbs O_2, non-reversibly, in aqueous solution in the ratio of one O_2 per two Fe, forming a red purple solution stable for up to 3 h at ambient temperature.[410]



(120) $m = n = 2$
(121) $m = 2$, $n = 3$
(122) $m = 3$, $n = 2$



(123)

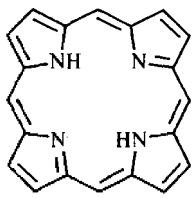


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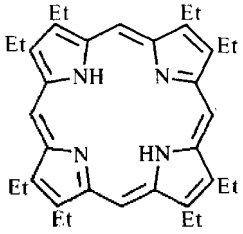
44.2.9.2 Porphyrins and Related Ligands

Iron porphyrins serve as the prosthetic group for the biologically important class of proteins known as the hemoproteins. These include the oxygen transport and storage proteins, hemoglobin and myoglobin, the electron carrier cytochromes, as well as various oxidase and oxygenase enzymes. As a result, the hemoproteins and synthetic iron porphyrin complexes have received much attention. A vast literature has now accumulated, particularly over the past few years, and it is therefore quite impossible to do other than indicate the principal classes of iron(III) porphyrin complex known to occur, together with a brief description of the structures and properties of some representative examples. Many comprehensive reviews are available.[411–416]

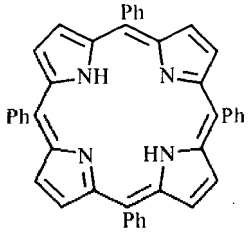
The parent ligand porphine has the planar conjugated tetrapyrrole ring structure (**125**) containing a 16-membered inner larger ring. In the naturally occurring metalloporphyrins all eight pyrrole carbon atoms are completely substituted. Commonly used synthetic porphyrins are octaethylporphyrin (H_2OEP) (**126**) and *meso*-tetraphenylporphyrin (H_2TPP) (**127**).



(125)



(126)



(127)

In the metal complexes the two pyrrole hydrogens are usually replaced by the metal ion so that porphyrin is coordinating as the dianion. Because of the conjugated nature of the dianionic porphyrin ring the hole size is fairly well fixed (some variability *via* ring puckering is permitted) at about 2.01 ± 0.08 Å. Thus, while some metal ions may sit in the hole in the same plane as the ring, others, being too large, may be forced to sit out-of-plane. Usually, though not always, the metal ion will be bound to all four nitrogen donors of the porphyrin ring. The metal ion can then acquire five- or six-coordination by binding one or two monodentate ligands in axial positions. Indeed, higher coordination numbers are found in several cases but for iron porphyrin complexes coordination numbers are restricted to four, five and six, and to five and six only for the case of Fe^{III} complexes.

The properties of a particular iron porphyrin are controlled in several different ways—by variation in the nature and position of porphyrin ring substituents, the number and nature of axial ligands, and the spin state and oxidation state of the metal ion. Not least, the protein itself in the natural systems plays a major role in the tailoring of the properties of the prosthetic group for the particular biological function it is to perform.

Most six-coordinate Fe^{III}–porphinato complexes, $[Fe(por)L_2]^+$, have low-spin ($S = \frac{1}{2}$) configurations.[413,417–420] In such cases, the equatorial Fe—N distances are close to 1.99 Å and Fe—N(axial) distances usually less than 2.0 Å. Displacements of the Fe atom out of the porphyrin 'N_4' plane are usually small. However, a number of complexes in which the axially ligating group is relatively weak field display high-spin ($S = \frac{5}{2}$) ⇌ low-spin ($S = \frac{1}{2}$) spin equilibria at accessible temperatures[421,422] or are actually fully high-spin as in the case of $[Fe(TPP)F_2]^-$ and $[Fe(TPP)(EtOH)_2]^+$.[423,424] The distinctive differences in magnetic properties and in Mössbauer and ESR spectra of the two classes are clearly reflected in the structural parameters as may be seen from an inspection of the data in Table 7. Thus, for the low-spin complexes the average Fe^{III}–N(porphyrin) distance in the low-spin complexes (vacant $d_{x^2-y^2}$ orbital) is < 2.00 Å whereas in the high-spin complexes (occupied $d_{x^2-y^2}$ orbital) this bond length is an excess of 2.00 Å.

Table 7 Structural Data for Some Six-coordinate $[Fe^{III}(porphyrin)L_2]$ Complexes

Porphyrin	*L*	*Spin state*	*Average Fe—N(por)* (Å)	*Fe—L* (Å)	*Ref.*
PP-IX	1-Meim	$\frac{1}{2}$	1.990	1.966 1.988	417
TPP	im	$\frac{1}{2}$	1.989	1.957 1.991	418
TPP	py	$\frac{1}{2}$	1.990	2.085	413
	N_3^-			1.926	
TPP	CN^-	$\frac{1}{2}$	2.000	1.975	419
TPP	THT[a]	$\frac{1}{2}$	1.985	2.357	420
TPP	PMS[b]	$\frac{1}{2}$	1.982	2.341	420
TPP	4-Meim	$\frac{1}{2}$	1.998	1.928, 1.958	428
OEP	3-Clpy	$\frac{1}{2}$ (98 K)[c]	1.994	2.031	421
		$\frac{1}{2} \leftrightarrow \frac{5}{2}$(293 K)[d]	2.014	2.194	
TPP	EtOH	$\frac{5}{2}$	2.03	2.14	423
TPP	F^-	$\frac{5}{2}$	2.064	1.966	424

[a] Tetrahydrothiophene. [b] Phentamethylenesulfide. [c] Predominantly low-spin at 98 K. [d] About 55% in high-spin form at 293 K.

Five-coordinate (square pyramidal) Fe^{III} complexes[425–427] containing a single axial ligand are generally high-spin ($S = \frac{5}{2}$) with the metal atom displaced from the porphyrin 'N_4' plane in the direction of the apical ligand.[413] Structural data for some representative examples are in Table 8.

Table 8 Structural Data for Some Five-coordinate [Fe^{III} (porphyrin)X] Complexes

Porphyrin	*X*	*Spin-State*	*Average Fe—N(por)* (Å)	*Fe—X* (Å)	*Displacement of Fe out of 'N$_4$' plane*	*Ref.*
PP-1X-DME	OMe	$\frac{5}{2}$	2.073	1.842	0.49	425
TPP	Cl	$\frac{5}{2}$	2.049	2.192	0.38	426
PP-1X-DME	SC_6H_4-*p*-NO_2	$\frac{5}{2}$	2.064	2.324	0.448	427
TPP[a]	O	$\frac{5}{2}$	2.087	1.763	0.50	439
TPP[b]	N	$\frac{5}{2}$	1.991	1.661	0.32	440

[a] In $[Fe_2(TPP)_2O]$. [b] In $[Fe_2(TPP)_2N]$.

However, more recently, a number of intermediate spin ($S = \frac{3}{2}$) iron(III) complexes have been prepared.[429–434] Stabilization of this spin state can be expected, in either square pyramidal or tetragonal symmetry, whenever the axial ligand field is very weak compared to the equatorial ligand field, such that $d_{x^2-y^2}$ lies well above d_{z^2} in energy and remains unoccupied. Examples of $S = \frac{3}{2}$ complexes are $[Fe(OEP)(ClO_4)]$[429] $[Fe(OEP)(EtOH)_2][ClO_4]$,[429,434] $[Fe(TPP)(ClO_4)]$[430] and $[Fe(TPP)(H_2O)_2][ClO_4]$[430] in which the axial ligands are the weakly bonding ClO_4^- ion or EtOH and H_2O molecules. Several of the complexes of thic class have effective magnetic moments at room temperature in the range 4.5–5.5 BM, significantly larger than expected for an $S = \frac{3}{2}$ state. Since Mössbauer spectra and other properties exclude the existence of a thermal equilibrium between magnetically distinct spin states, it has been postulated[435] that there is a quantum admixture of $S = \frac{3}{2}$ and $S = \frac{5}{2}$ states. Quantum mechanical admixing, presumed to occur *via* spin–orbit coupling when the energy separation between the pure states is small, may be recognized also on the basis of unusual $g \approx 4$ ESR signals as well as by a drop in magnetic moment at low temperatures.

A common product of the autoxidation of iron(II) porphyrins is the μ-oxo dimer[436,439] (equation 23), a reaction of importance in relation to O_2 transport and utilization in nature. These μ-oxo dimers contain two high-spin ($S = \frac{5}{2}$) Fe^{III} ions which are antiferromagnetically coupled through the oxo bridge,[437,438] as noted above for several other classes of μ-oxo Fe^{III} complex. An alternative route to the μ-oxo dimers is reaction of mononuclear [Fe(por)X] (X = *e.g.* Cl) with OH^-. The geometry[439] of the coordination sphere in the five-coordinate μ-oxo dimers approximates very closely to that found in the uncoupled five-coordinate monomers (see Table 8). In $[Fe_2(TPP)_2O]$ the bridge is near linear with Fe—O—Fe = 174.5°. It is interesting to compare the μ-oxo complex $[Fe_2(TPP)_2O]$[439] with the μ-nitrido complex $[Fe_2(TPP)_2N]$.[440] Structural parameters, specifically the short Fe—N(por) distance (1.99 Å) and the relatively small out-of-plane displacement (0.32 Å) of the Fe^{III} atom from the porphyrin ring are suggestive of a low-spin ($S = \frac{1}{2}$) ground state (compare with data in Table 8). Similar conclusions were reached on the basis of X-ray photoelectron studies.[441] On the other hand Mössbauer spectra[442] appear to favour a high-spin description with a formal oxidation state of Fe^{III}, Fe^{III} or rapidly exchanging Fe^{III}, Fe^{IV}, while a resonance Raman study[443] likewise favours the high-spin Fe^{III} formulation.

$$4Fe^{II} + O_2 \longrightarrow 2Fe^{III}—O—Fe^{III} \qquad (23)$$

The mechanism of the autoxidation of Fe^{II} porphyrins has been studied in detail by visible and ^1H NMR spectroscopy.[444] This is an important reaction and its understanding, and circumvention, have formed the basis of the strategies for the design of synthetic iron(II) complexes capable of the reversible binding of O_2. As mentioned above the usual ultimate product of Fe^{II} porphyrin autoxidation is the μ-oxo dimer. La Mar and Balch and co-workers[444] have shown that addition of O_2 to toluene solutions of $Fe^{II}P$ (**128**) (P = a porphyrin dianion) leads to the formation of an intermediate (**130**) which may be detected at -80°C by visible and ^1H NMR spectra. This intermediate has been formulated as a peroxo-bridged diiron(III) species on the basis of its antiferromagnetism in solution and the stoichiometry of its formation. Upon warming, this μ-peroxo complex decomposes quantitatively to the μ-oxo species (**132**) together with O_2. This reaction has been shown to be first order in (**130**). The overall mechanism for the autoxidation is summarized in equations (24)–(30). The formation of the Fe^{IV} species (**131**) is consistent with other information on this oxidation state of iron (*vide infra*). Evidence for a different kind of Fe^{III} porphyrin–peroxo complex in solution has been presented. This mononuclear species formulated as $[Fe^{III}(por)(O_2)]^-$ (por = TPP or OEP) appears to be produced *via* a redox reaction between Fe^{II} porphyrin and O_2^-. Visible, IR, resonance Raman and ESR spectra support a formulation of the complexes in which the peroxide is bidentately coordinated to Fe^{III} in the 'sideways-on' (Griffiths) fashion (structure **133**).[445]

The low temperature spectroscopic observation of the Fe^{IV} ferryl complex (**134**) [P = TPP, B = py, pip or *N*-Me-im] formed *via* reaction (31) has been followed by the demonstration by the same group of its role in oxygen atom transfer reactions. Thus, it was found[446] that PFe^{II} catalyzes

$$Fe^{II}P + O_2 \longrightarrow O_2Fe^{II}P \quad (24)$$
(128) (129)

$$PFe^{II}O_2 + Fe^{II}P \longrightarrow PFe^{III}—O_2—Fe^{III}P \quad (25)$$
(129) (128) (130)

$$PFe^{III}—O_2—Fe^{III}P \longrightarrow 2PFe^{IV}O \quad (26)$$
(130) (131)

$$PFe^{IV}O + PFe^{III}—O_2—Fe^{III}P \longrightarrow PFe^{III}—O—Fe^{III}P + PFe^{II}O_2 \quad (27)$$
(131) (130) (132) (129)

$$PFe^{II}O_2 \longrightarrow PFe^{II} + O_2 \quad (28)$$
(129) (128)

$$PFe^{IV}O + PFe^{II} \longrightarrow PFe^{III}—O—Fe^{III}P \quad (29)$$
(131) (128) (132)

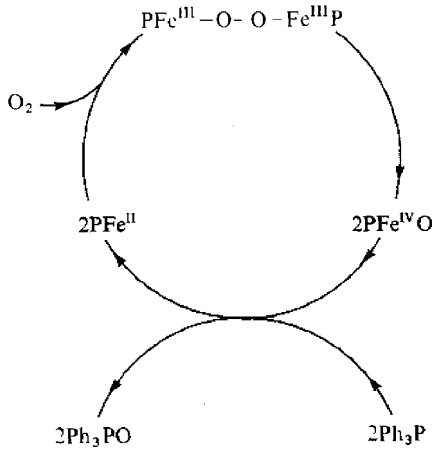
$$PFe^{IV}O + O_2Fe^{II}P \longrightarrow PFe^{III}—O—Fe^{III}P \quad (30)$$
(131) (129) (132)



(133)

the oxidation of triphenylphosphine in toluene to triphenylphosphine oxide. It is considered[446] that $PFe^{IV}O$ is the active oxidant and that the catalytic cycle in Scheme 6 applies. Fe^{III} species such as [FePCl], $[FePB_2]^+$ and [PFe—O—FeP] were inactive, though the μ-oxo dimer of phthalocyanatoiron(III) [PcFe—O—FePc] can apparently perform the same oxidation in the presence of pyridine under mild conditions.[447]

$$PFe^{III}—O—O—Fe^{III}P + 2B \longrightarrow 2BPFe^{IV} \quad (31)$$
(130) (134)



Scheme 6 Proposed catalytic cycle for the oxidation of triphenylphospine *via* Fe^{II} porphyrin complexes

44.2.9.2.1 The heme proteins

In the heme proteins the prosthetic group consists of iron coordinated to a substituted porphyrin. The versatility of the heme proteins is apparent in the range of different functions they perform, mediate or catalyze. These functions are associated with, for example, dioxygen transport (hemog-

lobin), dioxygen storage (myoglobin), electron transfer (cytochromes), catalysis of oxygenation reactions such as hydroxylation (cytochrome P_{450}), and of oxidation involving hydrogen peroxide (peroxidases and catalases). The adaptation of the heme protein to a particular function is controlled by a variety of structural and other factors, often in intriguing and subtle ways. These include alteration of the substitution pattern of the porphyrin ring (affecting *e.g.* the redox potential of the metal centre), the nature of the axial ligation at the iron centre (affecting spin state, reactivity and redox potential), and the conformational/structural/interactive relationships of the prosthetic group with the amino acid chain of the protein. In all of these metalloproteins the redox activity of the coordinated metal ion is central to the biological function, all involving changes in oxidation state during an operational cycle. Usually the cycling in oxidation state is between +2 and +3 but higher oxidation states may also be involved.

The dioxygen-carrying proteins, hemoglobin and myoglobin, as well as the many synthetic model systems that have been developed recently,[448] will not be considered here in this chapter since their chemistry is mainly that of iron in the +2 oxidation state. The present chapter is therefore restricted to a brief description of the structure and reactivity of some cytochrome and peroxidase proteins.

44.2.9.2.2 Electron transport heme proteins

The cytochromes are the electron carrier heme proteins occurring in the mitochondrial respiratory chain.[449] There are five cytochromes linking coenzymes Q (ubiquinone) and O_2 in this electron transport chain (Scheme 7). Cytochromes are also involved in energy transfer in photosynthesis. The iron atom in cytochromes cycles between the Fe^{II} and Fe^{III} states, *i.e.* they are one-electron carriers, in contrast to CoQ and the NADH flavins they act upon which are two-electron carriers. Thus, one molecule of reduced CoQ transfer its two high potential electrons to two molecules of cytochrome b, the next member of the electron transport chain.

$$\text{CoQ} \rightarrow \text{cyt b} \rightarrow \text{cyt } c_1 \rightarrow \text{cyt c} \rightarrow \text{cyt}(a + a_3) \rightarrow O_2$$

Scheme 7 The electron transport chain linking coenzyme Q and O_2

The five cytochromes between CoQ and O_2 (Scheme 7) increase incrementally in redox potential, spanning an overall potential of about one volt. The various cytochromes differ in structure and properties. In cyt b, cyt c_1 and cyt c the prosthetic group is heme itself, iron–protoporphyrin-IX, as in hemoglobin and myoglobin. Cytochrome c is structurally well defined in both the Fe^{II} and Fe^{III} states.[450] It consists of a polypeptide chain of 104 amino acid residues and a covalently attached heme group. One axial site of the iron atom is occupied by the nitrogen from a histidine residue and the other axial site by a sulfur atom from a methionine residue of the protein chain (Figure 12). Thus, unlike myoglobin and hemoglobin, cytochrome c functions without change in axial ligation. Indeed, as reinforced by studies on model compounds of low-spin Fe^{II} and Fe^{III} porphyrins containing axial thioether ligands, there is little alteration in Fe—S bond length as change of oxidation state of the metal.[451]

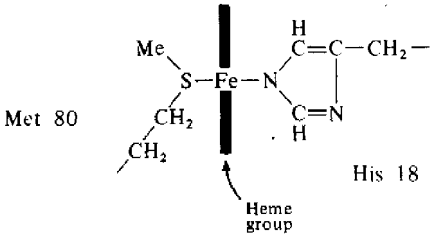


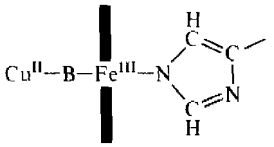
Figure 12 The heme group in cytochrome c showing the axial ligation to methionine and histidine residues of the protein chain

An interesting feature of cytochrome c, which is present in all organisms that contain a mitochondrial respiratory chain, is that it has remained virtually unchanged since it evolved more than 1.5×10^9 years ago.

Reduced cytochrome c passes its electron on to the next member of the respiratory chain, cytochrome $(a + a_3)$. These two cytochromes, together known as cytochrome c oxidase, comprise two iron–porphyrin prosthetic groups and two copper centres. Electrons are transferred to cytochrome a and then to a_3 which contains Cu which cycles between the +1 and +2 oxidation states. The net function performed by this terminal member of the electron transport chain is the four-elec-

tron reduction of O_2 to H_2O with release of energy which is stored in the ADP–ATP cycle, and the reoxidation of reduced cyt c to the oxidized form (equation 32).[452,453] Various spectroscopic (ESR,[454] MCD[455]) and magnetic studies[455] have shown that the enzyme contains one isolated heme unit (cytochrome a) which is low-spin in both the oxidized and reduced forms and one isolated copper centre which is ESR active. The second heme unit (cytochrome a_3), believed to be the O_2 binding site, is associated with the second copper atom which is EPR undetectable. Variable temperature magnetic susceptibility measurements have shown that the iron atom of the fully oxidized (resting) form of the enzyme is in the $S = \frac{5}{2}$ spin state and strongly antiferromagnetically coupled to the EPR non-detectable copper atom in the $S = \frac{1}{2}$ spin state.[456] The data indicate a coupling constant $-J$ of $\geqslant 200\,cm^{-1}$, leading to a resultant $S = 2$ ground state, for the spin-coupled [Fe—B—Cu] dimer. One axial position of the coordination sphere of the iron atom in cyt a_3 is believed to be an imidazole group[457] while the other is occupied by a bridging ligand B responsible for the superexchange interaction with the Cu^{II} ion (structure **135**). The nature of the bridging ligand B remains uncertain. Several candidates have been proposed on the basis of the properties of various model binuclear complexes containing coupled Fe^{III}–Cu^{II} pairs. These include the imidazolate ion (from a histidine residue of the protein),[454,456,458] an oxo (or hydroxo) bridge (derived from O_2 itself)[459,460] and a thiolate group (from a cystein residue).[461]

$$4\text{cyt c}^{II} + O_2 + 4H^+ \longrightarrow 4\text{cyt c}^{III} + 2H_2O \qquad (32)$$



(135)

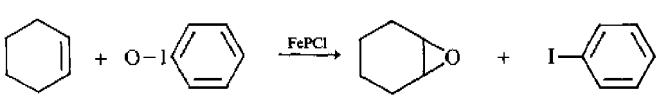
44.2.9.2.3 Cytochrome P_{450}, peroxidase and catalase enzymes

Cytochrome P_{450}, named after the wavelength (in nm) of the absorption maximum of the carbon monoxide complex of the reduced form, is not an electron transport protein but actually a monoxygenase enzyme which catalyzes the incorporation of one atom of O_2 into an organic substrate while the second atom is reduced to H_2O. A common activity is the catalytic hydroxylation of substrates (equation 33) which include hydrocarbons and steroids. Other oxidations mediated by P_{450} enzymes are epoxidation, oxidative group transfer involving involving a 1,2-carbon shift with concomitant incorporation of oxygen as a carbonyl group at the C-1 position, and heteroatom oxygenation.[462–464] The active site of P_{450} comprises an iron protoporphyrin IX moiety in a hydrophobic cleft in the surface of the apoprotein. The metal ion is always five- or six-coordinate. One axial ligand is believed to be the thiolate anion from a cysteine residue of the polypeptide chain. The second axial position is the site for O_2 binding. The mechanism of hydroxylation of substrates by cyt P_{450} was first proposed to be an oxenoid process in which an oxene species inserted into a carbon–hydrogen bond in a manner analogous to carbenes. Subsequently, Groves and co-workers[463,465] demonstrated that alkane hydroxylation proceeded by a stepwise process involving the formation of a carbon-centred free radical *via* hydrogen abstraction by a perferryl (Fe^V=O) intermediate (equation 34). A significant discovery was that exogenous oxygen donors such as iodosylbenzene and alkyl hydroperoxides are effective oxygen sources for the enzyme in the absence of dioxygen and a reducing agent. This suggested that dioxygen is bound and reduced to metal-bound peroxide at the active site. The epoxidation of alkenes by iodosylbenzene (equation 35) was also found to be catalyzed by synthetic iron porphyrins. The mechanism[466] for the epoxidation using either O_2 or PhIO is summarized in Scheme 8.

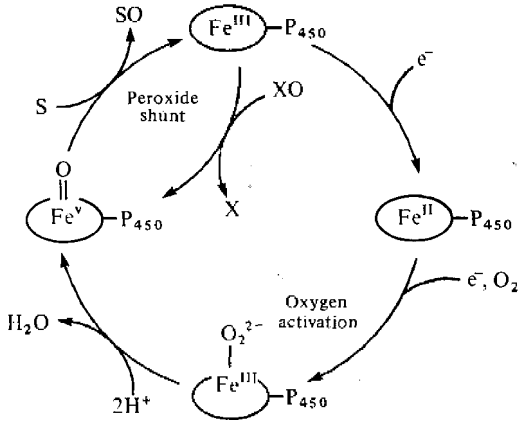
Peroxidase and catalase enzymes catalyze oxidations by hydrogen peroxide and the disproportionation of hydrogen peroxide into dioxygen and water (equations 36 and 37). The two classes of

$$RH + O_2 + 2H^+ + 2e^- \longrightarrow ROH + H_2O \qquad (33)$$

$$[Fe^V{=}O] \xrightarrow{RH} [Fe(OH) + R\cdot] \longrightarrow Fe^{III} + ROH \qquad (34)$$



(35)



Scheme 8 A catalytic cycle for oxygen activation and transfer by cytochrome P_{450} (S = substrate, *e.g.* alkene; X = *e.g.* iodosylbenzene)[466]

enzyme have strong similarities, not only in function but also in structure and mechanism of action.[467,468] These heme proteins have attracted much attention in recent years because, like cytochrome P_{450}, they appear to involve novel high oxidation state species of iron as intermediates in the redox cycles and because the oxo–iron species, in synthetic compounds, may have practical value as catalysts in the functionalization of organic molecules. The best characterized enzyme of this class is horseradish peroxidase (**HRP**). This contains protoporphyrin IX and in the resting state the iron is in the +3 oxidation state, probably coordinated to an imidazole nitrogen atom (from a histidine residue) in one axial position with, possibly, an exchangeable aquo group in the sixth position.[468,469] There is evidence for both high- and low-spin forms of the Fe^{III} ion. Upon reaction with H_2O_2 or organic peroxides the iron(III) prosthetic group undergoes a two-electron oxidation to generate a green compound HRP-I which then may undergo a one-electron reduction to give the red species HRP-II. The collective evidence of a variety of spectroscopic and other studies strongly favours a low-spin ($S = 1$) Fe^{IV} formulation for both HRP-I and HRP-II, with the porphyrin ring forming a π-cation radical in the case of HRP-I (equations 38 and 39).[470–473] Similar considerations probably apply to the catalase family of enzymes.[474]

$$H_2O_2 + SH_2 \xrightarrow{\text{peroxidase}} 2H_2O + S \quad (36)$$

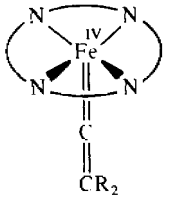
$$H_2O_2 + H_2O_2 \xrightarrow{\text{catalase}} 2H_2O + O_2 \quad (37)$$

$$[PFe^{III}] + H_2O_2 \longrightarrow \underset{\text{[HRP-I]}}{[\cdot PFe^{IV}{=}O]} + H_2O \quad (38)$$

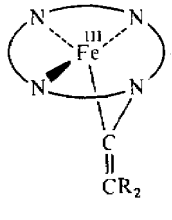
$$[\cdot PFe^{IV}{=}O] + R \longrightarrow \underset{\text{[HRP-II]}}{[PFe^{IV}{=}O]} + \cdot R \quad (39)$$

Oxidation products of Fe^{III} porphyrin complexes may not always involve Fe^{IV}, however. Thus, magnetic, Mössbauer and structural studies on [Fe(TPP)Cl][$SbCl_6$] allow assignment as an Fe^{III} ($S = \frac{5}{2}$) complex of a radical porphyrin cation.[475]

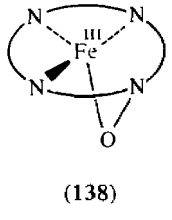
Recently synthesized iron porphyrin–carbene complexes (**136**) may be considered as carbon analogues of the oxo–iron(IV) porphyrin (HRP-II and CAT-II) species.[476] The one-electron oxidation of [Fe(TPP)(C=CR_2)] (R = aryl) by $CuCl_2$ affords the stable complex [Fe(TPP)(C=CR_2)] Cl (TPP = *meso*-tetra-*p*-tolyl porphyrin and R = *p*-ClC_6H_4) which has a visible spectrum very similar to that of CAT-I. X-Ray analysis of this complex has revealed a structure (**137**) in which the vinylidene moiety has inserted between the iron atom and one pyrrole ring of the porphyrin and it is suggested that this may constitute a model, *i.e.* structure (**138**), for the active site of CAT-I as an alternative to the Fe^{IV} cation radical model.[477]



(136)



(137)



(138)

44.2.10 IRON(IV), IRON(V) AND IRON(VI)

Usually, high oxidation states of metals are stabilized most effectively when in combination with the most electronegative atoms, fluorine and oxygen. Rather surprisingly, no Fe^{IV} or higher oxidation state compounds with fluorine are known. Indeed rather few stable or well-defined higher oxidation state iron compounds are known. Despite this, there can be no doubt about the importance of such compounds. We have already encountered the Fe^{IV} and Fe^{V} states in reactive intermediates in the reactions of several metalloproteins and of several synthetic porphyrin complexes.

The Sr^{2+} and Ba^{2+} salts of the ferrates(IV), Sr_2FeO_4 and Ba_2FeO_4, may be prepared by oxidation of a mixture of hydrated iron(III) oxide with the alkaline earth metal oxide or hydroxide with oxygen at 800–900°C (equation 40).[478] These black compounds do not contain discrete $[FeO_4]^{4-}$ ions and are really mixed metal oxides. They are readily decomposed by mineral acids to Fe^{III} and O_2. Vibrational spectra of some of these systems have been recorded.[479]

$$Sr_3[Fe(OH)_6]_2 + Sr(OH)_2 + \tfrac{1}{2}O_2 \longrightarrow 2Sr[FeO_4] + 7H_2O \qquad (40)$$

The oxidation of the iron(III) complexes $[Fe(DAS)_2X_2][FeX_4]$ (DAS = *o*-phenylenebisdimethylarsine, X = Cl, Br) with concentrated nitric acid followed by addition of the appropriate anion led to the isolation of black $[Fe(DAS)_2X_2]Y_2$ ($Y = BF_4^-$, ClO_4^-, ReO_4^-).[480] The magnetic properties indicate two unpaired electrons consistent with a low-spin t_{2g}^4 configuration in a tetragonal (*trans* halide) structure. Mössbauer quadrupole splittings are large ($\sim 3.2\,mm\,s^{-1}$) and temperature independent.[481]

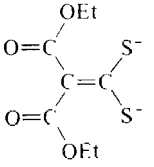
The most stable iron(IV) complexes are those containing dithiocarbamate and related ligands. Reaction of tris(dithiocarbamato)iron(III) complexes $[Fe^{III}(S_2CNR_2)_3]$ (R = Me, Et, Pr^i, cyclohexyl) with BF_3 in the presence of air yields the complexes $[Fe^{IV}(S_2CNR_2)_3]BF_4$. Salts containing other counterions such as PF_6^- and ClO_4^- may be obtained by variations in the preparative methods.[482,483] I_2 may be used as oxidant in certain cases.[483] These intensely coloured complexes have magnetic moments at room temperature in the range 3.2–3.4 BM, measured in chloroform solution. These values are consistent with low-spin ($S = 1$) ground states when allowance is made for some distortion from cubic symmetry. Mössbauer isomer shifts in the range 0.1–0.2 mm s^{-1} relative to iron metal are lower than those characteristic of Fe^{III} compounds consistent with the removal of one *d* electron from Fe^{III} (d^5) to give Fe^{IV} (d^4). Quadrupole splittings are in the range 2.0–2.5 mm s^{-1}, *i.e.* somewhat smaller than observed for the tetragonal $[Fe(DAS)X_2]^{2+}$ complexes mentioned above, but still much larger than the splitting usually observed for Fe^{III} complexes.[482,284] The structure of the cation in $[Fe(S_2CNR_2)_3]ClO_4$ [$R_2 = (CH_2)_4$] is very similar to that of the corresponding Fe^{III} complex. There is, however, a significant shortening (0.11 Å) in the average Fe—S distance as expected for a depopulation of the antibonding e_g orbital, as well as for the higher formal charge on the metal.[485] As found for many Fe^{III} complexes of 'sulfur' ligands, the 'FeS_6' core in the Fe^{IV} complex conforms neither to the ideal octahedral nor trigonal prismatic arrangements, the angle of twist between the triangular faces being 38°.

Despite the ambiguity regarding the assignment of formal oxidation states to metal and ligand in many dithiolate complexes, the structure and properties of the benzyltriphenylphosphonium salt of tris(1,1-dicarboethoxyethylene-2,2-dithiolato)ferrate $[BzPh_3P]_2[Fe(DED)_3]$ (DED = structure **139**) are considered[486] to be best described in terms of an Fe^{IV} complex. The structure is close in important details to that of the dithiocarbamate complex described above.[485]

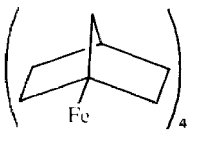
Mixed valence Fe^{III}, Fe^{IV} oxo-bridged dimers $[Fe_2L_2O]X$ (L = TPP or salen; X = PF_6, BF_4, ClO_4 or I_3) have been prepared by oxidation of the μ-oxo diiron(III) complexes.[487,488] Antiferromagnetic exchange interaction was indicated by the variable temperature magnetic susceptibility data which could be fitted to the theoretical equations for an isotropic exchange ($H = -2J\,S_1 \cdot S_2$) in an $S_1 = \frac{5}{2}$, $S_2 = 2$ dimer. The exchange parameter J was found to fall in the range -7.5 to $-17.6\,cm^{-1}$ for $[Fe_2(salen)_2O]X$ and in the range -82.5 to $-119\,cm^{-1}$ for $[Fe_2(TPP)_2O]X$. Mössbauer spectra of both series of complexes, recorded at 4.2 and 77 K, consisted of a single quadrupole-split doublet, showing that the rate of electron transfer between the metal centres is faster than $\sim 10^7\,s^{-1}$. The ESR spectra of the salen complexes were reported to consist of a single isotropic signal at $g \simeq 2.0$, this being somewhat temperature dependent in line width. This behaviour is consistent with a thermal intervalence electron transfer rate of the order of $10^{10}\,s^{-1}$. For the $[Fe_2(TPP)_2O]X$ complexes either a high-spin Fe^{III} ESR signal or no ESR signal was observed suggesting that thermal electron transfer rates are less than $10^{10}\,s^{-1}$ in these cases.[488] $[Fe_2(TPP)_2O]$ can also be oxidized electrochemically to $[Fe_2(TPP)_2O]^{2+}$ which may be formulated either as $[Fe^{IV}—O—Fe^{IV}]$ or $[Fe^{IV}—O—Fe^{III}(por^+)]$.[489]

An organometallic compound containing iron formally in the +4 oxidation state is the purple

tetralkyl $[Fe(nor)_4]$ (**140**) (nor = 1-norbornyl) formed by reaction of $FeCl_3 \cdot OEt$ with 1-norbornyllithium. The stability of this complex and of those of other transition metal ions is probably associated with the bulky nature of the alkyl ligand which serves to protect the metal from attack by reagents.[490]



(139)



(140)

The + 5 oxidation state of iron is very rare and has been firmly established only for the ferrate(V) oxyanion $[FeO_4]^{3-}$. The K^+ salt has been prepared by heating K_2FeO_4 with KOH in O_2 at 700–800°C or from KO_x and Fe_2O_3 in O_2 at similar temperatures.[491,492] An impure form of Na_3FeO_4 has been obtained on heating Na_3FeO_3 in O_2 at high pressure. X-Ray investigations indicate a tetrahedral structure for the $[FeO_4]^{3-}$ anion.

Iron(V) has been suggested to occur as intermediates in the reactions of various biological systems, *e.g.* in HRP-I. However, as noted above, this species is probably best regarded as an Fe^{IV} complex of the porphyrin radical cation.

The chemistry of iron(VI) is confined to that of the ferrate(VI) $[FeO_4]^{2-}$ ion. $K_2[FeO_4]$ may be prepared by the oxidation of hydrated Fe_2O_3 in concentrated aqueous alkali with KClO or KBrO (equation 41)[491,493]. Electrolysis of concentrated alkali solutions with an iron anode has also been employed as a method for the preparation of $[FeO_4]^{2-}$.[494,495] Pure materials appear to be limited to the salts with alkali metal ions and Ba^{2+}. The purple salts contain discrete tetrahedral $[FeO_4]^{2-}$ anions and the alkali metal salts have the orthorhombic β-K_2SO_4 structure.[493,496] The magnetic moments are in the range 2.8–3.2 BM consistent with the presence of two unpaired electrons.[493,497] Electronic,[498] ESR[499] and Mössbauer[500] spectra have been reported.

The ferrate(VI) ion is moderately stable in concentrated alkali solution but decomposes rapidly in neutral or acidic solutions according to equation (42). The strong oxidizing power of $[FeO_4]^{2-}$ is reflected in the redox couple of ~ 2.0 V for the half reaction (equation 43). The ferrate(VI) ion is a stronger oxidizing agent than permanganate and has found application in the oxidation of alcohols and other organic compounds.[501–503]

$$Fe_2O_3 \cdot 3H_2O + 4OH^- + 3ClO^- \longrightarrow 2[FeO_4]^{2-} + 3Cl^- + 5H_2O \quad (41)$$

$$2[FeO_4]^{2-} + 10H^+ \longrightarrow 2Fe^{3+} + 5H_2O + \tfrac{3}{2}O_2 \quad (42)$$

$$[FeO_4]^{2-} + 8H^+ + 3e^- \rightleftharpoons Fe^{3+} + 4H_2O \quad (43)$$

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45

Ruthenium

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45.1 INTRODUCTION

Ruthenium was discovered by Karl Karlovitch Klaus in 1844 in Tartu, Estonia (Ruthenia is latin for Russia). It is a rare metal with a natural abundance in the earth's crust of *ca.* 10^{-3} p.p.m. The main sources are laurite, the native alloys osmiridium and iridiosmium and other platinum metal concentrates.

Ruthenium has an atomic number of 44, electronic configuration $[Kr]4d^7 5s^1$ and an atomic weight of 101.07. It possesses seven stable isotopes ^{96}Ru ($I = 0$, 5.5%), ^{98}Ru ($I = 0$, 1.87%), ^{99}Ru ($I = \frac{3}{2}$, 12.72%), ^{100}Ru ($I = 0$, 12.62%), ^{101}Ru ($I = \frac{5}{2}$, 17.07%), ^{102}Ru ($I = 0$, 31.61%), ^{104}Ru ($I = 0$, 18.58%), and exists in four allotropes, the stable α-phase being grey–white in colour. The metal is insoluble in all acids including *aqua regia* and is resistant to oxygen up to 600°C whereupon it forms RuO_2. The metal dissolves in fused KOH to give $K_2[RuO_4]$.

Ruthenium exhibits a wide range of oxidation states from VIII to −II, the most common being III and II for 'classical-type' ligands. The least common oxidation states are VII, V, I and −I. The higher oxidation states are stabilized by small π donor ligands such as F^-, O^{2-}, N^{3-} (*e.g.* $[Ru^{VI}F_6]$, $[Ru^{VIII}O_4]$, $[Ru^{VI}NCl_4]^-$); conversely π acceptor ligands such as CO, PR_3 stabilize the lower oxidation states (*e.g.* $[Ru^{-II}(CO)_4]^{2-}$, $[Ru^0(CO)_5]$, $[Ru^0(CO)_3(PPh_3)_2]$). Ligands which are good σ donors but show no substantial π acceptor or donor properties (*e.g.* H_2O, NH_3) are usually associated with Ru^{III} and Ru^{II}. Table 1 summarizes the oxidation states and coordination numbers for complexes of ruthenium.

Ruthenium(0), d^8: The chemistry is primarily one of mononuclear, polynuclear carbonyls and tertiary phosphine complexes; a range of Ru^0 nitrosyls are known.

Ruthenium(I), d^7: Very few monomeric complexes are known with dimerization and polymerization reactions *via* Ru—Ru metal bond formation being prevalent.

Ruthenium(II), d^6: A wide range of Ru^{II} complexes incorporating carbonyl, phosphine, ammine and heterocyclic ligands are known. Virtually all Ru^{II} complexes are octahedral and diamagnetic with a t_{2g}^6 configuration (unless steric constraints are present). Catalytic processes utilizing Ru^{II} phosphine complexes, kinetic studies on substitution reactions of $[Ru(NH_3)_5L]^{2+}$ and the photophysics and photochemistry of $[Ru(bipy)_3]^{2+}$ and related systems have been areas of major advance in recent years.

Ruthenium(III), d^5: Ru^{III} is often associated with 'classical-type' ligands, *e.g.* ammine, water, halides. They are octahedral low spin t_{2g}^5 species with one unpaired electron and generally substitutionally inert. The electronic structure of polynuclear carboxylates and mixed valence $Ru_2^{II/III}$ complexes of the type $[Ru(NH_3)_5]_2L^{5+}$ has been the subject of much interest particularly with respect to the degree of unpaired electron delocalization within these molecules.

Ruthenium(IV), d^4: These complexes are often octahedral or distorted octahedral with a t_{2g}^4 low

Table 1

Oxidation state	*Coordination number*	*Complex*
Ru^{-II}	4	$[Ru(PF_3)_4]^{2-}$, $[Ru(CO)_4]^{2-}$
Ru^{0}	4	$[RuCl(NO)(PPh_3)_2]$
	5	$[Ru(CO)_3(PPh_3)_2]$, $[Ru(PF_3)_5]$, $[Ru(CO)(dmpe)_2]$, $[RuH(NO)(PR_3)_3]$
	6	$[Ru(dad)_3]$
Ru^{I}	6	$[Ru(\mu\text{-}I)(CO)_2PPh_3]_2$, $[Ru_2(\mu\text{-}H)(\mu\text{-}OH)(PMe_3)_6]$
Ru^{II}	5	$[RuCl_2(PPh_3)_3]$, $[RuHCl(PPh_3)_3]$
	6	$[Ru(NH_3)_6]^{2+}$, $[Ru(NH_3)_5py]^{2+}$, $[Ru(bipy)_3]^{2+}$, $[RuCl_5NO]^{2-}$, $[Ru(TPP)(CO)EtOH]$, $[Ru(OH_2)_6]^{2+}$, $[RuH_2(PPh_3)_4]$, $[Ru(CN)_6]^{4-}$, $[RuCl_3NO(PR_3)_2]$
Ru^{III}	6	$[Ru(NH_3)_6]^{3+}$, $[RuCl(NH_3)_5]^{2+}$, $[Ru(oxal)_3]^{3-}$, $[Ru(acac)_3]$, $[Ru(OH_2)_6]^{3+}$, *mer*-$[RuCl_3(PR_3)_3]$, $[RuCl_3(AsPh_3)_2MeOH]$, $[\{Ru(NH_3)_5\}_2O]^{4+}$
Ru^{IV}	4	$[RuF_4]$
	6	$[RuCl_6]^{2-}$, $[Ru_2Cl_8N(OH_2)_2]^{3-}$, $[Ru_2OCl_{10}]^{4-}$
	7	$[RuH_3(SiR_3)(PPh_3)_3]$, $[RuH_4(PPh_3)_3]$
Ru^{V}	6	$[RuF_5]_4$, $[RuF_6]^{-}$
Ru^{VI}	5	$[RuO_3(OH)_2]^{2-}$, $[RuNCl_4]^{-}$
	6	RuF_6, $[RuO_2Cl_4]^{-}$
Ru^{VII}	4	$[RuO_4]^{-}$
Ru^{VIII}	4	$[RuO_4]$

spin configuration giving μ_{eff} = 2.7–2.9 BM which decreases with decreasing temperature. Oxo- and nitrido-bridged polynuclear complexes of Ru^{IV} are of particular interest, while more recently organometallic and hydrido Ru^{IV} species have been synthesized.

Ruthenium(V), (VI), (VII), (VIII) (d^3, d^2, d^1, d^0): These complexes are restricted to halo, oxo and nitrido species such as $[RuNCl_4]^{-}$, $[RuNCl_5]^{2-}$ and $[RuO_4]^{2-/1-/0}$. Oxo complexes of ruthenium have been used as oxidation catalysts.

This article reviews the coordination chemistry of ruthenium up to mid-1984 with particular emphasis on work published since 1967. The organometallic chemistry of ruthenium has been reviewed[1] and is not covered herein. Previous reviews of the coordination chemistry of ruthenium have been published by Griffith,[2] Seddon[3–5] and Gmelin,[6] with a more general review by Cotton and Wilkinson.[7] Since ruthenium complexes often show multi-electron redox behaviour, the ordering of the contents within the review has been taken according to the ligands bound to the metal, with subdivisions where applicable, for metal oxidation states. The main reason for this approach is to facilitate data retrieval and cross referencing.

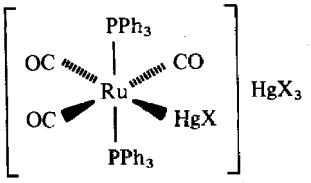
45.2 MERCURY-CONTAINING LIGANDS

Very few papers have been published on compounds containing direct ruthenium–mercury bonds and of these, several are strictly outwith the scope of this review since the other ligands present are either carbocyclic rings or other carbon-bonded groups, *e.g.* $[(Ru(\eta\text{-}C_5H_5)_2)_2Hg_2Br_4]$,[8] $[Ru_3(CO)_9(HgBr)(C_2Bu^t)]_2$[9] and $[RuCl_2(CNEt)_4(HgCl_2)]$.[10]

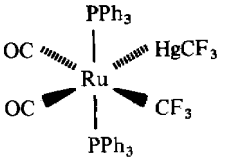
The first examples of compounds containing Ru—Hg bonds were $[Ru(HgX)(CO)_3(PPh_3)_2]HgX_3$ (**1**) (X = Cl, Br, I) prepared by the reaction of mercury(II) halides with $[Ru(CO)_3(PPh_3)_2]$.[11] Similar reactions, however, with $[RuI(CO)_2(PPh_3)_2]I$ and HgI_2 (1:1 molar ratio) give $[RuI(CO)_3(PPh_3)_2]HgI_3$ and $[\{RuI(CO)_3(PPh_3)_2\}_2]HgI_4$ (2:1 molar ratio).[12] Oxidation of $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ with HgX_2 affords $[Ru(X)(HgX)(CO)_3]_2$ (X = Cl, Br or SCN), in which the halogen bridge can be cleaved with pyridine to give $[RuX(HgX)(CO)_3py]$ (X = Cl, Br).[13]

Reaction of $[Ru(CO)_3(PPh_3)_2]$ or $[Ru(CO)_2(PPh_3)_3]$ with $Hg(CF_3)_2$ has been shown by X-ray analysis to give $[Ru(HgCF_3)(CF_3)(CO)_2(PPh_3)_2]$ (**2**).[14] The average C—F distance in the Ru-bound CF_3 group is 0.1 Å longer than in the Hg-bound CF_3 group and the Ru—Hg bond length is 2.628(1)Å. The compound reacts with aqueous $HClO_4$ to convert the CF_3 group to a CO group with retention of the Ru—Hg linkage, *viz.* $[Ru(HgCF_3)(CO)_3(PPh_3)_2]ClO_4$. Treatment of $RuCl_3$ in acetone with $HgCl_2$ followed by EPh_3 is claimed to give $[RuCl_2(HgCl_2)(EPh_3)_2]$ (E = P, As, Sb) (ν_{RuHg} 178–172 cm^{-1}).[15] Interaction of *cis*-$[RuClMe(PMe_3)_4]$ with 1% sodium amalgam over a period of three days at ambient temperature yields the trimetallic complex (**3**) in which the methyl groups are orientated *ca.* 90° from one another.[16a] Reaction of $[Ru_3(NO)(CO)_{10}]$ with $HgCl_2$ gives $[Ru_3(NO)(CO)_{10}]_2Hg$.[16b] Finally, the Hg^{2+}-catalysed aquation of the $[RuCl(NH_3)_5]^{2+}$ cation has been studied in both aqueous solution and in a variety of mixed water–organic solvents.[17] Kinetic

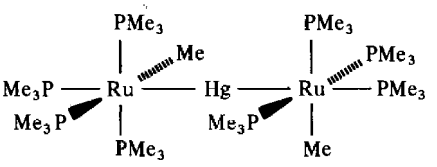
data in aqueous solution are consistent with preequilibrium formation of a chloro-bridged intermediate $[(NH_3)_5Ru—Cl—Hg]^{4+}$ followed by dissociation to release $[HgCl]^+$ and the rapid addition of water to give $[Ru(NH_3)_5(OH_2)]^{3+}$.



(1)



(2)



(3)

45.3 GROUP IV LIGANDS

45.3.1 Cyanides and Fulminates

45.3.1.1 Ruthenium(I) cyanides

Gamma-ray irradiation at 77 K and X-ray irradiation at room temperature of single crystals of the diamagnetic $K_4[Ru(CN)_6]\cdot 3H_2O$ produce paramagnetic low spin Ru^I species.[18] At room temperature, the ESR spectra were interpreted in terms of the species $[Ru(CN)_5(NC)]^{5-}$ whereas at liquid nitrogen temperature $[Ru(CN)_4(NC)_2]^{5-}$ is observed. However, parallel studies by Symons and Wilkinson on $K_4[Ru(CN)_6]$ in various host lattices suggest that γ irradiation produces such species as $[Ru(CN)_4(CN')H_2O]^{4-}$, $[Ru(CN)_4(CN')_2]^{5-}$, $[Ru(CN)_4(CN')X]^{5-}$ and $[Ru(CN)_4X_2]^{5-}$ (X = Cl, Br), where CN′ indicates a cyanide ligand tilted off the z axis.[19]

45.3.1.2 Ruthenium(II) cyanides

(i) $Ru(CN)_2$ and the $[Ru(CN)_6]^{4-}$ ion

$Ru(CN)_2$ was prepared in 1920 by addition of KCN to the blue 'ruthenium dichloride' solution.[20] No structural information is available on the material. $K_4[Ru(CN)_6]$ was first made in 1896 either by the action of KCN on $K_2[RuO_4]$ or by boiling a solution of $RuCl_3$ with an excess of KCN until the solution loses its colour.[21] As described elsewhere,[2] various other metal salts of this anion have been prepared together with the anhydrous free acid $H_4[Ru(CN)_6]$ and in several earlier studies, the electronic, IR and Raman spectra[22] have been recorded and assignments proposed. The IR spectra of solid $Y_4[Ru(CN)_6]$ (Y = H, D) have been measured and interpreted as showing unsymmetrical (N—Y···N) bonds.[23] The ^{99}Ru NMR spectrum of $K_4[Ru(CN)_6]$ has been recorded.[24]

The X-ray structure of $Mn_2[Ru(CN)_6]\cdot 8H_2O$ confirms that the ruthenium ion is coordinated by six cyanide ions in a slightly distorted octahedron (average Ru—C and C—N distances are 2.028(6) and 1.160(8) Å respectively) and all the CN groups are bonded through nitrogen to manganese.[25]

A detailed investigation of the surface-enhanced Raman scattering from adsorbed $K_4[Ru(CN)_6]$ clearly demonstrates that the molecule interacts with the metal surface *via* a CN bridge. The strength of this interaction is dependent upon the metal surface (Ag or Cu) and the applied potential. Furthermore, the spectra from both metals show vibrational modes which are only IR active in bulk phase, indicating a symmetry lowering on adsorption.[26] Mössbauer parameters for $K_4[Ru(CN)_6]$ and other ruthenium–cyano compounds such as $K_4[Ru(CN)_5NO_2]\cdot 2H_2O$ and $K_2[Ru(CN)_5NO]\cdot 2H_2O$ have been reported and discussed.[27]

A method for the preparation of thin films of $Fe_4[Ru(CN)_6]_3$ ('ruthenium purple') involving electrochemical reduction of $K_3[Ru(CN)_6]$ in a solution of $Fe_2(SO_4)_3$ has been developed.[28] This 'ruthenium purple' modified electrode is claimed to be one of the best catalysts for evolution of oxygen and chlorine. Electrochemical studies on polyammonium macrocyclic complexes of $[Ru(CN)_6]^{4-}$ indicate a 1:1 stoichiometry with a monoelectronic, reversible, oxidation for these complexes; this illustrates the control of redox potential of anions by complexation with appropriate receptor molecules.[29] The kinetics of oxidation of $[Ru(CN)_6]^{4-}$ by $[MnO_4]^-$ in $HClO_4$ have been investigated by stopped-flow techniques. It is found that $[Ru(CN)_6]^{4-}$ is quantitatively oxidized to $[Ru(CN)_6]^{3-}$ in accordance with equation (1) and that two protonated intermediates $[RuH(CN)_6]^{3-}$ and $[RuH_2(CN)_6]^{2-}$ are involved in the oxidation process.[30]

$$MnO_4^- + 5Ru^{II} + 8H^+ \longrightarrow Mn^{2+} + 5Ru^{III} + 4H_2O \quad (1)$$

Finally, reaction of $[Ru(CN)_6]^{4-}$ with alkylating agents such as dimethyl sulfate[31] or triethyloxonium tetrafluoroborate in acetone[32] gives high yields of the isocyanide cations $[Ru(CNMe)_6]^{2+}$ and $[Ru(C{\equiv}N{-}C(Me)_2CH_2(CO)Me)_6]^{2+}$ respectively. Treatment of the former with simple amines leads to various carbene complexes such as $[Ru(CNMe)_4(C(NHMe)_2)_2]^{2+}$.[31]

(*ii*) *Monomeric Ru^{II} cyanides containing N donor ligands*

$K_2[Ru(CN)_5(NO)]$, the only fully established nitrosyl cyanide ruthenium complex, is prepared by reaction of $K_4[Ru(CN)_6]$ with HNO_3.[33] Its Mössbauer spectrum,[27b] which shows a more positive isomer shift than $K_4[Ru(CN)_6]$, is ascribed to the greater π acceptor ability of NO^+ compared to CN^-. For $K_4[Ru(CN)_5(NO_2)]$, prepared by reaction of $K_2[Ru(CN)_5NO]$ with OH^-,[34a] a decrease in isomer shift[27b] is attributed to the poor π acceptor ability of NO_2^-. The X-ray structure of $Na_2[Ru(CN)_5NO]\cdot 2H_2O$, prepared from '$RuCl_3\cdot xH_2O$' and NaCN by oxidation with HNO_3 has been reported. Some reactions of this anion with various nucleophiles are discussed.[34b] Interestingly, a recent paper claims that the final product of the $[Ru(CN)_6]^{4-}/HNO_3$ reaction is $[Ru(CN)_3(NO)(H_2O)_2]$.[35]

Reaction of $[Ru(NH_3)_5OH_2]^{2+}$ and $Na[BH_3CN]$ under argon leads to the formation of $[Ru(BH_3CN)(NH_3)_5]^+$ which on exposure to air gives the ruthenium(III) dication $[Ru(BH_3CN)(NH_3)_5]^{2+}$. Dissolution of the former in 3 M HCl produces the hydrogen cyanide complex $[Ru(NCH)(NH_3)_5]^+$ coordinated at the nitrile nitrogen.[36] More recent studies by Isied and Taube[37] have shown that this HCN complex can be prepared by direct reaction of HCN with $[Ru(NH_3)_5OH_2]^{2+}$ and that its instability is due to intramolecular rearrangement of N- to C-bound ligand, followed by labilization of the *trans* ammonia group and subsequent polymerization to $[RuCN(NH_3)_4]_n^{n+}$. Similarly reaction of $[RuCN(NH_3)_5OH_2]^{2+}$ with equimolar amounts of NaCN gave $[RuCN(NH_3)_5]^+$. Reaction of either the latter or $[Ru(NCH)(NH_3)_5]^{2+}$ with isonicotinamide (isn) gave *trans*-$[Ru(CN)(NH_3)_4(isn)]^+$.

The synthesis of $[Ru(CN)_5pz]^{3-}$ (pz = pyrazine) has been described (equations 2 and 3); the *N*-methylated derivative is similarly prepared. The effective pK_a of $[Ru(CN)_5pzH]^{2-}$ (0.4 ± 0.1) has been measured by spectrophotometric titration and its value contrasted with that of $[Fe(CN)_5pzH]^{2-}$ (0.065 ± 0.06) and $[Ru(NH_3)_5(pzH)]^{3+}$ (2.85 ± 0.1).[38] The electronic spectra[39a] and voltammetric behaviour[39b] of a series of $[Ru(CN)_5L]^{3-}$ anions (L = various aromatic nitrogen heterocycles) have been reported and fully discussed.

$$[Ru(CN)_6]^{4-} + Br_2 \xrightarrow{H_2O} [Ru(CN)_5OH_2]^{3-} + BrCN + Br^- \quad (2)$$

$$[Ru(CN)_5OH_2]^{3-} + \text{N}\!\!\diagup\!\!\diagdown\!\!\text{N} \longrightarrow \left[Ru(CN)_5\text{N}\!\!\diagup\!\!\diagdown\!\!\text{N}\right]^{3-} + H_2O \quad (3)$$

A substantial amount of work has been published on *cis*-$[Ru(CN)_2(bipy)_2]$ and the corresponding $[Ru(CN)_2(phen)_2]$. Much of this is concerned with their interesting photochemical and photophysical properties and these are fully discussed, together with those of the well-known and exhaustively studied $[Ru(bipy)_3]^{2+}$ in Sections 45.4.3.1.viii.a and 45.4.3.1.vi.b respectively.

The compound *cis*-$[Ru(CN)_2(bipy)_2]\cdot 3H_2O$ was first prepared from NaCN, 2,2′-bipyridyl and $K_2[RuCl_5(OH_2)]$ followed by reduction with bisulfite ion. It is protonated on the cyanide nitrogen atoms by perchloric acid in acetic acid[40] and its IR spectrum has been recorded and discussed.[41] An alternative synthesis from reaction of $[Ru(C_2O_4)(bipy)_2]\cdot 4H_2O$ with NaCN is available.[42]

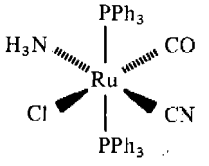
(*iii*) *Monomeric Ru^{II} cyanides containing other ligands*

A few cyano phosphine and arsine complexes of ruthenium(II) have been reported. These include *trans*-$[RuH(CN)(dmpe)_2]$ (dmpe = $Me_2P(CH_2)_2PMe_2$) obtained from the corresponding chloro complex and aqueous KCN[43] or more recently by treatment of $[RuH(2\text{-np})(dmpe)_2]$ (2-np = 2-naphthyl) with HCN. The latter gives a 85% *cis*, 15% *trans* isomer mixture (^1H NMR evidence).[44]

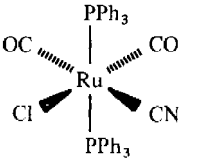
The complex *trans*-$[Ru(CN)_2(eda)_2]$ {eda = ethylene-1,2-bis(diphenylarsine)}[45] and quadridentate tertiary phosphine and arsine complexes such as $\{Ru(CN)_2[E(o\text{-}C_6H_4EPh_2)_3]\}$ (E = P, As) are

prepared by reaction of the corresponding chloro compounds with NaCN.[46] Reaction of $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]ClO_4$ with CN^- gives $[RuCN(\eta^1\text{-}CS_2Me)(CO)_2(PPh_3)_2]$ which then loses CO to generate $[Ru(CN)(\eta^2\text{-}CS_2Me)CO(PPh_3)_2]$.[47]

Two carbonyl complexes $K_2[Ru(CN)_2I_2(CO)_2]$ (from ruthenium carbonyl iodide and KCN)[48] and $[RuCl(CN)(NH_3)(CO)(PPh_3)_2]$ (**4**) (from treatment of $[RuCl_2(CCl_2)(CO)(PPh_3)_2]$ with ammonia) are known. Reaction of the latter with CO gives $[RuCl(CN)(CO)_2(PPh_3)_2]$ (**5**).[49]



(4)



(5)

(iv) Binuclear Ru^{II} cyanides

Most of these complexes are formed *via* reaction of $[Ru(CN)_6]^{4-}$ with other transition metal compounds and involve bridging cyano groups. For example, DMF solutions of *cis*-$[Ru(CN)_2(bipy)_2]$ and either $K[PtCl_3(C_2H_4)]$ or *cis*- or *trans*-$[PtCl_2LL']$ (L = C_2H_4, Me_2S, L' = 4-methylpyridine) react to give 1:1 and 1:2 adducts. Spectroscopic studies indicate that adduct formation results in appreciably enhanced emission lifetimes. The compound $\{Ru(CN)_2(bipy)_2[PtCl_2(C_2H_4)]_2\}$ can be isolated but no structural information is available as yet.[50] Similarly aqueous solutions of $[Ru(CN)_6]^{4-}$ and bis(histidinato)cobalt(III) develop an orange–red colour when exposed to visible light and the formation of the single cyano-bridged complex anion $[(L\text{-hist})_2Co(NC)Ru(CN)_5]^{3-}$ is proposed.[51] The closely related species $[(en)_2NH_3Co(NC)Ru(CN)_5]^-$ has been synthesized[52a] and many other references to cyano-bridged Ru^{II}/metal complexes are to be found in references 52b and 53 with the latter describing the synthesis, photophysical properties and excited state redox behaviour of $[CN(bipy)_2RuCNPtdien]^{2+}$ and $[dienPtNC[Ru(bipy)_2]CNPtdien]^{4+}$. Polymeric cations made up of $Ru(bipy)_2$ units linked by cyanide bridges can be prepared by reacting $[Ru(CN)_2(bipy)_2]$ with $[Ru(C_2O_4)(bipy)_2]$.[54]

The mechanism of formation of these species probably involves initial formation of an outer sphere complex and then reorganization to form a cyano-bridged compound. For example, mixing of $[RuCl(NH_3)_5]^{2+}$ and $[Ru(CN)_6]^{4-}$ solutions produces a new absorption maximum at 510 nm ($\varepsilon = 20$) assigned to an outer sphere intervalence transfer transition from Ru^{II} to Ru^{III}. Irradiation of this band leads to the formation of $[(NH_3)_5Ru(NC)Ru(CN)_5]^-$ as a stable photoproduct whereas intervalence excitation of the starting ion pair yields its redox isomer $[Ru^{II}Cl(NH_3)_5]^+/[Ru^{III}(CN)_6]^{3-}$ which can diffuse apart.[55] Similarly, saturated DMSO solutions of $[Co(NH_3)_6]^{3+}/[Ru(CN)_6]^{4-}$ exhibit an absorption band at 360 nm ($\varepsilon = 580$) assigned to the intervalence transfer from a reducing Ru^{II} to an oxidizing Co^{III} centre,[56] and in a very thorough study, Curtis and Meyer have examined outer sphere charge transfer (OSCT) transitions for a series of mixed metal ion pairs $[M(CN)_6, Ru(NH_3)_5L]^-$ (M = Fe, Ru, Os; L = pyridine or substituted pyridine). From a detailed analysis of these OSCT bands, a number of proposals regarding the 'structure' and the extent of electronic coupling in these species are made.[57,58a] Related studies on the binuclear $[(NH_3)_5RuNC\text{-}Ru(bipy)_2CN]^{3+}$ and trinuclear $[(NH_3)_5RuNCRu(bipy)_2CNRu(NH_3)_5]^{6+}$ have been published.[58b]

Finally, the action of H_2SO_4 on $K_4[Ru(CN)_6]$ is reported to give the formally mixed valence $[Ru_2(CN)_5OH_2]$ as a blue powder, which reacts with ammonia to produce $NH_4[Ru_2(CN)_5(NH_3)_4]$.[59] However this is old work and more evidence is required to substantiate these claims.

45.3.1.3 Ruthenium(III) cyanides

Treatment of a solution of $K_4[Ru(CN)_6]$ with Cl_2 results in several colour changes and warming with H_2SO_4 then precipitates a green–black product of composition $Ru(CN)_3 \cdot 5H_2O$; with concentrated ammonia this gives $Ru(CN)_3 \cdot 2NH_3 \cdot H_2O$ which is also insoluble.[59] Much more recently, because coordinated methylamine ligands are more susceptible to oxidation than the free base, it has been found that exposure of $[Ru(NH_2Me)_6]^{2+}$ cations to oxygen under ambient conditions produces $Ru(CN)_3 \cdot 3H_2O$.[60]

Earlier studies reveal that a yellow solution is obtained by reaction of $[Ru(CN)_6]^{4-}$ with H_2O_2,

Ce^{IV} or bismuthate in acid conditions, or with ozone in neutral. This solution presumably contains the $[Ru(CN)_6]^{3-}$ ion {*cf.* more recent work involving $[MnO_4]^-$ oxidation—equation (1), Section 45.3.1.2.i}. The potential of the $[Ru(CN)_6]^{3-}/[Ru(CN)_6]^{4-}$ couple is $+0.86 \pm 0.05$ V *vs.* SCE.[61] Hydroxyl radicals produced by pulse radiolysis also converts $[Ru(CN)_6]^{4-}$ into $[Ru(CN)_6]^{3-}$.[62] Studies on the decomposition of aqueous solutions of $[Ru(CN)_6]^{3-}$ reveal that reactions such as aquation (to $[Ru(CN)_5OH_2]^{2-}$), dimerization and ligand oxidation to form $[Ru(CN)_5(CNO)]^{4-}$ are involved.[63]

Finally, Gillard *et al.* report that the $[Ru(CN)_2(bipy)_2]^+$ cation (obtained by oxidation of $[Ru(CN)_2(bipy)_2]$ with Cl_2 or cerium(IV) nitrate) reacts with water to give the $[Ru(bipy)_2(H_2O)_2]^{3+}$ cation. Reduction of this solution in the presence of SCN^- gives $[Ru(SCN)_2(bipy)_2]\cdot 4H_2O$.[64]

45.3.1.4 Ruthenium(IV), (V) and (VII) cyano complexes

Treatment of $K_3[Ru_2NCl_8(OH_2)_2]$ with KCN gives the very stable species $K_5[Ru_2N(CN)_{10}]\cdot 3H_2O$. On the basis of IR and Raman studies, an eclipsed (D_{4h}) structure with a linear RuNRu unit is proposed, although of course, these indirect methods cannot distinguish between this and the staggered (D_{4d}) configuration. Cyano complexes of Ru^{IV} are unusual and it is suggested that in this compound the strong π donor effects of the nitrido ligand force the ruthenium to behave as a Ru^{III} or even Ru^{II} centre.

Reaction of RuO_4 with ice cold solutions of NaCN in the presence of caesium ion did not yield the expected $Cs_2[Ru(CN)_4(O)_2]$ anion (*cf.* $Cs_2[RuCl_4(O)_2]$, Section 45.9.9). Instead a green paramagnetic salt formulated as $Cs_3[Ru^V(CN)_4(CNO)_2(O)]$ is formed. The reaction of $K_2[RuO_4]$ with NaCN in the presence of Cs^+ give a yellow paramagnetic material $Cs_5[Ru_2(CN)_9(O)_5]$ (containing formally Ru^{VII}?).[65]

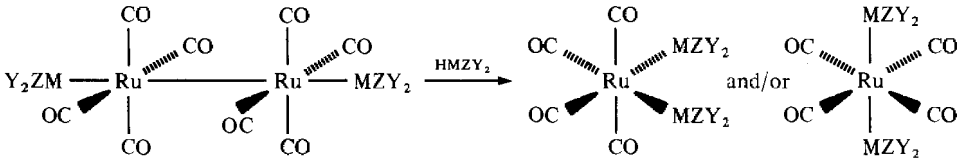
45.3.2 Silicon-containing Ligands

45.3.2.1 Carbonyl complexes

Many of the complexes with silicon-containing ligands and carbonyl groups are outwith the scope of this review in that they are octahedral with four CO groups per ruthenium. Nevertheless, since these compounds are often the precursors for species with three or less CO groups per ruthenium, a brief outline of their syntheses and characterization is given in this section.

$$[Ru_3(CO)_{12}] \xrightarrow[\text{or } h\nu]{\Delta} [Ru(CO)_4] \xrightarrow{HMZY_2} [RuH(MZY_2)(CO)_4] \xrightarrow[-H_2]{\Delta}$$

(6)



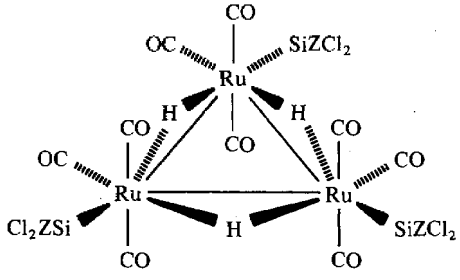
(7) (8)

Scheme 1

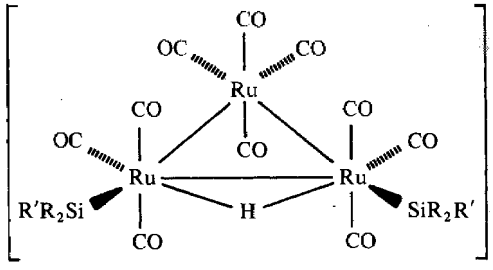
As discussed in detail elsewhere,[1] most of these silicon-containing tetracarbonyl complexes are made *via* either photochemical or thermal reaction of $[Ru_3(CO)_{12}]$ with a silicon hydride (Scheme 1; M = Si). This yields an intermediate $[RuH(SiZY_2)(CO)_4]$ (**6**) which may decompose to $[Ru(SiZY_2)(CO)_4]_2$ (**7**) by loss of H_2 or may react with more $HSiZY_2$ to give *cis*- and/or *trans*-$[Ru(SiZY_2)_2(CO)_4]$ (**8**) [Z = Y = Me, Et, Pr,[66] Cl;[66,67] Z = Me, Y = Cl;[66,68,69] Z = Cl, Y = Me[69] (not all combinations of products formed)]. The latter can also be formed by direct reaction of $[Ru(SiZY_2)(CO)_4]_2$ with $HSiZY_2$. The stereochemically non-rigid behaviour of (**8**) (M = Si, Ge, Sn) has been investigated by $^{13}C\text{-}\{^1H\}$ NMR spectroscopy.[69] Related tetracarbonyl complexes with chelating disilanyl ligands have been formed directly from $[Ru_3(CO)_{12}]$ and an extensive range of mixed Group IVB ligand complexes have been made from $[Ru(SiMe_3)(CO)_4]^-$. (See reference 1, p. 909 for details.)

It has been reported that reaction of $[Ru_3(CO)_{12}]$ with $HSiZCl_2$ (Z = Me, Cl) at elevated temperature gives the trinuclear clusters $[Ru_3(\mu\text{-}H)_3(CO)_9(SiZCl_2)_3]$ (**9**) in addition to $[Ru(SiZCl_2)_2(CO)_4]$. A mechanism of formation of these species is tentatively proposed[70] although attempts to synthesize the corresponding $SiMe_2Cl$ and $SiMe_3$ trinuclear clusters were unsuccessful. A related cluster anion $Na[Ru_3H(CO)_{10}(SiR_2R')_2]$ can be synthesized from $Na[Ru_3H(CO)_{11}]$ and $HSiR_2R'$. On the basis of NMR evidence, structure (**10**) is proposed.[71]

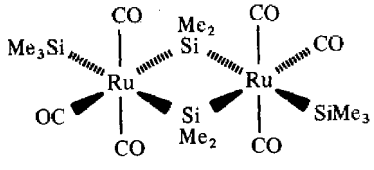
Pentamethyldisilane reacts with $[Ru_3(CO)_{12}]$ to form $[Ru(\mu\text{-}SiMe_2)(SiMe_3)(CO)_3]_2$ (**11**), also obtained from HSi_2Me_5 and $[Ru(MMe_3)(CO)_4]_2$ (M = Si or Ge);[72] the structure of (**11**) has been verified by X-ray analysis (Ru···Ru, 2.96 Å).[73] In contrast, 1,1,2,2-tetramethyldisilane reacts with $[Ru(MMe_3)(CO)_4]_2$ to give $[Ru_2(CO)_6(\mu\text{-}SiMe_2)_3]$ (**12**).[72]



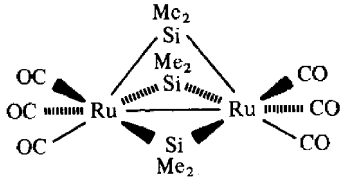
(9)



(10)

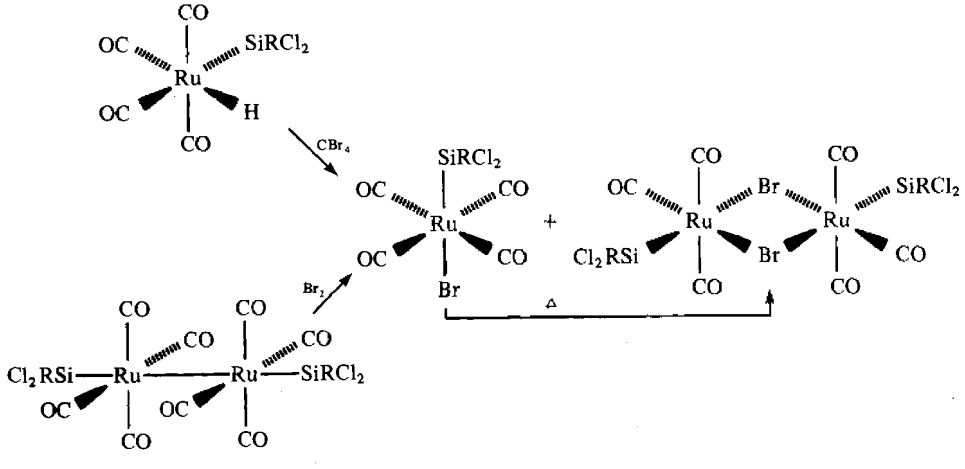


(11)



(12)

Reaction of $[Ru(SiMe_3)(CO)_4]_2$ with bromine or iodine gives *trans*-$[RuX(SiMe_3)(CO)_4]$ and pyrolysis of these materials produces the halide-bridged species $[RuX(SiMe_3)(CO)_3]_2$ as an isomeric mixture.[74] However, as shown in Scheme 2, treatment of *cis*-$[RuH(SiRCl_2)(CO)_4]$ with CBr_4 results in the formation of $[RuBr(SiRCl_2)(CO)_3]_2$ (single isomeric form) together with *trans*-$[RuBr(SiRCl_2)(CO)_4]$. Similar products are obtained when the Ru—Ru bond in $[Ru(SiRCl_2)(CO)_4]_2$ is cleaved with Br_2.[68] Reaction of $[Os(CO)_5]$ with *trans*-$[RuBr(SiCl_3)(CO)_4]$ at 0°C gives $[(CO)_5Os\text{-}RuBr(SiCl_3)(CO)_3]$ which on standing in solution isomerized to $[Br(CO)_4OsRu(SiCl_3)(CO)_4]$.[75]



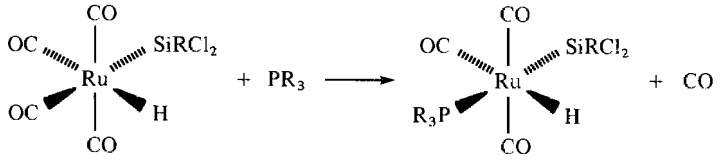
Scheme 2

45.3.2.2 Carbonyl complexes containing group IV, V or VI donor ligands

In *cis*-$[Ru(SiCl_3)_2(CO)_4]$ only the CO groups *trans* to silicon exchange with ^{13}CO.[76] Substitution by PPh_3 to giver *mer*-$[Ru(SiCl_3)_2(CO)_3PPh_3]$ has a similar rate and a wide range of other *mer*-

$[Ru(SiCl_3)_2(CO)_3L]$ (L = PF_3, $P(OPh)_3$, $AsPh_3$, $SbPh_3$, $CNC(Me)_3$ *etc.*) are readily prepared.[67] Similar results are obtained with *cis*-$[Ru(SiMeCl_2)_2(CO)_4]$, and likewise with $[RuH(SiRCl_2)(CO)_4]$, P donor ligands displace the CO group *trans* to $-SiRCl_2$ (equation **4**).[68] Synthesis of the related $[RuX(SiZY_2)(CO)_3L]$ (L = $P(OMe)_3$, PPh_3 *etc.*, X = Cl, Br, I, $ZY_2 = Me_3$; Cl_3; Z = Me, Y = Cl) are readily achieved by cleavage of $[RuX(SiZY_2)(CO)_3]_2$ with L.[68,74]

Further substitution in *mer*-$[Ru(SiCl_3)_2(CO)_3L]$ could only be accomplished when L had a small cone angle. Thus, the second CO group is not replaced by PPh_3 even at 80°C whereas $P(OMe)_3$ reacts at room temperature to give $[Ru(SiCl_3)_2(CO)_2PPh_3\{P(OMe)_3\}]$ and $[Ru(SiCl_3)_2(CO)_2L_2]$ (L = PF_3, $PPhMe_2$ *etc.*) are also formed under mild conditions.[67] Kinetic studies on CO substitution reactions of $[Ru(SiCl_3)_2(CO)_3L]$ complexes indicate a dissociative mechanism and a *cis* effect of L which is almost entirely steric in origin.[77] The dicarbonyl complex $[Ru(SiMe_3)_2(CO)_2(PPh_3)_2]$ can however by synthesized by reaction of $[Ru(SiMe_3)(CO)_4]_2$ (**7**) with PPh_3 (equation 5) or by oxidative addition of $HSiMe_3$ to $[Ru(CO)_3(PPh_3)_2]$ under UV irradiation.[66] Reaction of $[RuH_2(CO)_2(PEt_3)_2]$ with $SiClMe_3$ also gives $[Ru(SiMe_3)_2(CO)_2(PEt_3)_2]$.[78a] A study of the photochemistry of $[RuH(SiEt_3)(CO_3)PPh_3]$ indicates that both facile loss of CO and reductive elimination of Et_3SiH can occur.[78b]

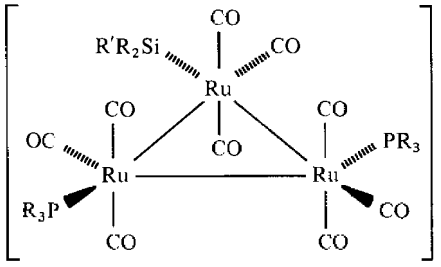


(4)

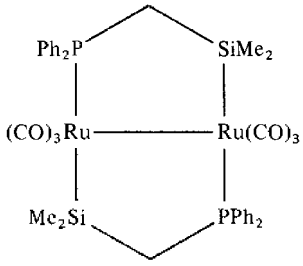
$$[Ru(SiMe_3)(CO)_4]_2 + PPh_3 \longrightarrow Ru(SiMe_3)_2(CO)_2(PPh_3)_2 + Ru(CO)_3(PPh_3)_2 \quad (5)$$

Substitution of the equatorial groups in *cis*-$[Ru(SiCl_3)_2(CO)_4]$ by a variety of bidentate ligands (L–L) gives $[Ru(SiCl_3)_2(CO)_2(L–L)]$ *via* monodentate intermediate $[Ru(SiCl_3)_2(CO)_3(L–L)]$ complexes (L–L = diene, $MeS(CH_2)_2SMe$, $Ph_2P(CH_2)_2PPh_2$, *o*-$C_6H_4[AsMe_2]_2$ *etc.*). With $Ph_2E(CH_2)_2EPh_2$ (E = P, As), it is also possible to isolate the binuclear complexes $\{[Ru(SiCl_3)_2(CO)_3]_2(L–L)\}$.[79]

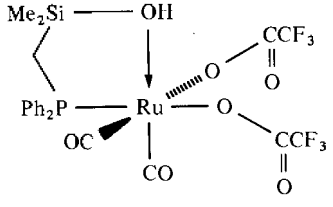
The trinuclear cluster anions $[Ru_3(SiR_2R')(CO)_9(PR_3)_2]^-$ are prepared from $Na[Ru_3H(CO)_{10}(SiR_2R')_2]$ and isolated as the $[N(PPh_3)_2]^+$ salts. Structure (**13**) is proposed on the basis of NMR data.[80] Finally, reaction of $[Ru_3(CO)_{12}]$ with $Ph_2PCH_2SiMe_2H$ affords the symmetrically bridged diruthenium compound (**14**) (Ru—Ru 3.056(1) Å). Treatment of (**14**) with CF_3CO_2H gives the mononuclear phosphinomethyl–dimethylsilanol complex $[Ru(PPh_2CH_2SiMe_2OH)(CO)_2(CO_2CF_3)_2Et_2O]$ (**15**) in which the Et_2O molecule is hydrogen-bonded to the silanol-O with O···O 2.64 Å.



(13)



(14)



(15)

45.3.2.3 Tertiary phosphine and arsine complexes

Silyl–ruthenium(IV) complexes $[RuH_3(SiR_3)L_n]$ (R_3 = various combinations of H, F, Cl, Me, Ph, OMe, OEt; L = PPh_3, $AsPh_3$, $P(C_6H_4Me\text{-}p)_3$; n = 2, 3) are formed by reaction of an excess of $HSiR_3$ with $[RuH_2L_4]$, $[RuHClL_3]$, $[RuCl_2L_3]$ or $[RuCl_3(AsPh_3)_3]$. Complexes of the type $[RuH_2X(SiR_3)L_3]$ (X = Cl, I) are obtained by reaction of the chlororuthenium(II) complexes with $HSiCl_3$ or of $[RuH_3(Si(OEt)_3)(PPh_3)_3]$ with $CDCl_3$ or I_2. These dihydrides are unstable in solution in the absence of an excess of silane and revert to $[RuHX(PPh_3)_3]$. In some cases, $[Ru(SiR_3)_2(PPh_3)_3]$ are formed.[82,83,84]

These silyl–ruthenium complexes are very reactive. For example, incomplete H–D exchange occurs between $[RuH_3(SiR_3)L_3]$ and D_2 at room temperature. Treatment with excess HCl gives the free silane and $[RuCl_2(PPh_3)_3]$, whereas with CO, $[RuH_2CO(PPh_3)_3]$ is formed. Exchange of silyl groups occurs on reaction of $[RuH_3(SiR_3)(PPh_3)_3]$ (R_3 = $(OEt)_3$, Cl_2Me) with $HSiF_3$ whereas iodine gives $[RuH_2I(Si(OEt)_3)(PPh_3)_3]$ and H_2.

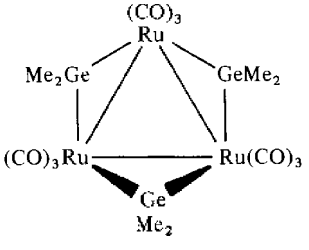
Finally, extensive investigations of the ability of $[RuCl_2(PPh_3)_3]$ to catalyse the hydrosilation of a range of organic substrates have been made. (See references 1 and 85 for full details.)

For details of other silyl–ruthenium compounds containing polyalkenes, azulenes and arenes, see reference 1, pp. 915–919.

45.3.3 Germanium-containing Ligands

Although in comparison to Si much less work has been published on the reactions of germyl hydrides with $[Ru_3(CO)_{12}]$, reaction with $HGeMe_3$ gives compounds $[Ru(GeMe_3)(CO)_4]_2$ (**7**), $[Ru(GeMe_3)_2(CO)_4]$ (**8**) and $[Ru(\mu\text{-}GeMe_2)(GeMe_3)(CO)_3]_2$ (*cf.* **11**) (Scheme 1, M = Ge). In addition, pyrolysis of $[Ru(GeMe_3)_2(CO)_4]$ (**8**) at 140°C gave $[Ru(\mu\text{-}GeMe_2)(CO)_3]_3$ (**16**) and a small amount of $[Ru_2(\mu\text{-}GeMe_2)_3(CO)_6]$ (*cf.* **12**).[86] A number of tetracarbonyl complexes containing different Group IVB ligands can be made from the $[Ru(GeMe_3)(CO)_4]^-$ anion which is obtained by reduction of $[Ru(GeMe_3)(CO)_4]_2$ with Na/Hg (see reference 1, p. 912 for details). X-Ray structural analysis of the *cis* and *trans* isomers of $[Ru(GeCl_3)_2(CO)_4]$ reveals a short Ru—Ge distance (2.48 Å) indicative of the high π-bonding ability of the $GeCl_3^-$ anion.[87]

The compound $[Ru(GeMe_3)_2(CO)_2(PPh_3)_2]$ (isomeric mixture) is formed from $[Ru(GeMe_3)_2(CO)_4]$ and PPh_3.[86] No germyl–ruthenium(IV) compounds of type $[RuH_3(GeR_3)L_n]$ have been reported although in one instance hydrogermylation of 1-hexene catalysed by $[RuCl_2(PPh_3)_3]$ is observed (equation 6).[88] Treatment of $RuCl_3$ with $GeCl_2Et_2$ followed by EPh_3 is reported to give $[RuCl_2(GeEt_2Cl)(EPh_3)_3]$ (E = P, As, Sb). Other germyl–ruthenium compounds containing hydrocarbon moieties are discussed in reference 1, p. 915.



(16)

$$C_4H_9CH{=}CH_2 + GeHPh_3 \xrightarrow[60°C]{[RuCl_2(PPh_3)_3]} C_6H_{13}GePh_3 \qquad (6)$$

45.3.4 Tin-containing Ligands

45.3.4.1 Ruthenium(II) halide complexes

It has long been known that interaction of tin(II) chloride with solutions of platinum metal salts gives coloured species which have been utilized analytically but until recently, the nature of the

species present in solution was uncertain. Reactions of $SnCl_2$ with hydrated $RuCl_3$ or RuO_4 in dilute hydrochloric acid give yellow or orange salts containing the $[RuCl(SnCl_3)_5]^{4-}$ anion,[89] previously described as $[RuCl_2(SnCl_3)_2]^{2-}$.[90] The structure has been confirmed by X-ray analysis and the first example of ^{119}Sn–^{99}Ru coupling has been observed in the ^{119}Sn FT NMR spectrum of this anion.[91] The ^{119}Sn Mössbauer spectrum of '$[RuCl_2(SnCl_3)_2]^-$' is reported.[92] Reaction of $[RuCl(SnCl_3)_5]^{4-}$ with L (L = thiourea or its substituted derivatives) is claimed to give $Me_4N[Ru(SnCl_3)_3L_3]$, $[Ru(SnCl_3)_2L_4]$ and $[RuL_6](SnCl_3)_2$.[93]

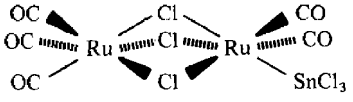
Another route to the $[RuCl(SnCl_3)_5]^{4-}$ anion is from reactions between $SnCl_2$ and $[RuCl_5NO]^{2-}$ in HCl solution; intermediates such as orange $[RuCl_3(SnCl_3)_2NO]^{2-}$ and brownish-black $[Ru_2Cl_6(SnCl_3)_2(NO)_2]^{4-}$ were characterized.[94] The $[RuCl_2(SnCl_3)_4]^{4-}$ ion is reported in a Japanese patent[95] and further work has substantiated this claim.[96]

Reaction of '$RuCl_3 \cdot xH_2O$' with SnF_2 in aqueous HF followed by addition of MF (M = Na, K or NH_4) gives $M_4[Ru(SnF_3)_6]$ which on treatment with HX in the presence of $[Me_4N]^+$ gives $[Me_4N]_4[RuX(SnF_3)_5]$ (X = Cl, Br).[97] The $[Ru(SnF_3)_6]^{4-}$ anion is also formed by treatment of $H_4[RuCl(Sn(OH)_3)_5]$ with $SnCl_2$ in HF.[98] The ^{119}Sn NMR spectrum of the corresponding $[Ru(SnCl_3)_6]^{4-}$ (made *in situ* by reaction of '$RuCl_3 \cdot xH_2O$' with a ten-fold excess of $SnCl_2 \cdot 2H_2O$ in 3 M HCl) has been published.[96,99]

45.3.4.2 Ruthenium(II) carbonyl and carbonyl halide complexes

As for silicon and germanium, reaction of $[Ru_3(CO)_{12}]$ with $HSnR_3$ gives good yields of $[Ru(SnR_3)_2(CO)_4]$; for R = Me, a small amount of $[Ru(\mu\text{-}SnMe_2)(SnMe_3)(CO)_3]_2$ (*cf.* **11**) is also produced;[100] the structure of the latter has been confirmed by X-ray analysis.[101] Other ways of forming the $[Ru(SnR_3)_2(CO)_4]$ complexes are by treatment of $[RuH_2(CO)_4]$ with $HSnMe_3$ or $SnPh_3Cl$, reaction of $[Ru(MMe_3)_2(CO)_4]$ (M = Si,Ge)[66,86] with $HSnMe_3$, or by reaction of $Me_3SnCH_2NMe_2$ with $[Ru_3(CO)_{12}]$.[102] Reaction of the $[Ru(MMe_3)(CO)_4]^-$ anions (M = Si,Ge) with SnR_3Cl gives the mixed group IVB ligand complex $[Ru(MMe_3)(SnR_3)(CO)_4]$ and treatment of these with SnR'_3Cl gives $[Ru(SnR'_3)(SnR_3)(CO)_4]$. With $SnCl_2Me_2$, the anion $[Ru(SiMe_3)(CO)_4]^-$ yields $[Ru(\mu\text{-}SnMe_2)(CO)_4]_2$.[66] The X-ray structure of $[Ru(SnMe_3)(CO)_4]_2$ shows the linear Sn—Ru—Ru—Sn unit and eclipsed configuration of the CO groups (*cf.* **7**; Scheme 1).[103]

The reaction of $SnCl_4$ with $[Ru_3(CO)_{12}]$ (xylene, 135°C) gives $[Ru_2Cl_3(SnCl_3)(CO)_5]$ (**17**); a trinuclear derivative $[Ru_3(CO)_{12}SnCl_4]$ is formed at room temperature and is thought to contain a linear Ru_3 sequence. On heating this may form $[RuCl(SnCl_3)(CO)_4]$ which can dimerize with loss of $SnCl_2$ to form (**17**). Under CO (70 atm) the product is *trans*-$[Ru(SnCl_3)_2(CO)_4]$ which does not isomerize to the *cis* form in solution.[104,105]

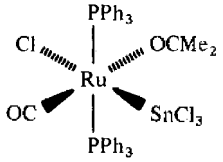


(17)

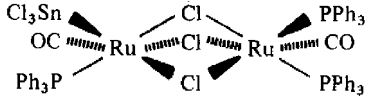
The 'RuCOX' (X = Cl or Br) solutions react with SnX_2 to form lemon-yellow $[RuCl_2(SnX_3)_2(CO)_2]^{2-}$; the chloro complex is also formed from $[RuCl_2(CO)_2]_n$ and $SnCl_2$ in HCl solution.[106,107,108] The related $[RuCl(SnMe_3)(CO)_4]$ is prepared by cleavage of one of the Ru—Sn bonds in $[Ru(SnMe_3)_2(CO)_4]$, using I_2 at −5°C.[74]

45.3.4.3 Ruthenium(II) complexes containing group IV, V or VI donor ligands

Treatment of the 'RuCOCl' solutions with PPh_3 and $SnCl_2$ in acetone gives lemon-yellow crystals initially formulated as $[Ru_2Cl_3(SnCl_3)(CO)_2(PPh_3)_3(Me_2CO)_2]$[106] but shown by X-ray analysis to be the monomer (**18**). This is converted to the bridged derivative (**19**) by warming in benzene; both complexes readily eliminate $SnCl_2$, the latter giving $[Ru_2Cl_4(CO)_2(PPh_3)_3]$[109] (see Section 45.5.5.1).



(18)



(19)

White *trans*-$[Ru(SnCl_3)_2(CNEt)_4]$ and *cis*-$[RuCl(SnCl_3)(CNEt)_2(EPh_3)_2]$ are formed by insertion of $SnCl_2$ into $[RuCl_2(CNEt)_4]$ or *cis*-$[RuCl_2(CNEt)_2(EPh_3)_2]$ (E = P, As, Sb) respectively.[10,110] Similarly reaction of $RuCl_3$ with $SnCl_2$ followed by EPh_3 gives $[RuCl(SnCl_3)(EPh_3)_3]$[15] and treatment of *trans*-$[RuHX(PHPh_2)_4]$ or $[RuCl_2(DMSO)_4]$ with $SnCl_2$ gives *trans*-$[RuH(SnCl_3)(PHPh_2)_4]$[111] and $[Ru(SnCl_3)_2(DMSO)_4]$[112] respectively.

Reaction of the $[RuCl_2(SnX_3)_2(CO)_2]^{2-}$ anions with pyridine (X = Cl, Br) gives $[Ru(SnX_3)_2(CO)_2(py)_2]$; with SEt_2, the cationic complex $[Ru(SnCl_3)(CO)_2(SEt_2)_3]^+$ is formed.[108]

Finally, reaction of $[RuI(CO)_3(PPh_3)_2]I$ with SnI_2 (1:1 mole ratio) gives $[RuI(CO)_3(PPh_3)_2]SnI_3$. The same compound is formed by oxidation of $[Ru(CO)_3(PPh_3)_2]$ with SnI_4; in C_6H_6 under reflux the latter reaction produces *cis*-$[RuI_2(CO)_2(PPh_3)_2]$ and SnI_2.[12]

45.3.5 Lead-containing Ligands

The only reference to ruthenium–lead complexes is the preparation of *cis*-$[Ru(PbMe_3)_2(CO)_4]$ from reaction of $[Ru(CO)_4]^{2-}$ with $PbClMe_3$ (reference 1, p. 912).

45.4 NITROGEN LIGANDS

45.4.1 Ammines

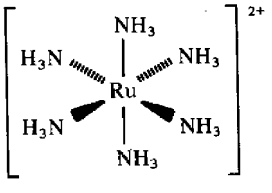
45.4.1.1 Mononuclear complexes $[Ru(NH_3)_6]^{x+}$

Ruthenium(II): $[Ru(NH_3)_6]^{2+}$ (**20**) is a diamagnetic orange complex which can be prepared by reaction of $RuCl_3$ with NH_4OH in the presence of zinc dust (equations 7 and 8),[113–115] by treatment of $RuCl_3$, $[RuCl_5H_2O]^{2-}$, $[RuCl(NH_3)_5]^{2+}$ or $[RuCl_6]^{2-}$ with hydrazine and NH_4Cl,[116,117] by refluxing $[Ru(NH_3)_5N_2]^{2+}$ with concentrated NH_3 solution[117] or by reduction of $[Ru(NH_3)_6]^{3+}$ (see below). The single crystal X-ray structures of $[Ru(NH_3)_6]X_2$ (X = I^-, Cl^-) (**20**) have been reported[118,119] and show octahedral geometry around ruthenium(II) with Ru—N = 2.144 Å for the I^- salt.[118] The UV visible spectrum of (**20**) shows an absorption at 267 nm,[116] while its Mössbauer spectrum has also been reported.[120] The IR spectrum of $[Ru(NH_3)_6]^{2+}$ has been analysed,[117,121–123] and on the basis of deuteration shifts using highly concentrated nujol mulls the band predominantly due to the T_{1u} (Ru—N) stretching vibration, $\nu_{Ru\ N}$, has been reassigned to the absorption at 430 cm^{-1}.[123]

$$2RuCl_3 + Zn + 16NH_3 \longrightarrow 2[Ru(NH_3)_6]Cl_2 + [Zn(NH_3)_4]Cl_2 \quad (7)$$

(**20**)

$$[Ru(NH_3)_6]Cl_2 + [Zn(NH_3)_4]Cl_2 + 4HCl \longrightarrow [Ru(NH_3)_6][ZnCl_4] + 4NH_4Cl \quad (8)$$



(20)

$[Ru(NH_3)_6]^{2+}$ is a good reducing agent ($E^\circ = -0.214$ V *vs.* SHE for $[Ru(NH_3)_6]^{2+/3+}$ couple),[124] and has been studied in relation to outer-sphere electron transfer reactions.[118,124–126] The self exchange between $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_6]^{3+}$ (equation 9) has a rate constant $k = 3.2 \times 10^3\ M^{-1}s^{-1}$ in CF_3SO_3H,[127] with $\Delta H^{\neq} = 43.1 \pm 1.0$ kJ mol^{-1} and $\Delta S^{\neq} = -11 \pm 3$ J K^{-1} mol^{-1}.[128] Reductive quenching[128] of excited state $[Ru(bipy)_3]^{2+*}$ by $[Ru(NH_3)_6]^{2+}$ *via* an outer-sphere mechanism has been reported[129] (see Section 45.4.3.1). Oxidation of $[Ru(NH_3)_6]^{2+}$ by $[Ru(NH_3)_5py]^{3+}$ occurs with a rate constant, $k = 7.2 \times 10^5\ M^{-1}s^{-1}$.[130] Electron transfer reactions between $[Ru(NH_3)_6]^{2+}$ and a series of cobalt(III) complexes have been studied.[131–134] The one electron reduction of $[Co(L)(OH_2)_2]^{5+}$ (L = tetra-4-*N*-methylpyridyl porphine) (equation 10) occurs at a rate ($k_{12} = 1.2 \times 10^5\ M^{-1}s^{-1}$ at 15.5°C; $K_{equil} = 8.9 \times 10^5$) higher than that observed for the reduction of $[Co(NH_3)_5(OH_2)]^{3+}$ and $[Co(NH_3)_6]^{3+}$.[135,136] This is consistent with the $E_{1/2}$ values for the Co^{III}/Co^{II} couples, with the rate of reaction decreasing with increasing pH.[137] The reduction of

$[CoX(NH_3)_5]^{2+}$ (X = NCS^-, SCN, N_3^-, F^-, Cl^-, Br, I^-, OAc^-, RCO_2^-)[124,126,131,133,138–141] $[CoX(NH_3)_5]^{3+}$ (X = H_2O,[142] nitrile,[143] glycine, alanine[144]) and $[Co(en)_2(L–L)]^{n+}$ (L–L = thiolate, thioether, alkoxy, carboxylate)[145] by $[Ru(NH_3)_6]^{2+}$ has been studied kinetically, the specific rates for reduction of the nitrile complexes being increased due to electron withdrawal by the C≡N moiety.[143] For the glycine and alanine complexes, no pH dependence was observed,[144] the electron transfer being thought not to occur *via* coordination of carboxylate to ruthenium.[144,145] Kinetic studies have also been carried out on the reduction of $[Fe(L)(OH_2)_2]^{5+}$ (L = tetra-4-*N*-methylpyridyl porphine),[146] $[Fe(edta)]^-$,[147] cytochrome aa_3,[148] cytochrome c(III),[149] platinum(IV)[150] and copper(II)/(III)[124,151] complexes and perchlorate salts.[124] The reduction of Fe^{III} is found to be faster than that of $[FeOH]^{2+}$.[128] The importance of non-adiabaticity in the above outer-space mechanisms has been discussed.[129,152]

$$[Ru(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} \longrightarrow [Ru(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+} \quad (9)$$

$$[Ru(NH_3)_6]^{2+} + [Co^{III}(L)(OH_2)_2]^{5+} \rightleftharpoons [Ru(NH_3)_6]^{3+} + [Co^{II}(L)(OH_2)_2]^{4+} \quad (10)$$

Under protic conditions $[Ru(NH_3)_6]^{2+}$ is oxidized by O_2 to give $[Ru(NH_3)_6]^{3+}$ and H_2O_2 (equation 11),[153] the reduction of O_2 being 10^4 faster than the corresponding reduction of H_2O_2.[153] The reduction of H_2O_2 to H_2O by $[Ru(NH_3)_6]^{2+}$ shows first order dependence on $[Ru^{II}]$ and saturation dependence on $[H_2O_2]$.[154] A mechanism involving addition of H_2O_2 to a distorted, activated six-coordinate complex $*[Ru(NH_3)_6]^{2+}$ to give a seven-coordinate intermediate (**21**) (equation 12) has been postulated.[154] The photooxidation of $[Ru(NH_3)_6]^{2+}$ at a ferrocene derivatized photoanode has been reported.[155] The aquation of $[Ru(NH_3)_6]^{2+}$ is found to be $[H^+]$ catalysed with rate constant $k = 1.24 \times 10^{-3}\,M^{-1}s^{-1}$ at 25°C,[156] an interaction of H^+ and Ru^{II} π–d electron density being proposed to labilize the Ru—N bond.[157a] The hydroformylation of ethylene is catalysed by $[Ru(NH_3)_6]^{2+}$ on zeolites; the active species is thought to be $[Ru(OH)(NH_3)_5]^{2+}$.[157b]

$$\frac{-d[O_2]}{dt} = k[[Ru^{II}(NH_3)_6]^{2+}][O_2] \qquad k = 1.26 \times 10^2\ M^{-1}s^{-1} \text{ at } 25°C,\ \mu = 1 \quad (11)$$

$$[Ru(NH_3)_6]^{2+} \rightleftharpoons *[Ru(NH_3)_6]^{2+} \xrightarrow{H_2O_2} [Ru(NH_3)_6(H_2O_2)]^{2+} \xrightarrow[2H^+]{[Ru(NH_3)_6]^{2+}}$$

(21)

$$2[Ru(NH_3)_6]^{3+} + 2H_2O \quad (12)$$

Ruthenium(III): $[Ru(NH_3)_6]^{3+}$ (**22**) is colourless and is prepared usually by the oxidation of $[Ru(NH_3)_6]^{2+}$.[115] Oxidizing agents that have been used include hydrazine hydrochloride,[116] $Na_2[PtCl_6]$,[115] $Na[AuCl_4]$,[115] acidified NO_2^- salts,[158] Br_2 in the presence of NaBr[113] and Br_2 vapour.[159] Heating of $[RuCl(NH_3)_5]Cl_2$ with hydrazine hydrochloride,[160] or treatment of $[Ru(NH_3)_5(OH_2)]^{2+}$ with hydrazoic acid[161] also gives $[Ru(NH_3)_6]^{3+}$. The latter reaction is proposed to occur *via* a nitrene intermediate (**23**) (equations 13–15).[161] $[Ru(NH_3)_6]^{3+}$ shows an absorption band at 276 nm,[116,162] while X → Ru charge transfer bands for $[Ru(NH_3)_6]X_3$ (X = Cl^-, Br^-, I^-) have also been assigned;[156] for X = I^- and Br^-, two maxima are observed due to $^2P_{3/2}$–$^2P_{1/2}$ doublet splitting of the halide ion.[156] The Ru—N stretching vibration ν_{Ru-N} for the complexes $[Ru(NH_3)_6]X_3$ (X = Cl^-, Br^-, I^-, BF_4^-) occurs in the IR in the region 485–424 cm^{-1}.[117] The single crystal X-ray structures of $[Ru(NH_3)_6]X_3$ (X = BF_4^-,[118] Cl^-[119]) confirm an octahedral geometry for ruthenium(III) with Ru—N = 2.104 Å for the BF_4^- salt.[118] Magnetic susceptibility measurements in the range 80–300 K show $[Ru(NH_3)_6]X_3$ to have a low spin d^5 configuration with μ_{eff} = 1.90 BM (87 K), 2.17 BM (292 K) for the Br^- salt.[163] Aqueous solutions of $[Ru(NH_3)_6]^{3+}$ turn yellow on addition of NaOH with a new absorption at 400 nm due to the formation of $[Ru(NH_2)(NH_3)_5]^{2+}$ (**24**) (equation 16).[164] $[Ru(NH_2)(NH_3)_5]^{2+}$ is believed to play an important role in the base catalysed proton exchange reactions of $[Ru(NH_3)_6]^{3+}$ in H_2O.[164] When $[Ru(NH_3)_6]^{3+}$ is dissolved in HPO_4^{2-}/NaOH buffer (pH 12), however, no yellow solution is obtained; in addition absorptions for $[Ru(NH_2)(NH_3)_5]^{2+}$ were found to show marked dependence on anions.[165] Subsequently the optical spectra of basic solutions of $[Ru(NH_3)_6]^{3+}$ were analysed assuming the presence of a hydroxide ion pair and $[Ru(NH_2)(NH_3)_5]^{2+}$, the formation constants of which were 5.4 M^{-1} and 1.8 M^{-1} respectively.[166] The aquation of $[Ru(NH_3)_6]^{3+}$ proceeds *via* two parallel reaction pathways: (a) pH independent, (b) base catalysed, pK_a of $[Ru(NH_3)_6]^{3+}$ = 13.1.[166]

$[Ru(NH_3)_6]^{3+}$, like $[Ru(NH_3)_6]^{2+}$, participates in outer-sphere electron transfer reactions, a range of such reactions involving the reduction of $[Ru(NH_3)_6]^{3+}$ having been reported. $[Ru(NH_3)_6]^{3+}$ quenches the excited state $[Ru(bipy)_3]^{2+*}$ and has been suggested as a possible oxidant in related redox systems.[167] The reduction of $[Ru(NH_3)_6]^{3+}$ by Cr^{2+},[125] $[V(bipy)_3]^{2+}$,[168] $[V(H_2O)_6]^{2+}$ ($\Delta H^{\neq}$ = 2.5 kJ mol^{-1}, $\Delta S^{\neq} = -42$ J K^{-1} mol^{-1} at 298 K[169] and U^{III} ($\Delta H^{\neq}$ = 1.0 kJ mol^{-1},

$$[Ru(NH_3)_5(OH_2)]^{2+} \xrightarrow{N_3H} [Ru(NH_3)_5(N_3H)]^{2+} \longrightarrow [(H_3N)_5Ru^{IV}{-}\ddot{N}H]^{2+} + N_2 \quad (13)$$

(23)

$$[(H_3N)_5Ru^{IV}{-}\ddot{N}H]^{2+} \xrightarrow{H^+} [(H_3N)_5Ru^{IV}{-}NH_2]^{3+} \quad (14)$$

$$[(H_3N)_5Ru^{IV}{-}NH_2]^{3+} + [Ru(NH_3)_5(OH_2)]^{2+} \xrightarrow{H^+} [Ru(NH_3)_6]^{3+} + [Ru(NH_3)_5(OH_2)]^{3+} \quad (15)$$

(22)

$$[Ru(NH_3)_6]^{3+} + {}^-OH \rightleftharpoons [Ru(NH_2)(NH_3)_5]^{2+} + H_2O \quad (16)$$

(22) (24)

$\Delta S^{\neq} = -39\,J\,K^{-1}\,mol^{-1}$)[170,171] has been studied. No acid dependence was observed in the oxidation of Np^{III} by $[Ru(NH_3)_6]^{3+}$,[172] while the second order reduction by Ti^{III} was found to be inversely proportional to $[H^+]$, suggesting that $Ti(OH)^{2+}$ was the active reductant.[173] $[Ru(NH_3)_6]^{3+}$ forms a range of mixed valent salts with $[Ru(CN)_6]^{4-}$, $[Fe(CN)_6]^{4-}$[58,174] and $[Fe(CN)_5L]^{3-}$ (L = CO, DMSO, pz, py, imid)[174] which show outer-sphere intervalence charge transfer bands in the visible-near IR region. A plot of optical electron transfer energy *versus* difference in redox potential of the complexes increases linearly; these results have been discussed[58,174] in terms of Hush theory.[175,176] Photolysis of $[Ru(NH_3)_6]^{3+}$ at 185 nm leads to substantial photoreduction in the presence of 2-propanol, methanol or ethanol which act as radical scavengers of the excited state $[Ru(NH_3)_6]^{3+*}$.[177] $[Ru(NH_3)_6]^{3+}$ has been reduced by $e^-_{(aq)}$[178] and by organic radicals *via* outer-sphere mechanisms, the order of reactivity being $\dot{C}H_2OH < CH_3\dot{C}HOH < (CH_3)_2\dot{C}OH < CH_3\dot{C}OH\text{-}CO_2^- < CH_3CO\dot{C}(O^-)CH_3$;[178,179] in general $R\dot{C}(OH)CO_2H$ was found to be less reactive than $R\dot{C}(OH)CO_2^-$.[180] The low yield UV photoaquation of $[Ru(NH_3)_6]^{3+}$ has been reported.[181] The adsorption–desorption of $[Ru(NH_3)_6]^{3+}$ on pyrolytic graphite electrodes coated with Nafion 125 and on clay-modified electrodes has been described.[182,183]

Ruthenium(IV) and (V): Oxidation of $[Ru(NH_3)_6]^{3+}$ by $\dot{O}H$ gives $[Ru(NH_3)_6]^{4+}$ which rapidly decays to $[Ru(NH_3)_6]^{5+}$ and $[Ru(NH_3)_6]^{3+}$ with a rate constant $k = 4.5 \times 10^9\,M^{-1}\,s^{-1}$.[178]

45.4.1.2 Mononuclear complexes $[RuL_n(NH_3)_{6-n}]^{x+}$

Ruthenium ammine–phosphine and –selenium complexes are discussed in Sections 45.5.4.6 and 45.8 respectively.

(*i*) *Carbon donor ligand complexes*

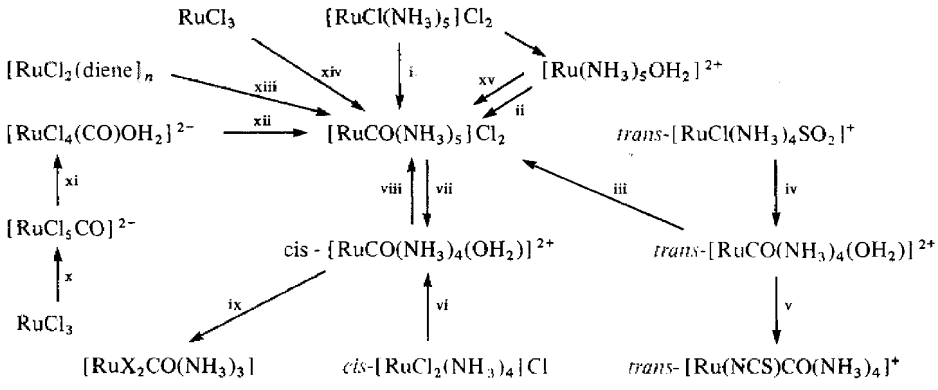
(a) Cyanides and related ligands

Cyano–ammine complexes are also discussed in Section 45.3.1.2.ii $[Ru(NH_3)_5OH_2]^{2+}$ reacts with isocyanide L in ethanol to give $[Ru(L)(NH_3)_5]^{2+}$, and on further reaction, the bis adduct *trans*-$[Ru(L)_2(NH_3)_4]^{2+}$ (L = benzyl isocyanide, cyclohexyl isocyanide).[184a] Aquation of *trans*-$[Ru(CNC_7H_7)_2(NH_3)_4]^{2+}$ yields *trans*-$[Ru(CNC_7H_7)(NH_3)_4(OH_2)]^{2+}$.[184a] Measurements on the rate of aquation of $[Ru(CNC_7H_7)(NH_3)_5]^{2+}$ to *trans*-$[Ru(CNC_7H_7)(NH_3)_4(OH_2)]^{2+}$ indicate that isocyanide labilizes the *trans* NH_3 by a factor of forty compared with the aquation of $[Ru(NH_3)_6]^{2+}$.[184a] Likewise the rate of aquation of *trans*-$[Ru(CNC_7H_7)(NH_3)_4(isn)]^{2+}$ is also enhanced by isocyanide, a low affinity of ruthenium(II) for isn being observed in these systems.[184a] $E_{1/2}$ values for the above complexes have been measured, the electrolysis of $[Ru(CNC_7H_7)(NH_3)_5]^{2+}$ at 0.79 V *vs.* NHE yielding the ruthenium(III) species $[Ru(CNC_7H_7)(NH_3)_5]^{3+}$.[184a] The solid state thermal reactions of $[Ru(NH_3)_5L]^{2+}$ (L = MeNC, CO) have been analysed and compared with the reactivity of analogous complexes of N_2, NCMe and NO.[184b]

(b) Carbonyls and alkenes

Carbonyl and alkene complexes of ruthenium have been previously reviewed.[1] The syntheses of $[Ru(CO)(NH_3)_5]^{2+}$ are summarized in Scheme 3. The dependence of $\nu_{C\equiv O}$ upon counterion and upon solvent has been discussed.[188] The Mössbauer spectrum of $[Ru(CO)(NH_3)_5]^{2+}$ has been reported.[27c,120] The replacement of H_2O by isn in *trans*-$[Ru(L)(NH_3)_4(OH_2)]^{2+}$ has been assessed, the lability increasing in the order L = CO = N_2 < isn < py < imid (N bound) ≃ NH_3 < OH^- < CN^- < SO_3^{2-} < imid (C bound).[189] For π acid ligands good correlation between specific rate and $E_{1/2}$ values for the ruthenium(II)/(III) couple was observed.[189]

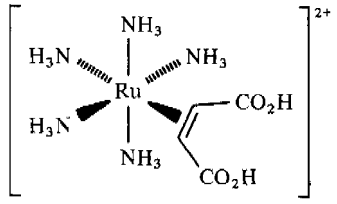
Treatment of $[RuCl(NH_3)_5]^{2+}$ with Ag^+ followed by reduction by zinc amalgam in aqueous



i, Zn/Hg, H^+, CO;[159] ii, CO, H_2SO_4, 48 h;[185] iii, NH_3;[159] iv, CO, HCO_2H, 70 °C, 3 h;[159]
v, NaNCS;[159] vi, Zn/Hg, H^+, CO;[159] vii, H^+, H_2O;[159] viii, NH_3;[159] ix, HX;[159]
x, CO, HCl, 80 °C, 16 h;[186] xi, H_2, 80 °C, 5 h;[186] xii, NH_4OH, 25 °C, 48 h;[186]
xiii, CO, NH_2NH_2;[187a] xiv, (a) CO, EtOH, (b) NH_2NH_2;[187a] xv, CO_2, Zn/Hg;[187b]

Scheme 3

solution and addition of L yields $[Ru(L)(NH_3)_5]^{2+}$ (L = fumaric acid, ethylene, isobutene, 1,4-cyclohexadiene, acetylene, phenylacetylene, 3-hexyne).[190] The complex of 3-hexyne has also been prepared by addition to $[Ru(NH_3)_5(acetone)]^{2+}$.[191] The complexes show $d \rightarrow \pi^*$ charge transfer bands in the range 200–300 nm while the C=C and C≡C stretching vibrations $\nu_{C=C}$, $\nu_{C\equiv C}$ are lowered in energy by 100–200 cm^{-1} on complexation. The single crystal X-ray structure of the fumaric acid adduct (**25**) shows the alkene to be carbon η^2 bound to the metal centre, C=C = 1.413 Å, Ru—C = 2.172 Å, Ru—N = 2.143–2.154 Å, with the axial NH_3 ligands bending away from the equatorially bound alkene.[190] The stabilization of ruthenium(II) in these systems ($E_{1/2}$ = 0.54 V *vs.* NHE for $[Ru^{II}(3\text{-hexyne})(NH_3)_5]^{2+}$) is ascribed to back-bonding from metal to alkene.[190]



(25)

Carbon bonded imidazole derivatives are discussed in Section 45.4.1.2.ii.b.

(*ii*) *Nitrogen donor ligand complexes*

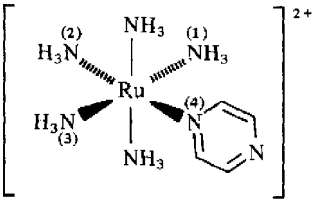
(a) Amines

Treatment of $[RuCl(NH_3)_5]^{2+}$ with $Ag(O_2CCF_3)$, followed by zinc amalgam reduction and addition of amine yields $[Ru(L)(NH_3)_5]^{2+}$ (L = cyclohexylamine, benzylamine, methylamine).[192] Oxidation of these complexes with Br_2 produces the corresponding ruthenium(III) species $[Ru(L)(NH_3)_5]^{3+}$.[192] Subsequent oxidation of the amine ligand can readily occur to give imine and nitrile products, explaining the relatively few complexes of this type that have been isolated (see Section 45.4.2).

(b) Monodentate heterocycles

Ruthenium(II): A range of complexes of the type $[Ru(L)(NH_3)_5]^{2+}$ (*e.g.* L = pyridine,[193–196] pyridazine,[193] pyrazine,[193,195,197] pyrimidine,[193] triazine,[193] 2-cyanopyridine, 3-cyanopyridine, 4-cyanopyridine,[198] 2-, 3- and 4-RC(O)-substituted pyridines (R = $CHMe_2$, CH_2Et, CH_2Pr^i,[199] OMe, NH_2, OH,[194] H,[193] Ph[195]), *N*-methylpyrazine,[197] 4,4′-bipyridine,[195] 1,2-bis(4′-pyridyl)ethylene,[195] hypoxanthine,[200] guanine,[201] xanthine,[202] 4-dimethylaminopyridine[196]) have been prepared by reaction of $[RuCl(NH_3)_5]Cl_2$ with a Ag^+ salt (AgO_2CCF_3 is often used) followed by zinc amalgam reduction

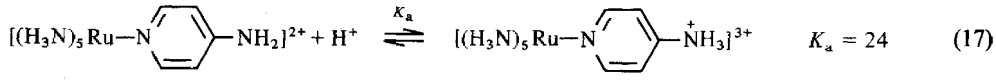
and addition of ligand L. Alternatively L may be added directly to $[Ru(NH_3)_5(OH_2)]^{2+}$. Reduction of $[RuL(NH_3)_5]^{3+}$ chemically by H_2S[203] or electrochemically[204] has been used to generate $[RuL(NH_3)_5]^{2+}$ (L = pyridine, 4-aminopyridine). The single crystal X-ray structure of $[Ru(NH_3)_5pz]^{2+}$ (**26**) shows octahedral ruthenium(II) with Ru—N(NH_3) = 2.15–2.17 Å, and a shortened Ru—N(pz) = 2.006 Å due to $d\pi(Ru) \rightarrow {}^*\pi(pz)$ back-bonding.[205] The plane of the pyrazine ring intersects the equatorial plane containing N-1, N-2, N-3 and N-4 at 45° thus minimizing steric effects.



(26)

The electronic spectra of these complexes show solvent dependent $Ru^{II} \rightarrow L$ charge transfer bands[193,196] which have been used to assess the degree of metal → ligand back-bonding.[206] The Ru^{II}/Ru^{III} redox couples for the complexes have been correlated with the energies of the $Ru^{II} \rightarrow L$ charge transfer bands,[193] *e.g.* for L = py, $\lambda = 407$ nm ($\varepsilon = 7700\,M^{-1}cm^{-1}$), $E_{1/2} = +0.38$ V *vs.* SSCE.[191] Mössbauer studies of $[Ru(NH_3)_5L]^{2+}$ (L = pyridine, pyrazine) have been reported.[120] The degree of back-donation from the ruthenium(II) centre has been probed by ^1H and ^{13}C NMR for the complexes $[Ru(L)(NH_3)_5]^{2+}$ (L = pyridine, 4-methyl pyridine, 4-benzoyl pyridine, pyrazine, methyl pyrazine).[38,207] The shifts in the ^{13}C NMR spectra for the 3- and 4-positions were found to be consistent with back-bonding to the ligand from the metal centre.[207] In addition, the C≡N stretching vibration $\nu_{C\equiv N}$ for 4-cyanopyridine shifts to low energy on coordination to the $[Ru(NH_3)_5]^{2+}$ moiety.[198] $[Ru(NH_3)_5L]^{2+}$ (**27**) (L = 4-aminopyridine) shows a Ru → L charge-transfer band at 360 nm. At low pH this absorption decreases in intensity due to protonation of the free amine (equation 17),[204] suggesting that the lone pair on the uncoordinated NH_2 influences the M → L charge transfer process. On protonation of (**27**), LH^+ becomes a better π acceptor shifting λ_{max} to longer wavelength.[204] On coordination of pyrazine, 4,4′-bipyridine and 1,2-bis(4′-pyridyl)-ethylene to $[Ru(NH_3)_5]^{2+}$, the basicity of the free N site is increased (pK_a for complexes = 2.6, 4.4, 5.0 respectively).[195] This effect has been discussed in relation to stronger metal → ligand back-donation in the protonated complexes[193] and in terms of the degree of delocalization of the protonated species.[195] The enthalpy of protonation of $[Ru(NH_3)_5pz]^{2+}$ is found to be $-20.5\,kJ\,mol^{-1}$.[208] This work has been further extended by the synthesis of complexes $[Ru(NH_3)_5LH]^{3+}$ incorporating potentially bidentate ligands (L = *e.g.*, 1,1′-bis(4′-pyridyl)amine).[209] The rate of reduction of pyrazine *N*-oxide was found not to be increased on coordination to the $[Ru(NH_3)_5]^{2+}$ moiety in spite of the N—O stretching vibration ν_{N-O} decreasing from 1313 cm^{-1} in the free oxide to 1258 cm^{-1} in the complex.[210] The synthesis,[196] electronic, IR and resonance Raman spectra of $[Ru(L)(NH_3)_5]^{3+}$ (L = 1-methyl-4,4′-bipyridine) have been published.[211]

The pseudoexchange rate for the $[Ru(NH_3)_5py]^{2+/3+}$ couple has been determined as $k = 4.7 \times 10^5\,M^{-1}s^{-1}$ at 25°C.[212] The reduction of cytochrome c,[213,214] myoglobin,[215–217] Co^{III} and $Cu^{II/III}$ complexes by $[Ru(L)(NH_3)_5]^{2+}$ (L = histidine, pyridine, pyrazine, 4,4′-bipyridine) has been reported.[151,218,219] The reduction of O_2 by $[Ru(NH_3)_5(isn)]^{2+}$, and *cis*- and *trans*-$[Ru(NH_3)_4(isn)(OH_2)]^{2+}$ occurs *via* outer-sphere formation of O_2^- with rate constants $k = 1.08 \times 10^{-1}$, 1.38×10^{-1} and $3.03 \times 10^{-2}\,M^{-1}s^{-1}$ respectively (equation 18).[220] Ruthenium(III) and decreasing acidity were found to inhibit the reduction due to competition between the reaction of O_2^- and Ru^{III} and protonation of O_2^- followed by reaction of Ru^{II} (equations 19–22).[220] $[Ru(NH_3)_5(isn)]^{2+}$ is oxidized by HO_2 with a rate constant $k = 9.07 \times 10^6\,M^{-1}s^{-1}$ *via* an outer-sphere mechanism that shows anomalous behaviour with regard to Marcus theory.[221] The mechanism and kinetics of the reduction of O_2 in the presence of Cl^- has been discussed.[220] Reduction of H_2O_2 by $[RuL(NH_3)_5]^{2+}$ (L = 1-methylimidazole) is first order in $[Ru^{II}]$.[154]



(27)

$$\frac{-d[Ru^{II}]}{dt} = 2k[Ru^{II}][O_2] \quad (18)$$

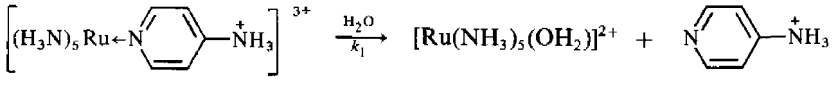
$$Ru^{II} + O_2 \rightleftharpoons Ru^{III} + O_2^- \quad (19)$$

$$O_2^- + H^+ \rightleftharpoons HO_2 \quad (20)$$

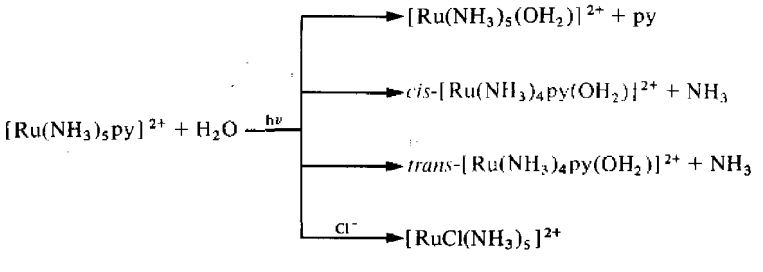
$$Ru^{II} + HO_2 \longrightarrow Ru^{III} + HO_2^- \quad (21)$$

$$H^+ + Ru^{II} + HO_2 \longrightarrow Ru^{III} + H_2O_2 \quad (22)$$

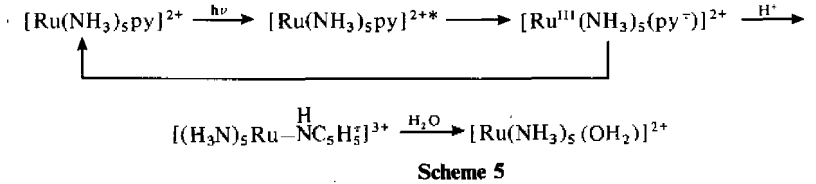
$[Ru(NH_3)_5py]^{2+}$ aquates at a slower rate than $[Ru(NH_3)_6]^{2+}$, while electron withdrawing groups on coordinated pyridine slow the aquation still further.[157,222] The kinetics of aquation of protonated (**27**) have been studied to give a rate law (equation 23) with rate constant $k_1 = 4.4 \times 10^{-2}\,s^{-1}$.[204] The photoactivation of the relatively non-labile $[Ru(NH_3)_5py]^{2+}$ has been reported. Photosubstitution of $[Ru(NH_3)_5py]^{2+}$ is found to be wavelength dependent and often leads to the formation of several products[223,224] (Scheme 4) (*cf.* the photochemistry of $Ru(bipy)_3^{2+}$ which shows photoluminescence and is relatively photosubstitution inert,[225,226] see Section 45.4.3.1.vi). The quantum yield for the aquation of $[Ru(NH_3)_5py]^{2+}$ on irradiation at the Ru → L charge transfer band was found to be pH dependent suggesting competitive acid-catalysed and acid independent reaction pathways.[227] A proposed mechanism for photoaquation of $[Ru(NH_3)_5py]^{2+}$ is given in Scheme 5.[225] Studies on charge transfer excited species $[RuL(NH_3)_5]^{2+*}$ showed evidence for ligand field excited states, and indicated that the metal → ligand charge transfer excited state (MLCT) was in fact substitutionally unreactive;[226] the excited state responsible for photosubstitution in $[Ru(NH_3)_5py]^{2+}$ is therefore believed to be ligand field (LF) in character.[228] Thus, if the LF state is of lower energy relative to the MLCT state, photolability and substitution would be expected to readily occur, whereas for systems where the MLCT state is of lowest energy, photostability would be prevalent.[228] The role of solvent in the relative ordering of these levels has been intimated.[228] Flash photolysis experiments on a series of complexes $[RuL(NH_3)_5]^{2+}$ (L = substituted pyridines, aromatic heterocycles) show the formation of long-lived transients for those complexes that are photosubstitution inert.[229] These intermediates have been proposed to involve a pyridine ligand π-bonded to Ru^{II} with an uncoordinated N which can be reversibly protonated with aquation of the complex.[229] UV irradiation of $[Ru(NH_3)_5py]^{2+}$ in aqueous NaCl solution yields initially $[Ru(NH_3)_5(OH_2)]^{2+}$ which is oxidized to $[RuCl(NH_3)_5]^{2+}$.[230] The photolysis of the pyridyl complex (**28**) at 313 nm leads to a novel carbon–carbon bond cleavage reaction on the ligand site (equation 24).[199]



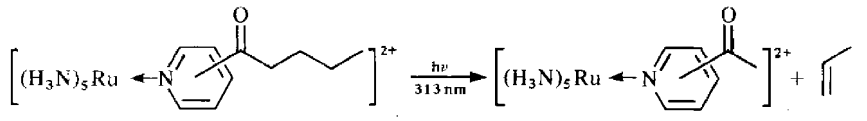
$$-\frac{d[Ru^{II}L]}{dt} = \frac{k_1 K_a[H^+][Ru^{II}L]}{1 + K_a[H^+]} \quad (23)$$



Scheme 4



Scheme 5

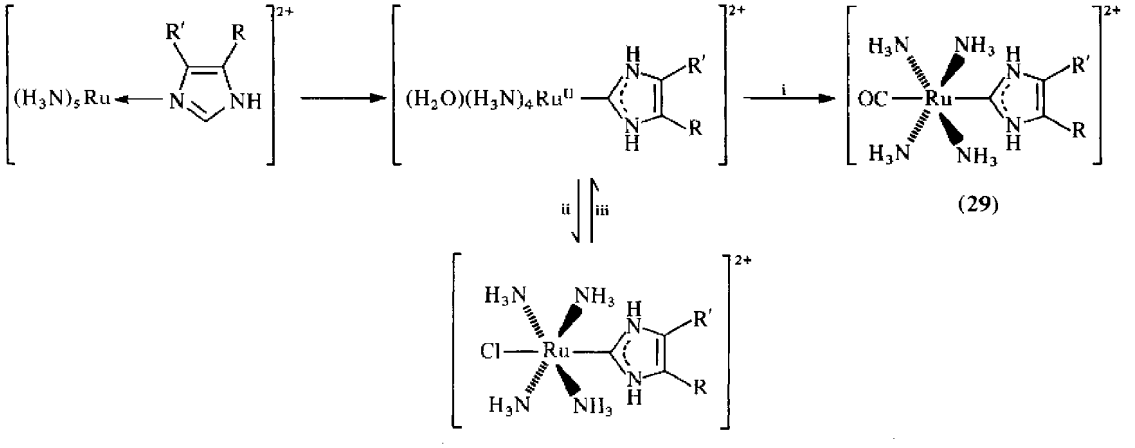


(28)

(24)

The rate of aquation of $[Ru(NH_3)_5(imid)]^{2+}$ was found to be 500 times faster than for the pyridyl derivative. A series of substituted imidazole adducts was therefore prepared and studied by ^1H NMR. This clearly showed an intramolecular arrangement of N-bound to C-bound imidazole (Scheme 6).[231–234] The single crystal X-ray structure of (**29**) confirms[232] the formation of a Ru—C bond (2.218 Å), with CO *trans* to imidazole ($R^1 = R = Me$). In general, the N-bound imidazole complexes are unstable below pH 2 due to facile aquation *via* highly labilizing[189] C-bound intermediates.[232] The electrochemistry and reactions with H_2O_2 and O_2 of N- and C-bound imidazole complexes have been reported.[235] C-bound xanthine derivatives have also been prepared.[202,236] The binding of $[Ru(NH_3)_5]^{2+}$ to double helical and single stranded DNA has been reported to occur at N-7 of guanine.[201,237] $[Ru(NH_3)_5]^{2+}$ has been anchored to graphite electrodes using polyvinylpyridine and polyacrylonitrile.[238]

The rates of substitution of H_2O in *cis*- and *trans*-$[RuL(NH_3)_4(OH_2)]^{2+}$ have been measured, and the effect of L on the lability of H_2O assessed[189] (see Section 45.4.1.2.i.b). Equilibrium constants for equation (25) have been measured[239] for a range of ligands L (Table 4).



(29)

i, CO; ii, O_2, Cl^-; iii, Zn/Hg, H_2O

Scheme 6

$$trans\text{-}[Ru(SO_3)(NH_3)_4(OH_2)] + L \underset{}{\overset{K_{equil}}{\rightleftharpoons}} [Ru(SO_3)(NH_3)_4L] + H_2O \qquad (25)$$

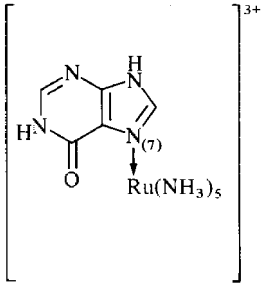
Complexes of the type *trans*-$[RuL_2(NH_3)_4]^{2+}$ can be prepared by treatment of $[RuCl_2(NH_3)_4]^+$ with $Ag(O_2CCF_3)$, reduction by zinc amalgam and addition of L (L = pyridine, pyrazine, 3- and 4-RCO pyridine; R = OMe, NH_2, OH).[194,240] Reaction of *cis*- or *trans*-$[RuCl_2(NH_3)_4]^+$ with pyHCl and zinc amalgam gives *cis*- or *trans*-$[Ru(NH_3)_4py_2]^{2+}$,[241] while reduction of $[Ru(NH_3)_4py_2]^{3+}$ by H_2S also yields $[Ru(NH_3)_4py_2]^{2+}$.[203] A series of mixed ligand complexes of type *trans*-$[RuLL'(NH_3)_4]^{2+}$ (L = pyridine, L′ = pyrazine, pyrazine H^+, 4-acyl pyridine; L = pyrazine, L′ = pyrazine, pyrazine H^+;[240,242] L = pyridine, 3-chloropyridine, 3,5-dichloropyridine, L′ = 4-cyano-*N*-methyl pyridinium, *N*-methyl-4,4′-bipyridine[196]) have been prepared by treatment of *trans*-$[Ru(SO_4)L(NH_3)_4]^+$ with zinc amalgam and L′. The basicity of these complexes was found to decrease in the order $[Ru(NH_3)_5pz]^{2+}$ > *trans*-$[Ru(NH_3)_4(py)(pz)]^{2+}$ > *trans*-$[Ru(NH_3)_4(pz)_2]^{2+}$ > pz > *trans*-$[Ru(pzH)(NH_3)_4pz]^{3+}$ > $[Ru(NH_3)_5pz]^{3+}$.[240] The visible spectrum of some of the mixed ligand complexes shows two metal → ligand charge transfer absorption bands,[240] these being found to be highly solvent dependent.[196] The single crystal X-ray structure of *cis*-$[Ru(NH_3)_4(isn)_2]^{2+}$ shows a net decrease in the Ru^{II}–N(isn) distance relative to Ru^{III}–N(isn) in *cis*-$[Ru(NH_3)_4(isn)_2]^{3+}$;[243] this is attributed to metal → isn $d \rightarrow \pi^*$ back-bonding in the ruthenium(II) complex.[243] Reaction of $[Ru(NH_3)_5N_2]^{2+}$ with py yields $[Ru(NH_3)_4py_2]^{2+}$ and $[Ru(NH_3)_2py_4]^{2+}$,[244]

while photolysis of *trans*-$[RuLL'(NH_3)_4]^{2+}$ in the visible region leads to photoaquation of NH_3.[240,245] The redox couples for a series of complexes $[RuL(NH_3)_5]^{2+/3+}$ and $[Ru(L)_2(NH_3)_4]^{2+/3+}$ have been measured and correlated with the electronic properties of L.[246]

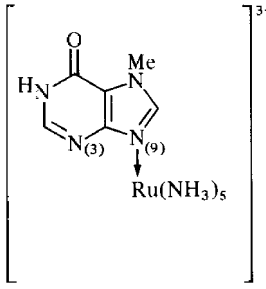
Ruthenium(III): $[RuL(NH_3)_5]^{3+}$ and $[Ru(L)_2(NH_3)_4]^{3+}$ (L = pyridine,[194] *N*-methylpyrazine$^+$,[197] 3- and 4-RCO pyridine; R = OMe, NH_2, OH[194]) have been prepared by Ag^I or Ce^{IV} oxidation of the corresponding ruthenium(II) complexes. The preparation of $[RuL(NH_3)_5]^{3+}$ by air oxidation of $[RuL(NH_3)_5]^{2+}$ (L = imidazole, 1-methylimidazole, 4-methylimidazole, 3,5-dimethylimidazole, benzimidazole) has also been achieved,[231,232] with the formation of $[RuCl(NH_3)_4(imid)]^{2+}$ as a side product.[231] Reaction of *cis*-$[Ru(NH_3)_4(OH_2)_2]^{2+}$ with isn in HCl yields $[RuCl(NH_3)_4isn]^{2+}$,[222] while *cis*- or *trans*-$[RuCl(NH_3)_4SO_2]^+$ with L in aqueous solution gives *cis*- or *trans*-$[Ru(SO_4)(L)(NH_3)_4]^+$ (L = pyridine, isonicotinamide,[222] 3-chloropyridine, 3,5-dichloropyridine,[196] substituted imidazole[239,247]) which reacts with HX to form $[RuX(L)(NH_3)_4]^{2+}$ (X = Cl^-, Br^-, I^-).[222,239] The $E_{1/2}$ values for the $Ru^{III/II}$ couples in these complexes are influenced by X rather than L, while the energy of the $Ru^{III} \rightarrow L$ charge transfer is also markedly dependent on X.[222] The electronic and vibrational spectra of $[RuL(NH_3)_5]Cl_3$ (L = 4-dimethylaminopyridine) have been analysed;[211] For L = 4-aminopyridine protonation of the complex leads to loss of the $L \rightarrow M$ charge transfer band at 505 nm indicating lone pair involvement in the CT process.[204]

The single crystal X-ray structure of $[Ru(NH_3)_5pz]^{3+}$, prepared by PbO_2 oxidation of $[Ru(NH_3)_5pz]^{2+}$,[197] shows a longer Ru^{III}–N(pz) distance (2.076 Å) and slightly shorter Ru^{III}–$N(NH_3)$ bonds (2.10–2.13 Å) as compared with the ruthenium(II) analogue which has bond lengths of 2.006 Å and 2.15–2.17 Å for those linkages.[205] Similar lengthening of the Ru^{III}–N(isn) distances is also observed for *cis*-$[Ru(NH_3)_4(isn)_2]^{3+}$.[243] $[Ru(NH_3)_5pz]^{3+}$ is less basic than the ruthenium(II) analogue,[240] a similar decrease in pK_a being observed[235,248] for $[RuL(NH_3)_5]^{3+}$ (L = C-bound, N-bound imidazole, pK_a for coordinated imidazole = 11.00, 7.06 respectively) compared with free imidazole (pK_a = 14.2). The synthesis of the protonated complex $[Ru(LH)(NH_3)_5]^{4+}$ (L = 1,1′-bis(4-pyridyl)amine) by Cl_2 oxidation of $[Ru(LH)(NH_3)_5]^{3+}$ in HCl has been achieved.[209]

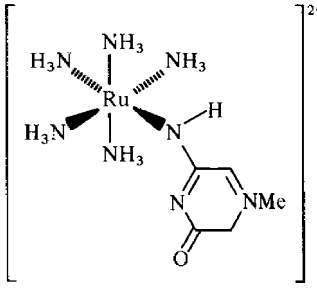
The interaction of ruthenium(III) with biologically active ligands has been studied in complexes $[RuL(NH_3)_5]^{3+}$ (L = guanine,[201,249] xanthine derivatives,[202] hypoxanthine,[200] cytidine, adenosine tubercidin,[249] histidine,[236] histidine of ribonuclease A[250]). These products show low energy $L \rightarrow M$ charge transfer bands, the cytidine and adenosine adducts dissociating or isomerizing on reduction to ruthenium(II).[249] The single crystal X-ray structures of $[RuL(NH_3)_5]Cl_3$ (L = hypoxanthine, 7-methylhypoxanthine) have been determined.[257] Hypoxanthine is bound through N-7 (Ru—N-7 = 2.087 Å) (**30**), while for 7-methylhypoxanthine, N-3 to N-9 linkage isomerization can occur,[200,251] the crystal structure of (**31**) showing Ru^{III} bound to N-9 (Ru—N-9 = 2.094 Å).[251] The X-ray structure of $[Ru^{III}L(NH_3)_5]^{2+}$ (L = 1-methylcytosine$^-$) (**32**) shows a short Ru—N(cytosine) bond (1.983 Å), with hydrogen bonding between a ring N atom of cytosine and two NH_3 ligands.[252]



(30)



(31)



(32)

The outer-sphere reduction of $[Ru(NH_3)_5py]^{3+}$ with $[Fe(CN)_6]^{4-}$ and $[Ru(NH_3)_6]^{2+}$ (k = 4.3 × 10^6, 7.2 × 10^5 $M^{-1}s^{-1}$ respectively) has been studied.[130] $[RuL(NH_3)_5]^{3+}$ (L = pyridine, substituted pyridine) forms ion pairs with $[M^{II}(CN)_6]^{4-}$ (M = Fe, Ru, Os) which show in concentrated solutions outer-sphere charge transfer bands in the near IR (λ = 915 nm for $[Ru(NH_3)_5py]_4[Fe(CN)_6]_3$), interactions between $[M(CN)_6]^{4-}$ and an ammine face or with the pyridine ligand being postulated.[57,130,215] The reduction of $[Ru(NH_3)_5isn]^{3+}$ by Cr^{II} has been noted to be 2 × 10^4 faster than Cr^{II} reduction of Co^{III};[194] the formation of a binuclear Ru^{III}–Cr^{II} intermediate with Cr^{II} bound to the amide or carbonyl of isonicotinamide was proposed[194] (see Section 45.4.1.3). Kinetic studies on the reduction of $[Ru(NH_3)_5py]^{3+}$ by Cr^{II},[253] V^{II},[253] Ti^{III}[254] and $[Co(edta)]^{2-}$[219] (k = 3.4 × 10^{-3}, 1.2 × 10^5, 4.2 × 10^3, 32 $M^{-1}s^{-1}$ respectively), $[Ru(NH_3)_5pz]^{3+}$ and *cis*-$[Ru(NH_3)_4(isn)_2]^{3+}$ by Ti^{III} (k = 1.5 × 10^5, 1 × 10^6 $M^{-1}s^{-1}$ respectively)[254] and $[RuL(NH_3)_5]^{3+}$ (L = pz, 4,4′-bipy) by $[Co(edta)]^{2-}$ (k = 77 $M^{-1}s^{-1}$ for 4,4′-bipy complex)[219,255] have been reported

and the mechanisms discussed. The oxidation of horseheart ferrocytochrome and related species by $[Ru(NH_3)_5L]^{3+}$ at low pH has been studied.[215–217,256,257] O_2^- reduces $[Ru(NH_3)_5isn]^{3+}$ with a rate constant $k = 2.18 \times 10^8\,M^{-1}s^{-1}$.[221] The efficient hydrolysis of *p*-nitrophenylacetate in the presence of $[Ru(imid^-)(NH_3)_5]^{2+}$,[258] and the reduction of $[RuL(NH_3)_5]^{3+}$ (L = py, isn) and $[Ru(NH_3)_4(isn)_2]^{3+}$ by Cu^I have been reported.[259] Outer-sphere ligand to metal charge transfer absorption bands have been observed in the electronic spectra of $[Ru(NH_3)_5py]^{3+}$ with halide ions.[260]

Ruthenium(IV): $[Ru(NH_3)_5py]^{3+}$ disproportionates at high pH to give $[Ru(NH_3)_5py]^{2+}$ and $[Ru(NH_3)_5py]^{4+}$.[261] Formation of Ru^{II} is second order in $[Ru^{III}]$, with $[Ru(NH_3)_5py]^{3+}$ being reformed from $[Ru(NH_3)_5py]^{4+}$ at pH 8–8.5.[261]

(c) Bidentate heterocycles

Ruthenium(II): (See also Section 45.4.3.1.ix). Reaction of $[Ru(NH_3)_4(OH_2)_2]^{2+}$, $[Ru(NH_3)_5(OH_2)]^{2+}$ or $[Ru(NH_3)_5(acetone)]^{2+}$ with L–L gives complexes $[Ru(L–L)(NH_3)_4]^{2+}$, while $[Ru(L–L)_2(NH_3)_2]^{2+}$ may be prepared by treatment of $[Ru(L–L)_2Cl_2]$, or preferably $[Ru(L–L)_2(OH_2)_2]^{2+}$ with NH_3 (L–L = 2,2′-bipyridine, 1,10-phenanthroline, 2,2′-bipyrimidine, or related heterocycles.[196,203,262–267] The ruthenium(II) complexes show intense metal → ligand charge transfer bands (not present in ruthenium(III) products)[267] and a related one electron $Ru^{II/III}$ redox couple. The electrochemistry of $[Ru(bipy)_2(NH_3)_2]^{2+}$ ($E_{1/2} = +1.27$ V *vs.* SCE) has been reported,[196,268a] and a spatially isolated redox orbital model proposed for this and related systems.[268b] Aerial oxidation of $[Ru(L–L)(NH_3)_4]^{2+}$ (L–L = 2-aminomethylpyridine) yields the corresponding 2-pyridinalimine adduct.[263] ^1H NMR of $[Ru(L–L)_2(NH_3)_2]^{2+}$ (L–L = 4,4′-dimethyl-2,2′-bipyridine) indicates that the complex is in the sterically preferred *cis* configuration.[269] Exchange rates have been measured[127] for $[Ru(bipy)(NH_3)_4]^{3+/2+}$ ($k = 7.7 \times 10^5$ in CF_3SO_3H, $2.2 \times 10^6\,M^{-1}s^{-1}$ in $HClO_4$, $\Delta H^{\neq} = 16.7\,kJ\,mol^{-1}$, $\Delta S^{\neq} = -100\,J\,K^{-1}\,mol^{-1}$), and for $[Ru(bipy)_2(NH_3)_2]^{3+/2+}$ ($k = 8.4 \times 10^7\,M^{-1}s^{-1}$ in $HClO_4$). Reduction of O_2 by $[Ru(phen)(NH_3)_4]^{2+}$ occurs with a rate constant $k = 7.73 \times 10^{-3}\,M^{-1}s^{-1}$,[220] while exchange reactions with $[Co(OH_2)_6]^{3+}$ have also been reported.[270]

Ruthenium(III): $[Ru(L–L)_2(NH_3)_2]^{3+}$ and $[Ru(L–L)(NH_3)_4]^{3+}$ may be prepared by chemical or electrochemical oxidation of ruthenium(II) analogues and are found to be strong oxidizing agents. Reduction of $[Ru(terpy)(bipy)(NH_3)]^{3+}$, $[Ru(bipy)_2(NH_3)_2]^{3+}$, $[Ru(terpy)(NH_3)_3]^{3+}$ and $[Ru(bipy)(NH_3)_4]^{3+}$ with $[Fe(OH_2)_6]^{2+}$ has been reported and related to Marcus theory.[271] Oxidation of $[(NH_3)_4Ru]_2bipym^{4+}$ at +1.02 V *vs.* NHE leads to binuclear cleavage and the formation of $[Ru(bipym)(NH_3)_4]^{3+}$ and $[Ru(NH_3)_4(OH_2)_2]^{3+}$.[262] The reduction of $[Ru(bipy)(NH_3)_4]^{3+}$ with Cu^I has been reported.[272]

(d) Nitrosyls

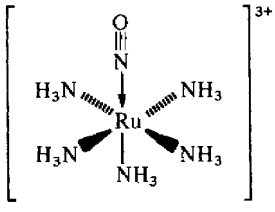
Transition metal nitrosyl complexes have been the subject of several reviews.[273–277]

Ruthenium(II): $[Ru(NO)(NH_3)_5]^{3+}$ was originally synthesized by treatment of $[Ru(NH_3)_6]^{3+}$ with NO_2^- in HCl.[158,278] It can also be prepared by aerial oxidation of $[Ru(NH_3)_6]^{3+}$ at pH 13 with NaOH[279] (equation 26), by reaction of $[Ru(NH_3)_6]^{3+}$ with NO under acidic conditions[280–282] (equation 27) or by direct substitution of H_2O in $[Ru(NH_3)_5(OH_2)]^{3+}$ by NO.[158] The N—O stretching vibration ν_{NO} for $[Ru(NO)(NH_3)_5]^{3+}$ occurs at 1908 cm^{-1};[279] the single crystal X-ray structure[283–285] of (**33**) shows Ru—N(NO) = 1.770, N—O = 1.172, Ru—N(NH_3) = 2.017–2.133 Å with a near linear nitrosyl ligand.[283] Thus the binding of NO in $[Ru(NO)(NH_3)_5]^{3+}$ should be regarded as $[Ru^{II}—NO^+]$ rather than $[Ru^{III}—NO]$, consistent with the diamagnetism of the complex. Analysis of the electronic absorption spectra of related complexes rules out a magnetically coupled $[Ru^{III}–NO]$ model.[286] Mössbauer studies of $[RuNO(NH_3)_5]^{3+}$ have been reported.[27c,120]

$$[Ru(NH_3)_6]^{3+} \xrightarrow[O_2]{pH\ 13} [Ru(NO)(NH_3)_5]^{3+} \qquad (26)$$

$$[Ru(NH_3)_6]^{2+} \xrightarrow[NO]{H^+} [Ru(NO)(NH_3)_5]^{3+} \qquad (27)$$

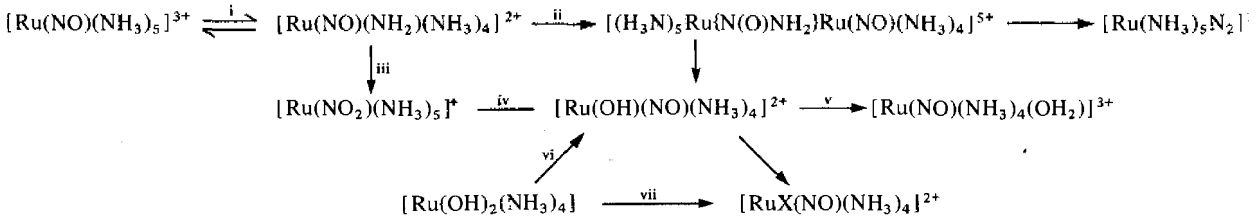
(33)



(33)

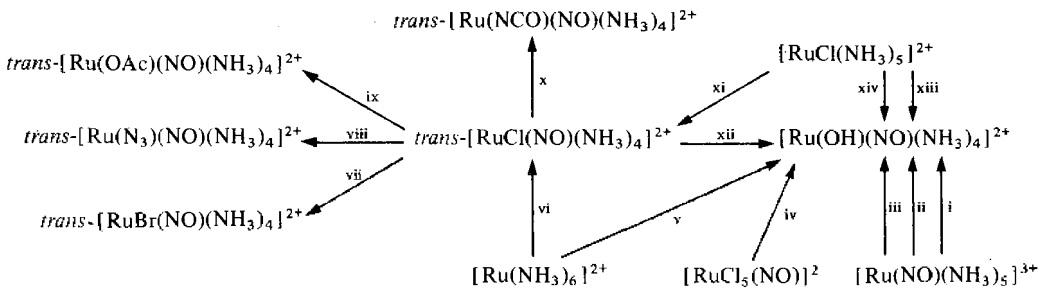
Whereas the aquation of $[Ru(NH_3)_6]^{3+}$ is very slow (several days), the reaction of $[Ru(NH_3)_6]X_3$ with NO is relatively fast with rate constants $k = 2.0 \times 10^{-1}$ for $X = Cl^-$, $1.9 \times 10^{-1} M^{-1} s^{-1}$ for $X = Br^-$ with first order dependence on [NO] and $[\{Ru(NH_3)_6\}^{3+}]$.[158] The dependence of the kinetics on pH has been discussed.[287] Reaction of $[RuBr(NH_3)_5]^{2+}$ with NO gives $[Ru(NO)(NH_3)_5]^{3+}$ and $[RuBr(NO)(NH_3)_4]^{2+}$.[158] The ^1H NMR of $[Ru(NO)(NH_3)_5]^{3+}$ shows increased H^+ exchange at the *trans* NH_3 group relative to $[Ru(NH_3)_5CO]^{2+}$. Schemes 7 and 8 summarize the reactivity of ruthenium ammine–nitrosyl complexes.

The single crystal X-ray structures of $[RuCl(NO)(NH_3)_4][Ru(NO_2)_4(OH)(NO)]$ and $[Ru(OH)(NO)(NH_3)_4][Os(NO_2)_4(OH)NO]\cdot 0.5H_2O$ have been reported.[296b]



i, 0.5 M[$^-$OH];[288] ii, $[Ru(NO)(NH_3)_5]^{3+}$;[289] iii, 5.0 M[$^-$OH];[288]
iv, Δ;[288] v, H^+;[290] vi, Ag^+, NO, H_2O;[290] vii, HX;[290]

Scheme 7



i, $^-$OH;[279, 288, 289, 291] ii, NH_3;[292] iii, $^-$OH, PhCHO catalyst;[293] iv, NH_3;[294]
v, (a) Cl_2 (b) NH_4OH reflux (c) 0 °C;[114] vi, (a) Cl_2 (b) NH_4OH (c) HCl;[114, 286, 295]
vii, Br^-;[286] viii, N_3^-, 75 °C, H_2O, H^+;[286] ix, NaOAc, HOAc, 90 °C;[286, 295]
x, KNCO, 90 °C;[286] xi, (a) NH_3 (b) Cl_2, NH_3 (c) Δ, 80 °C (d) HCl;[114, 286]
xii, NH_4OH;[114, 286] xiii, NaOH, NO;[280] xiv, $HClO_4$;[296]

Scheme 8

For *trans*-$[Ru^{II}X(NO)(NH_3)_4]^{x+}$, the N—O stretching vibration ν_{N-O} has been found to be a good indicator of *trans* effects of X; ν_{N-O} decreases in the order $NH_3 > NCO^- > N_3^- > -OAc > Cl^- > Br^-$.[268] ^1H NMR studies of *cis*- and *trans*-$[Ru(NO)(NH_3)_4(OH_2)]^{3+}$ in concentrated H_2SO_4 show the complexes to be stable for approximately fifteen minutes.[297] IR[298] and X-ray structural analyses[283] of *trans*-$[Ru(OH)(NO)(NH_3)_4]Cl_2$ have been reported and indicate binding of NO^+ to Ru^{II} (< RuNO = 173.8°).

For $[Ru(NO)(NH_3)_5]^{3+}$, $E° = -0.12$ V *vs.* SCE at 23°C.[299] Radiolysis of $[Ru(NO)(NH_3)_5]^{3+}$ yields a one-electron reduction product $[Ru(\dot{N}O)(NH_3)_5]^{2+}$ (**34**) which rapidly adds organic radicals (equations 28 and 29).[299] Reduction of $[Ru(NO)(NH_3)_5]^{3+}$ in the presence of a range of alcohols, amines and carboxylic acids RH yields products $[Ru(N(O)R)(NH_3)_5]^{2+}$.[300,301] $[Ru(\dot{N}O)(NH_3)_5]^{2+}$ is proposed as an intermediate in the redox catalysed aquation of $[Ru(NO)(NH_3)_5]^{3+}$ to *trans*-$[Ru(OH)(NO)(NH_3)_4]^{2+}$ which occurs with rate constants $k = 3.1 \times 10^9$, $5.5 \times 10^8 M^{-1} s^{-1}$ for $\dot{C}O_2$ and $CH_3\dot{C}OH$ respectively.[302] The rates of reaction are independent of $[\{Ru(NO)(NH_3)_5\}^{3+}]$ but depend linearly upon $[\{Ru(\dot{N}O)(NH_3)_5\}^{2+}]$ produced during the radical reaction. $[Ru(\dot{N}O)(NH_3)_5]^{2+}$ is scavenged by O_2 with a rate constant $k = 7.6 \times 10^6 M^{-1} s^{-1}$.[299]

Nitrosyl ammine intermediates have been detected when $[Ru(NH_3)_6]^{3+}$ is treated with O_2 in

$$[Ru(NO)(NH_3)_5]^{3+} + e^-_{(aq)} \longrightarrow [Ru(\dot{N}O)(NH_3)_5]^{2+} \quad (28)$$

(34)

$$[Ru(\dot{N}O)(NH_3)_5]^{2+} + R\cdot \longrightarrow [Ru\{N(O)R\}(NH_3)_5]^{2+} \quad (29)$$

(34)

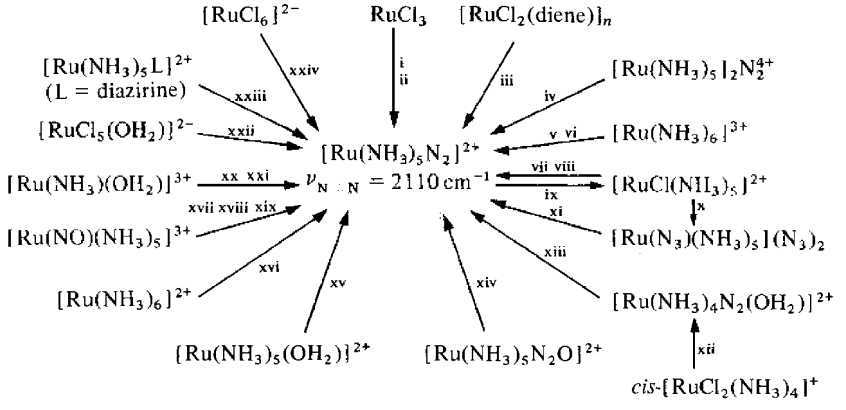
zeolites at 450 K[303] while reaction of $[Ru(NO)(NH_3)_5]^{3+}$ with $[Cr(OH_2)_6]^{2+}$ affords a dimeric species $[(NH_3)_4(OH_2)Ru—NH—Cr(OH_2)_5]^{5+}$.[282]

(e) Dinitrogen

The activation of N_2 by transition metal complexes has been reviewed.[304–308]

Ruthenium(I): Pulse radiolysis of $[Ru(NH_3)_5N_2]^{2+}$ yields $[Ru^I(NH_3)_5N_2]^+$ with a rate constant $k = 4.2 \times 10^9\,M^{-1}s^{-1}$. The product dismutes to $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5N_2]^0$ ($2k = 2.7 \times 10^9\,M^{-1}s^{-1}$) with subsequent deposition of Ru metal.[309]

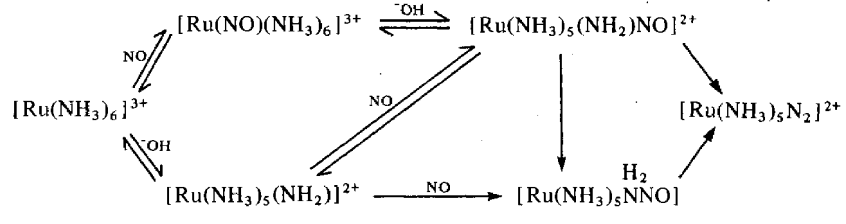
Ruthenium(II): The synthesis of $[Ru(NH_3)_5N_2]^{2+}$ was first prepared in 1965 by refluxing $RuCl_3$ in aqueous hydrazine.[310] Since then a range of methods have been developed for the synthesis of this complex. Scheme 9 summarizes the main routes to $[Ru(NH_3)_5N_2]^{2+}$.



i, NH_2NH_2;[160,244,310] ii, Zn, NH_4OH;[311,312] iii, NH_2NH_2;[187] iv, NH_3;[313]
v, NO, ^-OH;[280,314] vi, NH_2NH_2;[116] vii, Zn/Hg, CF_3SO_3H, N_2;[315] viii, Zn, N_2O;[316]
ix, concentrated HCl;[160] x, (a) Ag^+ (b) NaN_3;[317] xi, decomposition Δ;[317]
xii, NaN_3, H^+;[159] xiii, NH_3;[159] xiv, Cr^{2+};[314,318] xv, N_2;[319,320] xvi, Cl_2, 0 °C;[114]
xvii, RNH_2, pH ⩾ 10;[321] xviii, NH_2NH_2;[292,322] xix, ^-OH;[279] xx, NaN_3, NH_3, H^+;[160,244]
xxi, NH_2NH_2, 1 h;[244] xxii, NH_2NH_2; 12 h;[244] xxiii, O_2 or H_2O_2, H^+;[323]
xxiv, NH_2NH_2, 12 h;[244]

Scheme 9

High yields of $[Ru(NH_3)_5N_2]^{3+}$ can be obtained from the reaction of $[Ru(NH_3)_6]^{2+}$ with NO at pH 8.45,[280,314] the yield dropping with lowering of pH and falling to zero at pH 6.[280] The proposed mechanism for the formation of $[Ru(NH_3)_5N_2]^{2+}$ from $[Ru(NH_3)_6]^{3+}$ is illustrated in Scheme 10.[158,280,287] Labelling experiments confirm that N_2 formation in the complex arises from combination of NO and coordinated NH_3 (equation 30),[314] whereas in the reduction of $[Ru(NH_3)_5N_2O]^{2+}$ by Cr^{II}, N_2 arises solely from coordinated N_2O (equation 31).[314,318] The mechanism of formation of $[Ru(NH_3)_5N_2]^{2+}$ from $[Ru(NH_3)_6]^{3+}$ and N_2H_4 involves oxidation of coordinated N_2H_4 to N_2 (equation 32).[116] The kinetics of formation of $[Ru(NH_3)_5N_2]^{2+}$ from $[Ru(NH_3)_5OH_2]^{2+}$ and N_2 has been reported (equation 33); $k_1 = 7.3 \times 10^{-2}$, $k_{-1} = 2.03 \times 10^{-6}\,s^{-1}$, $K_{equil} = 3.3 \times 10^4$.[324,325]



$$-\frac{d[[Ru(NH_3)_6]^{3+}]}{dt} = k_H[Ru^{III}][NO] + k_{OH}[Ru^{III}][NO][^-OH]$$

Scheme 10

$$[Ru(NH_3)_6]^{3+} + {}^{15}NO \longrightarrow [Ru(NH_3)_5{}^{29}N_2]^{2+} \quad (30)$$

$$[Ru(NH_3)_5{}^{15}N{}^{15}NO]^{2+} \xrightarrow{Cr^{II}} [Ru(NH_3)_5{}^{30}N_2]^{2+} \quad (31)$$

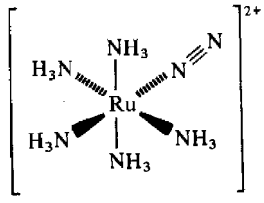
$$\underset{\lambda = 276\,nm}{[Ru(NH_3)_6]^{3+}} \xrightarrow{N_2H_4} \underset{\lambda = 380\,nm}{[Ru(NH_3)_5N_2H_4]^{3+}} \longrightarrow \underset{\lambda = 510\,nm}{[Ru(NH_3)_5(NH{=}NH)]^{2+}} \xrightarrow{O_2} \underset{\lambda = 221\,nm}{[Ru(NH_3)_5N_2]^{2+}} \quad (32)$$

(35)

$$[Ru(NH_3)_5(OH_2)]^{2+} + N_2(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(NH_3)_5N_2]^{2+} + H_2O \quad (33)$$

The single crystal X-ray structure of $[Ru(NH_3)_5N_2]^{2+}$ (**35**) confirms the linear linkage of N_2 (Ru—N = 2.11 Å, N≡N = 1.12 Å).[326]

Ab initio SCF–MO calculations[327] and Hartree–Fock–Slater studies[328] predict that the polarization of coordinated N_2 will be $Ru—\overset{\delta-}{N}—\overset{\delta+}{N}$. Bands in the vibrational spectrum have been assigned[329,330] to the N≡N and Ru—N(N_2) stretching modes. The frequency and intensity of $\nu_{N\equiv N}$ are found to be dependent upon counterion and solvent, due to electrostatic interactions in solution.[188,331] Mössbauer and ^{15}N NMR studies on $[Ru(NH_3)_5N_2]^{2+}$ have been reported.[27c,120,332,333] Linkage isomerism of coordinated N_2 has been detected in the solid state ($t_{1/2} = 2 \pm 1$ days at 22°C in the dark) and solution ($t_{1/2} = 2$ h at 25°C),[318] a weak π-bonded intermediate being postulated[318] (equation 34).



(35)

$$Ru \leftarrow {}^{15}N{\equiv}{}^{14}N \rightleftharpoons Ru \leftarrow \overset{{}^{15}N}{\overset{\|}{{}^{14}N}} \rightleftharpoons Ru \leftarrow {}^{14}N{\equiv}{}^{15}N \quad (34)$$

For $[Ru(NH_3)_5N_2]^{2+}$, $E_{1/2} = +0.72$ V *vs.* SCE.[334] *Cis*-$[Ru(NH_3)_4(OH_2)_2]^{2+}$ takes up one equivalent of N_2 to afford $[Ru(NH_3)_4(N_2)(OH_2)]^{2+}$,[320] while treatment of $[RuCl(NH_3)_5]^{2+}$ or *cis*-$[RuCl_2(NH_3)_4]^+$ with N_2H_4 at −23°C for 1 h and 10 min respectively is reported to yield $[Ru(NH_3)_4(N_2)_2]^{2+}$ ($\nu_{N\equiv N}$ = 2220, 2185 cm^{-1}).[335]

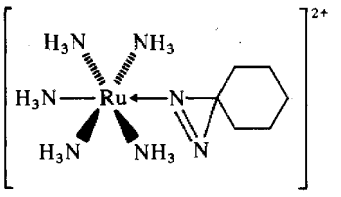
The N_2 ligand in $[Ru(NH_3)_5N_2]^{2+}$ may be displaced by other ligands; thus, with pyridine $[Ru(NH_3)_5py]^{2+}$ and $[Ru(NH_3)_4py_2]^{2+}$ are formed.[244] The photochemistry of $[Ru(NH_3)_5N_2]^{2+}$ has been studied in terms of oxidation of Ru^{II} to Ru^{III}, and of ligand substitution reactions *via* ligand field excited states.[336–338] For the N_2 complex, the principal photoreaction is redox in character[337] (equations 35–37). Thermolysis of solid $[Ru(NH_3)_5N_2]X_2$ (X = Cl^-, Br^-, I^-) at 165–213°C liberates NH_3 yielding initially $[RuX(NH_3)_4N_2]X$, with the rate increasing in the order $Cl^- < Br^- < I^-$. The Cl^- reaction is proposed to occur *via* an S_N1 mechanism, while for Br^- and I^-, S_N2 mechanism predominates.[339] Above 243°C N_2 is liberated.[339] The reactivity of $[Ru(NH_3)_5N_2]^{2+}$ in zeolites has been reported,[340–342] air oxidation yielding zeolite-bound ruthenium red.[342]

$$\underset{\lambda = 221\,nm}{[Ru(NH_3)_5N_2]^{2+}} \xrightarrow[HCl]{h\nu} \underset{\lambda = 330\,nm}{[RuCl(NH_3)_5]^{2+}} \quad (35)$$

$$[Ru(NH_3)_5N_2]^{2+} \xrightarrow[NH_3]{h\nu} \underset{\lambda = 276\,nm}{[Ru(NH_3)_6]^{3+}} \quad (36)$$

$$[Ru(NH_3)_5N_2]^{2+} \xrightarrow[H_2O]{h\nu} \underset{\lambda = 290\,nm}{[Ru(OH)(NH_3)_5]^{2+}} \quad (37)$$

Reaction of diazirine L with $[Ru(NH_3)_5OH_2]^{2+}$ yields $[Ru(NH_3)_5L]^{2+}$ (**36**) which is oxidized in air or by H_2O_2 to $[Ru(NH_3)_5N_2]^{2+}$ and cyclohexanone.[323] The single crystal X-ray structure of (**36**) indicates strong $d \rightarrow p\pi^*$ (N=N) back-bonding with Ru—N(N_2) = 1.911 Å, Ru—N(*trans* NH_3) = 2.147 Å, N=N = 1.28 Å, < RuNN = 141.6°.[323]



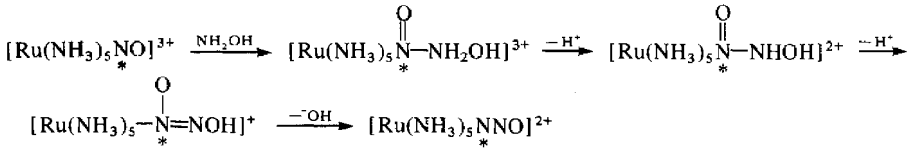
(36)

Ruthenium(III): Reaction of $[Ru(NH_3)_5N_2]^{2+}$ with $\dot{O}H$ yields $[Ru^{III}(NH_3)_5N_2]^{3+}$ which rapidly aquates to $[Ru(OH)(NH_3)_5]^{2+}$.[309] For $[Ru(NH_3)_5N_2]^{3+}$ the specific rate of aquation $k = 70\,s^{-1}$.[315]

(f) Nitrous oxide

Ruthenium(II): Reaction of $[Ru(NH_3)_5(OH_2)]^{2+}$ with oxygen free N_2O at 30–40 atm yields the adduct $[Ru(NH_3)_5N_2O]^{2+}$ (equation 38).[314,343,344] At lower pressures, $[Ru(NH_3)_5N_2]^{2+}$ and $\{[Ru(NH_3)_5]_2N_2\}^{4+}$ are formed. $[Ru(NH_3)_5N_2O]^{2+}$ may also be prepared by reaction of $[Ru(NO)(NH_3)_5]^{3+}$ with NH_2OH under basic conditions.[281,292,322] Scheme 11 gives the proposed mechanism for this reaction, with the N of NO remaining bound to the Ru centre.[322,345] $[Ru(NH_3)_5N_2O]^{2+}$ can be isolated as a by-product in the reaction of $[Ru(NO)(NH_3)_5]^{3+}$ with N_2H_4.[322] X-Ray powder results and the electronic and vibrational spectra of $[Ru(NH_3)_5N_2O]^{2+}$ are consistent with linear bound N_2O, $RuN{\equiv}NO$,[345] with characteristic IR bands at 1160 cm^{-1} and 2250 cm^{-1}.[322]

$$[Ru(NH_3)_5(OH_2)]^{2+} + {}^{15}N^{15}NO \longrightarrow [Ru(NH_3)_5{}^{15}N^{15}NO]^{2+} + H_2O \qquad (38)$$



Scheme 11

The reduction of complexed N_2O by Cr^{II} and V^{II} is increased by facts of 10^8 and 10^7 respectively over reduction of free N_2O.[346,347] The kinetics of these reactions have been discussed.[346,347]

(g) Cyanates and thiocyanates

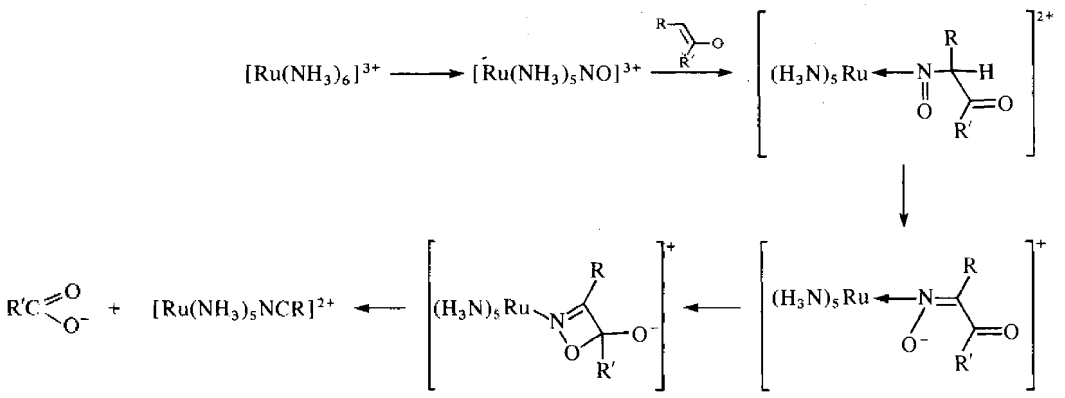
The complexes $[Ru(L)(NH_3)_5]^{2+}$ (L = $^-$NCO, $^-$NCS, $^-$NCSe) can be prepared by reaction of $[RuCl(NH_3)_5]^{2+}$ with L in refluxing aqueous solution, or by treatment of $[RuCl(NH_3)_5]^{2+}$ with Ag^+ followed by reduction with zinc amalgam and addition of L.[348,349] With excess NCS, further reaction leads to the formation of a range of amine–thiocyanate complexes including $[Ru(NCS)_2(NH_3)_4]^+$[350–352] and the proposed $[Ru(NCS)_2(SCN)_2(NH_3)_2]^-$.[352,353] A low energy charge transfer band is observed for $[Ru(NCO)(NH_3)_5]^{2+}$ and is assigned to $e(\pi L) \rightarrow t_2(4dRu)$ transition.[354] On the basis of the energy of *d–d* transitions in $[Ru(L)(NH_3)_5]^{2+}$, a spectrochemical series of L (NH_3 > $^-$NCO > $^-$OAc > $^-$NCS > $^-$NCSe) was proposed.[349] Reaction of the dimer $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$ with CN^- gives S-bound $[Ru(SCN)(NH_3)_5]^+$ which rearranges to the N-bound $[Ru(NCS)(NH_3)_5]^{2+}$.[355,356] An alternative preparation of $[Ru(SCN)(NH_3)_5]^{2+}$ has been reported.[352] The hydrolysis of $[Ru(NCO)(NH_3)_5]^{2+}$ is acid catalysed with the proposed formation of $[Ru(NH_2CO_2H)(NH_3)_5]^{3+}$ as a reactive intermediate.[348]

The reduction of $[Ru(NCS)(NH_3)_5]^{2+}$ by Ti^{III} and Ti(Hedta) shows second order kinetics with rate constants k = 840 and $2.8 \times 10^4\,M^{-1}\,s^{-1}$,[357] inner-sphere electron transfer *via* $^-$NCS bridges being proposed for both systems.[357]

(h) Nitriles

Ruthenium(II): Treatment of $[Ru(NH_3)_5(OH_2)]^{2+}$ or $[Ru(NH_3)_5(acetone)]^{2+}$ with L or $[RuCl(NH_3)_5]^{2+}$ with zinc amalgam in the presence of L yields $[RuL(NH_3)_5]^{2+}$ (L = acetonitrile, benzonitrile,[358] substituted benzonitrile,[196,358,359] acrylonitrile,[360] hydrogen cyanide,[36,37] ethyl cyanoformate,[361] dicyanamide, malononitrile, substituted malononitrile, tricyanomethanide,[362] 4-cyano-1-methylpyridinium[196]). Reaction of a hundred-fold excess of RCHO (R = Ph, Me) with $[Ru(NH_3)_6]^{2+}$ under alkaline conditions yields $[Ru(NH_3)_5NCR]^{2+}$.[363–365] The likely mechanism of this reaction is given in Scheme 12. An alternative route to nitrile complexes is by reaction of $[Ru(NH_3)_5OH_2]^{2+}$ with aldoximes, *e.g.* RMeC=NOH, to afford $[Ru(NH_3)_5(NCMe)]^{2+}$ and

ROH.[366,367] A wide range of alkoximes have been surveyed for this reactivity, the reaction proceeding *via* deaquation and elimination of ROH with no net redox change occurring at the metal centre.[366–368]



Scheme 12

Complexation of RCN to ruthenium(II) centres leads to shifts of the C≡N stretching vibration $\nu_{C\equiv N}$ to lower frequencies as compared with $\nu_{C\equiv N}$ for the free ligand.[369] This is due to strong $d\pi \rightarrow \pi^*$ back-bonding from Ru^{II} to the nitrile ligand,[358,360] and is consistent with the remarkable unreactivity of these d^6 complexes compared with the corresponding d^5 Ru^{III} species[370,371] (see below). The binding of acrylonitrile to the $[Ru(NH_3)_5]^{2+}$ moiety has been studied by ^1H NMR and confirms terminal N binding rather than π bonding through C≡N or C=C.[360] ^1H NMR has also been used to probe the degree of back-bonding from Ru^{II} to coordinated nitrile, the observed shielding of geminal protons for coordinated acrylonitrile and 1-methylacrylonitrile, and of the 3- and 4-protons of benzonitrile being consistent with an extensive back-bonding model.[372] The electronic and resonance Raman spectra of $[RuL(NH_3)_5]^{3+}$ (L = 4-cyano-1-methylpyridinium$^+$)[211] and Mössbauer studies on $[RuL(NH_3)_5]^{2+}$ (L = benzonitrile, acetonitrile)[120] have been published. The photolysis of $[Ru(NH_3)_5(NCMe)]^{2+}$ in aqueous conditions in the presence of Cl^- gives $[RuCl(NH_3)_5]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{2+}$.[224,337]

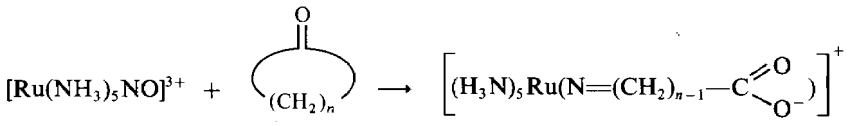
Ruthenium(III): Ruthenium(III) nitrile complexes $[RuL(NH_3)_5]^{3+}$ may be synthesized by reaction of L with $[Ru(NH_3)_5OH_2]^{3+}$,[196] oxidation of $[Ru(L)(NH_3)_5]^{2+}$ with Ce^{IV} or Ag^I,[359] by direct treatment of $[RuCl(NH_3)_5]^{2+}$ with L under reflux[358,360] or by aerial oxidation of coordinated amines.[192] The IR spectrum of these complexes shows the C≡N stretching vibration $\nu_{C\equiv N}$ to occur at higher frequencies than in the free ligand,[358,360] indicating net π back-donation from π^* (L) $\rightarrow d\pi$ (Ru^{III}). This is also reflected in the reactivity of nitrile ligands coordinated to Ru^{III}.

The specific rates of base hydrolysis of $[Ru(NH_3)_5NCR]^{3+}$ are 2.2×10^2 (R = Me) and $2 \times 10^3\ M^{-1}\ s^{-1}$ (R = Ph) which is 10^6 times more reactive than the corresponding Ru^{II} complex, and 10^8 times more reactive than the free ligand.[370,371,373] General base catalysis is observed in these reactions suggesting ^-OH attack on coordinated nitrile as an initial step leading to amido complexes $[Ru(NHC(O)R)(NH_3)_5]^{2+}$.[370,371] On coordination of *tert*-butylmalononitrile to $[Ru(NH_3)_5]^{3+}$ the pK_a of the ligand decreases from 13.1 to 3.85,[362] the enhanced acidity of *tert*-butylmalononitrile on coordination to Ru^{III} being attributed to the relative net π acceptor ability of the metal centre; *cf.* the increase in basicity and decrease in basicity of pyrazine on coordination to $[Ru(NH_3)_5]^{2+}$ and $[Ru(NH_3)_5]^{3+}$ respectively.[240] The acid hydrolysis of $[Ru(NH_3)_5NCR]^{3+}$ has been reported to occur with specific rates $k = 1.2 \times 10^{-5}$ (R = Me), $3.4 \times 10^{-5}\ M^{-1}\ s^{-1}$ (R = Ph).[373]

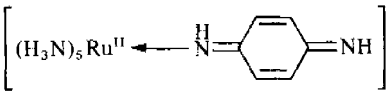
(i) Imines, amides and related ligands

Imine complexes have been involved as intermediates in the condensation of aldehydes with $[Ru(NO)(NH_3)_5]^{3+}$ under basic conditions to form nitrile complexes;[364,365] in certain cases the imine species have been isolated (equation 39).[364] Reaction of $[RuCl(NH_3)_5]^{2+}$ with $Ag(O_2CCF_3)$ followed by addition of ligands L (L = quinone diimine derivatives of 1,4-diaminobenzene, 1-amino-4-dimethylaminobenzene, 1,4-diaminonaphthalene, 4-aminophenol) gives complexes $[RuL(NH_3)_5]^{2+}$, *e.g.* (**37**).[374] These products show intense metal to ligand charge transfer bands near 550 nm ($\varepsilon = 3 \times 10^4\ M^{-1}\ cm^{-1}$), the basicity of the diimine ligand being increased on coordination to ruthenium(II). A reversible couple between Ru^{II}(diimine) and Ru^{II}(diamine) is observed.[374] Reaction of $[Ru(NH_3)_6]^{3+}$ with diketones such as biacetyl yields under basic conditions the corresponding bidentate diimine complexes (**38**).[375,376] The kinetics of the reaction have been elucidated and

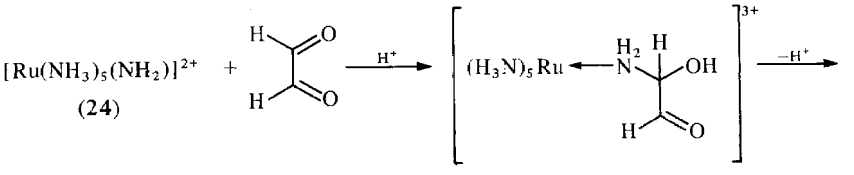
shown to proceed with [$^-$OH] dependence *via* the intermediate $[Ru(NH_2)(NH_3)_5]^{2+}$ (**24**) (Scheme 13). The diimine complex (**38**) shows a reversible oxidation couple at +0.56 V *vs.* SCE, controlled potential electrolysis of chemical oxidation with Br_2 yielding the ruthenium(III) analogue.[375,376]

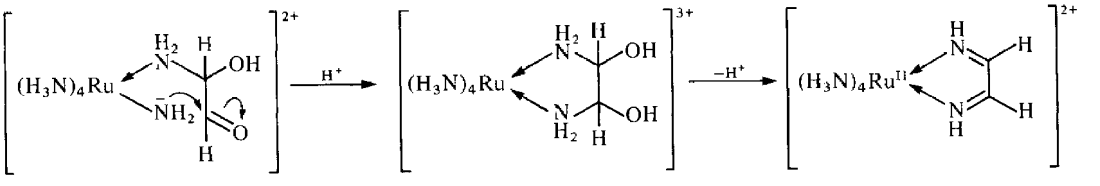


(39)



(37)



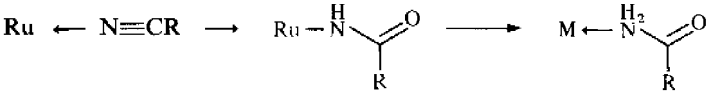


(38)

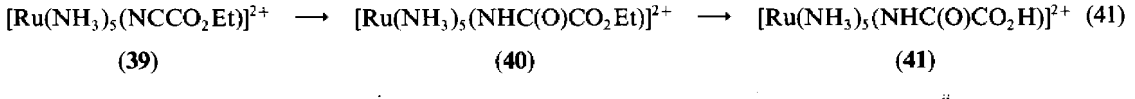
$$\frac{d[Ru^{II}]}{dt} = k[Ru^{III}][\text{biacetyl}][^-OH]$$

Scheme 13

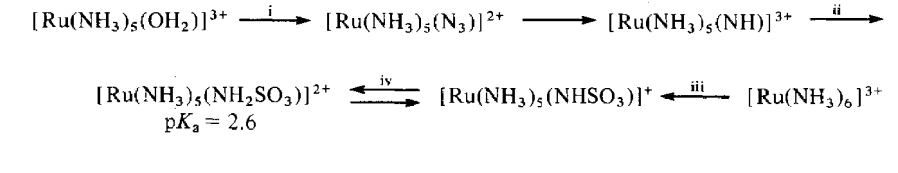
The base hydrolysis of Ru^{III} nitrile complexes to amido products has been reported (equation 40).[370] Reaction of $[Ru^{II}(NH_3)_5(NCCO_2Et)]^{2+}$ (**39**) with AgO yields $[Ru^{III}(NHC(O)CO_2Et)(NH_3)_5]^{2+}$ (**40**) which in mild alkali gives the oxamic acid derivative (**41**) (equation 41).[361] The hydrolysis of $[Ru(NCO)(NH_3)_5]^{2+}$ gives $[Ru(NH_2CO_2H)(NH_3)_5]^{3+}$.[348] Amide derivatives of $[Ru(NH_3)_5]^{3-}$ may also be prepared directly from the reaction of $[Ru(NH_3)_5OH_2]^{2+}$ with $RCONH_2$ (R = Me, Ph),[371] while sulfamide complexes have been synthesized by reaction of SO_3^{2-} on azide complexes[377] or by attack of $S_2O_3^{2-}$ on coordinated NH_3 (Scheme 14).[378]



(40)



(39) (40) (41)



i, (a) LiOH (b) LiN_3, H^+;[378] ii, SO_3^{2-}, H^+;[378] iii, $Na_2S_2O_3$, O_2, 26 h, dark;[378] iv, HBr[378]

Scheme 14

(iii) Oxygen donor ligand complexes

(a) Aqua and hydroxy ligands

Ruthenium(II): $[Ru(NH_3)_5OH_2]^{2+}$ can be most efficiently prepared by zinc amalgam reduction of $[RuCl(NH_3)_5]Cl_2$ in aqueous solution.[208,319,325] More recently, an alternative route avoiding Zn^{2+} and Cl^- ion has been developed based on the aquation of electrochemically reduced $[Ru(O_3SCF_3)(NH_3)_5]^{2+}$.[208] Alternative routes include the photolysis[379] and acid-catalysed hydrolysis[380] of $[Ru(NH_3)_6]^{2+}$ and the reduction of $[Ru(NH_3)_5(OH_2)]^{3+}$.[203] The lability of the aqua ligand in these systems makes $[Ru(NH_3)_5OH_2]^{2+}$ an excellent starting material for the synthesis of substituted pentaammine complexes, and for the study of their kinetics of formation.

Tables 2 and 3 give data on the substitution reactions of $[Ru(NH_3)_5OH_2]^{2+}$ with a range of ligands L.[381-383] The kinetics of substitution on $[Ru(NH_3)_5OH_2]^{2+}$ are first order in $[[Ru(NH_3)_5(OH_2)]^{2+}]$ and [L] with rate constant in the range $k = 0.048 \rightarrow 0.32\ M^{-1}s^{-1}$ at 25°C for L = pyridine, 3- and 4-cyanopyridine, acetonitrile, benzonitrile, perfluorobenzonitrile.[384,385] Electron-donating groups on L were found to enhance the rate of substitution, while electron-withdrawing groups decreased the rate. An S_N1 mechanism was suggested, with pyridines reacting relatively slowly due to steric factors.[384] The enthalpies for substitution of $[Ru(NH_3)_5OH_2]^{2+}$ by acetonitrile, imidazole, pyridine, thiodiethanol, $[Ru(NH_3)_5pz]^{2+}$, isonicotinamide, pyrazine, *N*-methylpyrazinium$^+$, dimethyl sulfoxide and CO have been found to be -38.4, -38.9, -53.1, -57.3, -57.7, -64.0, -70.3, -75.3, -80.3 and $-160.3\ kJ\ mol^{-1}$ respectively.[208]

Table 2 Kinetic Data for Substitution Reactions

$$[Ru(NH_3)_5(OH_2)]^{2+} + L \xrightarrow{k} [Ru(NH_3)_5L]^{2+} + H_2O$$

L	*Rate constant k* ($M^{-1}s^{-1}$)
NH_3	5.5×10^{-2}
MeCN	30.2×10^{-2}
py	9.3×10^{-2}
pz	5.6×10^{-2}
pzH^+	3.1×10^{-3}
isn	10.5×10^{-2}
$isnH^+$	3.6×10^{-3}
imid	20×10^{-2}
$imidH^+$	2.7×10^{-3}
3-Methylpyridine	3×10^{-3}
2,6-Dimethylpyridine	$< 4 \times 10^{-5}$
Isoniazid	9.2×10^{-2}
Cyanoacetate	1.2
Pyrazine *N*-oxide	3×10^2

Table 3 Selected Equilibrium Quotient Data for Reactions[383]

$$[Ru(NH_3)_5(OH_2)]^{n+} + L \overset{K}{\rightleftharpoons} [Ru(NH_3)_5L]^{n+} + H_2O$$

L	$n = 2+$ K_{equil} (M^{-1})	$n = 3+$ K_{equil} (M^{-1})
NH_3	3.5×10^4	3.6×10^5
Ethyl glycinate	3.2×10^3	5.5×10^2
Methylamine	3.5×10^3	3.5×10^3
Methyl sarcosinate	50 ± 10	2.0

The kinetics of substitution of L on *trans*-$[Ru(SO_3)(NH_3)_4(OH_2)]$ have been reported (Table 4) and indicate that replacement of NH_3 by SO_3^{2-} lowers the affinity for the incoming ligand approximately ten-fold, but increases the rate of substitution approximately 100-fold, a much greater lowering of affinity being observed with methionine methyl ester.[386] Reaction of $[Ru(NH_3)_5(OH_2)]^{2+}$ with $P(OEt)_3$ in acetone gives $[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ from which the derivatives *trans*-$[RuL(NH_3)_4(P(OEt)_3)]^{2+}$ could be prepared;[387] for aquation (L = H_2O) of the diphosphite complex the rate constant $k = 1.12 \times 10^{-5}\ s^{-1}$. Substitution reactions of *trans*-$[Ru(NH_3)_4(OH_2)[P(OEt)_3]^{2+}$ were studied and an order for the affinity of the complex for the entering ligand was found to be $P(OEt)_3 > SO_3^{2-} >$ imid(N bound) > isn > pz > $Mepz^+$.[387] For SO_3^{2-} and N-bound imid, bond making was proposed to be substantial in the activated complex, whereas for isn, pz and $Mepz^+$, noticeable outer-sphere complex formation was indicated.[387] Reaction of *trans*-$[Ru(SO_4)(NH_3)_4isn]^+$ with CF_3SO_3H and zinc amalgam gives *trans*-$[Ru(NH_3)_4isn(OH_2)]^{2+}$.[388] The labilizing effect of L in *trans*-$[RuL(NH_3)_4(OH_2)]^{2+}$ was probed by kinetic measurements and the labilizing

effect of L was found to increase in the order L = N_2 < CO < isn < pz < imid(N bound) < $-NH_3$ < ^-OH < $P(OEt)_3$ < ^-CN < SO_3^{2-} < imid(C bound).[387] The kinetics of substitution of *cis*- and *trans*-$[Ru(NH_3)_4(OH_2)_2]^{2+}$ to $[RuL(NH_3)_4(OH_2)]^{2+}$ and then to $[RuL_2(NH_3)_4]^{2+}$ have been studied;[385] for L = pyridine, the second order rate constants $k_1 = 9 \pm 1$ (*cis* isomer) and $0.74\ M^{-1}s^{-1}$ (*trans* isomer) for initial substitution, and $k_2 = 1.2 \pm 0.5$ (*cis* isomer) and $0.5 \pm 0.5\ M^{-1}s^{-1}$ (*trans* isomer) for the second substitution reaction.[385] Photolysis of $[Ru(NH_3)_5(OH_2)]^{2+}$ in the presence of Cl^- affords $[RuCl(NH_3)_5]^{2+}$.[379]

Table 4 Selected Kinetic and Equilibrium Data for Reactions[239,386]

trans-$[Ru(SO_3)(NH_3)_4(OH_2)] + L \rightleftharpoons$ *trans*-$[Ru(SO_3)(NH_3)_4L] + H_2O$

L	*Association quotient K*	*Specific rate constant k* (M^{-1})
NH_3	1.5×10^3	13.8
Methylamine	5.4×10^2	1.9
Ethyl glycinate	4.7×10^2	20
Prolinato	5	5.3
Methyl sarcosinate	3.1	2.9
Adenosine	8 ± 7	
1-Methylguanosine	7.6×10^2	
1-Histidine	1.1×10^3	
1,9-Dimethylguanine	1.4×10^3	
Imidazole	11.8×10^3	
1-Methylimidazole	$> 46 \times 10^3$	

Electron transfer between $[Ru(NH_3)_5(OH_2)]^{2+}$ and $[RuCl(NH_3)_5]^{2+}$ ($k = 1.0 \times 10^3\ M^{-1}s^{-1}$) yields $[Ru(NH_3)_5OH_2]^{3+}$ and $[RuCl(NH_3)_5]^+$.[178] The rate of electron transfer is reported to be independent of $[H^+]$, and decreases in the order $I^- > Br^- > Cl$, the reaction proceeding *via* an outer-sphere type mechanism.[389] Subsequent aquation of $[RuCl(NH_3)_5]^+$ occurs to give $[Ru(NH_3)_5OH_2]^{2+}$ ($k = 4.7\ s^{-1}$) thus rendering the overall aquation of $[RuCl(NH_3)_5]^{2+}$ catalysed by reducing agent.[125,178] The kinetics of reduction of $[CoX(NH_3)_5]^{2+}$ (X = F^-, Cl^-, Br^-, I^-, ^-NCS, ^-SCN, N_3^-) and $[Co(ox)(NH_3)_4]^-$ by $[Ru(NH_3)_5OH_2]^{2+}$ have been reported and discussed in terms of inner- and outer-sphere electron transfer mechanisms.[133,139,390] $[Ru(NH_3)_5(OH_2)]^{2+}$ with VO^{2+} yields green binuclear complexes $[(NH_3)_5Ru^{II}OV^{IV}(L)_n]^{4+}$ (L = H_2O,[380] edta derivatives[391]) which show M → L charge transfer bands near 600 nm. The ESR spectra and electron transfer processes in these systems have been reported.[391] Reduction of H_2O_2 and cytochrome c by $[Ru(NH_3)_5OH_2]^{2+}$ has been studied,[154,392] while $[Ru(NH_3)_5OH_2]^{2+}$ has been bound to polyvinyl pyridine coated electrodes.[393]

Ruthenium(III): $[Ru(NH_3)_5OH_2]^{3+}$ has been prepared by reaction of $[RuCl(NH_3)_5]Cl_2$ with dilute NH_3 and acidification to pH 3,[394] by reaction of $[Ru(O_3SCF_3)(NH_3)_5)](O_3SCF_3)_2$ with H_2O,[208] by protonation of $[Ru(OH)(NH_3)_5]^{2+}$ with 3 M CF_3SO_3H[362] or by treatment of $[Ru(NH_3)_6]Cl_2$ with HCl.[395] $[Ru(OH)(NH_3)_5]^{2+}$[278,396] can be isolated from the reduction of $[RuCl(NH_3)_5]Cl_2$ with zinc amalgam followed by air oxidation of the product, from the reaction of $[RuCl(NH_3)_5]Cl_2$ with NH_3,[290,397] and from the aquation of $[Ru(NH_3)_6]^{3+}$ under basic conditions.[164] The latter reaction proceeds *via* two independent pathways: (a) pH independent, and (b) base-catalysed aquation *via* $[Ru(NH_2)(NH_3)_5]^{2+}$ intermediate;[166] for $[Ru(NH_3)_5OH_2]^{3+}$ $pK_a = 4.2$.[235,398]

Substitution reactions of $[Ru(NH_3)_5OH_2]^{3+}$ have been reported (Table 3).[383] Thermolysis of $[Ru(NH_3)_5OH_2]X_3$ in the solid state takes place *via* a two step process to give initially $[RuX(NH_3)_5OH_2]^{2+}$ in a rate-determining step, with subsequent formation of $[RuX(NH_3)_5]^{2+}$ (X = Cl^-, Br^-, I^-, NO_3^-);[399a] the activation energies and entropies for these reactions have been assessed.[399a,399b] In solution, anation of $[Ru(NH_3)_5OH_2)]^{3+}$ shows second order kinetics.[124,399c,400] The photolysis of $[Ru(NH_3)_5(OH_2)]^{3+}$ has been reported.[177]

Electron transfer reactions of $[Ru(NH_3)_5OH_2]^{3+}$ with Sm^{II},[401,402] Yb^{II},[401,402] Eu^{II},[401,402] Fe^{III},[128] $[Fe^{III}OH]^{2+}$,[128] U^{III},[170] Cr^{II},[125,402] V^{II}[402] and $[Ti^{III}(OH)]^{2+}$[254] have been studied. $[Ru(NH_3)_6]^{3+}$ on zeolites can be converted to a complex of the type $[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$ which is an active catalyst for the water gas shift reaction.[403]

$[Ru(NH_3)_4(OH_2)_2]^{3+}$ is prepared *via* addition of CF_3SO_3H to $[Ru(ox)(NH_3)_4]^+$;[404a] the affinity of *trans*-$[Ru^{III}L(NH_3)_4OH_2]^{3+}$ (L = C-bound imidazole) for imidazole, py, isn, Cl^-, Br^-, I^- is very low ($K_{assoc} = 1.2$ for isn) except for NCS^- ($K_{assoc} = 3.3 \times 10^4\ M^{-1}$); a large kinetic labilization by C-bound imidazole is implied.[235]

Electrochemical evidence for the interconversion of $[Ru^{IV}(O)(NH_3)_5]^{2+}$, $[Ru^{III}(OH)(NH_3)_5]^{2+}$ and $[Ru^{III}(NH_3)_5(OH_2)]^{3+}$ has been obtained using activated glassy carbon electrodes.[404b]

$[Ru(O)_2(NH_3)_4]^{2+}$ and related ruthenium(VI) complexes incorporating the *trans* dioxo moiety have been reported.[65]

(b). Carboxylates

Ruthenium(II): The polarographic reduction of $[Ru^{III}L(NH_3)_5]^{2+}$ (L = formate, acetate, propionate, butyrate, glycolate, glycinate) shows a reversible one electron transfer to give Ru^{II} at a DME in aqueous solution.[405,406] $E_{1/2}$ values for this couple were found to become more positive with increasing $[H^+]$.[406] The reversible uptake of CO_2 by $[Ru(NH_3)_5(OH_2)]^{2+}$ has been described.[187b]

Ruthenium(III): Reaction of $[Ru(OH)(NH_3)_5]Cl_2$ with acetic anhydride followed by acid hydrolysis and treatment with Ag^+ gives $[Ru(OAc)(NH_3)_5]^{2+}$.[397] Oxalic acid with $[Ru(OH)(NH_3)_5]^{2+}$[290] or $[RuCl(NH_3)_5]^{2+}$[404a] affords *cis*-$[Ru(ox)(NH_3)_4]^+$. Carboxylato complexes can be prepared generally by treatment of $[RuCl(NH_3)_5]^{2+}$ with $Ag(O_2CCF_3)$ followed by addition of carboxylate buffer in DMF.[402] Charge transfer bands for the complexes $[Ru(O_2CR)(NH_3)_5]^{2+}$ are observed near 300 nm, and are related to the $E_{1/2}$ values for reduction of the complexes.[405]

Aquation of $[Ru(O_2CR)(NH_3)_5]^{2+}$ proceeds *via* two pathways: (a) an acid-catalysed S_N1 process, and (b) an acid independent S_N2 process for R = CH_2F, CH_2Cl, CH_2Br, CH_2I.[407] For R = $CHCl_2$, CCl_3 the aquation reaction is not catalysed by H^+ due to the high acidity of the coordinated ligand.[407–409] Data for the aquation of non-halo carboxylate complexes are given in Table 5; the mechanisms of the reactions have been discussed.[410–412] Anation of $[Ru(O_2CCH_2Cl)(NH_3)_5]^{2+}$ is reported to proceed *via* predominantly an S_N1 mechanism.[409]

Table 5 Kinetic Data for Aquation of $[Ru(O_2CR)(NH_3)_5]^{2+}$[410] for which Aquation Rate Law is Rate = [complex]($k_{H_2O} + k_H[H^+]$)

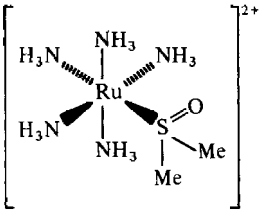
RCO_2^-	$k_{H_2O}(s^{-1})$	$k_H(M^{-1}s^{-1})$
Formate	5.37×10^{-5}	3.3×10^{-3}
Acetate	11.8×10^{-5}	2.3×10^{-3}
Propionate	14×10^{-5}	2.5×10^{-3}
Isobutyrate	13.7×10^{-5}	1.7×10^{-3}
Glycolate	5.7×10^{-5}	0.75×10^{-3}
Glycinate	6.75×10^{-5}	3.1×10^{-3}

The reduction of *cis*-$[Ru(ox)(NH_3)_4]^+$, $[Ru(oxH)(NH_3)_5]^{2+}$ and $[Ru(OAc)(NH_3)_5]^{2+}$ by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5OH_2]^{2+}$ has been studied;[413] the rates of reduction are acid dependent and increase with increasing $[H^+]$ with outer-sphere mechanisms being proposed.[413] Inner-sphere reductions of $[Ru(O_2CR)(NH_3)_5]^{2+}$ have been reported with Cr^{II}[402] and Ti^{III}.[414,415] Acid dependent second order kinetics were observed for Ti^{III} reactions which occur *via* electron transfer in a deprotonated binuclear intermediate, the rate constant for reduction being identified as the rate constant for substitution on Ti^{III}.[414] For the salicylato complex, no acid dependence was observed;[415] cross-bridging between Ru^{III} and Ti^{III} through the π-system of carboxylate was proposed.[415] Reaction of $[Ru(NH_3)_6]^{3+}$, $[RuCl(NH_3)_5]^{2+}$ or *cis*-$[RuCl_2(NH_3)_4]^+$ with LH_2 (LH_2 = catechol, 2,3-dihydroxynaphthalene) yields *cis*-$[RuL(NH_3)_4]^+$, while reaction with LH_3 (LH_3 = 3,4-dihydroxybenzoic acid, 3-(3,4-dihydroxyphenyl)propanoic acid) yields $[RuL(NH_3)_4]$;[416] the properties of these complexes have been discussed.[416]

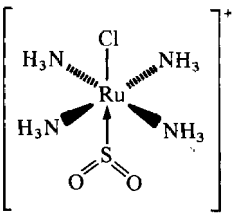
(c) Sulfoxides and related ligands

Ruthenium(II): Refluxing $[Ru(NH_3)_5N_2]^{2+}$ in aqueous DMSO yields $[Ru(NH_3)_5DMSO]^{2+}$ (**42**).[417] ^1H NMR and IR spectral data for $[Ru(NH_3)_5\{S(O)(Me)_2\}]^{2+}$, $[Ru(ND_3)_5\{S(O)(Me)_2\}]^{2+}$, $[Ru(ND_3)_5\{S(O)(CD_3)_2\}]^{2+}$ and $[Ru(NH_3)_5\{S(O)(CD_3)_2\}]^{2+}$ indicate that the DMSO ligand is S-bonded.[417] This is confirmed by the single crystal X-ray structure of $[Ru(NH_3)_5DMSO]^{2+}$ (**42**) which shows Ru—S = 2.188 and S—O = 1.527 Å with lengthening of Ru—N distance *trans* to S to 2.209 Å.[418]

A range of SO_2, HSO_3^- and SO_3^{2-} complexes of $[Ru(NH_3)_5]^{2+}$ and $[Ru(NH_3)_4]^{2+}$ have been prepared.[2,419,420] Reaction of $[RuCl(NH_3)_4SO_2]^+$ with NH_3 yields $[Ru(SO_3)(NH_3)_5]$ which on acidification gives $[Ru(NH_3)_5SO_2]^{2+}$,[419,420] the Mössbauer of which has been reported.[120] Treatment of $[RuCl(NH_3)_5]^{2+}$ with HSO_3^-/SO_2 yields *trans*-$[Ru(HSO_3)_2(NH_3)_4]$ which can be converted to *trans*-$[RuX(NH_3)_4SO_2]^+$ with HX (X = Cl^-, Br^-).[196,419–421] The single crystal X-ray structure of *trans*-$[RuCl(NH_3)_4SO_2]Cl$ (**43**) shows[421] the SO_2 ligand to be S bonded with Ru—S = 2.072 Å, S—O = 1.462, 1.394 Å Ru—Cl = 2.415 Å with a planar $RuSO_2$ moiety. *Trans*-$[RuL(NH_3)_4SO_2]^{2+}$ may be prepared by reaction of *trans*-$[RuCl(NH_3)_4SO_2]^+$ with L (L = pz, isn, imid).[239,422] Photolysis of *trans*-$[RuCl(NH_3)_4SO_2]^+$ leads to linkage isomerism of the SO_2 ligand, from S-bonded SO_2 (ν_{SO} = 1255, 1110 cm^{-1}) to η^2-bonded SO_2 (ν_{SO} = 1165, 940 cm^{-1}) (equations 42 and 43).[423]

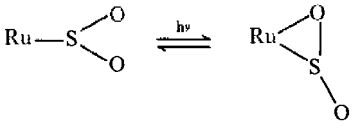


(42)



(43)

$$[RuCl(NH_3)_4SO_2]^+ \underset{h\nu\ 365\,nm\ 195\,K}{\overset{h\nu\ 365\,nm\ 25\,K}{\rightleftharpoons}} [RuCl(NH_3)_4(\eta^2\text{-}SO_2)]^+ \quad (42)$$



(43)

$[Ru(NH_3)_4(OH_2)(SO_2)]^{2+}$ may be prepared by reaction of *cis*-$[RuCl_2(NH_3)_4]Cl$ with zinc amalgam, HSO_3^- followed by acidification.[239,422] In solution, the SO_2 complex is in equilibrium with HSO_3^- and SO_3^{2-} derivatives (equations 44 and 45).[422] The rates of substitution of pyrazine into the SO_2 (**44**), HSO_3^- (**45**) and SO_3^{2-} (**46**) complexes have been measured; rate constants $k = 0.033$, 0.2, 13.5 $M^{-1}s^{-1}$ at 25°C respectively.[422] The rate of substitution for *cis*-$[Ru(SO_3)(NH_3)_4OH_2]$ is independent of [pz], the rate-determining step being release of NH_3 *trans* to SO_3^{2-}.[422]

$$\underset{\textbf{(44)}}{\textit{trans}\text{-}[Ru(NH_3)_4(OH_2)SO_2]^{2+}} + H_2O \rightleftharpoons \underset{\textbf{(45)}\ pK_a = 2.15}{\textit{trans}\text{-}[Ru(HSO_3)(NH_3)_4(OH_2)]^+} + H^+ \quad (44)$$

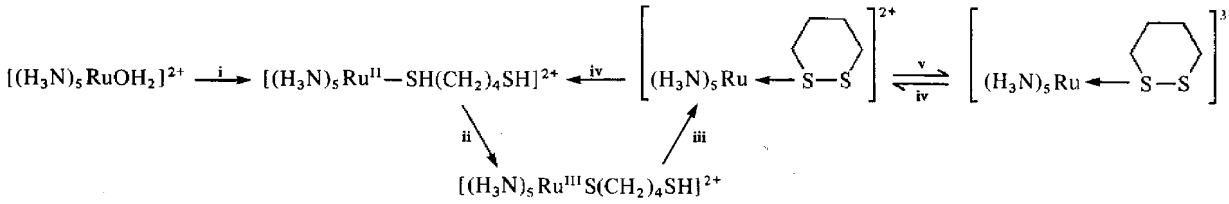
$$\underset{\textbf{(45)}}{\textit{trans}\text{-}[Ru(HSO_3)(NH_3)_4(OH_2)]^+} \rightleftharpoons \underset{\textbf{(46)}\ pK_a = 5.05}{\textit{trans}\text{-}[Ru(SO_3)(NH_3)_4(OH_2)]} + H^+ \quad (45)$$

Ruthenium(III): Oxidation of $[Ru(NH_3)_5\{S(O)(Me)_2\}]^{2+}$ (**42**) to the Ru^{III} complex leads to S → O isomerization at a specific rate $k = 7.0 \times 10^{-2}\,s^{-1}$; reduction back to Ru^{II} reverses the isomerization ($k = 30\,s^{-1}$) reforming (**42**).[424] Aquation is associated with both reactions. The 3+/2+ couples are 1.0 V and 0.01 V *vs.* SCE for the S- and O-bonded complexes respectively.[424] The electrochemistry of $[Ru(NH_3)_5SO_2]^{2+}$ has been studied;[425] oxidation at +0.5 V *vs.* SCE leads to the formation of the Ru^{III} complex with hydrolysis of coordinated SO_2 at a rate constant $k = 2.4 \times 10^{-2}\,s^{-1}$.[425] Treatment of $[RuCl(NH_3)_5]Cl_2$ with CF_3SO_3H leads to a high yield of labile $[Ru^{III}(OSO_2CF_3)(NH_3)_5]^{2+}$,[426,427] which readily undergoes substitution reactions to $[RuL(NH_3)_5]^{3+}$.[208,426,427] Reaction of $[Ru(NH_3)_5OH_2]^{3+}$ with $S_2O_3^{2-}$ yields $[Ru(S_2O_3)(NH_3)_5]^+$[378] while *trans*-$[Ru(SO_4)(L)(NH_3)_4]^+$ can be prepared by reaction of *trans*-$[RuCl(NH_3)_4SO_2]^+$ with L (L = pyridine, 3-chloropyridine, 3,5-dichloropyridine) in aqueous solution.[196] Oxidation of $[RuCl(NH_3)_4SO_2]^+$ with H_2O_2 in the presence of Na_2CO_3 and py gives $[Ru(SO_4)(NH_3)_4py]^+$.[428]

(*iv*) *Sulfur donor ligand complexes*

(See also Section 45.7). Reaction of $[Ru(NH_3)_5OH_2]^{2+}$ with an excess of L gives products $[RuL(NH_3)_5]^{2+}$ (L = 2,6-dithiaspiro[3.3]heptane,[429,430] $MeS(CH_2)_3SMe$,[429] H_2S,[431] $HS(CH_2)_4SH$,[432] Me_2S,[433] $S(C_2H_4)_2S$,[434] $S(C_3H_6)_2S$[434]). For $[Ru(NH_3)_5(SH_2)]^{2+}$ and $[Ru(NH_3)_5(SH_2)]^{3+}$, $pK_a = 4.0$ and −10 respectively, while for $[Ru(NH_3)_5(SHEt)]^{2+}$ and $[Ru(NH_3)_5(SHEt)]^{3+}$ $pK_a = 9$ and −7 respectively.[431] For the formation of $[Ru(NH_3)_5(SH_2)]^{2+}$ (equation 46), $K_{equil} = 1.5 \times 10^3\,M^{-1}$,[431] thioethers having generally a greater affinity for Ru^{II} than for Ru^{III}.[431] Reduction of $[RuL(NH_3)_5]^{3+}$ (L = $S(CH_2)_4S$) with zinc amalgam gives $[RuL(NH_3)_5]^{2+}$, which on further reduction yields $[Ru(NH_3)_5HS(CH_2)_4SH]^{2+}$;[432] reoxidation to $[RuL(NH_3)_5]^{3+}$ has been shown to occur with O_2 or Ce^{IV} (Scheme 15).[432] The aquation of $[Ru(NH_3)_5X(Me)_2]^{2+}$ to $[Ru(NH_3)_4(OH_2)X(Me)_2]^{2+}$ occurs with rate constants $k = 4.2 \times 10^{-6}$ (X = S), 1.0×10^{-5} (X = Se), 1.2×10^{-4} (X = Te) reflecting an increasing labilization order of $(Me)_2S < (Me)_2Se < (Me)_2Te$.[433]

$$[Ru(NH_3)_5(OH_2)]^{2+} + H_2S \overset{K_{equil}}{\rightleftharpoons} [Ru(NH_3)_5(SH_2)]^{2+} + H_2O \quad (46)$$



i, $HS(CH_2)_4SH$; ii, O_2 or Ce^{IV}; iii, [O]; iv, Zn/Hg; v, Ce^{IV}

Scheme 15

Oxidation of $[Ru^{II}(LH)(NH_3)_5]^{2+}$ with O_2 or Ce^{IV} gives $[Ru^{III}L(NH_3)_5]^{2+}$ (L = $\bar{S}CH_2Me$, $\bar{S}(CH_2)_3SH$, $\bar{S}(CH_2)_4SH$, $\bar{S}Ph$, $\bar{S}(Me)_2$),[432,433] while treatment of $[Ru(NH_3)_5OH_2]^{2+}$ with $[(Me)_3S]PF_6$ yields $[Ru^{II}(NH_3)_5S(Me)_3]^{3+}$.[435] The Ru^{III} complexes show strong ligand → metal charge transfer bands *e.g.* for $[Ru(NH_3)_5S(Me)_2]^{3+}$ $\lambda = 453$ nm ($\varepsilon = 3 \times 10^2\,M^{-1}\,cm^{-1}$).[434,435] The lability and reactivity of thioethers bound to Ru^{II} and Ru^{III} have been fully discussed in relation to the electronic and redox properties of these systems.[383,396,429–436]

(*v*) *Halide complexes*

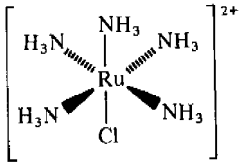
Ruthenium(II): $[RuCl(NH_3)_5]^+$ can be prepared by reduction of $[RuCl(NH_3)_5]^{2+}$ with Ti^{III} [173] or Ru^{II},[173] photolysis of $[Ru(NH_3)_5OH_2]^{2+}$ in the presence of Cl^- [379] or by radiolysis of $[RuCl(NH_3)_5]^{2+}$.[178] For $[RuCl(NH_3)_5]^{2+}$, *cis*- and *trans*-$[RuCl_2(NH_3)_4]^+$, $E_{1/2}$ for Ru^{II}/Ru^{III} couple = −0.282 V, −0.328 V and −0.412 V *vs.* SCE respectively.[334,425] $[RuCl(NH_5)_5]^+$ aquates rapidly to give $[Ru(NH_3)_5OH_2]^{2+}$ together with $[RuCl(NH_3)_5]^{2+}$ (equation 47).[379,425,437] The oxidation of $[RuCl(NH_3)_5]^+$ by CoL_3^{3+} (L = en, cyclohexanediamine) follows first order dependence on $[Co^{III}]$ and $[Ru^{II}]$ *via* an outer-sphere electron transfer with rate constant $k = 3.8 \times 10^{-3}$ and $6.2 \times 10^{-3}\,M^{-1}\,s^{-1}$ respectively.[438]

$$[RuX(NH_3)_5]^+ + H_2O \rightleftharpoons [Ru(NH_3)_5(OH_2)]^{2+} + X^- \qquad (47)$$

$X = Cl^-$, $K_{equil} = 0.7\,M$, $\Delta H^{\neq} = 50\,kJ\,mol^{-1}$, $\Delta S^{\ddagger} = -67\,J\,K^{-1}mol^{-1}$, $k = 6.3\,s^{-1}$

$X = Br^-$, $K_{equil} = 0.92\,M$, $\Delta H^{\neq} = 59\,kJ\,mol^{-1}$, $\Delta S^{\ddagger} = -42\,J\,K^{-1}mol^{-1}$, $k = 5.4\,s^{-1}$

Ruthenium(III): $[RuX(NH_3)_5]X_2$ can be prepared by treatment of $RuCl_3$ or $[RuCl_5(OH_2)]^{2-}$ with hydrazine followed by HCl,[117,325,439] by refluxing $[Ru(NH_3)_6]^{3+}$ in HX[113,114,193,394,421,440–442] or by solid state thermal substitution of $[Ru(NH_3)_6]X_3$ (X = Cl^-, Br^-, I^-).[443,444] The single crystal X-ray structure of $[RuCl(NH_3)_5]Cl_2$ (**47**) shows Ru—N = 2.07–2.11 Å, Ru—Cl = 2.34 Å.[439] Reaction of *cis*-$[Ru(ox)(NH_3)_4]^+$ or $[RuX(NH_3)_4SO_2]^+$ with refluxing HX (X = Cl^-, Br^-, I^-)[290,445–447] or thermolysis of $[RuCl(NH_3)_5]Cl_2$[444] yields $[RuX_2(NH_3)_4]^+$. $RuCl_3(NH_3)_3$ has been prepared by action of O_2 on blue solution of $[Ru(NH_3)_6]^{2+}$ in HCl,[442,448] by reaction of HCl with *cis*-$[RuCl_2(NH_3)_4]^+$[197] and by thermolysis of $[RuCl_2(NH_3)_4]Cl$.[444] The single crystal X-ray structure of *fac*-$[RuCl_3(NH_3)_3]$ shows Ru—N = 2.105–2.467 Å, Ru—Cl = 2.323–2.529 Å.[449]



(47)

Halo–ammine complexes show halide → Ru^{III} charge transfer bands[450] which have been characterized by circular dichroism studies.[354] Calculations predict that the Ru—N bond strength increases in the order *cis*-$[RuX_2(NH_3)_4]^+$ < $[RuX(NH_3)_5]^{2+}$ < $[Ru(NH_3)_5OH_2]^{3+}$ < $[Ru(NH_3)_6]^{3+}$, with Ru—NH_3 *trans* to X weaker than when *cis* to X.[451] The magnetic and ESR properties of $[RuCl(NH_3)_5]Cl_2$ have been reported.[163,452,453]

Anation of *trans*-$[Ru(NH_3)_4(isn)(OH_2)]^{3+}$ by Cl^- and Br^- proceeds *via* first order kinetics;[388] with I^- however, more complex kinetics are observed with the rate law being given by equation (48).[388] The k_a term can be accounted for by equations (49) to (51), with the k_b term suggesting a possible

electron transfer from I^- to Ru^{III} not involving free I_2.[388] The role of halide in the reduction of O_2 by *trans*-$[Ru(NH_3)_4(isn)(OH_2)]^{2+}$ has been discussed. *Trans*-$[RuI(NH_3)_4(isn)]I_2$ can also be prepared by treatment of *trans*-$[Ru(SO_4)(NH_3)_4(isn)]^+$ with NaI.[388]

$$\frac{-d[Ru^{III}(OH_2)]}{dt} = k_a[I^-]^{\frac{1}{2}}[I_3^-]^{-\frac{1}{2}} + k_b[I^-]^2 \quad (48)$$

$$2[Ru^{III}(OH_2)] + 3I^- \longrightarrow 2[Ru^{II}(OH_2)] + I_3^- \quad (49)$$

$$[Ru^{II}(OH_2)] + I^- \longrightarrow [Ru^{II}(I)] + H_2O \quad (50)$$

$$2[Ru^{II}(I)] + I_3^- \longrightarrow 2[Ru^{III}(I)] + 3I^- \quad (51)$$

The ligand exchange reactions of $[RuX(NH_3)_5]^{2+}$ ($X = Cl^-$, Br^-, I^-) (equation 52) have been studied and are proposed to take place *via* a two step process with the rate-determining step being the formation of $[Ru(NH_3)_5OH_2]^{3+}$ (equations 53 and 54).[454] The mechanisms for Br^- exchange for $[RuBr_2(NH_3)_4]^+$ in aqueous and mixed solvent systems have been discussed.[455] The aquation of $[RuX(NH_3)_5]^{2+}$ ($X = Cl^-$, Br^-, I^-) has been reported to occur *via* an associative S_N2 mechanism,[456,457] with base hydrolysis being substantially faster than the corresponding acid hydrolysis.[398,458] Scheme 16 illustrates the proposed S_N2cb and S_N2 processes for the base hydrolysis of $[RuX(NH_3)_5]^{2+}$ ($X = Cl^-$, Br^-, I^-) for $[^-OH] = 0.03$–0.2 M,[459a,459b] although an S_N1cb mechanism has been attributed to the reaction at lower ^-OH concentrations of 3.78×10^{-4}–2.65×10^{-3} M.[398] The aquation of $[RuCl(NH_3)_5]^{2+}$ is catalysed by Hg^{2+}[17] and $[Ru(NH_3)_5(OH_2)]^{2+}$,[125] the former reaction occurring *via* the formation of a chloro-bridged intermediate.[17] Acid hydrolysis of *cis*-$[RuCl_2(NH_3)_4]^+$ takes place with retention of configuration.[457] The UV photoaquation of $[RuCl(NH_3)_5]^{2+}$ has been reported in very low yield,[181] while photoaquation of *cis*-$[RuX_2(NH_3)_4]^+$ ($X = Br^-$, I^-) gives *cis*-$[RuX(NH_3)_4(OH_2)]^{2+}$.[460,461] No photoaquation is observed for $X = Cl^-$.[461] $[RuCl(OH)(NH_3)_4]^+$ has been prepared by treatment of $RuCl_3$ with NH_3 in aqueous ethanol.[462]

$$[RuX(NH_3)_5]^{2+} + X^{-*} \xrightarrow{k_1} [RuX^*(NH_3)_5]^{2+} + X^- \quad (52)$$

$$k_1 = 3.15 \times 10^{-4}\,s^{-1},\ X^- = Cl^-$$

$$k_1 = 3.63 \times 10^{-4}\,s^{-1},\ X^- = Br^-$$

$$k_1 = 1.1 \times 10^{-4}\,s^{-1},\ X^- = I^-$$

$$[RuX]^{2+} \xrightarrow[H_2O]{RDS} [RuOH_2]^{3+} + X^- \quad (53)$$

$$[RuOH_2]^{3+} \xrightarrow{X^{-*}} [RuX^*]^{2+} + H_2O \quad (54)$$

$$[RuX(NH_3)_5]^{2+} + {}^-OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RuX(NH_2)(NH_3)_4]^+ + H_2O$$

$$\downarrow k_3 \qquad\qquad \downarrow k_2$$

$$[Ru(OH)(NH_3)_5]^{2+} \qquad [Ru(OH)(NH_3)_5]^{2+}$$

For $X = Cl^-$, $[^-OH] = 0.03 - 0.2$ M; $k_1 = 9.29 \times 10^{-2}$, $k_{-1} = 2.65 \times 10^{-2}$, $k_2 = 6.78 \times 10^{-1}$, $k_3 = 1.13 \times 10^{-1}\,M^{-1}s^{-1}$

Scheme 16

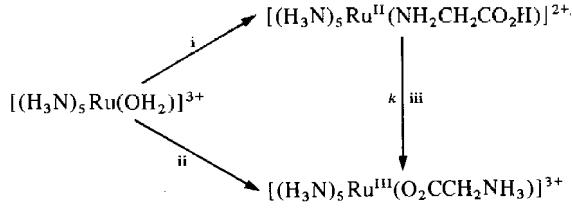
The solid state thermal deamination–anation of $[RuX(NH_3)_5]Y_2$ (s) to $[RuXY(NH_3)_4]Y$ (s) ($X = Cl^-$, Br^-; $Y = Cl^-$, Br^-, I^-, NO_3^-) has been investigated and the mechanism of the reactions discussed.[463] Thermal degradation of $[RuX(NH_3)_5]X_2$ occurs *via* the reduction of Ru^{III} by halide or by ammonia[444,464,465] with the initial formation of $[RuX_3(NH_3)_3]$ ($X = Cl^-$, Br^-). The thermal stability of $[RuX(NH_3)_5]^{2+}$ was found to decrease in the order $Cl^- > Br^- > I^-$.[443]

The reduction of $[RuX(NH_3)_5]^{2+}$ by Ti^{III} shows second order kinetics, with the rate of reaction being inversely proportional to $[H^+]$ indicating that $TiOH^{2+}$ and not Ti^{3+} is the reductant; rate constant $k = 12$, 56.0, 112.0 $M^{-1}s^{-1}$ for $X = Cl^-$, Br^-, I^- respectively.[173,466] The reduction of $[RuCl(NH_3)_5]^{2+}$, *cis*-$[RuCl_2(NH_3)_4]^+$ and *cis*-$[RuCl(NH_3)_4(OH_2)]^{2+}$ by Cr^{II} follows pseudo first order kinetics at higher $[Cr^{II}]$ with rate constant $k = 460$, 117 and 154 s^{-1} respectively.[402,467,468] For *trans*-$[RuCl_2(NH_3)_4]^+$ second order kinetics is observed.[468] Reductions with Cr^{II} occur *via* an

inner-sphere mechanism with the formation of binuclear chloro-bridged intermediates [Ru^{III}—Cl—Cr^{II}] followed by electron transfer to give [Ru^{II}—Cl—Cr^{III}] and dissociation to Ru^{II} and Cr^{III} products.[125,402,467,468] Reduction of $[RuX(NH_3)_5]^{2+}$ (X = Cl^-, Br^-, I^-) by U^{III} probably proceeds *via* an inner-sphere mechanism,[171] whereas for reduction by V^{II} an outer-sphere mechanism predominates;[402,468] by contrast, reduction of $[Ru(NH_3)_5OH_2]^{3+}$ by U^{III} is thought to occur *via* an outer-sphere process.[171] The reaction of $[RuX(NH_3)_5]^{2+}$ with organic radicals has been reported,[180] while I^-/I_2 coupling experiments using electrodes chemically modified with $[RuCl(NH_3)_5]Cl_2$ exhibited electrocatalysis.[469] An intervalence charge transfer band at $\lambda = 510$ nm has been observed on mixing $[RuCl(NH_3)_5]^{2+}$ with $[Ru(CN)_6]^{4-}$.[55,470]

(*vi*) *Amino acids, esters and mixed donor complexes*

Addition of L to $[Ru(NH_3)_5OH_2]^{2+}$ under basic conditions yields the complexes $[RuL(NH_3)_5]^{2+}$ (L = glycine,[471] ethyl glycine,[383] methyl sarcosine,[383] glycinamide,[472] *N*-ethyl glycinamide,[472] glycylglycine,[472] glycylglycinamide,[472] ethyl glycylglycine[472]). Oxidation of the glycine complex $[Ru^{II}(NH_3)_5(NH_2CH_2CO_2H)]^{2+}$ leads to N → O isomerization to give $[Ru^{III}(NH_3)_5(O_2CCH_2NH_3)]^{3+}$ (Scheme 17).[471] For the ethyl glycine complex $[Ru^{II}(NH_3)_5(NH_2CH_2CO_2Et)]^{3+}$, N → O rearrangement occurs within the Ru^{III} oxidation state to yield $[Ru^{III}(NH_3)_5OC(OEt)CH_2NH_3]^{3+}$ under acidic conditions.[473] $[H^+]$ inhibits reversion to the N-bonded complex, with the hydrolysis of the ethyl glycinate ligand being found to be much faster for this system than for the $[Co(NH_3)_5]^{3+}$ analogue.[473] Under acidic conditions (pH = 3) $[RuL(NH_3)_5]^{3+}$ (L = glycinamide, *N*-ethyl glycinamide, glycylglycine, glycylglycinamide, ethyl glycylglycine) reacts to form $[RuL(NH_3)_4]^{3+}$ in which the ligand L is N,O bonded.[472] At higher acidities aquation to $[Ru(NH_3)_5OH_2]^{3+}$ is a competing reaction, with the rate law being $k = k' + k''[H^+]$ where k' corresponds to chelate formation and k'' to aquation.[472] Treatment of *cis*-$[Ru(NH_3)_4(OH_2)_2]^{3+}$ at pH 1 with L gives $[Ru(L)(NH_3)_4]^{3+}$ (L = glycylglycine, glycinamide, *N'*-ethyl glycinamide) with the ligand L being *N,N'* bonded.[404a] Rearrangement to the N,O-bound isomer is slow, but can be achieved more readily by reduction to the Ru^{II} species in acidic solution and reoxidizing.[404a] It is interesting to note here that the N-bonded complex $[RuL(NH_3)_5]^{3+}$ (L = acetamide) does not rearrange to the O-bonded isomer. However, for L = formamide, reduction does lead to N → O isomerization to form the O-bonded Ru^{II} species which on reoxidation, decays with a specific rate $k = 1\,s^{-1}$ to the N-bonded starting material.[474] The above linkage isomerization reactions and relative stabilities of the products have been fully discussed.[404a,471–474] Radiolabelled Ru^{III}–ammine complexes of amino acids have been reported.[475]



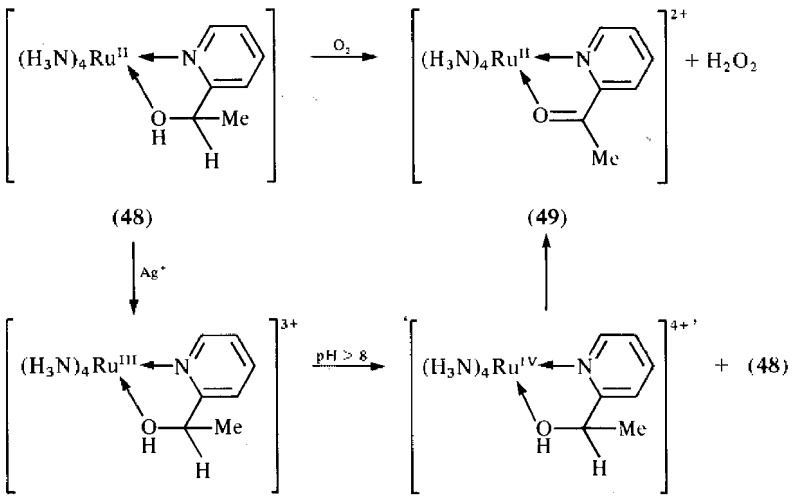
$$k = k_1 + \frac{k_2}{[H^+]},\quad k_1 = 2 \times 10^{-3}\,s^{-1},\quad k_2 = 1.25 \times 10^{-4}\,M^{-1}s^{-1}.$$

i, (a) Zn/Hg, (b) sodium glycinate; ii, glycine, 3 h; iii, [O]

Scheme 17

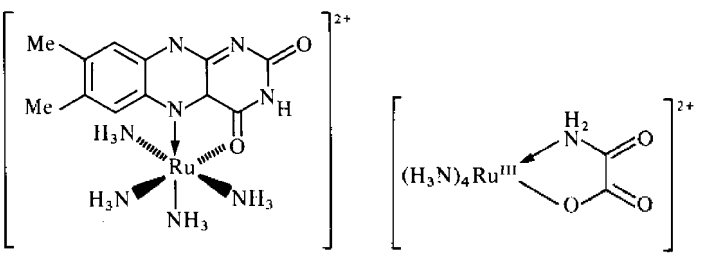
Reaction of $[Ru(NH_3)_4(OH_2)_2]^{2+}$ with L (L = 2-pyridine carboxaldehyde,[263] 2-pyridine alcohol[476a]) yields the complexes $[Ru^{II}L(NH_3)_4]^{2+}$. These products can be interconverted by oxidation of the pyridine alcohol derivative (**48**) to the acetyl pyridine complex (**49**) (Scheme 18).[476a] The complexes $[Ru(NH_3)_nL]^+$ (*n* = 4,5; LH = pyrazinecarboxylic acid) have been generated in which L can be mono- or bi-dentate.[476b]

Metalloflavin complexes of type $[RuL(NH_3)_4]^{2+}$ have been synthesized by reaction of $[Ru(NH_3)_5OH_2]^{2+}$ and *cis*-$[Ru(NH_3)_4(OH_2)_2]^{2+/3+}$ with flavin ligand, L.[477–479] The single crystal X-ray



Scheme 18

structure of the 10-methylisoalloxazine complex (**50**) has been reported and confirms a bidentate N,O chelate with Ru—O = 2.088 Å, Ru—N(flavin) = 1.980 Å, Ru—N(NH_3) = 2.12 Å, the short Ru—N(flavin) distance being consistent with back-bonding from Ru^{II}.[477,479] (**50**) shows two, one electron reductions.[478,480] More recently, resonance Raman studies on flavin derivatives of $[Ru(NH_3)_4]^{2+}$ have been published.[481] Condensation of $[Ru(NH_3)_6]^{3+}$ with oxalic acid is reported to yield (**51**).[375]



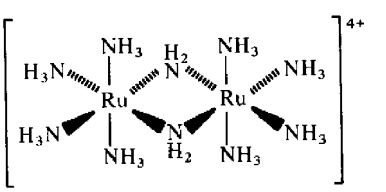
45.4.1.3 Binuclear complexes

Ruthenium ammine–phosphine and –selenium complexes are discussed in Sections 45.5 and 45.8 respectively.

(*i*) *Nitrogen donor bridged complexes*

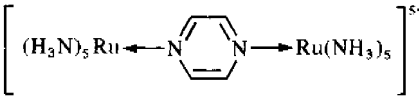
(a) Amines

Refluxing $RuCl_3$ for two hours in ethanol followed by treatment with NH_3 at 90°C for two to three hours yields a black product $[(NH_3)_4Ru(NH_2)_2Ru(NH_3)_4]Cl_4 \cdot 4H_2O$ (**52**).[482] The single crystal X-ray structure of (**52**) confirms the presence of two bridging NH_2 ligands with Ru—$N(NH_2)$ = 2.011, 2.029 Å, Ru—$N(NH_3)$ = 2.130–2.146 Å.[482]



(b) Heterocycles and nitriles

Several reviews on binuclear pentaammine ruthenium complexes have been published.[483–488] Since the initial report by Creutz and Taube in 1969 on the synthesis of the mixed valence dimer $[Ru(NH_3)_5]_2pz^{5+}$ (**53**),[489] a wide range of binuclear ruthenium ammine complexes have been prepared and characterized. The basis for this work was to study the extent of metal–metal interaction across the bridging ligand, and in particular to assess the charge distribution in the mixed valence complexes $[Ru(NH_3)_5]_2L^{5+}$. These complexes can be described as either (a) charge localized systems with no interaction between Ru^{II}/Ru^{III} centres (Class I), (b) having only partial metal–metal coupling (Class II) or (c) fully delocalized with $Ru^{II\frac{1}{2}}/Ru^{III\frac{1}{2}}$ centres (Class III).[175,490] Hush theory predicts[175,176] that a moderately coupled Class II mixed valence system will show an intervalence charge transfer band for the light-induced transition (equation 55). The analysis of intervalence bands, particularly their solvent dependence, has been the subject of much discussion.[484,491] More recently, the vibronic coupling model[492–494] has been applied to the analysis of intervalence charge transfer bands and good agreement has been observed for localized systems while discrepancies have occurred for supposed delocalized ones.[495] A full discussion of the theoretical basis for these models is outside the scope of this review, and is summarized in Creutz's review.[484] The measurement of comproportionation constant K_c for equation (56) has also been used to assess the stabilization due to delocalization of $[Ru(NH_3)_5]_2L^{5+}$ relative to $[Ru(NH_3)_5]_2L^{4+}$ and $[Ru(NH_3)_5]_2L^{6+}$.[491] The properties of intervalence charge transfer bands and evaluation of K_c have been commonly used parameters for the assignment of Class II or Class III behaviour to these types of mixed valence complexes.



(53)

$$[Ru^{II}, Ru^{III}]^{5+} \xrightarrow{h\nu} [Ru^{III}, Ru^{II}]^{5+} \quad (55)$$

$$[2,2]^{4+} + [3,3]^{6+} \overset{K_c}{\rightleftharpoons} 2[2,3]^{5+} \quad (56)$$

Reaction of $[Ru(NH_3)_5OH_2]^{2+}$ (generally prepared by treatment of $[RuCl(NH_3)_5]^{2+}$ with $Ag(O_2CCF_3)$ at 80°C, removal of precipitated AgCl, acidification with $NaHCO_3$ in aqueous solution to pH 2–3 and reduction by zinc amalgam) with half an equivalent of L yields the binuclear complex $[Ru(NH_3)_5]_2L^{4+}$ (L = for example, pyrazine,[195,197] pyrimidine,[496] 4,4′-bipyridine,[195,209,497] 1,2-bis(4-pyridyl)ethylene,[195] 1,1′-bis(4-pyridyl)methane,[209] 1,1′-bis(4-pyridyl)amine,[209] 1,2-bis(4-pyridyl)-acetylene,[209] 3,3′-dimethyl-4,4′-bipyridine,[209] dicyanobenzenes,[496] dicyanonaphthalenes,[496] cyanogen[498]). Dithionite has been used as a counterion for the isolation of the complexes in the solid state.[499] The [2,2] species $[Ru(NH_3)_5]L^{4+}$ can be oxidized to the $[2,3]^{5+}$ and $[3,3]^{6+}$ ions electrochemically or chemically.[209,500] Thus, the Creutz–Taube complex $[Ru(NH_3)_5]_2pz^{5+}$ may be prepared by oxidation of the $[2,2]^{4+}$ ion with Ag^+, while further oxidation with Ce^{4+} yields the $[3,3]^{6+}$ ion (equation 57).[197]

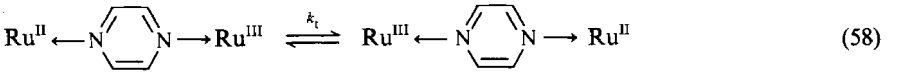
$$\underset{[2,2]^{4+}}{[Ru(NH_3)_5]_2pz^{4+}} \xrightarrow{Ag^+} \underset{[2,3]^{5+}}{[Ru(NH_3)_5]_2pz^{5+}} \xrightarrow{Ce^{4+}} \underset{[3,3]^{6+}}{[Ru(NH_3)_5]_2pz^{6+}} \quad (57)$$

$$\lambda = 547\,nm\ (Ru^{II} \rightarrow L) \qquad \lambda = 565\,nm\ (Ru^{II} \rightarrow L) \qquad no\ Ru^{II} \rightarrow L$$

$$no\ IVCT \qquad \lambda = 1562\,nm\ (IVCT) \qquad no\ IVCT$$

The single crystal X-ray structure of $[Ru(NH_3)_5]_2pz^{5+}$ (**53**) has been reported;[501,502a] this shows Ru—N(pz) = 2.002 Å, Ru—N(NH_3 *trans* to pz) = 2.135 Å, Ru—N(NH_3 *cis* to pz) = 2.110 Å.[502a] A full crystallographic study of the series $[(H_3N)_5Ru(pz)Ru(NH_3)_5]^{n+}$ (n = 4,5,6) has been published.[502b] The $[2,3]^{5+}$ complex shows an intervalence charge transfer band in the near IR at 1562 nm ($\varepsilon = 5 \times 10^3\,M^{-1}\,cm^{-1}$),[503] in addition to a $Ru^{II} \rightarrow$ ligand charge transfer band at 565 nm ($\varepsilon = 2.1 \times 10^4\,M^{-1}\,cm^{-1}$)[197,489] while the $[2,2]^{4+}$ complex shows an analogous charge transfer band at 547 nm ($\varepsilon = 3 \times 10^4\,M^{-1}\,cm^{-1}$).[489] Neither the $[2,2]^{4+}$ nor $[3,3]^{6+}$ ions show an intervalence charge transfer band at 1562 nm; the $[3,3]^{6+}$ ion shows no absorbance at 565 nm.[197] Although the observation[197,489] of an intervalence band for the mixed valent species $[Ru(NH_3)_5]_2pz^{5+}$ was consistent with Hush theory,[176] the solvent dependence of the absorption suggested that a more delocalized formalism for the complex should be invoked.[486] In addition, the comproportionation constant K_c of 4×10^6 indicated a relative stabilization of the $[2,3]^{5+}$ ion.[197] The question of whether the Creutz–Taube ion should be regarded as a Class II or Class III system is still the topic of much debate.

Highly contradictory reports on the degree of delocalization in the complex have been published, with many techniques being used in an attempt to distinguish between the two possible classifications. Conflicting IR,[197,486,489,502,504–506] photoelectron spectroscopy,[505,507–511] ^{99}Ru Mössbauer,[502,512] resonance Raman,[502,513] ^{1}H NMR,[506,514] powder ESR (8–50 K),[506] single crystal ESR,[502a,515,516] magnetic susceptibility,[506] electrochemical[197,486] and kinetic[486] studies have been published. The contradictory results obtained for the $[2,3]^{5+}$ complex may be partially reconciled however by regarding the rate of intramolecular electron transfer k_t in (**53**) as being rapid (equation 58). In principle, experiments with a faster resolution time than k_t could detect Class II behaviour, while techniques with a slower resolution time would suggest Class III characteristics for (**53**). A value for k_t of $10^{13}\,s^{-1} > k_t > 10^{11}\,s^{-1}$ has been proposed,[484,486] suggesting a substantial degree of delocalization in the molecule. The Creutz–Taube complex appears to be at the frontier of Class II/Class III behaviour, and as such, a description of delocalization within the molecule in terms of k_t would seem most appropriate.[484]



(58)

The complex $[Ru(NH_3)_5]_2$4,4-bipy^{4+} (4,4′-bipy = 4,4′-bipyridine) shows one, two electron oxidation,[517] the $[3,3]^{6+}$ ion being formed on addition of Br_2 or Cl_2 (Scheme 19).[497] $[Ru(NH_3)_5]_2$ 4,4-bipy^{5+} can not be prepared directly from the $[2,2]^{4+}$ ion, but is generated by addition of Ru^{II} to the $[3,3]^{6+}$ ion.[497,500] The mixed valence $[2,3]^{5+}$ ion shows an intervalence charge transfer band at 1030 nm ($\varepsilon = 880\,M^{-1}\,cm^{-1}$),[500] and has a comproportionation constant $K_c = 20$ near to a statistical value,[209,497] suggesting no special stability for this mixed valence complex. Solvent dependence of the intervalence charge transfer absorption agrees well with the Hush model,[518,519] and the rate of intramolecular electron transfer for $[Ru(NH_3)_5]_2$4,4-bipy^{5+} has been estimated as $k_t < 10^8\,s^{-1}$ [484] indicating weakly coupled Class II behaviour.

$$[(H_3N)_5Ru(OH_2)]^{2+} \xrightarrow{4,4'\text{-bipy}} [Ru(NH_3)_5]_2\text{4,4′-bipy}^{4+} \xrightarrow{Br_2 \text{ or } Cl_2} [Ru(NH_3)_5]_2\text{4,4′-bipy}^{6+} \xrightarrow{[Ru(NH_3)_5OH_2]^{2+}} [Ru(NH_3)_5]_2\text{4,4′-bipy}^{5+}$$

Scheme 19

A good example of a Class III binuclear complex is the cyanogen adduct $[Ru(NH_3)_5]_2NCCN^{5+}$; K_c is estimated as $> 10^{13}$ [498] with an intervalence charge transfer band at 1429 nm ($\varepsilon = 4.1 \times 10^2\,M^{-1}\,cm^{-1}$).[503] The IR spectrum of the $[2,3]^{5+}$ ion shows $\nu_{C\equiv N}$ at 2210 cm^{-1}, intermediate between the values of 1960 cm^{-1} and 2330 cm^{-1} for the $[2,2]^{4+}$ and $[3,3]^{6+}$ species respectively. Thus for $[Ru(NH_3)_5]_2NCCN^{5+}$, the rate of electron transfer k_t between metal centres has been estimated as $k_t > 10^{13}\,s^{-1}$.[484,486,498] A theoretical molecular orbital analysis of the mixed valence complexes $[Ru(NH_3)_5]_2L^{5+}$ has proposed[520] that for L = pz, the electron is in an orbital coupled over both metal centres. For L = non-conjugated dinitrile or 4,4′-bipyridine, non-equivalent metal centres were suggested, while for L = cyanogen, a highly coupled, symmetric ground state was found.[520]

Table 6 lists data for binuclear mixed valence pentaammine ruthenium complexes.

The bridging of dinitrile ligands in binuclear pentaammine ruthenium complexes can be accompanied by deprotonation of the nitrile. Thus, on oxidation of $[Ru(NH_3)_5]_2L^{4+}$ (L = malononitrile, *tert*-butylmalononitrile) to the mixed valence $[2,3]^{5+}$ species, deprotonation of the bridging ligand occurs to yield $[Ru(NH_3)_5]_2(L^-)^{4+}$ (equation 59).[362,428,526,527] The enormous enhancement of pK_a for the nitrile ligands on binding to Ru^{III} can be illustrated in the $[Ru^{II}—L—Ru^{III}]^{5+}$ and $[Ru^{III}—L—Ru^{III}]^{6+}$ complexes where $pK_a = -0.7$ and -4.8 for L = malonitrile, $pK_a = 1.6$, -3.0 for L = *tert*-butylmalononitrile respectively.[362] Similar pK_a enhancement has been observed for mononuclear systems.[362]

$$[(H_3N)_5Ru^{II}(L)Ru^{II}(NH_3)_5]^{4+} \longrightarrow [(H_3N)_5Ru^{II}(L^-)Ru^{III}(NH_3)_5]^{4+} \quad (59)$$
$$[2,L,2]^{4+} \qquad\qquad [2,L^-,3]^{4+}$$

$[Ru(NH_3)_4]_2$bipym^{4+} (bipym = 2,2′-bipyrimidine) has been prepared by treatment of $[Ru(NH_3)_5OH_2]^{3+}$ with bipym in the presence of zinc amalgam.[262] The complex shows two oxidations at +0.830 V and +1.02 V *vs.* NHE, the second oxidation leading to cleavage of the bimetallic unit. Photolysis of the $[Ru(NH_3)_4]_2$bipym^{4+} causes only slight decomposition of the complex.[262]

Table 6 Comproportionation Constants (K_c) and Intervalence Charge Transfer (IVCT) Bands for Mixed Valence Binuclear Complexes $[Ru(NH_3)_5]_2L^{5+}$ [484]

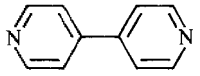
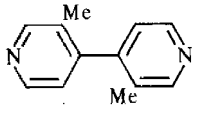
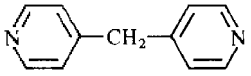
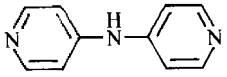
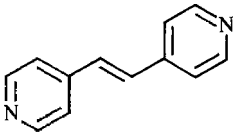
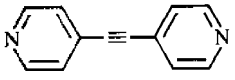
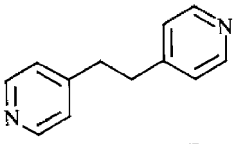
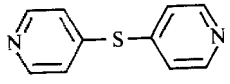
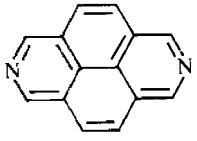
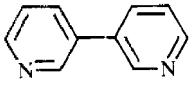
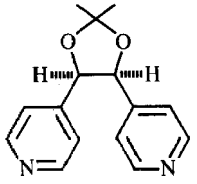
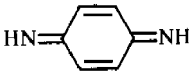
L	K_c	*IVCT* (nm)	$\varepsilon(M^{-1}cm^{-1})$	*Ref.*
	4×10^6	1562	5×10^3	197, 498, 503, 521
	4×10^7	1661	$> 2 \times 10^3$	495, 521
	3×10^2	1399	41	496, 503
	20	1030	880	209, 486, 495, 497, 500
	9.8	890	165	209, 486, 495
	6.7	810	30	209, 486, 495
	26	920	1010	209, 495, 519
	14	960	760	209, 486, 495
	14	920	640	209, 495
		—	< 10	522
		855	70	486, 495, 522
		1090	450	486
		830	60	523
		950	6	486, 524
	10^{10}	1710	900	525

Table 6 (*Continued*)

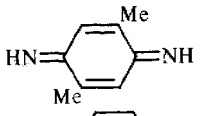
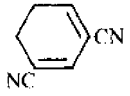
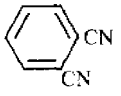
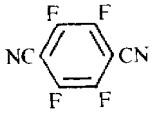
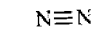
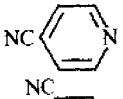
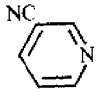
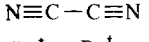
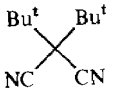
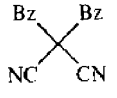
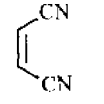
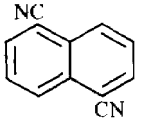
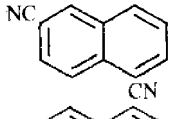
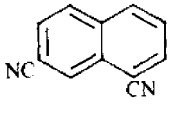
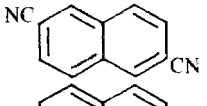
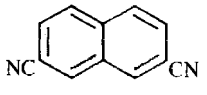
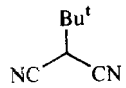
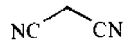
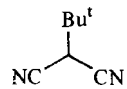
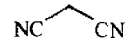
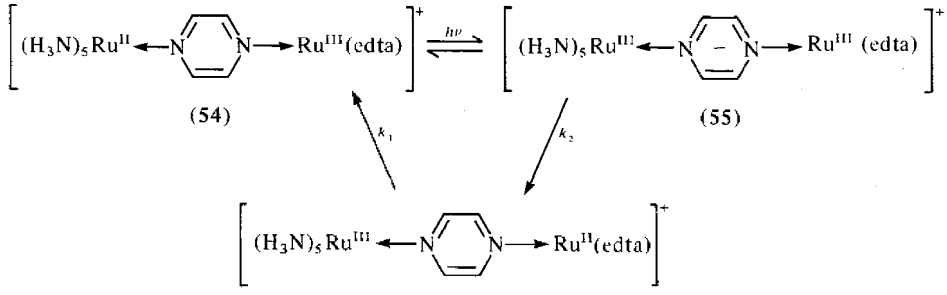
L	K_c	*IVCT* (nm)	ε($M^{-1}cm^{-1}$)	*Ref.*
	10^{10}	1770	800	525
	23	862	507	496, 503
	11	752	8	503
	33	1055	98	496, 503
		1000	600	495
	10^8	1020	1.4×10^3	315, 484, 503
	4.5×10^4	935	1100	503
	6.4×10^3	847	23	503
	$> 10^{13}$	1429	4.1×10^2	495, 498, 503
		925	180	526
	10	990	1.6×10^2	362
		975	150	527
	7	781	135	496, 503
	8.5	—	—	503
	10	769	20	503
	10	769	140	503
	9	—	—	503
1,3-Dicyanoadamantane	10	752	12	503
μ-Pseudo-*p*,*p*′-dicyanoparacyclophane	4	800	10	503

Table 6 (*Continued*)

L	K_c	*IVCT*(nm)	$\varepsilon(M^{-1}cm^{-1})$	*Ref.*
		784[a]	2.8×10^{4}[a]	362
		694[a]	1.7×10^{4}[a]	362
Tricyanomethanide		562[a]	4.5×10^{3}[a]	362
Dicyanamide		400[a]	2×10^{3}[a]	362
	$> 10^{10}$[b]	1170[b]	1.6×10^{4}[b]	362, 428, 526, 527
	$> 10^{11}$[b]	1280[b]	$> 10^{4}$[b]	362, 527
Tricyanomethanide	2.3×10^{3}[b]	1550[b]	6.2×10^{3}[b]	362
Dicyanamide	2×10^{2}[b]	1100[b]	2.8×10^{3}[b]	362, 428

[a] For $[(H_3N)_5Ru^{III}(L^-)Ru^{III}(NH_3)_5]^{5+}$. [b] For $[(H_3N)_5Ru^{II}(L^-)Ru^{III}(NH_3)_5]^{4+}$.

Reaction of *trans*-$[RuCl(NH_3)_4SO_2]Cl$ with $NaHCO_3$, pz and then H_2O_2 yields the binuclear complex $[(SO_4)(H_3N)_4Ru^{III}pzRu^{III}(NH_3)_4SO_4]^{2+}$ which can be converted to $[Hpz(H_3N)_4Ru^{II}pzRu^{II}(NH_3)_4pzH]^{6+}$ by treatment with zinc amalgam, pyrazine and acid.[242] This latter species is a useful intermediate in the synthesis of tri- and tetra-nuclear complexes. A range of complexes of type *trans*-$[L'(NH_3)_4Ru(imid)Ru(NH_3)_4L]^{n+}$ ($L' = SO_2$, SO_4^{2-}, H_2O; imid = imidazole derivatives; $L = SO_4^{2-}$, NH_3) have been synthesized by reaction of $[Ru(SO_3)(NH_3)_4OH_2]$ and the corresponding mononuclear fragment.[247,528a] These complexes have been studied electrochemically and intervalence charge transfer bands observed for mixed valence species.[247,528a] Irradiation of the $[RuCl(NH_3)_5]^{2+}/[Ru(CN)_6]^{4-}$ ion pair leads to the formation of $[(H_3N)_5Ru^{III}NCRu^{II}(CN)_5]^-$.[55] The binuclear species $[(H_3N)_5Ru(pz)Ru(CN)_5]^{-/0}$ have been prepared and their electronic properties compared with related symmetric and asymmetric complexes.[528b] Reaction of $[Ru(NH_3)_5pz]^{2+}$ with $[Ru^{III}(Hedta)OH_2]$ produces a trapped valence complex $[(H_3N)_5Ru^{II}pzRu^{III}(edta)]^+$ (**54**). Photolysis of (**54**) leads to an activated $[Ru^{III}—pz^{\cdot-}—Ru^{III}]$ dimer (**55**) which decays back to (**54**).[529]

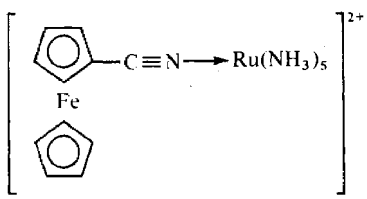


$k_1 = 0.8 \times 10^{10}\,s^{-1}$ $k_2 > 10^{11}\,s^{-1}$

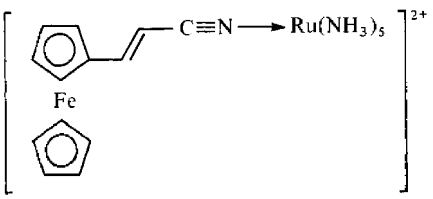
Binuclear complexes $[(H_3N)_5Ru(L)RuX(bipy)_2]^{3+}$ ($X = Cl^-$, L = pz, 4,4′-bipy, 1,2-bis(4-pyridyl)ethylene, 1,2-bis(4-pyridyl)ethane; $X = NO_2^-$, L = pz) have been synthesized by reaction of $[Ru(NH_3)_5OH_2]^{2+}$ with $[RuX(L)(bipy)_2]^+$.[530] The [2,3]$^{4+}$ and [3,3]$^{5+}$ complexes have been generated, and the intervalence charge transfer bands for the mixed valence species analysed.[531–533] For $X = Cl^-$, L = pz, 4,4′-bipy, 1,2-bis(4-pyridyl)ethylene, absorptions were observed at 960 nm ($\varepsilon = 530$), 695 nm ($\varepsilon > 300$) and 680 nm ($\varepsilon > 300\,M^{-1}cm^{-1}$) respectively.[530] No such band was observed for the 1,2-bis(4-pyridyl)ethane analogue.[530] The metal–metal coupling in $[(H_3N)_5Ru^{II}pzRu^{III}Cl(bipy)_2]^{4+}$ has been estimated to be three times lower than for the Creutz–Taube ion.[531,532] The preparation of $[(H_3N)_5RupzRu(NCCH_3)(bipy)_2]^{5+}$ has been reported.[530]

The interactions of the $[Ru(NH_3)_5]^{2+}$ moiety and its derivatives with other metal centres in ligand-bridged heterobimetallic complexes of the type $[(NH_3)_5Ru—L—M]$ have been investigated. Systems that have been studied include M = Cr^{III}, L = 4-amidopyridine;[534,535] M = Ni^{II}, L = pz;[536] M = Cu^{II}, L = pz;[536–538] M = Cu^{I}, L = 4-vinyl pyridine;[539,540a] M = Co^{III},[540b] L = 3-O_2Cpy,[541] 4-O_2Cpy,[541] 3-O_2CCH_2py,[541] 4-O_2CCH_2py,[541] 4-NCpy,[542] pz,[542] 4,4′-bipy,[522,542] 3,3′-bipy,[523] 1,1′-bis(4-pyridyl)methane,[523] 1,2-bis(4-pyridyl)ethane,[522] 1,2-bis(4-pyridyl)ethylene,[522] 1,1′-bis(4-pyridyl)-methanol,[523] 3,3′-dimethyl-4,4′-bipyridine,[522] bis-(4-pyridyl)sulfide,[522] 1,4-dicyanobicyclo[2.2.2]octane;[543] M = Rh^{III}, L = 4-NCpy,[542,544] pz,[542] 4,4′-bipy;[542] M = Fe^{II}, L = pz,[545] Cp derivatives.[546,547] Ni^{II}, Cu^{II} and Zn^{II} bind to $[Ru(NH_3)_5pz]^{2+}$ (equation 60) with association quotients K = 17, 32 and 3.1 M^{-1} respectively.[536] Photolysis of the Ru^{II}—pz—Cu^{II} complex leads to bleaching of the charge transfer band with the formation of a Ru^{III}—pz—Cu^{I} dimer.[537] Binding of Cu^{I} to $[RuL(NH_3)_5]^{3+}$ (L = 4-vinyl pyridine) *via* the alkene (K_{equil} = 8.4 × 10^3) has been reported, with subsequent electron transfer from Cu^{I} to Ru^{III} at a rate constant k = 9.7 $M^{-1}s^{-1}$.[539] The complex $[(NC)_5Fe^{II}pz-Ru^{II}(NH_3)_5]^{1-}$, prepared by reaction of $[Ru(NH_3)_5pz]^{2+}$ with $[Fe(CN)_5OH_2]^{3-}$, shows two, one electron oxidations at +0.45 V and +0.72 V *vs.* NHE for oxidation of Ru^{II} and Fe^{II} respectively.[545] The neutral species has been formulated as a trapped valence Class II system, with an intervalence charge transfer band at 1330 nm.[545] The first order specific rate constants for electron transfer from Ru^{II} to Co^{III} in $[(H_3N)_5Co^{III}L\ Ru^{II}(NH_3)_4OH_2]^{n+}$ (L = substituted pyridines, 4,4′-bipyridyl derivatives) are in the range $k = 1 \times 10^{-4}$ to $44 \times 10^{-3}\ s^{-1}$.[522,548] More recently, a range of Co–Ru dimers with polypeptide bridges have been prepared, and electron transfer reactions within the binuclear system investigated.[549–551] Ferrocene–ruthenium heterobinuclear complexes (**56**) and (**57**) have been synthesized and compared with polynuclear ferrocene derivatives.[546,547] The Fe^{II}, Ru^{II} dimers show one electron oxidations at +0.44 V and +0.85 V for (**56**) and +0.44 V and +0.66 V *vs.* SCE for (**57**) with intervalence charge transfer bands in the near IR being observed for the Fe^{II}, Ru^{III} species.[546]

$$[(H_3N)_5Ru\ pz]^{2+} + M^{II} \rightleftharpoons [(H_3N)_5Ru \leftarrow N \bigcirc N \rightarrow M^{II}]^{4+} \qquad (60)$$



(56)



(57)

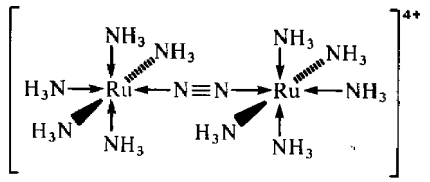
(c) Dinitrogen

$[(Ru(NH_3)_5)_2N_2]^{4+}$ can be synthesized by treatment of $[Ru(NH_3)_5OH_2]^{2+}$ with N_2,[313,338] by reaction of $[Ru(NH_3)_5OH_2]^{2+}$ with $[Ru(NH_3)_5N_2]^{2+}$,[324,338] by reduction of reaction solutions of N_2O and $[RuCl(NH_3)_5]^{2+}$ with zinc amalgam,[316] by reaction of $[Ru(NO)(NH_3)_5]^{3+}$ with $[Ru(NH_3)_6]^{3+}$ under basic conditions,[321] or by decomposition of $[Ru(N_3)(NH_3)_5]^{2+}$ under acidic conditions.[317] The formation of the dimer from the reaction of N_2 with $[Ru(NH_3)_5OH_2]^{2+}$ (equation 61) follows first order kinetics in $[N_2]$, with second order kinetics overall[553] with k_1 = 7.3 × $10^{-2}\ M^{-1}s^{-1}$, K_{equil} = 3.3 × 10^4, $\Delta H^\circ = -42.3\ kJ\ mol^{-1}$, $\Delta S^\circ = -54\ J\ K^{-1}\ mol^{-1}$.[324,325] For the reaction of $[Ru(NH_3)_5OH_2]^{2+}$ with $[Ru(NH_3)_5N_2]^{2+}$ (equation 62), K_{equil} = 7.3 × 10^3, $\Delta H^\circ = -46.9\ kJ\ mol^{-1}$, $\Delta S^\circ = -84\ J\ K^{-1}\ mol^{-1}$.[324] $[(Ru(NH_3)_5)_2N_2]^{4+}$ shows no strong IR band for the stretching vibration $\nu_{N\equiv N}$ suggesting a linear symmetric structure for the dimer.[338] The Raman spectrum of $[(Ru(NH_3)_5)_2N_2]^{4+}$ shows $\nu_{N\equiv N}$ at 2100 cm^{-1}, and $\nu_{^{15}N\equiv{}^{15}N}$ at 2030 cm^{-1}.[312,554] A linear structure with an eclipsed conformation is confirmed[555] by the single crystal X-ray structure of (**58**) with Ru—$N(N_2)$ = 1.928 Å, Ru· · · ·Ru = 4.979 Å, <Ru—N—N = 178.3°, N—N = 1.124 Å (N—N = 1.0976 for free N_2), consistent with back-donation of electron density from Ru^{II} to N_2.[328] A molecular orbital description for (**58**) has been discussed.[315] (**58**) shows a metal ligand charge transfer band at 263 nm (ε = 4.8 × $10^4\ M^{-1}\ cm^{-1}$).[315,555a] Replacement of NH_3 by H_2O in the dimer decreases ΔH of binding of N_2 by 25.1 $kJ\ mol^{-1}$.[556] The ^{15}N NMR of (**58**) has been reported recently.[555b]

$$2[Ru(NH_3)_5(OH_2)]^{2+} + N_2 \longrightarrow [Ru(NH_3)_5]_2N_2^{4+} \qquad (61)$$

$$[Ru(NH_3)_5(OH_2)]^{2+} + [Ru(NH_3)_5N_2]^{2+} \longrightarrow [Ru(NH_3)_5]_2N_2^{4+} \qquad (62)$$

(**58**)



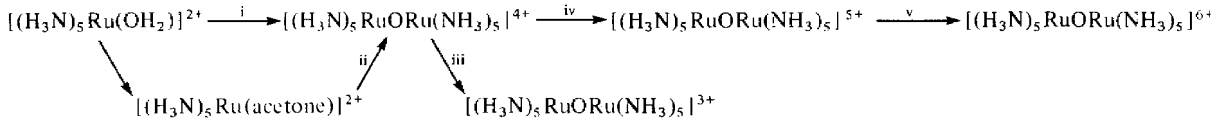
(58)

$[(Ru(NH_3)_5)_2N_2]^{4+}$ shows two, one electron oxidations at +0.73 V and +1.2 V *vs.* SCE.[315,334] The mixed valence $[2,3]^{5+}$ ion can be generated by oxidation of the $[2,2]^{4+}$ complex with Br_2 or Ce^{4+},[315,557] and shows an intervalence charge transfer band at 1020 nm, and a comproportionation constant $K_c = 10^8$ (see Table 6) indicating Class III delocalized behaviour.[315,484] $[(Ru(NH_3)_5)_2N_2]^{5+}$ decomposes (rate constant $k = 0.1\,s^{-1}$) to $[Ru(NH_3)_5N_2]^{2+}$ and $[RuX(NH_3)_5]^{n+}$ ($X = SO_4^{2-}$, $n = 1$; $X = HSO_4^-$, $n = 2$) in SO_4^{2-} electrolyte.[557] For the $[2,3]^{5+}$ complex, the specific rate of aquation $k = 2.4 \times 10^{-2}\,s^{-1}$.[315] Oxidation of $[(Ru(NH_3)_5)_2N_2]^{5+}$ at +1.2 V yields $[(Ru(NH_3)_5)_2N_2]^{6+}$, the specific rate of aquation of which has been estimated as greater than $10^3\,s^{-1}$.[315] This contrasts with the stability of $[(Os(NH_3)_5)_2N_2]^{5+}$ which is indefinitely stable in H_2O.[315]

The preparation of $[(RuX(NO)(NH_3)_4)_2N_2]^{4+}$ ($X = Cl^-$, Br^-) has been reported.[558] Reaction of *cis*-$[Ru(NH_3)_4(OH_2)_2]^{2+}$ with $[Os(NH_3)_5N_2]^{2+}$ yields $[(H_2O)(H_3N)_4Ru^{II}N_2Os^{II}(NH_3)_5]^{4+}$ *via* second order kinetics.[559] The heteronuclear dimer can be oxidized at +0.1 V *vs.* SSCE in H_2SO_4/K_2SO_4 at pH 3.3 to give the mixed valence Ru^{III}—Os^{II} product which shows an intervalence charge band at 755 nm.[559] There has been a report of an N_2O dimer $[(Ru(NH_3)_5)_2N_2O]^{4+}$.[560]

(*ii*) *Oxygen donor bridged complexes*

Oxidation of $[Ru(NH_3)_5acetone]^{2+}$ with O_2 or oxidation of $[Ru(NH_3)_5OH_2]^{2+}$ with $LiClO_4$ in acetone yields the Ru^{III}—Ru^{III} dimer $[Ru(NH_3)_5]_2O^{4+}$ (Scheme 20).[561] The complex shows oxidations at +0.32 V and +1.67 V and a reduction at −1.98 V *vs.* SSCE.[561] The mixed-valence Ru^{IV}—Ru^{III} complex can be generated by oxidation with Br_2. A molecular orbital description of the Ru—O—Ru moiety has been given. Electronic, vibrational, redox, photoelectron and magnetic data for these complexes have been described, with the 5+ ion being assigned as a delocalized system.[561] The complexes $[(Ru(NH_3)_4)_2L]^{2+/3+/4+}$ and $[(H_3N)_4RuLRu(bipy)_2]^{3+/4+}$ (L = pyrazine-2,5-dicarboxylate) have been synthesized, and their spectroscopic features discussed.[562] The formation of a linear CO_2 bridge in $[(Ru(NH_3)_5)_2CO_2]^{4+}$, prepared by reaction of $[Ru(NH_3)_5N_2]^{2+}$ with CO_2 at high pressure or by treatment of $[Ru(NH_3)_5(OH_2)]^{2+}$ with N_2O/Zn amalgam and CO_2, has been proposed.[187b]



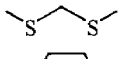
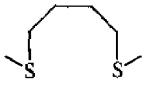
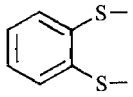
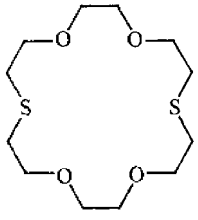
i, acetone, $LiClO_4$; ii, O_2; iii, −1.98 V; iv, +0.32 V; v, +1.67 V *vs.* SSCE[561]

Scheme 20

(*iii*) *Sulfur donor bridged complexes*

This area has been reviewed.[484,563] Reaction of $[RuL(NH_3)_5]^{2+}$ with $[Ru(NH_3)_5OH_2]^{2+}$ yields the dimeric complexes $[(Ru(NH_3)_5)_2L]^{4+}$ (L = thioether).[429,434] Table 7 summarizes intervalence charge transfer and K_c data for the complexes $[(Ru(NH_3)_5)_2L]^{5+}$. Treatment of $[Ru(NH_3)_5OH_2]^{2+}$ with C_2H_4S and COS, with H_2S followed by oxidation, or reduction of $[Ru(NH_3)_5SO_2]^{2+}$ with zinc amalgam gives $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$ (**59**), which reacts with HSO_3^- and CN^- to produce $[Ru(SSO_3)(NH_3)_5]^+$ and $[Ru(SCN)(NH_3)_5]^+$ respectively with the latter species isomerizing to $[Ru(NCS)(NH_3)_5]^{2+}$.[356] The single crystal X-ray structure of (**59**) shows Ru—S = 2.191, 2.195 Å.[565] The bridging unit has been proposed to have predominantly a Ru^{III}—S⋯S—Ru^{II} formulation,[565] although resonance Raman studies have preferred a Ru^{III}—S—S—Ru^{III} configuration.[566] Reaction

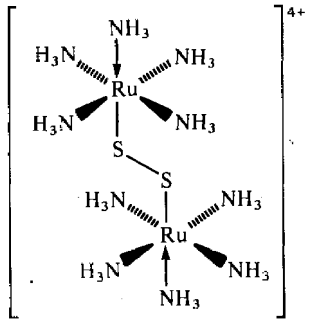
Table 7 Comproportionation Constants (K_c) and Intervalence Charge Transfer (IVCT) Bands for Mixed Valence Complexes $[Ru(NH_3)_5]_2L^{5+}$

L	K_c	*IVCT* (nm)	ε ($M^{-1}cm^{-1}$)	*Ref.*
	125	928	45	484, 563
	⩽10	840	21	484, 563
	<10	775	5	429
	⩽10	615	0.75	484, 563
	30	964	22	484, 563
	48	1132	35	484, 563
	890	1220	86	484, 563
	185	1000	64	484, 563
	100	996	55	484, 563
	40	972	6	434, 495
	<10	1180	75	434, 495
	⩽10	910	43	429, 564
	4	808	9	564
	4	690	2.3	564
	⩽10	860	3	484, 563

of *trans*-$[Ru(SO_4)(NH_3)_4isn]^+$ with zinc amalgam and L yields $[(Ru(NH_3)_4isn)_2L]^{4+}$ (L = $MeS(CH_2)_3SMe$, 2,6-dithiaspiro[3.3]heptane).[429]

(*iv*) *Halide-bridged complexes*

Blue chloro–ammine complexes can be prepared by treating $[Ru(NH_3)_6]Cl_2$ with HCl at 0 °C.[442,448] Oxidation of the blue Ru^{II}—Ru^{III} dimer $[Ru_2Cl_3(NH_3)_6]^{2+}$ with Ce^{IV} yields the corresponding yellow Ru^{III}–Ru^{III} complex.[448] The exact nature of these species is unknown, although a trichloro-



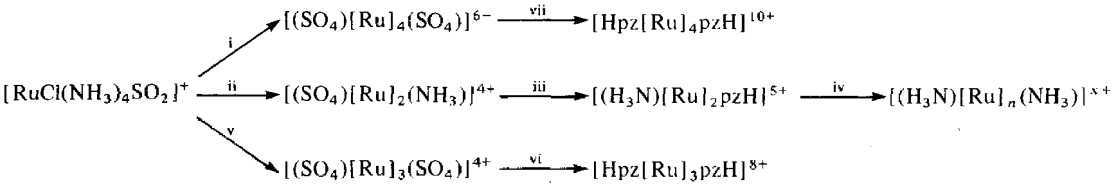
(59)

bridged structure has been proposed on the basis of one ν_{Ru-Cl} stretching vibration being observed in the IR at 270 cm^{-1}.[448]

45.4.1.4 Tri- and poly-nuclear complexes

(*i*) *Nitrogen donor bridged complexes*

A series of tri-, tetra-, penta- and hexa-nuclear pyrazine-bridged complexes have been prepared by Taube and co-workers (Scheme 21).[242,486] The mixed valence complexes show intervalence charge transfer absorptions in the near IR. The metal → ligand charge transfer band moves to lower energy as the chain length increases. On oxidation, this absorption decreases in intensity and moves to higher energy until, in the fully oxidized complexes, the band disappears.[242] The extent of end to end interactions in the mixed valence complexes has been discussed.[242,486,547]



i, $NaHCO_3$, $[Hpz[Ru]_2pzH]^{5+}$, H_2O; ii, $NaHCO_3$, $[Ru(NH_3)_5pzH]^{3+}$, HBF_4, H_2O; iii, Zn/Hg, pz; iv, $[RuCl(NH_3)_5]^{2+}$, Zn/Hg; v, $NaHCO_3$, $[Ru(NH_3)_4(pzH)_2]^{4+}$; vi, Zn/Hg, pz, H^+; vii, Zn/Hg, pz.

Scheme 21[242]

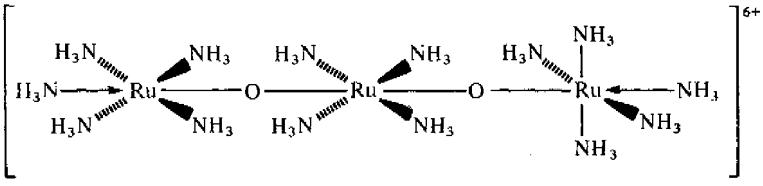
Reaction of $[Ru(L)_2(bipy)_2]^{2+}$ with $[Ru(NH_3)_5OH_2]^{2+}$ in the dark in acetone yields the [2,2,2]$^{6+}$ trimer $[(H_3N)_5Ru^{II}LRu^{II}(bipy)_2LRu^{II}(NH_3)_5]^{6+}$ (L = pz, 4,4′-bipy, 1,2-bis(4-pyridyl)ethylene, 1,2-bis(4-pyridyl)ethane);[567] oxidation with Br_2 to give the [2,2,3]$^{7+}$ and [3,2,3]$^{8+}$ systems was achieved. The sites of oxidation appear to be localized, with no long range interaction between remote pentaammine moieties.[567]

The tetranuclear complex $[(Ru(NH_3)_5)_4TCNE]^{8+}$ shows four, one electron oxidations and a one electron reduction.[527] The 10+ is more stable than the 9+ and 11+ species, with a strong coupling between metal centres being proposed.[527] A heteronuclear ferrocene–ruthenium complex $[(Ru(NH_3)_5)_2Fc(CN)_2]^{4+}$ ($Fc(CN)_2$ = 1,1′-dicyanoferrocene) has been prepared. No evidence was observed for an end to end interaction in the corresponding 5+ ion.[547]

(*ii*) *Oxygen donor bridged complexes*

Reaction of $RuCl_3$ in ethanol with ascorbic acid at 85°C for 3 h, reduction of volume and treatment with NH_3 for 1 h at 90°C in the air yields a brown [3,4,3]$^{6+}$ complex $[Ru_3O_2(NH_3)_{14}]^{6+}$ (**60**) commonly known as ruthenium red.[568–571] The single crystal X-ray structure of $[Ru_3O_2(NH_3)_{14}]^{6+}$ shows[572] a linear Ru—O—Ru—O—Ru backbone with Ru—O

= 1.857–1.845 Å, < RuORu = 171.5°. For the central and one end Ru atom, the Ru—N (equatorial) bonds are eclipsed, with the other end Ru—N (equatorial) bonds twisted by 31° to give a non-centrosymmetric ion. Reaction of $[Ru_3O_2(NH_3)_{14}]^{6+}$ with en yields $[Ru_3O_2(NH_3)_{10}(en)_2]^{6+}$,[568] the single crystal X-ray structure of which shows a linear backbone with the en ligands bound to the central Ru.[573] The central Ru—N bonds are eclipsed with respect to the Ru—N (equatorial) bonds of both end groups, which are themselves eclipsed relative to one another.[573] Ruthenium red is also identified as the product when $[Ru(NH_3)_5N_2]^{2+}$ is oxidized in air on Y-type zeolite.[342]



(60)

Oxidation of $[Ru_3O_2(NH_3)_{14}]^{6+}$ or $[Ru_3O_2(NH_3)_{10}(en)_2]^{6+}$ with HCl in air, or by Cl_2 water gives the $[4,3,4]^{7+}$ analogue ruthenium brown.[568] Mössbauer studies on the 6+ and 7+ ions are in agreement with linear structures for these complexes.[574] The resonance Raman spectra of ruthenium red and brown and of their en analogues have been reported.[575] Ruthenium brown is reduced by ^-OH in a second order reaction with rate constant $k = 1.9 \times 10^4\,s^{-1}\,mol^{-1}$, $\Delta H^{\neq} = 79.5\,kJ\,mol^{-1}$, reduction of the en derivative being faster.[568,576,577] The mechanism of the reaction was initially thought to proceed *via* formation of a peroxy-bridged Ru—O—O—Ru species,[578] but recent evidence suggests possible attack on coordinated NH_3 to give nitrosyl intermediates.[579]

The use of ruthenium red as a staining reagent for electron microscopy has been reviewed.[580] The complex is active for the staining of cell walls;[570,580] its possible binding modes to DNA[581] and interference with Ca^{2+} transport[582,583] have been discussed.[584]

45.4.2 Amines

45.4.2.1 Mononuclear complexes $[RuL_6]^{2+}$

Ruthenium(II) amine complexes have been reviewed.[585] The complexes $[Ru(NH_2R)_6]^{2+}$ (R = Me, Pr^n, Bu^i, Bu^n) can be prepared by treatment of $RuCl_3$ with the corresponding amine in the presence of zinc under argon (equation 63).[60,586] If the reaction is carried out under N_2, formation of $[Ru(NH_3)_5N_2]^{2+}$ is detected. The products $[Ru(NH_2R)_6]^{2+}$ are air sensitive and are readily oxidized by dioxygen to cyano complexes,[60,587] coordinated amine being more susceptible to oxidation than the free base. Reaction of $[RuX_4L_2]$ with L yields $[RuL_6]^{2+}$ (L = substituted anilines).[588] The value of $10\,Dq$ for the complexes $[RuL_6]^{2+}$ places aniline between en and H_2O in the spectrochemical series.[586]

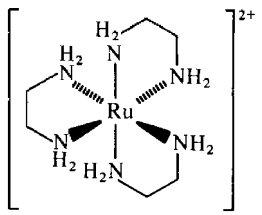
$$RuCl_3 + 6RNH_2 \xrightarrow[Ar]{Zn} [Ru(NH_2R)_6]^{2+} \qquad (63)$$

45.4.2.2 Mononuclear complexes $[RuL_3]^{2+/3+}$

Ruthenium(II): Reaction of $RuCl_3$ with en in the presence of Zn at pH 1–2 yields $[Ru(en)_3]^{2+}[ZnCl_4]^{2-}$ which can be converted to the canary yellow dichloro salt $[Ru(en)_3]Cl_2$ by treatment with lithium anthranilate (equations 64 and 65).[589–591] Reduction of (−)-$[Ru(en)_3]^{3+}$ with Zn gives (−)-$[Ru(en)_3]^{2+}$.[592] The single crystal X-ray structure of *rac*-$[Ru(en)_3]^{2+}[ZnCl_4]^{2-}$ (**61**) shows O_h geometry around the ruthenium with Ru—N = 2.132 Å (*cf.* with Ru—N = 2.11 Å for $[Ru(en)_3]^{3+}$) and average < NRuN = 81.6°.[593] The absolute configuration and axial rotational strength of $[Ru(en)_3](NO_3)_2$ have been resolved[594] and the conformational stability of $[RuL_3]^{2+}$ (L = en, 1,2-diaminopropane) probed by ^1H NMR studies.[595,596] IR,[590] electron absorption optical rotatory dispersion, circular dichroism[592] and Mössbauer[120] data for $[Ru(en)_3]^{2+}$ have been reported.

$$RuCl_3 + 3en \xrightarrow{Zn} [Ru(en)_3][ZnCl_4] \qquad (64)$$

$$[Ru(en)_3][ZnCl_4] \xrightarrow{2Li(an)} [Ru(en)_3]Cl_2 + Zn(an)_2 + 2LiCl \qquad (65)$$



(61)

Like $[Ru(NH_3)_6]^{2+}$, $[Ru(en)_3]^{2+}$ is a good outer-sphere oxidizing agent; redox reactions with Fe^{3+}, $FeOH^{2+}$,[128] O_2[153] and $[CoX(NH_3)_5]^{2+}$ (X = F^-, Cl^-, Br^-, I^-)[139] have been studied. For the reaction with $[CoF(NH_3)_5]^{2+}$, $\Delta H = 29.4\,kJ\,mol^{-1}$, $\Delta S = -120\,J\,K^{-1}\,mol^{-1}$.[139] The self-exchange between $[Ru(en)_3]^{2+/3+}$ is slower than for $[Ru(NH_3)_6]^{2+/3+}$.[128] Treatment of $[Ru(en)_3]^{2+}$ with I_2 in NaI solution gives an intense yellow colouration with an absorption band at 448 nm. The product of the reaction was initially formulated as a Ru^{VI} complex,[597] however oxidative dehydrogenation of an en ligand to a diimine species has been shown to occur.[598]

Reaction of $RuCl_3$ with *o*-phenylenediamine in the presence of Zn yields the tris(diimine) complex of *o*-benzoquinone diimine.[599]

Ruthenium(III): Oxidation of $[Ru(en)_3][ZnCl_4]$ by silver anthranilate or with $[enH_2](NO_3)_2$ gives the pale yellow complex $[Ru(en)_3]Cl_3$.[600–602] The single crystal X-ray structure of *rac*-$[Ru(en)_3]^{3+}$ shows the en rings to have *lcl* conformation with significant puckering, Ru—N = 2.11 Å.[603] The ESR spectrum of $[Ru(en)_3]^{3+}$ has been measured at 4 K diluted in single crystals of $[Rh(en)_3Cl_3]_2 \cdot NaCl \cdot 6H_2O$ and as a powder with $[Co(en)_3]Br_3 \cdot H_2O$ at K and X band respectively.[604,605] $[Ru(en)_3]I_3$ has $\mu_{eff} = 2.2$ BM consistent with low spin d^5 Ru^{III}.[600] Electronic absorption,[600,605] optical rotatory dispersion and circular dichroism data[592] for $[Ru(en)_3]^{3+}$ have been reported. The enantiomers of $[Ru(en)_3]I_3$ have been resolved by fractional precipitation with optically active $[Rh(ox)_3]$.[592]

$[Ru(en)_3]^{3+}$ undergoes outer-sphere electron transfer with Cu^{I}[606] and Ti^{III}.[607] An outer-sphere charge transfer band from anion to complex cation has been observed near 450 nm for concentrated solutions of $[Ru(en)_3]I_3$.[608] The oxidation of Np^{3+} by $[Ru(en)_3]^{3+}$ (equation 66) in trifluoromethane sulfonate has been studied; rate constant $k = 8.96\,M^{-1}\,s^{-1}$, $\Delta H^{\neq} = -52.7\,kJ\,mol^{-1}$, $\Delta S^{\neq} = -173.6\,J\,K^{-1}\,mol^{-1}$.[609] E_f for the $[Ru(en)_3]^{3+/2+}$ couple was assessed as 0.172 V *vs.* Ag/Ag^+.[128,609] Oxidation of U^{3+} in trifluoromethane sulfonate occurs with a rate constant $k = 1.62 \times 10^5\,M^{-1}\,s^{-1}$, $\Delta H^{\neq} = -1.3\,kJ\,mol^{-1}$, $\Delta S^{\neq} = -163\,J\,K^{-1}\,mol^{-1}$.[170]

$$[Ru(en)_3]^{3+} + Np^{3+} \xrightarrow{k} [Ru(en)_3]^{2+} + Np^{4+} \qquad (66)$$

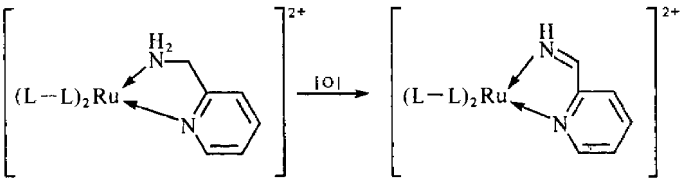
45.4.2.3 Mononuclear complexes with nitrogen donor ligands

Reaction of $[RuCl_2L_2]$ with en in refluxing aqueous ethanol yields $[RuL_2en]^{2+}$ (L = bipy,[264] phen,[610] 2-(phenylazo)pyridine[611]). The complexes $[RuL(en)_2]^{2+}$ may be prepared by reduction of $[RuCl_2(en)_2]^+$ with zinc amalgam in acetic acid followed by addition of L.[610] The electrochemistry of $[Ru(bipy)_2en]^{2+}$ has been reported.[268] The reduction of $[Ru(bipy)(tmed)_2]^{3+}$ to the Ru^{II} species has been achieved with H_2S,[203] while treatment of $[Ru(bipy)py_4]^{2+}$ with en gives $[Ru(bipy)(en)py_2]^{2+}$.[612]

Oxidation of amine complexes tends to occur at the coordinated amine to give imine and nitrile products.[587,610,613,614a] The aromatization of piperazine and piperidine (L) has been achieved by oxidation of $[Ru(NH_3)_5L]^{2+}$.[614b] Reaction of $[Ru(phen)_2en]I_2$ with Ag^+ and NaOCl gives $[Ru(phen)_2diim]^{2+}$,[610] while treatment of $[Ru(en)_3]^{2+}$ with NaOH, $AgNO_3$ and HI yields $[Ru(en)_2diim]^{2+}$ (**62**) (equation 67).[597,598,610] The four electron oxidation of $[Ru(bipy)_2L]^{2+}$ (L = en, *trans*-1,2-diaminocyclohexane) to the corresponding diimine species has been achieved chemically and electrochemically,[614a] while the two electron oxidation for L = 2-aminomethylpyridine and 1,2-diamino-2-methylpropane forms monoimine products (equations 68).[614a] The reactions are thought to proceed *via* Ru^{III} intermediates, a correlation between oxidative dehydrogenation and the $Ru^{II/III}$ couple for the complexes being noted.[610] The back-bonding from Ru^{II} to the diimine ligand has been discussed.[614a]

$$[Ru(en)_3]^{2+} \xrightarrow{[O]} \left[(en)_2Ru\right]^{2+} \qquad (67)$$

(61) (62)

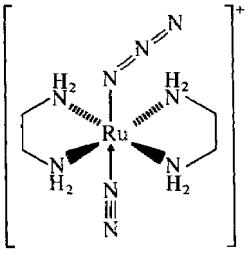


(68)

An amine ligand in $[Ru(NH_2R)_6]^{2+}$ can be replaced by an organic nitrile, *e.g.* PhCN, in the presence of Zn to give $[Ru(NH_2R)_5NCPh]^{2+}$.[60] Alternatively nitrile complexes can be prepared by oxidation of coordinated amines. Thus, oxidation of $[Ru(bipy)_2(NH_2CH_2R)_2]^{2+}$ (prepared by treatment of $RuCl_2(bipy)_2$ with RCH_2NH_2 in methanol) at 1.1 V, 0.8 V and 1.1 V *vs.* SSCE for RCH_2NH_2 = allylamine, benzylamine, *n*-butylamine respectively yields $[Ru(bipy)_2(NCR)_2]^{2+}$ *via* Ru^{III} and imine intermediates.[613] The same products may be prepared directly from the reaction of $[Ru(CO_3)(bipy)_2]$ with the corresponding nitrile.[613]

Cis-$[RuL_2(OH_2)_2]^{3+}$ reacts with NaN_3 to give *cis*-$[Ru(N_3)_2L_2]^+$ (L = en, ½trien);[317,615] *cis*-$[Ru(N_3)_2trien]^+$ can also be prepared by reaction of *cis*-$[RuCl_2trien]Cl$ with NaN_3.[394] On heating at 65°C for 25 min, *cis*-$[Ru(N_3)_2(en)_2]^+$ decomposes to *cis*-$[Ru(N_3)(N_2)(en)_2]^+$ with ν_{NN} at 2130 cm^{-1} and ν_{NNN} at 2050 cm^{-1}.[317,615,616] The trien analogue is formed on heating at 45°C for 3 h.[394]

Treatment of *cis*-$[Ru(N_3)(N_2)(en)_2]^+$ with cold HNO_2 affords a mixture of *cis*-$[Ru(N_2)_2(en)_2]^{2+}$ (ν_{NN} = 2220, 2190 cm^{-1}) and its aquation product *cis*-$[Ru(N_2)(en)_2OH_2]^{2+}$ (ν_{NN} = 2130 cm^{-1}).[317,616] These products can further aquate to $[Ru(en)_2(OH_2)_2]^{2+}$.[320] Reaction of *trans*-$[RuCl_2(en)_2]^+$ with Ag^+ followed by NaN_3 gives *trans*-$[Ru(N_3)(N_2)(en)_2]^+$ (**63**) the single crystal X-ray structure of which confirms a distorted O_h geometry around Ru^{II} with Ru—$N(N_2)$ = 1.894 Å, Ru—$N(N_3^-)$ = 2.191 Å, Ru—N(en) = 2.108–2.144 Å, < $RuNN(N_3^-)$ = 116.7°, < $RuNN(N_2)$ = 179.3°.[617]



(63)

The formation of *cis*-$[RuL_2(N_2)(OH_2)]^{2+}$ has been reported from the reaction of *cis*-$[RuL_2(OH_2)_2]^{2+}$ with N_2 with rate constants $k = 4.98 \times 10^5$, 8.55×10^5 s^{-1} for L = en and ½trien respectively.[320] Unlike $[Ru(NH_3)_5OH_2]^{2+}$, *cis*-$[Ru(N_2)(en)_2OH_2]^{2+}$ does not appear to react with N_2.[616] The trien complex $[Ru(N_2)(trien)OH_2]^{2+}$ can be prepared by solvolysis of $[RuX(trien)]_2N_2^{2+}$ (X = I^-, Br^-) under basic conditions.[618] Reaction of thiourea with *cis*-$[Ru(N_3)_2(en)_2]^+$ gives $[Ru\{NSC(NH_2)_2\}(en)_2OH_2]^{3+}$.[317] $[RuCl_3(NO)]$ reacts with amines NR_3 in EtOH to yield $[RuCl_3(NO)(NR_3)_2]$.[123,619]

45.4.2.4 Mononuclear complexes with oxygen donor ligands

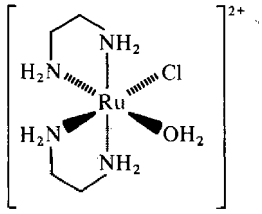
Photolysis of $[Ru(en)_3]^{2+}$ in aqueous acidic conditions yields $[Ru^{II}(enH)(en)_2OH_2]^{3+}$.[379]

Reaction of *cis*-$[RuCl_2(en)_2]^+$ with Ag^+ in H_2O yields *cis*-$[Ru(en)_2(OH_2)_2]^{3+}$.[462,615,616,620] The kinetics of anation of *cis*-$[Ru(en)_2(OH_2)_2]^{3+}$ and *cis*-$[RuX(en)_2OH_2]^{2+}$ (X = Cl^-, Br^-) have been reported to be first order with respect to [halide] and [complex].[400] The ligand field photolysis of *cis*- and *trans*-$[RuCl_2(en)_2]^+$ has been studied (equations 69 and 70) with *cis* and *trans* products $[RuCl(en)_2OH_2]^{2+}$ interconverting.[621,622] The single crystal X-ray structure of *cis*-$[RuCl(en)_2OH_2]^{2+}$ (**64**), prepared by reaction of $[RuCl_2(en)_2]^+$ with CF_3SO_3H followed by H_2O,[457,623] shows six-coordinate Ru^{III} with Ru—N = 2.10 Å, Ru—Cl = 2.323 Å, Ru—O = 2.093 Å.[623] The complex hydrolyses with retention of configuration in aqueous acid.[623] Treatment of $[Ru(NH_2Me)_6]^{2+}$ with O_2 in aqueous conditions yields $[Ru(OH)(NH_2Me)_5]^{2+}$ *via* a Ru^{III} aqua species;[587] the complex readily decomposes to cyano products.[587]

$$cis\text{-}[RuCl_2(en)_2]^+ \xrightarrow[H_2O/H^+]{h\nu} \underset{84\%}{cis\text{-}[RuCl(en)_2(OH_2)]^{2+}} + \underset{16\%}{trans\text{-}[RuCl(en)_2(OH_2)]^{2+}} \quad (69)$$

$$trans\text{-}[RuCl_2(en)_2]^+ \xrightarrow[H_2O/H^+]{h\nu} trans\text{-}[RuCl(en)_2(OH_2)]^{2+} + cis\text{-}[RuCl(en)_2(OH_2)]^{2+} \quad (70)$$

34% 66%

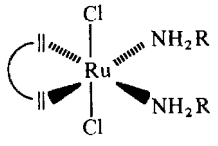


(64)

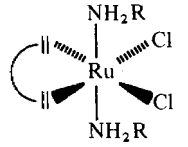
Reaction of $[Ru(ox)_3]^{3-}$ with L yields *trans*-$[Ru(ox)_2L_2]^-$ (L = aniline derivatives), which reacts with HX to produce $[RuX_4L_2]^-$ (X = Cl^-, Br^-).[586,588] The analogous reactions with en lead to the formation of the double salts $[Ru(ox)(en)_2]^+[Ru(ox)_2en]^-$ and $[RuX(en)_2]^+[RuX_4(en)]^-$ respectively.[620,624] Prolonged treatment with HX produces *cis*-$[RuX_2(en)_2]X$.[620] $[Ru(ox)L_2]^+$ (L = en, ½trien) can be isolated from the reaction of $[RuCl_2L_2]^+$ with Ag^+ and oxalate.[620]

45.4.2.5 Mononuclear complexes with halide ligands

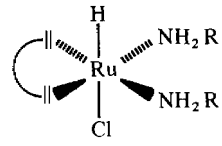
Ruthenium(II): The synthesis of $[RuX_2L_4]$ (X = halide, L = aniline derivative) has been mentioned.[586] Reaction of $[Ru(enH)(en)_2OH_2]^{3+}$ with Cl^- yields $[RuCl(enH)(en)_2]^{2+}$.[379] Red solutions produced by refluxing $RuCl_3$ under CO react with $C_6H_5NH_2$ in ethanol to give $[RuCl_2(CO)_2(NH_2C_6H_5)_2]$,[108] the electrochemistry of which has been reported.[625] Refluxing amines L with $[RuCl_2(diene)]_n$ yields two isomers of the complex $[RuCl_2L_2(diene)]$.[626a,626b] The single crystal X-ray structures of $[RuCl_2L_2diene]$ (L = piperidine, diene = norbornadiene (**65**),[626a] L = aniline, diene = norbornadiene (**66**),[627] L = 1-hexylamine, diene = 1,5-cyclooctadiene (**67**))[626a] have been carried out. For (**65**) Ru—N = 2.237, 2.248 Å;[626a] for (**67**) Ru—N = 2.174 Å, Ru—Cl = 2.458 Å;[626a] for (**66**) Ru—N = 2.213 Å, Ru—Cl = 2.415, 2.407 Å.[627] The ^1H and ^{13}C NMR spectra of these isomers have been discussed.[626a] Another product isolated from the reaction of $[RuCl_2(diene)]_n$ with amine was $[Ru(Cl)(H)(L)_2(diene)]$ (**68**),[626b] the single crystal X-ray structure of which shows Ru—H = 1.57 Å, Ru—Cl = 2.555 Å, Ru—N = 2.240 Å, with ν_{RuH} at 2040 cm^{-1} in the IR spectrum.[628] Reaction of $[RuCl(CO)_3]_2$ with RNH_2 yields $[RuCl(CONHR)(NH_2R)_2(CO)_2]$ which on acidification gives $[RuCl(NH_2R)_2(CO)_3]^+$.[629a] Treatment of $[RuCl_2(arene)]_2$ with en produces $[RuCl(en)(arene)]^+$ with the formation of small amounts of $[Ru(en)_3]^{2+}$.[629b]



(65) $[RuCl_2(nbd)(pip)_2]$
(66) $[RuCl_2(nbd)(anil)_2]$



(67) $[RuCl_2(cod)(hex)_2]$



(68)

Ruthenium(III): Reaction of $[Ru(ox)_3]^{3-}$ with amine L followed by HX yields *cis*-$[RuX_2L_2]^+$ (L = en, 1,2-diaminopropane, ½trien);[457,618,620] $[RuX_4(en)]^-$ has been isolated from these reactions.[620] The absolute configuration of (−)-*cis*-$[RuCl_2(en)_2]^+$ has been determined,[630] and can be converted to the *trans* isomer by heating for 1 min at 60°C with ethylene glycol.[631] *Trans*-$[RuX_2L]^+$ may be alternatively prepared by treatment of $[RuCl_5(OH_2)]^{2-}$ with L (L = $(en)_2$, $(1,2\text{-diaminopropane})_2$, $(1,2\text{-diamino-}N,N'\text{-dimethylethane})_2$, 1,9-diamino-3,7-diazanonane, 1,10-diamino-4,7-diazadecane, 1,11-diamino-4,8-diazaundecane).[632–634] Oxidation of $[RuCl(enH)(en)_2]^{2+}$ with $[Ru(en)_3]^{3+}$ gives $[RuCl(enH)(en)_2]^{3+}$[379] while solvation effects in *cis*-$[RuBr_2(en)_2]^+$, *trans*-$[RuX_2(en)_2]^+$ (X = Cl^-, Br^-, I^-, NCS^-) and *trans*-$[RuX_2L]^+$ (X = Cl^-, Br^-; L = 1,9-diamino-3,7-diazanonane) have been probed by ESR spectroscopy.[635]

The acid and base hydrolysis of *cis*- and *trans*-$[RuCl_2L]^+$ (L = $(NH_3)_4$, $(en)_2$, $(1,2\text{-diaminopropane})_2$, trien, 1,9-diamino-3,7-diazanonane) have been studied;[457,631,634,636–638] the role of increased chelation in the observed rates of hydrolysis has been assessed[457,634,637] and related to the $E_{1/2}$ values

for the $Ru^{III/II}$ redox couples.[636,639] *Trans*-$[RuCl_2(en)_2]^+$ hydrolyses more slowly than the *cis* isomer, the aquation of *cis*-$[RuCl_2(en)_2]^+$ being Hg^{2+} catalysed (equation 71).[640] An S_N1 mechanism *via* a square pyramidal intermediate has been proposed,[634,636,637,640] hydrolysis occurring with retention of configuration.[457,458,634,637] Base hydrolysis occurs *via* a conjugate base mechanism, with a second order rate law (equation 72).[458] The ligand field (LF) and ligand–metal charge transfer (LMCT) excited state photochemical aquation of *trans*-$[RuX_2(en)_2]X$ has been studied.[641–643] For $X = I^-$, LF excitation led to aquation with greater than 85% stereochemical change, whereas for LMCT excitation retention of configuration was observed. For $X = Cl^-$, Br^-, the LF and LMCT bands overlap and stereochemical mixing was found in the products.[641]

The reduction of *trans*-$[RuXL]^+$ ($X = 2Cl^-$, $2Br^-$, $2I^-$, $BrCl^{2-}$; $L = (en)_2$, 1,9-diamino-3,7-diazanonane) by Cr^{II} and V^{II} has been reported.[644,645] Reduction by Cr^{II} follows a rate expression (equation 73) consistent with an inner-sphere mechanism involving bridging chloro species;[644,645] an outer-sphere mechanism has been suggested for reductions with V^{II}.[644]

$$cis\text{-}[RuCl_2(en)_2]^+ \xrightarrow{Hg^{2+}} cis\text{-}[RuCl(en)_2(OH_2)]^{2+} \longrightarrow cis\text{-}[Ru(en)_2(OH_2)_2]^{3+} \quad (71)$$

(HCl)

$$\frac{-d[\text{complex}]}{dt} = k[^-OH][\text{complex}] \quad (72)$$

$$k_{obs} = (k_1 + k_x[X^-])[Cr^{II}] \quad (73)$$

Thermolysis of $(LH)_2[RuCl_6]$ ($L = Et_2NH$) has been proposed to yield $[RuCl_4L_2]$ ($L = Et_2NH$).[646]

45.4.2.6 Binuclear complexes

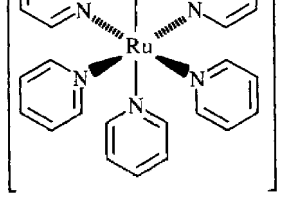
Treatment of $[RuL_2(N_2)(OH_2)]^{2+}$ with $[RuL_2(OH_2)_2]^{2+}$ (L = en, ½trien) yields the dimer $[RuL_2(OH_2)]_2N_2^{4+}$.[320] On reduction with zinc amalgam *cis*-$[RuBr_2(trien)]$ reacts with N_2 in the presence of KX to give $[(trien)XRu^{II}(N_2)Ru^{II}X(trien)]X_2$ ($X = Br^-$, I^-).[618] $[(en)_2ClRu(OH)RuCl(en)_2]^{3+}$ is reported to be the product of photolysis of *cis*-$[RuCl(en)_2OH_2]^{2+}$.[621] The nitrido-bridged complex $[Ru_2N(en)_5]^{5+}$[647] is discussed in Section 45.4.6.

45.4.3 Heterocycles

45.4.3.1 Mononuclear complexes

(*i*) *Monodentate heterocyclic complexes* $[RuL_6]^{2+/3+}$

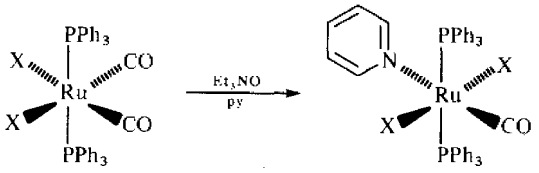
Reaction of $[Ru(OH_2)_6]^{2+}$ with excess of L (L = pyridine, pyrazine, pyridazine) yields $[RuL_6]^{2+}$.[648] Analogous products have also been prepared by extended reflux of pyridine with $[RuH(HOMe)_3(PPh_3)_2]^+$ or $[RuH(OH_2)_3(PPh_3)_2]^+$,[649] or by reaction of $[Ru(cod)(N_2H_4)_4]^{2+}$ with 2-methylpyridine.[650] The single crystal X-ray structure of $[Rupy_6]^{2+}$ (**69**) shows Ru—N = 2.10–2.14 Å with octahedral Ru^{II}. (**69**) shows a metal to ligand charge transfer band at 341 nm, with a larger Ru—N force constant compared with data for the Ru—NH_3 bond.[649] For the $[Rupy_6]^{3+/2+}$ couple $E^\circ = +1.29$ V *vs.* NHE.[649]



(**69**)

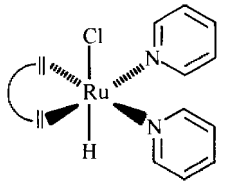
(ii) Monodentate heterocyclic complexes with carbon donor ligands

Treatment of $[RuCl_2(CO)_3]_2$ with py in THF yields $[RuCl_2(CO)_3py]$[651] which reacts further to give $[RuCl_2(CO)_2py_2]$.[651-653] Reaction of $[RuX_2(CO)_4]$ (X = Br^-, I^-) with L at room temperature leads to the formation of $[RuX_2(CO)_3L]$ (L = py, 3-methylpyridine, 3,4-dimethylpyridine).[654] The complexes $[RuCl_2(CO)L_3]$ (L = py, 3-methylpyridine) have been isolated from the reactions of $[RuCl_2(CO)diene]_2$ (diene = 1,5-cod, nbd) with L;[655] for L = quinoline, the complex $[RuCl_2(CO)_2L_2]$ was obtained.[655] Replacement of Cl^- in $[RuCl_2(CO)_2py_2]$ has been achieved by treatment with Ag^+ to yield $[Ru(OAc)_2(CO)_2py_2]$ in the presence of ^-OAc, or $[Ru(CO)_2(NCMe)_2py_2]^{2+}$ in acetonitrile.[656] The decarbonylation of $[RuCl_2(CO)_2L_2]$ with bidentate ligands has been reported.[657] Decarbonylation of $[RuX_2(PPh_3)_2(CO)_2]$ (X = Cl^-, Br^-) with Et_3NO in pyridine gives $[RuX_2(PPh_3)_2(CO)py]$ (equation 74) with inversion of stereochemistry.[658]



(74)

Reaction of $[RuCl_3(CO)nbd]^-$ with py yields $[RuCl_3(CO)py_2]^-$ and $[RuCl_2(CO)(nbd)py]$[659] while refluxing $[Ru(cod)(N_2H_4)_4]^{2+}$ with excess of L affords $[Ru(cod)L_4]^{2+}$ (L = py, 4-methylpyridine);[650] the catalytic reduction of nitroalkenes and *N*-oxides by CO and H_2O has been achieved using $[Ru(cod)py_4]^{2+}$.[660] The complex $[Ru(NCS)_2(CO)_2py_2]$ has been prepared by reaction of $[Ru(NCS)_2(CO)_2]_n$ with pyridine.[661] Amine exchange reactions of $[RuClH(cod)L_2]$ (L = amine) with pyridine, 4-methylpyridine and 4-dimethylaminopyridine have been studied; the single crystal X-ray structure of $[RuClH(cod)py_2]$ (**70**) shows[662] Ru—N = 2.167, 2.153 Å, Ru—Cl = 2.584 Å, Ru—H = 1.60 Å.

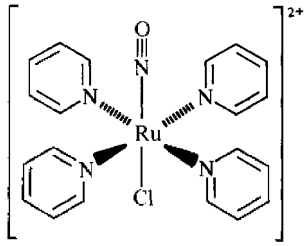


(70)

The pK_a of $[Ru(CN)_5(pzH)]^{2-}$ is 0.4 compared with 2.85 for $[Ru(pzH)(NH_3)_5]^{2+}$.[38] Ruthenium–cyano complexes are discussed in Section 45.3.1

(iii) Monodentate heterocyclic complexes with nitrogen donor ligands

Treatment of $[Ru(NO_2)_2py_4]$ with HX yields $[RuX(NO)py_4]^{2+}$ (X = Cl^-, Br^-); with X = ClO_4^-, $[Ru(OH)(NO)py_4]^{2+}$ is obtained.[663] The single crystal X-ray structure of *trans*-$[RuCl(NO)py_4]^{2+}$ (**71**) shows a linear RuNO unit with < RuNO = 174.8°, Ru—NO = 1.760 Å, N—O = 1.132 Å, Ru—Cl = 2.314 Å shortened due to the *trans* effect of nitrosyl, Ru—N(py) = 2.111 Å.[664] The nitrosyl in $[RuX(NO)py_4]^{2+}$ behaves as an electrophile, reaction with ^-OH leading to the reversible formation of $[RuX(NO_2)py_4]$.[663] The ClO_4^- salt of (**71**) reacts with N_3^- to give a mixture of $[RuCl(N_3)py_4]$ and $[Ru(Cl)py_4(OH_2)]^+$, while the PF_6^- salt of (**71**) yields $[RuCl(N_2)py_4]^+$ which rapidly loses N_2 in solution.[663] The one electron electrochemical reduction of (**71**) generates $[Ru(NO)py_4(OH_2)]^{2+}$; further reduction either electrochemically or with zinc amalgam produces $[RuCl(NH_3)py_4]^+$.[663] $[RuCl\{N(O)SO_3\}py_4]$ can be prepared by treatment of (**71**) with SO_3^{2-},[665] while reaction of $[RuI_2(NO)]$ with py is proposed to give a dimeric species of stoichiometry $[RuI_2(NO)py_2]_2$.[666]



(71)

Thermolysis of $(LH)_2[RuCl_5(NO)]$ (L = benzimidazole, imidazole, 5-nitrobenzimidazole, benzotriazole, py) leads to the initial formation of $[RuCl_4(NO)L]^-$ with subsequent reaction to afford $[RuCl_3(NO)L_2]$.[646] When solutions of $RuCl_3$ with NaNCS in pyridine are refluxed for three days, a product formulated as $[Ru(NCS)_2py_4]$ can be isolated.[667] Nitrosyl and thionitrosyl complexes containing heterocycles with arsine or phosphine ligands have been reported.[668]

(*iv*) *Monodentate heterocyclic complexes with oxygen donor ligands*

The complexes $[RuL(OH_2)_5]^{3+}$ (L = *N*-methylpyrazinium$^+$), $[RuL_2(OH_2)_4]^{2+}$ (L = py, pz) and $[Rupy_4(OH_2)_2]^{2+}$ can be isolated from the reaction of L with $[Ru(OH_2)_6]^{2+}$.[648] Reaction of $K_3[Ru(ox)_3]$ with py under reflux for 1 h followed by reduction with zinc amalgam yields $[Ru(ox)py_4]$.[669] Treatment of $[RuCl_2py_4]$ with NO_2^- produces $[Ru(NO_2)_2py_4]$.[663] The ruthenium(VI) complex $[RuO_2Cl_2py_2]$ with a *trans*-dioxo O=Ru=O moiety can be prepared by reaction of RuO_4 with py in the presence of HCl.[65] A product of stoichiometry RuO_4py_2 has been isolated from the reaction of RuO_4 with pyridine; the exact nature of this complex is unknown but is likely to involve Ru^{III} and/or Ru^{IV}.[670–674a] *Trans*-$[Ru^{IV}(O)Cl(py)_4]^+$ can be prepared by oxidation of *trans*-$[RuCl(NO)(py)_4]^{2+}$; the single crystal X-ray structure of the Ru^{IV}–oxo product shows an unusually long Ru—O distance of 1.862 Å.[674b]

(*v*) *Monodentate heterocyclic complexes with halide ligands*

Treatment of $[RuCl_6]^{2-}$ with L under reflux conditions yields $[RuCl_2L_4]$ (L = py, 2-, 3- and 4-methylpyridine.[675,676] $[Ru(ox)py_4]$ reacts with HCl to give *cis*-$[RuCl_2py_4]$. Recrystallization of *cis*-$[RuCl_2py_4]$ from pyridine leads to the isolation of the more stable *trans* isomer.[669] Extended reflux of $[RuCl_2(PPh_3)_3]$ or $[RuCl_2(AsPh_3)_2]_2$ with L yields $[RuCl_2L_4]$ (L = quinoline, 2-methylpyridine, 2-aminopyridine) together with mixed phosphine– and arsine–amine complexes.[677] The IR spectra of complexes of type $[RuCl_2L_4]$ have been reported.[669,675]

The complexes $[RuCl_3L_3]$ can be prepared by reaction of $[RuCl_2L_4]$ with HCl (L = py, 2-, 3- and 4-methylpyridine),[675] by reflux of $RuCl_3$ with L (L = imidazole, substituted imidazoles)[678] or by fusion of RuX_3 (X = Cl^-, Br^-, I^-) with molten L (L = thiazolidine-2-thione).[679] $[RuCl_3py_3]$ and $[RuCl_3pyL_2]$ (L = 2-methylbenzonitrile) show a reversible $Ru^{II/III}$ couple near 0.0 V *vs.* SCE, and a reversible $Ru^{III/IV}$ couple.[680] The differences between *fac* and *mer* isomers towards redox reactions have been discussed.[680] Treatment of $[RuCl_4(NCR)_2]^-$ with pyridine gives $[RuCl_4py_2]^-$.[681] The IR and magnetic properties of complexes $[RuCl_3L_3]$ have been reported.[675] Halo complexes of 3-methyl rhodanine, adenosine and xanthosine have been prepared by reflux of $RuCl_3$ with ligand in alcoholic solvents.[682,683]

Thermolysis of $(LH)_2[RuCl_6]$ yields $[RuCl_4L_2]$ (L = imidazole, 5-nitrobenzimidazole, benzimidazole, pyridine, benzotriazole, Et_2NH);[646,684] for L = pyridine thermolysis at higher temperatures gives $[RuCl_3py_2]_2$.[684]

(*vi*) *Bidentate heterocylic complexes* $[RuL_3]^{n\pm}$

(*a*) $[RuL_3]^+$

$[Ru(bipy)_3]^+$ can be generated by reductive quenching of excited state $[Ru(bipy)_3]^{2+}$* (see below) or by controlled potential electrolysis of $[Ru(bipy)_3]^{2+}$ at -1.42 V.[685,686] $[Ru(bipy)_3]^{1+/0/1-}$ have been generated electrochemically and their absorption spectra are consistent with the formation of charge localized ruthenium(II)–bipy radical species.[687,688] Comparison of the electronic spectra for $[Ru(bipy)_3]^{2+/1+/0/1-}$ shows the progressive growth of a band near 340 nm which is observed also for free ($bipy^-$) radical anion, and the concomitant collapse of the ($bipy^0$) $\pi \rightarrow \pi^*$ transition near 290 nm.[687–690] Bands assigned to intervalence charge transfer transition between coordinated ($bipy^0$) and ($bipy^-$) occur at 4500 cm^{-1} (ε = 210, 345 M^{-1} cm^{-1}) for $[Ru(bipy)_3]^{1+/0}$ respectively;[691] no such absorptions are observed for $[Ru(bipy)_3]^{2+/1-}$.[691] $[Ru(bipy)_3]^+$ shows a metal to ligand charge transfer band at 495–510 nm.[685,688,689,692–695] The ESR spectra of $[Ru(bipy)_3]^{1+/0}$ indicate interligand electron hopping with line broadening of the isotropic signal near g = 2,[696,697] no such line broadening being observed for $[Ru(bipy)_3]^{1-}$.[697] The charge localized assignment for $[Ru(bipy)_3]^{+/0}$ is further confirmed by resonance Raman data[698] which show bands assigned to both ($bipy^0$) and ($bipy^-$) in

the complexes. The redox orbital localization in $[Ru^{II}(bipy^{-})(bipy)_2]^{+}$ has been compared to the electron distribution in charge transfer excited state $[Ru(bipy)_3]^{2+*}$[687,688,691,697–700] (see below). Spectro–electrochemical studies on reduced complexes of $[RuL_3]^{2+}$ (L = 3,3′-biquinoline,[701] 5,5′-bis(ethoxycarbonyl)-2,2′-bipyridine,[687] 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine,[687,702] 4,4′-dimethyl-2,2′-bipyridine,[687] 4,4′-bis(diethylcarbamyl)-2,2′-bipyridine[687]) have been published. Voltammetry of $[RuL_3]^{2+}$ (L = bipy, 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine) at low temperatures indicates spatially isolated, localized orbitals for these complexes.[703–705a]

$[Ru(bipy)_3]^{+}$ is oxidized to $[Ru(bipy)_3]^{2+}$ by O_2, $[Co(bipy)_3]^{3+}$ and $[NiCN_4]^{2-}$ at pH 11 with rate constants $k = 7.4 \times 10^9$, 1.6×10^9 and $4.1 \times 10^7\ M^{-1}\ s^{-1}$ respectively.[685,689,692] $[Ru(bipy)_3]^{0}$ obtained by controlled potential electrolysis of $[Ru(bipy)_3]^{2+}$ at -1.65 V generates H_2 on reaction with H_2O;[686] no evolution of H_2 is observed on treatment of $[Ru(bipy)_3]^{+}$ with H_2O.[686]

(b) $[RuL_3]^{2+}$

Over the past fifteen years a vast literature has built up around tris(diimino) complexes of Ru^{II}, particularly $[Ru(bipy)_3]^{2+}$. This has been based upon the photochemical behaviour of $[Ru(bipy)_3]^{2+}$ and the nature of its excited state $[Ru(bipy)_3]^{2+*}$ in relation to the use of such complexes as potential solar energy converters. $[Ru(bipy)_3]^{2+}$ is stable up to 300°C irrespective of the nature of the anion, the decomposition product being metallic Ru or RuO_2.[705b] Early preparations of $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ were achieved by fusion of $RuCl_3$ with molten ligand at 250°C[706,707] or by refluxing $[RuCl_5(OH_2)]^{2-}$ with ligand in the presence of tartrate[708,709] or hypophosphite.[707,710,711] The preparation of $[Ru(bipy)_3]^{2+}$ by reduction of $RuCl_3$ with H_2 over Pt black followed by treatment with bipy in MeOH has been recommended.[712] By addition of optically active tartrate salt, Λ-$[Ru(bipy)_3]^{2+}$ has been isolated[708,709,713] and ion association measurements for $[Ru(phen)_3]^{2+}$[714,715] and the optical activity of $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$[716] have been studied. Λ-$[Ru(phen)_3]^{2+}$ has been used in clay column chromatography for the optical resolution of metal complexes.[717,718] The intercalation of $[Ru(phen)_3]^{2+}$ into DNA has been reported.[719] NMR studies of bipy complexes of Ru^{II} have been published.[267,269] Table 8 summarizes selected data on the synthesis, electronic spectra and redox properties of complexes of type $[RuL_3]^{2+}$. A comprehensive account of the photochemistry, photophysics and theoretical models derived from absorption and luminescent data for $[Ru(bipy)_3]^{2+}$ is beyond the scope of this review. Several excellent reviews of this area have appeared in the literature,[3–5,487b,727,731,767–784] the accounts by Seddon and Seddon,[3–5] and Kalyanasundaram[768] being particularly detailed.

The electronic absorption spectrum of $[Ru(bipy)_3]^{2+}$ shows bands at 185 nm, 208 nm and 285 nm assigned to bipy $\pi \rightarrow \pi^*$ transitions, and *d–d* transitions at 323 nm, 345 nm, 238 nm, 250 nm.[727,731] The intense absorption at 454 nm ($\varepsilon = 14600\ M^{-1}\ cm^{-1}$)[724] is assigned to a metal to ligand charge transfer;[267,785–790] this latter transition shows a long tail absorption above 500 nm which has been assigned to a spin-forbidden metal to ligand charge transfer.[711,790] The luminescence of $[Ru(bipy)_3]^{2+}$ was first reported by Paris and Brandt in 1959 as an emission near 600 nm and was assigned as charge transfer in nature.[791] Later this was reassigned to a singlet *d–d* transition[792,793] and then to a spin-forbidden triplet–singlet charge transfer from $(t_{2g})^5(\pi^*)^1$ to $(t_{2g})^6$ (equation 75).[790,794,795] The orbital nature of the MLCT absorption and emission spectra of $[Ru(bipy)_3]^{2+}$, and hence the electronic structure of the excited state $[Ru(bipy)_3]^{2+*}$, has been the subject of much controversy.

$$\underset{(t_{2g})^6}{[Ru(bipy)_3]^{2+}} \xrightarrow{h\nu} \underset{(t_{2g})^5(\pi^*)^1}{[Ru(bipy)_3]^{2+*}} \xrightarrow{h\nu'} \underset{(t_{2g})^6}{[Ru(bipy)_3]^{2+}} \qquad (75)$$

To rationalize the luminescence characteristics of $[Ru(bipy)_3]^{2+*}$ Crosby and co-workers have developed in a series of papers[727,736,787,793,802–807] an electron-ion parent (EIP) coupling model[804,805] to describe the orbital symmetries of the excited states. In this model, the electronic structure of $[Ru(bipy)_3]^{2+*}$ could not be simply described as singlet or triplet; since the luminescence is charge transfer *d–π** in character, spin-orbit coupling would be expected to occur thus mixing the emitting states and thus the emission was described as occurring from a 'manifold' of spin-orbit states ${}^3CT \rightarrow {}^1A_{1g}$,[790,803–805,808] with three emitting levels of A_1, E and A_2 symmetries. $[Ru(bipy)_3]^{2+*}$ was therefore described as a d^5 Ru^{III} centre with one electron delocalized over three bipy ligands[685,787] and the temperature dependence and polarization of the luminescence predicted.[3–5,768]

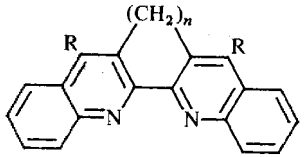
More recently, however, the EIP model has been modified and alternative models that generate the requisite manifold of emitting levels have gained favour. Photoselection data for the emission of $[Ru(bipy)_3]^{2+*}$ were found to be inconsistent with the EIP model[789,809,810] with a far greater degree of polarization than would be expected for an ion of D_3 symmetry.[811–813] Since the single crystal X-ray structure of $[Ru(bipy)_3]^{2+}$ shows[814] the complex to have D_3 symmetry with short Ru—N = 2.056 Å

Table 8 Synthesis, Absorption Spectra and Redox Properties of Complexes $[RuL_3]^{2+}$

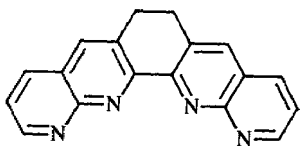
Ligand (L)	*Synthesis*	*λ (ε) (nm × 10^{-4} $M^{-1}cm^{-1}$)*	$E_{1/2}$ (V)	*Reference electrode (solvent)*
2,2′-bipy[a]	$RuCl_3$, L, 250°C[706]	454 (1.46), 428 (1.17), 345 (—),	+1.354, −1.332, −1.517, −1.764,	SCE (MeCN)
	$RuCl_3$, L, EtOH, 72 h, Δ[720,721]	323 (—), 285 (7.92), 250 (2.56)[711,724]	−2.4[725]	
	$RuCl_3$, L, DMF, Δ[712]		+1.03, +2.78[723,726]	SCE (SO_2)
	$RuCl_3$, L, H_2O, NaH_2PO_2, Δ[711,712,722]		−1.76, −1.92, −2.14, −2.78,	$Fc^{+/0}$ (DMF)
	$RuCl_3$, Pt, H_2, MeOH, L, Δ[712]		−3.0, −3.3[599,703]	
	$Ru(bipy)_2Cl_2$, L, DMF, Δ[723]		−1.06, −1.24, −1.49, −2.17[688]	SHE (MeCN)
	$[RuCl_5(OH_2)]^{2-}$, L, NaH_2PO_2, Δ[707,710]			
	$[RuCl_5(OH_2)]^{2-}$, tartrate, L, Δ[708,709]			
3,3′-$(Me)_2$bipy	$RuCl_3$, L, DMF, phosphate, pH 7[721,732]	456 (1.16), 348 (1.18), 296 (4.94), 236 (3.23)[732,733]	+1.15, −1.46[733]	SHE (MeCN)
4,4′-$(Me)_2$bipy[b]	$RuCl_3$, L, DMF[687,721]	459 (1.49), 435 (1.2), 285 (8.0),	+1.17, −1.34, −1.51, −1.77, −2.57[687,697]	SCE (DMF)
	$[RuCl_5(OH_2)]^{2-}$, NaH_2PO_2, H_2O, HCl, L[728]	247 (2.52)[687,728,732]		
5,5′-$(Me)_2$bipy[c]	$RuCl_3$, L, DMF[687]		+1.15, −1.41, −1.59, −1.80[687]	SCE (DMF)
6,6′(Me_2)bipy	$RuCl_3$, Pt, H_2, MeOH, L, ethylene glycol[724]	446 (0.74), 297 (5.18), 248 (2.15)[724]		
6-Mebipy	$RuCl_3$, Pt, H_2, MeOH, L, ethylene glycol[724]	448 (1.11), 293 (7.13), 247 (2.93)[724]		
4,4′-$(Ph)_2$bipy	$RuCl_3$, H_2O, HCl, L, DMF, Δ, 3 h[721,728]	~480 (4.0), ~350 (−3.0),	+1.17[728]	SHE (1 M H_2SO_4)
	$RuCl_3$, EtOH, NH_2OH, HCl, NaOAc, L, Δ[735,736]	~310 (10.0), ~290 (9.0), ~230 (10.0)[735,736]		
4,4′-$(Bu^t)_2$bipy	$RuCl_3$, EtOH, L, 72 h, Δ[737]	456 (1.68)[733]	+1.11, −1.44[733,737]	SHE (MeCN)
4,4′-$(CO_2Et)_2$bipy	$RuCl_3$, L, DMF, Δ, 2 weeks[687]	471 (2.5), 442 (2.1), 362 (2.4)[687]	+1.54, −0.89, −1.01, −1.19, −1.63,	SCE (DMF)
			−1.83, −2.15[687]	
			−1.34, −1.46, −1.62, −2.02, −2.19,	$Fc^{+/0}$ (DMF)
			−2.42, −2.88, −2.97, −3.19, −3.34[703]	
5,5′-$(CO_2Et)_2$bipy	$RuCl_3$, L, DMF, Δ[687]	505 (1.0), 465 (0.88)[687]	+1.53, −0.66, −0.75, −0.91, −1.37,	SCE (DMF)
			−1.57, −1.82[687]	
4,4′-$(CONEt_2)_2$bipy	$Ru(DMSO)_4Cl_2$, L, Δ, MeOH[687]	459 (2.0), 435 (1.8)[687]	+1.28, −1.12, −1.26, −1.43[687]	SCE (DMF)
4-(CO_2Et)bipy			−0.98, −1.10, −1.42, −1.76, −1.95,	SCE (MeCN)
			−2.22[702]	
5-(CO_2Et)bipy			−0.82, −0.93, −1.23, −1.76, −1.92,	SCE (MeCN)
			−2.24[702]	
4-(NO_2)bipy	$[RuCl_5(OH_2)]^{2-}$, H_2O, HCl, L, Δ[737]	480 (2.04), 384 (0.63)[737]	+1.425, −1.060, −1.210(i)[737]	SHE (MeCN)
			+1.54[738]	SCE (MeCN)
4-(Et_3P^+)bipy	$[RuCl_5(OH_2)]^{2-}$, H_2O, HCl, L, Δ[738]	466 (1.82)[738]	+1.52[738]	SCE (MeCN)
4,4′$(Cl)_2$bipy	$[RuCl_5(OH_2)]^{2-}$, H_2O, HCl, L, Δ[737]	462 (1.7), 433 (1.4)[737]	+1.55, −0.545(i)[737]	SHE (MeCN)
1,10-phen[d]	$RuCl_3$, L, DMF[721,732]	446 (1.9), 417 (1.81), 263 (11.3),	+1.4, −1.41, −1.54, −1.84, −2.24[725]	SCE (MeCN)
	$RuCl_3$, tartrate, L[709]	224 (8.0)[724]		
	$RuCl_3$, Pt, H_2, MeOH, L, ethylene glycol[724]			
	$[RuCl_5(OH_2)]^{2-}$, H_2O, HCl, H_3PO_2, L[728]		+1.03, +2.60[726]	SCE (SO_2)
2,9-$(Me)_2$phen	$RuCl_3$, Pt, H_2, MeOH, L, ethylene glycol[724]	501 (2.6), 270 (8.2), 232 (13.2)[724]		
5,6-$(Me)_2$phen	$RuCl_3$, H_2O, HCl, H_3PO_2, L[728]	453 (2.04), 425 (1.84)[728]	+1.266, −1.288, −1.452, −1.710,	SSCE (DMF)
			−2.45[697,728]	
3,4,7,8-$(Me)_4$phen	$RuCl_3$, H_2O, HCl, H_3PO_2, L[728]	438 (2.45)[728]	+1.02[728]	SHE (1 M H_2SO_4)
3,5,6,8-$(Me)_4$phen	$RuCl_3$, H_2O, HCl, H_3PO_2, L[728]	440 (1.98), 417 (1.96)[728]	+1.09[728]	SHE (1 M H_2SO_4)
4,7-$(Ph)_2$phen[e]	$RuCl_3$, EtOH, NH_2OH, HCl, NaOAc, L[735]	460 (2.95), 440 (3.0), 270 (15.0)[735]	+1.20[728]	SHE (1 M H_2SO_4)
	$[RuCl_5(OH_2)]^{2-}$, H_2O, HCl, DMF, L, H_3PO_2[721,728]		−1.22, −1.34, −1.53, −1.99, −2.13,	SCE (DMF)
			−2.31[741]	

Table 8 (*Continued*)

Ligand (L)	*Synthesis*	*λ (ε)* (nm × 10^{-4} $M^{-1}cm^{-1}$)	$E_{1/2}$ (V)	*Reference electrode (solvent)*
2-(Me)phen	$RuCl_3$, MeOH, Pt, H_2, L, ethylene glycol[724]	446 (1.44), 267 (10.4), 224 (9.53)[724]		
5-(Me)phen[f]	$RuCl_3$, H_2O, HCl, H_3PO_2, L[728]	450 (1.94), 420 (1.79)[728]	+1.23[728]	SHE (1 M H_2SO_4)
5-(Ph)phen[f]	$RuCl_3$, H_2O, HCl, H_3PO_2, L[728]	448 (2.46), 420 (2.32)[728]	+1.26[728]	SHE (1 M H_2SO_4)
5-(Cl)phen[f]	$RuCl_3$, H_2O, HCl, H_3PO_2, L[728]	447 (1.84), 422 (1.78)[728]	+1.36[728]	SHE (1 M H_2SO_4)
5-(Br)phen	$RuCl_3$, H_2O, HCl, H_3PO_2, L[728]	448 (1.88), 420 (1.82)	+1.37[728]	SHE (1 M H_2SO_4)
5-(NO_2)phen[g]	$RuCl_3$, H_2O, HCl, H_3PO_2, L[728]	449 (2.0)[728]	+1.46[728]	SHE (1 M H_2SO_4)
5-(NH_2)phen	$RuCl_3$, DMF, L, Δ, 10 h[745]	470 (1.61), 364 (2.07)[745]		
2,2′-Bipyrimidine[h]	$RuCl_3$, EtOH, L, H_2O, Δ, 30 h[746]	454 (0.86), 418 (0.82), 362 (—),	+1.69, −0.91, −1.08, −1.28[747]	SSCE (MeCN)
	$RuCl_3$, L, DMF[728]	332 (1.7), 252 (4.9)[747]		
	$RuCl_3$, L, ethylene glycol, Δ[747]			
2,2′-Biquinoline	$RuCl_3$, Pt, H_2, MeOH, L, ethylene glycol, 8 h, Δ[748]	524 (0.9), 370 (4.0), 345 (5.0), 270 (11.0)[749]	+1.47, −0.895, −1.25, −1.84[737]	SHE (MeCN)
3,3′-Biquinoline		390 (2.3), 340 (10.0), 330 (9.0), 260 (11.0)[749]	−1.51, −1.60, −1.735[701]	SHE (MeCN)
2,2′-Bipyrazine	$RuCl_3$, L, ethylene glycol, Δ[747]	440 (1.3), 415 (—), 338 (—),	+1.86, −0.8, −0.98, −1.24, −2.075[751,752]	Ag (MeCN)
	$Ru(DMSO)_4Cl_2$, L, Δ, H_2O[750,751]	291 (5.1), 240 (2.0)[747]		
2,2′-Biimidazole	$[Ru(H_2O)_6]^{2+}$, L, 50°C, H_2O[648]	396 (1.07), 279 (4.0)[648]	+0.44[648]	SHE (MeCN)
2,2′-Bibenzimidazole	$RuCl_3$, glycerol, L, 100°C, 10 h[753]	483 (—)[753]	+0.80[753]	SCE (MeCN)
2-(2′-Pyridyl)quinoline	$RuCl_3$, MeOH, Pt, H_2, ethylene glycol, L[748]	480 (—)[740,754]		
	Ru blue, L[740,754]			
2-(2′-Pyridyl)imidazole	$RuCl_3$, tartrate, L, Δ, water[755]	482 (3.3), 298 (41.0)[755]		
2-(2′-Pyridyl)benzimidazole	$RuCl_3$, tartrate, L, Δ, water[755]	428 (6.5), 410 (3.7), 318 (55.3), 311 (55.3), 243 (55.8)[755]		
2-(2′-Pyridyl)thiazole	$[Ru_2OCl_8]^{4-}$, glycerol, L[756]	463 (—)[756]	+1.28[756]	SHE (1 M HNO_3)
1-(2′-Pyridyl)-3,5-Me_2pyrazole	$RuCl_3$, Pt, H_2, L, MeOH[757]	382 (1.52)[757]	+1.17[757]	SCE (MeCN)
2-(Phenylazo)pyridine	$[RuL_2(OH_2)_2]^{2+}$, L, Δ[611,758]	498 (1.35), 470 (—), 377 (3.8), 323 (2.04), 277 (2.2)[611]	+0.06, −0.3, −0.89, −1.53[611]	SCE (CH_2Cl_2)
			+2.10, −0.13, −0.45, −0.94, −1.59, −1.92, −2.06[758]	SCE (MeCN)
2-(3′-Tolylazo)pyridine	$[RuL_2(OH_2)_2]^{2+}$, L, Δ[758]	494 (1.39), 464 (1.3), 372 (3.8), 320 (2.3)[758]	+2.23, −0.10, −0.43, −0.93, −1.59, −1.89, −1.95[758]	SCE (MeCN)
2-(4′-Nitrophenylazo)pyridine	$[RuL_2Cl_2]$, HNO_3, Ag^+, L, Δ, 4 h[759]	505 (1.4), 470 (—), 343 (3.58)[759]	+0.015, −0.265, −0.608, −0.737, −0.785[759]	Ag/Ag^+ (MeCN)
1,4,5,8-Tetraazaphenanthrene	$Ru(DMSO)_4Cl_2$, L, EtOH, H_2O, Δ, 20 h[760]	435 (1.6), 407 (1.7), 270 (3.2)[760]	+1.93, −0.76, −0.89, −1.15, −1.59(i)[760]	SCE (MeCN)
2-Picolylamine	$RuCl_3$, EtOH, L, Δ, 14 h[761]	500 (—)[761]		
2-(4′-Tolyl)pyridine carboxaldimine	$[RuCl_5(OH_2)]^{2-}$, L, MeOH, Δ, 1.5 h[762]	552 (0.72), 496 (0.63)[762]	+1.17[726]	SCE (MeCN)
2-Benzoquinone diimine	$RuCl_3$, 1,2-diaminobenzene, Zn, NH_3[599]	671 (1.27), 656 (1.3), 485 (2.29), 403 (0.47), 220 (3.0)[599]	+1.38, +0.03, −0.31, −1.08, −1.2[599]	SCE (MeCN)



$n = 2$, R = H	$RuCl_3$, Pt, H_2, ethylene glycol, L, 200°C[737]	544 (0.96), 522 (0.90)[737]	+1.425, −0.755, −0.965, −1.3, −1.88[737]	SHE (MeCN)
$n = 2$, R = Me	$RuCl_3$, Pt, H_2, ethylene glycol, L, 200°C[737]	540 (1.06), 496 (0.76)[733,737]	+1.26, −0.895, −1.065, −1.37[733,737]	SHE (MeCN)
$n = 2$, R = Ph	$RuCl_3$, Pt, H_2, ethylene glycol, L, 200°C[737]	540 (1.7), 493 (0.98)[737]	+1.42, −0.9, −1.215, −1.825[737]	SHE (MeCN)
Naphthyridine $[RuL_4]^{2+}$	$RuCl_3$, PtO_2, H_2, MeOH, L, glycerol[763,764]	500 (0.73), 434 (0.96), 304 (1.19)[763]	+1.05[763]	SSCE (MeCN)
2-Methylnaphthyridine $[RuL_4]^{2+}$	$RuCl_3$, PtO_2, H_2, MeOH, L, glycerol[763,764]	465 (0.86), 277 (4.11)[763]	+1.08[763]	SSCE (MeCN)
2,7-Dimethylnaphthyridine	$[RuCl_5(OH_2)]^{2-}$, glycerol, 100°C[763,764]	455 (0.87), 286 (5.0)[763]	+1.37, −1.24(i), −1.42(i), −1.56(i)[763]	SSCE (MeCN)
2-(2′-Pyridyl)naphthyridine	$[RuCl_5(OH_2)]^{2-}$, glycerol, 24 h; Δ, 24 h[765]	526 (1.25), 317 (6.94), 245 (5.03)[765]	+1.08, −0.99, −1.23, −1.53, −0.87(i)[765]	SSCE (MeCN)

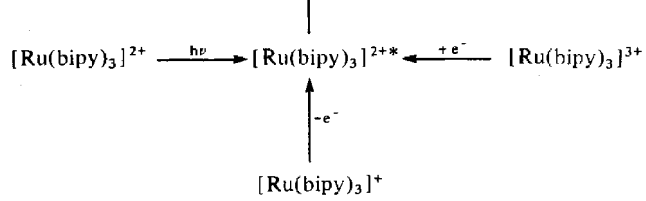


	$[RuCl_5(OH_2)]^{2-}$, glycerol, 24 h; L, Δ, 24 h[765]	585 (0.99), 553 (0.75), 390 (3.15), 358 (5.22), 272 (3.03), 243 (6.46)[765]	+0.97, −0.83, −1.06, −1.36, −1.71(i)[765]	SSCE (MeCN)
1,1′-Bis(2′-pyridyl)amine (HDPA)	$RuCl_3$, L, H_2O, H_3PO_2[766]	380 (5.4), 290 (1.1)[766]		
{1,1′-Bis(2′-pyridyl)amine}$^-$ (DPA^-)	$[Ru(HDPA)_3]^{2+} \xrightarrow{-OH} [Ru(DPA)_3]^-$[766]	430 (1.2), 370 (1.6), 305 (4.2)[766]		

[a] See also references 268a, 687, 692, 702, 727–731. [b] See also references 269, 692, 728, 734. [c] See also references 692, 734. [d] See also references 728, 737, 739, 740. [e] See also reference 737. [f] See reference 742 for complexes of 4-(Me)phen, 4-(OPh)phen, 4-(Cl)phen. [g] See also references 743, 744. [h] See also reference 734.

distances (consistent with strong $Ru^{II} \rightarrow$ bipy back-donation), more recent proposals have led to the thesis that the excited state in $[Ru(bipy)_3]^{2+*}$ is of lower symmetry than D_3; *e.g.* with a localized bipy radical such as $[Ru^{III}(bipy^-)(bipy)_2]^{2+}$. Direct experimental evidence for localized charge distribution in $[Ru(bipy)_3]^{2+*}$ has come from absorption[699,700,815–817] and resonance Raman spectral studies[818–823] on the excited state species. The absorption spectrum of $[Ru(bipy)_3]^{2+*}$ shows a band near 360 nm assignable to coordinated ($bipy^-$) radical anion,[699,700,815–817] while frequency shifts between $[Ru(bipy)_3]^{2+}$ and $[Ru(bipy)_3]^{2+*}$ have been found to be analogous to those observed in the IR spectra for ($bipy^0$) and ($bipy^-$).[818–822] This has led to the conclusion that on the vibrational time scale, the electron is localized on only one bipy ligand, rather than delocalized over all three. Voltammetric data suggest[703–705a] a localized formalism for the redox orbitals of $[Ru(bipy)_3]^{2+}$ and this is confirmed by spectroscopic studies on $[Ru(bipy)_3]^{+}$. Polarized single crystal emission,[824] absorption data,[720,825,826] and resonance Raman studies[827,828] on $[Ru(bipy)_3]^{2+}$ have been published. Analysis of the charge transfer absorption spectrum of $[Ru(bipy)_3]^{2+}$ by CD[786,825,826,829,830] and by molecular orbital X_α and Hückel calculations[789,831,832] has led to a model[789] which involves only weak coupling ($\sim 600\,cm^{-1}$) between bipy ligands. This is consistent with spectral studies for $[Ru(bipy)_3]^{2+*}$ and $[Ru(bipy)_3]^{+}$. More recently an electronic structural model[833] based on the absorption spectrum of $[Ru(bipy)_3]^{2+}$ has indicated that the luminescent excited state can be regarded as a triplet with less than 10% singlet character. The exact nature of the excited state species $[Ru(bipy)_3]^{2+*}$ is still the subject of much discussion and is likely to remain so in the near future.

$[Ru(bipy)_3]^{2+*}$ can not only be generated by photolysis of $[Ru(bipy)_3]^{2+}$, but also *via* electron transfer reactions in the dark to give chemiluminescent activity. This has been achieved by the reduction of $[Ru(bipy)_3]^{3+}$ with ^-OH,[834] N_2H_4, $NaBH_4$, edta,[834,835] e^-_{aq},[836] H_2SO_4,[837] oxalate[838] or $[Ru(bipy)_3]^{+}$[729] (Scheme 22). The chemiluminescent spectrum obtained from the reduction of $[Ru(bipy)_3]^{3+}$ was found to be identical to that of the photoluminescent spectrum of $[Ru(bipy)_3]^{2+}$.[836] Chemiluminescence has been extended to electrogenerated chemiluminescence (ECL) in which reduced and oxidized forms of $[Ru(bipy)_3]^{2+}$ are cogenerated by rapid cycling between E_{ox} of the $Ru^{II/III}$ couple and E_{red} of the first reduction potential followed by annihilation of $[Ru(bipy)_3]^{3+}$ with $[Ru(bipy)_3]^{+}$ (equation 76).[725,729,838,839] Electron transfer during ECL experiments occurs *via* an outer-sphere mechanism conforming to Marcus theory.[840,841] The efficiency obtained from ECL and pulse radiolysis[836] experiments is generally higher than that for photoluminescence[842–845] and more recently ECL studies have been carried out at electrodes modified by polymer surface films.[846,847] The photoinduced disproportionation of $[Ru(bipy)_3]^{2+}$ on photolysis in a glass matrix to yield $[Ru-(bipy)_3]^{+}$ and $[Ru(bipy)_3]^{3+}$ has been reported (equation 77 and 78).[848]



Scheme 22

$$[Ru(bipy)_3]^{3+} + [Ru(bipy)_3]^{+} \longrightarrow [Ru(bipy)_3]^{2+*} + [Ru(bipy)_3]^{2+} \quad (76)$$

$$[Ru(bipy)_3]^{2+*} \longrightarrow [Ru(bipy)_3]^{3+} + e^-_{glass} \quad (77)$$

$$[Ru(bipy)_3]^{2+} + e^-_{glass} \longrightarrow [Ru(bipy)_3]^{+} \quad (78)$$

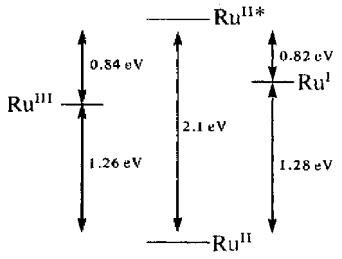
Quenching of the luminescence of $[Ru(bipy)_3]^{2+*}$ by a quencher Q can occur *via* energy transfer to give $[Ru(bipy)_3]^{2+}$, by reductive quenching to $[Ru(bipy)_3]^{+}$ or by oxidative quenching to yield $[Ru(bipy)_3]^{3+}$ (equations 79–81).[849] The parallels between quenching mechanisms and photodiode behaviour at a molecular level have been made.[850] The relative $E_{1/2}$ values for $[Ru(bipy)_3]^{3+/2+/1+}$ and $Q^{1-/0/1+}$ play an important role as to which mechanism is observed.[849] The oxidation potential of $[Ru(bipy)_3]^{2+*}$ has been estimated at -0.84 V *vs.* NHE[686,851] making it a stronger reducing agent by approximately 2.1 V compared with $[Ru(bipy)_3]^{2+}$.[694] $[Ru(bipy)_3]^{2+*}$ is more reactive towards both reduction and oxidation than the ground state molecule[695] (Scheme 23)[767,775] consistent with its

formalism as $[Ru^{III}(bipy^{-})(bipy)_2]^{2+}$. A range of inorganic and organic reagents have been used to quench the excited state $[Ru(bipy)_3]^{2+*}$ species.[852,853] Oxidative quenching of $[Ru(bipy)_3]^{2+*}$ and related excited state complexes has been reported with $S_2O_8^{2-}$,[695,808,839,854–856] O_2,[769,857–863] $[Co(NH_3)_6]^{3+}$,[864] $[CoX(NH_3)_5]^{2+}$ (X = Cl^-, Br^-, I^-),[851,864] $[CoL(NH_3)_5]^{3+}$,[865,866] $[Co(ox)_3]^{3-}$,[867,868] $[Co(acac)_3]$,[869] Co^{III} macrocyclic complexes,[870,871] $[CoCl(Hedta)]^-$,[864] $[Co(phen)_3]^{3+}$,[863] binuclear Co^{III} species,[872,873] $[Fe(CN)_6]^{3-}$,[863,874] $[Fe(ox)_3]^{3-}$,[864,867] Fe^{3+},[129,728,863,875–880] $[Cr(ox)_3]^{3-}$,[867,868] Tl^{III},[878] $[Os(bipy)_3]^{3+}$,[863] $[Ru(NH_3)_6]^{3+}$,[863,880] Hg^{II},[881–883] bipy derivatives[865,879,880,884–890] and nitrobenzene.[884,891] Reductive quenching has been studied with $[Fe(CN)_5L]^{3-}$,[849] $[Mo(CN)_6]^{4-}$,[874,892] Eu^{II},[694,695,892,893] $[Os(CN)_6]^{4-}$,[695,873,874] amines,[884,894–897] dopamine,[898] adrenaline,[898] L-dopa,[898] dtc^-,[899] methoxybenzenes,[895] aromatic ethers,[894] hydroquinone[894] and water,[894] while energy transfer mechanism has been observed for Cr^{III},[728,868,874,900–904] Ti^{III} [905] and O_2.[906] Quenching reactions with Fe^{II},[129,878] Ru^{II},[851] Ru^{III},[907] Cu^{II},[908,909] Ag^{I},[910,911] Eu^{III},[129,695] $[PtCl_4]^{2-}$,[868] $[Ni(CN)_4]^{2-}$,[874] Os^{II},[907] Os^{III}, Os^{IV}, Os^{VI} [912] and *N*,*N*′-dimethylaniline,[888,913,914] have also been reported. Quenching of $[Ru(bipy)_3]^{2+*}$ does not occur with $[Co(CN)_6]^{3-}$, $[Pt(CN)_4]^{2-}$ or $[Pd(CN)_4]^{2-}$.[874] Energy transfer quenching is thought to be favoured when absorption and emission spectra of the reacting species overlap.[905,915]

Energy transfer quenching $[Ru(bipy)_3]^{2+*} + Q \longrightarrow [Ru(bipy)_3]^{2+} + Q^*$ (79)

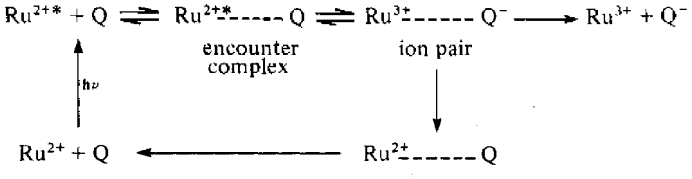
Reductive quenching $[Ru(bipy)_3]^{2+*} + Q \longrightarrow [Ru(bipy)_3]^{+} + Q^{+}$ (80)

Oxidative quenching $[Ru(bipy)_3]^{2+*} + Q \longrightarrow [Ru(bipy)_3]^{3+} + Q^{-}$ (81)



Scheme 23

The use of electron transfer quenching of $[Ru(bipy)_3]^{2+*}$ (equations 80 and 81) for the conversion of photolysis energy to generate radical species has been developed. Bipyridinium salts such as *N*,*N*′-dimethyl-4,4′-bipyridinium^{2+} (MV^{2+}) and *N*-methyl-4,4′-bipyridinium^{+} have been used successfully as electron acceptors.[865] Flash photolysis studies indicate that the formation of free radicals occurs *via* one electron transfer from $[Ru(bipy)_3]^{2+*}$,[865] while the quenching of $[Ru(bipy)_3]^{2+*}$ by nitrobenzene has been described in terms of encounter complex and ion pair formation (Scheme 24).[891] Quenching by binuclear superoxy Co^{III} species has been formulated as being due to 90% electron transfer and 10% energy transfer.[873] The relaxation processes of excited state polypyridyl complexes[916] and electron transfer kinetics in these systems[768] have been discussed. The oxidation of Ph_3N to Ph_3N^+ has been achieved using photosensitized $[Ru(bipy)_3]^{2+}$ and MV^{2+} (equations 82–84).[917]



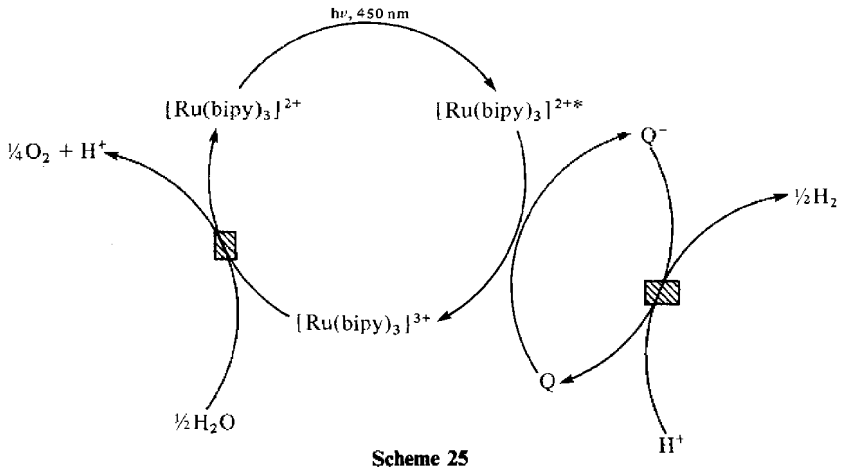
Scheme 24

$Ru^{2+} \longrightarrow Ru^{2+*}$ (82)

$Ru^{2+*} + MV^{2+} \longrightarrow Ru^{3+} + MV^{+}$ (83)

$Ru^{3+} + NPh_3 \longrightarrow Ru^{2+} + {}^{+}NPh_3$ (84)

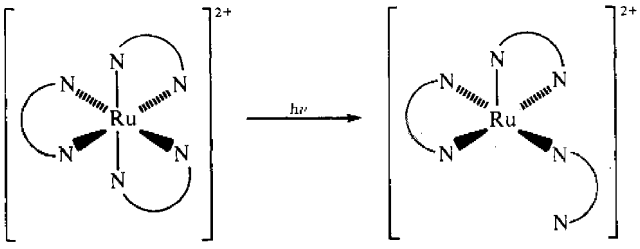
With the ability of photolytically sensitizing $[Ru(bipy)_3]^{2+}$ to $[Ru(bipy)_3]^{2+}*$ and transferring an electron to a quencher Q to generate a strong oxidant $[Ru(bipy)_3]^{3+}$ and reductant Q^- simultaneously, much attention has been focused on the possible utilization of $[Ru(bipy)_3]^{2+}$ as a photocatalyst for the photochemical splitting of water to H_2 and O_2. Although $[Ru(bipy)_3]^{2+}*$ does not cleave water itself, a series of papers have appeared in the literature describing the decomposition of H_2O to H_2 and/or O_2 and related redox processes using $[Ru(bipy)_3]^{2+}$ or a derivative as a photosensitizer in conjunction with a range of radical carriers and homogeneous and heterogeneous catalysts.[854,894,918–949] Scheme 25 illustrates a typical cycle utilizing the oxidative quenching of $[Ru(bipy)_3]^{2+}*$.[918] The photochemical splitting of H_2O by tris(diimino) Ru^{II} complexes is discussed in Chapter 62.5. $[Ru(bipy)_3]^{2+}$ mediates the photoreduction of alkenes with 1-benzyl-1,4-dihydronicotinamide[950] and the photooxidation of phenols.[951] More recently, electron transfer reactions of $[Ru(bipy)_3]^{2+}$ derivatives (particularly those incorporating vinyl substituents) have been studied in polymeric films at electrode surfaces,[183,846,952–977] with colloids,[978] at ion exchange surfaces,[979] in zirconium phosphate lattices,[897] and zeolites[980] in order to investigate the formation of photocurrents; surfactant bipy derivatives have also been studied in micellar solutions.[854,888,963,964,981–987a] Work has been directed also to the development of new photosensitizers of type $[RuL_3]^{2+}$.[987b] The cation $[Ru(bpz)_3]^{2+}$ (bpz = 2,2′-bipyrazine) is a superior photosensitizer to $[Ru(bipy)_3]^{2+}$ and shows emission at 603 nm with a half-life of the excited state $t_{1/2} = 1.04\,\mu s$,[750–752] compared with a $t_{1/2} = 6.0\,\mu s$ for $[Ru(bipy)_3]^{2+}*$.[711,753] Whereas $[Ru(bipy)_3]^{2+}*$ is oxidatively quenched by triethanolamine to $[Ru(bipy)_3]^{3+}$, $[Ru(bpz)_3]^{2+}*$ is reductively quenched to $[Ru(bpz)_3]^{+}$ which undergoes electron transfer with MV^{2+} to yield MV^{+}.[750] This is consistent with the redox properties of $[Ru(bpz)_3]^{2+}$ which is oxidized and reduced at potentials ~0.5 V more positive than $[Ru(bipy)_3]^{2+}$.[752] Protonation equilibria for $[Ru(bpz)_3]^{2+}*$ have been measured[988] and ECL has been generated by reaction of $[Ru(bpz)_3]^{+}$ with $[Ru(bpz)_3]^{3+}$.[752] The single crystal X-ray structure of $[RuL_3]^{2+}$ (L = 4,7-dimethyl-2,3,8,9-dibenzo-5,6-dihydrophenanthroline) has been reported.[989] Photochemical studies on $[RuL_3]^{2+}$ (L = 2,2′-bithiazoline) indicate that aromatized cyclic ligands are not essential for charge-transfer emission,[990] while $[RuL_3]^{-}*$ (LH = 2,2′-dipyridyl amine) has been reported to show spatially isolated single ring emission.[766] The luminescence of complexes containing nitro and phosphonium bipy ligands has been studied.[991a] More recently, covalently linked photosensitizer (bipy) and electron acceptor (MV^{2+}) complexes have been synthesized.[991b]



Scheme 25

The photochemical stability of $[Ru(bipy)_3]^{2+}$ towards ligand substitution reactions has been the mainstay of its use as a photosensitizer.[992,993] More recently however photosubstitution reactions have been reported.[767,768,994] The EIP model has been modified by Houten and Watts[995,996] to take into account high temperature substitution reactions by introducing a higher set of non-luminescent levels.[997,998] Substitution photochemistry of $[Ru(bipy)_3]^{2+}$ by Br^- is quenched by ferrocene three times as strongly as luminescence suggesting that the photoreactive LF state is not in thermal equilibrium with the luminescent excited state.[999] Photolysis of $[Ru(bipy)_3]^{2+}$ with X^- yields $[RuX_2(bipy)_2]$ ($X^- = Cl^-$,[1000] Br^-,[1001] I^-,[1002] ^-NCS,[1003] ^-NCO,[1004] ^-NCSe,[1004] NO_2^-,[1002] N_3^-,[1002] malonate,[1002] ^-CN[1002]). Solvolysis may also occur to give the complexes $[Ru(bipy)_2(NCMe)_2]^{2+}$,[757,1005] $[RuCl(bipy)_2S]$ (S = MeCN, $MeNO_2$)[1006] and $[RuX(bipy)_2DMF]^+$ (X = Br^-,[1001] ^-NCS[1003]); the role of chlorinated solvents in these photoreactions has been discussed.[1000] Association of H^+ in ground

state and excited state $[Ru(bipy)_3]^{2+}$ has been suggested[225,1007] leading to decomposition *via* loss of bipy ligands.[994,1008,1009] Monodentate bipy intermediates have been proposed in these reactions[767,994,1010,1011] which is consistent with data for the photoracemization of $[Ru(bipy)_3]^{2+}$ *via* rotation of five-coordinate intermediate species (**72**) (equation 85).[1012] The photoanation of $[Ru(bpz)_3]^{2+}$ in MeCN by Cl^- yields *cis*-$[RuCl(bpz)_2(NCMe)]^+$ and *cis*-$[RuCl_2(bpz)_2]$.[751]



(85)

(72)

There have been several reports of covalent hydration and pseudo-base formation in the reactions of $[RuL_3]^{2+}$ (L = bipy,[64,709] phen, 5-nitro-1,10-phenanthroline,[743,1013–1022] 2,2′-bipyrimidine[1023]) with a range of nucleophiles. These reactions are proposed to involve nucleophilic attack on the coordinated heterocyclic ligand to give in the case of CN^- attack on phen and 5-nitro-1,10-phenanthroline complexes, 2-, 6- or 9-cyano derivatives.[1014] The proposals for pseudo-base formation have come under severe criticism[1024–1029] although the yields of these products in solution are likely to be low.[1023,1030,1031] For $[RuL_3]^{2+}$ (L = 2,2′-bipyrimidine) ring cleavage is reported to occur in the presence of ^-OH to yield $[Ru(OH)(bipym)_2(pym)]^+$.[1023] The acidity of the 3,3′-protons in $[Ru(bipy)_3]^{2+}$ has been noted although covalent hydration was not observed directly.[1029,1032]

(c) $[RuL_3]^{3+}$

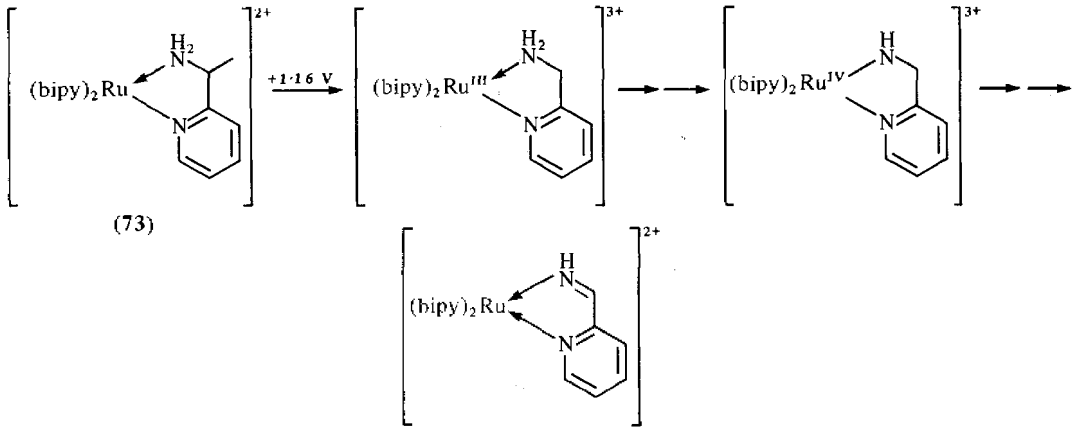
Complexes of type $[RuL_3]^{3+}$ can be prepared by chemical or electrochemical oxidation of $[RuL_3]^{2+}$ (Table 8) or as a product in the oxidative quenching of excited state $[RuL_3]^{2+}*$ (see above). The oxidation of $[Ru(bipy)_3]^{2+}$ by PbO,[837] Tl^{III},[1033] Cl_2,[722] and Ce^{IV}[1034] has been reported. $[Ru(bipy)_3]^{3+}$ shows a band near 680 nm ($\varepsilon = 407\,M^{-1}\,cm^{-1}$)[267,723] with no MLCT band near 454 nm as observed for $[Ru(bipy)_3]^{2+}$.[724] The ESR spectrum of $[Ru(bipy)_3]^{3+}$ is consistent with a Ru^{III} d^5 configuration.[604] $[RuL_3]^{3+}$ (L = bipy, phen) have been reported not to racemize or dissociate in water, but react to give covalently hydrated species.[64] The electrochemical formation and spectroscopy of $[Ru(bipy)_3]^{3+}$ in $AlCl_3$/*N*-(1-butyl)pyridinium chloride melts have been described.[1035]

$[Ru(bipy)_3]^{3+}$ undergoes outer-sphere electron transfer with reducing agents such as alkyl radicals,[1036] BH_4^-,[1037] cyclohexanone,[1038] ^-OH,[1039] $[Ru(bipy)_3]^{2+}$,[152,1040] Co^{II},[1040–1043] Co^{III},[1044] $[Cr(bipy)_3]^{3+}*$,[1045] $[Fe(OH_2)_6]^{2+}$,[271,1046–1048] $[Fe(CN)_6]^{4-}$,[1047] $[Mo(CN)_6]^{2-}$,[1047] $SbCl_3$[860] and Hg^I.[722] For the oxidation of $[Fe(OH_2)_6]^{2+}$ by $[Ru(phen)_3]^{3+}$ and $[Ru(bipy)_3]^{3+}$, $\Delta H^{\neq} = -5.65, -1.26\,kJ\,mol^{-1}$; $\Delta S^{\neq} = -151, -138\,J\,K^{-1}\,mol^{-1}$ respectively.[1043] The reaction of $[Ru(phen)_3]^{3+}$ with $[Ru(bipy)_3]^{2+}$ proceeds with a rate constant $k = 1.2 \times 10^9\,M^{-1}\,s^{-1}$ and $\Delta H^{\neq} = 32.2\,kJ\,mol^{-1}$, $\Delta S^{\neq} = -27.6\,J\,K^{-1}\,mol^{-1}$.[1046] The oxidation of H_2O to O_2 has been achieved using Co^{II} in the presence of $[Ru(bipy)_3]^{3+}$.[1049]

The electrochemistry of $[RuL_3]^{2+}$ (L = bipy, phen) has been extended by the measurement of the $[RuL_3]^{4+/3+}$ redox couples in liquid SO_2 at +2.78 V and +2.60 V *vs.* SCE respectively.[723,726]

(vii) Bidentate heterocyclic complexes $[RuL_2L']^{n+}$, $[RuLL'L'']^{n+}$

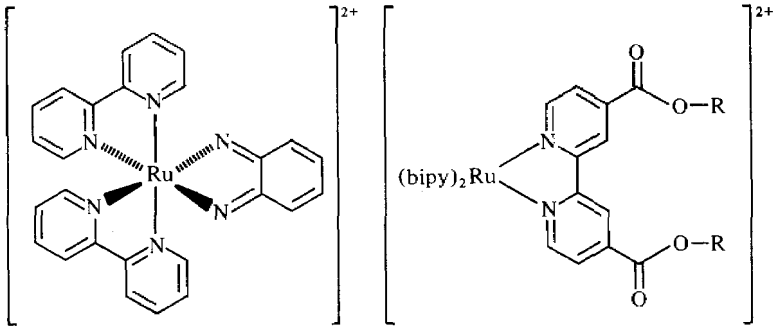
A range of mixed ligand complexes $[RuL_2L']^{2+}$ have been prepared and their spectroscopic, luminescent and redox properties studied (Table 9). The absorption and CD spectra of $[Ru(phen)_2(bipy)]^{2+}$ and $[Ru(bipy)_2(phen)]^{2+}$ have been discussed.[1052] $[Ru(bipy)_2L]^{2+}$ [L = 2-(aminomethyl)pyridine, 2-(1-aminoethyl)pyridine (**73**)] undergoes oxidative dehydrogenation on oxidation at +1.16 V *vs.* SCE (Scheme 26).[1068,1074] The rate-determining step of reaction is deprotonation at the α carbon atom with concomitant two electron transfer from ligand to metal.[1074] The single crystal X-ray structure of (**73**) shows[1074] Ru—N(py) = 2.062 Å, Ru—$N(NH_2)$ = 2.121 Å, Ru—N(bipy) = 2.064, 2.046, 2.044, 2.057 Å. The single crystal X-ray structure of the related complex $[Ru(bipy)_2(NH)_2C_6H_4]^{2+}$ (**74**) has been reported and shows short Ru—$N(NH)_2C_6H_4$ distances of 2.038, 1.996 Å suggesting strong back-bonding from Ru^{II} to the diimino ligand.[1069]



(73)

Scheme 26

The luminescent properties of the excited state species $[RuL_2L']^{2+}$* have been investigated with the aim of developing more efficient photosensitizers than $[Ru(bipy)_3]^{2+}$.[733] Mixed ligand Ru^{II} complexes incorporating surfactant long chain ester derivatives of bipy have been synthesized, for example (**75**) and (**76**),[888,1055,1061–1063,1075–1083] and their luminescence investigated in micellar solutions.[1061–1063,1079,1081] These surfactant complexes are generally found to be inactive for the photochemical cleavage of water,[986,1059,1060,1084,1085] hydrolysis of the ester moieties and destruction of assemblies being a particular problem with these systems.[986] Irradiation of $[Ru(bipy)_2L]^{2+}$ (L = 2,2′-bipyridine-4,4′-dicarboxylic acid) in the presence of edta, MV^{2+} and Pt catalyst produces H_2 at one tenth of the rate as observed for $[Ru(bipy)_3]^{2+}$.[1086] This is ascribed to the electron withdrawing effect of the carboxyl or ester functions to bimolecular quenching of the excited state by water;[1086] H^+ transfer in the excited state species has been studied and the luminescence measured as a function of pH.[1087] The deprotonated complex was found to be a stronger base in the excited state than in the ground state,[1087] while for complexes of 4,7-dihydroxy-1,10-phenanthroline, an increase in acidity has been observed in the excited state.[1053] The linking of complexes $[RuL_2L']^{2+}$ to polystyrene supports,[1088] and the preparations of vinyl polymers[953,1056,1089] and chemically modified electrodes[1090,1091] have been reported.



(74)

(75) R =

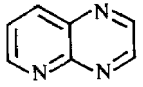
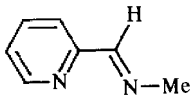
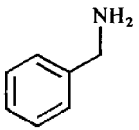
(76) R = $C_{18}H_{37}$

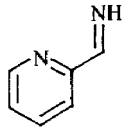
The lifetimes of excited state $[Ru(bipy)_2L]^{2+}$* vary according to L; for example, the half-life for $[RuL_3]^{2+}$* (L = 2,2′-bibenzimidazole) $t_{1/2} = 1.00\,\mu s$, for $[Ru(bipy)_2L]^{2+}$* $t_{1/2} = 3.00\,\mu s$ as compared with $t_{1/2} = 6.0\,\mu s$ for $[Ru(bipy)_3]^{2+}$*.[711,753] This has led to the study of excited state species for mixed ligand systems particularly with regard to localized and delocalized formalisms for $[RuL_2L']^{2+}$*. Using the EIP model, Crosby has proposed ligand–ligand coupling in the excited and ground state of $[Ru(bipy)_2L]^{2+}$ (L = 4,4′-dimethyl-2,2′-bipyridine, 4,4′-diphenyl-2,2′-bipyridine, 5,6-dimethyl-1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline),[806]

Table 9 Synthesis, Absorption Spectra and Redox Properties of Complexes $[RuL_2L']^{2+}$

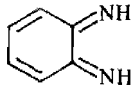
Ligand (L)	*Synthesis*	*λ (ε)* (nm × 10^{-4} $M^{-1}cm^{-1}$)	$E_{\frac{1}{2}}$ (V)	*Reference electrode (solvent)*
$[Ru(bipy)_2L]^{2+}$				
1,10-phen	$[RuCl_2(bipy)_2]$, L, EtOH, Δ, 12 h[1050–1052]	449 (1.57), 286 (6.32), 264 (5.76)[739]	+1.29, −1.45, −1.65, −1.75[701,739]	SSCE (MeCN)
2,9-$(Me)_2$phen	$[RuCl_2(bipy)_2]$, L, EtOH, H_2O, Δ[762]	452 (1.36)[762]	+1.18[762]	SCE (MeCN)
4,7-$(Ph)_2$phen	$[RuCl_2(bipy)_2]$, L, EtOH, H_2O, Δ, 4.5 h[1051]	452 (1.48), 428 (1.39), 388 (0.7), 280 (11.7), 255 (4.5)[737]	+1.245, −1.320, −1.50 −1.73[737]	SHE (MeCN)
4,7-$(OH)_2$phen (pH 1)	$[RuCl_2(bipy)_2]$, L, MeOH, H_2O, Δ, 1 h[737]	460 (1.26), 445 (1.29), 288 (6.53), 253 (7.06)[1053]		
4,7-$(O^-)_2$phen (pH 13)		495 (1.0), 450 (0.97), 370 (1.87), 292 (6.64), 258 (7.15)[1053]		
2-(OMe)phen	$[RuCl_2(bipy)_2]$, L, Δ, EtOH[1054]	446 (1.55)[1054]	+1.47, −1.11, −1.33, −1.65[1054]	Ag/Ag^+ (acetone)
2-$(C(O)NHC_3H_7)$phen	$[RuCl_2(bipy)_2]$, L, Δ, EtOH[1054]	446 (1.62)[1054]	+1.50, −1.03, −1.33, −1.59[1054]	Ag/Ag^+ (acetone)
5-(NH_2)phen	$[RuCl_2(bipy)_2]$, L, H_2O, Δ, 24 h[745]	455 (1.59), 370 (1.06)[745]	+1.31[745]	SSCE (MeCN)
3,3-$(Me)_2$bipy	$[RuCl_2(bipy)_2]$, L, EtOH, Δ[732]	453 (1.26), 287 (7.14), 239 (2.43)[732]	+1.22, −1.37[733]	SHE (MeCN)
4,4′-$(Me)_2$bipy	$[RuCl_2(bipy)_2]$, L, EtOH, Δ, 3 h[1055]	457 (1.1), 433 (1.0), 394 (0.48), 354 (0.4), 287 (6.5)[1055]		
4,4′-$(Bu^t)_2$bipy	$[RuCl_2(bipy)_2]$, MeOH, H_2O, L, Δ, 1 h[737]	450 (1.45), 429 (1.3), 390 (0.7), 356 (0.69), 325 (1.09)[733,737]	+1.21, −1.37, −1.53, −1.82[733,737]	SHE (MeCN)
4,4′-$(Cl)_2$bipy	$[RuCl_2(bipy)_2]$, L, MeOH, ethylene glycol, Δ[737]	448 (1.26), 396 (0.68), 357 (0.66), 350 (0.63), 327 (0.95)[737]	+1.30, −1.41, −1.49, −1.74[737]	SHE (MeCN)
4-(NO_2)bipy	$[RuCl_2(bipy)_2]$, L, MeOH, H_2O, Δ, 2 h[737]	493 (1.11), 429 (1.12), 338 (0.88), 286 (6.09), 254 (2.47)	+1.37, −0.56, −1.17, −1.53, −1.78[737]	SHE (MeCN)
6-(4′-Tolyl)bipy	$[RuCl_2(bipy)_2]$, L, MeOH, H_2O, Δ, 43 h[1056]	618 (10.0), 480 (13.5)[1056]		
6-(4′-Styryl)bipy	$[RuCl_2(bipy)_2]$, L, Δ, MeOH, H_2O[1056]	616 (10.0), 480 (13.8)[1056]		
4,4′-$(COOEt)_2$bipy[a]	$[RuCl_2(bipy)_2]$, L, EtOH, Δ, 5 h[687]		+1.38, −0.93, −1.36, −1.56, −1.90[687]	SCE (DMF)
4,4′-$(COOH)_2$bipy	$[Ru(ox)(bipy)_2]$, L, $(CaOAc)_2$, Δ, EtOH[687,986,1059]	475, 420 (pH = 0.6), 455 (pH = 12.5)[986]	+1.36, −1.38, −1.58[1058]	SSCE (MeCN)
	$[RuCl_2(bipy)_2]$, L, Δ, EtOH[1058]			
4,4′-$(COOC_{27}H_{46})_2$bipy	$[RuCl_2(bipy)_2]$, L, Δ[986]			
	$[Ru(bipy)_2(bipy(CO_2H)_2)]$, SO_2Cl_2, ROH[986]			
4,4′-$(COOC_{18}H_{37})_2$bipy	$[RuCl_2(bipy)_2]$, L, Δ[1060]	478 (1.31), 420[986]		
4-$(COOC_{18}H_{37})$bipy	$[RuCl_2(bipy)_2]$, L, Δ[1059]	485 (—), 425 (—)[1059]		
4-$(COOC_{18}H_{37})$4′(COOEt)bipy	$[RuCl_2(bipy)_2]$, L, Δ[1059]	485 (—), 425 (—)[1059]		
4,4′-$(C(O)NHC_{12}H_{25})$bipy	$[RuCl_2(bipy)_2]$, L, EtOH, Δ[1061,1062]	482 (—)[1063]		
Naphthyridine	$[RuCl_2(bipy)_2]$, L, H_2O, acetone, Δ[739]	434 (1.12), 286 (5.26), 253 (—), 243 (2.25)[739]	+1.26[739]	SSCE (MeCN)
2-Methylnaphthyridine	$[RuCl_2(bipy)_2]$, L, H_2O, acetone, Δ[739]	434 (1.13), 286 (5.07), 255 (—), 243 (2.21)[739]	+1.25[739]	SSCE (MeCN)

Table 9 (*Continued*)

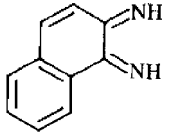
Ligand (L)	*Synthesis*	*λ(ε)* (nm, 10^{-4} M^{-1} cm^{-1})	$E_{\frac{1}{2}}$ (V)	*Reference electrode (solvent)*
2,7-Dimethylnaphthyridine	$[RuCl_2(bipy)_2]$, L, H_2O, acetone, Δ[739]	453 (1.26), 286 (7.92), 254 (2.51), 243 (—)[739]	+1.32[739]	SSCE (MeCN)
	$[RuCl_2(bipy)_2]$, L, H_2O, acetone, Δ[739]	434 (1.02), 284 (5.0), 254 (—), 245 (2.07)[739]	+1.32[739]	SSCE (MeCN)
4,4′-Dimethylbipyrimidine	$[RuCl_2(bipy)_2]$, L, EtOH, H_2O[762]	442 (1.09)[762]	+1.25[762]	SCE (MeCN)
2,2′-Bipyrimidine[b]	$[RuCl_2(bipy)_2]$, L, Δ, EtOH, H_2O, Δ[746,762] $[RuCl_2(bipy)_2]$, Ag^+, acetone, L, Δ[1064] $[RuCl_2(bipy)_2]$, L, ethylene glycol[747]	480 (—), 422 (0.97), 360 (0.64), 322 (—), 294 (4.8), 236 (4.0)[747,1064]	+1.36, −1.01, −1.45[1064]	SSCE (MeCN)
2,2′-Biquinoline[c]	$[RuCl_2(bipy)_2]$, L, ethylene glycol, Δ, 1 h[737] $[RuCl_2(bipy)_2]$, L[1065]	526 (0.87), 494 (0.58), 439 (0.81), 400 (0.44), 370 (1.71), 350 (2.04)[737,1065]	+1.33, −0.905, −1.37, −1.66[737]	SHE (MeCN)
2,2′-Bipyrazine	$[RuCl_2(bipy)_2]$, L, ethylene glycol, Δ[747]	473 (0.99), 414 (1.0), 386 (—), 343 (—), 283 (6.3), 242 (2.4)[747]	+1.49, −0.91, −1.45, −1.68[747]	SSCE (MeCN)
2-(2′-Pyridyl)quinoline	$[RuCl_2(bipy)_2]$, L, EtOH, Δ, 4 h[754,1065]	476 (—), 452 (1.05), 289 (5.16), 275 (4.97), 247 (3.58)[1065]		
2-(Phenylazo)pyridine	$[RuCl_2(bipy)_2]$, L, MeOH, H_2O, Δ, 3.5 h[1066]	494 (0.88), 364 (1.22), 278 (4.5)[1066]	+1.6, −0.52, −1.26, −1.81, −2.15, −2.53[758]	SCE (MeCN)
2-(3′-Tolylazo)pyridine	$[RuCl_2(bipy)_2]$, L, MeOH, Δ[1066]	494 (0.86), 368 (1.16), 280 (4.45)[1066]	+1.6, −0.52, −1.26, −1.81, −2.13, −2.47[758]	SCE (MeCN)
1-(2′-Pyridyl)-3,5-dimethylpyrazole	$[RuCl_2(bipy)_2]$, L, EtOH, H_2O, Δ, 2 h[757]	450 (1.08), 413 (—), 368 (—), 350 (—)[757]	+1.22[757]	SCE (MeCN)
2-(2′-Pyridyl)thiazole	$[RuCl_2(bipy)_2]$, L, MeOH, H_2O, Δ, 2 h[756]	453 (—)[756]	+1.26[756]	SHE (1 M HNO_3)
2,3-Bis(2′-pyridyl)pyrazine	$[RuCl_2(bipy)_2]$, L, Δ[1067]		+1.58[1067]	SHE (MeCN)
	$[RuCl_2(bipy)_2]$, MeOH, H_2O, L, Δ, 2 h[737]	459 (1.46), 430 (1.2), 344 (0.59), 322 (0.85), 286 (11.6)[737]	+1.28, −1.25, −1.55, −1.79[737]	SHE (MeCN)
	$[RuCl_2(bipy)_2]$, L[1068]	471 (1.02), 340 (1.08)[1068]	+1.16[1068] +1.12 +0.76	SSCE (propylene carbonate) SSCE (MeCN) SSCE (1M H_2SO_4)



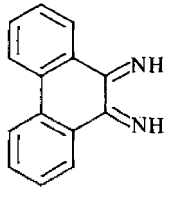
[Ru(bipy)$_2$LH$_2$], +1.16 V[1068] | 470 (1.36)[1068] | +1.33[1068] | SSCE (MeCN)



[RuCl$_2$(bipy)$_2$], LH$_2$, Zn, 100°C; NH$_3$[1069]



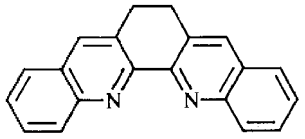
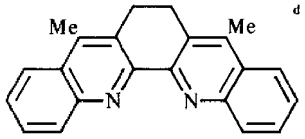
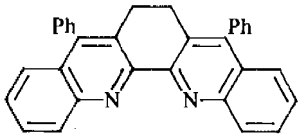
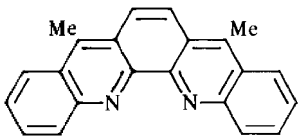
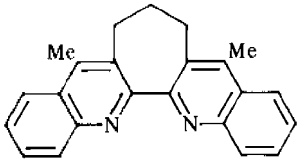
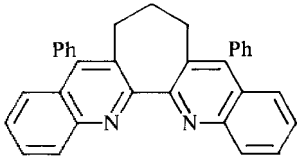
[RuCl$_2$(bipy)$_2$], LH$_2$, Zn, 100°C; NH$_3$[1069]



[RuCl$_2$(bipy)$_2$], LH$_2$, Zn, 100°C; NH$_3$[1069]

(2-Pyridyl)imidazole	[RuCl$_2$(bipy)$_2$], L, CaCO$_3$, Δ, 3 h[1070]	460 (1.05), 426 (1.00), 388 (—), 289 (7.08), 244 (2.24)[1070]	+1.14, −1.52, −1.78[1070]	SCE (MeCN)
(2-Pyridyl)imidazole$^-$	[Ru(LH)(bipy)$_2$]$^{2+}$, NaOMe[1070]	500 (0.91), 446 (—), 377 (—), 293 (5.75), 245 (2.14)[1070]	+0.76(i), −1.49, −1.73[1070]	SCE (MeCN)
(2-Pyridyl)benzimidazole	[RuCl$_2$(bipy)$_2$], L, CaCO$_3$, Δ, 3 h[1070] [RuCl$_2$(bipy)$_2$], L, EtOH, H$_2$O, Δ[1071]	458 (1.29), 317 (2.57), 289 (6.03), 244 (3.16)[1070]	+1.17, −1.49, −1.76[1070,1071]	SCE (MeCN)
(2-Pyridyl)benzimidazole$^-$	[Ru(LH)(bipy)$_2$]$^{2+}$, NaOMe[1070,1071] [RuCl$_2$(bipy)$_2$], L, EtOH, H$_2$O[762]	493 (0.95), 328 (2.29), 293 (6.03), 246 (3.89)[1070]	+0.72, −1.46, −1.70[1070,1071]	SCE (MeCN)
Biimidazole	[RuCl$_2$(bipy)$_2$], L, CaCO$_3$, Δ[1070]	473 (0.93), 340 (1.07), 289 (6.03), 242 (2.34)[1070]	+1.04, −1.66, −1.96[1070]	SCE (MeCN)
Biimidazole$^-$	[Ru(LH$_2$)(bipy)$_2$]:NaOMe (1:1)[1070]	513 (0.95), 334 (1.0), 292 (5.37), 244 (2.51)[1070]	+0.59(i), −1.64, −1.92[1070]	SCE (MeCN)
Biimidazole^{2-}	[Ru(LH$_2$)(bipy)$_2$]:NaOMe (1:2)[1070]	562 (0.85), 360 (0.83), 294 (4.90), 244 (3.09)[1070]	+130.2(i), −1.63, −1.92[1070]	SCE (MeCN)
Bibenzimidazole	[RuCl$_2$(bipy)$_2$], L, CaCO$_3$, Δ[1070,1072]	463 (1.17), 350 (4.36), 332 (3.72), 291 (6.17), 243 (3.80)[753,1070,1072]	+1.12, −1.60, −1.90[1070,1072]	SCE (MeCN)
Bibenzimidazole$^-$	[Ru(LH$_2$)(bipy)$_2$]:NaOMe (1:1)[1070,1072]	507 (0.91), 341 (3.39), 327 (3.09), 294 (5.89), 243 (4.37)[1070,1072]	+0.72, −1.53, −1.86[1070,1072]	SCE (MeCN)
Bibenzimidazole^{2-}	[Ru(LH$_2$)(bipy)$_2$]:NaOMe (1:2)[1070,1072]	551 (0.91), 334 (3.02), 298 (5.50), 245 (6.17)[1070,1072]	+0.43, −1.58, −1.87[1070,1072]	SCE (MeCN)

Table 9 (*Continued*)

Ligand (L)	*Synthesis*	*λ (ε)* (nm, $10^{-4}M^{-1}cm^{-1}$)	$E_{\frac{1}{2}}$ (V)	*Reference electrode (solvent)*
	$[RuCl_2(bipy)_2]$, L, ethylene glycol, 196°C, 45 min[737]	528 (0.92), 440 (0.84), 393 (2.19), 372 (1.80), 345 (2.02)[737]	+1.31, −0.91, −1.385, −1.665[737]	SHE (MeCN)
 [d]	$[RuCl_2(bipy)_2]$, L, ethylene glycol, 160°C, 2 h[737]	528 (0.94), 448 (0.83), 391 (1.82), 370 (1.73), 347 (2.06)[737]	+1.255, −1.0, −1.41, −1.675[737]	SHE (MeCN)
	$[RuCl_2(bipy)_2]$, L, ethylene glycol, 196°C, 1 h[737]	532 (1.09), 496 (0.64), 441 (0.82), 394 (2.18), 372 (2.09)[737]	+1.3, −0.905, −1.370, −1.66[737]	SHE (MeCN)
	$[RuCl_2(bipy)_2]$, L, ethylene glycol, 160°C, 2 h[737]	554 (0.85), 518 (0.63), 444 (1.54), 390 (0.72), 360 (1.4)[737]	+1.275, −0.94(i), −1.47(i) −1.71(i), −1.645[737]	SHE (MeCN)
	$[RuCl_2(bipy)_2]$, L, ethylene glycol, 196°C, 1 h[737]	501 (0.53), 438 (0.83), 350 (1.60), 327 (1.72)[737]	+1.24, −1.08, −1.435, −1.685[737]	SHE (MeCN)
	$[RuCl_2(bipy)_2$, L, ethylene glycol, 196°C, 2 h[737]	516 (0.82), 440 (0.91), 441 (0.77), 354 (2.47), 286 (5.98)	+1.29, −0.99, −1.4, −1.67[737]	SHE (MeCN)

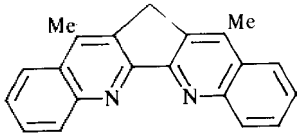
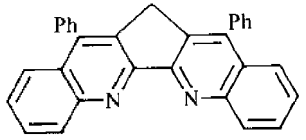
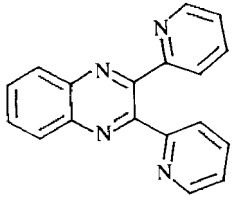
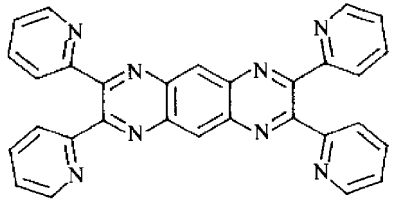
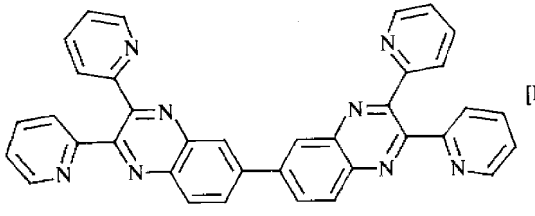
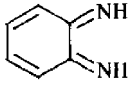
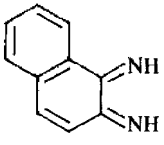
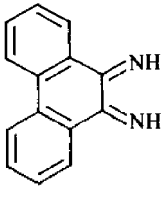
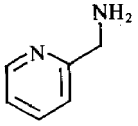
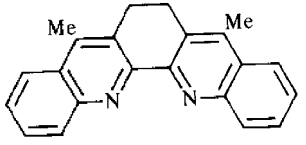
	$[RuCl_2(bipy)_2]$, L, ethylene glycol, 160°C, 2 h[737]	496 (0.78), 449 (0.93), 376 (3.94) 366 (1.90), 355 (2.21)[737]	+1.26, −1.03, −1.485, −1.71[737]	SHE (MeCN)
	$[RuCl_2(bipy)_2]$, L, ethylene glycol, 160°C, 2 h[737]	511 (0.34), 446 (0.25), 385 (0.60) 373 (0.47), 363 (0.54)	+1.295, −0.895, −1.44, −1.645, −1.985[737]	SHE (MeCN)
	$[RuCl_2(bipy)_2]$, Ag^+, acetone, L, Δ, 24 h[1064]	515 (0.81), 427, 348, 284 (68.0), 253[1064]	+1.41, −0.78, −1.41[1064]	SSCE (MeCN)
	$[RuCl_2(bipy)_2]$, Ag^+, acetone, L, Δ, 24 h[1064]	573 (0.8), 415 (2.3), 398 (2.3), 285 (8.8), 256 (—)[1064]	+1.42, −0.42, −0.92[1064]	SSCE (MeCN)
	$[RuCl_2(bipy)_2]$, H_2O, MeOH, HCl, L, Δ, 4 h[1073]	525 (0.85), 420 (—), 381 (0.32), 284 (9.5), 244 (5.7)[1073]	+1.41, −0.62, −1.41[1073]	SSCE (MeCN)
$[Ru(bipy)L_2]^{2+}$				
1,10-phen	$[RuCl_3(bipy)]$, L, EtOH, H_2O, Δ, 48 h[1051] $[Ru(bipy)py_4]$, L, Δ^{612}	448 (1.65), 430 (—), 284 (—), 262 (9.17)[739]	+1.30[739]	SSCE (MeCN)
4,7-$(Ph)_2$phen 5-(NH_2)phen	$[RuCl_3(bipy)]$, L, EtOH, H_2O, Δ, 8 h[1051] $[RuCl_4(bipy)]^-$, L, DMF, Δ^{745}	462 (1.66), 364 (1.69)[745]	+1.39[745]	SSCE (MeCN)

Table 9 (*Continued*)

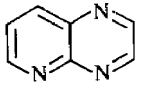
Ligand (L)	*Synthesis*	*λ (ε)* (nm, 10^{-4} M^{-1} cm^{-1})	$E_{\frac{1}{2}}$ (V)	*Reference electrode (solvent)*
3,3′-$(Me)_2$bipy	$[RuCl_2L_2]$, bipy, EtOH, Δ[732]	454 (1.23), 342 (1.09), 289 (6.06), 235 (2.82)[732]	+1.18, −1.41[733]	SHE (MeCN)
4,4′-$(Bu^t)_2$bipy		454 (1.53)[733]	+1.16, −1.39[733]	SHE (MeCN)
2,2′-Biquinoline	$[RuCl_2L_2]$, bipy, Δ[1065]	546 (0.73), 480 (0.56), 444 (0.28), 407 (0.42), 379 (2.16)[737,1065]	+1.395, −0.82, −1.05, −1.61, −1.855[737]	SHE (MeCN)
	$[RuCl_3(bipy)]$, L, ethylene glycol, Δ, 2 h[737]			
2,2′-Bipyrazine	$[RuCl_4(bipy)]^-$, L, ethylene glycol[747]	463 (1.2), 415 (0.92), 375 (0.56), 338 (—)[747]	+1.72, −0.79, −1.02, −1.58[747]	SSCE (MeCN)
2,2′-Bipyrimidine	$[RuCl_4(bipy)]^-$, L, ethylene glycol[747]	460 (—), 420 (0.94), 368 (0.98), 326 (1.2)[747]	+1.55, −0.95, −1.13[747]	SSCE (MeCN)
2-(2′-Pyridyl)quinoline	$[RuCl_3(bipy)]$, L, EtOH, H_2O, Δ, 24 h[754]	480 (1.11), 455, 307 (4.26), 274 (5.38)[1065]		
	$[RuCl_2L_2]$, bipy, Δ[1065]			
2-(Phenylazo)pyridine (pap)	$[Ru_2L_2(OH_2)_2]^{2+}$, bipy, Δ[611]	514 (0.93), 436 (0.42), 368 (2.06), 312 (2.06), 282 (3.06)[611,758]	+1.88, −0.21, −0.72, −1.47, −1.75, −2.06, −2.44[758]	SCE (MeCN)
2-(3′-Tolylazo)pyridine (tap)		510 (1.04), 364 (2.43), 314 (2.39), 288 (3.23)[758]	+1.89, −0.21, −0.72, −1.48, −1.78, −2.11, −2.49[758]	SCE (MeCN)
2-(2′-Pyridyl)thiazole	$[RuCl_4(bipy)]^-$, L, EtOH, H_2O, Δ, 2 h[756]	458[756]	+1.27[756]	SHE (1 M HNO_3)
1-(2′-Pyridyl)-3,5-dimethylpyrazole	$[RuCl_3(bipy)]$, L, H_2O, Δ, 24 h[757]	435 (1.22), 377, 272[757]	+1.21[757]	SCE (MeCN)
	$[RuCl_3(bipy)]$, LH_2, Zn; NH_3[1069]			
	$[RuCl_3(bipy)]$, LH_2, Zn; NH_3[1069]			
	$[RuCl_3(bipy)]$, LH_2, Zn; NH_3[1069]			



[Ru(bipy)py$_4$], L, Δ^{612}



	[$RuCl_2L_2$], bipy, ethylene glycol, 150°C, 3 h[737]	559 (0.96), 489 (0.63), 421 (0.26), 395 (2.75), 375 (2.43), 355 (3.20)[733,737]	+1.255, −0.92, −1.135, −1.665, −1.925[733,737]	SHE (MeCN)
[Ru(phen)$_2$L]$^{2+}$				
2-(2′-Pyridyl)quinoline	[$RuCl_2$(phen)$_2$], L, $\Delta^{740,1065}$	476 (—), 442 (1.31), 390 (—), 358 (0.75), 314 (2.04)[1065]		
2,2′-Biquinoline	[$RuCl_2$(phen)$_2$], L, Δ^{1065}	523 (0.95), 439, (0.96), 378 (2.25), 359 (1.98), 336 (2.19)[1065]		
3,3′-(Me)$_2$bipy	[$RuCl_2$(phen)$_2$], L, EtOH[732]	450 (1.52), 423 (1.47), 264 (7.96), 224 (6.04)[732]		
4,7-(OH)$_2$phen		460 (1.36), 440 (1.36), 288 (6.18), 245 (6.23)[1053]		
Naphthyridine	[$RuCl_2$(phen)$_2$], L, H_2O, acetone, Δ^{739}	426 (1.45), 413 (—), 262 (7.59)[739]	+1.27[739]	SSCE (MeCN)
2-Methylnaphthyridine	[$RuCl_2$(phen)$_2$], L, H_2O, acetone, Δ^{739}	417 (1.38), 262 (8.15)[739]	+1.26[739]	SSCE (MeCN)
2,7-Dimethylnaphthyridine	[$RuCl_2$(phen)$_2$], L, H_2O, acetone, Δ^{739}	448 (1.40), 262 (9.12)[739]	+1.33[737]	SSCE (MeCN)



	[$RuCl_2$(phen)$_2$], L, H_2O, acetone, Δ^{739}	428 (1.20), 262 (7.97)[739]	+1.33[739]	SSCE (MeCN)
[Ru(phen)L$_2$]$^{2+}$				
2-(2′-Pyridyl)quinoline (pq)	[$RuCl_2L_2$], phen, $\Delta^{740,1065}$	480 (—), 453 (1.17), 393 (0.55), 360 (—), 315 (3.23),[1065]		
2,2′-Biquinoline (biq)	[$RuCl_2L_2$], phen, Δ^{1065}	551 (0.87), 478 (0.65), 422 (—), 406 (—), 380 (2.55)[1065]		
[Ru(pq)$_2$(biq)]$^{2+}$	[$RuCl_2$(pq)$_2$], biq, Δ^{1065}	530 (0.74), 478 (0.94), 380 (1.32), 314 (4.69), 268 (6.86)[1065]		
[Ru(pq)(biq)$_2$]$^{2+}$	[$RuCl_2$(biq)$_2$], pq, Δ^{1065}	533 (0.76), 517 (0.76), 483 (0.78), 379 (2.49), 325 (4.84)[1065]		
[Ru(bipyrim)(4,4′-Me$_2$bipy)$_2$]$^{2+}$	[$RuCl_2$(4,4′-Me$_2$bipy)$_2$], bipyrim, EtOH, Δ^{762}		−1.52, −2.05, −2.26[734]	Ag/Ag$^+$ (MeCN)
[Ru(bipyrim)(5,5′-Me$_2$bipy)$_2$]$^{2+}$	[$RuCl_2$(5,5′-Me$_2$bipy)$_2$], bipyrim, EtOH, Δ^{762}		−1.53, −2.12, −2.36[734]	Ag/Ag$^+$ (MeCN)
[Ru(pap)$_2$(tap)]$^{2+}$	[Ru(pap)$_2$(OH$_2$)$_2$]$^{2+}$, tap, Δ^{758}	492 (1.14), 464 (1.04), 370 (3.01), 320 (1.81)[758]	+2.14, −0.11, −0.43, −0.91, −1.57, −1.92, −2.04[758]	SCE (MeCN)
[Ru(pap)(tap)$_2$]$^{2+}$	[Ru(tap)$_2$(OH$_2$)$_2$]$^{2+}$, pap, Δ^{758}	492 (1.31), 464 (1.22), 372 (3.43), 320 (2.09)[758]	+2.19, −0.08, −0.41, −0.91, −1.57, −1.93, −2.03[758]	SCE (MeCN)

Table 9 (*Continued*)

Ligand (L)	*Synthesis*	*λ (ε)* (nm, 10^{-4} M^{-1} cm^{-1})	$E_{\frac{1}{2}}$ (V)	*Reference electrode (solvent)*
$[Ru(pap)_2(dithiazole)]^{2+}$	$[Ru(pap)_2(OH_2)_2]$, dithiazole, Δ[611]			
$[Ru(4,4'\text{-}Me_2bipy)_2(4,7\text{-}(OH)_2phen)]^{2+}$		460 (1.36), 440 (1.36), 288 (6.18), 245 (6.23)[1053]		
$[Ru(3,4,7,8\text{-}Me_4phen)_2(4,7\text{-}(OH)_2phen)]^{2+}$		450 (1.67), 425 (1.85), 270 (9.41), 255 (7.56)[1053]		
$[Ru(bipy)(phen)(di\text{-}(2\text{-}pyridyl)amine)]^{2+}$ a	$[Ru(CO)_2(bipy)(phen)]^{2+}$, L, Δ[657]			

[a] See also reference 1057. [b] See also references 262 and 734. [c] See also reference 701. [d] See also references 701 and 733.

$[Ru(bipy)_2phen)]^{2+}$ and $[Ru(bipy)(phen)_2]^{2+}$.[806,1050,1092,1093] More recently, the absorption spectra of $[Ru(bipy)_x(phen)_{3-x}]^{2+}$ have been interpreted as superpositions of the tris chelate $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ end points,[1051] suggesting localized, weakly coupled excited states. For the complexes $[Ru(bipy)_2L]^{2+}$ (L = 2-(2′-pyridyl)quinoline,[754,1065,1094] 2,2′-biquinoline,[1065,1094,1095] 3,3′-biquinoline,[1094] 2,2′-bipyridine-4,4′-dicarboxylic acid,[1057] 2,2′-bipyridine-4,4′-diethyl carboxylate,[1057] 4,4′-dinitro-2,2′-bipyridine[1094]), $[Ru(bipy)L_2]^{2+}$ (L = 3,3′-biquinoline)[1094] and $[Ru(phen)_2L]^{2+}$ (L = 2-(2′-pyridyl)quinoline,[1094] bipy,[1096] 2,2′-biquinoline,[1094] dmch[1094]) no clear dual emission has been observed, emission occurring from the lowest energy charge transfer excited state localized on the ligand which is easiest to reduce.[754,1094,1097] A degree of energy transfer from phen to 2-(2-pyridyl)quinoline (L) has been suggested however for $[Ru(phen)_xL_{3-x}]^{2+}$.[740] The electrochemistry of $[RuL_2L']^{2+}$ (L = 2,2′-bipyrimidine, L′ = bipy, 4,4′-dimethyl-2,2′-bipyridine, 5,5′-dimethyl-2,2′-bipyridine) indicates that for the primary reduction product, the electron is localized on a single 2,2′-bipyrimidine ligand.[734] Kinetic and emission data for a range of mixed ligand complexes $[Ru(bipy)_{3-x}L_x]^{2+}$ (L = 2,2′-bipyrazine, 2,2′-bipyrimidine), $[RuL_{3-x}L'_x]^{2+}$ (L = 2,2′-bipyrimidine, L′ = 2,2′-bipyrazine) and $[RuLL'L'']^{2+}$ (L = bipy, L′ = 2,2′-bipyrimidine, L″ = 2,2′-bipyrazine) have been reported.[1098a] For synthetic and electrochemical work in this area see references 1098a–d. Spectro–electrochemical studies on $[Ru(bipy)_2L]^{1+/0/1-}$ (L = 2,2′-biquinoline, phen, dmch) have been carried out and the results related to a localized redox orbital model.[701]

$[Ru(bipy)_2L]^{2+}$ (L = 4,4′-dichloro-2,2′-bipyridine) is susceptible to attack by nucleophiles at the 4,4′ positions of the substituted bipy, reactivity being higher for the coordinated than for the free ligand.[1099]

(*viii*) *Bidentate heterocyclic complexes with carbon donor ligands*

A wide range of complexes of type $[RuL_2XY]^{2+/1+/0}$ (L = bidentate heterocycle) have been prepared and their chemical and photochemical properties investigated.[264–267,611,785,1100]

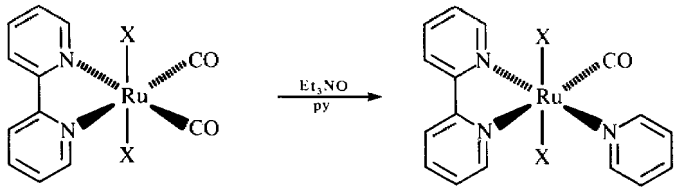
(a) Cyanides (see Section 45.3.1)

Cis-$[Ru(CN)_2(bipy)_2]$ can be isolated by treatment of $[Ru(ox)(bipy)_2]$ with NaCN in aqueous MeOH and chromatography on silica or alumina,[40,41,55,266] by photolysis of $[Ru(bipy)_3](CN)_2$[1002] or by reaction of $RuCl_3$ with L (L = bipy, phen or heterocyclic derivatives) followed by NaCN to yield $[Ru(CN)_2(L)_2]$.[1055,1082] The interaction of $[Ru(CN)_2(bipy)_2]$ with Ag^+,[1101] $[Pt(dien)]^{2+}$ (dien = diethylenetriamine),[1102] $[PtCl_3(C_2H_4)]^-$ and *cis*- and *trans*-$[PtCl_2(L)(L')]$ (L = C_2H_4, Me_2S; L′ = 4-methylpyridine)[50,1103] yields CN bridged 1:1 and 1:2 adducts and the luminescence properties of these complexes have been described. The excited state chemistry[1100] and electron transfer quenching reactions of $[Ru(CN)_2(L)_2]$* with pyridinium salts,[1104] O_2,[857] Cu^{2+},[1105] Fe^{3+},[879] paraquat[879] and aqueous acid[1106,1107] have been reported. The electrochemistry of $[Ru(CN)_2(bipy)_2]$ has been reported.[268b]

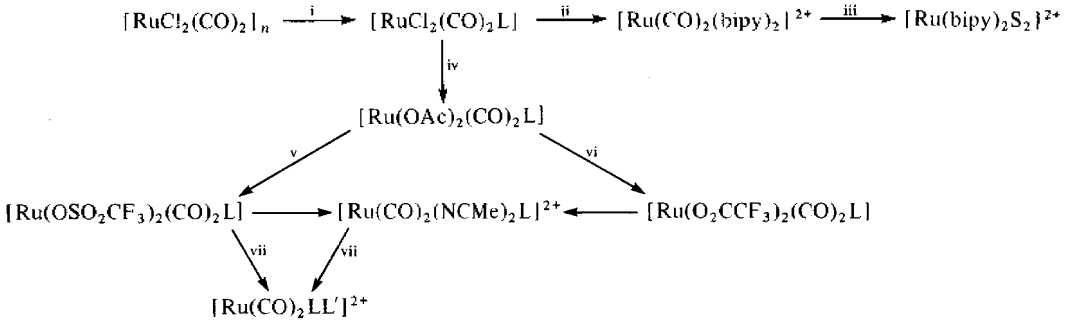
Hydrolysis of $[Ru^{III}(CN)_2(bipy)_2]^+$ yields $[Ru(bipy)_2(OH_2)_2]^{3+}$.[64]

(b) Carbonyls and related ligands

Reaction of the red solution obtained from refluxing RuX_3 with CO in EtOH with L yields $[RuX_2(CO)_2L]$ (X = Cl^-, Br^-; L = bipy, phen,[48,108,652,1108–1111] diphos[652,653]). Treatment of $[RuX_2(CO)_2L]$ with HX′ gives $[RuX'_2(CO)_2L]$ (X′ = $CF_3CO_2^-$, $MeCO_2^-$, $CF_3SO_3^-$) from which $[Ru(CO)_2(NCMe)_2L]^{2+}$ can be generated.[1108] The electrochemistry of $[RuCl_2(CO)_2L]$ (L = bipy, phen) has been reported.[625] The decarbonylation of $[RuX_2(CO)_2L]$ (**77**) (L = bipy, X = Cl^-, $CF_3CO_2^-$; L = phen, X = Cl^-, Br^-) with Et_3NO in pyridine yields $[RuX_2(CO)L(py)]$ (**78**) with retention of stereochemistry (equation 86),[658] while treatment of $[RuCl_2(CO)_2L]$, $[RuCl_2(CO)py(phen)]$ or $[Ru(CO)_2(phen)_2]^{2+}$ with Me_3NO in 2-methoxyethanol in the presence of L′ gives $[RuL(L')_2]^{2+}$ (L = phen, bipy, L′ = bipy, phen, 3,4,7,8-tetramethyl-1,10-phenanthroline).[657] $[RuCl_3(C_7H_8)CO]^-$ reacts with L to produce $[RuCl_2(CO)L]_n$ and $[RuCl_3(CO)L]^-$ (L = bipy, phen).[659] Treatment of $[Ru(O_3SCF_3)_2(CO)_2phen]$ with L (L = bipy, phen, 3,4,7,8-tetramethyl-1,10-phenanthroline,[1108] 4,4′-dimethyl-2,2′-bipyridine,[1112a] 4,4′-diisopropyl-2,2′-bipyridine[1112a]) yields the complexes $[Ru(CO)_2(phen)L]^{2+}$; likewise reaction of $[Ru(CO)_2(NCMe)_2L]^{2+}$ with L gives *cis*-$[Ru(CO)_2L_2]^{2+}$.[1108,1112a] $[Ru(CO)_2(bipy)_2](PF_6)_2$ catalyses the reduction of CO_2 to formic acid and CO under alkaline conditions, and to CO only under acidic conditions.[1112b] The formation of $[Ru(CO)_2py_2L]^{2+}$ (L = bipy, phen) has been achieved by treatment of $[Ru(CO)_2(NCMe)_2py_2]^{2+}$ with L.[656] Reaction of $[RuCl_2(CO)_2L]$ with L′H (L′H = acetylacetone, benzoylacetone, dibenzoylmethane, 2-hydroxyacetophenone, 2-hydroxbenzophenone, 3-hydroxy-4-methoxy-benzophenone, 8-hydroxyquinoline, salicylaldehyde, L = phen, bipy) yields $[Ru(CO)_2LL'_2]$.[1113] Scheme 27 illustrates the synthesis of some heterocyclic complexes of ruthenium carbonyls.



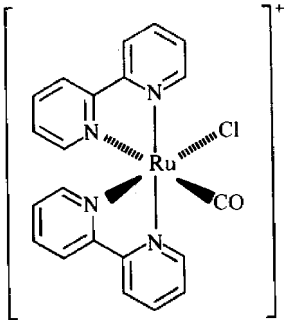
(77) (78) (86)



i, L (L = phen, bipy);[1108,1112,1114] ii, bipy, H_2O, EtOH, Δ;[1114] iii, hν, S (S = MeOH, H_2O, MeCN);[1114]
iv, HOAc or AgO_2CR;[656] v, CF_3SO_3H (L = phen);[656] vi, AgO_2CCF_3;[656]
vii, L′ (L′ = phen, bipy, 3,4,7,8-tetramethyl-1,10-phenanthroline)[656,1108,1112]

Scheme 27

Reaction of $RuCl_3$ with two equivalents of bipy in DMF yields $[RuCl_2(bipy)_2]$ together with *cis*-$[RuCl(CO)(bipy)_2]^+$ (**79**) in 30–50% yield.[1115–1117] *Cis*-$[RuCl(CO)L_2]^+$ (L = bipy, phen) can also be prepared by carbonylation of $[RuCl_2L_2]$[1116,1118] or by reaction of *cis*-$[RuCl(bipy)_2OH_2]^+$ with Ph-C≡CH in water at 100°C.[1119] Extended carbonylation of $[RuCl_2(bipy)_2]$ in the presence of Ag^+ yields $[Ru(CO)_2(bipy)_2]^{2+}$.[1116,1118] The single crystal X-ray structure of *cis*-$[RuCl(CO)(bipy)_2]^+$ (**79**) shows a six-coordinate Ru^{II} centre with Ru—C = 1.861, Ru—Cl = 2.396, Ru—N = 2.097, 2.066, 2.177, 2.104 Å.[1115] (**79**) catalyses the photochemical water-gas shift reaction.[1117,1120] $[RuCl(CO)(bipy)_2]^+$ reacts with N donor ligands L′ under reflux to give *cis*-$[Ru(CO)(bipy)_2L']^{2+}$, whereas the photochemical reaction yields *cis*-$[RuCl(bipy)_2L']^+$.[1115] The relevance of this reactivity to the possible synthesis of $[RuCl(bipy)_2(\eta^1\text{-bipy})]^+$ has been discussed.[1115] *Cis*-$[RuH(CO)L_2]^+$ can be prepared by treatment of $[RuCl(CO)L_2]^+$ (L = bipy, 4,4′-dimethyl-2,2′-bipyridine) with BH_4^-, and reacts with aqueous acid to give $[Ru(CO)(bipy)_2OH_2]^{2+}$ and H_2 (equation 87).[1121] Reaction of $[Ru(CO_3)(bipy)_2]$ with HCO_2H for 1 h affords $[Ru(O_2CH)(bipy)_2CO]^+$ which loses CO_2 in refluxing 2-methoxyethanol to yield *cis*-$[RuH(bipy)_2CO]^+$.[1121] The role of $[RuH(CO)(bipy)_2]^+$ as a possible intermediate in the photochemical generation of H_2 from H_2O by $[Ru(bipy)_2]^{2+}$ has been intimated.[1121]



(79)

$$[Ru(H)(CO)(bipy)_2]^+ + H_3O^+ \longrightarrow [Ru(CO)(bipy)_2(OH_2)]^{2+} + H_2 \quad (87)$$

Reaction of *cis*-$[Ru(bipy)_2(OH_2)_2]^{2+}$ with PhC≡CH yields *cis*-$[Ru(CO)(\eta^1\text{-}CH_2Ph)(bipy)_2]$,[1119] while treatment of *cis*-$[Ru(bipy)_2(acetone)_2]^{2+}$ with nbd gives $[Ru(C_7H_8)(bipy)_2]^{2+}$ ($\lambda = 421$ nm, $\varepsilon = 6780\,M^{-1}cm^{-1}$, $E_{1/2} = +1.70$ V *vs.* SSCE, in MeCN.[191] *Trans*-$[RuCl_2(C_7H_8)(bipy)]$ ($\lambda = 390$ nm, $\varepsilon = 1460\,M^{-1}cm^{-1}$, $E_{1/2} = +1.04$ V *vs.* SSCE in MeCN) has been prepared by reaction of $[RuCl_2(C_7H_8)]_n$ with bipy in acetone.[191]

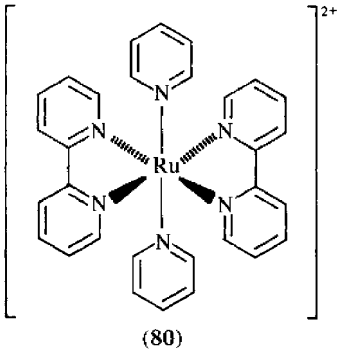
The single crystal X-ray structure of *trans*-$[Ru(bipy)_2(PPh_3)_2]^{2+}$[1122,1123] and the synthesis of related bis(phosphine) complexes[1005] have been reported. Reaction of $[RuCl_2L_2]$ (L = bipy,[1124], 2-(arylazo)pyridine[1066]) with phosphine, arsine and stibine ligands (L′) affords the complexes $[RuCl(L)_2L']^+$ while with bidentate ligands L′ $[Ru(bipy)_2L']^{2+}$ can be isolated.[1124] (See Section 45.5).

(*ix*) *Bidentate heterocyclic complexes with nitrogen donor ligands*

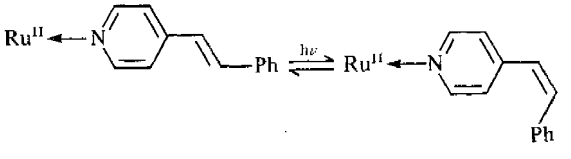
(a) Tertiary amines

A range of complexes of type *cis*-$[RuL_2L'_2]^{2+}$ and $[RuLL'_4]^{2+}$ (L = bidentate heterocycle; L′ = tertiary amine) has been synthesized and their electronic spectra analysed.[267,785] The synthesis of $[Ru^{II}L_2L'_2]^{n+}$ (L = bipy, phen, L′ = py,[264–266] pz,[1125] pyrazole,[1126] *cis*- and *trans*-4-stilbazole,[1127,1128] ^-NCS[64,266] substituted triazoles,[1129] MeCN,[266,757,1126] N_3^-,[266,1130] 3- and 4-nicotinic acid,[1058] 3- and 4-aminopyridine,[745] 4,4′-bipyridine;[850,1091] L = 4,4′-dimethyl-2,2′-bipyridine, L′ = py[1122,1123]) can be typically achieved by refluxing $[RuCl_2L_2]$ with L′,[611,1126,1127,1131] treatment of $[RuCl_2L_2]$ with Ag^+ followed by L′[1126,1132] or by reaction of L′ with $[RuL_2(OH_2)_2]^{2+}$.[1125,1133] The absolute configuration of *cis*-$[Ru(phen)_2py_2]^{2+}$ has been assigned *via* absorption and CD spectra.[266,1134] Reaction of *trans*-$[RuL_2(OH_2)_2]^{2+}$ with L′ (L = bipy, phen, L′ = py, MeCN, pyrazole) yields the complexes *trans*-$[RuL_2L'_2]^{2+}$.[612,1005,1122,1131,1133] The single crystal X-ray structure of *trans*-$[Ru(phen)_2py_2]^{2+}$ (**80**) shows Ru—N(py) = 2.097, Ru—N(phen) = 2.096, 2.100 Å[1122,1133] with unfavourable α-H interactions being proposed between heterocyclic rings;[1005] structural analysis of *trans*-$[RuL_2py_2]^{2+}$ (L = 4,4′-dimethyl-2,2′-bipyridine) confirms distorted bipyridyl ligands.[619,1123] Photolysis of *trans*-$[Ru(phen)_2py_2]^{2+}$ yields the *cis* isomer in good yield.[1133] Photolysis of $[Ru(bipy)_3]^{2+}$ or $[Ru(bpz)_3]^{2+}$ yields substituted products *via* loss of one bipy or bpz ligand.[751,757,1002,1004,1005] The electrochemistry of *cis*- and *trans*-$[Ru(bipy)_2py_2]^{2+}$ has been reported[268a,268b,691]; *cis*- and *trans*-$[Ru(bipy)_2py_2]^+$ have been electrogenerated and show intervalence charge transfer bands at 4350 cm^{-1} ($\varepsilon = 121\,M^{-1}cm^{-1}$) and 4090 cm^{-1} ($\varepsilon = 100\,M^{-1}cm^{-1}$) respectively.[691] Deprotonation reactions of $[Ru(bipy)_2L_2]^{2+}$ (L = pyrazole) have been studied,[1126] while photochemical isomerization reactions of $[Ru(bipy)_2L_2]^{2+}$ (L = *trans*- and *cis*-stilbazole) and $[Ru(bipy)_2LX]^+$ have been reported to occur in butyronitrile *via* CT excited state to give ligand radical anions (equation 88).[1127,1128] The formation of pseudo-base adducts between nucleophiles and $[Ru(bipy)_2py_2]^{2+}$ has been reported,[1135] but later refuted by other workers as a simple substitution reaction with pyridine loss.[1029]

Reaction of $[RuCl_3(bipy)]$ with py in refluxing EtOH for 24 h gives $[Ru(bipy)py_4]^{2+}$;[612,1131] further reaction with L (L = en, 2-methylaminopyridine, 2-ethylaminopyridine, phen, bipy) yields $[Ru(bipy)(L)py_2]^{2+}$.[612]



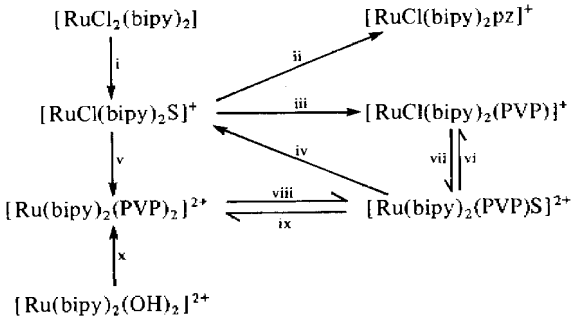
(80)



(88)

$[RuCl(bipy)_2py]^+$ can be prepared by treatment of $[RuCl_2(bipy)_2]$ with py followed by NaCl;[1136] substitution reactions of *cis*-$[Ru(phen)_2py_2]^{2+}$ with a range of anions proceed with retention of configuration.[1130] Photolysis of $[Ru(bipy)_2py_2]^{2+}$ and $[Ru(bipy)_2(NCMe)_2]^{2+}$ in CH_2Cl_2 with X^- yields $[RuX(bipy)_2py]^+$, $[RuX(bipy)_2(NCMe)]^+$ and $[RuX_2(bipy)_2]$ ($X = ClO_4^-$, NO_3^-, ^-NCS, Br^-, Cl^-, NO_2^-) *via* a dissociative mechanism.[1137]

A range of vinyl and carboxypyridyl derivatives of $[Ru(bipy)_2]^{2+}$ have been prepared and electron transfer reactions and the photochemical activity of these complexes as polymer films at electrode surfaces studied.[745,861,953,1058,1138–1148] Some chemical transformations involving polyvinyl pyridine (PVP) are illustrated in Scheme 28.[1138,1142–1144,1149] The charge transfer luminescence spectra of *cis*- and *trans*-$[Ru(bipy)_2py_2]^{2+}$,[1096,1150] *cis*-$[Ru(bipy)_2L_2]^{4+}$ (L = 2-methyl-4,4′-bipyridinium$^+$),[1151] *cis*- and *trans*-$[Ru(bipy)(phen)py_2]^{2+}$, $[Ru(bipy)py_2(L)]^{2+}$ (L = en, $(NH_3)_2$, 2-methylaminopyridine, 2-ethylaminopyridine) and $[RuCl(bipy)py_3]^+$ have been measured.[1096]



i, solvent S; ii, pz; iii, PVP, Δ; iv, Cl^-; v, PVP, Δ; vi, Cl^-, Δ; vii, hν, solvent S; viii, hν, solvent S, ix, PVP, Δ; x, PVP

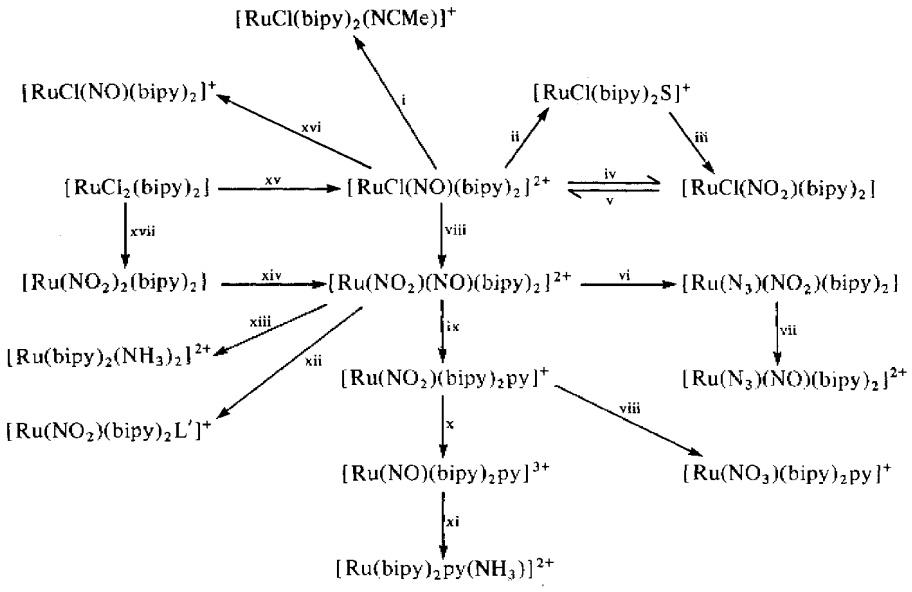
Scheme 28

For electron transfer reaction between $[Ru(bipy)_2py_2]^{3+}$ and $[Fe(OH_2)_6]^{2+}$, $\Delta H^{\neq} = +1.26\,kJ\,mol^{-1}$ and $\Delta S^{\neq} = -130\,J\,K^{-1}\,mol^{-1}$.[1043]

(b) Nitrosyls and related ligands

Reaction of $[RuX_2L_2]$ ($X = Cl^-$, Br^-; L = bipy, phen) with NO_2^- yields $[Ru(NO_2)_2L_2]$; acidification with HCl forms $[RuCl(NO)L_2]^{2+}$ while with HPF_6 $[Ru(NO_2)(NO)L_2]^{2+}$ is produced.[1152–1154] The thermal decomposition of $(phenH)_2[RuCl_5(NO)]$ gives $[RuCl(NO)phen]^{2+}$,[646] while reaction of $[RuCl_3(NO)]_n$[619,1155,1156] or $[RuCl_5(NO)]^{2-}$[1157] with L yields $[RuCl_3(NO)L]$. Treatment of *trans*-$[Ru(bipy)_2(OH_2)_2]^{2+}$ with $NaNO_2$ followed by acidification gives *trans*-$[Ru(NO)(OH)(bipy)_2]^{2+}$.[1005] Scheme 29 summarizes work on the interconversion of NO^+, NO_2^- and NO_3^- complexes.[1158] The reduction of $[Ru(NO)(bipy)_2L]^{3+}$ (L = NH_3, py, MeCN) and $[RuX(NO)(bipy)_2]^{2+}$ ($X = N_3^-$, Cl^-, NO_2^-) electrochemically or by I^- yields $[Ru(NO)(bipy)_2L]^{2+}$ and $[RuX(NO)(bipy)_2]^+$ respectively.[1159,1165,1166] There was found to be a linear correlation between ν_{NO} and $E_{1/2}$ for the reversible one electron reduction of these complexes. The site of reduction is essentially π^* (NO) in character and thus can be regarded as reduction of coordinated NO^+ to NO with a lowering in frequency of the N—O stretching vibration ν_{NO} from 1940 and 1970 cm^{-1} for $[RuCl(NO)(bipy)_2]^{2+}$ and $[Ru(NO)(bipy)_2NCMe]^{3+}$ to 1650 and 1610 cm^{-1} for $[RuCl(NO)(bipy)_2]^+$ and $[Ru(NO)(bipy)_2NCMe]^{2+}$ respectively.[1159,1165,1166] $[RuCl_2(bipy)_2]$ reacts with $[Ru(NO)(bipy)_2NCMe]^{3+}$ (rate constant $k > 10^6\,M^{-1}\,s^{-1}$) to give $[RuCl_2(bipy)_2]^+$ and $[Ru(NO)(bipy)_2NCMe]^{2+}$.[1159,1166] The oxidation of $[RuCl(NO)(bipy)_2]^+$ at chemically modified electrodes has been reported.[1145] *Cis*-$[RuCl(NO_2)(bipy)_2]$ can be oxidized to give a transient Ru^{III} complex $[RuCl(NO_2)(bipy)_2]^+$ which decomposes *via* O transfer to yield $[RuCl(NO)(bipy)_2]^{2+}$ (**81**) and $[RuCl(NO_3)(bipy)_2]^+$ (**82**) (equation 89).[1167,1168] This observation has led to the use of $[RuCl(NO_2)(bipy)_2]$ and $[Ru(NO_2)(bipy)_2py]^+$ for the electrocatalytic oxidation of PPh_3 under alkaline conditions whereby the NO_2^- complex can be regenerated from the NO^+ species by reaction with base ($\bar{O}H$ or lutidine) (Scheme 30).[1167] This electrocatalytic cycle has been extended by immobilization of $[Ru(NO_2)(isn)(bipy)_2]^+$ on alkyl amine silanized modified PtO electrodes, thus enabling the catalytic oxidation of PPh_3 at a modified electrode surface.[1169,1170]

A series of electrophilic reactions of coordinated nitrosyl group has been reported. $[RuCl(NO)(bipy)_2]^{2+}$ reacts with aryl amines $ArNH_2$ to give $[RuCl(N_2Ar)(bipy)]^{2+}$ which shows a degree of diazonium ion character with $\nu_{N\equiv N}$ in the range 1980–2100 cm^{-1}.[1171,1172] Cleavage of these complexes occurs with KI in aqueous solution at 60°C to yield $[RuI_2(bipy)_2]$, N_2 and iodoaryl

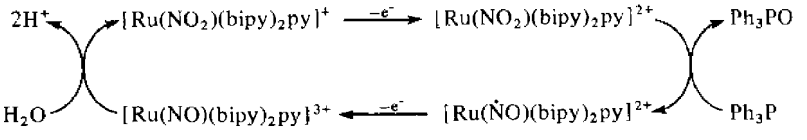


i, hν, MeCN;[1159] ii, N_3^-; S (S = H_2O, MeCN, MeOH, acetone);[1149, 1160–1162] iii, NO_2^-;[1161] iv, ^-OH;[1154, 1163] v, H^+, $SnCl_4$ or BF_3;[1163] vi, N_3^-;[1159] vii, HPF_6;[1159] viii, Ce^{IV};[1153] ix, (a) KN_3 (b) py (NH_3, MeCN, H_2O);[1153, 1159, 1161] x, H^+;[1153, 1159] xi, $+6e^-$; $+5H^+$;[1164] xii, L' (L' = MeCN, NH_3, PPh_3, pz);[1153] xiii, $+12e^-$, $+12H^+$;[1164] xiv MeCN, HPF_6;[1153] xv, (a) NO_2^- (b) HCl;[1152] xvi, I^-;[1159] xvii, NO_2^- [1152]

Scheme 29

$$2[RuCl(NO_2)(bipy)_2] \xrightarrow{-3e^-} [RuCl(NO)(bipy)_2]^{2+} + [RuCl(NO_3)(bipy)_2]^+ \quad (89)$$

(81) **(82)**



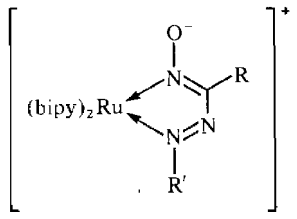
Scheme 30

products.[1171] $[RuCl(p\text{-}N_2C_6H_4Me)(bipy)_2]^{2+}$ shows an irreversible one electron reduction to give a coordinated N_2Ar radical product which decomposes in MeCN to $[RuCl(bipy)_2NCMe]^+$.[1165] Reaction of $[RuX(NO)(bipy)_2]^{2+}$ with C_6H_5NRR' yields $[RuX\{N(O)C_6H_4NRR'\}(bipy)_2]^+$ (X = Cl^-, R = R' = Me, R = H, R' = Me; X = NO_2^-, R = R' = Me, R = H, R' = Me).[1173] ^{15}N labelling experiments indicate that the N of nitrosyl remains bound to the metal centre.[1174] The same complexes can be prepared by reaction of $[RuCl(bipy)_2(acetone)]^+$ with $4\text{-}N(O)C_6H_4NMe_2$ and show $d\pi \rightarrow \pi^*$ (nitrosoarene) charge transfer bands near 600 nm in addition to bands assigned to $d\pi \rightarrow \pi^*$ (bipy) transitions.[1173] $[RuCl\{N(O)C_6H_4NRR'\}(bipy)_2]^+$ shows a $Ru^{II/III}$ couple and a one electron reduction on the nitrosoarene ligand.[1175] Further reaction with a second mole of arylamine can occur to yield $[Ru\{N(O)C_6H_4NMe_2\}_2(bipy)_2]^{2+}$ (**83** in equation 90).[1173,1174] Addition of arylhydrazones RCH=NNHR' (R = Me, Ph, $p\text{-}MeC_6H_4$, R' = Ph, $p\text{-}MeC_6H_4$) to $[RuCl(NO)(bipy)_2]^{2+}$ gives the products $[Ru(bipy)_2L]^+$ (**84**) in $MeOH/MeO^-$.[1176] (**84**) can also be synthesized by direct reaction of NaL with $[RuCl_2(bipy)_2]$. Protonation raises the $Ru^{III/II}$ couple from +0.8 V for (**84**) to +1.0 V *vs.* SCE for $[Ru(LH)(bipy)_2]^{2+}$.[1176] Treatment of $[RuCl(NO)(bipy)_2]^{2+}$ with phenol yields $[RuCl\{N(O)C_6H_4OH\}(bipy)_2]^+$.[1174]

Reactions of $[RuCl(NO)(bipy)_2]^{2+}$ and $[Ru(NO)(bipy)_2py]^{3+}$ with RO^- (R = Me, Et, Pr^i) yield the products $[RuCl\{N(O)OR\}(bipy)_2]^+$ and $[Ru\{N(O)OR\}(bipy)_2py]^{2+}$ respectively;[1177]

$$[Ru(NO_2)(bipy)_2\{N(O)C_6H_4NMe_2\}]^+ \underset{-OH}{\overset{H^+}{\rightleftharpoons}} [Ru(NO)(bipy)_2\{N(O)C_6H_4NMe_2\}]^{3+} \xrightarrow{C_6H_5NMe_2} [Ru(bipy)_2\{N(O)C_6H_4NMe_2\}_2]^{2+} \quad (90)$$

(83)



(84)

$d\pi Ru^{II} \rightarrow \pi^*$ (N(O)OR) back-bonding is significant in these species, the N(O)OR ligand being a better π acceptor than NO, py or MeCN.[1177] The photo induced addition of ^-OH to $[RuCl(NO)(bipy)_2]^{2+}$ gives the metastable product $[RuCl(NO_2H)(bipy)_2]^+$ which regenerates the starting material in the dark.[1178] SO_3^{2-} reversibly adds to $[RuX(NO)(bipy)_2]^+$ (X = Cl^-, Br^-) to give $[RuX\{N(O)SO_3\}(bipy)_2]$.[665] The single crystal X-ray structure of the chloro complex shows a distorted octahedral environment around Ru^{II} with Ru—N(N(O)SO_3) = 1.90 Å and a long N—S bond length of 1.82 Å.[665] Addition of Hacac to $[RuCl(NO)(bipy)_2]^{2+}$ gives N-bound MeCOC(NO)COMe.[1179]

(c) Other nitrogen donors

Thermal substitution reactions of $[RuCl_2(bipy)_2]$ with diazadienes (dad) yield $[Ru(bipy)_2dad]^{2+}$ species.[1180] The N-bound thiocyanate complex $[Ru(NCS)_2(bipy)_2]$[355] can be prepared by treatment of $RuCl_3$ with bipy in refluxing EtOH for 48 h followed by NaNCS for 24 h,[667,1181] or by photolysis of $[Ru(bipy)_3](NCS)_2$.[355,1003] The latter method also yields $[Ru(NCS)(bipy)_2DMF]^+$ as a side product.[1003] $[Ru(N_3)_2(bipy)_2]$ and $[Ru(N_3)(bipy)_2L]^+$ (L = py, MeCN) can be electrochemically or chemically oxidized with Br_2 or Ce^{IV} to the corresponding Ru^{III} species which undergo thermal and photo induced decomposition in MeCN *via* electron transfer from N_3^- to Ru^{III} (equation 91).[1182] Treatment of $[Ru(nbd)(NCMe)_4]^{2+}$ with L (L = bipy, phen, 5-methyl-1,10-phenanthroline) yields $[Ru(L)(NCMe)_4]^{2+}$.[1183] Oxidation of $[Ru(bipy)_2(NH_2CH_2R)_2]^{2+}$ by eight electrons leads to the formation of the dinitrile complex $[Ru(bipy)_2(NCR)_2]^{2+}$.[1184]

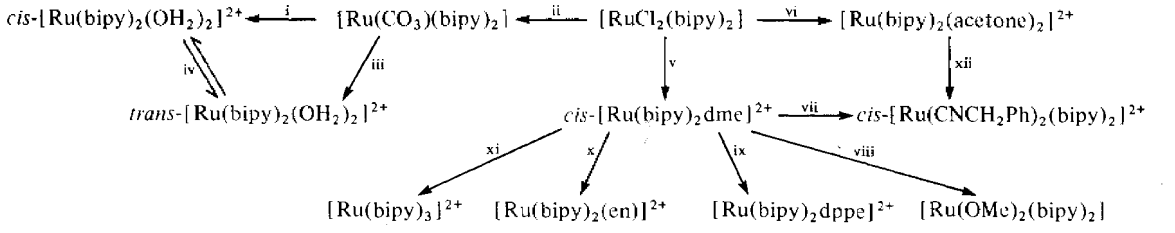
$$[Ru(N_3)_2(bipy)_2] \xrightarrow[MeCN]{h\nu} [Ru(N_3)(bipy)_2(NCMe)] + \tfrac{3}{2}N_2 \quad (91)$$

(x) Bidentate heterocyclic complexes with oxygen donor ligands

Ruthenium(II): Acidification of $[Ru(CO_3)L_2]$ (L = phen, bipy, bpz) in aqueous solution yields *cis*-$[Ru(bipy)_2(OH_2)_2]^{2+}$[1119,1133,1185–1187] which on photolysis gives the *trans* isomer *via* a five-coordinate intermediate.[1005,1133,1187] $[RuCl_2L_2]$ (L = 2-(phenylazo)pyridine, 2-(3-tolylazo)pyridine) undergoes stereoretentive displacement of Cl^- in the presence of Ag^+ to yield $[RuL_2(OH_2)_2]^{2+}$ which can be deprotonated to $[Ru(OH)L_2(OH_2)]^+$ and $[Ru(OH)_2L_2]$.[1186,1188] The diaqua complexes are useful starting materials for the synthesis of products of type $[Ru(bipy)_2XZ]^{n+}$ (X, Z = *e.g.* py, pz, MeCN, NO_2^-, NO^+, halides, PR_3).[611,1005,1133,1161,1181,1185,1188] Scheme 31 shows some substitution chemistry of the $[Ru(bipy)_2]^{2+}$ moiety. The second order rate constants for substitution on $[Ru(bipy)_2(OH_2)_2]^{2+}$ decrease in the order $N_3^- > NO_2^- > SCN^- >$ py.[1158,1181] The catalytic photooxidation of water using *trans*-$[Ru(bipy)_2(OH_2)_2]$ on hectorite has been reported, the active complex being thought to be $[Ru(bipy)_2(OH_2)]_2O^{4+}$.[1190]

Treatment of $[RuX(NO)(bipy)_2]^{2+}$ with KN_3 in solvent S yields $[RuX(bipy)_2S]^+$ (X = Cl^-, NO_2^-; S = acetone, methanol, H_2O).[1161,1162] Likewise $[Ru(bipy)_2py(OH_2)]^{2+}$ can be prepared by reaction of $[Ru(NO)(bipy)_2py]^{3+}$ with KN_3 in water or by treatment of $[RuCl(bipy)_2py]^+$ with Ag^+ in water.[1136]

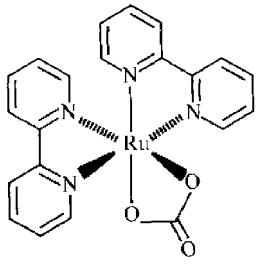
Cis-$[RuCl_2(bipy)_2]$ in refluxing DMSO yields *cis*-$[RuCl(bipy)_2DMSO]^+$,[1191] while $[RuCl_2(DMSO)_4]$ with 8-aminoquinoline (L) gives $[RuCl_2(L)(DMSO)_2]$.[1192] The single crystal X-ray structure of $[Ru(CO_3)(bipy)_2]$ (**85**), prepared by reaction of $[RuCl_2(bipy)_2]$ with $NaHCO_3$,[1160,1193] shows bidentate CO_3^{2-} with Ru—O = 2.087, Ru—N(*cis* to O) = 2.042, Ru—N (*trans* to O) = 2.013 Å.[1194] Treatment of $[RuCl_2L_2]$ (L = bipy and phen derivatives) with carboxylates (L′) gives products of type $[RuL'L_2]^{n+}$ (L′ = 2,5-pyrazine dicarboxylate,[562] oxalate,[264,369,1195] acac[268a,269]). Reaction of



i, HPF_6, H_2O;[1186,1187] ii, $NaHCO_3$;[1160] iii, $h\nu$, $HClO_4$;[1187] iv, $h\nu$;[1187] v, $AgPF_6$, DME;[1189] vi, Ag^+, acetone;[1189] vii, $CNCH_2Ph$;[1189] viii, MeO^-;[1189] ix, dppe;[1189] x, en;[1189] xi, bipy;[1189] xii, $CNCH_2Ph$[1189]

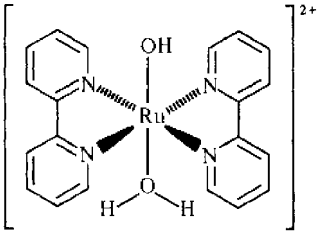
Scheme 31

$[Ru(CO_3)(bipy)_2]$ with hydroxamates (H_2L) yields the complexes $[Ru^{II}(HL)(bipy)_2]^+$ and $[Ru^{II}(L)(bipy)_2]$, which show $Ru^{II/III}$ and $Ru^{III/IV}$ couples in MeCN.[1196] A series of partially characterized complexes involving hydroquinone have been reported.[1195]

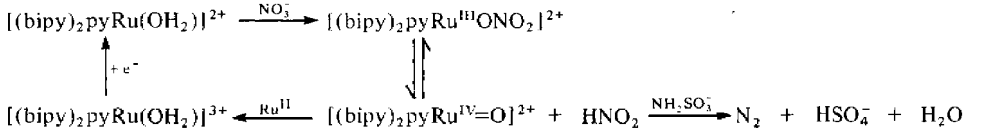


(85)

Ruthenium(III): $[Ru(bipy)_2(OH_2)_2]^{3+}$ has been proposed as an intermediate in the reaction of $RuCl_3$ with bipy in aqueous conditions at pH 2.[1197] In the presence of ClO_4^{2-}, $[Ru(bipy)_2(OH_2)_2]^{2+}$ is oxidized to $[Ru(OH)(bipy)_2OH_2]^{2+}$. The single crystal X-ray structure of *trans*-$[Ru(OH)(bipy)_2OH_2]^{2+}$ (**86**) shows Ru—N = 2.090, 2.099 and Ru—O = 2.007 Å with intermolecular hydrogen bridges between coordinated OH_2 and OH ligands.[1187] Oxidation of $[Ru(bipy)_2py(OH_2)]^{2+}$ at +0.8 V *vs.* SCE yields $[Ru^{III}(OH)(bipy)_2py]^{2+}$,[1136] while oxidation by NO_3^- gives in acidic conditions $[Ru^{III}(bipy)_2py(OH_2)]^{3+}$ *via* a Ru^{IV} intermediate (Scheme 32).[1198] In the presence of $NH_2SO_3^-$, the HNO_2 produced is reduced to N_2 and on electrochemical regeneration of the Ru^{II} starting material, the system becomes catalytic for the reduction of NO_3^- to N_2.[1198] The oxidation of H_2O_2 by $[Ru(OH)(bipy)_2py]^{2+}$ has been studied.[1199] $[Ru(bipy)_2py(OH_2)]^{3+}$ has a $pK_a = 0.85$ compared to its Ru^{II} analogue which has a pK_a of 10.79.[1136] The formation of $[Ru(OH)(bipy)_2py]^{2+}$ from $[Ru(bipy)_2py(OH_2)]^{2+}$ and $[Ru(O)(bipy)_2py]^{2+}$ is first order in $[Ru^{II}]$ and $[Ru^{IV}]$.[1200] Oxidation of hydroxamate complexes $[Ru^{II}(LH)(bipy)_2]^+$ and $[Ru(L)(bipy)_2]$ with Ce^{IV} yields the corresponding Ru^{III} species.[1196]



(86)



Scheme 32

Ruthenium(IV): $[Ru(bipy)_2py(OH_2)]^{2+}$ can be oxidized by Ce^{IV} or by controlled potential electrolysis to $[Ru(O)(bipy)_2py]^{2+}$ (ν_{Ru-O} at 792 cm^{-1}) which oxidizes PPh_3 to $OPPh_3$ (Scheme 33).[1136,1201–1204] ^{18}O labelling shows that O transfer from Ru=O to PPh_3 occurs *via* first order kinetics with rate constant $k = 1.75 \times 10^5\ M^{-1}\ s^{-1}$.[1202] $[Ru(O)(bipy)_2py]^{2+}$ has been used electrocatalytically for the oxidation of alkenes, alcohols, aldehydes, aromatics[1204] and chloride to chlorine.[1205] The H–D kinetic isotope effects for the oxidation of H_2O_2 by Ru^{III} and Ru^{IV} have been measured as 16 and 22 respectively.[1199] The oxidation of 2-propanol by $[Ru(O)(bipy)_2py]^{2+}$ occurs *via* a two electron hydride transfer from the α-carbon to Ru=O; no transfer of coordinated O was observed, while a slower oxidation of substrate by Ru^{III} *via* a one electron transfer was detected.[1203] Electrode supported oxidation catalysts based on Ru^{IV} have been achieved by deposition of films containing $[Ru(bipy)_2(OH_2)]^{2+}$ bound to poly-4-vinylpyridine.[1186] $[Ru(O)L_2py]^{2+}$ (L = 2-(phenylazo)pyridine), prepared by Ce^{4+} oxidation of $[RuL_2py(OH_2)]^{2+}$ ($E^\circ = +1.20$ V), catalyses the oxidation of H_2O to O_2.[1206]

$$[Ru(bipy)_2py(OH_2)]^{2+} \xrightarrow{+0.53\ V} [Ru(bipy)_2py(OH)]^{2+} \xrightarrow{+0.42\ V} [Ru(bipy)_2py(O)]^{2+} \xrightarrow{PPh_3}$$

$$[Ru(bipy)_2py(OPPh_3)]^{2+} \xrightarrow{MeCN} [Ru(bipy)_2py(MeCN)]^{2+} + OPPh_3$$

Scheme 33

Ruthenium(V), (VI), (VII), (VIII): Electrochemical studies on *cis*-$[Ru(bipy)_2(OH_2)_2]^{2+}$ show a series of one electron couples to $Ru^{III/IV/V/VI}$ (Scheme 34),[1207,1208] the Ru^{VI} species being thought to be the active complex in the oxidation of Cl^-.[1205] Reaction of RuO_4 with bipy and phen yield products of stoichiometry RuO_4bipy and $Ru_2O_7phen_2$ which have been assigned as Ru^{VIII} and Ru^{VII} complexes respectively;[1209] from their spectroscopic and chemical properties however they appear to be lower valent species. A series of partially characterized products have been synthesized by reaction of these complexes with bipy in MeOH.[674a,1195,1210] A genuine Ru^{VI} complex $[Ru(O)_2Cl_2(bipy)]$ has been prepared from the reaction of RuO_4 with HCl and bipy.[65,1211]

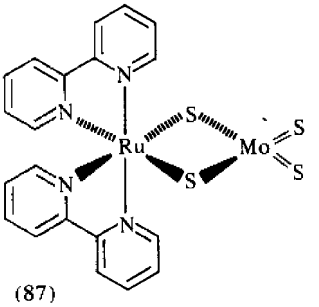
$$cis\text{-}[Ru(bipy)_2(OH_2)_2]^{2+} \xrightarrow{+0.53\ V} [Ru(bipy)_2(OH)(OH_2)]^{2+} \xrightarrow{+0.76\ V} [Ru(bipy)_2(O)(OH_2)]^{2+} \xrightarrow{+0.94\ V}$$

$$[Ru(bipy)_2(O)(OH)]^{2+} \xrightarrow{+1.07\ V} [Ru(bipy)_2(O)_2]^{2+}$$

Scheme 34

(*xi*) *Bidentate heterocyclic complexes with sulfur donor ligands*

The synthesis and catalytic behaviour of $[Ru(S_2MoS_2)(bipy)_2]$ (**87**) have been described.[1212a]

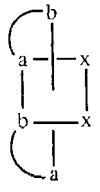


(87)

(*xii*) *Bidentate heterocyclic complexes with halide ligands*

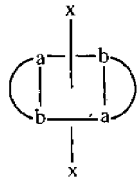
Ruthenium(II): A range of complexes of type $[RuCl_2L_2]$ have been prepared by a variety of routes.[264–266,738] *Cis*-$[RuCl_2(bipy)_2]$ can be prepared by reaction of $RuCl_3$ with bipy in refluxing DMF for 8 h in the presence of LiCl,[1115,1124] by substitution of py in *cis*-$[Ru(bipy)_2py_2]^{2+}$ by Cl^-,[1131] or by activation of $RuCl_3$ in refluxing H_2O/EtOH, followed by evaporation and dissolution in aqueous HCl and addition of bipy in H_2O/acetone.[1212b] *Trans*-$[RuCl_2(bipy)_2]$ has been synthesized by

addition of LiCl to *trans*-$[Ru(bipy)_2(OH_2)_2]^{2+}$ or by photolysis of $[Ru(CO_3)(bipy)_2]$ in HCl.[1005] Refluxing solutions of $[Ru(bipy)py_4]^{2+}$ with bipy in EtOH followed by addition of HCl yield mixtures of *cis*- and *trans*-$[RuCl_2(bipy)_2]$.[1131] The *cis* isomer can be prepared by repeated treatment of the *cis*/*trans* mixture with py to give $[Ru(bipy)_2py_2]^{2+}$ followed by conversion to the dichloro complex with HCl.[1131] Other routes to $[RuCl_2(bipy)_2]$ include reaction of $[RuCl_3(Hdma)]$ (dma = dimethylacetamide) with bipy,[1213] $[RuCl_5(OH)]^{2-}$ with bipy and X^- ($X^- = Cl^-$, Br^-, I^-),[369,708,1214] photolysis of $[Ru(bipy)_2py_2]X_2$[1137] or $[Ru(bipy)_3]Cl_2$ in acetone,[1006] heating $[RuCl(bipy)_2(NCMe)]Cl$ in CH_2Cl_2,[1006] vacuum pyrolysis of $[Ru(bipy)_3]Cl_2$ at 290°C for 2 h[369] or treatment of $[Ru(ox)(bipy)_2]$ with HCl.[369] The electronic spectra of $[RuX_2(bipy)_2]$ ($X = Cl^-$, Br^-, I^-) have been reported.[267,738,785,1214] Thermolysis of $(phenH)[RuCl_4phen]$[266,1112] or reaction of $[Ru(phen)_2py_2]^{2+}$ with X^-[1130] yields $[RuX_2(phen)_2]$ while 2,2′-bipyrazine[1185,1215] and 2,2′-biquinoline[1065] derivatives of $[RuCl_2L_2]$ have also been reported. Treatment of (Hpq)$[RuCl_4(pq)]$ with HCl, Hg and KCl yields $[RuCl_2(pq)_2]$ (pq = 2-(2′-pyridyl)quinoline).[1065] Refluxing $RuCl_3$ with 2-(phenylazo)pyridine (L) in EtOH gives blue β-$[RuCl_2L_2]$ (**88**).[1216] Reaction of L with $[RuCl_2(DMSO)_4]$ in acetone for 17 h[1216] or refluxing $RuCl_3$ with L in MeOH for 8 h[1066] leads to the formation of green γ-$[RuCl_2L_2]$ (**89**) which can be converted to the blue α isomer $[RuCl_2L_2]$ (**90**) by reflux in xylene for 3 h.[1216] Substitution reactions of $[RuCl_2L_2]$ have been reported.[611,1066]



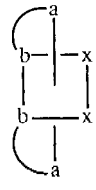
(88)

β



(89)

γ



(90)

α

$[RuCl_2(bipy)_2]$ undergoes solvolysis in H_2O,[1181] DMSO[1191] and MeCN.[1006] $[RuCl(bipy)_2OH_2]^+$ has been partially resolved by (+)-tartrate.[1217] Reduction of $[RuCl_4(bipy)]^-$ by Ti^{2+} yields $[RuCl_4(bipy)]^{2-}$ which catalyses the hydrogenation of maleic acid to succinnic acid *via* a $[RuCl_3(H)bipy]^{2-}$ intermediate.[1218] The reductive electrochemistry of $[RuCl_2(bipy)_2]$ and related $[Ru(bipy)_2]^{2+}$ species has been interpreted in terms of a spatially isolated redox orbital model with π^* electron density localized on individual bipy ligands.[268a]

Ruthenium(III): For $[RuCl_2(bipy)_2]$, $E_{1/2}(Ru^{II/III}) = +0.35$ V *vs.* SCE, with electron withdrawing groups on bipy increasing $E_{1/2}$.[268a,738] $[RuCl_2(bipy)_2]^+$ can be prepared by oxidation of $[RuCl_2(bipy)_2]$,[369,675,1197] by Cl^- substitution on $[RuCl(p\text{-}N_2C_6H_4Me)(bipy)_2]^{2+}$[1145] or by Cl_2 oxidation of $[Ru(ox)(bipy)_2]$ in the presence of Cl^-.[369] $[RuCl_2(bipy)_2]^+$ undergoes rapid solvolysis in H_2O to yield $[RuCl(bipy)_2OH_2]^{2+}$; both $[RuCl_2(bipy)_2]^+$ and $[RuCl(bipy)_2OH_2]^{2+}$ have been resolved with (+)-tartrate.[1197,1217,1219]

$[RuCl_3(bipy)OH_2]$ can be prepared by reduction of $[RuCl_4(bipy)]$ in H_2O and EtOH[265] or by refluxing $RuCl_3$ with aqueous HCl and bipy for several days.[612,712,1131] The complex is often used for the preparation of tris chelate species $[Ru(bipy)L_2]^{2+}$ (Table 9).[612,712,745,1131] Refluxing $[RuCl_5OH]^{2-}$ with L in the presence of Cl^-,[264,265] or treatment of $RuCl_3$ with H_2 in MeOH followed by aerial reflux of the resulting green solution with L and KCl has been reported to give $[RuCl_4L]^-$ (L = bipy, phen).[1220] The magnetic properties of $[RuCl_4bipy]^-$ have been studied.[163]

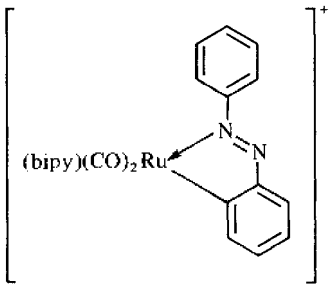
Ruthenium(IV): $[RuCl_4L]$ has been reported to be the product of the oxidation of $LH[RuCl_4L]$ with Cl_2 or Ce^{IV} in HNO_3,[264,265] while thermolysis of $(phenH_2)[RuCl_6]$ yields $[RuCl_4phen]$.[684] The magnetic properties of these complexes have been reported.[1221]

(*xiii*) *Bidentate heterocyclic complexes with mixed donor ligands*

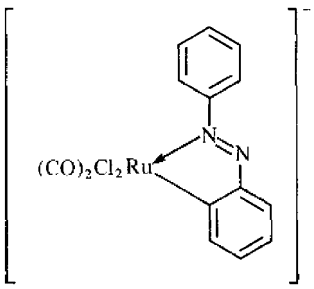
Reaction of $[Ru(azb)Cl(CO)_2]_2$ (azb = 2-(phenylazo)phenyl) with bipy gives $[Ru(azb)(CO)_2bipy]^+$ $[Ru(azb)Cl_2(CO)_2]^-$ (**91**) with the azb ligand binding through N and C.[1222]

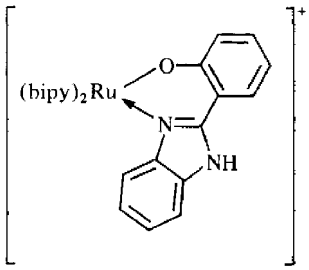
Treatment of $[RuCl_2(bipy)_2]$ with L^- yields $[RuL(bipy)_2]^+$ (**92**) which shows redox activity at $E_{1/2} = +0.39$, -1.67 and -2.00 V *vs.* SCE.[1070,1071] Complexes (**93**) have been prepared by reaction of L with $[Ru(CO_3)(bipy)_2]$ or $[Ru(bipy)_2(EtOH)_2]^{2+}$;[1223] oxidation of (**93**) to $[Ru^{III}L(bipy)_2]^{2+}$ can be achieved chemically or electrochemically, the energy of the L → metal charge transfer band in the Ru^{III} complexes correlating with the values for the $Ru^{II/III}$ redox couple.[1223] The complexes [Ru-

$(bipy)_2L]^+$ (L = azophenols, azonaphthols) have been reported.[1224] Reaction of $[RuCl_2(bipy)_2]$ with isonitrosoketonates yields complexes of type $[RuL(bipy)_2]^+$ (**94**).[1225,1226] As for the complexes (**93**), (**94**) show correlation between $E_{1/2}$ for the $Ru^{II/III}$ couple and the energy of L → metal charge transfer bands in the Ru^{III} species; protonation of (**94**) raises the $Ru^{II/III}$ redox potential.[1226] An alternative route to (**94**) is by the reaction of *cis*-$[RuCl(NO)(bipy)_2]^{2+}$ with propiophenone in $MeOH/MeO^-$.[1227]

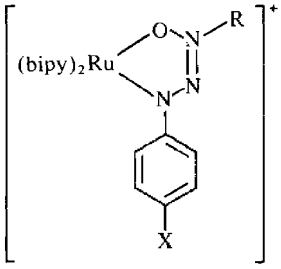


(91)

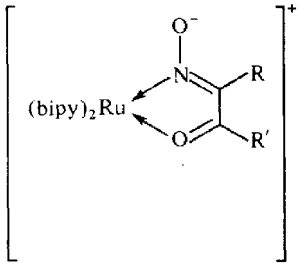




(92)



(93)



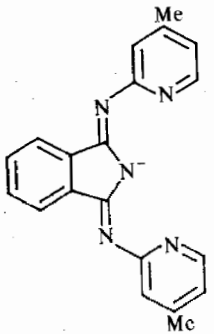
(94)

Chiral complexes of amino acids and related ligands of type Δ and Λ $[RuL(bipy)_2]^+$ (L = (−)-serine,[1228] (−)-tryptophane,[1229] 5-hydroxytryptophane,[1230] phenylalanine,[1230] (−)-alanine[1231,1232]) and $[RuL(bipy)_2]$ (L = (−)-aspartate,[1233] (−)-glutamate[1234a]) have been reported. Inversion of the Δ and Λ isomers has been studied and equilibrium constants for the isomerization reactions determined[1228,1229,1233,1240a]. More recently, chiral complexes Δ, Λ-$[Ru(L)_2L']^+$ (L = bipy, phen; L'H = *S*-threonine, *S*-allothreonine) have been prepared and studied crystallographically.[1234b] Reaction of $[RuCl_2(bipy)_2]$ with 8-mercaptoquinoline (L) under basic conditions yields the N,S complex $[RuL(bipy)_2]^+$; alkylation of the coordinated ligand at S has been achieved with MeI.[1235]

(*xiv*) *Tridentate heterocyclic complexes* $[RuL_2]^{n+}$

$[Ru(terpy)_2]^{2+}$ can be prepared by fusion of $RuCl_3$ with the ligand at 250–260°C,[1236] reduction of $RuCl_3$ with H_2 over Pt black followed by reaction with terpy in MeOH[807] or by reaction of $[RuCl_5(OH_2)]^{2-}$ with terpy in the presence of H_3PO_2.[728] The synthesis, electronic spectra and redox properties of related bis chelate complexes $[RuL_2]^{2+}$ are summarized in Table 10. The electrochemistry of $[Ru(terpy)_2]^{2+}$ has been studied;[723,725,1241,1242] cyclic voltammetry shows a one electron oxidation at + 1.264 V, *vs.* SSCE in DMF.[697] ESR studies on the reduced products indicate that the first two reductions are ligand based with the redox orbitals being located on single chelate rings.[1242] The charge transfer luminescence of $[RuL_2]^{2+}$ (L = terpy, 4′-phenyl-2,2′,6′,2″-terpyridine, 4,4′,4″-triphenyl-2,2′,6′,2″-terpyridine) has been interpreted on the basis of a delocalized excited state,[1243] but more recently, also interpreted using a charge-trapped model[1244] (see Section 45.4.3.1.vi). The half-life of $[Ru(terpy)_2]^{2+*}$ is estimated as approximately 1.2 ns and undergoes electron transfer quenching with $[Fe(OH_2)_6]^{3+}$ to give $[Ru(terpy)_2]^{3+}$ and $[Fe(OH_2)_6]^{2+}$.[1245] The reduction of $[Ru(terpy)_2]^{3+}$ by $[Fe(OH_2)_6]^{2+}$ is first order in $[Ru^{III}]$ and $[Fe^{II}]$ with $\Delta H^{\neq} = -11.72\,kJ\,mol^{-1}$, $\Delta S^{\neq} = -172\,J\,K^{-1}\,mol^{-1}$.[1043] The luminescence of $[RuL_2]^{2+}$ (L = 2.6-di(2′-quinolyl)pyridine) has been studied and assigned as charge transfer in nature.[1238] $[RuL_2]^{2+}$ (L = 2,4,6-tri(2′-pyridyl)-1,3,5-triazine) is reported to undergo pseudo-base formation by attack of ^-OH on the triazine ring.[1246,1247a] More recently, the complex $[Ru(L)_2]^{2+}$ (L = 5,5″-diphenyl-2,2′,2″-terpyridine) has been synthesized.[1247b]

Table 10 Synthesis, Absorption Spectra and Redox Properties of Complexes $[RuL_2]^{2+}$

Ligand (L)	*Synthesis*	$\lambda(\varepsilon)$ (nm × 10^{-4} M^{-1} cm^{-1})	$E_{\frac{1}{2}}$(V)	*Reference electrode (solvent)*
2,2′:6′,2″-terpy	$RuCl_3$, L, Δ, 250°C[1236] $RuCl_3$, Pt, H_2, MeOH, L, glycerol, 70°C[807] $[RuCl_5(OH_2)]^{2-}$, HCl, L, H_2O, H_3PO_2[728]	470 (1.6), 330 (3.8), 310 (7.23), 280 (2.8), 270 (4.8)[728,807]	+1.26, −1.27, −1.510, −1.948, −2.35[697,725]	SSCE (DMF)
4′-Ph-2,2′:6′,2″-terpy	$RuCl_3$, Pt, H_2, MeOH, 2,2′-oxydiethanol, 70°C, 1 h[807]	560 (0.82), 490 (2.42), 310 (6.67), 280 (8.19)[807]		
4′-(4-R-Ph)-2,2′:6′,2″-terpy (R = OMe, Br, Cl, OH, Me)	$RuCl_3$, L, EtOH, Δ, 100 h[1237]	~490 (2.9)[1237]		
4,4′,4″-Ph_3-2,2′:6′,2″-terpy	$RuCl_3$, Pt, H_2, MeOH, glycerol, 70°C, 1 h[807]	500 (3.84), 330 (9.84), 290 (8.92), 240 (7.19)[807]		
2,6-Di(2′-quinolyl)pyridine	$[RuCl_5(OH_2)]^{2-}$, L, ethylene glycol, H_2O[1238]	610 (0.22), 560 (0.48), 510 (0.9), 470 (0.7), 370 (5.39)[807]		
2,4,6-Tri(2′-pyridyl)-1,3,5-triazine	$RuCl_3$, Pt, H_2, MeOH, L, ethylene glycol[807,1238] $RuCl_3$, L, pH 2.2–4, EtOH, 87°C, 1 h[1239]	501 (1.92)[728,1239]	−0.67, −0.80, −1.41, −1.69, −2.25, −2.4[725,741]	SCE (DMF)
	$RuCl_2(DMSO)_4]$, LH, MeOH, Et_3N[1240] $RuCl_3$, LH, NaOMe, MeOH[1240]	665 (0.98)[1240]	+0.278, −1.381, −1.662[1240]	SHE (DMF)

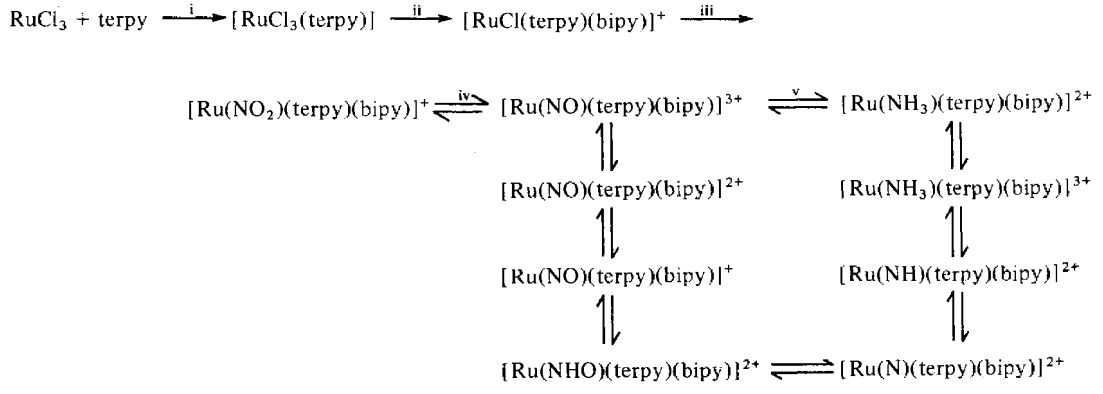
(xv) Tridentate heterocyclic complexes with carbon donor ligands

Reaction of $RuCl_3$ with terpy in refluxing DMF gives *trans*-$[RuCl_2(CO)terpy]$[1116,1248] the single crystal X-ray structure of which shows Ru—N = 2.070, 2.013, 2.084 Å, Ru—Cl = 2.400, 2.403 Å, Ru—C = 1.865 Å.[1248] The single crystal X-ray structure of *cis*-$[RuCl_2(CO)terpy]$, prepared by decarbonylation of $[RuCl_2(CO)_2terpy]$ with Me_3NO in CH_2Cl_2, shows Ru—N = 2.080, 1.969, 2.081 Å, Ru—Cl = 2.420, 2.438 Å, Ru—C = 1.886 Å.[1248] $[RuX_2(CO)_2]_n$ (X = Cl^-, Br^-) reacts with terpy to give $[RuX_2(CO)_2terpy]$; the single crystal X-ray structure of two forms of $[RuBr_2(CO)_2terpy]$ shows bidentate terpy ligand which can be protonated to yield $[RuX_2(CO)_2(H\text{-}terpy)]^+$.[1248] $[RuCl_3terpy]$ reacts with L (L = PPh_3, $PTol_3$) to give *trans*-$[RuCl_2(terpy)L]$ which can be converted to the *cis* isomer in refluxing 1,2-dichloroethane.[1249] The *cis* isomer can also be isolated from the reaction of $[RuCl_2(PPh_3)_3]$ with terpy; carbonylation of *cis*- or *trans*-$[RuCl_2(terpy)(PPh_3)]$ gives *cis*- or *trans*-$[RuCl_2(CO)(terpy)]$. *Cis*-$[Ru(terpy)(OH_2)_2PPh_3]^{2+}$ with PhC≡CH yields $[Ru(\eta^1\text{-}CH_2Ph)(CO)(terpy)(PPh_3)]^+$ and PhMe.[1119] The preparation of *trans*-$[RuCl(terpy)(PPh_3)_2]^+$ has been reported.[1249]

Reaction of $[Ru_3(CO)_{12}]$ with $KHB(pz)_3$ yields $[RuX(CO)_2L]$ (X = Cl^-, Br^-, I^-; L = tris(pyrazolyl)borate).[1250] Treatment of $[RuCl_2(C_6H_6)]_2$ with $B(pz)_4^-$ (tetrakis(1-pyrazolyl)borate) in MeCN gives $[Ru(B(pz)_4)(C_6H_6)]^+$, the single crystal X-ray structure of which shows octahedral Ru^{II} with Ru—N = 2.105, Ru—C = 2.20 Å.[1251]

(xvi) Tridentate heterocycles with nitrogen donor ligands

Reaction of $[Ru(terpy)(bipy)(OH_2)]^{2+}$ or $[Ru(terpy)(bipy)Cl]^+$ with L (L = NH_3,[1184] py,[1252] 4-vinylpyridine,[1252] cyclohexylamine,[259] (α-methylbenzyl)amine,[259] isopropylamine,[1253] 4-chlorostilbazole,[1254] 1,2-bis(4′-pyridyl)ethylene,[1254] benzonitrile[259]) yields the complexes $[Ru(terpy)(bipy)L]^{2+}$. The 4,4′-dimethyl-2,2′-pyridyl species have been prepared.[259] Oxidation of $[Ru(terpy)(bipy)(NH_2CHMe_2)]^{2+}$ and related amine complexes by four electrons gives the Ru^{IV} product $[Ru(NCMe_2)(terpy)(bipy)]^{3+}$ *via* a two electron oxidation intermediate $[Ru(terpy)(bipy)(NH{=}C\text{-}Me_2)]^{2+}$.[259,1253] The single crystal X-ray structure of $[Ru(NCMe_2)(terpy)(bipy)]^{3+}$ shows a linear Ru—N—C moiety with a short Ru—N($NCMe_2$) bond of 1.831 Å suggesting multiple bonding between Ru—N.[259] The oxidation of coordinated NH_3 in $[Ru(terpy)(bipy)NH_3]^{2+}$ to NO_3^- in $[Ru(NO_3)(terpy)(bipy)]^{2+}$ has been achieved by controlled potential electrolysis at +0.8 V *vs.* SCE in water.[1164,1184] The reaction occurs *via* $[Ru(NO)(terpy)(bipy)]^{3+}$ and $[Ru(NO_2)(terpy)(bipy)]^+$ intermediates. The reverse process, reduction of NO_2^- to NH_3, has also been observed (Scheme 35).[1164,1184] Comparisons between this redox system and its osmium analogue have been made in relation to $E_{1/2}$ values and the differences between Ru—NO and Os—NO mixing.[1255] Quenching of the excited state $[Ru(terpy)(bipy)NH_3]^{2+}$* using Fe^{3+}(aq) and paraquat has been reported.[879]



i, EtOH, Δ, 3 h;[259] ii, bipy, EtOH, H_2O, Δ, 3 h;[259] iii, NO_2^-, H_2O, Δ, 3 h;[259] iv, HPF_6, MeOH;[259] v, $-6e^-$, $+H_2O$, $-5H^+$[1164,1184]

Scheme 35

Reaction of $[RuCl_3(terpy)]$ with L yields the *mer* isomers of $[Ru(terpy)L_3]$ (L = 4-vinylpyridine, *trans*-stilbazole, 4-chlorostilbazole, 1,2-bis(4-pyridyl)ethylene); $[RuCl(terpy)(stilbazole)_2]^+$ was also

isolated from the reaction.[1254] Likewise, treatment of the tripyrazolylmethane complex $[RuCl_3\{HC(pz)_3\}]$ with 4-vinylpyridine gives $[RuCl_3\{HC(pz)_3\}(vpy)_3]^{2+}$.[1254]

$[RuCl_2(NO)terpy]^+$ is the product from the reaction of $[RuCl_5(NO)]$ with terpy.[1157] [RuCl(NO)(tetrapy)] has been reported.[1157]

(*xvii*) *Tridentate heterocyclic complexes with oxygen and sulfur donor ligands*

$[Ru(terpy)(bipy)OH_2]^{2+}$ can be prepared by treatment of $[RuCl(terpy)(bipy)]^+$ with Ag^+ in water,[265,1068,1252] or by aquation of $[Ru(O_3SCF_3)(terpy)(bipy)]^+$.[1256] A range of substitution products of $[Ru(terpy)(bipy)OH_2]^{2+}$ has been prepared.[1158] Oxidation to $[Ru^{III}(OH)(terpy)(bipy)]^{2+}$ and $[Ru^{IV}(O)(terpy)(bipy)]^{2+}$ has been achieved electrochemically in solution and on surface film (equation 92).[1186,1203,1204,1257a,1257b] This system has been used for the catalytic oxidation of 2-propanol, *p*-toluic acid and xylenes.[1186,1203,1204,1258] The kinetics and mechanism of the oxidation of aromatic hydrocarbons[1258] and 2-propanol[1203] by $[Ru(O)(terpy)(bipy)]^{2+}$ have been discussed.[1203,1258] A slower reaction of $[Ru^{III}(OH)(terpy)(bipy)]^{2+}$ occurs *via* a one electron outer-sphere transfer.[1203]

$$[Ru(terpy)(bipy)(OH_2)]^{2+} \xrightarrow{0.49\,V} [Ru(terpy)(bipy)OH]^{2+} \xrightarrow{0.62\,V} [Ru(terpy)(bipy)(O)]^{2+} \quad (92)$$

Treatment of $[RuCl(terpy)(bipy)]^+$ with CF_3SO_3H under N_2 gives $[Ru(O_3SCF_3)(terpy)(bipy)]^+$, which when treated with dry air at 110°C for 5 h yields the Ru^{III} analogue $[Ru(O_3SCF_3)(terpy)(bipy)]^{2+}$.[1256] Aquation of $[Ru(O_3SCF_3)(terpy)(bipy)]^{2+}$ occurs readily to give $[Ru(terpy)(bipy)OH_2]^{3+}$.[1203,1204,1256] The luminescence and redox chemistry of $[Ru(terpy)(bipy)L]^{2+}$ (L = OH_2, phenothiazine, *N*-methylphenothiazine, thianthrene) have been reported.[1259]

(*xviii*) *Tridentate heterocyclic complexes with halide ligands*

$[RuCl_3(terpy)]$ can be prepared by reaction of $RuCl_3$ with terpy in refluxing EtOH for 3 h.[259,1249,1252] The corresponding complex of 1,3-bis(4-methyl-2-pyridylimino)isoindoline (L) $[RuCl_3L]$ can be prepared by the same method[1240,1260] and has been used for the catalytic oxidation of alcohols.[1260]

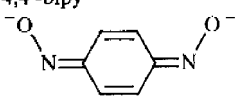
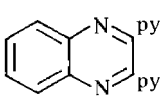
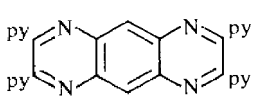
The preparation of $[RuCl(terpy)(bipy)]^+$ has been achieved by reaction of $[RuCl_4(bipy)]$ or $[RuCl_4bipy]^-$ with terpy,[264,265,1181] by treatment of $[RuCl_3terpy]$ with bipy[259,1252] and by decarbonylation of $[RuCl_2(CO)_2(bipy)_2]$ with Me_3NO in the presence of terpy in 2-methoxyethanol.[657] A range of substitution products of $[RuCl(terpy)(bipy)]^+$[1068,1181] and related complexes have been reported.[264,265]

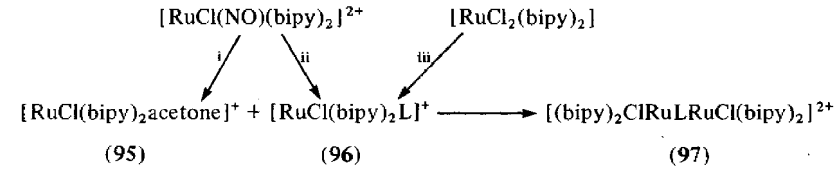
45.4.3.2 Binuclear and polynuclear complexes

(*i*) *Nitrogen donor bridged complexes*

This area has been reviewed.[484] A range of binuclear [2,2], [2,3] and [3,3] complexes of type $[RuCl(bipy)_2]_2L^{n+}$, $[Rupy(bipy)_2]_2L^{n+}$ and $[Ru(bipy)_2]L^{n+}$ and related systems have been prepared (Table 11). Dimerization reactions have been carried out using a general strategy involving labile solvent coordinated mononuclear substrates. For example, $[RuCl(NO)(bipy)_2]^{2+}$ can be activated by N_3^- in acetone to give $[RuCl(bipy)_2(acetone)]^+$ (**95**) which readily adds $[RuCl(bipy)_2L]^+$ (**96**) to produce the binuclear complexes $[RuCl(bipy)_2]_2L^{2+}$ (**97**) (L = pz,[1125,1149,1261,1263,1265] 4,4′-bipyridine,[1149,1265] 1,2-bis(4′-pyridyl)ethylene[1149,1265] 1,2-bis(4′-pyridyl)ethane,[1265] pyrimidine[1266,1265]) (Scheme 36). $[Ru(bipy)_2py]_2$ (4,4′-bipy)$^{4+}$ can be prepared by an analogous route.[1269] The purification of these binuclear complexes has been discussed.[1271] Oxidation of the [2,2] complexes to the [3,3] species can be carried out electrochemically or chemically, while the mixed valence [2,3] species may be generated directly from the [2,2] species, or by reaction of [2,2] with [3,3] in 1:1 molar ratios.[1132,1149,1263,1265,1266] The degree of delocalization in the mixed valence [2,3] complexes has been assessed. Magnetic properties of the complexes $[RuCl(bipy)_2]_2L^{5+}$ (L = pz, pyrimidine, 4,4′-bipyridine, 1,2-bis(4′-pyridyl)ethylene, 1,2-bis(4′-pyridyl)ethane) suggest very little interaction between the metal centres;[1272] this, together with electrochemical, K_c and intervalence charge transfer absorption data (Table 11), indicates trapped valence Class II behaviour for these complexes.[484,530,1261,1263,1265–1267] Electron transfer in these systems has been likened to the outer-sphere electron transfer between $[RuCl(bipy)_2py]^{2+}$ and $[RuCl(bipy)_2py]^+$.[1261,1263,1265,1267] No dramatic dif-

Table 11 Comproportionation Constants (K_c) and Intervalence Charge Transfer (IVCT) Bands for Mixed Valence Binuclear Complexes $[RuXL_2]_2L'^{n+}$[484]

L	*X*	*L'*	*n*	K_c	*IVCT* (*ε*) (nm, $M^{-1}cm^{-1}$)	*Ref.*
bipy	Cl^-	pz	3+	100	1300 (455)	495, 1125, 1149, 1261–1265
bipy	Cl^-	pyrimidine	3+	100	1360 (40)	495, 1265, 1266
bipy	Cl^-	4,4′-bipy	3+	4	980 (100)	1149, 1263, 1265
bipy	Cl^-	1,2-bis(4′-pyridyl)ethylene	3+	4	930 (200)	1149, 1263, 1265
bipy	Cl^-	1,2-bis(4′-pyridyl)ethane	3+	4		1265
bipy	Cl^-	$Ph_2PCH_2PPh_2$	3+	230	1245 (25)	1267, 1268
phen	Cl^-	pz	3+		1316 (650)	1132
5-(NO_2)phen	Cl^-	pz	3+		1266 (458)	1132
4,7-$(Me)_2$phen	Cl^-	pz	3+		1333 (735)	1132
3,4,7,8-$(Me)_4$phen	Cl^-	pz	3+		1299 (589)	1132
bipy	py	4,4′-bipy	5+		1270 150	1269
bipy	H_2O		3+		910 42	1270
bipy	—	2,2′-bibenzimidazole^{2-}	3+	9.8×10^4	1062, 1950 (1.3×10^3, 3.4×10^3)	1072
bipy	—	2,2′-bipyrimidine	5+	1.63×10^3		746, 762, 1064
bipy	—	phen$O(CH_2CH_2O)_n$phen (n = 2–4)	5+	$\leqslant 1$	1135	1054
bipy	—		5+	$\leqslant 1$		1054
bipy	—		5+	$\leqslant 1$		1054
bipy	—	3,3′$(Me)_2$2,2′-bipyrimidine	5+			762
bipy	—	(pyrazole)$_2$	3+			1126
bipy	—		5+			1064
bipy	—		5+		1900	1064

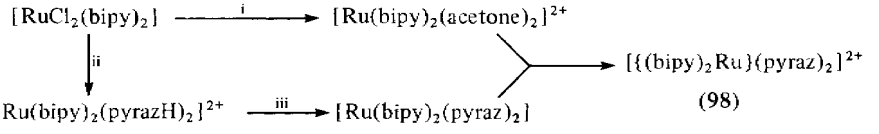


i, KN_3, acetone;[1261] ii, KN_3, L;[1125,1261] iii, Ag^+, L[1125,1261]

Scheme 36

ference was observed in metal–metal interactions in $[RuCl(phen)_2]_2L^{3+}$ compared with $[RuCl(bipy)_2]_2L^{3+}$.[1132]

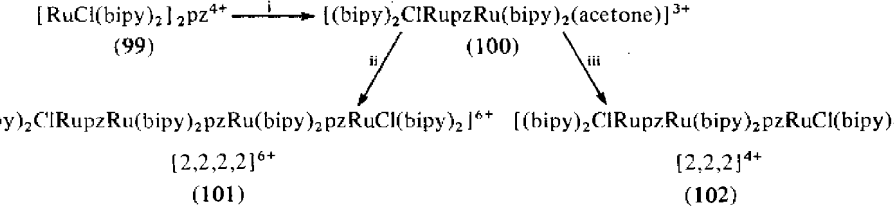
A range of tetradentate ligands have been used to bridge $[Ru(bipy)_2]^{2+}$ moieties (Table 11).[746,762,1054,1064,1067,1072,1073,1240,1260,1273] Reaction of $[RuCl_2(bipy)_2]$ with L under refluxing conditions gives $[Ru(bipy)_2]_2L^{4+}$ (L = 2,2′-bipyrimidine),[746,762,1064] while for L = 2,3-dipyridylquinoxaline, $[RuCl_2(bipy)_2]$ was treated with Ag^+ in acetone followed by addition of L.[1064] Binuclear complexes incorporating pyrazole and benzimidazole anion bridging ligands have been developed (Scheme 37).[1072,1126] Oxidation of the pyrazole $[2,2]^{2+}$ species (**98**) to the $[3,2]^{3+}$ product leads to the formation of a very strong Ru^{III}–pyrazole bond with concomitant bridge cleavage.[1126] $[Ru(bipy)_2]_2L^{4+}$ (L = 2,3-bis(2′-pyridyl)pyrazine) has been prepared from $[RuCl_2(bipy)_2]$; the $[3,2]^{5+}$ ion decomposes in solution.[1067] The synthesis and electrochemistry of bi-, tri- and tetra-nuclear species incorporating a 2,2′,3,3′-tetra-2-pyridyl-6,6′-biquinoxaline bridge have been described,[1073] while binuclear complexes of isoindoline derivatives and the binding of Cu and Pd salts to related monomeric complexes have also been reported.[1240,1260] The characteristics of intervalence transfer in mixed metal Ru/Os dimers have been fully discussed.[1273b] Hetero-binuclear species based on $[Ru(CN)_2(bipy)_2]$ are discussed in Section 45.4.3.1.viii.



i, Ag^+, acetone; ii, pyrazH; iii, KOH

Scheme 37[1126]

A series of trinuclear,[1054,1149] tetranuclear[746,1149] and higher polynuclear[1125] products have been prepared. Treatment of $[RuL_3]^{2+}$ (L = 2,2′-bipyrimidine) with three equivalents of $[RuCl_2(bipy)_2]$ in refluxing water yields the tetranuclear species $[Ru(bipy)_2(bipym)]_3Ru^{8+}$.[746] The $[2,2]^{2+}$ species $[RuCl(bipy)_2]_2pz^{2+}$ (**99**) reacts with N_3^- in acetone to give the dimer $[(bipy)_2ClRuL-Ru(bipy)_2(acetone)]^{3+}$ (**100**); reaction with half an equivalent of pz, or one equivalent of $[RuCl(bipy)_2pz]^+$ leads to the formation of the tetramer $[2,2,2,2]^{6+}$ (**101**) and trimer $[2,2,2]^{4+}$ (**102**) respectively (Scheme 38).[1149] The electrochemistry of (**101**) and (**102**) has been investigated (equations 93 and 94) and metal–metal interactions in the mixed valence products discussed.[1149,1272] The trinuclear complex $[N\{CH_2CH_2OphenRu(bipy)_2\}_3]^{6+}$ has been prepared.[1054]



i, KN_3, acetone; ii, ½pz; iii, $[RuCl(bipy)_2pz]^+$

Scheme 38[1149]

$$[2,2,2]^{4+} \xrightarrow{-2e^-} [3,2,3]^{6+} \xrightarrow{-e^-} [3,3,3]^{7+} \quad (93)$$

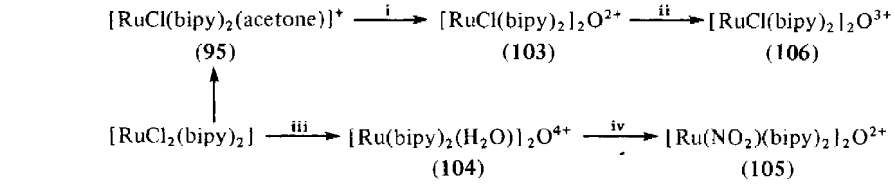
$$[2,2,2,2]^{6+} \xrightarrow{-2e^-} [3,2,2,3]^{8+} \xrightarrow{-e^-} [3,3,2,3]^{9+} \xrightarrow{-e^-} [3,3,3,3]^{10+} \quad (94)$$

(*ii*) *Oxygen donor complexes*

Reaction of $[RuCl(L)_2 \text{ acetone}]^+$ (**95**), prepared from $[RuCl(NO)(L)_2]^{2+}$ with N_3^- in acetone, with O_2 for 72 h yields the oxo-bridged dimer $[RuCl(L)_2]_2O^{2+}$ (**103**) (L = bipy, phen).[1274] Treatment of $[RuCl_2(bipy)_2]$ with Ag^+ for 8 h in refluxing water gives $[Ru(bipy)_2(OH_2)]_2O^{4+}$ (**104**) which can be readily converted to the nitro derivative $[Ru(NO_2)(bipy)_2]_2O^{2+}$ (**105**) on reaction with $NaNO_2$ (Scheme 39).[1207,1212b,1274] The redox properties of $[RuCl(bipy)_2]_2O^{2+}$ have been investigated and the oxidized $[3,4]^{3+}$ (**106**), $[4,4]^{4+}$ and reduced $[2,3]^{1+}$ ions generated.[1274] PES studies on the mixed valence $[3,4]^{3+}$ ion indicate strong coupling between equivalent Ru atoms.[1274] The single crystal X-ray structure of $[Ru(NO_2)(bipy)_2]_2O^{2+}$ (**105**) shows < RuORu = 157.2° with Ru—O = 1.876, 1.890 Å, with a Ru to Ru distance of 3.692 Å.[1275]

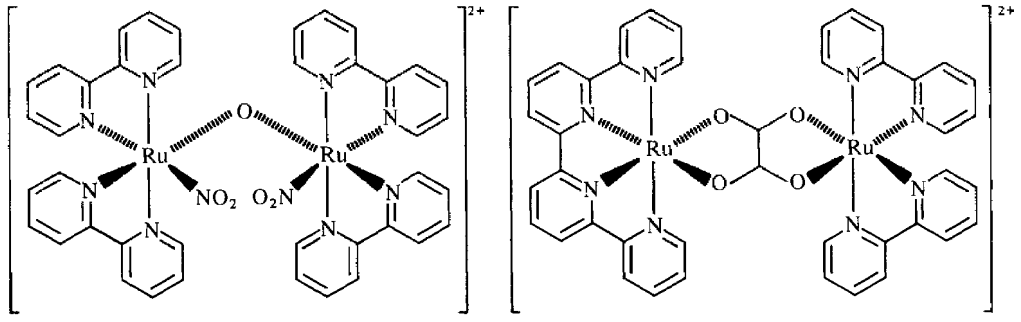
The oxo-bridged dimers $[Ru(L)_2OH_2]_2O^{2+}$ (L = bipy, phen) catalytically oxidize H_2O to O_2[1207] and $2Cl^-$ to Cl_2[1205,1207] in the presence of excess of Ce^{IV}. The mechanism of H_2O oxidation is believed to occur *via* the four electron oxidation species $[5,5]^{4+}$ (equation 95).[1207] The use of these binuclear complexes on chemically modified electrodes has been reported,[1205] and their involvement in the photooxidation of H_2O at the surface of hectorite mentioned.[1190]

Reaction of $[RuCl_2(bipy)_2]$ with L^{2-} (L^{2-} = pyrazine-2,5-dicarboxylate) gives $[Ru(LH)(bipy)_2]^+$ and a green binuclear species $[Ru(bipy)_2]_2L^{2+}$.[562] No intervalence charge transfer absorption was observed for the mixed valence $[2,3]^{3+}$ ion in contrast to the complexes $[Ru(NH_3)_4]_2L^{3+}$ and $[(NH_3)_5Ru(L)Ru(bipy)_2]^{4+}$.[562] The single crystal X-ray structure of $[Rupy_4]_2(ox)^{2+}$ (**107**) shows a centrosymmetric planar oxalate bridging Ru^{II} ions with Ru—O = 2.096, 2.133 Å.[1276]



i, O_2, 72 h; ii, Cl_2; iii, $AgNO_3$, H_2O, Δ, 8 h; iv, $NaNO_2$

Scheme 39[1274]

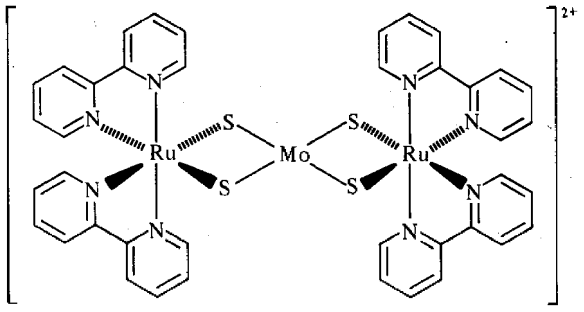


$$[(bipy)_2Ru^{V}(=O)-O-(O=)Ru^{V}(bipy)_2]^{4+} + 2H_2O \longrightarrow [(bipy)_2Ru^{III}(OH_2)-O-(H_2O)Ru^{III}(bipy)_2]^{4+} + O_2 \quad (95)$$

Reaction of RuO_4 with phen in CCl_4 yields a supposed oxy-bridged Ru^{VII} dimer $[Ru_2O_7(phen)_2]$.[1209] (see Section 45.4.3.1.x).

(*iii*) *Sulfur donor complexes*

The binuclear complex (**108**) has been synthesized and its use as a catalyst for the electrochemical reduction of acetylene in MeOH/DMF discussed.[1212a]



(108)

(*iv*) *Halide complexes*

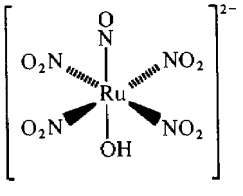
Reaction of $[RuCl_2(AsPh_3)_2]_2$ with bipy is reported to yield a dimer of stoichiometry $[Ru_2Cl_4(bipy)_3]$.[677] Reaction of $[Ru(CO_3)(bipy)_2]$ with *cis*-$[RuCl_2(bipy)_2]$ under acidic conditions gives $[RuCl(bipy)_2]_2^{2+}$; the complex can be oxidized to a $[3,2]^{3+}$ ion which decomposes in MeCN to $[RuCl_2(bipy)_2]^+$ and $[Ru(bipy)_2(NCMe)_2]^{2+}$.[1160] The weakness of the Cl^- bridge in the mixed valence compound is assigned to the high strength of the Ru^{III}—Cl bond leading to bridge cleavage.[1126,1160]

45.4.4 Nitrosyls

Ruthenium shows a wide nitrosyl chemistry and several reviews of the area have been published.[273–277] ^{15}N NMR studies on nitrosyl complexes show that N is deshielded by up to 450 p.p.m. in bent as compared with linear NO ligands.[1277] PES studies of core binding energies for nitrosyl complexes have been reported and comparisons between coordinated NO^+ and ^+N_2R assessed.[1278,1279] ^{99}Ru Mössbauer spectra of $[RuX_5(NO)]^{n+}$ (X = ^-CN, NH_3, ^-NCS, Cl^-, Br^-) have been measured at 4.2 K, and the chemical isomer shift found to decrease as ligand field strength of X decreases;[27c,1280] the changes in quadrupolar splitting have been discussed in terms of σ donor and π acceptor abilities of coordinated ligands.[1280]

45.4.4.1 Nitrogen donor complexes

Nitrosyl ammine, amine, heterocyclic and phosphine complexes are discussed in Sections 45.4.1, 45.4.2, 45.4.3 and 45.5 respectively. A range of nitrosyl complexes incorporating NO_2^- and NO_3^- ligands have been reported. Treatment of $RuCl_3$ with $NaNO_2$ yields $[Ru(OH)(NO_2)_4(NO)]^{2-}$ (**109**),[1281–1283] the single crystal X-ray structure of which shows a linear Ru—N—O(nitrosyl) with ^-OH and NO^+ mutually *trans*; Ru—N(NO_2) = 2.079 Å, Ru—N(NO) = 1.748 Å.[1284] The IR spectrum of $[Ru(OH)(NO_2)_4(NO)]^{2-}$ has been assigned by ^{14}NO and ^{15}NO labelling experiments.[298] Reaction of ruthenium(II) nitrosyls with HNO_3 gives a wide range of products of general type $[Ru(NO_2)_x(NO_3)_y(NO)_2]^{n+}$; the separation of some of the products has been achieved,[2,1285–1292a] *e.g.* $[Ru(NO_3)_3(NO)(OH_2)_2]$, $[Ru(NO_2)(NO_3)(NO)(OH_2)_3]^+$, $[Ru(NO_2)(NO_3)_2(NO)(OH_2)_2]$. In the presence of tributyl phosphate (tbp), $[Ru(NO_3)_3(NO)(OH_2)_2]$ gives an equilibrium mixture of $[Ru(NO_3)_3(NO)(tbp)_2]$, which can be extracted into dodecane.[1286]



(109)

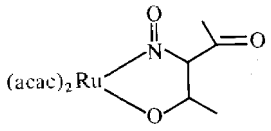
Treatment of $[RuCl_5(NO)]^{2-}$ with KNCS yields $[Ru(NCS)_5(NO)]^{2-}$[1292b] the Mössbauer spectrum of which has been reported.[27c] The reaction between $[Ru(CN)_6]^{4-}$ and HNO_3 yields $[Ru(CN)_5NO]^{2-}$[1281,1283,1293] (see Section 45.3.1).

45.4.4.2 Oxygen donor complexes

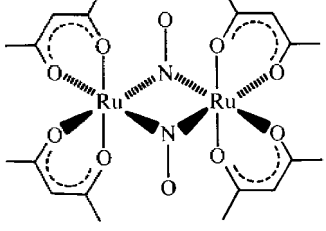
$[Ru(NO)(OH_2)_5]^{3+}$ can be prepared by reaction of $[Ru(OH_2)_6]^{2+}$ with NO,[282] or by protonation with HNO_3 of $[Ru(OH)_3NO]_n$ formed by alkaline hydrolysis of $[RuCl_3(NO)]_n$.[1294–1296] Reaction of $[Ru(NO)(OH_2)_5]^{3+}$ with $[Cr(OH_2)_6]^{2+}$ yields the dimeric product $[(H_2O)_5Ru—NH—Cr(OH_2)_5]^{5+}$, the rate of formation of which is first order in $[Cr^{II}]$ and $[Ru^{II}]$.[282]

$[RuCl_3(NO)(OH_2)_2]$ reacts with diketones, *e.g.* acacH, to give the halo-bridged dimer $[RuCl_2(acac)(NO)]_2$.[619] At pH 3 *cis*-$[RuCl(acac)_2(NO)]$ is formed while a tetramer $[Ru(acac)_2(NO)]_4$ has also been proposed;[1297] at pH 6 $[RuCl_3(NO)(OH_2)_2]$ with Hacac yields $[Ru(acac)_2(hia)]$ (**110**) which can also be prepared directly from *cis*-$[RuCl(acac)_2(NO)]$.[1297] The single crystal X-ray structure of the dimer $[Ru(acac)_2(NO)]_2$ (**111**) shows Ru—O = 2.031 Å, Ru—N = 1.918 Å with a planar $Ru(\mu\text{-}NO)_2Ru$ unit.[1298] The structure of $[RuL_2(NO_2)(NO)]^{2-}$ (L = 2,4,5,6-(1*H*,3*H*)pyrimidinetetrone-5-oximate) has been reported, chelation of L being through O of oximate and the 6-carbonyl moiety with *cis* NO and NO_2.[1299] Reaction of $[RuCl_3(NO)(OH_2)_2]$ with glycinate gives $[Ru(OH)_3(gly)(NO)]^-$.[1300]

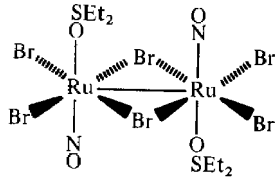
Oxidation of $[RuBr_3(SEt_2)_2(NO)]$ produces $[RuBr_3(NO)(OSEt_2)]_2$ (**112**), the X-ray structure of which shows a Br^--bridged dimer with sulfoxide *trans* to NO; Ru—N = 1.71 Å, Ru—O = 2.058 Å.[1301]



(110)



(111)



(112)

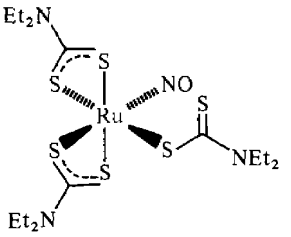
45.4.4.3 Sulfur donor complexes

Reaction of $[RuCl_3(NO)]$ with thioethers (L) in EtOH gives complexes $[RuCl_3(NO)L_2]$ (L = SEt_2, SEtPh, SPr_2 $S(CH_2Ph)_2$, SPrPh, SMePh, $SeEt_2$, SePhEt) with L being mutually *trans*;[619,1302,1303] the synthesis of $[RuBr_3(NO)(SEt_2)_2]$ has been reported.[1301] The ^1H and ^{13}C NMR and IR spectra of these complexes have been analysed.[1302,1303] The complexes $[RuX_3(NO)L_2]$ (X = Cl^-, Br^-; L = PPh_3, $AsPh_3$) react with elemental sulfur to give the sulfide dimers $[RuX_2(NO)L_2]_2S$ which can be oxidized with perbenzoic acid to the sulfoxy-bridged species $[RuX_2(NO)L_2]_2SO$.[1304]

Reaction of $[RuCl_3(NO)]$ with dithioacetylacetonate ($sacsac^-$) in water yields *trans*-$[Ru(sacsac)_2Cl(NO)]$.[1305] Polarography of this product shows two reversible reductions at −0.27 V and −1.43 V *vs.* Ag/AgCl, compared with $[Ru(sacsac)_3]$ which shows only one redox couple at +0.04 V *vs.* Ag/AgCl corresponding to the $Ru^{III/II}$ couple.[1305–1307] More recently dithiocarbamate derivatives *cis*- and *trans*-$[RuX(S_2CNRR')_2(NO)]$ (X = Cl^-, Br^-, I^-, Fe^-, NO_2^-, ^-OH, ^-NCO, N_3^-, SCN^-; R = R′ = Me, Et; R = Me, R′ = Et; R = Me, R′ = Ph) have been prepared from $[RuCl_3(NO)]$ and $Na^+(^-S_2CNRR')$ in MeOH followed by acidification and treatment with X^-.[1308] *Cis*-$[Ru(S_2CNMe_2)_2(^{15}NO_2)(NO)]$ undergoes exchange between NO and NO_2 ligands.[1308] *Cis*-$[Ru(S_2CNRR')_3(NO)]$ can also be isolated from the above reactions[1308] or prepared directly from $[Ru(S_2CNRR')_3]$ with NO.[1309] The ^1H NMR spectrum of the complex with R = R′ = Me differentiates between unidentate and bidentate dtc ligands;[1308] this is confirmed by the single crystal X-ray structure of $[Ru(S_2CNEt_2)_3(NO)]$ (**113**) which shows two bidentate dtc ligands with Ru—S = 2.415 Å and one monodentate dtc with Ru—S = 2.398 Å *cis* to NO, Ru—N = 1.72 Å.[1310]

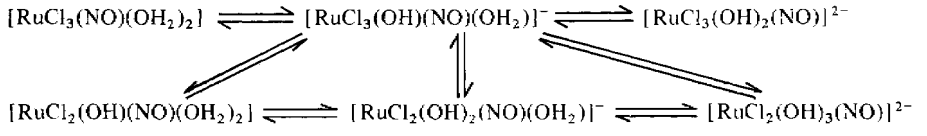
45.4.4.4 Halide complexes

Reaction of $RuCl_3$ with NO in EtOH yields $[RuCl_3(NO)]$[1292,1300,1302] while $[RuX_3(NO)]_n$ (X = Cl^-, Br^-, I^-) can be prepared by treatment of RuO_4 with HX and HNO_3.[1311,1312] In aqueous solution,



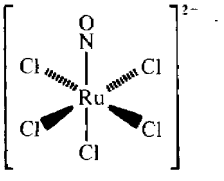
(113)

these complexes may be regarded as $[RuX_3(NO)(OH_2)_2]$[1313] and are highly useful starting materials for the synthesis of ruthenium nitrosyls. The kinetics of hydrolysis of $[RuCl_3(NO)(OH_2)_2]$ show displacement of three Cl^- ligands at decreasing rates with no loss of NO^+, pK_1 and pK_2 for $[RuCl_3(NO)(OH_2)_2]$ being 4.9 and 7.5 respectively (Scheme 40).[1313] The interaction of $[RuCl_3(NO)(OH_2)_2]$ with glycine and alanine has been reported.[1314]



Scheme 40[1313]

Anation of $[RuX_3(NO)]$ with halide,[1311,1312,1315] reaction of $RuCl_3$ with HCl and NO for 48 h followed by NH_4Cl[1315] or treatment of $RuCl_3$ with NOCl in EtOH[282,1316] yield $[RuCl_5(NO)]^{2-}$. $[RuCl_5(NO)]^{2-}$ with X^- gives $[RuX_5(NO)]^{2-}$ ($X = Br^-$, I^-).[1316] The single crystal X-ray structure of $[RuCl_5(NO)]^{2-}$ (**114**) shows octahedral Ru^{II} with Ru—Cl(equatorial) = 2.373–2.379, Ru—Cl(*trans* to NO) = 2.357, Ru—N = 1.738, N—O = 1.131 Å, < RuNO = 176.7°,[1317a] with $[RuF_5(NO)]^{2-}$ being found to be isostructural.[1317b] The IR spectrum of $[RuCl_5(NO)]^{2-}$ has been assigned,[298,1318–1324] with $\nu_{^{14}NO}$ = 1876, 1850, 1844 cm^{-1} for X = Cl^-, Br^-, I^- respectively.[1318] The ^{19}F NMR spectrum[1325] and Mössbauer data[27] for $[RuX_5(NO)]^{2-}$ have been reported. The rate of hydrolysis of $[RuCl_5(NO)]^{2-}$ is more rapid under basic conditions although hydrolysis of $[RuCl_4(OH)(NO)]^{2-}$ is pH independent at pH < 2.5 and pH = 7.5–9.5.[1315,1326] The crystal structure of $[RuCl_4(OH)(NO)]^{2-}$ (Ru—N = 2.04 Å) has been reported.[1327]



(114)

$[RuCl_5(NO)]^{2-}$ shows a reversible one electron oxidation, the electrogenerated product being assigned on the basis of IR, ESR and magnetic data to low spin $[Ru^{III}Cl_5(NO)]^-$.[1328,1329a]

Reaction of $RuCl_3$ with $S_3N_3Cl_3$ gives a brown product '$[RuCl_3(NS)]$' which, on treatment with Ph_4PCl in aqueous solution, yields $PPh_4[RuCl_4(NS)(OH_2)]$, the single crystal X-ray structure of which shows octahedral geometry with H_2O *trans* to NS and < RuNS = 170.9° and N—S = 1.504 Å.[1329b]

45.4.5 Hydrazines, Diimines and Related Ligands

Refluxing solutions of $[RuCl_2(cod)]_n$ with hydrazines yield complexes of type $[Ru(cod)(NH_2NRR')_4]^{2+}$ and $[Ru(H)(cod)(NH_2NRR')_3]^+$.[650] These products are converted to $[Ru(NH_2NCRR')_2(PR_3)_4]^{2+}$ (R = R' = Me) on reaction with PR_3, while with LiX, $[Ru(H)(X)(cod)]_2NH_2NMe_2$ ($X = Cl^-$, Br^-) is isolated.[650] PES studies indicate that aryldiazo and aryldiimine

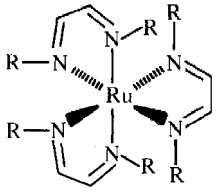
ligands possess low overall charge and are less polar than coordinated N_2.[1279] $[Ru(cod)(NH_2NH_2)_4]^{2+}$ reacts with isocyanides CNR in refluxing acetone to give *trans*-$[Ru(CNR)_4(NH_2NMe_2)_2]^{2+}$;[1330] in ethanol reaction of $[Ru(cod)(NH_2NH_2)_4]^{2+}$ and $CNCMe_3$ yields *mer*-$[Ru(CNCMe_3)_3(NH_2NH_2)_3]^{2+}$, which in cold acetone is converted to *trans*-$[Ru(CNCMe_3)_4(NH_2NH_2)_2]^{2+}$ and under refluxing conditions to *mer*-$[Ru(CNCMe_3)_3(NH_2NMe_2)_3]^{2+}$.[1330] $[Ru(cod)(NH_2NHMe)_4]^{2+}$ with CNR yields *trans*-$[Ru(CNR)_4(NH_2NHMe)_2]^{2+}$.[1330] Interaction of $[RuCl_2(PPh_3)_3]$ with hydroxylamine under basic conditions gives $[RuCl(NH_2O)(NH_2OH)(PPh_3)_2]$ which has been postulated as having an η^2-NH_2O^- ligand.[1331]

The syntheses of $[Ru(N_2C_6H_4\text{-}4\text{-}R)(CO)_2L_2]^+$ (R = NO_2, F, H, OMe, NMe_2, L = PPh_3; R = OMe, L = $PPh_2(4\text{-}MeC_6H_4)$ and $[Ru(N_2C_6H_3\text{-}2,6\text{-}R'_2)(CO)_2(PPh_3)_2]^+$ (R = Me, Cl) from $[Ru(CO)_3L_2]$ have been reported.[1332] Protonation with HX yields $[Ru(N_2HC_6H_4\text{-}4\text{-}R)(CO)_2L_2]^{2+}$ reversibly together with $[Ru(I)(N_2HC_6H_4\text{-}4\text{-}F)(CO)_2(PPh_3)_2]^+$ and $[RuCl_2(N_2HC_6H_4\text{-}4\text{-}R)(CO)(PPh_3)_2]$ as isolable products.[1332] Ruthenium blue solutions with PhN_2Ph give the postulated dimeric product $[Ru_2Cl_4(C_6H_4N_2Ph)(PhN_2Ph)]$ with an *ortho*-metallated PhN_2Ph ligand.[676]

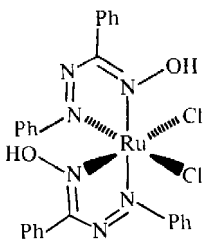
Reaction of $[RuH_2(PPh_3)_4]$ or $[Ru(H)(C_6H_4PPh_2)(PPh_3)(C_2H_4)]$ with dad (dad = (4-$MeOC_6H_4N{=}CH)_2$) yields a dark product $[Ru(dad)_3]$ (**115**), the single crystal X-ray structure of which confirms a tris-chelate configuration, formally Ru^0 with Ru—N(average) = 2.06 Å;[1333,1334] the diamagnetic solid is rapidly oxidized in air to $[Ru(dad)_3]^{2+}$.[1333,1334] Treatment of $RuCl_3$ in THF with Zn powder followed by dad gives *cis*-$[RuCl_2(dad)_2]$.[1335] A range of organometallic derivatives of dad ligands, *e.g.* $[Ru_3(CO)_8(dad)]$, $[Ru(CO)_3(dad)]$, $[Ru_2(CO)_6(dad)]$, $[Ru_4(CO)_8(dad)_2]$, have been synthesized and their reactivity and rearrangement chemistry investigated.[1,1336–1346]

RuX_3 reacts with a range of arylazooximes to give *cis*- and *trans*-$[RuCl_2(HL)_2]$ (HL = RN=NC(=NOH)R').[1347,1348] The X-ray structure of the *cis* isomer for R = R' = Ph (**116**) shows Ru—N = 1.986 Å indicating strong back-bonding.[1348] $[RuCl_2(HL)_2]$ with PR_3 in the presence of NEt_3 produces $[RuL_2(PR_3)_2]$ (PR_3 = PPh_3, ½diphos).[1347] Reaction of $RuCl_3$ or $[RuCl_2(HL)_2]$ with HL in the presence of NEt_3 however gives the Ru^{III} tris chelate product $[RuL_3]$ (HL = PhN=NC(=NOH)Me).[1347] The Ru^{III} complexes $[RuCl_2(L)(HL)]$ and $[RuCl_2L_2]^-$ have also been generated and show ligand to metal charge transfer bands near 580 and 1000 nm; the corresponding Ru^{II} species show metal to ligand charge transfer bands near 680 nm.[1349]

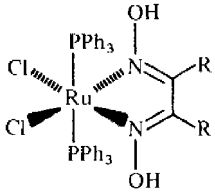
$[RuCl_2(PPh_3)_3]$ reacts with oximes L to give complexes of type $[RuCl_2(PPh_3)_2L]$ (**117**) which have been characterized by IR and ^1H and ^{31}P NMR spectroscopy.[1331]



(115)



(116)



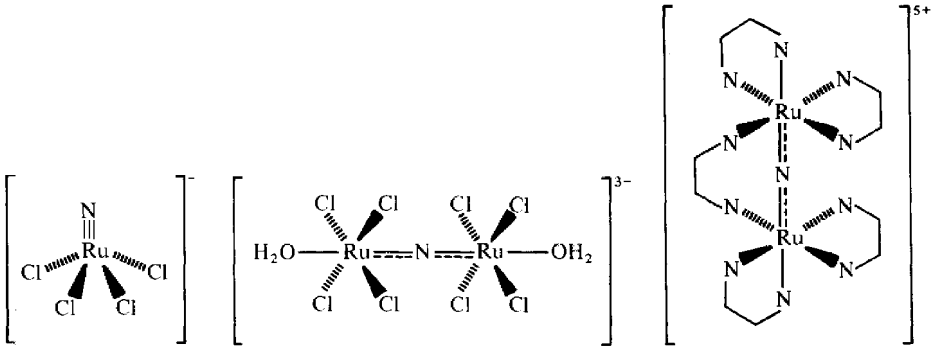
(117)

45.4.6 Nitrides

The chemistry of transition metal nitrido[1350] and organoimido[1351] complexes has been reviewed. Few mononuclear nitrido complexes are known. Reaction of *trans*-$[Ru(O)_2X_4]^{2-}$ with N_3^- and HX yields $Cs_2[RuNX_5]$ (X = Cl^-, Br^-) on addition of CsX while with larger cations (Ph_4As^+, Bu_4N^+) $[RuNX_4]^-$ was isolated.[65] The single crystal X-ray structure of $[RuNCl_4]^-$ (**118**) shows square pyramidal Ru^{VI} with Ru—N = 1.570 Å, Ru—Cl = 2.310 Å.[1352] Addition of L (L = py, pyridine *N*-oxide, isoquinoline, DMSO) or L' (L' = hexamethylenetetramine, pz or dioxane) to $[RuNCl_4]^-$ gives adducts $[RuNCl_4(L)]^-$ and $[RuNCl_4]_2L'^{2-}$.[1353]

Reaction of $[RuCl_5(NO)]^{2-}$ with $SnCl_2$ or HCHO yields the centrosymmetric binuclear nitrido complex $[Ru_2NCl_8(OH_2)_2]^{3-}$.[94,1354,1355] The single crystal X-ray structures of $K_3[Ru_2NCl_8(OH_2)_2]$[1356,1357] and $(NH_3)_3[Ru_2NCl_8(OH_2)_2]$ (**119**)[1358] show Ru—N = 1.718 Å Ru—O = 1.80 Å, < ORuN = 179.7°.[1356] A range of other substituted nitrido dimers have been prepared, *e.g.* $[Ru_2NX_8(OH_2)_2]^{3-}$ (X = Br^-, NCS^-), $[Ru_2N(NO_2)_6(OH)_2(OH_2)_2]^{3-}$, $[Ru_2NX_2(NH_3)_8]^{3+}$ (X = Cl^-, Br^-, NO_3^-), $[Ru_2NX_3(NH_3)_6(OH_2)]^{2+}$ (X = Cl^-, NCS^-, N_3^-),[1355] $[Ru_2NCl_8(CO)_2]^{3-}$,

$[Ru_2N(CN)_{10}]^{5-}$.[65] Vibrational spectra of these complexes are consistent with linear Ru—N—Ru units with $\nu_{Ru_2N} = 1083\,cm^{-1}$ for $[Ru_2NCl_8(OH_2)_2]^{3-}$.[65,1355] The resonance Raman[1359] and Mössbauer spectra[1360] of binuclear nitrides have been reported. Prolonged treatment of $[Ru_2NCl_8(OH_2)_2]^{3-}$ with en yields $[Ru_2N(en)_5]^{5+}$ (**120**) the single crystal X-ray structure of which shows a bridging en ligand and Ru—N(nitride) = 1.742 Å with < RuNRu = 174.6°; $\nu_{Ru_2N} = 1048\,cm^{-1}$.[647]



(118) (119) (120)

In the original preparation of ruthenium red $[Ru_3O_2(NH_3)_{14}]^{6+}$, an impurity 'ruthenium violet' was isolated.[570] This compound has been proposed to be a trinuclear species $[Ru_3N_2(NH_3)_8(OH)(OH_2)_5]^{5+}$ with a linear Ru_3N_2 backbone; a closely related osmium system has been synthesized.[1361]

45.4.7 Thiocyanates

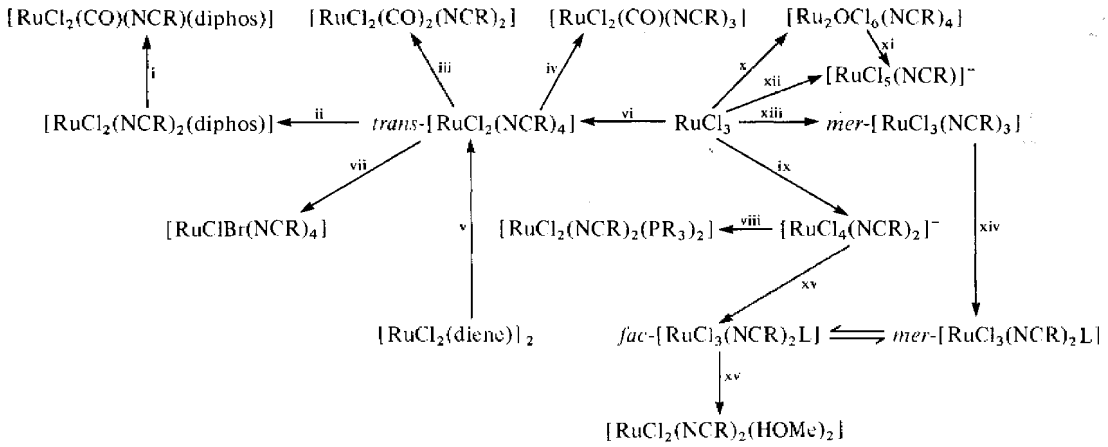
Ruthenium(II): $[Ru(SCN)_6]^{4-}$ is reported to be formed on treatment of $[Ru(NCS)_6]^{3-}$ with molten thiocyanate.[355,1362] $RuCl_3$ with CO in EtOH reacts with NH_4NCS to give proposed dimers $[Ru_2(NCS)_6(CO)_4]^{2-}$ and the monomer $[Ru(NCS)_4(CO)_2]^{2-}$.[1363]

Ruthenium(III): Reaction of $RuCl_3$ or $RuCl_6^{3-}$ with NCS^- yields $[Ru(NCS)_6]^{3-}$.[1362,1364–1366] Using high voltage electrophoresis, this product has been shown to be a mixture of four isomers of the type $[Ru(NCS)_n(SCN)_{6-n}]^{3-}$[1367,1368] with mixed N- and S-bound NCS^-. The far IR spectra of these complexes confirm mixed S and N bonding.[353] Heating solid Bu_4N^+ salts of the above mixture yields $[Ru(NCS)_5(SCN)]^{3-}$, while the PPN^+ salt rearranges to $[Ru(NCS)_6]^{3-}$ above 160°C.[1368] $[Ru(NCS)_6]^{3-}$ may also be prepared by treating $(Bu_4N)_3[Ru(NCS)_5SCN]$ with a one-hundred-fold excess of $Bu_4N^+Br^-$ in EtOH.[1368]

45.4.8 Nitriles

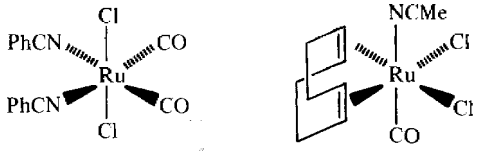
Ruthenium(II): Transition metal complexes of organonitriles have been reviewed.[1369] $[Ru(\pi\text{-allyl})_2(nbd)]$ reacts in MeCN to give $[Ru(nbd)(NCMe)_4]^{2+}$ with further reflux yielding $[Ru(NCMe)_6]^{2+}$.[1183] Refluxing solutions of $[Ru(cod)(N_2H_4)_4]^{2+}$ and $[Ru(H)(cod)(NH_2NRR')_3]^+$ in MeCN yield $[Ru(cod)(NCMe)_4]^{4+}$ and $[RuH(cod)(NCMe)_3]^+$ respectively.[650] $[RuCl_2(cod)]_n$ in MeCN gives $[RuCl(cod)(NCMe)_3]^+$ which is converted to $[Ru(cod)(NCMe)_4]^{2+}$ and $[Ru(cod)(NCMe)_3(MeOH)]^{2+}$ on treatment with $AgPF_6$ in MeCN and MeOH respectively.[1370] Treatment of $[Ru(cod)(NCMe)_4]^{2+}$ with L yields $[Ru(cod)(NCMe)_2L_2]^{2+}$ (L = py, propylamine, 4-picoline) and $[Ru(cod)(NCMe)_3L]^{2+}$ (L = Et_2S).[1370] Ruthenium blue solution with PhCN produces $[RuCl_2(NCPh)_3]_2$ which reacts with L to give $[RuCl_2(NCPh)_2L_2]$ (L = $PhNH_2$, $\frac{1}{2}$bipy).[676] Scheme 41 summarizes the reactivity of halo–nitrile complexes.

Trans-$[RuCl_2(NCR)_4]$ can be prepared by reaction of $[RuCl_2(diene)]_2$ with nitrile,[1372] or by reduction of $RuCl_3$ with H_2 over Adams catalyst and treatment with RCN;[676,1371] $[RuCl_2(NCMe)_4]$ catalytically oxidizes decylmethyl sulfide under O_2 at 100 PSI ($7 \times 10^{-5}\,kg\,m^{-2}$) at 100°C to the sulfoxide.[1375] Carbonylation of *trans*-$[RuCl_2(NCR)_4]$ yields $[RuCl_2(CO)_2(NCR)_2]$ (R = Me, Et, Pr, Pr^i, Ph, $PhCH_2$);[1371] the single crystal structure of $[RuCl_2(CO)_2(NCPh)_2]$ (**121**) has been reported.[1376] $[RuX_2(CO)_3]_2$ (X = Cl^-, Br^-) with RCN produces $[RuX_2(CO)_3(NCR)]$[651] while $[RuCl_2(CO)(cod)]_2$ with RCN gives $[RuCl_2(CO)(cod)(NCR)]$; the structure of the MeCN adduct (**122**) has been published.[1377]



i, CO;[1371] ii, diphos;[1371] iii, CO, acetone, Δ;[1371] iv, CO, MeOH, Δ;[1371] v, RCN;[1372] vi, Pt, H_2, RCN;[676, 1371] vii, LiBr;[1371] viii, PR_3;[681] ix, MeOH, RCN;[681] x, RCN, 45–70 °C, 2 h;[1373, 1374] xi, CH_2Cl_2, Et_4NCl;[681] xii, RCN, 4 h, Δ;[681] xiii, RCN, MeOH, 70 °C, 1–3 h;[1373, 1374] xiv, L (L = py, PhSMe, R'CN);[1373, 1374] xv, MeOH, 48 h;[681]

Scheme 41



(121) (122)

Ruthenium(III): $RuCl_3$ with RCN in refluxing MeOH gives $[RuCl_3(NCR)_3]$ together with the novel side product $[RuCl(NCR)_5][RuCl_4(NCR)_2]$ which reacts with L to yield $[RuCl_2(NCR)_2L_2]$ (L = py, PPh_2Me).[1373,1374] The electrochemistry of $[RuCl_3L_3]$ (L = 2- and 3-methylbenzonitrile) and $[RuCl_3L_2L']$ (L = 2-methylbenzonitrile, L' = MeCN, py) shows $Ru^{II/III}$ and $Ru^{III/IV}$ redox couples, the *fac* isomers being more difficult to reduce than the corresponding *mer* isomers.[680]

45.5 PHOSPHORUS, ARSENIC AND ANTIMONY LIGANDS

45.5.1 Mononuclear Ruthenium(0) Complexes

45.5.1.1 $[RuL_5]$, $[RuL_nL'_{5-n}]$, $[RuL_nL'_{4-n}]$ complexes (L = P donor; L' = donor, MeCN, alkene)

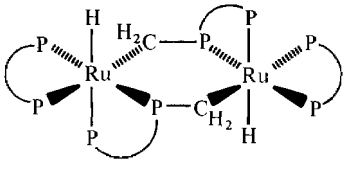
$[Ru\{P(OMe)_3\}_5]$ can be prepared either by Na/Hg reduction in THF of $[RuCl_2\{P(OMe)_3\}_4]$ in the presence of excess $P(OMe)_3$[1378,1379] or by photolysis of $[Ru_3(CO)_{12}]/P(OMe)_3$ mixtures.[1380] At low temperatures (−125°C), its $^{31}P-\{^1H\}$ NMR spectrum consists of a limiting A_2B_3 pattern but variable temperature studies suggest that facile intramolecular scrambling of $P(OMe)_3$ ligands occurs at higher temperatures.[1378] Heating $[Ru\{P(OMe)_3\}_5]$ to 120°C in *n*-hexane results in a novel rearrangement to form *cis*-$[Ru(Me)(P\{OMe\}_3)_4P(O)(OMe)_2]$ and both these compounds will react with MeI to give $[Ru(Me)(P\{OMe\}_3)_5]I$.[1380]

The related $[Ru(PF_3)_5]$ compound was first prepared by reaction of $RuCl_3$ and PF_3 (500 atm/250°C) in the presence of copper,[1381,1382] and more recently by treatment of $[Ru_3(CO)_{12}]$ with PF_3 at high pressure (500 atm/160°C/12 h).[1383] This extremely volatile white solid which is fluxional even at −160°C[1384] sublimes at room temperature and decomposes to an unidentified red polynuclear compound at 155°C. It also reacts with K/Hg to give the colourless liquid $K_2[Ru(PF_3)_4]$.[1381,1382]

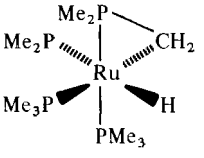
$[Ru(PF_2NMe_2)_5]$ can be directly synthesized by cocondensation of ruthenium vapour and PF_2NMe_2[1385] or by reductive elimination of acetic acid from $[RuH(OCOMe)(PPh_3)_3]$ on treatment with PF_2NMe_2 at elevated temperatures.[1386] Under milder conditions, hydrido/acetato/phosphine

compounds are formed (see Section 45.10.3.2). The compounds $[Ru(PF_2NC_4H_8)_5]$, $[Ru(PF_3)_3(PPh_3)_2]$ and $[Ru(PF_3)_4PPh_3]$ can be prepared by the same route. The latter complex is also formed if $[Ru(PPh_3)(\eta^4\text{-}C_4H_6)_2]$ is treated with an excess of PF_3, whereas with other L ($P(OMe)_3$, $P(OCH_2)_3CMe$, PF_2NMe_2), only one butadiene molecule is displaced and $[Ru(PPh_3)L_2(C_4H_6)]$ is formed.[1387] High resolution NMR studies establish fluxional behaviour for all these complexes.

Treatment of $[RuH(2\text{-np})(dmpe)_2]$ (2-np = 2-naphthyl) with L (L = CO, C_2H_4, $P(OMe)_3$) gives the five-coordinate zerovalent complexes $[Ru(dmpe)_2L]$,[1388] whereas pyrolysis of the hydride results in loss of naphthalene and formation of a compound of empirical formula $[Ru(dmpe)_2]$. However its IR spectrum contains a ν(RuH) band at *ca.* 1800 cm^{-1}[1389] and an X-ray analysis shows its solid state structure to be the novel dimeric Ru^{II} complex (**123**) which results from intermolecular oxidative addition of methyl groups to ruthenium.[1390] Similarly reaction of *trans*-$[RuCl_2(PMe_3)_4]$ with Na/Hg in C_6H_6 gives '$Ru(PMe_3)_4$', shown by NMR studies to be $[RuH(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3]$ (**124**).[1391a,1391b] However, reduction of $[RuCl_2(PMe_3)_2\{P(OMe)_3\}_2]$ with Na/Hg in the presence of $P(OMe)_3$ gives $[Ru(PMe_3)_2\{P(OMe)_3\}_3]$.[1391c]



(123)



(124)

The genuine Ru^0 complex $[Ru(dppe)_2L]$ (L = $P(OMe)_3$, CO) can be prepared by reaction of $[Ru(dppe)_2$ styrene] (synthesized from $[Ru(PPh_3)_2(styrene)_2]$ and dppe) with L;[1392] $[Ru(PMe_3)_4C_2H_4]$ has been synthesized both by reaction of $[Ru(PMe_3)(\eta\text{-}C_6H_6)(C_2H_4)]$ with PMe[1391a] and by the interaction of *trans*-$[RuCl_2(PMe_3)_4]$ with $MgEt_2$. NMR data for the latter suggest that the C_2H_4 group is bound in the η^2 or metallacyclopropane form and this is confirmed by X-ray analysis.[1393]

Although strictly outside the scope of this review, other genuine Ru^0 alkene (or arene) phosphine complexes include $[Ru(PPh_3)_2(styrene)_2]$,[1394] $[Ru(PPh_3)_2(C_2H_4)_2(styrene)]$,[1394] $[Ru(dppm)_2$-styrene],[1392] $[Ru(P\{OCH_2\}_3CEt)_3nbd]$,[1395] $[Ru(PR_3)(\eta^4\text{-}C_4H_6)_2]$,[1394,1396] $[Ru(PPh_3)_3(\eta^4\text{-}C_4H_6)]$,[1394] $[Ru(PR_3)_2(C_6H_6)]$,[1397] $[Ru(PMe_3)(cod)(cot)]$,[1398] $[Ru(dppm)_2(cod)]$,[1399] $[Ru(PR_3)_3$-$(CH_2C_6H_4CH_2)]$,[1400] $[Ru(CO)(PPh_3)_2(\eta^4\text{-}C_5H_6)]$ and $[Ru(L)(\eta^4\text{-}C_5H_6)]$ (L = $MeC(CH_2PPh_2)_3$, $PhP(CH_2CH_2PPh_2)_2$).[1401] However, many have been reformulated as *ortho*-metallated Ru^{II} compounds[1402] (see also reference 1 and Section 45.5.4.5.v for more information).

Finally, electrochemical reduction of $[RuCl_2(PPh_3)_4]$ in MeCN gives a complex formulated as $[Ru(\eta^2\text{-}MeCN)(PPh_3)_4]\cdot MeCN$.[1403] However, chemical reduction of $[RuCl_2(PPh_3)_n]$ (n = 3 or 4) with Na/Hg or Mg/Hg in MeCN/THF gives the isomeric *ortho*-metallated $[RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2]$.[1404] It is claimed that these products are identical[1404] but this has been refuted.[1405] Labile intermediates such as $[Ru(MeCN)_2(PPh_3)_2]$ (paramagnetic and presumably tetrahedral), $[RuMeCN(PPh_3)_3]$ and $[Ru(MeCN)_3PPh_3]$ are also observed on chemical reduction of $[RuCl_2(PPh_3)_4]$.[1404]

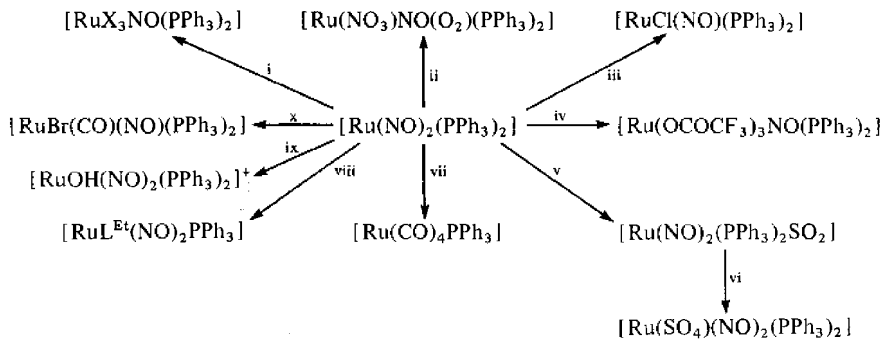
45.5.1.2 Nitrosyl complexes

Ruthenium forms more nitrosyl complexes than any other element. The dinitrosyl complex $[Ru(NO)_2(PPh_3)_2]$ was first prepared from $[RuCl_2(CO)_2(PPh_3)_2]$ and $Na[NO_2]$ in DMF; $[Ru(ONO)_2(CO)_2(PPh_3)_2]$ is formed initially but this isomerizes to $[Ru(NO_2)_2(CO)_2(PPh_3)_2]$ which decomposes to the $[Ru(NO)_2(PPh_3)_2]$ complex,[1406] probably *via* $[Ru(ONO)(CO)(NO)(PPh_3)_2]$.[1407]

Other synthetic routes to this useful compound are by reaction of $[RuH_4(PPh_3)_3]$ with NO,[1408] by treatment of $[RuHCl(PPh_3)_3]$, $[RuH(NO)(PPh_3)_3]$ or $[RuCl(NO)(PPh_3)_2]$ with $[Co(NO)(DMG)_2]$[1409] or by reaction of $RuCl_3/PPh_3$ (1:2 mole ratio) with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in the presence of Et_3N.[1410a] Direct reaction of $[RuCl_2(PPh_3)_3]$ with NO in acetone or C_6H_6 gives both $[Ru(NO)_2(PPh_3)_2]$ and $[RuCl_3NO(PPh_3)_2]$ (see Section 45.5.4.6.iii); in $CHCl_3$ only $[RuCl_3$-$(NO)(PPh_3)_2]$ is formed.[1411]

The X-ray crystal structures of $[Ru(NO)_2(PPh_3)_2]\cdot nC_6H_6$ (n = 0,[1412] 0.5[1413]) reveal that the compound is pseudotetrahedral with linear NO groups and is thus best described as a formally Ru^{-II}, NO^+ complex. Physical measurements performed on this compound include ^{15}N NMR spectro-

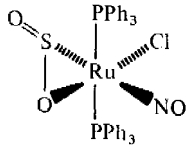
scopy (which supports the presence of linear RuNO groups in the solid state and in solution),[1414] XPS studies[1278] and electrochemical studies in MeCN which reveal an irreversible two electron oxidation process. In the presence of excess chloride ion, it gives a stable product (possibly $[RuCl_2(NO)_2(PPh_3)_2]$) from which $[Ru(NO)_2(PPh_3)_2]$ can be electrochemically regenerated.[1415] Some reactions of $[Ru(NO)_2(PPh_3)_2]$ are shown in Scheme 42.



i, X_2;[1413] $PhCH_2Br/\Delta$;[1416] ii, O_2;[1406, 1413] iii, $[RuCl_2(PPh_3)_3]/Zn$;[1413] iv, CF_3CO_2H;[1417] v, SO_2;[1418] vi, air;[1418] vii, CO/100 atm/24 h;[1418, 1419] viii, L_2^{Et} = (EtNCH$_2$CH$_2$NEtC=)$_2$;[1420] ix, air;[1406] x, CO, $PhCH_2Br$, toluene/Δ[1416]

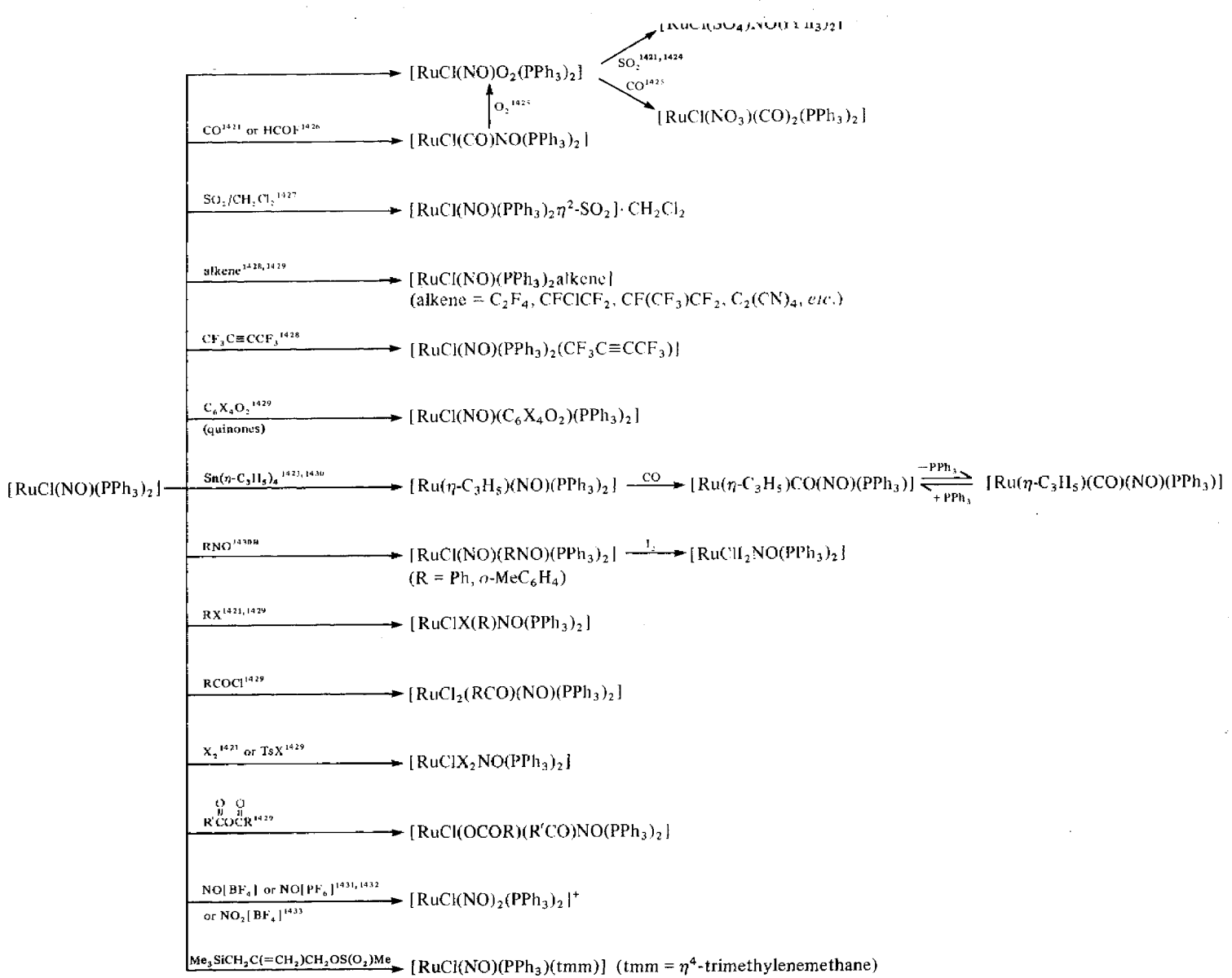
Scheme 42

The ruthenium analogue of Vaska's compound, $[RuCl(NO)(PPh_3)_2]$, can be prepared by reaction of $[RuCl_3NO(PPh_3)_2]$ with Zn dust or Zn/Cu in boiling C_6H_6.[1421–1423] Some of the reactions exhibited by this useful starting material, namely addition of neutral molecules such as alkene, CO, SO_2 *etc.*, chloride displacement by allyl anion or oxidative addition to form Ru^{II} nitrosyls are shown in Scheme 43. Similar studies have been made on $[RuCl(NO)(AsPh_3)_2]$[1434] and the related complexes [RuCl(NO)(L–L)], [RuCl(CO)(NO)(L–L)], [RuCl(NO)(P(OCH$_2$)$_3$CEt)(L–L)] and $[RuCl(CO)(NO)(PPh_2CH_2Ph)_2]$ (L—L = *trans*-spanning 2,11-bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene) are known.[1435] X-Ray structural analysis on $[Ru(NO)(PPh_3)_2(\eta\text{-}C_3H_5)]$ reveals a distorted tetrahedral structure with an almost linear RuNO group[1423] whereas $[RuCl(NO)_2(PPh_3)_2PF_6$[1432] has a square based pyridimidal structure containing one bent apical and one linear equatorial nitrosyl group (ν_{NO} 1687, 1845 cm^{-1}); recent solid state ^{15}N NMR studies support this conclusion.[1414b] However, ^{15}N NMR studies suggest that in solution an equilibrium mixture of isomeric structures is present,[1277] and that the linear and bent NO ligands undergo rapid intramolecular interconversion.[1436] The sulfate complex $[RuCl(SO_4)NO(PPh_3)_2]$ contains pseudooctahedral ruthenium with *trans* phosphines and a bidentate sulfato group (see Section 45.5.4.6.iii);[1424] $[RuCl(NO)(PPh_3)_2\eta\text{-}SO_2]\cdot CH_2Cl_2$ (**125**)[1427] has a very similar geometry except the η^2-SO_2 is S/O bonded. Another Ru^0 sulfur dioxide complex briefly mentioned in the literature is $[Ru(SO_2)_2(PPh_3)_2]$ (from $[RuH_4(PPh_3)_3]$ and SO_2).[1408,1437]



(125)

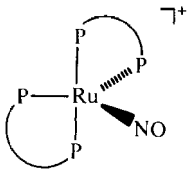
A high yield route to the preparation of $[RuCl(CO)(NO)(PPh_3)_2]$ is *via* treatment of [RuHCl(CO)(PPh$_3$)$_3$] with *N*-nitroso-*N*-methyltoluene-*p*-sulfonamide.[1438] The low frequency of the ν(RuCl) bond in the IR spectrum (266 cm^{-1}) indicates a weak Ru—Cl bond and indeed the chloride group is readily replaced by a range of anionic ligands to give $[RuX(CO)NO(PPh_3)_2]$ (X = OH, Br, I, N_3, NCO, NCS, HCO_2).[1438] The iodide has a trigonal bipyramidal geometry[1439] but the other members of the series may be closer to tetragonal pyramidal and may have a bent nitrosyl group.[1438] The dioxygen adducts $[RuX(NO)(O_2)(PPh_3)_2]$ (X = Cl, OH, CN, NCS) can be prepared by treatment of $[RuX(CO)(NO)(PPh_3)_2]$ with O_2.[1440] Reaction of $[RuCl(CO)(NO)L_2]$ (L = PPh_3, PCy_3) with


[RuCl(NO)(PPh3)2]
[RuCl(NO)O2(PPh3)2]
SO2 1421, 1424
CO 1425
O2 1425
[RuCl(NO3)(CO)2(PPh3)2]
CO 1421 or HCOF 1426
[RuCl(CO)NO(PPh3)2]
SO2/CH2Cl2 1427
[RuCl(NO)(PPh3)2η2-SO2]·CH2Cl2
alkene 1428, 1429
[RuCl(NO)(PPh3)2alkene]
(alkene = C2F4, CFClCF2, CF(CF3)CF2, C2(CN)4, etc.)
CF3C≡CCF3 1428
[RuCl(NO)(PPh3)2(CF3C≡CCF3)]
C6X4O2 1429
(quinones)
[RuCl(NO)(C6X4O2)(PPh3)2]
Sn(η-C3H5)4 1423, 1430
[Ru(η-C3H5)(NO)(PPh3)2]
CO
[Ru(η-C3H5)CO(NO)(PPh3)]
−PPh3
+PPh3
[Ru(η-C3H5)(CO)(NO)(PPh3)]
RNO 1430b
[RuCl(NO)(RNO)(PPh3)2]
I2
[RuClI2NO(PPh3)2]
(R = Ph, o-MeC6H4)
RX 1421, 1429
[RuClX(R)NO(PPh3)2]
RCOCl 1429
[RuCl2(RCO)(NO)(PPh3)2]
X2 1421 or TsX 1429
[RuClX2NO(PPh3)2]
O O
R'COCR 1429
[RuCl(OCOR)(R'CO)NO(PPh3)2]
NO[BF4] or NO[PF6] 1431, 1432
or NO2[BF4] 1433
[RuCl(NO)2(PPh3)2]+
Me3SiCH2C(=CH2)CH2OS(O2)Me
[RuCl(NO)(PPh3)(tmm)] (tmm = η4-trimethylenemethane)

Scheme 43

CO in CH_2Cl_2 in the presence of large anions gives $[Ru(CO)_2(NO)L_2]Y$ ($Y = BPh_4$, PF_6). These cations can also be prepared by reaction of $[Ru_3(CO)_9(PPh_3)_3]$ with $NO[PF_6]$ in MeOH. Unlike the isoelectronic $[Ru(CO)_3(PR_3)_2]$, these nitrosyl cations undergo further substitution with PPh_3 to yield $[Ru(CO)NO(PPh_3)_3]^+$. Complete CO replacement is not possible with monodentate phosphines but dppe gives both $[Ru(CO)(NO)PPh_3(dppe)]^+$ and $[Ru(NO)(dppe)_2]^+$. A more convenient route to all these cations is by addition of ligands to the highly reactive solvated species obtained *in situ* by treatment of $[RuCl(CO)(NO)(PPh_3)_2]$ with $Ag[PF_6]$ in acetone. The $[Ru(CO)_2(NO)L_2]^+$ cations react with halide ion (X^-) to regenerate the neutral complexes $[RuX(CO)(NO)L_2]$.[1441]

Crystallographic studies on the $[RuNO(dppe)_2]^+$ and $[RuNO(dppp)_2]^+$ cations[1442] (dppp = $Ph_2P(CH_2)_3PPh_2$) confirm the expected trigonal bipyramidal structure (**126**) with basal almost linear NO groups. Variable temperature ^{31}P NMR studies indicate that these compounds undergo facile intramolecular rearrangement probably *via* a Berry pseudorotation process.[1443]

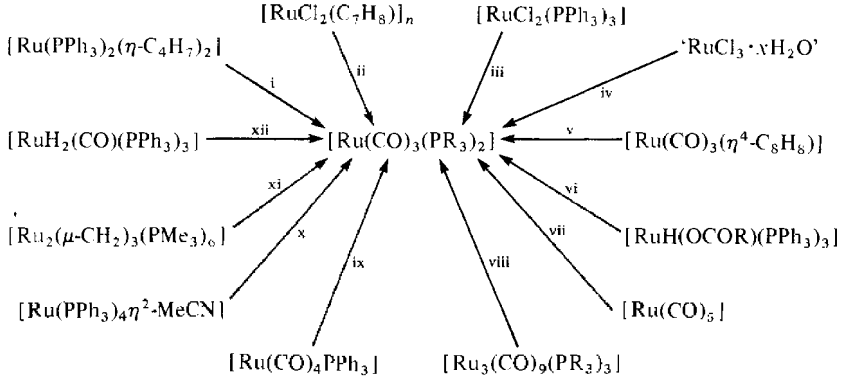


(126)

The related sterochemically non-rigid hydrido complexes $[RuH(NO)(PR_3)_3]$ can be prepared by refluxing $[RuCl_3(NO)(PR_3)_2]$ with ethanolic KOH in the presence of excess PR_3 (R_3 = Ph_3, Ph_2Me, Ph_2Pr^i, Ph_2Cy).[1444] The $[RuH(NO)(PPh_3)_3]$ complex has a slightly distorted trigonal bipyramidal structure with equatorial PPh_3 groups and a linear NO group.[1442a,1445] The ESCA spectrum of this compound is available.[1446]

45.5.1.3 Carbonyl and/or isocyanide complexes

$[Ru(CO)_3(PPh_3)_2]$ was first prepared by reduction of $[RuCl_2(CO)_2(PPh_3)_2]$ with Zn dust in DMF under four atmospheres pressure of CO.[1447] A number of alternative syntheses have since been developed (Scheme 44) and X-ray analysis has just confirmed its trigonal bipyramidal[1457] structure. $[Ru(CO)_3dppe]$ can be prepared from either $[Ru_3(CO)_{12}]$[1458] or $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$, the mechanism of the latter involving bimolecular attack of the tertiary phosphine on the substrate.[1450] A high yield synthesis of $[Ru(CO)_3(Ph_2Ppy)_2]$ from $[Ru_3(CO)_{12}]$ is also available.[1459]



i, CO, C_6H_6/Δ;[1448] ii, CO, N_2H_4, PPh_3;[187] iii, NaOR or Na/Hg, CO;[1449]
iv, PR_3 + aqueous HCHO/KOH in $MeOCH_2CH_2OH$ (R = Ph, *p*-Tol, *p*-$MeOC_6H_4$);[1410]
v, PR_3 (R_3 = Ph_3, Bu_3, $MePh_2$);[1450] vi, CO, MeOH;[1451] vii, $2PPh_3$, THF/130 °C;[1452]
viii, PPh_3 or PBu^n_3; MeEtCO;[1453] ix, PPh_3;[1454] x, excess CO;[1403] xi, CO (5 atm)/60 °C;[1455]
xii, $h\nu$[1456b]

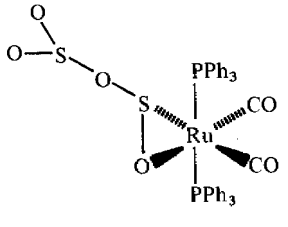
Scheme 44

Treatment of $[Ru(CO)_5]$ with PPh_3 under UV irradiation gives $[Ru(CO)_4PPh_3]$,[1452] also formed by heating $[Ru_3(CO)_9(PPh_3)_3]$ with CO under pressure[1453,1460] or more conveniently (along with $[Ru(CO)_3(PPh_3)_2]$) by photolysis of $[Ru_3(CO)_{12}]$ and PPh_3 in hexane. The latter route can be extended to PBu^n_3 and $PMePh_2$ derivatives.[1461a] An almost quantitative yield of $[Ru(CO)_4PPh_3]$ is obtained from the carbonylation under pressure of $[Ru(CO)_3(PPh_3)_2]$[1461b] or $[Ru(NO)_2(PPh_3)_2]$.[1418,1419] The reaction of $[Ru_3(CO)_{12}]$ with PBu^t_3 is solvent dependent; in boiling *n*-butanol $[Ru(CO)_4(PBu^t_3)]$ is isolated, whereas in MeOH, the sole product is $[Ru(CO)_3(PBu^t_3)_2]$.[1462] X-Ray analyses of $[Ru(CO)_4\{P(OMe)_3\}]$[1463] and $[Ru(CO)_4(AsPh_3)]$[1464] reveal a trigonal bipyramidal structure with an axial non-carbonyl ligand. In contrast, $[Ru(CO)_4(SbPh_3)]$ (from $[Ru_3(CO)_{12}]$ and $SbPh_3$ irradiated in *n*-hexane) has a trigonal bipyramidal structure with an equatorial $SbPh_3$ group.[1465] The corresponding $[Ru(CNBu^t)_4PPh_3]$ (trigonal bipyramidal structure with an equatorial PPh_3 group) is also known.[1466] IR studies however indicate that both axial and equatorial isomers are present in solution for $[Ru(CO)_4(EPh_3)]$ (E = As, Sb) and it is believed that the σ donor properties of EPh_3 are an important factor in determining the site preference.[1464]

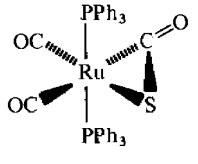
Under high pressures (35 atm/160°C/12 h) of PF_3, $[Ru_3(CO)_{12}]$ reacts to give mononuclear $[Ru(CO)_{5-n}(PF_3)_n]$ (n = 3,4 and 5) with only traces of n = 1 or 2. Increasing the CO content only increases the amounts of complexes with n = 3 and 4; in the absence of added CO, $[Ru(PF_3)_5]$ (see Section 45.5.1.1) is formed, in 95% yield. All these mononuclear species are fluxional (^{19}F NMR evidence) and their IR spectra show that a mixture of all possible isomers is obtained.[1383]

Similar stepwise displacement of CO from $[Ru_3(CO)_{12}]$ with $P(OMe)_3$ (under UV irradiation) can be monitored by ^{31}P NMR spectroscopy. This shows evidence for $[Ru(CO)_{5-n}\{P(OMe)_3\}_n]$ (n = 1–5) intermediates. The stable $[Ru(P(OMe)_3)_5]$ is ultimately isolated (see Section 45.5.1.1).[1380]

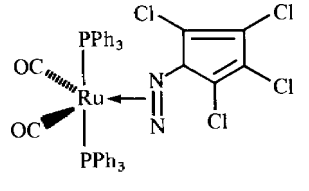
The very reactive compound $[Ru(CO)_2(PPh_3)_3]$ is synthesized either by deprotonation of $[RuH(CO)_2(PPh_3)_3]^+$,[1467] reaction of $Li[OEt]$ with $[Ru(N_2C_6H_4R)(CO)_2(PPh_3)_2]^+$[1468] or by reaction of $[Ru(\eta^2\text{-MeCN})(PPh_3)_4]$ with a deficiency of CO.[1403] It is probably trigonal bipyramidal with axial CO groups and readily adds hydrogen to give *cis*-$[RuH_2(CO)_2(PPh_3)_2]$;[1467] the hydrogen is displaced by π acceptor ligands to give $[Ru(CO)_2(PPh_3)_2L]$ (L = O_2, CO, C_2H_4, CH_2=CHCN).[1467,1469] A wide range of other ruthenium complexes of type $[Ru(CO)_2(PR_3)_2L]$, (*e.g.* L = CS_2,[1470] CSe_2,[1470] S_2,[1471] R'NCO,[1472] NHCOR,[1472] R'NCONR',[1472] $CF_3CHFCF_2N_3$,[1473] SO_2,[1474] C_2F_4,[1475] $(CN)_2C(CF_3)_2$,[1475] $(CF_3)_2C$=O,[1475] RNCS[1476]), are readily synthesized from either $[Ru(CO)_2(PPh_3)_3]$ or $[Ru(CO)_3(PR_3)_2]$. Low temperature crystallography[1477] on the SO_2 compound (**127**) shows the presence of a second molecule of SO_2 coordinated to the terminal oxygen of the η^2-SO_2 group. Reaction of $[Ru(CO)_3(PPh_3)_2]$ with COS first gives $[Ru(CO)_2(PPh_3)_2(\eta^2\text{-COS})]$ (**128**) which with additional COS produces $[Ru(S_2CO)(CO)_2(PPh_3)_2]$; reaction of (**128**) with PPh_3 gives $[Ru(CO)_3(PPh_3)_2]$ and $SPPh_3$.[1478] The complexes $[Ru(CO)_2(PPh_3)_2N_2R]$ (**129**) shown by X-ray analysis (for R = C_5Cl_4) to have η^2-coordination of the diazo group are prepared from $[Ru(CO)_2(PPh_3)_2(C_2H_4)]$ and the appropriate diazo derivative.[1479] Other diazenido complexes are discussed in Section 45.5.4.6.iv.



(127)



(128)



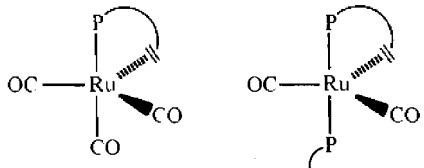
(129)

The zerovalent isocyanide complexes $[Ru(CO)_2(CNp\text{-Tol})(PPh_3)_2]$ and $[Ru(CO)(CNp\text{-Tol})(PPh_3)_3]$ can be prepared by deprotonation of the cationic hydride complexes $[RuH(CO)_2(CNp\text{-Tol})(PPh_3)_2]^+$ and $[RuH(CO)(CNp\text{-Tol})(PPh_3)_3]^+$ respectively. The latter reacts with O_2 to give $[Ru(CO)(CNp\text{-Tol})(O_2)(PPh_3)_2]$ whereas in the former, one of the CO ligands is oxidized to give the ruthenium carbonate $[Ru(CO_3)(CO)(CNp\text{-Tol})(PPh_3)_2]$.[1480] Reaction of $[Ru(CO)(CNR)(PPh_3)_3]$ (R = *p*-Tol, *p*-$MeOC_6H_4$) or $[Ru(CO)_2(PPh_3)_3]$ with electrophilic alkenes such as fumaronitrile, maleonitrile *etc.* gives $[Ru(CO)Y(PPh_3)_2(alkene)]$ (Y = CO, CNR). The dicarbonyl compounds exist as two geometric isomers in solution and interchange by a combined alkene rotation–Berry mechanism.[1481] $[RuCO(CNp\text{-Tol})(PPh_3)_3]$ is also obtained by dehydrochlorination of $[RuHClCO(CNp\text{-Tol})(PPh_3)_2]$ with 1,8-diazabicyclo[5.4.0]undec-7-ene in the presence of PPh_3; similar treatment of $[RuHCl(CO)(PPh_3)_3]$ in a CO atmosphere gives $[Ru(CO)_3(PPh_3)_2]$.[1482] Further reactions of $[Ru(CO)_3(PPh_3)_2]$ and $[Ru(CO)_2(PPh_3)_3]$ which involve oxidation to Ru^{II} are discussed

in Section 45.5.4 and monomeric Ru^0 carbonyl phosphine complexes containing NO groups, *e.g.* $[RuX(CO)NO(PPh_3)_2]$, $[Ru(CO)_2NO(PPh_3)_2]^+$, are covered elsewhere (Section 45.5.1.2). Reference 1 p.932 contains a review on the catalytic properties of $[Ru(CO)_3(PPh_3)_2]$.

Related species with bi- and multi-dentate P and As donor ligands include $[Ru(CO)_3f_6fos]$ {$f_6fos = (CF_2)_3C(PPh_2)=C(PPh_2)$},[1483] $[Ru(CO)_3L—L]$ (L—L = dppe[1450,1458] and *trans*-spanning 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene),[1484] $[Ru(CO)_2MeC(CH_2PPh_2)_3]$,[1485] $[Ru(CO)_2PhE(o\text{-}C_6H_4EPh_2)_2]$ (E = P, As) and $[Ru(CO)\ E(o\text{-}C_6H_4EPh_2)_3]$ (E = P, As).[46] All these compounds are obtained by treatment of $[Ru_3(CO)_{12}]$, (or sometimes $[Ru(CO)_3(PPh_3)_2]$), with the appropriate ligand and are believed to have trigonal bipyramidal structures. $[Ru(CO)_2ttp]$ and $[Ru(CO)_2(Cyttp)]$ [tpp = $PhP\{(CH_2)_3PPh_2\}_2$; Cytpp = $PhP\{(CH_2)_3PCy_2\}_2$] have been synthesized both from $[Ru_3(CO)_{12}]$ and by Na/Hg reduction of $[RuCl_2(ttp)]$, $[RuCl_2(Cyttp)]$, $[Ru(CO)_2(ttp)](BF_4)_2$ or $[RuH(CO)_2(tpp)]BF_4$.[1486] The very air sensitive $[Ru(CO)(dppe)_2]$ can be prepared by decarboxylation of $[Ru(O_2CH)Me(CO)(PPh_3)_2]$ in the presence of dppe,[1487] whereas the analogous $[Ru(CO)(dmpe)_2]$ is obtained by carbonylation of $[RuH(2\text{-}np)(dmpe)_2]$.[1388] Reaction of $[Ru(\eta^2\text{-}MeCN)(PPh_3)_4]$ with a deficiency of CO is also claimed to give $[Ru(CO)(PPh_3)_4]$.[1403] Treatment of $[Ru(dppm)_2(cod)]$ with CO gives $[Ru(CO)(dppm)(cod)]$ and $[Ru(CO)_2(dppm)(cod)]$.[1399]

Reaction of $o\text{-}CH_2{=}CHC_6H_4PPh_2$ (SP) with $[Ru_3(CO)_{12}]$ gives $[Ru(CO)_3SP]$ (**130**) and $[Ru(CO)_2(SP)_2]$ (**131**), the proportions of which depend on the ratio of reactants. An excess of SP reacts with $[Ru_3(CO)_{12}]$ to give $[Ru(CO)(SP)_2]$ which has a trigonal bipyramidal structure with the vinyl groups and CO coordinated in the equatorial plane.[1488] Reaction of $o\text{-}Ph_2PC_6H_4CH{=}CHCHMeC_6H_4PPh_2$ (1-BDPB) with $[Ru_3(CO)_{12}]$ gives $[Ru(CO)_2(1\text{-}BDPB)]$ in which the P atoms are believed to span the axial position of a trigonal bipyramid.[1489]

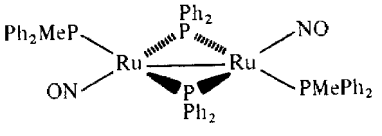


(130) (131)

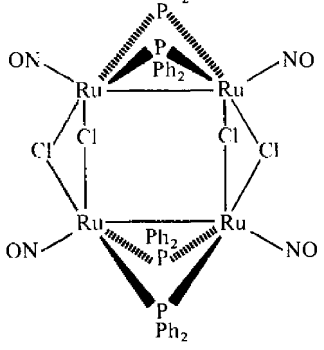
45.5.2 Bi-, Tri- and Tetra-nuclear Ruthenium(0) Complexes

45.5.2.1 Nitrosyl complexes

The reaction of $[RuCl_3(NO)(PMePh_2)_2]$ with Ph_2PH and a Zn/Cu couple yields the binuclear phosphido-bridged complex $[Ru(NO)(\mu\text{-}PPh_2)(PMePh_2)]_2$ (**132**); the tetranuclear species (**133**) (formally a mixed Ru^0/Ru^{II} complex) is also obtained in poor yield. Compound (**132**) can also be obtained from $[RuH(NO)(PMePh_2)_3]$,[1490,1491] and the PPh_3 analogue is known.[1491,1492]



(132)



(133)

Kinetic studies on the reaction of $[Ru_3(CO)_{10}(NO)_2]$ with PPh_3 suggest a dissociative process involving stepwise displacement of CO to give first $[Ru_3(CO)_9(NO)_2PPh_3]$ and then $[Ru_3(CO)_8(NO)_2(PPh_3)_2]$.[1493] The ^{13}C NMR spectrum of the latter shows that it is the equatorial CO groups in $[Ru_3(CO)_{10}(NO)_2]$ which are replaced.[1494] $[(Ph_3P)_2N][Ru_3(CO)_{10}NO]$ has been synthesized in high yield by reaction of $[(Ph_3P)_2N]NO_2$ with $[Ru_3(CO)_{12}]$.[1495]

45.5.2.2 Carbonyl complexes

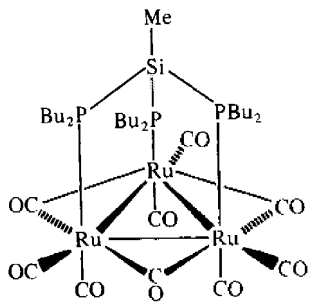
A substantial amount of work has been published on the reactions of $[Ru_3(CO)_{12}]$ particularly with P donor ligands and this is very thoroughly reviewed in references 1 and 3–5. The usual products from thermal reaction of $[Ru_3(CO)_{12}]$ with PR_3 are $[Ru_3(CO)_9(PR_3)_3]$, the mono- and di-substituted derivatives normally not being isolated unless bulky phosphines such as PCy_3 are used. With phosphines with small substituents *e.g.* PH_3, PMe_3 it is also possible to isolate $[Ru_3(CO)_8(PR_3)_4]$. Likewise reaction of $[Ru_3(CO)_{12}]$ with PF_3/CO mixtures gives in addition to $[Ru(CO)_{5-n}(PF_3)_n]$ (Section 45.5.1.3) a less volatile residue of red crystals identified by mass spectrometry as a mixture of $[Ru_3(CO)_{12-n}(PF_3)_n]$ (n = 1–6).[1383] Similar results are obtained with AsR_3 although fewer data are available. For SbR_3, only a cursory mention of $[Ru_3(CO)_9(SbPh_3)_3]$ appears in the literature.[1496]

However, it has been shown that an excellent route to many $[Ru_3(CO)_{12-n}L_n]$ (n = 1–4) species is *via* the radical anion $[Ru_3(CO)_{12}]^-$, generated by addition of sodium diphenylketyl. An extensive list of products obtained by this novel method is given in ref. 1497a and X-ray structures of $[Ru_3(CO)_{11}PCy_3]$, $[Ru_3(CO)_{10}\{P(OMe)_3\}_2]$, $[Ru_3(CO)_9(PMe_3)_3]$[1498] and $[Ru_3(CO)_{10}Ph_2PCH_2PPh_2]$[1499a] are now available. These reactions also provide routes to mixed ligand derivatives such as $[Ru_3(CO)_9(PMe_3)(PPh_3)P(OMe)_3]$ and $[Ru_3(CO)_9(PMe_3)(dppe)]$. Studies have shown that irradiation of $[Ru_3(CO)_{12}]$ and PMe_2Ph in THF containing $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ gives $[Ru_3(CO)_{11}PMe_2Ph]$.[1499b] Detailed electrochemical studies on $[Ru_3(CO)_{12}]$ are also reported.[1499c]

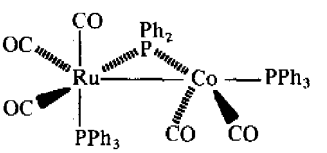
As discussed elsewhere (references 1, 3–5 and Section 45.5.1.3), reactions between $[Ru_3(CO)_9(PR_3)_3]$ and CO or PR_3 result in break-up of the cluster with formation of $[Ru(CO)_4PR_3]$ and $[Ru(CO)_3(PR_3)_2]$ respectively. The extensive kinetic studies on these substitution and dissociative reactions are reviewed in reference 1, p. 878. There is a paper which details the characterization and photochemistry of SiO_2-modified $LRu(CO)_4$ and $L_3Ru_3(CO)_9$ (L = $PPh_2(CH_2)_2Si(OEt)_3$), prepared from $[Ru(CO)_4L]$ and $[Ru_3(CO)_9L_3]$ respectively with a hydrocarbon suspension of SiO_2.[1500]

Related trinuclear carbonyl complexes $[Ru_3(CO)_{10}(L\text{–}L)]$ can be synthesized from thermal reactions of $[Ru_3(CO)_{12}]$ and L–L (*e.g.* L–L = dppm,[1501] dppe[1502]) and with $MeSi(PBu_2)_3$[1503] the 'capped' $[Ru_3(CO)_9\{(Bu_2P)_3SiMe\}]$ (**134**) is formed. Again, the radical ion-initiated route provides a better method to the above and also $[Ru_3(CO)_8(L\text{–}L)_2]$ (dppm, dpam) and the dppm bridged $[Ru_3(CO)_{11}]_2$dppm.[1497a] Reaction of $[Ru_3(CO)_{12}]$ with an equimolar amount of $(RO)_2PNR'P(OR)_2$ gives $[Ru_3(CO)_{10}\{\mu\text{-}(RO)_2PNR'P(OR)_2\}]$ which reacts further with excess ligand under UV irradiation to give $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(R')P(OR)_2\}_2]$.[1497b] Treatment of $[Ru_3(CO)_8(dppm)_2]$ with $Ag(OCOCF_3)$ gives the adduct $[Ru_3(CO)_8(dppm)_2][\mu\text{-}Ag(O_2CCF_3)]$.[1497c] With the fluorocarbon tertiary phosphine or arsine ligands (ffos, ffars or $f_6$fos), thermal reaction with $[Ru_3(CO)_{12}]$ under mild conditions gives $[Ru_3(CO)_{12-2n}(L\text{–}L)_n]$ (n = 1 and 2); refluxing in toluene for several hours produces $[Ru_2(CO)_6(L\text{–}L)]$ and on irradiation $[Ru(CO)_3L\text{–}L]$ is formed.[1483]

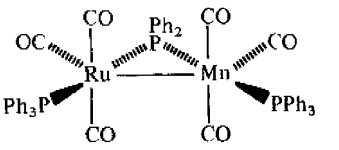
A number of interesting heterobimetallic carbonyl complexes containing phosphido bridges have been synthesized. These include $[RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2]$ (**135**) made by reaction of $[RuHCl(CO)(PPh_3)_3]$ with $Na[Co(CO)_4]$. The Ru—Co bond length of 2.05 Å implies a single bond between the atoms. Stepwise displacement from (**135**) of PPh_3 by CO gives $[RuCo(\mu\text{-}PPh_2)(CO)_6PPh_3]$ and $[RuCo(\mu\text{-}PPh_2)(CO)_7]$ respectively whereas with HCl two isomers of $[RuCoHCl(\mu\text{-}PPh_2)(CO)_4]$ are formed.[1504] Treatment of $[RuCl_2(PPh_2Cl)(p\text{-cymene})]$ with $[Co_2(CO)_8]$ provides an alternative route to $[RuCo(\mu\text{-}PPh_2)(CO)_7]$.[1505a] Reaction of $[RuCo(\mu\text{-}PPh_2)(CO)_7]$ with $NaBH_4$ gives $[RuCoH(\mu\text{-}PPh_2)(CO)_6]^-$ shown by X-ray analysis to have a terminal Ru—H linkage *cis* to the μ-PPh_2 group.[1505b] Preliminary results on the related binuclear Ru—Mn complexes $[RuMn(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2]$ (**136**) and $[RuMnCl(\mu\text{-dppm})_2(\mu\text{-}CO)_2(CO)_3]$ (**137**), isolated from reaction of $Na[Mn(CO)_5]$ with $[RuCl_2(PPh_3)_3]$ and *cis*-$[RuCl_2(dppm)_2]$ respectively have been published.[1506] Reaction of $[Ru(dppm)_2cod]$ with $[RuCl(CO)_2]_2$[1507a] in the presence of excess CO at 70°C produces the binuclear $[RuRhCl(\mu\text{-}CO)(dppm)_2]$ (**138**), whereas $[RuH_2(dppm)_2]$ and $Mo(CO)_6$ give $[RuMo(\mu\text{-dppm})_2(CO)_6]$ which has an interesting chemistry.[1507b]



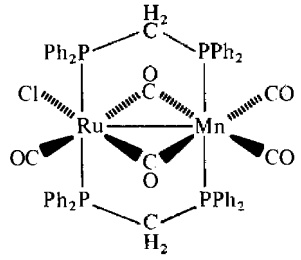
(134)



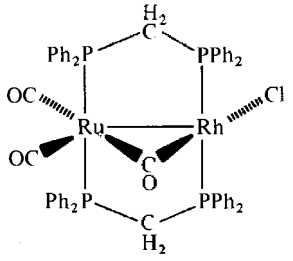
(135)



(136)



(137)



(138)

For references to related heterotrimetallic complexes such as $[Ru_2Pt(CO)_7(PR_3)_3]$, $[RuPt_2(CO)_5(PR_3)_3]$, $[RuPt_2(CO)_4\{P(OPh)_3\}_4]$ and $[(dppe)PtRu_2(CO)_8]$, see reference 1, p. 927.

45.5.3 Ruthenium(I) Complexes

45.5.3.1 Mononuclear complexes

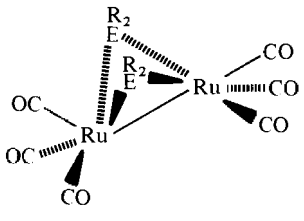
There are very few monomeric Ru^I complexes containing P or As donor ligands; dimerization with formation of a metal–metal bond is preferred in most instances. Brief references are made to $[RuCl_2(NO)(PPh_3)_2]$ obtained as a minor side-product in the preparation of $[RuCl_3NO(PPh_3)_2]$[1508] and also by reaction of $[RuCl_2NO(PPh_3)]_2$ with PPh_3.[1329] This product shows an ESR spectrum indicative of a paramagnetic $Ru^I(d^7)$ complex. However, reaction of $[RuI_2(NO)]_n$ with $AsMePh_2$ gives a compound of empirical formula '$[RuI_2NO(AsMePh_2)_2]$' which is essentially diamagnetic and is therefore tentatively formulated as the metal–metal bonded dimer $[RuI_2(NO)(AsMePh_2)_2]_2$.[1509]

Electroreduction of $[RuCl(dppp)_2]PF_6$ leads to the Ru^I species $[RuCl(dppp)_2]$ and then the Ru^0 anion $[RuCl(dppp)_2]^-$ although only the *ortho*-metallated product $[\overline{RuH(C_6H_4PPh(CH_2)_3PPh_2)}\text{-}(dppp)]$ was isolated;[1509a] $[Ru(NO)(dppp)_2]^+$ also undergoes two reversible reductions.[1510]

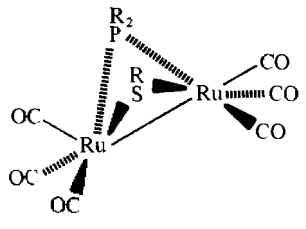
A series of compounds such as $[RuCl_2(NO)(AsMePh_2)_3]$, $[RuCl_2NO(DMSO)L_2]$, (L = $AsPh_3$, $SbPh_3$, $AsMePh_2$, $AsMe_2Ph$) and $[RuCl_2NO(L\text{–}L)_2]$ (L–L = dppm, dpae) have been reported. These have been formulated as Ru^{II} species but have ν_{NO} bands characteristic of NO^+ (!!).[1511] A further critical examination of these complexes is very desirable.

45.5.3.2 Bi- and tetra-nuclear complexes

In contrast to Ru^0, Ru^{III} and especially Ru^{II}, relatively few Ru^I complexes containing P or As donor ligands are reported. Reaction between $[Ru_3(CO)_{12}]$ and E_2R_4 in C_6H_6 gives $[Ru(\mu\text{-}ER_2)(CO)_3]_2$ (**139**) (E = P, As; R = Me, C_6F_5).[1512–1514] Reduction of (**139**; $ER_2 = PMe_2$) produces the Ru^0 diamagnetic dianion; a paramagnetic radical anion (formally $Ru_2^{I,0}$ is formed on mixing (**139**) with its dianion and analysis of the NMR spectra of the latter and the ESR spectrum of the radical anion indicates that the general geometry, including the Ru—Ru bond, is preserved in all three complexes. Iodine cleaves the Ru—Ru bond of (**139**; $ER_2 = PMe_2$) to give the Ru^{II} dimer $[RuI(\mu\text{-}PMe_2)(CO)_3]_2$.[1515] The complex (**139**) ($ER_2 = PPh_2$) has been synthesized, together with various trinuclear hydrido complexes, by irradiation (> 300 nm) of $[Ru_3(CO)_9(PPh_2H)_3]$.[1516] The mixed P- and S-bridged complex $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6]$ (**140**) is obtained from $[Ru_3(CO)_{12}]$ and Ph_2PSPh by cleavage of the P—S bond.[1517]

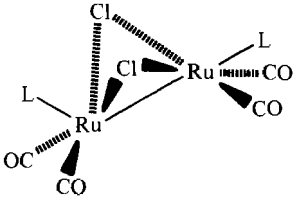


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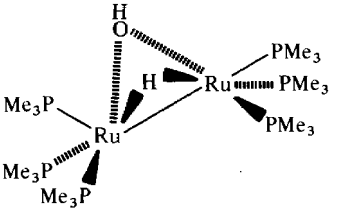


(140)

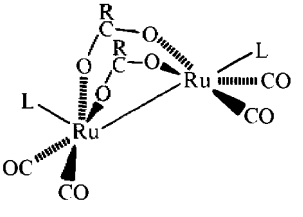
Closely related binuclear Ru^{I} complexes $[Ru(\mu\text{-}Cl)(CO)_2(PBu^t{}_2R)]_2$ (**141**) are generated by reaction of the 'Ru(CO)Cl' solution with the bulky phosphines $PBu^t{}_2R$ (R = Bu^t, Ph or *p*-Tol).[1518,1520] With smaller substituents, $[RuCl_2(CO)_2(PR_3)_2]$ are formed (see Section 45.5.4.5.i). Compounds (**141**) undergo facile PR_3 exchange to yield $[Ru_2(\mu\text{-}Cl)_2(CO)_4(PR_3)(PR'_3)]$ and metathetical reactions with heavier halides give the bromo and iodo analogues; $[Ru(\mu\text{-}I)(CO)_2(PPh_3)]_2$ is also formed by reaction of $[Ru_2(\mu\text{-}Cl)_2(\mu\text{-}Fe(CO)_4)(CO)_4(PPh_3)_2]$ (Section 45.5.5) with KI[1519a] whereas interaction of $[Ru_2(CH_2)_3(PMe_3)_6]$ (Section 45.5.8) with water gives $[Ru_2(\mu\text{-}H)(\mu\text{-}OH)(PMe_3)_6]$ (**142**).[1521] [Ag(OCOMe)] and (**141**) produce $[Ru(\mu\text{-}OCOMe)(CO)_2(PBu^t{}_2R)]_2$ (**143**), and other routes to these carboxylate compounds are by reaction between $[Ru_3(CO)_{12}]$ and RCO_2H in the presence of $PBu^t{}_3$,[1522] treatment of $[Ru_3(CO)_9(PPh_3)_3]$ with $MeCO_2H$[1523] or reaction of $[Ru(OCOR)(CO)_2]_n$ with equimolar amounts of L (L = PBu_3, PPh_3, $P(p\text{-}C_6H_4F)_3$, $AsPh_3$; R = H, Me, Et — not all combinations).[1524] The corresponding $[Ru(\mu\text{-}OMe)(CO)_2(PBu^t{}_3)]_2$ is readily obtained from reaction of $[Ru(CO)_3(PBu^t{}_3)_2]$ with MeOH.[1522a,1520]



(141)



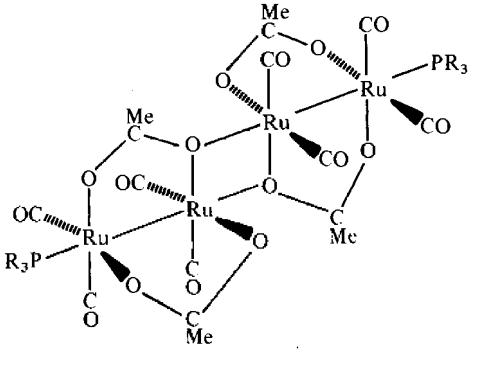
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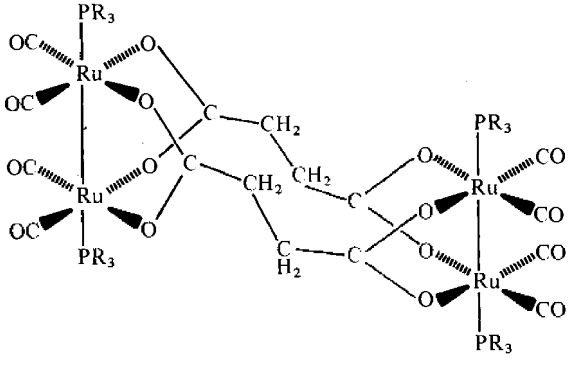
(143)

Reaction of $[Ru(OCOMe)(CO)_2]_n$ with PBu_3 (2:1 mole ratio of Ru:P) at 150°C in C_6H_6 has yielded the tetrameric $[Ru_4(OCOMe)_4(CO)_8(PBu_3)_2]$ (**144**) together with a minor amount of (**143**). Compound (**144**) can also be prepared by reacting $[Ru(OCOMe)(CO)_2]_n$ with (**143**) in C_6H_6 at 150°C. Treatment of the tetramer (**144**) with the stoichiometric amounts of PBu_3 then gives (**143**). Similarly $[Ru_3(CO)_{12}]$ and glutaric acid in boiling toluene give $[Ru_2(OCO(CH_2)_3OCO)(CO)_4]_n$ which on treatment with PBu_3 (1:1 mole ratio of Ru:P) yields $[Ru_4(OCO(CH_2)_3OCO)_2(CO)_8(PBu_3)_4]$ (**145**). X-Ray analyses of (**144**) and (**145**) reveal that the structures consist of couples of dimers linked by carboxylate groups.[1525,1526] The corresponding $[Ru_4(OCO(CH_2)_nOCO)_2(PBu_3)_4]$ (n = 0–2) are also known.[1527]

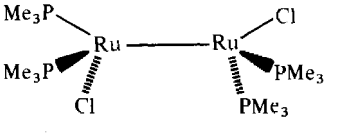
Another Ru^{I}/PR_3 complex is $[RuCl(PMe_3)_2]_2$ obtained in low yield from the reaction of $[Ru_2(OCOMe)_4Cl]$ and $[Mg(MeOC_6H_4)_2]$ in the presence of excess PMe_3[1528] and formulated as the dimer (**146**) on the basis of its diamagnetism, ^{31}P NMR and far IR spectra.[1529] The binuclear Ru^{I} nitrosyls $[RuI_2NO(AsMePh_2)_2]_2$ and $[RuCl_2NO(PPh_3)]_2$ are covered in Section 45.5.3.1.



(144)



(145)



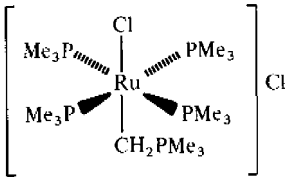
(146)

For completion, although carbocyclic ring complexes are not the province of this review, $[Ru_2(CO)_3PR_3(\eta\text{-}C_5H_5)_2]$, made by treatment of $[Ru(CO)_2(\eta\text{-}C_5H_5)]_2$ with PR_3, are other formally Ru^I binuclear complexes.[1530]

45.5.4 Mononuclear Ruthenium(II) Complexes

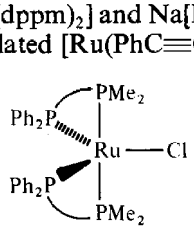
45.5.4.1 $[RuL_6]^{2+}$, $[RuXL_n]^+$ (n = 4,5), $[RuX(L\text{–}L)_2]^+$, $[RuL']^{2+}$ cations (X = halide, alkyl etc.)

To date the only routes to the fully substituted cations $[RuL_6]^{2+}$ are by reaction in MeOH of $[RuX_2(nbd)]_n$[1531,1532] (X = Cl, Br) or $[RuCl_2(PPh_3)_3]$[1533] with an excess of $P(OMe)_3$ or $P(OMe)_2Ph$. For L = $P(OMe)_3$, some $[RuCl\{P(OMe)_3\}_5]^+$ is also isolated from the mother liquor. If less $P(OMe)_2Ph$ is used, the binuclear cations $[Ru_2X_3(P(OMe)_2Ph)_6]^+$ are formed, (see Section 45.5.5.1), and these are the only products isolated on reaction of $[RuX_2(nbd)]_n$ with bulkier PR_3 groups such as $P(OEt)_3$, $P(OEt)_2Ph$, $P(OR)Ph_2$ (R = Me, Et).[1531,1532] Reaction of $[Ru\{P(OMe)_3\}_5]$ or $[RuMe\{P(O)(OMe)_2\}\{P(OMe)_3\}_4]$ with MeI gives $[RuMe\{P(OMe)_3\}_5]I$,[1380] and one of the products from the reaction of *trans*-$[RuCl_2(PMe_3)_4]$ with the lithiated ylide $Li[Me_2P(CH_2)_2]$ is $[RuCl(PMe_3)_4(CH_2\text{-}PMe_3)]Cl$ (**147**).[1380,1534]



(147)

Treatment with $Ph_3C[BF_4]$ of the reaction mixture from $[Ru_2(OCOMe)_4Cl]$, $[Hg(MeOC_6H_4)_2]$ and PMe_3 gives $[RuCl(PMe_3)_4]BF_4$ ($^{31}P\text{-}\{^1H\}$ NMR spectrum is a sharp singlet), formulated as a fluxional five-coordinate monomer. A compound of empirical formula $[RuCl(PMe_3)_4]Cl$ is also obtained from *trans*-$[RuCl_2(PMe_3)_4]$ left in C_6H_6 for several weeks. However its $^{31}P\text{-}\{^1H\}$ NMR spectrum consists of an A_2X_2 pattern at ambient temperature which suggests that it is the binuclear dication $[RuCl(PMe_3)_4]_2Cl_2$.[1529] The analogous cations $[RuCl(P(OMe)Ph_2)_4]^+$ and $[RuCl(P(OEt)Ph_2)_4]_2^{2+}$ can be synthesized by reaction of $[RuCl_2(PPh_3)_3]$ or $[RuCl_2(P(OR)Ph_2)_3]$ with an excess of $P(OR)Ph_2$ in EtOH. These undergo further rearrangement to form $[Ru_2Cl_3(P(OMe)Ph_2)_6]^+$ and $[Ru_3Cl_5(P(OEt)Ph_2)_9]^+$ respectively (see Section 45.5.5.1).[1533] The deeply coloured pentacoordinate cations $[RuX(L\text{—}L)_2](PF_6)$ (L—L = dppp, 2-(diphenylphosphinoethyl)pyridine; X = Cl, Br) are formed by treatment of *trans*-$[RuX_2(L\text{—}L)_2]$ with ethanolic solutions of $NH_4[PF_6]$, and these take up small neutral ligands to give *trans*-$[RuXL'(L\text{–}L)_2]PF_6$ (L′ = CO, MeCN).[1535] Five-coordinate cations are not obtained by this route with the less bulky dppm or dppe ligands,[1535] but they have been prepared for the unsymmetrical diphosphine ligands $Ph_2P(CH_2)_3PMe_2$ and $Ph_2P(CH_2)_3PMePh$. Non-fluxional trigonal bipyramidal structures (**148**) are proposed on the basis of ^{31}P NMR spectral studies.[1536a] However, there is evidence for square pyramidal geometry (when L = PMe_2Ph).[1536b] Preliminary studies have also indicated that one of the products from reaction of *cis*-$[RuCl_2(dppm)_2]$ and $Na[Mn(CO)_5]$ in THF is the very air-sensitive $[RuCl(dppm)_2THF]Mn(CO)_5$.[1506] The related $[Ru(PhC{\equiv}C)(PMe_2Ph)_5]PF_6$ is known.[1537]



(148)

A number of Ru^{II} cations containing polydentate P or As donor ligands have been reported. For example, prolonged reflux of $[RuCl_2(PPh_3)_3]$ in C_6H_6 with the hexatertiary phosphine *P,P,P′,P′*-tetrakis(2-diphenylphosphinoethyl)-α,α′-diphospha-*p*-xylene (TDDX) gives as the main product the binuclear $[Ru_2Cl_4(PPh_3)_2(TDDX)]$ (see Section 45.5.5.3), but treatment of the filtrate

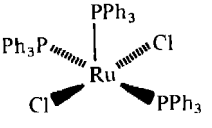
with $NH_4[PF_6]$ precipitates some $[Ru(TDDX)](PF_6)_2$ in which pentadentate coordination of the ligand is tentatively suggested.[1538] The corresponding ligand *As,As,As',As'*-tetrakis(2-diphenylarsinoethyl)α,α'-diphospha-*p*-xylene (TDADX) gives the chocolate brown [RuCl(TDADX)]Cl under the same conditions. In this case TDADX acts as a tetradentate ligand which may be coordinated to a single Ru^{II} atom either through one P and three As or through all four As atoms. Carbonylation yields [RuCl(CO)(TDADX)]Cl.[1539] The five-coordinate cation [RuCl(tet-1)]Cl (tet-1 = $Ph_2P(CH_2)_2PPh(CH_2)_2P(Ph)(CH_2)_2PPh_2$) is also obtained by reaction of $[RuCl_2(PPh_3)_3]$ with tet-1 in dry C_6H_6, and again carbonylation affords [RuCl(CO)(tet-1)]Cl. In contrast, direct reaction of $[RuCl_2(DMSO)_4]$ with either tet-1 or tet-2 $\{P[(CH_2)_2PPh_2]_3\}$ in C_6H_6/MeOH gives the S-bonded DMSO cations [RuCl(DMSO)tet]Cl.[1540]

45.5.4.2 [RuXYL$_n$] complexes (n = 2,3,4; X,Y = halide)

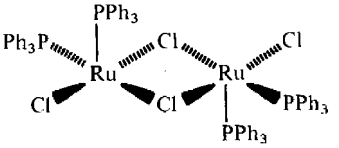
(i) L = monodentate P donor ligand

The products of reaction of tertiary phosphines with '$RuCl_3 \cdot xH_2O$' are very dependent upon the nature of PR_3 and the reaction conditions. Thus with an excess of PPh_3 in MeOH,[106,1541] EtOH[1542] or isopropanol[1542] at reflux for several hours, red-brown $[RuCl_2(PPh_3)_3]$ is formed whereas shaking the reaction mixture at room temperature yields $[RuCl_2(PPh_3)_4]$[106] (shown by $^{31}P\text{-}\{^1H\}$ NMR studies[1543,1544] to be best formulated as $[RuCl_2(PPh_3)_3 \cdot PPh_3]$ with one PPh_3 group trapped in the lattice). Prolonged reaction at room temperature in MeOH using a 1:2 molar ratio of Ru to PPh_3 gives green $[RuCl_3(PPh_3)_2MeOH]$[106] (see Section 45.5.7.1), whereas these reactants in isobutanol or cyclohexanol yield black, polymeric $[RuCl_2(PPh_3)_2]_n$[1542] (which can also be made by heating $[RuCl_2(PPh_3)_3]$ under reflux in methyl ethyl ketone,[1545] or by reduction of $[RuCl_3(PPh_3)_2MeOH]$ with hydrogen).[1546,1547] Solvents such as 2-methoxyethanol and benzyl alcohol take part in the reaction producing $[RuHCl(CO)(PPh_3)_3]$ (see Section 45.10.3.2.iii)[1542,1548] and $[RuCl_2(CO)(PPh_3)_3]$ (Section 45.5.4.5.i)[1542] respectively.

Other routes to $[RuCl_2(PPh_3)_3]$ include the treatment of $[RuH_2(N_2)(PPh_3)_3]$ or $[RuH_2(PPh_3)_4]$ with HCl[1549] or reaction of $Cs[Ru(\eta\text{-}C_6H_6)Cl_3]$[1550] (or the reduced 'ruthenium blue' solution)[676] with PPh_3. An X-ray structural analysis confirms the five-coordinate structure (**149**); a distorted square pyramidal structure with one of the phenyl *ortho* hydrogens blocking the sixth coordination position.[1551] Osmometric molecular weight studies in acetone on $[RuCl_2(PPh_3)_n]$ ($n = 3,4$)[106] suggest extensive dissociation in solution and spectrophotometric measurements in deoxygenated C_6H_6 supported these conclusions (equations 96 and 97).[1552] However, variable temperature ^{31}P NMR studies indicate that the dissociation product $[RuCl_2(PPh_3)_2]_n$ is a five-coordinate dimer (**150**) ($n = 2$) rather than a four-coordinate monomer ($n = 1$) and equation (98) rather than (97) is a better representation of the species present in non-polar media.[1543,1544] Note that the different ^{31}P NMR spectrum of '$RuCl_2(PPh_3)_2$' reported later by Vrieze *et al.*[1553] is in fact a spectrum of $[RuCl_2(PPh_3)_2(2\text{-}MeCOC_5H_4N)]$.[1554] The ^{31}P NMR spectra also reveal the fluxional nature of all the ruthenium complexes shown in equation (98) and quantitative kinetic and thermodynamic data are available.[1543]



(149)



(150)

$$[RuCl_2(PPh_3)_4] \rightleftharpoons [RuCl_2(PPh_3)_3] + PPh_3 \quad (96)$$

$$[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl_2(PPh_3)_2] + PPh_3 \quad (97)$$

$$2[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl_2(PPh_3)_2]_2 + 2PPh_3 \quad (98)$$

In more polar media, conductometric,[106] spectrophotometric[1552] and ^{31}P NMR spectroscopic studies[1544] reveal the presence of an alternative dissociation pathway for $[RuCl_2(PPh_3)_3]$, namely loss of Cl^- to produce Ru^{II} cations (equations 99 and 100) although unpublished work indicates that the triply-bridged chloride dimer $[Ru_2Cl_4(DMA)(PPh_3)_4]$ is present.[1555] Synthesis of pure $[RuBr_2(PPh_3)_3]$ by reaction of methanolic '$RuCl_3 \cdot xH_2O$'/LiBr solutions with PPh_3 has also been

claimed,[106] but subsequent ^{31}P NMR studies revealed that a mixture of $[RuCl_xBr_{2-x}(PPh_3)_3]$ ($x = 0$–2) is formed.[1543] However, pure $[RuBr_2(PPh_3)_3]$ can be synthesized by reaction of $[Ph_3(PhCH_2)P]_3[Ru_2Br_9]$ with PPh_3 in MeOH. This has very similar properties to $[RuCl_2(PPh_3)_3]$.[1556]

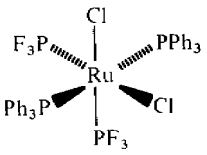
$$[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl(PPh_3)_3]^+ + Cl^- \quad (99)$$

$$[RuCl(PPh_3)_3]Cl \rightleftharpoons [RuCl(PPh_3)_2]Cl + PPh_3 \quad (100)$$

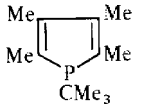
A number of other complexes of type $[RuCl_2L_n]$ (L = P donor ligand, $n = 2,3$ or 4) can be made by either direct reaction of '$RuCl_3 \cdot xH_2O$' or the reduced 'ruthenium blue' solution with L. These include L = P(*p*-Tol)$_3$ ($n = 3,4$),[1557,1558] P(*p*-MeOC$_6$H$_4$)$_3$ ($n = 3$),[1559] $PMe_2(CH_2Ph)$ ($n = 4$),[1560] PMe_2(1-*np*) ($n = 3$),[1561] $P(OMe)_3$ ($n = 4$, *trans*),[1562] $PPh_2(C_6H_4SO_3H)$ ($n = 2$),[1563] $PHPh_2$ ($n = 4$, *trans*),[1564,1565] $PHEt_2$ ($n = 4$),[1564] various substituted phospholes ($n = 3,4$),[1566,1567] and 3,3′,4,4′-tetraMe-1,1′-diphosphaferrocene ($n = 4$, *trans*).[1568] The *trans* isomer of $[RuCl_2(PHMe_2)_4]$ is also prepared from '$RuCl_3 \cdot xH_2O$' and Me_2PPMe_2 in H_2O or EtOH, the hydrogen being abstracted from the solvent,[1569] whereas treatment of $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ with $PHPh_2$ gives the *cis* isomer.[1565] For the preparation of $[RuCl_2\{P(OEt)_3\}_4]$, '$RuCl_3 \cdot xH_2O$' and $P(OEt)_3$ are reacted in the presence of $Na[BH_4]$.[1570] Treatment of $[RuH(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3]$ (**124**) with HX (X = Cl, Br) leads to *cis*-$[RuX_2(PMe_3)_4]$ whereas with CH_2X_2 (X = Cl, Br, I) or MeI, a mixture of $[RuX_2(PMe_3)_4]$ and $[RuX(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3]$ is produced.[1391b]

However, most P donor ligands react with '$RuCl_3 \cdot xH_2O$' in aqueous EtOH or 2-methoxyethanol to give the triple chloride-bridged complexes $[Ru_2Cl_3L_6]Cl$, (see Section 45.5.5.1), which do *not* generally react with an excess of L to give $[RuCl_2L_4]$. A better route to the latter is therefore *via* reaction of L with $[RuCl_2(PPh_3)_{3\text{ or }4}]$, usually in non-polar media to minimize formation of ionic species. This method affords both $[RuCl_2L_3]$ (L = $PEtPh_2$,[1544] P(OR)Ph_2 (R = Me, Et),[1533] $PRPh_2$ (R = Me, $MeCH_2CH(Ph)CH_2$),[1571] $PMe(Ph)(PhCH_2)$,[1572] *etc.*) and $[RuCl_2L_4]$ (L = $P(OPh)_3$[1573] PMe_2Ph (*cis*;[1544] *trans*[1400]), $P(OMe)_2Ph$,[1533] $P(OMe)_3$,[1533] PEt_3,[1400] $PMePh_2$,[1400] PMe_3,[1529,1574] $PRPh_2$ (R = Me, $MeCH_2CH(Ph)CH_2$)[1571] and various 1-substituted 3,4-dimethylphospholes[1575] *etc.*). For $n = 4$, both *cis* and *trans* isomers are found and these undergo thermal and photochemical isomerization in solution (see references 1533 and 1575 for details). Reaction of $[RuH(C_6H_4PPh_2)(PMe_3)_3]$ with HCl gives $[RuCl_2(PMe_3)_3]$.[1391c] Many of these monomeric complexes also undergo facile rearrangement in solution to form various bi- and sometimes tri-nuclear species as discussed in Section 45.5.5.1.

A number of mixed P donor ligand complexes $[RuX_2L_xL'_y]$ are also known. Most of the compounds in this category involve a combination of PPh_3 and fluorophosphines. For example, treatment of *cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$ with gaseous HX gave *cis*-$[RuX_2(PF_3)_2(PPh_3)_2]$ (X = Cl, Br)[1576] whose structure (**151**) was verified by X-ray analysis for X = Cl.[1577] Other routes to (**151**) include reaction of $[RuCl_2(PPh_3)_3]$ or $[RuHCl(CO)(DMA)(PPh_3)_2]$ with two moles of PF_3[1578] and of $[RuCl_2(C_{10}H_{16})(PF_2NMe_2)]$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) with PF_3 and then PPh_3.[1579] Compound (**151**) is also formed *via* binuclear, triple chloride-bridged intermediates (Section 45.5.5.1), on treatment of $[RuCl_2(PPh_3)_3]$ with equimolar amounts of PF_3.[1580] Reaction of $[RuCl_2(PPh_3)_3]$ with allyl difluorophosphite gives $[RuCl_2(PF_2CH_2CH{=}CH_2)_2(PPh_3)_2]_n$[1581] whereas the sterically bulky phosphole 1-Me_3CDMP (**152**) gives the stereochemically rigid, pentacoordinate $[RuCl_2(PPh_3)(Me_3CDMP)_2]$ (*cf.* other 1-substituted 3,4-dimethylphospholes (RDMP) which afford $[RuCl_2(RDMP)_4]$ (R = Me, Bu, Ph, $PhCH_2$)].[1575] It has been shown that *trans*-$[RuCl_2(PMe_3)_4]$ reacts with $P(OMe)_3$ to give *trans, mer*-$[RuCl_2(PMe_3)_3P(OMe)_3]$ and *all trans*-$[RuCl_2(PMe_3)_2\{P(OMe)_3\}_2]$ whereas *trans*-$[RuCl_2\{P(OMe)_3\}]$ and PMe_3 gives *trans,cis,cis*-$[RuCl_2(PMe_3)_2\{P(OMe)_3\}_2]$.[1391c]



(151)



(152)

These monomeric $[RuCl_2L_n]$ complexes (particularly L = PPh_3) are very useful precursors for the synthesis of a wide range of Ru^{II} compounds of type $[RuCl_2Y_{4-x}L_x]$ ($x = 1$–3; Y = C, N, O or S donor ligands). Complete displacement of the chloride groups with other anionic ligands is also

readily achieved to give the six-coordinate complexes $[Ru(X–X)_2L_2]$ (X–X = $^-S_2CNR_2$, ^-SOCPh, ^-OCOR, ^-acac, *etc.*). For detailed examples see reference 85 and Sections 45.5.4.5 to 45.5.4.9. References to the widespread catalytic properties of $[RuCl_2(PPh_3)_3]$ are given in Section 45.10.6, together with those for the closely related $[RuHCl(PPh_3)_3]$ and other catalytically active species.

(*ii*) *L = monodentate As donor ligand*

In contrast to the large amount of work on $[RuCl_2(PR_3)_n]$ compounds, relatively little has been published on the corresponding tertiary arsine complexes. Attempts to synthesize $[RuCl_2(AsR_3)_3]$ *via* '$RuCl_3 \cdot xH_2O$' and AsR_3 in MeOH gave $[Ru^{III}Cl_3(AsR_3)_2MeOH]$ (R = Ph,[106] *p*-Tol[625,1582]); the bromo derivatives are also available. The above reaction in EtOH gives a mixture of $[RuCl_3(AsPh_3)_3]$ and $[RuCl_3(AsPh_3)_2EtOH]$[1547] and not $[RuCl_2(AsPh_3)_3]$ as previously claimed.[1583] However extended reflux (17 h) of '$RuCl_3 \cdot xH_2O$' and $AsMe_2Ph$ in MeOH gives *cis*- and *trans*-$[RuCl_2(AsMe_2Ph)_4]$ whereas shorter reflux times (1 h) in 2-methoxyethanol yield $[RuCl_3(AsMe_2Ph)_3]$.[1584] Similar extended reflux in EtOH produces $[RuCl_2L_4]$ [L = $AsRPh_2$ (R = Me, Et, Pr, Bu);[1585] $AsMe_2(PhCH_2)$[1560]]. Another route to these compounds is *via* ligand exchange in non-polar solvents with either $[RuCl_2(PPh_3)_3]$ or $[RuCl_3(AsPh_3)_2MeOH]$ in the presence of Zn/Hg.[1586] Treatment of the reduced 'ruthenium blue' solution with $AsMe_2Ph$ and $AsMePh_2$ in alcohol is reported to give the five-coordinate $[RuCl_2(AsR_3)_3]$ complexes.[1511]

Earlier claims[1587] that reaction of '$RuCl_3 \cdot xH_2O$' and an excess of $AsPh_3$ in boiling 2-butanol gives the brown solid $[RuCl_2(AsPh_3)_2]_n$ are incorrect. On the basis of magnetic, ESR and electrochemical evidence, this has been reformulated as the mixed valence $[Ru_2Cl_5(AsPh_3)_4]$ (see Section 45.5.6).[1588] It is likely that $[Ru_2Cl_5(AsPh_3)_4]$ and not $[RuCl_2(AsPh_3)_2]_n$ is also formed on treatment of $[RuCl_3(AsPh_3)_2MeOH]$ with $AsPh_3$ in propanol.[1586] The insoluble mixed ligand polymer $[RuCl_2(AsPh_3)(PPh_3)]_n$ is claimed[1586] but this may also be a mixed valence species. However, it appears that genuine $[RuCl_2(AsPh_3)_2]_n$ can be prepared by treatment of $[RuCl_3(AsPh_3)_2MeOH]$ with 1 atm H_2 in DMA at 25°C.[1546,1547]

(*iii*) *L = monodentate Sb donor ligand*

The only complexes of this type are with $SbPh_3$. Reaction of '$RuCl_3 \cdot xH_2O$' and $SbPh_3$ in MeOH at ambient temperature gives the very insoluble deep red $[RuCl_2(SbPh_3)_3]_n$; the same compound is obtained under reflux in MeOH or 2-methoxyethanol.[106] A more soluble pink form (presumably monomeric) has been prepared by reaction of alcoholic solutions of the reduced 'ruthenium blue' solution with $SbPh_3$.[1511] An earlier report on the preparation of $[RuCl_2(SbPh_3)_4]$ from $K_2[RuCl_6]$ and $SbPh_3$ is available[1589] and the corresponding $[RuBr_2(SbPh_3)_4]$ is known.[1590]

45.5.4.3 [RuXY(L–L)$_n$] complexes (n = 2,3; X,Y = halide)

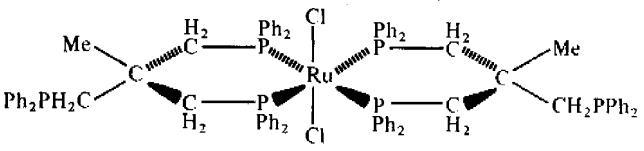
Earlier work by Chatt *et al.* on reactions of '$RuCl_3 \cdot xH_2O$' with various diphosphines $R_2P(CH_2)_2PR_2$ (R = Me, Et or Ph) and Nyholm *et al.* with *o*-$C_6H_4(AsMe_2)_2$(diars) led to the preparation of *cis*- and *trans*-$[RuCl_2(R_2P(CH_2)_2PR_2)_2]$[43,1591] and *trans*-$[RuCl_2(diars)_2]$[1592] respectively. Replacement of chloride with Br^-, I^-, ^-OCOMe, SCN^- was achieved. More recently, a wider range of the *trans* compounds $[RuCl_2(L–L)_2]$ have been obtained by treatment of either $[RuCl_2(PPh_3)_3]$, $[RuCl_2(py)_4]$, $K_2[RuCl_5(OH_2)]$ or '$RuCl_3 \cdot xH_2O$' with L–L in alcoholic solution (L–L = dppm,[1593–1595] dppe,[1571,1594,1595] dppp,[1535a,1536a,1594] 2-(diphenylphosphinoethyl)pyridine,[1535b] $Ph_2As(CH{=}CH)AsPh_2$ (eda),[45,1593] diars,[1596] *o*-$C_6H_4(PMePh)_2$,[1597] *o*-$C_6H_4(AsMePh)_2$,[1597] $Ph_2P(CH_2)_3PMe_2$,[1536a] $Ph_2P(CH_2)_3PMePh$,[1536a] *etc.*), or with excess dppm, eda and $Ph_2As(CH_2)_2AsPh_2$, by displacement of all the CO from 'RuCOCl' solutions.[1593] Some *trans*-$[RuCl_2(dmpe)_2]$ is also formed by treating $[RuH(2\text{-np})(dmpe)_2]$ with $CDCl_3$.[44] Metathesis of *trans*-$[RuCl_2(eda)_2]$ with NaX (X = NCS, I, N_3, CN) yields *trans*-$[RuX_2(eda)_2]$ but with NaBr, $[RuClBr(eda)_2]$ is formed.[45]

The complexes *cis*- and *trans*-$[RuCl_2(dppm)_2]$ undergo isomerization reactions induced by light, heat or oxidation to Ru^{III}. The conversion *trans* → *cis* occurs thermally while *cis* → *trans* occurs photochemically apparently by irradiation of the lowest lying *d–d* transition.[1598] In water/alcohol mixtures photolysis of *cis*- or *trans*-$[RuCl_2(dmpe)_2]$ gives *trans*-$[RuCl(OH_2)(dmpe)_2]^+$, while *trans*-$[RuCl(DMSO)(dmpe)_2]^+$ is always observed in DMSO. These results are consistent with the

formation of a five-coordinate excited-state fragment as the primary photochemical process and the thermodynamic preference for $[RuCl(dmpe)_2^+]^*$ to rearrange to the isomer with Cl^- in the apical position.[1599]

A detailed investigation of the stereochemistry of *cis*- and *trans*-$[RuCl_2(L\text{–}L)_2]$ (L–L = *o*-$C_6H_4(EMePh)_2$; E = As, P) has been undertaken. The optically active, racemic, *meso*, *syn*, and *anti* forms of the *trans* compound were isolated for both ligands; each of these subsequently isomerized to the corresponding *cis* complex by reaction with $AlEt_3$ and the various diastereoisomers of the latter separated and characterized. Whereas the *trans* isomers are relatively inert, the *cis* complexes readily undergo stereospecific halogen substitution by I^- and CO.[1597] A minor product obtained from the reaction of '$RuCl_3 \cdot H_2O$' with $\pm$*o*-$C_6H_4(PMePh)$, in the presence of formaldehyde is *trans*-$[RuCl_2\{(\pm)\text{-}o\text{-}C_6H_4(PMePh)_2\}\{(\pm)\text{-}o\text{-}C_6H_4(PMePh)P(O)MePh]$ containing P,P′ and O,P′ bidentate ligands respectively.[1600a]

Reaction of $[Ru(OH_2)_6](tos)_2$ with dppe gives $[Ru(dppe)_2(tos)_2]$ (tos = *p*-toluenesulfonate).[1600b] Reaction of $[RuCl_2(PPh_3)_3]$ with $MeC(CH_2PPh_2)_3$ (triphos) affords the white compound $[RuCl_2(triphos)_2]$ shown by ^{31}P NMR spectroscopy to have structures (**153**) with non-coordinated P atoms,[1594] whereas $Ph_2AsCH_2AsPh_2$ (dpam) forms $[RuCl_2(dpam)_3]$ which contains one bi- and two mono-dentate dpam ligands.[1593] The reinvestigation of the reaction of $[RuCl_2(PPh_3)_3]$ with equimolar amounts of $Ph_2P(CH_2)_nPPh_2$ (n = 1–4) has been reported. Only for n = 4 is the complex $[RuCl_2(PPh_3)(chelate)]$ isolatable. ^{31}P NMR evidence is also presented for binuclear species such as $[Ru_2Cl_4(L\text{–}L)_2(PPh_3)_2]$[1601] (see Section 45.5.5).



(153)

Various $[RuCl_2(L\text{–}L)_2]$ have been prepared starting from either $[RuCl_2(DMSO)_4]$[1511] or reduced solutions of $[Ru_2OCl_{10}]^{4-}$ and X-ray structures of *cis*- and *trans*-$[RuCl_2(dppm)_2]$ are reported.[1602a] Reaction of $[RuCl_2(PPh_3)_3]$ with $Ph_2P(CH_2)_nPPhCH_2CH_2CpH$ (LH) (n = 3,4) has been shown to give neutral [RuLCl] complexes containing a coordinated Cp group.[1602b]

45.5.4.4 Polydentate P, As or Sb donor ligand halide complexes

Although reaction of $MeC(CH_2PPh_2)_3$ (triphos) with $[RuCl_2(PPh_3)_3]$ gives compound (**153**) where triphos acts as a bidentate ligand,[1594] the analogous reaction with $PhP\{(CH_2)_2PPh_2\}_2$ gives the five-coordinate monomer $[RuCl_2PhP\{(CH_2)_2PPh_2\}_2]$.[1540] In contrast, reaction of this tritertiarz phosphine with '$RuCl_3 \cdot xH_2O$' in boiling EtOH gives a binuclear chloride-bridged complex (see Section 45.5.5.2). Likewise, reaction of '$RuCl_3 \cdot xH_2O$' with $PhP\{(CH_2)_3PPh_2\}_2$ (ttp) and $PhP\{(CH_2)_3PCy_2\}_2$ (Cyttp) affords $[RuCl_2(ttp)]_x$ and $[RuCl_2(Cyttp)]$ respectively. The former is polymeric and the latter monomeric, presumably due to steric effects of the larger cyclohexyl groups.[1486] Incomplete displacement of PPh_3 from $[RuCl_2(PPh_3)_3]$ occurs on treatment with $P[(CH_2)_2PPh_2]_3$ (tet-2) to produce $[RuCl_2(PPh_3)(tet\text{-}2)]$, in which tet-2 acts as a terdentate ligand.[1540] Interestingly, the same reaction with $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$ (tet-1) gives the five-coordinate cation [RuCl(tet-1)]Cl,[1540] although the product from reaction of tet-1 with $[RuCl_2py_4]$ is formulated elsewhere as $[RuCl_2(tet\text{-}1)]$, and $[RuCl_2N\{(CH_2)_2PPh_2\}_3]$ is also reported.[1595]

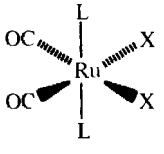
A series of six-coordinate complexes $[RuCl_2(ligand)]$ containing the quadridentate ligands (*o*-$Ph_2L \cdot C_6H_4)_3L'$, (L = P or As; L′ = P, As or Sb but not all combinations), have been prepared by reaction of '$RuCl_3 \cdot xH_2O$' or $[RuCl_2(PPh_3)_3]$ with the appropriate ligand. Metathesis with NaX gives the corresponding $[RuX_2(ligand)]$ (X = Br, I, NCS, CN but not all combinations).[46] An X-ray analysis of $[RuBr_2\{As(o\text{-}C_6H_4AsPh_2)_3\}]$ confirms the distorted octahedral structure.[1603a] Reaction of $[RuCl_2py_4]$ with $Ph_2P(CH_2)_2P(Ph)(CH_2)_2P(Ph)(CH_2)_2PPh_2$ (L) gives *trans*-$[RuCl_2L]$.[1603b]

45.5.4.5 Carbon donor ligand complexes

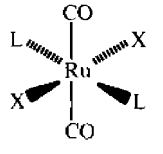
(*i*) *Carbonyl halides*

A very large number of compounds of general formula $[RuX_2(CO)_xL_{4-x}]$ (X = Cl, Br, I; L = PR_3, AsR_3, $SbPh_3$; x = 1–3) have been synthesized in the last 25 years. Since this is the subject

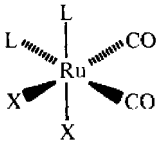
of detailed reviews,[1,3,4,5,1604,1605] only a brief account is presented here. For $x = 3$, the best route is *via* reaction of the cluster compounds $[Ru_3(CO)_9L_3]$ with halogens or hydrocarbon solvents[1560] (*e.g.* L = PPh_3, $PMe_2(CH_2Ph)$, $AsMe_2(CH_2Ph)$; x = Cl, Br, I).[1560,1606] For $x = 2$ and 1, several methods are available and these lead to the various geometrical isomers (**154–157**; $x = 2$) and (**158, 159**; $x = 1$) which can also interconvert under thermal or photochemical stimulation (see references 1607–1610). For example, reaction of $[RuI_2(CO)_2]_n$ with L gives $[RuI_2(CO)_2L_2]$ (**154**) whereas $[RuI_2(CO)_2(p\text{-}MeC_6H_4NH_2)_2]$ and L under mild conditions gives products of stereochemistry (**155**) which isomerize thermally to (**154**). These iodo compounds are converted into the corresponding chloro or bromo compounds by treatment with the appropriate halogen, usually with preservation of the original stereochemistry.[1611] The dicarbonyl species can also be obtained by direct reaction of $[RuX_2(CO)_3]_2$ (X = Cl, Br), $[RuCl_2(CO)_2]_n$, $[RuCl_2(CO)_3THF]$[1612] or $[RuCl_4(CO)_2]^{2-}$[1613] with L or by treatment of carbonylated, alcoholic solutions of $RuCl_3$ with L.[106,1584,1614a] As detailed in Table 1, reference 1, p. 693, the latter route also leads to $[RuCl_2COL_3]$ in some instances. Bromo and iodo analogues of $[RuCl_2COL_3]$ can be obtained by metathesis, the ease of replacement of Cl dependent upon the *trans* ligand; Cl *trans* to PR_3 is substituted more rapidly than Cl *trans* to Cl or CO which allows the isolation of some intermediate $[RuClY(CO)(PR_3)_3]$ complexes (X = Br, I, SCN).[1614a] The same intermediates can be obtained by treatment of $[RuHCl(CO)(PR_3)_3]$ with HX (X = Br, I), together with some $[RuX_2(CO)(PR_3)_3]$ (**158**).[1614b]



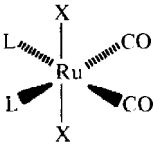
(154)



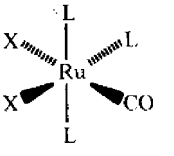
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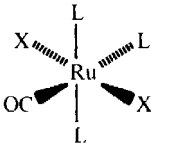
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(157)



(158)



(159)

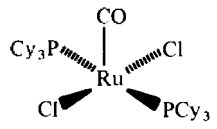
An alternative method is by carbonylation of complexes of Ru^{II} or Ru^{III} containing P, As or Sb donor ligands, *e.g.* $[RuCl_2(PPh_3)_3]$ reacts with CO to give $[RuCl_2(CO)_2(PPh_3)_2]$ (the isomer formed depending on conditions),[106,1607] whereas $[RuCl_2(P(OMe)Ph_2)_3]$ produces $[RuCl_2(CO)(P(OMe)Ph_2)_3]$ (isomer **158**),[1615] and $[RuCl_2(PMe_3)_4]$ forms $[RuCl_2CO(PMe_3)_3]$ (isomer **159**).[1391c] More examples are given in Table 2, reference 1, p.695. Solvento complexes $[RuCl_2(CO)(PR_3)_2(solvent)]$ (solvent = DMA, DMF, DMSO, MeOH) have also been isolated from these reactions.[1558,1607,1616]

In some instances, decarbonylation of the solvent provides the source of CO, *e.g.* reaction of '$RuCl_3 \cdot xH_2O$' and PPh_3 in benzyl alcohol gives $[RuCl_2(CO)(PPh_3)_3]$;[1542] $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ decarbonylates saturated aldehydes RCHO to give $[RuCl_2CO(PEt_2Ph)_3]$[1617] and reaction of '$RuCl_3 \cdot xH_2O$', PPh_3, KOH, 2-methoxyethanol and aqueous HCHO, followed by CCl_4 produces $[RuCl_2(CO)_2(PPh_3)_2]$;[1410b] a similar recipe yields $[RuX_2CO(AsRPh_2)_3]$ (R = Me, Et, Pr).[1618] Other routes to $[RuCl_2COL_3]$ are by reaction of $[RuCl_2(PPh_3)_3]$ with CO_2[1619] and cocondensation of Ru with $(COCl)_2$, followed by addition of PMe_3.[1620] Reaction of $[Ru(CO)_3(PPh_3)_2]$ with $(NSCl)_3$ gives $[RuCl_2(CO)_2(PPh_3)_2]$,[1621] and X-ray structures of some of these mono- and di-carbonyl complexes have been published.[1575,1610,1622]

Detailed studies of the thermally and photochemically induced interconversions of the various isomers of $[RuX_2(CO)_2L_2]$ reveal that the key step is dissociation of CO to form five-coordinate intermediates.[1608,1610] A similar study on $[RuCl_2CO(PMe_2Ph)_2L]$ (L = $P(OMe)_3$, $P(OMe)_2Ph$) suggests that the isomerization mechanisms involve phosphorus ligand dissociation.[1609] An electrochemical study of $[RuCl_2(CO)(PMe_2Ph)_3]$ reveals that the compound undergoes a reversible one-electron oxidation.[625]

Treatment of carbonylated, 2-methoxyethanol solutions of $RuCl_3$ with bulkier phosphines such as PCy_3 gives the five-coordinate $[RuCl_2CO(PCy_3)_2]$[1623a,1623b] shown by X-ray analysis to have the distorted square pyramidal structure (**160**);[1624] a cyclohexyl hydrogen atom blocks the sixth coordination position (Ru···H = 2.31 Å). Reaction of (**160**) with L′ (CO, fumaronitrile, $CH_2{=}CHCN$) gives $[RuCl_2(CO)L'(PCy_3)_2]$.[1623a,1625] Even bulkier phosphines such as $PBu^t{}_2Ph$ and $PBu^t{}_2(p\text{-Tol})$ react with the 'RuCOCl' solution to give dimeric ruthenium(I) complexes $[Ru(\mu\text{-Cl})(CO)_2PR_3]_2$ (see Section 45.5.3.2). These probably form because the $PBu^t{}_2Ph$ groups are too bulky to permit six coordination. As discussed elsewhere, related compounds containing $SnCl_3^-$, {*e.g.* $[RuCl(SnCl_3)CO(Me_2CO)(PPh_3)_2]$},[109] $SiMe_3$ {*e.g.* $[RuCl(SiMe_3)(CO)_3PPh_3]$},[68,74] and $SiCl_3$ {*e.g.* $[Ru(SiCl_3)_2(CO)_2PPh_3(P(OMe)_3)]$}[67] (Section 45.3.2) are available.

There are relatively few examples of cationic and anionic carbonyl halides containing monodentate P, As or Sb donor ligands. Reaction of $[Ru(CO)_3(PPh_3)_2]$ with I_2 or SnI_4 gives



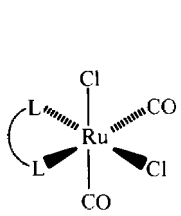
(160)

$[RuI(CO)_3(PPh_3)_2]Z$ (Z = I,[1626] SnI_3[12]); on heating, these form $[RuI_2(CO)_2(PPh_3)_2]$. Similar cations $[RuX(CO)_3(PR_3)_2]^+$ are obtained by reaction of phosphine-substituted carbonyl halides with Lewis acids ($AlCl_3$, $AlBr_3$, $FeCl_3$) in benzene under CO (X = Cl, Br; R = Cy, Et, Ph).[1627] In some systems, Lewis acid adducts can be isolated. Thus treatment of $[RuCl_2(CO)_2(PMe_3)_2]$ with $FeCl_3$ in CH_2Cl_2 at 25°C gives $[RuCl(Cl \rightarrow FeCl_3)(CO)_2(PMe_3)_2]$. Addition of more $FeCl_3$ affords $[Ru(Cl \rightarrow FeCl_3)_2(CO)_2(PMe_3)_2]$.[1628] The related cations $[RuCl(CO)_2(CS)(L–L)]BPh_4$ are known (see Section 45.5.4.5.ii).[1629a] Dissolving $[RuCl_2CO(P(OMe)Ph_2)_3]$ in MeOH and adding $Na[BPh_4]$ gives the five-coordinate cation $[RuCl(CO)(P(OMe)Ph_2)_3]^+$; with $[RuCl_2CO(P(OEt)Ph_2)_3]$, the binuclear $[RuCl(CO)(P(OEt)Ph_2)_3]_2$ $(BPh_4)_2$ is formed[1615] (*cf.* $[RuCl(P(OMe)Ph_2)_4]^+$ and $[RuCl(P(OEt)Ph_2)_4]_2^{2+}$ (Section 45.5.4.1).[1533] The chiral octahedral cations $[RuR(CO)_2L^*(PMe_3)_2]^+$ (L* = PhPMeR′ *etc.*) have been prepared and $^2J_{PP}$ between the diastereotopic PMe_3 groups determined.[1629b]

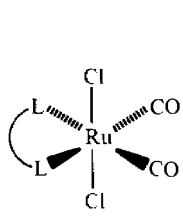
Reaction of $[Ru(CO)_3(PPh_3)_2]$ or $[RuI_2(CO)_2(PPh_3)_2]$ with MeI gives $MePh_3P[RuI_3(CO)_2PPh_3]$.[1630] Closely related carbonyl anions $[RuCl_3COL_2]^-$ (L = $AsPh_3$, $SbPh_3$) are prepared by treatment of $Ph_3(PhCH_2)P[RuCl_3CO(nbd)]$ with stoichiometric amounts of L; some $[RuCl_2COL(nbd)]$ (Section 45.5.4.5.vi) is also formed. With excess $SbPh_3$, $[RuCl_2CO(SbPh_3)_3]$ (**158**) is the main product.[659] Treatment of $[RuCl_2CO(MeOH)(PPh_3)_2]$ with $[AsPh_4]Cl \cdot HCl$ in acetone gives $AsPh_4[RuCl_3CO(PPh_3)_2]$.[1616]

Relatively little work has been published on carbonyl halide complexes of polydentate phosphines and arsines. Thus reaction of $[RuX_2(CO)_2]_n$ (X = Cl, Br, I) with dppe, eda and $Ph_2E(CH_2)_4EPh_2$ (E = P, As) gives $[RuX_2(CO)_2(L–L)]$ (**161**; X = Cl),[1631] whereas treatment of the ethanolic 'RuCOCl' solution with dppm or eda gives isomer (**162**). With dpam, $[RuCl_2(CO)_2(dpam)_2]$ (**163**) with unidentate dpam coordination is formed.[1593] Detailed studies on the analogous dicarbonyl complexes *cis*- and *trans*-$[RuCl_2(CO)_2(L–L)]$ (L–L = *o*-$C_6H_4(EMePh)_2$; E = As, P) have appeared. The *trans* isomers were prepared from $[RuCl_2(CO)_2]_n$ and L–L in boiling EtOH or 2-methoxyethanol whereas treatment of $[RuCl_2(CO)_3]_2$ with L–L in EtOH at room temperature affords the less stable *cis* isomers. For L–L = *o*-$C_6H_4(PMePh)_2$, the tricarbonyl cations $[RuCl(CO)_3L–L]Cl$ can be prepared and the dicarbonyls undergo reversible decarbonylation to give the chloro-bridged dimers $[RuCl_2(CO)(L–L)]_2$. Reaction of these dimers or the netural dicarbonyls with DMSO gives exclusively *cis*-$[RuCl_2(CO)(DMSO)(L–L)]$ (with S-bonded DMSO).[1632,1633] Carbonylation of $[RuCl_2(ttp)]_x$ gives *cis*- and *trans*-$[RuCl_2(CO)ttp]$ whereas only *trans*-$[RuCl_2(CO)Cyttp]$ is formed with $[RuCl_2(Cyttp)]$.[1486] The cations $[RuX(CO)_2(Cyttp)]X'$ (XX′ = HCl, HBr, HBF_4, Cl_2, Br_2) are prepared by oxidative addition of halogens and acids to $[Ru(CO)_2(Cyttp)]$ whereas treatment of $[RuCl_2(tpp)]_x$ with CO and $Tl[BF_4]$ gives $[Ru(CO)_2(tpp)](BF_4)_2$.[1486]

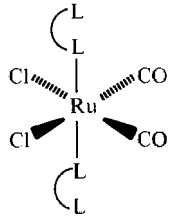
Halogenation of $[Ru(CO)_2triphos]$ (triphos = $MeC(CH_2PPh_2)_3$) gives initially the salts $[RuX(CO)_2triphos]X$ (X = Cl, Br) which lose CO reversibly to give $[RuX_2(CO)(triphos)]$. The neutral chloro complex contains a labile Ru—P bond since it also reacts reversibly with SO_2 to give $[RuCl_2CO(SO_2)(triphos)]$ (**164**).[1485] Treatment of these and related $[RuX(CO)_2(triphos)]X'$ cations with a variety of neutral ligands L (L = Bu^tNC, $P(OMe)_3$, PMe_2Ph *etc.*) in the presence of trimethylamine *N*-oxide yields chiral complexes of the type $[RuX(CO)L(triphos)]X'$. The compound $[RuMe(CO)(CNBu^t)(triphos)]PF_6$ has been resolved, and the absolute configuration of the (+)-enantiomer has been determined.[1634]



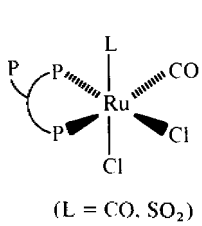
(161)



(162)



(163)



(L = CO, SO_2)

(164)

Reactions of $[RuCl_2(L\text{–}L)_2]$ (L–L = dppm or dppe) with CO and silver salts of non-coordinating anions produce $[Ru(CO)_2(L\text{–}L)_2]^{2+}$ (both *cis* and *trans* isomers). A series of compounds of general formula $[Ru(CO)_2(dppm)_2AgY]X_2$ may also be isolated (Y = O_2PF_2, Cl, ClO_4, $BF(OH)_3$; X = BF_4, AsF_6, ClO_4), which are proposed to contain a dppm ligand bridging Ru and Ag, the bond between which is reversibly cleaved by $MeNO_2$ on the NMR time scale.[1635] Treatment of the dicarbonyl cations $[Ru(CO)_2(L\text{–}L)_2]^{2+}$ with $Na\{HB(OEt)_3\}$ produces the formyl species $[Ru(CHO)(CO)(L\text{–}L)_2]^+$ as confirmed by the X-ray analysis of *trans*-$[Ru(CDO)(CO)(dppe)_2]SbF_6 \cdot CH_2Cl_2$.[1636] Studies have revealed that *trans*-$[Ru(CHO)(CO)(dppe)_2]SbF_6$ decomposes in CH_2Cl_2 to give *cis*-$[RuH(CO)(dppe)_2]SbF_6$ which subsequently isomerizes to the *trans* isomer. However, *cis*-$[Ru(CHO)(CO)(dppm)_2]SbF_6$ gives $[RuH(CO)_2(dppm)_2]SbF_6$ with a monodentate dppm ligand but chelation occurs on photolysis in CH_2Cl_2 to give *trans*-$[RuCl(CO)(dppm)_2]SbF_6$ *via* *trans*-$[RuH(CO)(dppm)_2]SbF_6$.[1637a] It has been shown that *trans*-$[Ru(CHO)(CO)(dp)_2]SbF_6$ [dp = 1,2-bis(diphenylphosphine)benzene] decomposes to *trans*-$[RuH(CO)(dp)_2]SbF_6$ *via* a free radical mechanism.[1637b] Monocarbonyl cations of type $[RuCl(CO)(L\text{–}L)_2]^+$ are also prepared by direct reaction of *trans*-$[RuCl_2(dppm)_2]$ with CO[1593] or by reaction of the five-coordinate cations $[RuCl(L\text{–}L)_2]^+$ (L–L = dppp, 2-diphenylphosphinoethylpyridine) with CO.[1535]

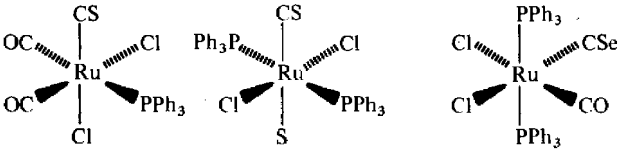
Hydridocarbonyls and carbonyl complexes containing C, N, O or S donor ligands are covered in later sections of this review.

(*ii*) *CS and CSe complexes*

Reaction of $[RuCl_2(CS)(CO)_3]$ (made from $[Ru_3(CO)_{12}]$ and $CSCl_2$) with PPh_3 gives $[RuCl_2(CO)_2CS(PPh_3)]$ (**165**). With bidentate ligands L–L (L–L = $Ph_2E(CH_2)_2EPh_2$; E = P, As) a mixture of species is obtained and only $[RuCl(CO)_2CS(L\text{—}L)]BPh_4$ could be isolated in pure form.[1629a] Bridge cleavage of $[RuCl_2(CS)(PPh_3)_2]_2$ (Section 45.5.5.2) with CO gives $[RuCl_2CO(CS)(PPh_3)_2]$, the isomer formed depending on the reaction conditions,[1638] whereas with MCl/HCl, $M[RuCl_3(CS)(PPh_3)_2]$ (M = Ph_4As, Et_4N, $Ph_3(PhCH_2)P$) is obtained.[1639] Treatment of the double chloride-bridged dimer with DMF gives $[RuCl_2(CO)DMF(PPh_3)_2]$ which on recrystallization from $MeOH/CH_2Cl_2$ produces $[RuCl_2(CS)MeOH(PPh_3)_2]$ (**166**);[1616] the aqua analogue $[RuCl_2(OH_2)(CS)(PPh_3)_2]$ is formed by reaction of $[RuCl_2(PPh_3)_3]$ with CS_2 in xylene.[1640] Reaction of $[RuCl_2(PPh_3)_3]$ with neat CS_2 gives the binuclear complexes $[RuCl_2(CS)(PPh_3)_2]_2$ and $[Ru_2Cl_4(CS)(PPh_3)_4]$[1639,1641] (see Section 45.5.5.1) and the monomeric $[RuCl_2CO(CS)(PPh_3)]$ (?) is claimed.[1642]

The alkoxyphenylphosphine complexes $[RuCl_2(CS)L_3]$ [L = $P(OR)Ph_2$ (R = Me, Et), $P(OMe)_2Ph$] are prepared by reaction of either $[Ru_2Cl_4(CS)(PPh_3)_4]$ or $[RuCl_2CS(PPh_3)_2]_2$ with an excess of L in C_6H_6. Addition of $Na[BPh_4]$ to alcoholic solutions of these $P(OR)Ph_2$ complexes then gives $[RuCl(CS)(P(OMe)Ph_2)_3]BPh_4$ and $[RuCl(CS)(P(OEt)Ph)_3]_2(BPh_4)_2$. No cationic complexes are generated under these conditions for $[RuCl_2(CS)\{P(OMe)_2Ph\}_3]$.[1615]

The Ru^0 complex $[Ru(CO)_2(PPh_3)_3]$ reacts readily with CY_2 (Y = S, Se) to form $[Ru(CY_2)(CO)_2(PPh_3)_2]$.[1470] These compounds are readily methylated with MeI to give $[Ru(CY_2Me)(CO)_2(PPh_3)_2]^+$. Displacement of CO with X^- affords neutral $[RuX(CY_2Me)(CO)(PPh_3)_2]$ and treatment of these dithio- or diseleno-methyl ester complexes with HX produces the mixed thio- or seleno-carbonyl complexes $[RuX_2(CO)(CY)(PPh_3)_2]$ (X = Cl, Br).[1643] These compounds are also formed on treatment of $[RuCl_2(CCl_2)(CO)(PPh_3)_2]$ with H_2Y.[49] An X-ray structure determination shows $[RuCl_2CO(CSe)(PPh_3)_2]$ to have structure (**167**). The long Ru—Cl bond (2.477 Å) *trans* to CSe compared to 2.428 Å (Ru—Cl *trans* to CO) demonstrates the strong *trans* influence of the CSe ligand.[1643,1644] Chromatography of $[RuI_2(CO)(CSe)(PPh_3)_2]$ on alumina affords $[RuI(OH)(CO)(CSe)(PPh_3)_2]$ (with OH *trans* to CSe).[1643] A report on the preparation of hydride complexes such as $[RuHCl(CS)(PPh_3)_3]$, and $[RuH(\eta^2\text{-}OCOR)CS(PPh_3)_2]$ (R = H, Me) has appeared (see Section 45.10.3.2.iii). The corresponding $[RuCl(\eta^2\text{-}OCOH)CS(PPh_3)_2]$ is also synthesized from $[RuCl_2(OH_2)(CS)(PPh_3)_2]$ and $Na[OCOH]$.[1645] Some CNR complexes containing CS and CSe are described in the next section.



(**165**) (S = DMF, MeOH) (**167**)

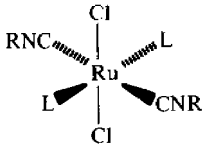
(**166**)

(iii) CNR, CNHR and related carbene complexes

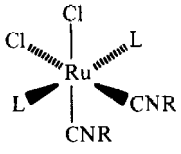
Reaction of $[RuX_3(AsRPh_2)_3]$ (X = Br, Cl; R = Et, Me, Ph) with *p*-tolyl isocyanide in acetone or alcohol gives $[RuX_2(AsRPh_2)_2(CN\text{-}p\text{-}Tol)_2]$.[1646] A more detailed study on $[RuCl_3L_3]$ (L = PMe_2Ph, $PPr^n{}_2Ph$, $PBu^n{}_2Ph$) shows that the ruthenium(III) cations $[RuCl_2(CNR)L_3]^+$ are first formed and these undergo reduction to various isomers (**168–170**) of $[RuCl_2(CNR)_2L_2]$.[1647] Other routes to $[RuX_2(CNR)_2(ER_3)_2]$ involve direct reaction of $[RuCl_2(PPh_3)_3]$, $[RuX_3(AsPh_3)_2MeOH]$ or $[RuX_2(SbPh_3)_n]$ (X = Cl, *n* = 3; X = Br, *n* = 4) with CNR;[1411,1590,1648] the ^{13}C NMR spectrum of $[RuCl_2(CNPh)_2(PPh_3)_2]$ (**170**) is reported.[1649] These isomers undergo facile interconversion in solution on thermal or photochemical excitation, and the mechanism of isomerization is proposed to occur *via* the photoelimination of PPh_3.[1590,1650] The analogous $[Ru(OCOMe)_2(CNMe)_2(PPh_3)_2]$ are prepared from the action of CNMe on $[Ru(OCOMe)_2(PPh_3)_2]$[1651] and treatment of *cis*-$[RuCl_2(CNEt)_2(EPh_3)_2]$ (**169**) with $SnCl_2$ in 2-methoxyethanol gives *cis*-$[RuCl(SnCl_3)(CNEt)_2(EPh_3)_2]$ (E = P, As, Sb).[110]

Direct reaction of $[RuX_2CO(AsRPh_2)_3]$ (X = Cl, Br; R = Me, Et, Pr) with *p*-tolyl isocyanide gives $[RuX_2(CO)(CN\text{-}p\text{-}Tol)(AsRPh_2)_2]$[1652] and the X-ray structures of $[RuCl_2(CO)(CN\text{-}p\text{-}ClPh)(PPh_3)_2]$[1653] (**171**) and $[RuCl(Ph)CO(CNCMe_3)(PMe_2Ph)_2]$ (**172**)[1654] have been reported. Treatment of the five-coordinate $[RuCl(R')(CO)(PPh_3)_2]$ with CNR affords $[RuCl(R')(CO)(CNR)(PPh_3)_2]$ (R = R′ = *p*-Tol). Heating this in boiling CH_2Cl_2 gives an orange material, shown by X-ray analysis to be the iminoacyl complex (**173**). Protonation of (**173**) with HCl gives the aminocarbene complex $[RuCl_2[C(NHR)R'](CO)(PPh_3)_2]$.[1655] Reaction of O_2 with the zerovalent $[Ru(CO)_2(CN\text{-}p\text{-}Tol)(PPh_3)_2]$ (Section 45.5.1.3) gives the carbonate (**174**).[1480]

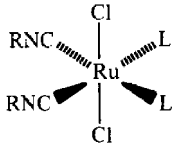
The product of reaction between $[RuCl_2(PPh_3)_3]$ and CS_2 in boiling xylene reacts with CNR to give the yellow *trans* isomer of $[RuCl_2(CNR)(CS)(PPh_3)_2]$. Isomerization to a colourless *cis* isomer occurs in toluene under reflux and this reacts with $Ag[ClO_4]$ to give $[RuCl(OClO_3)(CNR)(CS)(PPh_3)_2]$ which in turn gives $[RuCl(CNR)(CO)(CS)(PPh_3)_2]ClO_4$ on carbonylation. This cation reacts with SeH^- to give (**175**) which on methylation with MeI affords $[Ru(\eta^2\text{-}Se{=}CSMe)(CNR)(CO)(PPh_3)_2]^+$ (**176**). Treatment of (**176**) with aqueous HCl in toluene/EtOH solution under reflux liberates MeSH and produces $[RuCl_2(CNR)(CSe)(PPh_3)_2]$ in high yield.[1640,1645] The dicarbonyl complexes $[RuCl_2(CNR)(CO)_2PPh_3]$ can be made by reaction of $[RuCl_2(CO)_2(CS)PPh_3]$ with NH_2R; this reaction goes *via* a labile amino(mercapto)carbene complex which eliminates H_2S.[1629a] Other, isocyanide complexes containing hydride ligands are covered in Section 45.10.



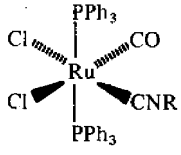
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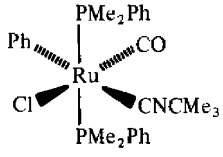
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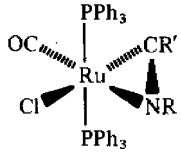
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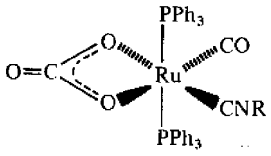
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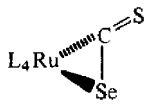
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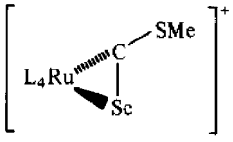
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(174)

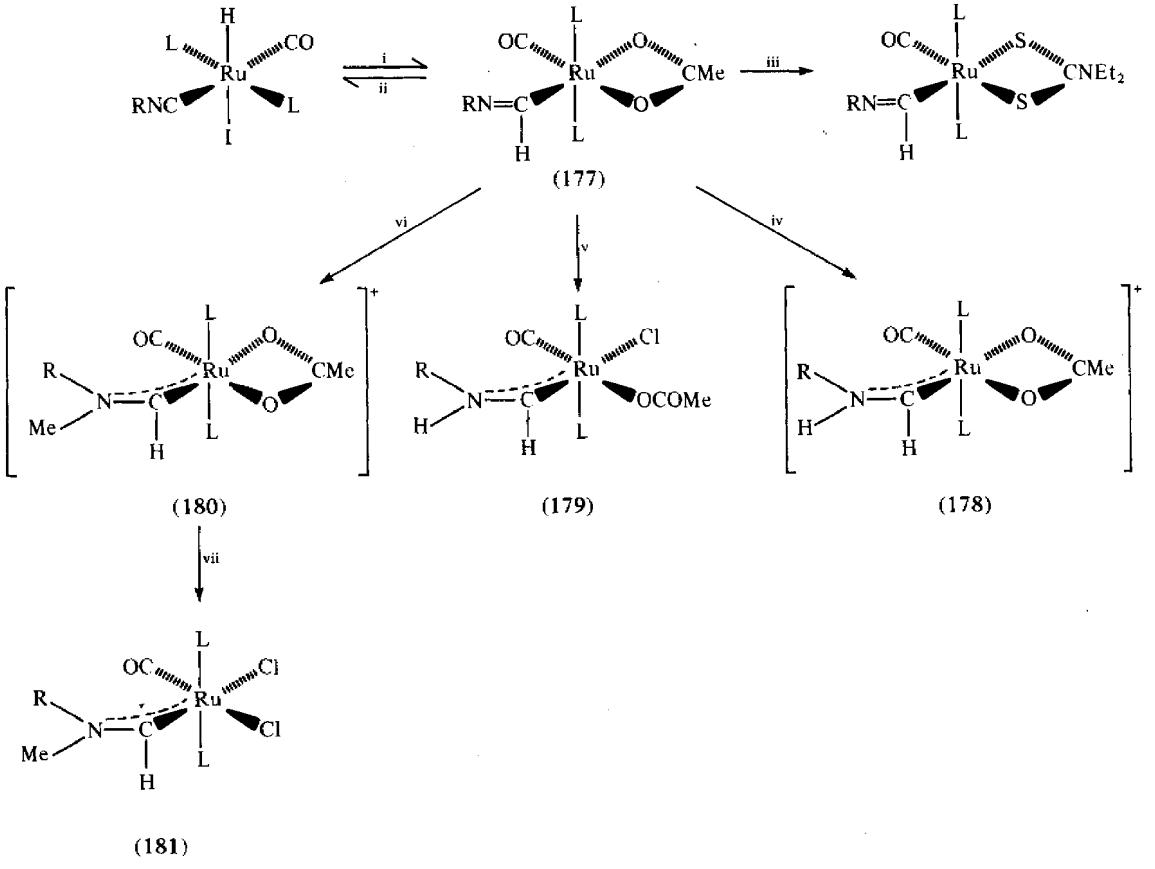


(175) L_4 = (CO)(CNR)$(PPh_3)_2$



(176)

Roper and co-workers[1656] have reported the synthesis of a number of formimidoyl (CNHR) complexes. For example reaction of $[RuHI(CN\text{-}p\text{-}Tol)(CO)(PPh_3)_2]$ with acetate ion promotes hydrogen migration from ruthenium to isocyanide to give the formimidoyl complex (**177**) (L–L = OCOMe). Treatment with $^-S_2CNEt_2$ gives (**177**) (L–L = S_2CNEt_2). The nitrogen atom of the CNHR group is attacked by electrophiles to generate a range of secondary carbene complexes such as (**178**) (with $HClO_4$) and (**179**) (with HCl) (Scheme 45). With dimethylsulfate, methylation of (**177**) (L–L = OCOMe) leads to the cationic *N*-*p*-tolylmethylaminocarbene complex (**180**). The bidentate acetato group is then removed by addition of LiCl to give the neutral carbene (**181**). Other examples of P donor ligand compounds containing these C-bonded ligands are to be found in the above references.

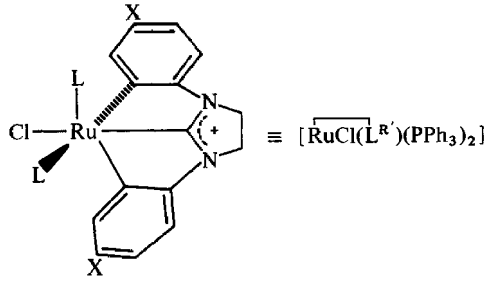


L = PPh_3; R = *p*-Tol

i, ^-OCOMe; ii, HI; iii, $^-S_2CNEt_2$; iv, $HClO_4$; v, HCl; vi, Me_2SO_4; vii, LiCl

Scheme 45

Reaction of $[RuCl_2(PPh_3)_3]$ with electron-rich alkenes $(R\overline{NCH_2CH_2NRC}=)_2$ ($L^R{}_2$, R = Me, Et, CH_2Ph) affords *trans*-$[RuCl_2(L^R)_4]$ which for R = Me react with PF_3 and $P(OMe)_3$ to give *trans*-$[RuCl(L^{Me})_4(PF_3)]Cl$ and *trans*-$[RuCl(L^{Me})_2\{P(OMe)_3\}_3]Cl$ respectively. More complicated reactions occur with aryl-substituted electron-rich alkenes. Thus, reaction of $L^{R'}{}_2$ (R′ = Ph, *p*-Tol or *p*-$MeOC_6H_4$) with $[RuCl_2(PPh_3)_3]$ in refluxing xylene gives the cyclometallated product (**182**). Further reactions undergone by this stereochemically rigid five-coordinate complex include displacement of both PPh_3 groups by other PR_3 to give $[\overline{RuCl(L^{R'})}(PR_3)_2]$ or of one PPh_3 group by $L^{Et}{}_2$ to give $[\overline{RuCl(L^{R'})}(L^{Et})PPh_3]$. The latter compound is also formed by treatment of $[\overline{RuCl_2(L^{R'})}(NO)PPh_3]$ (made from $[RuCl_3NO(PPh_3)_2]$ and $L^{R'}{}_2$) with $L^{Et}{}_2$. Small ligands L′ add to (**182**) and $[\overline{RuCl(L^{R'})}(PR_3)_2]$ to give the six-coordinate $[\overline{RuCl(L^{R'})}(PR_3)_2L']$ (L′ = CO, PF_3, $P(OMe)_3$, N_2, MeCN).[1420,1657,1658a] The compound $[RuCl_2(L^{Me})_4]$ is a good hydrosilylation catalyst.[1658b]



(182) X = H, Me or OMe; L = PPh_3

(iv) Alkyl, aryl and acyl complexes

Most of the early work in this area[1659] was concerned with reactions between *cis*- and *trans*-$[RuX_2(L–L)_2]$ (X = halide; L–L = dmpe, dppe or dppm) and various alkylating and arylating reagents. Thus, *cis*-$[RuCl_2(L–L)_2]$ and LiR (R = Me, Ph) give the corresponding dimethyl and diphenyl complexes, *cis*-$[RuR_2(L–L)_2]$ respectively. *Cis*-$[RuEt_2(dmpe)_2]$ has been prepared from *trans*-$[RuCl_2(dmpe)_2]$ and $MgEt_2$ whereas with *trans*-$[Ru(OCOMe)_2(dmpe)_2]$, the *trans* diethyl isomer is formed.[16a] Use of the less reactive AlR_3 compounds affords only the monoalkyl derivatives $[RuClR(L–L)_2]$ (alkyl = Me, Et, Pr^n) from both the *cis* and *trans* dichloro complexes; the monoaryl analogues (R = Ph, *p*-MeC_6H_4) are also available. Further reaction of *cis*-$[RuClMe(L–L)_2]$ with LiMe gives *cis*-$[RuMe_2(L–L)_2]$ whereas treatment with Br^-, I^- or SCN^- produces $[RuXR(L–L)_2]$. The latter are also formed by reaction of $[RuHR(L–L)_2]$ (see Section 45.10.3.2.i) with hydrogen halides. The compound *cis*-[Ru(2-np)(Cl)(dmpe)$_2$] is also the major product together with *ca.* 20% $[RuCl_2(dmpe)_2]$ on treatment of *cis*-[Ru(2-np)H(dmpe)$_2$] with $CDCl_3$,[44] and $[RuClMe(diars)_2]$ is obtained from $[RuCl_2(diars)_2]$ and LiMe.[1659] Detailed NMR studies are reported on many of these alkyl and aryl complexes.[1659,1660]

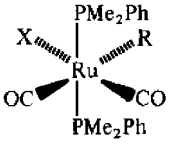
The corresponding dialkyl and diaryl complexes *cis*-$[RuR_2(PMe_3)_4]$ (R = Me,[1661] Ph[1528]) are best prepared by treatment of $[Ru_2(OCOMe)_4Cl]$ with MgR_2 and PMe_3 in THF. The dimethyl derivative has also been synthesized by reaction of *trans*-$[RuCl_2(PMe_3)_4]$ and LiMe in ether.[1380a,1534] Studies[16] have shown that treatment of this di-Me compound with one equivalent of HCl at −78°C gives *cis*-$[RuCl(Me)(PMe_3)_4]$ whereas with $MeCO_2H$, *cis*-$[Ru(\eta^1\text{-}OCOMe)Me(PMe_3)_4]$ is formed; more HCl produces $[RuCl(PMe_3)_4]_2Cl_2$. The mono-Me complex also reacts with 1% Na/Hg to give *cis*-$[RuMe(PMe_3)_4]_2Hg$ (see Section 45.2). The five-coordinate PPh_3 complex $[RuCl(Me)(PPh_3)_3]$ results from the reaction of $[RuCl_2(PPh_3)_3]$ with $AlMe_3$ in C_6H_6.[1662] Related mono-Me complexes include *cis*-$[RuMe\{P(O)(OMe)_2\}\{P(OMe)_3\}_4]$ generated by heating $[Ru\{P(OMe)_3\}_5]$ in *n*-hexane in a sealed tube and $[RuMe\{P(OMe)_3\}_5]I$, obtained by reaction of MeI with either of these isomers.[1380] The ylide complex $[RuCl(CH_2PMe_3)(PMe_3)_4]Cl$ (Section 45.5.4.1) results from reaction of *trans*-$[RuCl_2(PMe_3)_4]$ with $Li[Me_2P(CH_2)_2]$.[1534]

Trifluoroiodomethane oxidatively adds to *trans*-$[Ru(CO)_3\{P(OCH_2)_3CEt\}_2]$ in C_6H_6 to give $[RuI(CF_3)(CO)_2L_2]$[1663] whereas the photochemical reaction of chlorotrifluoroethylene with *trans*-$[Ru(CO)_3(PMe_2Ph)_2]$ affords an isomeric mixture of $[RuCl(\eta^1\text{-}CF{=}CF_2)(CO)_2(PMe_2Ph)_2]$.[1664a] Various compounds containing a Ru—CF_3 bond, *e.g.* $[Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2]$ (Section 45.2) and $[RuCl(CF_3)(CO)_2(PPh_3)_2]$, are also reported and conversions to difluorocarbene species discussed.[14] Reaction of $[RuCl_2(CF_2)CO(PPh_3)_2]$ with $HOCH_2CMe_3$ gives $[RuCl_2(CFOCH_2CMe_3)CO(PPh_3)_2]$.[1664b] A preliminary communication on reactions of $[RuCl_2(CCl_2)CO(PPh_3)_2]$ is available.[49]

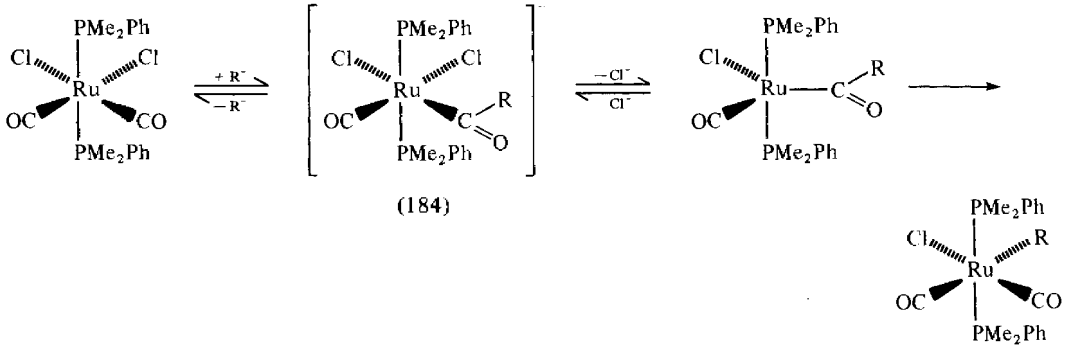
In an interesting insertion reaction, $[RuHCl(CO)(PPh_3)_3]$ and RCH=CHR′ dimethyl fumarate, methyl sorbate, methyl acrylate, *N,N*′-dimethylacrylamide or CH_2=CH-2-py) give $[RuCl(CO)(RCH{-}CH_2R')(PPh_3)_2]$ in which the alkyl residue is bidentate, coordinated through the σ-alkyl bond and also *via* R′. With CH_2=CHCN, however, the halide-bridged $[RuCl\{CHMe(CN)\}CO(PPh_3)_2]_2$ with a more normal monodentate alkyl group is formed.[1665a,b] Alkyl acrylates insert into $[RuHClCO(PPh_3)_3]$ under mild conditions to give Ru—C σ-bonded compounds $[RuCl(CH_2CH_2CO_2R)CO(PPh_3)_2]$.[1665c]

Reaction of *trans*-$[RuCl_2(CO)_2(PMe_2Ph)_2]$ with HgR_2 (R = Me, Ph) provides a convenient route to $[RuCl(R)(CO)_2(PMe_2Ph)_2]$ since even when HgR_2 is added in large excess, there is no replacement of the remaining chloride ligand.[1666] The methyl derivative $[RuCl(Me)(CO)_2(PMe_3)_2]$ is also obtained by photolysis of $[RuCl_2(CO)_2(PMe_3)_2]$ and dimethyltitanocene.[1667] Treatment however of either the *cis* or *trans* isomer with LiR leads to $[RuR_2(CO)_2(PMe_2Ph)_2]$ (R = Me, Ph, 3- and 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-FC_6H_4), and the mixed $[RuRR'(CO)_2(PMe_2Ph)_2]$ are readily synthesized from $[RuCl(R)(CO)_2(PMe_2Ph)_2]$ and LiR′.[1668] Spectroscopic (IR, NMR) studies reveal that all these compounds have configuration (**183**) irrespective of the stereochemistry of the starting material.[1666,1668] The proposed mechanism of formation of the monoalkyl or aryl complexes involves loss of CO and formation of intermediate Hg adducts. However, for reactions with LiR (Scheme 46) it is suggested that the mechanism involves nucleophilic attack by R^- on the carbon atom of a CO ligand to yield the acyl intermediate (**184**). In support of this proposal, reaction of $[RuMe_2(CO)_2(PMe_2Ph)_2]$ with CO gives first $[RuMe(COMe)(CO)_2(PMe_2Ph)_2]$ and then $[Ru(COMe)_2(CO)_2(PMe_2Ph)_2]$. Similarly, $[RuClMe(CO)_2(PMe_2Ph)_2]$ and $[RuMePh(CO)_2(PMe_2Ph)_2]$ afford $[RuCl(COMe)(CO)_2(PMe_2Ph)_2]$ and $[RuPh(COMe)(CO)_2(PMe_2Ph)_2]$ respectively on carbonylation and with L′ (L′ = PR_3, $P(OR)_3$, $AsMe_2Ph$), $[RuX(COMe)(CO)(PMe_2Ph)_2L']$ (X = Cl, Ph) are formed.[1668,1669] However no evidence is found for benzoyl complexes when $[RuX(Ph)(CO)_2(P-$

$Me_2Ph)_2$] (X = Cl, Br, I, Me, COMe, Ph) are treated with CO at atmospheric pressure or with PMe_2Ph. This is in contrast to studies on related complexes [Ru(C_6H_4Me-4)X$(CO)_2(PPh_3)_2$] (X = Cl, Br, I) (for preparation, see Scheme 47) which are in equilibrium in solution with acyl species [RuX(COC_6H_4Me-4)$(CO)(PPh_3)_2$].[1670] The low value of ν_{CO} (1550 cm^{-1}) suggests the acyl group is dihapto rather than monohapto and this is confirmed by crystal structure analyses of [RuI(η^2-COC_6H_4Me-4)$(CO)(PPh_3)_2$] and of the related [RuI(η^2-COMe)$(CO)(PPh_3)_2$] (**185**; X = I; R = Me) which is prepared from [Ru$(CO)_2(PPh_3)_3$] and MeHgI in benzene.[1671] Interestingly, it has been suggested that the corresponding [RuCl(COEt)$(CO)(PPh_3)_2$] contains an η^1-acyl group and that it does not isomerize to [RuCl(Et)$(CO)_2(PPh_3)_2$] in solution.[1672] Complexes of formula [RuCl(COEt)$CO(PPh_3)_2$Solvent] (Solvent = C_6H_6, CH_2Cl_2, THF) can be obtained by reaction of PPh_3 with [RuCl(COEt)$(CO)_2]_2$ (prepared by treating [RuCl$(CO)_3(\eta$-$C_3H_5)$] with C_2H_4 under pressure).[1673] Reaction of [RuHCl$(PPh_3)_3$] and [RuHCl$(CO)(PPh_3)_3$] with aldehydes has also been claimed to give [RuCl(COR)$(CO)(PPh_3)_2$] (R = Me, Et).[1674] However, it has been pointed out[1670] that the IR and NMR spectra of these compounds are identical with those of [RuCl(OCOR)$(CO)(PPh_3)_2$], and since it is known that [$RuCl_2(PPh_3)_3$] and PhCHO give [RuCl(OCOPh)$CO(PPh_3)_2$][1675a] (see Section 45.5.4.7.vi), the acyl formulation seems unlikely here. The binuclear complex [$Ru_2(CO)_5PPh_3(\mu$-$PPh_2)(\mu$-O=CPh)] containing bridging phosphido and acyl groups is obtained by pyrolysis of [$Ru_3(CO)_9(PPh_3)_3$].[1675b] The double acyl-bridged compound [$Ru_2(\mu$-O=$CEt)_2(CO)_6$] undergoes facile substitution of a CO by PPh_3 *etc.*[1675c]

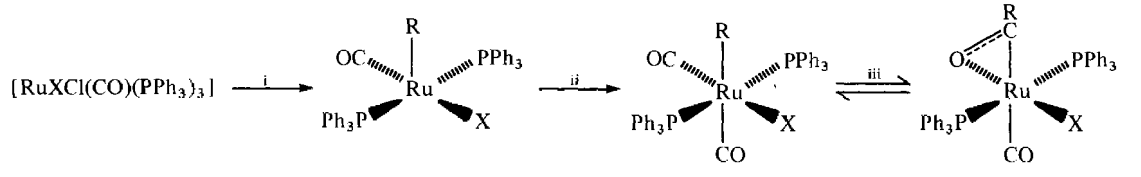


(**183**) X = Cl, Me, aryl



(**184**)

Scheme 46



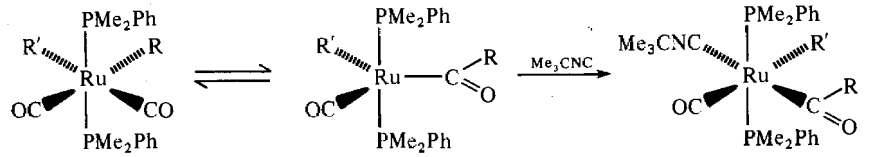
i, [Hg(p-Tol)$_2$] or [Hg(p-Tol)Cl]/toluene/Δ; ii, CO; iii, CH_2Cl_2

(**185**)

Scheme 47

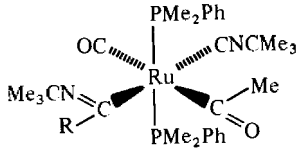
It has been revealed[1676] that the diaryl complexes [RuRR′$(CO)_2(PMe_2Ph)_2$] will react with Me_3CNC to give [RuR′(COR)$(CO)(CNCMe_3)(PMe_2Ph)_2$] shown by X-ray analysis (for R = R′ = Ph) to have structure (**186**).[1677] Kinetic studies indicate that the rate-determining step is combination of the aryl and CO ligands followed by rapid attack of the isonitrile *trans* to the acyl ligand (Scheme 48). In unsymmetrical diaryl compounds, the aryl ligand bearing the more electron-releasing substituent becomes incorporated in the acyl ligand. Similar complexes [RuR(COMe)$(CO)(CNCMe_3)(PMe_2Ph)_2$] are formed from [RuMeR$(CO)_2(PMe_2Ph)_2$] (R = Ph, COMe, Me) and Me_3CNC. In this instance [RuMe(COMe)$CO(CNCMe_3)(PMe_2Ph)_2$] (**186**) reacts with more Me_3CNC to form (**187**); in the absence of added Me_3CNC, complex (**186**) (R = R′ = Me)

slowly disproportionates into $[RuMe_2(CO)_2(PMe_2Ph)_2]$ and (**187**).[1678a] Treatment of $[RuH(CO)_3]_n$ with PPh_3, followed by elution from a silica gel column with EtOH gives $[Ru(OH)(OCEt)(CO)_2PPh_3]$.[1678b]



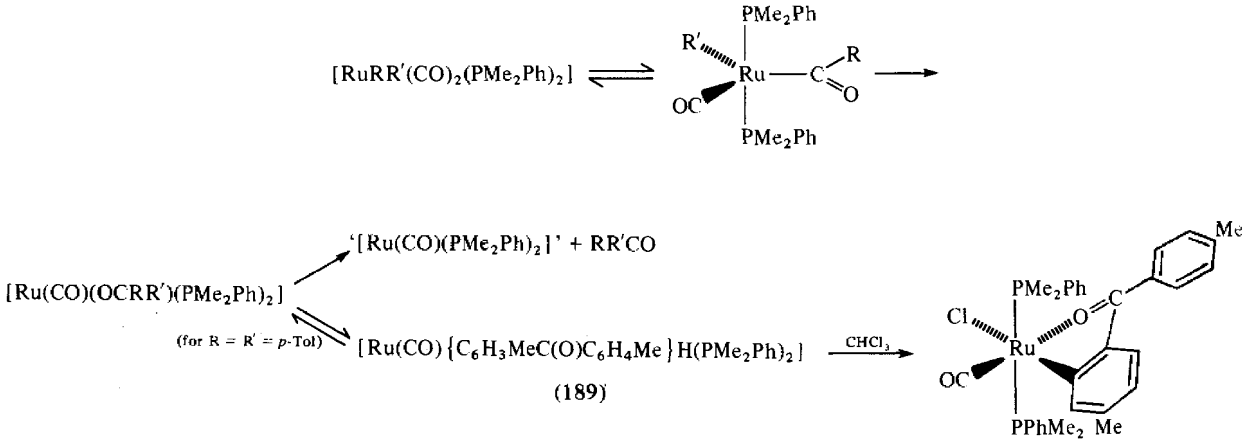
(186)

Scheme 48



(187)

The complexes $[RuRR'(CO)_2(PMe_2Ph)_2]$ also decompose intramolecularly in $CHCl_3$ at 298 K to yield ketones RR'CO. A proposed mechanism (Scheme 49) involves reductive elimination by C—C bond formation. For R = R' = *p*-Tol, the unusual product (**188**) is isolated and it is suggested that this arises from oxidative addition of the ketone in the proposed Ru^0 intermediate to form (**189**) and subsequent reaction with $CHCl_3$ replaces hydride by chloride.[1679a] There is a report of the crystal structure of (**188**) and further examples of the synthesis of *ortho*-metallated ketone complexes.[1679b]



Scheme 49

(188)

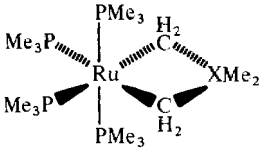
Alkyl, aryl and acyl nitrosyl phosphines and hydridophosphine complexes of Ru^{II} are covered in Sections 45.5.4.6.iii and 45.10 respectively.

(*v*) *Cyclometallated complexes*

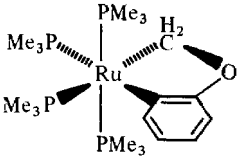
Cyclometallation is a reaction in which a chelate metal alkyl or aryl is generated by cleavage of a C—H bond in a coordinated ligand, a new metal–carbon σ bond being formed at the point of cleavage (*e.g.* compound (**182**) in Section 45.5.4.5.iii). Since most of the work on these types of complex is contained in another review (reference 1, p.734), only a brief survey is included here.

Reaction of $[Ru_2(OCOMe)_4Cl]$ with $[Mg(Me_3SiCH_2)_2]$ and PMe_3 in THF gives the metallacycle (**190**; X = Si). On reaction with $[Mg(CH_2Bu^t)_2]$ the neopentyl compound (**190**; X = C) is formed,[1661] whereas $[Mg(2\text{-}MeOC_6H_4)_2]$ produces (**191**).[1528] Compound (**190**; X = C) is also obtained by reaction of *cis*-$[RuClMe(PMe_3)_4]$ or $[Ru_2Cl_3(PMe_3)_6]BF_4$ with $[MgCl(CH_2Bu^t)]$; reaction of *cis*-

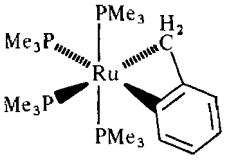
$[RuCl(Me)(PMe_3)_4]$, *trans*-$[RuCl_2(PMe_3)_4]$ or $[RuCl(PMe_3)_4]_2Cl_2$ with $[MgCl(CH_2Ph)]$ gives (**192**).[16] Treatment of *trans*-$[RuCl_2(PMe_3)_4]$ with the lithiated ylide $Li[Me_2P(CH_2)_2]$ gives complex (**193**) containing both a three- and four-membered metallacycle together with the cation $[RuCl(PMe_3)_4(CH_2PMe_3)]Cl$ (**147**) (Section 45.5.4.1).[1380,1534] Another example of a three-membered metallacycle is $[RuI(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3]$ obtained by reaction of $[RuH(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3]$ with MeI; some *trans*-$[RuI_2(PMe_3)_4]$ is also formed.[1391] The metallacycle $[RuCl(CH_2PMe_2)(PMe_3)_3]$ and spirocycle $[Ru(CH_2PMe_2)_2(PMe_3)_2]$ have been prepared by reaction of *cis*-$[Ru(OCOMe)Cl(PMe_3)_4]$ and *cis*-$[Ru(OCOMe)_2(PMe_3)_4]$ respectively with $Li[N(SiMe_3)_2]$.[1680] Reaction of $[RuHCl(CO)(PPh_3)_3]$ with alkenes such as dimethyl fumarate and 2-vinylpyridine give the metallacycles (**194**) and (**195**) respectively,[1665] and with 2-formylpyridines, insertion into the Ru—H bond gives *cis*-$[RuCl(OCH_2C_5H_4N)(CO)(PPh_3)_2]$.[1681] The related complex (**196**) is prepared by reaction of $[RuCl(OCOMe)(CO)(PPh_3)_2]$ with acetophenone at elevated temperatures[1682] [*cf.* compound (**188**) in Section 45.5.4.5.iv].



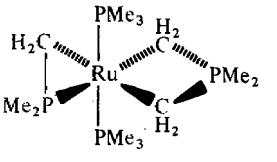
(190)



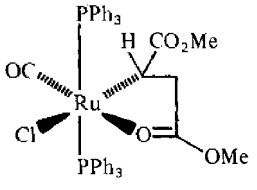
(191)



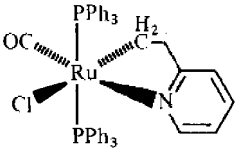
(192)



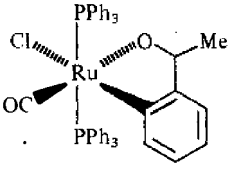
(193)



(194)



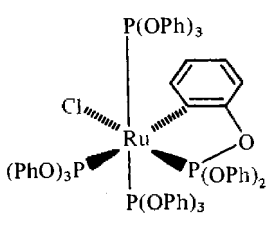
(195)



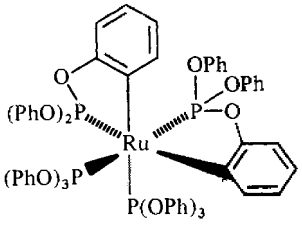
(196)

A number of complexes containing one or more *ortho*-metallated tertiary phosphite or phosphine ligands are known. For example, reaction of $[RuHCl(PPh_3)_3]$ and $P(OPh)_3$ in C_6H_6 at room temperature gives hydrogen and the *ortho*-bonded complex (**197**); on treatment with H_2 (or D_2), $[RuX\{(2,6\text{-}X_2C_6H_3O)_3P\}_4]$ (X = H, D) is readily formed,[1683] while CO in boiling benzene affords $[RuCl\{(C_6H_4O)P(OPh)_2\}CO\{P(OPh)_3\}_2]$.[1684] Reaction of $[RuHCl(CO)(PPh_3)_3]$ with $P(OPh)_3$ in boiling xylene leads to displacement of PPh_3 to give low yields of $[RuCl(CO)P(OPh_3)_2(P—C)]$ (P—C = $C_6H_4OP(OPh)_2$) whereas with $[RuH_2(PPh_3)_4]$, the dimetallated product (**198**) is obtained.[1685] Sodium amalgam reduction of $[RuCl_2(P(OPh)_3)_4]$ also gives (**198**),[1686a] (as does reaction of (**197**) with sodium phenoxide)[1686b] and the analogous dimetallated phosphite species *cis*-$[Ru(P—C)_2(cod)]$[1687] and *cis*-$[Ru(P—C)_2(CO)_2]$[1688] are reported.

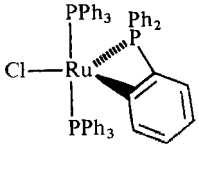
Most of the cyclometallated tertiary phosphine complexes also contain Ru—H bonds (see Section 45.10.3.2.ii). However, the yellow cyclometallated PPh_3 complex $[RuCl(C_6H_4PPh_2)(PPh_3)]_2$ has been identified as the product of stoichiometric hydrogenation of alkenes such as maleic acid with $[RuHCl(PPh_3)_3]$. It reacts with CO in solution to give $[RuCl(C_6H_4PPh_2)(CO)(PPh_3)]$.[1689] Reaction of $[RuHCl(PPh_3)_3]$ with an excess of Li, Zn or Mg methyls gives some $[RuMe(C_6H_4PPh_2)(PPh_3)_2]Et_2O$ together with various hydridomethyl complexes (Section 45.10.3.2.i).[1690] The chloride analogue $[RuCl(C_6H_4PPh_2)(PPh_3)_2]$ (**199**) is prepared by reaction of $[RuCl_2(PPh_3)_3]$ with $[Zr(\eta\text{-}C_5H_5)_2Me_2]$,[1691] and thermal decomposition of $[RuH(C_6H_4PPh_2)L(PPh_3)_2]$ (L = MeCN, py) gives a mixture of products including the bis-*ortho*-metallated complex $[Ru(C_6H_4PPh_2)_2L(PPh_3)]$.[1404]



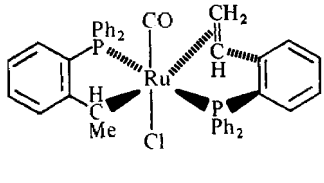
(197)



(198)



(199)



(200)

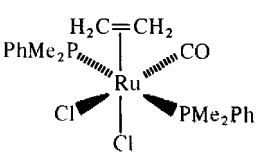
Finally, as detailed in reference 1, p.739 various *ortho*-metallated complexes have been generated from the ligand *o*-CH_2=$CHC_6H_4PPh_2$ (SP); *e.g.* reaction of $[RuCl_2(CO)_2(SP)_2]$ with boiling 2-methoxyethanol gives, as the major product $[Ru(o\text{-}CHMeC_6H_4PPh_2)Cl(CO)(SP)]$ (**200**). Other more complex products from this reaction are discussed in reference 1489. See Section 45.5.4.6.v for an example of a cyclometallated formazan derivative.

(*vi*) *Alkene complexes*

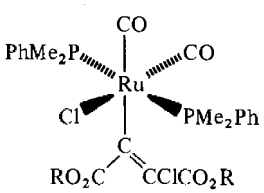
Reaction of all-*trans*$[RuCl_2(CO)_2(PMe_2Ph)_2]$ with C_2H_4 in $CHCl_3$ gives $[RuCl_2(CO)(PMe_2Ph)_2\text{-}C_2H_4]$, shown by X-ray analysis to have structure (**201**). The ^1H and ^{13}C NMR data are consistent with retention of this structure in solution, and show free rotation of the C_2H_4 group about the Ru—C_2H_4 axis down to $-40°C$.[1692] The alkenyl complexes $[RuCl(CO)_2(EMe_2Ph)_2\{CCO_2R)$=$C(CO_2R)Cl\}]$ (**202**) (E = P, As; R = Me, Et) have been synthesized by reaction of *trans*-$[RuCl_2\text{-}(CO)_2(EMe_2Ph)_2]$ with the alkynes $RO_2CC{\equiv}CCO_2R$. The proposed mechanism of formation of (**202**) involves initial formation of the alkyne complexes $[RuCl_2(CO)(EMe_2Ph)_2(RO_2CC{\equiv}CCO_2R)]$ which then undergo intramolecular nucleophilic attack by a chloride ligand. Further reaction of (**202**; R = Me) with EMe_2Ph gives $[RuCl(CO)(EMe_2Ph)_3\{C(CO_2Me)$=$C(CO_2Me)Cl\}]$.[1693] Treatment of the dimer $[RuCl(\eta^1\text{-}C_3H_5)(CO)_2(\eta^2\text{-}CH_2{=}CHCN)]_2$ with PPh_3 gives $[RuCl(\eta^1\text{-}C_3H_5)(CO)_2(PPh_3)(\eta^2\text{-}CH_2{=}CHCN)]$.[1694] Other monoalkene complexes include $[RuCl_2CO(PCy_3)_2L']$ (L′ = fumaronitrile, CH_2=$CHCN$), $[\{RuCl_2CO(PCy_3)_2\}_2TCNE]$ (with a bridging TCNE ligand)[1625] and $[RuCl(NO)(PPh_3)_2$alkene] (see Section 45.5.1.2).

Treatment of '$RuCl_3{\cdot}xH_2O$' with *o*-CH_2=$CHC_6H_4EPh_2$ (E = P, As) gives $[RuX_2(L\text{–}L)_2]$ (X = Cl, Br). The compound $[RuCl_2(SP)_2]$ (E = P) exists in three isomeric forms all with both vinyl groups coordinated, two with *trans* chlorides and hence *cis* and *trans* phosphines, the most stable isomer having structure (**203**). The bromo phosphine and the arsine complexes exist only in form (**203**).[1695] Treatment of $[RuCl_2(SP)_2]$ in refluxing 2-methoxyethanol with CO results in displacement of the vinyl groups to form $[RuCl_2(CO)_2(SP)_2]$ whereas direct reaction of '$RuCl_3{\cdot}xH_2O$', SP and CO in 2-methoxyethanol yields $[RuCl_2(CO)_2SP]$ (**204**), which decomposes to $[RuCl_2(CO)SP]_2$ on further heating. On reaction of $[RuCl_2(CO)_3]_2$ and SP, $[RuCl_2(CO)_3SP]$ (**205**) is initially produced.[1695] The X-ray structural analysis of $[RuCl_2CO(BDPH)]$ (BDPH = 1,6-bis(diphenylphosphino)-*trans*-3-hexene), in which the BDPH moiety is bound *via* the alkenic group and two P atoms occupying mutually *trans* positions, has been reported.[1696]

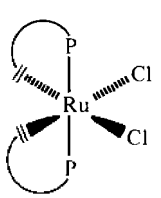
Reaction of $[RuCl_2(PPh_3)_n]$ (n = 3,4) or $[RuX_3(EPh_3)_2MeOH]$ with norbornadiene gives the very insoluble $[RuX_2(EPh_3)_2(nbd)]$ (E = P, As; X = Cl, Br),[106,655,1697] shown by X-ray analysis (for E = P) to have structure (**206**).[1698a] A more soluble analogue $[RuX_2(PMe_2Ph)_2(nbd)]$ is prepared from $Ph_3(PhCH_2)P[RuX_3CO(nbd)]$ and PMe_2Ph. With $[RuCl_3CO(nbd)]^-$ and $PMePh_2$ (1:2 molar ratio), a mixture of $[RuCl_2(PMePh_2)_2(nbd)]$ and $[RuCl_2CO(PMePh_2)_3]$ is formed. Reaction of the nbd anion with EPh_3 in 1:2 molar ratio gives $[RuCl_2CO(EPh_3)nbd]$ and some $[RuCl_3CO(EPh_3)_2]^-$ anion (E = As, Sb).[659]



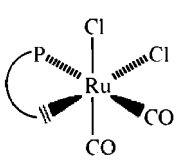
(201)



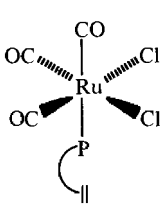
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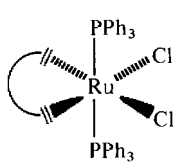
(203)



(204)



(205)



(206)

The insoluble cycloheptatriene complex $[RuCl_2(chpt)]_n$ undergoes bridge cleavage reactions to give $[RuCl_2L(chpt)]$ (L = $AsPh_3$, PBu_3, PPh_3, $P(OPh)_3$). These Lewis base derivatives react with thallium β-diketonates to give the cyclohexadienyl complexes $[Ru(dike)L(C_7H_8\text{-}dike)]$ resulting from attack of diketone on the coordinated hydrocarbon as well as on the metal.[1372]

Ru^{II} hydride alkene complexes are covered in Section 45.10, but other Ru^{II} P, As or Sb donor

ligand complexes containing delocalized π-electron ligands such as η^3-allyl, η^5-cyclopentadienyl, η^5-cyclohexadienyl, η^5-carborane and η^6-arene are outside the scope of this review (see references 1, 3 and 1698b for further information).

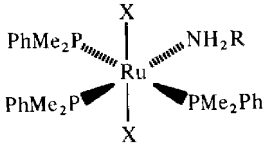
Binuclear compounds containing tertiary phosphines and ethene are discussed in Sections 45.5.5.1 and 45.5.5.2.

45.5.4.6 Nitrogen donor ligand complexes

(*i*) *Ammine, amine, hydrazine and carbamoyl complexes*

Surprisingly few ammine or amine complexes containing P or As donor ligands are known. The cations *trans*-$[Ru(NH_3)_4\{P(OR)_3\}_2]^{2+}$ (R = Me, Et, Bu, Pr^i) can be prepared by treatment of $[Ru(NH_3)_5OH_2]^{n+}$ (n = 2,3) or *trans*-$[Ru(NH_3)_4(OH_2)(SO_2)]^{2+}$ cations with $P(OR)_3$ in acetone. In aqueous CF_3SO_3H, hydrolysis to *trans*-$[Ru(NH_3)_4(OH_2)\{P(OEt)_3\}]$ occurs and reaction of this with $P(OR)_3$ gives *trans*-$[Ru(NH_3)_4P(OR)_3\{P(OEt)_3\}]$ (R = Me, Bu, Pr^i). Displacement of water by pyrazine affords *trans*-$[Ru(NH_3)_4P(OEt)_3pz]^{2+}$.[1699,1700a] The binuclear complex μ-TEPP-*trans*-$[Ru(NH_3)_4P(OEt)_3]_2(PF_6)_4$ has been prepared. This readily hydrolyses to form *trans*-$[Ru(NH_3)_4(OH_2)(P(OEt)_3)]^{2+}$.[1700b] Reaction of *trans*-$[RuCl(N_3)(diars)_2]$ with dry HCl gas, followed by addition of BPh_4^-, gives first *trans*-$[RuCl(N_2)(diars)_2]BPh_4$ and then *trans*-$[RuCl(NH_3)(diars)_2]BPh_4$.[1701]

The neutral $[RuX_2(NH_2R)(PMe_2Ph)_3]$ (**207**) (X = Cl, Br; R = H, Me, Bu) arise from reaction of *mer*-$[RuX_3(PMe_2Ph)_3]$ with NH_2R in anhydrous ethanol. Hydrazines also yield $[RuCl_2(NH_2NHR)(PMe_2Ph)_3]$ (R = H, Ph) and the binuclear $[RuCl_2(N_2H_4)(PMe_2Ph)_2]_2$ but secondary and tertiary amines give only $[RuX_2(EtOH)(PMe_2Ph)_3]$. However, when small amounts of water are present, dealkylation of secondary amines occurs to produce the corresponding $[RuX_2(NH_2R)(PMe_2Ph)_3]$.[1702] Similar monosubstituted compounds are obtained by reaction of $[RuCl_2(PPh_3)_2]_n$ with aniline, *o*-chloroaniline and *o*-toluidine.[1703] However NH_3, most hydrazines and amines react with $[RuCl_2(PPh_3)_2]_n$ or $[RuCl_2(PPh_3)_3]$ to form the disubstituted $[RuCl_2L_2(PPh_3)_2]$ (L = NH_2R; R = H, $PhCH_2$, *p*-$MeOC_6H_4$, $Me(CH_2)_4$, $(PhCH_2)HNNH_2$, $NHEt_2$, NEt_3; L_2 = en, 1,2-$(H_2N)_2C_6H_3Me$-*p*, *etc.*);[677,1545,1703] $[RuCl_2(NH_2CH_2Ph)_2(PPh_3)_2]$ catalyses the oxidation of NH_2CH_2Ph to PhCN.[1703] The $AsPh_3$ analogues $[RuCl_2L_2(AsPh_3)_2]$ (L = $NHEt_2$, NEt_3, N_2H_4, NH_3, $MeNH_2$, *etc.*) are also known.[677,1704] Treatment of $[Ru(N_2H_4)_4cod](BPh_4)_2$ with various PR_3 in acetone gives the hydrazone complexes *trans*-$[Ru(NH_2NCMe_2)_2L_4](BPh_4)_2$ (L = $P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$, $P(OCH_2)_3CR$; R = Me and Et) whereas $[Ru(NH_2NHMe)_4(cod)](PF_6)_2$ and $P(OMe)_2Ph$ produces $[Ru(NH_2NHMe)_2(P(OMe)_2Ph)_4](PF_6)_2$.[650,1705] Reaction of $[RuH_2(PPh_3)_4]$ and *o*-phenylenediamine gives the diimine complex $[Ru\{o\text{-}C_6H_4(NH)_2\}(PPh_3)_3]$.[1706]



(207)

Other ammine, amine and hydrazine complexes include $[RuCl_2L(CO)(PPh_3)_2]$ (L = NH_2p-Tol, NH_2-*p*-$OMeC_6H_4$, $PhHNNH_2$) from $[RuCl_2(PPh_3)_3]$, L and CO;[629a] $[RuCl(CN)NH_3(CO)(PPh_3)_2]$ from reaction of $[RuCl_2(CCl_2)CO(PPh_3)_2]$ with NH_3,[49] $[Ru(SOCPh)_2L_2(PR_3)_2]$ (L = NH_3, NH_2Et; L_2 = $HNC(Me)CH_2CMe_2NH_2$, en) (see Section 45.5.4.8.v),[1707,1708] and $[Ru(dttd)(N_2H_4)PPh_3]$ (see Section 45.5.4.8.iii).[1709]

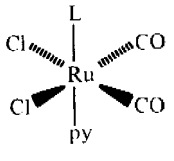
The carbamoyl complexes $[RuCl(CO)_2(CONHp\text{-}Tol)(PPh_3)_2]$ are generated by displacement of NH_2R from $[RuCl(CO)_2(NH_2R)_2(CONHp\text{-}Tol)]$[629a] whereas $[Ru(CO)_2(CONHR)(PPh_3)_2]BF_4$, (prepared from $[Ru(CO)_2(PPh_3)_2(RNCO)]$ and HBF_4), gives $[RuCl(CO)(CONHR)(PPh_3)_2]_n$ (R = COPh) on addition of LiCl.[1472]

(*ii*) *Mono-, bi- and tri-dentate N-heterocyclic complexes*

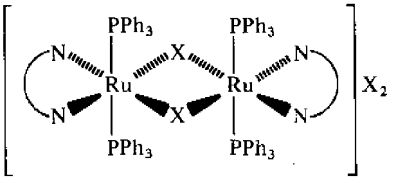
Treatment of $[RuCl_2(PPh_3)_2]_2$ or $[RuX_2(PPh_3)_3]$ (X = Cl, Br) with pyridine leads to stepwise replacement of PPh_3 groups giving $[RuCl_2(py)_2(PPh_3)_2]$, $[RuX_2(py)_3PPh_3]$ and *trans*-

$[RuX_2(py)_4]$;[1545,1587,1697] 4-acetylpyridine affords $[RuCl_2(4\text{-}MeCOC_5H_4N)_2(PPh_3)_2]$[1553] whereas 2-methyl- and 2,6-dimethyl-pyridine are apparently too sterically congested to react.[1545] $[RuCl_2(PPh_3)_3]$ with Li[PhNpy] in toluene (PhNpy = anion of 2-(*N*-anilino)-pyridine) gives two isomers of $[Ru(PhNpy)_2(PPh_3)_2]$. In one isomer the coordinating atoms *N*-py, *N*-Ph and PPh_3 are all in a *cis* arrangement; in the other, the py rings are *trans* to each other. Both isomers display two quasi-reversible oxidation waves assignable to Ru^{III}/Ru^{II} and Ru^{IV}/Ru^{III} couples.[1710] Similarly, $[Ru(NCS)_2(PPh_3)_2]_n$ and pyridine affords $[Ru(NCS)_2(py)_3(PPh_3)]$.[1711] Cleavage of the chloro-bridged species $[RuCl_2(CO)_2L]_2$ (L = $PBu^t{}_2Ph$, $PBu^t{}_2p$-Tol) and $[RuCl_2(CS)(PPh_3)_2]_2$ with pyridine gives $[RuCl_2(CO)_2pyL]$ (**208**)[1519] and $[RuCl_2(CS)py(PPh_3)_2]$[1638] respectively, whereas $[RuHCl(CO)(PBu^t{}_2Me)_2]$ (after treatment with HCl) reacts with pyridine to form $[RuCl_2CO(py)_2(PBu^t{}_2Me)]$.[1712]

The nature of the product from reaction of $[RuCl_2(CS)(PPh_3)_2]_2$ and 2,2′-bipyridyl (or 1,10-phenanthroline) is reported to be solvent dependent. Thus in CS_2, work-up gives $[RuCl_2(CS)(N\text{–}N)PPh_3]$ whereas in MeOH, $[RuCl(bipy)(PPh_3)_2]_2Cl_2$ (**209**) (or $[RuCl_2(phen)(PPh_3)_2]$) are isolated.[1638] However since the major species from $[RuCl_2(PPh_3)_3]$ and CS_2 is the triple chloride-bridged $[(PPh_3)_2CSRuCl_3RuCl(PPh_3)_2]$ rather than $[RuCl_2CS(PPh_3)_2]_2$ (see Section 45.5.5.1),[1639,1641] it is likely that these products arise from bridge cleavage of the asymmetric binuclear complex. Direct reaction of $[RuX_2(PPh_3)_3]$ (X = Cl, Br) with these heterocycles in CH_2Cl_2 provides a high yield route to (**209**). However reaction of $[RuCl_2(PPh_3)_3]$ or $[RuCl_3(PPh_3)_2(MeOH)]$ with an excess of N–N in MeOH gives red solutions from which the monomeric cations $[RuCl(N\text{–}N)_2PPh_3]Cl$ are isolated. The corresponding $[RuCl(bipy)_2AsPh_3]^+$ cation is obtained as its BPh_4^- salt from reaction of $[RuCl_3(bipy)AsPh_3]$ (Section 45.5.7.1), bipy and $Na[BPh_4]$ in MeOH.[1697,1713] An alternative route to a wider range of $[RuCl(bipy)_2L]^+$ cations (L = PPh_3, $P(p\text{-Tol})_3$, $PMePh_2$, $PBu^n{}_3$, $Ph_2P(CH_2)_nPPh_2$ (n = 1,3), $Ph_2PC{\equiv}CPPh_2$, $Ph_2As(CH_2)AsPh_2$, $AsPh_3$, $SbPh_3$) is *via* treatment of $[RuCl(bipy)_2S]^+$ (S = H_2O, acetone) with the appropriate L.[1124] In some instances the dications $[Ru(bipy)_2L_2]^{2+}$, (L = $P(p\text{-Tol})_3$, $PMePh_2$, $Ph_2P(CH_2)_nPPh_2$ (n = 1,2,3), *cis*-$Ph_2PCH{=}CHPPh_2$), can be isolated as their PF_6^- salts.[1124,1189] The electronic spectra and redox properties of all these cations are discussed[1124] and the X-ray crystal structure of $[Ru(bipy)_2(PPh_3)_2](PF_6)_2$ reveals a *trans* arrangement of PPh_3 groups.[1122,1123] The related $[Ru(NO_2)(bipy)_2PPh_3]^+$ cation has also been reported.[1153]



(208)

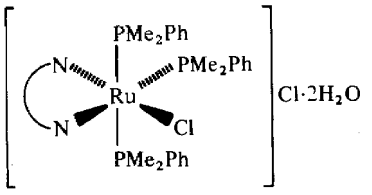


(209) N–N = bipy, phen

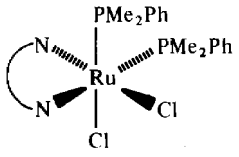
Reaction of *mer*-$[RuCl_3(PMe_2Ph)_3]$ and an excess of bipy in MeOH followed by recrystallization from acetone–light petroleum gives $[RuCl(bipy)(PMe_2Ph)_3]Cl\cdot 2H_2O$ (**210**) and $[RuCl(bipy)(PMe_2Ph)_2(OCMe_2)]Cl$, whereas in CH_2Cl_2 $[RuCl_2(bipy)(PMe_2Ph)_2]$ (**211**) and a small amount of $bipyH[RuCl_3(bipy)(PMe_2Ph)]$ are formed. With phen in CH_2Cl_2, $[RuCl_2(phen)(PMe_2Ph)_2]$ is produced but in MeOH followed by recrystallization from CH_2Cl_2–light petroleum, the main product is $[RuCl(phen)(PMe_2Ph)_2(CH_2Cl_2)]Cl$, together with small amounts of $phenH[RuCl_3(phen)PMe_2Ph]\cdot H_2O$. Treatment of *mer*-$[RuCl_3(PMe_2Ph)_3]$ with 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen) in MeOH gives $[RuCl(Me_4phen)(PMe_2Ph)_3]Cl$. In contrast, with 2,9-dimethyl-1,10-phenanthroline (Me_2phen) only $[Ru_2Cl_2(Me_2phen)_4]Cl_2$ and $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ are isolated.[1713]

Other bipy and phen compounds include $[Ru(SC_6F_5)bipy(PPh_3)_2]_2Cl_2$ (from reaction of (**209**); N–N = bipy, X = Cl) with $[Pb(SC_6F_5)_2]$)[1714] and the two isomers of $[Ru(SOCPh)_2(N\text{–}N)(PMe_2Ph)_2]$ (see Section 45.5.4.8.v).[1708]

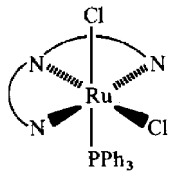
The reaction of $[Ru(terpy)Cl_3]$ with an excess of L (L = PPh_3, $P(p\text{-Tol})_3$) in the presence of Et_3N yields violet *trans*-$[RuCl_2L(terpy)]$ (terpy = 2,2′,2″-terpyridyl). This complex can be converted into *cis*-$[RuCl_2L(terpy)]$ (**212**) by boiling in 1,2-dichloroethane and the *cis* isomer can also be prepared by treatment of $[RuCl_2(PPh_3)_3]$ with terpy in boiling C_6H_6. The chloride in the *cis* isomer is significantly more labile than that in the *trans* isomer and addition of PPh_3 gives the *trans*-$[RuCl(PPh_3)_2(terpy)]^+$ cation. With CO, the *cis* and *trans* isomers give *cis*- and *trans*-$[RuCl_2CO(terpy)]$ respectively.[1249] Reaction of *cis*-$[Ru(OH_2)_2(PPh_3)(terpy)]^{2+}$ with PhC≡CH gives the alkyl complex $[Ru(\eta\text{-}CH_2Ph)CO(PPh_3)(terpy)]^+$.[1119]



(210)



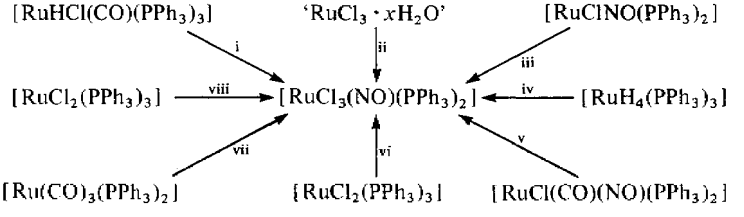
(211)



(212)

(iii) Nitrosyl, thionitrosyl, azido and dinitrogen complexes

The ruthenium(II) nitrosyl complexes $[RuCl_3(NO)L_2]$ (L = PR_3, AsR_3, SbR_3) were first prepared by the reaction of $[RuCl_3NO(OH_2)_n]$ with L in ethanol; treatment with NaBr or LiI gave the corresponding $[RuX_3NOL_2]$ (X = Br, I).[123,1715,1716] Alternative routes to $[RuCl_3NO(PPh_3)_2]$ are shown in Scheme 50. Compounds of this type are also generated by the method shown in equations (101)–(104). A reinvestigation of the original synthetic route by Townsend and Coskran[1720] revealed that for L = PMe_2Ph, $AsMe_2Ph$, the kinetically favoured isomer (**213**) could be isolated which readily converts on heating to the thermodynamically favoured isomer (**214**). For other L, only isomer (**214**) is observed. X-Ray analyses of $[RuCl_3(NO)L_2]$ (L = PPh_3,[1718] $PMePh_2$[1721]) confirm this observation and reveal a linear RuNO group; multinuclear NMR studies are also reported.[1722] Studies have indicated that irradiation (at 365 nm) of both (**213**) and (**214**) (for L = PMe_2Ph) induces isomerization to (**215**); reconversion to (**214**) requires thermal energy. For L = PPh_3, the photochemical reaction is reversible at ambient temperature and in the presence of $SbPh_3$, $[RuCl_3NO(PPh_3)(SbPh_3)]$ is produced.[1723]



i, N_2O;[1717] ii, PPh_3/*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide;[1410a, 1508] iii, TsCl;[1430] iv, NOCl;[1408] v, Cl_2;[1438] vi, NO_2/LiCl;[1718] vii, NOCl;[1719] viii, NO/$CHCl_3$[1411]

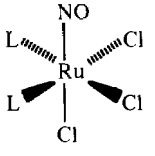
Scheme 50

$$[Ru(CO)_2(NO)(PPh_3)_2]^+ + Cl_2 \longrightarrow [RuCl_3NO(PPh_3)_2] + \textit{cis}\text{-}[RuCl_2(CO)_2(PPh_3)_2]^{1441} \quad (101)$$

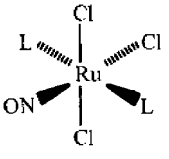
$$[RuCl_2(PPh_3)_3] + NO \xrightarrow[\text{or benzene}]{\text{acetone}} [RuCl_3NO(PPh_3)_2] + [Ru(NO)_2(PPh_3)_2]^{1411} \quad (102)$$

$$[RuCl_2(PPh_3)_4] + [CoNO(DMG)_2] \longrightarrow [RuCl_3NO(PPh_3)_2] + [RuCl(NO)O_2(PPh_3)_2]^{1409} \quad (103)$$

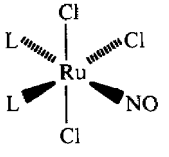
$$[Ru(NO)_2(PPh_3)_2] + PhCH_2Br \xrightarrow[\Delta]{\text{toluene}} [RuBr_3NO(PPh_3)_2] + [RuBr_2(NCPh)_2(PPh_3)_2]^{1416} \quad (104)$$



(213)



(214)



(215)

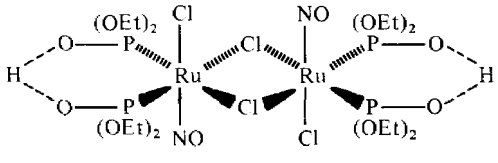
Reaction of $[RuCl_3NO(EPh_3)_2]$ (E = As, Sb) with various $P(OR)_3$ and dppe gives $[RuCl_3(NO)L_2]$ [L = $P(OR)_3$ (R = Me, Et, Bu), $\frac{1}{2}$dppe] and kinetic studies indicate that ligand dissociation to generate a five-coordinate $[RuCl_3NO(EPh_3)]$ intermediate is an important step.[1724]

Other complexes $[RuCl_3NO(L—L)]$ (L—L = dppm, *cis*-$Ph_2AsCH{=}CHAsPh_2$, $Ph_2PCH_2OCH_2PPh_2$) are formed from $[RuCl_3NO]$ but again dpam is anomalous forming $[RuCl_3$-

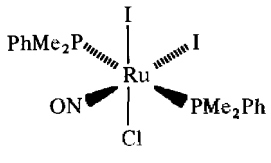
$NO(dpam)_2]$.[1593] Some studies on anchoring of $[RuCl_3NO(SbPh_3)_2]$ to polymer-bound phosphinic ligands are reported,[1725] and the mixed ligand complex $[RuCl_3NO(AsPh_3)OAsPh_3]$ is known.[1726] Treatment of '$RuCl_3 \cdot xH_2O$' and $P(OPh)_3$ with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in dry *tert*-butanol gives green $[RuCl_3NO\{P(OPh)_3\}_2]$. However, the same reaction in EtOH affords the unusual yellow dimer (**216**), shown by X-ray analysis to contain unsymmetrical RuPOHOP moieties.[1727] Other binuclear nitrosyl complexes are the unusual $[RuX_2NO(EPh_3)]_2Y$ (X = Cl, Br; E = P, As; Y = S, SO).[1304]

As detailed in Scheme 43 (Section 45.5.1.2), $[RuCl(NO)(PPh_3)_2]$ undergoes oxidative addition reactions with various halogens, alkyl, aryl and acyl halides to give the corresponding Ru^{II} NO complexes.[1421,1429] Similar studies are reported for $[RuCl(NO)(AsPh_3)_2]$.[1434] With $[RuCl(NO)(PMePh_2)_2]$ and I_2, *trans* halide addition is followed by facile isomerization in solution to give (**217**).[1428] Mixed halide derivatives are also prepared by treatment of $[RuX(CO)(NO)(PPh_3)_2]$ with halogens Y_2 giving $[RuXY_2NO(PPh_3)_2]$ (with *trans* PPh_3 groups).[1438] The corresponding sulfato complex $[RuCl(SO_4)(NO)(PPh_3)_2]$ is obtained by reaction of $[RuCl(NO)(PPh_3)_2]$ or $[RuH(NO)(PPh_3)_3]$ with SO_2,[1424] whereas $[Ru(NO)_2(PPh_3)_2]$ or $[RuH(NO)(PPh_3)_3]$ and R_FCO_2H afford $[Ru(OCOR_F)_3NO(PPh_3)_2]$ (R = CF_3, C_2F_5)[1417,1728a,1728b] and $[RuCl(NO)(PPh_3)_2]$ gives $[RuCl(NO)(C_6X_4O_2)(PPh_3)_2]$ (X = Cl, Br) on treatment with quinones.[1429]

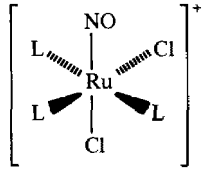
In reactions of $[RuCl_3NO]$ with L in ethanol, the cations $[RuCl_2(NO)L_3]^+$ (L = PMe_2Ph, $AsMe_2Ph$) can be isolated from the filtrate as either BPh_4^- or Cl^- (for L = PMe_2Ph) salts. NMR evidence suggests configuration (**218**).[1720] The cations *trans*-$[RuCl(NO)(diars)_2]^{2+}$ can be similarly prepared from $[RuCl_3(NO)]$ and diars.[1729] As shown in Scheme 51, this cation exhibits a rich chemistry producing azido, dinitrogen, ammine and nitro complexes.[1701,1730] Reaction of *cis*-$[RuCl_2(diars)_2]$ with NaN_3 in boiling 2-methoxyethanol gives *cis*-$[Ru(N_3)_2(diars)_2]$[1701] and similarly, *trans*-$[Ru(N_3)_2(eda)_2]$ is formed from *trans*-$[RuCl_2(eda)_2]$[45] and $[Ru(N_3)_2\{N(CH_2CH_2PPh_2)_3\}]$ from $[RuCl_2\{N(CH_2CH_2PPh_2)_3\}]$.[1595] *Cis*-$[Ru(N_3)_2(PMe_3)_4]$ has been synthesized from *cis*-$[RuMe_2(PMe_3)_4]$ and Me_3SiN_3.[1731] Addition of N_2 to the electron rich carbene complex (**182**) gives $[RuCl(L^{R'})(PR_3)_2N_2]$ (see Section 45.5.4.5.iii).



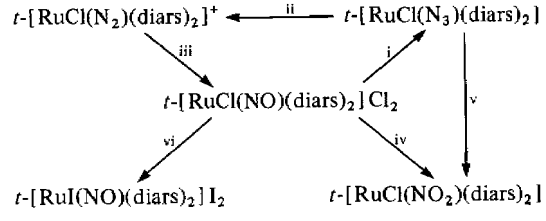
(216)



(217)



(218)



i, NaN_3 or N_2H_4; ii, $[NO_2][SbF_6]$, or $[NO][PF_6]$ or HCl;
iii, $[NO][PF_6]$; iv, NaOH; v, $h\nu/O_2$; vi, excess LiI

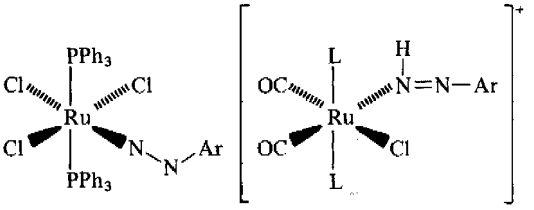
Scheme 51

Finally, reaction of various ruthenium(II) and (III) compounds with $[NSCl]_3$ in THF gives thionitrosyl complexes. Examples include $[RuCl_3(NS)(EPh_3)_2]$ (partial X-ray analysis has been reported for E = P),[1732] $[RuBr_2Cl(NS)(EPh_3)_2]$ (E = P, As) and $[RuCl_3(NS)(AsPh_3)(EPh_3)]$ (E = P, Sb).[668]

(*iv*) *Diazenido (NNR) and diazene (RN=NR) complexes*

Reaction of $[RuCl_2(PPh_3)_3]$ with various aryl diazonium tetrafluoroborates in the presence of LiCl gives the diazenido complexes $[RuCl_3(NNAr)(PPh_3)_2]$ (Ar = *p*-Tol, *p*-$MeOC_6H_4$, *p*-ClC_6H_4,

p-$O_2NC_6H_4$). X-Ray analysis for the tolyl complex[1718] and its acetone solvate[1733] confirms structure (**219**) with a bent diazenido ligand (formally ArN_2^+). A ^{15}N NMR method to distinguish between the different geometries exhibited by diazenido ligands is also available.[1734] In the absence of LiCl, reaction of $[RuCl_2(PPh_3)_3]$ with $[p\text{-}MeOC_6H_4N_2]PF_6$ in acetone gives a mixture of the cations $[RuCl_2(NNAr)(PPh_3)_2]_n^{n+}$ and $[Ru_2Cl_3(NNAr)_2(PPh_3)_3]^+$ whereas in MeCN, $[Ru_2Cl_2(MeCN)_3(NNAr)_2(PPh_3)_4]^{2+}$ is isolated.[1717]



(219) (220)

In contrast, treatment of $[RuHCl(PPh_3)_3]$ with $[ArN_2]X$ affords $[RuCl(NNAr)_2(PPh_3)_2]X$ (X = BF_4, PF_6) which undergoes chlorination to produce $[RuCl_3(NNAr)(PPh_3)_2]$ (**219**).[1717] The five-coordinate compound $[RuHCl(CO)_2PBu^tPr^n_2)]$ reacts with $[PhN_2]BF_4$ to give a phenyldiazene complex $[RuCl(NH{=}NPh)(CO)_2(PBu^tPr^n_2)]BF_4$ for which spectroscopic data suggest structure (**220**; L = $PBu^tPr^n_2$),[1519] whereas $[RuHCl(CO)(PPh_3)_3]$ and $[ArN_2]BF_4$ give '$[RuCl(FBF_3)(NH{=}NAr)CO(PPh_3)_2]$' which has a weakly coordinated BF_4^- ligand. Acetone solutions of the latter yield $[RuCl(NH{=}NAr)(CO)_2(PPh_3)_2]BF_4$ (**220**; L = PPh_3) with CO and $[RuCl_2(NH{=}NAr)(CO)(PPh_3)_2]$ with LiCl. The complex $[RuH(NH{=}NAr)(CO)(PPh_3)_3]BF_4$ (from $[RuH_2CO(PPh_3)_3] + [ArN_2]BF_4$[1735]) reacts with LiCl to give the same dichloro compound.[1736]

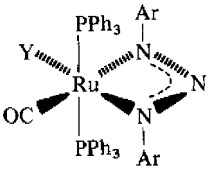
Addition of $[ArN_2]^+$ to $[Ru(CO)_3(PPh_3)_2]$ affords $[Ru(NNAr)(CO)_2(PPh_3)_2]^+$.[1735,1737] This gives $[RuX(NNAr)(CO)_2(PPh_3)_2]$ (X = Cl, F, Br, I) on treatment with X^- which then protonate readily to form the phenyldiazene salts (**220**) as confirmed by a structural analysis on $[RuCl(NH{=}NPh)(CO)_2(PPh_3)_2]ClO_4 \cdot CH_2Cl_2$.[1738] The preparations of analogous hydrido diazenide and diazene complexes such as $[RuH(NH{=}NPh)(CO)_2(PPh_3)_2]^+$, $[RuH(NNPh)(CO)_2(PPh_3)_2]$ and $[RuH(NNPh)(CO)(PPh_3)_2]$ are discussed in reference 1735.

Finally, *trans*-$[RuX_2L_2]$ (X = Cl, Br, I; L = 2-(arylazo)pyridine) reacts with various PR_3 and $Ph_2P(CH_2)_nPPh_2$ ($n = 2,3$) to give the cations $[RuX(PR_3)L_2]^+$, $[Ru(PR_3)_2L_2]^{2+}$ and $[Ru(Ph_2P(CH_2)_nPPh_2)L_2]^{2+}$ respectively. A correlation between the Ru^{III}/Ru^{II} electrode potential and the visible spectra of these compounds is demonstrated.[1739]

(*v*) *Triazenido (RNNNR), formamidinato (RNC̄(H)NR), formazan (RNNC(R)NNR), formamido (RNC̄(H)O), thioformamido (RNC̄(H)S) and ureylene (RNCONR^{2-}) complexes*

Bidentate 1,3-diaryltriazenido complexes can be synthesized by reaction of 1,3-diaryltriazenes, (ArNNNHAr), with either Ru^0 or Ru^{II} hydride complexes. For example, $[RuHXCO(PPh_3)_3]$ (X = H, Cl) and $[Ru(CO)_3(PPh_3)_2]$ give $[RuH(ArNNNAr)(CO)(PPh_3)_2]$ in boiling C_6H_6 or EtOH, whereas $[RuHCl(CO)(PPh_3)_3]$ affords $[RuCl(ArNNNAr)(CO)(PPh_3)_2]$ in C_6H_6 at room temperature. An X-ray analysis on $[RuH(p\text{-}TolN_3Tol\text{-}p)(CO)(PPh_3)_2]$ confirms configuration (**221**).[1740,1741] Alternative routes to triazene complexes involve displacement of halide ion from halo–ruthenium complexes with triazenido anions (*e.g.* equations 105 and 106).[1742,1743]

Diarylcarbodiimides (ArN=C=NR) insert into Ru—H bonds to give the corresponding formamidinato (ArN===C̄H===NAr) complexes (equation 107). Configuration (**222**) assigned on the basis of NMR evidence has been confirmed for X = H by X-ray analysis.[1744] Compound (**222**; X = H) is also prepared from $[RuH_2(PPh_3)_4]$ and *p*-TolNCO.[1745] In boiling C_6H_6, Pr^iNCNPr^i inserts into the Ru—H bond of $[RuHCl(CO)(PPh_3)_3]$ but concomitant dehydrogenation of a Pr^i group gives $[RuCl\{CH_2{=}C(Me)NCHNCHMe_2\}CO(PPh_3)_2]$ (**223**) as confirmed by X-ray analysis.[1746]



(221) Y = H, Cl

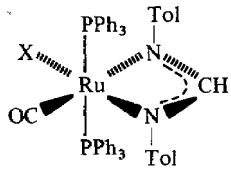
$$[RuHCl(PPh_3)_3] + Li[N_3Ph_2] \longrightarrow [RuH(PhN_3Ph)(PPh_3)_3] + LiCl \quad (105)$$

$$[RuCl_2(PPh_3)_n] + Li[N_3Ph_2] \longrightarrow [Ru(PhN_3Ph)_2(PPh_3)_2] + 2Cl^- \quad (106)$$

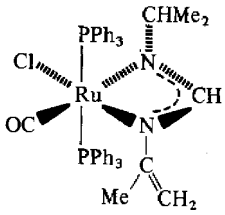
(or $HN_3Ph_2 + Et_3N$)

$$[RuHX(CO)(PPh_3)_3] + TolNCNTol \longrightarrow \quad (107)$$

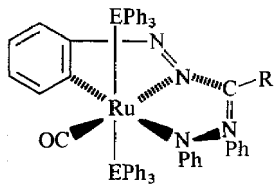
(X = H, Cl, Bv, $OCOCF_3$)



(222)



(223)



(224)

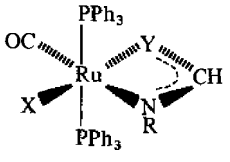
Reaction of $[RuH_2(CO)(EPh_3)_3]$ (E = P, As) or $[RuHCl(CO)(PPh_3)_3]$ with 1,5-diphenylformazans (PhN=NC(R)=NNHPh) in boiling 2-methoxyethanol or DMF affords the deep green cyclometallated formazan derivatives $[Ru\{(O—C_6H_4)N=NC(R)=NNPh\}CO(EPh_3)_2]$, (**224**) (as established by X-ray analysis for R = Ph, E = P). Isomeric hydrido intermediates of form $(RuH(PhN=NCH=NNPh)CO(PPh_3)_2]$ have been isolated as pink (with *cis*-PPh_3) or purple (with *trans*-PPh_3) complexes and convert to the green cyclometallated compound on further heating.[1747]

Alkyl and aryl isothiocyanates, RNCS, undergo insertion reactions into Ru—H bonds to give thioformamido, (RN=CH=S), complexes (equations 108 and 109)[1748] whereas aryl isocyanates, RNCO, and $[RuHX(CO)(PPh_3)_3]$ (X = H, Cl, Br) afford the analogous formamido complexes (**225**; Y = O). Under more forcing conditions, reaction of the dihydride with *p*-TolNCO results in cleavage of a molecule of isocyanate and formation of the ureylene complex $[Ru(TolNCONTol)(CO)_2(PPh_3)_2]$ (**226**).[1745] Compound (**226**; R = *p*-$TolSO_2$) is also obtained by reaction of $[Ru(CO)_3(PPh_3)_2]$ with toluene-*p*-sulfonyl isocyanate at room temperature in C_6H_6.[1472]

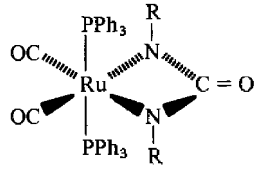
$$[RuHX(CO)(PPh_3)_3] + RNCS \longrightarrow [RuX(RNCHS)(CO)(PPh_3)_2] \quad (108)$$

(X = H, Cl, Br, $OCOCF_3$) (R = Me, Et, Ph, *p*-Tol)

$$[RuH_2(PPh_3)_4] + RNCS \longrightarrow [Ru(RNCHS)_2(PPh_3)_2] \quad (109)$$



(225) Y = O, S

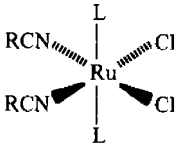


(226) R = *p*-Tol, *p*-$TolSO_2$

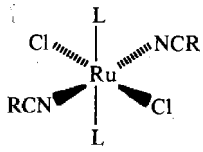
(*vi*) *Nitriles and N bonded thiocyanates and selenocyanates*

Reaction of $[RuCl_2(PPh_3)_3]$ and various alkyl or aryl nitriles RCN gives $[RuCl_2(RCN)_2(PPh_3)_2]$ (R = Me, Pr^n, Pr^i, Ph, $PhCH_2$, CH_2=CH *etc.*); in boiling acetone the *cis* isomer (**277**) is obtained whereas toluene yields the *trans* isomer (**228**). Recrystallization of (**228**) from acetone gives (**227**). With dinitriles, $[RuCl_2L_2(PPh_3)_2]$ is formed (L = $NC(CH_2)_nCN$ (*n* = 1–4), phthalonitrile).[1545] Recrystallization of the bis(MeCN) complex from C_6H_6 affords the binuclear $[RuCl_2(MeCN)(PPh_3)_2]_2$.[1404] The corresponding $[RuCl_2(RCN)_2(AsPh_3)_2]$ (R = Me, Pr, CH_2=CH)

are known,[677,1749] and also the ethyl(diphenylphosphino)acetate analogue (equation 110).[1750] An alternative route to (**228**) (L′ = various PR_3) is *via* bridge cleavage of $[RuCl_2(PhCN)_3]_2$ while treatment of $Et_4N[RuCl_4(RCN)_2]$ with $PMePh_2$ yields $[RuCl_2(RCN)_2(PMePh_2)_2]$.[681] Treatment of the polymeric $[Ru(NCS)_2(PPh_3)_2]_n$, (made from $[RuCl_2(PPh_3)_3]$ and SCN^-), with MeCN gives $[Ru(NCS)_2(MeCN)_2(PPh_3)_2]$,[1711] and the closely related $[Ru(NCE)_2(CO)_2(PPh_3)_2]$ (E = S, Se) are prepared from $[Ru(CO)_3(PPh_3)_2]$ and $(ECN)_2$.[661,1626]



(227)



(228)

$$[RuCl_3(o\text{-}MeC_6H_4CN)_3] + PPh_2CH_2C(O)OEt \longrightarrow [RuCl_2(o\text{-}MeC_6H_4CN)_2(PPh_2CH_2C(O)OEt)_2] \quad (110)$$

(228)

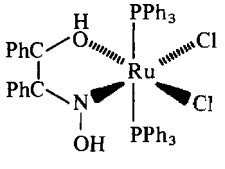
The cations *fac*-$[Ru(RCN)_3L_3]^{2+}$ are generated either by treatment of $[Ru_2Cl_3L_6]Cl$ (L = PMe_2Ph, $PMePh_2$) with $Ag[BF_4]$ and RCN (R = Me, Et, Pr, Ph, $MeOC(O)CH_2^-$),[1752] by protonation of $[Ru_2(OH)_3(PMe_2Ph)_6]^+$ with HPF_6 in MeCN[1753] or by reaction of $[Ru(MeCN)_4(cod)]^{2+}$ with $P(OMe)_2Ph$ or $P(OMe)_3$ in nitromethane.[1370] The *fac* isomer isomerizes to the *mer* form on recrystallization.[1753] In MeCN, $[Ru(MeCN)_4cod]^{2+}$ and L give $[Ru(MeCN)_4L_2]^{2+}$ (L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OMe)_2Ph$ and $P(OMe)_3$). The monocations $[RuCl(MeCN)_3L_2]^+$ (L = PPh_3, $PMePh_2$, PMe_2Ph) can be synthesized from $[RuCl(MeCN)_3(cod)]PF_6$ and L in refluxing MeCN,[1370] and treatment of $[RuX(L\text{–}L)_2]PF_6$ (L–L = dppe, $Ph_2P(CH_2)_2NC_5H_4$) with MeCN gives the six-coordinate *trans*-$[RuX(MeCN)(L\text{–}L)_2]PF_6$.[1535] Treatment of $[Ru(OCOMe)(OH_2)(PPh_3)_3]BF_4$ with MeCN gives $[Ru(OCOMe)(MeCN)(PPh_3)_3]^+$ which reacts with aqueous HBF_4 to produce the $[Ru(OH_2)(MeCN)_2(PPh_3)_2]^{2+}$ dication.[1754]

Nitrile complexes containing Ru—H bonds are covered in Section 45.10.

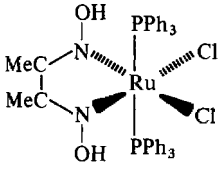
(*vii*) *Oxime and Schiff base complexes*

In the absence of alkali, hydroxyoximes, α-dioximes and α-carbonyloximes displace PPh_3 from $[RuCl_2(PPh_3)_3]$ and form complexes of type (**229**), (**230**) and (**231**) respectively. Small simple oximes give the six-coordinate bis(oxime) compounds (**232**) whereas with more bulky substituents the pentacoordinate $[RuCl_2\{N(OH)C(Me)(Bu^t)\}(PPh_3)_2]$ is formed. In MeOH, reductive decarboxylation of solvent occurs with formation of $[RuHCl(CO)(LH)(PPh_3)_2]\cdot MeOH$ (L—H = cyclohexanone oxime, acetophenone oxime and *n*-butylphenylketone oxime). In the presence of base, chloride displacement occurs and both α-dioximes and α-carbonyloximes give *trans*-$[Ru(oxime)_2(PPh_3)_2]$. Similar products are formed with pyrinaldoxime but with salicyaldoxime, stepwise replacement of chloride produces first (**233**) and then (**234**).[1755]

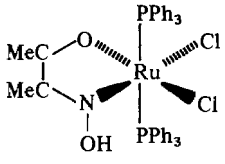
Treatment of $[RuCl_2(PPh_3)_3]$ with the sodium salts of Schiff bases also leads to chloride displacement. For example, *N*-benzylsalicylideneimine gives (**235**) whereas *N,N′*-ethylenebis(pentane-2,4-dione-monoimine) yields (**236**).[1756,1757a,1757b] The air sensitive compound (**237**) has been reported.[1758a] Redox reactions of the compound $[RuC_2H_4(N{=}CHC_6H_4O\text{-}o)_2(PPh_3)_2]$ with I_2, $FeCl_3$ and O_2 have been reported.[1758b] Reaction of $[RuCl_2(PPh_3)_3]$ with the sodium salt of *N,N′*-bis(salicylaldehydo)ethylenediamine (salenH_2) gives $[Ru(salen)(PPh_3)_2]$ whereas with the free ligand in methanol, the ruthenium(III) complex $[RuCl(salen)PPh_3]$ is formed.[1756,1758c]



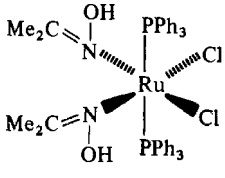
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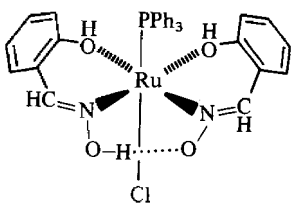
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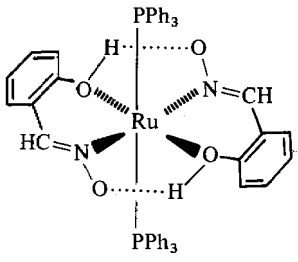
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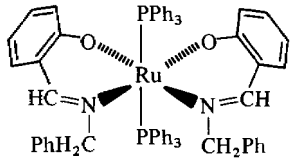
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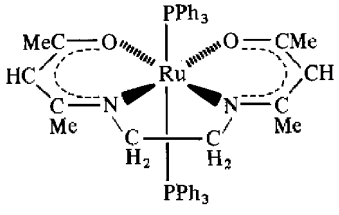
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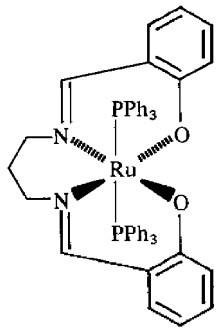
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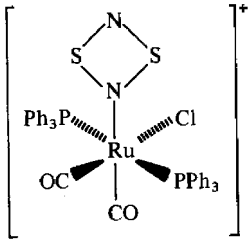
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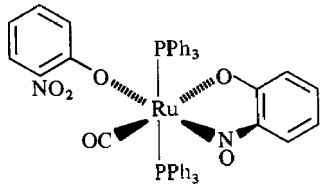
(237)

(*viii*) *Miscellaneous*

Reaction of $[RuCl_2(CO)(PPh_3)_2]$ and $S_2N_2 \cdot 2AlCl_3$ in CH_2Cl_2 gives $[RuCl(S_2N_2)(CO)_2(PPh_3)_2]$-$AlCl_4$, (**238**), the first example in which the S_2N_2 group acts as a monodentate ligand through nitrogen.[1759]



(238)



(239)

Aminoacid complexes $[RuClL(PPh_3)_2]$ (LH = glycine, L-serine, L-hydroxyproline and L-allohydroxyproline) can be prepared by reaction of $[RuCl_2(PPh_3)_3]$ with the appropriate amino acid in the presence of $Na[HCO_3]$. Glycerin is oxidatively dehydrogenated in the presence of $[RuClL(PPh_3)_2]$ and *N*-methylmorpholine-*N*-oxide.[1760] On heating $[RuH_2(PPh_3)_4]$ with 2-hydroxypyridine and 8-hydroxyquinoline, $[RuX_2(PPh_3)_2]$ (X = 2-OC_5H_4N, 8-OC_9H_6N) is formed whereas 2-mercaptopyridine, 2-aminothiophenol and 2-aminophenol form $[Ru(chelate)_2(PPh_3)_2]$ even at room temperature.[1706] Reaction with *N*-sulfinylaniline (NSA) gives $[RuCl_2(EPh_3)_2(NSA)_2]$ (E = P, As) *via* *N*-coordination.[1761]

Reaction of $[Ru(CO)_3(PPh_3)_2]$ with 2-nitrophenol in boiling C_6H_6 gives the unusual Ru^{II} complex (**239**) in which on nitrophenol ligand has undergone reduction to a nitrosophenolate anion and another coordinates *via* only the phenolate group.[1762]

45.5.4.7 Oxygen donor ligand complexes

(i) Water, alcohol, acetone, dimethylformamide, dimethylacetamide and tetrahydrofuran complexes

A number of O donor solvento complexes containing P donor ligands have been reported. Treatment of $[RuCl_2(CS)(PPh_3)_2]_2$ with DMF gives $[RuCl_2(CS)(PPh_3)_2DMF]$ which on recrystallization from $MeOH/CH_2Cl_2$ produces $[RuCl_2(CS)MeOH(PPh_3)_2]$.[1616] Similarly $[RuCl_2(CO)DMF(PPh_3)_2]$, (from $[RuCl_2(PPh_3)_3]$ and CO in DMF), forms $[RuCl_2(CO)MeOH(PPh_3)_2]$[659,1616] and not the five-coordinate $[RuCl_2(CO)(PPh_3)_2]$ as originally suggested.[1607] The aqua analogues are obtained as shown in equations (111) and (112), and carbonylation of $[RuCl_2(PPh_3)_3]$ in DMA gives $[RuCl_2(CO)DMA(PPh_3)_2]$.[1607]

$$\text{'}RuCl_3\cdot xH_2O\text{'} + HCO_2H \longrightarrow \text{'}RuCl_2(OH_2)(CO)\text{'} \xrightarrow{PPh_3} [RuCl_2(OH_2)(CO)(PPh_3)_2]^{1763} \quad (111)$$

$$[RuCl_2(PPh_3)_3] + CS_2 \xrightarrow[\Delta]{\text{xylene}} [RuCl_2(OH_2)CS(PPh_3)_2]^{1640} \quad (112)$$

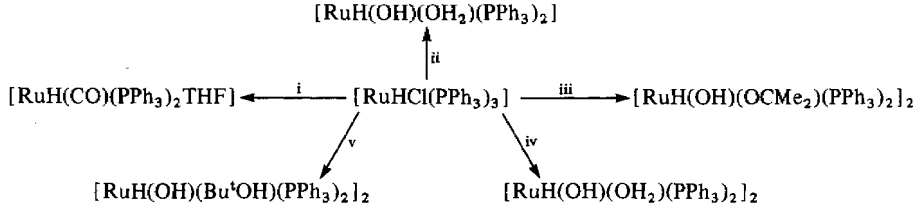
On heating $[RuCl_2(PPh_3)_3]$ in acetone, red $[RuCl_2Me_2CO(PPh_3)_2]_n$ precipitates whilst with higher ketones, black $[RuCl_2(PPh_3)_2]_n$ is produced.[1545] Secondary and tertiary amines react with *mer*-$[RuX_3(PMe_2Ph)_3]$ in anhydrous EtOH to give $[RuX_2(EtOH)(PMe_2Ph)_3]$ (X = Cl, Br)[1702] and treatment of $[RuH_2(PPh_3)_4]$ with SO_2 in wet toluene gives the aqua intermediate $[RuSO_4(OH_2)(SO_2)(PPh_3)_2]$.[1764] Complexes of formula $[RuCl(COEt)CO(PPh_3)_2Solvent]$ (Solvent = C_6H_6, THF, CH_2Cl_2) arise from reaction of PPh_3 with $[RuCl(COEt)(CO)_2]_2$.[1673] Direct reaction of $[Ru(OH_2)_6](tos)_2$ with PPh_3 gives $[Ru(tos)_2(OH_2)_2(PPh_3)_2]$ (tos = *p*-toluenesulfonate).[1600b]

The aqua cation $[RuCl(OH_2)(CNR)(CS)(PPh_3)_2]ClO_4$ has been synthesized by reaction of *cis*-$[RuCl_2(CNR)(CS)(PPh_3)_2]$ with $Ag[ClO_4]$ in $EtOH/CH_2Cl_2$[1645] and protonation of $[RuH(OCOMe)(PPh_3)_3]$ with aqueous HBF_4 in acetone gives $[Ru(OCOMe)(OH_2)(PPh_3)_3]BF_4$ as the end product. Intermediate hydrido cations such as $[RuH(Solvent)(PPh_3)_3]^+$ are produced in this reaction (see Section 45.10.3.2.v).[1754] Other solvated hydrido complexes include $[RuH(OH_2)(CO)_n(PPh_3)_{4-n}]BF_4$ (n = 1,2),[1765] $[RuH(MeOH)(PMe_2Ph)_4]PF_6$, $[RuH(EtOH)(dppe)_2]PF_6$,[1766] $[RuH(OH_2)(CO)_2(PPh_3)_2]^+$, $[RuH(OH_2)_2(MeOH)(PPh_3)_2]^+$[1754] (Section 45.10.3.2.v) and various hydroxo species containing H_2O, THF, acetone and *tert*-butanol (Section 45.5.4.7.ii).

The reactive intermediate $[Ru(Me_2CO)_3(PMe_2Ph)_3]^{2+}$ is generated by treatment of $[Ru_2(OH)_3(PMe_2Ph)_6]^+$ with HPF_6 in acetone.[1753] $[RuCl(SnCl_3)(Me_2CO)CO(PPh_3)_2]$[109] and $[RuCl(dppm)_2THF]Mn(CO)_5$[1506] are discussed in Sections 45.2 and 45.5.4.1 respectively.

(ii) Hydroxo complexes

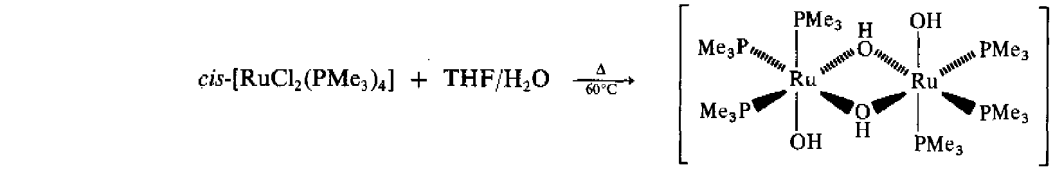
Reaction of $[RuCl_2(PPh_3)_3]$ with NaOH in THF containing 10% water gives $[RuCl(OH)(OH_2)(PPh_3)_2]_2$ but on prolonged heating this is converted to $[RuH(OH)(PPh_3)_2(THF)]_2$. As shown in Scheme 52,[1767] these and other hydrido–hydroxo dimers, together with their monomeric analogues $[RuH(OH)(PPh_3)_2Solvent]$ (Solvent = H_2O, THF), are obtained by treatment of $[RuHCl(PPh_3)_3]$ with aqueous carbonate-free NaOH or KOH in THF or acetone. Another route to $[RuH(OH)(OH_2)(PPh_3)_2]$ is by reaction of $[RuH(C_6H_4PPh_2)Et_2O(PPh_3)_2]$ (Section 45.10.3.2.ii) with water in THF.[1402] Further complications arise because of subsequent transformation of some of these products into tetranuclear complexes containing terminal carbonyls and bridging OH, H and PPh_2 ligands, *e.g.* $[Ru_4H_4(OH)_2(PPh_2)_2(CO)_2(Me_2CO)_2(PPh_3)_6]$.[1767]



i, NaOH or KOH in THF/H_2O; 25 °C; ii, NaOH or KOH in Me_2CO/> 10% H_2O;
iii, KOH, Me_2CO/< 1% H_2O; Δ; iv, KOH, Me_2CO/< 1% H_2O; 25 °C; v, $KOBu^t$ in Bu^tOH

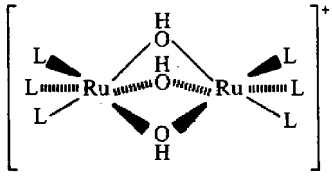
Scheme 52

Other binuclear hydroxo species are $[Ru(OH)_2(PMe_3)_3]_2$ (**240**)[1521] (equation 113), $[Ru_2(OH)_3L_6]^+$ (**241**) (L = PMe_2Ph, $PMePh_2$, $P(OMe)Ph_2$, PMe_3) and $[Ru_2(OH)_2(PPh_3)_4(BF_4)_2]$ (**242**). The PMe_3 cation is best prepared by reaction of $[Ru_2(CH_2)_3(PMe_3)_6]$ with $[Ph_3C]BF_4$ in THF[1768] whereas treatment of $[RuH(NH_2NMe_2)_3(cod)]^+$ with PR_3 in acetone/MeOH followed by addition of water provides a high yield route to the others.[1753] Compound (**242**) arises from reaction of [RuH(OCOMe)$(PPh_3)_3$] with HBF_4 in MeOH. The low conductivity in $MeNO_2$ suggests anion coordination or ion-pairing.[1769] The related hydroxo-bridged complex (**243**) is produced by reaction of $[RuHCl(Pr^iNCHCHNPr^i)(PPh_3)_2]$ with water in toluene.[1770]

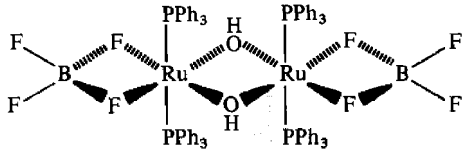


(113)

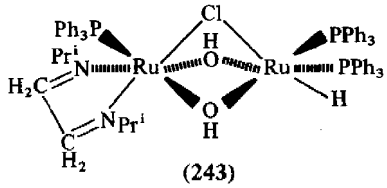
(240)



(241)



(242)



(243)

Trimetallic hydroxo-bridged complexes such as $[Ru_2(\mu\text{-}OH)_2\{\mu\text{-}Fe(CO)_4\}(CO)_4L_2]$ (L = PPh_3, PMe_3, $AsPh_3$) and $[Ru_2(\mu\text{-}OH)(\mu\text{-}H)\{\mu\text{-}Fe(CO)_4\}(CO)_4(PPh_3)_2]$ are covered in Section 45.5.5.

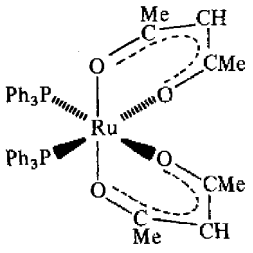
(*iii*) *Ketoenolate (dike) and quinone complexes*

Reaction of $[RuH_2(PPh_3)_4]$ with acetylacetone in boiling 2-methoxyethanol in the presence of Et_3N gives orange crystals of $[Ru(acac)_2(PPh_3)_2]$ shown by ^1H NMR spectroscopy to have the *cis* configuration (**244**). Similar compounds are obtained using trifluoroacetylacetone and hexafluoroacetylacetone.[1771] The rate of inversion between the optical isomers of (**244**) is slow at ambient temperature and hence the enantiomers can be resolved.[1772] $[Ru(acac)_2(PPh_3)_2]$ can also be prepared from $[RuCl_2(PPh_3)_3]$, acacH and Et_3N in boiling C_6H_6 and on recrystallization from MeOH and C_6H_6 gives orange and green forms respectively. These products have identical NMR and electronic spectral properties and it is suggested that they may differ in the solid either in the orientation of the phenyl groups or because of the existence of a *trans* isomer.[1545] In the absence of base, compounds such as $[RuCl(acac)(PPh_3)_2]_2$, which are formulated as chloride-bridged dimers are isolated; the corresponding $AsPh_3$ compounds are also known.[1704]

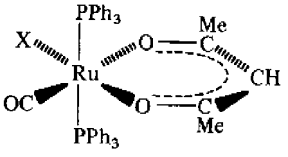
Treatment of $[RuHCl(CO)(PPh_3)_3]$ with acacH in boiling 2-methoxyethanol gives $[RuCl(acac)(CO)(PPh_3)_2]$ (**245**) whereas in the presence of Et_3N, the hydrido complex $[RuH(acac)CO(PPh_3)_2]$ (**245**) is produced. The latter also arises from direct reaction of $[RuH_2(CO)(PPh_3)_3]$, $[RuH(NO_3)CO(PPh_3)_2]$ or $[Ru(CO)_3(PPh_3)_2]$ with acacH,[1771,1773] or $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$ with acacH/KOH.[1774] Complexes of similar stoichiometry result from reaction of $[RuHX(CO)(PPh_3)_3]$ (X = H, Cl) with acacH in C_6H_6.[1775] The fluorinated β-diketonates $[Ru(dike)_2(PPh_3)_2]$ and $[RuX(dikete)CO(PPh_3)_2]$ (X = H, Cl) are also known.[1771,1776] Interestingly, reaction of $[RuH_2(CO)(PPh_3)_3]$ with $[Pd(facfac)_2]$ in boiling C_6H_6 gives a mixture of [RuH(facfac)$(CO)(PPh_3)_2$] and *cis*-[Ru$(facfac)_2CO(PPh_3)$] which can be separated by chromatography.[1776] Treatment of $[Ru(NO_3)_2CO(PPh_3)_2]$ (Section 45.5.4.7.v) with acetylacetone gives $[Ru(NO_3)(acac)CO(PPh_3)_2]$ containing a monodentate NO_3^- ligand,[1773] and likewise $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$ gives [Ru(OCOCF$_3$)(dike)$(CO)(PPh_3)_2$] (dike = acac, facfac).[1774]

Tetrachloro- and tetrabromo-1,2-benzoquinone react with $[Ru(CO)_3(PPh_3)_2]$ to give the orange complexes (**246**). The same compounds are obtained using tetrachloropyrocatechol and base. Cyclic voltammetry indicates that compounds (**246**) undergo reversible one-electron transfer reactions and these oxidation products can be chemically generated.[1777a] Treatment of $[RuCl(NO)(PPh_3)_2]$ with various quinones yields $[RuCl(NO)(C_6X_4O_2)(PPh_3)_2]$[1430] whereas $[RuCl_2(PPh_3)_3]$ affords the ruthenium(IV) complexes $[RuCl_2(C_6X_4O_2)(PPh_3)_2]$ (X = Cl, Br).[1777a] The catecholate-bridged dimer

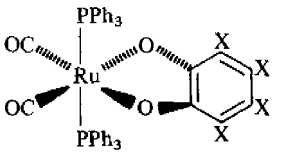
$[Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)]_2$ undergoes bridge cleavage with Group V donors and halide ions to give $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)]$ (L = PPh_3, $AsPh_3$ *etc.*) and $[RuX(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]^-$ (X = Cl, Br, I) respectively. Chemical oxidation of these monomers gives semiquinone complexes.[1777b] Direct reaction of $[RuCl_2(CO)_n(PPh_3)_{3-n}]$ (n = 0–3) with *o*-semiquinolates of Na, Tl or Cu gives $[RuClL(CO)_n(PPh_3)_{3-n}]$ (HL = 3,6-di-*tert*-butyl-1,2-semiquinone *etc.*).[1777c]



(244)



(245) X = H, Cl



(246) X = Cl, Br

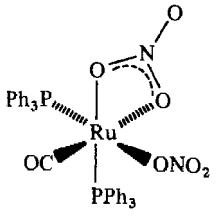
(*iv*) *Dioxygen complexes*

Apart from the formally Ru^0 compounds $[RuX(NO)O_2(PPh_3)_2]$ and $[Ru(CO)(CNR)O_2(PPh_3)_2]$,[1480] the only claims for $Ru^{II}O_2$ species are concerned with O_2 absorption by $[RuCl_2(PPh_3)_3]$ and '$RuCl_2(AsPh_3)_3$'. However, the green material obtained by exposure of solutions of $[RuCl_2(PPh_3)_3]$ to air is attributed to formation of unspecified triphenylphosphine oxide complexes[1411,1544,1547] and the compound $[RuCl_2(AsPh_3)_3O_2]$ has been reformulated as the binuclear μ-peroxo complex $[(AsPh_3)_3Cl_2RuO_2RuCl_2(AsPh_3)_3]Cl_2$.[1778] Note however that earlier workers[1547] suggested that Ru^{III} arsine oxide complexes may be present here.

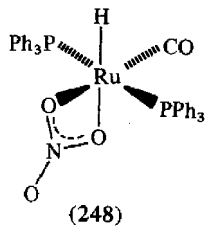
(*v*) *Nitrato, sulfato, carbonato and perchlorato complexes*

Reaction of $[RuHCl(CO)(PMe_2Ph)_3]$ with aqueous HNO_3 gives $[RuCl(NO_3)(CO)(PMe_2Ph)_3]$ containing a monodentate NO_3^- ligand.[1614c] Similarly, treatment of $[RuH_2CO(PPh_3)_3]$ with HNO_3 gives $[Ru(NO_3)_2CO(PPh_3)_2]$ (**247**) which exhibits facile intramolecular exchange of its uni- and bi-dentate NO_3^- groups. A preliminary communication reports the preparation of $[Ru(NO_3)_2(PMe_2Ph)_3]$ from reaction of $[Ru_2X_3(PMe_2Ph)_6]^+$ (X = OH, H) with HNO_3; $[RuH(PMe_2Ph)_5]^+$ and HNO_3 give $[Ru(NO_3)(PMe_2Ph)_5]^+$.[1753] The dicarbonyl complex $[Ru(NO_3)_2(CO)_2(PPh_3)_2]$ (with unidentate NO_3^- ligands) is prepared either by reaction of (**247**) with CO or treatment of $[Ru(CO)_3(PPh_3)_2]$ with HNO_3. Reaction of (**247**) with EtOH or propanol gives the hydrido complex $[RuH(NO_3)(CO)(PPh_3)_2]$ (**248**) and with $PMePh_2$, $[Ru(NO_3)_2CO(PMePh_2)_3]$ is formed. Facile cleavage of one or more Ru—O bonds in (**247**) or (**248**) with ligands such as acacH (Section 45.5.4.7.iii), $^-$OCOMe (Section 45.5.4.7.vi) and dithioacid anions (Section 45.5.4.8.ii) can also occur. Compound (**247**) is a good catalyst for dehydrogenating primary and secondary alcohols.[1773,1779]

Treatment of $[Ru(CO)_3(PR_3)_2]$ (PR_3 = PPh_3, $PPh_2(p\text{-Tol})$] with SO_2 in C_6H_6 gives the air sensitive compounds $[Ru(CO)_2(PR_3)_2(SO_2)]$ (see (**127**) in Section 45.5.1.3) which on exposure to air affords $[Ru(SO_4)(CO)_2(PR_3)_2]$.[1474] Other routes to this compound are shown in equation (114).[1474,1477] An X-ray structure analysis confirms the presence of bidentate sulfate.[1780] The related complex $[RuCl(SO_4)(NO)(PPh_3)_2]$ (Section 45.5.4.6.iii) is well characterized.[1424] An unusual reaction occurs between $[RuH_2(PPh_3)_4]$ and SO_2 in toluene. The first product is the yellow aqua complex $[RuSO_4(OH_2)(SO_2)(PPh_3)_2]$ which slowly rearranges in solution to the binuclear toluene solvate (**249**). X-Ray analysis reveals that this contains unidentate SO_2 and bridging SO_4^{2-} groups.[1764]



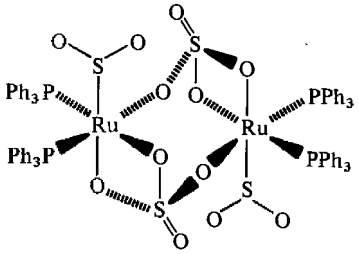
(247)



(248)

$$[Ru(CO)_3(PPh_3)_2] + \text{concentrated } H_2SO_4 \xrightarrow{THF} [Ru(SO_4)(CO)_2(PPh_3)_2] \quad (114)$$

$$[Ru(CO)_2(PPh_3)_2SO_2] + SO_2 \text{ (or } PPh_3) \longrightarrow [Ru(SO_4)(CO)_2(PPh_3)_2]$$



(249)

Aerial oxidation of the $[RuH(CO)_2(PPh_3)_2(CN\text{-}p\text{-}Tol)]^+$ cation gives the carbonate complex $[Ru(CO_3)(CO)(PPh_3)_2(CN\text{-}p\text{-}Tol)]$[1480] and a rare example of an O-bound perchlorate compound is $[RuCl(OClO_3)(CNR)(CS)(PPh_3)_2]$ obtained by reaction of $[RuCl_2(CNR)(CS)(PPh_3)_2]$ with $Ag[ClO_4]$.[1640]

(*vi*) *Carboxylato complexes*

A considerable amount of work has been published on Ru^{II} carboxylate complexes containing P donor ligands. Thus reaction of $[RuCl_2(PPh_3)_3]$ with sodium acetate in boiling *tert*-butanol gives $[Ru(\eta^2\text{-}OCOMe)_2(PPh_3)_2]$.[1769] A range of analogous carboxylates are formed using the appropriate RCO_2H in acetone (R = Et, Ph, Bu^t) in the presence of $Na[HCO_3]$.[1545] As described elsewhere (Section 45.10.3.2.i) reactions in lower boiling point alcohols lead to $[RuH(OCOR)(PPh_3)_3]$.[1451] Treatment of $[RuH_2(PF_2NMe_2)_2(PPh_3)_2]$ with CF_3CO_2H gives the mixed phosphine complex $[Ru(\eta^2\text{-}OCOCF_3)_2(PF_2NMe_2)(PPh_3)]$ whereas with $[RuH_2L(PPh_3)_3]$, $[Ru(OCOF_3)_2L(PPh_3)_2]$ (L = PF_3, PF_2NMe_2) with bi- and uni-dentate $OCOCF_3$ ligands is formed.[1576] The corresponding $[Ru(OCOR)_2(PMe_2Ph)_3]$ are also reported (equations 115 and 116) and $[Ru\{C_6H_4OP(OPh)_2\}_2(P(OPh)_3)_2]$ (**198**) gives $[Ru(\eta^1\text{-}OCOR_F)_2\{P(OPh)_3\}_4]R_FCO_2H$ (R_F = CF_3, C_2F_5), with only unidentate $^-OCOR_F$ groups, on treatment with the appropriate carboxylic acid.[1685] The preparations of *cis*-$[Ru(\eta^1\text{-}OCOMe)Me(PMe_3)_4]$ from *cis*-$[RuMe_2(PMe_3)_4]$ and $MeCO_2H$,[16a] and $[Ru(\eta^2\text{-}OCOMe)Cl(PPh_3)_3]$ and $[Ru(\eta^2\text{-}OCOMe)Cl(PMe_3)_4]$[1680] have been reported.[1680]

$$[Ru_2X_3(PMe_2Ph)_6]PF_6 + CF_3CO_2H \longrightarrow [Ru(OCOCF_3)_2(PMe_2Ph)_3]^{1753} \quad (115)$$

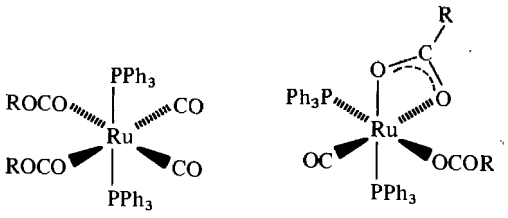
(X = H, OH)

$$mer\text{-}[RuH(BH_4)(PMe_2Ph)_3] + RCO_2H \longrightarrow [Ru(OCOR)_2(PMe_2Ph)_3]^{1752} \quad (116)$$

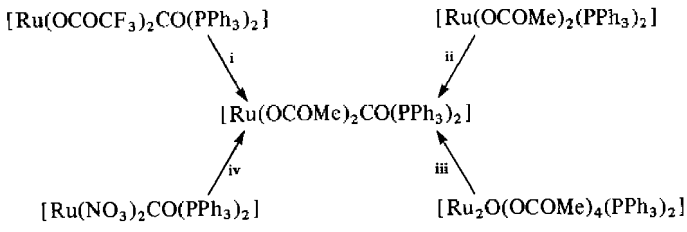
(R = Me, Bu^t)

A wide range of PR_3, carbonyl carboxylates have been prepared. For example $[Ru(CO)_3(PPh_3)_2]$ and RCO_2H in boiling C_6H_6 or 2-methoxyethanol give $[Ru(\eta^1\text{-}OCOR)_2(CO)_2(PPh_3)_2]$ (**250**) (R = H, Me, Et, CF_3 *etc.*).[1447,1523,1728a,1781,1782] This method has been employed to synthesize the open chain polyether carboxylate complexes $[Ru(\eta^1\text{-}L)_2(CO)_2(PPh_3)_2]$ (L = 1-(*o*-carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)ethanato(1−)].[1783] The monocarbonyls $[Ru(OCOR)_2(CO)(PPh_3)_2]$ (**251**), (with mono- and bi-dentate ^-OCOR groups which undergo facile intramolecular exchange), are obtained from $[RuH_2(CO)(PPh_3)_3]$ and RCO_2H (R = CF_3, C_2F_5, C_6F_5, *p*-C_6H_4Cl, *p*-$C_6H_4NO_2$], whereas weaker RCO_2H give the hydrido complexes $[RuH(\eta^2\text{-}OCOR)(CO)(PPh_3)_2]$.[1728a,1781,1782,1784] The acetate analogue $[Ru(OCOMe)_2(CO)(PPh_3)_2]$ can be prepared by several routes (Scheme 53) and the related compounds $[Ru(OCOCF_3)_2CO(PPh_3)_m(L\text{–}L)]$ (L–L = $C_6H_4(PPh_2)_2$, m = 0, 1; $Ph_2P(CH_2)_2AsPh_2$, m = 1 and $Ph_2P(CH_2)_nPPh_2$, n = 3,4; m = 0) have been synthesized by reaction of $[RuH_2(CO)(PPh_3)(L\text{–}L)]$ with CF_3CO_2H.[1786]

Reaction of $[RuHCl(CO)(PMe_2Ph)_3]$ with RCO_2H under mild conditions affords $[RuCl(\eta^1\text{-}OCOR)(CO)(PMe_2Ph)_3]$ (R = Me, Et, Ph) with a unidentate ^-OCOR group[1614c] but under more vigorous conditions, $[RuHCl(CO)(PPh_3)_3]$ gives the chelate derivatives $[RuCl(\eta^2\text{-}OCOR)CO(PPh_3)_2]$.[1728a,1781,1782] Other routes to the benzoate complex (**252**) are shown in Scheme 54. The thiocarbonyl analogue $[RuCl(\eta^2\text{-}OCOH)CS(PPh_3)_2]$ has been prepared by reaction of $[RuCl_2(OH_2)CS(PPh_3)_2]$ with $Na[OOCH]$[1645] and treatment of $[RuCl(p\text{-}Tol)CO(PPh_3)_2]$ with for-



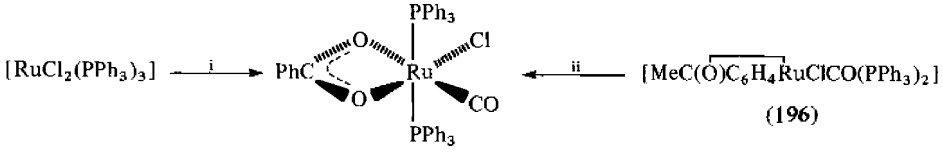
(250) (251)



i, Na[OCOMe], MeOH, Δ;[1774] ii, CO/MeOH;[1785] iii, CO, PPh_3;[1785] iv, Na[OCOMe];[1773]

Scheme 53

mate ion gives the aryl carbonyl derivative [Ru(η^2-OCOH)(*p*-Tol)CO(PPh_3)$_2$]. Thermal decarboxylation of the latter yields [Ru(CO)(PPh_3)$_3$] (see Section 45.10.3.2.ii) which on reaction with HCHO affords [Ru(η^2-OCOH)(Me)CO(PPh_3)$_2$].[1487] The nitrosyl complexes [RuCl(OCOR)(COR)(NO)(PPh_3)$_2$] are known (Section 45.5.4.6.iii).[1429] Reactions of these CO compounds with other O-donor ligands such as NO_3^- and β-diketonates are discussed elsewhere and many of these neutral complexes catalyse the dehydrogenation of alcohols and the hydrogenation of ketones and alkenes.[1786,1787,1788]



(252)

i, PhCHO/Δ;[1675] ii, $PhCO_2H$[1682]

Scheme 54

A number of cationic tertiary phosphine complexes containing carboxylate ligands have been synthesized. Examples include [Ru(η^1-$OCOCF_3$)(PMe_2Ph)$_5$]$^+$ (from [RuH(PMe_2Ph)$_5$]$^+$ and CF_3CO_2H), [Ru(η^2-OCOR)(PMe_2Ph)$_4$]PF_6[1753] (confirmed by X-ray analysis[1789] for R = Me) and [Ru(η^2-OCOMe)(OH_2)(PPh_3)$_3$]BF_4[1754] obtained as the end product by protonation of [RuH(η^2-OCOMe)(PPh_3)$_3$] with aqueous HBF_4 in acetone. The various hydrido intermediates are discussed in Section 45.10.3.2.v. Other carboxylate cations described in reference 1754 are [Ru(η^2-OCOMe)L(PPh_3)$_3$]BF_4 (L = MeCN, CO) from reaction of the aqua cation with L. An X-ray analysis of the [Ru(η^2-OCOMe)CO($PMePh_2$)$_3$]PF_6 analogue has been published.[1790]

Other references to carboxylato complexes containing P donor ligands are to be found in Sections 45.3.2, 45.5.4.5.iii, 45.5.8, 45.6.5 and 45.10.

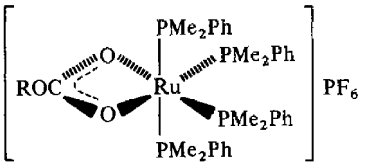
(*vii*) *Carbonate ester and carbamato complexes*

Treatment of [RuH(PMe_2Ph)$_5$]PF_6 with CO_2 in MeOH or EtOH gives the bidentate monoalkylcarbonate esters (**253**). Recrystallization of [Ru(η^2-OCOH)(PMe_2Ph)$_4$]PF_6 from ROH/acetone also gives (**253**). The hydrido complex [RuH(O_2COR)(PPh_3)$_3$] is obtained from [$RuH_2(PPh_3)_4$], CO_2 and

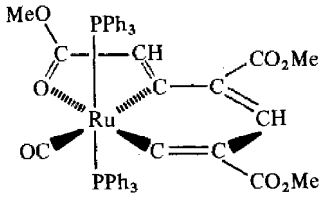
ROH[1791] and similar reactions (equations 117 and 118) yield the corresponding dimethylcarbamato complexes;[1792] X-ray analysis[1793] confirms the structure of $[Ru(O_2CNMe_2)(PMe_2Ph)_4]BF_4$. Structural analysis also reveals that the product from reaction of $[RuH_2(CO)(PPh_3)_3]$ with methyl propiolate is the novel metallocycle (**254**).[1794]

$$[RuH(PMe_2Ph)_5]BF_4 + CO_2 \xrightarrow{NMe_2H/EtOH} [Ru(O_2CNMe_2)(PMe_2Ph)_4]BF_4 \quad (117)$$

$$[RuH_2(PPh_3)_4] + CO_2 \xrightarrow{NMe_2H/EtOH} [RuH(O_2CNMe_2)(PPh_3)_3] \quad (118)$$



(253)

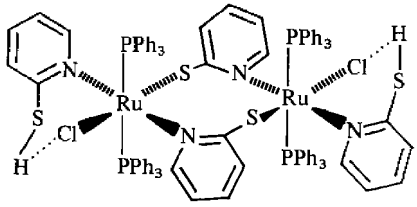


(254)

45.5.4.8 Sulfur donor ligand complexes

(*i*) *Thiolato and sulfido complexes*

Very few complexes containing SH^- or SR^- and P donor ligands have been reported. Rare monomeric complexes are $[RuH(SR)(PPh_3)_3]$ (R = H, Ph, $PhCH_2$) obtained by treatment of $[RuH_2(PPh_3)_4]$ or $[RuH_4(PPh_3)_3]$ with RSH (or S_8 for R = H); the corresponding SMe derivative is obtained from $[RuH_2(PPh_3)_4]$ and dimethyldisulfide.[1795a,1795b] Aniline-2-thiol in the presence of base displaces both chloro ligands from $[RuCl_2(PPh_3)_3]$ to give the chelate complex $[Ru(2\text{-}H_2NC_6H_4S)_2(PPh_3)_2]$ whereas pyridine-2-thiol produces a dimeric species (**255**) with pyridine-2-thiolato bridges.[1545] Several other binuclear complexes containing these ligands are known (equations 119–121). Reaction of $[Ru(CO)_3(PPh_3)_2]$ with 2,2′-dipyridyldisulfide (RSSR) gives $[Ru(SR)_2(CO)_2PPh_3]$ (with mono- and bi-dentate SR groups) which on standing for several days converts to $[Ru(SR)_2(CO)PPh_3]$ (with bidentate SR groups).[1796b] The preparation of $[Ru(tddtH)_2(CO)(PPh_3)_2]$ by reaction of $[Ru(CO)_3(PPh_3)_2]$ with 1,3,4-thiadiazole-2,5-dithiol($tddtH_2$) has been reported. The mono- and bi-dentate ligands display dynamic interchange.[1796c]



(255)

$$[RuCl(bipy)(PPh_3)_2]_2Cl_2 \xrightarrow[acetone]{Pb(SC_6F_5)_2} [Ru(SC_6F_5)(bipy)(PPh_3)_2]_2Cl_2^{1714} \quad (119)$$

$$[RuH(cod)(NH_2NMe_2)_3]^+ \xrightarrow[ii.\ YSH\ (Y = Me, H)]{i.\ PR_3\ acetone/MeOH} [(PR_3)_3Ru(SY)_3Ru(PR_3)_3]^{+\,1753} \quad (120)$$

$$[RuI(\eta^2\text{-}CS_2Me)(CO)(PPh_3)_2] \xrightarrow[C_6H_6/\Delta]{RNH_2} [RuI(SH)(CO)(CNR)PPh_3]_2^{1796} \quad (121)$$

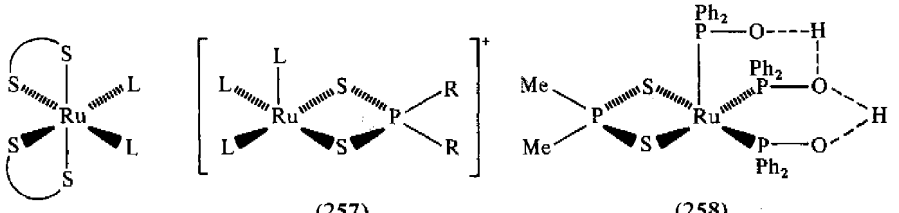
(R = Me, Bu^n, Bu^i, Pr^i, Pr^n, $PhCH_2$)

Examples of bridging sulfido complexes are $[RuX_2NO(EPh_3)]_2S$ (X = Cl, Br, E = P, As) made by reaction of $[RuX_3NO(EPh_3)_2]$ with sulfur; oxidation with perbenzoic acid gives $[RuX_2NO(EPh_3)]_2SO$.[1304] A polymeric complex of empirical formula '$[Ru_3Cl_3S_2(PPh_3)_3]$' is purported to be the product from $[RuCl_2(PPh_3)_3]$ and sulfur[1449] and species such as $[Ru(CO)_2(PPh_3)S]_2$ and $[Ru(CO)_2(SPPh_3)_2S]CH_2Cl_2$ also appear in the literature.[1642] Treatment of $[RuH(PMe_3)_3(CH_2PMe_2)]$ with S_8 in C_6H_6 has given $[Ru(PMe_3)_3S_6]$ which on dissolution in acetone gave $[Ru(PMe_3)_3S_7]$. The S_7^{2-} is tridentate, forming two five-membered rings.[1796d]

(*ii*) *Dithio-phosphinato, -phosphato, -carbamato, -carbonato, -ester and -carbonimidato complexes*

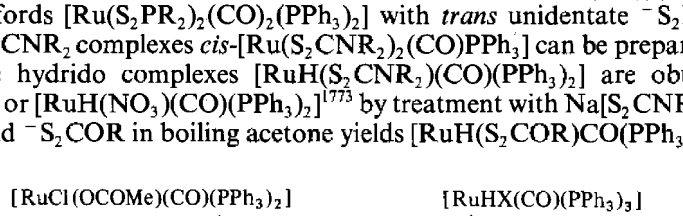
Complexes of general formula $[Ru(S–S)_2L_2]$ (S–S = S_2PR_2 (R = Me, Et, Ph), S_2CNR_2 (R = Me, Et), S_2COR (R = Me, Et); L = PPh_3, PMe_2Ph, $PMePh_2$, $PEtPh_2$, $P(OPh)_3$, $P(OMe)Ph_2$, $P(OEt)Ph_2$, $P(OMe)_2Ph$) can be synthesized by the prolonged reaction of compounds such as $[RuCl_2L_3]$, (L = PPh_3, $PEtPh_2$, $P(OR)Ph_2$), $[RuCl_2L_4]$ (L = PMe_2Ph, $PMePh_2$, $P(OMe)_2Ph$, $P(OPh)_3$) and *mer*-$[RuCl_3(PMe_2Ph)_3]$ with the appropriate Na[S–S].[1797–1799] Reaction of $[RuCl_2(diene)]_n$ with $Na[S_2PMe_2]\cdot 2H_2O$ gives $[Ru(S_2PMe_2)_2diene]$ (diene = cod, nbd) and the labile diene moiety is readily replaced by other bidentate ligands to give $[Ru(S_2PMe_2)_2(L–L)]$ (L–L = dppm, dppe, diars); for diars, *trans*-$[Ru(S_2PMe_2)_2(diars)_2]$ is also formed.[1800] Tetramethylthiuram disulfide and $[RuH_2(PPh_3)_4]$ also gives $[Ru(S_2CNMe_2)_2(PPh_3)_2]$.[1801] In most instances, NMR spectroscopic studies indicate the *cis* configuration (**256**), verified by X-ray analysis for $[Ru(S_2PEt_2)_2(PMe_2Ph)_2]$,[1802] and also reveal facile interconversion at ambient temperature of optical isomers (for the $^-S_2PR_2$ compounds) and restricted rotation about the C—N bond (for the $^-S_2CNR_2$ compounds). Rate constants and associated activation parameters for these processes have been determined by line shape analysis of their ^1H NMR spectra and a mechanism of optical inversion involving Ru—S bond cleavage proposed.[1798,1799,1803]

Under mild conditions of reaction, several intermediates can be isolated from treatment of $[RuCl_2L_n]$ with $S–S^-$ anions. These include the six-coordinate $[RuCl(S_2PR_2)L_3]$ which rearrange in alcoholic media to the red five-coordinate cations $[Ru(S_2PR_2)L_3]^+$ (**257**) and $[Ru(S_2COMe)_2L_3]$ (with uni- and bi-dentate $^-S_2COMe$ groups) which on heating give $[Ru(S_2COMe)_2L_2]$ [L = PMe_2Ph, $P(OR)Ph_2$ (R = Me, Et)]. Reaction of $[RuCl_2(PMe_2Ph)_4]$ with $Na[S_2CNR_2]$ in EtOH gives the $[Ru(S_2CNR_2)(PMe_2Ph)_4]^+$ cations whereas in C_6H_6 $[Ru(S_2CNR_2)_2(PMe_2Ph)_3]$ are formed.[1799] The tetrakisphosphine cation is also prepared from reaction of $[RuH(PMe_2Ph)_5]^+$ with CS_2 in a $NHMe_2$/EtOH mixture.[1792] Treatment of some of these $[Ru(S—S)_2L_2]$ complexes with ligands (L′) of greater basicity gives either $[Ru(S–S)_2LL']$ (L = PPh_3, PMe_2Ph; L′ = $P(OPh)_3$) and/or $[Ru(S–S)_2L'_2]$ [L′ = $P(OPh)_3$, PMe_2Ph, $PHPh_2$, $P(OMe)_2OH$, $PCl_{3-n}Ph_n$ (n = 0–2)] whereas with $PClPh_2$ in a H_2O/MeOH mixture, the unusual product (**258**) is isolated *via* the intermediate $[Ru(S_2PMe_2)PPh_3\{(Ph_2PO)_2H\}]$.[1798,1804] ^{31}P NMR spin-lattice relaxation times are reported for some of these $^-S_2PMe_2$ complexes.[1805]



(256) (257) (258)

The yellow monocarbonyls *cis*-$[Ru(S_2PR_2)_2(CO)L]$ are obtained by carbonylation of $[Ru(S_2PR_2)_2L_2]$. For L = PMe_2Ph, two isomers of formula $[Ru(S_2PMe_2)_2CO(PMe_2Ph)_2]$ (with uni- and bi-dentate $^-S_2PMe_2$ groups) are also formed.[1798] Reaction of $[Ru(CO)_3(PPh_3)_2]$ with R_2PS_2H (R = Ph, OPh) affords $[Ru(S_2PR_2)_2(CO)_2(PPh_3)_2]$ with *trans* unidentate $^-S_2PR_2$ groups.[1806] The corresponding $^-S_2CNR_2$ complexes *cis*-$[Ru(S_2CNR_2)_2(CO)PPh_3]$ can be prepared by several routes (Scheme 55). The hydrido complexes $[RuH(S_2CNR_2)(CO)(PPh_3)_2]$ are obtained from $[RuHCl(CO)(PPh_3)_3]$[1801] or $[RuH(NO_3)(CO)(PPh_3)_2]$[1773] by treatment with $Na[S_2CNR_2]$. Likewise, $[RuHCl(CO)(PPh_3)_3]$ and ^-S_2COR in boiling acetone yields $[RuH(S_2COR)CO(PPh_3)_2]$ (R = Me, Et).[1801]

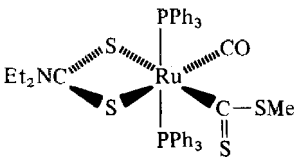


i, $Na[S_2CNR_2]$ (R = Me, Et);[1801] ii, $[Me_2NCS_2]_2$, C_6H_6, Δ;[1801]
iii, $Na[S_2CNR_2]$/MeOH;[1773] iv, $[Me_2NCS_2]_2$, C_6H_6, Δ[1801]

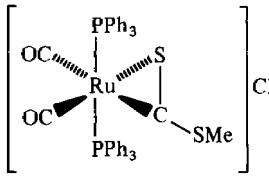
Scheme 55

Other examples of complexes containing $^{-}S_2CNR_2$ groups are $[Ru(S_2CNEt_2)(CNH\textit{p}\text{-Tol})(CO)(PPh_3)_2]$ (**177**) (Section 45.5.4.5.iii) and $[Ru(S_2CNEt_2)(CO)(CS)(PPh_3)_2]^+$, obtained by protonation of $[Ru(S_2CNEt_2)(\eta^1\text{-}CS_2Me)CO(PPh_3)_2]$ (**259**).[47] In compound (**259**), the dithioester group, CS_2Me, is bound through carbon only but examples of complexes containing chelated CS_2Me ligands are $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]ClO_4$ (**260**)[1470,1807] and $[RuCN(\eta^2\text{-}CS_2Me)\text{-}CO(PPh_3)_2]$.[47]

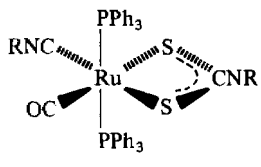
Addition of an excess of aryl or alkyl isothiocyanates to $[Ru(CO)_2(PPh_3)_3]$ gives the dithiocarbonimidato complexes $[Ru(S_2CNR)(CNR)(CO)(PPh_3)_2]$ (R = Me, Et, Ph) (**260a**).[1476] The related $[Ru(S_2CO)(CO)_2PPh_3]$ is made by addition of COS to the Ru^0 complex $[Ru(CO)_2(PPh_3)_2(\eta^2\text{-COS})]$ (**128**) (Section 45.5.1.3).[1478] Reaction of *fac*-$[RuH(\eta^2\text{-}C_6H_4PPh_2)(PMe_3)_3]$ with CS_2 and COS gives *fac*-$[Ru(SCHS)(\eta^2\text{-}C_6H_4PPh_2)(PMe_3)_3]$ and *fac*-$[Ru(S_2CO)CO(PMe_3)_3]$ respectively.[1391c]



(259)



(260)



(260a)

(*iii*) *Dithiolene complexes*

Bis(perfluoromethyl)dithiolene, $S_2C_2(CF_3)_2$, reacts with $[Ru_3(CO)_{12}]$ in boiling *n*-heptane to give an orange product which on treatment with PPh_3 affords $[Ru\{S_2C_2(CF_3)_2\}CO(PPh_3)_2]$ as a mixture of orange and violet crystals. These two complexes are structural isomers which interconvert in solution, the orange form being the more stable.[1808] X-Ray structural analyses reveal both isomers to be square pyramidal, with the axial group being CO in the orange form and PPh_3 in the violet form.[1809] Reaction of the orange product with $AsPh_3$ gives $[Ru\{S_2C_2(CF_3)_2\}CO(AsPh_3)_2]$ but with $P(OMe)Ph_2$ and $P(OMe)_3$, $[Ru\{S_2C_2(CF_3)_2\}L_3]$ are formed.

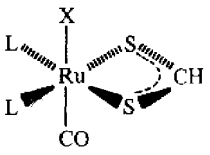
In boiling *n*-decane, $S_2C_2(CF_3)_2$ and $[Ru_3(CO)_{12}]$ give a green material which reacts with an excess of EPh_3 to produce $[Ru\{S_2C_2(CF_3)_2\}_2(EPh_3)_2]$ (E = P, As, Sb); with less EPh_3, $[Ru\{S_2C_2\text{-}(CF_3)_2\}_2EPh_3]$ (E = P, As) are isolated and if the latter (for E = P) is treated with hydrazine hydrate and then $Ph_4AsCl\cdot HCl$, $Ph_4As[Ru\{S_2C_2(CF_3)_2\}_2PPh_3]$ (μ_{eff} = 1.79 BM) is generated. Electronic spectral studies reveal that in solution, $[Ru\{S_2C_2(CF_3)_2\}_2(EPh_3)_2]$ is extensively dissociated into the monoadducts.[1808]

Reaction of $[RuCl_2(PMe_3)_4]$ with $Li_2[dttd]$ and $[RuCl_2(PPh_3)_3]$ with H_2dttd gives $[Ru(dttd)L_2]$ (H_2dttd = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane). The PMe_3 ligands are inert but one PPh_3 ligand is readily substituted by CO or N_2H_4 to yield $[Ru(dttd)(CO)PPh_3]$ and $[Ru(dttd)(N_2H_4)PPh_3]$ respectively. However, refluxing $[Ru(C_6H_4S_2)_2(CO)_2]^{2-}$ (see Section 45.7.6) in EtOH in the presence of excess PMe_3 and subsequent alkylation with $1,2\text{-}C_2H_4Br_2$ provides a route to $[Ru(dttd)\text{-}(CO)PMe_3]$.[1709]

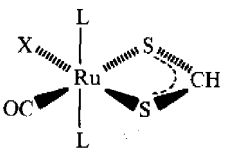
(*iv*) *Dithiocarboxylato complexes*

The best synthetic route to dithioformate complexes is by insertion of CS_2 into ruthenium–hydride bonds. Thus $[Ru(S_2CH)_2(PPh_3)_2]$ can be prepared by reaction of CS_2 with $[RuH_2(PPh_3)_4]$,[1437] $[RuH_4(PPh_3)_3]$,[1408,1810] $[RuH_3(SiR_3)(PPh_3)_2]$[83] or $[RuH(OCOH)(PPh_3)_3]$.[1811] X-Ray analysis confirms a *cis* configuration.[1812] Carbonyl complexes $[RuX(S_2CH)(CO)L_2]$ (**261**) (L = PCy_3, PPh_3) are obtained from treatment of $[RuHCl(CO)((PCy_3)_2]$[1623,1813] or of $[RuHX(CO)(PPh_3)_3]$ (X = Cl, Br, O_2CCF_3,[1810] NO_3[1773]) with CS_2. These isomerize to (**262**) on heating in C_6H_6 or toluene. The orange cation $[Ru(S_2CH)(PMe_2Ph)_4]^+$ (X-ray structure of PF_6^- salt available)[1814] results from reaction of CS_2 on $[RuH(PMe_2Ph)_5]^+$.[1792] In boiling MeOH this isomerizes to the purple five-coordinate $[Ru\{S_2C(H)PMe_2Ph\}(PMe_2Ph)_3]PF_6$ (**263**) which reacts with excess $P(OMe)_3$ to give the yellow octahedral complex $[Ru(S_2CH)(PMe_2Ph)_2\{P(OMe)_3\}_2]PF_6$ whereas with the larger $P(OMe)Ph_2$, the purple $[Ru\{S_2C(H)(PMe_2Ph\}(P(OMe)Ph_2)_3]PF_6$ is formed.[1815] Equimolar amounts of $P(OMe)_3$ and (**263**) give the intermediate $[Ru(S_2CH)(PMe_2Ph)_3P(OMe)_3]PF_6$, and a study of the kinetics and mechanism of this substitution reaction is available.[1816]

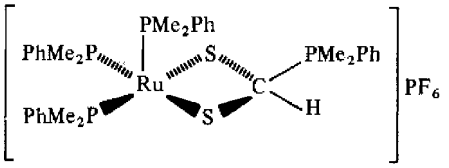
Reaction of $[RuCl_2(PPh_3)_3]$ with CS_2 gives several binuclear products (Section 45.5.5.1) and also a product initially formulated as $[RuCl(\eta^2\text{-}CS_2)(PPh_3)_3]Cl$.[1638] Further studies on the more soluble $PEtPh_2$ analogue suggest it should be reformulated as the phosphoniodithiocarboxylate complex (**264**). Dissolving (**264**) in MeOH and adding BPh_4^- gives $[RuCl(MeOH)(S_2CPEtPh_2)(PEtPh_2)_2]$-$BPh_4$.[1558] The cation $[RuH(S_2CPCy_3)CO(PCy_3)_2]^+$ is prepared in similar fashion from $[RuHCl(CO)(PCy_3)_2]$ and CS_2 and the closely related $[RuCl(S_2CPCy_3)CO(PCy_3)_2]^+$ arises from treatment of $[RuCl_2CO(PCy_3)_2]$ with the zwitterion ligand $S_2\bar{C}\overset{+}{P}Cy_3$.[1817]



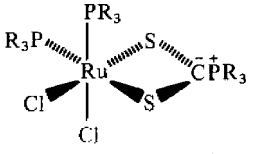
(261)



(262)



(263)

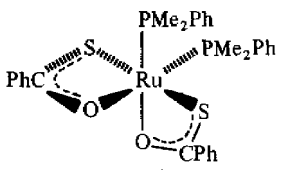


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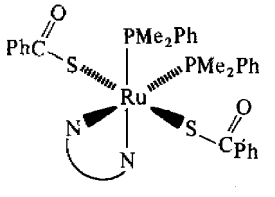
(*v*) *Monothio-carboxylato, -carbamato and -carbonato complexes*

$[RuCl_2(PPh_3)_3]$ reacts with excess sodium or ammonium monothiobenzoate in boiling MeOH or acetone to give $[Ru(SOCPh)_2(PPh_3)_2]$ while *mer*-$[RuCl_3(PMe_2Ph)_3]$ with Na[SOCPh] in acetone yields $[Ru(SOCPh)_2(PMe_2Ph)_2]$ (**265**). These complexes which have *trans* and *cis* phosphine ligands respectively and contain bidentate $[SOCPh]^-$ react with monodentate Lewis bases to give $[Ru(SOCPh)_2L_2(PR_3)_2]$ (L = CO, NH_3, NH_2Et) which contain monodentate *trans* S-bonded $[SOCPh]^-$.[1707] Reaction of (**265**) with bidentate nitrogen donors gives $[Ru(SOCPh)_2$-$(N\text{–}N)(PMe_2Ph)_2]$ but various isomers are formed, namely (**266**; N–N = en; **267** [major] and **268** [minor]; N–N = bipy and phen).[1708] The unusual compound (**266**; N–N = $HNC(Me)CH_2C$-Me_2NH_2) is isolated by reaction of *mer*-$[RuCl_3(PMe_2Ph)_3]$ with $[NH_4][SOCPh]$ in acetone.[1707]

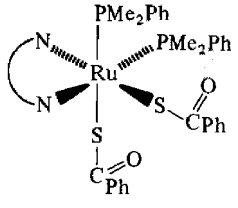
Treatment of (**265**) with dppe gives the two isomers (**269**) and (**270**) (NMR evidence) and the structure of (**269**) has been verified by X-ray analysis. An isomeric mixture of *mer*-$[Ru(SOCPh)_2$-$(PMe_2Ph)_3]$ (with uni- and bi-dentate $[SOCPh]^-$) arises from addition of PMe_2Ph to (**265**) whereas shaking *cis*-$[RuCl_2(PMe_2Ph)_4]$ in MeOH for short periods with $NH_4[SOCPh]$ gives the *facial* isomer; prolonged interaction gives the $[Ru(SOCPh)(PMe_2Ph)_4]^+$ cation.[1818] Thioacetic acid reacts with $[Ru(NO_3)_2CO(PPh_3)_2]$ in MeOH to give $[Ru(SOCMe)_2CO(PPh_3)_2]$ (with bi- and uni-dentate $[SOCMe]^-$). Two isomers are formed depending on reaction conditions.[1773] The thioformate complex $[Ru(SOCH)_2(CO)_2(PPh_3)_2]$ is claimed.[1642]



(265)

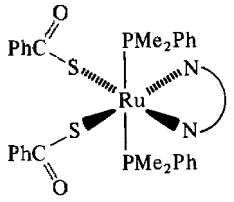


(266)

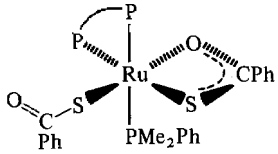


(267)

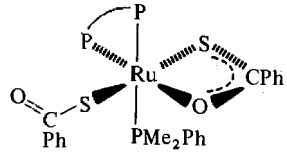
The monothiocarbonate and monothiocarbamate cations $[Ru(SOCY)(PMe_2Ph)_4]PF_6$ (Y = OEt, NMe_2) can be prepared by treating $[RuH(PMe_2Ph)_5]PF_6$ with COS in EtOH or EtOH/$NHMe_2$ respectively.[1792]



(268)



(269)



(270)

(*vi*) *Sulfur dioxide and dimethyl sulfoxide complexes*

Few ruthenium(II) sulfur dioxide complexes are reported. These include the monomeric $[RuSO_4(OH_2)(PPh_3)_2SO_2]$ (from $[RuH_2(PPh_3)_4]$ and SO_2) which slowly rearranges to the binuclear $[RuSO_4(PPh_3)_2SO_2]_2$ [see Section 45.5.4.7.v and (**249**)][1764] and the poorly characterized $[RuXCl(PPh_3)_2SO_2]$ (X = Cl, H) from reaction of SO_2 with $[RuCl_2(PPh_3)_3]$ and $[RuHCl(PPh_3)_3]$ respectively. Prolonged reaction of the hydride complex with SO_2 gives rise to $[Ru_3Cl_3(PPh_3)_4(SO_2)_2]$(?)[1411,1449] while treatment of $[RuHX(CO)(PCy_3)_2]$ with SO_2 in C_6H_6 for 4 h yields $[RuHX(CO)(PCy_3)_2SO_2]$ (X = Cl, Br);[1813] $[RuCl_2(CO)(triphos)SO_2]$ (**164**) is discussed in Section 45.5.4.5.i.

Reaction of $[RuCl_2(DMSO)_4]$ with PPh_3 affords $[RuCl_2(DMSO)_2PPh_3]$ whereas $P(OPh)_3$ leads to $[RuCl_2(DMSO)\{P(OPh)_3\}_3]$; IR and NMR studies indicate S-bonded DMSO groups.[112] Related complexes include $[RuCl_2(DMSO)_2(triphos)]$, [RuCl(DMSO)L]Cl (L = tet-1 or tet-2),[1540] $[RuCl_2(DMSO)L_3]$ (L = $AsMePh_2$, $AsMe_2Ph$, $SbPh_3$), $[RuCl_2(DMSO)_2(AsPh_3)_2]$[1511] and references to the preparation of other Ru^{II} DMSO compounds such as $[RuCl_2CO(DMSO)(PPh_3)_2]$, *cis*-$[RuCl_2(CO)(DMSO)(L–L)]$ (Section 45.5.4.5.i) and *trans*-$[RuCl(DMSO)(dmpe)_2]^+$ (Section 45.5.4.3) are given elsewhere.

(*vii*) *Miscellaneous*

Reaction of $[RuCl_2(PPh_3)_3]$ with *N*-phenylcarbamoylpyrrole-2-thiocarboxamide (PTH) gives $[RuCl_2(PTH)_2PPh_3]$ which contains a strong ruthenium–sulfur bond.[1819] With an excess of 1-arylte-traazole-5-thiones in boiling C_6H_6, S-coordinated $[RuCl_2\{ArN_4H(CS)\}_3PPh_3]$ (Ar = Ph, *o*-Tol, *p*-ClC_6H_4, *p*-$MeOC_6H_4$) are formed;[1820] reaction of $[RuCl_2(PPh_3)_3]$ with COS gives $[RuCl_2(SPPh_3)PPh_3]_2$ and $OPPh_3$. In the presence of PPh_3, the black dimeric carbonyl complex $[RuCl_2(SPPh_3)CO]_2$ is isolated; the corresponding Ph_3AsS complex has also been reported.[1642]

45.5.4.9 Mixed donor atom (P—N, P—O, P—S) ligands

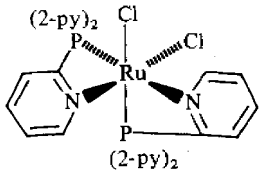
(*i*) *P–N ligand complexes*

Reaction of $[RuCl_2(PPh_3)_3]$ with tris(2-pyridyl)phosphine in C_6H_6 at room temperature produces the two isomers (**271**) and (**272**) whereas with $[RuHCl(PPh_3)_3]$, compound (**273**) with only one bidentate P(2-py)$_3$ ligand is formed.[1821] Treatment of '$RuCl_3 \cdot xH_2O$' with $PPh_2(C_6H_4NMe_2)$ (PN) gives $[RuCl_2(PN)_2]$;[1822] $[RuCl_5(OH_2)]^{2-}$ or $[RuCl_2(PPh_3)_3]$ with 2-(diphenylphosphinoethyl)pyridine in boiling aqueous EtOH affords *trans*-$[RuCl_2\{Ph_2P(CH_2)_2(py)\}_2]$. Treatment of the latter with ethanolic solutions of $NH_4[PF_6]$ gives the five-coordinate cation $[RuCl\{Ph_2P(CH_2)_2(py)\}_2]PF_6$ which readily reacts with CO or MeCN (L′) to give *trans*-$[RuClL'\{Ph_2P(CH_2)_2(py)\}_2]PF_6$.[1535b] The neutral dicarbonyl (**274**) is obtained by chlorination of $[Ru_3(CO)_9(PPh_2py)_3]$ and this reacts with more 2-(diphenylphosphino)pyridine to give $[RuCl_2(CO)_2(PPh_2py)_2]$ (with *trans* P-bound $PPh_2(py)$ and *cis* CO, *cis* Cl groups).[1459,1823]

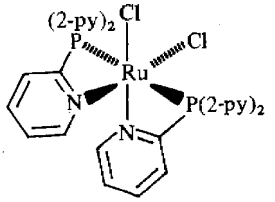
The binuclear complexes (**275**) and (**276**), which interconvert on heating in solution, have been synthesized either by reaction of $[RuCl_2(CO)_2(PPh_2py)_2]$ with $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) or from $[Ru(CO)_3(PPh_2py)_2]$ and $[PdCl_2(cod)]$.[1459]

(*ii*) *P–O ligand complexes*

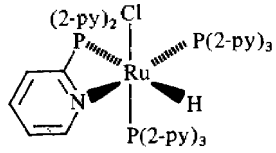
The octahedral chelate complex *trans*-$[RuCl_2(PO)_2]$, formed by reaction of '$RuCl_3 \cdot xH_2O$' with 2-(diphenylphosphino)anisole, $PPh_2(2\text{-}MeOC_6H_4)$, in boiling EtOH, reacts with CO at room temperature, the weak Ru—O bonds being broken stepwise, to give first $[RuCl_2(CO)(PO)_2]$ (**277**) and



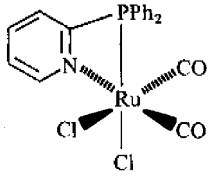
(271)



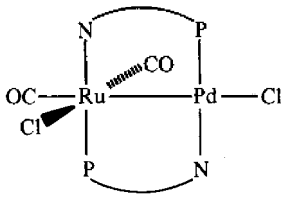
(272)



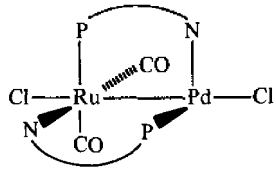
(273)



(274)



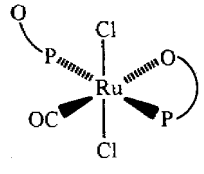
(275)



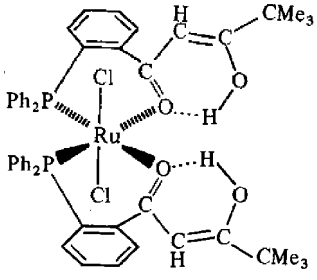
(276)

then $[RuCl_2(CO)_2(PO)_2]$ (all *trans* isomer). At higher temperatures in alkane solvents, the *cis* Cl, *cis* CO isomer of the latter is obtained. Similar complexes are produced with *tert*-butyl isocyanide.[1822,1824] The related complex $[RuCl_2\{PPh_2(2\text{-}OCC_6H_4)\}_2]$ (from '$RuCl_3 \cdot xH_2O$' and $PPh_2(2\text{-}OHCC_6H_4)$] undergoes decarbonylation on heating to give *cis*, *cis*, *trans*-$[RuCl_2(CO)_2(PPh_3)_2]$.[1825] Phosphine exchange of $PPh_2(2\text{-}C_6H_4COCH_2COBu^t)$ with $[RuCl_2(PPh_3)_3]$ affords (**278**) which further reacts with copper acetate to form a bimetallic complex in which copper is bound to the four oxygen atoms.[1826]

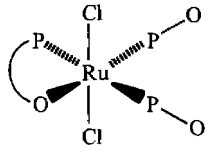
In contrast, reaction of '$RuCl_3 \cdot xH_2O$' with $PPh_2(CH_2C(O)OEt)$ in hot EtOH gives $[RuCl_2\{PPh_2(CH_2C(O)OEt)\}_3]$ shown by X-ray analysis to have structure (**279**). This compound exhibits facile intramolecular exchange of the bi- and one of the uni-dentate PO ligands and reacts readily with CO to give both mono- and di-carbonyl derivatives $[RuCl_2(CO)_n\{PPh_2(CH_2C(O)OEt)\}_2]$. The corresponding $[RuCl_2\{o\text{-}MeC_6H_4CN\}_2\{PPh_2CH_2C(O)OEt\}_2]$ (**228**) is known (see equation 110 and Section 45.5.4.6.vi).[1750]



(277)



(278)



(279)

In common with all these P—O ligand complexes which contain long Ru—O bonds, X-ray structural analysis of $[RuCl(Me)(cod)P(2\text{-}MeOC_6H_4)_3] \cdot CH_2Cl_2$, (prepared from $[RuCl(Me)(cod)\text{-}MeCN]_2$ and $P(2\text{-}MeOC_6H_4)_3$), reveals a distorted octahedral configuration with a 2-methoxyphenyl oxygen atom occupying the sixth coordination site [Ru—O = 2.58 Å).[1827] An analogous structure is found for $[RuCl(Me)(cod)\{PPh_2(2\text{-}MeOC_6H_4)\}]$.[1828] The complex *trans*-$[RuCl_2\{(\pm)\text{-}o\text{-}C_6H_4(PMePh)_2\}$ $(\pm)\text{-}o\text{-}C_6H_4(PMePh)(O)MePh)]$ containing P,P′ and O,P′ bidentate ligands respectively is covered in Section 45.5.4.3.

(*iii*) *P–S ligand complexes*

The only reference found to complexes of this type is a paper by Sanger and Day on reactions of $Ph_2P(CH_2)_2SPh$ (PS) with $[RuCl_2(CO)_3]_2$ which gives P-bonded $[RuCl_2(CO)_3PS]$ and then $[RuCl_2(CO)_2(PS)_2]$. However, when an ethanolic solution of '$RuCl_3 \cdot xH_2O$' and excess $Ph_2P(CH_2)_2SPh$ are refluxed for a prolonged period, an insoluble pink solid $[RuCl_2(PS)_2]_x$ which

probably contains bidentate $Ph_2P(CH_2)_2SPh$ is precipitated. Reaction of '$RuCl_3 \cdot xH_2O$' with $Ph_2P(CH_2)_2SPh$ under an atmosphere of CO gives first $[RuCl_2(CO)(PS)_2]$ and then some $[RuCl_2(CO)_2(PS)_2]$.[1829] The complexes $[RuCl_2(4\text{-}R_2PDBT)_2]$ (R = Ph, *p*-Tol; DBT = dibenzothiophene) were prepared in high yield from $[RuCl_2(PPh_3)_3]$ and $4\text{-}R_2PDBT$. X-Ray diffraction studies reveal that for R = *p*-Tol, an all *cis* geometry is adopted.[1830]

A range of P—C ligand complexes are known and these are fully discussed under the headings cyclometallated (Sections 45.5.4.5.v and 45.10.3.2.iii) and alkene complexes (Section 45.5.4.5.vi).

Macrocycle complexes containing P, As or Sb donor ligands are covered in Section 45.12.

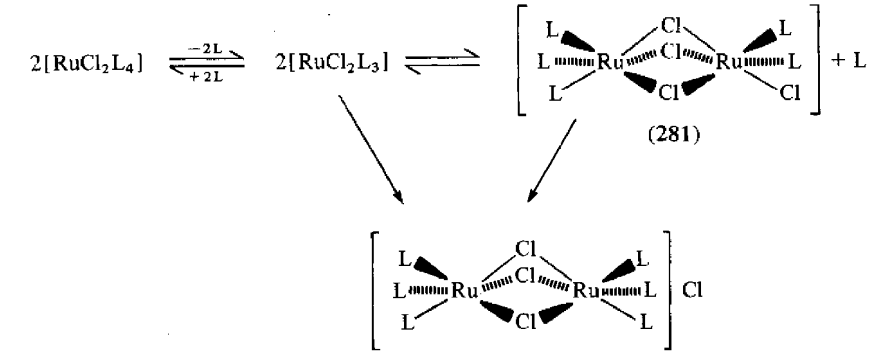
45.5.5 Bi-, Tri-, Tetra- and Poly-nuclear Ruthenium(II) Complexes

45.5.5.1 Triple halide-bridged complexes (and related species)

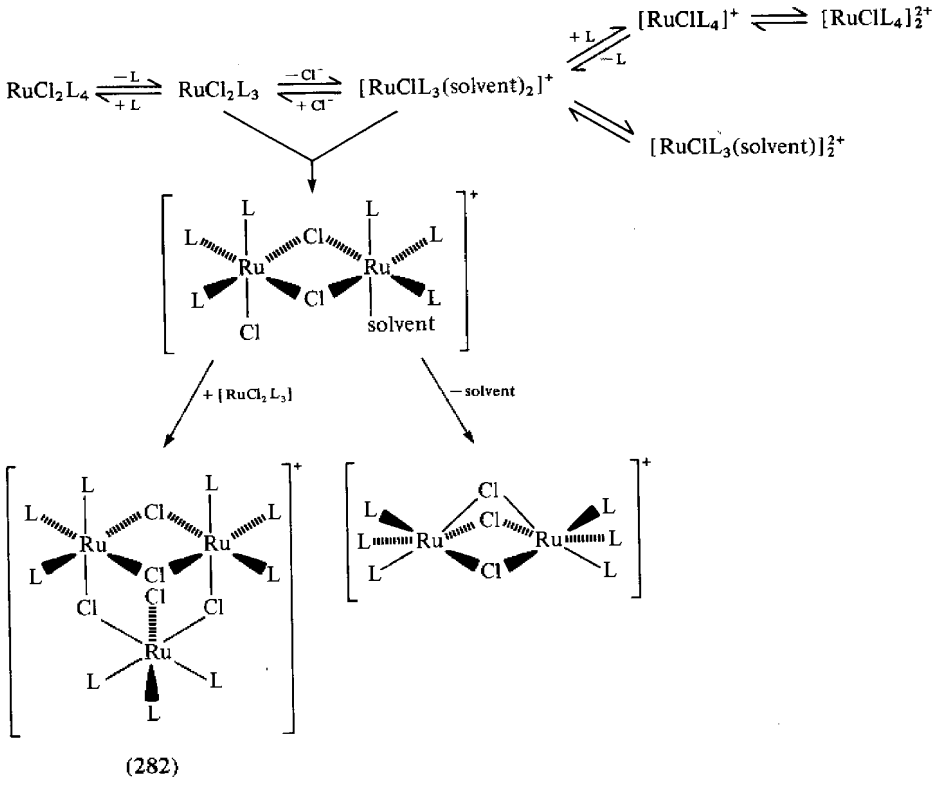
Compounds of the type $[L_3RuCl_3RuL_3]Y$ (L = various alkyl and aryl substituted PR_3; Y = Cl, ClO_4, SCN, BPh_4) were first prepared in 1961 by reaction of '$RuCl_3 \cdot xH_2O$' with L in aqueous MeOH or EtOH.[1591a] A wider range of these cations (L = $P(OR)Ph_2$, $P(OR)_2Ph$, $P(OR)_3$ (R = Me, Et), $AsRPh_2$, AsR_2Ph *etc.*) are now available, usually from reaction of '$RuCl_3 \cdot xH_2O$', $[RuCl_2(nbd)]_n$, $[RuCl_2(PPh_3)_n]$, Ru–arenes or the reduced 'ruthenium blue' solution with L in polar media.[629b,676,1531,1532,1533,1544,1550,1561,1585,1614b] The confacial bioctahedral geometry (**280**) has been verified by X-ray structural analyses for L = PEt_2Ph (Y = *mer*-$[RuCl_3(PEt_2Ph)_3]^-$),[1831] PMe_2Ph (Y = PF_6)[1832] and PMe_3 (Y = BF_4).[16a]

The related cations $[L_3RuX_3RuL_3]^+$ (X = OH^-, L = PMe_2Ph, $PMePh_2$, $P(OMe)Ph_2$; X = F, I, SH, SR; L = PMe_2Ph, $PMePh_2$) are synthesized by treatment of $[RuH(NH_2NMe_2)_3(cod)]^+$ with L in acetone/MeOH followed by addition of HX.[1753] The $[Ru_2(OH)_3(PMe_3)_6]^+$ cation is obtained from $[Ru_2(CH_2)_3(PMe_3)_6]$ and $[Ph_3C]BF_4$ in THF[1768] and crystal structures for this and the PMe_2Ph analogue are published. The $[Ru_2H_3L_6]^+$ cations [L = PMe_2Ph, PMe_3) are discussed in Section 45.10.4. Treatment of these hydroxo complexes with HX in $MeNO_2$ provides a high yield route to the pure $[Ru_2X_3L_6]^+$ cations (L = PMe_2Ph; X = Cl, Br, I).[1556] The iodo and bromo derivatives can also be prepared from $[Ru_2Cl_3L_6]^+$ and NaI or '$RuCl_3 \cdot xH_2O$', LiBr and L respectively[1614b] but ^{31}P NMR evidence indicates that these are a mixture of $[Ru_2Cl_nX_{3-n}L_6]^+$ cations.[1556]

Pyrolysis of $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ in methyl acetate or *n*-propyl propionate gives $[Ru_2Cl_3(PEt_2Ph)_6][RuCl_3(PEt_2Ph)_3]$ and/or the neutral binuclear complexes $[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]$ (**281**) (X-ray analyses available).[1617,1831,1833] An alternative route to the latter is by reaction of $[RuCl_2(PPh_3)_3]$ with L in non-polar solvents such as hexane or petroleum ether. Monomeric $[RuCl_2L_{3\text{ or }4})$ are first produced (see Section 45.5.4.2.i) and in solution these rearrange to $[Ru_2Cl_4L_5]$ and/or $[Ru_2Cl_3L_6]Cl$ depending on the nature of L and of the solvent (Scheme 56). High yields of $[Ru_2Cl_4L_5]$ (L = $PClPh_2$, $PEtPh_2$, PEt_2Ph) can be prepared by this intermolecular coupling method.[1544] For L = $P(OR)_2Ph$, $P(OR)Ph_2$ no neutral $[Ru_2Cl_4L_5]$ are observed and this is attributed to the high nucleophilicity of the Ru—P bonds. Instead, various ionic species such as $[Ru_2Cl_3L_6]^+$, $[RuCl\{P(OMe)Ph_2\}_4]^+$, $[RuCl\{P(OEt)Ph_2\}_4]_2^{2+}$ and $[Ru_3Cl_5\{P(OEt)Ph_2\}_9]^+$ (**282**) are isolated (Scheme 57).[1533] Reaction of $[Ru_2Cl_5(PEtPh_2)_4]$ with equimolar amounts of AgCl gives the fluxional heterotrimetallic complex $[Ru_2Cl_5(PEtPh_2)_4AgPEtPh_2]$ in which a Ag^I ion is linked to one terminal and two bridging-chloride ligands.[1832a] The double chloride-bridged $[RuCl(PMe_3)_4]_2Cl_2$ can be synthesized by leaving *trans*-$[RuCl_2(PMe_3)_4]$ in C_6H_6 for several weeks.[1529] Pyrolysis of $[Ru_2Cl_3\{P(OMe)Ph_2\}_6]Cl$ produces the unusual compound (**283**) in which all the Ru—P bonds are

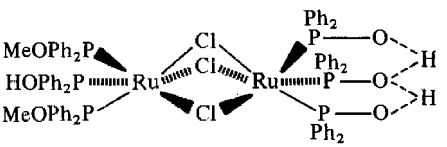


Scheme 56



(282)

Scheme 57



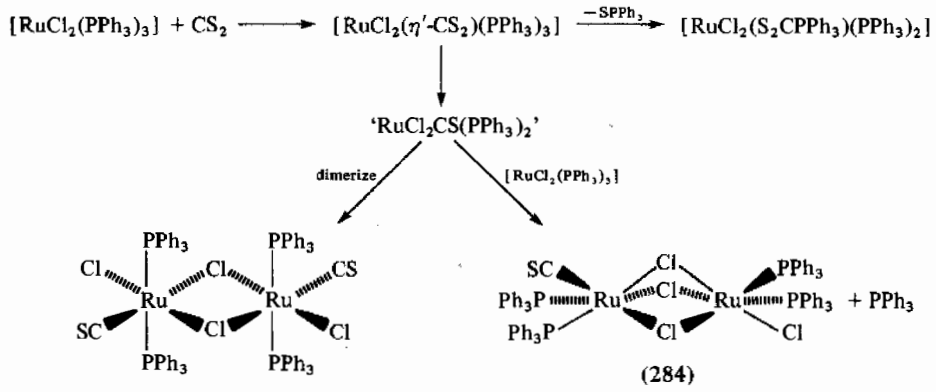
(283)

retained but some cleavage and partial hydrolysis of O—Me bonds has occurred[1834] (*cf.* (**258**) in Section 45.5.4.8.ii).

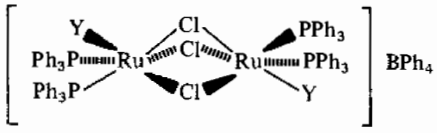
The neutral, binuclear complex $[(PPh_3)_2(CS)RuCl_3RuCl(PPh_3)_2]$ (**284**) (X-ray analysis available)[1835] together with some $[RuCl_2(CS)(PPh_3)_2]_2$ and $[RuCl_2(S_2CPPh_3)(PPh_3)_2]$ are obtained by reaction of $[RuCl_2(PPh_3)_3]$ with CS_2.[1639,1641] Possible reaction pathways are shown in Scheme 58 and these suggestions are supported by the high yield synthesis of $[Ru_2Cl_4Y(PR_3)_4]$ (Y = CO, CS; PR_3 = PPh_3, P(*p*-Tol)$_3$) from $[RuCl_2(PR_3)_3]$ and $[RuCl_2Y(PR_3)_2DMF]$ (equation 122).[1558,1616] Extension of this intermolecular coupling method to prepare $[(PPh_3)_2(CO)RuCl_3RuCl\{P(p\text{-}Tol)_3\}_2]$[1558] and $[(PPh_3)_2CORuCl_3OsCl(PPh_3)_2]$[1836a] is possible. Furthermore, heating $[RuCl_2Y(PPh_3)_2MeOH]$ in CH_2Cl_2 gives an isomeric mixture of $[PPh_3Cl(Y)RuCl_3Ru(Y)(PPh_3)_2]$ and reaction of these with PPh_3 and $Na[BPh_4]$ then affords the cations $[(PPh_3)_2YRuCl_3RuY(PPh_3)_2]BPh_4$ (**285**) (Y = CO, CS).[1616] Other routes to $[Ru_2Cl_4(CO)_2(PPh_3)_3]$ are by reaction of $[RuCl_3CO(nbd)]^-$ with an excess of PPh_3 in CH_2Cl_2,[1616] treatment of $[RuHX(CO)(PPh_3)_3]$ (X = H,[1580] Cl[1717]) with HCl in C_6H_6 or elimination of $SnCl_2$ from $[Ru_2Cl_3(SnCl_3)(CO)_2(PPh_3)_3]$ (**19** and Section 45.3.4.3).[109] Some NMR evidence for compounds of formulation '$[Ru_2Cl_4(L\text{–}L)_2(PPh_3)_2]$' (L–L = dppe, dppp) has been published[1601] and unpublished work[1555] suggests that the anionic $[Ru_2Cl_5(PPh_3)_4]^-$ is formed by addition of Cl^- to $[Ru_2Cl_4(DMA)(PPh_3)_4]$. A high yield method of incorporating ligands such as N_2, alkenes, alkynes *etc.* into the terminal positions of $[L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}]$ by displacement of terminal chloride using $Tl[BF_4]$ has been published.[1836b]

$$[RuCl_2Y(PR_3)_2DMF] + [RuCl_2(PR_3)_3] \xrightarrow[\Delta]{\text{acetone}} [(PR_3)_2YRuCl_3RuCl(PR_3)_2] + PR_3 + DMF \quad (122)$$

An isomeric mixture of the analogous PF_3 complex $[Ru_2Cl_4(PF_3)_2(PPh_3)_3]$ can be generated by reaction of $[RuH_2(PF_3)(PPh_3)_3]$ with HCl. Other methods of preparation of this compound are shown in Scheme 59. Methods (iii) and (iv) also afford $[(PPh_3)Cl(PF_2NMe_2)RuCl_3Ru(PF_2\text{-}NMe_2)(PPh_3)_2]$ whereas reaction of *cis*-$[RuCl_2(PF_2NMe_2)_2(PPh_3)_2]$ with equimolar amounts of

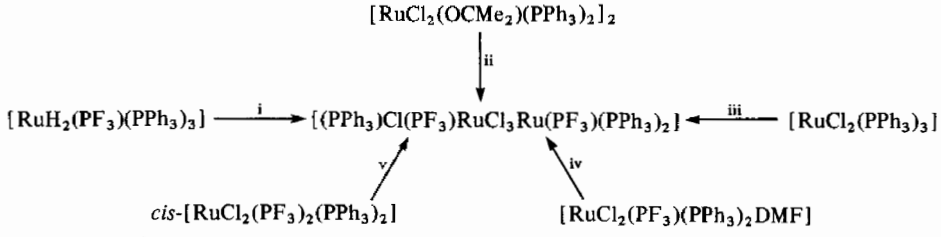


Scheme 58



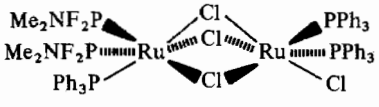
(285) Y = CO, CS

$[RuCl_2(PPh_3)_3]$ gives the isomers (**286**) and (**287**). The mono-PF_3 complex $[Ru_2Cl_4(PF_3)(PPh_3)_4]$ is obtained from reaction of $[RuCl_2(PPh_3)_3]$ with PF_3 in 2:1 molar ratio and the mixed PF_3/CO complex $[Ru_2Cl_4(CO)PF_3(PPh_3)_3]$ from $[Ru_2Cl_4CO(PPh_3)_4]$ and PF_3 (1:1 mole ratios).[1580] The heterobimetallic complexes (**288**) can be synthesized by intermolecular coupling of equimolar amounts of $[RuCl_2(PPh_3)_3]$ and *mer*-$[RhCl_3L_3]$ (L = PMe_2Ph, PEt_2Ph, PBu_3, PBu_2Ph, PPh_3).[1837]

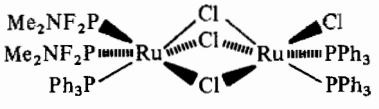


i, HCl gas; ii, PF_3; iii, PF_3 (1:1 mole ratio); iv, Δ; v, $[RuCl_2(PPh_3)_3]$ (1:1 mole ratio)

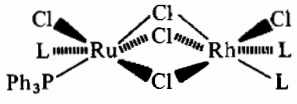
Scheme 59



(286)



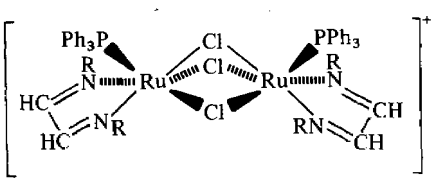
(287)



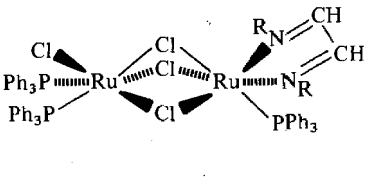
(288)

Another example of a neutral triple halide-bridged complex of this type is $[(PPh_3)_2ClRuCl_3RuN_2(PPh_3)_2]$ formed by treating $[RuCl_2(PPh_3)_4]$ in THF, in a reverse osmosis cell with nitrogen under pressure. This compound reacts with $N_2B_{10}H_8SMe_2$ to give $[(PPh_3)_2ClRuCl_3$-$Ru(N_2B_{10}H_8SMe_2)(PPh_3)_2]$.[1838] The interesting diazadiene complexes (**289**) and (**290**) have been prepared by reaction of $[RuCl_2(PPh_3)_3]$ with diazadiene in 1:2 and 2:1 molar ratios respectively. The unusual hydroxo-bridged complex $[(PPh_3)(Pr^iNCHCHNPr^i)RuCl(OH)_2RuH(PPh_3)_2]$ (**243**) (Sec-

tion 45.5.4.7.ii) is produced by the reaction of $[RuHCl(Pr^iNCHCHNPr^i)(PPh_3)_2]$ with water in toluene.[1770] A similar reaction between $[RuCl_2(PPh_3)_3]$ and a 1.5-fold molar excess of the electron-rich alkene $(MeNCH_2CH_2NMeC{=})_2$ $(L^{Me})_2$ affords $[Ru_2Cl_4(L^{Me})_3(PPh_3)_2]$.[1657a]



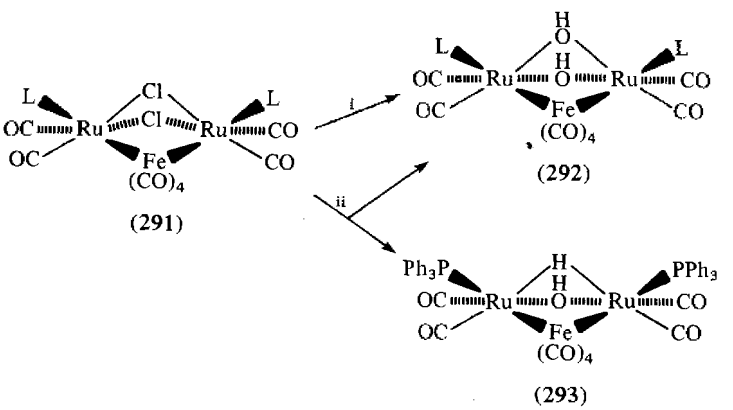
(289)



(290)

Some examples of electrogenerated triple halide-bridged ruthenium(II) anions are given in Section 45.5.6.

Finally, a series of related trimetallic halide- and hydroxo-bridged complexes have been reported. Thus reaction of $[Ru(arene)Cl_2L]$ with $[Fe_2(CO)_9]$ gives the novel complex $[Ru_2(\mu\text{-}Cl)_2\{\mu\text{-}Fe(CO)_4\}(CO)_4L_2]$ (**291**) which undergoes further reaction with aqueous Na_2CO_3 in acetone to give (**292**) and in isopropanol to give (**293**) and (**292**) (Scheme 60).[1519a] A report on the preparation of $[Ru_2(\mu\text{-}Cl)_2\{\mu\text{-}Fe(CO)_4\}(CO)_4Ph_2P(CH_2)_2PPh_2]$ is available.[1499]



(291)

(292)

(293)

L = PPh_3, PMe_3, $AsPh_3$, $Ph_2P(C{\equiv}CBu^t)$

i, Na_2CO_3/acetone; ii, Na_2CO_3/isopropanol

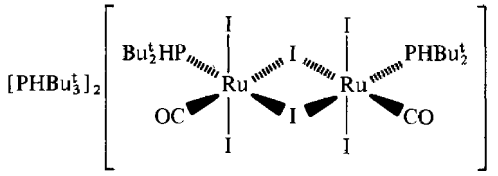
Scheme 60

45.5.5.2 Double halide-bridged complexes (and related species)

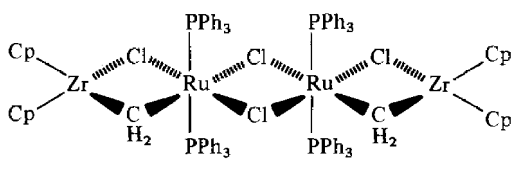
Reaction of $[Ru(CO)_4PPh_3]$ with halogens in boiling acetone or with chlorinated solvents at room temperature gives the dimeric species $[RuX_2(CO)_2PPh_3]_2$ (X = Cl, Br, I).[1454] The same compounds are formed by heating $[RuX_2(CO)_3PPh_3]$ in C_6H_6.[1606c] Related complexes $[RuX_2(CO)_2L]_2$ (X = Cl, Br; L = $PBu^t{}_2Ph$, $PBu^t{}_2(p\text{-Tol})$, $PBu^t{}_3$) are obtained by treatment of the ruthenium(I) dimers $[RuCl(CO)_2L]_2$ with halogens.[1519,1520b] or (for X = I) by reaction of $[RuI_2(CO)_3]_2$ with $PBu^t{}_3$ for short periods in 2-methoxyethanol;[1839] $[RuCl_2(CO)_2L_3]_2$ (L = PMe_3, PEt_3) are also known.[1840] All these compounds have terminal CO groups and bridging and terminal halides. Reaction of '$RuCl_3 \cdot xH_2O$' with ethylene-1,2-bis(diphenylarsine) (eda) in boiling 2-methoxyethanol gives $[RuCl_2CO(eda)]_2$.[45] Analogous compounds $[RuCl_2CO(L)_2]_2$ with PR_3 and AsR_3 ligands are obtained by treatment of $[RuCl_3CO(nbd)]^-$ with PPh_3,[659] heating $[RuCl_2CO(AsPh_3)_3]$ in toluene[1841a] or by leaving all *trans*-$[RuCl_2(CO)_2(PMe_2Ph)_2]$ to stand in acetone for several days.[1608] The thiocarbonyl complexes $[RuCl_2(CS)(L)_2]_2$ (L = PPh_3,[1638,1639,1641] $P(p\text{-Tol})_3$[1558]) are also available *via* $[RuCl_2L_3]$ and CS_2. Reaction of '$RuCl_3 \cdot xH_2O$', PMe_3 and CO gave $[RuCl_2(CO)_2(PMe_3)]_2$ which catalysed the alcoholysis of Et_3SiH.[1841b]

Other CO and CS double halide-bridged species include the cations $[RuClY\{P(OEt)Ph_2\}_3]_2(BPh_4)_2$ (Y = CO, CS) obtained by dissolution of $[RuCl_2Y\{P(OEt)Ph_2\}_3]$ in EtOH containing $Na[BPh_4]$,[1615] and the novel anionic complex (**294**) from reaction of '$RuCl_3 \cdot x$-

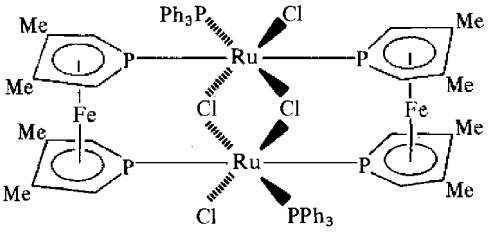
H_2O', NaI, PBu^t_3 with CO in refluxing 2-methoxyethanol.[1839] As discussed elsewhere (Scheme 57, Section 45.5.5.1) the $[RuCl\{P(OEt)Ph_2\}_4]^{2+}_2$ cation can be prepared from $[RuCl_2(PPh_3)_3]$ or $[RuCl_2(P(OEt)Ph_2)_3]$ treated with $P(OEt)Ph_2$ in EtOH[1535] and $[RuCl(PMe_3)_4]^{2+}_2$ is also known.[1529] Under UV irradiation, reaction of $[RuCl_2(PPh_3)_3]$ and $[ZrCp_2MeCl]$ affords the interesting zirconium–ruthenium complex (**295**)[1691] and direct reaction of '$RuCl_3 \cdot xH_2O$' tritertiary phosphine $PhP\{(CH_2)_2PPh_2\}_2$ (L) in boiling EtOH gives the binuclear chloride-bridged $[RuCl_2L]_2$.[1842] Treatment of $[RuCl_2(PPh_3)_3]$ with 3,3',4,4'-tetraMe-1,1'-diphosphaferrocene (DPF) gives the unusual binuclear complex $[RuCl_2(DPF)PPh_3]_2$ whose structure (**296**) was confirmed by X-ray analysis.[1568] Reduction of $[Ru_2Cl_5(PEt_2Ph)_4]$ with $Na[BH_4]$ in the presence of C_2H_4 or PhC≡CH(L') leads to the double halide-bridged complexes $[(PEt_2Ph)_3ClRu(\mu\text{-}Cl)_2RuL'_2Cl(PEt_2Ph)]$.[1836b]



(294)



(295)

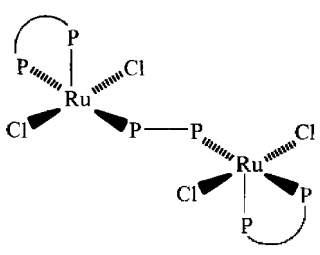


(296)

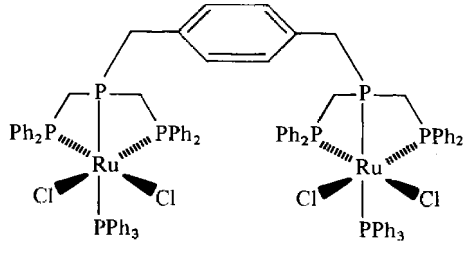
The following double halide-bridged compounds are discussed elsewhere: $[RuCl_2(PPh_3)_2]_n$ (Section 45.5.4.2.i), $[RuCl_2(AsPh_3)_2]_n$ (?) (Section 45.5.4.2.ii), $[RuCl_2(CO)L\text{–}L]_2$ (L–L = *o*-$C_6H_4(EMePh)_2$; E = P, As) (Section 45.5.4.5.i), $[RuCl_2CO(SP)]_2$ (Section 45.5.4.5.vi), $[RuCl(CO)(CONHR)(PPh_3)_2]_n$ (Section 45.5.4.6.i), $[RuCl(N\text{–}N)(PPh_3)_2]_2Cl_2$ (N–N = bipy, phen) (Section 45.5.4.6.ii), $[RuCl\{CHMe(CN)\}CO(PPh_3)_2]_2$ (Section 45.5.4.5.iv), $[RuCl_2NO(\{P(OEt)_2O\}_2H)]_2$ (Section 45.5.4.6.iii), $[RuCl_2(NNAr)(PPh_3)_2]^{n+}_n$, $[Ru_2Cl_2(MeCN)_3(NNAr)_2(PPh_3)_4]^{2+}$ (Section 45.5.4.6.iv), $[RuCl_2(MeCN)(PPh_3)_2]_2$ (Section 45.5.4.6.vi), $[RuCl_2(PPh_3)_2Me_2CO]_n$ (Section 45.5.4.7.i), $[RuCl(acac)(EPh_3)_2]_2$ (Section 45.5.4.7.iii), $[RuCl_2(SPPh_3)PPh_3]_2$ and $[RuCl_2(SPPh_3)CO]_2$ (Section 45.5.4.8.vii).

45.5.5.3 Binuclear complexes with polydentate phosphine bridges

The chiral ditertiary phosphine, diop, displaces all three PPh_3 groups from $[RuCl_2(PPh_3)_3]$ to give the green binuclear complex $[Ru_2Cl_4(diop)_3]$ (**297**),[1571,1843] which is a good catalyst for asymmetric transfer hydrogenation of prochiral unsaturated acids or esters by alcohols.[1571,1844,1845] The analogous compound $[Ru_2Cl_4(dppb)_3]$ is obtained either by reaction of dppb with $[RuCl_2(PPh_3)_3]$ or $K_2[RuCl_5(OH_2)]$[1535] or by decomposition of $[RuHCl(dppb)_2]$.[1846a] Reaction of $[RuCl_2(cod)]_n$ with 2,2'-bis-(diphenylphosphine)-1,1'-binaphthyl (BINAP) gives the chiral $[Ru_2Cl_4(BINAP)_2NEt_3]$ which is an



(297)



(298)

excellent catalyst for asymmetric hydrogenation of alkenes and some cyclic anhydrides.[1846b] Prolonged reaction of $[RuCl_2(PPh_3)_3]$ in hot C_6H_6 with the hexadentate ligand TDDX gives the bridged complex (**298**),[1538] and the related complexes $[RuCl_2(CO)_2]_2L$ (L = $Ph_2P(CH_2)_2P(Ph)(CH_2)_2$-$P(Ph)(CH_2)_2PPh_2$ (tet-1) and $P[(CH_2)_2PPh_2]_3$ (tet-2) are also known.[1540] The cation $[(bipy)_2ClRu(\mu$-dppm$)RuCl(bipy)_2]^{2+}$ can be prepared by treatment of $[RuCl_2(bipy)_2]$ with dppm in EtOH.[1267]

45.5.5.4 Miscellaneous

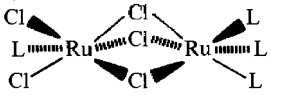
Other bi-, tri-, tetra- or poly-nuclear Ru^{II} complexes mentioned in earlier sections are $[(RuCl_2$-$CO(PCy_3)_2)_2TCNE]$ (Section 45.5.4.5.vi), $[RuCl_2(N_2H_4)(PMe_2Ph)_2]_2$ (Section 45.5.4.6.i), $[Ru(NCS)_2(PPh_3)_2]_n$ (Section 45.5.4.6.ii), various bi- and tetra-nuclear hydrido and halo/hydroxo compounds (Section 45.5.4.7.ii), $[RuX_2NO(EPh_3)_2]_2Y$ (Y = S, SO) (Section 45.5.4.8.1), $[Ru(SC_6$-$F_5)(bipy)(PPh_3)_2]_2$, $[RuI(SH)(CO)(CNR)PPh_3]_2$, $[RuCl(2\text{-}HSC_5H_4N)(2\text{-}SC_5H_4N)PPh_3]_2$, $[Ru_3Cl_3S_2(PPh_3)_3]$ (Section 45.5.4.8.i), $[RuSO_4(SO_2)(PPh_3)_2]_2$ (Section 45.5.4.7.v), $[Ru_3Cl_3$-$(SO_2)_3(PPh_3)_4]$ (Section 45.5.4.8.vi) and $[RuPdCl_2(CO)(PPh_2py)_2]$ (Section 45.5.4.9.i).

45.5.6 Mixed Valence Ruthenium(II)/Ruthenium(III) Complexes

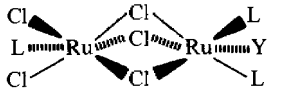
The first formally mixed valence $Ru_2^{II/III}$ complexes, namely $[Ru_2Cl_5L_4]$ (L = PBu^n_3, $P(pent)^n_3$) were synthesized in 1967 by the prolonged interaction of excess L on '$RuCl_3 \cdot xH_2O$' in EtOH[1847] and the 'symmetric' structure (**299**) was later confirmed by X-ray analysis for L = PBu^n_3.[1848] More recently, the corresponding red-brown $As(p\text{-}Tol)_3$ and $AsPh_3$ complexes have been prepared by reaction of '$RuCl_3 \cdot xH_2O$' with excess AsR_3 in EtOH and butan-2-ol respectively.[1588] The latter was previously reported as the Ru^{II} polymer $[RuCl_2(AsPh_3)_2]_n$.[1587] However, reaction of '$RuCl_3 \cdot xH_2O$' with $As(p\text{-}Tol)_3$ in butan-2-ol or with $As(p\text{-}C_6H_4Cl)_3$ in MeOH gives the yellow-green isomer (**300**). Evidence for these formulations comes from detailed ESR, magnetic and electrochemical studies and is supported by the single crystal X-ray structure of $[(PEt_2Ph)Cl_2RuCl_3Ru(PEt_2Ph)_3]$ (**300**), synthesized by aerial oxidation of $[(PEt_2Ph)_2ClRuCl_3Ru(PEt_2Ph)_3]$ (Section 45.5.5.1) in HCl/$MeNO_2$ solution.[1588] The related complexes $[(PR_3)_2YRuCl_3RuCl_2PR_3]$ (Y = CO, CS; R = Ph, *p*-Tol) are produced by aerial oxidation of $[(PR_3)_2YRuCl_3RuCl(PR_3)_2]$ (Section 45.5.5.1) and are believed to have structure (**301**).[1556,1639,1836a,1849] The mixed valence complexes $[Ru_2Cl_5(mppl)_4]$[1567] (mppl = 3-methyl-1-phenylphosphole) and $[Ru_2Cl_5(dpae)_2]$[1588] are also known.



(299)



(300)

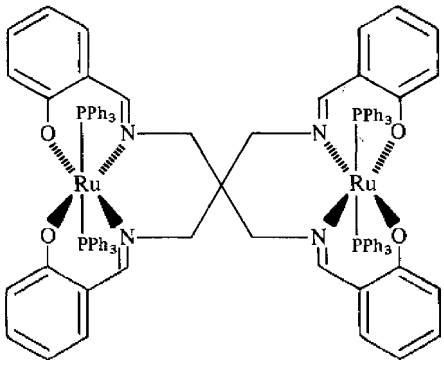


(301)

Other mixed valence triple halide-bridged $Ru_2^{II,III}$ complexes can be generated electrochemically from stable $Ru_2^{II,II}$ or $Ru_2^{III,III}$ compounds and characterized by *in situ* spectroscopic measurements. Examples include $[Ru_2Cl_3(PEt_2Ph)_6]^{2+}$ $[Ru_2Cl_4(PEt_2Ph)_5]^+$, $[Ru_2Cl_4Y(PPh_3)_4]^+$ (Y = CO, CS), and $[Ru_2Cl_6\{As(p\text{-}Tol)_3\}_3]^-$. An examination of the intervalence charge transfer bands in the optical spectra of these complexes reveals that the degree of metal–metal interaction decreases as the molecular asymmetry increases. Bulk electrogeneration, followed by *in situ* characterization, of $Ru_2^{II,II}$ anions such as $[(PEt_2Ph)Cl_2RuCl_3Ru(PEt_2Ph)_3]^-$ and $[As(p\text{-}Tol)_3Cl_2RuCl_3RuCl\{As(p$-$Tol)_3\}_2]^{2-}$ is also possible.[1556,1850]

The mixed valence $[(bipy)_2ClRu(\mu$-dppm$)RuCl(bipy)_2]^{3+}$ cation, which is a valence-trapped species with an intervalence charge transfer band at 8020 cm^{-1}, is synthesized by stoichiometric oxidation of $[(bipy)_2ClRu(\mu$-dppm$)RuCl(bipy)_2]^{2+}$ with $[Fe(bipy)_3]^{3+}$.[1267] Compound (**302**) has been prepared and in the semioxidized $Ru^{III} \cdots Ru^{II}$ complex derived from (**302**), some interaction between Ru atoms is proposed although no intervalence charge transfer band is detected.[1758a]

The synthesis and reactivity of complexes such as $[Ru_3O(OCOMe)_6(PPh_3)_3]$ in which the ruthenium has a mean oxidation state of $+2\frac{2}{3}$ are covered in Section 45.6.5.



(302)

45.5.7 Mononuclear Ruthenium(III) Complexes

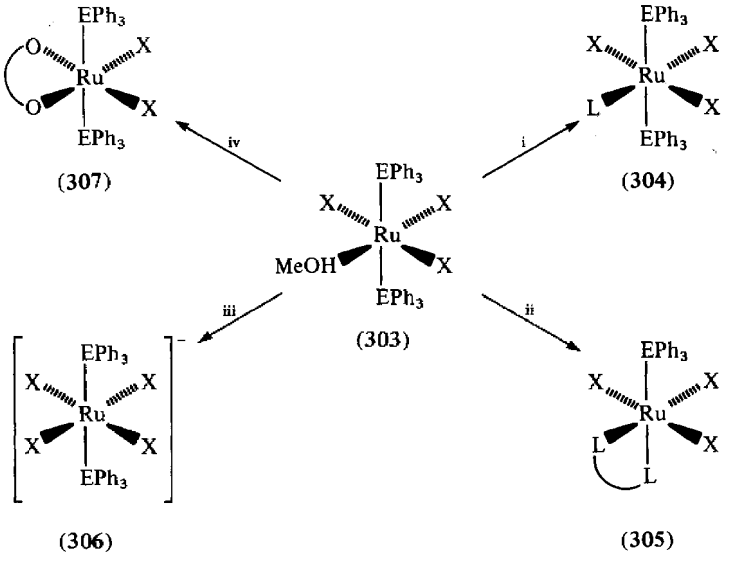
45.5.7.1 Monodentate P, As and Sb donor ligand complexes

An extensive series of paramagnetic Ru^{III} complexes $[RuCl_3L_3]$ ($L = PR_3$ or AsR_3) can be synthesized from '$RuCl_3 \cdot xH_2O$' concentrated HCl and L in EtOH, using much shorter reaction times than those required to give $[Ru_2Cl_3L_6]Cl$ or $[RuCl_2L_4]$.[1584,1585,1851] The bromo compounds are also available and IR and ESR studies suggest meridional structures.[1722,1852,1853] The phosphole complex $[RuCl_3(dmppl)_3]$ (dmppl = 3,4-dimethyl-1-phenylphosphole) is also reported.[1567] However, for $L = AsPh_3$[106] and $As(p\text{-}Tol)_3$[625,1582] reaction with '$RuCl_3 \cdot xH_2O$' in boiling MeOH gives the green methanolates $[RuCl_3(AsR_3)_2MeOH]$ (**303**) and the PPh_3 analogue is obtained in low yield by shaking MeOH solutions of PPh_3 with '$RuCl_3 \cdot xH_2O$' (2:1 molar ratio).[106] The bromo compounds are known and the preparation of $[RuCl_3(AsPh_3)_3]$ (two isomers?) and $[RuCl_3(AsPh_3)_2OAsPh_3]$[1726] (previously formulated as $[RuCl_3(AsPh_3)(OAsPh_3)_2]$)[1854] is also published. Note however that the compound reported as $[RuCl_2(AsPh_3)_3O_2]$[1583] has been reformulated as the binuclear μ-peroxo complex $[(AsPh_3)_3Cl_2RuO_2RuCl_2(AsPh_3)_3]Cl_2$[1778] although earlier workers[1547] suggested that all the physicochemical properties could be ascribed to Ru^{III} arsine oxide complexes. Further work to resolve these differences is now required.

As shown in Scheme 61, these $[RuX_3(EPh_3)_2MeOH]$ complexes are excellent precursors for the synthesis of a wide range of low spin Ru^{III} compounds containing O, N or S donor ligands.[106,1697,1855,1856] The same types of compound can be prepared from $[RuX_3\{As(p\text{-}Tol)_3\}_2MeOH]$,[625,1582] $[RuCl_3(AsPh_3)_3]$ or '$[RuCl_3(AsPh_3)_2OAsPh_3]$'.[1726,1749] Thus the labile MeOH group can be replaced by a variety of donor ligands L to give $[RuX_3(EPh_3)_2L]$ (**304**). For L = pyridine, the monopyridine complex could be isolated only by adding a large excess of light petroleum to quench the reaction immediately after addition of pyridine.[1855] The related *mer,trans*-$[RuCl_3(NH_3)\{P(OMe)_3\}_2]$ is obtained as a by-product from reaction of '$RuCl_3 \cdot xH_2O$' (containing nitrogen impurity) with $P(OMe)_3$ in refluxing MeOH.[1562] Ligands such as pyridine, Me_2S, isocyanides and the bidentate bipy and phen also displace one of the EPh_3 groups from (**303**) to give $[RuX_3(EPh_3)L_2]$ (**305**). The mixed $[RuCl_3(PPh_3)py(CNR)]$ is prepared by treatment of the reactive $[RuCl_3(PPh_3)_2py]$ with CNR.[1855] Spectroscopic and dipole moment measurements support the proposed structures. Treatment with halide ion in the presence of a large cation gives the Ru^{III} anions (**306**). For E = P, the same compound is produced by reaction of $[RuCl_2(PPh_3)_3]$ with MCl/HCl ($M = AsPh_4^+$, Me_4N^+) or $Ph_4As[Ru(N)Cl_4]$ with PPh_3 in cold acetone.[1857] Other anions can be prepared either by direct exchange with $[RuCl_4(EPh_3)_2]^-$ (*e.g.* $L = P(OPh)_3$, PEt_3, PMe_2Ph) or, as their phosphonium salts, by reaction of the 'RuCOCl' solution with excess L ($L = PEt_3$, PEt_2Ph, PMe_2Ph).[1749,1858] The *trans* structure is established by ESR and IR spectroscopy[1852,1858,1859] and their magnetic circular dichroism and optical spectra have been analysed.[1860] Under more forcing conditions, reduction of (**303**) to Ru^{II} complexes generally occurs (see Section 45.5.4 for examples). However, rather surprisingly, *mer*-$[RuCl_3L_3]$ ($L = PPh_3$, $PMePh_2$, PMe_2Ph, $PEtPh_2$) have been synthesized by reaction of $[RuCl_3(AsPh_3)_2MeOH]$ with an excess of L in boiling C_6H_6.[1586]

An electrochemical survey of many of these compounds has been reported. Most of the neutral compounds show a reversible one-electron reduction and an irreversible one-electron oxidation whereas the anions (**306**) exhibit irreversible reduction and quasi-reversible oxidation behaviour.[625]

Reaction of (**303**) or $[RuCl_3(EPh_3)_3]$ with β-diketones leads to partial replacement of halide and

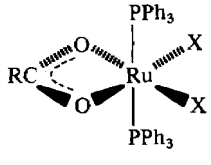


(X = Cl, Br; E = P, As – not all possible combinations)

i, L = Me_2CO, THF, $MeNO_2$, DMF, DMSO, RCHO, NH_3, $MeNH_2$, Et_2S, CS, py, RCN (R = Me, Pr, Ph, $PhCH_2$, CH_2=CH) *etc.*; ii, L = ½ bipy, ½ phen, Me_2S, py, 2-MeC_5H_4N, pyrazine, 4,4′-bipy, 1,4-dithian, CNR; iii, X = Cl^-; Br^-; iv, various β-diketones

Scheme 61

formation of $[RuX_2(dike)(EPh_3)_2]$ (**307**);[1861,1862] $[RuCl_2(acac)(dppe)]$ is also known.[1863] The bromotropolonate complexes $[RuCl_2L(EPh_3)_2]$ (L = bromotropolonate, E = P, As) are given by reaction of L with $[RuCl_3(EPh_3)_3]$,[1864] whereas $[RuCl_3(PPh_3)_3]$ and *N*-phenylcarbamoylpyrrole-2-thiocarboxamide (PTH) afford S-bonded $[RuCl_3(PTH)_2(PPh_3)]$.[1819] Treatment of $[RuX_2(PPh_3)_3]$ with RCO_2H in aerated solvents affords $[RuX_2(OCOR)(PPh_3)_2]$ (R = Me, Et, Ph, *p*-Tol *etc.*) whose structure (**308**) is established by X-ray analysis (for X = Cl; R = Ph).[1865] This compound is also prepared by reaction of $[RuCl_2(PPh_3)_3]$ with dibenzoyl peroxide.[1866] A route to $[RuCl_2(OCOR)(AsPh_3)_2]$ (R = Me, Et) is published although it was suggested these are dimeric with chloride bridges and unidentate ^-OCOR ligands.[1704]



(308)

A number of cationic Ru^{III} compounds containing P or As donor ligands are known. Examples include $[RuCl_2(CNR)(PR_3)_3]^+$ (from reaction of *mer*-$[RuCl_3(PR_3)_3]$ and CNR, see Section 45.5.4.5.iii),[1647] $[RuCl_2bipy(PPh_3)_2]BPh_4$ (from $[RuCl_3(PPh_3)_2(MeNO_2)]$, bipy and $Na[BPh_4]$ heated in MeOH) and $[RuCl_2(PhCN)(bipy)(PPh_3)]Cl\cdot H_2O$ (from $[RuCl_3(bipy)PPh_3]$ in MeOH treated with an excess of PhCN).[1713] Studies have revealed that oxidation of $[RuCl_2(PMe_3)_4]$ with $AgPF_6$ gives $[RuCl_2(PMe_3)_4]PF_6$.[1391c]

45.5.7.2 Bi- and poly-dentate P and As donor ligand complexes

The ruthenium(III) cations *cis*- or *trans*-$[RuCl_2(L–L)_2]ClO_4$ (L–L = dmpe, depe) are readily prepared by treatment of the corresponding *cis*- or *trans*-$[RuCl_2(L–L)_2]$ with $HClO_4$; their ESR spectra are reported.[1591a,1852] Oxidation of *trans*-$[RuCl_2(dppm)_2]$ with $NO[BF_4]$ affords *trans*-$[RuCl_2(dppm)_2]BF_4$ although this must be isolated rapidly to avoid conversion to nitrosyl complexes.[1593] Chemical or electrochemical oxidation of *cis*-$[RuCl_2(dppm)_2]$ also gives *trans*-

$[RuCl_2(dppm)_2]^+$.[1598] Oxidation of $[RuCl_2(diars)_2]$ with Cl_2 in the presence of X^- produces *trans*-$[RuX_2(diars)_2]X$ (X = Cl, Br, I)[1592] and other Ru^{III} cations generated by oxidation of their neutral Ru^{II} precursors include $[Ru(1,2\text{-}O_2C_6X_4)(CO)_2(PPh_3)_2]^+$ (X = Cl, Br)[1777a] and $[RuCl_2\{PPh_2(2\text{-}MeOC_6H_4)\}_2]^+$.[1824] Direct reaction of '$RuCl_3 \cdot xH_2O$' with the neopentyldi(tertiary phosphine), $(Me_3CCH_2)_2P(CH_2)_2P(CH_2CMe_3)_2$, gives $[RuCl_2(L\text{–}L)_2]^+$[1867] whereas with $Ph_2P(CH_2)_2SPh$ (SP), $[RuCl_3SP]$ is first produced.[1829]

Few Ru^{III} complexes containing polydentate P or As donor ligands are known. Thus, reaction of '$RuCl_3 \cdot xH_2O$' with the hexatertiary phosphine $[Ph_2PCH_2CH_2]_2P(CH_2)_2P[CH_2CH_2PPh_2]_2$ (L) in boiling EtOH gives the brown Ru^{III} cation $[RuCl_2L]^+$ isolatable as its PF_6^- salt (μ_{eff} = 1.7 BM); tetradentate coordination of the ligand is proposed.[1868] In contrast, reaction of the closely related TDDX ligand (see Section 45.5.4.1) with '$RuCl_3 \cdot xH_2O$' gives the binuclear Ru^{III} cation $[Ru_2Cl_4(TDDX)](PF_6)_2$ (*cf.* $[Ru_2Cl_4(PPh_3)_2TDDX]$ (**298**), Section 45.5.5.3).[1538] Chlorine oxidation of $[RuCl_2\{N(CH_2CH_2PPh_2)_3\}]$ affords the corresponding Ru^{III} cation.[1595]

45.5.8 Bi- and Tri-nuclear Ruthenium(III) Complexes

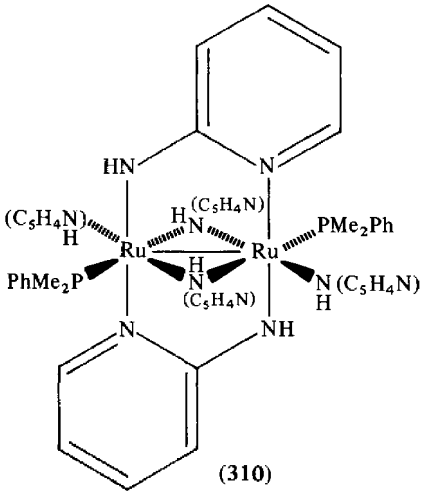
Heating the methanolates $[RuX_3(AsR_3)_2MeOH]$ (**303**) (X = Cl, Br; R = Ph, *p*-Tol) in non-coordinating solvents such as C_6H_6 or CH_2Cl_2 provides a high yield route to the paramagnetic triple halide-bridged complexes $[(AsR_3)X_2RuX_3RuX(AsR_3)_2]$ (**309**). These undergo stepwise, one-electron reductions to form the $[Ru_2X_6(AsR_3)_3]^{n-}$ anions (n = 1,2).[1850] Under milder conditions, loss of MeOH from (**303**) in the above solvents gives brown compounds of empirical formula $[RuX_3(AsR_3)_2]$. Monomeric trigonal bipyramidal structures were initially proposed for these species[1582,1697,1859] but on the basis of electrochemical evidence (two reversible one-electron reductions), they were reformulated as the double halide-bridged $[(AsR_3)_2X_2RuX_2RuX_2(AsR_3)_2]$.[625] However a comparison of electrochemical, magnetic, ESR and optical spectral properties strongly indicates that the latter are also the triple halide-bridged $[Ru_2X_6(AsR_3)_3]$ (**309**) containing one molecule of clathrated AsR_3.[1869] (*cf.* $[RuCl_2(PPh_3)_3] \cdot PPh_3$).[1543,1544]

Related binuclear complexes $[Ru(NCS)_3(EPh_3)_2]_2$ (E = As, Sb) can be prepared by reaction of $[RuCl_3(EPh_3)_3]$ with $NH_4[NCS]$.[1704,1711] These are formulated as double bridged species but they might be $[Ru_2(NCS)_6(EPh_3)_3]EPh_3$. There are two brief references to $[RuX_3(PPh_3)_2]_n$ complexes; $[RuI_3(PPh_3)_2]_2$ from reaction of $[RuH_2(PPh_3)_4]$ with I_2[1870] and $[RuCl_3(PR_3)_2]_2$ (R = Bu, Pr, Pent) from '$RuCl_3 \cdot xH_2O$' and PR_3 in EtOH.[1847] The latter is formulated as a double chloride-bridged species but more definitive evidence is now required. The interesting complex $[RuCl_3(mppl)]$ (mppl = 3-methyl-1-phenylphosphole) is also known.[1567] Electrogeneration and *in situ* spectroscopic characterization of triply halide-bridged binuclear $Ru_2^{III,III}$ cations such as $[Ru_2Cl_5(PEt_2Ph)_4]^+$, $[Ru_2Cl_3(PEt_2Ph)_6]^{3+}$ and $[Ru_2Cl_4(PEt_2Ph)_5]^{2+}$ have been accomplished;[1850] oxygenation of $[RuCl_3(AsPh_3)_3]$ is claimed to give the binuclear μ-peroxo complex $[(AsPh_3)_3Cl_2RuO_2RuCl_2(AsPh_3)_3]Cl_2$ rather than $[RuCl_3(AsPh_3)_2(OAsPh_3)]$ (see Section 45.5.7.1).[1778]

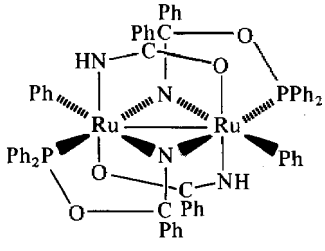
Reaction of $[Ru_2(OCOMe)_4Cl]$ with $Li[C_5NH_4NH]$ in THF followed by addition of PMe_2Ph gives dark red crystals of $[Ru_2(C_5NH_4NH)_6(PMe_2Ph)_2]$, shown by X-ray analysis to have structure (**310**), in which the anionic ligand exhibits three modes of coordination. This is the first edge-sharing



(309)



(310)



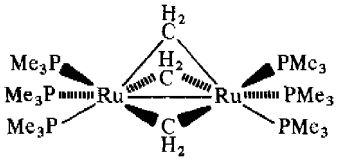
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biooctahedral molecule having a bond between two d^5 metal atoms and also the first in which the (μ_2, η^1) bridging atoms are imido nitrogen atoms.[1817a]

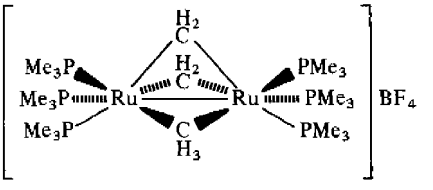
Treatment of $[Ru_2(OCOMe)_4Cl]$ with excess molten benzamide ($PhCONH_2$) affords $[Ru_2(PhCONH)_4Cl]$ which reacts with PPh_3 in DMSO/MeOH to generate the novel complex $[Ru_2(Ph)_2(PhCONH)_2(\mu\text{-}NC(Ph)OPPh_2)_2]$ (**311**). This consists of two equivalent Ru^{III} atoms surrounded by a distorted octahedron of ligand atoms. The $Ph_2POC(Ph)N^-$ ligand coordinates through its P and N atoms to form a five-membered chelate ring and the nitrogen atom also serves as a bridge to the other Ru atom. This chelating ligand is (at least formally) the product of attack of a $PhCONH^-$ oxygen atom on Ph_3P with concomitant shift of a phenyl group to Ru and loss of H.[1871b]

The reaction between $[Ru_3O(OCOMe)_6(OH_2)_3]OCOMe$ and $MgMe_2$ in the presence of PMe_3 yields the diamagnetic tri-μ-methylene complex (**312**). The short Ru^{III}—Ru^{III} distance of 2.650(1) Å probably indicates the presence of a metal–metal bond and hence accounts for the observed diamagnetism. Compound (**312**) reacts with one equivalent of HBF_4 or $[Ph_3C]BF_4$ to give $[(Me_3P)_3Ru(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)Ru(PMe_3)_3]BF_4$ (**313**) and with an excess of HBF_4 or CF_3SO_3H to eliminate methane and produce $[(Me_3P)_3Ru(\mu\text{-}CH_2)_2Ru(PMe_3)_3](BF_4)_2$ (**314**). The above protonation can be readily reversed by addition of alkyllithiums.[1521,1768,1872]

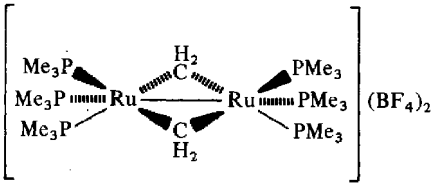
The remarkable trinuclear cation (**315**) is isolated by protonation with HBF_4 of the red oil which is also obtained from the $[Ru_3O(OCOMe)_6(OH_2)_3]OCOMe$, $MgMe_2$, PMe_3 reaction mixture. This formally contains two Ru^{III} and a central, tetrahedrally coordinated Ru^{IV} ion.[1521,1768,1872]



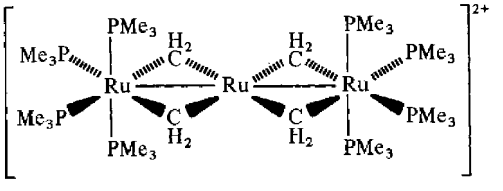
(312)



(313)



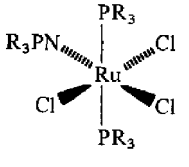
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(315)

45.5.9 Ruthenium(IV) and Higher Oxidation State Complexes

There are few Ru^{IV} complexes containing soft P, As or Sb donor ligands. Treatment of $Bu^n{}_4N[RuNCl_4]$ with EPh_3 in boiling acetone gives the diamagnetic $[Ru^{VI}Cl_3N(EPh_3)_2]$ (E = Sb, As). Further reaction of the $AsPh_3$ compound with various PR_3 in cold acetone produces the novel phosphineimidato complexes $[RuCl_3(NPR_3)(PR_3)_2]$ (PR_3 = PPh_3, $PEtPh_2$, PEt_2Ph, $PMePh_2$, PEt_3); with PMe_2Ph, the intermediate $[RuCl_3(NPMe_2Ph)(AsPh_3)_2]$ is isolated.[1857] Magnetic moments typical of Ru^{IV} (μ_{eff} *ca.* 2.8 BM at room temperature) are observed and the structure (**316**) is confirmed by X-ray analysis of the $[RuCl_3(NPEt_2Ph)(PEt_2Ph)_2]$ complex.[1873]



(316)

Other Ru^{IV} complexes discussed elsewhere include $[RuCl_2(C_6X_4O_2)(PPh_3)_2]$ (X = Cl, Br) (Section 45.5.4.7.iii), $[RuH_3(SiR_3)(PPh_3)_3]$ (Section 45.3.2.3), $[RuH_4(PPh_3)_3]$, $[RuH_4(PPh_3)_2]_2$, $[RuH_3(PR_3)_4]^+$ (Section 45.10.5), $[RuF_4(PF_3)]_n$ and $RuF_4 \cdot AsF_5$ (Section 45.9.7.2).

Higher oxidation state complexes are confined to $[RuO_4PF_3]$ and $[RuO_4(PF_3)_2]$ (from RuO_4 and PF_3). Similar reactions with PCl_3 or PBr_3 reduce the tetroxide to RuO_2PX_3 (X = Cl, Br).[1874] Preliminary communications on the hexahydrides $[RuH_6(PR_3)_2]$ (R = Ph, Cy) have recently appeared (see Section 45.10.5).

45.5.10 Useful Books and Reviews

For more detailed information about P, As, and Sb donor ligand complexes, the following books and reviews are recommended. 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands' edited by C. A. McAuliffe, McMillan, 1973; 'Phosphine, Arsine and Stibine Complexes of the Transition Elements' by C. A. McAuliffe and W. Levason, Elsevier, 1979; 'Comprehensive Organometallic Chemistry' edited by Sir Geoffrey Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, 1982, Volume 4, Sections 32.1 to 32.9, 'The Chemical and Catalytic Reactions of Dichlorotris(triphenylphosphine)ruthenium(II) and its Major Derivatives' by F. H. Jardine in *Progress in Inorganic Chemistry*, 1984, volume 31, pp. 265–370, 'The Chemistry of Ruthenium' by E. A. Seddon and K. R. Seddon, Elsevier, 1984, chapters 7–14, and volume 7 (Comprehensive Review Index) of this series.

45.6 OXYGEN LIGANDS

Ruthenium complexes of oxygen donor ligands incorporating other donor ligands are discussed in the corresponding section for the other ligand. Ternary and related compounds are outside the scope of this review.

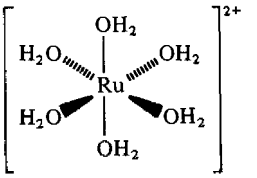
45.6.1 Aqua Complexes

The chemistry of ruthenium aqua complexes has been compared to the corresponding ammine species.[1875]

Ruthenium(II): $[Ru(OH_2)_6]^{2+}$ can be prepared by reduction of RuO_4 with metallic Pb[648,1876] or Sn[1877] or by electrochemical[1878] or chemical reduction of $[RuCl_5(OH_2)]^{2-}$ using Pt/H_2.[282,1879] Purification of the pink product as its ditosylate salt by ion exchange column chromatography has been described.[1876,1879] The single crystal X-ray structure of $[Ru(OH_2)_6](tos)_2$ (**317**) shows an average Ru—O distance of 2.122 Å.[1876] EXAFS,[1880] IR, Raman[1881] and electronic[601] spectral data for $[Ru(OH_2)_6]^{2+}$ have been reported, Dq and B being evaluated as 2100 cm^{-1} and 423 cm^{-1} respectively.[1878] The force constant for the symmetric Ru—OH_2 stretching vibration has been calculated as 1.91 mdyn $Å^{-1}$.[1881]

For the redox couple $[Ru(OH_2)_6]^{3+/2+}$, $E_{\frac{1}{2}} = +0.205$ V *vs.* NHE.[648,1882] The rate of self exchange between $[Ru(OH_2)_6]^{3+/2+}$ (equation 123) has been determined as $\sim 50\,M^{-1}s^{-1}$ by ^{17}O, ^{99}Ru NMR,[1883] IR force constant[1881] and kinetic (Marcus Theory) measurements.[1884] $[Ru(OH_2)_6]^{2+}$ is readily oxidized to $[Ru(OH_2)_6]^{3+}$ by O_2,[282] ClO_4^-,[1885] $[RuL(NH_3)_5]^{3+}$ (L = py, isn),[1884] $[Ru(bipy)_3]^{3+}$, $[Os(bipy)_3]^{3+}$, $[Co(phen)_3]^{3+}$ and $[Fe(OH_2)_6]^{3+}$.[1884] The oxidation of $[Ru(OH_2)_6]^{2+}$ by ClO_4^- in the presence of halides follows kinetics given by equation (124), where $k_1 = 3.2 \times 10^{-3}\,M^{-1}s^{-1}$, $K = 1.2\,M^{-1}$, the rate being limited by slow substitution on Ru^{II}.[1885,1886] The same rate-determining step has been invoked in the $[Ru(OH_2)_6]^{2+}$ catalysed substitution reactions of $[Ru(OH_2)_6]^{3+}$ by halide ion X^- with second order rate constant $k = 8.5 \times 10^{-3}$, 10.2×10^{-3}, $9.8\,M^{-1}s^{-1}$ for $X = Cl^-$, Br^-, I^- respectively.[1877] The rate of water exchange on $[Ru(OH_2)_6]^{2+}$ has been measured as $1.44 \times 10^{-2}\,s^{-1}$ at 24.5°C by ^{17}O NMR studies.[1883]

$[Ru(OH_2)_6]^{2+}$ is a good starting material for the synthesis of substituted aqua complexes, *e.g.* $[Ru(NO)(OH_2)_5]^{3+}$,[282] $[Ru(py)_x(OH_2)_{6-x}]^{2+}$ ($x = 4,2,0$);[648] reaction of $[Ru(OH_2)_6]^{2+}$ with N_2 at



(317)

5 atm for 72 h yields the N_2-bridged dimer $[Ru(OH)_5]_2N_2^{4+}$.[1879] Addition of N_2 to $[Ru(OH_2)_6]^{2+}$ to give $[Ru(N_2)(OH_2)_5]^{2+}$ was found to proceed approximately 35 times more slower than the addition of N_2 to $[Ru(NH_3)_5OH_2]^{2+}$.[1879]

$$[Ru(OH_2)_6]^{2+} + [Ru(OH_2)_6]^{3+} \overset{k}{\rightleftharpoons} [Ru(OH_2)_6]^{3+} + [Rh(OH_2)_6]^{2+} \quad (123)$$

$$\frac{d[[Ru(OH_2)_6]^{3+}]}{dt} = 2k_1[ClO_4^-][Ru^{II}](1 + K[Cl^-])^{-1} \quad (124)$$

Ruthenium(III): $[Ru(OH_2)_6]^{3+}$ is readily prepared by oxidation of $[Ru(OH_2)_6]^{2+}$.[1876,1887] The single crystal X-ray structure of $[Ru(OH_2)_6](tos)_3$ shows an average Ru—O distance of 2.029 Å.[1876] The temperature independent magnetic moment of $[Ru(OH)_6]^{3+}$ has been measured as 1.92 BM[1888] with powder and single crystal ESR spectra in $CsGa(SO_4)_2 \cdot 12H_2O$ giving $g_\parallel = 1.494$, $g_\perp = 2.517$, $A_\parallel = 2.2 \times 10^{-3}\,cm^{-1}$ and $A_\perp = 1 \times 10^{-4}\,cm^{-1}$.[1888] IR and Raman[1881] spectra of $[Ru(OH_2)_6]^{3+}$ have been reported, the force constant for the symmetrical Ru—OH_2 stretching vibration being estimated as 2.98 mdyn $Å^{-1}$;[1881] molecular orbital calculations,[1890] EXAFS[1880] and NMR[1889] data have also been published. Absorption spectra for $[Ru(OH_2)_6]^{3+}$ give values for Dq and B of 3000 cm^{-1} and 600 cm^{-1} respectively.[1881,1891] For the formation of $[Ru(OH)(OH_2)_5]^{2+}$, $pk = 2.4$ at 20°C.[1891] The reduction of $[Ru(OH_2)_6]^{3+}$ by $[Ru(NH_3)_6]^{2+}$, $[RuCl(OH_2)_5]^{2+}$ and $[V(OH_2)_6]^{2+}$ has been reported.[1884] The preparation of $[Ru(OH_2)_6]^{4+}$ in solution has been claimed.[1892]

45.6.2 Hydroxy Complexes

The chemistry of hydroxy and high valence aqua complexes of ruthenium is generally very ill-defined; for a full discussion see reference 3.

The most important hydroxy complex is the red/brown Ru^{IV} product formulated as $[Ru_4(OH)_{12}]^{4+}$ prepared by oxidation of Ru^{III} nitrosyls and nitrates with HNO_3,[1893] by electrolytic[1894] or chemical[1895–1898] reduction of RuO_4 or in potentiometric studies of Ru^{IV} in methylsulfonic and nitric acid at pH 1.5–4.[1899] $[Ru_4(OH)_{12}]^{4+}$ shows multi-redox behaviour, the generation of intermediates formulated as $[Ru_4(OH)_{10}]^{5+}$, $[Ru_4(OH)_8]^{6+}$, $[Ru_4(OH)_6]^{7+}$ and $[Ru_4(OH)_4]^{8+}$ being available.[1893,1895,1897,1899,1900] The direct formation of $[Ru_4(OH)_4]^{8+}$ by electrolysis of $[Ru_4(OH)_{12}]^{4+}$ at a Pt electrode has been reported, the Ru^{III} complex decomposing to a binuclear species of type $[Ru_2(OH)_5]^{4+}$ *via* first and zero dependence in $[Ru^{III}]$ and $[H^+]$ respectively.[1901] Ruthenium hydroxy species are active hydrogenation catalysts.[1902]

45.6.3 Oxo Complexes

Oxo (M=O) complexes of ruthenium,[1903] associated high valence chemistry[1904] and the properties of ruthenium(II) and (III) oxides[3–5] have been reviewed.

Ruthenium(IV): RuO_2 can be prepared by high temperature oxidation of Ru metal[1905,1906] or $RuCl_3$,[1907–1910] by dehydration of hydrated RuO_2,[1911,1912] or reduction of RuO_4, $[RuO_4]^-$ or $[RuO_4]^{2-}$ by $NaBH_4$.[1913,1914] The compound has a rutile structure in crystalline form with octahedral Ru with Ru—O = 1.984 Å for four connectivities and Ru—O = 1.942 Å for the other two;[1915–1918] no direct Ru—Ru bonding occurs within the structure.[1919] PES,[1920] Mössbauer[27a,1921,1922] and magnetic susceptibility[1908,1923] data for RuO_2 have been published with $\chi = 1.10 \times 10^{-6}$ and 1.76×10^{-6} EMU g^{-1} at 1.3 and 1033 K respectively. In recent years RuO_2 and related oxides have found uses in catalytic systems, particularly in the generation of O_2 from H_2O[1924–1929] (see Section 45.4.3.1.vi) and the water-gas shift reaction.[1930]

The chemistry of ruthenates $MRuO_3$ has been reviewed (see reference 3, pp. 116–135).

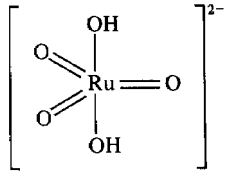
Ruthenium(V): Several reports on the preparation of hydrated ruthenium(V) oxide have appeared.[1910,1913–1936] These products are not well characterized and require further detailed analysis. Cluster species of type $[Ru_4O_{16}]^{2-}$ have been proposed to exist in Na_3RuO_4.[1937]

Ruthenium(VI): $[RuO_4]^{2-}$ is stable in aqueous alkaline conditions and can be generated by fusion of $RuCl_3$ or RuO_2 with KNO_3 and KOH,[1938–1942] reduction of RuO_4 with aqueous KOH (equations 125 and 126),[1943a] oxidation of RuO_2 by Na_2O[1943b] or $NaBiO_3$[1944,1945] and by the oxidation of $RuCl_3$ with alkaline $K_2S_2O_8$[1211,1946,1947] or hypochlorite.[1948] Problems with overoxidation to Ru^{VII} and Ru^{VIII} exist with reactions using Na_2O[1943b] and hypochlorite.[1948,1949] $[RuO_4]^{2-}$ can be isolated most con-

veniently in the solid state as its relatively insoluble barium salt, the single crystal X-ray structure of which shows the complex to be $Ba[Ru(O)_2(OH)_3]$ (**318**) with trigonal bipyramidal Ru^{VI} and *trans* hydroxides, Ru=O = 1.755 Å, Ru—OH = 2.02 Å.[1950–1952] The IR and Raman spectra of the solid are consistent with this structure,[1211,1953,1954] although solution studies suggest that the major species is $[RuO_4]^{2-}$, deuteration experiments indicating the absence of hydroxy species.[1953–1956] $[RuO_4]^{2-}$ shows absorptions near 480 and 380 nm[1949,1957–1962] and an isotropic ESR signal at $g = 2.0$, with a magnetic moment $\mu_{eff} = 2.75$ BM.[1963] The Mössbauer spectrum of $[RuO_4]^{2-}$ has been reported.[1964]

$$4RuO_4 + 4OH^- \longrightarrow 4[RuO_4]^- + 2H_2O + O_2 \quad (125)$$

$$4[RuO_4]^- + 4OH^- \longrightarrow 4[RuO_4]^{2-} + 2H_2O + O_2 \quad (126)$$



(318)

$K_2[RuO_4]$ and $Na_2[RuO_4]$ are stable in aqueous alkali giving a bright orange solution, disproportionation to Ru^{VII} and Ru^{IV} occurring in acidic and neutral conditions.[1936,1949] The electrochemistry of $[RuO_4]^{2-}$ has been reported.[1965] $[RuO_4]^{2-}$ acts as a two electron oxidant for the stoichiometric and catalytic oxidation of alcohols, aldehydes and amines to carboxylic acids and ketones.[1211,1944–1947,1966–1974] The reagent is less reactive towards carbon–carbon double bonds than RuO_4, $[RuO_4]^-$ or OsO_4 and has been used for the oxidation of unsaturated alcohols.[1211,1969] The use of $Ba[Ru(O)_2(OH)_3]$, $[Ru(O)_2Cl_3]^-$ and $[Ru(O)_2Cl_2(bipy)]$ for the oxidation of alcohols to aldehydes and ketones has been described.[1211]

Ruthenium(VI) complexes of periodate[1948] and sulfate[1953,1975,1976] have been reported. RuO_3 can be generated in the vapour phase at 1200°C[1905,1977–1980] and has been proposed to be an intermediate in the oxidation of substrates by RuO_4.[1966,1981,1982]

Ruthenium(VII): $[RuO_4]^-$ may be most readily prepared by reaction of $[RuO_4]^{2-}$ with Cl_2 or NaOCl.[1948,1957,1960] Alternative preparations include fusion of $RuCl_3$ with KNO_3 and KOH[1983] or reduction of RuO_4 with KOH at 0°C (equation 125).[1960,1969] $K[RuO_4]$ is less soluble than $K_2[RuO_4]$ forming very dark green almost black crystals. The single crystal X-ray structure of $[RuO_4]^-$ shows a distorted tetrahedral Ru centre with Ru—O = 1.79 Å and ⟨ORuO = 106°[1984] (*cf.* with $Ba[Ru(O)_2(OH)_3]$). IR and Raman spectra for $[RuO_4]^-$ have been reported.[1954–1956,1984] The electronic spectrum of $[RuO_4]^-$ shows absorptions near 390 and 320 nm; the assignment of these transitions and their relationship to absorption bands observed for RuO_4 and $[RuO_4]^{2-}$ have been the subject of much debate.[1948,1949,1957–1961,1985,1986] The Mössbauer spectrum of $[RuO_4]^-$ has been reported.[1964]

$[RuO_4]^-$ is reduced under alkaline conditions to $[RuO_4]^{2-}$ (equation 126) *via* a rate law given in equation (127); the proposed mechanism of reaction is given in equations (128)–(132).[1935,1987] Electron exchange between $[RuO_4]^-$ and $[RuO_4]^{2-}$ occurs with second order kinetics, rate constant $k > 3 \times 10^4\,M^{-1}s^{-1}$ at 0°C; with $[MnO_4]^{2-}$ the specific rate constant for electron transfer $k = 5.7 \times 10^2\,M^{-1}s^{-1}$ at 20°C with $\Delta H^\circ = 17\,kJ\,mol^{-1}$, $\Delta S = -46\,J\,K^{-1}mol^{-1}$, $\Delta H^{\neq} = 29\,KJ\,mol^{-1}$, $\Delta S^{\neq} = -46\,J\,K^{-1}\,mol^{-1}$.[1988a]

$$\text{Rate} = k[[RuO_4]^-]^2[OH^-]^3 \quad (127)$$

$$[RuO_4]^- + 2[OH^-] \rightleftharpoons [RuO_4(OH)_2]^{3-} \quad (128)$$

$$[RuO_4(OH)_2]^{3-} + [RuO_4]^- \rightleftharpoons [RuO_4(OH)_2]^{2-} + [RuO_4]^{2-} \quad (129)$$

$$[RuO_4(OH)_2]^{2-} \rightleftharpoons [RuO_4]^{2-} + H_2O_2 \quad (130)$$

$$H_2O_2 + OH^- \rightleftharpoons H_2O + HO_2^- \quad (131)$$

$$HO_2^- + OH^- \longrightarrow H_2O + O_2 \quad (132)$$

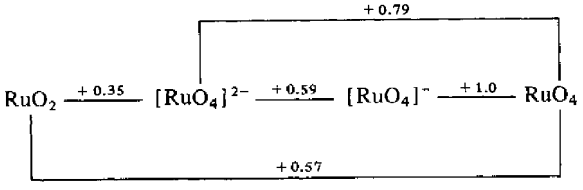
$[RuO_4]^-$ oxidizes alcohols and aldehydes to ketones and carboxylic acids, and readily cleaves carbon–carbon double bonds.[1211,1968,1969] The use of $Bu_4N[RuO_4]$, prepared by the fusion of $RuCl_3$ with KNO_3 and KOH and subsequent reaction with Cl_2 and addition of Bu_4NOH, for the oxidation of alcohols to aldehydes and ketones in acetone or CH_2Cl_2 has been described.[1988b]

Ruthenium(VIII): The chemistry of RuO_4 has been reviewed (reference 3, pp.45–55).

RuO_4 is a toxic, highly volatile yellow product (m.p. 25.4°C, b.p. 40°C) which tends to explode in the solid state. It can be prepared by oxidation of $RuCl_3$, RuO_2 or $[RuCl_6]^{2-}$ with Ce^{IV},[1989,1990] $NaIO_4$,[1943a,1991] NaOCl,[1992,1993] ClO_4^-,[1994] $Cr_2O_7^{2-}$,[1995] BiO_3^-[1957] or BrO_3^-,[1996,1997] oxidation of $[RuO_4]^{2-}$ with Cl_2[1998] or $K[MnO_4]$,[1999] or by hydrolysis of $RuOF_4$, RuF_5 or RuF_4 followed by oxidation with F_2.[2000] The most convenient method of preparation is by oxidation of RuO_2 by aqueous $NaIO_4$ at 0°C followed by extraction of RuO_4 into CCl_4;[1943a,1981,1991,2001] RuO_4 can be stored as a yellow solution in CCl_4 over $NaIO_4$.

Electron diffraction studies on RuO_4 in the gaseous phase show the Ru—O distance to be 1.705 Å, with no deviation from tetrahedral geometry being observed.[2002] The photoelectron spectrum of RuO_4 has been reassigned to give an orbital ionization sequence $2t_2 < 2a_1 < 1e < 3t_2 < 1t_1$,[2003,2004] previously studied samples being contaminated with CO_2[2005] or N_2.[2006] Theoretical calculations based on SCF-Xα,[2007] extended Hückel[2008] and Hartree–Fock–Slater Discrete Variation MO[1958,1986] methods have been used to predict the energy level sequence and have inverted the energies of the $1e$ and $2a_1$ levels. The electronic absorption spectrum of RuO_4 has been reported,[2008–2013] a CD study showing that the absorption near 390 nm is due to a $1t_1 \rightarrow 2e$ transition.[2001,2014] Mössbauer,[1964] and IR and Raman[1954,2015–2019] spectra for RuO_4 in the gaseous, liquid and solid states have been published, RuO_4 retaining its T_d symmetry in CCl_4. ^{99}Ru, ^{101}Ru and ^{17}O NMR studies on RuO_4 show the coupling constant $J_{^{17}O-^{99}Ru} = 23.4$ Hz.[24,2020]

The redox chemistry of RuO_4 has been investigated, Scheme 62 illustrating the potentials for the interconversion of the oxy anions of ruthenium.[1949,2021,2022] Electrochemical reduction of RuO_4 in the presence of a series of anions yields partially characterized nitrato and hydroxy complexes of Ru^{II} and Ru^{III}.[2023] Reaction of RuO_4 with two electron donors L (L = NH_3, PF_3) yields adducts $RuO_4 \cdot L$.[1874] In the case of L = PF_3, an apparent binuclear complex $[RuO_4]_2PF_3$ was formed at −100°C.[1874]



Scheme 62

RuO_4 is an extremely powerful oxidizing agent that has found important uses in the stoichiometric and catalytic[1991,2024] oxidation of organic substrates.[1982,2025] The reactivity of RuO_4 towards organic substrates has been reviewed,[3,1982,2025] and compared with corresponding reactivity of OsO_4.[2026] The oxidations of alcohols,[1957,1966,1981,1997,2027–2030] aldehydes,[1977] alkenes,[1993,1997,2031,2032] alkynes,[2033,2034] ethers,[1997,2035–2038] lactones,[2039] amines,[2040,2041] amides,[1997] aromatics,[2024,2035,2042–2050] sulfides,[2048] oxalic acid,[2051] and Se^{IV}[1989] by RuO_4 have been reported, with reaction occurring *via* two successive, two electron transfers.[1966] The oxidation of 2-propanol in 1–6.5 M $HClO_4$ solution occurs *via* a pathway where hydride abstraction is rate determining, while at high pH, the rate-determining step is carbonium ion formation.[1981,2036]

45.6.4 Ketoenolate Complexes

A range of ketoenolate complexes $[Ru^{III}L_3]$ (HL = $RC(O)CH_2C(O)R^1$, R = R^1 = Me,[163,2052] CF_3,[2052–2056] Ph,[2052,2057,2058] 4-NO_2Ph,[2058,2059] Bu^t;[2052,2055,2060] R = CF_3, R′ = Ph,[2055,2061] Bu^t,[2061] Me;[2054,2056,2057,2061,2062] R = Me, R′ = Ph;[2062] HL = $RC(O)CHR'C(O)R''$, R = R″ = Ph, Me, CF_3, Bu^t, R′ = Ph)[2052] have been prepared by reaction of blue ruthenium(III) chloride with the corresponding diketone under basic conditions or by ligand exchange with [Ru(acac)$_3$]. The tris chelate complexes of (+)-3-acetylcamphor[2063] and (+)-3-trifluoroacetylcamphor[2064] $[RuL_3]$, for example, have been prepared by ligand exchange reaction with [Ru(acac)$_3$] in ethyl benzoate at 160°C; the diastereomers have been separated by tlc on silica and assigned by ^1H NMR studies.[2063] For tris complexes of

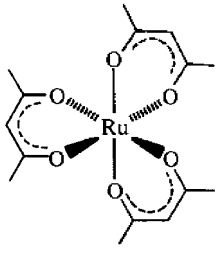
asymmetric ligands (L = A–B), *mer* and *fac* isomers of $[Ru(A–B)_3]$ can be isolated.[2054,2057,2062] The formation of ^{103}Ru labelled $[Ru(acac)_3]$ has been described.[2060] $[Ru(acac)_3]$ has been resolved by chromatography on montmorillonite containing Δ-$[Ni(phen)_3]^{2+}$,[2065,2066] by complex formation with (2*R*,3*R*)-(−)-dibenzoyl tartaric acid[2067] and partially resolved by chromatography on D-(+)-lactone.[2068]

The single crystal X-ray structure of $[Ru(acac)_3]$ (**319**) shows octahedral Ru^{III} with average Ru—O distance of 2.0 Å.[2069] The magnetic properties of $[Ru(acac)_3]$ are consistent with low spin d^5 Ru^{III} with $\mu_{eff} = 1.91$ and 1.75 BM at 298 K and 85.2 K respectively,[163,2057,2070] while the ESR spectrum of $[Ru(acac)_3]$ in $[Al(acac)_3]$ shows a three line signal with $g_x = 1.28$, $g_y = 1.74$, $g_z = 2.82$[2071] suggesting a dynamic Jahn–Teller effect in the complex.[2072] IR[2073] and NMR[2062,2074,2075] spectra for $[Ru(acac)_3]$ have been reported. $[Ru(acac)_3]$ shows absorptions at 476 nm ($\varepsilon = 1.68 \times 10^3$), 324 ($\varepsilon = 1.7 \times 10^3$) and 265 nm ($\varepsilon = 2.7 \times 10^4\,M^{-1}\,cm^{-1}$) in methanol[2057,2070] with Dq being estimated as 1540 cm^{-1}.[2076] Kinetic studies on ligand exchange in $[Ru(acac)_3]$ in acetyl acetone have been carried out; the first order rate constant $k = 9.5 \times 10^{-5}\,s^{-1}$ at 158°C with exchange occurring without decomposition. The rate-determining step was proposed to be formation of complex involving unidentate acac.[2077,2078]

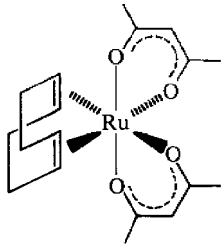
Mass spectral data for $[RuL_3]$ (HL = $RC(O)CH_2C(O)R'$, R = R′ = Me, CF_3; R = Me, R′ = CF_3) suggest relatively little tendency for internal redox reactions in these complexes.[2056] Several studies on the electrochemistry of tris ketoenolate complexes have been published.[2052,2055,2062,2064,2079] $[Ru(acac)_3]$ shows a one electron redox couple to $[Ru(acac)_3]^-$ at $E_{\frac{1}{2}} = -0.72$ V and −0.51 V *vs.* SCE in MeCN and H_2O respectively.[2079] The effect of substitution on acac on the $Ru^{III/II}$ redox couples for the corresponding complexes has been assessed and related to the redox couples $[Ru(NH_3)_6]^{2+/3+}$, $[Ru(en)_3]^{2+/3+}$ and $[Ru(CN)_6]^{3-/4-}$.[2055] A linear relationship was observed between $E_{\frac{1}{2}}$ values for the $Ru^{IV/III/II}$ couples and the sum of the Hammett constants for the functionalities on the coordinated ketoenolate.[2052] Association between $[RuL_3]^-$ and alkali metal ions has been noted;[2052] the rate of aquation of $[Ru(acac)_3]^-$ was found to be relatively slow, with a rate constant $k < 1 \times 10^2\,M^{-1}\,s^{-1}$.[2078] $H[Ru(acac)_3]$ is observed to be a relatively strong acid with $pK_a < 3.5$.[2078]

The complex $[RuL_3]$ (LH = (+)-3-acetylcamphor) can be reduced by treatment with Na/Hg for 40 h, or oxidized by controlled potential electrolysis to the corresponding Ru^{II} and Ru^{IV} species respectively with retention of configuration.[2064] The Ru^{III} diastereomers are found to isomerize at 170°C.[2064] Electron transfer and reduction of derivatives of $[Ru(acac)_3]$ by Ti^{III} have been investigated,[2080,2082] the electron transfer in the ketoenolato bridged Ru—L—Ti binuclear intermediate occurring with a rate constant $k = 21\,s^{-1}$.[2081] $[Ru(acac)_3]$ has been found to be an active catalyst in carbonylation and homologation reactions.[2083–2088]

$[Ru(acac)_2(CO)_2]$ has been synthesized by reduction of $[Ru(acac)_3]$ in THF at 160°C with H_2 and CO at high pressure,[2089] in benzene with CO at 150°C,[2090] by treatment of $[Ru(acac)_2(NCMe)_2]$ with CO at 110°C[2091] or reaction of $Ru_3(CO)_{12}$ with Hacac at 150°C in THF.[2089] $[Ru(acac)_2(cod)]$ (**320**) can be prepared by treatment of $RuCl_3$ with cod and oxalic acid in refluxing ethanol for 2 h, followed by treatment with acetic acid, Hacac and K_2CO_3.[2053,2092,2093] A similar route yields $[Ru(acac)_2(nbd)]$.[2094] $[Ru(acac)Cl_2(OH_2)_2]$ has been synthesized by reaction of $RuCl_3$ with acac in aqueous HCl.[1863] A highly unusual pentanuclear $RuFe_4$ complex linked by ketoenolate and Cp^- functions has been reported; the complex is capable of undergoing an eight electron change, four at the Ru atom and one each at the Fe atoms.[2095d]



(319)



(320)

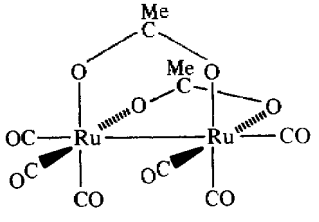
The complexes $[RuL_3]$ (LH = tropolone, α-isopropenyltropolone) have been prepared by reaction of $RuCl_3$ with LH in the presence of $NaHCO_3$; the NMR spectra of these products show them to have predominantly the *mer* configuration.[2095a] Ketoenolate complexes incorporating phosphine, ammine and amine ligands are discussed in Sections 45.5, 45.4.1 and 45.4.2 respectively.

45.6.5 Carboxylate Complexes

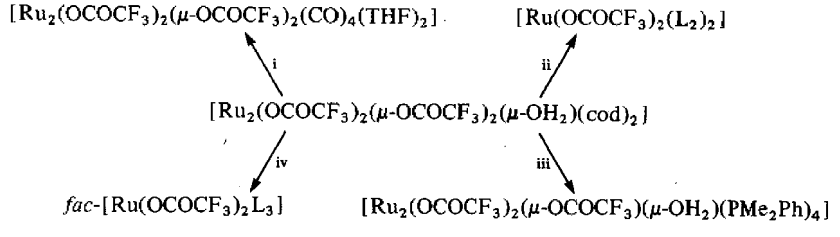
45.6.5.1 Monocarboxylates

Treatment of $[Ru_3(CO)_{12}]$ with carboxylic acids at reflux gives, as the major product, the insoluble polymeric species $[Ru(OCOR)(CO)_2]_n$ (R = Me, Et, C_9H_{19}).[1524] For R = Me, this is also formed by carbonylation (1 atm) of '$RuCl_3 \cdot xH_2O$' and Na[OCOMe] in $MeCO_2H$/acetone at 80°C.[2096] Interestingly, reaction of $[Ru_3(CO)_{12}]$ with 4-fluorobenzoic acid (HL) gives $[Ru_2L_2(CO)_5OH_2]$, shown by X-ray analysis to have bridging carboxylate groups and a terminal aqua ligand.[2095b] The reaction of $[Ru_3(CO)_{12}]$ with C_2H_4 and H_2O under pressure also gives a propionato complex containing the $[Ru(CO)_2(\mu\text{-}O_2CEt)]_2$ unit.[2095c] Reaction of $[Ru(\mu\text{-}OCOMe)(CO)_2]_n$ with CO (50 atm; 80°C) in hexane[1524] or carbonylation (1 atm) of '$RuCl_3 \cdot xH_2O$' and Na[OCOMe] in aqueous $MeCO_2H$ at 80°C[2096] affords $[Ru_2(OCOMe)_2(CO)_6]$ of probable structure (**321**). Both $[Ru(OCOR)(CO)_2]_n$ and $[Ru_2(OCOMe)_2(CO)_6]$ react with a wide range of ligands to yield the complexes $[Ru(\mu\text{-}OCOMe)(CO)_2L]_2$ (L = MeCN, $AsPh_3$, py, piperidine and various PR_3) (**143**; Section 45.5.3.2).[1519,1524,2097,2098] Tetrameric $[Ru_4(OCOMe)_4(CO)_8(PBu_3)_2]$ (**144**; Section 45.5.3.2) can also be prepared from $[Ru(OCOMe)(CO)_2]_n$.[1525,1526] The complexes $[Ru(OCOMe)(CO)_2]_n$ and $[Ru_2(\mu\text{-}OCOMe)(CO)_2(pip)]_2$ have been shown to be active catalysts for the selective homogeneous carbonylation of a variety of cyclic secondary amines;[2098,2099] $[Ru(OCOMe)(CO)_2]_2$ also catalyses the isomerization of alkenes.[2100]

The binuclear Ru^{II} carboxylates $[Ru_2(OCOR)_2(\mu\text{-}OCOR)_2(\mu\text{-}OH_2)(cod)_2]$ (R = CF_3, CCl_3, CH_2Cl) have been synthesized *via* protonation of $[Ru(\eta^3\text{-}C_3H_4R)_2(cod)]$ with haloacetic acids. Some reactions of these complexes (R = CF_3) are shown in Scheme 63.[2101]



(321)

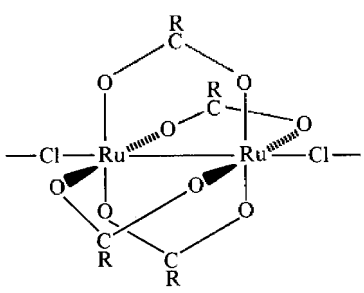


i, CO(1 atm), THF/50 °C; ii, L_2 = dppm or dppe (4 equiv), Et_2O, 25 °C;
iii, PMe_2Ph (4 equiv), THF/25 °C; iv, L = PMe_2Ph, $PMePh_2$, PPh_3 (6 equiv), Et_2O, 25 °C

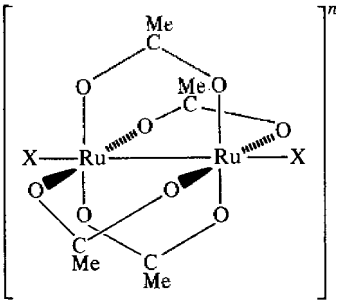
Scheme 63

Reaction of '$RuCl_3 \cdot xH_2O$' with acetic acid/acetic anhydride mixtures gives the brown solid $[Ru_2(OCOMe)_4Cl]$ (**322**) and a green solution (see below).[2102] Higher yields of (**322**) are obtained if the reaction is performed in the presence of an excess of LiCl.[1769] A range of complexes of type $[Ru_2(OCOR)_4X]$ (R = Me; X = Cl, Br, I, SCN, NO_3, OCOMe; R = Ph, H; X = Cl, Br; R = Et, Pr^n, CH_2Cl; X = Cl) can be prepared either from '$RuCl_3 \cdot xH_2O$' or by carboxylate or anion exchange reactions on (**322**).[2102–2104] X-Ray structural analyses on the butyrate,[2105] propionate,[2106] acetate[2106–2108] (X = Cl) and formate[2109] (X = Br) reveal $[Ru_2(OCOR)_4]^+$ units linked into infinite chains by axially bridging halide groups (Ru····Ru ≈ 2.28 Å). Variable temperature magnetic susceptibility studies on all these compounds show $\mu_{eff} \approx 4$ BM per molecule at 300 K (Curie–Weiss constant $\theta = 20$ K for R = Pr^n), which indicates the presence of three unpaired electrons (quartet ground state).[2102–2104,2110] This information together with extensive spectroscopic evidence (ESR,[2110] electronic,[2102,2105,2108,2111–2114] resonance-Raman,[2111,2114] IR, Raman,[2111,2115] and SCF–Xα–SW calculations[2112] suggest the ground state electronic configuration $\sigma^2p^4\delta^2\pi^{*2}\delta^{*1}$. The ESR spectrum[2110]

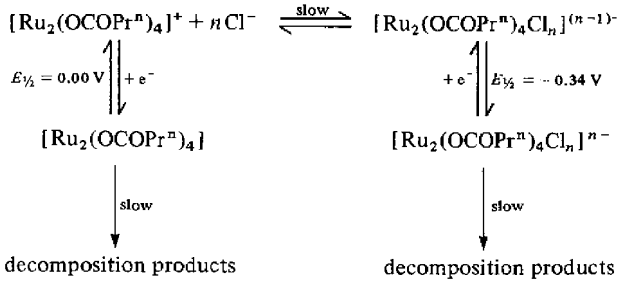
indicates that the three unpaired electrons are fully delocalized. Cyclic voltammetric studies (*vs.* SCE) on $[Ru_2(OCOPr^n)_4Cl]$ in CH_2Cl_2 reveal two reduction waves, one of which disappears on addition of an excess of Cl^- ion.[2110,2113] The proposed reduction process is shown in Scheme 64 and the electronic spectra of the reduced species have been published.[2116] Rate constants for the reduction of $[Ru_2(OCOMe)_4]^+$ by Ti^{3+} are available.[2080] $[Ru_2(OCOMe)_4(THF)_2]$ has been successfully isolated by reaction of $[Ru_2(OCOMe)_4Cl]$ with one equivalent of Me_3SiCH_2MgCl and its structure confirmed by X-ray analysis. Magnetic measurements ($\mu_{eff} \approx 3.1$ BM per molecule at 305 K) suggest a $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*3}$ electronic configuration.[2117]



(322)

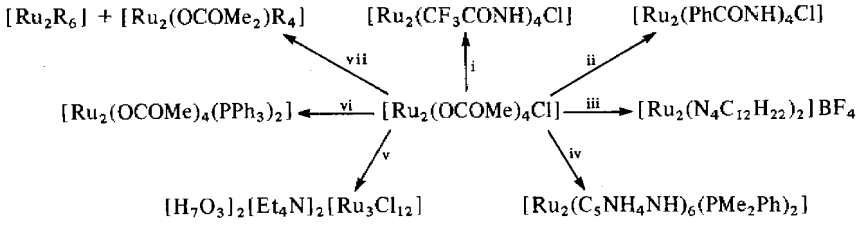


(323) X = Cl ($n = -1$); OH_2 ($n = +1$)



Scheme 64

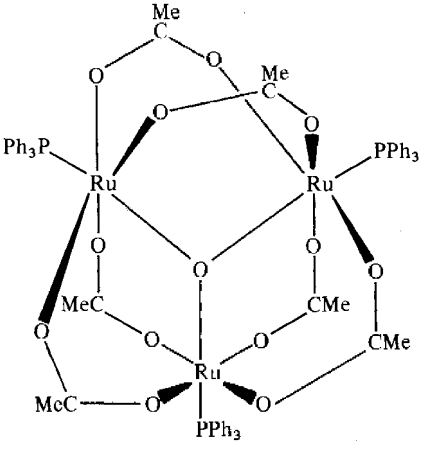
Hydrolysis of (**322**) affords $[Ru_2(OCOMe)_4(OH_2)_2]^+$ whereas treatment with CsCl gives $Cs[Ru_2(OCOMe)_4Cl_2]$; these have the discrete dimeric structure (**323**).[2106] With pyridine, (**322**) gives $[Ru(OCOMe)_2py_4]$ and $[Ru(OCOMe)_2py_2]$, with uni- and bi-dentate OCOMe coordination respectively,[2102] whereas Bu^tNC produces *trans*-$[Ru(OCOMe)_2(Bu^tNC)_4]$.[2118] The corresponding $[Ru(OCOH)_2py_n]$ ($n = 2,4$) can be prepared from reaction of $[Ru_3O(O_2CH)_6(OH_2)_3]O_2CH$ with pyridine.[2119] Related complexes include $Na[Ru(OCOH)_3(OH_2)]$ (from '$RuCl_3 \cdot xH_2O$' and Na[OCOH])[2119] and $[Ru(OCOMe)(azb)(CO)_2]$ (from $[RuCl(azb)(CO)_2]_2$ and Ag[OCOMe]).[1222] Some other reactions of $[Ru_2(OCOMe)_4Cl]$ are shown in Scheme 65 and further discussed in the appropriate section. Calorimetric measurements of the enthalpies of adduct formation to $[Ru_2(OCOPr^n)_4Cl]$ by various Lewis bases are now available.[2121c] Reaction of (**322**) with HBF_4 in MeOH, followed by addition of PPh_3 gives a solution which contains a very active alkene and alkyne hydrogenation catalyst.[2122] Other monocarboxylate complexes containing P or As donor ligands are discussed in Sections 45.5.4.7.vi and 45.10.



i, CF_3CONH_2/Δ;[2116] ii, molten $PhCONH_2$;[1871b] iii, $C_{22}H_{22}N_4^{2-}$, $Na[BF_4]$, EtOH;[2120] iv, $Li(C_5NH_4NH)$; PMe_2Ph;[1871a] v, 12 M HCl, $[Et_4N]Cl$;[2121] vi, PPh_3/MeOH;[1769] vii, RMgCl ($R = Me_3SiCH_2$, Me_3CCH_2)[2218,2219]

Scheme 65

The main component of the green solution, formed by reaction of '$RuCl_3 \cdot xH_2O$' with acetic acid/acetic anhydride, was believed to contain a binuclear ruthenium acetato complex,[2102] but an X-ray structure determination on its PPh_3 adduct, $[Ru_3O(OCOMe)_6(PPh_3)_3]$ (**324**), (mean oxidation state $+2\frac{2}{3}$), suggested it should be reformulated as an oxotriruthenium species.[2123] Later, more detailed investigations[2124] of the reaction of '$RuCl_3 \cdot xH_2O$' with Na[OCOMe], $MeCO_2H$ in EtOH showed the product to be the dark green $[Ru_3O(OCOMe)_6(OH_2)_3]OCOMe$ (**325**) (μ_{eff} at 298 K is 1.77 BM/molecule). In aqueous solution the hydrolytic equilibrium shown in equation (133) is established with the cation favoured at pH < 2 and the anion at pH > 9. Compound (**325**) is an active catalyst for the conversion of unsaturated carbinols to saturated ketones,[2125] and some oxidative transfer dehydrogenation reactions.[2126] Detailed vibrational spectral studies on (**325**) and related species are available.[2127]



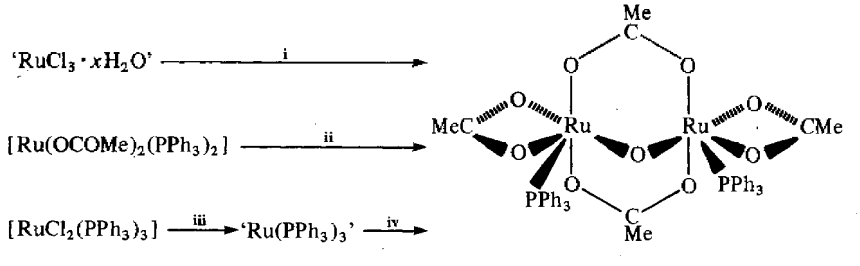
(324)

$$[Ru_3O(OCOMe)_6(OH_2)_3]^+ \underset{}{\overset{-H^+}{\rightleftharpoons}} [Ru_3O(OCOMe)_6OH(OH_2)_2] \overset{-H^+}{\rightleftharpoons} [Ru_3O(OCOMe)_6(OH)_2(OH_2)]^- \quad (133)$$

(**325**)

Reduction of (**325**) with H_2 in aqueous media gives the light green, diamagnetic intermediate $[Ru_3O(OCOMe)_6(OH_2)_3]$ which undergoes a further two electron reduction to yield yellow $[Ru_3(OCOMe)_6(OH_2)_3]$ (μ_{eff} at 298 K is 0.4 BM/molecule). The latter is very oxygen sensitive and rapidly reinserts oxygen to regenerate $[Ru_3O(OCOMe)_6(OH_2)_3]$. Reaction of (**325**) with pyridine affords the corresponding blue $[Ru_3O(OCOMe)_6py_3]^+$ cation which is readily reduced by H_2 to $[Ru_3O(OCOMe)_6py_3]$ and then $[Ru_3(OCOMe)_6py_3]$.[2124]

The diamagnetic $[Ru_3O(OCOMe)_6(PPh_3)_3]$ (**324**), formed by reaction between PPh_3 and $[Ru_3O(OCOMe)_6(OH_2)_3]^{n+}$ ($n = 1,0$), is not reduced by H_2 at ambient temperature although it does form an extremely air-sensitive, reduced yellow solution (formulated as '$Ru(OCOMe)_2PPh_3$') under more forcing conditions. Reoxidation of this does not regenerate (**324**) but instead the purple, diamagnetic $[Ru_2O(OCOMe)_4(PPh_3)_2]$ (**326**). Some other routes to (**326**) are shown in Scheme 66.[1769,2124] Related complexes are known for other carboxylates (OCOH,[2119] OCOEt,[2124] OCOPr,[2124] $OCOCH_nCl_{3-n}$ ($n = 0$–2)[2128] *etc.*).



(326)

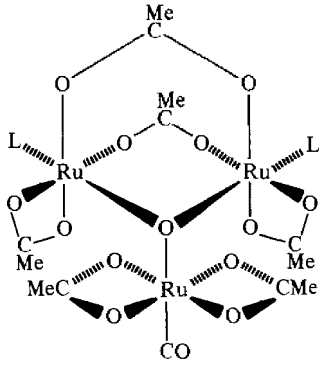
i, PPh_3, Na[OCOMe], MeOH; ii, O_2/MeOH; iii, Ag^+; iv, O_2/Na[OCOMe]

Scheme 66

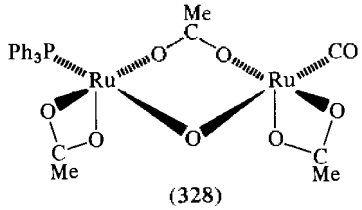
If $[Ru_3O(OCOMe)_6(OH_2)_3]OCOMe$ is treated with H_2 at 80°C in DMF, the monohydride $[Ru_3(H)O(OCOMe)_5(DMF)_3](OCOMe)$ is first formed which undergoes a subsequent intramolecular reduction to produce $[Ru_3O(OCOMe)_4(DMF)_n][OCOMe]$. Further reduction with H_2 yields dimeric ruthenium(I) species such as $[Ru_2(OCOMe)_2(HO_2CMe)MeOH]$ together with $[Ru(OCOMe)(CO)L]_2$ (L = PPh_3, $SbPh_3$, py *etc.*), isolated by addition of L to the DMF solution. The final products are a mixture of $[Ru(OCOMe)(CO)_2L]_2$ and $[RuH(CO)_3]_n$.[2129] Further studies indicate that $[Ru_3(H)O(OCOMe)_5(DMF)_3](OCOMe)$ catalyses the hydrogenation and isomerization of alkenes. Interestingly, only one ruthenium centre is involved in the catalytic process.[2130]

Carbon monoxide reacts slowly with $[Ru_3O(OCOMe)_6(MeOH)_3]^+$ in MeOH but the reduced forms, $[Ru_3O(OCOMe)_6(MeOH)_3]$ and $[Ru_3(OCOMe)_6(MeOH)_3]$ rapidly give purple, paramagnetic $[Ru_3O(OCOMe)_6(CO)(MeOH)_2]$ (**327a**); with pyridine (**327a**) gives $[Ru_3O(OCOMe)_6(CO)py_2]$ (**327b**) which is also prepared from $[Ru_3O(OCOMe)_6py_3]^+$ and CO. Reaction of (**327a**) with PPh_3 yields turquoise $[Ru_2O(OCOMe)_3CO(PPh_3)]$ (**328**) also formed from $[Ru_3O(OCOMe)_6(PPh_3)_3]$ and CO.[1651] Note, however that other workers suggest that $[Ru_3O(OCOMe)_6(CO)py_2]$ has a symmetric structure of type (**324**).[2131]

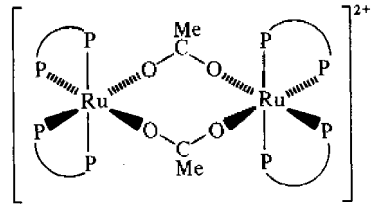
Treatment of $[Ru_3O(OCOMe)_6(MeOH)_3]^+$ with dppm or dppe gives the binuclear cations (**329**) whereas dppm and $[Ru_3O(OCOMe)_6(MeOH)_3]$ affords two isomers of $[Ru_2(OCOMe)_4(dppm)_2]$; some $[Ru(OCOMe)_2(dppm)_2]$ is also produced. With dppe and $[Ru_3O(OCOMe)_6(MeOH)_3]$, the product analyses for $[Ru_6O_2(OCOMe)_{12}(dppe)_3]$ and this is tentatively formulated as two $[Ru_3O(OCOMe)_6]$ units linked by three bridging dppe groups.[2119]



(327) (a) L = MeOH; (b) L = py



(328)



(329)

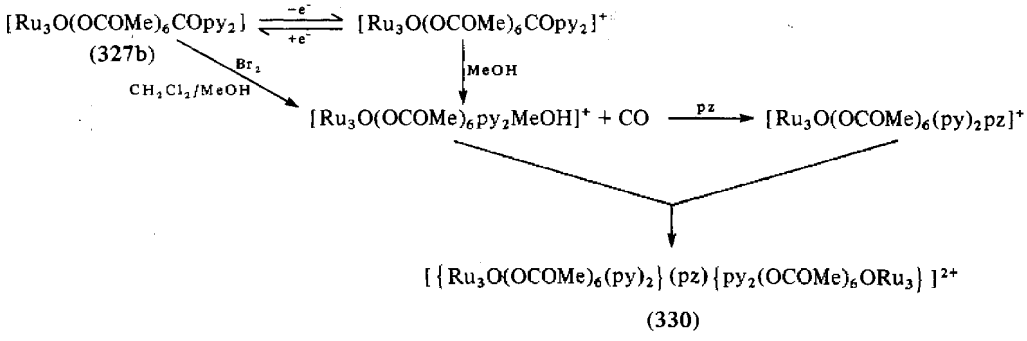
Reactions of $[Ru_3(OCOMe)_6(MeOH)_3]$ with MeNC, NO, SO_2 are fully discussed in reference 1651. For example MeNC gives $[Ru_3O(OCOMe)_6(NCMe)_2MeOH]$ and NO followed by PPh_3 affords $[Ru_3O(OCOMe)_6(NO)(PPh_3)_2]$.

Electrochemical studies on $[Ru_3O(OCOMe)_6py_2L]^+$ (L = pyrazine, *etc.*) (see Scheme 67 for synthesis) reveal the existence of a series of redox states $[Ru_3O(OCOMe)_6py_2L]^n$ ($n = +3$ to -2). The electronic properties have been interpreted *via* a MO scheme which assumes strong Ru—Ru interaction *via* the central oxygen atom and also direct metal–metal bonding.[2131,2132] Rates of electron self-exchange between $[Ru_3O(OCOMe)_6(py)_3]^+$ and $[Ru_3O(OCOMe)_6(py)_3]$ have been determined by ^1H NMR line broadening experiments.[2133]

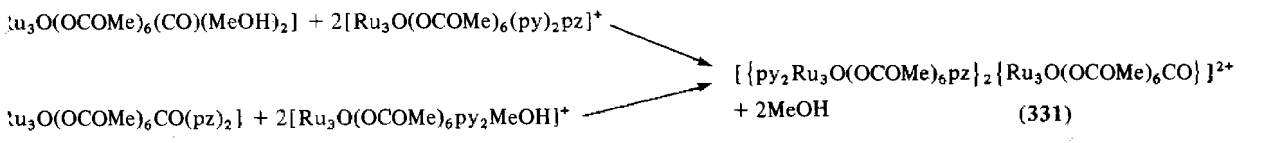
The pyrazine-bridged dimer (**330**) is prepared as shown in Scheme 67. Detailed cyclic voltammetric studies on this and related N-heterocyclic ligand bridged dimers indicate a weak cluster–cluster interaction across the bridge at anodic potentials but significant interactions at cathodic potentials as the electron content of the clusters increases. Electronic spectral measurements support this conclusion.[2132,2134]

The ligand bridged trimeric cluster (**331**) (PF_6^- salt) has been prepared as shown in Scheme 68. This complex shows spectacular electron-transfer behaviour with a total of ten one- or two-electron waves between +2.2 and −1.7 V (in MeCN *vs.* SSCE). Again, these electrochemical studies suggest that when the total electron content is low, interelectronic cluster interactions are weak but as the

electron content increases, electronic coupling between the cluster sites is enhanced. In fact at negative potentials, a series of closely spaced, one electron waves suggests the beginning of band-like behaviour in this discrete molecular system.[2135]



Scheme 67



Scheme 68

Reaction of $[NH_4]_2[RuCl_6]$ with 10% HCO_2H gives $[NH_4]_2[RuCl_4(OCOH)(OH_2)]$ whereas with Na[OCOH], $[NH_4]_3[RuCl_5(OCOH)]\cdot 2H_2O$ is produced.[2136]

45.6.5.2 Dicarboxylates

The ruthenium(III) trisoxalato anion $[Ru(C_2O_4)_3]^{3-}$ was first prepared by Charonnat as its potassium salt by reaction between $K_2[RuCl_5(OH_2)]$ and $K_2[C_2O_4]$.[2137] Later workers[2138] found that this method led to KCl contamination and prepared $K_3[Ru(C_2O_4)_3]\cdot 3H_2O$ by reaction of $K_4[Ru_2OBr_{10}]$ with $H_2[C_2O_4]$ and HCHO, followed by neutralization with $K[HCO_3]$. Treatment of $RuO_2\cdot xH_2O$ with an excess of ammonium hydrogen oxalate gives $[NH_4]_3[Ru(C_2O_4)_3]\cdot 1.5H_2O$.[588] The magnetic properties,[588,2139] electronic[2139,2140] and ESR spectra[604] and electrochemical behaviour[2141] of this anion are fully documented.

The $[Ru(C_2O_4)(OH_2)_4]^+$ ion has been reported to exist in aqueous solution and the $[Ru(C_2O_4)_2(OH_2)_2]^-$ anion has been isolated as its sodium salt by treatment of $[Ru_2(OCOMe)_4Cl]$ with aqueous $Na_2[C_2O_4]$ under an oxygen atmosphere. This anion undergoes a facile one-electron reduction by Ti^{III} *via* an inner-sphere mechanism.[2143] Other $[Ru(C_2O_4)_2L_2]^-$ anions (L = N donor ligands) are discussed in Section 45.4. Reaction of $K_3[Ru(C_2O_4)_3]$ with $[enH_2][C_2O_4]$ gives the *cis*-$[Ru(C_2O_4)(en)_2]^+$ cation.[620]

Other oxalato complexes include various nitrosyl species such as $K_2[RuCl_3(C_2O_4)NO]$, $K_2[RuCl(C_2O_4)_2NO]$, $K[Ru(C_2O_4)_2NO(py)]$, $[RuCl(C_2O_4)NO(py)_2]$,[2144] the black $K_2[Ru(C_2O_4)_3]$[2145] from oxidation of $K_3[Ru(C_2O_4)_3]$ with H_2O_2 and $Cs_2[RuO_2(C_2O_4)_2]$,[65] obtained by treatment of RuO_4 with ice cold solutions of $Cs_2[C_2O_4]$ and oxalic acid. The latter contains a *trans* RuO_2 unit. The mixed valence anion $[Ru_2(OCOMe)_2(C_2O_4)_2(OH_2)_2]^-$ has been synthesized by reaction of $[Ru_2(OCOMe)_4Cl]$ with oxalic acid. Reduction with Ti^{III} gives $[Ru_2(OCOMe)_2(C_2O_4)_2]^{2-}$ *via* an intermediate containing two ruthenium atoms and one titanium atom.[2146]

Aqueous solution studies between Ru^{III} or Ru^{IV} with citric acid indicate that 1:3 and 1:2 complexes respectively are formed.[2147]

45.6.6 Miscellaneous

Ruthenium complexes incorporating only nitrate, sulfate[2148] or related oxy-anion ligands are generally ill-defined.[3] The chemistry of heavy metal nitrates,[2149] nitrites[2150] and dioxygen[2151a] com-

plexes has been reviewed. The fluorosulfate complexes $[Ru(SO_3F)_3]$, $[Ru(SO_3F)_4]^-$, $[Ru(SO_3F)_5]^-$ and $[Ru(SO_3F)_6]^{2-}$ have been reported.[2151b]

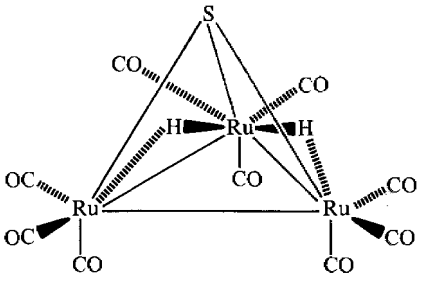
Reaction of $[RuBr_2(CO)_4]$ with L (L = pyridine *N*-oxide, $OPPh_3$) in $CHCl_3$ yields the complexes $[RuBr_2(CO)_3L)$.[2152] The products $[RuCl_3L_3]$ (L = 2,6-lutidine *N*-oxide,[2153] phosphole *N*-oxide derivatives,[2154] 8-hydroxyquinoline-*N*-oxide[2155,2156]) and O bonded $[RuCl_3L_2]$ (L = thiomorpholin-3-one)[679] have been prepared.

45.7 SULFUR LIGANDS

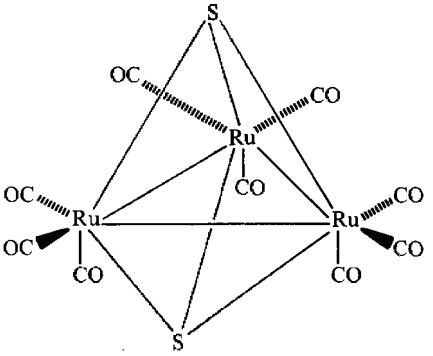
45.7.1 Sulfido, Thiolato and Thiazole Complexes

No simple sulfides of Ru in formal oxidation states less than four are apparently known; thus 'Ru_9S_8' has been shown to be a mixture of RuS_2 and Ru.[2157] Earlier work[2] reveals that the Ru^{IV} complex RuS_2 can be made from the elements at high temperatures and that it has the pyrite structures.[2158] More recently, poorly crystallized samples of diamagnetic RuS_2 were prepared by reaction of the anhydrous $[NH_4]_2[RuCl_6]$ with H_2S at 180°C for 4 h. These amorphous products were annealed under various conditions and the resulting degree of crystallinity was determined.[2159,2160] The high temperature enthalpy and decomposition pressure of RuS_2 (to form Ru(s) and $S_2(g)$)[2161] and IR data and normal coordinate calculations[2162] are available. Synthesis of members of the $Co_{1-x}Ru_xS_2$ ($0 \leqslant x \leqslant 1$) and $Rh_{1-x}Ru_xS_2$ ($0.5 \leqslant x \leqslant 1$) systems has been accomplished by the sulfurization of mixtures of $[NH_4]_2[RuCl_6]$ with either $[Co(NH_3)_5Cl]Cl_2$ or $[NH_4]_3[RhCl_6]$ and variable temperature magnetic susceptibility measurements recorded.[2163] The polysulfides RuS_3 and RuS_6 can also be prepared by reaction of $K_2[RuCl_6]$ and H_2S; RuS_6 is oxidized by air to a pyrosulfite $[Ru(S_2O_5)_2]$ and a 'thiometallate', possibly $[Ru(SH)_6]^{3-}$, can be obtained from polysulfides and $[RuCl_6]^{2-}$.[2] However, this is old work and further studies in this area are desirable.

Reaction of RuO_4 with SCl_2 in CCl_4 gives the brown, moisture sensitive $[RuCl_4S]_x$. A binuclear structure with a RuS_2Ru bridge is proposed.[2164] Another sulfido-bridged complex is $[Ru_3H_2(\mu_3\text{-}S)(CO)_9]$ (**332**) from reaction of $[Ru_3(CO)_{12}]$ with $Na_2[SO_3]$ and alcoholic KOH.[2165] A higher yield route to (**332**) is by reaction of $[Ru_3(CO)_{12}]$ with sulfur under a CO/H_2 atmosphere in refluxing octane; some $[Ru_3S_2(CO)_9]$ (**333**) is also formed.[2166] Compound (**332**) is also generated by addition of water to the trihydrido cation $[Ru_3H_3(\mu\text{-}S)(CO)_9]^+$.[2167,2168] Variable temperature ^{13}C NMR studies on (**332**) reveal both H and CO scrambling processes.[2169] With $[Ru_3(CO)_{12}]$ and cyclohexene sulfide, a yellow solid of composition $[RuS(CO)_3(C_6H_{10})]_n$ has been isolated.[2165]



(332)



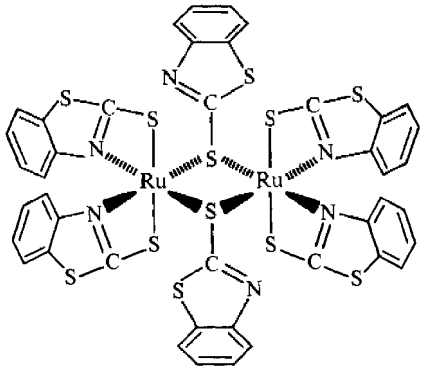
(333)

Sulfido complexes containing P or As donor ligands, *e.g.* $[RuX_2NO(EPh_3)]_2S$ (X = Cl, Br; E = P, As), $[Ru_3Cl_3S_2(PPh_3)_3]$, $[Ru(CO)_2(PPh_3)S]_2$ *etc.*, are discussed in Section 45.5.4.8.i.

Reaction of $NEt_4[RuCl_4(MeCN)_2]$ with 4 equivalents of the Li salt of either 2,3,5,6-tetramethylbenzenethiol or 2,4,6-triisopropylbenzenethiol (LH) and 0.5 equivalents of the corresponding sulfide in MeOH/MeCN solutions give high yields of $[RuL_4(MeCN)]$, shown by X-ray analyses to have trigonal bipyramidal structures with axial MeCN groups. Electrochemical studies reveal that both $[RuL_4MeCN]^+$ and $[RuL_4MeCN]^-$ can be generated.[2170a] Reaction of $[RuL_4MeCN]$ with CO at room temperature gives $[RuL_4CO]$, a rare example of a Ru^{IV} carbonyl complex.[2170b] A series of six-coordinate octaethylporphyrin complexes [Ru(SR)(OEP)(CO)] can be synthesized by treatment of [Ru(OEP)CO] with SR^- (R = CMe_3, Et, $CH_2CH_2CO_2Me$).[2171]

Reaction of the reduced 'ruthenium blue' solution with thiols such as 2-aminobenzenethiol and 4-toluenethiol (LH) gives highly insoluble compounds of stoichiometry $[Ru(L)_2]_n$ which are prob-

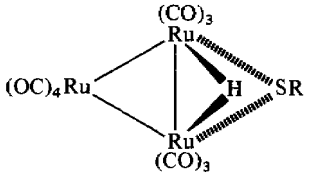
ably polymeric with sulfur bridges. Attempts to cleave these bridges with PPh_3 and *p*-toluidine were unsuccessful. The benzothiazole-2-thiol (LH) complex of stoichiometry $[RuL_3]$ is weakly paramagnetic, dimeric in $CHCl_3$ and structure (**334**) is proposed. Reaction of the reduced 'ruthenium blue' solution with pyridine-2-thiol gives the highly insoluble and polymeric $[RuCl_2(pySH)_2]_n$ which reacts with PPh_3 to yield $[Ru(pyS)_2(PPh_3)_2]$.[676] A Ru^{III} complex of 3,4,5-pyridazinetrithiol has also been reported.[2172a] Also reaction of $[Ru(acac)_3]$ with HSPh has been shown to give polymeric $[Ru(SPh)_3]_n$.[2172b]



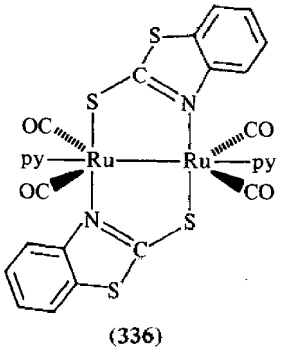
(334)

Treatment of the 'RuCOCl' solution with thiophenol produces the light brown $[Ru(SPh)_2(CO)_2]_3$, formulated as a trimer on the basis of an osmometric molecular weight determination. Similar reactions with dithiols gave yellow complexes of uncertain composition[107] but with 2-aminothiophenol, the orange brown $[Ru(SC_6H_4NH_2)_2(CO)_2]$ was isolated.[108] Reaction of $[Ru_3(CO)_{12}]$ with thiols (including thiophenol) affords the binuclear $[Ru(SR)_2(CO)_3]_2$ and the polymeric $[Ru(SR)_2(CO)_2]_n$ (R = Me, Et, Bu^n, Ph); the formation of $[Ru(SPh)_3]$ is also mentioned.[2173] Similar products are formed with organic disulfides. For example, Ph_2S_2 and $[Ru_3(CO)_{12}]$ produces $[RuSPh(CO)_3]_2$, $[RuSPh(CO)_3]_n$, $[Ru(SPh)_2(CO)_3]_n$ and two forms of $[Ru(SPh)_2(CO)_2]_n$; Et_2S_2 gives $[RuSEt(CO)_3]_2$ and $[Ru(SEt)_2(CO)_2]_n$[2174] whereas Me_2S_2 generates $[Ru(SMe)_2(CO)_2]_n$ ($n = 242$) which on bromination gives $[RuBr(SMe)_2(CO)_2]_2$.[2175] The mixed P- and S-bridged complex $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6]$ [(**140**); Section 45.5.3.2] is obtained from $[Ru_3(CO)_{12}]$ and Ph_2PSPh.[1517] Under milder conditions, $[Ru_3(CO)_{12}]$ and RSH afford the trinuclear hydrido complexes $[Ru_3H(\mu\text{-}SR)(CO)_{10}]$ (**335**) (R = Et, Br^n)[2176] which for R = Et undergo protonation in 98% H_2SO_4 to generate the $[Ru_3H_2(\mu\text{-}SEt)(CO)_{10}]^+$ cation.[2167,2168]

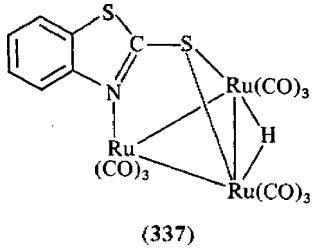
Treatment of $[Ru(azb)Cl(CO)_2]_2$ (azb = 2-phenylazophenyl) with sodium benzenedithiolate gives $[Ru(azb)(SPh)(CO)_2]_2$, a compound containing bridging SPh groups whereas sodium 2-aminobenzenethiolate (abt) yields the monomeric $[Ru(azb)(abt)(CO)_2]$ with a chelating abt ligand.[1222] Reaction of mercaptobenzothiazole (mbtH) with $[Ru_3(CO)_{12}]$ in MeOH gives a mixture of products but addition of pyridine and recrystallization affords $[Ru(mbt)_2(py)_2(CO)_2]$, (with *cis* CO, *cis* py and mutually *trans* mbt ligands coordinated in the thiolate form *via* the exocyclic sulfur atom), and $[Ru(mbt)py(CO)_2]_2$ (**336**), probably *via* initial formation of $[Ru_2(mbt)_2(CO)_6]$. In the latter, the Ru—Ru bond is bridged by the thiazole ligand.[2177,2178] Under mild conditions (toluene, 50°C/1 h), $[Ru_3(CO)_{12}]$ and mbtH generate $[Ru_3H(C_7H_4NS_2)(CO)_9]$ (**337**) in which the heterocyclic ligand is attached to the cluster *via* a bridging thiolato group and a third ruthenium by nitrogen. Under the same mild conditions, mercaptoethanoic acid and $[Ru_3(CO)_{12}]$ afford $[Ru_3H(\mu\text{-}SCH_2CO_2H)(CO)_{10}]$ with a structure similar to that of other $[Ru_3H(\mu\text{-}SR)(CO)_{10}]$ (**335**) complexes.[2179] Reaction of $[Ru_3(CO)_{12}]$ with thiobenzophenones produces the novel *ortho*-metallated complex (**338**) in high yield.[2180]



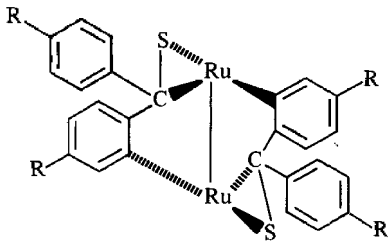
(335)



(336)



(337)



(338) R = OMe, Me

Other examples of carbonyl clusters containing sulfido or thiolato ligands include the hydrocarbon complexes $[Ru_2(\mu\text{-}SBu^t)(CO)_4(\mu_2\text{-}\eta^7\text{-}C_7H_7)]$, $[Ru_3(\mu_3\text{-}S)(CO)_6(\mu_3\text{-}\eta^8\text{-}C_8H_8)]$[2181] and also $[Ru_6H_2(SEt)_2(CO)_{15}]$ and $[Ru_6HC(SEt)_3(CO)_{15}]$.[2182]

Cations such as $[Ru(SR)(NH_3)_5]^{2+}$, $[(NH_3)_5RuS_2Ru(NH_3)_5]^{4+}$, are discussed in Sections 45.4.1.2.iv and 45.4.1.3.iii respectively and thiolato complexes containing P donor ligands in Section 45.5.4.8.i. References to the preparation of other ruthenium-thiol and -thione complexes are given in reference 3. Reaction of $[Ru(edta)(OH_2)]$ with RSH gives $[Ru(edta)SR]^{2-}$ (see Section 45.11.1.5).

Finally, although outside the scope of this review, various $\eta\text{-}C_5H_5$ and $\eta\text{-}C_6H_6$ complexes containing thiolato groups are known. Examples include $[Ru(SR)(CO)_2(\eta\text{-}C_5H_5)]$, $[Ru(\mu\text{-}SR)(CO)(\eta\text{-}C_5H_5)]_2$, $[Ru_3(\mu\text{-}SR)_3(CO)_2(\eta\text{-}C_5H_5)_3]$ (reference 1, p.781) and $[Ru_2(\mu\text{-}SEt)_3(\eta\text{-}C_6H_6)_2]BPh_4\cdot MeOH$.[2183]

45.7.2 Thioethers

The Ru^{III} monomers $[RuCl_3(SRR')_3]$ (R = Ph; R′ = Me, Et, Pr^n, Bu^n; R = R′ = Me, Et) are generally prepared by heating under reflux an ethanolic solution of '$RuCl_3\cdot xH_2O$' with an excess of RR′S.[2184–2186] The corresponding bromides are prepared by shaking the chlorides with LiBr in acetone. With Me_2S and Et_2S, the red $[RuCl_3(SR_2)_3]$ was contaminated with black $[RuCl_3(SR_2)_2]_2$ which can be separated by fractional crystallization. Under milder conditions of reaction, small amounts of yellow $[RuCl_2(SMe_2)_4]$ are also formed.[2185] The low μ_{eff} of the binuclear species (*ca.* 1.0 BM/Ru at 293 K) suggests some Ru—Ru interaction probably *via* chloro bridges. Initially, $[RuCl_3(SEt_2)_3]$ was assigned a *fac* configuration on the basis of its IR spectrum and the similarity of its X-ray powder pattern to *fac*-$[IrCl_3(SEt_2)_3]$.[2184,2187] However, further ^1H NMR studies on the latter indicate it has a *mer* configuration which suggests that all the $[RuX_3L_3]$ have a *mer* structure;[2188] their ESR spectra are consistent with this conclusion.[1852,2185]

Interestingly, reaction of '$RuCl_3\cdot xH_2O$' with $PhPr^iS$ in boiling MeOH gives $[RuCl_3(SPhPr^i)_2MeOH]$ (*cf.* $[RuCl_3(EPh_3)_2MeOH]$ (E = P, As); Section 45.5.7.1). Treatment of this with MeCN gives first $[RuCl_3(SPhPr^i)_2MeCN]$ and then $[RuCl_3(MeCN)_3]\cdot MeCN$. Facile SR_2 displacement is a general feature of the $[RuCl_3(SPhR)_3]$ complexes (see equation 134).[2185]

$$[RuCl_3(SPhR)_3] + L \xrightarrow{C_6H_6} [RuCl_3L_3]\cdot 0.5C_6H_6 \quad (L = PhNH_2, py) \qquad (134)$$

Other dialkyl sulfide complexes include the unusual cation $[Ru(SnCl_3)(CO)_2(SEt_2)_3]^+$, obtained by treating $[RuCl_2(SnCl_3)_2(CO)_2]^{2-}$ with three moles of Et_2S,[108] $[Ru(MeCN)_3(SEt_2)(cod)]^{2+}$ (from $[Ru(MeCN)_4cod]^{2+}$ and Et_2S),[1370] various $[RuCl_3NO(SRR')_2]$ (see Section 45.4.4.3),[123,1301,1302,1303] $[RuCl_3(PPh_3)(SMe_2)_2]$ (see Section 45.5.7.1), $[RuCl_3CO(SMe_2)_2]^-$ (from reaction of $[RuCl_3CO(nbd)]^-$ and Me_2S),[659] and ammine complexes such as $[Ru(NH_3)_5SMe_2]^{2+}$, $[Ru(NH_3)_4(OH_2)SMe_2]^{2+}$, $[Ru(NH_3)_4L_2]^{2+}$ (L = $MeS(CH_2)_2CH(NH_2)CO_2Me$), and $[(NH_3)_5RuL\text{-}Ru(NH_3)_5]^{n+}$ (L = 1,4-dithiane, 1,5-dithiocane; n = 4,5) *etc.* (see Sections 45.4.1.2.iv and 45.4.1.3.iii).

The reaction of '$RuCl_3\cdot xH_2O$' with various disulfides in boiling EtOH affords $[RuCl_3(RS(CH_2)_2SR)_{1.5}]_n$ (R = Et, Pr^n, Ph). For R = Et, reaction with pyridine gives $[RuCl_3(ES(CH_2)_2SEt)py]$ suggesting that one sulfide molecule is bridging and the other chelating in the parent molecule.[2185] Parallel work by Rice *et al.*[2189] reports the synthesis of other examples of $[RuCl_3L_{1.5}]_n$ [L = 1,4-dithiane, $RS(CH_2)_2SR$ (R = Me, Et)] and also $[RuCl_3(RS(CH_2)_2SR)]_n$ (R = Me, Ph; n = probably 2) and $[RuCl_3(PhS(CH_2)_2SPh)_2]_n$ (n = probably 2).

In boiling 2-methoxyethanol, reduction occurs to give $[RuX_2(RS(CH_2)_2SR)_2]$ (X = Cl, Br) (see reference 2190 for variable temperature ^1H NMR studies on $[RuX_2(MeS(CH_2)_2SMe)_2]$) and for

R = Et, chemical oxidation with $HClO_4$ or Br_2 then generates the Ru^{III} cations $[RuX_2(EtS(CH_2)_2SEt)_2]^+$. For R = Ph, carbonylation in boiling 2-methoxyethanol gives $[RuX_2(CO)_2(PhS(CH_2)_2SPh)$ (with *cis*-CO and *trans* X groups).[2185] Compounds of this type are also formed as shown in equation (135). Similarly, $[RuX_2(CO)_2(SR_2)_2]$ (various isomers) and in some instances $[RuX_2(CO)(SR_2)_3]$ can be prepared.[1611,2191,2192] Interestingly, reaction of ethane-1,2-dithiol with $[RuI_2(CO)_2]_n$ gives the unstable $[RuI_2(CO)_2(HS(CH_2)_2SH)_2]$ in which the sulfur ligands may be monodentate.[1611]

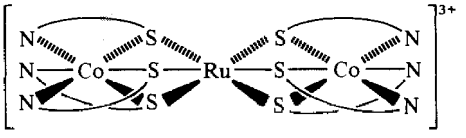
$$[RuI_2(CO)_2]_n + RS(CH_2)_2SR \longrightarrow [RuI_2(CO)_2(RS(CH_2)_2SR)] \quad (R = Et, Ph)^{1611,2191} \quad (135)$$

The Ru^{III} anion $[RuCl_4(MeS(CH_2)_2SMe)]^-$ is obtained as its $AsPh_4^+$ and NMe_4^+ salts from '$RuCl_3 \cdot xH_2O$', 2,5-dithiahexane and $[AsPh_4]HCl_2$ in acetone or $[NMe_4]Cl$ in absolute alcohol.[2193]

Treatment of '$RuCl_3 \cdot xH_2O$' with the trisulfide 1,1,1-tris(ethylthiomethyl)ethane in boiling 2-methoxyethanol gives $[RuCl_3\{MeC(CH_2SEt)_3\}]$ which on further heating with DMF affords $[RuCl_2(CO)\{MeC(CH_2SEt)_3\}]$. This is a rare example of a solvent decarbonylation reaction with a sulfide complex. Carbonylation in 2-methoxyethanol also yields $[RuCl_2(CO)_2\{MeC(CH_2SEt)_3\}]$ formulated as a seven-coordinate Ru^{II} compound.[2185] The corresponding $[RuCl_3\{S(CH_2CH_2CH_2SMe)_2\}]$ is obtained by reaction of '$RuCl_3 \cdot xH_2O$' with the trithioether in EtOH.[2194]

45.7.3 Metallothioanions as Ligands

The complexes $[Ru(CoL_3)_2]X_3 \cdot nH_2O$ (**339**) (X = Cl, I, BPh_4) (μ_{eff} = 1.8 BM at 303 K) are prepared by reaction of $RuCl_3$ with a large excess of CoL_3 (L = $NH_2CH_2CH_2S^-$), followed by addition of NaI or $Na[BPh_4]$. A study of the ESR spectra of this and the corresponding Fe^{III} complex suggests severe distortion from octahedral geometry. Hyperfine structure from the two equivalent cobalt nuclei indicates that the unpaired electron is delocalized over all three metal ions.[2195]



(339)

Treatment of $[RuCl_2(bipy)_2] \cdot 2H_2O$ with equimolar amounts of $[NH_4]_2[MoS_4]$ in aqueous EtOH for 18 h at room temperature produces the bimetallic complex (**87**). Reaction of (**87**) with more $[RuCl_2(bipy)_2] \cdot H_2O$ then affords the trimetallic cation (**108**), isolated as its PF_6^- salt. Electrochemical reduction of these species at −1.7 V in the presence of acetylene produces some ethylene and ethane[1212] (see Sections 45.4.3.1.xi and 45.4.3.2.iii respectively).

45.7.4 Dithiocarbamato and Related Complexes

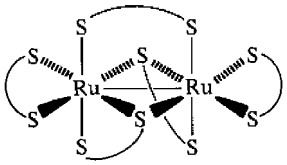
Several reviews which cover the chemistry of ruthenium dialkyldithiocarbamates have appeared in the last fifteen years.[2196–2199] Cambi and Malatesta[2200] and later Malatesta[1309] reported the low spin, monomeric $[Ru(S_2CNR_2)_3]$ (R = Me, Et, Bu^n) which they prepared by reacting $K_2[RuCl_6]$ with aqueous $Na[S_2CNR_2]$. More recently, compounds of this type have been prepared by the reaction of $Na[S_2CNR_2]$ with solutions of '$RuCl_3 \cdot xH_2O$'.[2201,2202] A crystal structure determination for R = Et shows the RuS_6 core to have approximate D_3 symmetry and a twist towards trigonal prismatic geometry.[2203,2204] Essentially the same RuS_6 core geometry is found for $[Ru(S_2CN(CH_2)_4O)_3] \cdot 2.5CHCl_3$ with the hydrogen atom of each $CHCl_3$ hydrogen-bonded to the sulfur atoms of various ligands.[2202] The temperature-dependent ^1H NMR spectra of various $[Ru(S_2CNRR')_3]$ reveal both intramolecular metal-centred inversion and ligand-centred geometric isomerization which are attributed to a trigonal twist mechanism and S_2C—N bond rotation respectively. The distortion of the RuS_6 core towards trigonal prismatic coordination may be the reason for ease of metal-centred inversion which involves a trigonal twist pathway.[2201] Mass spectral[2205] and ESR data[604] on several $[Ru(S_2CNR_2)_3]$ are available.

Several studies[2206–2210] have been published on the redox behaviour of $[Ru(S_2CNR_2)_3]$. A one electron reversible reduction to $[Ru(S_2CNR_2)_3]^-$ is observed but the one electron oxidation is

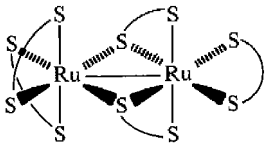
quasi-reversible and the product $[Ru(S_2CNR_2)_3]^+$ is unstable towards further reaction or decomposition. For example, in MeCN, the electrochemical oxidation product of $[Ru(S_2CNEt_2)_3]$ is the diamagnetic $[Ru(S_2CNEt_2)_3MeCN]^+$ cation.[2210] Earlier studies[2206,2207] had indicated that $[Ru(S_2CNEt_2)_3]^+$ was synthetically accessible and aerial oxidation in the presence of BF_3 was reported to yield $[Ru(S_2CNEt_2)_3]BF_4$.[2207] However, X-ray analysis revealed the product to be the binuclear $Ru_2^{III,III}$ cation $[Ru_2(S_2CNEt_2)_5]BF_4$ (**340**) (β-isomer). Electrochemical studies on (**340**) in MeCN showed a four member series (equation 136) and the one electron reduction product $[Ru_2^{II,III}(S_2CNEt_2)_5]$ was isolated.[2208]

Independent studies involving chromatographic separation of the reaction products of '$RuCl_3 \cdot xH_2O$' and $Na[S_2CNPr^i_2]$ led to the isolation of some $[Ru_2(S_2CNPr^i_2)_5]X$ ($X = Cl^-$, $Ru_2Cl_6^{2-}$), shown by X-ray analysis to have structure (**341**) (α-isomer).[2211] The α-$[Ru_2(S_2CNMe_2)_5]^+$ cation is converted to the β-isomer by heating in $CHCl_3$ and the interconversion can be monitored by ^1H NMR spectroscopy. Reduction of the α-isomers is more facile than the β-isomers but the β-$[Ru_2(S_2CNR_2)_5]^-$ rapidly isomerizes to give the α-$[Ru_2(S_2CNR_2)_5]^-$ anion which is the reverse of the situation for the cations.[2209] A detailed reexamination[2210] of the preparation of compounds (**340**) and (**341**) reveals that chemical oxidation of $[Ru(S_2CNR_2)_3]$ using BF_3 gas in the absence of oxygen yields the α-isomer; in the presence of oxygen, only the β-isomer is formed. The ^1H NMR spectra of α- and β-$[Ru_2(S_2CNMe_2)_5]^+$ have been assigned by variable temperature and ligand-exchange studies and an isomerization reaction mechanism proposed.

$$Ru_2(S_2CNR_2)_5]^{2+} \longleftarrow [Ru_2(S_2CNR_2)_5]^+ \rightleftharpoons [Ru_2(S_2CNR_2)_5] \rightleftharpoons [Ru_2(S_2CNR_2)_5]^- \quad (136)$$



(340)



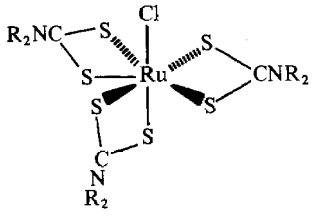
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The α- and β-isomers of $[Ru_2(S_2CNR_2)_5]^+$ can be reduced to the paramagnetic α- and β-$[Ru_2(S_2CNR_2)_5]$ respectively by reaction with $Na[BH_4]$ in ethanol. For R = Et, the green α-isomer converts in toluene to the purple β-isomer with a first-order rate constant of $8 \times 10^{-4} s^{-1}$ at 30°C. Photolysis in $CHCl_3$ yields the oxidized cations with chloride counterions and retained α and β stereochemistry.[2210]

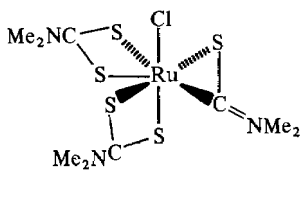
Seven-coordinate, diamagnetic Ru^{IV} complexes $[RuCl(S_2CNR_2)_3]$ (R = Me, Et) are obtained by photolysis of $[Ru(S_2CNR_2)_3]$ in $CHCl_3$ or CH_2Cl_2 or by reaction with gaseous HCl in C_6H_6. X-Ray analysis reveals a distorted pentagonal bipyrimidal structure (**342**) although the compound is non-rigid in CD_2Cl_2 solution even at −95°C.[2212] More detailed photochemical studies on $[Ru(S_2CNR_2)_3]$ at λ = 265–366 nm in various chlorinated solvents show that in addition to (**342**), some α-$[Ru_2(S_2CNR_2)_5]Cl$ is formed; a reaction pathway involving the formation of an excited Ru^{II} species $[Ru(S_2CNR_2)_2(S_2^+CNR_2)]^*$ is proposed to explain these results.[2213] Interestingly, photolysis at 366 nm in the presence of a large excess of benzophenone gives the unusual product $[RuCl(S_2CNMe_2)_2(\eta^2\text{-}SCNMe_2)]$ (**343**) in greater than 90% yield. Variable temperature ^1H NMR studies on this non-rigid, pentagonal bipyramidal molecule are reported.[2214] In donor-type solvents S such as MeCN and DMSO, compound (**342**) forms $[Ru(S_2CNEt_2)_3S]Cl$; further reaction with PPh_3 gives $[Ru(S_2CNEt_2)_3PPh_3]Cl$ and all these seven-coordinate Ru^{IV} complexes are stereochemically non-rigid. In propylene carbonate, $[Ru(S_2CNEt_2)_3Cl]$ is undissociated and exhibits a one electron oxidation and a two electron reduction step to form $[Ru(S_2CNEt_2)_3]^-$.[2210]

Addition of iodine to $[Ru(S_2CNRR')_3]$ in $CHCl_3$ affords the diamagnetic Ru^{IV} complexes $[Ru(S_2CNRR')_3I_3]$ (**344**) (R = R′ = Me, Et, Ph, $PhCH_2$; R = Me; R′ = Ph). X-Ray analysis (for R = R′ = Me) shows the molecule to be seven-coordinate with one iodide ion coordinated in an axial position while an I_2 molecule strongly solvates the iodide atom. Again all the R groups are magnetically equivalent on the ^1H NMR timescale even at −90°C.[2210,2215] Addition of $Ag[BF_4]$ in acetone to these $[Ru(S_2CNR_2)_3X]$ compounds gives ultimately $[Ru_2(S_2CNR_2)_5]BF_4$ and with $Na[S_2CNR_2]$, $[Ru(S_2CNR_2)_3]$ is formed. Both these reactions illustrate the lability of the Ru—X bond.[2210,2212,2215]

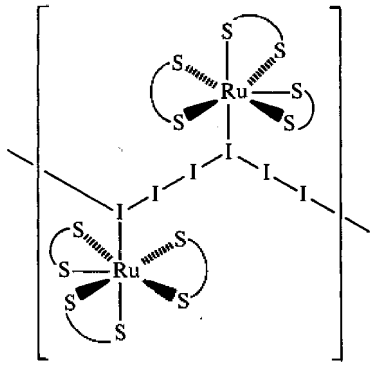
Interestingly, $[Ru(S_2CNEt_2)_3NO]$ is six-coordinate with one of the $^-S_2CNEt_2$ groups monodentate. This is not too surprising since the complex contains a Ru^{II} d^6 ion which has a marked preference for an octahedral t_{2g}^6 configuration.[2203] Hydrogen-1 and ^{13}C NMR studies of $[Ru(S_2C-$



(342)



(343)



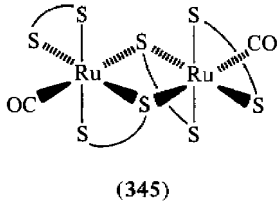
(344)

$NR_2)_3NO]$ (R = Me, Et) (made by passing NO through $CHCl_3$ solutions of $[Ru(S_2CNR_2)_3]$), show hindered rotation about the C=N bond in the two bidentate sulfur ligands but free rotation at ambient temperature in the monodentate ligand; there is no exchange between mono- and bi-dentate ligands at room temperature.[1308,2216]

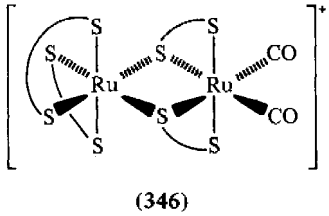
The complexes *trans*-$[RuCl(S_2CNR_2)_2NO]$ (R_2 = Me, Et, MePh, MeEt) are prepared by reaction of $[RuCl_3NO]$ with two equivalents of $Na[S_2CNR_2]$. A series of *cis*-$[RuX(S_2CNR_2)_2NO]$ (X = Cl, Br, I, NO_2, SCN, N_3, NCO, F) can be synthesized by treatment of the *trans* chloro compound with either HX or AgX. Heating some of these *cis* isomers to 160–210°C results in quantitative conversion to the *trans* isomer. Several cationic solvates *trans*-$[Ru(S_2CNR_2)_2NO(S)]^+$ (S = H_2O, MeOH) were also isolated and ^1H and ^{13}C NMR studies on all these compounds indicate stereochemical rigidity at ambient temperature.[1308]

The binuclear $[Ru_2N(S_2CNEt_2)_4]Cl$ has been prepared by reaction of $K_3[Ru_2NCl_8(OH_2)_2]$ with $Na[S_2CNEt_2]$. It is a non-electrolyte in acetone solution and may be polymeric in the solid state with ---Ru—Cl—Ru—N—Ru—Cl--- chains.[65]

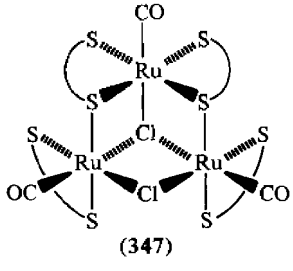
The yellow crystalline '$Ru(S_2CNR_2)_2CO$' (R = Me, Et) and $[Ru(S_2CNR_2)_2(CO)_2]$ (R = Me, $PhCH_2$) were prepared by reaction of ethanolic 'RuCOCl' solutions with $Na[S_2CNR_2]$ or tetrasubstituted thiuramdisulfide.[107] The latter (R = Me) is also prepared by treating $[Ru_3(CO)_{12}]$ with tetramethylthiuramdisulfide or by the prolonged reaction of $[RuCl_2(CO)_2(PPh_3)_2]$ with $Na[S_2CNMe_2]$.[1798] The related thioxanthate complex $[Ru(S_2CSMe)_2(CO)_2]$ is formed by addition of CS_2 to THF solutions of $Na_2[Ru(CO)_4]$, followed by reaction with methyl iodide.[2217] Prior ageing of the 'RuCOCl' solution and treatment with tetrabenzylthiuramdisulfide gives $[Ru\{S_2CN(CH_2Ph)_2\}_2(CO)_2]Cl$ (μ_{eff} = 1.8 BM).[107] However, X-ray analyses by Raston and White[2218] reveal that '$Ru(S_2CNEt_2)_2CO$' has the dimeric structure (**345**) in the solid state. Compound (**345**) is also formed, together with some *cis*-$[Ru(S_2CNEt_2)_2(CO)_2]$ by reaction of β-$[Ru_2(S_2CNEt_2)_5]$ with CO under UV irradiation.[2210] Slow electrochemical oxidation of (**345**) affords the mixed valence $Ru_2^{II,III}$ cation, $[Ru_2(S_2CNEt_2)_4(CO)_2]^+$ (**346**), isolated in high yield as its BF_4^- salt. The most important feature of this structure is that the CO groups are now both coordinated to the same Ru atom, which indicates that the oxidation reaction has resulted in an unusual CO rearrangement. The Ru—Ru distance of 3.614(1) Å indicates no significant Ru—Ru bonding.[2219] Another interesting Ru^{II} trinuclear complex (**347**) was isolated in minute quantities by prolonged reaction of methanolic solutions of 'RuCOCl' with the ester $MeSC(S)NEt_2$.[2220]



(345)



(346)



(347)

Treatment of (**345**) (R_2 = Me_2, Et_2 or MePh) with bis(perfluoromethyl)-1,2-dithietene in boiling THF gives violet, diamagnetic crystals of $[Ru(S_2CNR_2)_2(S_2C_2(CF_3)_2)]$ which were characterized by ^1H NMR and IR spectroscopy.[2221] Some $[Ru(S_2CNMe_2)_2diene]$ (diene = nbd, cod) have been prepared by reaction of $[RuX_2diene]_n$ with $Na[S_2CNMe_2]$.[2222] For the preparation of pentamethylenedithiocarbamate and related ligands, see references 2223–2225.

A range of complexes containing dithiocarbamate or dithiocarbonate groups and P donor ligands are described in Section 45.5.4.8.ii.

45.7.5 Dithio-phosphinato and -phosphato Complexes

The violet complex $[Ru(S_2PPh_2)_3]$ can be prepared by the reaction of $[RuCl_3(AsPh_3)_2MeOH]$ (or '$RuCl_3 \cdot xH_2O$') with $Na[S_2PPh_2]$ in acetone.[1697] Its NMR[1697] and ESR spectra[604] have been reported. The black compound $[Ru(S_2PEt_2)_3]$ ($\mu_{eff} = 1.93$ BM) is mentioned but no preparative details are given.[2226] The analogous $[Ru\{S_2P(4\text{-}ClC_6H_4)_2\}_3]$ ($\mu_{eff} = 1.7$ BM), (from '$RuCl_3 \cdot xH_2O$' and $Na[S_2PR_2]$ in water)[2227] and $[Ru\{S_2P(OEt)_2\}_3]$ (from $K_2[RuCl_5(OH_2)]$ and $NH_4[S_2P(OEt)_2]$),[2228] are also known. The reaction between $[Ru_3(CO)_{12}]$ and Ph_2PS_2H gives *cis*-$[Ru(S_2PPh_2)_2(CO)_2]$.[1798]

Various Ru^{II} complexes containing P or As donor ligands as well as $[Ru(S_2PMe_2)_2(diene)]$ (diene = cod, nbd)[1800] are described in Section 45.5.4.8.ii.

45.7.6 Dithiolene, Dithiocarboxylate and Related Complexes

Apart from early reports of the preparation of $[Ru(S_2C_2Ph_2)_3]$ (originally formulated as $[Ru(S_2C_2Ph_2)_2]$),[2229] and the synthesis[2229] and ESR spectrum of the $[Ru(mnt)_3]^{3-}$ anion,[604] the chemistry of ruthenium dithiolenes is relatively unexplored. Other examples of dithiolenes and related complexes include $(AsPh_4)_3[Ru\{S_2C{=}C(CN)_2\}_3]$ (from $[RuCl_6]^{2-}$ and $[S_2C{=}C(CN)_2]^{2-}$ in water),[230] $[RuL_3]$ (L = S_2CCH_2Ph,[2231] S_2CPh,[2232] $S_2CC_6H_4$-4Me,[2232] 2-hydroxybenzenedithiocarboxylate,[2233] 8-quinolinedithiocarboxylate),[2234] $(Ph_4As)_3[Ru(dto)_3]$ (dto = dithiooxalate)[604] and various Ru^{II} and Ru^{III} quinazoline-2,4(1*H*,3*H*)-dithione (QH) complexes such as $[RuCl_2(Q)(QH)py_2]$, $[RuCl_2(Q)(QH)(OH_2)_2]$, $[Ru(Q)_2(py)_2]$.[2235] The ESR spectra of several of these compounds are analysed in detail.[604,2230] Ruthenium(III) complexes with the following ligands have also been reported: piperazinedithiocarboxylate, piperazinebis(dithiocarboxylate),[2236] 1,2,4-triazoline-5-thione derivatives.[2237]

As discussed elsewhere (Section 45.5.4.8.iii), reaction of $[Ru_3(CO)_{12}]$ with $S_2C_2(CF_3)_2$ in boiling *n*-heptane gives an impure orange coloured carbonyl adduct which reacts with various P and As donor ligands to give clean products. In boiling *n*-decane, $[Ru_3(CO)_{12}]$ and $S_2C_2(CF_3)_2$ produces an impure green material, believed to be $[Ru\{S_2C_2(CF_3)_2\}_2]_2$ which also reacts with P and As donor ligands.[1808] Reaction of the reduced 'ruthenium blue' solution with toluene-3,4-dithiol ($L'H_2$) gives dark brown, polymeric $[Ru_2L'_3]$ ($\mu_{eff} = 0.6$ BM).[676]

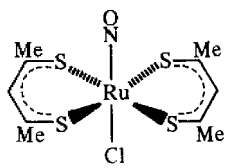
Reaction of $[RuCl_2(CO)_3THF]$ with $Li(SC_6H_4SMe\text{-}o)$ yields *cis*-$[Ru(MeSC_6H_4S)_2(CO)_2]$; with Li[1,2-$S_2C_6H_4$], *cis*-$[Ru(C_6H_4S_2)(CO)_2]^{2-}$ is obtained and isolated as its NMe_4^+ salt. Treatment of the latter with 1,2-$C_2H_4Br_2$ gives *cis*-$[Ru(dttd)(CO)_2]$ (H_2dttd = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane).[1709] Further reactions of these compounds with PR_3 ligands are discussed in Section 45.5.4.8.iii. Dithiocarboxylate complexes containing P donor ligands are covered in Section 45.5.4.8.iv.

45.7.7 Dithio- and Monothio-β-diketonate Complexes

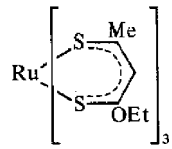
There is a review on transition metal dithio-β-diketonate complexes[2238] but very little work has been published on those of ruthenium. Treatment of $[RuCl_3NO(OH_2)]$ and acetylacetone with H_2S in a saturated HCl/EtOH solution affords the red-brown $[RuCl(sacsac)_2NO]$ for which a *trans* structure (**348**) was proposed on the basis of ^1H NMR spectroscopy. Polarographic studies in acetone/$Et_4N[ClO_4]$ reveal two reversible one electron reductions at -0.27 V and -1.44 V,[1305] whereas $[Ru(sacsac)_3]$, (made as above starting from '$RuCl_3 \cdot xH_2O$'), undergoes a one electron reduction at $+0.04$ V (relative to Ag/AgCl). The magnitude and reversible nature of these reduction potentials suggest that the isolation of sacsac compounds in unusually low formal oxidation states should be possible.[1306,1307,2055] The ESR spectrum of $[Ru(sacsac)_3]$ is consistent with low spin Ru^{III} (t_{2g}^5) with a large low symmetry distortion[604,2239] and its μ_{eff} of 1.72 BM at 290 K supports this conclusion. Detailed electronic spectra (35 000–10 000 cm^{-1}) are reported and some tentative assignments proposed.[2239]

The related *O*-ethylthioacetothioacetate ruthenium(III) complex $[Ru(EtOsacsac)_3]$ (**349**) is prepared by direct reaction of '$RuCl_3 \cdot xH_2O$', EtOsacsacH and Na[OCOMe] in EtOH. The dark green solid is thermally unstable above 60°C.[2240]

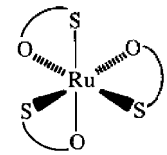
A series of papers[2241–2244] have appeared on the preparation and physicochemical properties of the monothio-β-diketonates $[Ru(RC(S)=CHCOCF_3)_3]$ (R = Ph, *p*-MeC_6H_4, *m*-MeC_6H_4, 2-thienyl, β-naphthyl, Pr^i, *m*-ClC_6H_4, *m*-BrC_6H_4) and $[Ru(RC(S)XC(O)Ph)_3]$ (X = CH, R = Ph, NHPh, NBu_2; X = N, R = piperidino, NBu_2).[1751a] Information given includes mass spectra (molecular ion peak observed), dipole moments (which suggest a facial octahedral configuration (**350**) in which all S atoms are mutually *cis*), and magnetic data over the temperature range 83–293 K. The compounds are all low spin Ru^{III} with magnetic moments in the range 1.68–1.84 BM (at 293 K). They obey the Curie–Weiss Law with large negative values for the Weiss constant. Brown, diamagnetic $[Ru(PhC(S)CHC(O)Ph)]_4$ was reported as the product from the reaction between $K_2[RuCl_6]$ and PhC(S)CHC(O)Ph but it was very poorly characterized.[1751b]



(348)



(349)



(350)

Some monothio-carboxylate, -carbonate and -carbamate complexes have also been synthesized but these all contain P donor ligands (see Section 45.5.4.8.v).

45.7.8 Thiourea Complexes

The reaction of thiourea with Ru^{III} ions is of analytical importance and much work has been done towards developing a reliable method of analysis.[2245] Although earlier studies[2246] suggested that only two thiourea complexes were present in $HClO_4$ solution, namely $[Ru(tu)]^{2+}$ and $[Ru(tu)_3]$, Youmans has shown that reaction of aqueous HCl solutions of '$RuCl_3 \cdot xH_2O$' with an excess of thiourea at 100°C gives $[Ru(tu)_6]^{3+}$ isolated as its $[HgI_4]^{2-}$ salt. Magnetic measurements (μ_{eff} = 2.0 BM at 300 K) support the Ru^{III} formulation and IR studies indicate Ru—S bonding.[2247]

More recently,[2248] $[RuCl(tu)_5]Cl_2$ has been isolated as have a number of complexes containing substituted thioureas such as diphenylthiourea, allylthiourea, naphthylthiourea *etc.* For other (mainly Russian) references to studies of the interaction of thiourea and substituted thioureas with ruthenium(III), see reference 3, p. 212.

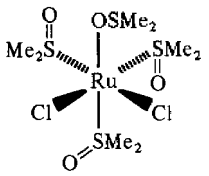
For ammine complexes containing SO_2, *e.g.* $[Ru(NH_3)_4(SO_2)(OH_2)]^{2+}$, $[RuCl(NH_3)_4SO_2]Cl$ *etc.*, see Section 45.4.1.2.iii.c.

45.7.9 Sulfoxide Complexes

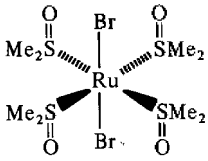
These are covered in this section because most ruthenium sulfoxide complexes contain predominantly S-bonded groups. Two reviews on transition metal sulfoxides have been published.[2249,2250] Yellow $[RuX_2(DMSO)_4]$ (X = Cl, Br) were first prepared by the reduction of '$RuCl_3 \cdot xH_2O$' (or $RuBr_3$) in DMSO at 80°C with H_2.[2251] Later studies revealed that the same compounds are formed in quantitative yield by heating the halides for a few minutes with DMSO under reflux.[112] The bromo compound is also formed by prolonged shaking of $[RuBr_3(AsPh_3)_2MeOH]$ with DMSO.[1697] The deuterated products $[RuX_2(d^6\text{-DMSO})_4]$ are obtained in analogous fashion.

The IR,[112,2251] ^1H[112,2252] and ^{13}C[2253] NMR spectra of yellow $[RuCl_2(DMSO)_4]$ suggest the presence of both S- and O-bonded DMSO groups and X-ray analysis[2254] confirms structure (**351**) with a facial arrangement of S-bonded ligands. A less stable, red isomer of $[RuCl_2(DMSO)_4]$ has also been described and it was concluded on the basis of IR evidence that it should be formulated as $[Ru(OSMe_2)_n(SOMe_2)_{4-n}Cl_2]$ ($n \geq 2$).[2186]

For $[RuBr_2(DMSO)_4]$ however, spectroscopic evidence indicates exclusively S-bonded groups[1697,2252] and an X-ray study[2255] confirms structure (**352**), with a *trans* arrangement. IR measurements suggest that $[RuI_2(DMSO)_4]$ has a similar structure.[2252] This difference in structure between the chloro and bromo complexes helps to rationalize the fact that the latter is a much more active sulfide oxidation catalyst.[2256,2257] Compounds of tetramethylene sulfoxide of type $[RuX_2(TMSO)_4]$ (X = Cl, Br, I) with only S-bonded groups are known,[2258,2259] and the thermal decomposition of $[RuCl_2(DMSO)_4]$ has been studied by tga and dta techniques.[2186] Hydrolysis of $[RuCl_2(DMSO)_4]$ can be monitored by ^1H NMR spectroscopy and various aqua complexes detected.[2252,2260a]

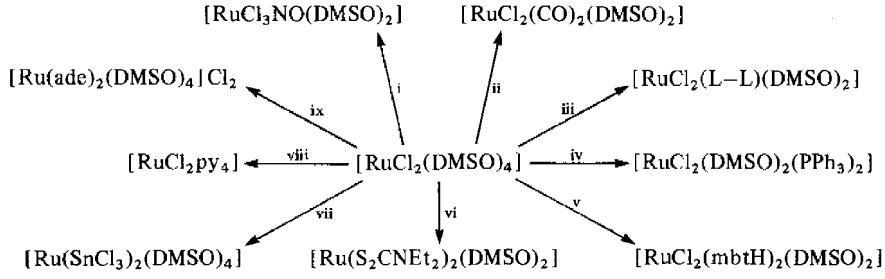


(351)



(352)

Some reactions of $[RuCl_2(DMSO)_4]$ in which either the chloride or some or all of the DMSO groups are replaced are shown in Scheme 69.[112] Similar studies have been reported using *trans*-$[RuBr_2(DMSO)_4]$.[2260b] Note that in the absence of DMSO, adenine and cytosine are claimed to react with $[RuCl_2(DMSO)_4]$ to give the binuclear species $[Ru_2Cl_4(ade)_3(DMSO)_4]$ and $[Ru_2Cl_4(cyt)_4(DMSO)_2(MeOH)_4]$ respectively.[2261] A paper has revealed that reaction of $[RuCl_2(DMSO)_4]$ with various anionic bidentate ligands such as *o*-$HO_2CC_6H_4NHCOMe$ (AABH) *etc.* provides a convenient route to $[Ru(AAB)_2(DMSO)_2]$. With uninegative terdentate ligands, (L), complexes of formula $[Ru(L)_2]$ are formed.[2262]



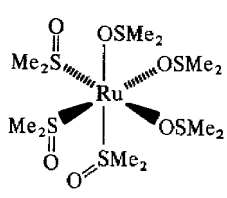
i, NO; ii, CO; iii, L–L = 2,2′-bipy, 1,10-phen or 2-aminopyridine; iv, PPh_3; v, 2-mercaptobenzothiazole (mbtH); vi, $Na[S_2CNEt_2]$; vii, $SnCl_2$; viii, py; ix, adenine/DMSO[2260]

Scheme 69

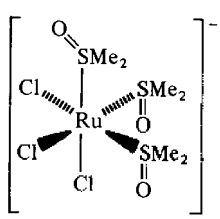
In the presence of Ag^+ in D_2O, $[RuCl_2(DMSO)_4]$ gives *fac*-$[Ru(DMSO)_4(OD_2)_2]^{2+}$ and in DMSO, this provides a route to the $[Ru(DMSO)_6]^{2+}$ cation, with counterion ClO_4^-[112] or BF_4^-.[2263] Equation (137) shows another route to this cation. The diene/DMSO cation is made by reaction of $[Ru(N_2H_4)_4cod](BPh_4)_2$ with DMSO in acetone. IR,[650,2263] ^1H[650,2252,2263] and ^{13}C[2253] NMR studies on this hexakis cation suggest both S- and O-bonded DMSO groups which is confirmed by crystallographic evidence (structure **353**).[2263] Hydrolysis of (**353**) leads to stepwise displacement of O-bonded DMSO to form $[Ru(DMSO)_{6-n}(OD_2)_n]^{2+}$ (n = 1–3) respectively.[2252,2260a,2263] Reaction of (**353**) (BF_4^- salt) with adenine in DMSO gives $[Ru(ade)_2(DMSO)_4](BF_4)_2$.[2260a] Treatment of $[RuCl_2(DMSO)_4]$ with stoichiometric amounts of $Ag[BF_4]$ in DMSO generates $[RuCl(OSMe_2)_2(SOMe_2)_3]^+$.[2252]

Reduction of '$RuCl_3 \cdot xH_2O$' with H_2 at 80°C in the presence of a stoichiometric amount of DMSO in DMA solution affords yellow $NMe_2H_2[RuCl_3(DMSO)_3]$, the cation being a reduction product of the solvent. The deuterated analogue is readily prepared and X-ray analysis shows the *fac* S-bonded structure (**354**).[2264] In water loss of chloride produces some $[RuCl_2(DMSO)_3(OH_2)]$ and treatment with Ag^+/D_2O forms $[Ru(DMSO)_3(OD_2)_3]^{2+}$.[2252,2263] With adenine in DMSO, $[RuCl_2(ade)(DMSO)_3]$ is produced.[2260a]

$$[Ru(DMSO)_4cod](BPh_4)_2 \xrightarrow{DMSO} [Ru(DMSO)_6](BPh_4)_2^{650} \qquad (137)$$



(353)



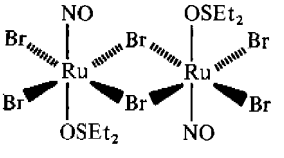
(354)

Complexes (**351**), (**353**) and (**354**) will catalyse the hydrogenation (DMA, 60°C, 1 atm) of acrylamide to 1-aminopropane[2263,2264] but are inactive for the hydrogenation of alkenes.[2263] Compounds (**351**) and (**354**) catalyse the hydrogenation of methyl vinyl ketone to methyl ethyl ketone and the reduction of unsaturated carboxylic acids.[2265]

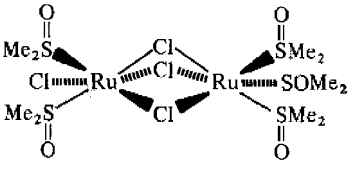
Neutral, monomeric ruthenium(II) complexes containing chiral sulfoxide ligands have been prepared by sulfoxide exchange reactions with $[RuCl_2(DMSO)_4]$, and these show some catalytic activity for the hydrogenation of prochiral unsaturated carboxylic acid substrates.[2266] With bulkier sulfoxide ligands (L), trimeric complexes $[RuCl_2L_2]_3$ are formed and racemic methyl phenyl sulfoxide (mpso) affords polymeric $[RuCl_2(mpso)_2]_n$.[2265,1843]

Other monomeric Ru^{II} complexes containing DMSO ligands include S-bonded $[Ru(NH_3)_5(DMSO)]^{2+}$ (from $[Ru(NH_3)_5N_2]^{2+}$ and DMSO),[244,418] $[RuCl_3NO(DMSO)_2]$ (from '$RuCl_3 \cdot xH_2O$', DMSO and NO),[112] $[RuClX(DMSO)(\eta\text{-}C_6H_6)]$ (X = Cl, H).[2250] References to the preparation of DMSO compounds containing P or As donor ligands are given in Section 45.5.4.8.vi.

The binuclear O-bonded $[RuBr_3NO(OSEt_2)]_2$ (**355**) is formed by photochemically-induced aerial oxidation of $[RuBr_3NO(Et_2S)_2]$ in $CHCl_3$,[1301] whereas heating moist toluene solutions of $[RuCl_2(DMSO)_4]$ affords $[Ru_2Cl_4(DMSO)_5]$.[1192] Detailed IR and NMR (^1H and ^{13}C) studies establish the triple chloride-bridged structure (**356**) containing exclusively S-bonded DMSO groups. In contrast to $[RuCl_2(DMSO)_4]$, (**356**) undergoes a reversible one electron oxidation to generate *in situ* the mixed valence cation $[Ru_2Cl_4(DMSO)_5]^+$.[2253]



(355)



(356)

Relatively little evidence exists for monomeric Ru^{III} sulfoxide complexes. Thus $[RuCl_3(DMSO)_3]$ was prepared by the reaction between DMSO and the reduced 'ruthenium blue' solutions[676] but later reports[112] indicate that it is unrepeatable. However, direct reaction of '$RuX_3 \cdot xH_2O$' with di-*n*-propyl or di-*n*-butyl sulfoxide (L) is claimed to give $[RuX_3L_3]$ (X = Cl, Br) and IR data suggest the presence of both O- and S-bonded ligands.[2258] Other Ru^{III} sulfoxides include $[Ru(DMSO)_6]X_3$ (X = Cl, ClO_4), $[Ru(DMSO)_5Cl]Cl_2$ and $M[RuCl_4(DMSO)_2]$ (M = Bu_4N^+, Na^+). The first two contain both O- and S-bonded DMSO but the latter only S-bonded.[2186,2267] Reaction of $[RuBr_3(AsPh_3)_2MeOH]$ with $DMSO/H_2O$ (1:1 v/v) gives O-bonded $[RuBr_3(AsPh_3)_2DMSO]$; in neat DMSO, $[RuBr_2(DMSO)_4]$ is formed.[1697]

45.8 SELENIUM AND TELLURIUM LIGANDS

In contrast to sulfur (Section 45.7), relatively little has been published on ruthenium complexes containing selenium and tellurium ligands.

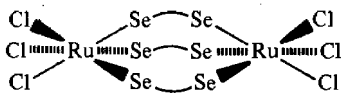
$RuSe_2$ and $RuTe_2$ are normally prepared from the elements at high temperature or by heating $RuCl_3$ with Se or Te.[2] These have the pyrite structure.[2158,2268] Other measurements on these compounds include IR spectra, force constant and normal coordinate calculations,[2162] a ^{125}Te Mössbauer spectrum[2269] and the determination of the high temperature enthalpy and decomposition pressure of $RuSe_2$.[2270] A low temperature modification of $RuTe_2$ of the marcasite type has been prepared. At 620°C, this transforms monotropically into the pyrite type form.[2271] $Rh_{1-x}Ru_xSe_2$ ($x < 0.45$) is known and exhibits superconductivity.[2272]

Reaction of $[Ru_3(CO)_{12}]$ with selenium or tellurium under a CO/H_2 atmosphere in refluxing octane gives $[Ru_3H_2(\mu_3\text{-}E)(CO)_9]$ (E = Se, Te) (see (**332**) Section 45.7.1) and $[Ru_3Se_2(CO)_9]$ (see (**333**), Section 45.7.1).[2166] Low yields of (**332**) are also obtained from reaction of $[Ru_3(CO)_{12}]$ with EO_2 and alcoholic KOH.[2165] The interesting binuclear complex $[(NH_3)_5RuSe_2Ru(NH_3)_5]Cl_4$ has recently been synthesized.[2273]

The yellow binuclear compounds $[Ru(EPh)(CO)_3]_2$ (E = Se, Te) are minor products from reactions between $[Ru_3(CO)_{12}]$ and Ph_2E_2. These react further with Ph_2E_2 to give two forms of orange, polymeric $[Ru(EPh)_2(CO)_2]_n$ (n = 6–7 and 12–14) as major products. The seleno compound $[Ru(SePh)(CO)_3]_2$ may exist as two isomers, but only one, probably with the *anti* conformation was isolated.[2274] Irradiation of $[Ru(CO)_2(\eta\text{-}C_5H_5)]_2$ with Ph_2Se_2 gives $[Ru(SePh)(CO)_2(\eta\text{-}C_5H_5)]$ and

$[Ru(\mu\text{-SePh})(CO)(\eta\text{-}C_5H_5)]_2$ (reference 1, p. 781). $[RuL_4(MeCN)]$ and $[RuL_4(CO)]$ (LH = 2,3,5,6-$(CH_3)_4C_6HSeH$ or 2,4,6-$(Pr^i)_3C_6H_2SeH$) have been prepared.[2170b]

A number of seleno- and telluro- ether complexes are known. For example, treatment of $[RuI_2(CO)_2]_n$ with various selenides or tellurides affords $[RuI_2(CO)_2L_2]$ and/or $[RuI_2(CO)L_3]$ [L = Et_2Se, Ph_2Se, Bu_2Te, Ph_2Te]. Isomeric mixtures are frequently formed and separated by fractional crystallization. The chloro and bromo analogues can be prepared by treatment of the iodo complex with Cl_2 or Br_2 respectively.[1611,2191] Similarly, Ph_3PSe gives $[RuI_2(CO)_2(SePPh_3)_2]$ which decomposes in DMF to produce $[Ru_2I_4(CO)(SePPh_3)_2DMF]$. $[RuI_2(CO)_2PhSe(CH_2)_2SePh]$ is formed unexpectedly from $[RuI_2(CO)_2]_n$, Ph_2Se_2, EtOH and C_6H_6 at 150°C. The ethano bridge is presumably generated by catalytic dehydration of EtOH.[1611] On the basis of ^1H NMR and molecular weight measurements, the complex of empirical formula $[RuCl_3(Pr^iSe(CH_2)_2SePr^i)]_{1.5}$ is proposed to have the dimeric structure (**357**).[2275]



(357)

Complexes of type $[RuX_3NOL_2]$ (L = Et_2Se, EtPhSe) are readily prepared[1302] and exhibit facile inversion at selenium.[1303] Ammine cations such as $[Ru(NH_3)_5EMe_2]^{2+}$, $[Ru(NH_3)_4(OH_2)(EMe_2)]^{2+}$ (E = Se, Te),[433] $[Ru(SePh)(NH_3)_5]^{2+}$[432] are also known (*cf.* SR_2 analogues in Section 45.4.1.2.iv).

The only diselenocarbamates of ruthenium mentioned in the literature are $[Ru(Se_2CNEt_2)_3]$ (from Et_2NCSe_2H and $Na_2[RuCl_6]$),[2276] and $[Ru(Se_2CNMe_2)_3NO]$.[2216] Selenourea is reported to form a blue-green complex with Ru^{IV} solutions in 6 M HCl[2277] and interactions between selenourea and Ru^{III} have been investigated.[2278]

Other selenium-containing complexes include the benzeneseleninato compounds $[Ru(RC_6H_4SeO_2)_3]$ and $[Ru(RC_6H_4SeO_2)_2X]$, (R = H; *p*- and *m*-Cl, Br; *p*-Me; X = Cl, Br), whose IR spectra indicate *O,O'*-seleninato coordination. The tris-complexes are octahedral and the bis are polymeric, octahedral with bridging halides.[2279,2280] Reaction of $[Ru(CO)_3(PPh_3)_2]$ with $(SeCN)_2$ affords $[Ru(NCSe)_2(CO)_2(PPh_3)_2]$.[2281]

Selenocarbonyl complexes and related species are discussed in Sections 45.5.4.5.ii and 45.5.4.5.iii.

45.9 HALOGEN LIGANDS

This section covers the chemistry of pure halides, aqua-, hydroxo-, oxo- and carbonyl halides. For nitrido and nitrosyl halides see Sections 45.4.6 and 45.4.4.4 respectively. Unlike most other sections of this article, much of the published work on ruthenium halides is pre-1970 and excellent, detailed reviews[2,3] have appeared in the literature. Therefore in order to conserve space and avoid undue repetition, only a relatively brief account containing earlier key references and more recent data is presented here.

45.9.1 Ruthenium(I) Halides

Although reactions of hypophosphorous acid with aqueous solutions of RuX_3 (X = Cl, Br, I) are claimed to give RuX *in situ*,[2282] further work in this area is now required. More recently, Ru^I chloro compounds of possible formula $H[Ru_2Cl_3(DMA)_2]$ have been isolated from reaction of '$RuCl_3 \cdot xH_2O$' with H_2 in DMA; these species are effective catalysts for hydrogenation of alkenes and unsaturated carboxylic acids.[2283]

45.9.2 Ruthenium(I) Carbonyl Halides

Brief reports on the preparation and properties of colourless $[RuBr(CO)]_n$, (from $RuBr_3$ and CO at 350 atm and 180°C),[2284] and orange $[RuI(CO)_x]_n$, (from $RuCl_3$ or $[RuI_2(CO)_2]_n$ with CO or $[Ru(CO_5)]$ and I_2),[1110] have appeared in the literature. A reinvestigation of these compounds would be of considerable interest.

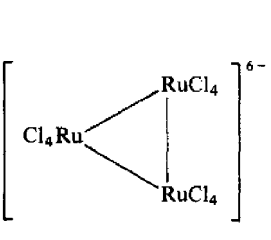
45.9.3 Ruthenium(II) Halides

Although there are a number of reports of the preparation of $RuCl_2$ in the early literature, it appears that this species has never been prepared in a pure state. In fact the reported method of preparation is similar to that established for β-$RuCl_3$ (see Section 45.9.6.1)[2285] and incomplete chlorination with consequent contamination of $RuCl_3$ by ruthenium metal was probably responsible for the erroneous claims. However, residues with Ru:Cl ratios of *ca.* 1:2 have been isolated from the reduced 'ruthenium blue' solution (see below); a black solid with a Ru:Br ratio of *ca.* 1:2 is obtained from the corresponding violet–blue Ru^{II} bromide solution.[2286,2287] No RuX_2 (X = F, I) are known.

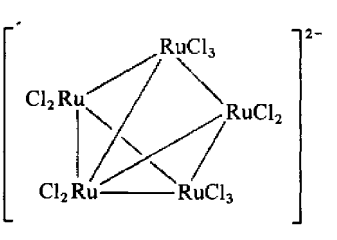
Chemical or electrochemical reduction of aqueous or alcoholic solutions of '$RuCl_3 \cdot xH_2O$', $K_2[RuCl_6]$ or $K_4[Ru_2OCl_{10}]$ produce the well-known reduced 'ruthenium blue' solutions which are both useful synthetic precursors for many ruthenium(II) and (III) complexes[676] and active catalysts for alkene hydrogenation and isomerization.[2283] However in spite of 180 years of effort the composition of these blue solutions still remains uncertain. For an excellent and detailed account of this fascinating but extremely complicated topic, see reference 3, p. 342. In brief, a survey of the experimental data clearly reveals that there are several species present in solution, in an equilibrium whose position depends on the pH and chloride ion concentration of the solution. Earlier workers suggested that an important component of these solutions was $[RuCl_4]^{2-}$ and various solids purporting to contain this anion were isolated by addition of cations such as Cs^+, pyH^+, enH_2^{2+} *etc.* Later workers[2288] have proposed a trimeric structure (**358**) for this anion.

Rose and Wilkinson,[2288] by treatment of the methanolic blue solutions with various cations, have trapped out stable solids of composition $M[Ru_5Cl_{12}]$ ($M = Fe(bipy)_3^{2+}$, $Ru(bipy)_3^{2+}$, $[C_6H_4(CH_2PPh_3)_2]^{2+}$ and proposed structure (**359**). The ESR spectra of these materials are essentially identical to those of the blue solutions in various solvents, so it is reasonable to assume that the ion present in the solids is also present in the blue solutions. However, the ESR spectrum and magnetic properties of (**359**) (μ_{eff} = 1.3 BM per five ruthenium atoms) are not consistent with what might be expected to be a diamagnetic cluster. Furthermore, the blue solutions obtained by electrolytic reduction of $K_2[RuCl_5(OH_2)]$ in 0.01 M HCl and which can be separated into the binuclear blue components $[Ru_2Cl_3]^{2+}$, $[Ru_2Cl_4]^+$, $[Ru_2Cl_5]$, (and unidentified anionic species), by ion exchange techniques at 0°C have the same ESR spectra as (**359**).[2289] It has been suggested that these $Ru_2^{II,III}$ mixed valence complexes are isostructural with the ammines $[(NH_3)_3Ru(\mu\text{-}Cl)_3Ru(NH_3)_3]^{2+}$ (see Section 45.4.1.3.iv), *e.g.* $[(H_2O)_3RuCl_3Ru(H_2O)_3]^{2+}$ *etc.* Clearly more work is now required to resolve these differences of structural formulation.

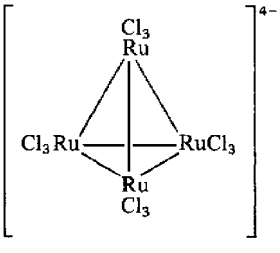
Upon saturation with HCl gas, the blue methanolic solutions turn green and addition of a cation gives green solids of empirical formula $M[RuCl_3]$ ($M = pyH^+$, Et_4N^+) for which the tetrameric structure (**360**) has been proposed.[2288] Interestingly, reaction between '$RuCl_3 \cdot xH_2O$' and $Na[S_2CNPr^i_2]$ gives as one of the minor products, $[Ru_2(S_2CNPr^i_2)_5]_2[Ru_2Cl_6] \cdot 2CHCl_3$, which contains the only crystallographically characterized chloro complex (**361**) of Ru^{II}.[2211] Clearly this dimeric formulation must be considered as a possibility for Rose and Wilkinson's green complexes $M_n[RuCl_3]_n$.[2290] The claim of brown trimeric anions $[Ru_3Cl_9]^{3-}$ (from reaction of aqueous solutions of '$RuCl_3 \cdot xH_2O$' with H_2O_2)[2290] has been withdrawn; they are now reformulated as the binuclear Ru^{IV} anions $[Ru_2OCl_9(OH_2)]^{3-}$ (reference 5, p. 97).



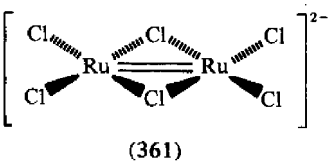
(358)



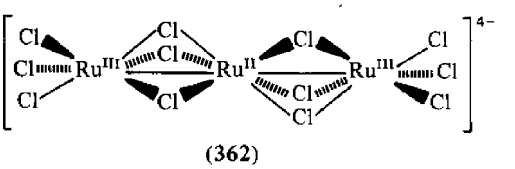
(359)



(360)



(361)



(362)

Dissolution of $[Ru_2(OCOMe)_4Cl]$ in 12 M HCl also gives a deep blue solution and addition of $[Et_4N]Cl$ and solvent evaporation leads to the slow precipitation of the deep green, mixed valence $[H_7O_3]_2[Et_4N]_2[Ru_3Cl_{12}]$ (**362**) which has been characterized crystallographically.[2121a] It is believed that this complex is derived from the components of the ruthenium blue solution by trace amounts of aerial oxidation. The ground state electronic structure and electronic spectra of (**362**) have been calculated by the SCF–Xα–SW method.[2291]

Violet-blue solutions are obtained from chemical reduction of $RuBr_3$ in ethanolic or HBr/H_2O media.[2287,2292] These give similar electronic[2292] and ESR spectra[2288] to their chloride analogues. Blue solutions are also generated by reduction of green ethanolic solutions of RuI_3.[2287]

45.9.4 Ruthenium(II) Aquahalide Complexes

Polarographic half-wave potentials for the reduction of various monomeric aquachlororuthenium(III) complexes $[RuCl_n(OH_2)_{6-n}]^{(3-n)+}$ $(0 \leqslant n \leqslant 3)$ have been reported. The various Ru^{II} products then undergo rapid aquation to give $[Ru(H_2O)_6]^{2+}$ (see Section 45.6.1). A cyclic voltammetric study on $[RuCl(OH_2)_5]^+$ reveals that at high sweep rates, only the oxidation wave due to $[RuCl(OH_2)_5]^+$ is observed; at lower rates, a wave due to $[Ru(H_2O)_6]^{2+}$ grows in. The $[RuCl_3(OH_2)_3]^-$ anion aquates too rapidly to be studied by cyclic voltammetry but the rates of aquation of *cis*- and *trans*-$[RuCl_2(OH_2)_4]$ were calculated as 0.13 and 0.14 s^{-1} respectively.[2293]

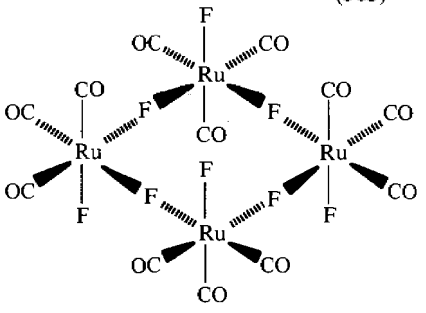
45.9.5 Ruthenium(II) Carbonyl Halides

45.9.5.1 Carbonyl fluorides

Reaction of $[RuF_2(CO)_3 \cdot RuF_5]_2$ (see Section 45.9.8) with CO (100 atm/200°C) gives pale yellow $[RuF_2(CO)_3]_4$ of structure (**363**). Compound (**363**) is also formed as shown in equation (138). The mass spectrum of (**363**) has been analysed in terms of an initial fragmentation to yield $[Ru_2F_3(CO)_6]^+$ and $[Ru_2F_4(CO)_5]^+$. It reacts with HCl to give $[RuCl_2(CO)_3]_2$ and with an excess of XeF_2 to form *fac*-$[RuF_3(CO)_3]$.[2294,2295]

$$[Ru_3(CO)_{12}] + XeF_2 \xrightarrow[\text{or HF}]{CFCl_2CF_2Cl} [RuF_2(CO)_3]_4 \qquad (138)$$

(**363**)



(**363**)

45.9.5.2 Neutral carbonyl chlorides, bromides and iodides

For detailed references, see the excellent accounts of this area in references 1 and 3. The first report of ruthenium(II) carbonyl halides was in 1924 when polymeric $[RuX_2(CO)_2]_2$ were prepared by passing CO over RuX_3 (X = Cl, Br, I) at *ca.* 270°C.[2296] Other routes to these compounds include reaction of $[Ru_3(CO)_{12}]$ and halogens in inert solvents above 140°C,[2297] evaporation of aqueous HX solutions containing $[RuX_4(CO)_2]^{2-}$,[1613,2298] thermal decomposition of $[RuX_2(CO)_4]$ (or $[Ru_2X_4(CO)_6]$) at 200°C *in vacuo*,[2297] or carbonylation of $[RuCl_2(cht)]_2$.[1372] IR data show two ν_{CO} bands, indicating a *cis*-$(CO)_2$ arrangement in a 'kinked' structure (**364**).[2299]

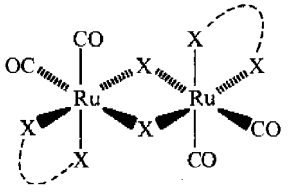
Other neutral Ru^{II} carbonyl halides are of the type *cis*-$[RuX_2(CO)_4]$, $[RuX_2(CO)_3]_2$ and $[Ru_3X_6(CO)_{12}]$. The best route to *cis*-$[RuI_2(CO)_4]$ is shown in equation (139).[2300] Treatment of

$[RuBr_2(CO)_3]_2$ with CO (80–90 atm/20–120°C) gives pure *cis*-$[RuBr_2(CO)_4]$; the chloride reacts similarly but rapidly reforms $[RuCl_2(CO)_3]_2$ in the absence of CO.[651] For other preparations see reference 1, p. 672. X-Ray (for X = I),[2301] IR, ^{13}C NMR and mass spectral data are available.[2300,2302]

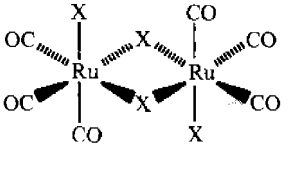
$$[Ru_3(CO)_{12}] + I_2 \xrightarrow[100°C/40\,atm/13\,h]{CO/C_6H_6} \underset{(90\%)}{cis\text{-}[RuI_2(CO)_4]} \qquad (139)$$

Carbonylation of '$RuCl_3 \cdot xH_2O$' in methanol (60°C/10 atm/24 h) and subsequent evaporation of solvents is the best route to $[RuCl_2(CO)_3]_2$.[2303] Treatment of $[Ru_3(CO)_{12}]$ with CHX_3 in the presence of ethanol also affords $[RuX_2(CO)_3]_2$ (X = Cl, Br)[653] and oxidation of $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ with I_2 gives $[RuI_2(CO)_3]_2$.[2304] Other routes include thermal decomposition of *cis*-$[RuX_2(CO)_4]$[654] and carbonylation of $[RuCl_2(nbd)]_n$ or $[RuCl_2(C_6H_6)]_2$ in alcohols.[187a] Detailed mass spectral data have been recorded.[2302] The structure (**365**) of $[RuX_2(CO)_3]_2$ (X = Cl, Br)[2305] is consistent with the IR data obtained in pure $CHCl_3$. Discrepancies between authors in the earlier IR solution spectral results in $CHCl_3$ are ascribed to the presence of ethanol stabilizer producing solvated monomers such as $[RuCl_2(CO)_3(EtOH)]$.[651] Reactions with Lewis bases to give $[RuX_2(CO)_3L]$ and $[RuX_2(CO)_2L_2]$ are covered in other sections. Reaction with $SbCl_5$ and HCl in CH_2Cl_2 gives $[RuCl_2(CO)_3]_2SbCl_3$.[2306]

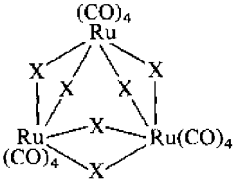
At room temperature $[RuX_2(CO)_4]$ rapidly trimerize to form $[Ru_3X_6(CO)_{12}]$ which are proposed to have structure (**366**). The chloride is most conveniently prepared by direct chlorination of $[Ru_3(CO)_{12}]$ in refluxing $CHCl_3$. In solution, they readily lose CO to give $[RuX_2(CO)_3]_2$.[2297,2307]



(364)



(365)



(366)

45.9.5.3 Anionic carbonyl halides

Reaction of '$RuCl_3 \cdot xH_2O$' with HCl/HCO_2H (1:1 mixtures), under reflux produces a series of striking colour changes (deep red to green to orange to yellow), over a period of 30 h.[2298,2308] Treatment of the solution at the appropriate time with CsCl led to isolation of red $Cs_2[RuCl_5CO]$, green $Cs_2[trans\text{-}RuCl_4CO(OH_2)]$ (confirmed by X-ray analysis),[2309] orange $Cs_2[cis\text{-}RuCl_4(CO)_2]$ and yellow $Cs[fac\text{-}RuCl_3(CO)_3]$ salts respectively. Evaporation of the final solution gave $[RuCl_2(CO)_2]_n$. Less convenient routes to these anions include carbonylation and subsequent reduction by H_2 of '$RuCl_3 \cdot xH_2O$'/H_2O/HCl solutions, carbonylation of reduced 'ruthenium blue' solutions and addition of chloride to $[RuCl_2(CO)_2]_n$ and $[RuCl_2(CO)_3]_2$, (giving $[RuCl_4(CO)_2]^{2-}$ and $[RuCl_3(CO)_3]^-$ respectively).[1613,2310]

Analogous bromo and iodo anions are formed by reaction of '$RuX_3 \cdot xH_2O$' with HX/HCO_2H[2298,2308] or, for $Cs_2[RuX_4(CO)_2]$, by treatment of $Cs_2[RuCl_4(CO)_2]$ with HX. The red 'RuCOCl' solution exchanges with iodide to give a red-brown solution from which dark brown $[Et_4N]_2[Ru_2I_6(CO)_4]$ (with *cis* $Ru(CO)_2$ groups) is obtained by addition of $[Et_4N]Cl$.[2311] For schemes and further details see reference 1, p. 670. For reactions with Lewis bases see Sections 45.4.3.1.ii and 45.5.4.5.i.

45.9.6 Ruthenium(III) Halides

45.9.6.1 Pure neutral halides

Ruthenium(III) fluoride can be prepared by the reduction of ruthenium(V) fluoride with either iodine or sulfur at elevated temperatures[2312] or in an impure form by reduction of $[RuF_5]_4$ with ruthenium metal.[2313] It is a dark brown powder shown by X-ray powder diffraction studies to consist of RuF_6 corner shared octahedra, (with Ru----Ru separations of 3.37 Å).[2314] Neutron diffraction studies reveal no evidence of magnetic ordering even at 4.2 K.[2315]

After considerable confusion and effort (see reference 3, p. 156 for a comprehensive review of the earlier literature), it was shown by Fletcher and co-workers[2316] that two modifications of water

insoluble $RuCl_3$ (namely α and β) could be prepared in a pure state. The dark brown β-form is best obtained by heating ruthenium sponge at 330–340°C in a 1:3 mixture of CO and Cl_2 and the black α-form by heating the β-form in a current of chlorine to 700°C. The $\beta \rightarrow \alpha$ transition occurs at 450°C and is irreversible.[3] The α-form is isostructural with violet $CrCl_3$ and α-$TiCl_3$ and has a strongly defect-ordered layer structure with Ru----Ru = 3.46 Å. The β-form has a distorted octahedral environment of chloride ions, with a Ru----Ru distance of 2.83 Å. Detailed magnetic measurements reveal that β-$RuCl_3$ is antiferromagnetic below 600 K and shows extremely low values of χ_m, whereas α-$RuCl_3$ has much higher magnetic susceptibilities, *e.g.* μ_{eff} = 2.14 BM at room temperture, and only becomes antiferromagnetic below 13 K.[2317] The optical properties of the latter have been studied in IR, visible and UV regions by reflectance spectroscopy.[2318] Information on other physicochemical properties is to be found in reference 3.

Water soluble hydrated or commercial $RuCl_3$ (*i.e.* '$RuCl_3 \cdot xH_2O$') is usually prepared by the evaporation of a solution of $[RuO_4]$ in hydrochloric acid. However, it is important to note that it is a heterogeneous, ill-defined mixture of variable oxidation-state, oxochloro and hydroxochloro monomeric and polymeric ruthenium complexes. Nevertheless, it is by far the most common starting material for the preparation of ruthenium complexes. Note that evaporation of aqueous solutions of '$RuCl_3 \cdot xH_2O$' (pH *ca.* 1.5) several times on a waterbath removes most of the HCl contaminant and this purified '$RuCl_3 \cdot xH_2O$' is much more reactive towards, for example, various organic ligands such as 1,3-cyclohexadienes.[2319]

Commercial '$RuCl_3 \cdot xH_2O$' is widely used as a catalyst (see references 3 and 2320 for details of earlier studies). Examples include the oxidation of amines and alcohols,[2321] the production of glycol esters from synthesis gas,[2322] and the generation of 1,3-diol derivatives from reaction of dienes and alkenes with aldehydes and carboxylic acids.[2323]

Pure samples of water insoluble, black-brown $RuBr_3$ can be prepared by prolonged reaction between ruthenium and bromine at 450–500°C and 20 atm.[2324] X-Ray analysis reveals that the structure is based upon chains of $(Ru_2Br_3)Br_{\frac{3}{2}}$ groups with the metal in approximately octahedral coordination with a Ru----Ru separation of 2.73 Å.[2325,2326] It exhibits only a very weak temperature-independent paramagnetism, indicative of strong metal–metal interactions.[2326] A water soluble version of '$RuBr_3 \cdot xH_2O$' prepared from $[RuO_4]$ (or ruthenium(III) hydroxide) and HBr is also known.[2327]

RuI_3 can be synthesized either by the metathetical reaction between '$RuCl_3 \cdot xH_2O$' and KI in aqueous solution, by the action of hydriodic acid on $[RuO_4]$,[2327,2328] or by thermal decomposition of $[RuI(NH_3)_5]I_2$ or *cis*-$[RuI_2(NH_3)_4]I$.[464,465] The black powder is sparingly soluble in water with a similar structure to $RuBr_3$.[2325] For other properties see reference 3, p. 161.

45.9.6.2 Pure anionic halides

$K_3[RuF_6]$ can be prepared by fusing RuX_3 (X = Cl, I) with $K[HF_2]$ in the absence of oxygen. It is a brownish-grey powder, isomorphous with $K_3[RhF_6]$, with μ_{eff} = 1.25 BM at room temperature. Its electronic and IR spectra are available.[2329,2330]

Virtually all the methods of preparing $[RuCl_6]^{3-}$ are a variation on a method developed by Charonnat which involves recrystallizing salts of $[RuCl_5(OH_2)]^{2-}$ from 12 M hydrochloric acid.[2331] A convenient synthesis of $K_3[RuCl_6]$ is to add the correct molar ratio of KCl to the methanolic 'ruthenium blue' solution, heat under reflux in air and then recrystallize the product from 12 M HCl.[1220] Reduction of $[RuCl_6]^{2-}$ by H_2[2332] and by $H\cdot$[2333] (generated by pulse radiolysis) has been studied. Extensive physicochemical studies on this anion with a variety of cations include X-ray analysis (for $[Al(H_2O)_6]^{3+}$[2331] and $[PhNH_3]^+$ cations[2334]), electronic and IR spectra,[3,2333,2335,2336a,2336b] magnetic circular dichroism,[2337] magnetic measurements (*ca.* 2 BM at 300 K),[2338] ESR,[2339] WHMO[2340] and SCF–Xα–SW calculations on the ground state electronic structure[2291] and measurement of the kinetics of isotope exchange for the reaction shown in equation (140).[2341]

$$[RuCl_6]^{3-} + {}^{36}Cl^- \rightleftharpoons [RuCl_5{}^{36}Cl]^{3-} + Cl^- \qquad (140)$$

$[RuCl_6]^{3-}$ in aqueous HCl solution will activate H_2 homogeneously and hence catalyse its reduction of Ru^{IV} and Fe^{III}.[2342] It will also catalyse the isotopic exchange between H_2O and D_2[2343] and the hydration of alkynes, although the active species in the latter process are probably the aquachloro species $[RuCl_5(OH_2)]^{2-}$ and $[RuCl_4(OH_2)_2]^-$.[1613] The preparation and properties of these and related aquahalide Ru^{III} complexes are discussed in the next section.

There are many reports in the early literature of complexes of the general formula $A_4[RuCl_7]$

which are probably the crystal aggregates $A_3[RuCl_6]ACl$.[2] Thus, $[N(CH_2CH_2NH_3)_3]H[RuCl_7]\cdot 2H_2O$ has spectroscopic properties identical to $K_3[RuCl_6]$ and is formulated as $[N(CH_2CH_2NH_3)_3][RuCl_6]HCl\cdot 2H_2O$,[2338] and $[PhNH_3]_6[RuCl_9]$ is isomorphous with its bromide analogue, whose crystal structure reveals the formulation $[PhNH_3]_6[RuBr_6]Br_3$.[2334] Compounds of formula $A_2[RuCl_5]$ are also known but attempts to repeat many of these preparations have resulted only in the isolation of $A_4[Ru_2OCl_{10}]$[2334] (see Section 45.9.7.3). Nevertheless dehydration of $K_2[RuCl_5(OH_2)]$ or heating $K_2[RuCl_6]$ in HCl at 600°C gives $K_2[RuCl_5]$. Magnetic susceptibility measurements on this material (μ_{eff} = 1.64 BM at 350 K; 1.14 BM at 80 K) are significantly lower than for the $[RuCl_6]^{3-}$ ions (*ca.* 2 BM at 300 K),[2338] which might suggest it should be formulated as a $[Ru_2Cl_{10}]^{4-}$ ion.[2344] Thermal stability studies on this anion and other chlororuthenates such as α-$RuCl_3$ and $K_3[RuCl_6]$ have been reported.[2345]

Earlier Russian work[2346] on the preparation of the $[Ru_2Cl_9]^{3-}$ anion has been verified. $Cs_3[Ru_2Cl_9]$ can be prepared by solid state reaction at 700°C between stoichiometric proportions of CsCl and $RuCl_3$.[2347] Its X-ray structure (Ru—Ru = 2.725(3) Å), magnetic susceptibility (μ_{eff} = 0.51 BM per Ru at 300 K),[2347] redox properties (see equation 141 for $[NBu_4]^+$ salt in CH_2Cl_2; $E_{\frac{1}{2}}$ values *vs.* Ag/AgCl reference electrode)[2348] and electronic spectra[2291,2346] have been reported and SCF–Xα–SW calculations performed which establish a '$a_1'^2e'^4e''^4$' ground state electronic structure.[2291] The analogous $K_3[Ru_2Br_9]$ is readily prepared by reaction of '$RuCl_3\cdot xH_2O$' with a concentrated HBr/ethanol mixture followed by addition of KBr. The magnetic, redox and electronic spectral properties and Ru—Ru internuclear distance (2.86 Å) of this anion are very similar to those of $[Ru_2Cl_9]^{3-}$.[2335,2348]

$$\underset{35e^-}{[Ru_2^{II,III}Cl_9]^{4-}} \overset{-0.57\,V}{\rightleftharpoons} \underset{34e^-}{[Ru_2^{III,III}Cl_9]^{3-}} \overset{+0.92\,V}{\rightleftharpoons} \underset{33e^-}{[Ru_2^{III,IV}Cl_9]^{2}} \overset{+1.58\,V}{\rightleftharpoons} \underset{32e^-}{[Ru_2^{IV,IV}Cl_9]^{-}} \quad (141)$$

Salts of the $[RuBr_6]^{3-}$ anion (with counterions such as $[PhNH_3]^+$[2334] and $[N(CH_2CH_2NH_3)_3]^{3+}$[2338]) have been prepared by analogous routes to those of the chloride derivatives and fully characterized by structural and spectroscopic techniques.[3] Compounds of formulation $A_4[RuBr_7]$ (probably $A_3[RuBr_6]ABr$) and $A_2[RuBr_5]$ (probably $A_4[Ru_2OBr_{10}]$) are also reported.[3]

45.9.6.3 Aqua- and hydroxo-halide complexes

Ion exchange techniques have been used to separate the species present in aqueous solutions of ruthenium trichloride. The species present are $[RuCl_n(OH_2)_{6-n}]^{(3-n)+}$ ($0 \leqslant n \leqslant 6$) and their electronic spectra are available.[1887,2349–2351]

A number of these aquachloro complexes have been isolated and characterized by X-ray analysis. Thus, red $M_2[RuCl_5(OH_2)]$ can be prepared by ethanolic reduction of $[RuO_4]$ in HCl in the presence of MCl (M = K, Rb, Cs, NH_4),[2352] by reduction of $K_4[Ru_2OCl_{10}]$,[2335] or by reaction between $K_3[Ru(C_2O_4)_3]$ and HCl.[2353] The bromo derivatives $M_2[RuBr_5(OH_2)]$ are made by exactly analogous routes.[2354] The X-ray structure of the potassium[2355] and caesium chloro salts[2356] confirm the octahedral structure with Ru—Cl = 2.311 (*trans* to H_2O), 2.353 Å (*cis* to H_2O). Detailed magnetic (μ_{eff} *ca.* 2 BM at 300 K)[2357] and IR studies[2358] have been reported. Oxidation in $HCl/HClO_4$ solutions give dimeric oxo-bridged Ru^{IV} species[2359] whereas in 2 M HCl, $[RuCl_6]^{2-}$ is formed reversibly.[2360,2361]

The red *cis*-$[RuCl_4(OH_2)_2]^-$ anion is prepared (as the H^+ salt) by evaporation of a solution of $[RuO_4]$, HCl and ethanol,[2362] or, as its NH_4^+, Rb^+ or Cs^+ salts, by reduction of ammonium ruthenate with $SnCl_2$ and HCl in the presence of the appropriate cation.[2363] The latter type of route also gives $M[RuBr_4(OH_2)_2]$.[2364] Interconversion between H[*cis*-$RuCl_4(OH_2)_2$] and the green *trans* isomer is possible (equation 142).[2362] Solutions of *trans*-$[RuCl_4(OH_2)_2]^-$ are also obtained by aerial oxidation of the reduced methanolic blue solutions and addition of $[AsPh_4]Cl$ then precipitates green $AsPh_4$[*trans*-$RuCl_4(OH_2)_2$] (ν(Ru—Cl) 336 cm^{-1}).[2288] The X-ray structure of the red $AsPh_4$[*cis*-$RuCl_4(OH_2)_2$] complex has been reported with Ru—Cl = 2.325 (*trans* to H_2O), 2.355 Å (*cis* to Cl).[2365]

$$cis\text{-}H[RuCl_4(OH_2)_2] \underset{\Delta(HCl)}{\overset{\Delta(EtOH)}{\rightleftharpoons}} trans\text{-}H[RuCl_4(OH_2)_2] \quad (142)$$

Orange *mer*- and *fac*-$[RuCl_3(OH_2)_3]$ can be separated by elution at low temperature of aged ruthenium(III) chloride[2350] (or $K_2[RuCl_5(OH_2)]$)[2366] solutions through successive cation and anion exchange columns, which removes any charged species. Studies on these solution species include

dipole moment,[2366] IR[2367] and electronic[2350] spectral measurements. The kinetics of interconversion of the two isomers have been determined and it is found that the *mer* isomer is more labile than the *fac* isomers towards aquation, producing *cis*-$[RuCl_2(OH_2)_4]^+$.[2351]

Both *cis*- and *trans*-$[RuCl_2(OH_2)_4]^+$ cations can be successfully separated from aged solutions of '$RuCl_3 \cdot xH_2O$' in 0.3 M HCl by elution from a cation exchange column.[2349] The *trans* isomer, which is also made by heating blue hydrochloric acid solutions of Ru^{II} under N_2, has an ESR spectrum consistent with axial symmetry.[2288] For the interconversion $cis \rightleftharpoons trans$, $K = 1$.[2351]

The pentaaqua cation $[RuCl(OH_2)_5]^{2+}$ can be isolated in solution using cation exchange techniques.[1887] It electronic spectrum[1887] and rate of aquation ($t_{\frac{1}{2}} > 1$ year) have been measured (*cf.* for $[RuCl_6]^{3-}$, aquation to $[RuCl_5(OH_2)]^{2-}$ takes only a few seconds). Thus, cationic and neutral aquachlororuthenium(III) species are relatively substitutionally inert, compared to anionic species.[2351]

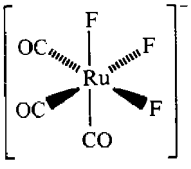
As mentioned earlier (Section 45.9.6.2) aqueous solutions of '$RuCl_3 \cdot xH_2O$' catalyse the hydration of alkynes. Detailed mechanistic studies indicate that the catalytic activity is dependent upon the combined concentrations of $[RuCl_4(OH_2)_2]^-$ and $[RuCl_5(OH_2)]^{2-}$.[1613]

The binuclear mixed valence chloro species $[Ru_2Cl_{n+3}]^{(2-n)+}$ $(0 \leqslant n \leqslant 2)$ are discussed in Sections 45.9.3.

Finally, there are some earlier reports of ill-defined hydroxo- and oxo-halide species such as $[Ru_2Cl_2(OH)_2]$, $[Ru_2OCl_4]$, $[RuCl_2(OH)(H_2O)]$ and $[en_2H_2]_5[RuCl_5OH]$ *etc.* (see reference 2, p. 135).

45.9.6.4 Carbonyl halides

Reaction between $[Ru_3(CO)_{12}]$ and an excess of XeF_2 in either $CFCl_2CF_2Cl$ or anhydrous HF at room temperature affords the air sensitive, paramagnetic, ($\mu_{eff} = 1.92$ BM), solid $[RuF_3(CO)_3]$. It is also formed by reaction of $[RuF_2(CO)_3]_4$ with an excess of XeF_2. The ESR spectrum in HF solution at 77 K confirms the monomeric, facial structure (**367**).[2295]



(367)

As discussed in Section 45.9.5.3, reaction of '$RuX_3 \cdot xH_2O$' with HX/HCO_2H (1:1 mixtures) under reflux produces initial deep red solutions containing the $[RuX_5CO]^{2-}$ anions (X = Cl, Br) which can be precipitated (for X = Cl) as its caesium salt.[2298,2308] For X = Cl, the same anion is formed by carbonylation of aqueous HCl solutions of '$RuCl_3 \cdot xH_2O$',[186,1613,2310] or treatment of $[RuCl_2CO(nbd)]_2$ with $[Ph_3(PhCH_2)P]Cl/HCl$ in acetone.[2368,2369] X-Ray structures of the $M_2[RuCl_5CO]$ salt ($M = Cs^+$,[2309] $Ph_3(PhCH_2)P^+$ [2368,2369]) are available. Evaporation of these red solutions yields an impure form of 'RuX_3CO' (possibly contaminated with RuX_3). No Ru^{III} iodocarbonyl complex has been isolated owing to its facile reduction but some IR evidence for its existence in solution is reported.[2298]

45.9.7 Ruthenium(IV) Halides

45.9.7.1 Pure neutral halides

Yellow crystals of RuF_4 can be synthesized by reaction of $[RuF_5]_4$ with iodine and iodine pentafluoride. It has a room temperature magnetic moment of 3.04 BM which drops to 2.51 BM at 88 K.[2370] Reaction with water gives RuO_2.[2000,2370]

Ruthenium(IV) chloride has been detected in the vapour phase on heating $RuCl_3$ and Cl_2 between 400–800°C.[2371] It is the principal vapour phase species up to 853°C[2372] and it is reported that solid $RuCl_4$ can be isolated by cooling the above vapour to liquid air temperatures. Above −30°C, it decomposes to $RuCl_3$ and Cl_2.[2373,2374] Note however that Fletcher and co-workers[2285] suggest that the above observations are compatible with oxochlorides such as $[Ru_2OCl_6]$ and are not, *per se*, evidence for the existence of $RuCl_4$.

All attempts to prepare RuX_4 (X = Br, I) have given only the trihalides (see Section 45.9.6.1).

45.9.7.2 Pure anionic halides and related species

$K_2[RuF_6]$ can be prepared by the action of water on $K[RuF_6]$[2375] and has a trigonal structure.[2376] An alternative preparation, which gives a cubic structure, is to fuse $K_2[Ru(NO_2)_4OH(NO)]$ (or $RuCl_3$) with $K[HF_2]$ at 250°C.[2376,2377] Other alkali metal salts (Na^+, Rb^+, Cs^+) are available,[2378] and also rhombohedral $Ba[RuF_6]$ (from $RuCl_3$, $BaCl_2$, F_2 at 350°C)[2379] and $[NO]_2[RuF_6]$ (by prolonged reaction between $[NO][RuF_6]$ and an excess of NOF at 150°C).[2380] Magnetic data,[2381] IR[2382] and electronic spectral studies[2330,2383] have been published. The enthalpy of solution of $K_2[RuF_6]$ in water at 298 K has been measured and the single ion hydration enthalpy of gaseous $[RuF_6]^{2-}$ determined.[2384] Reaction of $[RuF_6]$ with PF_3 in anhydrous hydrogen fluoride gave polymeric $[RuF_4(PF_3)]_n$. The low magnetic susceptibility values (μ_{eff} = 1.81 BM per Ru at 293 K) probably arise from strong magnetic exchange in the solid state. Treatment of RuF_6 with AsF_3 gives the adduct $RuF_4 \cdot AsF_5$ formulated on the basis of IR evidence as $(RuF_3)_n^{n+}$ $(AsF_6)_n^{n-}$.[2385]

Earlier methods of preparation of $K_2[RuCl_6]$ include the oxidation of $K_2[RuCl_5(OH_2)]$ with Cl_2, reaction of $K_2[RuO_4]$ with cold dilute HCl, recrystallization of $K_4[Ru_2OCl_{10}]$ from concentrated HCl and the reduction of $[RuO_4]$ with concentrated HCl in the presence of KCl.[3] Unfortunately most of these methods produce some $K_4[Ru_2OCl_{10}]$ contaminant and, therefore, more elaborate preparations to obtain purer samples have been devised.[2360,2386] For example, reduction of $K_4[Ru_2OCl_{10}]$ to $K_2[RuCl_5(OH_2)]$ with ethanol and then oxidation by Cl_2 to $K_2[RuCl_6]$. Other alkali metal and organic cation salts are available. For example, '$RuCl_3 \cdot xH_2O$' and $[Et_4N]Cl$ in thionyl chloride gives $[Et_4N]_2[RuCl_6]$.[2387]

The potassium salt forms black crystals which have a cubic lattice and a Ru—Cl distance of 2.29(4) Å.[2388,2389a] Extensive magnetic measurements (μ_{eff} *ca.* 2.8 BM at room temperature), IR, Raman and electronic spectral studies have been published on the $[RuCl_6]^{2-}$ anion (see reference 3, p. 94 and references 2336b and 2389b for details), although much of the earlier work is suspect because of contamination by diamagnetic $K_4[Ru_2OCl_{10}]$. The results are consistent with a model in which both the spin-orbit coupling constants and the interelectronic coupling factors are close to their free-ion values, although the possibility of contributions from higher excited states cannot be ruled out.[2390] Similar results are obtained for the $[RuBr_6]^{2-}$ anion, prepared as its potassium salt, either by oxidation of concentrated aqueous solutions of $K_2[RuBr_5(OH_2)]$ with Br_2[2391] or by passing Br_2 through solutions of $K_2[RuCl_6]$, $K_3[RuCl_6]$, $K_2[RuCl_5(OH_2)]$, $K_4[Ru_2OCl_{10}]$ or $RuCl_3$ in hydrobromic acid.[2335]

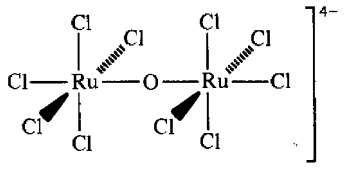
The NQR spectrum of $K_2[RuCl_6]$ shows a single resonance frequency over the temperature range 77–298 K[2386] but on standing its aqueous solutions are slowly reduced and polarographic studies show this involves irreversible reduction to $[RuCl_5(OH_2)]^{2-}$ probably *via* $[RuCl_6]^{3-}$.[2360] The latter is formed directly by reaction of $[RuCl_6]^{2-}$ with H_2,[2332,2392] H·[2333] or Br^-[2393] and the kinetics of this process have been measured. Heating $K_2[RuCl_6]$ *in vacuo* gives $K_3[RuCl_6]$, α-$RuCl_3$ and Cl_2,[2394] and treatment of $Et_4N[RuCl_5(RCN)]$ with DMF affords the $[RuCl_5(DMF)]^-$ anion.[681]

The binuclear mixed valence anions $[Ru_2^{III,IV}X_9]^{2-}$ (X = Cl, Br) have been electrogenerated from $[Ru_2X_9]^{3-}$. Variable temperature magnetic measurements on analyte solutions of these 33 valence electron anions (μ_{eff} = 4.40 BM per molecule at 273 K for X = Br), indicate three unpaired electrons per molecule suggesting a spin quartet electronic ground state. Electrogeneration of the $[Ru_2^{IV,IV}X_9]^-$ anions is possible but compound instability makes quantitative magnetic measurements impossible.[2348] Observation of the intervalence charge transfer transition in the near IR spectrum of $[Ru_2Cl_9]^{2-}$ [but not $[Ru_2Cl_9]^{n-}$ (n = 3,1)] supports a spin-trapped description of the bonding.[1869]

No hexaiodoruthenates(IV) have been prepared

45.9.7.3 Oxo-, hydroxo- and aqua-halide complexes

$K_4[Ru_2OCl_{10}]$, originally formulated as $K_2[RuCl_5(OH)]$, can be made by the reaction of $[RuO_4]$, $K_2[RuO_4]$ or $RuO_2 \cdot xH_2O$ with potassium chloride dissolved in 5 M HCl. The rubidium and caesium salts are made by similar methods.[2395] Its formulation as a binuclear complex followed the observation that the complex was diamagnetic, and structure (**368**) with a linear Ru—O—Ru skeleton was subsequently confirmed by X-ray analysis.[2389a] A molecular orbital description of the bonding in (**368**) has been given, which accounts for both the diamagnetism and the short Ru—O bond lengths.[2396] Extensive electronic, resonance Raman and IR spectral measurements have been reported for this anion and various detailed assignments proposed.[2397,2398] Polarographic reduction of (**368**) leads to irreversible formation of $[RuCl_5(OH_2)]^{2-}$.[2399]



(368)

Black crystals of $K_4[Ru_2OBr_{10}]$ can be prepared from $[RuO_4]$, HBr and KBr and measurements of its IR, electronic and resonance Raman spectra suggest it is isostructural with $[Ru_2OCl_{10}]^{4-}$.[3] Hydrolysis of $[RuF_6]^{2-}$ in neutral or acid solution is reported to form the corresponding $[Ru_2OF_{10}]^{4-}$ anion. This will react with Cl^- to give $[Ru_2OCl_{10}]^{4-}$ which polymerizes to $[Ru_2Cl_2(OH)_2]_n$.[2400] Reaction of '$RuCl_3 \cdot xH_2O$' with Cl_2 is claimed to give $[Ru_2OCl_6]$ and $[Ru_2OCl_5]$[2285] (see Section 45.9.7.1).

Other studies on the Raman spectra of aqueous solutions of $K_4[Ru_2OCl_{10}]$ or $K_2[RuCl_6]$ indicate the presence of a range of aqua- or hydroxo-chloride species. These include $[Ru_2OCl_9(OH_2)]^{3-}$ (isolated by Crisp and Seddon[5]), $[Ru_2OCl_8(OH_2)_2]^{2-}$ and $[RuCl_4(OH)_2]^{2-}$ anions.[2401] In aqueous methanol solutions containing Ru^{IV} chlorides, $[Ru_2Cl_6(MeOH)(OH_2)(OH)_2]$ is claimed to be present.[2402] The preparation and properties of $[Ru_2OCl_6(NCR)_4]$ are discussed in references 1373 and 1374.

A number of publications have appeared on the effect of adding halide ions to solutions of Ru^{IV} in $HClO_4$. Although there is now general agreement as to the colour and electronic spectra of the various species formed, there has as yet been no hard identification of any of the chromophores. A range of formulations have been suggested which include monomers such as $[RuCl_4(OH)_2]^{2-}$, $[RuOCl_4]^{2-}$, $[RuCl_2(OH)_2(OH_2)_2]$, binuclear $[Ru_2OCl_9(OH_2)]^{3-}$, $[Ru_2OCl_8(OH_2)_2]^{2-}$, $[Ru_2O_2Cl_6(OH_2)_3]^{2-}$ and a variety of polynuclear species. For detailed references to this complicated area see reference 3, p. 108.

Finally, treatment of aged '$RuCl_3 \cdot xH_2O$' in 12 M HCl with $[Et_4N]Cl$ in the presence of a few drops of Hg produces a complex described as '$[Et_4N]_2[Ru_2Cl_7(OH)_3]$'. This may contain a Ru—O—Ru linkage.[681]

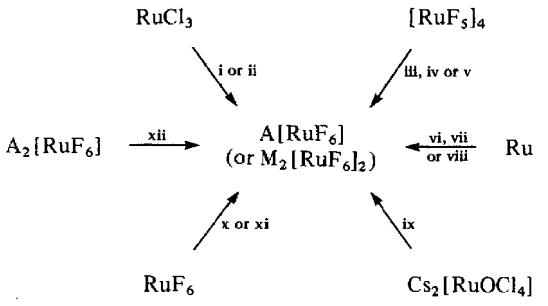
45.9.8 Ruthenium(V) Halides

The only ruthenium(V) halides reported are those containing fluoride. Green ruthenium(V) fluoride can be prepared by direct fluorination of the metal at 300°C,[2403] by reduction of $[RuF_6]$ with B_2O_3,[2404] BiF_3, SbF_3, Ru or H_2[2385] or by reaction of the metal and BrF_3. The latter method first generates $[BrF_2][RuF_6]$ which decomposes at 120°C *in vacuo* to give $[RuF_5]_4$ and BrF_3.[2375] The tetrameric structure (**369**) has been confirmed by X-ray analysis,[2405] but its mass spectrum[2403] indicates that the vapour consists of an equilibrium between monomer, dimer, trimer and tetramer units. Magnetic measurements reveal the presence of significant interactions between adjacent metal ions.[2406,2407] Mössbauer[2408] and IR[2409] spectral measurements are also available. Some of the reactions of $[RuF_5]_4$ are discussed below but further details are to be found in reference 3, p. 79.

The hexafluororuthenate(V) anion $[RuF_6]^-$ is readily prepared with a variety of cations such as alkali metals, alkaline earths, Ag^+, Tl^+, $[XeF]^+$, $[Xe_2F_3]^+$, $[O_2]^+$, $[NO]^+$, $[SF_3]^+$, $[BrF_2]^+$. Some of the synthetic routes are shown in Scheme 70. Measurements on this anion include various X-ray structural analyses, magnetic data (*ca.* 3.60 BM at room temperature), IR, Raman and diffuse reflectance spectra.[3] Interestingly, $XeF[RuF_6]$ can be oxidized by F_2 at 350°C to give $[XeF_5][RuF_6]$. X-Ray structures of both species have been determined and reveal significant interaction between the $[XeF_n]^+$ cation and $[RuF_6]^-$ anion, producing substantial distortion (particularly for $n = 1$), of the latter from regular octahedral geometry.[2418] All the $[RuF_6]^-$ metal salts are stable in dry air but in water dissolve to produce $[RuF_6]^{2-}$, O_2 and RuO_4. This is believed to be due to two competing reactions, a reduction and a disproportionation (equations 143 and 144).[2375]

Reaction of XeF_2 and $[RuF_5]_4$ in 1:2 molar ratio yields $[XeF][Ru_2F_{11}]$.[2411,2412] The same binuclear anion is produced upon prolonged storage at room temperature of $O_2[RuF_6]$;[2419] $[KrF][Ru_2F_{11}]$ is also known.[2420]

The mixed Ru^{II}–Ru^{V} complex $[RuF_2(CO)_3 \cdot RuF_5]_2$ can be prepared by reaction of $[RuF_5]_4$ with CO in a flow system at 200°C or by heating $[Ru_3(CO)_{12}]$ with a large excess of XeF_2 at 100°C in $CFCl_2CF_2Cl$. A tetrameric structure (**370**) has been proposed on the basis of IR and magnetic



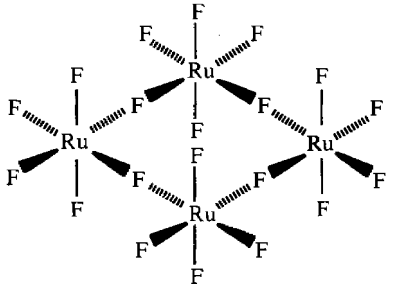
i, ACl, BrF_3 (A = Li, Na);[2410] ii, ACl, F_2 (A = K, Rb, Cs);[2379] iii, TlF, SeF_4 (A = Tl);[2375] iv, XeF_2, BrF_5 (A = XeF^+ or $Xe_2F_3^+$ depending on mole ratio of $[RuF_5]_4$ to XeF_2)[2411] or XeF_2(fuse) (A = XeF^+);[2412] v, SF_4, 108 °C (A = SF_3^+);[2413] vi, BrF_3, AX (AX = KBr, CsBr, AgBr) or $M[BrO_3]_2$ (M = Ca, Sr, Ba);[2375, 2379] vii, F_2/O_2, Δ, 300 °C (A = O_2^+);[2414] viii, KF, anhydrous HF (A = K);[2385] ix, F_2, 150 °C (A = Cs); x, H_2O (A = H_3O^+);[2415] xi, NO or NOF (A = NO^+);[2416] xii, F_2, 200–300 °C (A = Na, K, Rb, Cs)[2417]

Scheme 70

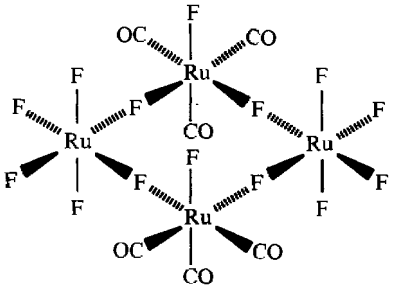
measurements. Further reaction of (**370**) with CO (100 atm/200 °C) gives the pale yellow $[RuF_2(CO)_3]_4$ (**363** and Section 45.9.5.1).[2294,2295]

$$4[RuF_6]^- + 6H_2O \longrightarrow 4[RuF_6]^{2-} + 4H_3O^+ + O_2 \quad (143)$$

$$4Ru^V \longrightarrow Ru^{VIII} + 3Ru^{IV} \quad (144)$$



(369)



(370)

45.9.9 Ruthenium(VI) Halides

Dark brown $[RuF_6]$ can be made by direct fluorination of the metal at elevated temperatures, the product being distilled rapidly out of the reaction zone or condensed at low temperature.[2385] $[RuF_5]_4$ which is much less volatile is also formed during the reaction. X-Ray powder patterns show the molecule to be isostructural with other platinum metal hexafluorides[2421,2422] and, together with the IR spectrum,[2423] suggest an octahedral structure. The solid is volatile at room temperature decomposing rapidly at 200 °C to give $[RuF_5]_4$ and F_2. It is also highly reactive and will attack Pyrex glass at room temperature.[2421] A recent paper describes the redox reactions of RuF_6 to produce species such as $[RuF_4(PF_3)]_n$ (with PF_3) $RuF_4 \cdot AsF_5$ (with AsF_3), $RuF_5 \cdot ClF_3$ (with ClF_3) and RuF_5 (using various reagents — see Section 45.9.8).[2385]

The compound originally formulated as $K_2[RuF_8]$[2312] has now been shown to be a mixture of $K[RuF_6]$ and $K[HF_2]$.[2375]

Ruthenium(VI) oxide tetrafluoride, $[RuOF_4]$, is reported to have been prepared by the action of a mixture of BrF_3 and Br_2 on ruthenium. The enthalpy and entropy of vaporization, X-ray powder pattern and magnetic properties (μ_{eff} = 2.91 BM at room temperature) have been measured.[2406] However more recently other workers also claim to have prepared $[RuOF_4]$ (by the fluorination of RuO_2 at 400–500 °C), but it shows different properties to the earlier product. Evidence for its formulation is based on mass spectroscopy (which shows the molecular ion $[RuOF_4]^+$), elemental analysis and IR spectrum (ν(Ru=O) = 1040 cm^{-1}). The solid is unstable, even at room temperature, decomposing to $[RuF_4]$ and O_2.[2000] A report on the physical and chemical properties of RuF_6 and $RuOF_4$ is available.[2424]

The diamagnetic, tetrachlorodioxoruthenate(VI) salts $A_2[RuO_2Cl_4]$ (A = Cs, Rb) can be prepared by treating $[RuO_4]$ with an excess of ACl in dilute HCl. Likewise, CsBr/HBr affords $Cs_2[RuO_2Br_4]$. Their IR spectra suggest they contain a *trans* RuO_2 unit.[65] $Cs_2[RuO_2Cl_4]$ reacts with F_2 at 150°C to give $Cs[RuF_6]$, with boiling 10 M HCl to give $Cs_2[RuCl_6]$, and with water to produce $[RuO_4]$ and RuO_2.[2455]

45.9.10 Ruthenium(VIII) Halides

Several claims for the formation of $[RuF_8]$ by fluorination of Ru or RuO_2, have been published. It is a highly reactive yellow solid which exists only at low temperatures (or in the presence of an excess of fluorine), and is far more volatile than $[RuF_5]_4$.[2426]

45.10 HYDROGEN AND HYDRIDE LIGANDS

45.10.1 Ruthenium(0) Complexes

Apart from hydridoruthenium carbonyl cluster compounds (see Sections 45.10.3.3 and 45.10.4) the only Ru^0 hydride complexes are the deep brown $[RuH(NO)(PR_3)_3]$ (R_3 = Ph_3, Ph_2Me, Ph_2Pr^i, Ph_2Cy) which are fully discussed in Section 45.5.1.2.

45.10.2 Ruthenium(I) Complexes

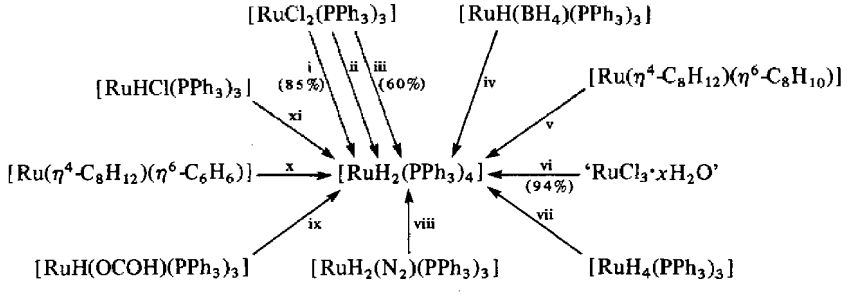
The only hydrido complex containing a formally Ru^I centre is the diamagnetic, air-sensitive $[Ru_2H(OH)(PMe_3)_6]$, obtained by heating $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ at 60°C in light petroleum or THF with an excess of water. On the basis of ^{31}P, ^{13}C and ^1H NMR spectra, structure (**142**) (see Section 45.5.3.2) is proposed.[1521]

45.10.3 Mononuclear Ruthenium(II) Complexes

45.10.3.1 Dihydrido complexes

(i) $[RuH_2L_xL'_{4-x}]$ (L = L' = P donor ligand, x = 4,3,2), $[RuH_2(L—L)_2]$ and related species

The yellow compound $[RuH_2(PPh_3)_4]$ was first prepared in 24% yield by the reduction of $RuCl_3$ or $[Ru(acac)_3]$ with $AlEt_3$ in the presence of PPh_3.[1870] Some higher yield routes to this complex are shown in Scheme 71. An X-ray analysis shows a distorted octahedral configuration with essentially *cis* hydride ligands,[2434] and in solution facile dissociation occurs to give free PPh_3 and $[RuH_2(PPh_3)_3]$.[1838,1870] A compound of the latter formula can be isolated by successive addition of '$RuCl_3 \cdot xH_2O$' and $Na[BH_4]$ to hot ethanolic PPh_3 (three moles/mole Ru).[2427] As discussed elsewhere (Section 45.10.3.1.ii), these $[RuH_2(PPh_3)_n]$ complexes exhibit a range of interesting reactions.



i, $Na[BH_4]$, PPh_3, H_2, $MeOH/C_6H_6$;[1408] ii, $Na[BH_4]$, PPh_3, $MeOH/C_6H_6$;[1408, 2427–2429] iii, $Li[NMe_2]$ (2 equiv.);[2430] iv, PPh_3, $EtOH/\Delta$;[2431] v, PPh_3, H_2, THF;[2432] vi, $Na[BH_4]$, PPh_3, $EtOH/\Delta$;[1402, 2427] vii, PPh_3;[1549, 2429, 2433] viii, PPh_3;[2428, 2429, 2433] ix, PPh_3;[1811, 2433] x, $PPh_3/h\nu$;[2434] xi, KOH/Bu^tOH[1767]

Scheme 71

Similar routes to those shown in Scheme 71 can be used to prepare other $[RuH_2L_4]$ complexes. For example, method (v) works well for L = $PMePh_2$, PMe_2Ph and $P(OMe)_3$,[2432] and method (vi) is excellent for the preparation of various tertiary phosphine and phosphite complexes.[1570,2435] The reaction of $[Ru_2Cl_3(PMePh_2)_6]Cl$ with hydrazine, $PMePh_2$ and H_2 under pressure[2436] or with KOH in isopropanol[1752] affords $[RuH_2(PMePh_2)_4]$ which is also produced by treatment of $[RuH(PMePh_2)_4(MeOH)]PF_6$ with H_2.[1766] $[RuH_2(PMe_3)_4]$ can be prepared by reduction of either $[Ru_2(OCOMe)_4Cl]$ or $[Ru_3O(OCOMe)_6(H_2O)_3]OCOMe$ with Na/Hg in THF under H_2 (3 atm) in the presence of PMe_3,[1521] or from *cis*-$[RuClMe(PMe_3)_4]$ and $LiAlH_4$ or NaOMe,[16a] whereas $[RuH_2(PHPh_2)_4]$ is prepared by reaction of *cis*- or *trans*-$[RuCl_2(PHPh_2)_4]$ with an excess of LiOMe in boiling MeOH.[111]

The majority of these $[RuH_2L_4]$ complexes adopt the *cis* configuration in the solid state, although *cis–trans* mixtures are sometimes observed in solution,[2437,2438] and crystals of *trans*-$[RuCl_2(P(OEt)_2Ph)_4]$ can be grown.[2439] Some of these compounds (but not for PMe_3) are stereochemically non-rigid in solution, undergoing intramolecular ligand exchange which can be monitored by ^1H and ^{31}P NMR spectroscopy.[2436,2437] The tertiary phosphines (except for PMe_3), unlike the phosphite complexes, readily lose a PR_3 group on heating and hence provide a ready synthesis of $[RuH_2YL_3]$ compounds (*e.g.* L = $PMePh_2$, Y = CO, PhCN;[2435,2436] see Section 45.10.3.1.ii for more examples).

The PF_3 complex *cis*-$[RuH_2(PF_3)_4]$ is obtained in high yield from the reaction of PF_3 (400 atm) and H_2 (120 atm) with anhydrous $RuCl_3$ and Cu powder at 250°C for 20 h. Reaction with Et_3N generates the monoanion $[RuH(PF_3)_4]^-$, which is stereochemically non-rigid,[1384] and with K/Hg, $K_2[Ru(PF_3)_4]$ is formed.[1381b] The mixed fluorophosphine/PPh_3 complexes $[RuH_2L(PPh_3)_3]$, $[RuH_2L_2(PPh_3)_2]$ {L = PF_3, $PF_2(NMe_2)$} and $[RuH_2(PF_3)(PF_3NMe_2)(PPh_3)_2]$ are also reported.[2440] Reaction of $[RuH_2(PPh_3)_4]$ with dppm gives $[RuH_2(dppm)(PPh_3)_2]$.[1399]

Reduction of *trans*-$[RuHCl(L–L)_2]$ (see Section 45.10.3.2.i) with an excess of $LiAlH_4$ gives $[RuH_2(L–L)_2]$ (L–L = depe, *o*-$C_6H_4(PEt_2)_2$) which were initially formulated as *trans* isomers.[1591c] However, the ^1H NMR spectrum for the depe compound indicates a *cis* configuration[2437] and this is supported by the X-ray analysis of *cis*-$[RuH_2(dppe)_2]$,[2432] made by method (v), Scheme 71. Other routes to these types of compound are by displacement of 2-naphthyl by H_2 (or D_2) from *cis*-$[RuH(2\text{-np})(dmpe)_2]$,[1388] treatment of $[RuH(L–L)_2]^+$ (L–L = dppe, dppp, dppb) with H_2, deprotonation of $[RuH_3(dppp)_2]PF_6$ with Et_3N,[1766] or reaction of [Ru(cod)(cot)] with dppe or dppm under H_2.[1398,1399]

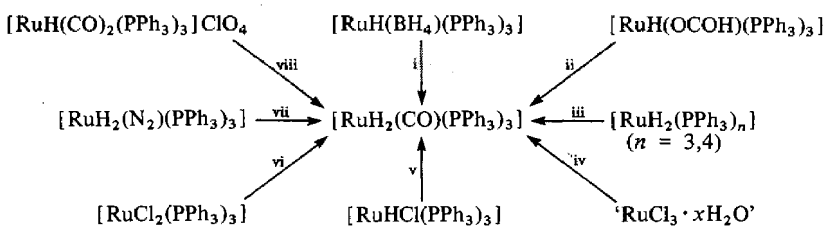
Finally rare examples of polydentate P donor ligand complexes containing two hydrido groups are *cis*-$[RuH_2\{P(OMe)_3\}(ttp)]$ and *trans*-$[RuH_2(PPh_3)(ttp)]$ (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$), prepared by reaction of $[RuH(BH_4)(ttp)]$ (Section 45.10.3.2.i) with the appropriate P donor ligand and Et_3N in THF.[1486,2441]

(ii) *$[RuH_2Y_xL_{4-x}]$ (L = P donor ligand, Y = C, N or O donor ligand; x = 1,2,3,4)*

Reaction of $[RuHCl(PPh_3)_3]$ with $AlEt_3$ in ether in a N_2 atmosphere,[1549,2428,2442] reverse osmosis of $[RuH_2(PPh_3)_4]$ under N_2 pressure[1838] or treatment of $[RuH(OCOH)(PPh_3)_3]$ with N_2[1811,2433] affords the dinitrogen compound $[RuH_2(N_2)(PPh_3)_3]$ as an air-sensitive white solid (ν_{NN} = 2147 cm^{-1}). The $P(p\text{-Tol})_3$ analogue is obtained by borohydride reduction of $[RuCl_2\{P(p\text{-Tol})_3\}_3]$ under N_2.[1599,2428] The N_2 group is readily displaced by various Lewis bases to give $[RuH_2Y(PPh_3)_3]$ (Y = PPh_3, CO, PhCN, NH_3, $N_2B_{10}H_8SMe_2$) and by H_2 to form $[RuH_4(PPh_3)_3]$[2428] (see Section 45.10.5); treatment of the latter with N_2 regenerates $[RuH_2N_2(PPh_3)_3]$ and with CO, and RCN, $[RuH_2CO(PPh_3)_3]$ and $[RuH_2(RCN)(PPh_3)_3]$ (R = Me, Ph) respectively are formed.[1408] Interestingly, IR and NMR evidence indicates that N_2 has a much greater affinity than 2-pentene for $[RuH_2(PPh_3)_3]$.[2443] X-Ray analysis reveals that $[RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3]\cdot 3C_6H_6$ has a linear RuNNR linkage with *cis* hydrides, *trans* PPh_3 groups.[2444] Some other routes to the white $[RuH_2CO(PPh_3)_3]$ (**371**) are shown in Scheme 72. Similarly $[RuH_2CO(PMePh_2)_3]$ is obtained by reaction of $[RuH_2(PMePh_2)_4]$ with CO,[2435,2436] treatment of $[RuH(\eta^2\text{-}BH_4)(PMePh_2)_3]$ with CO in the presence of Et_3N or heating $[Ru_2Cl_3(PMePh_2)_6]Cl$ with ethanolic KOH.[1752] Reaction of the 'RuCOCl' solution with $PEtPh_2$ and a large excess of $Na[BH_4]$ or $Na[BH_3CN]$ affords $[RuH_2CO(PEtPh_2)_3]$.[2431]

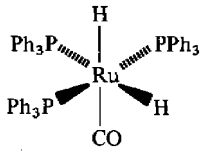
Other compounds of type $[RuH_2YL_3]$ are $[RuH_2(CO)(PPh_3)(L–L)]$ (L–L = $Ph_2P(CH_2)_nPPh_2$ (*n* = 1–4), $Ph_2P(CH_2)_2AsPh_2$, 1,2-$(Ph_2P)_2C_6H_4$),[1786] $[RuH_2CO(ttp)]$,[2441] $[RuH_2(PPh_3)_3(\eta^2\text{-}C_5H_{10})]$,[2446] $[RuH_2(PPh_3)_3THF]$ (from $[RuCl_2(PPh_3)_3]$ and Na/Hg or Mg/Hg in THF),[1404] and $[RuH_2(RNCHCHNR)(PPh_3)_n]$ (*n* = 2,3; R = Ph, $CHMe_2$, CMe_3, 4-MeO-Ph) which are believed to contain monodentate diazadiene ligands in some instances.[2447]

The dicarbonyl complexes $[RuH_2(CO)_2(PPh_3)_2]$ (**372**) can be synthesized by treatment of [Ru-

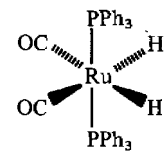


i, EtOH/Δ;[2431] ii, CO;[1811,2433] iii, HCHO;[1767,2427] iv, PPh_3, HCHO/KOH(Δ);[1410a] v, NaOMe/MeOH;[1767] vi, H_2, Et_3N, ROH;[2445] vii, EtOH;[2445] viii, ^-OEt[1467]

Scheme 72



(371)



(372)

$(CO)_3(PPh_3)_2$] with H_2 under pressure[1452] or [$Ru(CO)_2(PPh_3)_3$] with H_2 (1 atm).[1469] Other methods involve the reaction of the thermally unstable [$RuH_2(CO)_4$] with L (either PEt_3 or PPh_3) and treatment of [$RuCl_2(CO)_2L_2$] with $LiAlH_4$.[78a] The latter method can also be used to prepare [$RuH_2(CO)_2$(dppe)] and reaction of the 'RuCOCl' solution with 5-phenyl-5*H*-dibenzophosphole (DBP) and $Na[BH_4]$ yields [$RuH_2(CO)_2(DBP)_2$].[2431] Evidence for the existence of a hydrido–tricarbonyl complex has been presented; at high pressures [$RuH_2(CO)_3PPh_3$] is in reversible equilibrium with [$Ru(CO)_4(PPh_3$] and H_2.[2448]

Other [$RuH_2Y_2L_2$] complexes are [RuH_2(bipy)$(PPh_3)_2$] (from [$RuH_2(PPh_3)_4$] and bipy), [$RuH_2\{C_6H_4(CN)_2\}(PPh_3)_3$],[1706] [$RuH_2(CNBu^t)_2(PMe_3)_2$] (from [$RuMe_2(PMe_3)_4$] and $CNBu^t$ in THF),[2444] and [RuH_2(MeCN)$(PPh_3)_3$].[1404]

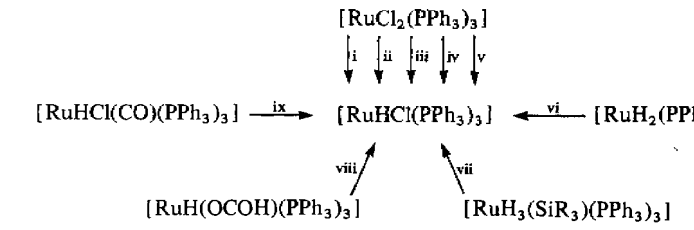
Finally, information on the preparation, Raman, IR, ^1H, ^{13}C NMR spectra and reactions of [$RuH_2(CO)_4$] is given in references 78a, 2448 and 2450 and references to dihydridoruthenium carbonyl cluster compounds are cited in Sections 45.10.3.3 and 45.10.4.

45.10.3.2 Monohydrido complexes

(i) [RuHXL$_n$], [RuHX(L–L)$_2$] (n = 3,4; L = P, As donor ligand; X = halide, alkyl, aryl, BH$_4$, OCOR) and related species

Treatment of [$RuCl_2(PPh_3)_3$] in C_6H_6/EtOH with H_2 for several days gives violet–black crystals of [$RuHCl(PPh_3)_3$]. This compound is also formed if the reaction is carried out under H_2 pressure (100 atm; 12 h) or in pure C_6H_6 in the presence of an organic base.[2445,2451] Other routes to this reactive material are shown in Scheme 73. In method (viii), use of HX or MeI gives the corresponding [$RuHX(PPh_3)_3$] (X = Br, I)[1437,1811,2433] and [$RuH_2(PPh_3)_4$] with EtBr and I_2 respectively also affords these complexes.[1870] A single crystal X-ray analysis of [$RuHCl(PPh_3)_3$]·C_6H_6 reveals a highly distorted trigonal bipyramid with the two axial PPh_3 groups being bent away from the perpendicular position to accommodate the equatorial PPh_3 group.[2454] Another compound of empirical formula 'RuHCl$(PPh_3)_3$' results from treatment of [$RuH_2(PPh_3)_4$] in C_6H_6 with 1,4-$Cl_2Si_4Ph_8$ in the presence of excess Et_3N. However, this is a red dimeric compound with different physical and spectroscopic properties from purple [$RuHCl(PPh_3)_3$]·C_6H_6.[2455] Other monomeric [$RuHClL_3$] complexes [L = $AsPh_3$,[2431] $AsMePh_2$,[1511] $PPh_2(C_6H_4SO_3H)$,[1563,2456] P(2-py)$_3$,[1821] dmppl;[1566,1567] L_3 = triphos, tet-1[1539,1540]) are available.

Several compounds of type [$RuHXL_4$] are known. For example, *trans*-[$RuHX(PHPh_2)_4$] (X = Cl, Br, I, SCN) are made by reaction of *cis*-[$RuH_2(PHPh_2)_4$] with NaX. The chloro compound is also prepared as shown in equation (145); it reacts with $SnCl_2$ to give *trans*-[$RuH(SnCl_3)(PHPh_2)_4$].[111] Low yield routes to *cis*-[$RuHCl(PMe_3)_4$] are shown in equation (146), but high yield routes have been reported, namely by dropwise addition of one equivalent of HCl to an etherial solution of



i, $Na[BH_4]$, C_6H_6/H_2O (Δ);[2445] ii, R_3SiH (R = Me, Et);[82] iii, $Li[NMe_2]$ (1:1 mole ratio)/THF;[2430] iv, Et_3SiH, PPh_3, Et_3N in C_6H_6;[83] v, RCH_2OH;[2452,2453] vi, $CHCl_3$;[2430] vii, $CDCl_3$;[84] viii, HCl;[1811,2433] ix, $h\nu$ (366 nm)[1456]

Scheme 73

cis-$[RuH_2(PMe_3)_4]$ at $-78°C$ or by reaction of *cis*-$[RuClMe(PMe_3)_4]$ with one equivalent of either $Li[BH_4]$ or $LiAlH(OMe)_3$.[16a]

Bidentate P and As donor ligand monohydrido complexes *trans*-$[RuHCl(L–L)_2]$ were first prepared by reduction of *cis*-$[RuCl_2(L–L)_2]$ with an excess of $Li[AlH_4]$ in THF (L–L = diars, dmpe, depe, dppm, *o*-$C_6H_4(PEt_2)_2$).[1591] More recently, *trans*-$[RuHCl(Ph_2P(CH_2)_nPPh_2)_2]$ (n = 2–4) and $[RuHCl(diop)_2]$ were synthesized by exchange of the appropriate L–L with $[RuHCl(PPh_3)_3]$. Reaction of $[RuHCl(PPh_3)_3]$ with $Ph_2As(CH_2)_2AsPh_2$ gives $[RuHCl(Ph_2As(CH_2)_2AsPh_2)_2]$ but $Ph_2As(CH_2)AsPh_2$ yields $[RuHCl(PPh_3)_2(Ph_2As(CH_2)AsPh_2)]$.[1846] Equation (147) shows another route to this type of complex. Although both ^1H and ^{31}P NMR studies on $[RuHCl(diop)_2]$ show inequivalent P atoms characteristic of a *cis* configuration, X-ray analysis reveals a distorted octahedron with H *trans* to Cl.[2457] This compound is also an active alkene hydrogenation catalyst.[2458] Treatment of $[Ru(dppe)_2(styrene)]$ with $P(OPh)_3$ (or $P(OMe)_3$ at higher temperatures) gives $[RuH\{P(O)(OR)_2\}(dppe)_2]$ (R = Me, Ph).[1392]

$$\text{*cis*- or *trans*-}[RuCl_2(PHPh_2)_4] \xrightarrow{LiOMe} \text{*trans*-}[RuHCl(PHPh_2)_4] \quad (145)$$
$$\text{*cis*-}[RuCl_2(PHPh_2)_4] \xrightarrow{H_2/Et_3N}$$

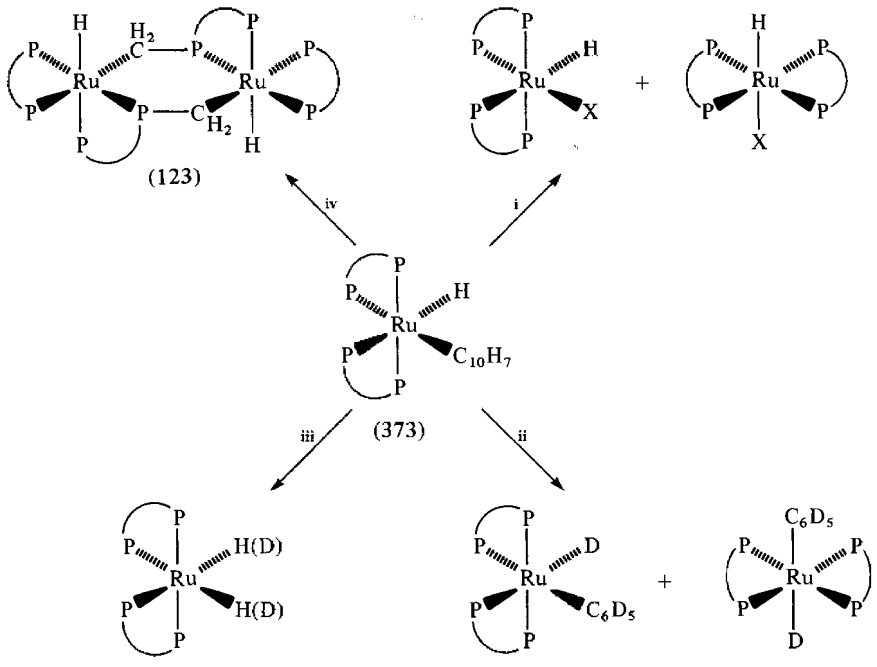
$$\text{*trans*-}[RuCl_2(PMe_3)_4] \xrightarrow[THF]{Na/Hg} \text{*cis*-}[RuHCl(PMe_3)_4]^{1529} \quad (146)$$
$$[Ru_2(OCOMe)_4Cl] \xrightarrow[\text{excess } PMe_3]{MgEt_2}$$

$$[RuCl_2(PPh_3)_3] + L–L \xrightarrow[\text{2-methoxyethanol}]{Et_3N,\ H_2} [RuHCl(L–L)_2] \quad (147)$$
$$(L–L = dppp,\ Ph_2P\{CH_2\}_3PMePh,\ Ph_2P\{CH_2\}_3PMe_2)^{1536}$$

$$\text{*cis*-}[RuH(2\text{-}C_{10}H_7)(dmpe)_2] \rightleftharpoons [Ru(C_{10}H_8)(dmpe)_2] \quad (148)$$

The corresponding hydrido/alkyl (and aryl) complexes *cis*-$[RuHR(L–L)_2]$ (L–L = dppe, dppm, dmpe; R = Me, Et, Ph) are readily prepared from *cis*-$[RuClR(L–L)_2]$ and $Li[AlH_4]$[1659] whereas treatment of *cis*- or *trans*-$[RuCl_2(dmpe)_2]$ with arene radical anions affords *cis*-$[RuH(\eta^1\text{-aryl})(dmpe)_2]$ (aryl = phenyl, 2-naphthyl, anthryl, phenanthryl).[1389] In solution, these compounds are in tautomeric equilibria with significant concentrations of Ru^0 complexes (*e.g.* equation 148) although X-ray analysis for aryl = 2-naphthyl confirms the presence of the six-coordinate Ru^{II} species (**373**) in the solid state.[2459] Some reactions of (**373**) with various substrates to produce other hydrido complexes are shown in Scheme 74.[44,2460a] Note that the compound of empirical formula ['$Ru(dmpe)_2$'] obtained by pyrolysis of $[RuH(2\text{-np})(dmpe)_2]$ (reaction (iv); Scheme 74) is a binuclear Ru^{II} hydrido complex, resulting from intermolecular oxidative addition of methyl groups to ruthenium.[1390]

Reaction of *cis*-$[RuClMe(PMe_3)_4]$ with excess NaOMe in THF affords *cis*-$[RuHMe(PMe_3)_4]$ which is also obtained by methylation of *cis*-$[RuHCl(PMe_3)_4]$ with MeMgCl.[16a] Higher homologues such as *cis*-$[RuHR(PMe_3)_4]$ (R = Et, Pr^n) can be prepared from *trans*-$[RuCl_2(PMe_3)_4]$ and excess MgR_2 in THF.[1393] The reaction of $[RuHCl(PPh_3)_3]$ with LiMe in diethyl ether also affords alkyl derivatives but the product is dependent on the Li:Ru ratio used. Thus, with a small excess of LiMe,

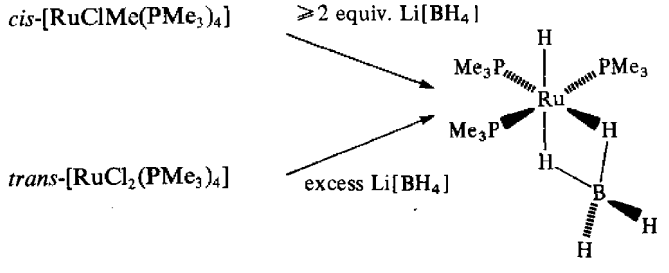


i, HX (X = CN, CH_2CN, CH_2OMe, C_6H_4CN); ii, C_6D_6, 60 °C; iii, $H_2(D_2)$; iv, Δ

Scheme 74

yellow $[RuHMe(PPh_3)_2(Et_2O)_2]$ contaminated with some LiCl is formed; a large excess of LiMe gives $[RuHMe(PPh_3)_2(LiMeOEt_2)_2]$. These complexes are extremely reactive *e.g.* dissolution in THF and warming gives methane and $[RuH(C_6H_4PPh_2)(PPh_3)(THF)_2]$.[1689]

The preparation of hydrido complexes by means of $[BH_4]^-$ may involve Ru—BH_4 intermediates and in some cases these can be isolated. Thus reaction of '$RuCl_3 \cdot xH_2O$', $[RuCl_2(PPh_3)_3]$ or the 'reduced ruthenium blue' with $Na[BH_4]$ in the presence of a large excess of PPh_3 gives $[RuH(BH_4)(PPh_3)_3]$.[2431] Treatment of $[RuCl_2(ttp)]_x$ with excess $Na[BH_4]$ in boiling THF gives $[RuH(\eta^2\text{-}BH_4)ttp]$ which at ambient temperature shows discrete ^1H NMR signals for the Ru—H, each of the two bridging protons and the two terminal BH's. Variable temperature studies indicate scrambling of the BH_4^- protons at two different temperatures which is interpreted as a two-step process. The latter compound in the presence of Et_3N catalyses the hydrogenation of 1-octene to octane at rates comparable to that with $[RhCl(PPh_3)_3]$.[2441] The active hydrogenation catalyst $[RuH(\eta^2\text{-}BH_4)(PMePh_2)_2]$ is synthesized from *fac*-$[Ru(MeCN)_3(PMePh_2)_3](BF_4)_2$ and $Na[BH_4]$[1752] and $[RuH(\eta^2\text{-}BH_4)(PMe_3)_3]$ is also known (equation 149). X-Ray analysis of the latter confirms the *mer* octahedral configuration (**374**).[16a] The analogous *mer*-$[RuH(\eta^2\text{-}BH_4)(PMe_2Ph)_3]$ has been prepared by treatment of *mer*-$[RuCl_3(PMe_2Ph)_3]$ with $NaBH_4$ in EtOH at 25°C.[2460b]

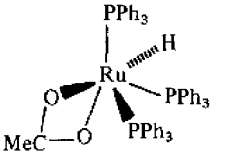


(149)

(374)

A suspension of $[RuCl_2(PPh_3)_3]$ in boiling MeOH containing the sodium salt of a carboxylic acid is reduced by H_2 or sodium hypophosphite to give the yellow $[RuH(OCOR)(PPh_3)_3]$ (R = Me, CH_2Cl, CF_3, Et, Pr, Pr^i, Ph *etc.*),[1451,2461] shown by X-ray analysis (R = Me)[2462] to have the distorted octahedral structure (**375**) which is retained in solution.[2463] A more rapid preparation of these active

homogeneous catalysts for hydrogenation of 1-alkenes is by treatment of $[RuH_2(PPh_3)_4]$ with the appropriate RCO_2H in boiling 2-methoxyethanol or by rapid successive addition of '$RuCl_3 \cdot xH_2O$', RCO_2H and KOH to a solution of PPh_3 in boiling EtOH;[1781] the latter method can be used to give $[RuH(OCOMe)(Ph_2PPhSO_3H\text{-}m)_3]$.[1563] Carbon dioxide reacts readily with $[RuH_2(PPh_3)_4]$, $[RuH_4(PPh_3)_3]$ or $[RuH_2(N_2)(PPh_3)_3]$ in aromatic solvents to give the formato complex $[RuH(OCOH)(PPh_3)_3]$[1437,1811,2433] whereas $[RuH_2(PPh_3)_4]$ and CO_2 in ROH produce $[RuH(O_2COR)(PPh_3)_3]$[1791] and in $NHMe_2$/EtOH, the carbamato complex $[RuH(O_2CNMe_2)(PPh_3)_3]$ is formed.[1792]



(375)

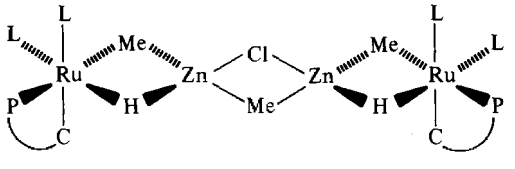
Reaction of $[RuH_2(PPh_3)_4]$ and dicarboxylic or α-hydroxy acids in boiling isopropanol yields $[RuH(OCOCH_2OCOH)(PPh_3)_3]$, $[RuH(OCOH(OH)R)(PPh_3)_3]$ and the dimeric complexes $[\{RuH(PPh_3)_3\}_2(OCO(CH_2)_nOCO)]$ ($n = 2$–4);[2464] with five-membered cyclic dicarboxylic anhydrides such as phthalic anhydride, C—O bond cleavage occurs to give $[RuH(o\text{-}OCOC_6H_4CHO)(PPh_3)_3]$.[2465]

Displacement of PPh_3 groups from $[RuH(OCOR)(PPh_3)_3]$ is also possible. Thus $[RuH(OCOMe)(PPh_3)_nL_{3-n}]$ ($n = 0$–3; L = $P(OMe)_3$, $P(OCH_2)_3CMe$, PF_2NMe_2, Bu^tNC, ½dppe — not all combinations) are reported[1386] and $[RuH(OCOMe)(Ph_2P(CH_2)_nPPh_2)_2]$ ($n = 2,3$) is mentioned.[1594] The complex $[RuH(OCOCF_3)(PF_3)_2(PPh_3)_2]$ can be prepared by reaction of $[RuH_2(PF_3)_2(PPh_3)_2]$ with CF_3CO_2H.[1576]

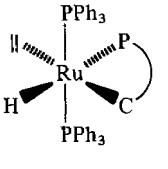
(*ii*) *Cyclometallated complexes*

Cyclometallation is defined in Section 45.5.4.5.v where some examples of complexes which do not contain Ru—H bonds are given. The majority of *ortho*-metallated ruthenium tertiary phosphine complexes are also monohydrides. For example reaction of $[RuHCl(PPh_3)_3]$ with LiR (R = Me, Me_3SiCH_2) in ethers at ambient temperature produces $[RuH(C_6H_4PPh_2)(PPh_3)_2S]$ (S = Et_2O, THF) which are formed by loss of CH_4 or $SiMe_4$ from $[RuHR(PPh_3)_2S_2]$. By use of an excess of LiMe, $ZnMe_2$ or $MgMe_2$ in Et_2O, yellow crystalline compounds containing Li, Mg or Zn as well as *ortho*-metallated PPh_3 ligands are obtained *e.g.* (**376**).[1690]

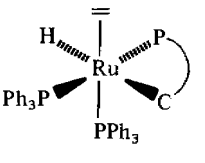
Treatment of $[RuH(C_6H_4PPh_2)(PPh_3)_2Et_2O]$, $[RuH_2(PPh_3)_4]$ or $[RuH_4(PPh_3)_3]$ with C_2H_4 gives a white solid of empirical formula $[Ru(PPh_3)_3C_2H_4]$ which converts to a pale orange isomer on heating. Initially these were formulated as Ru^0 complexes[2466] but further studies reveal that they are the Ru^{II} *ortho*-metallated species (**377**) and (**378**) respectively. An analogous reaction with cod gives (**379**) and a mechanism of formation involving Ru^{II} hydrido intermediates is proposed.[1402] Reduction of $[RuCl_2(PPh_3)_n]$ ($n = 3$ or **4**) with Na/Hg or Mg/Hg in MeCN/THF gives $[RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2]$ whereas reduction in THF/py affords a mixture of two isomers of the corresponding $[RuH(C_6H_4PPh_2)(py)(PPh_3)_2]$; in the presence of 2,2′-bipy, the dark red $[RuH(C_6H_4PPh_2)(bipy)(PPh_3)]$ is produced.[1404]



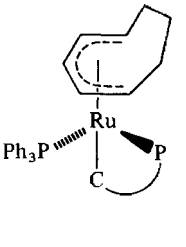
(376) L = PPh_3



(377)



(378)

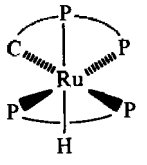


(379)

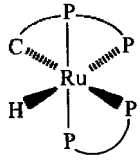
Electrochemical reduction of $[RuCl(dppp)_2]PF_6$ affords unstable anionic complexes which rapidly internally metallate to give $[RuH(C_6H_4P(Ph)(CH_2)_3PPh_2)(dppp)]$.[1509a] Direct synthesis of this complex is achieved by reaction of $[Ru(styrene)_2(PPh_3)_2]$ with dppp and $[RuH(C_6H_4P(Ph)(CH_2)_2PPh_2)(dppe)]$ (two isomers) is formed by treating $[Ru(styrene)(dppe)_2]$ with toluene. Hot toluene gives (**380**) whereas at room temperature isomer (**381**) is isolated. On standing for three days at room temperature, the dimetallated complex (**382**) can be isolated.[1392]

Other cyclometallated tertiary phosphine complexes include $K[RuH_2(C_6H_4PPh_2)(PPh_3)_2]\cdot C_{10}H_8\cdot Et_2O$ (formed by reaction of $[RuHCl(PPh_3)_3]$ with potassium naphthalide in THF at $-80°C$),[2467] $[RuH(C_6H_4PPh_2)(CO)(PPh_3)_2]$ (from thermal decarboxylation of $[Ru(o\text{-}Tol)(OCOH)CO(PPh_3)_2]$,[1487] $[RuH(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3]$ (see Section 45.5.1.1) and 'Ru(dmpe)$_2$' (see reaction (iv), Scheme 74 in Section 45.10.3.2.i). Reaction of *trans*-$[RuCl_2(PMe_3)_4]$ with Na/Hg in the presence of PPh_3 gives *fac*-$[RuH(C_6H_4PPh_2)(PMe_3)_3]$ which reacts with MeI and CS_2 to give *mer*-$[RuI(C_6H_4PPh_2)(PMe_3)_3]$ and *fac*-$[Ru(SCHS)(C_6H_4PPh_2)(PMe_3)_3]$ respectively.[1391c] Several *ortho*-metallated tertiary phosphite ruthenium hydrides have been characterized. For example treatment of $[Ru(CO)_2\{P(OMe)_3\}_3]$ with $P(OPh)_3$ produces (**383**)[1380] and likewise reaction of $[RuH(\eta^2\text{-}BH_4)ttp]$ with $P(OPh)_3$ yields the *ortho* metallated complex (**384**) even at room temperature.[2441] In boiling C_6H_6, $[RuH_2(CO)(PPh_3)_3]$ and $P(OPh)_3$ affords $[RuH\{(C_6H_4O)P(OPh)_2\}CO(PPh_3)P(OPh)_3]$ whereas more forcing conditions also produce some $[RuH\{(C_6H_4O)P(OPh)_2\}CO\{P(OPh)_3\}_2]$.[1685]

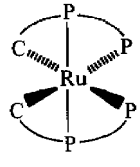
The compound $[RuH_2(PPh_3)_4]$ will cleave the vinyl CH bonds of neat alkylmethacrylates to give the five-membered metallacyclic complex (**385**), confirmed by an X-ray analysis of the *n*-butyl derivative.[2468]



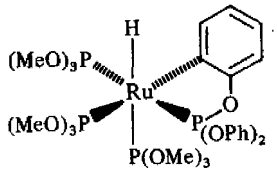
(380)



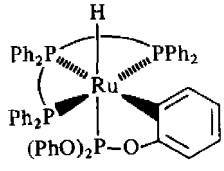
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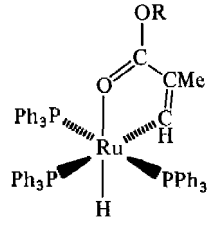
(382)



(383)



(384)



(385)

(iii) [RuHXY$_x$L$_{4-x}$] (L = P or As donor ligand, X = halide, OCOR, NO$_3$, dike, BF$_4$, dithioacid; Y = CO and/or CNR; x = 1,2)

Many hydrido–carbonyl complexes of ruthenium are obtained by decarbonylation of oxygen containing solvents (commonly alcohols). Thus Ru^{III} halides react with EPh_3 in high boiling point alcohols such as 2-methoxyethanol or ethylene glycol to give $[RuHX(CO)(EPh_3)_3]$ (E = P, As; X = Cl, Br).[2469] Later papers reporting the preparation of these complexes include HCHO in the recipe.[1410b,1841a] Ruthenium tertiary phosphine halide compounds also react with alcohols, particularly in the presence of base to give stable hydrido–carbonyl complexes (equation 150).[1584,1614b] The strong *trans* labilizing effect of the hydride ligand in $[RuHCl(CO)(PR_3)_3]$ can then be used to effect substitution with various P and As donor ligands (L) to form $[RuHCl(CO)(PR_3)_2L]$ (often in equilibrium with starting material).[1581,1685,2470,2471] The corresponding $[RuHCl(CS)(PPh_3)_3]$ is prepared by reaction of $[RuCl(OCOH)CS(PPh_3)_2]$ (Section 45.5.4.7.vi) with PPh_3.[1645]

$$[Ru_2Cl_3(PR_3)_6]Cl \xrightarrow[\Delta]{KOH/EtOH} [RuHCl(CO)(PR_3)_3] \qquad (150)$$

Decarbonylation of 2-methoxyethanol provides the CO ligands for formation of the five-coordinate bulky phosphine complexes $[RuHCl(CO)L_2]$ (L = PCy_3,[2472] PBu^t_2R (R = Me, Et)[1712]). These compounds readily take up CO to give $[RuHCl(CO)_2L_2]$ (L = PCy_3,[1813] PBu^t_2R[1712]) with *trans* L and

cis CO ligands. Treatment of *cis*-$[RuCl_2(CO)_2(PBu^tPr^n_2)_2]$ with 2-methoxyethanol/KOH yields $[RuHCl(CO)_2(PBu^tPr^n_2)_2]$[1519] and $[RuHCl(PPh_3)_3]$ and CO affords $[RuHCl(CO)_2(PPh_3)_2]$.[1449] The latter is also produced from $[RuCl_2(PPh_3)_3]$ in DMA treated with a H_2/CO mixture.[1607]

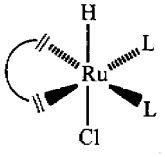
The five-coordinate $[RuHCl(CO)(PBu^t_2Et)_2]$ also reacts with MeNC to give $[RuHCl(CO)(CNMe)(PBu^t_2Et)_2]$[1712] and other neutral isocyanide monohydrido complexes include $[RuHX(CO)(CNR)(PPh_3)_2]$ (X = Cl, Br, I).[1480,1652,1656a,1717] Pyridine and SO_2 add to $[RuHCl(CO)(PCy_3)_2]$ to give $[RuHCl(CO)py(PCy_3)_2]$[2472] and $[RuHCl(CO)(SO_2)(PCy_3)_2]$[1813] respectively. With acetylene or phenylacetylene (L), $[RuHCl(CO)L(PCy_3)_2]$ is formed.[1623b]

Reaction of a six-fold excess of PPh_3 with 'Ru(CO)Cl' in EtOH in the presence of $Na[BH_4]$ affords a mixture of isomers of $[RuH(BH_4)(CO)(PPh_3)_3]$ which both contain a monodentate BH_4 ligand. The bulky PCy_3 generates $[RuH(BH_4)(CO)(PCy_3)_2]$ and with DBP and $Na[BH_3CN]$, $[RuH(BH_3CN)(CO)_2(DBP)_2]$ is formed.[2431]

Other carbonyl complexes of type $[RuHX(CO)_xL_2]$ ($x = 1,2$) include $[RuH(OCOR)(CO)_x(PPh_3)_2]$ (from $[RuH_2(CO)(PPh_3)_3]$ and RCO_2H),[1728a,1774] $[RuH(NO_3)(CO)_x(PPh_3)_2]$ (Section 45.5.4.7.v), $[RuH(dike)CO(PPh_3)_2]$ (Section 45.5.4.7.iii) and $[RuH(S–S)CO(PPh_3)_2]$ (S–S = $^-S_2CNR_2$, ^-S_2COR) (Section 45.5.4.8.ii).

(*iv*) *Other neutral monohydrido complexes containing C, N, O or S donor ligands*

Norbornadiene reacts with $[RuHCl(PPh_3)_3]$ in C_6H_6 to give $[RuHCl(PPh_3)_2(nbd)]$,[2445] shown[2473] to exist in solution as a single isomer. The analogous complexes $[RuHClL_2(cod)]$ (L = piperidine, $C_6H_{11}NH_2$, $NHMe_2$) are formed by reaction of $[RuCl_2(cod)]_n$ with amines at high temperature; X-ray analysis for L = piperidine establishes structure (**386**).[628] Reaction of the unusual dimer $[\{RuHX(cod)\}_2(NH_2NMe_2)]$ (X = Cl, Br) with Lewis bases in boiling acetone or MeOH generates a range of $[RuHX(cod)L_2]$ (L = $PMePh_2$, $SbPh_3$, $AsPh_3$, py). These are stable in the solid state but decompose in solution; spectroscopic (NMR, IR) data suggest structure (**386**).[2474]



(386)

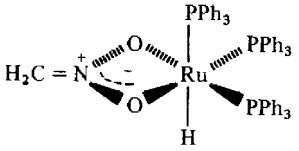
Propene oxidatively adds to $[\overline{RuH(C_6H_4PPh_2)}MeCN(PPh_3)_2]$ (or to the isomeric $[Ru(\eta\text{-}MeCN)(PPh_3)_4]MeCN$ to give $[RuH(\eta\text{-}C_3H_5)(MeCN)(PPh_3)_2]$[1404,2475] which then reacts with an excess of isobutene to give the 2-methylallyl complex $[RuH(\eta^3\text{-}C_4H_7)(MeCN)(PPh_3)_2]$, whereas treatment with $PHPh_2$ affords $[RuH(\eta\text{-}C_3H_5)(PMePh_2)_3]$.[2475] A similar hydrido-η^3-1-phenylallyl complex $[RuH(\eta^3\text{-}C_3H_4Ph)(MeCN)(PPh_3)_2]$ is isolated in high yield from reaction of $[Ru(\eta\text{-}MeCN)(PPh_3)_4]MeCN$ with allylbenzene in MeCN.[1405] A series of η-1-3 and η-1-5 cyclohexadienyl Ru^{II} hydrides such as $[RuH(PPh_3)_2(\eta\text{-}C_6H_7)]$ can be obtained by reaction of $[Ru(PPh_3)_2(styrene)_2]$ with cyclohexane,[2476] whereas 1-hexene gives a mixture of *syn*- and *anti*-$[RuH(PPh_3)_2(styrene)(1\text{-}3\text{-}\eta\text{-}C_6H_{11})]$.[1394] Other C donor ligand complexes include $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$, $[RuHCl(PPh_3)(\eta\text{-}C_6Me_6)]$, and a range of carborane complexes (reference 1, p. 806).

The diamagnetic red complex $[RuH\{N(SiMe_3)_2\}(PPh_3)_2]$ can be isolated from reaction of $[RuHCl(PPh_3)_3]$ with $Li[N(SiMe_3)_2]$. It is a rare example of a d^6 14-electron species and is proposed to have a distorted tetrahedral geometry.[2477] With diazadienes, $[RuHCl(PPh_3)_3]$ yields $[RuHCl(dad)(PPh_3)_2]$ which disproportionates in polar media to give $[RuH_2(dad)(PPh_3)_2]$, $[RuH_2(CO)(PPh_3)_3]$ and $[Ru_2Cl_3(dad)_2(PPh_3)_2]Cl$.[1770] Treatment of $[RuH_2(PPh_3)_4]$ with cyclic imides such as (+)-camphorimide, phthalimide, succinimide gives $[RuH(imido)(PPh_3)_3]$ in which the imide acts as a bidentate ligand coordinating *via* its N and O atoms.[2478] The potentially bidentate ligands 2-hydroxypyridine and 8-hydroxyquinoline react with $[RuH_2(PPh_3)_4]$ at room temperature to give $[RuHX(PPh_3)_3]$ (X = 2-OC_5H_4N, 8-OC_9H_6N) and 2-aminopyridine yields $[RuH(HNC_5H_4N)(PPh_3)_3]$. With pyrocatechol and resorcinol, the yellow crystalline complexes $[RuH(OC_6H_4OH)(PPh_3)_2]\cdot n[(OH)_2C_6H_4]$ ($n = 2$ and 0 respectively) are isolated and ^1H NMR studies indicate that the phenolic rings are π-bonded.[1706]

In contrast, $[RuHCl(PPh_3)_3]$ and 2,2′-bipyridyl give a poorly soluble red-brown material which may be $[RuHCl(bipy)(PPh_3)_2]_2$ although it could not be purified.[2445] There is also a brief mention in the literature of the reaction of $[RuH(PhN_3Ph)(PPh_3)_3]$ (see Section 45.5.4.6.v) with N_2 in a reverse osmosis cell to give $[RuH(N_2)(PhN_3Ph)(PPh_3)_2]$.[1838]

As noted elsewhere, various monohydrido complexes containing diazenido, diazene (Section 45.5.4.6.iv), triazenido, formazan and thioformamido (Section 45.5.4.6.v) ligands are available.

The yellow compound $[RuH(CH_2NO_2)(PPh_3)_3]$, obtained from the reaction of $MeNO_2$ with $[RuH_2(PPh_3)_4]$ or $[RuH(C_6H_4PPh_2)(PPh_3)_2Et_2O]$ is thought to contain bidentate O bonded $CH_2NO_2^-$ as in (**387**).[1402] Reaction of $[RuCl_2(PMe_3)_2\{P(OMe)_3\}_2]$ with Na/Hg in benzene gives the aryl hydrido complex *cis*-$[RuH(C_6H_5)(PMe_3)_2\{P(OMe)_3\}_2]$.[1391c]

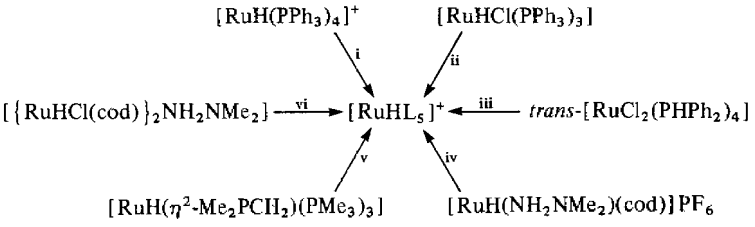


(387)

A range of Ru hydrido/hydroxo complexes are known, *e.g.* $[RuH(OH)(PPh_3)_2solvent]$ (solvent = H_2O, THF) (see Section 45.5.4.7.ii for details) and the related $[RuH(SR)(PPh_3)_3]$ (R = H, Me, Ph, $PhCH_2$) have been prepared (see Section 45.5.4.8.i). The sulfoxide complexes $[RuHCl(DMSO)_2(triphos)]$, $[RuHCl(DMSO)(tet\text{-}1)]$,[1540] $[RuHCl(DMSO)_2(AsPh_3)_2]$, $[RuHCl(DMSO)(AsMePh_2)_3]$ and $[RuHCl(DMSO)(AsMe_2Ph)_3]$[1511] are also reported.

(*v*) *Cationic monohydride complexes*

Triphenylmethyl hexafluorophosphate abstracts one hydride ion from $[RuH_2(PPh_3)_4]$ to give $[RuH(PPh_3)_4]PF_6$.[2479] The formation of a five-coordinate sixteen electron cation in preference to the eighteen electron species $[RuH(PPh_3)_5]^+$ is attributed to the steric bulk of the PPh_3 ligands since smaller ligands such as $P(OR)_2Ph$, $P(OR)_3$ (R = Me, Et), $PHPh_2$, PMe_2Ph, PMe_3 do form $[RuHL_5]^+$ cations. Some methods of synthesizing the latter are shown in Scheme 75. In method (iv), treatment with only four equivalents of PMe_2Ph in MeOH gives $[RuH(MeOH)(PMe_2Ph)_4]^+$[1766] and the mixed cations $[RuH(PF_3)_2(PPh_3)_2]BF_4$ are generated from $[RuH_2(PF_3)_2(PPh_3)_2]$ and HBF_4.[1576] Interestingly, $[Ru(CNBu^t)_5]$ deprotonates *nido*-2,3-Me_2-2,3-$C_2B_4H_6$ to give the related $[RuH(CNBu^t)_5]^+$ cation stabilized by a carborane anion.[2482]



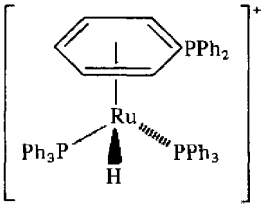
i, L = $P(OR)_2Ph$ (R = Me, Et) or $PHPh_2$;[2479] ii, $P(OMe)_3$ or $P(OMe)_2Ph$, or $PHPh_2$; PF_6^-;[111, 1531, 1532] iii, $PHPh_2$/MeOH; PF_6^-;[1565] iv, excess L ($P(OEt)_3$ or $P(OMe)_2Ph$ or PMe_2Ph), MeOH/Δ;[1766, 2480] v, PMe_3; PF_6^-,[1391] vi, $P(OMe)_3$ or $P(OMe)_2Ph$[2474, 2481]

Scheme 75

The $[RuH(PMe_2Ph)_5]^+$ cation has a distorted octahedral structure[2480] which shows evidence of the strain caused by non-bonded repulsions between the substituents on phosphorus and is consequently very reactive. For example, reaction with CO_2 in ROH gives the monoalkylcarbonate esters $[Ru(O_2COR)(PMe_2Ph)_4]^+$ (**253**; Section 45.5.4.7.vii) and with CS_2, $[Ru(S_2CH)(PMe_2Ph)_4]^+$ is formed (Section 45.5.4.8.iv).

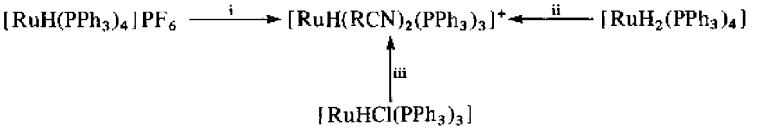
The red solution of $[RuH(PPh_3)_4]PF_6$ turns yellow on standing and a pale yellow solid of empirical formula $[RuH(PPh_3)_3]PF_6$ can be isolated. Spectroscopic data are consistent with struc-

ture (**388**) in which one of the PPh_3 ligands in η-bonded to Ru *via* one of the phenyl rings,[1754,2479] and this has been confirmed by X-ray analysis. Compound (**388**) is also formed in good yield by reaction of $[RuH_2(PPh_3)_4]$, $[RuH_4(PPh_3)_3]$ or $[RuH(OCOMe)(PPh_3)_3]$ with HBF_4/MeOH in the presence of excess PPh_3.[1754]



(388)

In the absence of an excess of PPh_3, the initial red species on protonation of [RuH(OCOMe)$(PPh_3)_3$] with HBF_4 is $[RuH(solvent)(PPh_3)_3]^+$ (solvent = MeOH, acetone) which in MeOH forms the yellow $[RuH(H_2O)_2(MeOH)(PPh_3)_2]^+$ cation. This cation is also obtained by treatment of $[Ru(OCOMe)(H_2O)(PPh_3)_3]BF_4$ with aqueous HBF_4 under hydrogen. Treatment of [RuH(OCOMe)$(PPh_3)_3$] in MeOH or acetone containing MeCN with aqueous HBF_4 gives the $[RuH(MeCN)_2(PPh_3)_3]^+$ cation.[1754] Cations of this type are also prepared as shown in Scheme 76 and assigned an octahedral structure with RCN *trans* to hydride.[2479]



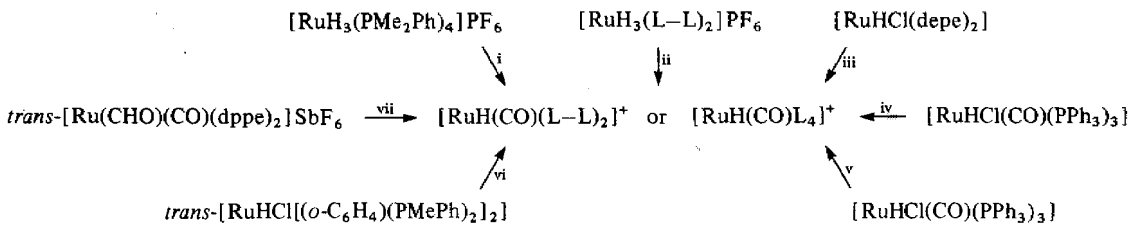
i, MeCN/MeOH, Δ; ii, $Ph_3C[BF_4]$, CH_2Cl_2, MeCN; iii, RCN, MeOH, KPF_6
(R = Me, Pr, Pr^i, Ph, *p*-Tol, $MeOC_6H_4$, ClC_6H_4)

Scheme 76

Reaction of $[RuH(NH_2NMe_2)cod]PF_6$ (see later) with the ditertiary phosphines dppp and dppb gives the five-coordinate $[RuH(L–L)_2]PF_6$ whereas dppe in EtOH yields the six-coordinate $[RuH(EtOH)(dppe)_2]PF_6$.[1766b] Protonation of $[RuH_2(dppm)_2]$ with HBF_4 in aqueous MeOH gives *trans*-$[RuH(OH_2)(dppm)_2]BF_4$.[1399] The corresponding $[RuH(Me_2P(CH_2)_3PPh_2)_2]BPh_4$ has been synthesized from *trans*-$[RuHCl(Me_2P(CH_2)_3PPh_2)_2]$ stirred with ethanolic solutions of $Na[BPh_4]$. It is not fluxional at room temperature and a trigonal bipyramidal structure is proposed.[1536a] More recent work suggests these compounds are square pyramidal in structure.[1536b]

Several routes to the monocarbonyl hydrido cations $[RuH(CO)(L–L)_2]^+$ and $[RuH(CO)L_4]^+$ are available (Scheme 77). Method (iii) with $CNBu^t$ in place of CO gives *trans*-[RuH(CNBu^t)$(depe)_2]^+$.[2484] Other monocarbonyl cations include $[RuH(S_2CPCy_3)(CO)(PCy_3)_2]^+$ (from CS_2 and $[RuHCl(CO)(PCy_3)_2]$),[1817] *cis*-$[RuH(CO)(bipy)_2]^+$ (prepared by heating *cis*-$[Ru(\eta^1$-OCOH)$CO(bipy)_2]^+$ in 2-methoxyethanol[1121a,b] or by treatment of *cis*-$[RuCl(CO)(bipy)_2]^+$ with $NaBH_4$)[1121c] and $[RuH(H_2O)(CO)(PPh_3)_3]BF_4$ (from treatment of $[RuH_2(CO)(PPh_3)_3]$ with aqueous HBF_4). Further reaction of the latter with CO gives $[RuH(H_2O)(CO)_2(PPh_3)_2]BF_4 \cdot EtOH$ (**389**) whose X-ray analysis reveals an extensive hydrogen-bonding network between the BF_4^- ion, the coordinated water molecule and the EtOH of crystallization.[1765] Compound (**389**) is also prepared by carbonylation of $[RuH(acetone)(PPh_3)_3]BF_4$.[1754] Treatment of $[RuHCl(CO)(PPh_3)_3]$ with $Ag[ClO_4]$ in MeCN gives $[RuH(CO)(MeCN)_2(PPh_3)_2]ClO_4$ (**390**) and since the MeCN groups are of different lability (*trans* to H and CO), a range of complexes are accessible by stepwise replacement. For example, treatment with CO, followed by PPh_3 gives $[RuH(CO)_2(PPh_3)_3]^+$ with *trans* CO groups.[1467] The tricarbonyl hydrido cation $[RuH(CO)_3(PPh_3)_2]^+$ is obtained by treatment of $[Ru(CO)_3(PPh_3)_2]$ with $NO[BF_4]$ or $NO[PF_6]$[2486a] and a preparative route to the cations $[RuH(N_2)(DMSO)_2(AsPh_3)_2]Cl$ and $[RuH(N_2)(DMSO)(AsMePh_2)_3]Cl$ has appeared.[1511]

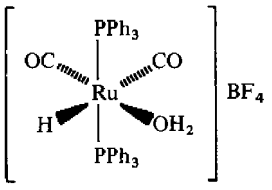
A series of monohydrido cations containing the tridentate ligands ttp and Cyttp have been reported. For example, reaction of $[RuH(\eta^2\text{-}BH_4)(ttp)]$ with HBF_4 and the appropriate ligand gives $[RuHL_2(ttp)]BF_4$ (L = $P(OMe)_3$, MeCN, CO). For L = $P(OMe)_3$, three different isomers (*i.e. trans, cis- syn* and *cis- anti*) are obtained depending on such factors as solvent used, reaction conditions



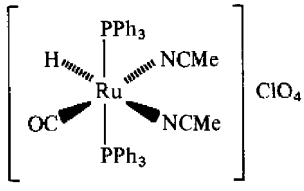
i, CO;[1766] ii, CO (L–L = dppe or dppp);[1766] iii, CO/acetone;[2484] iv, $Me_2P(CH_2)_3PPh_2$, $Li[ClO_4]$, EtOH;[1536] v, $PHPh_2$;[1565] vi, CO, PF_6^-;[2485] vii, CH_2Cl_2[1637]

Scheme 77

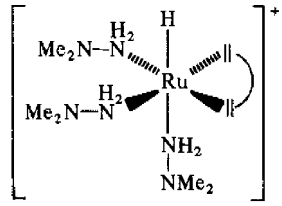
and sequence of addition of reagents. Some mixed ligand complexes such as $[RuH(MeCN)(PF_3)(ttp)]BF_4$ and $[RuH(CO)(P(OMe)_3)(ttp)]BF_4$ are also reported. Oxidative addition of acids to $[Ru(CO)_2(Cyttp)]$ affords the $[RuH(CO)_2(Cyttp)]^+$ cation[1486a,2441] whereas $[RuH(CO)_2triphos]Cl$ is formed from $[Ru(CO)_2triphos]$ and acetyl chloride.[2486b]



(389)



(390)



(391)

Treatment of a suspension of $[RuCl_2(cod)]_n$ in MeOH with *N,N*-dimethylhydrazine gives $[RuH(NH_2NMe)_2cod]^+$ isolated as its BPh_4^- or PF_6^- salts[650] and shown by X-ray analysis[2487] to have structure (**391**) with coordination *via* the less basic but more sterically favoured NH_2 nitrogen atoms. The NH_2NMe_2 groups are readily replaced by other N and P donor ligands to give $[RuHL_3(cod)]^+$ (L = N_2H_4, MeNHNH$_2$, py, 4-Mepy, $P(OMe)_3$, $P(OCH_2)_3CMe$, PPh_2OMe, PMe_2Ph, $PMePh_2$).[650,2488] Reaction of the dimer $[\{RuHX(cod)\}_2NH_2NMe_2]$ (X = Cl, Br) with 4-methylpyridine in EtOH or with $AgNO_3$ in MeCN also produces $[RuHL_3cod]^+$ (L = 4-Mepy, MeCN) respectively,[2474] and the coordinated cod in $[RuH(PMe_2Ph)_3(cod)]PF_6$ is readily replaced by 1,3-dienes to give $[RuH(PMe_2Ph)_3(diene)]PF_6$ (diene = buta-1,3-diene, hexa-1,3-diene).[2489]

45.10.3.3 Anionic complexes

There are relatively few examples of anionic ruthenium hydrido complexes. Thus, several papers have discussed the preparation of the $[RuH_6]^{4-}$ ion from Ru, H_2 and various lanthanide dihydrides at 800°C.[2490,2491] The ^{99}Ru Mössbauer spectra at 4.2 K for various $M_2[RuH_6]$ (M = Ca, Sr, Eu, Y) are consistent with diamagnetic Ru^{II} centres.[2492]

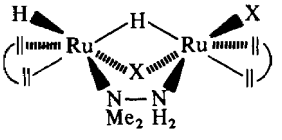
An unusual anionic dihydrido ruthenium complex is formed by reduction of $[RuHCl(PPh_3)_2]_2$ with potassium naphthalide at low temperature in THF, followed by recrystallization from toluene containing a small amount of diglyme. The physicochemical evidence is consistent with its formulation as the binuclear $[\{Kdiglyme\}^+\{RuH_2(PPh_2)(PPh_3)\}^-]_2$. Note that reduction of $[RuHCl(PPh_3)_3]$ with potassium naphthalide gives the *ortho*-metallated complex $K[RuH_2(C_6H_4PPh_2)(PPh_3)_2]C_{10}H_8 \cdot Et_2O$.[2467,2493]

A number of new anionic ruthenium hydrides have been synthesized by Halpern *et al.* These include *fac*-$[RuH_3(PPh_3)_3]^-$, isolated as its K^+ salt by reaction of $K[RuH_2(C_6H_4PPh_2)(PPh_3)_2]$ with H_2 (1 atm) in THF at 25°C, and $K[RuH(PPh_3)_2(anthracene)]$. Treatment of the latter with H_2 gives $K[RuH_5(PPh_3)_2]$ whose spectral data are consistent with a fluxional pentagonal bipyramidal structure. This pentahydride complex exhibits a rich chemistry, reacting with 1-hexene to produce the coordinatively unsaturated $[RuH_3(PPh_3)_2]^-$ anion and with cyclohexadiene to give $[RuH(PPh_3)_2cyclohexadiene]^-$. Anthracene regenerates $[RuH(PPh_3)_2anthracene]^-$ whereas ethylene affords the *ortho*-metallated $[Ru(C_6H_4PPh_2)(PPh_3)(C_2H_4)]^-$. Several of these complexes are good catalysts for the hydrogenation of anthracene to 1,2,3,4-tetrahydroanthracene.[2494]

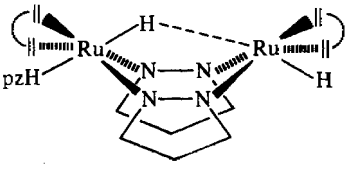
Other anionic ruthenium hydrides include the stereochemically non-rigid $[RuH(PF_3)_4]^-$ (from reaction of *cis*-$[RuH_2(PF_3)_4]$ with Et_3N),[1384] the protonated intermediates $[RuH(CN)_6]^{3-}$ and $[RuH_2(CN)_6]^{2-}$ (see Section 45.3.1.2.i) and an extensive range of tri-, tetra- and hexa-nuclear ruthenium hydride carbonyls, such as $[Ru_3H(CO)_{11}]^-$, $[Ru_4H(CO)_{13}]^-$, $[Ru_4H_3(CO)_{12}]^-$ and $[Ru_6H(CO)_{18}]^-$ (see reference 1, pp. 889–906).

45.10.4 Bi-, Tri-, Tetra- and Poly-nuclear Ruthenium(II) Complexes

The unusual hydrido-bridged complex $[\{RuHX(cod)\}_2NH_2NMe_2]$ (X = Cl, Br) is prepared by addition of either LiCl or LiBr to a boiling acetone/MeOH solution of $[RuH(NH_2NMe_2)_3(cod)]Y$ (Y = PF_6 or BPh_4).[2474] An X-ray analysis[2495] (for X = Cl) shows that its structure (**392**) consists of two Ru atoms linked by three different bridging ligands. Some reactions of this compound involving bridge cleavage and substitution are discussed in earlier sections. The X-ray structure of $[\{RuH(pz)cod\}_2pzH]$ has shown structure (**393**) with a semi-bridging hydride ligand.[2496]

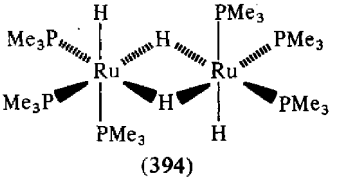


(392)

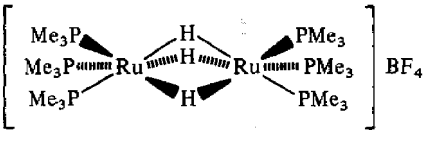


(393)

Treatment of $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ with H_2 (3 atm) in light petroleum affords the red crystalline diamagnetic $[Ru_2H_4(PMe_3)_6]$ shown by X-ray analysis to have structure (**394**). This double bridged species is quantitatively converted to $[Ru_2H_3(PMe_3)_6]BF_4$ (**395**) by reaction with aqueous HBF_4 in THF. It can also be obtained by reaction of H_2 (3 atm) with either $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6]BF_4$ or $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6][BF_4]_2$ in MeOH. The Ru—Ru distance in (**395**) is 2.540(1) Å.[1521] A complex analysing for $[Ru_2H_3(PMe_2Ph)_6]PF_6$ is produced by refluxing $[Ru(OCOH)(PMe_2Ph)_4]PF_6$ in MeOH in air.[1753] The related hydroxo-bridged complex $[PPh_3(Pr^iNCHCHNPr^i)Ru(\mu\text{-}OH)_2(\mu\text{-}Cl)RuH(PPh_3)_2]$ (**243** and Section 45.5.4.7.ii) is produced by the reaction of $[RuHCl(Pr^iNCHCHNPr^i)(PPh_3)_2]$ with water in toluene.[1770] The novel compound $[Ru_2H_4N_2(PPh_3)_4]$ with three bridging hydrides and a multiple metal–metal bond is known.[2497a] In the ruthenium catalysed conversion of methanol to methyl formate, $[RuCl_2(PPh_3)_3]$ is converted to the dinuclear cation $[(PPh_3)_2(CO)Ru(\mu\text{-}H)(\mu\text{-}Cl)_2Ru(CO)(PPh_3)_2]^+$, isolated as its PF_6^- salt.[2497c]



(394)

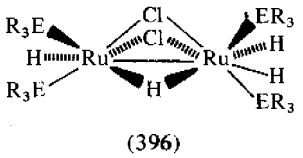


(395)

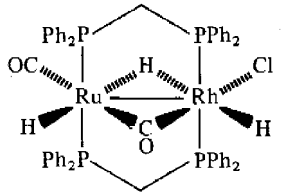
As discussed elsewhere (Section 45.10.3.2.i) reaction of $[RuH_2(PPh_3)_4]$ with 1,4-dichlorooctaphenyltetrasilane in the presence of Et_3N gives the dimeric $[RuHCl(PPh_3)_3]_2$, tentatively formulated on the basis of ^1H, ^{31}P NMR and IR spectroscopy as a bis-μ-chloro complex with terminal hydrido ligands.[2455] Reaction of H_2 with $[RuX_3(EPh_3)_2MeOH]$ in toluene or DMA in the presence of bases such as 'proton sponge' is reported to yield five-coordinate halide-bridged dimers $[RuHX(EPh_3)_2]_2$ (X = Cl, Br; E = P, As). Some evidence was also found for the existence of $[Ru^{III}HBr_2(AsPh_3)_2]$.[1546] However, unpublished work[1555] indicates that the above reactions also produce the Ru^{III} dimers $[RuH_2X(ER_3)_2]_2$ with possible structure (**396**) and these are in equilibrium with $[RuHX(ER_3)_2]_2$. Reduction of anhydrous $RuCl_3$ with sodium sand in neat Me_3P gives $[\{RuH(PMe_3)_3\}(\mu\text{-}Me_2PCH_2)_2]$.[2497d]

In a communication, reaction of the Ru^0 complex [Ru(cod)(cot)] with two equivalents of dppm in the presence of H_2 gives a compound of empirical formula $[RuH_2(dppm)_2]$. On the basis of ^{31}P and ^1H NMR evidence, this was tentatively formulated as a trinuclear complex,[1398] but further studies indicate that a mixture of monomeric *cis*- and *trans*-$[RuH_2(dppm)_2]$ is formed.[1399] A similar reaction with dppe gives $[RuH_2(dppe)_2]$,[1398] also formed by reaction of $[Ru(tos)_2(dppe)_2]$[1600a] with $NaAlH_4$. Pyrolysis of [RuH(2-np)(dmpe)$_2$] gives a compound of empirical formula '$[Ru(dmpe)_2]$' which is shown by structural analysis to be the dimeric Ru^{II} hydride (**123**; Section 45.5.1.1).

Treatment of $[RuH_2(PPh_3)_4]$ with an excess of hydroquinone in THF gives a highly insoluble compound tentatively formulated as the binuclear complex $[Ru_2H_2(O_2C_6H_4)_3(PPh_3)_4]$ (with a bridging hydroquinone ligand)[1706] whereas $[RuH_2(dppm)_2]$ and $[RhCl(CO)_2]_2$ affords the unusual $[RuRhH_2Cl(\mu\text{-}CO)CO(dppm)_2]$ (**397**).[1507a] Reaction of $[RuH_2(dppm)_2]$ with $[RhCl(cod)]_2$ produces $[RuRhH_2Cl(cod)(dppm)_2]$ (containing one bridging Cl, H and dppm group).[2497b] Treatment with $Na[BH_4]$ gives the coordinatively unsaturated $[RuRhH_3(dppm)_2]$.[2497c] Reactions with CO, $P(OMe)_3$ and LiMe are also reported. Reaction of $[MoRu(CO)_5(dppm)_2]$ with H_2 gives the dihydrogen-bridged complex $[MoRuH_2(CO)_5(dppm)_2]$.[1507b]



(396)



(397)

Examples of trinuclear hydrido complexes containing ruthenium include $[Ru_2(\mu\text{-}H)(\mu\text{-}OH)\{\mu\text{-}Fe(CO)_4\}(CO)_4(PPh_3)_2]$ (**293** and Section 45.5.5.1), $[Ru_3(\mu\text{-}H)_2(\mu\text{-}P, \eta^2\text{-}CH_2{=}CHC_6H_4PPh_2)(CO)_8]$ (from pyrolysis of $[Ru_3(CO)_{10}SP]$ at 80°C; SP = *o*-$CH_2{=}CHC_6H_4PPh_2$),[2498a] $[Ru_3(\mu\text{-}H)_3(CO)_9(SiZCl_2)_3]$ (**9** and Section 45.3.2.1) $[RuRh_3H(CO)_{12}]$, $[RuCo_3H(CO)_{10}(PPh_3)_2]$[2498b] and a series of phosphido-bridged clusters derived from photolysis of $[Ru_3(CO)_9(PHPh_2)_3]$ or reaction of $[Ru_3(CO)_{12}]$ with $PHPh_2$ *e.g.* $[Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8]$, $[Ru_3(\mu\text{-}H)_2\{\mu\text{-}PPh_2\}_2(CO)_7(PHPh_2)]$ *etc.*[1516] Many other hydrido carbonyl clusters containing three to six ruthenium atoms are known but these are outside the scope of this review {see reference 1, p. 889 for further details and reference 2499 for the X-ray structural analysis of the chiral cluster $[Ru_4H_4(CO)_9(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3][P(OCH_2)_3CEt]$}.

45.10.5 Higher Oxidation State Hydrido Complexes

In the presence of proton sponge, the complexes $[RuCl_2(PPh_3)_2]_2$, $[RuHCl(PPh_3)_2(nbd)]$ or $[RuX_2YL_2]$, (X = Y = Cl, Br, or X = Cl, Br; Y = O_2CR; L = PPh_3, $P(p\text{-Tol})_3$ or $AsPh_3$), react with H_2 in DMA or toluene to give the compounds $[RuH_2XL_2]_2$ (X = Cl, Br). The Ru^{III} product $[RuH_2Cl\{P(p\text{-Tol})_3\}_2]_2$ has been characterized by analytical, molecular weight, ^1H and ^{31}P NMR methods and chemical reactions and the data suggest the asymmetric structure (**396**). A reinvestigation of the reaction between $[RuCl_2(PPh_3)_3]$ and H_2 in DMA to form $[RuHCl(PPh_3)_3]$ also indicates that in the presence of excess Cl^-, a long lived intermediate, tentatively formulated as $[Ru_2H_3Cl_3(PPh_3)_4]$, is formed.[1555] In earlier work, reaction of $[RuBr_3(AsPh_3)_2]$ with H_2 in DMA at 25°C was claimed to give $[RuHBr_2(AsPh_3)_2]$.[1546]

The tetrahydrido complex $[RuH_4(PPh_3)_3]$ is readily obtained as very air sensitive white crystals by reaction of $[RuCl_2(PPh_3)_3]$ with $NaBH_4$ in C_6H_6/MeOH; in the presence of excess PPh_3, $[RuH_2(PPh_3)_4]$ is produced and this can be converted to the tetrahydride by passing a stream of H_2 through a C_6H_6 solution of the compound.[1408,1549,2427,2428] The tetrahydride is also generated from $[RuH_2(N_2)(PPh_3)_3]$ and H_2, a conversion which is readily reversed on exposure to nitrogen. Other routes are shown in equation (151).[1811,2433,2442] Solid $[RuH_4(PPh_3)_3]$ reacts with various other substrates (CO, NO, SO_2, NOCl, RCN) with displacement of H_2 to give compounds containing these ligands.[1408] Thus it might be effectively considered as a Ru^{II} complex containing neutral dihydrogen. The corresponding $[RuH_4(DBP)_3]$ (DBP = 5-phenyl-5*H*-dibenzophosphole) can be synthesized from $[RuCl_3(DBP)_3]$ and $NaBH_4$[2431] and it has been shown that $[RuH_4(PR_3)_3]$ (R = Pr^i, Cy, NEt_2) can be prepared by treatment of $[Ru(cod)(cot)]$ with three equivalents of PR_3 under H_2. These complexes in deuterated aromatic solvents exhibit H–D exchange between the solvent and the coordinated phosphines.[2500] $[RuH_4\{P(p\text{-}FC_6H_4)_3\}]$ is also known and has been shown to dehydrogenate cyclooctane at 150°C in the presence of a hydrogen acceptor.[2501]

$$\begin{matrix}[RuHCl(PPh_3)_3] \\ [RuH(OCOH)(PPh_3)_3]\end{matrix} \xrightarrow[H_2]{H_2/Et_3Al} [RuH_4(PPh_3)_3] \qquad (151)$$

The cationic Ru^{II} monohydrides $[RuH(MeOH)(PMe_2Ph)_4]PF_6$, $[RuH(EtOH)(dppe)_2]PF_6$ and $[RuH(dppp)_2]PF_6$ oxidatively add H_2 under ambient conditions to form the Ru^{IV} trihydrido cations $[RuH_3(PMe_2Ph)_4]PF_6$ and $[RuH_3(L\text{–}L)_2]PF_6$ (L–L = dppe, dppp), a process which can be reversed

on heating. Addition of HPF_6 to $[RuH_2(PMePh_2)_4]$ and $[RuH_2(dppb)_2]$ also gave very unstable trihydrido cations which revert to the dihydride on recrystallization.[1766] The corresponding $[RuH_3(PPh_3)_4]^+$ has been obtained, together with the dimer $[RuHCl(PPh_3)_3]_2$, by treatment of $[RuH_2(PPh_3)_4]$ with 1,4-$Cl_2Si_4Ph_8$ in the presence of Et_3N.[2502] A related 16 electron species $[RuH_3(PPh_3)_3]^+$ is tentatively claimed[1754] but no NMR data were reported because of rapid H_2 evolution in solution. The novel compound $[Ru_2H_6N_2(PPh_3)_4]$ can be prepared by recrystallization under nitrogen of the hydrogenation product of $[Ru(PPh_3)_2(styrene)_2]$. An X-ray analysis reveals structure (**398**) with four bridging hydrides and a short Ru—Ru distance (2.556(3) Å), consistent with a Ru—Ru double bond (although it is possible that this compound might be $[Ru_2H_4N_2(PPh_3)_4]$).[2497a] ^1H and ^{31}P NMR spectra indicate that the crude hydrogenation product is a mixture of $[RuH_6(PPh_3)_2]$ and $[Ru_2H_8(PPh_3)_4]$.[2503] Similar diamagnetic binuclear complexes $[Ru_2H_8L_4]$ (L = PPr^i_3, PBu^t_3), are produced by reaction of [Ru(cod)(cot)] with L at 40°C (although further work suggests these should be reformulated as $[Ru_2H_6L_4]$ species),[2497a] whereas with PCy_3, $[RuH_6(PCy_3)_2]$ is isolated.[1398] The latter loses H_2 thermally, photochemically or *in vacuo* to give $[Ru_2H_6(PCy_3)_4]$. Protonation of $[RuH_6(PCy_3)_2]$ with HBF_4/H_2O leads to $[Ru(OH_2)_5(PCy_3)]BF_4$ whereas reaction with ethylene produces the metallated complex $[RuH\{C_6H_{10}P(C_6H_{11})_2\}(PCy_3)(C_2H_4)_2]$.[2497a]



(398)

The silyl–ruthenium(IV) complexes $[RuH_3(SiR_3)L_n]$ (n = 2,3; L = PPh_3, $AsPh_3$, P(p-Tol)$_3$) and $[RuH_2X(SiR_3)L_3]$ (X = Cl, I) are discussed in Section 45.3.2.3.

45.10.6 References to Catalytic Reactions of Ruthenium Hydrido and Related Complexes

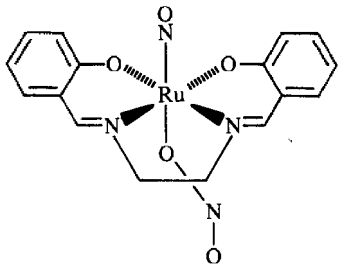
A number of the compounds discussed in this section *e.g.* $[RuHCl(PPh_3)_3]$, $[RuH(OCOR)(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$, $[RuHCl(CO)(PPh_3)_3]$, *etc.* and some from other sections *e.g.* $[Ru(CO)_3(PPh_3)_2]$, $[RuCl_2(PPh_3)_3]$, $[RuCl_3(EPh_3)_2MeOH]$ (Section 45.5) $[RuCl_2(DMSO)_4]$ (Section 45.7.9), '$RuCl_3 \cdot xH_2O$' (Section 45.9) are excellent homogeneous catalysts (or catalyst precursors) for such reactions as hydrogenation, isomerization, hydroformylation, polymerization, oxidation *etc.* of various organic substrates. Further references to these catalytic reactions are to be found in Chapters 61.1–61.5 and 67 of the present work and also in the following books and reviews. 'Comprehensive Organometallic Chemistry' edited by Sir Geoffrey Wilkinson, F. G. A. Stone and E. W. Abel, Volume 4 Section 32.9, Volume 8 and Volume 9 (Table 9 of Review Index), Pergamon Press, 1982. 'The Chemical and Catalytic Reactions of Dichlorotris(triphenylphosphine)ruthenium(II) and its Major Derivatives' by F. H. Jardine in 'Progress in Inorganic Chemistry', 1984, Volume 31, pp. 265–370. 'The Chemistry of Ruthenium' by E. A. Seddon and K. R. Seddon, Elsevier, 1984.

45.11 MIXED DONOR ATOM LIGANDS

45.11.1 N–O Ligands

45.11.1.1 Schiff base complexes

Treatment of $[Ru_3(CO)_{12}]$ with *N*,*N*′-bis(salicylaldehydo)ethylenediamine (salenH_2) in either DMF[2089] or toluene[2504] gives the dimeric yellow complex $[Ru(salen)CO]_2$; this compound is also formed by carbonylation of *trans*-$[Ru(salen)(PPh_3)_2]$[1756] (see Section 45.5.4.6.vii). Reaction with pyridine forms [Ru(salen)COpy] which undergoes facile oxidation with $[PhN_2]BF_4$, $[p\text{-}NO_2C_6H_4N_2]BF_4$ or $[Et_3O]BF_4$ to generate $[Ru(salen)COpy]BF_4$.[2504] Interaction of $[RuCl_2(CO)_2]_n$ or $[RuCl_2(CO)_3]_2$ with Na_2[salen] yields *cis*-$[Ru(salen)(CO)_2]$ and with $[RuCl_2(nbd)]_n$, [Ru(salen)(nbd)] is obtained.[1756] Nitrosation of $[Ru(salen)(PPh_3)_2]$ in THF at 60°C affords *trans*-[Ru(ONO)(salen)NO] (**399**) with an O-bonded nitrito group.[2505] Reaction of $[Ru(acac)_3]$ with *N*-benzylethylsalicylideneimine (LH) in ethyl benzoate gives the chiral tris complex $[RuL_3]$ which can be separated by TLC into its enantiomers.[2506]



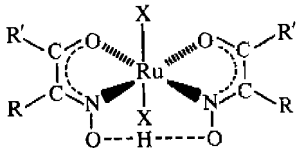
(399)

For Schiff base complexes containing tertiary phosphines, see Section 45.5.4.6.vii.

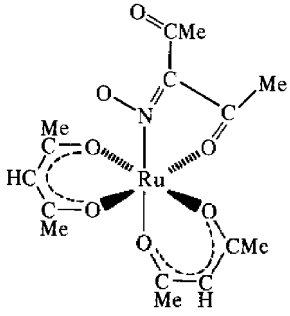
45.11.1.2 Oxime complexes

(i) Isonitrosoketones

Reaction of '$RuX_3 \cdot xH_2O$' with α-benziloxime [PhC(=O)C(=NOH)Ph] (HB) gives products formulated on the basis of IR, ESR, magnetic and electrochemical data as *trans*-$[Ru^{III}X_2(HB)B]$ (**400**) (X = Cl, Br).[1347,2507] A wider range of isonitrosoketone (hydroxyiminoketone) complexes of type (**400**) are now available, (R = R′ = Me; R′ = Ph, R = H, Me; R′ = Me, R = Ph), and these undergo both chemical and electrochemical reduction to generate the blue $[RuX_2(HB)B]^-$ anions. Addition of Et_3N deprotonates (**400**) to give $[RuX_2B_2]^-$ and reprotonation occurs on treatment with $HClO_4$.[2508] Similar reactions occur with arylazooximes [RC(=NOH)N=NAr] to give $[RuX_2(HL)L]$ (see Section 45.4.5),[1347,1349] and some ruthenium isonitrosoketonates containing 2,2′-bipyridyl ligands are described in Section 45.4.3.1.xiii.



(400)

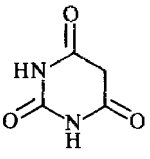


(401)

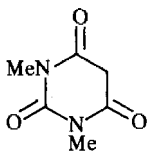
An unusual hydroxyiminoketone complex is (**401**) obtained by reaction of '$Ru(OH)_3NO$' with acacH at pH 6.5. At lower pH values either *cis*-$[Ru(acac)_2(Cl)NO]$ or $[Ru(acac)_2NO]_4$ is formed.[1297]

(ii) Ketoximes

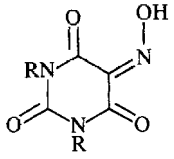
Treatment of $Na_2[RuOH(NO_2)_4NO]$ with an excess of the barbituric acids (**402**) yields the violurato anions $[Ru^{II}(VR_2)_3]^-$ (R = H, Me) which have been isolated with a variety of cations.[2509] These anions can also be prepared by either reaction of '$RuCl_3 \cdot xH_2O$' with violuric acid (VR_2H; **403**) in EtOH or $K_2[RuCl_5(OH_2)]$ and $Na[VR_2]$ in aqueous media.[2510] X-Ray analyses on $H_3O[Ru(VH_2)_3] \cdot 3H_2O$[2511] and $Ba[Ru(VH_2)_3]_2 \cdot 9H_2O$[2512] reveal an octahedral geometry with the violurato ligand coordinated as shown in (**404**). Retention of this geometry in solution is confirmed by ^1H NMR spectroscopy,[2509,2513] and the ^{13}C and ^{15}N NMR spectra of these $[Ru(VR_2)_3]^-$ are available.[2514] The analogous $H[Ru(dmho)_3]$ (dmho = 5,5-dimethylcyclohexane-1,2,3-trione-2-oxime) can be prepared by treatment of aqueous solutions of $Na[RuOH(NO_2)_4NO]$ with dmh (5,5-dimethylcyclohexane-1,3-dione).[2515] Further studies on the reaction of $Na_2[RuOH(NO_2)_4NO]$ with stoichiometric amounts of barbituric acid have led to the isolation of the intermediates $Na[RuOH(NO_2)_2(VH_2)NO]$ and *cis*-$[RuOH(VH_2)_2NO]$ and a detailed reaction mechanism is proposed.[2516]



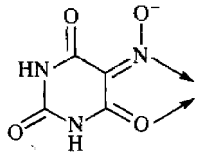
and



(402)



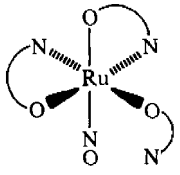
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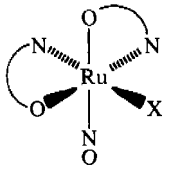
(404)

A number of reactions of these $[Ru(VR_2)_3]^-$ anions have been examined. Thus, deprotonation of aqueous solutions of $K[Ru(VH_2)_3]$ with KOH gives $K_4[Ru(VH)_3]$, whereas $Na[Ru(VH_2)_3]$ and NaOH followed by addition of $BaCl_2$ affords the dark blue $Ba_{2.5}[Ru(VH)_2(V)]$.[2513] Heating $[Ru(VR_2)_3]^-$ in dilute aqueous HCl produces the $[RuCl_2(VR_2)_2]^-$ anions.[2510] Reaction with $Na[NO_2]$ in $HClO_4$ gives $[Ru(VR_2)_3NO]$ (**405**), whereas treatment with $Na[NO_2]$ in hydrohalic media yields $[RuX(VR_2)_2NO]$ (**406**) (R = H, Me; X = Cl, Br). The rate determining step in the latter reaction involves breaking of the ring chelate.[2509,2517] Further complexes of type $[RuX(VR_2)_2NO]$ (X = Cl, OH, NO_3) and $[Ru(VR_2)_2Y(NO)]ClO_4$ (Y = H_2O, py, DMSO *etc.*) can be prepared by substituting the labile MeCN group of $[Ru(VR_2)_2(MeCN)NO]ClO_4$ (synthesized by refluxing $[Ru(NO_3)(VR_2)_2NO]$ with MeCN and $HClO_4$) with the appropriate ligand.[2510] A detailed study on the reactions of $[RuX(VR_2)_2NO]$ with β-diketones is also available.[2518]

Finally, treatment of $K_2[RuCl_5NO]$ with barbituric acid gives the $[Ru(barb)Cl_3NO]^{2-}$ and $[Ru(barb)_5NO]^{2-}$ anions which can undergo further deprotonation.[2519]



(405)

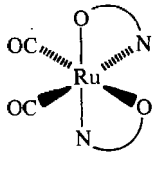


(406)

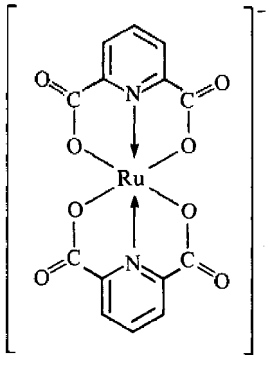
For oxime complexes containing tertiary phosphines, see Section 45.5.4.6.vii.

45.11.1.3 Amino acid, 8-hydroxyquinoline, dipicolinic acid and related complexes

Treatment of $[RuCl_2(diene)]_n$ (diene = nbd, 1,5-cod) with aqueous glycine (GlyH) at reflux yields two isomers of $[Ru(Gly\text{-}O)_2(diene)]\cdot H_2O$ which were successfully separated.[2520] The corresponding 8-hydroxyquinoline complex can be prepared by reaction of $[RuCl_2(1,5\text{-cod})]_n$ with 8-hydroxyquinoline and $Na_2[CO_3]$ in hot DMF.[2222] The dicarbonyl complex (**407**) is obtained in 6% yield together with $[Ru_3(CO)_8(8\text{-hq})_2]$ (76%), from reaction of $[Ru_3(CO)_{12}]$ with 8-hydroxyquinoline. On heating to 170°C, (**407**) isomerizes to a species with *cis* CO groups and equivalent 8-hydroxyquinoline ligands.[2521a] Treatment of $[RuHCl(CO)(PPh_3)_3]$ with 8-hydroxyquinoline (HL) gives $[RuCl(CO)(PPh_3)_2L]$.[2521b]



(407)



(408)

The nitrosyl complexes K[Ru(Gly-O)(OH)$_3$NO] and K[Ru(Ala)(OH)$_3$NO] arise from reaction of aqueous [RuCl$_3$(OH$_2$)$_2$NO] with glycine[1300] and L-α-alanine[2522] respectively, followed by anion exchange with 2 M KCl; [RuCl$_2$(Ala)$_4$] has also been claimed.[2523] Brief reports have been published on the reaction of '$RuCl_3 \cdot xH_2O$' with tris(hydroxymethyl)aminomethane (thamH) which gives [RuCl(tham)]$_2$Cl$_2$[2524] and [RuCl$_2$(DMSO)$_4$] and *N*-glycylglycine (Gly-Gly), which forms [Ru(Gly-Gly)(DMSO)$_3$].[112]

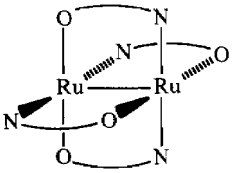
The [Ru^{III}(dipic)$_2$]$^-$ anion (**408**) has been synthesized starting from K$_2$[RuCl$_5$(OH$_2$)][2525] or '$RuCl_3 \cdot xH_2O$'.[2526] Compound (**408**) undergoes facile reduction with zinc or ascorbic acid to give burgundy coloured solutions of [Ru^{II}(dipic)$_2$]$^{2-}$ and the kinetics of electron transfer with the latter have been studied.[2525] Reaction of '$RuCl_3 \cdot xH_2O$' with equimolar amounts of dipicolinic acid and various mixed donor ligands such as glycine, nicotinic acid, isonicotinic acid, *o*-aminobenzoic acid *etc.* (N–O) gives the polymeric [Ru^{III}(dipic)(N–O)]$_n \cdot$H$_2$O.[2526] Some complexes of isonicotinic acid hydrazide (L) of type [Ru^{III}Cl$_2$L$_2$]Cl are known.[2527]

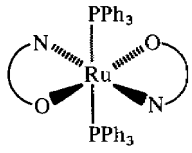
References to ammine, 2,2′-bipyridyl and tertiary phosphine complexes containing these ligands are to be found in Sections 45.4.1.2.vi, 45.4.3.1.xiii and 45.5.4.6.viii, 45.10.3.2.iv.

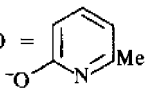
45.11.1.4 6-Methyl-2-pyridinolate and acetamide complexes

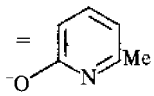
Reaction of [Ru$_2$(OCOMe)$_4$Cl] with sodium 6-methyl-2-pyridinolate [Na(mph)] at ambient temperature gives an 8% yield of [Ru$_2$(mhp)$_4$]$\cdot$CH$_2$Cl$_2$ (**409**) (r(Ru----Ru) = 2.238(1) Å). Magnetic (μ_{eff} = 2.9 BM/molecule) and PE spectral measurements suggest a $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*3}$ ground state electronic configuration.[2528] A detailed comparison of the structure of (**409**) with other [M$_2$(mhp)$_4$] complexes (M = Mo, Rh, Pd) has appeared.[2529]

In contrast, reaction of '[Ru$_2$(OCOMe)$_4$(PPh$_3$)$_2$]' with Na(mhp) in MeOH under reflux affords the monomeric species (**410**), the first example reported in which mhp acts as a chelating ligand.[2530]





(**409**) N–O = 

(**410**) N–O = 

The mixed valence Ru$_2^{II,III}$ complexes [Ru$_2$(RCONH)$_4$Cl] (R = CF$_3$,[2116] Me,[2531a] Ph[1871b]) have been prepared by reaction of [Ru$_2$(OCOMe)$_4$Cl] with RCONH$_2$. Like the corresponding carboxylato complexes, these molecules contain three unpaired electrons and detailed spectroelectrochemical studies indicate that the corresponding Ru$_2^{III,III}$ (for R = Me only), Ru$_2^{II,II}$ and possibly Ru$_2^{II,I}$ species can be generated in solution. However, the redox behaviour is very sensitive to the nature of the solvent and the amount of chloride ion present. The mixed valence Ru$_2^{II,III}$ complexes [Ru$_2$L$_4$Cl] (L = 2-hydroxypyridine, 2-anilinopyridine, 6-chloro-2-hydroxypyridine) were prepared from [Ru$_2$(OCOMe)$_4$Cl]. All these complexes exhibit a polar arrangement of the bonding ligands.[2531b]

The reaction of [Ru$_2$(PhCONH)$_4$Cl] with PPh$_3$ to give the novel [Ru$_2$Ph$_2$(PhCONH)$_2$(μ-NC(Ph)OPPh$_2$)$_2$] (**311**) is described in Section 45.5.8. For tertiary phosphine complexes of related ligands, see Sections 45.5.4.5.v and 45.5.4.6.v.

45.11.1.5 Edta and related complexes

Reaction between '$RuCl_3 \cdot xH_2O$' and Na$_2$[H$_2$edta] gives the yellow paramagnetic [Ru^{III}(Hedta)(OH$_2$)]$\cdot$4H$_2$O and [RuCl(H$_2$edta)(OH$_2$)]$\cdot$3.5H$_2$O.[2532] In water, stepwise hydrolysis of the former occurs to give [Ru(edta)(OH$_2$)]$^-$ and [Ru(OH)(edta)]$^{2-}$ respectively. Electrochemical studies reveal that electron transfer is rapid and reversible for the [Ru(edta)(OH$_2$)]$^{-/2-}$ couple and that [Ru^{II}(edta)(OH$_2$)]$^{2-}$ is oxidized by perchlorate ion.[2533] Reaction of the latter with formate ion affords the carbonyl complex [Ru(edta)(CO)]$^{2-}$.[2534]

Matsubara and Creutz[2535] have investigated the kinetics of substitution on $[Ru^{III}(edta)(OH_2)]^-$ and $[Ru(edta)(OH_2)]^{2-}$ anions and found rate constants higher than those of corresponding ruthenium compounds with oxygen and nitrogen donor ligands, especially for Ru^{III} in which substitution is faster by as much as ten orders of magnitude. Thus they generated an extensive series of $[Ru(edta)L]^{-/2-}$ anions (L varying from water to aromatic N-heterocycles), and measured their electronic spectra and redox potentials.

Ruthenium(III) edta complexes can be attached to a graphite electrode surface *via* the uncoordinated carboxylate function and some redox couples for several $[Ru(edta)L]^{-/2-}$ complexes are reported.[238]

In a subsequent paper, Diamantis *et al.*[2536] have reported the synthesis of compounds of type $[Ru(H_nedta)L_n]$ [L = CO, NO *etc.* (n = 1) and L = RCN (n = 2)] by reaction of $[Ru(Hedta)OH_2]^-$ with the appropriate ligand in the presence of H_2/Pt. The compounds were characterized by a range of spectroscopic techniques which indicate that the ligands L are accommodated in equatorial positions. For L = N_2, the anions $[Ru(edta)N_2]^{2-}$ and $[\{Ru(edta)\}_2N_2]^{4-}$ were isolated. The corresponding $Na_2[Ru(pdta)N_2]\cdot 2H_2O$ (H_4pdta = propylenediaminetetraacetic acid) has been prepared from $[Ru(Hptda)(OH_2)]\cdot H_2O$ and NaN_3,[2537]

The complexes $[Ru^{II}(H_2edta)L_2]$ (L = py, 4-MeC_5H_4N, ½bipy, ½phen, ½dppe, *etc.*) and $[Ru^{III}(H_2edta)L'_2]$ (L′ = HSCN, ½acac, ½DMG, ½S_2CNEt_2 *etc.*) have been prepared from $[Ru(Hedta)(OH_2)]^-$ and $[Ru(Hedta)(OH_2)]$ respectively. These have been fully characterized and also further reactions of the carboxylic acid functions in the free glycinate arms investigated (with CH_2N_2 and *p*-toluidine).[2538] Reaction of $[Ru(edta)OH_2]$ with RSH gives $[Ru(edta)SR]^{2-}$.[2539]

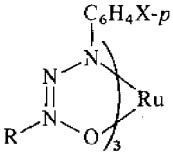
A range of other Ru^{III} edta complexes have been prepared starting from '$RuCl_2\cdot xH_2O$' and H_4edta *e.g.* $[RuCl(H_2edta)]$ and $[RuCl_2(H_3edta)]\cdot H_2O$[2540] or $K_2[RuCl_5(OH_2)]$ and $Na_2(H_2edta)$ *e.g.* $K[RuCl(Hedta)]\cdot 2H_2O$ and $K[RuCl_2(H_2edta)]\cdot H_2O$.[2536,2541]

Oxidation of $[Ru^{III}(edta)(OH_2)]^-$ by chlorate ion gives the green mixed valence, μ-oxo dimer $[(edta)Ru^{IV}ORu^{III}(edta)]^{3-}$ which can be reduced at a mercury electrode to $[(edta)Ru^{III}ORu^{III}(edta)]^{4-}$; facile decomposition of the latter to regenerate $[Ru^{III}(edta)(OH_2)]^-$ then occurs.[2542a] A preliminary report on the synthesis of $(Et_4N)_3$ $[LRu(\mu\text{-}OH)(\mu\text{-}O_2)RuL]$ (L = edta, Hedta) has also been published.[2543] The binuclear compound *trans*-$[Ru(NH_3)_4(NCS)LRu(edta)]$ (L = 4-vinylpyridine) has recently been synthesized.[2542b]

Finally, there is a brief report on the synthesis of the dark brown $[Ru^{IV}Cl_2(H_2edta)]\cdot 3H_2O$ {from $K_2[RuCl_6]$ and $Na_2(H_2edta)$}, which further reacts with acetate ion to give the violet complexes $M_2[Ru^{IV}Cl_2(edta)]\cdot xH_2O$ (M = K^+, x = 3; M = NH_4^+, x = 2).[2540]

45.11.1.6 Triazene 1-oxide complexes

The low spin Ru^{III} triazene 1-oxide complexes (**411**) (R = Et, X = Me, H, Cl, NO_2, CO_2Et; R = Ph, X = Me, H, Cl, CO_2Et) have been synthesized and assigned a meridional RuN_3O_3 coordination sphere. In MeCN, these complexes exhibit a quasi-reversible Ru^{III}/Ru^{II} and a nearly reversible Ru^{IV}/Ru^{III} couple and the electronic spectra of $[RuL_3]^-$ and $[RuL_3]^+$ are reported.[2544]



(411)

Treatment of (**411**) with either aqueous or gaseous HX (X = Cl, Br) gives the diamagnetic *trans,trans,trans*-$[Ru^{IV}X_2L_2]$ complexes, the first example of a Ru^{IV} chelate with centrosymmetric hexacoordination. Redox studies reveal that these compounds undergo stepwise reduction to $[RuX_2L_2]^{n-}$ (n = 1,2) and, furthermore, that the Ru^{III} monoanion loses halide ion to generate the redox active dimer $[L_2XRuXRuXL_2]^-$, ($[L_2RuX_2RuL_2]$).[2545]

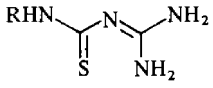
45.11.2 N–S Ligands

Reaction of $[RuCl_2(diene)]_n$ (diene = nbd, 1,5-cod) with 2(1*H*)-pyridinethione (pyridine-2-thiol), 2(1*H*)-pyrimidinethione or benzothiazole-2-thiol (2-mercaptobenzothiazole) (HL) in hot DMF in

the presence of $Na_2[CO_3]$ gives the chelate complexes $[RuL_2(diene)]$ (one isomer).[2222,2546] Treatment of these compounds with an excess of methyl iodide gives the iodide-bridged dimers $[RuIL(diene)]_2$.[2546] Other pyridine-2-thiol (pySH) and 2-mercapto-benzothiazole (mbtH) complexes such as $[RuCl_2(pySH)_2]_n$, $]Ru(pyS)_2(PPh_3)_2]$, $[Ru(mbt)_2(py)_2(CO)_2]$, $[Ru(mbt)py(CO)_2]_2$ *etc.* are described in Sections 45.5.4.8.i and 45.7.1. Reaction of $[RuCl_2(DMSO)_4]$ with mbtH gives $[RuCl_2(mbtH)_2(DMSO)_2]$. (Scheme 69, Section 45.7.9) while 2-aminothiophenol and $[RuCl_2(PPh_3)_3]$ afford $[Ru(chelate)_2(PPh_3)_2]$.[1706] Reaction of '$RuCl_3 \cdot xH_2O$' and 4-amino-3,5-dimercapto-1,2,4-triazole (H_2amt) gives $[Ru(Hamt)_2]$[2547] whereas 1,3,4-thiadiazole-2,5-dithiol produces polymeric ruthenium(II) and (III) complexes involving only S coordination.[2548] The reactions of 8-mercaptoquinoline with $[RuCl_2(bipy)_2]$ are discussed in Section 45.4.3.1.xiii.

Treatment of '$RuCl_3 \cdot xH_2O$' with 4-benzylamidothiosemicarbazide (btsc) and α-pyridylthiosemicarbazide (apt) gives the Ru^{III} cations $[RuCl_2(btsc)_2]Cl \cdot 2H_2O$ and $[RuCl_2(apt)_2]Cl$ respectively. With 1-benzilidine-4-α-pyridylthiosemicarbazone (bpt), $[RuCl_3(bpt)]$ is produced.[2549,2550]

Reaction of '$RuCl_3 \cdot xH_2O$' with *N*-amidinothiourea (Hatu) or *N*-methylamidinothiourea (HNmatu) (**412**) in the presence of NO gives $[Ru^{II}Cl_2(atu)(OH_2)NO] \cdot 2H_2O$ and $[RuCl_2(Nmatu)(OH_2)(NO)] \cdot H_2O$ respectively. Further reaction with aqueous NaOH produces the corresponding nitro complexes $[Ru^{II}(NO_2)atu(OH_2)_3]$[2551] *etc.*



(412)

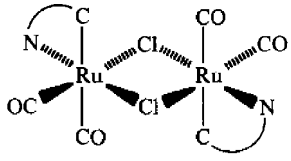
Thioformamido complexes containing tertiary phosphine ligands are discussed in Section 45.5.4.6.v.

45.11.3 N–C Ligands

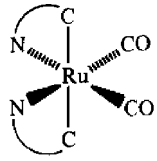
Reaction of $[RuCl_2(CO)_3]_2$ with molten azobenzene (azbH) gives the chloride-bridged dimer $[Ru(azb)Cl(CO)_2]_2$ (**413**) which undergoes an extensive range of reactions involving chloride displacement and/or bridge cleavage.[1222,1250] For examples see $[Ru(azb)(CO)_2bipy]^+$ $[Ru(azb)Cl_2(CO)_2]^-$ (**91**) (Section 45.4.3.1.xiii), $[Ru(azb)(SPh)(CO)_2]_2$, $[Ru(azb)(abt)(CO)_2]$ (abt = 2-aminobenzenethiolate) (Section 45.7.1) and reference 3, p. 702.

Related cyclometallated complexes $[RuCl(C–N)(CO)_2]_2$ (HC–N = 2-phenylpyridine,[2552] *N*-phenylpyrazole,[2552] PhCH=NMe,[2553] 2-(2-thienyl)pyridine[2554]) can also be synthesized from $[RuCl_2(CO)_3]_2$ and the appropriate ligand.

Some $[Ru(azb)(CO)_3]_2$ is obtained by reaction of $[Ru_3(CO)_{12}]$ with azobenzene,[2555] whereas treatment of $[Ru_3(CO)_{12}]$ with PhCH=NR (R = Me, Ph),[2553] azophenetole[2556] or benzo[*h*]quinolin-10-yl[2557] gives the monomeric $[Ru(C–N)_2(CO)_2]$. An X-ray analysis on the latter confirms structure (**414**).[2558]



(413)



(414)

Finally, reaction of azobenzene with the methanolic ruthenium blue solution gives $[\{Ru(azb)Cl_2\}_2(\mu\text{-PhN=NPh})]$ which on treatment with PPh_3 in MeOH produces $[Ru(azb)Cl(PPh_3)_3]$.[676]

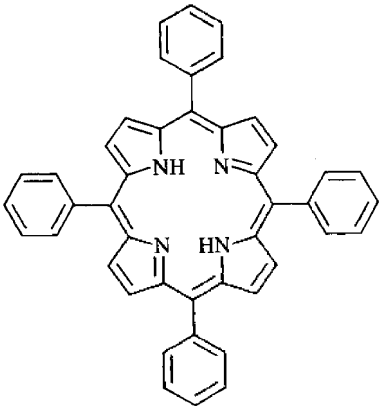
45.11.4 S–O Ligands

Monothio-β-diketonate complexes are described in Section 45.7.7 and monothio-carboxylate, -carbonate and -carbamate complexes in Section 45.5.4.8.5 and SO_2 complexes in Sections 45.4.1.2.iii.c and 45.5.4.8.vi.

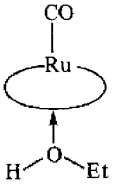
45.12 MACROCYCLIC COMPLEXES

45.12.1 Porphyrins

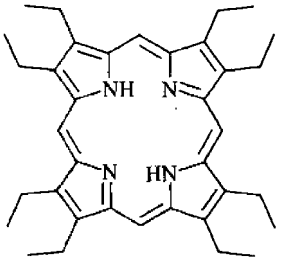
The chemistry of ruthenium porphyrins has been reviewed.[2559–2562] Reaction of $RuCl_3$ with H_2TPP (H_2TPP = *meso*-tetraphenylporphyrin, **415**) in refluxing ethanol/acetic acid under CO for 21 h yields an orange product originally formulated as $[Ru^{III}(TPP)(Cl)(CO)]$ with the ν_{CO} stretching vibration occurring near 1955 cm^{-1}.[2563] The complex was later proposed to be a ruthenium(II) species.[2564] A single crystal X-ray structural analysis of the product reported it to be [Ru(TPP)$(CO)_2$],[2565] but later it was correctly reformulated as the ethanol adduct [Ru(TPP)(CO)(HOEt)] (**416**) with Ru—O = 2.21, Ru—C = 1.77 Å and < RuCO = 175.8°.[2566] In non-coordinating solvents, the complexes [Ru(porph)(CO)(HOEt)] lose EtOH to yield [Ru(porph)CO] (porph = porphyrin dianion), the association constant K for [Ru(OEP)(CO)(HOEt)] (OEP = octaethylporphyrin, **417**) being estimated as 550 M^{-1} at room temperature in CH_2Cl_2 (equation 152).[2567,2568]



(415) H_2TPP



(416)

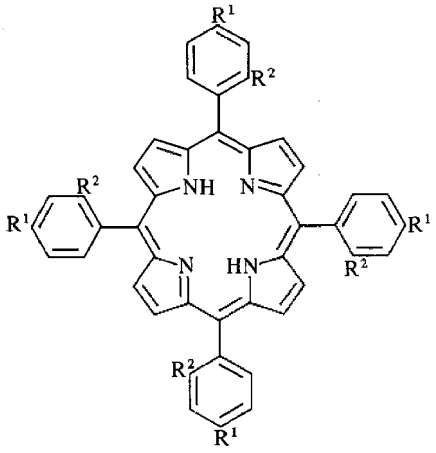


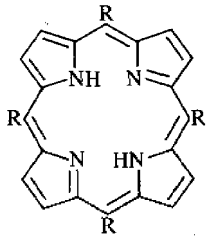
(417) H_2OEP

$$[Ru(OEP)(CO)] + EtOH \overset{K}{\rightleftharpoons} [Ru(OEP)(CO)(HOEt)] \quad (152)$$

Ruthenium(II) carbonyl complexes of the type [Ru(porph)CO] can be prepared by reaction of $Ru_3(CO)_{12}$ with H_2porph in toluene, decalin or benzene,[2566,2568–2576] $[RuCl_2(CO)_3]_2$ or $Ru_3(CO)_{12}$ with H_2porph in acetic or propionic acid,[2564] $RuCl_3$ with H_2porph under CO in 2-methoxy ethanol,[2567,2573,2577] or by reaction of $[Ru(porph)(CN)_2]$ with CO and N_2H_4 in MeOH,[2571] the product being purified by column chromatography. Porphyrin ligands that have been coordinated to ruthenium(II) include H_2TPP (**415**),[2566,2567,2570,2573,2576–2579] H_2OEP (**417**),[2567,2568,2571–2575,2577,2579,2580] substituted derivatives of *meso*-tetraphenylporphyrin, $H_2$4-XTPP (X = CF_3 (**418**),[2575,2580–2583] CH_3 (**419**),[2576,2577,2582,2583] Pr^i (**420**),[2566,2575,2580–2582,2584,2585] Cl (**421**),[2576,2582,2583] Br (**422**),[2576] F (**423**),[2576] MeO (**424**),[2576,2582,2583] Et_2N (**425**),[2582,2583] SO_3^- (**426**)[2569]), $H_2$2-XTPP (X = Me (**427**),[2580,2581] nicotinamide (**428**)[2586]), *meso*-tetramesitylporphyrin (**429**),[2581] *meso*-tetra-*n*-propylporphyrin (TPr^nP, **430**),[2573] *meso*-porphyrin IX dicarboxylic acid (**431**),[2587] dimethyl ester (**432**),[2570,2588–2590] dioctadecyl ester (**433**),[2591] etioporphyrin I (H_2EtioI (**434**)[2592,2593]) and myoglobin.[2587,2594,2595] Adducts [Ru(porph)(CO)L] can be readily prepared by addition of L to [Ru(porph)CO] {L = for example; py,[2566,2572,2578,2581,2585,2591] substituted pyridines,[2580–2585] 3-hydroxyaniline, benzylamine, pyrazole,[2585] 3,5-dimethyl pyrazole,[2584] 4,5-dimethyl pyridazine,[2584] 3,6-dimethyl pyridazine,[2584,2588] aliphatic amines,[2585] imidazole,[2570,2585,2588,2596] substituted imidazoles,[2585,2588] THF,[2575,2580,2583,2585,2592] H_2O,[2583] CO,[2575,2580] PPh_3,[2567,2568] PBu_3^n,[2568,2579] PBu_3^t,[2579] bidentate diphosphines,[2579] RS^- (R = Bu^t, Et, $MeO_2CCH_2CH_2$).[2171] The single crystal X-ray structure of [Ru(TPP)(CO)py] (**435**) shows Ru—C = 1.838 Å, Ru—N(py) = 2.193 Å, average Ru—N(TPP) = 2.052 Å, < RuCO = 178.4°.[2578] The strength of binding of CO to [Ru(porph)CO] is found to decrease in the order porph = OEP ≫ TPP > 4-Pr^iTPP > 4-CF_3TPP (equation 153), [Ru(OEP)$(CO)_2$] (**436**) being stable to loss of CO under vacuum over several hours.[2575]

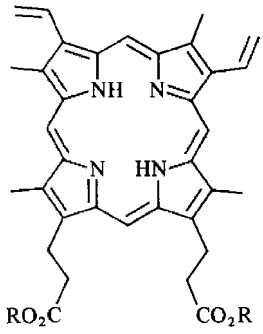
The rates of phenyl ring rotation and ring current effects in ruthenium complexes of TPP derivatives have been probed by NMR spectroscopy.[2580–2582,2596] Exchange of 4-*t*-butylpyridine in [Ru(porph)(CO)(4-Bu^tpy)] (porph = 4-XTPP; X = Cl, Me, OMe, Et_2N, CF_3) occurs *via* a dissociative mechanism with $\Delta G^{\neq}$ = 77.4–82.8 kJ mol^{-1}, $\Delta H^{\neq}$ = 82.0–92.5 kJ mol^{-1} and $\Delta S^{\neq}$ = 21–42 J K^{-1} mol^{-1}.[2583] Multiple resonance studies on [Ru(porph)(CO)(imid)] show that imidazole tautomerism (equation 154) occurs *via* a dissociative, intermolecular exchange ($\Delta G^{\neq}$ = 76.5 kJ mol^{-1}),[2596] rather than intramolecularly as suggested previously.[2570,2588] Inter- and



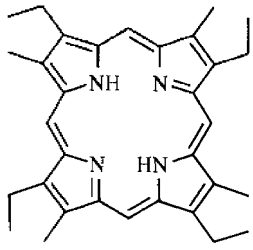


(429) R = mesityl
(430) H_2TPr^nP R = Pr^n

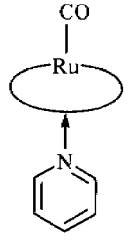
R^1	R^2	Formulae	
H	H	(415)	H_2TPP
CF_3	H	(418)	$H_2$4-CF_3TPP
Me	H	(419)	$H_2$4-MeTPP
Pr^i	H	(420)	$H_2$4-Pr^iTPP
Cl	H	(421)	$H_2$4-ClTPP
Br	H	(422)	$H_2$4-BrTPP
F	H	(423)	$H_2$4-FTPP
OMe	H	(424)	$H_2$4-MeOTPP
Et_2N	H	(425)	$H_2$4-Et_2NTPP
SO_3^-	H	(426)	$H_2$4-SO_3TPP
H	Me	(427)	$H_2$2-MeTPP
H	nicotinamide	(428)	$H_2$2-nicotinamide TPP



(431) R = H
(432) R = Me
(433) R = $C_{18}H_{37}$



(434) H_2Etio I



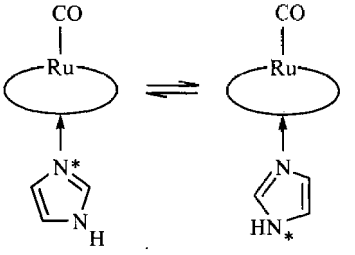
(435)

$$[Ru(OEP)CO] + CO \rightleftharpoons [Ru(OEP)(CO)_2] \quad (153)$$

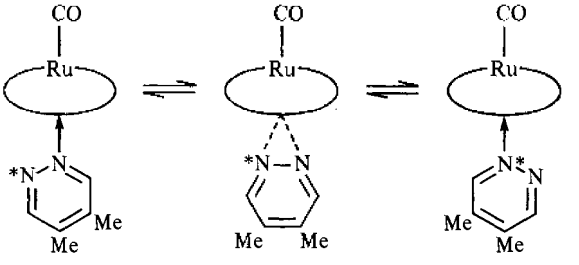
(436)

intra-molecular exchange reactions have been observed for 4,5- and 3,6-dimethylpyridazine adducts, intramolecular site exchange *via* a seven-coordinate ruthenium(II) intermediate (**437**) (equation 155) occurring at 20–85 times faster than intermolecular processes.[2584] ^{31}P NMR data for adducts of [Ru(OEP)CO] with bidentate phosphine ligands have been tentatively attributed to the formation of seven-coordinate adducts (**438**) (equation 156).[2579] A molecular orbital scheme for [Ru(porph)(CO)L] has been published.[2592]

The complexes [Ru(porph)(CO)L] generally show two, one electron oxidations and one, one electron reduction. For [Ru(OEP)(CO)(THF)] and [Ru(EtioI)(CO)(THF)], $^1E_{\frac{1}{2}} = +0.61$ and $+0.64$ V *vs.* SSCE respectively[2592] while for [Ru(4-XTPP)CO] (X = H, Me, MeO, F, Cl, Br), $^1E_{ox} =$ 0.74–0.86, $^2E_{ox} = 1.18$–1.27 and $E_{red} = -1.24$ to 1.35 V *vs.* SSCE in DMSO.[2576,2593] On the basis of electronic, IR and ESR data, the first oxidation has been assigned as ligand-based to give the π-cation radical $[Ru^{II}(porph^+)(CO)L]^+$.[2576,2592,2593,2597,2598] Interestingly the osmium analogue $[Os^{II}(OEP)(CO)py]$ is oxidized at the metal centre at $+0.4$ V *vs.* SSCE to afford $[Os^{III}(OEP)$-

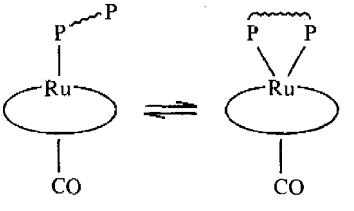


(154)



(155)

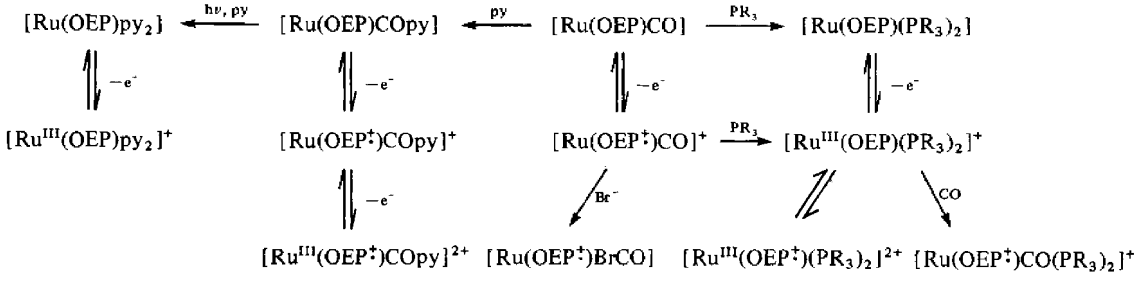
(437)



(156)

(438)

$(CO)py]^+$.[2592] The effect of variation of porphyrin ligand,[2597] solvation and axial ligation[2585,2599,2600] on the porphyrin ring oxidation has been assessed. The ^1H NMR spectra of π-cation radical complexes incorporating OEP and *meso*-porphyrin IX dimethyl ester have been reported and related to data on horseradish peroxidase and myoglobin derivatives.[2598] The second oxidation has been assigned to a metal-based redox couple to yield $[Ru^{III}(porph^+)(CO)L]^{2+}$, with the reduction process being sited on the porphyrin.[2576,2593] The stabilization of ruthenium(I) in the reduced complexes has also been proposed.[2601] For [Ru(4-Et_2NTPP)(CO)(4-Bu^{t}py)] three oxidation couples at $E_{\frac{1}{2}} = +0.50$, $+0.73$ and $+1.06$ V *vs.* SCE in CH_2Cl_2 are observed.[2597] Intramolecular electron transfer reactions between porphyrin and metal centres induced by changes in axial ligation have been studied and are summarized in Scheme 78.[2568,2592,2602,2603] For example, addition of Br^- to purple ($^2A_{2u}$ ground state) $[Ru(OEP^+)CO]^+$ yields green ($^2A_{1u}$ ground state) $[Ru(OEP^+)Br(CO)]$ which can be converted to $[Ru^{III}(OEP)(PBu^n{}_3)_2]^+$ on addition of $PBu^n{}_3$.[2568] Addition of CO to $[Ru^{III}(OEP)(AsPh_3)_2]^+$ yields $[Ru^{II}(OEP^+)(CO)(AsPh_3)]^+$ reversibly.[2603]

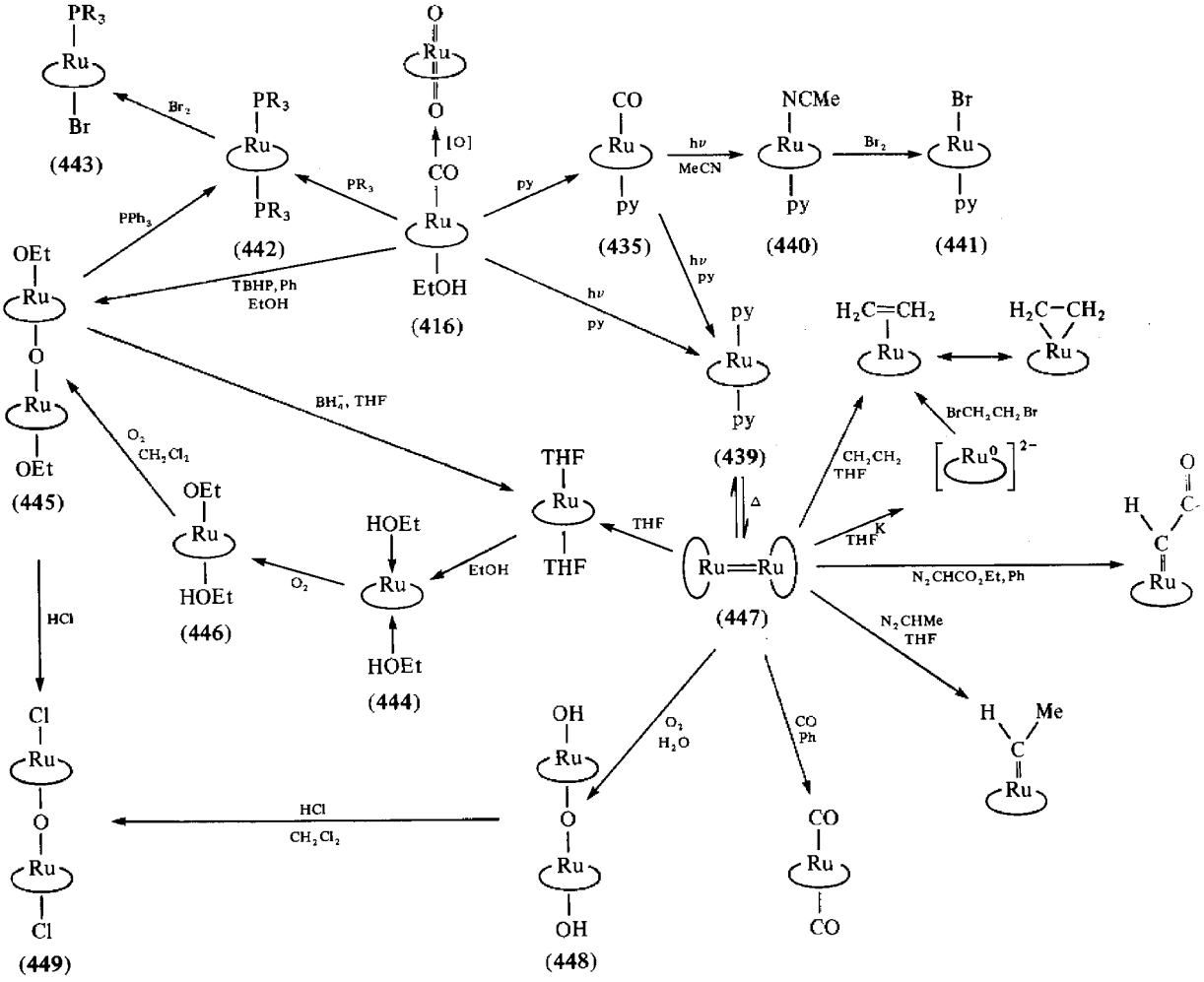


Scheme 78

Flash photolysis of [Ru(OEP)CO] has been investigated.[2604] The lifetime of the excited state species [Ru(porph)CO]* (porph = TPP derivatives) has been measured as $\sim 30\,\mu s$ with emission occurring near 730 nm.[2576] Oxidative and reductive quenching of [Ru(TPP)CO]* and related species has been reported, $E_{\frac{1}{2}}$ for the $[Ru(TPP)CO]^{*/+}$ redox couple being assessed as -0.57 V *vs.* SSCE.[2576] [Ru(TPP)CO] photocatalyses the generation of H_2 from H_2O in aqueous micellar solutions in the presence of hydrogenase,[2605] and catalyses the oxidation of sulfides to sulfoxides under O_2 at 100 psi ($7 \times 10^5\,kg\,m^{-2}$) and 100°C.[1375] $[Ru(4\text{-}SO_3TPP)CO]^{4-}$ has been reported to catalyse the water-gas-shift reaction.[2569]

Reaction of two equivalents of [Ru(TPP)CO] with one equivalent of 4,4′-bipy produces the binuclear species $[Ru(TPP)CO]_2 \cdot 4,4'\text{-bipy}$.[2584]

Photolysis of [Ru(porph)(CO)(HOEt)] at 300 nm in the presence of L yields $[Ru(porph)L_2]$ (L = py, porph = TPP,[2564] OEP,[2571,2572,2606–2608] Etio I,[2606] *meso*-porphyrin IX dioctadecyl ester;[2591] L = MeCN, porph = OEP, TPP;[2609] L = DMSO, porph = OEP[2608]). The single crystal X-ray structure of *trans*-$[Ru(OEP)py_2]$ (**439**) shows octahedral ruthenium(II) in the plane of the porphyrin ligand with Ru–N(py) = 2.1 Å.[2608] The resonance Raman spectrum of $[Ru(OEP)py_2]$ has been reported.[2610] Oxidation of $[Ru(porph)py_2]$ (porph = TPP, OEP) at $+0.08$ V *vs.* SSCE yields $[Ru^{III}(porph)py_2]^+$;[2592,2593] $[Ru(TPP)py_2]^+$ has been detected in redox quenching reactions of excited state $[Ru(TPP)py_2]^*$ with $[Ru(NH_3)_6]^{3+}$.[1245] Photolysis of [Ru(OEP)(CO)py] in MeCN yields [Ru(OEP)(NCMe)py] (**440**) which can be converted to [Ru(OEP)Brpy] (**441**) on oxidation with Br_2.[2611] Reaction of [Ru(OEP)Brpy] with $AgPF_6$ in MeCN affords $[Ru(OEP)(NCMe)py]^+$.[2611] Scheme 79 summarizes the synthetic routes to ruthenium porphyrins complexes.[2573,2607,2611]



Scheme 79

Refluxing solutions of [Ru(porph)(CO)(HOEt)] with phosphines L yields the complexes $[Ru(porph)L_2]$ (porph = OEP, TPP; L = PPh_3, $\frac{1}{2}PPh_3$, PBu^n_3, $P(4\text{-}MeOC_6H_4)_3$, $\frac{1}{2}P(4\text{-}MeOC_6H_4)_3$,[2564,2567,2568] PEt_3, PMe_2Ph, $P(OMe)_3$,[2601] bis(diphenylphosphino)methane (dpm), bis-(diphenylphosphino)ethane, bis(diphenylphosphino)butane, bis{(diphenylphosphino)ethyl}ethyl-

amine;[2579,2612] porph = 4-CF_3TPP, L = $P(OMe)_3$[2580]). The single crystal X-ray structure of *trans*-[Ru(OEP)(PPh_3)$_2$] (**442**) shows six-coordinate ruthenium(II), Ru—P = 2.438, Ru—N = 2.057, 2.044 Å with the central metal atom in the plane of the macrocyclic ring.[2567] An X-ray structural analysis of [Ru(TPP)(dpm)$_2$] shows monodentate dpm ligands with Ru—P = 2.398, Ru—N = 2.038, 2.045 Å.[2612] The dissociation of phosphine ligand L in the complexes [Ru(porph)L$_2$] has been assessed,[2567,2568] equilibrium constant $K = 1.2 \times 10^{-5}$ M for dissociation of [Ru(OEP)(PPh_3)$_2$] in toluene at room temperature (equation 157).[2613] [Ru(TPP)(PPh_3)$_2$] is an efficient catalyst for the decarbonylation of aldehydes.[2614]

$$[Ru(OEP)(PPh_3)_2] \rightleftharpoons [Ru(OEP)(PPh_3)] + PPh_3 \qquad (157)$$

The electrochemistry of bis-phosphine ruthenium porphyrin complexes has been reported (Scheme 78).[2568,2601–2603] Oxidation of [Ru(porph)L$_2$] (porph = OEP, TPP; L = PPh_3, $PBu^n{}_3$) affords the ruthenium(III) species [Ru(porph)L$_2$]$^+$ which converts to [Ru(porph)BrL] in the presence of Br^-.[2568,2602,2611] Likewise direct oxidation of [Ru(porph)(CO)L] or [Ru(porph)L$_2$] with Br_2, or HBr in air gives [Ru(porph)BrL].[2568,2602,2611] The complexes [Ru(OEP)ClL] have been prepared by an analogous procedure using Cl_2, or HCl in air.[2611] The single crystal X-ray structure of [Ru(OEP)BrPPh_3] (**443**) shows ruthenium(III) out of the porphyrin plane by 0.049 Å towards the PPh_3 ligand, with Ru—Br = 2.552 Å, Ru—P = 2.415 Å, Ru—N = 2.025–2.047 Å.[2611] Reduction of [Ru(OEP)BrPPh_3] by zinc amalgam yields [Ru(OEP)PPh_3].[2613] [Ru(OEP)BrPPh_3] in the presence of iodosyl benzene catalyses the oxidation of alkenes, cyclohexane and PPh_3.[2615] The ruthenium(IV) species [Ru(OEP)(O)] and [Ru(OEP$^+$)(O)Br] have been tentatively proposed as intermediates in the oxidation of PPh_3 to $OPPh_3$.[2615] The formation of ruthenium(I) species in the reduction of [Ru(TPP)(PR_3)$_2$] has been proposed.[2601]

Treatment of [Ru(OEP)py$_2$] with KCN over a prolonged period affords [Ru^{III}(OEP)$(CN)_2$]$^-$ which can be converted to [Ru(OEP)(CN)py] on reaction with py.[2574] Reduction of [Ru(OEP)(CN)py] with sodium amalgam in the presence of $CSCl_2$ yields [Ru(OEP)(CS)py]; the species [Ru^{II}(OEP)(CN)L]$^-$ (L = py, CO) have been identified in solution.[2574] Isocyanide adducts [Ru(porph)(CNR)$_2$] (porph = OEP, TPP, R = Bz;[2616,2617] porph = 4-CF_3TPP, R = Bu^t[2580]) can be isolated from reactions of [Ru(porph)CO] with RNC; for [Ru(TPP)(CNBz)$_2$], ν_{NC} = 2148 cm^{-1}.[2617] Addition of L (L = py, 1-methylimidazole, 4-*tert*-butylpyridine) gives [Ru(porph)(CNBz)L].[2616,2617] Kinetic measurements on axial ligand exchange in these compounds indicate that their lability increases in the order Ru(Pc) < Ru(porph) ≪ Fe(Pc) < Fe(porph) (Pc = phthalocyanine).[2616,2617]

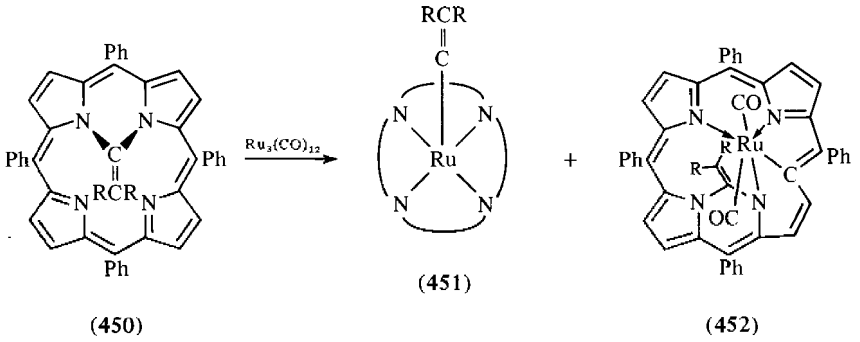
Reaction of [Ru(porph)CO] (porph = *meso*-porphyrin IX dimethyl ester) with NO in benzene yields [Ru(porph)$(NO)_2$], ν_{NO} = 1786 and 1838 cm^{-1}.[2589,2590] [Ru(OEP)(CO)py] with NO in MeOH affords [Ru(OEP)(OMe)NO].[2572] The aryldiazonium adducts [Ru(porph)(N_2Ar)solvent]$^+$ (porph = TPP, Ar = Ph, 4-MeOPh, solvent = acetone; porph = TPP, Ar = 4-NO_2Ph, solvent = EtOH; porph = OEP, Ar = 4-NO_2Ph, solvent = EtOH) have been prepared by reaction of [Ru(porph)(CO)(HOEt)] with ArN_2^+ in refluxing CH_2Cl_2.[2618] The stretching vibration $\nu_{N\equiv N}$ occurs near 1800 cm^{-1} for these complexes.[2618]

The binding of O_2 to ruthenium(II) porphyrins has been investigated; the formation of adducts [Ru(porph)(O_2)py] (L = *meso*-porphyrin IX dioctadecyl ester)[2609] and [Ru(OEP)(O_2)(NCMe)][2591] has been reported. [Ru(OEP)PPh_3] and [Ru(OEP)(PPh_3)$_2$] react with O_2 in toluene to give $OPPh_3$, RuO_2 and H_2OEP.[2613] The reaction is thought to occur *via* initial binding of O_2 to [Ru(OEP)PPh_3] and subsequent formation of [Ru(OEP)OH]$_2$O as a proposed intermediate.[2613] An outer-sphere electron transfer between [Ru(OEP)(PPh_3)$_2$] and O_2 to give superoxide and Ru^{III} has been noted.[2611,2613] [Ru(TPP)(HOEt)$_2$] (**444**), prepared by reduction of [Ru(TPP)OR]$_2$O (**445**) with $NaBH_4$ in THF and addition of EtOH, is oxidized by O_2 to [Ru(TPP)(OEt)]$_2$O.[2573] [Ru(TPP)(OEt)(HOEt)] (**446**) can be isolated from the reaction (Scheme 79) and its single crystal X-ray structure shows a centrosymmetric Ru^{III} with Ru—O = 2.019 Å.[2573] Oxidation of [Ru(porph)]$_2$ (**447**) with O_2 in the presence of trace H_2O,[2607] or oxidation of [Ru(porph)CO] (porph = OEP, TPP) with *tert*-butylhydroperoxide[2619] gives the binuclear Ru^{IV} complex [Ru(porph)OH]$_2$O (**448**). An X-ray structural analysis of [Ru(OEP)OH]$_2$O shows a linear RuORu backbone with Ru—O(bridge) = 1.847 Å, Ru—OH = 2.195 Å, Ru—N = 2.067 Å with a staggered conformation of porphyrin rings.[2620] A range of related binuclear Ru^{IV} species [Ru(porph)X]$_2$O (porph = OEP, TPP, TPrP; X = Cl^-, Br^-, $^-$OAc, $CF_3CO_2^-$, HSO_4^-, $^-$OMe, $^-$OEt, 4-$^-OC_6H_4Me$, 2-$^-OC_6H_4OH$) have been prepared.[2573,2607,2619,2621] The single crystal X-ray structure of [Ru(OEP)Cl]$_2$O (**449**) shows a linear RuORu moiety with Ru—O = 1.793, Ru—Cl = 2.320, Ru—N = 2.038 Å,[2621a] while an X-ray structural analysis of [Ru(TPP)OR]$_2$O (OR = 4-OC_6H_4Me) shows < RuORu = 177.8°, Ru—O (bridge) = 1.789 and Ru—OR = 1.964 Å.[2573] Cyclic voltammetry of the binuclear Ru^{IV} complexes

$[Ru(OEP)X]_2O$ (X = Cl^-, Br^-, ^-OH) shows three, two electron redox couples in CH_2Cl_2 assigned to $Ru^{IV}Ru^{IV}/Ru^{III}Ru^{III}$ and $Ru^{III}Ru^{III}/Ru^{II}Ru^{II}$ processes and oxidation of the porphyrin rings.[2619] More recently, oxidation of [Ru(porph)CO] (porph = **429**) with MCPBA or iodosyl benzene has yielded the *trans*-dioxo ruthenium(VI) species $[Ru(porph)O_2]$ which reacts with $P(OMe)_3$ to give two equivalents of Me_3PO and $[Ru(porph)(P(OMe)_3)_2]$. Interestingly, oxidation of the tolyl complex (**419**) yielded the Ru^{IV} μ-oxo dimer, suggesting that steric hindrance of (**429**) is important for the generation of the mononuclear Ru^{VI} oxo derivative.[2621b]

Vacuum pyrolysis (210°C, 10^{-5} torr) of red $[Ru(porph)py_2]$ (**439**) yields a green dimeric product $[Ru(porph)]_2$ (porph = TPP, OEP, 4-MeTPP).[2577,2606–2608] The single crystal X-ray structure of $[Ru(OEP)]_2$ (**447**) shows Ru—Ru = 2.408 Å, Ru—N = 2.050 Å with the Ru^{II} ion 0.30 Å out of the plane of the porphyrin ligands which are twisted by 23.8° with respect to one another.[2577,2622] Paramagnetic shifts in the ^1H NMR spectra of these complexes have been analysed and related to a qualitative molecular orbital diagram suggesting a formal Ru—Ru bond order of two with an electronic configuration $a_{1g}^2 e_u^4 b_{1g}^2 b_{1u}^{*2} e_g^{*2}$.[2577,2622] The binuclear complexes bind CO in the presence of py to yield [Ru(porph)(CO)py].[2608]

The binding of first row metal ions Mn^{III}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} to [Ru(porph)CO] (porph = *meso*-tetra(2-nicotinamidophenyl)porphyrin, **428**) has been investigated by electronic spectra and cyclic voltammetry.[2586] Reaction of $Ru_3(CO)_{12}$ with (**450**) in refluxing THF for 3 h leads to metal insertion to yield (**451**), together with the complex (**452**), formed by oxidative addition of ruthenium into a pyrrole carbon–nitrogen bond (Scheme 80).[2623a] The single crystal X-ray structure of (**452**) shows *cis* carbonyl ligands on six-coordinate Ru^{II} with direct bonding of ruthenium to a carbon atom of the macrocyclic ligand (Ru—C = 2.086 Å) and a non-bonding pyrrole nitrogen atom.[2623a] Very recently, the synthesis of alkylidene and alkene complexes of ruthenium porphyrins has been reported;[2623b,c] reduction of (**447**) with K in THF yields a violet-black precipitate of the ruthenium porphyrin dianion $K_2[Ru^0(porph)]$ (Scheme 79).[2623b]

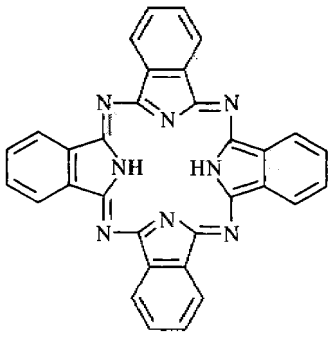


(450) (451) (452)

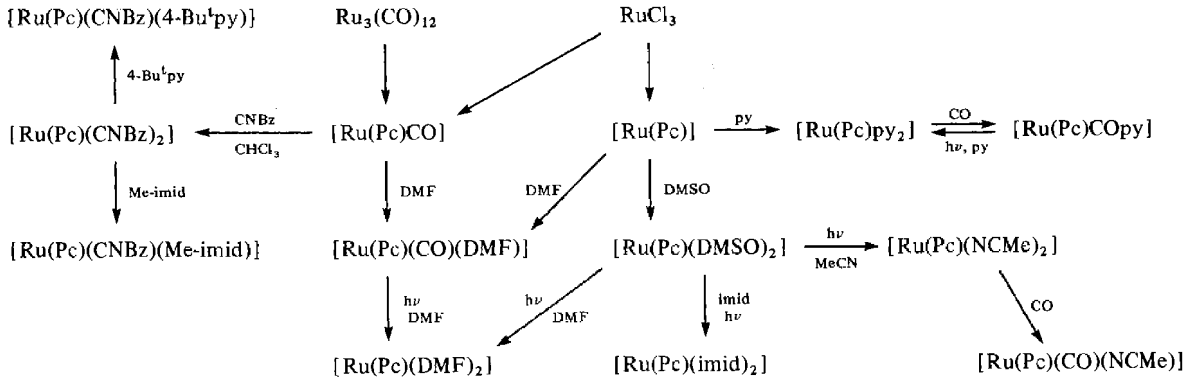
Scheme 80

45.12.2 Phthalocyanines

The coordination chemistry of the phthalocyanine dianion Pc^{2-} (H_2Pc = **453**) has been reviewed.[2562,2624–2626] Early work on the complexation of ruthenium by phthalocyanines reported the reaction of 2-cyanobenzamide or 1,2-dicyanobenzene with $RuCl_3$ to give '[Ru(Pc)]', '[Ru(Pc)Cl]' or '[Ru(ClPc)]'.[2627–2631] More recently treatment of $RuCl_3$ with 2-cyanobenzamide or 1,2-dicyanobenzene at 250°C for 4 h is reported to yield $[Ru^{II}(Pc)]$ together with $[Ru^{III}(Pc)Cl]$ as a minor product and less than 5% yield of [Ru(Pc)CO].[2632] Alternatively [Ru(Pc)] can be prepared by reaction of $RuCl_3$ with 2-cyanobenzamide in naphthalene at 290°C for 1 h,[2633] while the direct synthesis of [Ru(Pc)CO] has been achieved by treatment of $Ru_3(CO)_{12}$ or $RuCl_3$ under CO with 1,2-dicyanobenzene or H_2Pc at elevated tempeatures (greater than 200°C).[2632–2634] Extraction of [Ru(Pc)] and [Ru(Pc)CO] with ligands L affords the adducts $[Ru(Pc)L_2]$ (L = py,[2632,2633] 4-methyl pyridine,[2633] 4-*tert*-butylpyridine,[2633] aniline,[2627,2632] 2-methylaniline,[2627] PBu^n_3, $P(OBu^n)_3$,[2634] DMSO[2635]) and [Ru(Pc)(CO)L] (L = py,[2632,2633] 4-methyl pyridine, 4-*tert*-butyl pyridine[2633]) respectively. The species $[Ru(Pc)(DMSO)_2]$ is likely to incorporate S-bonded sulfoxide and has been found to be a useful precursor to a series of bis-adduct complexes $[Ru(Pc)L_2]$ (L = MeCN, py, imid, DMF) formed by photolysis of the DMSO adduct in the presence of L.[2635] Carbonylation of $[Ru(Pc)L_2]$ affords [Ru(Pc)(CO)L].[2633,2635] Refluxing solutions of [Ru(Pc)] in DMF gives [Ru(Pc)CO(DMF)] which can be converted to $[Ru(Pc)L_2]$ on photolysis in L.[2635] The polymeric pyrazine-bridged species $[Ru(Pc)pz]_n$ has been reported.[2636] Scheme 81 illustrates the synthetic chemistry of ruthenium phthalocyanines.[2617,2635]



(453) H_2Pc



Scheme 81

For [Ru(Pc)COpy] $\nu_{C\equiv O}$ occurs at 1965 cm^{-1} compared with 1939 cm^{-1} for [Ru(TPP)COpy] indicating that back-bonding from Ru^{II} to CO is greater in the latter complex.[2632] Pc complexes are found to be less labile than the corresponding porphyrin species, ligand substitution occurring *via* a dissociative mechanism.[2617,2634]

The complexes [Ru(Pc)(CO)L] and [Ru(Pc)L_2] (L = py, 4-methylpyridine, 4-*tert*-butylpyridine, imid, MeCN, DMF, DMSO) each show a reversible one electron oxidation in CH_2Cl_2; $E_{\frac{1}{2}} = +0.91$ V and $+0.77$ *vs.* SCE for [Ru(Pc)COpy] and [Ru(Pc)py_2] respectively.[2635] Quantitative oxidation gives the π radical cation products [Ru(Pc^+)(CO)L] and [Ru(Pc^+)L_2] which have been characterized by electronic and ESR spectroscopy;[2635] the redox activity of ruthenium phthalocyanines have been compared to the corresponding porphyrin analogues.[2635]

The photochemistry of [Ru(Pc)py_2][2637] and the quenching of excited state species [Ru(Pc)L_2]* (L = DMSO) and [Ru(Pc)(CO)L]* (L = py, DMF)[2638] have been investigated. [Ru(Pc)-{$(CD_3)_2SO$}$_2$] has been used as a ^1H NMR shift reagent.[2639] Protonation of [Ru(Pc)] at uncoordinated N atoms of the macrocyclic ring has been studied;[2628,2640,2641] '[RuPc]' has been found to catalyse the decomposition of H_2O_2,[2629] the oxidation of propene by O_2[2642] and the carbonylation of nitro compounds to isocyanates.[2643]

The exact nature of the complex '[Ru(Pc)Cl]' remains unknown. Formulations of a ruthenium(III) complex with axial Cl^-, [Ru(Pc)Cl],[2628] or a ruthenium(II) species with chlorinated Pc, [Ru(ClPc)],[2644] have been proposed, although ^1H, ^{13}C NMR and electronic spectral data appear to show no evidence for chlorination at the Pc ring.[5,2634] The complexes [Ru(ClPc)L_2] (L = PPh_3, py, methyl imidazole, $P(OBu^n)_3$, $P(Bu^n)_3$) have been reported.[2634,2644] The synthesis of [Ru{Pc-$(SO_3)_4$}]$^{4-}$ (H_2Pc-SO_3H = phthalocyanine tetrasulfonic acid) has been mentioned.[5]

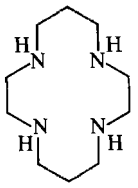
45.12.3 Tetraaza Macrocycles

A range of low spin, octahedral ruthenium(III) complexes incorporating tetraaza macrocyclic ligands have been synthesized. Reaction of $[RuCl_5(OH_2)]^{2-}$ with L in alcoholic solvent under reflux affords *trans*-[$RuCl_2$(L)]$^+$ (L = **454**–**463**).[632a,632b,634,2645–2649] Oxidative dehydrogenation of the coordinated macrocyclic ligand can occur[2646] and has been used to prepare *trans*-[$RuCl_2$(L)]$^+$ (L = **460** and **461**) by aerial oxidation of *trans*-[$RuCl_2$(L)]$^+$ (L = **458** and **459**) respectively.[2648] The single

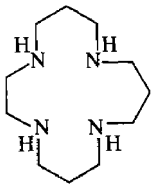
crystal X-ray structure of *trans*-$[RuCl_2(L)]^+$ (L = **454**) shows distorted octahedral Ru^{III} with Ru—Cl = 2.343, Ru—N = 2.083 Å.[2647] ESR spectra of *trans*-$[RuCl_2(L)]^+$ (L = **454**) have been reported.[635] Reaction of $[RuCl_5(OH_2)]^{2-}$ with cyclam (**454**) in MeOH over three days yields a mixture of *cis*- and *trans*-$[RuCl_2(L)]^+$ which can be separated by ion exchange and gel filtration and characterized by UV–visible spectroscopy.[2645a] The single crystal X-ray structure of the *cis* isomer shows Ru—Cl = 2.371 Å with Ru—N = 2.104–2.117 Å.[2645b] Reduction of these products by zinc amalgam yields the corresponding Ru^{II} species ($E_{\frac{1}{2}} = -0.23$ V, -0.19 V *vs.* NHE for *cis*- and *trans*-$[RuCl_2(L)]^+$ respectively) which react with isn to afford *cis*- and *trans*-$[Ru(L)(isn)_2]^{2+}$.[2645a] *Cis*-$[RuX_2(L)]^+$ may also be prepared by reaction of $[Ru(ox)_3]^{3-}$ with L (L = **454**, **455**) in the presence of HX (X = Cl^-, Br^-).[633] More recently, the complexes *cis*-$[Ru(L)(L')_2]^{2+}$ (L = **454**, L′ = py_2, bipy, phen) have been synthesized.[2645b]

Substitution reactions of *trans*-$[RuCl_2(L)]^+$ to give *trans*-$[RuX_2(L)]^+$ (X = for example, Br^-, I^-, NCS^-, NO_2^-, OAc^-) by direct reaction with X^- or *via* reduction to Ru^{II} have been described.[632a,2646,2648,2649] The kinetics of ligand substitution in $[RuX_2(L)]^+$ and $[RuX_2(L)]$ (X = Cl^-, Br^-) have been measured and suggest a dissociative mechanism for Ru^{III} complexes with the rate of halide release decreasing in the order L = **459** > **458** > **454**.[638,2650] The acid and base hydrolysis of complexes of cyclam (**454**) have been studied and related to data for tetraammine, bis-en and related open chain species, an S_N1cb mechanism being operative for base hydrolysis.[634,636,637,2650]

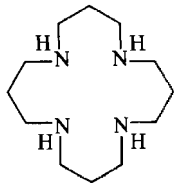
The electrochemistry of the ruthenium macrocycles *cis*- and *trans*-$[RuX_2(L)]^{n+/(n-1)+}$ (L = **454–462**, X = Cl^-, Br^-, I^-, NCS^-, OH_2, NO_2^-) have been investigated; the $Ru^{III/II}$ couple was found to vary over the range -0.80 to $+0.83$ V *vs.* Ag/Ag^+ and was related to the electronic and steric effects of L and X.[633,639,2647] Kinetic data for the reduction of *trans*-$[RuCl_2(L)]^+$ (L = **454**, **455**, **458**, **459**) by Cr^{II} and V^{II} suggest that electron transfer occurs *via* inner- and outer-sphere mechanisms respectively.[644,645] The variation in redox properties of $[Ru(CN)_6]^{3-/4-}$ in the presence of macrocyclic polyamine receptors has been investigated.[29]



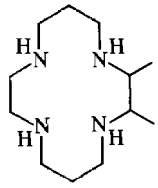
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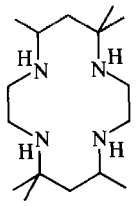
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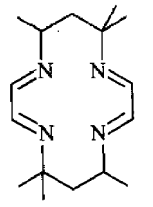
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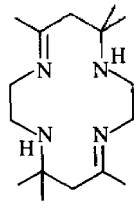
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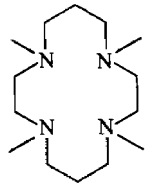
(458) C-*meso*
(459) C-*rac*



(460) C-*meso*
(461) C-*rac*



(462)

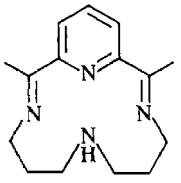


(463)

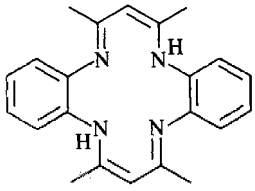
The absorption spectra of *trans*-$[RuX_2(L)]^+$ (L = **454–456**, **458**, **459**, X = Cl^-, Br^-, I^-) show two ligand to metal charge transfer bands. Irradiation at the lower energy CT band leads to stereoretentive aquation of X^-; the effects of L on the photoreactivity of these complexes have been discussed and related to their open chain analogues.[642]

Reduction of $[RuCl_2(L)]^+$ (L = **463**) at -0.20 V *vs.* SCE in aqueous 4-toluene sulfonic acid affords $[Ru(L)(OH_2)_2]^{2+}$ which can be oxidized to $[Ru^{IV}(O)(L)(OH_2)]^{2+}$ with H_2O_2 or electrochemically at 0.6–0.7 V *vs.* SCE. This latter species shows a Ru=O stretching vibration $\nu_{Ru=O}$ at 855 cm^{-1}.[2649a] More recently, this work has been further developed, the single crystal X-ray structures of *trans*-$[Ru^{IV}(O)(L)(NCMe)]^{2+}$,[2649b] *trans*-$[Ru^{IV}(O)(Cl)(L)]^{+}$[2649c] and *trans*-$[Ru^{VI}(O)_2(L)]^{2+}$[2649d] being reported. The chemical and electrochemical interconversion of these products has been achieved, and the oxidative activity of Ru^V analogues assessed.[2649c] The template synthesis of $[Ru(L)(OH_2)](ClO_4)_2$ (L = **464**) has been reported although the exact nature of this product is unknown.[2651a] Reaction of $[Ru_2(OAc)_4Cl]$ with LH_2 (LH_2 = **465**) in ethanol yields the

mixed valence $Ru^{II}Ru^{III}$ binuclear cofacial species $[RuL]_2^+$ (μ_{eff} = 1.55 BM) the single crystal X-ray structure of which shows Ru—Ru = 2.267 Å, with a formal Ru—Ru bond order of 2.5.[2120] Reduction of $[RuL]_2^+$ with $NaBH_4$ in ethanol affords the $Ru^{II}Ru^{II}$ dimer $[RuL]_2$ (μ_{eff} = 2.88 BM) with a Ru—Ru bond distance of 2.379 Å and formal bond order of two.[2120] Reaction with CO and py yields [Ru(L)(CO] and $[Ru(L)py_2]$ respectively.[2120]



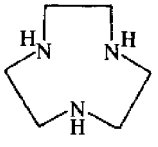
(464)



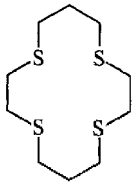
(465)

45.12.4 Triaza Macrocycles

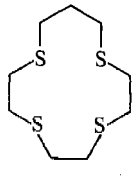
A range of complexes incorporating the triaza macrocycle, 1,4,7-triazacyclononane (**446**), have been synthesized;[2651b] these include $[Ru^{II}Cl(L)(DMSO)_2]^+$, $[Ru^{II}(L)_2]^{2+}$, $[Ru^{III}X_3(L)]$ (X = Cl^-, Br^-) and $[Ru^{III}(ox)(I)(L)]$ and the binuclear species, $[Ru^{III}{}_2(L)_2(\mu\text{-}OH)_2(\mu\text{-}MeCO_2)]^{3+/2+}$, $[Ru^{III}{}_2(L)_2(\mu\text{-}OH)_2Cl_2]^{2+}$ and $[Ru_2(L)_2(\mu\text{-}Cl)_3]^{2+}$. The single crystal X-ray structure of $[Ru^{III}{}_2(L)_2(\mu\text{-}OH)_2(\mu\text{-}MeCO)_2]I_3 \cdot H_2O$ shows a short Ru—Ru bond distance of 2.572 Å, indicating the presence of a single Ru—Ru bond for the diamagnetic complex.[2651b] The electrochemistry of the binuclear complexes was investigated.[2651b]



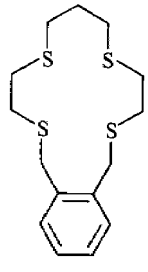
(466)



(467)



(468)



(469)

45.12.5 Tetrathia Macrocycles

Reaction of $RuCl_3$ or $[RuCl_5(OH_2)]^{2-}$ with L (L = **467**–**469**) in 2-(2-ethoxy)ethanol for two days gives *cis*-$[RuCl_2(L)]^+$.[632a,639,2652] The complexes incorporating (**467**) were originally formulated as *trans* isomers on the basis of IR data,[2652] but were later reformulated as *cis* products;[2653] the single crystal X-ray of *cis*-$[RuCl_2(L)]$ (L = **467**) shows Ru—Cl = 2.471, Ru—S = 2.262, 2.333 Å.[2653] A range of substituted derivatives $[RuX_2(L)]^+$ (X = Cl^-, Br^-, I^-, NCS^-, NO_2^-, N_3^-) have been prepared and their electrochemistry investigated.[639,2652] More recently the reaction of $RuCl_3$ with (**467**) in ethanol for 2 h has been reported to afford a brown product *fac*-$[RuCl_3(L)]$ in which the macrocycle is though to be tricoordinate; treatment with LiBr in acetone yields *fac*-$[RuBr_3(L)]$.[2194]

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46.1 INTRODUCTION

46.1.1 History

Since osmium was first isolated as the tetroxide, one of its most important and celebrated coordination complexes, a brief account of the history of its coordination chemistry is not out of place. The tetroxide, and subsequently the metal, was first isolated in 1803 by Smithson Tennant[1] (1761–1815) by distillation with nitric acid of the black material derived after *aqua regia* treatment of platinum metal concentrates. Of the tetroxide Tennant wrote:

> 'As the smell is one of its most distinguishing characters, I should on that account incline to call the metal *Osmium*'

(from $o\sigma\mu\eta$, a smell). Tennant narrowly escaped being overtaken by Fourcroy and Vauquelin[2,3] in the discovery of osmium. Early work on the coordination chemistry of the element was carried out by Berzelius,[4] but the most extensive of these early studies were those of Claus (1796–1864),[5] who in 1844 had discovered ruthenium.

46.1.2 Reviews on Osmium

The classic works of Gmelin[6,7] give the most extensive coverage of the coordination chemistry of the element, although the volumes on its organometallic chemistry have not yet appeared. The latest edition[7] covers the period 1939 to 1980 and the present author wrote the sections concerned with the coordination chemistry. There are other less comprehensive but useful sources of information. Pascal covers the literature up to 1958[8] while Mellor's treatise is still useful for the older work (up to 1936).[9] The author has written a book on the four rarer platinum metals (osmium, ruthenium, iridium, rhodium) covering the literature to 1967 and a short early review on osmium (1965);[11] Livingstone has written a book on the six platinum metals (1975).[12] There are recent reviews on the high oxidation state chemistry of osmium,[13a] and on standard potentials for osmium and ruthenium.[13b] Other reviews in the osmium chemistry of specific ligands are mentioned at appropriate points in the text. The organometallic chemistry of the element is of course covered up to 1982 in *Comprehensive Organometallic Chemistry* (vol. 4, p. 967).

46.1.3 General Features of the Coordination Chemistry of Osmium

It is hoped that these will become apparent as the text proceeds, so the following comments are very general.

46.1.3.1 Oxidation states

The three elements osmium, ruthenium and rhenium are distinguished from all others by the variety of the oxidation states which they display in their complexes, and of these three osmium is probably the most versatile in this respect. Examples of the main classes of complexes found for each oxidation state are listed in Table 1. It will be seen that all the states from VIII (d^0) to − II (d^{10}) are represented. It is this ability of the element to adopt different oxidation states at the behest of the surrounding ligands which gives osmium chemistry its special flavour and attractions. The principal reason for its versatility in this respect is surely its position within the block of transition metals in the Periodic Table. Its membership of the third row means that its outer ($5d$) orbitals are relatively exposed so that their electronic occupancy is susceptible to the nature of the coordinating ligands, and its central position within that third row means that attainment of the d^0 configuration typical of elements to the left, and of the d^{10} typical of elements to the right, are both possible for osmium. The element can thus be used as a convenient backdrop or exemplar of acceptor properties when discussing the donor properties of ligands. Thus, strong π donors such as F^-, O^{2-} and N^{3-}

favour high oxidation states (Os^{VIII}, Os^{VI}), strong π acceptors such as CO and NO^+ are associated with Os^{II} or Os^0 while NO^+ attains, in a formal sense at least, the Os^{-II} state. 'Conventional' ligands such as halide, ammonia and ethylenediamine tend to favour the III or IV states, while ligands with moderate π-acceptor capabilities (CN^-, bipy, phen) will tend to the Os^{II} (d^6) state.

Table 1 Oxidation States in Coordination Complexes of Osmium

Oxidation state	d^n	*Comments*	*Typical stabilizing ligands*	*Examples*[a]
VIII	d^0	Fairly rare but important	F^-, O^{2-}, N^{3-}	OsO_4, $[OsO_3F_3]^-$, $[OsO_3N]^-$
VII	d^1	Rare	F^-, O^{2-}	OsF_7, $[OsO_4]^-$, $OsOF_5$
VI	d^2	Relatively common	F^-, O^{2-}, N^{3-}	OsF_6, *trans*-$[OsO_2X_4]^{n-}$, $[OsNX_4]^-$
V	d^3	Rare	F^-	$[OsF_6]^-$, $[OsF_5]_4$
IV	d^4	Common	F^-, Cl^-, Br^-, I^-, OH^-, PR_3, OH^-, LR_3	$[OsX_6]^{2-}$, $[Os(NH_3)_4X_2]^{2+}$, *trans*-$Os(LR_3)_2X_4$
III	d^5	Common	Cl^-, Br^-, I^-, NH_3, acac, en, LR_3	$[OsX_6]^{3-}$, $[Os(NH_3)_6]^{3+}$, $[Os\ en_3]^{3+}$, $Os(LR_3)_3X_3$
II	d^6	Common	CN^-, bipy, phen, NO^+, terpy, LR_3	$[Os(CN)_6]^{4-}$, $[Os(bipy)_3]^{2+}$, $[Os(phen)_3]^{2+}$, $[Os(NO)X_5]^{2-}$, *trans*-$Os(LR_3)_4X_2$
I	d^7	Doubtful	? NO^+	$Os(NO)(PPh_3)_2Cl_2$
0	d^8	Fairly rare	CO, $P(OR)_3$, PF_3	$Os(CO)_5$, $Os_3(CO)_{12}$, $Os\{P(OR)_3\}_5$, $Os(PF_3)_5$
−I	d^9	Very rare	NO	$Os(NO)depe_2$
−II	d^{10}	Fairly rare	NO^+, CO, PF_3	$Os(NO)_2(PPh_3)_2$, $[Os(CO)_4]^{2-}$, $[Os(PF_3)_4]^2$

[a] L = P, As or Sb; R = alkyl or aryl; X = Cl, Br, I.

Since the oxidation state concept is so important for osmium we shall make extensive use of it as a means of classification of material within ligand groups, covering the lowest oxidation states first.

46.1.3.2 Coordination numbers

Osmium, and indeed all six platinum group metals, display rather little enterprise and versatility with respect to coordination numbers, although of course the ability to change coordination number lies at the heart of many catalytic reactions of platinum group complexes. The great majority of osmium complexes are octahedral. In Table 2 we give examples of the rarer coordination numbers. There are few examples of eight or seven coordination (nine coordination has not yet been observed for the element although its possibility for osmium has recently been briefly discussed[14]). There are examples of square-based pyramidal geometry, mainly for the higher oxidation states, and trigonal bipyramidal for the lower. Tetrahedral coordination is rare, though found both for osmium(VIII)

Table 2 Unusual Coordination Numbers for Osmium Complexes

Coordination number	*Examples*	*Page in text*	*Shape*
8	$[Os(en-H)_4]I_2$, $[Os(en-H)_3en]I_2$	531	Unknown
	$Os(PMe_2Ph)_2H_6$	571	Unknown
	? OsF_8	612	Unknown
7	$Os(edta)(H_2O)$	602	Monocapped octahedron
	OsF_7	612	Pentagonal bipyramidal
	$Os(PMe_2Ph)_4H_3$, $Os(PEt_2Ph)_4H_3$	571	Distorted pentagonal bipyramidal
	$[Os(PR_3)_4H_3]^+$, $Os(PPh_3)_3HCl_3$	570, 571	Unknown
5	$OsO(O_2R)_2$, $Os_2O_4(O_2R)_2$	584	Square-based pyramidal
	$[OsNX_4]^-$, $OsOCl_4$	563, 584	Square-based pyramidal
	$Os(PPh_3)_3X_2$	573	Square-based pyramidal
	$Os(CO)_5$		Trigonal bipyramidal
	$[Os(PF_3)_4H]^-$	576	Trigonal bipyramidal
	$Os\{P(OMe)_3\}_5$	575	Trigonal bipyramidal
4	OsO_4, $[OsO_4]^-$	588	Tetrahedral
	$[OsO_3N]^-$	562	Tetrahedral
	$Os(NO)_2(PPh_3)_2$	551	Distorted tetrahedral

(in OsO_4 and $[OsO_3N]^-$) and for osmium(−II) in $Os(NO)_2(PPh_3)_2$. Square planar coordination might be expected for osmium(0) (d^8) but does not seem to have been observed for it.

46.1.3.3 The ligands in the complexes

(*i*) *Group VII donors*

All four halide ions from octahedral complexes with the metal. Fluorides or fluoro complexes are known for osmium(VII) to osmium(IV) inclusive, with rather tenuous evidence for OsF_8; OsF_7 is a rare example of seven coordination for the metal. The other halides prefer the IV and III states, though osmium(V) chloride and chloro complexes have recently been made and also $[OsBr_6]^-$. Although $[RuF_6]^{3-}$ is well known there is no osmium analogue, in keeping with the general tendency of third-row elements to display higher oxidation states than their second-row partners.

(*ii*) *Group VI*

The oxo (O^{2-}) ligand is dominant in the coordination chemistry of osmium, participating in the VIII to IV oxidation states inclusive. The tetroxide OsO_4 is the single most important compound of osmium; OsO_4 and the recently discovered $[OsO_4]^-$ ion are tetrahedral. The *trans*-$[O{=}Os^{VI}{=}O]$ 'osmyl' moiety displays an extensive chemistry, comparable with that of the 'uranyl' O=U=O unit, and there is an extensive and unique cyclic oxo-ester chemistry (p. 584). There is surprisingly little information on hydroxo, aqua, sulfato, nitrato or phosphato complexes, but much recent work has been carried out on carboxylato species, and clearly much work remains to be done on the O-donor chemistry of the element. There are a reasonable number of sulfur-donor complexes but few with selenium or tellurium.

(*iii*) *Group V*

There are now a substantial number of nitrido complexes of osmium(VI) and osmium(IV) as well as the 'osmiamate' ion $[Os^{VIII}O_3N]^-$. In addition to the ammine and ethylenediamine complexes, much recent work has been carried out on the bipy, phen and terpy complexes, often in connection with research into the photodissociation of water. The nitrosyl chemistry of the element, though seemingly not as extensive as that of ruthenium, has received much attention, and there has been considerable work on the phosphine, arsine and stibine complexes.

(*iv*) *Group IV*

The wide area of osmium cluster carbonyl chemistry lies beyond the scope of this chapter (see refs. 15 and 16), though a few carbonyl complexes are covered, and of course there is full coverage of the cyanide chemistry of osmium.

46.1.3.4 Special aspects of osmium coordination chemistry

We have already alluded to the diversity of oxidation states, the dominance of oxo chemistry and the cluster carbonyls. Brief mention should be made too of the tendency of osmium (shared also by ruthenium and, to some extent, rhodium and iridium) to form polymeric species, often with oxo, nitrido or carboxylato bridges. Although it does have some activity in homogeneous catalysis (*e.g.* of *cis*-hydroxylation, hydroxyamination or amination of alkenes, see p. 558, and occasionally for isomerization or hydrogenation of alkenes, see p. 571), osmium complexes are perhaps too substitution-inert for homogeneous catalysis to become a major feature of the chemistry of the element. The spectroscopic properties of some of the substituted heterocyclic nitrogen-donor complexes may yet make osmium an important element for photodissociation energy research.

46.2 MERCURY AS A LIGAND

46.2.1 Osmium–Mercury Complexes

These are reported as 1:1 or 2:1 adducts with osmium phosphine or arsine complexes with mercury(II) chloride, but presumably involve Os—Hg—Cl units. They are the black $Os(PMePh_2)_3Cl_2 \cdot HgCl_2$, the white $Os(dppm)_2Cl_2 \cdot HgCl_2$ and the brown $Os(SbPh_3)_4Cl \cdot HgCl_2$, the grey $Os(PPh_3)_4Cl \cdot 2HgCl_2$ and $Os(dppe)_2Cl_2 \cdot 2HgCl_2$, the red $Os(dmpm)_2Cl \cdot 2HgCl_2$ and the black $Os(AsPh_3)_3Cl \cdot 2HgCl_2$. All are made from $(NH_4)_2[OsCl_6]$ and the phosphine, arsine and stibine ligands in water–methanol with $HgCl_2$.[17] Reaction of $Os(PEtPh_2)_3H_4$ and $Os(PEtPh_2)_4H_2$ with $HgCl_2$ gives unidentified species containing Hg:Os ratios of up to 9:1; evidence for the existence of $Os(HgCl)(PR_3)_3H(CO)$ and $Os(HgCl)_2(PR_3)_3(CO)$ (PR_3 = PMe_2Ph, PEt_2Ph) was presented.[18]

46.3 GROUP IV COMPLEXES

The chemistry of osmium is dominated here by the cyanide ligand; there is one fulminato complex, and a number of species containing Os—Sn bonds.

46.3.1 Cyanide Complexes

The cyanide ligand is a good σ donor and a fairly effective π acceptor,[19,20] so it is not surprising that the most stable osmium cyano complex is the d^6 species $[Os(CN)_6]^{4-}$, while $[Os(CN)_6]^{3-}$ (d^5) is fairly strongly oxidizing. In *trans*-$[OsO_2(CN)_4]^{2-}$ (p. 582) and *trans*-$[OsN(CN)_4H_2O]^-$ (p. 562) it is likely that the high oxidation state is sustained by the π-donor oxo ligands (the high ν_{CN} IR frequencies, 2151 cm^{-1} in $[OsO_2(CN)_4]^{2-}$[21] and 2155 cm^{-1} in $[OsN(CN)_4(H_2O)]$,[22] suggest that there is relatively little π bonding in these Os—C linkages).

Cyano complexes of osmium, amongst other transition metals, have been reviewed.[19] There is a brief section on osmium cyano complexes in ref. 16, p. 976.

46.3.1.1 Osmium(I)

A species believed to be $[Os(CN)_5]^{4-}$ can be generated by electron bombardment of $[Os(CN)_6]^{4-}$ in a KCl matrix at 77 K.[23] It was detected by EPR; if genuine it is one of the very few examples of monovalent osmium.

46.3.1.2 Osmium(II)

The potassium, barium, nickel(II) and copper(II) salts have long been known,[24] the normal method of preparation being to treat *trans*-$K_2[OsO_2(OH)_4]$ with excess aqueous potassium cyanide followed by fusion with potassium cyanide.[24,25] A free acid, $H_4[Os(CN)_6]$, can be made by addition of concentrated hydrochloric acid to $K_4[Os(CN)_6]$.[24] It is soluble in alcohol but can be precipitated as an etherate by diethyl ether. A study of its IR spectrum and that of its deuteriate suggests that it contains asymmetric —Os—C—N···H—N—C—Os— hydrogen bonds.[26,27]

There have been a number of studies on the vibrational spectra of $[Os(CN)_6]^{4-}$, mostly on the potassium salt.[28–30]. The latest data are given in Table 3 (with comparative results for $[Fe(CN)_6]^{4-}$ and $[Ru(CN)_6]^{4-}$); the T_{1g} and T_{2u} modes, which are inactive in the Raman and IR, were measured by IETS (inelastic electron-tunelling spectroscopy).[30] The increase in ν_{M-C} (*e.g.* ν_2, ν_4) from Fe to Os is consistent with an increase in M—C π bonding in the same sequence,[31] though it is interesting to note that this is apparently not borne out by ν_1. Electronic spectra of $[Os(CN)_6]^{4-}$ have been measured[32] and assigned;[33,34] the $10Dq$ value for the ion exceeds 34 000 cm^{-1}, much greater than those for $[Fe(CN)_6]^{4-}$ and $[Ru(CN)_6]^{4-}$.[34] Likewise, ^{13}C NMR chemical shifts for $[Os(CN)_6]^{4-}$ compared with $[Fe(CN)_6]^{4-}$ and $[Ru(CN)_6]^{4-}$ are consistent with greater ($\sigma + \pi$) metal–carbon overlap in the former.[35] There are also ESCA,[36] ^{183}Os Mössbauer[37a] and ^{14}N NMR data[25] for $[Os(CN)_6]^{4-}$, and spin–lattice relaxation times for the water molecules in $K_4[Os(CN)_6] \cdot 3H_2O$ have been determined.[37b]

Reaction rates between $[Os(CN)_6]^{4-}$ and $[MnO_4]^-$,[38] and also with OH^-,[39] have been measured. A mixed-valence complex of the Prussian blue type, $KFe^{III}[Os^{II}(CN)_6]$, has been reported.[32]

Table 3 Raman and Infrared data (cm^{-1}) on $[M(CN)_6]^{4-}$ (M = Fe, Ru, Os)[30]

	$[Fe(CN)_6]^{4-}$	$[Ru(CN)_6]^{4-}$	$[Os(CN)_6]^{4-}$
$\nu_1(A_{1g})^a$	2090	2108	2109
$\nu_2(A_{1g})^a$	385	425	458
$\nu_3(E_g)^a$	2055	2068	2061
$\nu_4(E_g)^b$	409	425	449
$\nu_5(T_{1g})^b$	354	344	362
$\nu_6(T_{1u})^c$	2044	2048	2038
$\nu_7(T_{1u})^c$	586	550	555
$\nu_8(T_{1u})^c$	415	371	(390)
$\nu_9(T_{1u})^c$	—	—	—
$\nu_{10}(T_{2g})^a$	506	465	476
$\nu_{11}(T_{2g})^a$	(105)	—	—
$\nu_{12}(T_{2u})^b$	474	491	513
$\nu_{13}(T_{2u})$	—	—	—

[a] Raman spectrum, aqueous solution. [b] IETS spectroscopy. [c] IR of $K_4[M(CN)_6]$ in KBr disc.

A few substituted osmium(II) cyano complexes are known (for $[Os(NO)(CN)_5]^{2-}$ see p. 546). Reaction of $(NH_4)_2[OsCl_6]$ and 2,2′-bipyridyl followed by treatment with NaCN gives $Os(CN)_2(bipy)_2 \cdot 2H_2O$ in which the CN groups may be *cis*. Protonation is said to occur in perchloric acid to give $Os(CN)_2(bipy)_2 \cdot 2HClO_4$.[40]

46.3.1.3 Osmium(III)

The salt $(Bu^n_4N)_3[Os(CN)_6]$ is made by an ion-exchange procedure from $[Os(CN)_6]^{4-}$ in air. The magnetic moment is 2.12 BM at 296 K. The electronic spectrum was measured and assigned; 10 *Dq* is 34 950 cm^{-1} for $[Fe(CN)_6]^{4-}$, and 38 000 cm^{-1} for $[Os(CN)_6]^{3-}$.[34] The $[Os(CN)_6]^{3-}/[Os(CN)_6]^{4-}$ couple of +0.634 V compares with +0.356 V for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple and with +0.860 V for $[Ru(CN)_6]^{3-}/[Ru(CN)_6]^{4-}$.[41] A higher value might have been expected for osmium, but apparently the palarographic value of +0.99 V, reported in the earlier literature,[42] may arise from reduction of cyanohydroxo complexes rather than from $[Os(CN)_6]^{3-}$.[19,33,41]

The redox potential for the $[Os(CN)_2(bipy)_2]^+/Os(CN)_2(bipy)_2$ complex is +0.778 V.[40] The species $[Os(CN)_2(OH)_4]^{3-}$ (by electrolytic reduction of an OsO_4/CN^- mixture) and $[Os(CN)_4(OH)_2]^{3-}$ (reduction of *trans*-$[OsO_2(CN)_4]^{2-}$) have been reported.[33,41]

46.3.1.4 Osmium(IV)

Although $[Os(CN)_6]^{2-}$ species have been claimed, it is clear that they are in fact $[Os(CN)_6]^{4-}$ salts.[11]

46.3.1.5 Osmium(VI)

For *trans*-$[OsO_2(CN)_4]^{2-}$ see p. 582; for *trans*-$[OsN(CN)_4(H_2O)]^-$, see p. 562. There are also reports of $[OsO_2(OH)_2(CN)_2]^{2-}$.[41]

46.3.2 Fulminato Complex

The only reported example of an osmium fulminato complex is $(Ph_4As)_2[OsO_2(CNO)_4]$, made by reaction of OsO_4 and potassium fulminate in a sealed tube followed by precipitation with tetraphenylarsonium chloride. The IR spectrum has $\nu(C{\equiv}N)$ at 2297 and 2181 cm^{-1} and ν^{as} (OsO_2) at 824 cm^{-1}.[44]

46.3.3 Osmium–Tin Complexes

Osmium forms relatively few non-organometallic metal–metal-bonded complexes (for species containing Os—Hg bonds see above, p. 525). In common with the other platinum group elements, however, it does form species of the type $[Os(SnX_3)_5X]^{2-}$, and these have received some recent study.

46.3.3.1 Complexes containing SnX_3^- and halo ligands

The known examples are listed in Table 4. The general method of preparation is the treatment of $K_2[OsCl_6]$ with SnX_2 in the presence of HX (for X = F, Cl, Br), while the hydroxo species is made by hydrolysis of the chloro complex.[44,46] The substituted complexes with phosphines, arsines and stibines are similarly made in the presence of the ligand.[17]

Table 4 Complexes Containing Osmium–Tin Bonds

Complex[a]	*Colour*	*Spectroscopic and other studies*
$[Os(SnCl_3)_6]^{4-}$		NMR[53b]
$K_4[Os(SnF_3)_6]$	White	IR, Mössbauer[45]
$(NH_4)_4[Os(SnCl_3)_5Cl]$	Pale yellow	IR,[45,46] UV/vis,[46] X-ray,[47,48] Mössbauer,[45] NMR[50]
$(Me_4N)_4[Os(SnBr_3)_5Br]$	Bright red	IR,[45,46] UV/vis,[46] Mössbauer[45]
$M_4[Os\{Sn(OH)_3\}_5Cl]$		Mössbauer[45]
$(Me_4N)_2[Os(SnCl_3)_4L_2]$	Red	IR, Mössbauer[45]
$(Me_4N)[Os(SnCl_3)_3L_3]$	Red	IR, Mössbauer[45]
$Os(SnCl_3)_3L_3$	Red	IR, Mössbauer[45]
$Os(SnCl_3)(PPh_3)_3Cl$		IR, Raman[17]

[a] L = thiourea.

The best studied of these species is the chloro complex, initially thought[45,47] to be a tetramethylammonium salt since $(Me_4N)Cl$ was used as the cation; subsequent X-ray data, however, showed it to be an ammonium salt or a mixed ammonium–tetramethylammonium salt,[48] so the same may be true for other anionic complexes listed in the table.

The structure shows the presence of two crystallographically independent but very similar anions in which five pyramidal $SnCl_3^-$ groups and a chloro ligand are at the apices of a slightly distorted octahedron. The Os—Cl distance is 2.42(2) Å; the mean Os—Sn distance *cis* to it is 2.580(5) Å and the *trans* Os—Sn distance is 2.530(5) Å. The Os—Cl bond length is some 0.08 Å longer than in other osmium(II) species so there appears to be a *trans* influence by the $SnCl_3^-$ ligand, manifested also in the shorter Os—Sn distance *trans* to the chloro ligand.[48] A force constant analysis was carried out on the molecule.[47,49]

A very high ^{117}Sn–^{119}Sn coupling constant of 18 600 ± 6 Hz was found for $[Os(SnCl_3)_5Cl]^{4-}$.[50] The complex catalyzes alkene isomerization, as does $[Os(SnBr_3)_5Br]^{4-}$.[51]

46.3.3.2 Complexes containing $SnCl_3^-$ and other ligands

Species of the type $Os(SnCl_3)_4L_2$ (L = methyl-, ethyl-, phenyl-, ethylphenyl- and diphenylthioureas and also thioacetamide) have been made from $[Os(SnCl_3)_5Cl]^{2-}$ and L, and the thiourea complexes $Os[SnCl_3)_2L_4]$, $[Os(SnCl_3)_3L_3]^-$, $Os(SnCl_3)_4L_2]^{2-}$ and $[OsL_6](SnCl_3)_2Cl$ can also be obtained.[52] The phosphonium salt $(Ph_3P)_4[Os(SnCl_3)Cl_5]^{4-}$ is obtained from $[Os(SnCl_5)Cl_4]^{4-}$ and Ph_3P or Ph_3PO.[53a]

The reaction of $(NH_4)_2[OsCl_6]$ and tin(II) chloride in concentrated hydrochloric acid and phosphines, arsines or stibines gives $Os(SnCl_3)(PR_3)_2Cl_2$ (PR_3 = $PMePh_2$, PPr^n_2Ph, PPh_3); $Os(SnCl_3)(LPh_3)_4Cl$ (L = As, Sb); $Os(SnCl_3)(L—L)_2Cl$ (L—L = dppm, dppe). IR spectra were measured and also, in the cases of $Os(SnCl_3)(PPh_3)_3Cl_2$, $Os(SnCl_3)(dppe)_2Cl$ and $Os(SnCl_3)(SbPh_3)_4Cl$, Raman spectra.[17]

The ^{119}Sn NMR spectra of $(PPH_4)_4[Os(SnCl_3)_6]$ and of $[OsCl(SnCl_3)_5]^{4-}$ have recently been measured,[53b] and $[Os(SnF_3)_6]^{4-}$ is also known.[45]

For the crystal structure of $(PPh_4)_2[Os(NO)Cl_3(SnCl_3)_2]$ see p. 549 below.

46.4 NITROGEN LIGANDS

Nitrogen is, after oxygen, the most frequently encountered donor atom in the coordination chemistry of osmium. There is a large and growing body of work on the ammine, pyridine, ethylenediamine and porphyrin complexes, but the most popular and rapidly growing field of study at the present time is that of the 'polypyridyls', the 2,2′-bipyridyl, 1,10-phenanthroline and 2,2′,2″,6′-terpyridyl complexes of the metal.

46.4.1 Ammine Complexes

Ammonia forms a number of complexes with osmium (see Table 5), though the only fully established unsubstituted osmium ammine which has been isolated is the hexaammine $[Os(NH_3)_6]^{3+}$; there is, however, electrochemical evidence for the existence both of $[Os(NH_3)_6]^{2+}$ and of $[Os(NH_3)_6]^{4+}$. Amongst the substituted ammines which have been isolated and characterized are several of osmium(II), all with supporting (or stabilizing) π-acceptor ligands, *e.g.* $[Os(NH_3)_5CO]^{2+}$, $[Os(NH_3)_5(NO)]^{3+}$ and $[Os(NH_3)_5(N_2)]^{2+}$.

Table 5 Representative Ammine Complexes

Complex	*Colour*	pK_a	*Spectroscopic and other studies*[a]
$[Os(NH_3)_6]^{3+}$	White	15	IR,[66,73] UV/vis,[55] M,[58] CV[63,65]
$[Os(NH_3)_6]^{4+}$		0	CV[55]
$[Os(NH_3)_5(H_2O)]^{3+}$			UV/vis,[62] CV[61,62]
$[Os(NH_3)_5(OH)]^{2+}$			CV[61]
$[Os(NH_3)_5(OSO_2CF_3)]^{2+}$			UV/vis[62]
$[Os(NH_3)_5Cl]^{2+}$ [b]	Yellow		Raman, IR,[74] UV/vis,[55,65,68] CV[63]
cis-$[Os(NH_3)_4Cl_2]Cl$[b]	Yellow		IR,[65] UV/vis[55,65]
trans-$[Os(NH_3)_4Cl_2]Cl$[b]	Bright yellow		IR,[65] UV/vis[55,65]
mer-$Os(NH_3)_3Cl_3$[b]			UV/vis, CV[55]
$K_2[Os(NH_3)Cl_5]$			IR,[66] UV/vis, CV[55]
cis-$[Os(NH_3)_4Cl_2]^{2+}$ [b]			UV/vis, CV[55]
trans-$[Os(NH_3)_4Cl_2]^{2+}$ [b]		4.0	UV/vis, CV[55]
mer-$[Os(NH_3)_3Cl_3]^{+}$ [b]		4.9	UV/vis, CV[55]
$Cs[Os(NH_3)Cl_5]$		6.5	UV/vis, CV[55]
$[Os(NH_3)_5(CO)Cl_2$	White		IR, UV/vis[69]
$[Os(NH_3)_5(CO)][IrCl_6]$	Lavender		IR[70]
$Os(NH_3)(PPh_3)_2Cl_3$			X-ray[71]

[a] M = magnetic studies; CV = cyclic voltammetry. [b] Bromo and iodo analogues also known.

There is also a wide range of osmium(III) species, *e.g.* $[Os(NH_3)_5X]^{2+}$ (X = Cl, Br, I, OH), *cis*- and *trans*-$[Os(NH_3)_4X_2]^{2+}$ and *mer*-$Os(NH_3)_3X_3$ (X = Cl, Br, I), and in fairly recent work the isolation of the corresponding osmium(IV) ammines has been demonstrated. In the presence of a strongly π-donating ligand such as N^{3-}, $[Os_2^{IV}N(NH_3)_8X_2]^{3+}$ (X = Cl, Br, I, NCS, N_3) and the ill-characterized $[Os^{IV}N(NH_3)_4(H_2O)]^{+}$ are formed, while two oxo ligands suffice to render *trans*-$[Os^{VI}O_2(NH_3)_4]^{2+}$ a stable species.

In this section we consider unsubstituted complexes first, then aqua, hydroxo, halo, carbonyl and phosphine ammines. For nitrido ammines see pp. 562, 563, nitrosylammines p. 546, and dinitrogen ammines p. 554. Other substituted ammines are dealt with under the section concerned with the substituting ligand.

46.4.1.1 Unsubstituted ammines, $[Os(NH_3)_6]^{n+}$

Although both the brown $[Os(NH_3)_6]$ and the yellow $[Os(NH_3)_6]Br$ have been claimed as products of the reaction of $[Os(NH_3)_6]Br_3$ with potassium in liquid ammonia,[54] the products were not well characterized and could be hydrido ammines or mixtures. There is evidence from the polarographic reduction of $[Os(NH_3)_6]^{3+}$ for the existence of $[Os(NH_3)_6]^{2+}$ but it appears to be labile to substitution and has not been isolated:[55] in this respect osmium differs significantly from ruthenium, for $[Ru(NH_3)_6]^{2+}$ is isolable and is in fact a useful synthetic precursor. The tetravalent complex $[Os(NH_3)_6]^{4+}$ has also been detected electrochemically, by cyclic voltammetric oxidation of $[Os(NH_3)_6]^{3+}$;[55] in acidic solution; however, the first product of one-electron oxidation of $[Os(NH_3)_6]^{3+}$ is probably $[Os(NH_3)_5(NH_2)]^{3+}$.[55]

Salts of $[Os(NH_3)_6]^{3+}$ are made from $[OsCl_6]^{2-}$ and ammonia with zinc dust[56] or from $(NH_4)_2[OsBr_6]$ and ammonia under pressure,[57] but a recently devised high-yield procedure involves reaction of $[Os(NH_3)_5(NO)]^{3+}$ with perchloric acid and amalgamated zinc.[55]

The magnetic moment of $[Os(NH_3)_6]Br_3$ has been measured from 77 to 300 K.[58] Both $[Os(NH_3)_6][OsBr_6]$[59] and $[Os(NH_3)_6]Br[OsBr_6]\cdot H_2O$[60] are known; presumably both contain $[Os(NH_3)_6]^{3+}$ though this is not immediately obvious.

46.4.1.2 Substituted ammines

(i) Aqua, hydroxo and triflato ammines

The aqua complex $[Os(NH_3)_5(H_2O)]^{3+}$ is best made from $[Os(NH_3)_5(N_2)]^{2+}$ with $HClO_4$ and cerium(IV);[55] a reversible polarographic reduction, presumably to $[Os(NH_3)_5(H_2O)]^{2+}$, is observed at pH 4.[61] The hydroxopentaammine $[Os(NH_3)_5(OH)]^{3+}$ is made by addition of base to the aqua complex, and this too exhibits a one-electron reversible polarographic reduction to the corresponding osmium(II) species.[61] The aqua complex of osmium(III) is a useful precursor for $[Os(NH_3)_5X]^{2+}$ species (X = Cl, Br, I; see below).

The 'triflato' complex $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$, made from $[Os(NH_3)_5(N_2)]^{2+}$ and triflic acid with bromine, is a very useful precursor for the preparation of mononuclear $[Os(NH_3)_5L]^{n+}$ species (L = pyridine, pyrazine, pyrimidine, *etc.*, see p. 534) and for binuclear pyrazine-bridged complexes (p. 526).[62] For *trans*-$[OsO_2(NH_3)_4]^{2+}$, see p. 582.

(ii) Halo ammines

For convenience we group chloro, bromo and iodo complexes together; no fluoroammines have yet been reported.

(*a*) *Osmium(II)*. Evidence from cyclic voltammetry suggests that $[Os(NH_3)_5X]^{2+}$ (X = Cl, I) can be reduced to the divalent state, presumably to $[Os(NH_3)_5X]^{+}$, but that these are labile to substitution.[63]

(*b*) *Osmium(III)*. The pentaammines $[Os(NH_3)_5X]^{2+}$ are made from $[Os(NH_3)_5(H_2O)]^{3+}$ and HX (X = Cl,[55,64] Br, I[55]). Both *cis* and *trans* isomers are known of $[Os(NH_3)_4X_2]^{+}$; the *cis* species are made from *cis*-$[Os(N_2)_2(NH_3)_4]^{2+}$ and HX,[65] and the *trans* complexes are prepared from *trans*-$[OsO_2(NH_3)_4]^{2+}$ and HX with $SnCl_2$ (X = Cl, Br), while for the iodo complex iron wire replaces $SnCl_2$ as the reducing agent.[55] There is a brief report of the trihalo species *mer*-$Os(NH_3)_3X_3$ (X = Cl, Br, I).[55]

The monoammine complex $K_2[Os(NH_3)Cl_5]$, made by reduction of $K[OsO_3N]$ with $SnCl_2$ in HCl[66] or with vanadium(II) or europium(II),[55] was once thought to be an amide, $K_2[Os(NH_2)Cl_5]$.[67]

Spectral data on osmium(III) haloammines are available (see Table 5); simplified MO theory has been applied to the charge-transfer spectra of $[Os(NH_3)_5X]^{2+}$ and $[Os(NH_3)_4X_2]^{+}$.[68]

(*c*) *Osmium(IV)*. No pentaammine halide species seem to be known of osmium(IV), but *cis*- and *trans*-$[Os(NH_3)_4X_2]^{2+}$ and *mer*-$[Os(NH_3)_3X_3]^{+}$ are made by oxidation of the corresponding osmium(III) complexes with iron(III) in the appropriate acid.[55]

Osmium(IV) ammines have unusually low pK_a values (see Table 5) and so persist only in strongly acidic media; the complexes are more acid by an order of five to six than their platinum(IV) counterparts but only slightly more acidic than the corresponding iridium(IV) complexes. This has been correlated with the decreasing t_{2g} electron occupancy in the series Pt^{IV}–Ir^{IV}–Os^{IV} and attributed to charge transfer from ligands to the empty π orbitals on osmium(IV). The *cis* isomers are more acidic than the *trans*, and this can be correlated with differences between the osmium(III) and osmium(IV) complexes for the isomers.[55]

Nitric oxide reacts rapidly with osmium(IV) di- and tri-haloammines giving, *via* a 'diazotization' reaction, osmium(III) dinitrogen ammine complexes (see p. 555).[64] At higher, pH, di- and tri-haloammines are unstable and undergo disproportionation reactions to osmium(III) haloammines and *trans*-$[OsO_2(NH_3)_4]^{2+}$.[64]

For $[Os(NH_2)X_5][Os(NH_3)_5X]$ (X = Cl, Br), see p. 557.

(iii) Carbonyl and phosphine ammines

Reaction of $[Os(NH_3)_5Cl]^{2+}$ with formic acid and zinc gives $[Os(NH_3)_5(CO)]^{2+}$,[69] and this can be oxidized to $[Os(NH_3)_5(CO)]^{3+}$ with $[IrCl_6]^{2-}$; oxidation of this with cerium(IV) leads to $[Os(N_2)(NH_3)_8(CO)_2]^{4+}$ in which there is a μ-dinitrogen bridge linking two *cis* tetraammine carbonyl osmium(II) moieties (see p. 556).[70]

The reaction of $N_2H_4 \cdot H_2O$ and PPh_3 with *trans*-$K_2[OsO_2(OH)_4]$ yields $Os(PPh_3)_2Cl_3(NH_3)$, and the X-ray crystal structure reveals the structure shown in Figure 1. In this, $a = 2.136(9)$, $b = 2.411(2)$, $c = 2.362(1)$ and the *trans* chloro distance $d = 2.360(3)$ Å. There is some distortion, the Cl(*cis*)—Os—Cl(*cis*) angle being 169.37(1)°.[71]

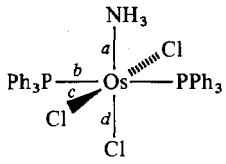


Figure 1 Structure of $Os(PPh_3)_2Cl_3(NH_3)$[71]

Reaction of $Os(PMe_2Ph)_3X_3$ (X = Cl, Br) with ammonia in dry ethanol gives $Os(PMe_2Ph)_3X_2(NH_3)$.[72]

(*iv*) *Miscellaneous ammines*

For *trans*-$[OsO_2(NH_3)_4]^{2+}$, see p. 582, and for $[OsN(NH_3)_4(H_2O)]^{3+}$, see p. 562.

(*v*) *Binuclear ammine complexes*

These constitute an important recent feature of osmium chemistry, but for convenience (and chemical sense) they are considered under the sections dealing with bridging ligands. For such complexes with bridging dinitrogen, see p. 556, with bridging pyrazine, see p. 536, and bridging nitride, see p. 563.

The ill-defined $[Os_2(NH_3)_6Br_4]Br_2$ is formed when $[Os(H_3)_6]Br_3$ is heated to 305 °C; the iodo complex $[Os_2(NH_3)_6I_4]I_2$ is formed when $[Os(NH_3)_6]I_3$ is heated to 234 °C.[75]

46.4.2 Complexes with Monodentate Amines

We consider here the remarkably small number of complexes of osmium with primary and aromatic amines RNH_2; all these involve phosphines as coligands. For complexes of pyridine and its analogues see p. 533; complexes of polydentate amines are considered in the sections which follow this one (p. 534).

Reaction of $Os(PMe_2Ph)_3X_3$ with RNH_2 (X = Cl, R = Me, Et, Pr^n, Pr^i, Bu^n; X = Br, R = Me, Bu^n) gives $Os(PMe_2Ph)_3X_2(RNH_2)$.[72] The *secondary* amines R_2NH give, with $Os(PMe_2Ph)_3Cl_3$, $Os(PMe_2Ph)_3Cl_2(RNH_2)$, which contains the coordinated primary amine (R = Me, Et, Pr^n, Pr^i, Bu^n, ^{n}hexyl, cyclohexyl, piperidine).[72]

46.4.3 Complexes with Bidentate Amines

46.4.3.1 Complexes with ethylenediamine

As ligands for osmium, ammonia and ethylenediamine (en; 1,2-diaminoethane) would be expected to have broadly similar properties, and this is on the whole true — there are stable osmium(III) complexes such as $[Os(en)_3]^{3+}$, *trans*-$[Os(en)_2X_2]^+$ (X = Cl, Br) and $[Os(en)Cl_4]^-$, and more recently the tetravalent $Os(en)X_4$ (X = Cl, Br, I) has been made. There is, however, an interesting chemistry of the 1,2-ethanediaminato-(1 −) and -(2 −) ligands with osmium in the higher IV, V and VI states, and another unusual feature is the existence of the hydride $[OsH_2(en)_2]^{2+}$.

Table 6 Representative Ethylenediamine Complexes

Complex	*Colour*	*Spectroscopic and other studies*[a]
$[Os(en)_3]I_3$	Yellow	IR,[79] M,[77] ESR,[85] CV[76]
$[Os(en)_2Cl_2]Cl\cdot H_2O$[b]		IR, Raman, UV/vis, M[78]
$[Os(en)_2H_2][ZnCl_4]$		IR, ^{1}H NMR, M[81]
$Os(en)Br_4$[c]		IR, UV/vis[79]
$[Os(en-H)en_2]Br_2$	Pink	X-Ray[76]

[a] M = magnetic studies; CV = cyclic voltammetry. [b] Bromo complex also known.[78] [c] Chloro and iodo complexes also known.[79]

We deal first with ethylenediamine complexes, then with 1,2-ethanediaminato-(1 −) and -(2 −) ligands (the so-called (en − H) and (en − 2H)), then related mono- and di-imines, and finally with substituted ethylenediamine complexes (see Table 6).

(*i*) *Osmium(II)*

There is a brief mention in the literature of $[Os(en)_3]^{2+}$, made by a one-electron reduction of $[Os(en)_3]^{3+}$. See also Scheme 1, p. 532.

(*ii*) *Osmium(III)*

The tris chelate $[Os(en)_3]^{3+}$ is most easily made by reduction of $[Os(en - H)(en)_2]^{3+}$ with ethanol, conc. HBr, $Na_2S_2O_4$[76] or $NaHSO_3$.[77] The iodide is paramagnetic with a magnetic moment close to 1.6 BM at room temperature.[77] The two *trans*-$[Os(en)_2X_2]X$ (X = Cl, Br) complexes can be made from $[Os(en)_2H_2]^{2+}$ and HX. The *trans* configuration for the chloro complex is suggested by the Raman and IR spectra, while that for the bromo species is indicated by a Br—Os—Br angle close to 180° from a partly resolved X-ray analysis of the compound. Both complexes are paramagnetic in solution (μ_{eff} = 1.91 and 1.95 BM at 323 K).[78] The salts $Cs[Os(en)X_4]$ (X = Cl, Br) were obtained from $[Os(en)(en - H)_2]Br_2$ and HX (a similar reaction with HI gave '$[Os(en)_3I_2]\ I_4$'). The bromo species with HCl gave $Cs[Os(en)Cl_nBr_{4-n}]$ (n = 1–3).[79] A rate of proton exchange with $[Os(en)_3]^{3+}$ has been given.[80]

(*iii*) *Osmium(IV)*

Although $[Os(en)_3]^{4+}$ has not been isolated, it seems possible that an oxidation wave for $[Os(en)_3]^{3+}$ near +2 V may be due to this species; a rate of proton exchange with $[Os(en)_4]^{4+}$ has been given.[80] It is clearly unstable with respect to $[Os(en)(en - H)_2]^{2+}$ and $[Os(en_2)(en - H)]^{3+}$ (p. 532).

There are however several substituted ethylenediamine complexes, the most unusual being the hydride $[Os(en)_2H_2]^{2+}$ which can be obtained as a $[ZnCl_4]^{2-}$ salt (by reaction of $[OsO_2(en)_2]Cl_2$ with zinc in HCl) or as a chloride. The salts are diamagnetic or almost so (μ_{eff} 0.22 BM at 298 K and 0.10 BM at 183 K for the $[ZnCl_4]^{2-}$ salt). Although this is formally an osmium(IV) complex there seems to be no abnormality in the ^{1}H NMR shift (δ_{OsH} = 15.4 p.p.m.); the Os—H stretch lies at 2150 cm^{-1} in the IR.[81]

The species $Os(en)X_4$ (X = Cl, Br) can be prepared from $[Os(en - H)_2(en)]\ Br_2$ and HX; a similar reaction with HI leads to '$[Os(en)_3I_2]\ I_4$', but $Os(en)I_4$ can be obtained from either $Os(en)Cl_4$ or $Os(en)Br_4$ with HI.[79] There is also an oxalato complex $Os(en)ox_2$, obtained from $[Os(en - H)_2(en)]Br_2$ and oxalic acid.[79]

(*iv*) *Osmium(VI)*

The osmyl complex *trans*-$[OsO_2(en)_2]^{2+}$ is discussed on p. 583 (see also Table 21). The only other species in this category is the deep red crystalline '$[Os(en)_3I_2]_4$', obtained by treatment of $[Os(en)(en - H)_2]Br_2$ with HI.[79] Although analytical data fit the formulation reasonably well it seems unlikely that this really is an eight-coordinate osmium(VI) species; an alternative possibility is $[Os(en)(en - H)_2](I_3)_2$.

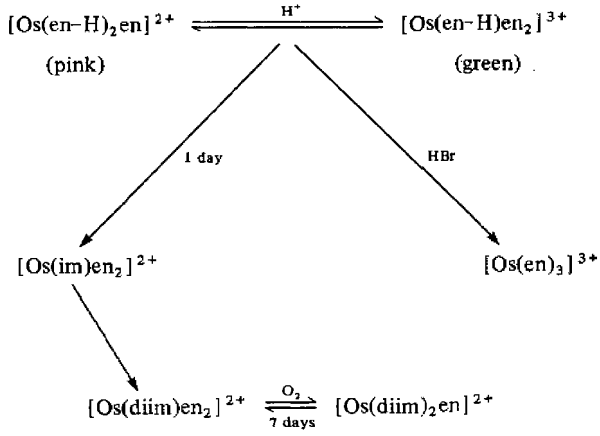
46.4.3.2 Complexes with deprotonated ethylenediamine

These species, in which the 1,2-ethanediaminato-(1 −) and -(2 −) ligands, $(HN(CH_2)_2NH_2)^-$ and $(HN(CH_2)_2NH)^{2-}$, are denoted by (en − H) and (en − 2H) respectively are relatively common for the higher oxidation states of osmium; indeed the normal preparation of the 'simple' $[Os(en)_3]^{3+}$ cation is by reduction of $[Os(en - H)_2en]^{2+}$. They are in effect π-donating amido ligands and so it is perhaps not surprising that osmium(IV) and osmium(VI) complexes should be formed with them. Precise characterization of some of them is lacking, however, particularly those of osmium(III), but there is a recent X-ray crystal structure of $[Os^{IV}(en - H)_2en]Br_2$.[76]

There is also evidence from NMR of the existence of mono- and di-imine complexes containing the coordinated $HN(CH_2)_2NH_2$ and $HN(CH_2)_2NH$ ligands; these we refer to below as im and diim respectively.

(*i*) *Osmium(II)*

The monoimine complex $[Os(im)(en)_2]^{2+}$ is formed at pH 6–7 by the spontaneous oxidative dehydrogenation of $[Os(en-H)(en)_2]^{3+}$; formation of other iminato complexes is given in Scheme 1.[76] The complexes were detected by electronic and ^1H and ^{13}C NMR spectroscopy.[76]



Scheme 1 Reactions of deprotonated ethylenediamine complexes[76]

(*ii*) *Osmium(III)*

Reaction of $[Os(en)_3]I_3$ with three, two or one moles of potassium amide yields respectively the brown $Os(en-H)_3$, the yellow-brown $[Os(en-H)_2en]I$ and the pink $[Os(en-H)(en)_2]I_2$; the magnetic moment of the latter is 1.58 BM at room temperature.[82] Formulation as iminato complexes would also be possible; structural data on these species would be of interest.

(*iii*) *Osmium(IV)*

The reaction of $(NH_4)_2[OsBr_6]$ and ethylenediamine at 60 °C yields the pink $[Os(en-H)_2en]Br_2$,[77] and this formulation of 1955 as an ethanediaminato(1 –) complex has recently been confirmed by a single crystal X-ray study. The two deprotonated ends of the ligands are *cis* to each other, and the Os—N bond length to these ends (*c* in Figure 2, is 1.90 Å, indicative of some multiple bonding, since the Os—NH_3 bond lengths *a* and *b* are respectively 2.19 and 2.11 Å.[76]

In Scheme 1 the reactions of this and other en – H complexes are depicted; the pK_a for the $[Os(en-H)_2en]^{2+}$–$[Os(en-H)en_2]^{3+}$ equilibrium is about 6.[76]

The pyrophoric species $[Os(en-H)_3]I$ has also been claimed, made by treatment of $[Os(en-H)_2en]I_2$ with potassium amide in liquid ammonia.[82]

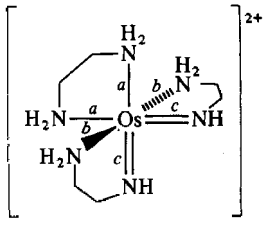


Figure 2 Structure of $[Os(en-H)_2en]^{2+}$[76]

(iv) Osmium(V) and Osmium(VI)

A black microcrystalline material formulated as $[Os(en-H)_3en]I_2 \cdot 4H_2O$ is obtained from $[Os(en-H)_2en]I_2$ and ethylenediamine at 100 °C,[77] and is paramagnetic (μ_{eff} = 1.78 BM).[83] A similar preparative method in the presence of air gives $[Os(en-H)_4]I_2 \cdot 3H_2O$,[77] a green-brown diamagnetic material thought to contain osmium(VI).[83] As formulated both these species presumably contain eight-coordinate osmium, a very rare coordination number for the element, and clearly they merit further investigation.

46.4.3.3 A complex of 2,3-butanediimine

Biacetyl reacts with $[Os(NH_3)_6]I_3$ in alkali, and the diammine-2,3-butanediimine species (Figure 3) is formed as brown-black crystals. The ^1H NMR spectrum is consistent with the *trans* structure.[84]

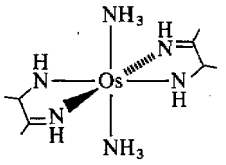


Figure 3 Proposed structure of the 2,3-butanediimine complex[84]

46.4.4 Complexes with Nitrogen Heterocycles

46.4.4.1 Complexes of pyridine and of substituted pyridines

(i) Complexes with pyridine

Osmium forms a number of complexes with pyridine (Table 7), mostly of the II oxidation state although there are examples of osmium(III) and osmium(IV) pyridine complexes. The important osmium(VI) species $Os_2O_6py_4$, a binuclear $\mu\mu'$-oxo 'osmyl' species, is considered on p. 595. There is also some important recent chemistry of osmium nicotinic and isonicotinic acid complexes (the 3- and 4-pyridinecarboxylic acids respectively).

Table 7 Complexes of Pyridine and of Substituted Pyridines

Complex	*Colour*	*Spectroscopic and other studies*[a]
cis-$Os(py)_2(CO)_2Cl_2$		IR, Raman, UV/vis[99]
trans-$Os(py)_2(CO)_2ClI$		IR, Raman, UV/vis, MS[89]
$Os(py)_3(PPh_3)Cl_2$	Red	ESCA, CV[93]
$[Os(py)(NH_3)_5]Cl_3 \cdot 2H_2O$		IR, Raman,[91,92] UV/vis,[62,90] CV[62,90,91]
$[Os(isonic)(NH_3)_5]Cl_3$[b]		UV/vis,[90,100] MCD,[100] CV[90]
$Os(py)_2(PPh_3)Cl_3$	Orange	ESCA, CV, M[93]
mer-$Os(py)_3Cl_3$		IR,[94] M,[101] ESR[102]
$[Os(py)(CO)Cl_4]^-$[c]	Orange	IR, Raman, UV/vis[95]
mer-$Os(3\text{-Mepic})_3I_3$		IR, M[101]
$[Os(py)Cl_5]^-$[c]		UV/vis[96,97]

[a] M = magnetic studies; CV = cyclic voltammetry. [b] isonic = *iso*nicotinamide. [c] Also bromo and iodo complexes.

(a) Osmium(II). The reaction of $[OsX_6]^{2-}$ and pyridine gives $Os(py)_4X_2$ (X = Cl, Br);[86] for the iodo complex a *trans* configuration has been postulated.[87] The carbonyl species $Os(py)_3(CO)X_2$ and $Os(py)_2(CO)XI$ (X = Cl, Br) are obtained from $[Os(CO)_2I_4]^-$ with pyridine followed by metathesis —the chloro ligands occupy *trans* position.[88] The dicarbonyls *cis*-$Os(py)_2(CO)_2X_2$ (X = Cl, Br, I) are made from pyridine and *cis*-$[Os(CO)_2X_4]^{2-}$ and their configurations have been determined by vibrational spectroscopy; on heating *in vacuo* the thermodynamically more stable *trans* isomers are formed.[89]

Cyclic voltammetry of $[Os(py)(NH_3)_5]^{3+}$ demonstrated the existence of $[Os(py)(NH_3)_5]^{2+}$,[62,90,91] and the surface-enhanced Raman spectra (SERS) of both species were measured recently,[91,92] with

normal, pyridine-d_5 and ammine-d_3 substitution. The metal–nitrogen, ammine and internal pyridine modes are enhanced; IR spectra were also recorded.[91]

Reaction of pyridine with $OsO_2Cl_2(PPh_3)_2$ yields $Os(py)_3(PPh_3)Cl_2$, which can be reversibly oxidized to the osmium(III) and osmium(IV) derivatives; electrochemical reduction of $Os(py)_2(PPh_3)Cl_3$ gives $[Os^{II}(py)_2(PPh_3)Cl_3]^-$.[93]

(*b*) *Osmium(III).* The iodo complex *mer*-$Os(py)_3I_3$ can be made from $[OsI_6]^{2-}$ and pyridine, and from this the corresponding $Os(py)_3X_3$ species (X = Cl, Br) can be obtained with X_2;[94] *fac*-$Os(py)_3Cl_3$ is made from $[OsCl_6]^{2-}$ and pyridine.[86] The mixed methyl pyrazine (R) complexes $Os(py)_nR_{3-n}X_3$ (n = 3, 1; X = Cl, Br, I) and $Os(py)_2RX_2I$ (X = Cl, Br, I) can be made from $[OsI_6]^{2-}$, pyridine and X^-.[94] The carbonyl halo species *trans*-$[Os(py)(CO)X_4]$ (X = Cl, Br, I) can be made from anhydrous pyridine with $[Os(CO)_2X_4]^{2-}$ or $[Os(CO)X_5]^-$.[95]

Replacement of the dinitrogen ligand in $[Os(N_2)(NH_3)_5]^{2+}$ by pyridine under aerobic conditions[90] or of the weakly bound triflate ligand in $[Os(OSO_2CF_3)(NH_3)_5]^{2+}$ by pyridine[62] yields $[Os(py)(NH_3)_5]^{3+}$; cyclic voltammetric studies show reversible reduction to $[Os(py)(NH_3)_5]^{2+}$ [62,90,91] and the surface-enhanced Raman spectrum[91,92] (SERS) of the complex (both normal and deuteriated) shows Os–N, ammine and internal pyridine vibrational modes. Infrared spectra were also measured.[91]

Reaction of *trans*-$Os(PPh_3)_2Cl_4$ with pyridine yields $Os(py)_2(PPh_3)Cl_3$, which can be oxidized or reduced by one-electron reactions, while electrochemical oxidation of $Os(py)_3(PPh_3)Cl_2$ gives $[Os(py)_3(PPh_3)Cl_2]^+$.[93]

(*c*) *Osmium(IV).* Salts of $[Os(py)X_5]^-$ (X = Cl, Br, I) can be obtained from $[OsX_6]^{2-}$ and pyridine, and the mixed species $[Os(py)Cl_4I]^-$ has also been isolated.[96] The chloro and bromo complexes can be made photochemically in the same way.[97] Electrochemical oxidation of $Os(py)_2(PPh_3)Cl_3$ gives $[Os(py)_2(PPh_3)Cl_3]^+$, and oxidation of $[Os(py)_3(PPh_3)Cl_2]^+$ gives $[Os(py)_3(PPh_3)Cl_2]^{2+}$.[93]

(*ii*) *Complexes of substituted pyridines*

(*a*) *Picoline (methylpyridine) complexes.* The 3- and 4-methylpyridine complexes $Os(pic)_3I_3$ have been made from $[OsI_6]^{2-}$ and the ligand.[94]

(*b*) *Isonicotinic acid (pyridine-4-carboxylic acid) and isonicotinamide complexes.* The dinitrogen ligand in $[Os(N_2)(NH_3)_5]^{2+}$ can be replaced by isonicotinic acid to give $[Os(nic)(NH_3)_5]^{2+}$,[90] and reaction of this ligand or of isonicotinamide with $[Os(N_2)_2(NH_3)_4]^{2+}$ yields $[OsL(N_2)(NH_3)_4]^{2+}$. The latter isonicotinic acid complex $[OsL(N_2)(NH_3)_4]^{2+}$ can be oxidized anaerobically in the presence of HCl to give *cis*-$[OsLCl(NH_3)_4]Cl_2 \cdot H_2O$, while the isonicotinamide complex $[OsL'(N_2)(NH_3)_4]^+$ reacts with $NaNO_2$ and HCl to give a triammine, $[OsL'(N_2)_2(NH_3)_3]Cl_2$. Evidence was also obtained for the existence of $[Os(\text{nicotinic acid})(N_2)(NH_3)_4]^{2+}$.[98]

46.4.4.2 Complexes with chelating pyridines

A number of unusual complexes in which pyridine is substituted in the 2 or *ortho* position with O- or N-donor ligands are known.

(*i*) *2-Hydroxypyridine (hp) complexes*

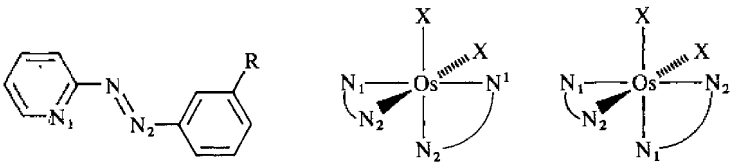
Reaction of the ligand with $OsCl_3$[103,104] or with $Os_2(OCOMe)_4Cl_2$[105] gives $Os_2hp_4Cl_2S_2$, where S is a solvent molecule. The X-ray crystal structure of $Os_2hp_4Cl_2 \cdot OEt_2$ shows this to have a 'lantern' type of structure similar to that found for $Os_2(OCOR)_4Cl_2$ (R = Me, Et, Pr^n; see Figure 34). In the complex the OsN_2O_2 moieties have a *trans* arrangement and the Os—Os distance is 2.344(2) Å,[103] while in $Os_2hp_4Cl_2 \cdot 2MeCN$ it is 2.357(1) Å.[104] The magnetic moment of $Os_2hp_4Cl_2$ is 1.44 BM at 300 K,[105] larger than that for the carboxylates $Os_2(OCOR)_4Cl_2$ (p. 601), possibly due to a greater population of states derived from configurations such as $\sigma^2\pi^4\delta^2\pi^{*2}$ or $\sigma^2\pi^4\delta^2\delta^*\pi^*$.[106]

Reduction of $Os_2hp_4Cl_2$ with $(\pi\text{-}C_5H_5)_2Co$ gives $[(\pi\text{-}C_5H_5)_2Co][Os_2hp_4Cl_2]$, which contains the Os_2^{5+} core. This olive-green material has a magnetic moment of 2.68 BM at 308 K and of 2.63 BM at 173 K in dichloromethane solution (unlike the corresponding carboxylates for which the moment drops substantially with temperature). The ESR spectrum of the complex was also measured.[107]

The ligand 2-aminomethylpyridine (Rpy) functions as a chelating ligand in its own right or as the monodeprotonated 2-iminomethylpyridine (RpyH) species. This reaction of Rpy with $[OsBr_6]^{2-}$

gives the red osmium(IV) complex $[Os(Rpy)(RpyH)_2]Br_2$, with a magnetic moment of 1.2 BM at room temperature, together with the green $[Os(Rpy)_2(RpyH)](ClO_4)_3$ (μ_{eff} = 1.1 BM) isolated from perchloric acid solution of the reactants. This can be reduced with HSO_3^- to the yellow-green $[Os(Rpy)_3](ClO_4)_3$, an osmium(III) complex (μ_{eff} = 1.8 BM).[108]

Isomeric complexes of 2-(phenylazo)pyridine (pap) and 2-(*m*-tolylazo)pyridine (tap) (Figure 4a) have been prepared from the ligand and $(NH_4)_2[OsX_6]$. These have stoichiometries corresponding to OsL_2X_2 (X = Cl, Br), but exist in various forms such that $Os(pap)_2Cl_2$ and $Os(tap)_2Cl_2$ have structures (b) and (c) shown in Figure 4.[109a] A recent X-ray crystal structure study shows that $Os(tap)_2Cl_2$ has the structure shown in Figure 4(b); mean Os—Cl, 2.394; mean Os—N, 2.06; mean Os—N_2, 1.974 Å.[109b]



(a) tap, R = H; pap, R = Me (b) (c)

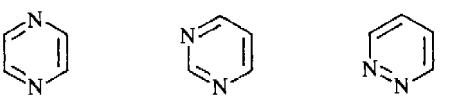
Figure 4 Isomers of 2-(arylazo)pyridine complexes[109a]

46.4.4.3 Piperidine ($C_6H_{11}N$) complexes

For convenience these are placed with pyridine. Only two complexes with osmium seem to have been reported. The ligand reacts with OsL_3Cl_3 (L = PMe_2Ph,[72] $As(p\text{-}MeC_6H_4)_3$[110]) to give OsL_3Cl_2(piperidine).

46.4.4.4 Bifunctional heterocyclic donors

In this section we consider the osmium complexes of the three potentially bifunctional ligands pyrazine (pyz), pyrimidine (pym) and pyridazine (pyd) (Table 8).* All form terminal complexes with



Pyrazine (pyz) Pyrimidine (pym) Pyridazine (pyd)

osmium, but only pyrazine forms binuclear species, the others not doing so presumably for steric reasons. Of particular interest is $[Os_2(pyz)(NH_3)_{10}]^{5+}$, the osmium analogue of the celebrated 'Creutz–Taube' complex $[Ru_2(pyz)(NH_3)_{10}]^{5+}$.[111]

Table 8 Pyrazine Complexes of Osmium

Complex	*Colour*	*Spectroscopic and other studies*[a]
mer-$Os(pyz)_3I_3$[b]	Blue-green	IR, UV/vis[94]
$[Os(pyz)(N_2)(NH_3)_4]Br_2$	Orange	IR, UV/vis[98]
$[Os(pyz)(NH_3)_5]Cl_3 \cdot 2H_2O$		UV/vis,[62] CV,[90,91] IR, resonance Raman[91]
cis-$[Os(pyz)(NH_3)_4Cl]Cl_2$	Orange	UV/vis[98]
$[Os_2(pyz)(NH_3)_{10}]^{4+}$	Violet	UV/vis, CV[114]
$[Os_2(pyz)(NH_3)_{10}]^{5+}$	Red	UV/vis, CV[114]
$[Os_2(pyz)(N_2)(NH_3)_9]^{5+}$		UV/vis, CV[114]
$[Os_2(pyz)(NH_3)_9Cl]^{4+}$		UV/vis, CV[114]
$[Os_2(pyz)(NH_3)_{10}]Cl_6 \cdot H_2O$		UV/vis,[100,114] MCD,[100] CV[113,114]
$[Os_2(pyz)(NH_3)_9Cl]^{5+}$		UV/vis, CV[114]
$[OsRh(pyz)(NH_3)_{10}]$-$Cl_6 \cdot H_2O$		UV/vis, MCD,[100] CV[114]
$[OsRuL(bipy)_4]^{3+}$[c]		UV/vis, CV[112]
$[Os_2(pyz)(NH_3)_{10}]^{6+}$		X-Ray[114b]

[a] CV = cyclic voltammetry. [b] Chloro and bromo complexes also known. [c] L = pyz, pyzc, bpm, pyz, pyzc, bpm.

* For bipyridyl, phenanthroline and terpyridyl see p. 537 *et seq.*

(*i*) *Mononuclear complexes*

(*a*) *Osmium(II)*. All three ligands form species of the type $[OsL(NH_3)_5]^{2+}$, these being obtained by electrochemical[62,90] or chemical[90] (zinc) reduction of the corresponding osmium(III) species. In basic solution these osmium(II) complexes are relatively stable in the absence of oxidizing agents, but are less so in acid: the values of pK_a for deprotonation of $[Os^{II}(LH)(NH_3)_5]^{3+}$ are 7.4, 2.1 and 3.7 for pyrazine, pyrimidine and pyridazine respectively, compared with pK_a values of 0.6, 1.3 and 2.33 for the ligands.[90] Recently the surface-enhanced Raman spectra (SERS) of $[Os(pyz)(NH_3)_5]^{2+}$ and of $[Os(pyz)(ND_3)_5]^{2+}$ have been recorded.[91]

The tetraammines *cis*-$[OsL(N_2)(NH_3)_4]^{2+}$ (L = pyrazine or 3,5-dimethylpyrazine) are made from *cis*-$[Os(N_2)_2(NH_3)_4]^{2+}$ and the ligand;[98] complexes of the monoprotonated species *cis*-$[Os(LH)(N_2)(NH_3)_4]^{+}$ (L = *N*-methylpyrazinium, pyrazinium and 3,5-dimethylpyrazinium) are also known.[98]

Recently the complex $[Os(pyzc)bipy_2]^{+}$ (pyzc = 2-pyrazinecarboxylic acid) has been made by reaction of $Os(bipy)_2Cl_2$ with the ligand.[112]

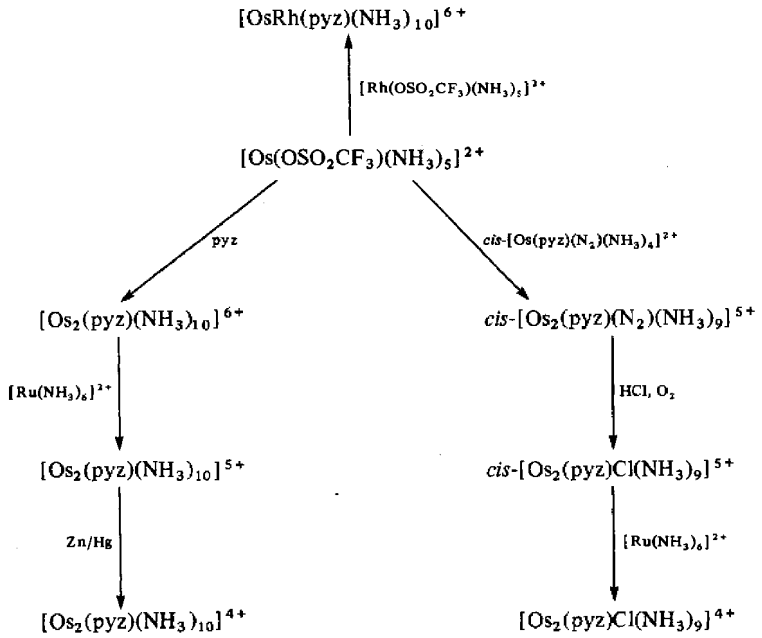
(*b*) *Osmium(III)*. The tris complex OsL_3X_3 (L = pyrazine, methylpyrazine and pyrimidine, X = Cl, Br, I) can be made from $[OsI_6]^{2-}$ and the ligands followed by metathesis where appropriate; *mer* configurations were assigned to $Os(pyz)_3Cl_3$, $Os(pyz)_3I_3$ and OsL_3X_3 (L = *N*-methylpyrazine, X = Cl, Br, I).[94] The mixed species $OsL(py)_2Br_nI_{3-n}$ (n = 1, 2) are made from *mer*-$OsL(py)_2I_3$ (L = *N*-methylpyrazine) and bromine.[113]

Salts of $[OsL(NH_3)_5]^{3+}$ (L = pyrazine, pyrimidine, pyridazine) can be made by displacement of nitrogen from $[Os(N_2)(NH_3)_5]^{2+}$[90] or from the triflato complex $[Os(OSO_2CF_3)(NH_3)_5]^{2+}$ and the ligands.[62] Cyclic voltammetry showed reduction to the osmium(II) species,[62,90] and the surface-enhanced Raman spectra (SERS) of $[Os(pyz)(HNH_3)_5]^{3+}$, $[Os(pyz)(NH_3)_5]^{2+}$ and of their ammine-d_5 derivatives were measured, as were the IR spectra.[91]

Reaction of *cis*-$[Os(pyz)(N_2)(NH_3)_4]^{2+}$ with HX yields *cis*-$[Os(pyz)X(NH_3)_4]^{2+}$ (X = Cl, Br).[98]

(*ii*) *Binuclear pyrazine-bridged complexes*

A number of these have been prepared using the synthetic procedures shown in Scheme 2. Of particular interest is $[Os_2(pyz)(NH_3)_{10}]^{5+}$ which has a radically different electronic absorption spectrum from either $[Os^{II}{}_2(pyz)(NH_3)_{10}]^{4+}$ or $[Os^{III}{}_2(pyz)(NH_3)_{10}]^{6+}$, and is believed to be a class III delocalized mixed-valence dimer, as is the dinitrogen analogue $[Os_2(N_2)(NH_3)_{10}]^{5+}$ (see p. 556). A similar situation probably obtains for $[Os_2(pyz)Cl(NH_3)_9]^{4+}$.[114a]



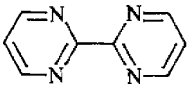
Scheme 2 Preparation of binuclear osmium ammines[114]

The pyrazine-bridged complex $[OsRu(pyz)bipy_4Cl_2]^{2+}$ has been reported and its electronic spectrum and cyclic voltammetry have been measured; two one-electron oxidations are observed.[112] In recent work the X-ray crystal structure of $[Os_2(pyz)(NH_3)_{10}]Cl_6 \cdot 2H_2O$ has been determined; the Os—N (pyrazine) distance is 2.101(7) Å.[114b]

Reaction of $[Os(pyzc)bipy_2]^+$ (pyzc = 2-pyrazinecarboxylic acid) with *cis*-$Ru(bipy)_2Cl_2$ gives the bridged complex $[OsRu(pyzc)bipy_4]^{2+}$; electronic absorption spectra and cyclic voltammograms were measured. Two one-electron oxidations were observed; the osmium(II) site is oxidized first and then the ruthenium site.[112]

46.4.4.5 Tetrafunctional ligands

The ligand 2,2-bipyrimidine (bpm) has been used to form terminal and bridging complexes with osmium. Reaction of *cis*-$Os(bipy)_2Cl_2$ and the ligand yields $[Os(bpm)bipy_2]^{2+}$, and with *cis*-



$Ru(bipy)_2Cl_2$ this gives the bipyrimidine-bridged complex $[OsRu(bpm)bipy_4]^{4+}$; the electronic absorption spectra and cyclic voltammetric properties were measured. Two one-electron oxidations were observed, the first probably occurring at the Os^{II} site and the second at Ru^{II}.[112]

46.4.4.6 Polypyridyl complexes of osmium

It has now become fashionable to call the bipyridyl, phenanthroline and terpyridyl ligands, and substituted forms of these, the 'polypyridyls' (see Table 9). In section 46.4.4.6.i. we consider the first two together, while terpyridyl complexes are dealt with in Section 46.4.4.6.iii.

Table 9 Properties of Bipyridyl, Phenanthroline and Terpyridyl Complexes

Complex	*Colour*	*Spectroscopic and other properties*[a]
$[Os(bipy)_3]^{2+}$	Green	Resonance Raman,[118,148] UV/vis, CD,[146,147] ^{1}H NMR,[118] CV,[40,157b,158] Mössbauer[184]
$[Os(phen)_3]^{2+}$	Brown	UV/vis, CD,[146,147] ^{1}H NMR,[185] CV[40,158]
$Os(bipy)_2Cl_2$[b]	Purple	Resonance Raman,[186] UV/vis,[174] CV[158]
$[Os(bipy)_2phen]^{2+}$	Green-brown	UV/vis,[120,175] CD[175]
$[Os(bipy)_3]^{3+}$	Violet	Resonance Raman,[118] UV/vis, CD,[146,147] ^{1}H NMR, ESR,[118,149,154] CV[40,157]
$[Os(phen)_3]^{3+}$	Red	UV/vis, CD,[146,147] ^{1}H NMR, ESR,[149,154] CV[40]
$[Os(bipy)_2Cl_2]^{+}$[b]	Brown	IR,[101] UV/vis,[151] M,[101] CV[158]
$[Os(terpy)_2]^{2+}$		UV/vis,[187] ^{1}H NMR,[188] CV[189]
$[Os(terpy)_2]^{3+}$	Green	CV[189]

[a] CV = cyclic voltammetry; M = magnetic studies. [b] Bromo and iodo complexes also known.

(*i*) *Complexes of 2,2′-bipyridyl and 1,10-phenanthroline*

In accordance with accepted practice we abbreviate these as bipy and phen, and the substituted ligands as Rbipy and Rphen (thus 5-Clbipy is 5-chloro-2,2′-bipyridyl and 4,7-Ph_2phen is 4,7-diphenyl-1,10-phenanthroline). The preparative routes to bipy and phen complexes are in general very similar, as are the chemistries of the two sets of complexes, so it is convenient to deal with them together. We consider first the tris species $[Os(LL)_3]^{2+}$ and $[Os(LL)_3]^{3+}$ and, in the following section, complexes involving LL and other ligands (LL = bipy, Rbipy, Rphen).

Since, like terpyridyl (p. 542), these ligands are good π acceptors by virtue of their considerable ring conjugation, it is the osmium(II) (d^6) state which is the commonest and generally the most stable; thus $[Os(LL)_3]^{3+}$ species are good one-electron oxidants. Nevertheless there are also examples of osmium(IV) and even a few of osmium(V) and osmium(VI) (the 'osmyl' osmium(VI) complexes are considered on p. 581).

The chemistry of these complexes has been extensively researched in the past two decades: the role of $[Os(LL)_3]^{3+}$ and $[Os(LL)_3]^{2+}$ in outer-sphere electron transfer processes has been much studied,

and two early papers in 1964 uncovered a large area of chemistry of bipy and phen complexes with other ligands. Recently, however, some of the considerable current interest in polypyridyl complexes of ruthenium as photosensitizers in the photodissociation of water has stimulated similar work on the corresponding complexes of osmium; as is indicated below it is the mixed complexes of osmium rather than $[Os(LL)_3]^{n+}$ which have excited the most interest. There is also much work likely to be done on electroactive polymeric species containing these ligands as electrode coatings.

(a) The tris complexes $[Os(bipy)_3]^{n+}$, $[Os(phen)_3]^{n+}$, $[Os(Rbipy)_3]^{n+}$ and $[Os(Rphen)_3]^{n+}$

Osmium(II). Salts of the green $[Os(bipy)_3]^{2+}$ ion can be made from OsO_4 and bipyridyl in the presence of hydrazine hydrate,[115] but the commonest procedure is to treat $K_2[OsCl_6]$ or $[Os(bipy)_2Cl_2]Cl$ with bipyridyl at 260 °C;[116] a similar reaction of $(NH_4)_2[OsBr_6]$ with phen at 270 °C gives the dark brown $[Os(phen)_3]^{2+}$.[117] Recent convenient preparations of both species involve refluxing solutions of the ligand with $Os_2(OAc)_4Cl_2$[105] or with $OsCl_3$[118]. Resolution of salts of both ions has been effected with the antimonyl tartrate anion.[117] The substituted complexes $[Os(R\text{-}bipy)_3]^{2+}$ and $[Os(Rphen)_3]^{2+}$ are normally made from $[OsX_6]^{2-}$ (X = Cl, Br) and the ligand (*e.g.* 6-Mebipy,[119] 4,4′-Me_2bipy,[120,121] 5,5′-Me_2bipy,[121] 6,6′-Me_2bipy,[119], 2-Mephen and 2,9-Me_2phen;[119] brief mention has been made of the complexes with 5-Mephen,[122] 4,7-Me_2phen and sulfonated 4,7-Me_2phen).[123]

The $[Os(phen)_3]^{2+}$ cation is said to be formed in aqueous solution from $[OsCl_6]^{2-}$ and the ligand at pH 2.5–5.0; in strong HCl, $Os(phen)_2Cl_2$ is formed.[124a] Recently EPR data on $[Os(bipy)_3]^-$ and $[Os(bipy)_3]^+$ have been reported.[124b]

An X-ray crystal structure determination of $[Os(phen)_3](ClO_4)_2 \cdot H_2O$ shows that the Os—N distances in the cation lie between 2.066(7) and 2.082(7) Å.[125]

Spectroscopic properties: the complexes as photosensitizers. The emphasis of these volumes is on the chemistry of the coordination complexes and so we can provide only a summary and brief guide to recent work on the photophysics and photochemistry of the polypyridyl complexes. Although most bipy and phen complexes of osmium, like their ruthenium analogues, are highly luminescent, it is only comparatively recently that the appropriate spectra have been measured and attempts made to harness their properties for such important applications as the photodissociation of water. The lifetimes of low-lying metal-to-ligand charge transfer (MLCT) excited states of $[Os(LL)_3]^{2+}$ complexes are in general much shorter than those of their ruthenium(II) counterparts.[126,127] This probably arises from the greater spin–orbit coupling in osmium than in ruthenium complexes leading to enhanced radiative and non-radiative decay rates for triplet–singlet transitions which have the effect of shortening the lifetimes of excited states.[127] The electronic absorption and emission spectra and in most cases quantum yields and lifetimes of excited states have been measured for $[Os(bipy)_3]^{2+}$,[119,123,126–137,145] $[Os(bipy\text{-}d_8)_3]^{2+}$,[126, 134,136] $[Os(phen)_3]^{2+}$,[119,123,127–131,134–137,139,145], and the following $[Os(Rbipy)]^{2+}$ and $[Os(Rphen)_3]^{2+}$ species with Rbipy: 6-Mebipy,[119] 4,4′-Me_2bipy,[126,134,137] 6,6′-Me_2bipy,[119] 4,4′-Ph_2bipy;[126] with Rphen: 5-Clphen and 5-Mephen,[126,134] 5,6-Me_2phen,[126,134,137] 5-NO_2phen,[134] 2,9-Me_2phen,[119] 4,7-Ph_2phen;[126,137] also for $[Os(phen)_2(Ph_2phen)]^{2+}$ and $[Os(phen)_2\text{-}SO_2Phphen]^{2+}$.[123] In most cases aqueous media were used but in some micellar solutions of sodium lauryl sulfate were employed.[138,139] The positions of MLCT absorption bands for $[Os(bipy)_3]^{2+}$ are solvent-dependent, this dependence being interpreted on the basis of dielectric continuum theory.[140] The lifetime of excited $[Os(bipy\text{-}d_8]^{2+}$ is approximately three times that for $[Os(bipy)_3]^{2+}$, an effect ascribed to radiationless decay theory.[136] A parametric model, including the effects of spin–orbit coupling, has been developed for the MLCT excited state of $[Os(bipy)_3]^{2+}$.[133]

Quenching of excited states of $[Os(bipy)_3]^{2+}$ and $[Os(5,6\text{-}Me_2phen)_3]^{2+}$ by copper(II) complexes,[143] by iron aqua complexes,[142] by $[Co(phen)_3]^{3+}$, $[Ru(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$;[141] of $[Os(phen)_3]^{2+}$ by $HgCl_2$,[138] by iron aqua complexes[142] and by cobalt(III) species[144] has been studied. Such quenching by iron aqua species was also studied for $[Os(5,5'\text{-}Me_2bipy)_3]^{2+}$ and for $[Os(5\text{-}Clphen)_3]^{2+}$[142] and by O_2 for $[Os(bipy)_3]^{2+}$,[141,145] $[Os\ phen_3]^{2+}$ and $[Os\ phen_2]^{2=}$ (LL = Ph_2phen, SO_2Phphen)[145].

Circular dichroism spectra for $[Os(bipy)_3]^{2+}$ and $[Os(phen)_3]^{2+}$ have been reported.[146,147] Resonance Raman spectra of $[Os(bipy)_3]^{2+}$ have also recently been measured.[148]

For redox and electron-transfer properties of $[Os(bipy)_3]^{2+}$ and $[Os(phen)_3]^{2+}$ see p. 539.

Osmium(III). Oxidation of $[Os(bipy)_3]^{2+}$ with chlorine yields the violet $[Os(bipy)_3]^{3+}$ ion,[115,149] while the red $[Os(phen)_3]^{3+}$ is similarly prepared by oxidation of $[Os(phen)_3]^{2+}$.[149,150] Resolution of $[Os(phen_3)]^{3+}$ has been achieved by oxidation of the corresponding $[Os(phen)_3]^{2+}$ species.[150]

Spectroscopic properties. The electronic absorption spectra of $[Os(bipy)_3]^{3+}$[136,145,146,151] and of $[Os(phen)_3]^{3+}$[145,146] have been measured, as have their circular dichroism spectra[145–147] and also the spectra of $[Os(4,4'\text{-}Me_2bipy)_3]^{3+}$.[151] The lifetimes of the charge transfer (MLCT) excited states of

$[Os(bipy)_3]^{3+}$ and $[Os(phen)_3]^{3+}$ are some 10^5 to 10^6 times shorter than those of the MLCT states for the corresponding $[Os(bipy)_3]^{2+}$ and $[Os(phen)_3]^{2+}$ species (see also p. 538); it is thought that the excited states of the trivalent complexes are so short-lived that their lower energy ligand field states are too high to be populated. The lifetime for $[Os(bipy\text{-}d_8)_3]^{3+}$ is roughly twice that for $[Os(bipy)_3]^{3+}$[136] (see also p. 538). A brief mention has been made of the use of $[Os(bipy)_3]^{3+}$ for the non-catalytic photooxidation of water in the presence of cobalt(II) hydroxo complexes.[152] The rate of quenching of luminescence of $[Ru(bipy)_3]^{2+}$ by $[Os(bipy_3)]^{3+}$ is close to the diffusion-controlled limit.[153]

The ^1H NMR spectra of $[Os(bipy)_3]^{3+}$ and of $[Os(phen)_3]^{3+}$ have been measured and contact, pseudo-contact and Fermi-contact shifts studied;[118,149,153] the ESR spectra were also measured.[149] The ^{13}C resonance spectra of $[Os(bipy)_3]^{2+}$, $[Os(4,4\text{-}Cl_2bipy)_3]^{2+}$, $[Os(4,4\text{-}(OEt)_2bipy)_3]^{2+}$, $[Os(4\text{-}OMebipy)_3]^{2+}$ and $[Os(4\text{-}NMe_2bipy)_3]^{2+}$ have been recorded.[153] The resonance Raman spectrum of $[Os(bipy)_3]^{2+}$ has been measured.[118]

Redox and electron transfer properties of $[Os(LL)_3]^{3+}$. There have been a number of determinations of the $[Os(LL)_3]^{3+}/[Os(LL)_3]^{2+}$ couples.[40,156,157a] Values of E_0 of $+0.858$ V for $[Os(bipy)_3]^{3+}/[Os(bipy)_3]^{2+}$ in 0.01 M H_2SO_4 and $+0.855$ V in 0.1 M HCl have been given; for $[Os(phen)_3]^{3+}/[Os(phen)]^{2+}$ it is $+0.859$ V in 0.1 M HCl.[157a]

Polarographic studies show, in addition to oxidation waves for $[Os(bipy)_3]^{2+}$, several reduction waves;[130,158] this is also the case for $[Os(4,4'\text{-}Me_2bipy)_3]^{2+}$, $[Os(5,5'\text{-}Me_2bipy)_3]^{2+}$[121] and $[Os(phen)_3]^{2+}$. Recent cyclic voltammetry and coulombetry studies on $[Os(bipy)_3]^{2+}$ and $[Os(phen)_3]^{2+}$ in liquid SO_2 show successive one-electron oxidations to $[Os(LL)_3]^{3+}$ and $[Os(LL)_3]^{4+}$.[118] There is a small but real difference in the $Os^{III/II}$ redox potential for $[Os(phen)_3]^{2+}$ in aqueous and in non-aqueous sodium lauryl sulfate micellar solutions.[138] Correlations have been made between the oxidation potentials and charge-transfer transition frequencies in complexes $[M(LL)_3]^{2+}$ (Me = Fe, Ru, Os; LL = bipy, 4,4′-Me_2bipy, 5,5′-Me_2bipy).[159]

These high potentials make $[Os(LL)_3]^{3+}$ systems efficient one-electron oxidants, and most of these oxidations proceed *via* an outer-sphere process with second-order rate constants often close to the diffusion-controlled limits. Amongst those reactions which have been studied are $[Os(bipy)_3]^{3+}$ with $[Mo(CN)_8]^{4-}$, $[Mn(NO)(CN)_5]^{3-}$;[160] $[Fe(CN)_6]^{4-}$, $[W(CN)_8]^{4-}$;[161] $[Ru(bipy)_3]^{3+}$, $[IrCl_6]^{2-}$,[161] Fe(phen)$_2$(CN)$_2$;[161] $[Ru(H_2O)_6]^{2+}$;[162] $[Os(LL)_3]^{3+}$ with $[Os(LL)_3]^{2+}$, (LL = bipy, phen,[163] 4,4′-bipy[164]); $[Os(bipy)_3]^{2+}$ with $[Mo(CN)_8]^{3-}$,[165] $[Fe(bipy)_3]^{3+}$;[161] $[Os(phen)_3]^{2+}$ with $[Fe(bipy)_3]^{3+}$, $[Fe(phen)_3]^{3+}$ and $[Fe(4,4'\text{-}Me_2phen)_3]^{2+}$;[166] $[Os(LL)_3]^{2+}$ with $[Fe(LL)_3]^{3+}$ (LL = 4,4′-Me_2phen, 4,7-Me_2phen, 5,6-Me_2phen, 3,5,6,8-Me_4phen).[166]

Detailed kinetics of some of these and other processes have been studied, e.g. oxidation by $[Os(bipy)_3]^{3+}$ of I^-, SCN^-,[167] OH^-;[122] reaction of $[Os(LL)_3]^{3+}$ with OH^- to give O_2 (LL = bipy, phen, 5-Mephen, 4,4-Me_2bipy),[168] oxidation of ascorbic acid by $[Os(LL)_3]^{3+}$ (LL = bipy, 4,4′-Me_2bipy);[169] and the photoinduced electron transfer reactions of acidopentaamminecobalt(III) complexes with $[Os(bipy)_3]^{2+}$.[170] The outer-sphere oxidation of ascorbic acid by $[Os(bipy)_3]^{2+}$ incorporated in a coating on a graphite electrode has recently been reported.[170]

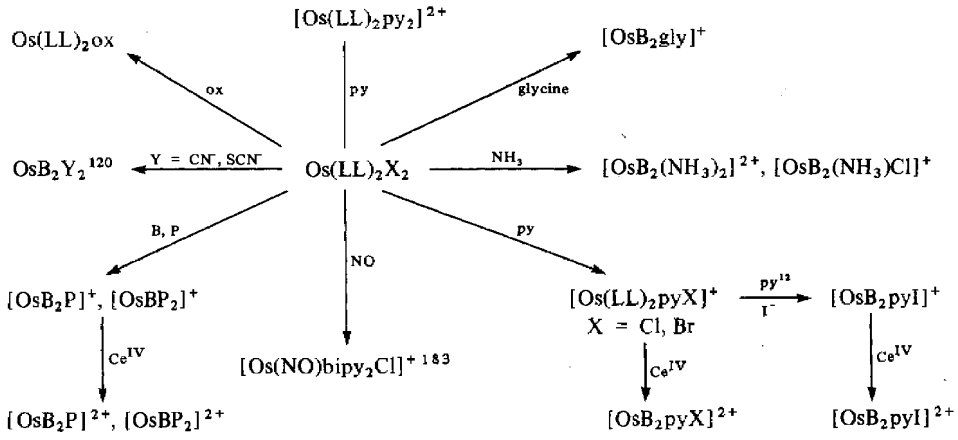
The thermodynamics of formation of outer-sphere complexes in solution, including those of osmium, have been reviewed.[172]

Osmium(IV). Evidence has been obtained from electrochemical oxidation of $[Os(bipy)_3]^{2+}$ and $[Os(phen)_3]^{2+}$ in liquid SO_2 for the existence of $[Os(phen)_3]^{4+}$. Magnetic susceptibility measurements show that $[Os(bipy)_3]^{4+}$ so generated is diamagnetic, and the ^1H NMR spectra and electrochemistry suggest that the oxidation is metal-centred for the bipy complex at least (whereas oxidation for the corresponding iron and ruthenium complexes is likely to be ligand-centred). Resonance Raman spectra of $[Os(bipy)_3]^{4+}$ are more complex than those of $[Os(bipy)_3]^{2+}$ or $[Os(bipy)_3]^{3+}$ suggesting that simple D_3 symmetry is not maintained: a Jahn–Teller splitting leading to inequivalent bond orders amongst the bipy rings was suggested as one explanation for this.[118]

(b) Substituted complexes $[Os(bipy)_xX_y]^{n+}$, $[Os(phen)_xX_y]^{n+}$, $[Os(Rbipy)_xX_y]^{n+}$, $[Os(Rphen)_xX_y]^{n+}$

Monomeric species. There are many of these, and for convenience and brevity we have illustrated the preparation of most of them schematically (see Schemes 3 and 4). The two main precursors are osmium(III) species: $[Os(LL)_2X_2]^-$ (LL = bipy, phen; X = Cl, Br, I), made by treatment of $K_2[OsX_6]$ with the ligands LL in dimethylformamide[173,174] (reduction with $Na_2S_2O_4$ gives $Os(LL)_2X_2$[173]); and $[Os(LL)Cl_4]^-$, made by heating the bipyridinium or phenanthrolinium salts $(LLH)_2[OsCl_6]$ to give $Os(LL)Cl_4$ which is then reduced with H_3PO_2 to $[Os(LL)Cl_4]^-$.[86]

Recently a number of complexes of the form *cis*-$[Os(LL)_2X_2]^{2+}$ (*e.g.* LL = bipy, phen; X = MeCN, $\frac{1}{2}(Ph_2PCH_2PPh_2)$, $\frac{1}{2}(Ph_2PCH{=}CHPPh_2)$, PMe_2Ph) have been made by reaction of



LL = coordinated bipy (B) or phen (P); X = Cl, Br, I. All from ref. 173 unless otherwise indicated.

Scheme 3 Reactions of $Os(LL)_2X_2$

cis-$Os(LL)_2Cl_2$ with X;[127] similar procedures are used to make complexes of the type $Os^{II}(LL)_2XX'$.[127,131,138] Some of these have been used as photosensitizers (see below).

Surface-enhanced Raman spectra (SERS) of $[Os(NH_3)_5bipy]^{3+}$ and its reduced form $[Os(NH_3)_5bipy]^{2+}$ have been measured.[91]

Electronic spectra and redox properties. The electronic absorption spectra of a number of osmium(II) bipy and phen complexes containing other ligands have been studied, *viz.* $[Os(bipy)_2LL]^{2+}$ (LL = phen, en, ox).[120] $Os(bipy)_2X_2$ (X = Cl,[120,172] Br, I,[120] CN[127]), $[Os(bipy)_2py_2]^{2+}$, $[Os(bipy)_2acac]^+$,[120] $[Os(bipy)_2X(py)]^+$ (X = Cl, Br, I),[173] $[Os(bipy)en_2]^{2+}$,[120] $[Os(bipy)en_2]^{2+}$,[151] $[Os(bipy)py_3X]^+$ (X = Cl, Br, I),[86] $Os(phen)_2ox$.[120] Circular dichroism spectra of $[Os(bipy)_2phen]^{2+}$ and of $[Os(bipy)phen_2]^{2+}$ have also been measured.[175]

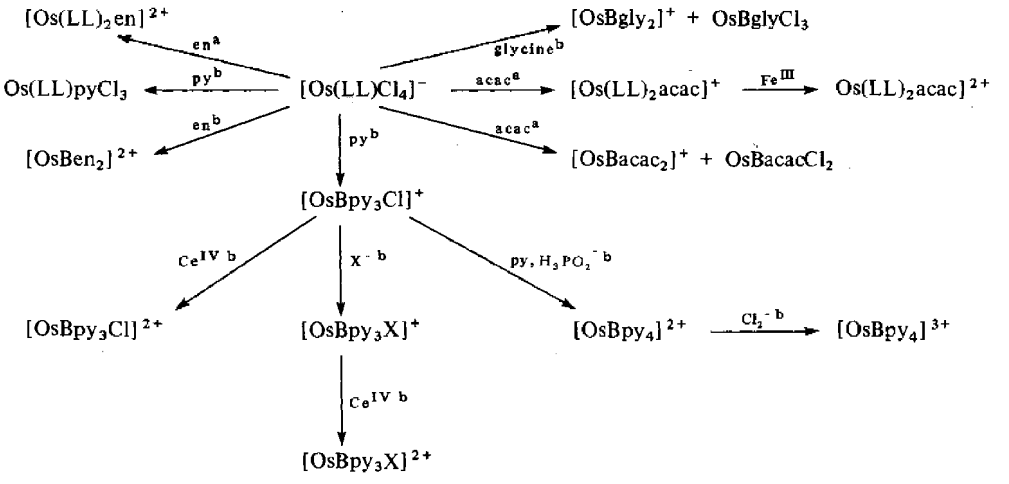
For electronic spectra of species in this category used as photosensitizers see below.

For redox properties of $[Os(bipy)_2acac]^+$ see p. 541. Polarographic data have been obtained for oxidation and reduction of $Os(bipy)_2X_2$ (X = Cl, Br) and $[Os(bipy)_2L_2]^{2+}$ (L = py, CN, ½en).[158] For electrochemical oxidation of *cis*-$[Os(bipy)_2(H_2O)_2]^{2+}$ see p. 000.[176] In $[Os(phen)_2(Ph_2PCH_2PPh_2)]^{2+}$, $[Os(phen)_2(cis\text{-}Ph_2PCH{=}CHPPh_2)]^{2+}$, $[Os(phen)_2(CO)Cl]^+$ and $[Os(bipy)_2(CNMe)_2]^{2+}$ there are small but real differences in the $Os^{II/III}$ couples in aqueous as compared with aqueous micellar sodium lauryl sulfate media.[138]

Spectroscopic properties: the complexes as photosensitizers. In general, substituted osmium polypyridyl complexes are more reactive electron transfer sensitizers than their ruthenium(II) counterparts and, more significantly, have longer MLCT excited state lifetimes than the corresponding $[Os(LL)_3]^{2+}$ species. The replacement of one of the polypyridyl ligands to enhance the MLCT state lifetime can be accomplished by choosing the ligand X (in $Os^{II}LLX_4$ or $Os^{II}LL_2X_2$) or X and X′ (in Os^{II} LL XX′) in such a way that its π-acceptor capacity controls the lifetime.[127] Species which have been studied in this way include $[Os(phen)py_4]^{2+}$, $[Os(bipy)diars_2]^{2+}$, $[Os(phen)_2py_2]^{2+}$, *cis*-$[Os(LL)_2(CO)Cl]^{2+}$;[131] *cis*-$[Os(LL)_2(CO)Cl]^{2+}$;[131] *cis*-$[Os(LL)_2(NCMe)_2]^{2+}$;[127,131,141] *cis*-$[Os(bipy)_2(NCMe)(PMePh_2)]^{2+}$;[131] *trans*-$[Os(phen)_2(PMe_2Ph)_2]^{2+}$;[127,131] $Os(bipy)_2(CN)_2$;[137] *trans*-$[Os(bipy)_2R_2]^{2+}$ (R = $PMePh_2$, PPh_3); *cis*-$[Os(bipy)_2(PMePh_2)_2]^{2+}$, $[Os(bipy)_2diars]^{2+}$;[131] $[Os(LL)_2dppm]^{2+}$;[127,131] $[Os(LL)_2dppe]^{2+}$;[130,131] $[Os(phen)_2dpp]^{2+}$, $[Os(phen)_2dape]^{2+}$,[131] $[OsL_2(cis\text{-}Ph_2PCH{=}CHPPh_2)_2]^{2+}$;[127,130,131,141] *trans*-$[Os(bipy)_2(trans\text{-}Ph_2PCH{=}CHPPh_2)]^{2+}$, $[Os(LL)_2dape]^{2+}$,[130] $[Os(bipy)_2(Ph_2PC_6H_4PPh_2)]^{2+}$ and $[Os(bipy)_2(Me_2SO)_2]$.[130,131]

The properties of a number of these photosensitizers have been studied in aqueous and sodium lauryl sulfate micellar media,[139] their electronic and emission spectra, electrochemistry and quenching of their luminescence by $HgCl_2$ in both media.[138] In some cases solvent dependence of MLCT excited state lifetimes has been observed, *e.g.* in $[Os(bipy)_2py_2]^{2+}$, $[Os(bipy)_2(NCMe)_2]^{2+}$ and $[Os(bipy)_2(Ph_2PC_6H_4PPh_2]^{2+}$. For these, dielectric continuum theory has been invoked to explain such solvent dependence, and it is necessary to assume that the excited electron in the excited state is localized on one ligand rather than delocalized over all three.[140]

There is a preliminary report of an excited state photoelectrochemical cell based on the reductive quenching of the MLCT excited state of $[Os(bipy)diars_2]^{2+}$ by $N(p\text{-}C_6H_4Br)_3$ in acidic, aerated acetonitrile: it produces H_2O_2 and bromine with high quantum efficiency.[177]



LL = coordinated bipy (B) or phen (P). [a]Ref. 173. [b]Ref. 86.

Scheme 4 Reactions of $[Os(LL)Cl_4]^-$

Osmium(III). The osmium(III) complexes $K[Os(LL)Cl_4]$ (LL = bipy, phen), made by reduction of $Os(LL)Cl_4$ with H_3PO_2 and KCl, are useful precursors for other osmium complexes (Scheme 4). In general, osmium(III) complexes in this category are made by oxidation of the corresponding osmium(II) species with chlorine or with cerium(IV) (see Schemes 3 and 4).

Magnetic susceptibilities of $[Os(bipy)_2Cl_2](ClO_4)$ were measured from 81 to 303 K (μ_{eff} is 1.61 BM at 81 K and 1.87 BM at 303 K); for $(Os(phen)_2Cl_2]ClO_4$ μ_{eff} is 1.61 BM at 85 K and 1.73 BM at 300.3 K.[101]

The complex $[Os(NH_3)_5(4,4'\text{-bipy})]^{3+}$ has been mentioned, and its resonance Raman and IR spectra recorded.[91]

Electronic spectra and redox properties. Electronic spectra have been measured for the following osmium(III) complexes: $[Os(bipy)_2phen]^{3+}$, $[Os(bipy)_2acac]^{2+}$,[151] $[Os(bipy)_2(py)X]^{2+}$ (X = Cl, Br, I),[171] $[Os(bipy)Cl_4]^-$, $[Os(bipy)acac_2]^+$,[151] $[Os(bipy)_2X_2]^+$ (X = Cl, Br, I)[151,172] $[Os(phen)_2X_2]^+$ (X = Br, I)[151,172] and $[Os(bipy)(py)_3X]^{2+}$ (X = Cl, Br, I).[86] Circular dichroism spectra were also measured for $[Os(bipy)_2phen]^{3+}$ and for $[Os(bipy)phen_2]^{3+}$.[175]

The redox potential for $[Os(bipy)_2acac]^{2+}/[Os(bipy)_2acac]^+$ is +0.1539 V as compared with +0.8836 V for $[Os(bipy)_3]^{3+}/[Os(bipy)_3]^{2+}$, showing graphically that osmium(III) is stablized relative to osmium(I) is stabilized relative to osmium(II) by replacement of one bipyridyl ligand.[151] For polarographic oxidation of $Os(bipy)_2Cl_2$, $Os(phen)_2X_2$ (X = Cl, Br), $[Os(bipy)_2LL_2]^{2+}$ (LL = py, ½en) and $[Os(bipy)_2(CN)_2]$ see p. 540, and of *cis*-$[Os(bipy)_2(OH)(H_2O)]^{2+}$, see below.[176] There are also electrochemical (redox) data for $[OsL_2(L—L)_2]^{2+}$ (L—L = $Ph_2P(CH_2)_2PPh_2$, $Ph_2PCH{=}CHPPh_2$, dape) and $[Os(biby)_2X_2]^{2+}$ (X = MeCN, DMSO).[130]

Osmium(IV), (V) and (VI). Heating $(LLH)_2[OsCl_6]$ to 300 °C gives $Os(LL)Cl_4$ (LL = bipy, phen).[86]

Cyclic voltammetry and differential pulse polarography of *cis*-$[Os(bipy)_2(H_2O)_2]^{2+}$ at pH 1.4 show oxidation to osmium(III) ($E_{\frac{1}{2}}$ + 0.16 V), followed by a two-electron step to osmium(V) ($E_{\frac{1}{2}}$ + 0.61 V) and the one-electron step to Os(VI) ($E_{\frac{1}{2}}$ 0.81 V); in the pH range 2.0–5.5 the Os^{III}–Os^V oxidation was resolved into two reversible one-electron waves showing an intermediacy of Os^{IV}. From pH dependence studies on the complexes the Os^{III} complex is likely to be *cis*-$[Os(bipy)_2(OH)(H_2O)]^{2+}$, the Os^{IV} probably *cis*-$[Os(bipy)_2O(H_2O)]^{2+}$ and the Os^V *cis*-$[Os(bipy)_2O(OH)]^{2+}$, while the Os(VI) species may be *cis*-$[OsO_2bipy]^{2+}$ (see also p. 584). As with the analogous ruthenium complexes the redox system occurs within a remarkably narrow potential window, with $\Delta E_{\frac{1}{2}}$ for $M^{VI/V}$ to $M^{III/II}$.[176,178]

Dimeric species. Reaction of *cis*-$Os(bipy)_2Cl_2$ and $Ph_2PCH_2PPh_2$ (dppm) gives $[Cl(bipy)_2Os^{II}(dppm)Os^{II}(bipy)_2Cl]^{2+}$ which, on oxidation with bromine, yields $[Cl(bipy)_2Os^{III}(dppm)Os^{III}(bipy)_2Cl]^{4+}$; mixture of these two dimers gives the weakly coupled mixed-valence species $[Cl(bipy)_2Os^{II}(dppm)Os^{III}(bipy)_2Cl]^{3+}$. The intervalence transitions were measured.[179] A $\mu\mu'$-hydroxo species $Os_2(OH)_2bipy_2Cl_4$ can be made by prolonged action of hot water on $K[Os(bipy)Cl_4]$.[86]

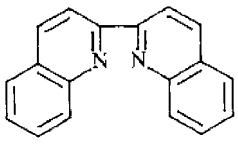
The near IR and magnetic circular dichroism spectra of $[(NH_3)_5Os(4,4'\text{-bipy})Os(NH_3)_5]^{6+}$ have

been recorded; exchange coupling is likely to occur in this species.[100] The mixed metal species $[OsRu(4,4'\text{-bipy})Cl_2(bipy)_4]^{2+}$ has been prepared from $[Os(4,4'\text{-bipy})Cl(bipy)_2]^{2+}$ and *cis*-$Ru(bipy)_2Cl_2$; cyclic voltammetric and electronic spectral data were recorded.[112]

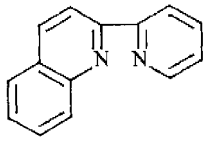
For the μ and $\mu\mu'$-imido complexes $[Os_2(NH)(bipy)_4]^{4+}$ and $Os_2(NH)_2(bipy)_4$ see p. 558.

Polymeric species. A field of rapidly growing interest is the reductive electrochemical polymerization of vinyl-containing ruthenium and osmium polypyridyl complexes. For osmium, the starting materials are *cis*-$[Os(bipy)_2L_2](PF_6)_2$ (L = 4-vinylpyridine ($n = 2$). *N*-(4-pyridyl)cinnamamide ($n = 1$)), made from the ligand and *cis*-$Os(bipy)_2(CO_3)$, and *cis*-$[Os(bipy)_2L'Cl](PF_6)$ (L' = 4-vinylpyridine and bis(4-pyridyl)ethylene), made from *cis*-$Os(bipy)_2Cl_2$ and the ligands. These species can be made to form polymeric fibres (homopolymer, copolymer or spatially segregated bilayer) and electrode coatings, and are electroactive because they contain a redox centre in each repeat unit.[180] The redox conduction of the film prepared from electrochemical polymerization of *cis*-$[Os(bipy)_2(N\text{-}(4\text{-pyridyl})\text{cinnamamide})_2]^{2+}$ has been measured by steady-state voltammetry and is close to the E° of the polymer Os^{III}/Os^{II} couple, involving the intermediacy of a mixed-valence state of the polymer.[181a–181c] Coated platinum electrodes using poly-$[Os(bipy)_2(4\text{-vinylpyridine})_2]^{3+}$ have been used to study the kinetically unfavourable oxidations of $Os(bipy)_2Cl_2$ and $[Os(Rphen)_3]^{2+}$ (Rphen = 5-Clphen, 5-NO_2phen and 3,4,7,8-Me_4phen).[182]

(*ii*) *Complexes of 2,2'-biquinoline and 2-(2'-pyridyl)quinoline*



biq



pq

These ligands are clearly related to 2,2'-bipyridyl. They react with $K_2[OsCl_6]$ in refluxing glycerol to give, after addition of sodium perchlorate, black crystals of $[Os(biq)_3](ClO_4)_2 \cdot H_2O$ and $[Os(pq)_3](ClO_4)_2 \cdot H_2O$. The absorption and luminescence spectra were measured; the difference between the energies of the π and π^* bands was less than that found for $[Os(bipy)_3]^{2+}$, as expected from the additional π-electron delocalization in these ligands.[190]

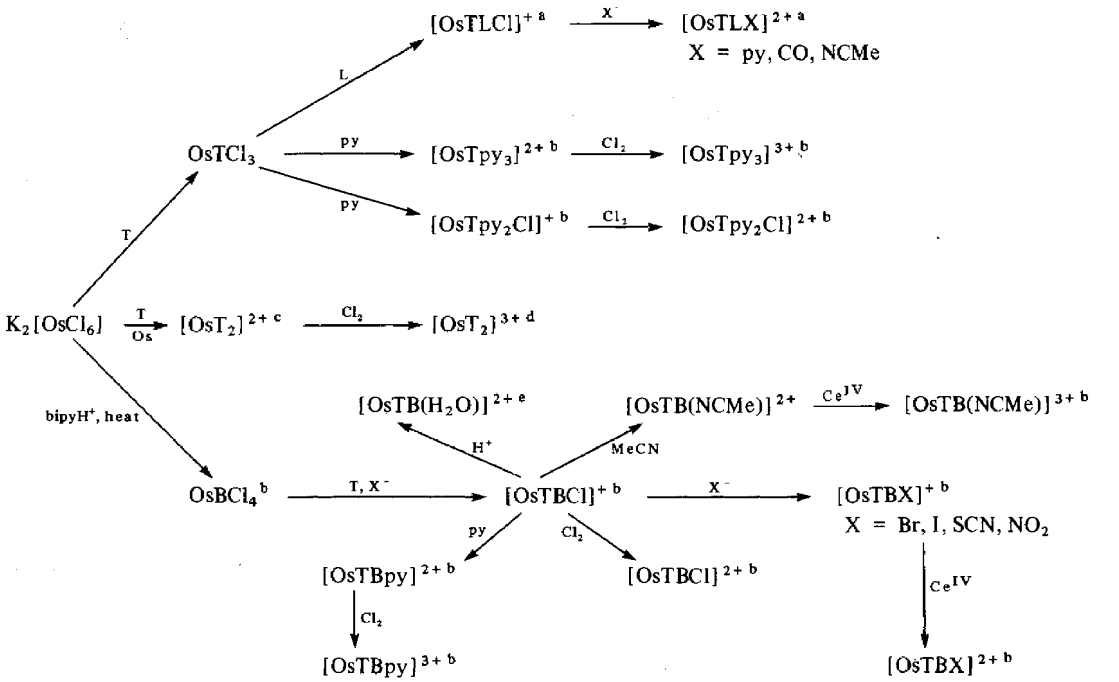
(*iii*) *Terpyridyl (terpy) complexes*

As a tridentate conjugated ligand this would be expected, like 2,2'-bipyridyl and 1,10-phenanthroline, to stabilize osmium(II) and this is indeed the case, with most of the reported complexes containing divalent osmium. The unsubstituted bis complex $[Os(terpy)_2]^{2+}$ is remarkably stable. It seems likely that terpyridyl complexes of osmium(II) are good candidates for further investigation as photosensitizers, having so far received less attention than the corresponding bipyridyl or phenanthroline species.

Osmium(II). The unsubstituted complex $[Os(terpy)_2]Cl_2$ was made in 1937 by fusion of the ligand with a mixture of $K_2[OsCl_6]$ and osmium metal, and is singularly unreactive towards either acids or alkalis.[191] The green chloride gives a red solution. For its redox and spectroscopic properties see below.

A number of substituted terpyridyl complexes have been reported, most of them made by Dwyer and co-workers in 1964.[192] Preparative routes are given in Scheme 5.

Spectroscopic properties: the complexes as photosensitizers. Spectroscopic (absorption and emission spectra),[128,138,187] redox and photochemical properties (MLCT lifetimes, quenching of the Os^{II} MLCT states by $HgCl_2$) have been studied for $[Os(terpy)_2]^{2+}$ in aqueous and in aqueous sodium lauryl sulfate micellar solutions;[138] the solvent accessibility of the complexes correlates with the hydrophilicity of the ligands (other osmium(II) bipy and phen complexes were included in the study).[139] Absolute luminescence, quantum yields and lifetimes of $[Os(terpy)_2]I_2$ in an alcohol glass at 77 K have been determined.[129] The complexes $[Os(terpy)LCl]^+$, $[Os(terpy)LR]^{2+}$ (L = *cis*-$Ph_2PCH{=}CHPPh_2$, dppm; R = py, MeCN, CO), $[Os(terpy)dppm_2]^{2+}$ and $[Os(terpy)(dppm)Cl]^+$ are the first complexes observed to exhibit strong MLCT-based luminescence in fluid solutions at room temperatures;[193] the absorption and emission spectra of $[Os(terpy)(dppm)Cl]^+$ and of



[a] Ref. 193. [b] Ref. 192. [c] Ref. 191. [d] Ref. 189. [e] Ref. 195. [f] Ref. 86.

T = terpyridyl; B = bipyridyl; L = dppm, *cis* $Ph_2PCH{=}CHPPh_2$

Scheme 5 Preparation of terpyridyl complexes

$[Os(terpy)(cis\text{-}Ph_2PCH{=}CHPPh_2)(NCMe)]^{2+}$ at room temperature have been measured.[193]

The ^1H resonance spectrum of $[Os(terpy)_2]^{2+}$ has been recorded.[188]

Redox properties. For oxidation of $[Os(terpy)_2]^{2+}$ see below. Treatment of $[Os(terpy)(bipy)Cl]^+$ with trifluoromethanesulfonic acid gives $[H_2O{-}Os(terpy)bipy]^{2+}$, and it has been shown by electrochemical and spectrophotometric studies (equation 1) to be a member of the series (at pH 7).[194]

$$[H_2O{-}Os(terpy)(bipy)]^{2+} \underset{c^-}{\overset{-e^-}{\rightleftharpoons}} [H_2O{-}Os(terpy)(bipy)]^{3+} \underset{2H^+,c^-}{\overset{-2H^+,-e^-}{\rightleftharpoons}} [O{=}Os(terpy)(bipy)]^{2+} \quad (1)$$

The hydroxo species $[HO{-}Os(terpy)bipy]^{2+}$ can also be made by oxidation of $[H_2O{-}Os(terpy)bipy]^{2+}$.[194] Redox properties of $[Os(terpy)LCl]^+$, $[Os(terpy)LR]^{2+}$ (L = *cis*-$Ph_2PCH{=}CHPPh_2$, R = py, CO, MeCN), $[Os(terpy)dppm\ Cl]^+$ and of $[Os(terpy)dppm]^{2+}$ have been measured.[193]

At pH 13, electrochemical reduction of $[OsO_2(terpy)(OH)]^+$ yields $[Os(terpy)O_2(OH)]$, at pH 7, $[Os(terpy)(OH)_3]$, and $[Os(terpy)(H_2O)_3]^{3+}$ at pH 1.[194]

Osmium(III). The unsubstituted $[Os(terpy)_2]^{3+}$ ion can be obtained as a sparingly soluble green perchlorate by oxidation of $[Os(terpy)_2]^{2+}$ with Cl_2.[189]

A number of substituted osmium(III) terpyridyl complexes are known (see Scheme 5).

Redox properties. In general $[M(terpy)_2]^{3+}$ ions are less stable than the corresponding $[M(bipy)_3]^{3+}$ species (M = Os, Ru, Fe); in 0.1 M H_2SO_4 the $[M(terpy)_2]^{3+}/[M(terpy)_2]^{2+}$ potentials are +0.951 (Os), +1.28 (Ru) and +1.08 V (Fe).[189] Although the colour change from green ($[Os(terpy)_2]^{3+}$) to red $[Os(terpy)_2]^{2+}$ is in principle favourable for redox titration purposes the instability of the tripositive complex renders it unsuitable for the purpose.[189] The complex $[HO{-}Os(terpy)bipy]^{2+}$ is obtained by electrochemical reduction of $[O{=}Os(terpy)bipy]^{2+}$ or oxidation of $[HO{-}Os(terpy)bipy]^+$ or $[H_2O{-}Os(terpy)bipy]^{2+}$,[195] and electrochemical reduction of $[OsO_2(terpy)(OH)]^+$ gives $[Os(terpy)(H_2O)_3]^{3+}$ at pH 1, and $Os(terpy)(OH)_3$ at pH 7.[194]

Osmium(IV), (V) and (VI). The existence of $[O{=}Os^{IV}(terpy)bipy]^{2+}$ has already been mentioned (see above).[195] Irreversible electrochemical oxidation of this occurs from pH 1 to 12 at +1.05 V, and the initial product is thought to be $[O{=}Os^{V}(terpy)bipy]^{3+}$ which then loses a bipyridyl ligand and undergoes a further one-electron oxidation to $[OsO_2(terpy)(OH)]^+$. At pH 13.5 a

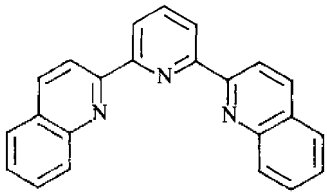
two-electron, one-proton reduction wave is observed (equation 2), while at lower pH the intermediate is $[HO—Os^{III}(terpy)bipy]^{2+}$.[195]

$$[O{=}Os(terpy)(bipy)]^{2+} \underset{-2e^-,H^+}{\overset{2e^-,H^+}{\rightleftharpoons}} [HO—Os^{II}(terpy)(bipy)]^{+} \quad (2)$$

The osmium(V) species $OsO_2(terpy)(OH)$ has also been detected electrochemically at pH 13, from reduction of $[OsO_2(terpy)(OH)]^+$; the latter is made from *trans*-$K_2[OsO_2(OH)_4]$ and terpy.[194]
Binuclear complexes. For $[Os_2O(terpy)_2(bipy)_2]^{4+}$ and $[Os_2O(terpy)_2(bipy)_2]^{2+}$, see p. 594.[192]

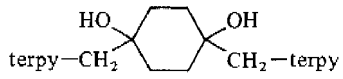
(*iv*) *Complexes of ligands related to terpyridyl*

(*a*) *Bis(2,6-di(2′-quinolyl)pyridine) complexes.* This ligand (dqp) is closely related to terpyridyl. It reacts with $K_2[OsCl_6]$ in refluxing ethylene glycol to give, after addition of sodium perchlorate, the dark purple $[Os(dqp)_2](ClO_4)_2$. The absorption and luminescence spectra were recorded; the luminescence spectrum is similar to that of $[Os(terpy)_2]^{2+}$, the benzo substitution in the dpq complex producing a slight red shift in some of the bands.[196]



dqp

(*b*) *(−)-Tubocurarine complexes.* Reaction of $Os(bipy)(Cl_4$ with (−)-tubocurarine (L) gave the binuclear complex $[Cl(bipy)Os(LL)Os(LL)Os(bipy)Cl]^{2+}$, dichloro-$\mu$-[1,4-cyclohexylbis(2,2′,2″-terpyridyl)-6″-methyl)-1,4-diol]bis(2,2′-pyridyl)diosmium(II) dichloride. The two coordinated chloro ligands can be replaced by pyridine on refluxing this with the complex in aqueous solution. The former complex has potent curariform biological activity[190] and there are possible applications as stains for electron microscopy for the complexes.[197]



L

46.4.5 Nitrosyl Complexes

As with nitrido and oxo complexes we shall consider osmium nitrosyl (NO) complexes as a group, irrespective of the nature of the other ligands present. Just as N^{3-} and O^{2-} are strong π donors and tend to dominate the overall bonding in their complexes, so too the nitrosyl ligand—certainly in its NO^+ guise—is a very effective π acceptor and is the dominant ligand in complexes containing it.

The normal classification of material by oxidation state is inappropriate for nitrosyl complexes because the oxidation state concept is very much a formalism for them. Instead we shall use the generally accepted $[M(NO)_x]^{n+}$ classification in which x is the number of coordinated NO groups and n the number of metal d electrons, the latter being calculated on the basis that NO^+ is the coordinated moiety. As will be apparent, osmium complexes within each such category do in fact show considerable similarities of structure and reactivity, and also with their ruthenium analogues. Osmium is unusual in forming an $[M(NO)]^5$ type of complex.

Since a far greater number of nitrosyl complexes have been isolated for ruthenium than for any other metal it might be expected that osmium should rival ruthenium in this respect. There seems no reason why this should not be so, and the present disparity in numbers of known osmium and ruthenium nitrosyls simply suggests that much less work has been carried out on the osmium systems.

There are several recent and comprehensive reviews on metal nitrosyl complexes which give good coverage to the osmium complexes;[198] a review on ruthenium nitrosyl complexes is particularly

useful for discussion of bonding aspects and is relevant to the analogous osmium nitrosyls.[199] The reader is also referred to the appropriate section in 'Comprehensive Organometallic Chemistry'.[200]

46.4.5.1 [Os(NO)]^5 and [Os(NO)]^6 complexes

(i) [Os(NO)]^5

The recently reported $[Os(NO)Cl_5]^-$ anion, isolated as NO^+ and PPh_3Me^+ salts from the reaction of Os_2Cl_{10} with nitric oxide, is a rare example of a 17-electron nitrosyl system.[201]

(ii) [Os(NO)]^6

This is the most numerous class and encompasses the widest diversity of coligands. Most of the known species are octahedral and in all the Os—N—O linkage is likely to be essentially linear with the nitrosyl moiety bound as NO^+, giving the osmium a formal oxidation state of II. An interesting area, well investigated for $[Ru(NO)]^6$ species but less studied for the osmium analogues, is that of the attack of the NO group in some of the species by nucleophiles.[199] As with the corresponding ruthenium complexes the N—O stretching frequency (ν_{NO}) lies between 1800 and 1900 cm^{-1} for most of the complexes which behave in this way.

Table 10 Representative Osmium Nitrosyl Complexes

Complex	*Colour*	ν_{NO} *(cm^{-1})*	*Spectroscopic and other properties*
[Os(NO)]^5			
$(PPh_3Me)[Os(NO)Cl_5]$	Golden-yellow	1823	IR[201]
[Os(NO)]^6			
$K_2[Os(NO)F_5]$	Red	1824	IR, EL,[202] NMR,[203] X-ray[235]
$K_2[Os(NO)Cl_5]$[a]	Red	1866,1854	Raman,[208,212] IR[208,212,250]
$(PPh_3Me)[Os(NO)Cl_4]$		1822	IR, X-ray[210]
$[Os(NO)(NH_3)_5]Cl_3$	Yellow	1891, 1870	Raman, IR,[251] ^{14}N NMR[252]
trans-$[Os(NO)(OH)(NH_3)_4]Br_2$[b]	Yellow	1808	IR,[214] X-ray[236]
trans-$[Os(NO)(NH_2)(NH_3)_4]Cl_2$	Yellow	1785, 1764	IR,[214] ^{15}N NMR[253]
$Os(NO)(OH)(NH_3)_2Br_2$		1807	IR,[216] X-ray[236,238]
$[Os(NO)(H_2O)(NH_3)_3Cl]Br_2$		1873	IR,[215] X-ray[236]
trans-$[Os(NO)(OH)(NO_2)_4]$-$[Ru(NO)(OH)(NH_3)_4]$	Yellow	1832	Raman,[208] IR,[208] X-ray,[237] ^{14}N NMR[252]
$K_2[Os(NO)(CN)_5]$	Red	1905	IR,[222,223] ESCA,[36] Mössbauer[184]
$(PPh_4)_2[Os(NO)(NCS)_5]$	Orange	1825	IR, UV/vis[234]
$Os(NO)Cl_3(PPh_3)_2$[c]	Brown	1850	IR[226]
$Os(NO)(NO_2)Cl_2(PMe_2Ph)_2$	Orange	1852	IR[254]
$[Os(NO)(CO)Cl_2(PPh_3)_2]BF_4$	Yellow	1899	IR, X-ray[233]
$Os(NO)(ON{=}C(O)CF_3)(OCOCF_3)(PPh_3)_2$	Orange	1820	IR, ^{19}F NMR,[224] X-ray[224,229]
$Os(NO)(HgCl)Cl_2(PPh_3)_2$	Yellow	1820	IR, X-ray[230]
cis-$[Os(NO)diars_2Cl]Cl_2 \cdot H_2O$	Yellow	1861, 1837	IR, ^1H NMR[205]
trans-$Os(NO)diars_2Cl]Cl_2 \cdot H_2O$[b]	Yellow	1872	IR, ^1H NMR[205]
$(Ph_4P)_2[Os(NO)Cl_3(SnCl_3)_2]$	Red	1805	IR, X-ray[231]
Os(NO)F(OEP)[d]	Deep red	1770	IR, UV/vis,[232] MS[232]
[Os(NO)]^7			
$[Os(NO)Cl_2(PPh_3)_2]$	Yellow	1845	IR[213]
[Os(NO)]^8			
$Os(NO)H(PPh_3)_3$	Brown	1635	IR, ^1H NMR[239]
$Os(NO)Cl(AsPh_3)_2$	Green	1795	IR[227]
$[Os(NO)(CO)_2(PPh_3)_2]ClO_4 \cdot CH_2Cl_2$	Orange	1750	IR, X-ray[244]
$[Os(NO)(CO)(CN(p\text{-tosyl}))(PPh_3)_2]ClO_4$	Orange	1700	IR, X-ray[245]
[Os(NO)$_2$]^8			
$[Os(NO)_2(OH)(PPh_3)_2]BF_4$	Orange	1842, 1632	IR,[247] X-ray[246]
[Os(NO)]^9			
Os(NO)dppe	Brown	1417	IR, CV[243]
[Os(NO)$_2$]^{10}			
$Os(NO)_2(PPh_3)_2 \cdot \frac{1}{2}C_6H_6$	Deep red	1665, 1616	IR, ESCA, X-ray,[248] ^{15}N NMR[253]
$Os(NO)_2(OEP)$	Red	1778, 1500	IR,[232] UV/vis,[232,255] ^1H NMR[255]

[a] Bromo and iodo complexes also known. [b] Chloro, bromo and iodo complexes also known. [c] Bromo and iodo complexes known, also with arsine and stibine ligands. [d] Methoxo and fluoro complexes also known.[232]

In Table 10 we list representative complexes of the $[Os(NO)]^6$ type; for conciseness we normally give only the potassium salts of anionic species and chloride salts of cationic complexes; for neutral species involving halide ligands we concentrate on the chloro examples. The coverage is representative but not comprehensive.

(*iii*) *Nitrosyl halides*

All four $[Os(NO)X_5]^{2-}$ species are now known. The fluoro complex is made from $[OsX_6]^{2-}$ with excess KHF_2,[202] the reaction yielding $[Os(NO)F_nX_{4-n}]^{2-}$ (X = Cl, Br);[203] stereochemistries of the products were deduced from ^{19}F NMR data.[203] For X-ray data see p. 548. The other nitrosylpentahalogeno complexes have been established longer. They are prepared from salts of *trans*-$[Os(NO)(OH)(NO_2)_4]^{2-}$ together with an excess of HX (X = Cl, Br, I);[204] another useful method is to react salts of $[OsX_6]^{2-}$ with nitrite ion and HX (X = Cl, Br, I).[205] Other salts for which relatively recent preparations have been given include $(NH_4)_2[Os(NO)X_5]$ (X = Cl, Br, I),[206,207] $Rb_2[Os(NO)X_5]$[207] and $Cs_2[Os(NO)X_5]$ (X = Cl,[205,207,208] Br,[205,208] I[205]).

More recently the preparation of $(NO)_2[Os(NO)Cl_5]$ from Os_2Cl_{10} and CCl_3NO has been reported; when the complex is heated to 170 °C the polymeric chloro-bridged species $[Os(NO)Cl_3]_n$ is formed.[209] With PPh_3Me^+, $(NO)_2[Os(NO)Cl_5]$ gives $(PPh_3Me)[Os(NO)Cl_4]$;[210] the X-ray crystal structure of this is described below on p. 548.

Studies on the ^{19}F NMR of $[Os(NO)F_5]^{2-}$ in aqueous solution provide evidence for the existence in such solutions of $[Os(NO)F_4(H_2O)]^-$, *cis*- and *trans*-$Os(NO)F_3(H_2O)_2$, $[Os(NO)F_2(H_2O)_3]^+$ and $[Os(NO)F(H_2O)_4]^{2+}$.[203] The hydrolytic behaviour of $[Os(NO)X_5]^{2-}$ (X = Cl, Br, I) indicates that NO^+ is exerting a *trans* effect in these complexes; the stability decreases from X = Cl to X = I, and the product is initially *trans*-$[Os(NO)(H_2O)X_4]^-$ which then deprotonates to *trans*-$[Os(NO)(OH)X_4]^-$.[211] Irradiation of $[Os(NO)X_5]^{2-}$ (X = Cl, Br) with mercury light gives $[Os(H_2O)X_5]^{2-}$.[211]

There are comprehensive Raman and IR spectroscopic data on $[Os(NO)X_5]^{2-}$ salts (X = Cl, Br, I).[208,212]

(*iv*) *Nitrosyl ammine and nitro complexes*

The chloride, bromide and iodide of $[Os(NO)(NH_3)_5]^{3+}$ are made from the corresponding $[Os(NH_3)_6]^{3+}$ salts and nitric oxide,[56] and X-ray data are available for *trans*-$[Os(NO)(OH)(NH_3)_4]Br_2$, $Os(NO)(OH)(NH_3)Br_2$ and $[Os(NO)(H_2O)(NH_3)_3Cl]Br_2$ (see p. 548). There does appear to be a *trans* influence of the NO group in that the protons in the *trans* ammine group in $[Os(NO)(NH_3)_5]^{3+}$ are acidic; treatment with base yields *trans*-$[Os(NO)(NH_2)(NH_3)_4]^{2+}$, and another product of the reaction is *trans*-$[Os(NO)(OH)(NH_3)_4]^{2+}$. This will react with HX (X = Cl, Br, I) to give *trans*-$[Os(NO)X(NH_3)_4]^{2+}$.[214]

Other substituted ammine complexes such as *cis*-$Os(NO)X_3(NH_3)_2$,$[Os(NO)X(NH_3)_3(H_2)]^{2+}$ (X = Cl, Br, I),[215] *trans*-$Os(NO)Cl_3(NH_3)_2$,[215] $Os(NO)X_2(NH_3)_2(OH)$ (X = Cl, Br,[216,217] I,[217] NO_2,[216] Bu, OAc[217]), *cis*-$Os(NO)Br_2(NH_3)_2Cl$[217] and $[Os(NO)(OH)_2(NH_3)_2(H_2O)]^+$[215] have been prepared.

Salts of '$[Os(NO_2)_5]^{2-}$' have long been reported in the literature[218] with sodium, potassium, ammonium, magnesium, calcium, strontium and barium cations, but the anion in these salts is now known to be *trans*-$[Os(NO)(OH)(NO_2)_4]^{2-}$.[219] The potassium salt, made from $[OsCl_6]^{2-}$ and excess KNO_2,[218] is a useful starting material for other nitrosyl complexes since the NO_2^- groups are easily displaced. The X-ray crystal structure of the anion is discussed below (p. 548). The anion exhibits a complex hydrolytic behaviour, alledgedly in accordance with the *trans* effect of the nitrosyl ligand.[220]

(*v*) *Nitrosyl azido and cyano complexes*

The complex $(Ph_4P)_2[Os(NO)(N_3)_5]$ is made from OsO_4, hydroxylamine and sodium azide. It has an unusually low ν_{N-O} frequency (1715 cm^{-1}). With *o*-phenanthroline, $Os(NO)(N_3)_3$ phen is produced. The red nitrosylpentacyano complex $K_2[Os(NO)(CN)_5]\cdot 2H_2O$ can be made from *trans*-$K_2[OsO_2(OH)_4]$, KCN and nitric acid.[222] The salt, which is unusual in that it is barely soluble in water, is like the nitroprusside ion in that it gives a coloured complex with sulfide ion.[222] With nitric acid it gives a number of species such as *trans*-$[Os(NO)(H_2O)(CN)_4]^-$ and $Os(NO)(CN)_3\cdot 2H_2O$.[223]

For nitrosylcyano complexes with thiourea see p. 608.

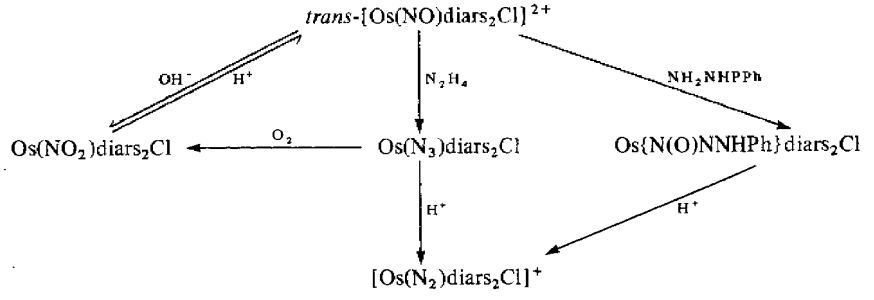
(*vi*) *Nitrosyl complexes with monoteriary phosphines, arsines and stibines*

The hydrido complexes $Os(NO)H(PPh_3)_2(OCOR)_2$ ($R = CF_3$, C_2F_5) have been prepared by reaction of RCO_2H with $Os(NO)H(PPh_3)_3$,[224] and a similar reaction will yield $[Os(NO)H_2(COCF_3)][H(OCOCF_3)_2]$;[224] $Os(NO)_2(PPh_3)_2$ and RCO_2H also give $[Os(NO)H(PPh_3)_2(OCOR)_2]^+$.[225] The neutral hydride is thought to have a structure in which the hydride is *trans* to the nitrosyl group and the monodentate carboxylato ligands are *trans* to each other.[224]

Reaction of $[OsX_6]^{2-}$ (X = Cl, Br) with MNTS (*N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide) in the presence of PR_3 (R = Bu^n, Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, X = Cl, R = Ph, X = Br) yields $Os(NO)X_3(PR_3)_2$;[226] other methods involve reaction of ClNO or BrNO with $OsCl_3$ in the presence of PPh_3[227] or reaction of $[OsX_6]^{2-}$ with nitric oxide and LPh_3 (L = As, Sb), this latter reaction giving $Os(NO)X_3(AsPh_3)_2$, and $Os(NO)X_3(SbPh_3)_2$ (X = Cl, Br, I).[228] The structure for all these species is likely to be that of Figure 12, with NO replacing NS.[226,227]

(*vii*) *With chelating arsines*

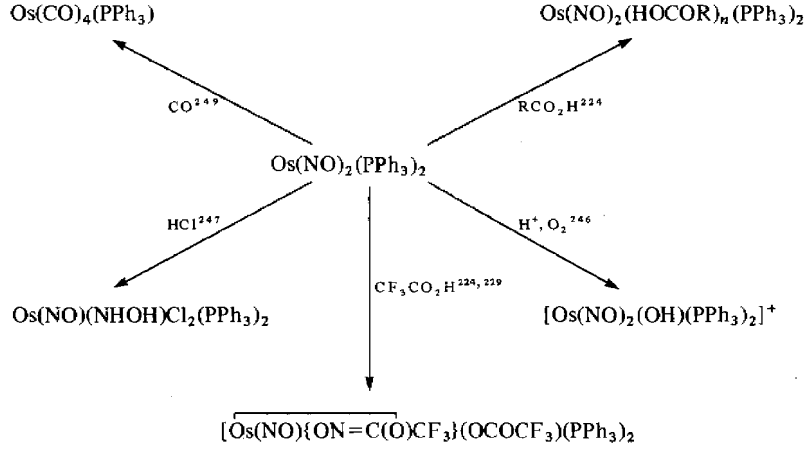
Reaction of $Cs_2[Os(NO)X_5]$ and *o*-phenylenebis(dimethylarsine) (diars) gave *trans*-$[Os(NO)(diars)_2X]^{2+}$ (X = Cl, Br, I); *cis*-$[Os(NO)(diars)_2Cl]Cl_2$ is made from $Os(N_3)(diars)_2Cl$ and HCl.[205] The systems provide a good illustration of attack by nucleophiles upon a coordinated nitrosyl group which has some electrophilic properties by virtue of the residual positive charge on its nitrogen atom (see Scheme 6).[205]



Scheme 6 Reactions of nitrosyl diarsine complexes[205]

(*viii*) *Miscellaneous [Os(NO)]^6 species*

Reaction of $Os(NO)_2(PPh_3)_2$ with trifluoroacetic acid gives $Os(NO)(ON{=}C(O)CF_3)(OCOCF_3)(PPh_3)$ (Scheme 7), in which both coordinated trifluoroacetate and *O,O'*-trifluoroacetato-hydroxamate ligands are present (see p. 548 for X-ray structure).[224,229] There are also two metal–metal-bonded species for which X-ray crystal structures have been determined (p. 548):



Scheme 7 Reactions of $Os(NO)_2(PPh_3)_2$

$Os(NO)Cl_2(HgCl)(PPh_3)_2$, made by the action of $HgCl_2$ on $Os(NO)(CO)Cl(PPh_3)_2$,[230] and $(Ph_4P)_2[Os(NO)Cl_3(SnCl_3)_2]$, obtained from $[Os(NO)Cl_3]_n$ and $PPh_4(SnCl_3)$.[231]

Octaethylporphyrin (OEP) affords three osmium nitrosyl complexes: Os(NO)(OMe)(OEP), made from Os(CO)py(OEP), methanol and NO;[232] with HF this yields Os(NO)F(OEP)[232] and with $HClO_4$ it gives $Os(NO)(OClO_3)(OEP)$.[255] The nitrosyl carbonyl complex $[Os(NO)(CO)Cl_2(PPh_3)_2]BF_4$ is made by reaction of $Os(NO)(CO)Cl(PPh_3)_2$ with HBF_4.[223]

Two complexes have recently been reported with polypyridyl ligands: $[Os(NO)(bipy)_2Cl](PF_6)_2$, obtained from $Os(bipy)_2Cl_2$ and nitric oxide with PF_6^-, and $[Os(NO)(terpy)(bipy)](PF_6)_3$, obtained from $[Os(terpy)(bipy)Cl]^+$, NO_2^- and HPF_6. The acid—base equilibrium (equation 3) was compared with that for the ruthenium analogue, and potentials for the $[Os(NO)(bipy)_2Cl]^{3+/2+}$ and $[Os(NO)(terpy)(bipy)]^{3+/2+}$ couples were compared with those for the ruthenium analogues. The differences were attributed to greater Os—NO electronic mixing and greater spin–orbit coupling at the osmium atom.[183]

$$[Os(NO)(terpy)(bipy)]^{3+} + 2OH^- \rightleftharpoons [Os(NO_2)(terpy)(bipy)]^+ + H_2O \quad (3)$$

Reaction of OsO_4 with hydroxylamine hydrochloride and thiocyanate ion gives $[Os(NO)(NCS)_5]^{2-}$; with 2,2′-bipyridyl or 1,10-phenanthroline (LL), $Os(NO)(NCS)_3(LL)$ complexes are formed.[234]

(*ix*) *X-Ray structural studies on* $[Os(NO)]^6$ *complexes*

Until fairly recently there were relatively few structural studies on osmium nitrosyls, but of late the field has received a fair amount of attention. As expected[198] the Os—N—O moiety is essentially linear in all these complexes, and most of them have octahedral coordination. There is evidence for a slight lengthening of the bond *trans* to the nitrosyl (there are more examples of this in the more extensively studied structural chemistry of $[Ru(NO)]^6$ complexes[198]); it has been noted that such *trans* bond shortening is a feature of octahedral $[M(NO)]^6$ complexes where the N—O stretching frequency exceeds 1800 cm^{-1},[198] as it does in all these compounds.

Structurally the simplest complexes to be studied are those of $NaK[Os(NO)F_5]\cdot H_2O$ (I) and $Cs_2[Os(NO)F_5]\cdot H_2O$ (II). For these the Os—N and N—O distances are 1.707(9) and 1.18(1) (I) and 1.675(16) and 1.21(2) Å (II); the mean Os—F (*cis*) distances are 1.991(8) and 1.986(9) Å in (I) and (II) respectively, while the corresponding Os—F (*trans*) distances are 1.966(5) and 1.947(5) Å. The Os—N—O angles are essentially linear in (I) and (II).[235] This slight shortening of *trans* ligands as against *cis* has been noted and discussed for $[Ru(NO)]^6$ complexes of the form $[Ru(NO)X_5]^{n-}$.[198] In $[PPh_3Me][Os(NO)Cl_4]$ there is no *trans* ligand, the structure being square-based pyramidal with an axial nitrosyl ligand (Os—N 1.89(2), N—O 0.90(3) Å, Os—N—O 177(2)°); the four equatorial ligands are at a mean distance of 2.36(1) Å from the osmium, with a mean N—Os—Cl angle of 93.8°.[210] The N—O distance of 0.90(3) Å is described as 'unnaturally short'[210] and presumably would have a more normal value if low-temperature data were obtained. It seems likely that the five-coordinate structure is a consequence of the presence of the large organic cation rather than a marked *trans* effect of the nitrosyl ligand; often 1:1 complexes rather than 2:1 cation:anion species are preferentially formed when the cation is bulky as is the case here (a similar instance is found for $[OsNX_4]^-$ species (X = Cl, Br, I); see p. 560).

Two other structures of highly symmetrical species are those for *trans*-$[Os(NO)(OH)(NH_3)_4]Br_2$ (III)[236] and the anion in *trans,trans*-$[Os(NO)(OH)(NO_2)_4][Ru(NO)(OH)(NH_3)_4]\cdot\frac{1}{2}H_2O$ (IV).[237] Here the Os—N and N—O distances are respectively 1.74(2) and 1.19(3) (III) and 1.762 and 1.15 Å (II);

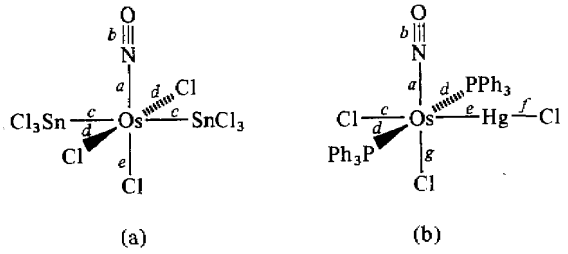


Figure 5 Structures of $[Os(NO)]^6$ complexes containing metal–metal bonds[230,23]

the Os—N—O angles are 176(1)° (I) and 175.7(8)° (IV). The *trans* Os—O (OH) distances are 2.01(2) (III) and 1.943 Å (IV), while the *cis* Os—N distances have mean values of 2.14 and 2.09 Å for (III) and (IV) respectively. For the *trans*-$[Ru(NO)(OH)(NH_3)_4]^{2+}$ cation in (IV) the Ru—N and N—O distances are 1.739 and 1.16 Å with the Ru—N—O angle at 178.4°, the *trans* Ru—O (OH) distance 1.956 Å and the mean *cis* Ru—N (NH_3) distance 2.115 Å.[237]

In $(PPh_4)_2[Os(NO)Cl_3(SnCl_3)_2]$ (V) the *trans* Os—Cl distance (*e*) is slightly but significantly shorter than that for the *cis* (*d*) (Figure 5a) (a = 1.734(2), b = 1.166(21), mean c = 2.648(1), mean d = 2.380(1), e = 2.364(4) Å; Os—N—O angle 180°).[231]

Another species containing a metal–metal bond is $Os(NO)(HgCl)Cl_2(PPh_3)_2$ (VI) (Figure 5b); this is an X-ray structure determination of rather lower accuracy (a = 1.79(4), b = 1.03(6), c = 2.42(2), mean d = 2.39(2), e = 2.577(6), f = 2.39(3), g = 2.37(2) Å, Os—N—O 180°).[230]

In $Os(NO)(OH)(NH_3)_3Br_2$[236,238] (VII) (Figure 6a) and $Os(NO)(H_2O)(NH_3)_3Cl$[236,238] (VIII) (Figure 6b) the bond distances are: a = 1.75(1), b = 1.16(2), mean c = 2.533, mean d = 2.11 e = 1.98(1) Å (for VII) a = 1.64(3), b = 1.21(4), c = 2.343(15), mean d = 2.34, e = 2.13(3).[236]

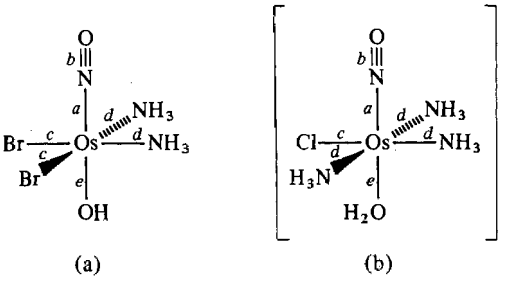


Figure 6 Structures of nitrosyl ammine complexes

In the unusual structure of $\overline{Os(NO)(ON{=}C(O)CF_3)}(OCOCF_3)(PPh_3)_2$ (VII) (Figure 7) the metal—ligand bond lengths between *cis* and *trans* ligands are the most marked for any $[Os(NO)]^6$ complexes, though the nature of the ligands is admittedly different. The coordinating atom *trans* to the nitrosyl group is from an *O,O'*-trifluoroacetohydroxamate ligand. In this a = 1.726(7), b = 1.209(9), c = 2.115(6), d = 2.063(6), e = 2.406(2), f = 2.375(2) and g = 1.984(6) Å[224] (see also ref. 229).

In $[Os(NO)(CO)Cl_2(PPh_3)_2]BF_4$ there is disorder between the carbonyl and nitrosyl ligands; the phosphine groups are *trans* to each other.[233]

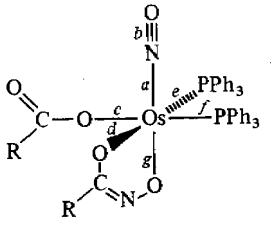


Figure 7 Structure of $\overline{Os(NO)(ON{=}C(O)CF_3)}(OCOCF_3)(PPh_3)_2$[299]

46.4.5.2 $[Os(NO)]^7$, $[Os(NO)]^8$ and $[Os(NO)_2]^8$ complexes

(i) $[Os(NO)]^7$ species

It has recently been shown that $OsCl_2(PPh_3)_3$ reacts with ONCl and ONBr to give $Os(NO)XCl(PPh_3)_2$ (X = Cl, Br); EPR data were reported.[213]

(ii)) $[Os(NO)]^8$ species

There are a few of these, all with phosphines or arsines and with six- or five-coordination. The ν_{NO} frequency in general for these lies lower than for those in $[Os(NO)]^6$ species, in the range 1650–1800 cm^{-1}.

The hydrides $Os(NO)H(PR_3)_3$ ($PR_3 = PMePh_2$, PPh_3) are made from $Os(NO)Cl_3(PR_3)_2$ with ethanolic KOH; the $PMePh_2$ complex may be fluxional in solution.[239]

The complex $Os(NO)Cl(PPh_3)_3$ is made from $Os(NO)(CO)Cl(PPh_3)_2$ in CH_2Cl_2 and air (a procedure giving $Os(NO)Cl(CO_3)(PPh_3)_2$) followed by treatment with PPh_3.[240] It reacts with diazomethane to give the carbene complex $Os(NO)(CH_2)Cl(PPh_3)_2$;[240,241] with the halogenated diazoalkane $IC(N_2)CO_2Et$ an aldoxime dinitrogen complex $Os(N_2)Cl_2\{N(OH)CHCO_2Et\}(PPh_3)_2$ is formed (see p. 556).[241]

The complexes $Os(NO)(NO_2)(PPh_3)_2$ and $Os(NO)Cl(AsPh_3)_2$, made from $OsCl_3$ and, in the first instance, N_2O_3 and PPh_3 and in the second ClNO and $AsPh_3$,[227] have unusually high ν_{NO} frequencies for $[OsNO]^8$ species (Table 10).

The complex $[Os(NO)(dppe)_2]^+$, made from $[Os(NO)(CO)_2(PPh_3)_2]BPh_4$ and dppe[242] will undergo electrochemical reduction in two reversible one-electron steps to give $[Os(NO)]^9$ and $[Os(NO)]^{10}$ species (equation 4).[243]

	$[Os(NO)dppe_2]^{2+}$	$\rightleftharpoons$	$Os(NO)dppe_2$	$\rightleftharpoons$	$[Os(NO)dppe_2]^-$	
$E_{\frac{1}{2}}$ (*vs.* SCE)		−1.33 V		−1.95 V		
ν_{NO} (cm^{-1})	1673		1417		1420	
Colour	Red		Brown		Red	(4)

There are also a number of nitrosyl carbonyl complexes in this category, a representative selection of which are listed in Table 10; general types are $[Os(NO)(CO)PR_3)_2]^+$, $[Os(NO)(CO)_2(PR_3)_2]^+$ and $Os(NO)(CO)X(PR_3)_2$.[242]

In the latter category the chloro complex $Os(NO)(CO)Cl(PPh_3)_2$ is of particular interest. It is made by reaction of $Os(CO)ClH(PPh_3)_3$ with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, and reacts with HCl to give $Os(HNO)Cl_2(CO)(PMe_3)_2$. This latter complex was shown by X-ray crystal structure analysis to contain an N-bonded HNO group,[233] so presumably electrophilic attack on NO has occurred, possibly *via* a 20-electron intermediate such as $[Os(NO)(CO)Cl_2(PPh_3)_2]^-$. Another curious feature of $Os(NO)(CO)Cl(PPh_3)_2$ is that it exhibits *three* ν_{N-O} frequencies (at 1769, 1629 and 1560 cm^{-1}, shifting to 1742, 1598 and 1534 cm^{-1} on ^{15}N substitution). It has been surmised that the solid may contain more than one form of the species in dynamic equilibrium.[233] Another carbonyl complex of interest is $Os(NO)H(CO)(PPh_3)_2$, made from $Os(NO)(CO)Cl(PPh_3)_2$ and $NaBPh_4$;[244] its X-ray crystal structure has been obtained (see p. 551, Figure 9).

(*iii*) *X-Ray studies on $[Os(NO)]^8$ species*

Two studies have been reported, both on carbonyl nitrosyl complexes, but in both cases disorder prevented the NO and CO groups being distinguished. In $[Os(NO)(CO)_2(PPh_3)_2]ClO_4$, made from $Os(NO)H(CO)(PPh_3)_2$ and $HClO_4$, the trigonal bipyramidal structure has apical phosphine ligands,[244] and this is also the case[245] in $[Os(NO)(CO)(CNR)(PPh_3)_2]ClO_4$[245] (R = *p*-tolyl). In both, however, the Os—N—O unit is essentially linear.

(*iv*) *$[Os(NO)_2]^8$ species*

Few of these are known but there is an X-ray study on one, $[Os(NO)_2(OH)(PPh_3)_2]PF_6$, made by reaction of oxygen with $Os(NO)_2(PPh_3)_2$ in the presence of HPF_6. The crystal structure shows a distorted square-based pyramidal structure in which there is a bent apical nitrosyl group (Os—N—O = 133.6(1)°) and a linear basal nitrosyl ligand (Os—N—O = 177.6(12)°). The bond distances are: a = 1.86(1), b = 1.17(2), mean c = 2.434, d = 1.935(8). e = 1.63(1), f = 1.24(2) Å (Figure 8).[246] The two stretching frequencies of 1842 and 1632 cm^{-1}, recorded for the BF_4^- salt,[247] presumably correspond to those of the linear and bent moieties.

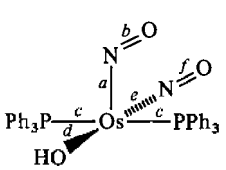


Figure 8 Structure of $[Os(NO)_2(OH)(PPh_3)_2]PF_6$[246]

There is a brief report of $[Os(NO)_2(OCOR)(PPh_3]_2OCOR$ ($R = CF_3$, C_2F_5);[225] reaction of $Os(NO)_2(PPh_3)_2$ with strong non-coordinating acids gives $[Os(NO)_2H(PPh_3)_2]^+$, but the species was not isolated.[247]

46.4.5.3 *[Os(NO)]^9, [Os(NO)]^{10} and [Os(NO)$_2$]^{10} complexes*

(i) [Os(NO)]^9 species

The only example would appear to be $Os(NO)dppe_2$, made by electrochemical reduction of $[Os(NO)dppe_2]^+$ (see below). It is dark brown and very air-sensitive, giving an ESR spectrum which seems to suggest that the unpaired electron is largely localized on the NO ligand. The very low ν_{NO} frequency of 1417 cm^{-1} suggests that it may contain a bent Os—N—O unit.[243]

(ii) [Os(NO)]^{10} species

Again the only example seems to be $[Os(NO)dppe_2]^-$ (see below);[243] the low ν_{N-O} frequency of 1420 cm^{-1} would be consistent with the presence of a bent Os—N—O ligand, equivalent to a coordinated NO^- group (a linear Os—N—O group would give an electron count of 20).

(iii) [Os(NO)$_2$]^{10} species

A very interesting complex is $Os(NO)_2(PPh_3)_2 \cdot \frac{1}{2}C_6H_6$, made from reaction of $Os(NO)H(PPh_3)_3$ with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide; it crystallizes as a hemisolvate from benzene.[248] The X-ray crystal structure shows it to be tetrahedral (N—Os—N = 139.1(3)°, P—Os—P = 103.51(6)°) with two essentially linear Os—N—O moieties (Os—N = 1.771(6) and 1.776(7) Å, N—O = 1.195(8) and 1.211(7) Å; Os—N—O = 178.7(7)° and 174.1(6)°).[248] Although the Os—N—O fragments are linear the ν_{N-O} frequencies are low, as is to be expected in view of competition for π-electron density on the osmium atom. ESCA studies suggest that the effective oxidation state of the osmium lies between II and 0.[248]

The hydrido complex $[Os(NO)_2H(PPh_3)_2]^+$ is formed by the action of strong acids on the complex, and the reaction of CO under pressure with this gives $Os(CO)_4(PPh_3)$, with CO_2 and N_2 as by-products.[249]

Another interesting complex in this category is $Os(NO)_2(OEP)$ (OEP = octaethylporphyrin), made from nitric oxide and Os(CO)py(OEP);[232,255] one ν_{NO} frequency is very low (1500 cm^{-1}) so that one Os—N—O group could be substantially more bent than the other.

46.4.6 Complex of HNO

As mentioned above (p. 550), reaction of $Os(NO)Cl(CO)(PPh_3)_2$ with HCl gives $Os(NHO)Cl_2(CO)(PPh_3)_2$, a rare example of a complex containing a coordinated HNO group. The X-ray crystal structure (Figure 9) has been determined. In this $a = 1.915(6)$, $b = 1.193(7)$, $c = 0.94(11)$, $d = 2.440(2)$, mean $e = 2.434(2)$, $f = 1.899(8)$, $g = 2.429(2)$ Å; ONH = 99(7)°. The ν_{NO} frequency is at 1410 cm^{-1}, shifting to 1393 cm^{-1} in ^{15}N substitution.[233]

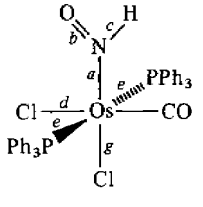


Figure 9 Structure of $Os(HNO)(CO)(PPh_3)_2$[233]

46.4.7 Diazenido Complexes

Reaction of $Os(PPh_3)_3X_3$, LiX and aryldiazonium salts $(RN_2)BF_4$ (X = Cl, R = Ph;[256] X = Br, R = Ph,[256] *p*-C_6H_4Me[257a]) gives $Os(N_2R)(PPh_3)_2X_3$, with the likely structure shown in Figure 10.[256]

ESCA data on $[Os(N_2\text{-}p\text{-}MeC_6H_4)(PPh_3)_2]Br_3$ and on $Os(N_2\text{-}p\text{-}C_6H_4F)(PPh_3)_2Br_3$ suggest that, in the latter case at least, the spectra could distinguish between the two nitrogen atoms.[257b]

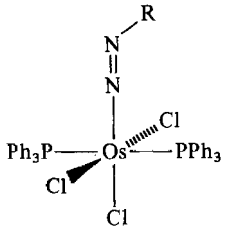


Figure 10 Likely structure of $Os(N_2R)(PPh_3)_2X_3$[256]

46.4.8 Thionitrosyl (NS) Complexes

Despite the relatively large number and diversity of osmium nitrosyl complexes (p. 544) rather few thionitrosyls of the metal are known (see Table 11), and this is clearly a field of potential interest for further study. It should in particular be possible to obtain complexes containing a bent Os—N—S moiety. It is interesting to note that two examples of bis-thionitrosyls, a very rare class of complex, are known with osmium. The formal oxidation state of the metal in all its known thionitrosyls is II with the exception of $(Ph_4As)[Os(NS)Cl_5]$; again by analogy with the nitrosyl chemistry, osmium(0) thionitrosyls might be expected to exist.

Table 11 Thionitrosyl and NSU Complexes

Complex	*Colour*	*M.p. (°C)*	ν_N	*Spectroscopic and other properties*
$Os(NS)_2Cl_4$	Brown		1388, 1326, 1308	IR[261]
$(Ph_4As)[Os(NS)_2Cl\cdot Cl_4]$	Black		1298, 1215	IR, X-ray[261]
$Os(NS)Cl_3(PMe_2Ph)_2$	Green		1285	IR, ^{1}H NMR[262]
$Os(NS)Cl_3(PPh_3)_2$	Green	145–147	1294,[263] 1290[160]	IR,[263] X-ray[260]
$Os(NS)Cl_3(AsPh_3)_2$	Green	150–152	1282,[262] 1290[263]	IR[262,263]
$Os(NS)Cl_3$bipy	Green		1282	IR[262]
$Os(NS)Cl_3py_2$	Green-yellow		1284	IR[262]
$(Ph_4P)_2[Os(NS)(NCS)_5)$	Green-brown		1270	IR[265]
$(Ph_4As)[Os(NS)Cl_5]$	Black		1340	IR[201]
trans-$(Ph_4P)[Os(NS)Cl_4(H_2O)]$	Green		1285	IR, X-ray[264]

Preparative routes involve sulfur abstraction by osmium(VI) nitrido complexes from S_2Cl_2 or SCN^-, though the mechanisms of these reactions are not clear; reaction of halides with $(NSCl)_3$ has also been used.

The subject of thionitrosyl coordination chemistry has recently been reviewed.[258] The NS ligand has been variously described as being a better σ donor and π acceptor[258,259] or a better σ donor but a worse π acceptor than NO.[260]

46.4.8.1 Osmium(II)

(i) Bis thionitrosyls

Two such species are known for osmium. Reaction of Os_2Cl_{10} with $(NSCl)_3$ yields $Os(NSCl)_2Cl_4$ (see p. 553 below) which, with $(Ph_4As)Cl$, gives $(Ph_4As)[Os(NS)_2Cl\cdot Cl_4]$. The X-ray crystal structure of this (Figure 11) shows the thionitrosyl ligands to be *cis* and deviating only slightly from linearity (the OsNS angle is 169.5°). A loosely bound chloro ligand is attached to the sulfur end of an NS group (S···Cl 2.28 Å); in the crystal it is statistically belongs to both sulfur atoms with an occupation probability of 50%.

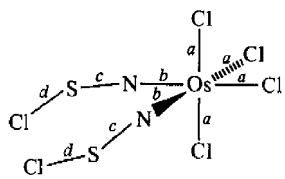


Figure 11 Structure of the anion in $(Ph_4As)[Os(NS)_2Cl\cdot Cl_4]$[261]

The Os—N distance of 1.83 Å is comparable with those found in nitrosyl complexes and is clearly indicative of a measure of back-bonding, but there is no apparent *trans* shortening or lengthening effect on the opposite chloro ligands.[261] In the structure, $a = 2.36$, mean $b = 1.835$, mean $c = 1.46$, mean $d = 2.27$ Å.[261]

Reaction of this material with $GaCl_3$ gave the neutral bis thionitrosyl, $Os(NS)_2Cl_4$. The IR spectrum suggests a *cis* configuration for the complex; although three bands appear in the N—S stretching region (1388, 1326 and 1308 cm^{-1}) the latter two are thought to arise from Fermi resonance. The Os—N stretches appear at 385 and 369 cm^{-1}, though the latter could be an Os—Cl mode.[261]

(*ii*) *Mono thionitrosyls*

The first thionitrosyl complexes of osmium, $Os(NS)X_3L_2$ (X = Cl, Br, L = $AsPh_3$, PMe_2Ph, $\frac{1}{2}$bipy), were made by Chatt by reacting the nitrido species $OsNX_3L_2$ with S_2Cl_2; the pyridine complex $Os(NS)Cl_3py_2$ was made from $[OsNCl_4]^-$, pyridine and S_2Cl_2.[262] The mechanism of the reaction is not at all clear. In the corresponding reaction of S_2Cl_2 with rhenium(V) nitrido complexes to give thionitrosyls it was postulated that nucleophilic attack of S_2Cl_2 at the sulfur atom by the nitrido ligand might occur, but this is less likely for osmium since osmium(VI) nitrido complexes exhibit pronounced electrophilicity at the N^{3-} ligand (p. 561). The ^{1}H NMR spectra of $Os(NS)Cl_3(PMe_2Ph)_2$ was measured and a structure proposed akin to that of Figure 12, with *trans* virtually coupled phosphorus ligands; the complexes are diamagnetic and probably contain linear Os—N—S units.[262]

Reaction of '$OsCl_3$' with $(NSCl)_3$ and L (L = PPh_3, $AsPh_3$) yields $Os(NS)Cl_3L_2$;[263] an improved method for preparation of $Os(NS)Cl_3(PPh_3)_2$ involves the use of $OsCl_2(PPh_3)_3$ and $(NSCl)_3$. The X-ray crystal structure (Figure 12) shows the Os—N—S unit to be linear;[259] the structure is analogous to those for $Os(NO)Cl_3(PPh_3)_2$ and $OsNCl_3(PPh_3)_2$, with $a = 1.779(9)$, $b = 1.503(10)$, mean $c = 2.459(2)$, mean $d = 2.387(3)$ and $e = 2.399(3)$ Å.

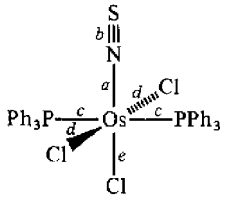


Figure 12 Structure of $Os(NS)Cl_3(PPh_3)_2$

A number of other monothionitrosyls of osmium have recently been reported. Reaction of Os_2Cl_{10} and $(NSCl)_3$ in the presence of $POCl_3$ yields $Os(NS)Cl_4(POCl)_3$ from which $(Ph_4As)[Os(NS)Cl_5]$ can be made,[201] and the latter can also be obtained, as the PPh_4^+ salt, from '$Os(NS)Cl_3$' (a polymer, made from $OsCl_3$, $(NSCl)_3$ and PPh_4^+[264]). Recrystallization of this from water–methanol gives *trans*-$(PPh_4)[Os(NS)Cl_4(H_2O)]$, the structure having been elucidated by X-ray diffraction (Os—N = 1.731(4), N—S = 1.514(5) Å with an Os—N—S angle of 174.9(3)°; Os—O = 2.165(4), mean Os—Cl = 2.356 Å, mean N—Os—Cl = 94.8°).[264]

46.4.8.2 Osmium(III)

Another example of sulfur abstraction by an osmium nitrido complex occurs in the reaction of $[OsNCl_4]^-$ with $(PPh_4)NCS$ to give $(Ph_4P)_2[Os(NS)(NCS)_5]$, in which the thiocyanate groups are thought to be bonded to the metal *via* nitrogen.[265] For reactions of the complex see Scheme 10, p. 563.

46.4.9 Complex of NSCl

The precursor species for $[Os(NS)_2Cl\cdot Cl_4]^-$ and $Os(NS)_2Cl_4$ is $Os(NSCl)_2Cl_4$, a black material obtained by reaction of $(NSCl)_3$ with Os_2Cl_{10}. It is thought to have a *cis* configuration with bent N—S—Cl ligands bound to osmium *via* the nitrogen atoms. The N—S stretching vibration appears at 1335 cm^{-1}.[261]

46.4.10 Dinitrogen (N_2) Complexes

The most stable osmium dinitrogen complexes occur with the metal in the divalent state, as would be expected for this π-acidic ligand, but a substantial number of osmium(III) dinitrogen complexes are also known, though these tend to lose N_2 readily and are kinetically much more labile than their osmium(II) counterparts (see Table 12). A few bis(dinitrogen) species are known with a *cis* arrangement of N_2 ligands; such a configuration is best adapted to π-acidic ligands, there being less competition for the metal t_{2g} orbitals than for the *trans* arrangement. An interesting feature of osmium dinitrogen chemistry is the formation of bridged species containing the Os—N≡N—Os and Os—N≡N—Ru units with apparently mixed oxidation states in some cases.

Dinitrogen complexes of osmium are often synthetically useful because the N_2 group can easily be displaced, especially by acids.

Table 12 Dinitrogen Complexes

Complex	*Colour*	ν_N (cm^{-1})	*Spectroscopic and other properties*[d]
$[Os(N_2)(NH_3)_5]Cl_2$	Yellow	2022	IR,[266,285,286] Raman,[285] UV/vis,[266,268] ESCA[282] X-ray[267]
cis-$[Os(N_2)(NH_3)_4(CO)]Cl_2$	White	2179	IR, UV/vis[64]
cis-$[Os(N_2)(NH_3)_4I]^+$		2028	IR, UV/vis, CV[64]
$Os(N_2)(NH_3)_3Cl_2$[a]		2003	IR, CV[64]
cis-$[Os(N_2)_2(NH_3)_4]Cl_2$	Yellow	2167, 2104	IR[266,271], Raman,[271] UV/vis,[64,266,268] CV,[64] ESCA[287]
cis-$[Os(N_2)_2(NH_3)_3L]Cl_2$[b]	Yellow	2180, 2125	IR, UV/vis[98]
$[Os(N_2)(NH_3)_5]Br_3$	Yellow	2212	IR, CV[64]
cis-$[Os(N_2)NH_3)_4Cl_2]^+$[a]			UV/vis, CV[64]
trans-$[Os(N_2)(NH_3)_3Cl_2]^+$[a]		2205	IR, UV/vis, CV[64]
mer-$Os(N_2)(NH_3)_2I_3$			UV/vis[64]
$Os(N_2)(PMe_2Ph)_3Cl(SC_6F_5)$	White	2080	IR, X-ray[279]
$Os(N_2)\{N(OH)CHCO_2Et\}(PPh_3)_2Cl_2$			IR, X-ray[241]
mer-$Os(N_2)(PMe_2Ph)_3Cl_2$[c]		2092	IR,[273,274] ^{1}H NMR,[273] ^{15}N NMR[288]
mer-$Os(NNAlMe_3)(PMe_2Ph)_3Cl_2$		1979	IR, ^{1}H NMR,[274] ^{15}N NMR[288]
$Os(N_2)(PMe_2Ph)_2HCl$		2059	IR, ^{1}H NMR,[277] ^{15}N NMR[288]
$Os(N_2)(PEtPh_2)_3H_2$	Brown	2085	IR, ^{1}H NMR[276]
$[Os(N_2)diars_2Cl]Cl$	Yellow	2080	IR, ^{1}H NMR[205]
$[Os_2(N_2)(NH_3)_{10}]Br_5$	Green	2015	IR, Raman, UV/vis,[280] CV,[280a,280b] MCD[280b]
$[Os_2(N_2)(NH_3)_{10}]^{4+}$			UV/vis, CV[280]
$[Os_2(N_2)(NH_3)_8Cl_2]Cl_5$	Green	1999	Raman, UV/vis,[281] ESCA[282,287]
$[Os_2(N_2)(NH_3)_8(CO)_2]Cl_4 \cdot H_2O$	White	2125	IR, Raman, CV[70]
$[Os_2(N_2)(NH_3)_{10}]Cl_6$	Blue		X-Ray[282b]

[a] Bromo and iodo complexes and *trans* isomers also known. [b] L = isonicotinamide. [c] Also PEt_3, $PMePh_2$, PEt_2Ph, $PEtPh_2$, PPr^n_2Ph, $AsMe_2Ph$, $AsEt_2Ph$. [d] CV = cyclic vultammetry.

46.4.10.1 Mononuclear complexes

(*i*) *Complexes with ammines and amines*

(*a*) *Osmium(II)*. Reaction of salts of $[OsCl_6]^{2-}$ with hydrazine hydrate gives $[Os(N_2)(NH_3)_5)^{2+}$;[266] chloride, bromide, iodide, perchlorate, tetrafluoroborate and tetraphenylborate salts have been made. The X-ray crystal structure (Figure 13) shows the *trans* ammine group to be slightly but significantly longer than the *cis* ammines ($a = 1.842(13)$, $b = 1.12(2)$, mean $c = 2.144$, $d = 2.151(15)$ Å) while the Os—N (N_2) distance is clearly much shorter than that expected for a pure σ bond.[267] Photolytic studies on the ion have been reported,[268] and γ irradiation of the complex in methanol generates the OH radical which reacts to give $[Os(N_2)(NH_2)(NH_3)_4]^{2+}$.[269] It is possible that a *trans* effect may be operative such that the *trans* ammine protons become more acidic.

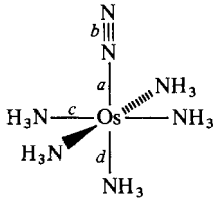


Figure 13 Structure of $[Os(N_2)(NH_3)_5]Cl_2$[267]

Reaction of $[Os(NH_3)_5CO]^{2+}$ with HCl and KNO_2 yields *cis*-$[Os(N_2)(NH_3)_4(CO)]^{2+}$; *trans*-$[Os(N_2)(NH_3)_4I]^+$ is made from $[Os(N_2)(NH_3)_5]^{2+}$ and chromium(II) with HCl and KNO_2. A slightly different route was used to make *cis*- and *trans*-$Os(N_2)(NH_3)_3X_2$ (X = Cl, Br, I), by treating *cis*- or *trans*-$[Os(NH_3)_4X_2]^+$ in HCl with KNO_2 and NO.[64] Complexes of the form *cis*-$[Os(N_2)(NH_3)_4L]^{2+}$ (L = isonicotinic acid, isonicotinamide, pyrazine and substituted pyrazines) are considered on p. 535.

There are also bis(dinitrogen) complexes of osmium(II). The first to be made was *cis*-$[Os(N_2)_2(NH_3)_4]^{2+}$ by a 'diazotization' procedure using $[Os(N_2)(NH_3)_5]^{2+}$ and nitrite in acid solution.[270] Vibrational spectroscopic data using both ^2H and ^{15}N substitution were obtained for the salts,[271] which are useful precursors for other osmium complexes involving pyrazine (see p. 536). A similar preparative procedure involving $[Os(N_2)(NH_3)_4L]^{2+}$ gives *cis*-$[Os(N_2)_2(NH_3)_3L]^{2+}$ (L = isonicotinamide).[98]

(*b*) *Osmium(III)*. Oxidation of $[Os(N_2)(NH_3)_5]^{2+}$ with cerium(IV) gives $[Os(N_2)(NH_3)_5]^{3+}$,[64] and the existence of the ion has also been shown electrochemically.[272] Reaction of *cis*- or *trans*-$[Os(NH_3)_4X_2]^+$ with HCl and NO_2^- gives *cis*- and *trans*-$[Os(N_2)(NH_3)_4X_2]^+$ respectively (X = Cl, Br, I), and a similar method yields *cis*- and *trans*-$[Os(N_2)(NH_3)_3X_2]^+$ from *mer*- and *fac*-$Os(NH_3)_3X_3$ (X = Cl, Br, I); *mer*-$Os(N_2)(NH_3)_2I_3$ was also prepared.[64]

The kinetic stability of these osmium(III) dinitrogen species, while less than that of the corresponding osmium(II) complexes, is far greater than for ruthenium(III) and shows that osmium(III) is capable of effective metal-to-ligand donation. Comparisons have been drawn, using electrochemical and pK_a data, between the π-acceptor properties of CO and N_2 in $[OsL(NH_3)_5]^{3+}$ (L = CO, N_2) species;[64] thus, the pK_a of $[Os(NH_3)_6]^{3+}$ lies near 16,[55] that of $[Os(N_2)(NH_3)_5]^{3+}$ is about 6.6 and that of $[Os(NH_3)_5CO]^{3+}$ about 2.5. In basic solution osmium(III) dinitrogen complexes disproportionate to an osmium(II) dinitrogen species and osmium(VI).[64]

(*c*) *Osmium(IV)*. The possibility of the existence of $[Os(N_2)(NH_3)_5]^{4+}$ has been mentioned.[272]

(*ii*) *Complexes with phosphines and arsines*

(*a*) *Osmium(II)*. These are summarized in Table 12. Most of them take the form *mer*-$(Os(N_2)(LR_3)_3X_2$ and are made by the reaction of $Os(LR_3)_3X_3$ in THF with zinc amalgam and N_2 under pressure.[273] The dinitrogen ligand has weakly basic properties; thus, *mer*-$Os(N_2)(PEt_2Ph)_3Cl_2$ forms a weak complex $Os(NNAlMe_3)(PEt_2Ph)_3Cl_2$ with the etherate of trimethylaluminum.[274] IR data (from comparison of intensities of the N≡N and C≡O stretching frequencies in $Os(N_2)(PEt_2Ph)_3Cl_2$ and $Os(CO)(PEt_2Ph)_3Cl_2$ suggest that N_2 is a weaker σ donor and weaker π acceptor than CO in these complexes.[275]

There are also hydrido dinitrogen complexes. Reaction of $OsH_4(PEtPh_2)_3$ with toluene-*p*-sulfonyl azide yields $Os(N_2)H_2(PEtPh_2)_3$,[276] while monohydrido complexes $Os(N_2)(PR_3)_3HX$ (PR_3 = PMe_2Ph, X = Cl, Br; PR_3 = PEt_2Ph, X = Cl) are made from $Os(N_2)(PR_3)_3X_2$ and sodium borohydride. The structure is thought to involve a *mer* arrangement of phosphine groups with the hydride *cis* to the coordinated dinitrogen.[277] A dinitrogen complex with the chelating phosphine depe, $[Os(N_2)H(depe)_2]BPh_4$, is made from *trans*-$[OsHCl(depe)_2]^+$, nitrogen and sodium tetraphenylboron.[278] With HCl, $Os(N_3)(diars)_2Cl$ gives $[Os(N_2)(diars)_2Cl]Cl$.[205] Two dinitrogen phosphine complexes of osmium have been studied by X-ray methods. Reaction of *mer*-$Os(N_2)(PMe_2Ph)_3Cl_2$ with $Pb(SC_6F_5)_2$ gave *mer*-$Os(N_2)(PMe_2Ph)_3Cl(SC_6F_5)$ which has the structure shown in Figure 14 in which a = 1.909, b = 1.112, mean c = 2.37, d = 2.507, e = 2.37 and f = 2.42 Å.[279]

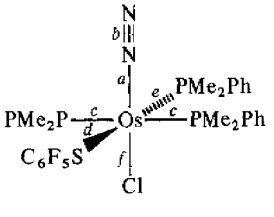


Figure 14 Structure of $Os(N_2)(PMe_2Ph)_3Cl(SPh)$[279]

An unusual dinitrogen complex generated from the halogenated diazoalkane $IC(N_2)CO_2Et$ and $Os(NO)Cl(PPh_3)_3$ in the presence of HCl yields $Os(N_2)[N(OH)CHCO_2Et](PPh_3)_2Cl_2$; an X-ray crystal study shows the structure to be that shown in Figure 15 in which a = 1.927(4), b = 1.063(5), c = 2.026(4), d = 2.412(1), mean e = 2.407 and f = 2.431(1) Å.[241]

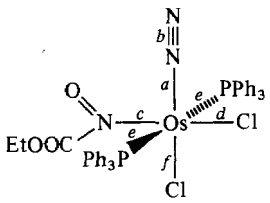
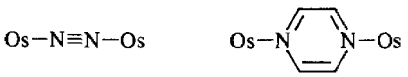


Figure 15 Structure of $Os(N_2)\{N(OH)CHCO_2Et\}(PPh_3)_2Cl_2$[241]

46.4.10.2 Binuclear dinitrogen-bridged complexes

A number of these have been isolated, including species with mixed oxidation states and heteronuclear species with ruthenium. In their general chemistry these remarkable complexes show clear analogies with bridging pyrazine complexes (p. 536):



The best characterized species is $[Os_2(N_2)(NH_3)_{10}]^{5+}$ made as a bromide or as a tosylate from reaction of $[Os(H_2O)(NH_3)_5]^{3+}$ with $[Os(N_2)(NH_3)_5]^{2+}$ in the presence of zinc amalgam. The stability of the mixed valence system (formally Os^{III-II}) has been ascribed to electronic delocalization effects and an MO scheme proposed,[280a] but it is not clear why it appears to be more stable than its reduction product, $[Os(N_2)(NH_3)_{10}]^{4+}$. Magnetic circular dichroism spectra and cyclic voltammetry of the ion have been measured.[280b] A number of other mixed homonuclear species are known, *viz.* $[Os_2(N_2)(NH_3)_9(H_2O)]^{5+}$, $[Os_2(N_2)(NH_3)_9Cl]^{4+}$, $[Os_2(N_2)(NH_3)_8Cl_2]^{3+}$ and $[Os_2(N_2)(NH_3)_9(N_2)]^{5+}$. The latter has one terminal and one bridging N_2 ligand, and is made by reaction of $[Os(N_2)(NH_3)_5]^{2+}$ with *cis*-$[Os(N_2)_2(NH_3)_4]^{2+}$.[281] There is some evidence from ESCA data that the ion $[Os_2(N_2)(NH_3)_8Cl_2]^{3+}$, as the trichloride, is indeed a delocalized Class III mixed valence species.[282a] Another binuclear dinitrogen-bridged complex is $[Os_2(N_2)(NH_3)_8(CO)_2]Cl_4$, made by oxidation of $[Os(NH_3)_5CO]^{2+}$ with persulfate, cerium(IV), permanganate or electrolytically. A possible route for formation of the complex by oxidation of $[Os(NH_3)_5CO]^{3+}$ to a nitrido species of higher oxidation state, possible osmium(V) with coupling of nitrido moieties to give the product, was suggested.[70] The isolation of the blue $[Os_2(N_2)(NH_3)_{10}]^{6+}$ by oxidation of the pentapositive species with chlorine has recently been reported.[282b]

Heteronuclear dinitrogen-bridged complexes are also known. Reaction of *cis*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$ with $[Os(N_2)(NH_3)_5]^{2+}$ yields $[(NH_3)_5Os(N_2)Ru(NH_3)_4(H_2O)]^{4+}$, and this can be oxidized to $[(NH_3)_5Os(N_2)Ru(NH_3)_4(H_2O)]^{5+}$.[283] There is also a very brief mention of $[OsRu(N_2)(NH_3)_{10}]^{n+}$ ($n = 4, 5$).[284]

46.4.11 Hydrazine Complexes

A few of these are known, all with osmium(II) and with phosphine or arsine coligands.

Reaction of $Os(PMe_2Ph)_3Cl_3$ with N_2H_4 or N_2H_3Ph in ethanol yields $Os(PMe_2Ph)_3Cl_2(N_2H_4)$ and $Os(PMe_2Ph)_3Cl_2(NH_2NHPh)$; the use of $Os(PR_2Ph)_3Cl_3$ (R = Et, Bu^n) as starting materials and N_2H_4 under reflux gives apparently binuclear species, $Os_2(PR_2Ph)_4Cl_4(N_2H_4)_2$, with the proposed structure shown in Figure 16.[72]

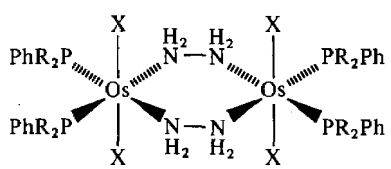


Figure 16 Proposed structure of $Os_2(PR_2Ph)_4Cl_4$[72]

The only reported example of an arsine complex is $Os\{As(p\text{-}MeC_6H_4)_3\}_3Cl_2(N_2H_4)$, made from $Os(As(p\text{-}MeC_6H_4)_3Cl_3$ and N_2H_4.[110]

46.4.12 Hydroxylamine Complex

It seems strange that no hydroxylamine complexes of osmium are established. There is a brief report of a deprotonated complex $Os(NO)(NHOH)Cl_2(PPh_3)_2$, made from $Os(NO)_2(PPh_3)_2$ and HCl. The ν_{NO} band is at 1860 cm^{-1}.[247]

46.4.13 Amino (—NH_2) and Organoamido (—NR_2) Complexes

Relatively few of these are known, though it might be anticipated that more osmium complexes with these ligands should exist.

46.4.13.1 Amino complexes

The only established example is *trans*-$[Os(NO)(NH_2)(NH_3)_4]^{2+}$ (see p. 546); the species $[Os(N_2)(NH_2)(NH_3)_4]^{2+}$ has also been claimed (see p. 554). Further investigation of '$[Os(NH_2)X_5][Os(NH_3)_5X]$' (X = Br, I), made by heating $[Os(NH_3)_6]X_3$,[75] is clearly needed; '$K_2[Os(NH_2)Cl_5]$' is known to be $K_2[Os(NH_3)Cl_5]$ (see p. 529). There is also a need to investigate $Cs_2[Os_2(NH_2)_2X_8]$ and $Cs_2[Os_5(NH_2)_8X_{14}]$ (X = Cl, Br, I), made from HX and $[Os(NH_3)_6][OsBr_6]$.[289] The amido ammine $[Os(NH_2)(NH_3)_5]^{3+}$ may be the first product of the one-electron oxidation of $[Os(NH_3)_6]^{3+}$ in acidic media.[55]

46.4.13.2 Alkanolaminato and diaminato complexes

Reaction of $OsO_2(NBu^t)_2$ with dimethyl or diethyl fumarate gives the osmium(VI) 'esters' $OsO_2(NBu^t(CHCO_2R)_2NBu^t)$ (R = Me, Et); the complex from diethyl fumarate is monomeric in benzene and the structure given in Figure 17(a) was proposed.[290] A related complex $OsO_2(NBu^t(CHCN)_2NBu^t)$ has recently been made from $OsO_2(NBu^t)_2$ and fumaronitrile.[291] Reaction of $OsO(NBu^t)_3$ and dimethyl fumarate gives $OsO(NBu^t)(NBu^t(CHCO_2Me)_2NBu^t)$,[290] presumably having the structure shown in Figure 17(b).

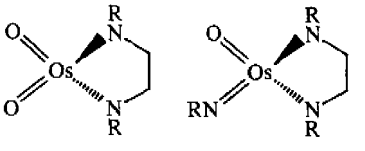


Figure 17 Proposed structures of diaminato complexes[290]

These monomeric and presumably tetrahedral complexes are intermediates in the diamination of alkenes (see p. 559). It is curious that, whereas OsO_4 and $OsO_3(NR)$ react with alkenes R′ to give square-based pyramidal dimers $Os_2O_4(O_2R')_2$ (p. 593) and $[OsO_2(OR'(NR))]_2$ (p. 559) respectively, the reaction products of $OsO_2(NR)_2$ (and presumably of $OsO(NR)_3$) with alkenes are monomeric:[290] there is no obvious reason for this. It is significant that Os—N rather than Os—O bonds are formed in these reactions.[290]

Alkanolaminato complexes $[OsO_2(OR'NR)]_2$ are made from $OsO_3(NR)$ and alkenes R′;[291,300] the X-ray crystal structure of $[OsO_2(OMeCH_2NBu^t)]_2$ shows this to have structure (I), Scheme 8.[291,291a]

46.4.14 Imido (=NH) and Organoimido (=NR) Complexes

This is an interesting area of osmium chemistry which stands much in need of development. Apart from the two incompletely characterized NH complexes, most of the organoimido chemistry is that of osmium(VIII); species such as $OsO_3(NR)$ will undergo oxyamination reactions with alkenic double bonds, and such reactions may be made catalytic. However, because of the high reactivity of osmium(VIII), only a small range of tertiary imido complexes have been prepared (R = Bu^t, Am^t, 1-adamantyl, Oct^t).

There is a good review on organoimide chemistry,[292] and organoimides are also mentioned in the course of a review on nitrido complexes.[293]

46.4.14.1 Complexes with =NH

Two binuclear complexes containing 2,2′-bipyridyl (bipy) have been reported in which the imido ligand appears to function in a bridging role. These are $[Os_2(NH)Cl_2(bipy)_4](ClO_4)_2$, made from $[Os(bipy)_2(NH_3)Cl]^+$ and cerium(IV), and $Os_2(NH_2)(bipy)_4$, made from $Os(bipy)_2Cl_2$ and ammonia.[173] The IR spectrum of the first complex has been recorded.[294] The oxidation states seem too low for these to be true imido complexes and further investigation would certainly be of interest.

46.4.14.2 Complexes with =NR

(i) Osmium(V) and osmium(VI)

It now appears that '$Os(NC_6H_4X)Cl_3(PPh_3)_2$' (X = H, *p*-MeO, *p*-Cl)[295] made from '$OsOCl_3(PPh_3)_2$' (now known to be a mixture containing $OsO_2Cl_2(PPh_3)_2$; see p. 584) are nitrile complexes $Os(NCC_6H_4X)Cl_3(PPh_3)_2$ (see p. 566).[296]

The complex $(PPh_4)[Os(NC(CCl_3)NCCl(CCl_3)Cl_5]$ may perhaps be regarded as an imido complex of osmium(VI); it is made by reaction of Os_2Cl_{10} with trichloroacetonitrile, and X-ray studies show it to have the structure shown in Figure 18. In this, $a = 1.97(1)$, $b = 1.34(1)$, mean $c = 2.32$, $d = 2.279(3)$, Os—N—C = 142.1(8)°. The Os—N distance (*a*) is slightly shorter than that expected for a single bond; the Os—N—C angle is 142.1(8)°.[297]

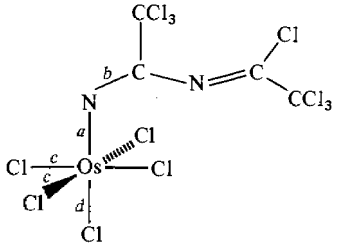


Figure 18 Structure of $(Ph_4P)[Os\{NC(CCl_3)NCCl(CCl_3)\}Cl_5]$[297]

(ii) Osmium(VIII)

The established organoimido complexes all contain osmium(VIII) and are listed in Table 13.

Table 13 Organoimido Complexes

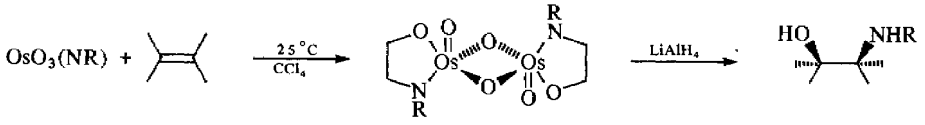
Complex	Colour	*M.p.* (°C)	ν_{OsN} (cm^{-1})	ν_{OsO} (cm^{-1})	Spectroscopic and other properties
$OsO_3(NBu^t)$	Yellow	100	1184	925, 912	IR,[299] UV/vis,[298] ^{13}C NMR[292,309]
$OsO_3(NAm^t)$		57–59	1210	930, 915	IR, ^1H NMR[301]
$OsO_3(NAd)$[a]	Yellow	176–177	1215	925, 915	IR, ^1H NMR,[301] X-ray[302]
$OsO_3(NOct^t)$	Yellow	51.5	1224	928, 910	IR,[291] UV/vis[290]
$[OsO_3(NOct^t)]_2DABCO$[b]	Red		1210	875, 850	Raman, IR, X-ray[308]
$OsO_2(NBu^t)_2$	Yellow	119–120 (d)	1200	888, 878	IR, ^1H NMR, MS,[290] X-ray,[302] ^{13}C NMR[309]
$OsO_2(NAm^t)_2$					
$OsO_2(NAd)_2$	Yellow	209–211	1175	880, 865	IR, ^1H NMR[290]
$OsO_2(NAm^t)(NAd)$	Yellow	72–74	1180	885, 875	IR, ^1H NMR[290]
$OsO(NBu^t)_3$	Yellow	114–116 (dec)	1190, 1100	838	IR, ^1H NMR, MS,[290] ^{13}C NMR[309]
$OsO(NAd)_2(NBu^t)$	Orange	146 (dec)	1160, 1100	838	IR, ^1H NMR[290]

[a] Ad = 1-adamantyl. [b] DABCO = 1,4-diazabicyclo[2.2.2]octane. [c] Not specifically assigned as such in reference.

(*a*) *Monoimido species, $OsO_3(NR)$.* The first to be made were $OsO_3(NBu^t)$ and $OsO_3(NOct^t)$, obtained from OsO_4 and the tertiary amine in ligroin.[298] Subsequent preparations of $OsO_3(NBu^t)$ used pentane[299–301] or water[290] as solvent. Other species made by similar routes are $OsO_3(NAm^t)$[290,301] and the 1-adamantyl complex OsO_3(N-1-Ad).[300,301]

The X-ray crystal structure of the latter complex has been determined. The coordination about the osmium is tetrahedral; the Os=N distance of 1.697(4) Å is slightly shorter than the mean Os =O distance of 1.714(4) Å and not much longer than the Os=N distance in terminal nitrido complexes below. The N—C distance is 1.448(6) Å and the Os—N—C angle 171.4(4)°.[302]

The complexes will effect oxyamination reaction with alkenes in a stereospecific reaction (Scheme 8).[290] After reductive cleavage of the intermediate alkanolaminato complex (I) (see below) vicinal amino alcohols (II) are formed. The reaction is unusual in that the new C—N bond is always formed at the least substituted terminal alkenic carbon atom, and there is a clear preference for the imido complex to use its NR group for coordination to the osmium despite the steric restraints of R.[299,300] However, the least sterically hindered part of the alkene moiety is attached to the nitrogen atom.[290,291,300] The yields of amino alcohols in the reaction can be improved by addition of tertiary alkyl bulkhead amines (see below).



(I) (II)

Scheme 8 Oxyamination by $OsO_3(NR)$[300,303]

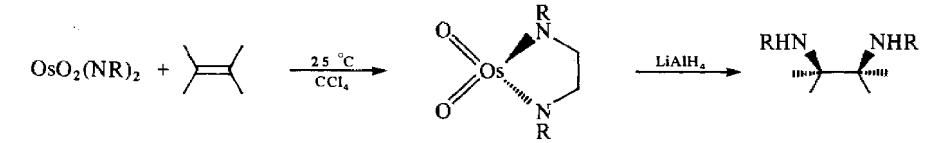
The oxyamination reactions can be rendered catalytic by using chloramine-T[303–305] or *N*-chloro-*N*-argentocarbamates.[306]

(b) The adducts $OsO_3(NR)\cdot L$ and $[OsO_3(NR)]_2L'$. Just as OsO_4 forms weak adducts with nitrogen donors (see p. 592), $OsO_3(NR)$ (R = Bu^t,[307] 1-Ad, Oct^t)[291] will form 1:1 species $OsO_3(NBu^t)\cdot L$ (L = quinuclidine, 3-quinuclidinone, 3-quinuclidinyl acetate[307]) and $OsO_3(NR)\cdot L$ (R = 1-Ad, Oct^t; L = quinuclidine).[291] There are also 2:1 species $[OsO_3(NBu^t)]_2\cdot L'$ with L′ = hexamethylenetetramine (HMT) or 1,4-diazabicyclo[2.2.2]octane (DABCO)[307] and the same nitrogen donors form similar complexes with $OsO_3(NR)$ (R = Am^t, Oct^t).[291] The X-ray crystal structure of $[OsO_3(NOct^t)]_2\cdot$DABCO has recently been determined; the DABCO ligand bridges two $OsO_3(NOct)^t$ moieties (Os—N = 2.45(1) Å), a little longer than the Os—N distance in $(OsO_4)_2\cdot$HMT due perhaps to a slightly greater *trans* weakening effect of the imido group over the oxo ligand). The osmium atoms have trigonal bipyramidal coordination, the apical positions being occupied by one DABCO nitrogen atom at the imido nitrogen (Os—N = 1.73(1) Å) while the equatorial positions are occupied by the oxo ligands (mean Os=O = 1.71 Å).[308]

(c) Bis imido species, $OsO_2(NR)_2$. Reaction of OsO_4 and *N-tert*-butyltriphenylphosphineimine or *tert*-butyltrimethylsilylamine[302] gives $OsO_2(NBu^t)_2$,[290] and the 1-adamantylimido complex $OsO_2(NAd)_2$ was similarly made; a mixed species $OsO_2(NAm^t)(NAd)$ was prepared from $OsO_3(NAm^t)$ and *N*-1-adamantyltriphenylphosphineimine.[290]

The X-ray crystal structure of $OsO_2(NBu^t)_2$ again shows the expected tetrahedral structure with Os=O at 1.744(6) Å; however, one of the imido groups is essentially linear (Os—N = 1.710(8) Å, Os—N—C = 178.9(9)°) and the other substantially bent (Os—N = 1.719(8) Å, Os—N—C = 155.1(8) Å.[301] The presence of one linear and one bent imido group in the complex has been partly rationalized on electron-counting procedures and MO considerations,[292,301] although both IR and ^{1}H NMR data indicate that both the imido groups are equivalent in solution.[302]

Reaction of $OsO_2(NBu^t)_2$ with alkenes followed by reductive cleavage gives vicinal diamines (IV; Scheme 9), and the intermediate 'ester' (I) (see p. 557) was isolated using dimethyl or diethyl fumarate as the reacting alkene. Again, the preference for Os—N rather than Os—O bond formation is noteworthy.[290]



(III) (IV)

Scheme 9 Diamination by $OsO_2(NR)_2$[290]

Efforts to obtain adducts of $OsO_2(NR)_2$ with nitrogen donors were unsuccessful;[291] this is not surprising since, if the osmium were to be trigonal bipyramidal as in $OsO_4\cdot L$ (p. 592) and $[OsO_3(NR)]_n\cdot L$ (p. 592), there would be considerable steric interaction between L and a necessarily equatorial NR group.

(d) Trisimido species, $OsO(NR)_3$. Reaction of OsO_4, $OsO_3(NBu^t)$ or $OsO_2(NBu^t)_2$ with *N-tert*-butyl-tri-*n*-butylphosphineimine gives $OsO(NBu^t)_3$, and the mixed complex $OsO(NAd)_2(NBu^t)$ can be made from $OsO_2(NAd)_2$ and *N-tert*-butyl-tri-*n*-butylphosphineimine.[290]

With alkenes, $OsO(NBu^t)_3$ effects vicinal diamination; the intermediate ester (III) (see Scheme 9) was isolated from the reaction with dimethy fumarate.[290]

(e) Tetrakisimido species, $Os(NR)_4$. Species of the type $Os(NBu^t)_3(NSO_3Ar)$ have been briefly mentioned (Ar = 2,4,6-trimethylphenyl, 2,4,6-triisopropylphenyl, *p*-tolyl).[292]

46.4.15 Nitrido Complexes

In this section we consider together all the osmium complexes involving the nitrido (N^{3-}) ligand since it appears that this is the dominant factor in the bonding of these complexes (for the same reason all oxo (O^{2-}) and nitrosyl (NO) complexes are grouped together).

Osmium forms a reasonably diverse number of nitrido complexes, particularly in the VI oxidation state (see Table 14); in this it resembles rhenium (as in many other respects). The terminal nitrido ligand is believed to be the strongest (or certainly one of the strongest) π donors[310,311] and will prefer, like the isoelectronic oxo (O^{2-}) ligand, to coordinate to metals in oxidation states of low d electron occupancy (*e.g.* d^0, Os^{VIII}, Re^{VII}; or d^2, Os^{VI}, Re^{V}). Such configurations are readily accessible to rhenium and osmium, placed as they are in the centre of the third row of the transition element block. When in a bridging role the nitrido (and oxo) ligands prefer a d^4 electron configuration and this of course is again readily accessible for osmium, for which the IV state is one of the commonest.

Table 14 Nitrido Complexes

Complex	*Colour*	ν_{OsO} *(cm^{-1})*	*Spectroscopic and other parameters*
$K_2[OsNCl_5]$	Purple	1084	IR,[22,318,325] Raman,[325] Mössbauer,[184]
$K_2[OsNBr_5]$	Purple	1085	IR, Raman[325]
trans-$K[OsNCl_4(H_2O)]$			UV/vis,[357] X-ray[323]
trans-$K[OsNBr_4(H_2O)]$		1109	IR,[318] UV/vis,[357] X-ray[326]
$Ph_4As[OsNCl_4]$	Pink	1123	IR, Raman,[325] UV/vis,[331,357] X-ray[329,330]
$Ph_4As[OsNBr_4]$	Pink	1119	IR, Raman,[325] UV/vis,[332,357] X-ray[331]
$Ph_4As[OsNI_4]$	Deep red	1107	IR,[265] UV/vis,[331] X-ray[332]
$OsNCl_3(PPh_2Me)_2$	Brown	1072, 1063	IR, ^{1}H NMR[315]
$K[OsO_3N]$	Yellow	1021	Raman,[325,340,358] IR,[325,341,358,359] UV/vis,[342,360–362] CV,[363] X-ray[335–338]
$K_3[Os_2NCl_8(H_2O)_2]$[a]	Brown	1137	Raman, IR,[344] UV/vis[344]
$Os_2N(S_2CNMe_2)_5 \cdot C_7H_{16}$	Black	1052	IR, UV/vis, ^{1}H NMR, CV,[350] X-ray[345]
$[Os_2N(NH_3)_8Cl_2]Cl_3$[b]	Yellow	1104	Raman, IR[344] UV/vis[344,353]

[a] Bromo analogue also known. [b] Bromo and iodo analogues also known.

All nitrido complexes of osmium so far reported are diamagnetic, with the exception of $[Os_3N_2(NH_3)_8(H_2O)_6]^{7+}$ (see p. 565).

The subject of transition metal nitrido complexes has been reviewed.[310,311]

46.4.15.1 Mononuclear complexes

(i) Osmium(IV) and osmium(V)

No mononuclear osmium(IV) nitrido complexes have been established, but μ-nitrido species containing a linear Os—N—Os unit are known, and there are trinuclear species of osmium(IV) and of mixed oxidation state containing Os—N—Os—N—Os units. The existence of both types is predictable from bonding considerations. They are dealt with on p. 564.

An osmium(V) nitrido complex $[OsN(CO)(NH_3)_4]^{2+}$ may be involved in the formation of $[Os_2(N_2)(NH_3)_8(CO)_2]^{4+}$ by oxidation of $[Os(NH_3)_5(CO)]^{2+}$.[70]

(ii) Osmium(VI)

This, having a d^2 configuration, is particularly suitable for octahedral mononitrido complexes such as $[OsNCl_5]^{2-}$, to which the Ballhausen–Gray bonding model for vanadyl species can be applied.[312] Taking the nitrido ligand to lie on the z axis the Os≡N triple bond is formed from a σ

bond and two π bonds, the latter being formed by overlap of filled $2p_x$ and $2p_y$ orbitals on N^{3-} with empty $5d_{xz}$ and $5d_{yz}$ orbitals on the osmium, the remaining *d* electrons pairing up in the $5d_{xy}$ orbital. It is curious that, whereas no $[Os^{VI}OX_5]^{n-}$ species are known, *trans* dioxo $[Os^{VI}O_2X_4]^{n-}$ complexes are numerous, the reverse being the case for the nitrido ligand: numerous octahedral osmium(VI) mononitrido complexes exist but no bis nitrido species. It may be that N^{3-} is too powerful a π donor[310,311] for a metal atom to sustain the presence of two such ligands, and indeed, as shown below, in some osmium(VI) nitrido species the ligand has electrophilic properties,[265,313–315] while in the less electronegative but isoelectronic rhenium(V) counterparts the nitrido ligand sometimes has weak nucleophilic properties.[316]

(a) Nitrido halogeno complexes. Reaction of salts of the 'osmiamate' ion $[OsO_3N]^-$ with HCl gives $[OsNCl_5]^{2-}$; the free acid and the potassium, rubidium, caesium and ammonium salts were made by Werner,[317] and more recent preparations of the potassium[299] and cesium[318] salts were described. Similarly, $[OsO_3N]^-$ with HBr gives $[OsNBr_5]^{2-}$; the rubidium and cesium salts have been isolated.[318,319]

The X-ray crystal structure of $K_2[OsNCl_5]$ shows the anion to be severely distorted with an apparently large *trans* weakening effect produced by the nitrido ligand[320] (an earlier X-ray study on '$K_2[OsNCl_5]$'[321,322] was later shown to concern *trans*-$K[OsNCl_4(H_2O)]$[323] and there is also another early, low-accuracy study of $K_2[OsNCl_5]$[324]).

In $K_2[OsNCl_5]$ (Figure 19a) = 1.614(13), mean $b = 2.361(4)$ and $c = 2.605(4)$ Å with an NOsCl (*cis*) angle of 96.5(5)°. The abnormal length of the *trans* Os—Cl bond was attributed to non-bonding steric interactions leading to N···Cl (*cis*) and Cl···Cl (*cis–cis*) distances of *ca.* 3.06 and 3.33 Å respectively.[320]

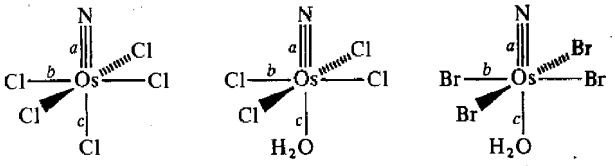


Figure 19 Octahedral halo nitrido complexes

Vibrational spectroscopic data on $[OsNX_5]^{2-}$ (X = Cl, Br) have been given.[325]

It is clear that the nitrido ligand exerts a *trans* weakening influence, however. The *trans* halide atoms in $[OsNX_5]^{2-}$ are easily replaced by water;[319] there are X-ray crystal structural studies on *trans*-$K[OsNCl_4(H_2O)]$ (Figure 19b)[323] and on *trans*-$K[OsNBr_4(H_2O)]$ (Figure 19c).[326] In (b), $a = 1.74(7)$, mean $b = 2.34(2)$ and $c = 2.50(3)$ Å,[323] and in (c) $a = 1.67(5)$, mean $b = 2.486$, and $c = 2.42(3)$ Å. The N—Os—Cl (*cis*) angle is 90.8°[323] and the N—Os—Br angle 101°.[326] Earlier determinations on the chloro complex (then thought to be $K_2[OsNCl_5]$[323,324]) and on the bromo complex are of lower accuracy. The Os—O distances are much longer than in other osmium(VI) species. Thus, Os—O (OH) in *trans*-$K_2(OsO_2(OH)_4]$ is 2.03 Å[327]; clearly a *trans* weakening effect is operative. The axial water molecules are easily removed (leading in the case of the bromo complex to a polymer, $K_n[OsNBr_4]_n$).[318] The larger the cation in *trans*-$M^I[OsNX_4(H_2O)]$ the more labile is the water molecule; salts of $[OsNCl_4(H_2O)]^-$ are known for M = K, Cs or Me_4N, but for M = Et_4N or larger organic cations the five-coordinate $M^I[OsNX_4]$ is formed. Presumably lattice energy forces are responsible for these differences.[328]

The square-based pyramidal halo complexes $[OsNX_4]^-$ can be made from $[OsNX_5]^{2-}$ (X = Cl, Br) with $(Ph_4As)X$,[318] and the deep red, beautifully crystalline iodo complex $Ph_4As[OsNI_4]$ is made from $[OsO_3N]^-$ and HI with $(Ph_4As)^+$.[265] There are X-ray crystal structure analyses of all three $[OsNX_4]^-$ species (Figure 20 and Table 15). They all have a distorted square-based pyramidal structure in which the four halo ligands lie well below the osmium atom, to such an extent that the X···X distances approach the van der Waals interaction distances. It has been suggested that steric N···X repulsion is not the main cause of the distortion since the N···X and X···X distances are virtually identical despite the differences in size between N and X. Rather it is likely to be an

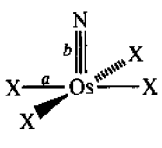


Figure 20 Structure of $[OsNX_4]^-$

Table 15 Bond Parameters for $[OsNX_4]^-$

Complex	Os—N (Å) (a)	Os—X (Å) (b)	NOsX (°)	N···X (Å)	cis-X···cis-X (Å)	Ref.
$[Ph_4As][OsNCl_4]$	1.604(10)	2.310(2)	104.53(5)	3.125(7)	3.162(4)	329, 330
$[Ph_4As][OsNBr_4]$	1.583(15)	2.457(1)	104.29	3.238(1)	3.364	331
$[Ph_4As][OsNI_4]$	1.626(17)	2.662(1)	103.73(2)	3.433(1)	3.657	332

electronic repulsion effect: the $2p_x^2$ and $2p_y^2$ π electrons on the nitrido ligand are drawn towards the electronegative osmium centre with concomitant repulsive interactions with the lone pairs on the halo ligands.[329,330,332a] Electronic spectral data on $[OsNCl_4]^-$ and $[OsNBr_4]^-$ [331] are consistent with such distortions. Vibrational spectroscopic data on $[OsNX_4]^-$ (X = Cl, Br)[325,331] and $[OsNI_4]^-$[265] have been obtained with ^{15}N substitution data in the case of the chloro and bromo complexes.[325]

Chemical reactions of $[OsNX_4]^-$ in acetone solution are summarised in Scheme 10. The electrophilicity of the nitrido ligand to phosphines has already been mentioned but it does not extend to arsine, stibine and simple nitrogen donors. Some of the latter, however, do form weak 1:1 complexes with monodentate ligands L and are presumably coordinated in positions *trans* to the nitrido ligand. Bifunctional ligands L′ give 2:1 complexes $[(OsNCl_4)_2L']^{2-}$.[265] The $[OsNCl_4]^-$ ion will abstract sulfur from thiocyanate[265] to give $[Os(NS)(NCS)_5]^{2-}$; another unusual feature is the relative lack of reactivity of $[OsNI_4]^-$ which, with its formal oxidation state of VI, is the highest oxidation state sustained by any transition metal iodo complex. It does not react with phosphines, arsines or aromatic amines, but with $SbPh_3$ it gives $OsNI_3(SbPh_3)_2$[265] in which there must be considerable steric strain and an overall symmetry similar to that of a lump of coal.

In recently reported work it has been shown that $[OsNCl_4]^-$ can be alkylated to $[OsNR_nCl_{4-n}]^-$ with MgR_2, XMgR or AlR_3 (n = 2 or 4, R = CH_2CMe_3 or CH_2CH_2Ph; n = 4, R = Me).[332b]

(b) Nitride complexes with other ligands. The existence of complexes with a water molecule *trans* to the nitride is quite common: thus, reaction of $K[OsO_3N]$ with HCN or oxalic acid gives *trans*-$K[OsN(CN)_4(H_2O)]$ and *trans*-$K[OsN(ox)_2(H_2O)]$, while *trans*-$K[OsNF_2(OH)_2(H_2O)]$ and *trans*-$K[OsN(ox)(OH)_2(H_2O)]$ are also known.[22]

In some osmium(VI) nitrido complexes the N^{3-} ligand is subject to nucleophilic attack by phosphines PR_3 to give phosphineiminato complexes $Os(NPR_3)X_3(PR_3)_2$;[313–315] similar complexes are formed by phosphinites.[265] The formation of these is illustrated in Scheme 10 below, see also p. 568.

The complexes $OsNL_2X_3$ (L = PR_3, AsR_3, $SbPh_3$, ½bipy, ½phen, py; X = Cl, Br) can be made as shown in Scheme 10 and are diamagnetic. IR spectra and, in the case of $OsN(PMe_2Ph)_2Cl_3$, ^1H NMR, suggest a *trans* structure similar to that shown in Figure 12, N replacing NS.[315] The abstraction reaction of sulfur from S_2 by $OsNL_2Cl_3$ (L = PMe_2Ph, $AsPh_3$, ½bipy, ½phen, py)[262] is noteworthy, as is a similar abstraction of sulfur from SCN^- by $[OsNCl_4]^-$ to give $[Os(NS)(NCS)_5]^{2-}$.[265]

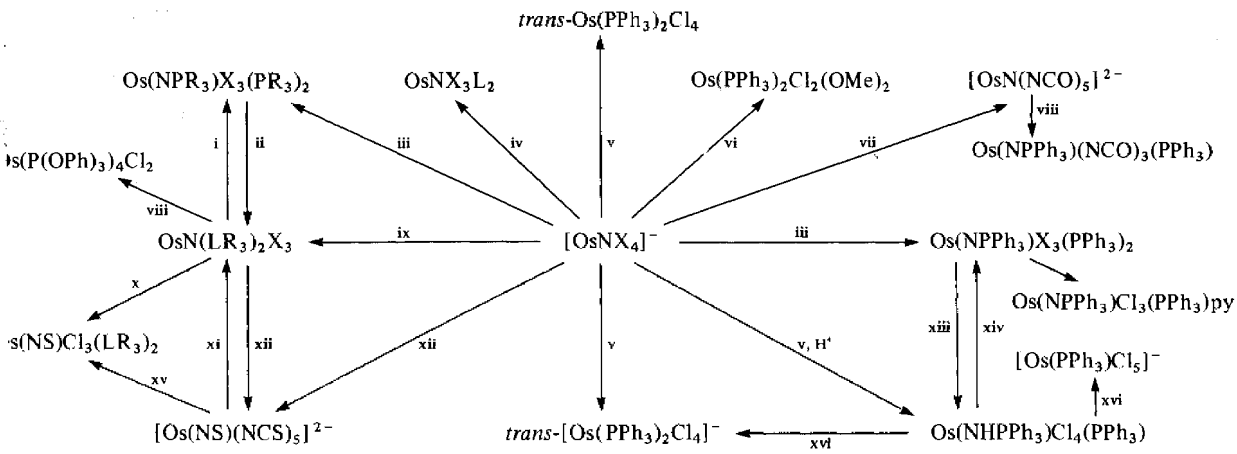
The porphyrin complexes *trans*-OsN(OEP)X (OEP = octaethylporphyrin; X = F, $OClO_3$, OMe) are made from OsO_2(OEP) and hydrazine hydrate with HF, $HClO_4$ or MeOH.[255] The existence of *trans*-$[OsN(NH_3)_4(H_2O)]^{3+}$ has been suggested though not fully confirmed.[55] Recently, the preparation of $(Bu^n_4N)[OsN(OSiMe_3)_4]$ has been accomplished by reacting $[OsNCl_4]^-$ with sodium siloxide; the product can be alkylated without cleavage of the Os≡N bond.[322a]

(c) Osmium(VIII). With a few minor exceptions the only established osmium(VIII) nitrido species are the 'osmiamates', salts of the tetrahedral $[OsO_3N]^-$ ion.

The osmiamate in is the source of most other osmium nitrido complexes. The free acid is said to be $OsN(OH)O_2$ in the solid state[22,333,334] and the $Bu^n_4N^+$, Ph_4P^+, Ph_4As^+, lithium, rhodium, potassium, rubidium, cesium, ammonium, silver, thallium, mercury, zinc, barium and lead salts are also known. The preparation of the potassium salt of OsO_4 in concentrated KOH solution with NH_4OH is a simple method for obtaining this useful starting material.[297]

A number of single crystal X-ray studies have been published, on the potassium,[335,336] rubidium[337] and cesium[338] salts. In the potassium and rubidium salts there appears to be a statistical distribution of nitrido and oxo ligands so that Os—N and Os—O bond lengths seem to be equal (*e.g.* 1.72 Å in $K[OsO_3N]$.[336] However, in $Cs[OsO_3N]$, the Os—N and Os—O distances are 1.676(15) and 1.739(8) Å respectively,[338] and an X-ray radial distribution analysis gave the Os—O and Os—N distances in $K[OsO_3N]$ as 1.78(3) and 1.63(3) Å respectively.[339]

Vibrational spectra of normal and isotopically substituted $[OsO_3N]^-$ have been measured (see Table 16).[325,340,341,358–360]



i, *Cl*: PEt_3, PMe_2Ph, $PMePh_2$, PEt_2Ph_2,[a] $P(OEt)Ph_2$;[b] *Br*: PEt_2Ph, $PEtPh_2$;[a] ii, Cl_2, PEt_3, PMe_2Ph, $PMePh_2$, PEt_2Ph, $PEtPh_2$;[a] iii, PPh_3 (Cl, Br);[a] iv, *Cl*: ½bipy;[a] ½phen;[b] *Br*: ½bipy;[a] v, PPh_3;[a] vi, PPh_3, MeOH;[a] vii, NCO^-; viii, PPh_3;[b] ix, *Cl*: $AsEt_3$, $AsPh_3$, $SbPh_3$;[a] *Br*: $AsPh_3$, $SbPh_3$;[a] *I*: $SbPh_3$;[b] x, S_2Cl_2, PMe_2Ph, $AsPh_3$;[c] xi, Cl_2: $AsPh_3$;[b] xii, SCN^-;[b] xiii, H^+;[a] xiv, py;[b] xv, S_2Cl_2, $AsPh_3$;[b] xvi, HCl.[a]

[a] Ref. 315 [b] Ref. 265 [c] Ref. 262.

Scheme 10 Reactions of $[OsNX_4]^-$

Table 16 Vibrational Spectra of $[OsO_3N]^-$

	ν_1 (A_1) ν_{OsN}	ν_2 ν_{OsO}	ν_3 δ_{OsO}	ν_4 (E) δ_{OsO}	ν_5 δ_{OOsN}	ν_6 δ_{OsO}	*Ref.*
$[OsO_3N]^-$	1021	897	309	871	372	309	340
	1029	898	309	872	374	302	325
$[OsO_3{}^{15}N]^-$	998	896	309	871	368	302	325
$K[Os^{18}O_3N]$[a]	1024	844		826	363	282	341

[a] IR data for the solid; others are Raman spectra in aqueous solution.

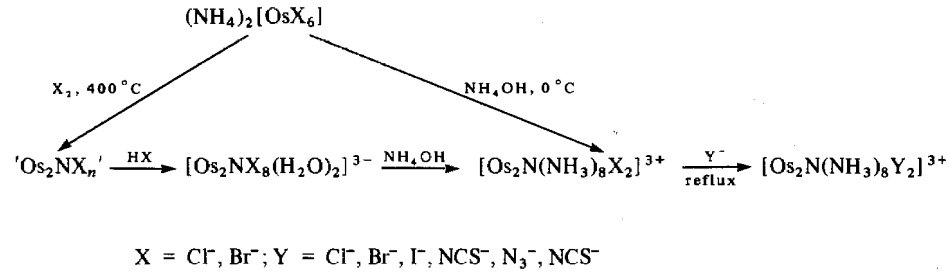
Electronic spectral data have also been measured for the ion.[342] The only other osmium(VIII) nitrido complexes claimed in the literature are of the type $[OOsN(Rbig)_2]OH \cdot SO_4 \cdot nH_2O$ (Rbig = biguanide, methylbiguanide).[343]

46.4.15.2 Polynuclear complexes

(*i*) *Binuclear species*

(a) Osmium(IV). The known dimers are of the form $[Os_2NX_8(H_2O)_2]^{3-}$ (X = Cl, Br) and $[Os_2N(NH_3)_8Y_2]^{3+}$ (Y = Cl, Br, I, NCS, N_3, NO_3);[344] there is also a dithiocarbamato complex $Os_2N(S_2CNMe_2)_5 \cdot C_7H_{16}$.[345] The first complexes of this type were $[Os_2N(NH_3)_8X_2]X_3$ (X = Cl, Br), made from $(NH_4)_2[OsX_6]$ and ammonia under pressure;[346–348] the routes in Scheme 11 were developed later.[344] The chloro species $[Os_2NCl_8(H_2O)_2]^{3-}$ can also be made in low yield by refluxing an aqueous solution of $K_3[Os(NH_2SO_3)Cl_5]$, and there is some evidence for the existence of $K_5[Os_2NCl_{10}]$.[349] However, although there is a brief mention in a review of an X-ray crystal structure of '$Cs_4[Os_2NCl_{10}]$'[310] this species is nowhere else reported in the literature, and it seems likely that the structure referred to is really that of $Cs_4[Os_2OCl_{10}]$ (see p. 593).

The dimethyldithiocarbamato complex was originally made from $OsCl_3 \cdot nH_2O$ and $Na(S_2CNMe_2)$,[345] and both it and the diethyldithiocarbamato analogue were later prepared from $Os(S_2CNR_2)_3$, $Na(S_2CNR_2)$ and $K_2[OsNCl_5]$.[350] The X-ray crystal structure of the 1:1 heptane



Scheme 11 Preparation of nitrido-bridged binuclear complexes [344]

adduct of $Os_2N(S_2CNMe_2)_5$ shows this to contain a slightly bent, symmetric nitrido bridge accompanied by a bridging dithiocarbamato ligand, the octahedron being completed by the other four chelating dithiocarbamato ligands. The Os—N distance is 1.76(3) Å and the OsNOs angle 164.6(18) °; the mean Os—S distance is 2.39(2) Å.[345]

Structure and bonding. All these osmium(IV) dimers are diamagnetic and Raman and IR spectra of $[Os_2NX_8(H_2O)_2]^{3-}$ and of $[Os_2N(NH_3)_8Y_2]^{3+}$ show no coincidences of fundamental skeletal vibrational modes, indicating a centrosymmetric structure.[344] Although, with the exception of $Os_2N(S_2CNMe_2)_5 \cdot C_7H_{16}$, there are no crystal structure studies on the osmium complexes, that of $K_3[Ru_2NCl_8(H_2O)_2]$ shows that this contains a centrosymmetric anion with a linear, symmetric Ru—N—Ru bridge. The Ru—N distance is 1.720 Å, indicating considerable multiple bonding in the linkage, and the chloro ligands are bent back from the nitrido group (N—Ru—Cl angle = 94.3 °). The long Ru—O (OH_2) distance of 2.175 Å is also suggestive of a *trans* weakening influence by the nitrido ligand.[351] The considerable similarities in the vibrational spectra of the ruthenium and osmium complexes[344] make it very likely that the structures will be similar in both groups. A similar structure has also been found recently from X-ray and vibrational spectroscopic studies on $K_5[Ru_2N(CN)_{10}]$.[352]

The bonding in these species is likely to be similar to that proposed for $[Os_2OCl_{10}]^{4-}$ (p. 594), p_π–d_π interactions for $2p$ orbitals on N^{3-} and $5d_{xz}$, $5d_{yz}$ orbitals on osmium giving rise to the observed diamagnetism.[353]

Raman and IR spectra of $[Os_2NX_8(H_2O)_2]^{3-}$ and $[OsN(NH_3)_8Y_2]^{3+}$ were recorded; isotopic substitution (^2H, ^{15}N) was used to aid assignments for $[Os_2N(NH_3)_8Br_2]Br_3$.[344]

(*ii*) *Trinuclear species*

The known chemistry of these species can all be systematized on the basis of the skeletal structure shown in Figure 21, though there are as yet no single crystal X-ray studies on complexes believed to contain it.

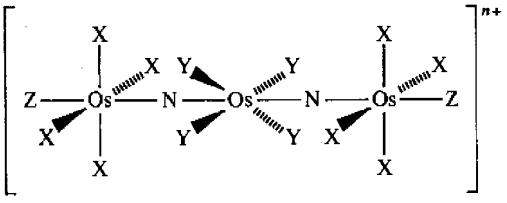


Figure 21 The likely basic structure of $[Os_3N_2X_8Y_4Z_2]^{n+}$ species[354]

Reaction of $(NH_4)_2[OsCl_6]$ or of $[Os(NH_3)_5Cl]Cl_2$ with ammonia gives the diamagnetic purple species $[Os_3N_2(NH_3)_8(H_2O)_6]Cl_6$, 'osmium violet', for which the structure above in Figure 21 (with X = NH_3, Y = Z = H_2O) was proposed; with aqueous cyanide, $[Os_3N_2(CN)_{10}(H_2O)_4]^{4-}$ is formed (X = Z = CN^-, Y = H_2O).[352,354] Resonance Raman and IR spectra were measured, and from these data it appears that the Os_3N_2 unit has considerable multiple bond character.[354] The bonding in the complex can be rationalized by using the molecular orbital scheme for ruthenium red, $[Ru_3O_2(NH_3)_{14}]^{6+}$,[355] and its ethylenediamine analogue $[Ru_3O_2(NH_3)_{10}en_2]^{6+}$.[356]

The complex '$Os_3N_7O_9H_{21}$', made from OsO_4 and ammonia,[344] is possibly $Os_3N_3(OH)_9(NH_3)_4$, with a structure related to that of Figure 21 but having an extra terminal nitrido ligand at the central atom (Y site).[344]

46.4.15.3 Polynuclear complexes of mixed oxidation state

Electrochemical oxidation of $Os_2N(S_2CNR_2)_5$ (R = Me, Et) showed that a reversible one-electron oxidation occurs to $[Os_2N(S_2CNR_2)_5]^+$, an osmium(IV)–(V) species and a further irreversible oxidation, possibly to an osmium(V) dimer.[350]

Trinuclear species apparently containing mixed oxidation states are also known. Reaction of $(NH_4)_2[OsCl_6]$ or $[Os(NH_3)_5Cl]^{2+}$ with air and ammonia gives, in addition to $[Os_3N_2(NH_3)_8(H_2O)_6]^{6+}$, 'osmium brown' $[Os_3N_2(NH_3)_8(H_2O)_6]Cl_7$; the latter is parammagnetic ($\mu_{eff} = 0.87$ BM per trimer unit). IR, resonance Raman and ESCA data are consistent with its formulation as in Figure 21 with X = NH_3 and Y = Z = H_2O. Treatment of 'Claus's salt', obtained from OsO_4 and aqueous ammonia, with cyanide ion gives $[Os_3N_2(CN)_8(H_2O)_6]^{4-}$ (X = CN^-, Y = Z = H_2O),[354] while HX gives $[Os_3N_2X_{11}(NH_3)_3]^{3-}$ (X = Cl or Br, Y = Cl or Br with one H_2O ligand, Z = NH_3).[344] Again, the bonding may be rationalized by the use of MO diagrams for trimeric ruthenium oxo-bridged species.[355,356]

46.4.16 Triazenido Complexes

The trihydro species $OsH_3(RNNNR)(PPh_3)_2$ have been made from $Os(PPh_3)_3H_4$ and the triazenes (R = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4); the complex $OsH_3(p\text{-}MeC_6H_4)NNN(p\text{-}MeOC_6H_4)$ was similarly prepared. These complexes are likely to be seven-coordinate and involve osmium(IV); ^{1}H NMR spectra suggest that they are stereochemically non-rigid. Their remarkable stability (the diphenyl complex is unaffected by boiling with PPh_3 in toluene) may arise from π-delocalization from the triazene to empty metal *d* orbitals.[364]

The osmium(II) species $Os(RNNNR)_2(PPh_3)_2$ (R = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$) are made from $[OsCl_6]^{2-}$ and the triazene with PPh_3 and KOH. On the basis of IR and ^{1}H NMR data the following structure shown in Figure 22 was proposed.

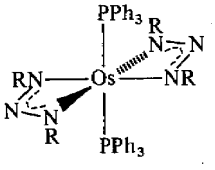


Figure 22 Likely structure of $Os(RNNNR)_2(PPh_3)_2$[364]

46.4.17 Azido Complexes

The only unsubstituted azido complex is $(Ph_4As)[Os(N_3)_6]$, made from NaN_3 and $(Ph_4As)Cl$ with $[OsCl_6]^{2-}$. It is an explosive yellow-orange complex.[365] The μ-nitrido complex $[Os_2N(NH_3)_8(N_3)_2](N_3)_3$ is a brown-yellow material obtained from $[Os_2N(NH_3)_8Cl_2]^{3+}$ and KN_3 under reflux (ν_{NN} = 2077 and 2040 cm^{-1}).[344]

The phosphine complexes $Os(N_3)(PR_3)_3Cl_2$ (PR_3 = PMe_2Ph, PEt_2Ph, $PPr^n{}_2Ph$, $PBu^n{}_2Ph$) are made from NaN_3 and *mer*-$Os(PR_3)_3Cl_3$; these purple complexes have ν_{NN} near 2060 cm^{-1} and probably have the structure shown in Figure 12, N_3 replacing NS.[366] A bis azido complex, *cis*-$Os(N_3)_2(PMe_2Ph)_4$, is a white material made from $Os(PMe_2Ph)_4Cl_2$ and NaN_3; ν_{NN} is at 2050 cm^{-1}.[366] The diarsine complex $Os(N_3)(diars)_2Cl$ is known, prepared from *trans*-$[Os(NO)diars_2Cl]^{2+}$ and $N_2H_4 \cdot HCl$; with HCl it gives the yellow $[Os(N_2)(diars)_2Cl]Cl$.[205]

46.4.18 Complexes of Pseudohalide Ligands

We have already considered azido complexes above; the only other pseudohalide to form complexes with the element is thiocyanate.

46.4.18.1 Thiocyanato complexes

Apart from a rather uncertain report of $[Os(SCN)_4]^{2-}$ the only unsubstituted thiocyanato complex to be fully established is $[Os(NCS)_6]^{3-}$. However, it appears that for the ambidentate NCS^-

ligand osmium(III) lies on the hard–soft boundary so that N or S bonding occurs almost in a random fashion; all the isomers of $[Os(NCS)_n(SCN)_{6-n}]^{3-}$ are known except for $[Os(SCN)_6]^{3-}$ ($n = 0$). This is probably the first system in which linkage isomerism and geometrical isomerism are so intertwined in an otherwise unsubstituted $[ML_6]^{n-}$ system.

(*i*) *Osmium(II)*

The only unsubstituted species claimed are $R_2[Os(NCS)_4]$ (R = diantipyrylmethane, $C_{23}H_{24}N_4O_2H^+$, and diantipyrylpropylmethane, $C_{26}H_{30}N_4O_2H^+$).[367] There are several substituted osmium(II) thiocyanato complexes, however. There is no indication from spectral data whether the ligand is N or S bonded in $(Ph_4P)_2[Os(NO)(NCS)_5]$ (see p. 545);[368] in the thionitrosyl complex $(Ph_4As)_2[Os(NS)(NCS)_5]$ (see p. 562) IR data suggest that there may be Os—N rather than Os—S bonding of the thiocyanate ligand. In $Os(diars)_2(SCN)_2$, made from $Os(diars)_2Cl_2$ and SCN^-, there are no spectral data to indicate the nature of binding of SCN^-,[369] but in $Os(Ph_2AsCH_2AsPh_2)_2(SCN)_2$, made from $(NH_4)_2[OsBr_6]$, SCN^- and the arsine, the IR spectrum is suggestive of S- rather than N-bonded thiocyanate.[370]

The complex $Os(SCN)_2(bipy)_2$ is made from KSCN and $Os(bipy)_2Cl_2$.[120]

(*ii*) *Osmium(III)*

Reaction of $K_2[OsCl_6]$ and KSCN with precipitation of the products by $(Bu^n_4N)^+$ yields $(Bu^n_4N)_3[Os(NCS)_6]$; IR,[371] electronic absorption[372] and Mössbauer spectra were measured,[184] and the magnetic susceptibility was measured from 90 to 295 K ($\mu_{eff} = 1.78$ BM at 295 K).[373] On the basis of the IR spectrum in particular no clear conclusion could be drawn as to whether the thiocyanate ligand was N or S bonded. Subsequent investigation showed that a mixture of isomers $(Bu^n_4N)_3[Os(NCS)_n(SCN)_{6-n}]$ is formed in the reaction,[374] and these may be separated by high-voltage electrophoresis or ion exchange.[375,376]

Of the ten possible isomers of $[Os(NCS)_n(SCN)_{6-n}]^{3-}$ nine have now been separated by ion exchange;[376] at high (refluxing) temperatures the $K_2[OsCl_6]$–KSCN reaction gives *cis* and *fac* complexes, while at lower temperatures (60 °C) the *trans* and *mer* species are formed.[376] In general, longer boiling periods produce a higher degree of N-bonded substitution while shorter reaction times at lower temperatures favour the formation of S-bonded isomers.[375] The only missing species is the fully N-bonded isomer, $[Os(NCS)_6]^{3-}$. The complexes were characterized by their Raman and IR spectra as well as electronic absorption spectra.[375,376] Confirmation of isomer assignment was given by EXAFS measurements on the various salts: the Os—N—C—S bonds are essentially linear while the Os—S—C—N bonds have an Os—S—C angle of approximately 110 °. The Os—N bond length decreases with increasing n in $[Os(NCS)_n(SCN)_{6-n}]^{3-}$ (2.21 Å for $n = 1$, 2.13 for $n = 6$) with the Os—S distance remaining relatively constant at 2.50 Å.[377]

(*iii*) *Osmium(IV)*

Four osmium(IV) complexes have been reported. The salts $[Os_2N(NH_3)_8(NCS)_2]Y_3$ (Y = Cl, NCS) are made from $[Os_2N(NH_3)_8Cl_2]^{2+}$ and NCS^-. The IR and Raman spectra suggest that it contains N-bonded thiocyanate,[344] consistent with the probable 'harder' nature of the $Os^{IV}_2N^{3+}$ moiety (see also p. 563). It has recently been reported, however, that osmium and ruthenium can be separated *via* their $[M(NCS)_6]^{2-}$ complexes using polyurethane foam.[378]

Recently, the isomeric pair $[Os(NCS)Cl_5]^{2-}$ and $[Os(SCN)Cl_5]^{2-}$ have been isolated by ion-exchange separation of the reaction product of $[OsCl_5I]^{2-}$ with $(SCN)_2$. IR, Raman and electronic spectra were measured.[379]

46.4.19 Nitrile Complexes

Surprisingly few osmium nitrile complexes are reported in the literature.

46.4.19.1 Osmium(II)

The reaction of $Os(PMe_2Ph)_3H_4$ and HBF_4 in acetonitrile gives $[Os(NCMe)_3(PMe_2Ph)_3](BF_4)_2$,[380] and there is a brief mention of $Os(NCMe)H_2(PR_3)_2$, made (but not isolated in the pure state) from $Os(PR_3)_3H_4$ (PR_3 = $PMePh_2$, PMe_2Ph, $PEtPh_2$).[276]

For $(PPh_4)[Os(NCMe)(CCl_3)NCCl(CCl_3)Cl_5]$, see under amides, p. 558.

46.4.19.2 Osmium(III)

The complexes $Os(NCAr)Cl_3(PPh_3)_2$ (Ar = Ph, *p*-tolyl) can be made from $OsCl_4(PPh_3)_2$, PPh_3 and ArNC; with MeCN, $Os(NCMe)Cl_3(PPh_3)_2$ is formed. These species are likely, on the basis of IR data, to have the structure shown in Figure 23(a). Reaction of $OsO_2Cl_2(PPh_3)_2$ and of $OsCl_2(PPh_3)_3$ respectively with *p*-toluenenitrile gives *cis*- and *trans*-$Os(NCR)_2(PPh_3)_2Cl_2$ (b and c; Figure 23) respectively.[296]

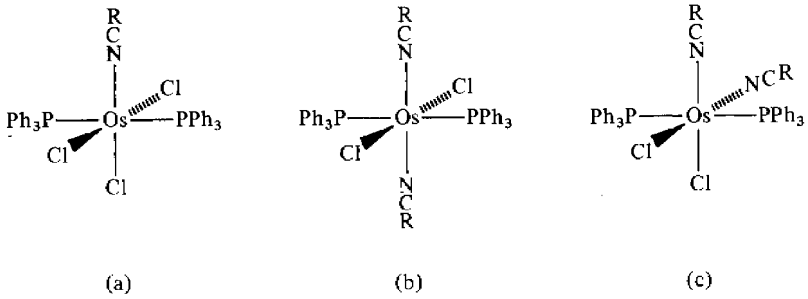


Figure 23 Structures of nitrile phosphine complexes[296]

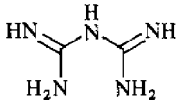
The acetonitrile complex $Os(NCMe)Cl_3(PPh_3)_2$ was found to be paramagnetic (μ_{eff} = 1.87 BM) with a broad room-temperature ESR spectrum (g = 2.16). The cyclic voltammogram showed a one-electron reversible reduction, and there is also a one-electron oxidation.[93]

The salt $(Et_4N)[Os(NCMe)Br_5]$, obtained from $[OsBr_6]^{2-}$ and PbO_2 in acetonitrile, has recently been reported.[381]

A recent X-ray crystal structure determination on *mer*-$Os(NCMe)Br_3(PPh_3)_2$ shows the Os—N distance to be 2.024(10) Å with the bromo ligand *trans* to it at 2.499(1) Å; the mean Os—P distance is 2.419 Å and the *trans* bromo ligands are at 2.490 Å. The complex was made by treating $(Bu^n{}_4N)_2[Os_2Br_{10}]$ in acetonitrile with triphenylphosphine.[382]

46.4.20 Miscellaneous Nitrogen Donor Complexes

46.4.20 Biguanide complexes



There seem to be no unsubstituted complexes of biguanide with osmium, though a few tris species of substituted biguanides have been reported.

(*i*) *Osmium(II)*

The tris complexes $[Os(Rbipy)_3]Br_2$ have been made from $(NH_4)_2[OsBr_6]$ and Rbig·HCl (Rbig = N^1,N^1-dimethylbiguanide, N^1-morpholinebiguanide, N^1-*p*-chlorophenyl-N^5-isopropylbiguanide (paludrine)). Electronic spectra were recorded, and the paludrine complex resolved *via* the antimonyl tartrate.[383]

(ii) Osmium(III)

Paludrine hydrochloride and $(NH_4)_2[OsCl_6]$ give $[Os(paludrine)_3]Cl_3$, or $[Os(paludrine)_3]^{2+}$ can be oxidized with hydrogen peroxide. The magnetic moment of the chloride at room temperature is 2.45 BM. The $[Os(paludrine)_2X_2]X$ complexes (X = Cl, Br) have also been prepared by reaction of $(NH_4)_2[OsX_6]$ with the ligand, and the magnetic moments at room temperature are respectively 1.60 and 1.68 BM. Electronic spectra were recorded.[383]

(iii) Osmium(VI)

Reaction of $(NH_4)_2[OsCl_6]$ and biguanides with alkaline H_2O_2 and OsO_4 with biguanide yields $OsO_2(big)_2$; with H_2SO_4 this gives $[OsO_2(bigH)_2]SO_4 \cdot H_2O$ and HCl yields $[OsO_2(bigH)_2]Cl$. The latter will react with 2,2′-bipyridyl (bipy) to give $[OsO_2(big)(bipy)]^+$. Piperazine biguanide (L′) reacts with *trans*-$[OsO_2(OH)_4]^{2-}$ to give $[OsO_2L'_4]^{2+}$.[384]

46.4.20.2 Benzotriazole complexes

Benzotriazole, $C_6H_4NHN_2$ (btz), forms a few complexes with osmium; fuller characterization would certainly be desirable.

(i) Osmium(III)

Osmium tetroxide in alkali with the ligand in ethanol yields $Os(btz)_3(OH)_3$; $Os(btz)_3X_3$ (X = Cl, Br) can be made from '$[OsO_3btz_4]^{3-}$, and HX.[385] Salts of $[OsO_3(btz)_4]^{3-}$ are said to be formed from the ligand and OsO_4 in alkali; red sodium, potassium, silver, barium, lead and calcium salts were isolated.[385]

46.4.20.3 Phosphineiminato (NPR_3) and phosphineaminato ($NHPR_3$) complexes

A number of osmium(IV) phosphineiminato complexes are known which also contain phosphine or arsine coligands; they are prepared by nucleophilic attack of phosphines on the nitrido ligand in osmium(VI) species. There is also one example of a phosphiteiminato complex, one of a phosphineaminato species, both formally involving osmium(IV), and two examples of osmium(I) aroylphosphineiminato complexes.

(i) Phosphineiminato complexes, $Os(NPR_3)X_3(LR_3)_2$

The preparation and principal properties of these species have been summarised in Scheme 10. They are made by reaction of alkyl aryl phosphines PR_3 (PEt_3, PMe_2Ph, $PMePh_2$, PEt_2Ph, $PEtPh_2$), with $OsN(AsPh_3)_2X_3$ (X = Cl, Br) while the triphenylphosphineiminato complexes $Os(NPPh_3)X_3(PPh_3)_2$ (X = Cl, Br) are best made directly from $[OsNX_4]^-$ and PPh_3. There is one example of a phosphineiminato complex containing an arsine group, $Os(NPPhMe_2)Cl_3(AsPh_3)_2$,[294] and there is a phosphiteaminato species $Os\{NP(OEt)Ph_2\}Cl_3\{P(OEt)Ph_2\}_2$.[265]

The complexes are paramagnetic with moments close to 1.8 BM at room temperature. The ^1H NMR and IR spectra of $Os(NPMe_2Ph)Cl_3(PMe_2Ph)_2$ suggest the *trans* configuration (I; Figure 24)[294] and this is indeed the type of structure found for the analogous ruthenium complex $Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2$ for which X-ray data have been obtained.[386] These complexes can be oxidized by chlorine to the nitrido species $OsN(PR_3)_2Cl_3$, and the triphenylphosphineiminato species can be protonated successively to $Os(NHPPh_3)Cl_4(PPh_3)$.[294] This bright red material is made by reaction of $[OsNCl_4]^-$ with PPh_3 and HCl, or by addition of one mole of HCl to $Os(NPPh_3)Cl_3(PPh_3)_2$. On the basis of IR data and on the ease of preparation of the complex from species of structure (a), structure (b) was proposed (Figure 24). The complex is readily deprotonated to $Os(NPPh_3)Cl_3(PPh_3)_2$, but its own further protonation by a mole of HCl leads to formation of $(Ph_3PNH_2)Cl$ and salts of $[Os(PPh_3)Cl_5]^-$.[294]

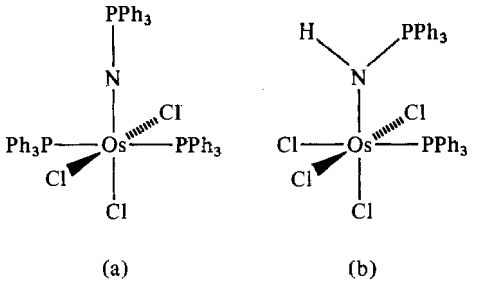


Figure 24 Structures of phosphineiminato and phosphineaminato complexes[294]

(*ii*) *Aroylphosphineiminato complexes, $Os\{NPPh_3C(O)Ar\}Cl_2(PPh_3)_2$*

The *N*-toluolyl and *N*-benzoyl complexes have been made from $OsO_2Cl_2(PPh_3)_2$, the phosphineimine and PPh_3, and the toluolyl complex was also obtained from $Os(PPh_3)_3Cl_2$, toluoylphosphineimine and PPh_3. A structure with the imine functioning as an N,O donor has been proposed (Figure 25).[296]

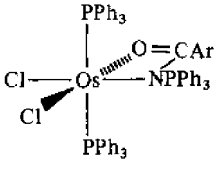


Figure 25 Structure of $Os(NPPh_3COAr)Cl_2(PPh_3)_2$[296]

46.4.20.4 Other nitrogen donor complexes

Two complexes have been reported with 8-amino-7-hydroxy-4-methylcoumarin, $NO_3C_{10}H_8$. Reaction of OsO_4 with this ligand in aqueous alkali and ethanol yields $[Os(NO_3C_{10}H_8)_2(OH)_2]\cdot 3H_2O$, a paramagnetic species ($\mu_{eff} = 1.22$ BM at room temperature, suggesting the presence of osmium(IV)). A similar reaction but in acidic aqueous ethanol yields the violet diamagnetic $[OsO_2(NO_3C_{10}H_8)_2]Cl_2$; IR and electronic spectra were measured.[387,388] Reaction of $OsCl_4$ with 4-*p*-dimethylaminoanilino-3-penten-2-one gives grey crystals of $OsL_4\cdot 2H_2O$; the electronic spectrum of this allegedly osmium(IV) complex was measured, but its diamagnetism[389] is unexpected —perhaps it is some type of 'osmyl' complex.

A complex formed between $Na_2[OsCl_6]$ and strychnine sulfate was formulated as $Os(N_2C_{21}H_{22}O_2)_3$[390] but later reformulated as a strychninium salt $(strychnineH)_2[OsCl_6]$.[391,392] For other complexes of osmium with alkaloids see p. 587.

46.5 PHOSPHORUS, ARSENIC AND ANTIMONY LIGANDS

The chemistry of these species with osmium is quite extensive, particularly in the case of the phosphines. In order to keep the sections to a manageable length we concentrate here on the hydrido and halo phosphines, arsines and stibines; when other ligands are involved the material is normally given under that ligand, but cross-references are provided. There are also separate sections on phosphorus trihalide complexes and on tertiary phosphites, while the relatively small sections on chelating phosphines and arsines are considered together. Also, in order to reduce the complexity of the treatment, much use has been made of reaction schemes, and it is in these rather than in the main text that some carbonyl complexes with these ligands are considered. For a fuller treatment of carbonyl phosphines, arsines and stibines the section in 'Comprehensive Organometallic Chemistry' is recommended,[16] as are the reviews of McAuliffe.[393,394]

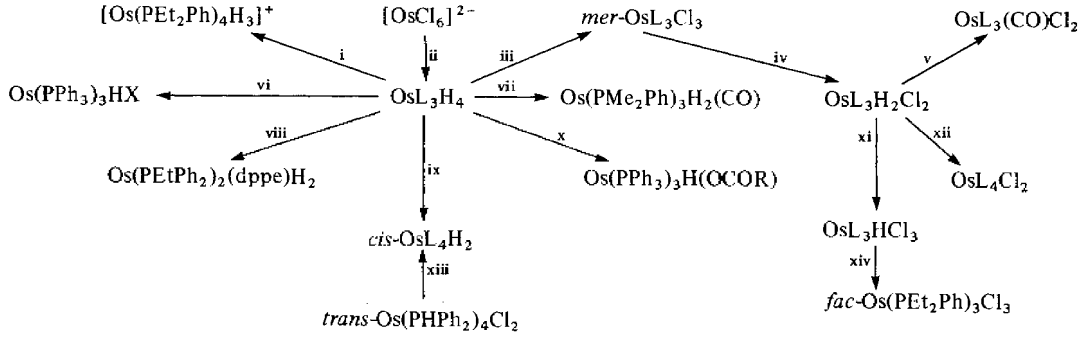
General chemistry. The commonest oxidation states in the phosphines, arsines and stibines of osmium are II and III, but there are a number of osmium(IV) species and, with oxo, nitrido and hydrido ligands, osmium(VI); with carbonyls there are examples of osmium(0) and with nitrosyls (pp. 549–551) also of the 0 and −II states. Although the stereochemistry is octahedral in most cases

there are examples of eight- and seven-coordination (the latter notably in the case of OsL_3H_4) and five-coordination; steric factors undoubtedly play a role particularly in the latter case. Osmium is not as catalytically active in its phospine, arsine and stibine chemistry as is, for example, ruthenium or rhodium, and most of the examples of catalytic reactions are with the carbonyls which are not covered in this chapter. The element nevertheless exhibits a rich chemistry with these ligands.

46.5.1 Tertiary Phosphine Complexes

46.5.1.1 Phosphine hydrido complexes

A wide variety of these are known, and the principal preparative routes to most of them are indicated in Scheme 12. The examples amongst these of seven- and even eight-coordination — very unusual stereochemistries for osmium — is noteworthy, as is the fact that, in a formal sense at least, some of them contain osmium(IV) or osmium(VI), very high oxidation states for phosphine-containing species.



i, HCl;[276] ii, BH_4^-, PPh_3;[405] iii, BH_4^- with L = PBu^n_3,[404] PMe_2Ph,[404] $PMePh_2$,[276] PEt_2Ph,[404] $PEtPh_2$;[276] iv, Zn and H_2 with L = $PMePh_2$, PEt_2Ph, $PEtPh_2$;[277] v, CO;[277] vi, HX;[397] vii, CO;[276] viii, dppe;[276] ix, L (L = PMe_2Ph, $PMePh_2$, PEt_2Ph, $PEtPh_2$);[276] x, OCOR;[406] xi, HCl with L = $PMePh_2$, PEt_2Ph;[277] xii, L = $PMePh_2$;[277] xiii, $[AlH_2(OH_2)_2OMe)_2]^-$;[407] xiv, heat.[277]

X = Cl, Br, I; R = Me, Et

Scheme 12 Some typical preparations and reactions of osmium hydrido phosphine complexes

The subjects of hydrido[395] and multihydrido[396] complexes have recently been reviewed.

(*i*) *Monohydrido species*

These span the formal oxidation states of II to IV. The carboxylato species $Os(PPh_3)_3H(OCOR)$ (R = Me, Et, CF_3, C_2F_5) are dealt with on p. 600; $Os(PPh_3)_3HX$ (X = Cl, Br, I) have been briefly reported as products of the reaction of $Os(PPh_3)_3H_4$ with HX, and the chloro complex is also made from $Os(PPh_3)_3Cl_2$ and H_2. With CO, $Os(PPh_3)_2HCl(CO)_2$ is formed and pyridine gives $Os(PPh_3)_3HCl(py)_2$. The chloro complex $Os(PPh_3)_3HCl$ catalyzes the homogeneous hydrogenation of terminal alkenes, and in some cases alkene isomerization occurs.[397]

The earlier reported[398] $Os(PBu^n_2Ph)_3HCl_n$ (n = 2 and 3) are now known to be mixtures,[399] but the formally tetravalent $Os(PR_3)_3HCl_3$ (PR_3 = $PMePh_2$, PEt_2Ph)[277] are well established.

For hydrido carboxylato phosphine complexes see p. 601.

(*ii*) *Dihydrido species*

There are two main classes: *cis*-$Os(PR_3)_4H_2$ and $Os(PR_3)_3H_2Cl_2$ (Scheme 12 and Table 17). The *cis* configuration of the former is established, in the case of $Os(PMePh_2)_4H_2$ at least, by phosphorus decoupling NMR experiments;[276] the high-field ^{1}N NMR spectra of $Os(PMePh_2)_2H_2Cl_2$ and of

$Os(PEt_2Ph)_2H_2Cl_2$ suggest that the hydrido ligands are in equivalent environments with respect to the phosphine ligands, a situation possibly caused by coupling effects.[277] The complex *cis*-$Os(PEtPh_2)_4H_2$ catalytically isomerizes and hydrogenates 1-octene, a process much more rapid in the presence than in the absence of hydrogen.[276]

Table 17 Hydrido Phosphine and Arsine Complexes

Complex	*Colour*	*M.p.* (°C)	ν_{OsH} (cm^{-1})	δ_{OsH} (cm^{-1})	τ_{OsH} (*p.p.m.*)	*Ref.*
$Os(PMePh_2)_3HCl_3$	Pink		2216, 2004, 1900		19.42q	277
cis-$Os(PMe_2Ph)_4H_2$		104–108	1950, 1920	830	20.35	276
$Os(PMePh_2)_3H_2Cl_2$	Grey	110–118 (d)	2171, 2029		19.55q	277
$[Os(PEt_2Ph)_4H_3]BPh_4$	White	199–203	–	842	21.09	276
$Os(PEt_2Ph)_3H_4$	White	79–80	2033, 1984, 1864	826	19.52q	404
$Os(PMe_2Ph)_2H_6$	Yellow oil		2028, 1980, 1869		18.60t	404
$Os(AsEtPh_2)_3H_4$		97–99	2041, 1986, 1813	810	19.66	276
cis-$Os(AsEtPh_2)_4H_2$		158–160	1992, 1975	845	23.74	276

Recently the complex *cis*-$Os(PMe_3)_4H_2$ has been obtained by reaction of *trans*-$Os(PMe_3)_4Cl_2$ and $NaC_{10}H_8$; with PF_6^- this gives $[Os(PMe_3)_4H_3]^+$ (see below).[400] Photolysis of $Os(PMe_2Ph)_3H_4$ gives a reactive intermediate $Os(PMe_2Ph)_3H_2$. This reacts with more phosphine to give *cis*-$Os(PMe_2Ph)_4H_2$, and a dimeric product $Os_2(\mu\text{-}H)_2(PMe_2Ph)_6H_2$ also results from the reaction (p. 572).[400]

(*iii*) *Tri- and tetra-hydrido species*

A number have been isolated: $[Os(PEt_2Ph)_4H_3]BPh_4$, made from *cis*-$Os(PEt_2Ph)_4H_2$ and HCl followed by addition of $NaBPh_4$,[276] and $[Os(PMe_3)_4H_3]PF_6$, from *cis*-$Os(PMe_3)_4H_2$ and $NH_4(PF_6)$.[401a] It seems from ^{1}H NMR data on the latter species that is fluxional at room temperature;[401a] an alarming observation on $[Os(PEt_2Ph)_4H_3]BPh_4$ (and its deuteriate) was than no IR band could be found to assign to the Os—H or Os—^{2}H stretches, though a band at 842 cm^{-1} was assigned to an Os—H deformation mode.[276] There is evidence for the existence of $[Os(PEt_2Ph)_2\{Ph_2P(CH_2)_2PPh_2\}H_3]^+$.[276] A recent X-ray crystal structure of $K[OsH_3(PMe_2Ph)_3]$ shows this to contain weak dimers with an H—K interaction; the main Os—H distance is 1.67 Å.[401b]

Tetrahydrido complexes of the form $Os(PR_3)_3H_4$ are the most important phosphine hydrides of osmium. Preparations are shown in Scheme 12 and typical data in Table 17, and some of the reactions are also given in Scheme 14. There is a full neutron diffraction study on $Os(PMe_2Ph)_3H_4$ which shows this to have a distorted pentagonal bipyrimidal structure with two apical and one equatorial phosphine ligand (mean Os—P apical distance 2.312 Å with a P—Os—P angle of 166.1(1)°; the bending occurs presumably as a result of the position of the equatorial phosphine ligand (Os—P = 2.347(3) Å). The hydride ligands are all in the equatorial plane (mean Os—H = 1.663 Å).[396,402] There are preliminary X-ray data on $Os(PEt_2Ph)_3H_4$ which indicate a similar structure (mean axial Os—P distance 2.296 Å, and an equatorial Os—P distance of 2.339 Å[403]). ^{1}H NMR data on the tetrahydrido complex indicate equivalence of the phosphine ligands, an effect which probably arises from fluxionality in solution.[276,404] IR spectra show three or four Os—H stretches in the 1800–2100 cm^{-1} region (though in some cases five stretches are observed in solution).[404] Both ^{1}H NMR and IR data are available for a number of OsL_3H_4 complexes (L = PBu^n_3, PMe_2Ph, PEt_2Ph) and also for $Os(PMe_2Ph)_2L'H_4$ (L′ = $P(OEt)_3$, $P(OMe)_2Ph$, PEt_2Ph, PPh_3, $AsMe_2Ph$); these latter species are made from *mer*-$Os(PMe_2Ph)_2L'Cl_3$ and BH_4^- in methanol.[404]

These OsL_3H_4 complexes have an extensive chemistry, representative examples of which are illustrated in scheme 12. In the presence of hydrogen, $Os(PEtPh_2)_3H_4$ catalyzes the hydrogenation of oct-1-ene.[276] Photolysis of $Os(PMe_2Ph)_3H_4$ gives a reactive intermediate $Os(PMe_2Ph)_3H_2$ (see above).

(*iv*) *Penta- and hexa-hydrido complexes*

Although salts of $[Os(PR_3)_2H_5]^+$ do not seem to have been isolated there is evidence from ^{1}H NMR spectra that $[Os(PMe_2Ph)_2H_5]^+$ is present in solutions of *cis*-$Os(PMe_2Ph)_4H_2$ in trifluoro-

acetic acid.[404] Such an $[OsL_3H_5]^+$ species would be a member of the series WL_3H_6, ReL_3H_5 and IrL_3H_3.[404]

The hexahydrido species $Os(PMe_2Ph)_2H_6$ is made by treatment of $Ph_4As[Os(PMe_2Ph)_2Cl_4]$ with $LiAlH_4$; it was detected by ^1H NMR.[404] The species $OsH_6(PPhPr^i_2)_2$ and $OsH_6(PPhPr^i_2)_2HgCl_2$ have recently been reported.

(v) *Polynuclear hydrido complexes*

Photolysis of $Os(PMe_2Ph)_3H_4$ in benzene or THF yields, amongst other products, red crystals of $Os_2(PMe_2Ph)_6H_4$. The X-ray crystal structure (Fig. 26) shows it to have a short Os—Os bond of 2.818(1) Å, formally a double bond if the electron-count of 18 is to be achieved; the Os_2H_2 bridge appears to be asymmetric with long and short distances of 2.18(10) and 1.59(10) Å respectively, while the Os—H terminal bonds are at 1.61(9) Å. The $Os(PMe_2Ph)_3$ unit about each metal atom has a *fac* geometry; the mean Os—P distance *trans* to the Os_2H_2 plane is 2.259 Å and that *trans* to the terminal hydrido ligand is substantially longer at 2.340(3) Å.[400] Reaction of this complex with HBF_4 leads to $[Os_2(PMe_2Ph)_6H_3]BF_4$, which has a tricapped trigonal prismatic type of structure (akin to that found in $K_2[ReH_9]$) with three bridging hydrido ligands (mean Os—H distance = 1.75(11) Å, Os—Os = 2.558(1) Å) and the mean Os—P distance is 2.291(4) Å. Formally there is an Os—Os triple bond here.[400] Finally, there is ^{31}P NMR evidence for the existence of $Os_2(PMe_2Ph)_5H_4$ in solutions of $Os_2(PMe_2Ph)_6H_4$, in which three hydrido ligands bridge two osmium atoms; one metal atom has three phosphine ligands with a *fac* arrangment and the other similarly bears two phosphine ligands and a terminal hydride ligand.[400]

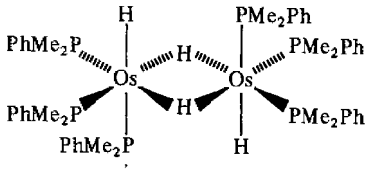


Figure 26 Structure of $Os_2(PMe_2Ph)_6H_4$[400]

46.5.1.2 Halo phosphine complexes

A very substantial number of these are known (examples are given in Table 18); as with the halo-arsines (p. 576) and -stibines (p. 577) the metal oxidation states represented are II, III and IV with a preponderance of the trivalent state; the early-reported '$Os(PPh_3)_3X$' (X = Cl, Br) complexes are now known to be hydrides, $Os(PPh_3)_3HX(CO)$.[408]

Table 18 Physical Data for Halo Phosphine, Arsine and Stabine Complexes

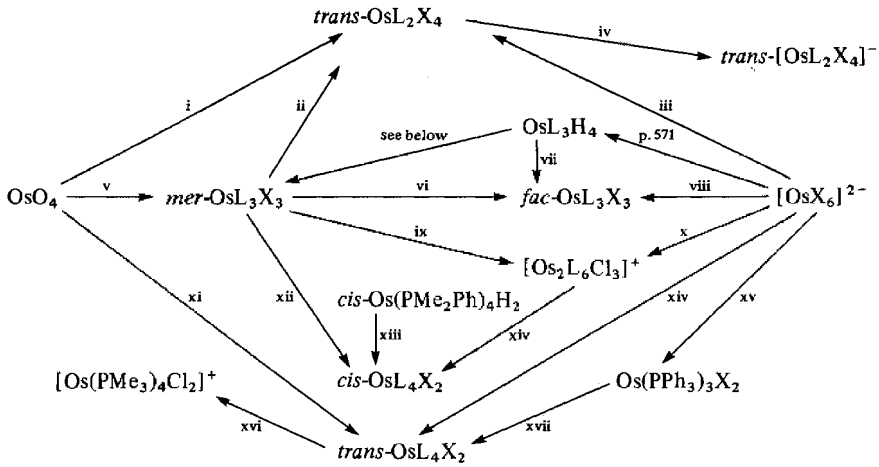
Complex	*Colour*	*M.p. (° C)*	*Spectroscopic and other properties*
trans-$Os(PMe_2Ph)_4Cl_2$	Yellow	252–258	ESCA[427]
trans-$Os(PPh_3)_4Br_2$[a]	Grey	202–205 (d)	IR[370]
mer-$Os(PMe_2Ph)_3Cl_3$	Red	200–204	IR,[404] ESR,[102,413] M,[411] ESCA,[418,427] X-ray[403]
fac-$Os(PBu_2Ph)_3Cl_3$	Maroon	161–162	IR,[413] UV/vis,[414] ESR[413]
trans-$Ph_4As[Os(PEt_2Ph)_2Cl_4]$	Yellow	198–202	IR[315]
$Os(PPh_3)_2(NH_3)Cl_3$	Orange	223–228	X-ray[71]
mer-$Os(AsPr^n_3)_3Cl_3$	Orange	159–160	IR,[413] UV/vis,[414,415] CD,[415] M[411]
fac-$Os(AsMe_2Ph)_3Cl_3$	Red-brown	158–186	M,[411] EPR[102,413]
mer-$Os(SbPh_3)_3Cl_3$	Green	238–240 (d)	IR, ^1H NMR, ESR[370]
fac-$Os(SbPh_3)_3Br_3$	Black	263–265 (d)	IR, ^1H NMR[370]
trans-$Os(PMe_2Ph)_2Cl_4$	Brown	206–207	IR, ^1H NMR,[413] M,[411,423] X-ray[403]
trans-$Os(AsPr^n_3)_2Cl_4$	Green-brown	155–156	IR,[413] UV/vis,[414] ^1H NMR,[428] M[411]
trans-$Os(SbPh_3)_2Cl_4$	Black	280–282 (d)	IR[370]

[a] $AsPh_3$ and $SbPh_3$ analogues also known.[370]

(i) *Osmium(II)*

Examples both of *cis*- and *trans*-$Os(PR_3)_4Cl_2$ and of the five-coordinate $Os(PPh_3)_3X_2$ (X = Cl, Br) are known. Preparations of these are outlined in Scheme 13; in addition, $Os(PMe_2Ph)_2\{P(OMe)_2Ph\}Cl_3$ can be obtained from $P(OMe)_2Ph$ and $Os(PMe_2Ph)_3(N_2)Cl$[409] and

trans-$Os(PMe_3)_4Cl_2$ from $Os(PPh_3)_2Cl_3$ and PMe_3 (a preliminary X-ray study of the complex was reported).[410] The *cis* form of $OsCl_2(PMe_3)_4$ is also known.[401]



i, HX, L (*Cl*: Bu^n_2Ph, Pr^n_2Ph, *Br*: PPr^n_3);[411] ii, Cl_2, L = PMe_2Ph, CCl_4, L = PMe_2Ph, PEt_2Ph;[404] iii, *Cl*: $PMePh_2$, PPr^n_2Ph, PPh_3;[370] iv, BH_4^-, PMe_2Ph, PEt_2Ph;[404] v, HX, L (*Cl*: PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph, PEt_2Ph, PPr^n_2Ph, PBu^n_2Ph,[411] PPh_2(1-naphthyl),[419] *Br*: PPr^n_3, PMe_2Ph, PEt_2Ph, PBu^n_2Ph);[411] vi, N_2H_4 (Cl, PBu_2Ph);[413] vii, HCl, PBu^n_3, PMe_2Ph, $PEtPh_2$;[404] viii, HX, PPh_3 (Cl, Br);[370] ix, Zn, PEt_3, PMe_2Ph, $PEtPh_2$;[254] x, $PMePh_2$, PEt_2Ph, $PEtPh_2$;[420] xi, Zn, HCl, PMe_2Ph;[276] xii, Zn, PMe_2Ph;[276] xiii, HCl;[276] xiv, $PHPh_2$;[407] xv, PPh_3 (Cl,[397,410] Br[421]); xvi, $AgPF_6$;[401] xvii, PMe_3 (Cl).[416]

Scheme 13 Preparative routes for osmium halo phosphine complexes

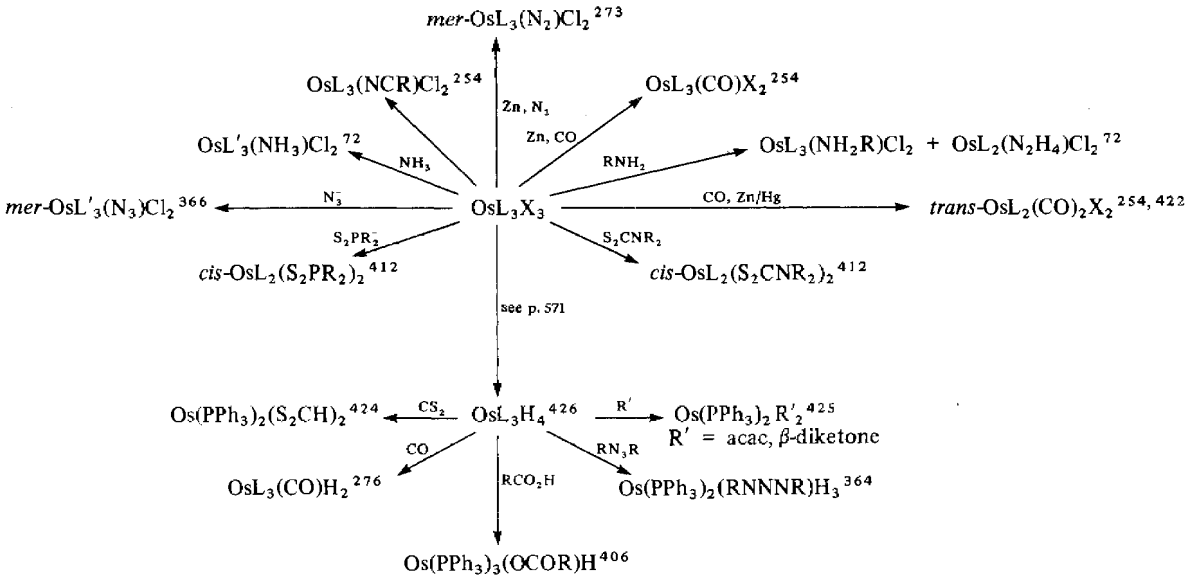
IR spectra were used to indicate configurations of *cis*- and *trans*-$Os(PHPh_2)_4Cl_2$[407] and of *trans*-$Os(PPh_3)_4Br_2$,[370] while ^{31}P NMR spectra of $Os(PPh_3)_3X_2$ (X = Cl, Br) suggested a square-based pyramidal structure for these in which, however, intramolecular rearangement renders the two phosphorus environments equivalent.[410a] In a recent paper electroreduction of *mer*-$OsCl_3(PMe_2Ph)_3$ to *mer*-$[OsCl_3(PMe_2Ph)_3]^-$ was described; this releases Cl^- to give the five-coordinate *trans*-$OsCl_2(PMe_2Ph)_3$.[410b]

(*ii*) *Osmium(III)*

mer- *and* fac-*OsL_3X_3*. These are important starting materials for other osmium phosphine complexes, particularly the *mer* isomers (see p. 574); general methods of preparation are given in Scheme 13. Other starting materials which have sometimes been used for *mer* complexes are $K_2[OsNCl_5]$, *trans*-$K_2[OsO_2(OH)_4]$ and *trans*-$OsO_2Cl_2(PPh_3)_2$.[411] In some cases *mer*-OsL_3Cl_3 can be converted to *mer*-OsL_3Br_3 with LiBr in refluxing ethanol.[411,412] The species $Os(PMe_2Ph)_2LCl_3$ (L = $P(OMe)_2Ph$, $P(OEt)_3$, PEt_2Ph, PPh_3) are made from *trans*-$Os(PMe_2Ph)_4Cl_2$ and L in hot benzene.[404]

These trivalent complexes are useful starting materials for other osmium phospine complexes, and some of the reactions are indicated in Schemes 13 and 14. In not all of the cases is it clear whether the *mer* or *fac* isomer was used and so we have omitted these prefixes, although it is likely in most cases that the *mer* was in fact the starting isomer. In order to simplify the schemes, general reactions only are indicated.

There is one X-ray crystal structure of a *mer* isomer, *mer*-$Os(PMe_2Ph)_3Cl_3$ (Figure 27). Bond lengths are $a = f = 2.347(6)$, $b = c = 2.408(6)$, $d = 2.350(5)$ and $e = 2.439(6)$ Å.[403] There are IR data on many *mer* and *fac* complexes (*mer*-OsL_3X_3; X = Cl, L = PPr^n_3,[413] PBu^n_3,[404] PMe_2Ph,[404] PEt_2Ph,[404] PBu^n_2Ph;[413] X = Br, L = PPr^n_3;[413] *fac*-OsL_3Cl_3; X = Cl, L = PBu^n_3, PMe_2Ph, PEt_2Ph,[404] PBu^n_2Ph,[413] PPh_3;[370] X = Br, L = PPh_3[370]), and electronic (*mer*-$Os(PPr^n_3)_3Cl_3$,[414] *mer*-$Os(PPr_2Ph)_3Cl_3$,[415] *mer*- and *fac*-$Os(PBu_2^nPh)_3Cl_3$,[414] *mer*-$Os(PBu^n_2Ph)_3Br_3$[414]) and ESR spectra (*mer*-$Os(PMe_2Ph)_3Cl_3$, *mer*-$Os(PEt_2Ph)_3Cl_3$,[102,413] *mer*- and *fac*-$Os(PBu^n_2Ph)_3Cl_3$[413]). Magnetic moments for these complexes lie in the range 1.9–2.1 BM at room temperature.[411] There are ESR data on *mer*-$OsCl_3(PR_3)_3$ (PR_3 = PMe_2Ph, PBu^n_2Ph, $AsMe_2Ph$) and on *mer*-$Os(PBu^n_2Ph)_3Br_3$.[102]



L = phosphine and arsine; L' = phosphine only

Scheme 14 Some reactions of OsL_3X_3 and OsL_3H_4

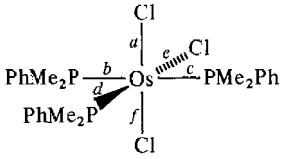


Figure 27 Structure of *mer*-$Os(PMe_2Ph)_3Cl_3$[403]

OsL_2X_3. Only one example of this type is reported; $Os(PPh_3)_2Cl_3$, made by refluxing *fac*-$Os(PPh_3)_3Cl_3$ in *t*-butanol.[416]

trans-*$[OsL_2X_4]^-$*. Apart from the preparative methods given in Scheme 13 *trans*-$Ph_4As[Os(PEt_2Ph)_2Cl_4]$ and *trans*-$Bu^n_4N[Os(PEt_2Ph)_2Br_4]$ are made from the phosphine and the corresponding $[OsNX_4]^-$ salts.[315]

$[Os(PMe_3)_4Cl_2]PF_6$. This is made from $AgPF_6$ and *trans*-$Os(PMe_3)_4Cl_2$, and reacts with CO to give *trans*-$Os(PMe_3)_3Cl_2(CO)$.[401]

$[Os_2L_6Cl_3]^+$. These are made as indicated in Scheme 13, and are likely to have a μ_3-chloro structure.[420]

trans-OsL_2X_4. Apart from the preparative routes outlined in Scheme 13, *trans*-$Os(PPh_3)_2Cl_4$ can be made from $Ph_4As[OsNCl_4]$ with PPh_3 or from $Os(PPh_3)_2Cl_2(NPPh_3)$ and HCl.[315]

A single crystal X-ray structure shows $Os(PMe_2Ph)_2Cl_4$ to have a *trans* configuration, with Os—P = 2.448(3) Å and Os—Cl = 2.319(3) Å.[403] A *trans* configuration in solution is also suggested by IR and ^1H NMR studies on species with L = PMe_2Ph, PEt_2Ph, PPr^n_2Ph and PBu^n_2Ph;[413,417] this is also the conclusion from Raman data on $Os(PMePh_2)_2Cl_4$ and $Os(PPh_3)_2Cl_4$,[370] and IR data on $Os(PMePh_2)_2Cl_4$, $Os(PPr^n_2Ph)_2Cl_4$, $Os(PPh_3)_2Cl_4$[370] and $Os(PPr^n_3)_2Br_4$.[413] There are electronic spectra for $Os(PPr^n_3)_2X_4$ (X = Cl, Br)[414] and ESCA data on $Os(PEt_3)_2Cl_4$, $Os(PMe_2Ph)_2Cl_4$[427] and $Os(PPh_3)_2Cl_4$;[93] magnetic moments are normally between 1.5 and 1.6 BM at room temperature for these complexes.[411]

$[OsLX_5]^-$. The sole example appears to be $Ph_4As[Os(PPh_3)Cl_5]$, a red complex made from $Os(PPh_3)Cl_4(NHPPh_3)\cdot Me_2CO$ and $Ph_4As(H_5O_2)Cl_2$.[315]

Miscellaneous phosphine complexes. For phosphine complexes with other ligands see as follows: acetonato, p. 598; alkoxo, p. 596; ammine, p. 529; azido, p. 565; carboxylato, p. 601; diazenido, p. 601; β-diketonate, p. 597; dinitrogen, p. 555; dithiocarbamate and dithiocarbonate, p. 604; hydrazine, p. 556; complexes with metal–metal bonds, p. 525; nitrile, p. 567; nitrido, p. 562; nitrosyl, p. 547; oxo, p. 584; phosphineiminato, p. 568; phosphinodithionato, p. 605; pyridine and piperidine, p. 533; sulfido, p. 603; triazenido, p. 565; trithiocarbonate, p. 605.

46.5.2 Tertiary Phosphite Complexes

It is a singular circumstance that the known chemistry of the tertiary phosphite complexes of osmium differs quite significantly from that of the tertiary phosphines, arsines and stibines. The closest analogue to $P(OR)_3$ in osmium coordination chemistry would seem to be PF_3, but even here the similarities are not marked. The oxidation states found are 0, II, III and IV (there are no established zerovalent unsubstituted osmium phosphine complexes), and the phosphites form unsubstituted species of the type OsL_5 and $[OsL_6]^{2+}$ which have no counterparts in phosphine chemistry. The reason for these differences must be associated in part at least with the different cone angles and basicities of $P(OR)_3$ ligands as against PR_3. Further similarities and differences between the chemistries of osmium phosphines, phosphites and phosphorus trihalide complexes would obviously constitute a worthwhile study.

46.5.2.1 Osmium(0)

Reaction of $Os\{P(OMe)_3\}_2Cl_4$ and $P(OMe)_3$ with sodium amalgam in THF yields the white $Os\{P(OMe)_3\}_5$. Study of the $^{31}P[^1H]$ NMR spectra showed simultaneous slow exchange of axial and equatorial ligands consistent with a Berry mechanism.[429]

46.5.2.2 Osmium(II)

Amongst the osmium(II) phosphito complexes known are the octahedral $[Os\{P(OR)_3\}_6]^{2+}$, made from $Os(PPh_3)_3Br_2$ and $P(OEt)_3$. The tetraphenylboronate is white; the trimethyl phosphite analogue could not be isolated.[430] Other osmium(II) species include $[Os\{P(OEt)_3\}_5X]^+$ (X = Cl, Br), made from $Os(PPh_3)_3X_2$ and $P(OEt)_3$,[430] $Os\{P(OR)_3\}_4Br_2$ (R = Ph, *p*-ClC_6H_4, *p*-MeC_6H_4), also made from $Os(PPh_3)_3Br_2$ and $P(OR)_3$,[431] and $Os(P(OPh)_3)_4Cl_2$, made from $OsNCl_3(AsPh_3)_3$ and $P(OPh)_3$.[265] For $Os\{P(OMe)_3\}_2$(octaethylporphyrin) see p. 618.

46.5.2.3 Osmium(III)

For $Os(PMe_2Ph)_2\{P(OR)_2Ph\}Cl_3$ (R = Me, Et) see p. 573.

46.5.2.4 Osmium(IV)

Reaction of $Na_2[OsCl_6]$ and $P(OMe)_3$ in the presence of amalgamated zinc gives $Os\{P(OMe)_3\}_2Cl_4$.[429]

46.5.3 Phosphorus Trihalide Complexes

The PF_3 ligand is similar to CO in many aspects of its coordination chemistry, and this is well exemplified by the small area of its osmium chemistry so far explored. The oxidation stages −II, 0 and II are represented, and there is an 'adduct' of osmium(VIII). Little is known about complexes of PCl_3 with osmium.

46.5.3.1 Osmium(−II)

The salt $K_2[Os(PF_3)_4]$ constitutes the most unequivocal instance in which osmium attains this rare oxidation state (it may always be argued for $Os(NO)_2(PPh_3)_2$, which has been crystallographically characterized, that −II is only a formal oxidation state). The salt is made from $Os(PF_3)_4H_2$ and potassium amalgam in ether. It is colourless, and the ^1H NMR and IR spectra are consistent with a symmetrical, presumably tetrahedral, structure.[432]

46.5.3.2 Osmium(0)

Osmium trichloride and Cu metal react with PF_3 at 250 °C under 500 atm to give the colourless $Os(PF_3)_5$, for which a trigonal bipyramidal structure was inferred.[433]

46.5.3.3 Osmium(II)

The dihydride $Os(PF_3)_4H_2$ is a colourless liquid (m.p. −72 °C), prepared from anhydrous $OsCl_3$ and PF_3 at 400 atm with H_2 at 120 atm at 250 °C. Both ^{31}P and ^1H NMR spectra suggest a *cis* structure.[432] With triethylamine $[Os(PF_3)_4H]^-$ is thought to be formed; the species was not isolated, but the ^1H NMR spectrum of a solution containing it was suggestive of a trigonal bipyramidal structure with the hydrido ligand occupying an axial position;[432] However, later ^1H and ^{19}F NMR data suggest that it is fluxional in solution.[434]

A number of tertiary phosphine complexes of osmium(II) substituted by PF_3 have been reported. Thus, reaction of $Os(PPh_3)_3H_4$ and PF_3 yields *cis*-$Os(PF_3)(PPh_3)_2H_2$ and *cis*-$Os(PF_3)(PPh_3)_3H_2$,[435] and the former reacts with HCl to give *cis*-$Os(PF_3)_2(PPh_3)_2HCl$.[436] This in turn with HCl under pressure gives *cis*-$Os(PF_3)_2(PPh_3)_2Cl_2$,[436] and reaction of PF_3 with *mer*-$Os(PMe_2Ph)_3Cl_3$ with zinc will give both the *cis* and *trans* forms of both $Os(PF_3)_2(PMe_2Ph)_2Cl_2$ and $Os(PF_3)(PMe_2Ph)_3Cl_2$.[437]

46.4.3.4 Osmium(III)

For $Os(PMe_2Ph)_2\{P(OR)_2Ph\}Cl_3$ (R = Me, Et) see p. 572. Reaction of osmium metal with PCl_5 at 600 °C gives a brown, volatile solid $OsCl_3 \cdot PCl_3$, the magnetic susceptibility of which was measured from 77 to 373 K; at the latter temperature μ_{eff} is 1.94 BM.[438] Presumably this material has a polymeric structure so as to give it octahedral coordination.

46.5.3.5 Higher oxidation states

At −100 °C OsO_4 will react with PF_3 to give $(OsO_4)_2 \cdot PF_3$; at 60 °C $OsO_4 \cdot PF_3$ is the product. With PCl_3, OsO_4 gives a black material, $OsO_2 \cdot PCl_3$.[439]

46.5.4 Tertiary Arsine Complexes

A substantial number of these have been reported for osmium, particularly with $AsPh_3$. Predictably the chemistry is quite similar to that for the analogous phosphine species.

46.5.4.1 Hydrido arsines

This is an area which has been much less explored in osmium chemistry than that of the hydrido phosphines. Some physical data are given in Table 17.

No monohydrido arsines seem to be known; reaction of $Os(AsR_3)_3H_4$ and AsR_3 in toluene gives the dihydrido species *cis*-$Os(AsR_3)_4H_2$ (AsR_3 = $AsEt_2Ph$, $AsEtPh_2$), and the ^1H NMR spectra of these suggest a *cis* configuration as is the case for the phosphine analogues.[276] No trihydrido complexes have been reported, but examples of $Os(AsR_3)_3H_4$ are known, made by reaction of *mer*-$Os(AsR_3)_3Cl_3$ with sodium borohydride (AsR_3 = $AsMe_2Ph$,[404] $AsEt_2Ph$,[276,404] $AsEtPh_2$,[276] $AsPh_3$[426]). Carbonylation of $Os(AsEtPh_2)_3H_4$ with CO yields $Os(AsEtPh_2)_3(CO)H_2$.[276]

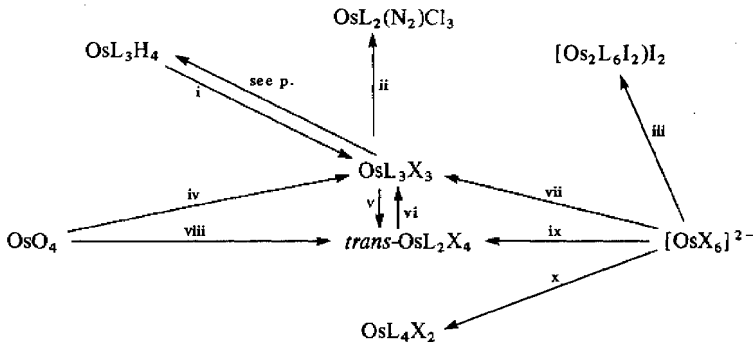
46.5.4.2 Halo arsine complexes

The general chemistry here, though not as extensively investigated as yet, follows the general pattern of the corresponding halo phosphine complexes. (see Table 18). As with these and with the halo stibines, oxidation states of II, III and IV are represented.

Reaction of $[OsX_6]^{2-}$ (X = Cl, Br) with H_3PO_4, HX and $AsMe_2Ph$ or $AsMePh_2$ gives $Os(AsR_3)_4X_2$; although the configurations were not established in this relatively early work[440] it

seems likely that they may be *trans*. The IR spectra of $Os(AsPh_3)_4Br_2$, made by refluxing $(NH_4)_2[OsCl_6]$ and HBr with $AsPh_3$ in 2-methoxyethanol, suggest that this has a *trans* configuration.[370]

There has been a more extensive study of osmium(III) complexes of the form $Os(AsR_3)_3X_3$, and these are summarized in Scheme 15 (see also Table 18).



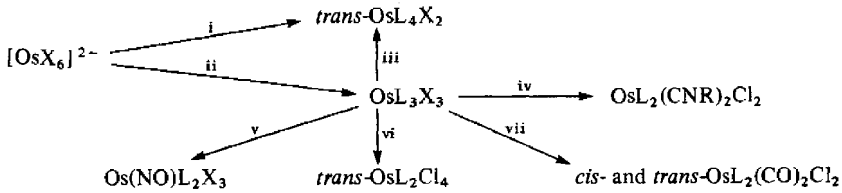
i, HCl ($AsMe_2Ph$, $AsEt_2Ph$);[404] ii, Zn, N_2 ($AsMe_2Ph$, $AsEt_2Ph$);[273] iii, HI ($AsMe_2Ph$, $AsMePh_2$);[440] iv, HX ($AsPr^n_3$,[411] $AsMe_2Ph$,[411] $AsEtPh_2$[276]); v, CCl_4 ($AsPr^n_3$, $AsMe_2Ph$,[411] $AsEt_2Ph$[404]); vi, N_2H_4 ($AsPr^n_3$);[411] vii, *Cl, Br*: $AsMe_2Ph$,[440] $AsMePh_2$,[422,440] $AsRPh_2$ (R = Et, Pr, Bu);[422] *Br*, $AsPh_3$.[421] viii, HCl ($AsPr^n_3$, $AsEt_2Ph$,[423] $AsPh_3$[370]); ix, $AsPh_3$ (Cl,[370] Br[421]); x, H_2PO_2, HX (X = Cl, Br) ($AsMe_2Ph$, $AsMePh_2$).[440]

Scheme 15 Preparative routes to haloarsine complexes

46.5.5 Tertiary Stibine Complexes

As is the case with most elements the stibine chemistry has been a largely neglected area and this is certainly so for osmium: very few osmium stibine complexes have been isolated. All of the species which have been isolated are with $SbPh_3$, though oxidation states span the range II to IV.

Preparative routes and typical properties are summarized in Scheme 16 (see also Table 18). The claimed *trans* configuration for $Os(SbPh_3)_4X_2$ (X = Cl, Br) and for $Os(SbPh_3)_2Cl_4$ is based at present on the simplicity of the IR spectra and, in the case of the black $Os(SbPh_3)_2Cl_4$, on the ^1H NMR spectrum also.[370] There is confusion however about the structure of $Os(SbPh_3)_3Cl_3$. On the basis of ESR, ^1H NMR and IR data a *mer* configuration has been proposed[370] and this would indeed seem to be the likely structure; an earlier IR study however was interpreted in favour of a *fac* structure.[441] The magnetic moment over a temperature range has been reported (100 to 300 K; μ_{eff} = 1.62 BM at 100 K rising to 1.73 BM at 300 K)[442] (or 1.92 BM at 293 K).[441] The bromo complex $Os(SbPh_3)_3Br_3$, made from $(NH)_2[OsBr_6]$ and $SbPh_3$ in 2-methoxyethanol, is purple, melting at 215 °C[421] or at 185–188 °C;[443] the same preparative route using methanol as the solvent gives a black



i, L (X = Cl, Br);[370] ii, L (X = Cl,[370,441] Br,[370] I[228]); iii, L, BH_4^- (X = Cl);[441] iv, Cl, RNC;[447] v, NO;[228,441] vi, Cl, CCl_4;[370] vii, CO.[441]

L = $SbPh_3$, R = *p*-MeC_6H_4

Scheme 16 Representative preparations and properties of triphenylstibine complexes

form melting at 263–265 °C.[370] On the basis of IR and ^{1}H NMR spectra a *fac* configuration for the black form was suggested;[370] a *mer* configuration for the purple form has been assigned on the basis of its IR spectra.[443] Clearly there is room for some further work in this area.

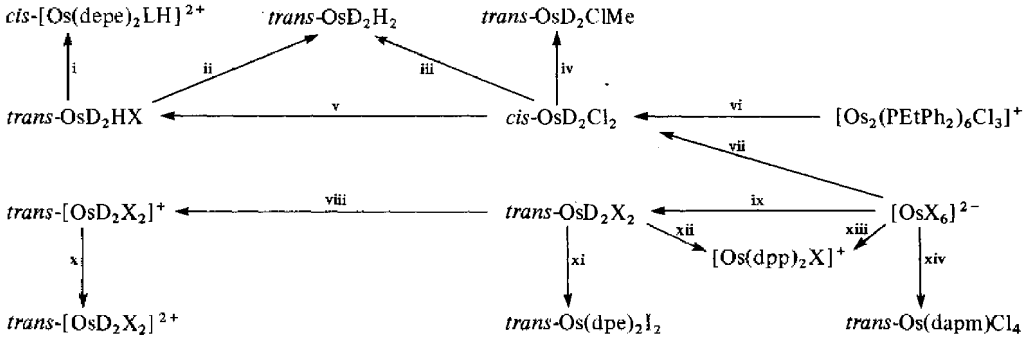
For nitrido stibines see p. 562, and for nitrosyl stibines see p. 547.

46.5.6 Bidentate Phosphine and Arsine Complexes

For convenience we consider these together. As with tertiary phosphines, arsines and stibines the oxidation states featured in the chemistry of these bidentate ligands are II, III and IV, with the former being predominant.

General preparative routes to these are summarized in Scheme 17. The abbreviations used below, in Scheme 17 and in Table 19 are the conventional ones, namely:

dmpe: bis(1,2-dimethylphosphino)ethane, $Me_2P(CH_2)_2PMe_2$
depe: bis(1,2-diethylphosphino)ethane, $Et_2P(CH_2)_2PEt_2$
dppm: bis(1,2-diphenylphosphino)methane, $Ph_2PCH_2PPh_2$
dppe: bis(1,2-diphenylphosphino)ethane, $Ph_2P(CH_2)_2PPh_2$
dpp: bis(1,2-diphenylphosphino)propane, $Ph_2P(CH_2)_3PPh_2$
pdmp: *o*-phenylenebis(dimethylphosphine), *o*-$C_6H_4(PMe_2)_2$
pdep: *o*-phenylenebis(diethylphosphine), *o*-$C_6H_4(PEt_2)_2$
diars: *o*-phenylenebis(dimethylarsine), *o*-$C_6H_4(AsMe_2)_2$
dapm: 1,2-bis(diphenylarsino)methane, $Ph_2AsCH_2AsPh_2$
dape: 1,2-bis(diphenylarsino)ethane, $Ph_2As(CH_2)_2AsPh_2$



i, BH_4^-, L= $P(OMe)_3$, $P(OPh)_3$, PhCN;[278] ii, $LiAlH_4$, dppe,[449] depm;[448] iii, $LiAlH_4$, pdep;[449] iv, Al_2Me_6, dppm, dppe;[450] v, X^-, $LiAlH_4$; *Cl*$^-$: dmpe, dppe,[449] dppm;[448] *I*$^-$: depe;[449] *SCN*$^-$: depe;[449] vi, dppm, dmpe, depe, dppe, pdep;[420] vii, Na/Hg, depm;[444] viii, *Cl*: $AgBF_4$, dppe, dpp;[445] H_2O_2, pdmp;[451] Cl_2, diars;[369] *Br*: Br_2, diars; *I*, *SCN*: $HClO_4$, I^- or SCN^-, diars;[369] ix, *Cl*: dmpe, dppm, depe, dppe,[420] pdmp,[451] dpp,[445] diars;[369] *Br*: diars;[369] *I*, *SCN*: I^- with X = Br, diars,[369] X = Br, SCN^-;[370] x, HNO_3: *Cl* (pdmp,[451] diars);[369] *Br*, *I*: (diars);[369] xi, I^- (dppe);[420] xii, BF_4^- (Cl, Br) dpp;[445] xiii, Cl, dpp;[445] xiv, dapm.[370]

Scheme 17 General preparations for chelating phosphine and arsine complexes

Table 19 Chelating Phosphine and Arsine Complexes

Complex	*Colour*	*M.p. (° C)*	*Spectroscopic and other properties*[a]
cis-$Os(dppm)_2Cl_2$	Yellow		X-ray[444]
cis-$Os(dppe)_2Cl_2$	Yellow	290–291	D[420]
trans-$Os(dmpe)_2Cl_2$	Yellow	298–300 (d)	UV/vis[453]
trans-$Os(dppe)_2Cl_2$	Yellow	293–296	UV/vis[454]
$[Os(dpp)_2Cl]BPh_4$	Brown	260	IR, UV/vis, ^{31}P NMR,[445] CV[452]
trans-$[Os(pdmp)_2Cl_2]ClO_4$	Purple		UV/vis, EPR, CV[451]

[a] CV = cyclic voltammetry; D = dipole moment

The X-ray crystal structure of $Os(dppm)_2Cl_2 \cdot CHCl_3$ shows this to be *cis*, with mean bond lengths of 2.452(2) (Os—Cl), 2.297 (P *cis* to Cl) and 2.339(1) Å (P *trans* to Cl), and a Cl—Os—Cl angle of 83.08(7)°.[444] The *cis* configuration of $Os(depe)_2Cl_2$ and of $Os(dppe)_2Cl_2$ in solution is demonstrated by the dipole moments of 9.3 and 8.3 D respectively.[420] The *trans* configurations of $[Os(dpp)_2Cl_2]BF_4$[445] and of the arsine complexes OsL_2Cl_2 (L = diars,[446,370] dape[370]) have been inferred from the relative simplicity of their far IR spectra. The complexes $Os(SCN)_2(dapm)_3$ and $OsI_3(dapm)_2$ have been reported; in the former the thiocyanate ligand is thought to be S-bonded.[370]

Magnetic susceptibility measurements on *trans*-$[OsL_2Cl]BF_4 \cdot \frac{1}{2}CH_2Cl_2$ (L = dppe, dpp) give surprisingly high magnetic moments at room temperature (μ_{eff} = 1.98 and 2.07 BM respectively),[455] while moments of $[Os(diars)_2X_2]$ are more normal (1.85 (Cl), 1.88 (Br), 1.93 (I) BM).[369] For the osmium(IV) species $[Os(diars)_2X_2](ClO_4)_2$ they are, not unexpectedly, lower: 1.25 (Cl), 1.22 (Br) and 1.16 (I) BM.[369] Another osmium(IV) complex is *trans*-$Os(dapm)Cl_4 \cdot EtOH$, made from the ligand and $[OsCl_6]^{2-}$ in ethanol.[370]

The IR and ^{31}P NMR spectra of $[Os(dpp)_2Cl]^+$ suggest that this has a trigonal bpyramidal structure in solution with a chloro ligand in an axial position.[445] On electrochemical reduction, it gives $Os(dpp)_2Cl$ (a rare case of osmium(I)) and, on further reduction, the osmium(0) species $[Os(dpp)_2Cl]^-$.[452]

For complexes of bidentate phosphines with metal–metal bonds see pp. 525, 527; for dinitrogen complexes see p. 555.

46.5.7 Complexes with Polydentate Phosphines and Arsines

The 'triphos' ligand (bis(2-diphenyl(phosphinoethyl)phenylphosphine, $[Ph_2P(CH_2)_2]_2PPh$) reacts with $[OsCl_6]^{2-}$ to give the yellow $Os(triphos)Cl_4$,[455] while reaction of bis(*o*-diphenylphosphinophenyl)phenylphosphine (QP) with $[Os(NO)(OH)(NO_2)_4]^{2-}$ and HCl gave the pale yellow $Os(QP)Cl_2$.[456]

One osmium complex of the phosphorus–arsenic chelate As—Pf—As (bis(2-diphenylarsinoethyl)phenylphosphine, $(Ph_2AsCH_2CH_2)_2PPh$) has been made from OsO_4 and the ligand in HCl; it is the orange $Os(As—Pf—As)Cl_3$.[457]

There is one complex with the tetradentate arsine qas (tris(*o*-diphenylarsinophenyl)arsine, $C_{54}H_{42}As_4$): $Os(qas)Cl_2$, made from $K_2[Os(NO)(OH)(NO_2)_4]$ and the ligand with HCl.[456]

46.6 OXYGEN-CONTAINING LIGANDS

46.6.1 Aqua and Hydroxo Complexes

No unsubstituted aqua complexes of osmium seem to have been reported, though we have already referred to a number of species in which H_2O is a ligand. Species such as $[Os(H_2O)_6]^{3+}$ and $[Os(H_2O)_6]^{4+}$ would be expected to exist.

There has also been little work on osmium hydroxo complexes apart from the now well-characterized *cis*-$[OsO_4(OH)_2]^{2-}$ (p. 592), *trans*-$[OsO_2(OH)_4]^{2-}$ (p. 581) and the two μ-hydroxo species structurally characterized, $M[Os_2(OH)O_8]$ (M = Rb, Cs) (p. 596). The $[Os(OH)_6]^{2-}$ species should certainly exist but does not seem to have been mentioned in the literature; even $[Os(OH)_6]^{3-}$ might be expected to be stable in the absence of oxygen. Other hydroxo (and aqua) complexes are considered in sections dealing with the other ligands present.

46.6.2 Osmium Oxo Complexes

The oxo complexes of osmium dominate the chemistry of the element, the cluster carbonyls notwithstanding, and the tetroxide is the single most important compound of the element.

In the area of osmium oxo chemistry there are three main topics of interest: the tetroxide itself, the 'osmyl' complexes which contain the *trans* $O{=}Os^{VI}{=}O$ unit, and the cyclic 'oxo ester' species which contain the Os^{VI} moiety. This is perhaps the most appropriate point at which to comment briefly on the reasons for the stability of these three systems.

Apart from ruthenium, osmium is the only element to form a neutral octavalent tetroxide, and certainly OsO_4 is chemically much more stable than RuO_4. It is a relatively mild oxidizing agent and

undoubtedly owes its stability largely to the ability of osmium, by virtue of its central position in the third row of the transition elements, to sustain the very high VIII oxidation state in the presence of π-donor ligands (O^{2-} alone, O^{2-} with N^{3-}, O^{2-} with F^-). The much greater oxidizing power of RuO_4 must surely derive from the fact that ruthenium is a second-row element and thus barely able to sustain the VIII state, while FeO_4 is unknown.

Whereas OsO_4 and the oxo esters considered below possess certain features unique to osmium, analogues of the 'osmyl' complexes are found for other elements capable of attaining a d^2 configuration (Ru^{VI}, Re^{V}, Tc^{V}, W^{IV}, Mo^{IV}), although it is true that the diversity of the coligands X in *trans*-$[Os^{VI}O_2X_4]^{n-}$ is rivalled only by that in the uranyl system. The reason for adoption of a *trans* geometry is electronic (see p. 579); *cis* dioxo species *cis*-$[MO_2X_4]^{n-}$ are found for the d° state (Re^{VII}, Mo^{VI}, W^{VI}, V^{V}) but are curiously missing from osmium(VIII) and ruthenium(VIII) chemistry.

The cyclic oxo esters are very much a feature of osmium(VI) chemistry but analogous rings are rare with other elements: they have been detected for ruthenium(VI) and manganese(V), but only for chromium(V) has any substantial oxo ester chemistry been uncovered. The osmium species are formed by two main routes: (a) by reaction of OsO_4 with alkenes, dienes or alkynes, in which case two electrons are transferred from the multiple bond to osmium(VIII) which is thus reduced to osmium(VI), or (b) by reaction of *cis*-glycols with *trans*-$[OsO_2(O_2R)_2]$ (R = H, Me) with elimination of water or methanol (see p. 582).

Both routes are facile for osmium and the d^2 osmium(VI) state is particularly stable for oxo species; the redox and kinetic properties of OsO_4 are such as to favour route (a) (whereas for RuO_4, for example, C=C cleavage would occur, and $[ReO_4]^-$ does not possess sufficient oxidizing power for the reaction to occur at all). Route (b) is facile because of the stability of the osmyl system in $[OsO_2(OH)_4]^{2-}$ and $[OsO_2(OMe)_4]^{2-}$ whereas analogues of these species are so far not known for other elements. Nevertheless, oxo ester rings for other elements should surely be commoner than they seem to be; the most fruitful approach to obtain them might be exploitation of a route analogous to (b) with, for example, *trans* dioxo species of ruthenium(VI) or of rhenium(V).

The arrangement of this large section on osmium oxo complexes follows the pattern of other sections in this chapter. We consider mononuclear complexes first, by increasing oxidation state and, within each oxidation state, we consider those complexes with the largest number of oxo ligands first. The same procedure is then followed for binuclear species. For convenience, however, mononuclear and polynuclear oxo esters are considered together.

46.6.2.1 Mononuclear complexes

(i) Osmium(IV) and (V) complexes

(a) Osmium(IV). For $[O{=}Os(terpy)(bipy)]^{2+}$ see p. 543.

(b) Osmium(V). The salt $Li_7[OsO_6]$ has been reported, made by reaction of $Li_5[OsO_6]$ and Li_2O with osmium metal. On the basis of X-ray studies of this hexagonal lattice the Os=O distance was estimated as 2.07 Å, suggesting that this is a lattice compound rather than a true complex.[459] There is a brief report of $Li_3[OsO_4]$[460] but again there is no evidence that $[OsO_4]^{3-}$ tetrahedra are involved.

(ii) Osmium(VI) complexes

As mentioned above the chemistry here is dominated by that of the osmyl species (see p. 581) and by oxo ester complexes (p. 584).

(a) Hexa-, penta- and tetra-oxo species. A substantial number of these have been reported, but in no single case is it certain that they contain discrete mononuclear species. Those reported include $[OsO_6]^{6-}$, $[OsO_5]^{4-}$ and $[OsO_4]^{2-}$ ions. Examples are $Li_6[OsO_6]$, $Na_4[OsO_5]$, $Ba_2[OsO_3]$, $Ba_3[OsO_6]$[460] and $Ba[OsO_4]\cdot nH_2O$;[461] the IR spectrum of $Ba_3[OsO_6]$ has been measured.[462]

For many years the 'osmates' $M^I_2[OsO_4]\cdot 2H_2O$ (M = Na, K)[463] and $Ba[OsO_4]\cdot H_2O$ were regarded as being tetrahedral osmium(VI) species, but it is now known that the sodium and potassium salts at least contain the *trans*-$[OsO_2(OH)_4]^{2-}$ ion;[327,464,465] the barium salt could be $Ba[OsO_2(OH)_4]$ or, possibly, contains the $[OsO_3(OH)_2]^{2-}$ anion (see below).

(b) Trioxo species. Few of these are known for osmium(VI). The species $[OsO_3(OH)_3]^{3-}$ is said to be present in solutions of $[OsO_2(OH)_4]^{2-}$.[466] It is possible that '$Ba[OsO_4]\cdot nH_2O$', made by reaction of $Ba(NO_3)_2$ with $K_2[OsO_2(OH)_4]$,[461] could be $Ba[OsO_3(OH)_2]$ since '$Ba[RuO_4]\cdot 2H_2O$' has been shown by X-ray studies to be $Ba[RuO_3(OH)_2]$ (in which there is a trigonal bipyramidal anion with three oxo ligands in equatorial positions).[467]

A number of trioxo species are claimed in the earlier literature. Thus, '$OsO_3(py)_2$' has long been regarded as such but is now known to be $Os_2O_6(py)_4$[468,469] (though in aqueous solution there is an equilibrium between the monomer and dimer[470,471]). Likewise the claimed 'oxy-oxmyl' salts $[OsO_3X_2]^{2-}$ (X = Cl, Br, NO_2^-, $\frac{1}{2}$ox)[204] are probably $[Os_2O_6X_4]^{4-}$ (see pp. 593 and 595).

(c) Dioxo ('osmyl') species.

As mentioned above (p. 579) this is one of the most important classes of osmium complexes, rivalling in number and diversity the oxo esters to be discussed in the next section. The trivial name 'osmyl' denotes the *trans* $Os{=}Os^{VI}{=}O$ grouping and, like 'uranyl' for $O{=}U^{VI}{=}O$, has passed into common parlance and will be used here.

We have already mentioned that the easily attained d^2 configuration for osmium favours the formation of these species (just as d^0, for other elements but apparently not for osmium, favours the formation of *cis* dioxo species[461,472]). The realization in 1960[464] that the long-known[463] and supposedly tetrahedral '$K_2[OsO_4]\cdot 2H_2O$' was diamagnetic and its consequent reformulation as *trans*-$K_2[OsO_2(OH)_4]$[464] (subsequently confirmed by X-ray studies[327,465]) led to a rationalization of the osmyl complexes.

Almost all osmyl complexes are octahedral (the few exceptions are treated on p. 582) and the great majority have linear or almost linear $O{=}Os{=}O$ systems (Table 20); most are mononuclear but a few are binuclear with a $\mu\mu'$-dioxo bridge.

Table 20 X-Ray Structural Data on 'Osmyl' Complexes

Complex	d_{OsO} (Å)	*OOsO* (°)	d_{OsX} (Å)	*XOsX* (°)	d_{OsY} (Å)	*YOsY* (°)	*Ref.*
(*a*) $[OsO_2X_4]^{n+}$							
trans-$K_2[OsO_2(OH)_4]$	1.77	180	2.03	90	—	—	327,465
trans-$K_2[OsO_2Cl_4]$	1.750(2)	180	2.379(5)	90	—	—	487
trans-$[OsO_2en_2](HSO_4)_2$	1.74(1)	180	2.11(1)	80.2	—	—	493
(*b*) $OsO_2(O_2R)py_2$							
$OsO_2(O_2C_5H_6N_2O_2)py_2$	1.85	162	1.90	85	2.16	94	515
$OsO_2(O_2C_6H_8N_2O_2)py_2\cdot H_2O\cdot 3py$	1.744	164.0	1.967	84.4(4)	2.169	89.8	498
$OsO_2(O_2C_{10}H_{13}N_5O_4)py_2$	1.78(4)	164(3)	1.95(5)	90(3)	2.18(6)	91(3)	516
$OsO_2(O_2C_{19}H_{12})py_2\cdot C_7H_8$	1.72	169	1.95	86	2.11	91	517
(*c*) *Miscellaneous*							
$OsO_2(OH)_2phen_2$ (X = O, Y = N)	1.742(4)	166.2(2)	1.983(4)	91.0(2)	2.130(5)	78.9(2)	469
$OsO_2(NH_2CH_2CO_2)_2$	1.731(3)	180.0	2.038(3)	78.9(1)[b]	2.114(3)		495
$K[OsO_2(OAc)_3]\cdot 2AcOH$	1.711	125.2(3)	2.026		2.148[b]	59.2[b]	483

[a] Chelating OOsN angle. [b] Chelating acetato ligand.

For $Os_2O_6py_4$ and $K_4[Os_2O_6(NO_2)_4]$ see Table 25 and p. 595; for $Os_2O_4(O_2C_6H_{10})_2(NC_7H_{13})_2$ see Table 25 and pp. 587; for $Os_2O_4(O_4C_8H_{12})py_4\cdot 4H_2O$ see p. 586 and Table 21.

They are all diamagnetic, and this can be attributed to the large tetragonal compression of the octahedron by the *trans* $O{=}Os$ bonds causing the two *d* electrons to pair up in the d_{xy} orbital (assuming the oxo ligands to lie on the *z* axis).[464]

Another approach is to envisage the formation of two three-centre, four-electron MOs involving $2p_x^2$–d_{xz}^0–$2p_x^2$ and $2p_y^2$–d_{yz}^0–$2p_y^2$ orbitals.

We classify here mononuclear osmyl complexes *trans*-$[OsO_2X_4]^{n-}$ by the nature of the ligand X; binuclear osmyl complexes are considered on p. 595.

Osmyl complexes with O-donor ligands. Preeminent amongst these are the 'osmates', sometimes called 'osmiates' in the early literature, and still often incorrectly formulated as salts of '$[OsO_4]^{2-}$'. The sodium, potassium and barium salts were reported in 1844,[474] but it is only recently that the rubidium and cesium salts were prepared.[475] The purple potassium salt is the best known and is a useful starting material for the preparation of other osmyl or osmium complexes. It is easily made from OsO_4 in excess KOH with added ethanol functioning both as reducing and precipitating agent,[464,476] and can also be made from osmium metal by fusion with KOH and KNO_3.[477] The sodium salt, though more soluble, is less easy to characterize and has a variable degree of hydration depending on the amount of ethanol added to the OsO_4–NaOH mixture.[478] The X-ray crystal structure of the potassium salt clearly shows it to have the *trans* structure (I)[327,465] (Table 20) postulated earlier on the basis of its diamagnetism and electronic spectra.[464] The acid dissociation constants of '$H_2[OsO_2(OH)_4]$' have been determined.[479] The possibility that '$Ba[OsO_4]\cdot nH_2O$' (and hence $Ba[OsO_2(OH)_4]\cdot 2H_2O$) could be $Ba[OsO_3(OH)_2]$ has been mentioned above (p. 580).

A closely related species is the olive-green $K_2[OsO_2(OMe)_4]$, made from KOH and OsO_4 in methanol.[480–482] Its use in electron microscopy of biological tissue has been proposed.[482] From it and acetic acid can be prepared the blue $K[OsO_2(OAc)_3]$;[480] on recrystallization from acetic acid this gives $K[OsO_2(OAc)_3]\cdot 2AcOH$ in which the osmyl group is emphatically *not* linear (Figure 28).

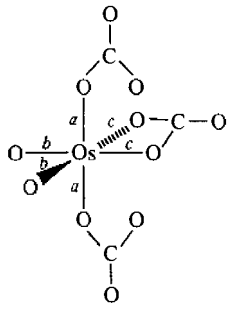


Figure 28 Structure of $K[OsO_2(OAc)_3]\cdot 2AcOH$[483]

The bent osmyl unit (OOsO angle = 125.2(3)°) is *trans* to a chelating acetato ligand, the octahedral coordination being completed by two monodentate acetato ligands. (mean $a = 2.026$, mean $b = 1.711$, mean $c = 2.148$.Å).[483]

The oxalato complex $[OsO_2ox_2]^{2-}$ has long been known as the sodium, potassium, ammonium, rubidium, cesium, magnesium and silver salts; the normal method of preparation is to treat OsO_4 with oxalic acid and the appropriate cation.[204] Recent electronic spectral studies on the tetrabutylammonium salt of $[OsO_2ox_2]^{2-}$ and $[OsO_2(malonate)_2]^{2-}$ show vibrational fine structure.[484] These are clearly true osmyl species, but the ion '$[OsO_3ox_2]^{2-}$'[204] may be better formulated as $[Os_2O_6ox_4]^{4-}$, rather than as the previously suggested $[OsO_2(OH)_2ox]^{2-}$.[21] The salts $M^I_2[OsO_2(salicylate)_2]$ are also reported (M = Na, K, NH_4, Rb, Cs).[485]

The diolato complexes $K_2[OsO_2(O_2R)_2]$ containing oxo ester rings are dealt with on p. 585 (see also Table 21). Formally related to these are the catecholato complexes $[OsO_2(Rcat)_2]^{2-}$, but they differ from them in that the metal–catecholato ring is likely to be planar (see p. 597). These are made for catechol or substituted catechols (Rcat = 4-methyl-, 4-*tert*-butyl-4-nitro-cholato) and $K_2[OsO_2(OH)_4]$. They react with pyridine to give $OsO_2(Rcat)py_2$.[486]

Table 21 Vibrational and Other Data for Osmyl Complexes

Complex	*Colour*	$\nu_{as}(OsO_2)$ (cm^{-1})	$\nu_s(OsO_2)$ (cm^{-1})	$\delta(OsO_2)$ (cm^{-1})	*Spectroscopic and other properties*[a]
$K_2[OsO_2(OH)_4]$	Purple	800	852	304	Raman,[461] IR,[21,462,518a] UV/vis,[464] ESCA,[93] X-ray[327,465]
$K_2[OsO_2(OMe)_4]$	Green	825			IR,[468] UV/vis[463]
$K[OsO_2(OAc)_3]$	Blue	845		300	IR,[468] X-ray[483]
$(Bu^n_4N)_2[OsO_2ox_2]$	Yellow	860	910	361	IR, Raman[484]
$(Bu^n_4N)_2[OsO_2(malonato)_2]$	Yellow	855	890	366	IR, Raman[484]
$K_2[OsO_2(O_2C_2H_4)_2]$	Red	803	859	330	Raman, IR[468]
$(PPh_4)_2[OsO_2cat_2]$	Red	824	864	290	Raman, IR,[468] ^{13}C NMR[518b]
$K_2[OsO_2Cl_4]$	Red	837	904	308	Raman, IR,[462,514] X-ray,[487] UV/vis[464,514]
$K_2[OsO_2Br_4]$	Red	843	899	292	Raman, IR,[462,514] UV/vis[514]
$[OsO_2(NH_3)_4]Cl_2$	Yellow	828	865	270	Raman,[462] IR[462,518a]
$[OsO_2en_2](HSO_4)_2$	Yellow		917		R,[476] X-ray[493]
OsO_2(glycinato)$_2$					X-ray[496]
$OsO_2(O_2C_2H_4)py_2$	Brown	824	870	292	IR[468]
$OsO_2(O_2C_2Me_4)(NC_9H_7)_2$	Brown	826		310	IR[519]
$OsO_2(O_2C_2Me_4)(NC_9H_7)$	Brown	898		310	IR[519]
OsO_2(OEP)	Olive-green	825			IR, UV/vis, ^1H NMR[504]
$K_2[OsO_2(CN)_4]$	Red	830	886	280	Raman,[461] IR,[21,461] CV[520]
$Na_6[OsO_2(SO_3)_4]\cdot 2H_2O$	Tan	842	858		Raman, IR[507]
$OsO_2Cl_2(PPh_3)_2$	Brown	840			IR, ESCA[93]
$OsO_2Br_2(PPh_3)_2$	Tan	847			IR, ESCA[513]
$Os_2O_4(O_4C_8H_{12})py_4\cdot 4H_2O$	Brown	830	879	290	Raman, IR[521] X-ray[522]
$OsO_2(OH)_2$phen	Brown	850	895		Raman, IR, X-ray[469]

[a] CV = cyclic voltammetry.

Halo osmyl complexes, $[OsO_2X_4]^{2-}$. The potassium, ammonium and cesium salts of $M^I_2[OsO_2Cl_4]$ and potassium and ammonium salts of $M^I_2[OsO_2Br_4]$ are known;[204] no fluoro or iodo osmyl complexes seem to have been reported, although *trans*-$[OsO_2F_4]^{2-}$ would be expected to be stable. Reaction of *trans*-$K_2[OsO_2(OH)_4]$ with HCl gives *trans*-$K_2[OsO_2Cl_4]$,[487] and a convenient preparation for salts of $[OsO_2Cl_4]^{2-}$ or $[OsO_2Br_4]^{2-}$ is to treat $K_4[Os_2O_6(NO_2)_4]$ with HCl or HBr.[204]

The X-ray crystal structure of $K_2[OsO_2Cl_4]$ shows it to have a *trans* structure for the anion (see Table 20).[487]

The so-called 'oxyosmyl' complex '$K_2[OsO_3Cl_2]$' has been made from $K_4Os_2O_6(NO_2)_4]$ and a deficiency of HCl.[204] Although the pyridinium analogue[488] of this has been reformulated as $(pyH)_2[OsO_2(OH)_2Cl_2]$,[461] a more attractive formulation is perhaps $K_4[Os_2O_6Cl_4]$, analogous to its nitro precursor.

The species $[OsO_2Cl_3(H_2O)]^-$ is thought to exist in equilibrium with $[OsO_2Cl_4]^{2-}$ (equation 5).[466]

$$[OsO_2Cl_4]^{2-} + H_2O \rightleftharpoons [OsO_2Cl_3(H_2O)]^- + Cl^- \quad (5)$$

The electrochemical reduction of $[OsO_2Cl_4]^{2-}$ to osmium(IV) and osmium(III) chloroaqua complexes has also recently been studied.[489]

Osmyl complexes with nitrogen donor ligands. The ammine $[OsO_2(NH_3)_4]Cl_2$ was first made by Frémy in 1844[474] and is still sometimes called 'Frémy's salt'. It is most easily made by reaction of *trans*-$K_2[OsO_2(OH)_4]$ with ammonium chloride[490] and is pale yellow and only sparingly soluble in water. On heating it decomposes to hydroxoammine complexes.[491]

The ethylenediamine complex *trans*-$[OsO_2en_2]Cl_2$ is made from *trans*-$K_2[OsO_2(OH)_4]$ and ethylenediamine dihydrochloride.[492] The X-ray crystal structure of the bisulfate salt (Table 20) confirms the *trans* geometry (the O=Os=O grouping, though linear, is not precisely perpendicular to the OsN_4 plane). The rate of exchange of $H_2{}^{18}O$ with *trans*-$[Os^{16}O_2en_2]^{2+}$ is slow but increases with increasing pH.[493] It reacts with $[Fe(H_2O)_6]^{2+}$ to give a deep blue species, possibly $[(H_2O)_5Fe—O—OsOen_2]^{4+}$, for which preliminary X-ray data were given.[494]

Direct reaction of OsO_4 with a series of amino acids in aqueous solution gives *trans*-$OsO_2(an)_2$ (an = glycinato, DL-glycinato, DL-valinato, DL-leucinato, DL-isoleucinato and DL-phenylalaninato), and the X-ray crystal structure of *trans*-$OsO_2(NH_2CH_2CO_2)_2$ has been elucidated (Table 20).[495] There are also X-ray data (Table 20) on $OsO_2(OH)_2phen \cdot 5H_2O$,[469] made by reaction of *trans*-$K_2[OsO_2(OH)_4]$ with 1,10-phenanthroline (phen).[496] The species exists in another monomeric form in which the hydrogen bonding of water molecules is slightly different; there is also a dimer, $Os_2O_6phen_2$.[496] Equilibria for this, and for $OsO_2(OH)_2TMEN \rightleftharpoons Os_2O_6(TMEN)_2$ (TMEN = *N,N,N',N'*-tetramethylethylenediamine), have been studied[496] and there are probably equilibria such as $OsO_2(OH)_2bipy \rightleftharpoons OsO_6bipy_2$ and $OsO_2(OH)_2py_2 \rightleftharpoons Os_2O_6py_4$.[471]

The oxo esters $OsO_2(O_2R)py_2$ are considered on p. 584 but since they are osmyl complexes we list X-ray data for four of these in Table 20; there are also IR data for them.[490,497]

It is worthwhile at this point to note that the O=Os=O moiety is linear only in complexes of the form *trans*-$[OsO_2X_4]^{n-}$, where D_{4h} symmetry exists by virtue of the equivalence of the four X ligands. In species of the type $OsO_2X_2Y_2$ (*e.g.* such as discussed above) it deviates substantially from linearity, by some 10° to 18°, in the complexes which have been studied by X-ray methods. In all cases the distortion is *away* from the relatively short Os—O (ester or hydroxo) bonds and *towards* the longer Os—N bonds. This effect has plausibly been explained on the basis that the π electrons in the O=Os=O system have a powerful repulsive effect towards electrons in the Os—O and Os—N moieties; these are minimized by bending of the O=Os=O system, and are also manifest in a relatively large OOsO angle (*ca.* 85°) and relatively large NOsN angle (*ca.* 94°) (though these are of course affected by ligand bite considerations).[498] There are obvious parallels here with the distortions observed in $OsO(O_2R)_2$ (p. 584),[499,500] $Os_2O_4(O_2R)_2$ (p. 584)[501] and $[OsNX_4]^-$ (p. 561);[329–332] similar effects are operative in the structures of $Os_2O_6py_4$ (Table 25)[469] and $K_4[Os_2O_6(NO_2)_4]$ (Table 25).[502]

The nitro complex '$K_2[OsO_3(NO_2)_2] \cdot 3H_2O$'[204] is not, as previously suggested, $K_2[OsO_2(OH)_2(NO_2)_2]$[21,503] but has been shown by X-ray studies to be $K_4[Os_2O_6(NO_2)_4]$ (p. 595).[502] For $[OsO_2(NO_2)_4]^{2-}$ and $[OsO_2(NO_3)_2(NO_2)_2]^{2-}$, see p. 598. An olive-green octaethylporphyrin (OEP) complex $OsO_2(OEP)$ can be made by oxidation of Os(CO)Cl(OEP) with H_2O_2.[504]

Osmyl complexes with miscellaneous donors. The cyano complex $K_2[OsO_2(CN)_4]$ is made from the action of aqueous KCN solution on OsO_4.[505] There are a number of osmyl complexes with sulfur donors. Reaction of OsO_4 with sodium sulfite in alkali gives $Na_2[OsO_2(SO_3)_4]$;[506] Raman and IR spectra suggest that the sulfite is S rather than O bonded.[507] There are complexes with thiourea, *e.g.*

$[OsO_2\{SC(NH_2)_2\}_2]SO_4$,[508] and dithiocarbamato species have been claimed.[509] Osmyl complexes with thiosemicarbazides are made from the ligand and OsO_4.[510,511] The species originally thought to be $OsOCl_3(PPh_3)_2$ and $OsOBr_3(PPh_3)_2$[512] are now known to be mixtures containing $OsO_2Cl_2(PPh_3)_2$[93,396] and $OsO_2Br_2(PPh_3)_2$;[513] they are made in a pure state by reaction of OsO_4 in HCl or HBr with ethanol, and a number of $OsO_2Cl_2(PR_3)_2$ species ($PR_3 = PMePh_2$, $PEtPh_2$, PEt_2Ph) have been so made.[513]

The 'osmyl' thioether complexes $OsO_2X_2(SR_2)_2$ ($SR_2 = SMe_2$, $MeS(CH_2)_2SMe$, *o*-$C_6H_4A(SMe_2)$, *o*-$C_6H_4(PPh_2)(SMe)$; X = Cl, Br) have recently been reported, made by reaction of the ligand with OsO_4 in concentrated HX. The IR, electronic and ^1H NMR spectra were recorded; the seleno complexes $MeSe(CH_2)_2SeMe$ were also prepared.[514]

One example of a *cis* dioxo complex has been reported, *cis*-$[OsO_2bipy_2](ClO_4)_2$, made by addition of Ce^{IV} to a solution containing *cis*-$[Osbipy_2(H_2O)_2]^{2+}$. The ^1H NMR and IR spectra ($\nu_{as}(OsO_2) = 878$, $\nu_s(OsO_2) = 858\,cm^{-1}$) support this very unusual structure for an osmium(VI) dioxo complex.[176] An X-ray crystal structure would clearly be of great interest.

For osmyl complexes with phthalocyanines see p. 619.

(d) Monooxo species. The simplest of these are the oxotetrafluoride and oxotetrachloride, but the large body of oxo esters come into this category also and are separately considered below.

Oxohalides (see Table 22). The oxotetrafluoride is a blue-green material, made by reaction of OsF_6 and OsO_4 at 175 °C,[523] and is diamagnetic. The oxotetrachloride $OsOCl_4$ is a dark-red diamagnetic liquid, very sensitive to moisture, made by reaction of an 8:1 Cl_2:O_2 mixture on osmium metal at 400 °C,[524] from OsO_4 and thionyl chloride under reflux[525a] or, in a new preparation, from OsO_4 and BCl_3.[525b] The IR spectrum of the gas suggested a square-based pyramidal structure for the compound.[526] It is isoelectronic with $[OsNCl_4]^-$ and so, like the latter, might be expected to undergo nucleophilic attack by phosphines at the axial ligand, but this does not appear to be the case.[265] The compound reacts with cesium fluoride in HCl to give the green '$Cs_2[OsOCl_6]$',[524] an apparently heptacoordinate material which should be further investigated. The so-called 'Os_2OCl_8', also made from osmium with a chloride:oxygen mixture,[527] is probably $OsOCl_4$.[525a]

Table 22 Monooxo Complexes

Complex	*Colour*	$\nu_{Os=O}$	*Spectroscopic and other properties*
$OsOF_4$	Blue-green		Raman[533]
$OsOCl_4$	Deep red	1028	IR,[525b,526] UV/vis[525b]
$OsOF_5$	Green	963	Raman, IR,[534] M,[535] X-ray[535]
$OsO(O_2C_2H_4)_2$	Black	992	IR,[497] X-ray[499,529]
$OsO(O_2C_2Me_4)_2$	Black	978	IR,[497] X-ray[500]

For $Os_2O_4(O_2C_2Me_4)_2$ see p. 000.

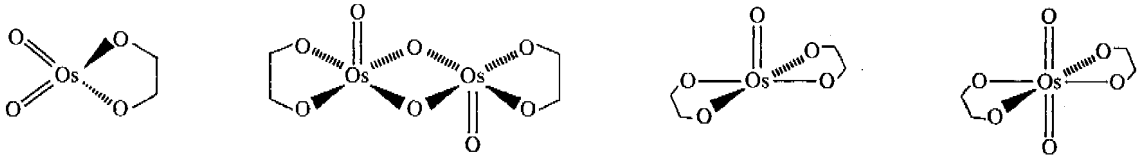
Osmium(VI) oxo esters. A large body of osmium(VI) complexes containing the cyclic system OsOCCO is known, generally made by reaction of OsO_4 with an alkene R. It is convenient to deal with these complexes as a group; we abbreviate the above ring as $Os(O_2R)$, the hypothetical O_2R^{2-} 'diolato' unit being derived from an alkene R (or diene or alkyne). Although ring complexes of this type are known for a few other metals it is only with osmium that such wide diversity and chemical stability are achieved.

The early work on the oxidation of alkenes and alkynes by OsO_4 (see p. 590) was little concerned with the osmium-containing intermediates. It was Criegee who showed, in 1936[528] and in 1942,[480] that alkenes R would react with OsO_4 to give isolable 'esters', formulated as $OsO_2(O_2R)$ ('monoesters') and, in some cases, $OsO(O_2R)_2$ ('diesters'); on hydrolysis these gave *cis* diols in high yield. He also showed in 1942 that the reaction of OsO_4 with alkenes was greatly accelerated by the presence of nitrogenous bases L (L = pyridine, isoquinoline) and that this reaction gave $OsO_2(O_2R)L_2$ which, on hydrolysis, gave the *cis* glycol. The possible mechanistic pathways for ester formation from alkenes are briefly considered on p. 590.

In this section we consider first the esters formed without nitrogenous bases (*i.e.* monoesters, diesters and salts of $[OsO_2(O_2R)_2]^{2-}$) and then the even larger body of information on esters containing nitrogenous bases. The latter section is sub-divided according to the Os:L ratio.

Ester complexes formed in the absence of nitrogenous bases. Criegee's 'monoesters' were formed by direct reaction of OsO_4 with the alkene R (*e.g.* tetramethylethylene, cyclopentene, indene, camphene, cholesterol) and were easily isolated.[480,528] He formulated them as presumably tetrahedral species (Figure 29a) (*i.e.* as $OsO_2(O_2R)$). Subsequent work showed them to be dimers, $Os_2O_4(O_2R)_2$ (b),[497] and the complex obtained from tetramethylethylene, $Os_2O_4(O_2C_2Me_4)_2$, was shown by X-ray

diffraction to have an *anti* structure (Figure 29b) the osmium having square-based pyramidal coordination. The terminal oxo ligand adopts the apical positions (Os=O = 1.675(7) Å) with the basal plane being formed by two diolato oxo ligands (mean Os—O = 1.870 Å) and the two bridging oxo ligands (Os—O = 1.922 Å, OsOOs (bridging) angle = 103.9(4)°). The bridging Os_2O_2 ring is planar. The mean O(terminal)OsO(based) angle is 111.1°,[501,529] a distortion comparable to that found in $[Os^{VI}NX_4]^-$ species (see p. 561) and probably arising from the same causes. A study of the ^1H NMR spectra of the complex showed that, in solution, there is a solvent-dependent mixture of the *syn* and *anti* isomers, the former being relatively more stable in solvents of high dielectric constant.[536]



(a) (b) (c) (d)

Figure 29 Strctures proposed for osmium ester complexes[501,529]

It has been shown that the hydrolysis of the monoester of 3-cyclohexenecarboxylic acid in $H_2{}^{18}O$ gave 3,4-dihydroxycyclohexanecarboxylic acid with no ^{18}O incorporation, which implies that cleavage occurs at the Os—O bonds.[530]

The 'diesters' of osmium(VI), $OsO(O_2R)_2$, are normally prepared by reaction of a *cis* diol $R(OH)_2$ with *trans*-$K_2[OsO_2(OMe)_4]$ or $K[OsO_2(OAc)_3]$, the resulting $K_2[OsO_2(O_2R)_2]$ (*vide infra*) then being acidified.[528] In a few cases diesters can be obtained directly from an alkene R with OsO_4[531] or by prolonged reaction of a diol $R(OH)_2$ with OsO_4.[497]

A single crystal X-ray of the species derived from ethylene glycol, $OsO(O_2C_2H_4)_2$, shows this to have a square-based pyramidal structure (Figure 29c).[449,532]

The coordination about the osmium is very similar to that found for the monoesters, the μ,μ'-dioxo bridge being replaced by a second oxo ester ring. The Os=O distance is 1.670(12) Å and the mean O(terminal)OsO(ester) angle is 110.1°; the mean Os—O (ester) distance is 1.885 Å and mean C—O distance 1.452 Å.[499,532] Very similar parameters have been found for $OsO(O_2C_2Me_4)_2$ (Os=O = 1.62, Os—O (ester) = 1.84.Å).[500]

There are a few examples of salts of the type $K_2[OsO_2(O_2R)_2]$, made, as mentioned above, by reaction of diols $R(OH)_2$ with *trans*-$K_2[OsO_2(OMe)_4]$ or $K[OsO_2(OAc)_3]$. No structural data are available but the IR and Raman spectra of $K_2[OsO_2(O_2C_2H_4)_2]$[468] are fully consistent with an osmyl structure (Figure 29d; see Table 21).

Oxo ester complexes with nitrogenous bases (L). Although most of these species contain the osmyl unit there are so many of them that it is appropriate to deal with them in a separate reaction. Most of the complexes have an Os:L ratio of 1:2 (the majority taking the form $OsO_2(O_2R)py_2$) and so we consider such species first and include those complexes of the type $OsO_2(O_2R)(L—L)$, where L—L is a bidentate N donor (usually 2,2′-bipyridyl). Within this first section we consider first the species derived from alkenes R or diols $R(OH)_2$, *viz.* $OsO_2(O_2R)L_2$ or $OsO_2(O_2R)L—L$, and then species derived from dienes, trienes and alkynes. We then deal with the much smaller body of complexes where the Os:L ratio is 1:1.

(1) Species containing OsL_2 or Os(L—L) units.

Complexes $OsO_2(O_2R)L_2$ and $OsO_2(O_2R)L—L$ formed from alkenes R or cis *diols $R(OH)_2$.* Criegee showed that the reaction of alkenes R with OsO_4 was greatly accelerated by the addition of N donors such as pyridine or isoquinoline (L); the products, of stoichiometry $OsO_2(O_2R)L_2$, were easy to isolate and crystallize, and on hydrolysis they would give the pure *cis* diol $R(OH)_2$.[480] Another route to $OsO_2(O_2R)L_2$ is the reaction[480] of a *cis* diol $R(OH)_2$ with 'OsO_3py_2' (now known to be $Os_2O_6py_4$,[469] though in solution the active species may well be OsO_3py_2 or $OsO_2(OH)_2py_2$).[470]

On p. 590 we discuss briefly the mechanism of the OsO_4–alkene–L reaction. The reaction in which *cis* diols $R(OH)_2$ react with 'OsO_3py_2' is thought to proceed *via* nucleophilic attack by the diol on osmium pyridine species. This is consistent with kinetic data and also with ^{18}O-labelling experiments on thymine glycols which demonstrated that there was no C—O bond cleavage.[530]

The reaction between 'OsO_3py_2', and $K_2[OsO_2(OMe)_4]$ or $K[OsO_2(OAc)_3]$ and $R(OH)_2$ normally occurs only with acyclic 1,2-diols and cyclic *cis* 1,2-diols; *trans* 1,2-diols do not react with the exception of *trans*-1,2-cyclohexanediol and *trans*-1,2-cycloheptanediol.[480] Behrman showed that *trans*-thyminediol, *trans*-thymidinediol and *trans*-1,3-dimethylthyminediol did react, albeit slowly,

with 'OsO_3py_2' as did the *cis* analogues;[470] presumably *trans–cis* isomerization had occurred. There are other kinetic data on the reaction of diols with oxoosmium pyridine,[537,538] substituted pyridine,[470] 2,2′-bipyridyl,[470,537,538,540] 1,10-phenanthroline[539] and TMEN[539,541] complexes. Studies have also been made of 'transesterification' reactions with L = pyridine,[537–539] ½bipyridyl,[537–539] ½phenanthroline[539] and ½TMEN.[539,541]

These $OsO_2(O_2R)L_2$ species are of course of the osmyl type; for convenience we give structural and vibrational data in the osmyl section (Table 21, pp. 581 and 582). There are four X-ray structures available (Table 20). In the complexes derived from thymine, $OsO_2(O_2C_5H_6N_2O_2)py_2$,[515] and from 1-methylthymine, $OsO_2(O_2C_6H_8N_2O_2)py_2 \cdot H_2O \cdot 3py$,[498] it is the erstwhile 5,6 double bond of the ligand which is spanned by the osmium, leading to a saturated pyrimidine ring system. The ester ring in the thymine complex has a twisted half-chair conformation[498,515] while that from 1-methylthymine is of a half-chair:[498] this difference may be due to disorder problems, however.[498] In the adenosine complex $OsO_2(O_2C_{10}H_{13}N_5O_4)py_2$ it is the *cis* 2′,3′-diol of the adenosine molecule which is so spanned, the nucleoside in the complex adopting a *syn* conformation rather than the *anti* arrangement in the free nucleoside.[516] The complex $OsO_2(O_2C_{19}H_{12})py_2 \cdot C_7H_8$ is derived from 9-methylbenzanthracene.[517] All of these complexes have O=Os=O units deviating substantially from linearity; this is discussed in the context of the osmyl complexes on p. 583.

The IR spectra of a number of $OsO_2(O_2R)L_2$ complexes (L = pyridine, isoquinoline) have been measured[468,497,519] and, in some cases, ^{18}O labelling used to help in assignments.[497] In general (see Table 21) $\nu_{as}(OsO_2)$ lies near 830 cm^{-1} and $\delta(OsO_2)$ near 300 cm^{-1}, as in other osmyl complexes.

From dienes and trienes. Reaction of OsO_4 and an excess of diene R in the presence of excess or isoquinoline[521] gives $OsO_2(O_2R)L_2$, while a similar reaction but with a 2:1 mole ratio of OsO_4:diene gives $Os_2O_4(O_4R)L_4$.[521] It is likely that $OsO_2(O_2R)L_2$ species have the structure illustrated for cycloocta-1,5-diene in Figure 30(a), since hydrolysis of $OsO_2(O_2C_8H_{12})py_2$ gives cyclooctene-5,6-diol. Raman and IR data are also consistent with this formulation.[521]

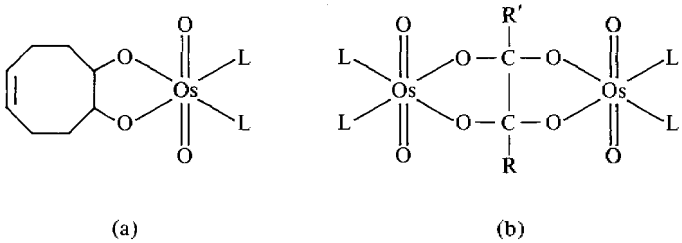


Figure 30 Likely structures of (a) $OsO_2(O_2C_8H_{10})L_2$ and (b) $Os_2O_4(O_2R)L_4$[521]

In the case of $Os_2O_4(O_4C_8H_{12})py_4 \cdot 4H_2O$ a crystal X-ray study shows that, as expected, a binuclear osmyl complex is formed with a bridging tetrolato ring (Figure 31).[522]

The conformation of the central ring is essentially that of a skewed chair–boat form. The osmyl units (Os=O = 1.72 Å) are substantially bent (OOsO angle = 163.5(7)°) from the ester group (Os—O (ester) = 1.95 Å) towards the nitrogen atoms (Os—N = 2.19 Å),[522] as in other osmyl complexes (p. 583).

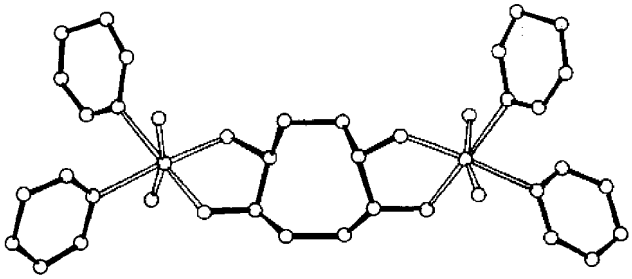


Figure 31 Structure of $Os_2O_4(O_4C_8H_{12})py_4 \cdot 4H_2O$ (reproduced with permission from B. A. Cartwright, W. P. Griffith, M. Schröder and A. C. Skapski, *Inorg. Chim. Acta*, **53**, L129, copyright 1981 Elsevier Sequoia SA)[522]

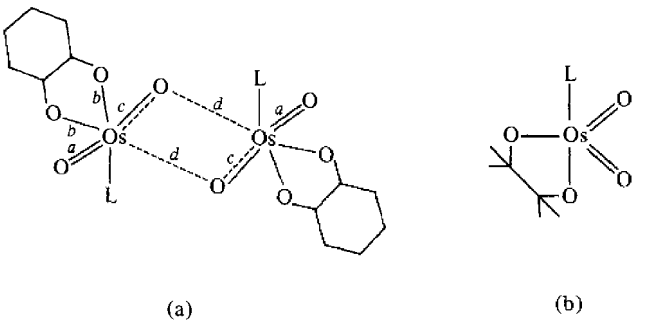
The formation of 1:1 and 2:1 OsO_4:furan oxo esters in the presence of pyridine and of 2,2′-bipyridyl has been studied kinetically using ^1H NMR.[543]

There are a few complexes with trienes. Reaction of methyl linolenate and OsO_4 in excess pyridine gives $Os_3O_6(O_6C_{19}H_{32})py_6 \cdot 2H_2O$ in which it seems that each of the three double bonds is spanned by an OsO_2py_2 moiety;[544] in $OsO_2(O_2C_{28}H_{44})py_2$, made from ergosterol, OsO_4 and pyridine, it seems that only one of the double bonds is so spanned since hydrolysis yields 3,5,6-ergostadientriol.[480]

From alkynes. Reaction of OsO_4 and pyridine[480,497,521] or isoquinoline[480,521] yields $Os_2O_4(O_4R)L_4$. On the basis of IR[497] and Raman, IR and ^1H NMR[521] spectroscopy a tetrolato structure was proposed with the inevitable osmyl unit (Figure 30b).[497,521]

(2) Species containing Os.L units.

(a) From alkenes. The propensity of OsO_4 to form 2:1 or 1:1 adducts with nitrogeneous bases (p. 592) led to a study of reactions of such species with unsaturated organic substrates. The complexes $OsO_4 \cdot L$ (L = pyridine, isoquinoline, phthalazine, quinuclidine) react with alkenes R to give $[OsO_2(O_2R)L]_2$.[519,545] The dimeric formulation derives from an X-ray crystallographic study carried out on $Os_2O_4(O_2C_6H_{10})_2(NC_7H_{13})_2$, the species obtained from cyclohexene with the $OsO_4 \cdot$ quinuclidine adduct. The structure is unusual, showing a weak Os_2O_2 bridge formed by one oxo ligand per metal atom of a distinctly bent osmyl moiety ($a = 1.73$, mean $b = 1.94$, $c = 1.78$, $d = 2.22$ Å; Figure 32a).[546] The OOsO osmyl angle is 154°; the terminal oxo bond length of 1.73 Å is slightly shorter than that involved in the asymmetric bridge (1.78 Å), the two bridge distances being 1.78 and 2.22 Å. The Os—O (ester) distances (1.90, 1.97 Å) and O (ester)OsO(ester) angles are comparable with those found[499,501] for other oxo ester complexes. In solution the complex is monomeric and is thought to have a trigonal bipyramidal structure with the oxo ligand in the equatorial plane (Figure 32b).



(a) (b)

Figure 32 Structure of $OsO_2(O_2R)L$: (a) in the solid state and (b) in solution[545]

Addition of excess ligand L to $OsO_2(O_2R)L$ solution gives $OsO_2(O_2R)L_2$;[545] reaction of 2:1 adducts such as $C_6H_{12}N_4 \cdot 2OsO_4$ formed from hexamethylenetetramine with alkenes R gives a mixture (equation 6).[519]

$$2C_6H_{12}N_4(OsO_4)_2 + 4R \rightarrow 2[C_6H_{12}N_4 \cdot OsO_2(O_2R)] + Os_2O_4(O_2R)_2 \quad (6)$$

It is a consequence of the unusual structure of these complexes in both the solid (dimer) and solution (monomer) states that the IR and Raman spectra show ν(Os=O) frequencies to be higher than in osmyl complexes.[519,545] In particular the IR band assigned to $\nu_{as}(OsO_2)$ lies near 890 cm^{-1} in all these oxo esters containing Os·L units rather than the 830 cm^{-1} absorption typical of those containing OsL_2 or Os(L) units; such behaviour is more typical[461] of *cis* rather than of *trans* dioxo complexes.

Finally we may mention the reaction products of the alkaloids brucine ($N_2O_4C_{23}H_{26}$) and strychnine ($N_2O_2C_{21}H_{22}$) with OsO_4. Initially red 1:1 adducts are formed when these are reacted with OsO_4 (p. 593) but then green osmium(VI) species $OsO_2(O_2R)$ are formed. Since brucine and strychnine (R) contain alkene linkages it is likely that an internal oxo ester has been formed in which an $OsO_4 \cdot N$ unit spans the double bond, with the N donor atoms within the molecule being coordinated to the osmium. Models show that such a structure, which would be analogous to that found for $OsO_2(O_2C_6H_{10})(NC_7H_{13})$ (see above), is feasible. Indeed, OsO_4 with brucine will react with cyclohexene to give $[OsO_2(O_2C_6H_{10})(\text{brucine})]_2$.[545,547a]

Complexes formed from dienes and alkynes. The quinuclidine adduct $OsO_4 \cdot L$ reacts with dienes R to give $Os_2O_4(O_4R)L_2$; this is likely to have a structure analogous to that found for $Os_2O_4(O_4C_8H_{12})py_4$ (p. 586) but with trigonal bipyramidal coordination about the osmium. With cyclooctadiene in excess, $OsO_4 \cdot L$ gives $OsO_2(O_2C_8H_{12})L$ for which vibrational ^1H NMR spectra suggest that only one double bond is spanned by an OsO_2L moiety.[545]

Just as OsO_4 in excess pyridine reacts with alkynes R to give $Os_2O_4(O_4R)py_4$, $OsO_4 \cdot L$ gives $Os_2O_4(O_4R)L_2$; again, there is likely to be trigonal bipyramidal coordination about the osmium.[545]

(iii) Osmium(VII)

(a) Hexa- and penta-oxo species. A few of these have been prepared, *e.g.* $M^I_5[OsO_6]$ (M = Li, Na),[460,547b] $Ba_5[OsO_6]_2$[460] (the IR spectrum of this was measured)[462] and $M^I_3[OsO_5]$ (M = Na, K).[460] On the basis of IR data it was tentatively suggested that $K_3[OsO_5]$ might in fact be $K_6[Os_2O_{10}]$.[462] Magnetic susceptibility measurements were made on $Li_5[OsO_6]$ from 39 to 251 K.[547b]

(b) Tetraoxo species. Recently the salt $(Ph_4As)[OsO_4]$ has been reported, made by reaction of $(Ph_4As)I$ with OsO_4 in CH_2Cl_2 solution. The grey-green complex has a magnetic moment of 1.37 BM at room temperature and the susceptibility follows the Curie–Weiss law from 4.2 to 140 K; (θ = 2.6 K). The low moment has been attributed to spin–orbit coupling effects. Cyclic voltammetric studies in CH_2Cl_2 show a reversible one-electron process for the OsO_4/OsO_4^- couple (E_0 = 0.1 V *vs.* standard calomel electrode). The IR spectrum shows bands at 834 and 852 cm^{-1} assigned to ν_1 (A_1) and ν_3 (F_2), and the deformations ν_2 and ν_4 are at 240 cm^{-1}.[548] The ion functions as an oxidant for activated alcohols, converting primary alcholos to aldehydes.[549]

(c) Monooxo species. The oxopentafluoride $OsOF_5$ is well characterised and is a discrete molecular species. It is made by reaction of osmium with a 5:1 F_2:O_2 mixture at 300 °C under 5 atm.[534] The emerald green crystals melt at 59.2 and boil at 100.5 °C with a transition point at 32.5 °C. The X-ray crystal structure shows it to have the expected C_{4v} structure (Os=O = 1.74, Os—F (*cis*) = 1.78(3), Os—F (*trans*) = 1.72(3) Å).[535] It is interesting that the *trans* fluoro ligand seems to be slightly closer to the metal than the *cis*.

Thermodynamic parameters were collected from vapour pressure data; magnetic susceptibility measurements from 77 to 295 K showed the solid to obey the Curie–Weiss law with θ = 6 °C at μ_{eff} 1.47 BM at 298 K.[535]

The compound OsO_2F_3 is probably polymeric (see p. 596).[533]

(iv) Osmium(VIII)

Obviously the chemistry here is dominated by that of the tetroxide. We briefly consider the hexa- and penta-oxo species, then OsO_4, followed by species of the type $OsO_4 \cdot L$ and $OsO_4 \cdot L_2$. The few tri-, di- and mono-oxo complexes of osmium(VIII) conclude the section. (see Table 23).

Table 23 Osmium(VIII) Oxo Complexes

Complex	ν_{OsO}	*Spectroscopic and other properties*
$Sr[OsO_5(H_2O)]$		X-ray[550]
OsO_4	see Table 24	Raman, IR, UV/vis (see p. 000), Mössbauer,[184] NMR,[583,584] ESCA,[582] X-ray,[561] electron diffraction[562]
$OsO_4 \cdot NH_3$	917, 885	IR[66]
$OsO_4 \cdot py$	928, 915, 907, 885	Raman, IR[468]
$OsO_4 \cdot NC_7H_{13}$	925, 910, 900	Raman, IR,[519] X-ray[634]
cis-$Li_2[OsO_4(OH)_2]$	920–850	IR,[628] X-ray[624]
cis-$Na_2[OsO_4(OH)_2]$	845–740	IR,[628,629] X-ray[625]
cis-$Ba[OsO_4(OH)_2]$	880–820	IR, Raman,[462,629] X-ray[627]
cis-$Cs_2[OsO_4F_2]$	950–900	Raman, IR[462,631]
$Ph_4P[OsO_4Cl] \cdot CH_2Cl_2$	910, 895, 885	X-ray[632]

For binuclear species see Table 25.

(a) Hexa- and penta-oxo species

Acid dissociation constants of 'H_4OsO_6, $H_{2n}OsO_{4+n}$, H_2OsO_5' and '$H_2OsO_5 \cdot H_2O$' have been published on the basis of measurements of the variation with pH of the electronic spectra of OsO_4 in aqueous solution.[479]

The X-ray crystal structure of the salt $Sr[OsO_5(H_2O)]$ shows this to have a distorted octahedral (C_{4v}) structure with Os=O distances varying from 1.72 to 1.93 Å and an Os—O (H_2O) distance of 2.12 Å.[550] However, it has recently been suggested that this is incorrect and that the salt is $Sr[OsO_3(OH)_2(H_2O)](OH)_2 \cdot H_2O$ (see p. 592).

(b) Tetraoxo species

Osmium tetroxide, OsO_4. This is undoubtedly the most important compound or complex of osmium, and it was as the tetroxide that osmium was first separated and, as explained on p. 522, gave its name to the element. It is industrially important both in the fine organic chemicals industry (for the *cis* hydroxylation of alkenes) and in biological chemistry and medicine for the 'fixation' or

preservation of biological tissue. Its use for the latter purpose can be dated to 1849[551] and for catalytic hydroxylation to 1913.[552] It is also an important precursor for other osmium complexes (p. 590).

The author has written a short general review on OsO_4[553] and there is a good recent review on the chemistry of its reactions with alkenes, dienes and alkynes.[554] In this section we describe its preparation, then its physical properties and chemical reactions.

Preparation. The oxidation of the metal or of any osmium salts will, if vigorous enough, produce the tetroxide; this is very volatile and can be distilled off or extracted from aqueous solution into an inert solvent such as CCl_4. Treatment of the metal at 300 °C with oxygen gives OsO_4,[477] and powdered osmium will also react with aqueous hypochlorite to give it.[497] Various methods of treating osmium residues to give OsO_4 have been described: oxidation with chromic acid and a nitric–sulfuric acid mixture followed by steam distillation;[555] oxidation by permanganate in acid solution[556] or conversion of residues to a thiourea complex followed by oxidation with H_2O_2 gives OsO_4[557] which, in both of these latter methods is then extracted into CCl_4.

Properties. Osmium tetroxide forms pale yellow crystals with a very characteristic odour (a possible description is that of a mixture of ozone and damp hay). It has a considerable vapour pressure at room temperature and so must be kept in stoppered container or (preferably) in sealed ampoules. The vapour is toxic (TLV 2.5 p.p.m.).[558a] The long-term occupational exposure limit (OEL) is 0.002 mg m^{-3}.[558b]

The compound melts at 40.46 ± 0.1 °C and there is a transition point at 72.54 ± 0.4 °C.[559] It is slightly soluble in water to give a very pale yellow solution but is very soluble in organic solvents, polar or non-polar (see below). Thermodynamic data of the compound have been reviewed.[560]

In the solid and gaseous states it is tetrahedral, with X-ray studies on the solid indicating a very slight distortion (two Os=O distances of 1.684(7) and two of 1.710(7) Å, with OOsO angles of 106.7(4) and 110.7(3)°).[561] It seems reasonable to ascribe these very slight distortions to solid-state effects (in the gas phase the Os—O distance is 1.711(3) Å[562]). Raman data (see below) suggest that the tetrahedral symmetry is retained in the pure liquid.[563]

OsO_4 in solution. The solubility of the tetroxide in water at 25 °C is 72.4 g dm^{-3}.[564] Although earlier studies on the partition coefficient of OsO_4 from its aqueous solution with CCl_4 seemed to indicate tht some $[OsO_4]_n$ polymers were present, this is now thought unlikely;[565] certainly the Raman spectrum of the aqueous solution is very similar to that of the solid.[563] There is, however, evidence of aggregation in propane or NF_3 solutions at 90 K.[566] In aqueous solution OsO_4 behaves as a very weak dibasic acid.[479] Extraction constants for OsO_4 in a variety of organic solvents have recently been measured.[567a]

Polarographic and electrochemical studies. Earlier polarographic data for OsO_4 have been reviewed.[567b] Most data concern alkaline aqueous solutions; the reductions $Os^{VIII} \rightarrow Os^{VI}$, $Os^{VI} \rightarrow Os^{IV}$ and sometimes $Os^{IV} \rightarrow Os^{III}$ have been observed, and in oxygen-free alkali the $Os^{VI} \rightarrow Os^{IV}$ and $Os^{IV} \rightarrow Os^{III}$ steps have $E_{\frac{1}{2}}$ values of −0.41 and −1.08 V (*vs.* SCE).[568]

Spectroscopic data. This attractive molecule has long been a favourite for spectroscopic studies and only the most comprehensive or recent data are given here. The four fundamental vibrational frequencies have often been measured for the molecule; since all four are Raman active but only two (the F_2) are IR active we concentrate on the Raman data (Table 24).

Table 24 Vibrational Spectra of OsO_4 (cm^{-1})

	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$	*Ref.*
Gas, 373 K	965.2	333.1	960.1	322.7	569
Pure liquid	964	338	953	334	563
Aqueous solution	962	333	952	333	563

IR spectra of gaseous $Os^{18}O_4$ show ν_3 and ν_4 to lie at 911.6 and 321.0 cm^{-1};[570] there are recent IR data on $^{192}OsO_4$.[571] Raman values for ν_1 and ν_2 are, for solutions in CCl_4, 964.5 and 335.2 cm^{-1} for $Os^{16}O_4$ and 909.7 and 316.5 cm^{-1} for $Os^{18}O_4$.[572]

There have been many force contact treatments (see for example ref. 573) and determinations of Coriolis coupling constants.[574] The use of transitions within the OsO_4 molecule as high-precision frequency standards using CO_2 lasers has been described in a number of publications.[575,576]

There have been detailed studies on the electronic absorption spectrum of the gas, and the magnetic circular dichroism spectrum has also been recorded and assigned;[577,578,580] such spectra were also obtained for the aqueous solution.[581] The electronic spectrum of the solid in an argon matrix at 20 K was measured and assigned.[580] An energy level diagram was constructed on the basis of the

gas phase spectrum.[579] There are also studies on the photoelectronic spectra of gaseous OsO_4[582] and the ^{189}Os Mössbauer spectrum was recorded.[184] Using molten OsO_4 a very weak ^{187}Os NMR resonance was observed.[583,584]

Chemical reactions of OsO_4. We concentrate on the important oxidation reactions.

(a) *Oxidation of alkenes.* The subject has been recently and comprehensively reviewed[554] so we give only an outline here.

The first observation that OsO_4 reacted with alkenes was apparently made in 1894;[585] by 1913 Hofmann had established that OsO_4 could be used catalytically for the *cis* hydroxylation of alkenes with ClO_3^- as cooxidant.[552] However, it was Criegee who, in three classic papers,[480,481,528] laid the foundations of our knowledge of this important reaction. He showed that OsO_4 would react with alkenes R to give '$OsO_2(O_2R)$' and in some cases $OsO(O_2R)_2$. The reaction was greatly accelerated by addition of bases such as pyridine to give $OsO_2(O_2R)py_2$.[480,528] Hydroloysis of any of these gave the *cis* glycol $R(OH)_2$. It is now known that '$OsO_2(O_2R)$' is in fact dimeric, $Os_2O_4(O_2R)_2$ (see p. 585).[501,529]

The reaction of alkenes with OsO_4 is commonly thought to involve a concerted six-π-electron cyclization leading directly to a five-membered ring (Figure 29a), accounting for the exclusively *cis* addition to alkenes. However, Sharpless[586] has suggested that the direct nucleophilic attack of carbon on oxygen that this entails is unlikely and that, moreover, the intermediate (Figure 29a) involves an uncomfortable angular strain on the ester ring. The proposed mechanism involves initial formation of an asymmetric oxametallacycle intermediate *via* initial nucleophilic attack of the alkene at the metal rather than at oxygen.[586] This then rearranges and could dimerize to give (b) in Figure 29.[586] The scheme also accounts for the observed[480] rate increase in the OsO_4–alkene reaction consequent on addition of pyridine: attack by the latter would induce a reductive insertion of the Os—C bond of the oxametallacycle into an oxo group giving an ester which then reacts with more pyridine giving $OsO_2(O_2R)L_2$.[586] Unequivocal direct evidence for this appealing mechanism is so far lacking[586–589] though intermediates $[OsO_4 \cdot L]_2$, albeit in dimeric form, have been isolated,[545,546] and there is a report of the existence (but not the isolation) of a complex of OsO_4 with adamantylideneadamantane.[590] Kinetics of the reaction of OsO_4 with alkenes in the absence of nitrogenous bases have been studied[530] as have those of the OsO_4–alkene reaction in the presence of ammonia,[591] pyridine,[537,592,593] substituted pyridines,[530] 2,2′-bipyridyl[537,538,592,594] and TMEN.[594] The OsO_4–alkene reaction is also substantially accelerated by methylamine,[595] cyanide[596] and thiocyanate.[596]

Although OsO_4 is thought of as a specific oxidant for *cis* alkenes there are a few examples of hydroxylation of *trans* alkenes, e.g. *cis*- and *trans*-cyclodecene can be hydroxylated to the respective *cis* and *trans* diols.[597] The OsO_4–alkene–pyridine reaction can be made catalytic by the use of suitable secondary oxidants such as H_2O_2, ClO_3^-, Bu^{t}OOH, *N*-morpholine *N*-oxide, IO_4^-, O_2 and ClO^-.[554]

(b) *Reaction with dienes and trienes.* Criegee noted that ergosterol could be oxidized to 3,5,6-ergostadientriol by OsO_4 and pyridine and he isolated the intermediate ester;[480] there are scattered reports in the literature of the *cis* hydroxylation of dienes and trienes, *e.g.* norbornadiene to *exo-cis*-norbornane-2,3-diol[598] and of *cis,trans*-1,5,9-cyclododecatriene to 8-cyclododecane-*trans*-1,2-diol.[599] The kinetics of reaction of OsO_4–pyridine and OsO_4–bipyridyl to furans have been studied.[543] For a discussion of the oxo esters formed from OsO_4 and dienes, see p. 586.

(c) *Reaction with alkynes.*[544] The first to react OsO_4 with alkynes was Phillips in 1894,[585] and an early analytical method for osmium was based on the reaction of OsO_4 with acetylene.[600] Again it was Criegee who in 1942 noted that acetylene reacted with OsO_4–pyridine to give an 'ester'.[480] Later work showed that alkynes R (acetylene, phenylacetylene, methylphenylacetylene, diphenylacetylene) with OsO_4–pyridine gave $Os_2O_4(O_4R)py_4$; on hydrolysis the esters of the latter three alkenes gave benzil, benzoic acid and 1-phenylpropane-1,2-dione respectively. The reactions can be rendered catalytic by use of an OsO_4–$KClO_3$ reagent.[521] The oxo esters derived from alkynes are considered above (p. 587).

(d) *Reaction with glycols and catechols.* It has been claimed on the basis of electronic spectra that OsO_4 reacts with ethylene glycol, pinacol or trimethylethyleneglycol (R) to give $OsO_2(OH)_2(O_2R)$;[601] kinetics of the oxidation of ethyleneglycol to formaldehyde by OsO_4 have been reported.[602] Certainly the *prolonged* reaction of OsO_4 with ethylene glycol gives $OsO(O_2C_2H_4)_2$, and in the presence of pyridine $OsO_2\{OC_2H_4(OH)\}_2py_2$ is formed.[497] With catechol or substituted catechols (Rcat), species of the form $Os(Rcat)_3$, $[OsO(Rcat)_2]_n$ and *trans*-$[OsO_2(Rcat)_2]^{2-}$ can be isolated (see p. 597).[486]

(e) *Reaction with amino acids, peptides and proteins.* The direct reaction of OsO_4 with amino acids can be difficult owing to the facile oxidation of the NH_2 group[544] but recently a number of osmyl complexes $OsO_2(an)_2$ have been isolated from amino acids and OsO_4 (see p. 583), and an X-ray crystal structure of $OsO_2(glycinate)_2$ has confirmed the osmyl formulation. Earlier studies, perhaps carried out under less rigorous conditions, indicated that amino acid oxidation occurred when

OsO_4[544,592,603] or OsO_4–pyridine[544,603] was used. Blocking of the reactive NH_2 group and esterification of the carboxylate group give complexes of the form $Os_2O_6L_4$ and the kinetics of reaction of OsO_4 and pyridine with 1-methy-α-*N*-acetyl-DL-tryptophan were studied; attack is across the double band of tryptophan.[592] Peptides seem relatively unreactive towards OsO_4[544] though some cleavage may occur.[603]

The reaction of OsO_4 with proteins is a complex subject needing much further study. The evidence so far suggests that OsO_4 can cross-link proteins[544,603] and that the tryptophanyl residue in particular may be implicated.[603] In biological tissue, where OsO_4 reacts with membranous material containing both unsaturated lipids and proteins, there is evidence for lipid–protein cross-linking (see below).[544,604]

(f) *Reaction with nucleosides, nucleotides and nucleic acids.* The literature up to 1977 has been reviewed.[605,606] Of the nitrogenous bases in nucleic acids the ones most likely to react with OsO_4 are the pyrimidines, and indeed there has been much work on its reaction with thymine and its derivatives,[470,539,541] adenine derivatives,[537] cytosine and 3-methylytosine.[594] A sequence-specific osmium reagent for thymine–cytosine pairs has been devised.[607] Nucleosides on their own react slowly with OsO_4 but in the presence of donors such as pyridine[538,608] or 2,2′-bipyridyl[537,538] the reaction is much faster, giving osmyl species $OsO_2(O_2R)py_2$ or $OsO_2(O_2R)$bipy. Reactions of this type are observed with thymidine,[608] cytidine,[538] adenosine[538] or substituted adenosine.[537] We have already discussed the crystal structure of the adenosine complex $OsO_2(O_2C_{10}H_{13}N_5O_4)py_2$ (Table 20 and p. 586).[516] In the presence of pyridine, nucleotides react with OsO_4; kinetic data were obtained for the reaction of desoxythymidine-5′-monophosphate (dTMP),[608] and other nucleotide–OsO_4 reactions were also investigated.[540,608] Polyuridylic acid (poly U) is easily oxidized by OsO_4 with ammonia,[591] and direct visualization of individual osmium atoms in polyuridylic acid treated with OsO_4–bipyridyl has been achieved (shown in the paper in a remarkable series of photographs).[609]

In *in vitro* studies there is little observable reaction between OsO_4 and native deoxyribonucleic acid (DNA), but it does react with denatured DNA, in which the thymine bases have probably been hydroxylated to 5,6-dihydroxythymine *via* an osmium(VI) ester.[610]

(g) *Osmium tetroxide and biological tissue.* The oldest use of OsO_4 is for the 'fixation' or preservation of biological tissue and dates back to 1849,[551] although in 1804 Tennant[1] had noted that it stained the hands; there is a considerable literature on the subject.[611] Osmium tetroxide is unique in having a dual role: applied as a dilute aqueous solution to tissue followed by dehydration and mounting procedures it both preserves the biological material and stains certain parts, particularly membranes, with an osmium-containing material. These stained parts are visible in optical microscopy as black or grey areas but also, by virtue of the electron-scattering power of osmium, delineate those areas in electron micrographs. It has been demonstrated that the uptake of OsO_4 by membranous material in particular is related to the content of unsaturated phospholipids,[612] and this with other evidence has led to the suggestion that cross-linking of double bonds in such lipids could occur[497,613,614] by 'monoester' or 'diester' formation (p. 584). An earlier suggestion that simple hydrogen bonding of OsO_4 was involved[615] has been disproved.[614] It is also possible that proteins and unsaturated lipids are cross-linked in membranes by OsO_4 to give osmyl species;[544,604] the presence of osmium(VI) as well as osmium(IV) and osmium(II) in tissue has been demonstrated by ESCA data,[616] though such data have to be treated with some caution.[617] It is also clear that OsO_4 reacts with catechols ('phenolics') in plant tissue to produce a very deep stain, probably arising from $[OsO(cat)_2]_n$,[486,618] and will almost certainly stain alkaloids.[545,547]

Miscellaneous sections of OsO_4 There is a recent review on the role of OsO_4 in the catalysis of redox reactions,[619] and the OsO_4–catalyzed decomposition of H_2O_2 is thought to proceed *via* peroxo intermediates.[620] With CO_3^{2-} or SO_3^{2-} in aqueous solution OsO_4 gives $[OsO_2(OH)_4]^{2-}$, but with a mixture of SO_3^{2-} and CO_3^{2-} it is said that $[OsO_2(SO_3)_4]^{6-}$ and $[Os(SO_3)_6]^{8-}$ are formed.[621]

(v) *Tetraoxo osmium(VIII) complexes with other ligands*

(a) Oxo hydroxo and oxo aqua species. It has long been known that OsO_4 will react with alkali metal hydroxides to give deep red solutions from which unstable solids can be isolated (called 'perosomates', 'perperosmates' or 'osmenates' in the older literature). Early workers made $M^I_2[OsO_4(OH)_2]$ (M = K,[622,623] Rb,[623] Cs[622,623]) and $Ba[OsO_4(OH)_2]$[622]; the ammonium salt was also claimed[622] (though it might be thought that $(NH_4)[OsO_3N]$ would be the product of the reaction of OsO_4 and NH_4OH). By using a deficiency of M^IOH with OsO_4, $M^I[OsO_4(OH)]$ (M = Rb, Cs[623]) and $Cs[Os_2(OH)O_8]$[623] were claimed. Recent X-ray work has shown the existence of *cis*-$[OsO_4(OH)_2]^{2-}$, $[Os_2(OH)O_8]^-$ and of $[OsO_5(H_2O)]^-$ also.

The X-ray crystal structures of *cis*-$Li_2[OsO_4(OH)_2]$,[624] *cis*-$Na_2[OsO_4(OH)_2]$[625] and *cis*-$M^{II}\{OsO_4(OH)_2\}$ (M = Ca, Sr[626] and Ba[626,627]) have been given, as have improved procedures for the isolation of *cis*-$M^I{}_2$ $[OsO_4(OH)_2]$ (M = Li,[628] Na, K,[628–630] Rb, Cs[629,630]). The anions have *cis* configurations,[629] as predicted by earlier Raman studies.[462] In $Li_2[OsO_4(OH)_2]$ the Os—O (OH) distance is 2.16 Å with mean Os=O 1.75 Å;[624] in the sodium salt there are two Os—O (OH) distances of 2.10 and 2.17 Å with the Os=O bond lengths varying from 1.74 to 1.82 Å;[625] in the barium salt there is disorder between one O—O (OH) and Os=O bond, while the other Os—O (OH) is 2.15 Å and the mean Os=O = 1.73 Å.[627] It has been suggested that the species formulated as $Sr[OsO_5(H_2O)]$ and for which a crystal structure has been reported (p. 588) is in fact $Sr[OsO_3(OH)_3](OH)\cdot 2H_2O$ or $Sr[OsO_3(OH)_2(H_2O)](OH)_2\cdot H_2O$.[629] For $M_2[Os_2O_8(OH)]$ (M = Rb, Cs) see p. 596.

The $[OsO_4(OH)_2]^{2-}$ ion has been implicated in the oxidation of ethylene glycol by OsO_4 in alkali, and a mechanism proposed for this reaction involving the $[OsO_3(OH)_3(OCH_2)_2OH]^{3-}$ ion.[602]

(b) Oxo halo complexes. The yellow $Cs_2[OsO_4F_2]$ has been made from excess CsF and OsO_4[622] and also the rubidium salt;[622] its Raman and IR spectra suggested a *cis* structure for the anion.[462,631] More recently, both it and $Rb_2[OsO_4F_2]$ have been made from RbF and OsO_4.[631] A salt of approximate composition $Cs[OsO_4F]$ has been obtained from OsO_4 and CsF; its Raman and IR spectra suggest that it may contain pentacoordinate osmium.[631]

The isolation and X-ray crystal structure of $(Ph_4)[OsO_4Cl]\cdot CH_2Cl_2$ have been reported. Reaction of OsO_4 in CH_2Cl_2 with $(PPh_4)Cl$ gives the orange-red crystals. The anion is trigonal bipyramidal with the chloro ligand axial; the mean Os—O distance is 1.72 Å and the Os—Cl distance is very long at 2.76(2) Å.[632]

(c) 'Adducts' of OsO_4 with N donors. Although '$OsO_4\cdot py_2$'[633] is now known to be $Os_2O_6py_4$,[469] there are loose 1:1 and 2:1 adducts of OsO_4 with N-donor ligands. These are unusual in that they appear to have very weak, long Os—N bonds such that the symmetry of the OsO_4 fragment is essentially undistorted and retains the reactivity of OsO_4 (see Figure 33 for structures of $OsO_4\cdot NC_7H_{13}$ and $[OsO_4]_2\cdot N_4C_6H_{12}$[634]).

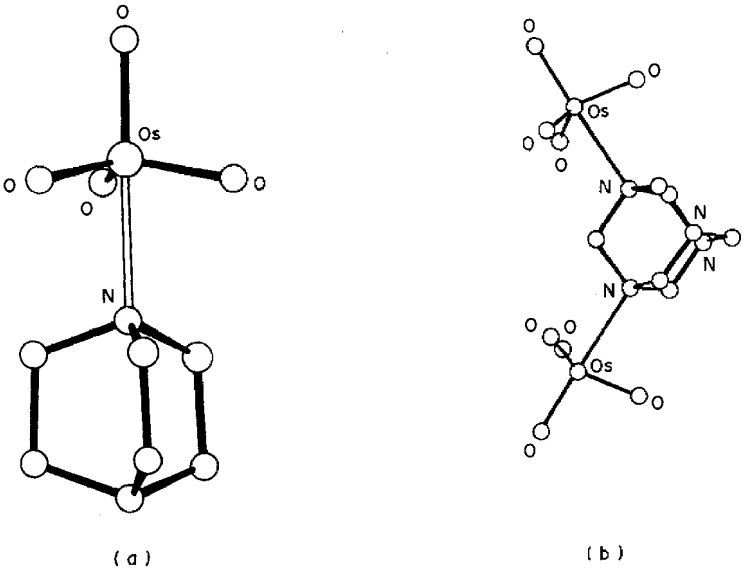


Figure 33 Structures of (a) $OsO_4\cdot NC_6H_{13}$ and (b) $(OsO_4)_2\cdot N_4C_6H_{12}$ (reproduced with permission from W. P. Griffith, A. C. Skapski, K. A. Woode and M. J. Wright, *Inorg. Chim. Acta*, **31**, L413, copyright 1978 Elsevier Sequoia SA)[634]

They are made by reaction of OsO_4 in aqueous solution or emulsion of the amine L to give $OsO_4\cdot L$ (L = pyridine,[468,480,519] NH_3,[66,333] pyridazine, quinuclidine (NC_7H_{13}), phthalazine and isoquinoline,[519] hexamethylenetetramine mandelate[635]) or $Os_2O_8\cdot L'$ (L' = hexamethylenetetramine ($N_4C_6H_{12}$), 1,4-diazabicyclo[2.2.2]octane, 5-methylpyrimidine and pyrazine).[519] With the exception of the pyridine, pyrazine and 5-methylpyrimidine adducts these produce little or no vapour pressure of OsO_4 at room temperature and so can be used as 'safe' forms of OsO_4; indeed, $[OsO_4]_2\cdot N_4C_6H_{12}$ is now commercially used in histochemistry as a replacement for OsO_4.[635]

The X-ray crystal structures of the quinuclidine and hexamethylenetetramine adducts show very long Os—N bonds (2.37 and 2.42 Å respectively) while the symmetry of the OsO_4 unit is little disturbed: the Os—O bond lengths are between 1.697 and 1.722 Å, and the O(axial)OsO(equatorial) angle of 100.6° is close to the tetrahedral angle of 109.47° (Figure 33).[634]

The reluctance of the remaining two nitrogen atoms in hexamethylenetetramine to coordinate may be due to unfavourable angles at these atoms brought about by coordination of the other two donor centres.[519]

It has been noted that a wide variety of alkaloids L containing one or more N-donor atoms will react with OsO_4 to give red solutions which almost certainly contain $OsO_4 \cdot L$ adducts (L = strychnine, brucine, quinine, sparteine, cinchonine, atropine, yohimbine, cocaine, emetine).[545,547] In the cases of strychnine and brucine an internal reaction subsequently occurs to give green osmium(IV) complexes $OsO_2(O_2L)$ (see p. 587). There is also evidence for the formation of 1:1 $OsO_4 \cdot L$ adducts with blocked amino acids (*e.g.* α-*N*-benzoyl-L-histidine, α-*N*-benzoyl-DL-methionine) and imidazoles.[544]

The reactions of $OsO_4 \cdot NC_7H_{13}$ with alkenes,[519,545,546] dienes[545] and alkynes[545] are considered on p. 590 and those of $[OsO_4]_2 \cdot N_4C_6H_{12}$ with alkenes[545] on p. 587.

6.2.1.4.3. Trioxo osmium(VIII) complexes

The salts $M^1{}_3[OsO_3F_3]$ are made by reaction of OsO_4 and KBr, CsBr or $AgIO_3$ in a 1:1 mole ratio with BrF_3,[533] or from MF (M = K, Rb, Cs) and OsO_3F_2.[631] The IR and Raman spectra of the solid cesium salt suggest a *fac* structure,[462] perhaps indicating that O^{2-} is a stronger π donor than is F^- for osmium(VIII) (there are also more recent vibrational data[634]). The postulated dimer $[OsO_3F_2]_2$ is considered on p. 596; the monomeric matrix-isolated OsO_3F_2 has been shown by Raman and IR spectra to have a trigonal bipyramidal (D_{3h}) structure.[636]

Two possible trioxo intermediates have been mentioned: $[OsO_3(OH)_3\{O(CH_2)_2OH\}]^{2-}$, from reaction of ethylene glycol with OsO_4 in base,[602] and $OsO_3(O_2R)$, thought to be formed when monoesters $Os_2O_4(O_2R)_2$ are oxidized with H_2O_2.[528]

6.2.1.4.4. Dioxo and monooxo osmium(VIII) complexes.

Reaction of glycols $R(OH)_2$ with OsO_4 is said to give $OsO_2(OH)_2(O_2R)$ as an intermediate.[601] There is no unequivocal evidence for the existence of these, though in view of the remarkable stability of the $Os^{VI}O_2R$ ring the existence of osmium(VIII) analogues seems feasible; a reductive route from alkenes is not of course possible. Two possible candidates, $OsO_3(O_2R)$ and $OsO_2(OH)_2(O_2R)$, are mentioned above and on p. 590.

The acid dissociation constant of '$OsO_2(OH)_4$' has been given.[479]

46.6.2.2 Binuclear oxo-bridged complexes.

A number of these are known (see Table 25), particularly with osmium(IV) and osmium(VI). It is clear that the bridging oxo ligands are functioning as π donors, particularly in the μ-oxo osmium(IV) dimers.

Table 25 Binuclear Oxo-bridged Complexes

Complex	$\nu_{as}(Os_2O)$	$\nu_s(Os_2O)$	*Spectroscopic and other properties*
$Cs_4[Os_2OCl_{10}]$	852	225	Raman,[640,643,653] IR,[462,640] UV/vis,[643] X-ray[641]
$(Me_4N)_4[Os_2OCl_6Br_4]$	846	223	Raman, IR[462]
$(Et_4N)_4[Os_2OBr_{10}]$	846	237	Raman,[462] IR[294,462]
$Os_2O(dppm)_2Cl_6 \cdot 2CHCl_3$			UV/vis, CV, X-ray[647]
$K_2[Os_2O(\eta^4\text{-chba-Et})_2(OPPh_3)_2$			X-ray[648]
$Os_2O(OAc)_2Cl_4(PPh_3)_2 \cdot Et_2O$			CV, ESCA, X-ray[649]
$Os_2O(OEP)_2(OH)_2$			UV/vis, CV, ^{1}H NMR[650]
$Os_2O_4(O_2C_2Me_4)_2$	981		IR,[497] ^{1}H NMR,[536] X-ray[501,529]
$Rb[Os_2(OH)O_8]$	960–800		IR,[630] X-ray[651]
$Cs[Os_2(OH)O_8]$	960–885		IR,[630] X-ray[629]
$[OsO_4]_2 \cdot N_4C_6H_{12}$	930, 917, 909		Raman, IR,[519] X-ray[634]
	$\nu_{as}(OsO_2)$	$\nu_s(OsO_2)$	$\nu(Os_2O_2)$	
$Os_2O_6py_4$	833	875	640, 448	Raman, IR,[468,469] X-ray[469]
$K_4[Os_2O_6(NO_2)_4]$	841	884		Raman, IR,[462] X-ray[502]
$Os_2O_4(O_2C_6H_{10})_2(NC_7H_{13})_2$	903	898		Raman, IR,[545] X-ray[546]
$Os_2O(OEP)_2(OMe)_2$				X-ray[646]

For $Os_2O_4(O_2C_2Me_4)_2$ see p. 000.

(*i*) *Osmium(II) and osmium(III)*

The complex $[Os^{III}_2O(bipy)_2(terpy)_2](ClO_4)_4$ has been claimed (made from reaction of [Os-Cl(bipy)(terpy)]Cl with $HClO_4$); reduction with $Na_2S_2O_4$ is said to give $[Os_2O(bipy)_2(terpy)_2](ClO_4)_2$, while oxidation with ceric ammonium nitrate gives $[Os_2O(bipy)_2(terpy)_2](ClO_4)_5$.[192] These are the only $Os^{II/III}$ μ-oxo complexes so far reported, but iron forms Fe^{III}—O—Fe^{III} and Fe^{III}—N—Fe^{IV} moieties.

(*ii*) *Osmium(IV)*

(a) Halo complexes. The most comprehensively studied example is $[Os_2OCl_{10}]^{4-}$ (isoelectronic with $[Os_2NCl_{10}]^{5-}$, see p. 563).

A number of salts containing $[Os(OH)Cl_5]^{2-}$ (*e.g.* $M^I_2[Os(OH)Cl_5]$; M = Na, K, Rb, Cs and some organic cations)[637] were reported in the earlier literature, but these almost certainly should be reformulated as $M^I_4[Os_2OCl_{10}]$. There is evidence for the existence in solution of the $[Os(OH)Cl_5]^{2-}$ ion, however (see p. 615).

The potassium, cesium and ammonium salts can be made by reaction of OsO_4 in concentrated HCl with OsO_4 in acid, in the presence of $FeSO_4$ functioning as the reducing agent.[638-640] The solids are diamagnetic[639] (this was one of the features which suggested that they were not in fact salts of $[Os(OH)Cl_5]^{2-}$, for which paramagnetism would be expected). The single crystal X-ray structure of $Cs_4[Os_2OCl_{10}]$ shows the anion to have a μ-oxo bridged structure with the equatorial chloro ligands in the eclipsed position. The Os—O distance is 1.778(15) Å with the Os—O—Os angle at 180°; the *cis* Os—Cl distance is 2.370 Å and the *trans* Os—Cl distance is only slightly longer at 2.433 Å.[641] It is instructive to compare the Os^{IV}—O—Os^{IV} grouping with the Os^{IV}—N—Os^{IV} moiety (see p. 615); clearly the nitrido ligand has a more powerful *trans* weakening effect, for the $[Os_2NCl_{10}]^{5-}$ ion has only a tenuous existence, the *trans* ligands being easily replaced by water to give $[Os_2NCl_8(H_2O)_2]^{3-}$.[344,349] The structural parameters for $[Os_2OCl_{10}]^{4-}$ can be compared with those found for $K_4[Ru_2OCl_{10}]$ and $K_3[Ru_2NCl_8(H_2O)_2]$; the Ru—O distance is 1.80 Å with a O—Ru—Cl angle of 94°,[642] while the Ru—N distance is 1.720(4) Å with an N—Ru—Cl angle of 94.7(2)°.[351]

Raman studies have been carried out on the potassium,[640] cesium[640] and ammonium salts[462,643] and on the $[Os_2OCl_{10}]^{4-}$ ion in acid solution;[643] resonance Raman enhancement was observed for the ν_1 (symetric Os—O—Os stretch) mode.[640,643] IR data have also been reported.[462,640] A molecular orbital scheme for the bonding in $[Os_2OCl_{10}]^{4-}$ can be derived from that proposed by Dunitz and Orgel[644] for the analogous $[Ru_2OCl_{10}]^{4-}$ species.[643,645] Such a scheme has been used to interpret the electronic and vibrational spectra of $[Os_2OCl_{10}]^{4-}$.[643]

A few other μ-oxo halo complexes have been reported but incompletely characterized, *viz.* salts of $[Os_2OCl_6Br_4]^{4-}$,[294] $[Os_2OI_{10}]^{4-}$ and $[Os_2OI_2Cl_8]^{4-}$.[518] The species $[Os_2OCl_8(H_2O)_4]^{2-}$ is thought to be a product of the reaction of *trans*-$[Os^{VI}O_2Cl_4]^{2-}$ with $[Os^{III}Cl_4(H_2O)_2]^{2-}$ in acid solution.[489]

There is a recent report of the X-ray crystal structure of *trans*-$Os_2O(OEP)_2]OMe)_2$, a deep violet material made by reaction of Os(OEP)(CO)(OMe) and 2,3-dimethylindole in dichloromethane. The Os—O—Os skeleton is essentially linear (Os—O—Os = 178°, Os—O = 1.808(3) Å); the octaethylporphyrin (OEP) ligands are twisted at a dihedral angle of 23° but are planar (mean Os—N = 2.033(78) Å); the Os—O (OMe) distance is 1.997(29) Å.[646]

(b) Other μ-oxo osmium(IV) complexes. Reaction of $OsCl_3$ in methanol with dppm ($Ph_2PCH_2PPh_2$) followed by recrystallization of the product from ethanol yields $Os_2O(\mu\text{-dppm})_2Cl_6\cdot 2MeCl$, in which a linear Os—O—Os unit (Os—O = 1.792(1) Å) is spanned by two bridging chelating phosphine ligands, the chloro ligands occupying equatorial (*cis* Os—Cl = 2.387(3) Å) and axial (*trans* Os—Cl = 2.307(3) Å) positions. The Os—P distance is 2.443(4) Å. As in $Cs_4[Os_2OCl_{10}]$ the configuration is eclipsed; unlike the interaction in the latter complex, though, the chloro ligands *trans* to the oxo ligand are slightly closer to the metal than are the *cis*. The OOsP angle is 85.51(8)°, brought in presumably by the strained bridge, while the OOsCl (*cis*) angle is 87.57(8)°. The complex could be electrochemically oxidized (presumably to a mixed $Os^{V/VI}$ species) and reduced in two one-electron steps.[647]

Reaction of the tetradentate N,N,O,O ligand 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane (abbreviated as H_4chbaEt; see p. 616) with *trans*-$K_2[OsO_2(OH)_4]$ in ethanol yields the osmyl complex $K_2[OsO_2(\eta^4\text{-chbaEt})]$, which can then be reduced by PPh_3 to the μ-oxo-bridged species $K_2[Os_2O(\eta^4\text{-chbaEt})(OPPPh_3)_2]$[648]. As in $Cs_4[Os_2OCl_{10}]$ the equatorial ligands are eclipsed, but the Os—O—Os bridge is not quite linear [OsOOs angle = 175.5°, Os—O (bridged) = 1.795 Å). The *trans* Os—O (PPh_3) distance is 1.971 Å so there is no obvious *trans* lengthening effect.[648].

Another μ-oxo complex containing a bent bridge is $Os_2O(OAc)_2Cl_4(PPh_3)_2$, made from *trans*-$OsO_2Cl_2(PPh_3)_2$ and acetic anhydride (other complexes, such as $Os_2O(OCOR)_2X_4(PR'_3)_2$, R = Me, Et; X = Cl, Br; $PR'_3 = PPh_3$ or PEt_2Ph, were made in similar fashion). In $Os_2O(OAc)_2Cl_4(PPh_3)_2 \cdot Et_2O$ the Os—O—Os moiety (OsOOs angle = 140.2(4)°, Os—O (bridge) = 1.830(10) Å) is spanned by two bridging acetato ligands (Os—O = 2.083(9)), and it is presumably these which cause the very substantial bending of the OsOOs unit and consequent lengthening, in comparison with the other systems, of the Os—O bridge distance. The complex is diamagnetic, and the Os···Os distance is 3.440(2) Å. The equatorial planes, as viewed down the Os···Os axis, are not eclipsed due to the strain imposed by the bridging acetato ligands. Both this and the other $Os_2O(OCOR)X_4(PR'_3)_2$ complexes exhibit a reversible one-electron reduction, and the purple paramagnetic osmium(III)/(IV) complexes $M[Os_2O(OAc)_2Cl_4(PPh_3)_2]$ were isolated (M = Na, Ph_4As); μ_{eff} was 1.3 BM for the sodium salt and 1.7 BM for the $[Ph_4As]^+$ salt.[649]

A number of μ-oxo osmium(IV) porphyrin complexes with octaethylporphyrin (OEP) have been obtained by reaction of $Os^{II}(OEP)(CO)(MeOH)$ with air and 2,3-dimethylindole in dichloromethane. The product is the dark purple $Os_2O(OEP)_2(OMe)_2$; the methoxo group is labile with respect to substitution and both $Os_2O(OEP)_2(OH)_2$ and $Os_2O(OEP)_2(OMe)(OH)$ can be made. The complexes are thought to contain a linear bridge with the methoxo or hydroxo ligands *trans* to the oxo bridge. Cyclic voltammetric studies show that $Os_2O(OEP)_2(OMe)_2$ can be reduced to an Os^{IV}—Os^{III} and then to an Os^{III}—Os^{III} dimer.[650]

The dimeric species Os_2OCl_6, made from OsO_4 and HCl, has been isolated; IR and mass spectral data were obtained.[525] The so-called '$OsBr_3$' may be Os_2OBr_6.[650a]

(*iii*) *Osmium(V)*

The so-called Os_2OCl_8, made from osmium metal and a 15:1 chlorine–oxygen mixture at 700 °C,[527] is thought from its IR spectrum to be $OsOCl_4$ (p. 584).[525]

(*iv*) *Osmium(VI)*

A number of these are known. Most fall into two categories: one, of the type $Os_2O_6L_4$ (A) contains *trans* dioxo osmyl moieties, and the other $Os_2O_4L_4$ (B) contains one terminal oxo ligand per osmium, as in the 'monoesters' already treated on p. 584. In both cases the two metal atoms are linked by a μ,μ'-dioxo bridge in which the Os—O distance is typically *ca.* 1.95 Å. There is clearly far less π bonding in this bridging system than in the linear Os—O—Os system found in osmium(IV) species; this may be a result of the fact that two of the three orbitals suitable for such bonding are used for π bonding to the terminal oxo ligand in these osmium(VI) systems, whereas in the osmium(IV) species two such orbitals are available for π bonding in the Os—O—Os bridge.

The compound $Os_2O_6py_4$, prepared by the reaction of OsO_4 with pyridine in the presence of a little ethanol as reducing agent,[470] is formulated in the older literature as OsO_3py_2[480] (the complex '$OsO_4 \cdot py_2$',[633] made from the slow reaction of OsO_4 with pyridine, is almost certainly $Os_2O_6py_4$[470]). The single crystal X-ray shows it to be a dimer, as previously proposed on the basis of vibrational spectroscopic data,[468] of type (A).[469]

The osmium is octahedral with *trans* osmyl linkages (Os=O = 1.73 Å, the osmyl OOsO angle being bent away from the Os_2O_2 bridge at 163.5(8)°); the Os–N (py) distance is 2.20(2) Å, and the mean Os—O (bridge) distance is 1.94 Å.[469]

There is evidence[471] that, in solution, the dimer is in equilibrium with monomer (equation 7) and there may be such equilibria between monomer and dimer forms with $Os_2O_6L_4$ (L = 3-picoline, 3-chloropyridine),[470] 2,2′-bipyridyl,[471] imidazole,[544] 1,10-phenanthroline[496] and *N,N,N′,N′*-tetramethylethylenediamine (TMEN)[496]). Species of the $Os_2O_6L_4$ type have also been found with imidazoles and α-*N*-benzoyl-L-histidine isobutyl ester.[544]

$$Os_2O_6py_4 \rightleftharpoons 2OsO_3py_2 \qquad (7)$$

Another example of the type (A) structure is $K_4[Os_2O_6(NO_2)_4] \cdot 6H_2O$, a deep brown crystalline material obtained by prolonged reaction at room temperature of KNO_2 with OsO_4 in aqueous solution. It was long formulated as '$K_2[OsO_3(NO_2)_2] \cdot 3H_2O$'[204] and is a useful precursor for other osmium(VI) and osmium(IV) complexes since it releases NO_2 with acids. A single crystal X-ray study showed it to be of type (A) with the osmyl Os=O distance 1.79(1) Å and the osmyl OOsO

angle 164.1°, bent away from the Os_2O_2 bridge; the Os—N distance is 2.17(2) Å and the Os—O bridge distance is 1.99 Å with an OsOOs bridge angle of 102°.[502]

The species formulated[478] as '$Na_4[O_2\{OsO_2(OH)_2\}_2]\cdot nH_2O$', a product of reaction of OsO_4 and NaOH in water–ethanol, could presumably be reformulated as $Na_2[Os_2O_6(OH)_4]\cdot nH_2O$.

An X-ray crystal structure of a type (B) complex, $Os_2O_6(O_2C_2Me_4)_2$, is discussed on p. 584. Other binuclear 'oxo ester' complexes which have been studied by X-ray methods are the 'tetrolato' species $Os_2O_4(O_4C_8H_{12})py_4$,[522] (see p. 586 and Table 21) and the species $Os_2O_4(O_2C_6H_{10})_2(NC_7H_{13})_2$,[546] (p. 587 and Table 25). It is known too that some complexes obtained from OsO_4 and nitrogenous bases are binuclear (p. 592).

(*v*) *Osmium(VII)*

The yellow-green OsO_2F_3, made by reaction of a 1:1 mixture of OsO_4 with OsF_6 at 750 °C, is probably a tetramer or an infinite chain structure with single fluoro bridges.[524]

(*vi*) *Osmium(VIII)*

The binuclear species $M^I[Os_2(OH)O_8]$ (M = Rb, Cs) are prepared by reaction of a deficiency of M^IOH with OsO_4.[629,630] The X-ray crystal structures of the rubidium[651] and cesium[629] salts show the osmium atoms to have a trigonal bipyramidal configuration with the bridging hydroxo ligand in the apical position. The Os=O distances vary from 1.66 to 1.75 Å in the rubidium salt, with the Os—O (OH) distance 2.16 Å and the OsOOs angle 153°.[651] In the cesium salt $Cs[Os_2(OH)O_8]$ the structure is similar (Os=O axial = 1.71(3), mean O=O equatorial = 1.67 Å) linked by a μ-hydroxo ligand constituting the remaining axial positions (Os—O = 2.22(2) Å) in an essentially symmetrical but bent bridge (OOsO angle 133(1)°).[629]

The compound OsO_3F_2 (indistinguishable by X-ray methods from OsO_2F_3)[533] is made by reaction of osmium metal with a 2:1 oxygen–fluorine mixture[523] or from OsO_4 and BrF_3.[524] There is much doubt about its structure, but the compound made at normal temperatures exists in at least three different crystalline forms and polymeric structures seem more likely.[652]

46.6.3 Dioxygen, Superoxo and Peroxo Species

Surprisingly, no non-organometallic complexes containing these ligands appear to have been isolated,[654] though peroxo species in particular might well be involved as intermediates in some reactions (*e.g.* in the OsO_4-catalyzed decomposition of H_2O_2[620]). The complex $Os(O_2)(CO)_2(PPh_3)_2$ is made by slow reaction of O_2 with $Os(CO)_2(PPh_3)_2$,[655] while $Os(O_2)(CO)HX(PCy_3)_2$ (X = Cl, Br) complexes are made from O_2 and $Os(CO)HX(PCy_3)_2$. With SO_2 the chloro species gives a sulfato complex.[656] It is likely that an η^2-peroxo (or 'dioxygen') complex is implicated in ligand oxidations at organic centres, *e.g.* oxidation of $Os(CO)Cl(NO)(PPh_3)_2$ to $Os(CO_3)Cl(NO)(PPh_3)_2$ by oxygen.[657]

46.6.4 Alkoxo Complexes

A few alkoxo complexes are known with phosphine coligands, and the methoxo species *trans*-$K_2[OsO_2(OMe)_4]$ is quite a useful synthetic reagent (see p. 584).

Reaction of $(Bu^n_4N)[OsNCl_4]$ with PPh_3 in methanol gives $Os(PPh_3)_2Cl_2(OMe)_2$,[315] and $Os(OMe_2Ph)_3Cl_3$ and Me_3N in ethanol yields the yellow $Os(PMe_2Ph)_3Cl_2(OEt)$.[72] The ethoxo species *fac*-$Os(PMe_2Ph)_3(S_2CNMe_2)(OEt)$ is made from *mer*-$Os(PMe_2Ph)_3(S_2CNMe_2)Cl$ and $K(S_2COEt)$ in ethanol.[412]

46.6.5 β-Diketonate Complexes

As might be expected for chelating O,O donor ligands it is the intermediate trivalent state of osmium which is stabilized by β-diketonates (as is the case for catechols, p. 597, and tropolonato complexes, p. 597). In the presence of π-acceptor chelates such as bipy, phen and terpy the II state is favoured, while with halides the IV state is preferred. The apparent absence of an osmyl complex, *e.g.* OsO_2acac_2, is surprising.

46.6.5.1 Osmium(II)

Although it has not been isolated, the product of polarographic reduction of $Os(acac)_3$ is probably $[Os(acac)_3]^-$.[658]

Reaction of $Os(PPh_3)_3H_4$ and β-diketonates L gives $Os(PPh_3)_2L_2$ (L = acetylacetonate, trifluoroacetylacetonate, hexafluoroacetylacetonate). A *cis* structure is thought to be likely; IR and ^1H NMR data were obtained.[429]

46.6.5.2 Osmium(III)

The neutral tris complex $Os(acac)_3$ is made from $[OsBr_6]^{3-}$ with acetylacetone under appropriate pH control.[659] It is paramagnetic (μ_{eff} = 1.81 BM at 289 K)[659] and is isomorphous with $Ru(acac)_3$ and $Co(acac)_3$.[660] The near IR spectrum has been measured and assigned.[660,661] A one-electron polarographic reduction wave at −1.244 V is observed (the redox potential for the corresponding thio β-diketonate, $Os(sacsac)_3$ (p. 606), is only −0.151 V); that of $Ru(acac)_3$ occurs at −0.728 V, in keeping with the general tendency of osmium(III) complexes being more difficlt to reduce than ruthenium(III).[658] There are mass spectral data on $Os(acac)_3$.[662]

46.6.5.3 Osmium(IV)

All the known examples also contain halides as coligands. Both *cis* and *trans* isomers of $Os(acac)_2X_2$ (X = Cl, Br, I) can be obtained from $[OsX_6]^{2-}$ and acetylacetone, separation being effected chromatographically;[663] $Os(acac)_2Cl_2$ can also be made by reaction of acetylacetone with $Os_2(OAc)_4Cl_2$[105] (the magnetic moment (1.29 BM) and electronic spectrum of the latter were obtained[105]). There are Raman, IR and electronic spectral data on *cis*- and *trans*-$Os(acac)_2Cl_2$.[663] Salts of $[Os(acac)X_4]^-$ (X = Cl, Br, I) are made from $[OsX_6]^{2-}$ and acetylacetone; IR and electronic spectral data were obtained for them.[664]

46.6.6 Tropolonato Complexes

The monoanion of this, trop, is a good O,O chelate, resembling the catecholato dianion in its platinum group chemistry. Reaction of $[OsCl_6]^{3-}$ (generated from $[OsCl_6]^{2-}$ and silver powder) with tropolone gives the yellow $Os(trop)_3$, for which IR, ^1H and ^{13}C NMR data were obtained. Similar data were obtained for the osmyl complex OsO_2trop_2, made from *trans*-$K_2[OsO_2(OH)_4]$ and tropolone.[665]

46.6.7 Catecholato Complexes

The 'non-innocent' ligand catechol forms very stable osmium(VI) complexes, as do a number of substituted catechols.

46.6.7.1 Tris catecholato complexes, Os(cat)$_3$ and Os(Rcat)$_3$

Reaction of OsO_4 with catechol or substituted catechols Rcat in chloroform yields the deep blue diamagnetic $Os(Rcat)_3$ species (Rcat = catechol, 4-*tert*-octyl-, 4-*tert*-butyl-, 3,5-di-*tert*-butyl-catechol).[486] X-Ray crystal structures of $Os(cat)_3$ and of the tris complex with 3,5-di-*tert*-butylcatechol show these to have D_3 symmetry; the Os—O distances fall within the range 1.947 to 1.985 Å (mean 1.960 Å) and the C—O distances are between 1.30 and 1.35 Å; the catecholato ($O_2C_6H_4$ or $O_2C_6H_2$) rings are essentially planar.[666] For $Os(cat)_3$, IR, Raman, ^1H NMR and electrochemical data were obtained; the latter showed two one-electron reversible reductions, presumably to $[Os(cat)_3]^-$ and $[Os(cat)_3]^{2-}$. The diamagnetism of these formally osmium(VI) species probably arises from the distortion from octahedral to D_3 symmetry.[486]

46.6.7.2 Bis catecholato complexes

Most of these are of the osmyl type, *trans*-$[OsO_2(Rcat)_2]^{2-}$ (Rcat = catechol, 4-methylcatechol, 4-*tert*-butylcatechol, 4-nitrocatechol), made from OsO_4 and the catechol in alkali or from the

catechol and *trans*-$K_2[OsO_2(OH)_4]$; cations were potassium or $(Ph_4P)^+$. The pyridine complexes *trans*-$OsO_2(Rcat)py_2$ were obtained from OsO_4, pyridine and the catechol (Rcat = cat, 4-Me-cat). IR and Raman data on these were measured; $\nu_s(OsO_2)$ appears near 860 cm^{-1} and $\nu_{as}(OsO_2)$ near 820 cm^{-1} (see also Table 21, p. 582).[486] IR and ^1H NMR data were obtained for the existence of $OsO(cat)(O_2C_2Me_4)$ in solution, made from $Os_2O_4(O_2C_2Me_4)_2$ and catechol.[536]

46.6.7.3 Polymeric catecholato complexes

Acidification of solutions containing $[OsO_2(Rcat)]^{2+}$ or direct treatment of the catechol with OsO_4 in acetone gives dark blue, polymeric species $[OsO(Rcat)_2]_n \cdot nH_2O$, thought to contain Os—O—Os—O···chains (R-cat = 4-methylcatechol, 4-*tert*-butylcatechol, 3,5-di-*tert*-butylcatechol). These are remarkably stable species, unreactive even towards boiling pyridine.[486]

46.6.7.4 Complexes with naturally occurring catechols

Preparative methods similar to those above with naturally occurring phenolics, particularly in plant cells, give *trans*-$[OsO_2(Rcat)_2]^{2-}$ (4-methyldaphnetinate), *trans*-$OsO_2(Rcat)py_2$ (gallate, quercetinate) and $[OsO(Rcat)_2]_n \cdot nH_2O$ (catechinate, gallate, digallate and caffeate). The specific site staining of 'phenolic' material (*i.e.* catechol-containing areas in plant tissue by OsO_4 solutions is likely to be due to formation of $[OsO(Rcat)_2]_n \cdot nH_2O$ species.[486,618]

46.6.8 Ketone Complex

The sole example seems to be $[Os(PMe_2Ph)_3Cl_2(OCMe_2)]ClO_4$, made from *mer*-$Os(PMe_2Ph)_3Cl_3$ in acetone in the presence of silver perchlorate.[366]

46.6.9 Oxoanions as Ligands

Some of the complexes in this category are in need of fuller characterization.

46.6.9.1 Nitrato and nitro complexes

There are very few of these for osmium, and no unsubstituted ones.

(*i*) *Nitrato complexes*

The '$K_2[OsO_2(NO_2)_4]$' reported in the early literature,[204] made by reaction of OsO_4 with nitric oxide in an aqueous solution of KNO_2, was later reformulated by the author as an osmyl complex, $K_2[OsO_2(NO_3)(NO_2)_3]$[503] and then, after second thoughts, as a different osmyl species, $K_2[OsO_2(NO_3)_2(NO_2)_2]$.[21]

The nitrato complex $[Os_2N(NH_3)_8(NO_3)_2]^{3+}$ is mentioned on p. 563.

(*ii*) *Nitro complexes*

The '$K_2[Os(NO_2)_5]$' reported in the early literature[204] and made by reaction of $[OsCl_6]^{2-}$ with aqueous KNO_2 is now known to be *trans*-$K_2[Os(NO)(OH)(NO_2)_4]$ (see p. 546).[219]

Recent work has been reported on the nitro complexes $[Os(NO_2)(terpy)(bipy)]^+$, made from $[Os(terpy)(bipy)Cl]^+$ and nitrite ion in ethylene glycol, and on $Os(NO_2)bipy_2Cl$, prepared from $[Os(NO)bipy_2Cl]^{2+}$ and sodium hydroxide. Oxidation of $[Os(NO_2)(terpy)(bipy)]^+$ with cerium(IV) to give $[Os(NO_2)(terpy)(bipy)]^{2+}$ is followed by its disproportionation (equation 8).

$$3[Os(NO_2)(terpy)(bipy)]^{2+} \longrightarrow [Os(NO_2(terpy)(bipy)]^+ + [Os(NO)(terpy)(bipy)]^{3+} + [Os(NO_3)(terpy(bipy]^{2+} \quad (8)$$

The kinetics of this second-order reaction have been studied. The equilibrium shown in

$$[Os(NO_2)terpy\ bipy]^+ + H_2O \rightleftharpoons [Os(NO)(terpy)(bipy)]^{3+} + 2OH^- \quad (9)$$

equation (9) was also measured. The osmium(III) complex $[Os(NO_2)(terpy)(bipy)]^{2+}$ will oxidize triphenylphosphine to Ph_3PO and $[Os(NO)(terpy)(bipy)].^{2+}$ Electronic spectra of $Os(NO_2)bipy_2Cl$ and of $[Os(NO_2)(terpy)(bipy)]^+$ were recorded. Reactions and data were compared with those for the corresponding ruthenium complexes.[183]

For $K_4[Os_2O_6(NO_2)_4]\cdot 6H_2O$ (formerly erroneously believed to be $K_2[OsO_3(NO_2)_2]\cdot 3H_2O$ or *trans*-$K_2[OsO_2(NO_2)_2(OH)_2]$), see p. 595.

46.6.9.2 Phosphato and sulfato complexes

(*i*) *Phosphato complexes*

None have been properly characterized for osmium, though a 1:1 complex between OsO_4 and PO_4^{3-} has been detected spectrophotometrically.[667]

(*ii*) *Sulfato complexes*

Athough sulfato complexes of osmium undoubtedly exist none have been definitely established or characterized.

(a) Osmium(IV). Osmium(IV) sulfato complexes are thought to be present in solutions made by chemical dissolution of osmium in sulfuric acid.[668,669a] Species thought to be $[Os(SO_4)_2(OH)_2]^{2-}$ have also been claimed.[668]

(b) Osmium(VI). Solutions of OsO_4 in H_2SO_4 are said to contain $OsO_2(OH)_2(SO_4)_2$,[669b] presumably an osmyl complex.

46.6.9.3 Sulfito and hydrosulfito complexes

(*i*) *Sulfito complexes*

There are early reports of sulfito complexes of osmium, but only recently has some of this work been reexamined. It appears that osmium binds to the sulfur atom rather than oxygen in SO_3^{2-}, even for the presumably 'hard' osmyl unit in $[OsO_2(SO_3)_4]^{6-}$.

(a) Osmium(II). The salt $Na_4[Os(SO_3)_3]\cdot 6H_2O$ was first made by reaction of osmium(VI) oxoesters with Na_2SO_3.[528] It is not clear whether this should be reformulated as $Na_4[Os(SO_3)_3(H_2O)_3]\cdot 3H_2O$ (with monodentate rather than bidentate SO_3^{2-} ligands) but recent work suggests that the potassium salt is $K_4[Os(SO_3)_3(H_2O)_3]$. It is made by reaction of $KHSO_3$ with $K_2[OsCl_6]$, and its Raman and IR spectra suggest that the SO_3^{2-} ligand functions as a monodentate S donor. The complex is diamagnetic.[507]

Other nominally osmium(II) sulfito species include $Na_6Os_4(SO_3)_7\cdot 24H_2O$, reported as a deep violet material obtained from $Na_2[OsCl_6]$ and $Na_2S_2O_4$.[670]

(b) Osmium(III). Treatment of $[Os(NH_3)_5Cl]Cl_2$ with SO_2 produces the pink-brown $Os(SO_3)(NH_3)_4Cl$; it is paramagnetic ($\mu_{eff} = 1.45$ BM at 294 K), and the Raman and IR spectra suggest a *trans* structure with S-bonded sulfite.[507]

(c) Osmium(IV). The salt $Na_8[Os(SO_3)_6]\cdot 3H_2O$ is reported to result from reaction of $NaHSO_3$ with $[OsCl_6]^{2-}$;[506] another product of this reaction is said to be $Na_6[Os(SO_3)_5(H_2O)]\cdot 4H_2O$.[506] Reaction of $NaHSO_3$ and $Na_2[OsCl_6]$ is also said to give $Na_7[Os(SO_3)_5Cl]\cdot 6H_2O$[506] and $Na_6[Os(SO_3)_4Cl_2]\cdot 10H_2O$.[671] There are also very ill-defined potassium salts: $K_6H_2[Os(SO_3)_6]\cdot 2H_2O$ and '$K_{11}H_3[Os_2(SO_3)_{11}(H_2O)]\cdot 5H_2O$' both being made from reaction of $KHSO_3$ with $K_2[OsCl_6]$.[506] It seems likely[507] that '$K_4H_2[Os(SO_3)_6]\cdot 2H_2O$' is actually $K_4[Os(SO_3)_3(H_2O)_3]$. A complex $K_6H_2[Os(SO_3)_4Cl_4]$ has been claimed as a product of reaction of $K_2[OsCl_6]$ with $KHSO_3$,[671] and OsO_4 with CO_3^{2-} and SO_3^{2-} in solution is said to give $[Os(SO_3)_6]^{8-}$.[621] A product of the K_2OsCl_6–K_2SO_3 reaction is said to be $K_6[Os(SO_3)_5(H_2O)]\cdot 4H_2O$.[506]

Reaction of $[Os_2N(NH_3)_8Cl_2]^{3+}$ with SO_2 gives $[Os_2N(NH_3)_8(SO_3)(H_2O)]Cl_3$; the sulfite is thought to be S-bonded.[507]

(d) Osmium(VI). There are some very ill-defined potassium salts which are said to result from

reaction of OsO_4 with SO_2 in water in the presence of KOH. The osmyl complex $Na_6[OsO_2(SO_3)_4]\cdot 5H_2O$ is well established, however (p. 582),[507] and has long been known.[506]

(*ii*) *Hydrosulfito complex*

The ESCA spectrum of $Na_4[Os(HSO_3)_6]$ has been reported but, irritatingly, no preparation was given.[36]

46.6.9.4 Triflato complex

The coordinated triflato $(SO_3CF_3)^-$ ligand is weakly bound to osmium in $[Os(OSO_2CF_3)(NH_3)_5]^{2+}$, made by reaction of triflic acid with $[Os(NH_{33})_5N_2]^{2+}$.[62] It is a useful reagent for preparation of other osmium pentaammines since triflate is a good leaving group (see p. 529).

46.6.9.5 Carboxylato complexes

In this section we consider the complexes of mono-, di- and poly-carboxylato complexes. There appear to be marked differences from ruthenium carboxylato chemistry particularly in respect of the II/III and III states. A number of osmyl complexes are known with monodentate or bidentate carboxylates (p. 582) but apparently none of ruthenium(VI). On the other hand, the binuclear ruthenium species $[Ru_3O(OCOR)_6L_3]^{n+}$, in which OCOR functions as a bidentate ligand, does not appear to have an osmium counterpart; both elements form 'lantern'-like species containing $[M_2(OCOR)_4]^{n+}$ cores, but again with marked differences between ruthenium and osmium. This is clearly an interesting and rewarding field for further study.

(*i*) *Monocarboxylato complexes*

For amino acids see p. 583.

(a) Monodentate. Few examples are known. The acetato species $K[OsO_2(OAc)_3]\cdot 2AcOH$ has been shown by X-ray studies to contain two monodentate and one bidentate acetato ligands in a plane about a bent osmyl unit (p. 582). The carbonyl complexes $OsH(OCOR)(CO)(PPh_3)_3$ and $Os(OCOR)_2(CO)_2(PPh_3)_2$ must contain monodentate OCOR ligands, and $Os(OCOR)_2(CO)(PPh_3)_2$ presumably contains one mono- and one bi-dentate OCOR group (R = CF_3, C_2F_5).[672]

(b) Bidentate monocarboxylates. A few of these are known, mainly with phosphines. The hydrides $Os(OCOR)H(PPh_3)_3$ are made from $OsH_4(PPh_3)_3$ and the appropriate acid (R = Me, Et,[406] CF_3[672]) and IR and ^1H NMR data suggest that the hydrido ligand is *trans* to the bidentate carboxylate group.[406,672] The bromo species $Os(OCOR)Br_2(PPh_3)_2$ are obtained from $OsBr_2(PPh_3)_3$ and the appropriate acid (R = Ph, *p*-C_6H_4Br, *p*-C_6H_4Me), and their IR spectra suggest that the two phosphine ligands are *trans* to the bidentate carboxylate.[673]

For osmyl salicylato complexes see p. 582, and for other osmyl carboxylato complexes see Tables 20 and 21, and p. 582.

(c) Bridging carboxylato complexes. The ability of carboxylato ligands to function in a bridging role is well exploited by the Group VIII metals. Thus there are many rhodium(II) carboxylates with the 'lantern' structure and a number of species of the type $[Ru_3O(OCOR)_6L_3]^{n+}$, $Re_2(OCOR)_4X_4$ and $Ru_2(OCOR)_4X$ where the carboxylate ligand is bridging. Until recently there have been few such examples with osmium, but new studies suggest that there is a rich chemistry of the element with bridging carboxylates, and that such species have an extensive redox chemistry.

Species containing the Os_2^{5+} core. Reaction of $Os_2(OCOR)_4Cl_2$ (R = Et, Pr^n) and $(\pi\text{-}C_5H_5)_2Co$ yields the salts $[(\pi\text{-}C_5H_5)_2Co][Os_2(OCOR)_4Cl_2]$, and these species are also produced by electrochemical reduction of $Os_2(OCOR)_4Cl_2$. Their magnetic properties in CH_2Cl_2 solution show moments per Os_2 unit higher than for the Os_2^{6+} core species (*e.g.* μ_{eff} of 2.47 BM at 275 K and 2.88 BM at 215 K for $[(\pi\text{-}C_5H_5)_2Co][Os_2(OCOEt)_4Cl_2]$, 2.65 BM at 240 K and 2.85 BM at 190 K for $[(\pi\text{-}C_5H_5)_2Co][Os_2(OCOPr^n)_4Cl_2]$).[674] These are nevertheless lower than moments observed for the analogous $Ru_2(OCOR)_4Cl$ species; this may arise from a greater separation of π^* and δ^* orbitals on Os_2^{5+}.[107]

Species containing the Os_2^{6+} core. Reaction of $[OsCl_6]^{2-}$ with acetic acid in acetic anhydride gives the brown, insoluble $Os_2(OCOMe)_4Cl_2$[105,675] and this will react with propionic or *n*-butyric acids to give $Os_2(OCOR)_4Cl_2$ (R = Et, Pr^n) which are more soluble in organic solvents.[105]

The X-ray crystal structures of the acetato, propionato and *n*-butyrato complexes show these to have the 'lantern' type of structure (Table 26 and Figure 34).

Table 26 Structural Data for Carboxylato Complexes (Å)

Complex	d_{Os-Os}	d_{Os-Cl}	d_{Os-O} *(mean)*	*Ref.*
$Os_2(OCOMe)_4Cl_2$	2.314(1)	2.448(2)	2.009(8)	106
$Os_2(OCOEt)_4Cl_2$	2.316(2)	2.430(5)	2.012(8)	106
$Os_2(OCOPr^n)_4Cl_2$	2.301(1)	2.417(3)	2.016	105, 676

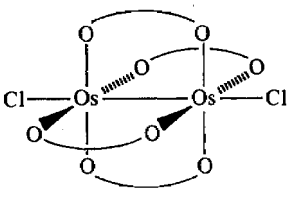


Figure 34 The 'lantern' structure for carboxylato complexes

Despite the short Os—Os distances the complexes are paramagnetic; thus, in solution, μ_{eff} for the butyrate is 1.15 BM per Os atom at 300 K and 1.02 BM at 188 K. It has been suggested that mixing of the triplet $\sigma^2\pi^4\delta^2\pi^{*2}$ or $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*1}$ states at room temperatures with the singlet ground state arising from $\sigma^2\pi^4\delta^2\delta^{*2}$ may occur, the latter state becoming increasingly favoured at lower temperatures.[105] Contributions from the two former states may, it has also been suggested, account for the greater Os—Os distance of 2.357 Å in Os_2(2-hydroxypyridine)$_4Cl_2 \cdot 2MeCN$ (see p. 534) than in these molecules.[106] The ^1H and ^{13}C NMR spectra of the *n*-butyrato complex show larger contact-shifted resonances to lower frequencies.[105]

Cyclic voltammetric studies show that the propionate and butyrate undergo reversible one-electron reductions ($E^\circ = +0.57$ and $+0.53$ V respectively) to $[Os_2(OCOR)_4Cl_2]^-$,[105,107,677] and there are also irreversible oxidation and reduction waves.

The acetato complex is a useful precursor for other species. In some reactions the bridges are partly or wholly displaced by other bridges, or monomeric osmium-(II), -(III) or -(IV) complexes are formed.[105]

In $Os_2(O_2CR)_2(Ph_2PC_6H_4)_2Cl_2$ [R = Me (made from $Os_2(OAc)_4Cl_2$ and triphenylphosphine) and R = Et (from a similar reaction but using propionic acid)] the phosphine groups function as cobridges with the acetato or propionato bridges; *ortho*-metallation occurs at one of the phenyl rings giving a P—C—C bridge. The short Os—Os distances (2.271(1) Å for R = Me,[678,679] 2.272(2) Å for R = Et[678]) corresponds effectively to a triple bond.[678]

For $Os_2O(OAc)_2Cl_4(PPh_3)_2$ see p. 595 and Table 25.

(*ii*) *Bidentate dicarboxylato complexes*

A few complexes of the oxalato (ox) ligand are known, though no one seems to have succeeded yet in isolating a tris oxalato complex.

In a recent series of papers, very comprehensive Raman, IR and electronic spectral data have been collected for $[Os(ox)X_4]^{2-}$ (X = Cl, Br, I; made from $[OsX_6]^{2-}$ and oxalic acid);[680] for $[Os(ox)Cl_nBr_{4-n}]^{2-}$[681] and for $[Os(ox)Cl_nI_{4-n}]^{2-}$[682] (n = 1–3, all geometrical isomers isolated, made from $[Os(ox)Br_4]^{2-}$ with Cl^- and $[Os(ox)I_4]^{2-}$ with Cl^- respectively). Similar spectroscopic studies were carried out on *mer*-$[Os(ox)(CO)X_3]^{2-}$, made from *trans*-$[Os(CO)_2X_4]^-$ or $[Os(CO)X_5]^{2-}$ with oxalate (X = Cl, Br, I).[683]

The species $Os(ox)bipy_2 \cdot H_2O$ and $Os(ox)phen_2$ are made from the corresponding chloro complexes and sodium oxalate.[173]

(iii) Tetradentate carboxylato complexes

Three edta complexes have been reported, and one of *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate.

(a) Osmium(II). The reaction of OsO_4 with the alkene 3-cyclohexenecarboxylic acid in the presence of H_4edta gives the brown $Na_6H_4[Os(edta)_3]$; maleic acid can also be used as the alkene, and the same species is obtained from $[OsO_2(OH)_4]^{2-}$ and edta. The complex $Na_5H_5[Os(dcta)_3]$ was made from OsO_4, H_4dcta and 3-cyclohexenecarboxylic acid.[684]

(b) Osmium(III). A yellow, paramagnetic 'free acid', $H[Os(H_2edta)Cl_2]\cdot 2\frac{1}{2}H_2O$, is obtained by reaction of $[OsCl_6]^{2-}$ and H_4edta; an anhydrous ammonium salt was also isolated. The material is paramagnetic (μ_{eff} = 1.79 BM at 286 K).[685]

(c) Osmium(IV). On aerial oxidation of $H[Os(H_2edta)Cl_2]\cdot 2\frac{1}{2}H_2O$ black crystals of Os(edta)$(H_2O)\cdot H_2O$ were obtained. An X-ray crystal structure determination showed the osmium to be heptacoordinate, a rare coordination number for the element. It has a distorted capped trigonal prismatic structure, the water occupying the capping position (Os—O (H_2O) = 2.049(7) Å); the four Os—O (edta) bonds form a distorted square (mean Os—O = 2.052 Å) and the two Os—N bonds (mean = 2.159 Å) are under the square, *trans* to the cap.[686]

(iv) Amino acid complexes

For convenience we deal with all the reported osmium complexes of amino acids in this section, apart from the osmyl species (p. 583).

(a) Glycine. The three complexes $[Os(bipy)_2(glycinate)]I\cdot 2H_2O$[173] (made from glycine and Os(bipy)$_2Cl_2$), $[Os(bipy)(glycinate)_2]I\cdot 2H_2O$[86] and Os(bipy)(glycinate)$Cl_2\cdot H_2O$[86] are reported; the latter two were made from glycine with $K[Os(bipy)Cl_4]$. The X-ray crystal structure of OsO_2(glycinate)$_2$ is described on p. 581 (Table 20).

(b) Lysine, arginine, proline and histidine. The methyl ester of α-*N*-benzoyllysine gives an orange solution with OsO_4 likely to contain a 1:1 adduct.[544]

Although α-*N*-benzoyl-L-arginine ethyl ester (L) does not react with aqueous OsO_4, it reacts with the 1-methylimidazole adducts $OsO_4\cdot N_2C_4H_6$ to give $Os_2O_6(N_2C_4H_6)L$; a similar reaction occurs with L-proline methyl ester. The blocked acid α-*N*-benzoyl-L-histidine isobutyl ester (L) gives a species $Os_2O_6L_4$ with OsO_4, and with α-*N*-acetyl-L-cysteine (L′) it gives $OsLL'_2$. With unsaturated lipids R (R = cyclohexene, oleic acid, methyl oleate, cholesteryl acetate) $OsO_2(O_2R)L_2$ is formed.[544]

(v) Miscellaneous acids

Complexes of nicotinic acids and isonicotinic acid with dinitrogen are considered on p. 554.
For methionine, cysteine, cystine and glutathione see pp. 554, 555.

46.6.10 Dimethyl Sulfoxide Complex

The complex $Os(DMSO)_3Cl_3$ is made from $[OsCl_6]^{2-}$ and DMSO under reflux; it is dark green and paramagnetic (μ_{eff} = 1.15 BM at room temperatures). The IR, electronic and ^{1}H NMR spectra were measured and a structure proposed[687] in which there is a *mer* configuration of two O- and one S-bonded DMSO ligands, unlike the rhodium analogue which, despite a similar stereochemistry, has one S- and two O-bonded ligands.[688] This suggests that osmium(III) lies at the borderline of hardness and softness towards DMSO (a similar situation is observed for thiocyanato complexes, *cf.* p. 565).

46.6.11 Complexes with Carbohydrates

In his classic work on the *cis* hydroxylation of alkenes, Criegee used mannitol with osmium(VI) esters (in a 2:1 sugar:osmium ratio) in order to complex the metal and thus hydrolyze the ester to the *cis* diol; the nature of the osmium sugar complex was not investigated.[480]

Reaction of $K_2[OsO_2(OAc)_3]$ with D-glucose[689] and other carbohydrates[690] gave brown, polymeric, largely uncharacterized osmium carbohydrate complexes,[689] called 'osmarins'. It has been suggested that these are osmium(IV) species,[689] although the mode of preparation would suggest that

osmyl complexes are formed. They have been used experimentally for the treatment of arthritis, and may possibly function by scavenging superoxide radicals.[691]

46.7 SULFUR-CONTAINING LIGANDS

Although there are areas of osmium–sulfur chemistry where recent and interesting work has been done (*e.g.* on dithio- and trithio-carbamates), there is also much poor work, often with complicated ligands where little more than the stoichiometry of the complex —and sometimes less— has been established. Much work remains to be done on the osmium chemistry of simple thio (and seleno) ligands.

In general sulfur and selenium, in keeping with their 'soft' character, tend to stabilize the 'intermediate' trivalent state of osmium.

46.7.1 Hydrosulfido and Disulfur Ligands

The species $[Os(SH)_6]^{2-}$ is possibly formed in solution when $[OsCl_6]^{2-}$ in alkali (*i.e.* presumably $[Os(OH)_6]^{2-}$) is treated with H_2S.[692]

Reaction of $Os(PPh_3)_3(CO)_2$ with S_8 gives $Os(S_2)(PPh_3)_2(CO)_2$; the X-ray crystal structure of the selenium analogue has also been determined.[693]

46.7.2 Sulfido Phosphine Complexes

Reaction of $Os(PMe_3)_3H(CH_2PMe_2)$ with S_8 gave $Os(PMe_3)_3S_6$ (dark brown) and $Os(PMe_3)_3S_7$ (orange). In the latter the S_7^{2-} ligand is coordinated in tridentate fashion, and this is shown by its X-ray crystal structure. There is distorted octahedral coordination about the osmium with a *fac* arrangement of phosphine ligands (mean Os—P = 2.235 Å), while the S_7 moiety forms two four-membered rings with S-1, S-4 and S-7 as donors (mean Os—S_1 and Os—S_4 = 2.435 Å, Os—S_4 2.310(2) Å). The rings are not planar; the S—S distances lie between 2.010 and 2.205 Å.[694]

46.7.3 Thioether Complexes

Only one dialkyl sulfide complex has been reported, *fac*-$Os(SEt_2)_3Cl_3$, but recently a number of osmium-(III), -(IV) and -(VI) complexes of chelating thioethers have been prepared. There is also only one DMSO complex, $Os(DMSO)_3Cl_3$ (see p. 602).

46.7.3.1 Dialkyl sulfides

The only example reported is *fac*-$Os(SEt_2)_3Cl_3$, made from $OsCl_4$ and Et_2S in refluxing ethanol. The configuration of this material was deduced from its IR and electronic spectra.[695]

For osmyl complexes with SR_2, see p. 584.

46.7.3.2 Chelating sulfides

A number of complexes of these with osmium(III) and osmium(IV) have appeared in two recent publications; the preferred oxidation state would seem to be IV, although the trivalent species, once made, are quite stable.

(i) Osmium(III)

The trithioether bis(3-methylthiopropyl) sulfide, $S(CH_2CH_2CH_2SMe)_2$ (L), gives $OsLX_3$ (X = Cl, Br) with $[OsX_6]^{2-}$ in addition to $OsLX_4$. The IR spectra in the ν_{OsCl} region suggested that these are *mer* isomers; electronic spectra were also measured. Other osmium(III) complexes of the form $OsL'_{1.5}X_3$ (L' = RSCH=CHSR, $RSCH_2CH_2SR$ (R = Me, Ph) and *o*-$C_6H_4(SMe)_2$; X = Cl, Br)

were made by prolonged reaction of L′ on $[OsX_6]^{2-}$; IR, electronic and ESR spectra were measured. A dithioether-bridged structure was proposed; in solution the chloro complexes have magnetic moments in the range 1.65–1.78 BM.[696]

(ii) Osmium(IV)

Species of the form $OsLX_4$ ($L = S(CH_2CH_2CH_2SMe)_2$, $MeC(CH_2SMe)_3$, X = Cl, Br and X = Cl, $L = S(CH_2)_2S(CH_2)_3S(CH_2)_3$[696]) and $OsL'X_4$[697] (X = Cl, L = RSCH=CHR, $RSCH_2CH_2R$, o-$C_6H_4(SR)_2$, R = Me, Ph; X = Br, L′ = MeSCH=CHSMe, $MeSCH_2CH_2SMe$)[697] have been made from $[OsX_6]^{2-}$ and the ligands. IR and electronic spectra have been reported for all of these, and magnetic moments are in the range 1.3–1.4 BM for most of them.[696,697] The tetrathioether $MeS(CH_2)_2S(CH_2)_2S(CH_2)_2SMe$ (L″) gave a species $Os_2L''Cl_8$.[696]

For osmium(VI) osmyl complexes see p. 584.

46.7.4 Dithiocarbamato ($S_2CNR_2^-$), Trithiocarbamato ($S_3CNR_2^-$), Dithiocarbonato (S_2COR^-) and Phosphinodithionate ($S_2PR_2^-$) Complexes

A number of osmium-(III) and -(IV) complexes involving dithiocarbamato ligands are known; there are some interesting binuclear species involving the ligand in a bridging role. Recently, complexes involving the novel trithiocarbamate and also selenodithiocarbamate ($SeS_2CNR_2^-$) ligands have been synthesized; indeed, they represent the first examples of these ligands in a coordinating role. Much of the work in this area has been carried out by Pignolet and his collaborators.

There is a recent review on the electrochemistry of osmium dithiocarbamato complexes.[698]

46.7.4.1 Dithiocarbamates

(i) Osmium(II)

Electrochemical evidence for the existence of $[Os(S_2CNEt_2)_3]^-$ from reduction of the neutral osmium(III) species $Os(S_2CNEt_2)_3$ has been presented.[699] Reaction of *mer*-$Os(PMe_2Ph)_3Cl_3$ and $Na(S_2CNMe_2)$ gives *cis*-$Os(PMe_2Ph)_2(S_2CNMe_2)_2$,[412] and *cis*-$Os(PPh_3)_2(S_2CNR_2)_2$ (R = Me, Et) can be made from $Os(PPh_3)_3H(OCOCMe)_2$ and $Na(S_2CNR_2)$;[700] *mer*-$Os(PMe_2Ph)_3(S_2CNMe_2)Cl$ is made from *mer*-$Os(PMe_2Ph)_3$ and $S_2CNMe_2^-$, and the *fac* isomer is made from the *mer* with $K_2(S_2COEt)$. Configurations were obtained from ^1H NMR spectra.[412]

The stable osmium(II) species $Os(S_2CNR)_2(PPh_3)_2$ (R = Me, Et) are made from $OsH(OCOCF_3)(PPh_3)_4$ and $Na(S_2CNMe_2)$.[700] Reaction of *mer*-$Os(PMe_2Ph)_3Cl_3$ with $Na_2(CNMe_2)$ yields *mer*- and *fac*-$Os(PMe_2Ph)_3(S_2CNMe_2)Cl$ and *cis*-$Os(PMe_2Ph)_2(S_2CNMe_2)_2$.[412]

(ii) Osmium(III)

A number of osmium(III) dithiocarbamates are known. The diethyl complex $Os(S_2CNEt_2)_3$ is made by reaction of $(NH_4)_2[OsCl_6]$ and $Na(S_2CNEt_2)$.[350,699] The molecule contains diastereotopic methylene protons and, from a study of the ^1H NMR spectra over a temperature range, rate constants were calculated from the metal-centred optical inversion of the complex.[350] The magnetic moment is 1.61 BM at 25 °C.[350] The dimeric species $Os_2(S_2CNMe_2)_5Cl$ is made from $(NH_4)_2[OsCl_6]$ and $Na(S_2CNMe_2)$.[350]

(iii) Osmium(IV)

The osmium(IV) complex $Os(S_2CNEt)_4$ is also made from the reaction of $(NH_4)_2[OsCl_6]$ with $Na(S_2CNEt_2)$,[699] whilst BF_3 reacts with $Os(S_2CNEt_2)_3$ in dichloromethane to give the paramagnetic $[Os(S_2CNEt_2)_3]BF_4$.[350] In solution $[Os(S_2CNEt_2)_3]PF_6$ (prepared in similar fashion[702]) shows a monomer–dimer equilibrium which has been studied by ^1H NMR and cyclic voltammetry. The X-ray crystal structure of $[Os_2(S_2CNEt_2)_6](PF_6)_2 \cdot nCH_2Cl_2$ (n = 1 or 2) shows the osmium atoms to

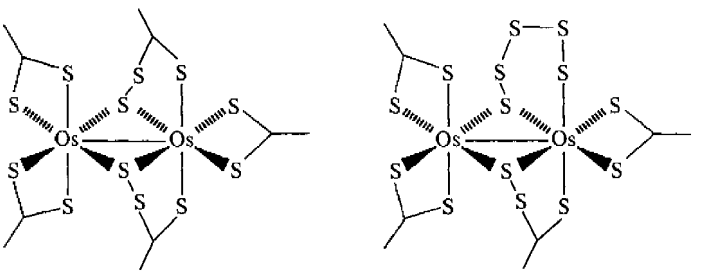
have distorted pentagonal bipyramidal coordination such that two sulfur atoms of two dithiocarbamato ligands bridge the metal atoms, one sulfur atom occupying the axial position of one pentagonal bipyramid and the equatorial position of the other. The Os···Os distance of 3.682(1) Å is too long for there to be significant metal–metal interaction. The mean Os—S distance is 2.415(3) Å.[701]

The diamagnetic and apparently seven-coordinate species $Os(S_2CNEt_2)_3X$ (X = Cl, I) were prepared from $Os(S_2CNEt_2)_3$ with HCl and I_2 respectively, and the chloro complex reacts with PPh_3 or MeCN (L) to give $Os(S_2CNEt_2)_3L$, also diamagnetic.[350] Reaction of $Os_2(OAc)_4Cl_2$ with $Na(S_2CNMe_2)$ gives $Os(S_2CNMe_2)_2Cl_2$.[105]

The diamagnetic μ-nitrido species $Os_2N(S_2CNEt_2)_5$ formally contains osmium(IV) and is considered on p. 563. For *fac*-$Os(PMe_2Ph)_3(S_2CNMe_2)(OEt)$, see p. 596.

46.7.4.2 Trithiocarbamates

The first trithiocarbamato complexes to be made were of osmium, and all these complexes are binuclear. In $[Os_2(S_3CNEt_2)_2(S_2CNEt_2)_3]BPh_4$, made from $(NH_4)_2[OsCl_6]$ and $Na(S_2CNEt_2)$ as a by-product in the synthesis of $Os(S_2CNEt_2)_3$, the 'extra' sulfur in $(S_3CNEt_2)^-$ has a bridging role (Figure 35a).[702]



(a) (b)

Figure 35 Structure of (a) $[Os_2(S_3CNEt_2)_2(S_2CNEt_2)_3]BPh_4$ and (b) $Os_2(S_5)(S_3CNEt_2)(S_2CNEt_2)_3$[703]

The mean Os—S (bridge) distances are 2.28 Å and mean Os—S (terminal dithiocarbamate) distances 2.44 Å. The Os···Os distance is 2.791 Å indicating metal–metal interaction which presumably accounts for the observed diamagnetism.[702] Reaction of elemental sulfur with $Os(S_2CNR_2)_3$ (R = Me, Et) in dimethylformamide gives $[Os_2(S_3CNR_2)_2(S_2CNR_2)_3]^+$ and $Os_2(S_5)(S_3CNR_2)(S_2CNR_2)_3$.[703] The X-ray crystal structure of $[Os_2(S_3CNMe_2)_2(S_2CNMe_2)_3]PF_6$ has a very similar structure to that of $[Os_2(S_3CNEt_2)_2(S_2CNEt_2)_3]BPh_4$, again with an Os···Os distance of 2.8782(1) Å and one Os—S (bridge) distance of 2.273 Å. In $Os_2(S_5)(S_3CNEt_2)$-$(S_2CNEt_2)_3$ (Figure 35b) there is a 'half-bridging' cyclic S_5^{2-} ligand, again with an Os···Os distance of 2.785 Å, while the Os—S (bridge) distance is 2.273 Å and the S_5 ring has a mean S—S distance of 2.06. Å.[703] Finally, in the selenodithiocarbamato species $[Os_2(SeS_2CNMe_2)_2(S_2CNMe_2)_3]PF_6$ there is an arrangement similar to that found in the trithiocarbamato analogue as in Figure 35(a) but with seleno instead of thio bridges.[704a]

The Os···Os distance is 2.836(1) Å and the mean Os—Se distance is 2.373 Å. The complex is made from red selenium and $Os(S_2CNEt_2)_3$.[704a]

46.7.4.3 Alkyl dithiocarbonato complexes

There are a few examples of these with phosphine coligands: $K(S_2COEt)$ will react with *mer*-$Os(PMe_2Ph)_3X_3$ (X = Cl, Br) to give *mer*-$Os(PMe_2Ph)_3(S_2COEt)X$, and *cis*-$Os(PMe_2Ph)_2$-$(S_2CNMe_2)(S_2COEt)$ is obtained from *mer*-$Os(PMe_2Ph)_3(S_2CNMe_2)Cl$ and $K(S_2COEt)$. The structures were derived from the ^1H NMR spectra.[412]

46.7.4.4 Alkyl- and aryl-phosphinodithionates

Reaction of *mer*-$Os(PMe_2Ph)_3Cl_3$ and $Na(S_2PMe_2)$ or $NH_4(S_2PPh_2)$ gives *cis*-$Os(PMe_2Ph)_2(S_2PR_2)$ (R = Me, Ph); slight variation of reaction conditions gives *mer*-

$Os(PMe_2Ph)_3(S_2PR_2)Cl_2$. From the methyl complex on recrystallization *trans*-$Os(PMe_2Ph)_2(S_2PMe_2)Cl_2$ and *mer*-$Os(PMe_2Ph)_3(S_2PMe_2)Cl$ can be obtained.[412] Reaction of $(2,4\text{-}Me_2C_6H_3)_2P(S)SH$ (HL) with $(NH_4)_2[OsCl_6]$ gave OsL_3; ESR data indicate distortion from octahedral symmetry.[704b]

46.7.5 Dithiolene Complexes

This is a largely unexplored area of osmium chemistry (in contrast to the situation for iron).

The two best characterized examples are $(Ph_4P)_3[Os(mnt)_3]$ (mnt = *cis*-1,2-dicyanoethylene-1,2-dithiolate), made from $[OsBr_6]^{2-}$ and the sodium salt of the ligand with $Na_2S_2O_4$;[85] $Os(tdt)_3$ (tdt = toluene-3,4-dithiol), a black material made from the liand and $[OsBr_6]^{2-}$ in base, and $(Me_4N)[Os(tdt)_3]$ for which a similar reaction is used but sodium dithionite is used as reducing agent.[705] The ESR spectrum of $[Os(mnt)_3]^{3-}$ has been measured[85] and also IR and electronic spectra on the tdt complexes.[705] Cyclic voltammetric studies on $Os(tdt)_3$ show that the redox system in equation (10) exists.[705]

$$Os(tdt)_3^{2-} \rightleftharpoons Os(tdt)_3^{-} \rightleftharpoons Os(tdt)_3 \rightleftharpoons Os(tdt)_3^{+} \quad (10)$$

An allegedly square planar complex OsL_2 (L = dithiobenzil) was claimed in 1964[706] but was later that year reformulated as the octahedral tris complex OsL_3.[707] No clear preparative details were given of this red complex, but the electronic spectrum and electrical conductance were later reported.[708]

Complexes between OsO_4 and 2,3-quinoxalinedithiol (2:1 and 1:4) have been shown to exist; both were isolated but not analyzed.[709] Further investigation is clearly desirable.

46.7.6 Sulfur Dioxide Complexes

It is surprising that so few of these have been reported for osmium.

The reaction of $[Os(NH_3)_5H_2O]^{3+}$ and $NaHSO_3$ with SO_2 at 80 °C gives $[Os(SO_2)(NH_3)_5]Cl_2$, the IR spectrum of which was measured.[90]

There is also a cyclohexylphosphine (PCy_3) complex: $Os(SO_2)(PCy_3)_2XH(CO)$, made from SO_2 and $Os(PCy_3)_2XH(CO)$ in benzene.[710]

46.7.7 Di- and Mono-thio-β-diketonates

As with much of osmium sulfur chemistry the data are scattered and incomplete; the best characterized complex is the dithioacetylacetonate complex $Os(sacsac)_3$.

46.7.7.1 Dithioacetylacetonate (4-thiolpent-3-ene-2-thione, $S_2C_5H_7^-$, sacsac)

The reaction between OsO_4 and acetylacetone with H_2S gives dark brown glossy plates of $Os(sacsac)_3$. IR and electronic spectra were recorded for the complex, as well as the ESR spectrum.[711] The magnetic susceptibility from 110 to 290 K shows that μ_{eff} is 1.65 BM at the latter temperature.[703] Polarographic reduction of $M(sacsac)_3$ (M = Ru, Os) shows reversible reduction at −0.01 and −0.151 V (vs. Ag/AgCl electrode),[658,711] while for $Os(acac)_3$ the potential is −1.244 V,[658] *i.e.* $Os(sacsac)_3$ is more easily reduced than $Os(acac)_3$, consistent with the 'softer' nature of sacsac as against acac, but less easily reduced than $Ru(sacsac)_3$, again as to be expected since ruthenium is a second row element.

A dark green complex, $Os(S_2C_6H_9)_3$, is made from 1-ethoxy-1-thiolobut-1-ene-3-thione and $[OsCl_6]^{2-}$.[712]

46.7.7.2 Monothio-β-diketonate complex

Monothiobenzoylmethane reacts with $[OsCl_6]^{2-}$ in aqueous ethanol to give the black complex $Os(SOC_{15}H_{12})_3$, which has a magnetic moment of 1.66 BM at room temperature. The same prepara-

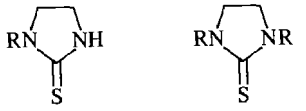
tion but with sodium acetate yields the black $Os(SOC_{15}H_{12})_4$, with a magnetic moment of 1.89 BM.[713]

46.7.8 Monothione Complexes

For the imidazolidine-2-thiones, which have received the most extensive study in this class of complexes, the monosubstituted imidazolidines stabilize osmium(III) while the disubstituted ones stabilize osmium(IV) and osmium(VI).[714]

46.7.8.1 Imidazolidine-2-thiones

The reaction of (I) or (II) with OsO_4 in aqueous ethanol gives $[OsL_6]^{3+}$ (L = (I), R = H, Me, Et)[714,715] and *trans*-$[OsL_2L_4]^{2+}$[716] (L = II, R = Me, Et); IR and electronic spectra were measured[714,715,717] and the kinetics of the reactions followed.[715,717]



The X-ray crystal structure of *trans*-$[OsL_4Cl_2](ClO_4)_2$ (L = II, R = Et, *i.e.* the *N,N'*-diethylimidazolidine-2-thione) confirms the *trans* configuration (Os—Cl = 2.351 Å, mean Os—S = 2.386 Å). The reaction is curious, for the chloro ligands were apparently derived from $HClO_4$ since the reaction was of OsO_4, the ligand and aqueous $HClO_4$. The osmyl complex *trans*-$[OsO_2L_4](ClO_4)_2$ can also be isolated from the reaction mixture.[716]

46.7.8.2 Thiazolidine-2-thione

This ligand (L) will react with OsX_3 (X = Cl, Br) to give OsL_3X_3; IR and electronic spectra of these were measured.[718]

46.7.9 Thiolato Complexes

46.7.9.1 Osmium(III)

The complex $Os(SC_{10}H_{13})_4(CNMe)$ is made from $OsCl_3$, the lithium salt of 2,3,5,6-tetramethylbenzenethiolate and 2,3,5,6-tetramethylphenyl sulfide; it is green-yellow. The X-ray crystal structure of the ruthenium salt shows it to be trigonal bipyramidal, with the acetonitrile in the axial position. The osmium complex is isomorphous; it would seem therefore to be the only example so far reported of a trigonal bipyramidal osmium(IV) complex. In an attempt to make a complex of lower coordination number 2,4,6-triisopropylbenzenethiolate ($SC_{15}H_{23}$) was used but the complex was still pentacoordinate, *i.e.* $Os(S_{15}H_{23})_4(MeCN)$.[719]

46.7.9.2 Osmium(IV)

The species $Na[Os(SNC_4H_{10})(OH)_4]$ and $Os(SNC_8H_{18})_2(OH)_2$ have been claimed, OsO_4 with dimethylaminoethanethiol giving the former[720] while diisopropylaminoethanethiol with 'osmic acid' gives the latter, which supposedly contains osmium(IV) (μ_{eff} is 1.2 BM at room temperature).

46.7.10 Dithiocarboxylate and Thiocarboxylate Complexes

There is some work on dithioformato complexes, but clearly thiocarboxylate osmium chemistry is an area in need of further study.

Complexes of the dithioformate ligand S_2CH^- have been made from $Os(PPh_3)_4H_3$ and CS_2. By analogy with the ruthenium analogue (for which an X-ray crystal structure has been obtained) a

structure involving bidentate S_2CH^- ligands *cis* to each other was proposed for $Os(PPh_3)_2(S_2CH)_2$. Reaction of CS_2 with $Os(PR_3)_3HX(CO)$ (PR_3 = PMe_2Ph, $PMePh_2$, PPh_3; X = Cl, Br) gives two forms of $Os(PR_3)_2(S_2CH)X(CO)$; in one the sulfur atoms are thought to be *trans* to the PR_3 ligands, and in the other the halide and PR_3 ligands are *trans* to the sulfur atoms.[424]

A number of complexes of *p*-chlorodithiobenzoate ($S_2C_7H_4Cl^-$; L) have been claimed, involving osmium(III) and osmium(IV); OsL_3 was isolated.[721] There is also $Os(SO_6C_{16}H_8)_2 \cdot 2H_2O$, a complex of 5,5′-thiodisalicylic acid, made from the ligand and 'osmic acid', and which has a magnetic moment of 1.35 BM at room temperature.[722]

46.7.11 Thiourea Complexes

The principal oxidation states involved in the rather few thiourea (thio) complexes which have been studied are II, III and (as the osmyl complex) VI. In no case is the mode of bonding properly established. In view of the uncertainty surrounding some of these species we consider both unsubstituted and substituted complexes together, using the apparent oxidation state for classification purposes.

46.7.11.1 Osmium(II)

Reduction of $[Os(thio)_6]^{3+}$ with $[Cr(H_2O)_6]^{2+}$ gives $[Os(thio)_6]^{2+}$.[508]

The reaction of thiourea with $[Os(NO)Cl_5]^{2-}$ is said to give a brown, seven-coordinate 'association complex', $K_2[Os(NO)(CN)_5 \cdot thio]$.[723] The X-ray photoelectron spectrum of $OsL_2 \cdot Cl_2$ (L = diphenylthiourea) has been measured.[724]

46.7.11.2 Osmium(III)

It appears that the main reaction product of OsO_4 with thiourea is $[Os(thio)_6]^{3+}$, together with formamidine disulfide, *via* initial formation of $[OsO_2thio_4]^{2+}$.[508,725] The earlier-reported species $[Os(thio)_6](OH)Cl_3$[726] is likely to have contained the osmium(III) species. Salts of $[Os(thio)_6]^{3+}$ with $[Cr(NH_3)_2(SCN)_4]^-$ and $[Cr(SCN)_6]^{3-}$ have been isolated using OsO_4, thiourea and the complex anion in HCl.[727,728] $[Os(thio)_6](SnCl_3)_2Cl$ has been reported;[52] ESCA data on $[Os(thio)_6]Cl_3$ have been given.[616]

The OsO_4–thiourea reaction has recently been investigated kinetically.[726,729]

Reaction of $[Os(NO)(CN)_5]^{2-}$ in hydroxide (which presumably generates $[Os(NO_2)(CN)_5]^{4-}$) and thiourea gives $K_2[Os(thio)(CN)_5]$.[723,730] The X-ray photoelectron spectrum of OsL_2Cl_3 has been measured (L = diphenylthiourea).[724]

46.7.11.3 Osmium(VI)

The osmyl-complex $[OsO_2thio_4]SO_4$ (brown, made from OsO_4 and the ligand in H_2SO_4)[508] and a dark green osmyl complex, made from *N*-α-pyridyl-*N*′-benzoylthiourea and *trans*-$K_2[OsO_2(OH)_4]$, have been reported.[731]

For ethylenethiourea complexes see imidazoline-2-thione, p. 607.

46.7.12 Miscellaneous S,S Donor Ligands

The diisopropyldithiophosphate complex, made by reaction of the ammonium salt of the ligand with $[OsCl_6]^{2-}$, has a dimeric structure with two bidentate $(Pr^iO)_2PS_2^-$ groups per metal atom and two bridging Pr^iP—S—S ligands, according to a preliminary X-ray study.[732]

Complexes of the form $Os(mdtp)_3$ and $Os(ptp)_3$ (mdtp = bis(2-methyl-5-chlorophenyl)dithiophosphinate and ptp is the corresponding *p*-tolyl derivative) were made from $[OsCl_6]^{2-}$ and the sodium salt of the ligand; the ESR data for these species were very briefly described. The complex $(Os(ptp)_2(PPh_3)_2]Cl$ and $[Os(ptp)_2phen]Cl$ were also prepared.[733]

46.8 SELENIUM- AND TELLURIUM-CONTAINING LIGANDS

There are relatively few of these, and it is obviously an area worthy of further investigation, as is that of osmium–tellurium chemistry.

46.8.1 Selenido Complexes

Reaction of $Os(PPh_3)_3(CO)_2$ with Se_8 yields $Os(\eta^2\text{-}Se_2)(PPh_3)_2(CO)_2$, the crystal structure of which shows a distorted octahedral structure. The side-bonded Se_2 ligand (Os—Se = 2.5403(8) and 2.5526(7) Å) with Se—Se = 2.321(1) Å) is *trans* to two carbonyl ligands (mean Os—C = 1.874 Å); the two phosphine ligands are *trans* to each other (mean Os—P = 2.406 Å).[693]

46.8.2 Selenoether Complexes

Reaction of $MeSe(CH_2)_2SeMe$ and also of Me_2Se with HX and OsO_4 gives $OsO_2X_2\{MeSe(CH_2)_2SeMe\}$ (X = Cl, Br); IR, electronic and ^1H NMR spectra were measured.[514]

46.8.3 Diethylselenocarbamato Complex

The species $Os(Se_2CNEt_2)_3$ is obtained from $[OsBr_6]^{2-}$ and $(NH_4)(Se_2CNEt_2)$. The complex has a magnetic moment of 1.63 BM at room temperature.[734]

46.8.4 Imidazolidine-2-selones

Reaction of these with OsO_4 in acid solution gives $[OsL_6]^{3+}$ (L = $SeN_2C_3H_5R$; R = H, Me, Et); the kinetics of the reactions were studied as well as the IR spectra of the complexes.[735]

46.8.5 Tellurium-containing Complexes

Attempts to prepare $OsO_2X_2(TeMe_2)$ (X = Cl, Br) from OsO_4, HX and Me_2Te failed.[514]

46.9 HALOGENS AS LIGANDS

The chemistry of osmium fluorides and fluoro complexes differs sufficiently from that of the chloro, bromo and iodo species to warrant separate treatment here. The early review of Canterford and Colton is still useful for the general halide chemistry of the element.[736]

46.9.1 Fluorides and fluoro complexes

Oxidation states IV to VIII inclusive are represented in the fluorine chemistry of osmium, as compared with III to VI for ruthenium and II and III for iron. Thus the fluorides of the iron–ruthenium–osmium triad well exemplify the greater tendency of second and third row elements to higher oxidation states with π-donor ligands.

The oxofluorides of osmium, amongst others, have recently been reviewed;[731] we have already dealt with them on p. 584.

46.9.1.1 Osmium(IV)

The tetrafluoride OsF_4 is not a discrete molecular species and so is not considered in detail here: it is a yellow material, prepared by reduction of $[OsF_5]_4$ with hydrogen over platinum gauze under UV irradiation at 50 °C.[738]

A number of salts of $[OsF_6]^{2-}$ are known: the free acid[739] (in aqueous solution only), the hydrazinium,[740] tridodecylammonium,[741] sodium,[742] potassium,[739,743] rubidium[739] and cesium[739,743] salts have been isolated. The general method of preparation is to treat the corresponding $[OsF_6]^-$ salt with aqueous alkali;[743] a convenient way of making $K_2[OsF_6]$ is to fuse $K_2[OsX_6]$ (X = Cl, Br or I) with KHF_2 at 400 °C.[744] They are white solids giving stable aqueous solutions.

Lattice parameters have been measured for the sodium, potassium and cesium salts; the sodium salt exists in a metastable orthorhombic form and a stable hexagonal form,[742] while $K_2[OsF_6]$ and $Cs[OsF_6]$ have hexagonal structures related to that of $K_2[GeF_6]$.[739] The IR stretching frequency (ν_3, F_{1u}) of $K_2[OsF_6]$ is 548 cm^{-1}.[745] Electronic spectra have been measured[746] and assigned for solid $K_2[OsF_6]$ and $Cs_2[OsF_6]$; for the $[OsF_6]^{2-}$ ion $10Dq$ is given as 26 000 cm^{-1}.[746,747]

Studies on the magnetic susceptibility of $K_2[OsF_6]$ and $Cs_2[OsF_6]$ from 89 to 291 K have been carried out and show that the molar susceptibility (χ_M) is essentially independent of temperature over this range (see Table 27).[748] The essential invariance of χ_M with temperature has been discussed.[748,749] It would be of considerable interest to study, as has been done for $K_2[OsX_6]$ (X = Cl, Br, I), the effect on the magnetic susceptibility of $M^I_2[OsF_6]$ salts of diluting them in isomorphous diamagnetic host lattices such as $M^I_2[PtF_6]$.

Table 27 Magnetic Data on $[OsX_6]^{2-}$ Complexes[748]

Complex	*Temperature range (K)*	*χ_a over same range (10^{-6} cgsu)*	*μ_{eff} at 300 K (BM)*
$K_2[OsF_6]$	88.9–291.0	713–713	1.31
$Cs_2[OsF_6]$	89.8–278.5	957–937	1.50
$K_2[OsCl_6]$	90–300	941–941	1.51
$Cs_2[OsCl_6]$	91.0–296.5	1257–1162	1.67
$K_2[OsBr_6]$	87.4–295.3	617–603	1.21
$Cs_2[OsBr_6]$	98.0–295.4	1392–1285	1.76
$K_2[OsI_6]$	88.4–296.2	877–789	1.38
$Cs_2[OsI_6]$	90.7–294.4	1191–1132	1.65

Studies on the ^{19}F NMR spectra of solid $M_2[OsF_6]$ (M = K, Rb, Cs) suggest that the anions have distorted structures.[750]

(*i*) *Mixed fluorohalo osmates(IV), $[OsF_nX_{6-n}]^{2-}$*

Many such complexes have been prepared. The fluorochloro series $[OsF_nCl_{6-n}]^{2-}$ has been made from $[OsCl_6]^{2-}$ and BrF_3; both *cis* and *trans* forms of $[OsF_4Cl_2]^{2-}$ were isolted as was *trans*-$[OsF_2Cl_4]^{2-}$.[751]

Recently the reaction of BrF_5 and $[OsCl_6]^{2-}$ has been shown to give all five members of $[OsF_nCl_{6-n}]^{2-}$ with the *cis* isomers for $n = 4$ and 2 and the *fac* isomer of $[OsF_3Cl_3]^-$; reaction of Cl^- with $[OsF_5Cl]^{2-}$ and with *cis*-$[OsF_4Cl_2]^{2-}$ gives *trans*-$[OsF_4Cl_2]^{2-}$, *trans*-$[OsF_2Cl_4]^{2-}$ and *mer*-$[OsF_3Cl_3]^{2-}$. The isomers were separated by ion exchange and their vibrational spectra measured;[752] in earlier work vibrational spectra and unit cell dimensions were listed for some isomers as the potassium salts.[751]

Most members of the series $[OsF_nBr_{6-n}]^{2-}$ and $[OsF_nI_{6-n}]^{2-}$ have been isolated from the reaction of $[OsX_6]^{2-}$ (X = Br, I) and tridodecylammonium fluoride.[753] The salt *trans*-$Cs[OsF_4ClBr]$, made by reaction of $K_2[OsF_5Cl]$ with HBr followed by ionophoresis and addition of cesium ion,[751] has been studied by single crystal X-ray analysis. The mean Os—F distance is 1.94 Å, with Os—Cl = 2.43(1) and Os—Br = 2.49(1) Å.[754]

(*ii*) *Miscellaneous osmium(IV) fluoro complexes*

Reaction of OsF_6 with PF_3 at −196 °C gives a yellow compound, amorphous to X-rays, giving analyses corresponding to $OsF_4 \cdot 2PF_3$. On the basis of IR data the formulation *trans*-$OsF_4(PF_3)_2$ was suggested. The essentially diamagnetic nature of the material (μ_{eff} = 0.3 BM at 300 K) is curious, but possibly it arises from the tetragonal distortion of the complex if it is indeed an osmium(IV) complex containing coordinated PF_3 ligands.[755]

46.9.1.2 Osmium(V)

This is an unusual oxidation state for osmium. We include osmium pentafluoride in our coverage here since it is a discrete molecular species. Osmium pentafluoride, $[OsF_5]_4$, is made by the reduction of OsF_6 with iodine and IF_5 at 55 °C[756] or from the action of silicon on OsF_6.[738] It is a blue-green solid melting at 70 °C to a viscous green liquid which becomes bluer as the temperature rises, boiling at 233 °C to a colourless vapour.[756]

The X-ray crystal structure of the solid shows it to be tetrameric in the solid state with a structure closely akin to that of $[RuF_5]_4$, the metal atoms lying at the corners of a rhombus and linked by *cis* fluoro bridges (Os—F (bridge) = 2.03 Å, mean Os—F(bridge)—Os angle = 137 °). The mean Os—F terminal distance is 1.84 Å (Figure 36).

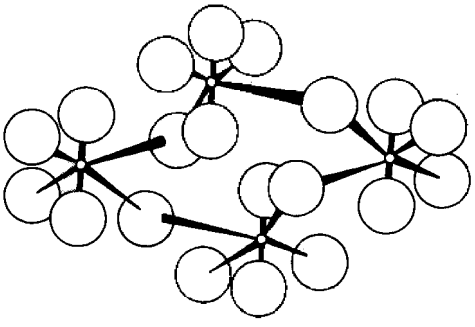


Figure 36 Structure of $[OsF_5]_4$ (reproduced with permission from J. H. Canterford and R. Colton, 'Halides of the Second and Third Row Transition Metals', p. 20, copyright 1968 Wiley)

The substantially bent Os—F(bridge)—Os angle is in agreement with the π-bonding hypothesis put forward by Canterford and Colton.[758] In pentafluorides $[MF_5]_4$ containing *cis* fluoro bridges, the degree of bridge fluoro-to-metal π bonding will be at a maximum if the M—F(bridge)—M angle is 180 ° and M has a d^0 configuration (*e.g.* M = Nb, Ta). As the *d* orbital electron occupancy increases with concomitant lower bridge F to M π bonding the angle is observed to decrease, from d^1 species (Mo, W), d^2 (Tc, Re), to d^3 (Ru, Os) and beyond; thus, in $[OsF_5]_4$, it is likely that such π bonding is of little importance.[758]

Magnetic interactions in $[OsF_5]_4$ have been studied by susceptibility and neutron diffraction measurements; it is magnetically ordered at $T_N = 6$ K.[759] The magnetic moment varies from 1.73 BM at 101.5 K to 2.06 BM at 295.4 K.[756]

(*i*) *Salts of* $[OsF_6]^-$

A number of salts of this ion are known; those of lithium,[760] sodium,[743] potassium,[742] rubidium,[761] cesium,[743] silver,[743,761] NO^+,[762] XeF^+ and $Xe_2F_3^+$[763] and BrF_3^+.[764] The alkali metal salts are made by reaction of a 1:1 $OsBr_4$, MBr mixture with fluorine(Li,[760] Na[742]) or with BrF_3 (K[742], Rb,[761] Cs[742]). These are colourless, decomposing in moist air, and in alkaline solution giving $[OsF_6]^{2-}$. These salts of non-metallic cations are made from OsF_5 or OsF_6 (NO^+,[762] Xe salts[763]).

Unit cell parameters have been measured for the alkali metal salts, which have rhombohedral structures.[760,761] A single crystal X-ray of $K[OsF_6]$ shows this to have a slightly distorted octahedral structure with a mean Os—F distance of 1.82 Å.[765] Raman spectra of $(NO)[OsF_6]$ and $Xe_2F_3[OsF_6]$ have been measured[763] and are listed in Table 28. From the electronic reflectance spectrum of $Cs[OsF_6]$ a value of 36 000 cm^{-1} was obtained for $10Dq$.[747] Magnetic susceptibility data for $K[OsF_6]$ and $Cs[OsF_6]$ show that the magnetic moment is essentially invariant from 115 to 295 K, giving μ_{eff} 3.34 and 3.23 BM for the potassium and cesium salts respectively.[766]

46.9.1.3 Osmium(VI)

(*i*) *Osmium hexafluoride*

OsF_6 is made by the direct fluorination of the metal;[767–769] as noted on p. 612 it now seems quite clear[767,769] that the 'OsF_8' of the early literature[770] is in fact OsF_6. It is a bright yellow solid, melting at 33.9 °C and boiling at 47.5 °C with a triple point at 33.4 °C (at 474.5 mmHg);[768] there is a phase transition at 1.4 °C.[771] In water it disproportionates to OsO_4 and $[OsF_6]^{2-}$.

Electron diffraction data on the vapour at −39 °C show the molecule to be octahedral in the gas phase with an Os—F distance of 1.831(8) Å; it is interesting to note that the Os—F distance for this d^2 species is very close to the value of 1.833(3) Å observed in WF_6 (d^0) and 1.830(8) Å in IrF_6 (d^3).[772] It has been plausibly suggested that this constancy of distance is a consequence of π donation from the fluoro ligands to the metal decreasing from W to Ir because of increased d electron occupancy, this effect being counterbalanced by the shrinkage of the M^{VI} size from left to right brought about by shielding effects.[773] In the solid state OsF_6 is cubic at room temperatures, undergoing a transition at 1.4 °C to a form of lower symmetry (probably orthorhombic).[772] Thermodynamic data have been calculated for the compound on the basis of vapour pressure data.[768]

There has been much work on the vibrational spectroscopy of the molecule; the best data for the vibrational frequencies are given in Table 28,[774] based on the IR spectrum of the gas and the Raman spectra of the liquid[775] and gas.[775–777] Electronic Raman spectra of a solution of OsF_6 in MoF_6 have recently been measured.[778] The unusual breadth and low intensity of the $\nu_2(F)$ and low intensities of combinations involving ν_2 suggest[774–777] that a dynamic Jahn–Teller effect is operative for this t_{2g}^2 molecule. There have been many force constant treatments for the molecule[774,779] and determinations of Coriolis coupling constants.[780,781] Electronic spectra of the gas[782] and its solutions in MoF_6[778] have been measured and assignments proposed. Magnetic susceptibility data were measured from 117 to 297 K and show that the Curie–Weiss law is obeyed ($\theta = 66°$, $\mu_{eff} = 1.47$ BM at 267.8 K).[769] Theoretical interpretions of these data have been given.[783,784]

Table 28 Vibrational Spectra for $[MX_6]^{n-}$ Complexes

Complex		ν_1 (A_{1g})	ν_2 (E_g)	ν_3 (F_{1u})	ν_4 (F_{1u})	ν_5 (F_{2g})	ν_6 (F_{2u})	*Ref.*
$(NO)[OsF_6]$[a]	R	690	606			261		763
OsF_6[b]	R, IR	731	668	720	268	276	205	777
$[OsCl_6]^{3-}$[c]	R, IR	310		294[e]	185[e]			791
$[OsCl_6]^{2-}$[d]	R	346	274			165		818
$K_2[OsCl_6]$[a]	R, IR	354	269	325	178	171		820
$(Et_4N)[OsCl_6]$[a]	R, IR	375	302	325	168	183		833
$[OsBr_6]^{3-}$[c]	R, IR	189	180[e]	200[e]	116[e]	94[e]	791	
$[OsBr_6]^{2-}$[d]	R	211	169			100		818
$K_2[OsBr_6]$[a]	R, IR	218	162	227	122			828, 829
$[OsI_6]^{3-}$[c]	R, IR	140	113[e]	140[e]	111[e]			791
$(Bu^n_4N)_2[OsI_6]$[a]	R, IR	155	120	170	91	80		821

[a] Solid. [b] Gas. [c] Solid and solution. [d] Solution. [e] On $[Co\ en_3][OsX_6]$.

The ^{19}F NMR resonance has been measured from 115 to 245 K at different field strengths of solid OsF_6 and spin–lattice relaxation times determined.[785] The electron affinity of OsF_6 has been compared with those of other metal hexafluorides.[762,786,787] The Mössbauer spectrum has been recorded.[184]

The apparently heptacoordinate $(NO)[OsF_7]$ has been made from FNO and OsF_6; it has a cubic structure.[762]

46.9.1.4 Osmium(VII)

The heptafluoride OsF_7 is made by fluorination of the metal at 600 °C under a fluorine pressure of 400 atm. The IR spectra suggest that the complex has a pentagonal bipyramidal (D_{5h}) structure. The magnetic susceptibility was measured from 90 to 195 K and, as with $[OsF_6]^{2-}$ salts, the moment is essentially invariant with temperature over this range ($\mu_{eff} = 1.08$ BM).[788]

46.9.1.5 Osmium(VIII)

The octafluoride OsF_8 was claimed in 1913 to be the product of reaction of Os with fluorine[770] but clearly OsF_6 had been made.[767,769] It is said that some OsF_8, however, may be produced by reaction of osmium with fluorine at very high pressures.[788]

For oxo fluorides and oxo fluoro complexes see p. 584, 588 and 596.

46.9.2 Chloro, Bromo and Iodo Complexes

There is only one binary halide, Os_2Cl_{10}, which can be classed as a 'complex' in the sense that it has a discrete molecular structure, and we consider it on p. 615 below. In this section we consider unsubstituted halo complexes $[OsX_6]^{n-}$, mixed species $[OsX_nY_{6-n}]^{x-}$ (X and Y both halides) and aqua and hydroxo halides. Other halo species substituted with other ligands are considered under the section dealing with the substituting ligand (*e.g.* oxo halo species on p. 584, nitrido halo complexes on p. 563, halo ammines on p. 529).

Although there is a small chemistry of $[OsX_6]^{3-}$ and an even smaller chemistry of $[OsCl_6]^-$, it is the IV oxidation state that predominates in the chloro, bromo and iodo chemistry of osmium, whereas for ruthenium it is probably true to say that the chemistry of $[RuX_6]^{3-}$ is more extensive, or at least has been more extensively investigated, that that of $[RuX_6]^{2-}$. Much work has been done on the mixed halo species $[OsX_xY_{6-n}]^{2-}$.

There is a short review on osmium halo complexes in solution.[789] For carbonyl halides of osmium, see p. 973 of ref. 16.

46.9.2.1 Osmium(III)

There are very early reports of the potassium and ammonium salts of $[OsCl_6]^{3-}$, made from $[OsO_3N]^-$ and HCl or for OsO_4 with NH_4Cl and H_2S,[5] but the compounds were not fully characterized. Reduction of $[OsX_6]^{2-}$ in acid solution with silver powder gives solutions thought to contain $[OsX_6]^{3-}$ (X = Cl, Br, I),[790] and recently the salts $[Co(en)_3][OsX_6]$ have been isolated from such solutions.[791] The potassium salt $K_3[OsBr_6]$ has been isolated by electrolytic reduction of $[OsBr_6]^{2-}$;[792] the $[OsBr_6]^{2-}/[OsBr_6]^{3-}$ couple is +0.31 V in 4 M HBr (*vs.* NHE).[793]

Vibrational spectroscopic data for $[OsX_6]^{3-}$ (X = Cl, Br, I) are given in Table 28,[791] and there are ESR data on apparently uncharacterized $[OsCl_6]^{3-}$ species.[794,795]

Dimeric $[Os_2X_8]^{2-}$ (X = Cl, Br) complexes have recently been made.

46.9.2.2 Osmium(IV)

Salts of $[OsX_6]^{2-}$, especially the chloride as $Na_2[OsCl_6]\cdot nH_2O$ (conveniently soluble in water or polar organic solvents), as $K_2[OsCl_6]$ or $(NH_4)_2[OsCl_6]$, are good precursors for preparations of other osmium complexes; indeed, $Na_2[OsCl_6]\cdot nH_2O$ rivals OsO_4 as a useful starting material.

(*i*) *Unsubstituted $[OsX_6]^{2-}$ species*

For $[OsCl_6]^{2-}$ the free acid[796] and salts with a variety of organic cations are known,[797–800] and the sodium,[801] potassium,[798,802] rubidium,[803] cesium[804] and ammonium[801,805] salts together with a number of heavy metal salts (*e.g.* silver and thallium(I)[806]). The best method of preparation is from OsO_4 and concentrated HCl in the presence of a reducing agent such as ascorbic acid,[798] iron(II) chloride[805] and the appropriate cation. The $[OsBr_6]^{2-}$ ion is obtainable as the free acid in solution[804] and salts of organic cations[797,807,808] as well as sodium,[506] potassium,[804,808] rubidium,[637] cesium[803,804] and ammonium,[809] while $[OsI_6]^{2-}$ is similarly represented by the acid in solution (and also, apparently, as a solid isomorphous with $(NH_4)_2[OsI_6]$[810]), with organic cations[811] and as the potassium[812–814] and ammonium[204] salts. For $[OsBr_6]^{2-}$ and $[OsI_6]^{2-}$ the acids themselves will reduce OsO_4,[809,814] or $[OsCl_6]^{2-}$ can be refluxed with HI.[813]

There is a single crystal X-ray structure of $(Ph_4P)_2[OsCl_6]$ which shows the mean Os—Cl distance to be 2.332 Å,[815] and unit cell data obtained for a number of cubic salts of $[OsCl_6]^{2-}$ and $[OsBr_6]^{2-}$.[816] In a recent paper correlations between Os—Cl distances and Os—Cl stretching frequencies have been made, and similar data presented for rhenium and iridium chloro species.[817] In particular there have been a number of studies on the Raman spectra, both non-resonance and resonance, of $[OsCl_6]^{2-}$[818–822] as well as electronic[823] and electronic resonance Raman spectra;[824] similar studies have been carried out with $[OsBr_6]^{2-}$[818,819,823–826,828,829] and $[OsI_6]^{2-}$[803,821,823,827] (for the latter, magnetic, electronic and Raman spectra and optical activity were also measured[827]). In Table 27 we also

include data on the IR spectra of $[OsCl_6]^{2-}$,[820,828,829] $[OsBr_6]^{2-}$[820] and $[OsI_6]^{2-}$,[791] There have been a number of studies on the electronic absorption spectra of $[OsX_6]^{2-}$ (X = Cl, Br,[790,798,806,811,819,824,830–832] I[811,823,824,831]); vibrational intervals were located in the luminescence spectra of solid $K_2[OsCl_6]$ doped into $K_2[PtCl_6]$.[832]

There have also been NQR[807,834] and ESCA[427] studies on $K_2[OsX_6]$ (X = Cl, Br) and Mössbauer work on $K_2[OsCl_6]$.[184] An MO description of the bonding in $[OsCl_6]^{2-}$ has been given.[835]

(a) Magnetic susceptibility data. The magnetic properties of $K_2[OsX_6]$ and $Cs_2[OsX_6]$ (X = F,Cl, Br, I) were first systematically studied by Earnshaw *et al.*, who found relatively little variation in the atomic susceptibility (χ_a) over a wide temperature range (Table 28).[748]

It was assumed from these data that the relative constancy of X_M with temperature arose from high spin–orbit coupling; where significant variation of χ_M did occur with temperature it was suggested that a small amount of paramagnetic impurity (*e.g.* $[OsX_6]^{3-}$) was perhaps responsible.[748] Later work showed that the susceptibilities of $K_2[OsCl_6]$ and $K_2[OsBr_6]$ diluted in the isomorphous diamagnetic host lattice $K_2[PtCl_6]$ or $K_2[PtBr_6]$ were much higher than for the pure salts, and a 'superexchange' mechanism *via* d_π–d_π metal ligand orbitals for the non-dilute systems was proposed to account for these observations.[836–838] Some of these measurements were repeated[808,839] and susceptibility data presented for $(NH_4)_2[OsX_6]$, $(Bu^n{}_4N)_2[OsCl_6]$ and $(Me_4N)_2[OsBr_6]$, and intermediate coupling schemes proposed.[807,840] Theoretical calculations on the basis of a cubic field successfully fitted experimental results for the susceptibility and electronic absorption spectra of $K_2[OsCl_6]$.[841]

(b) Other data for $[OsX_6]^{2-}$. Kinetics of the reaction shown in equation (11) were measured and compared with those for $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$;[842] there are also mechanistic studies on the reactions of $[OsCl_6]^{2-}$ with $[Fe(CN)_6]^{4-}$,[843] bromide[844] and iodide.[845] There are recent thermogravimetric and differential thermal analysis data for $M^I{}_2[OsX_6]$ (M = Rb, Cs; X = Br, I).[846]

$$[OsCl_6]^{2-} + H_2O \rightleftharpoons [OsCl_5(H_2O)]^- + Cl^- \qquad (11)$$

The species $OsCl_4 \cdot 2MCl_4$ (M = S,[847] Se, Te[848]) have been reported; their IR spectra suggest that they contain $[OsCl_6]^{2-}$ ions and so they have been formulated as $(MCl_3)_2[OsCl_6]$.[848]

(*ii*) *Mixed halo complexes, $[OsX_nY_{6-n}]^{2-}$*

Species of this type containing the fluoro ligand have already been considered (p. 610).

(a) $[OsCl_nBr_{6-n}]^{2-}$. All the geometrical isomers in this system, made from HBr and $[OsCl_6]^{2-}$, have been identified; ionophoresis,[849] chromatography[850,851] and HPLC[852] have been used, infrared spectra measured of the various complexes[831] and their stability constants determined.[853] Kinetics of exchange for the eighteen possible ligand exchange reactions were investigated by radiometry.[854,855]

(b) $[OsCl_nI_{6-n}]^{2-}$ and $[OsBr_nI_{6-n}]^{2-}$. Members of the former series were made from HI and $[OsCl_6]^{2-}$, and all the isomers were separated chromatographically,[850] whilst ionophoretic methods were used on the HBr–$[OsI_6]^{2-}$ system to give all the isomers. IR spectra of the members of the $Cs_2[OsBr_nI_{6-n}]$ series have been recorded[856a] as have electronic spectra.[856b] Hydrolysis of $[OsCl_nI_{6-n}]^{2-}$ is catalyzed by mercury(II).[857]

(*iii*) *Dimeric osmium(IV) species*

The dimeric salt $(Bu^n{}_4N)_2[Os_2Cl_{10}]$ can be made by heating $(Bu^n{}_4N)[OsCl_6]$ for a short time to 240 °C. The X-ray crystal structure analysis shows a chloro-bridged dimer structure (Os—Cl(bridge) = 2.411(2), mean Os—Cl *trans* to bridge = 2.306, mean Os—Cl *cis* to bridge = 2.301 Å). The Os···Os distance is 3.626(1) Å. The magnetic susceptibility was measured from 94 to 336 K; it obeys the Curie–Weiss law with $\theta = -6$ and $\mu_{eff} = 1.36$ BM (per metal atom).[858] Recently the bromo analogue has been made by refluxing $(Bu^n{}_4N)_2[OsBr_6]$ in trifluoroacetic acid. The structure is very similar to that of $[Os_2Cl_{10}]^{2-}$; the bridging Os—Br distances are 2.544(4) Å, the mean terminal Os—Br distance is 2.454 Å, and the Os···Os distance is 3.788(3) Å. Although there is clearly no direct Os—Os interaction in either of these complexes the magnetic moment μ_{eff} is remarkably low, 0.26 BM at 296 K.[382]

46.9.2.3 Osmium(V)

(i) Salts of $[OsX_6]^-$ (X = Cl, Br)

The tetraphenylarsonium salt is made from Os_2Cl_{10} and $(Ph_4As)Cl$[859] and tetraethylammonium salt from $(Et_4N)[OsX_4(CO)_2]$ (X = Br, I) and Cl_2 at 120 °C;[833] oxidation of $[OsCl_6]^{2-}$ by PbO_2 gives $[OsCl_6]^-$ [860,861] and $SCl_3[OsCl_6]$ can be got from OsO_4 and SCl_2.[861] The redox potential $[OsCl_6]^-/[OsCl_6]^{2-}$ is 0.8 V (*vs.* Hg/Hg_2SO_4).[833]

The X-ray crystal structures of $(Bu^n{}_4)[Oscl_6]$[858] and $(PPh_4)[OsCl_6]$[815] show these to be octahedral, with mean Os—Cl distances of 2.303 and 2.284 Å respectively. The difference is surprising given that only the cation has changed (see also ref. 861), but both are shorter than the Os—Cl distance of 2.332 Å in $(Ph_4P)_2[OsCl_6]$,[815] as expected in view of their higher oxidation states. The magnetic susceptibility of $(Bu^n{}_4N)[OsCl_6]$ over the range 94 to 336 K obeys the Curie–Weiss law (θ = 18 K, μ_{eff} = 3.03 BM)[858] The Raman, resonance Raman and IR spectra of $[OsCl_6]^-$ were recorded (see Table 28).[833]

Attempts to isolate pure salts of $[OsBr_6]^-$ were not successful, but the ion was generated in solution to form $[OsBr_6]^{2-}$ and solid PbO_2, and electronic spectra were recorded. The $[OsBr_6]^-/[OsBr_6]^{2-}$ potential is + 1.20 V.[860]

(ii) Dimeric osmium pentachloride, Os_2Cl_{10}

This is made by reaction of OsF_6 with BCl_3 at − 196 °C[862] or from OsO_4 and SCl_2.[859] The X-ray crystal struture shows it to be a chloro-bridged dimer with a bridging Os—Cl distance of 2.42 Å, and a mean terminal Os—Cl distance of 2.24 Å. The Os···Os distance is 3.63 Å. The magnetic susceptibility over the range 80 to 293 K obeys the Curie–Weiss law (θ = 230, μ_{eff} = 2.54 BM per Os atom). IR, electronic and ESR spectra were also recorded.[862]

(iii) Substituted halo complexes

(a) Aqua and hydroxo species. Recent work on the electrochemical oxidation of *trans*-$[OsO_2Cl_4]^{2-}$ gives evidence for the existence of labile $[Os^{III}Cl_n(H_2O)_{6-n}]^{(3-n)-}$ species; at high Cl^- concentrations $[OsCl_4(H_2O)_2]^-$ reacts with *trans*-$[OsO_2Cl_4]^{2-}$ to give $OsCl_4(H_2O)_2$.[489]

Although the main product of aquation of $[OsX_6]^{2-}$ appears to be $[OsX_5(H_2O)]^-$ (X = Cl, Br)[842,863] there is evidence for the existence of $[OsCl_5(OH)]^{2-}$,[863] *cis*-$[OsCl_4(OH)(H_2O)]^-$, *fac*-$[OsCl_3(OH)_2(H_2O)]^-$ and *mer*-$OsCl_3(OH)(H_2O)_2$ as well as oxo-bridged dimers in the hydrolysis products of $[OsCl_6]^{2-}$.[864] Evidence for the existence of $OsCl_4(H_2O)_2$,[489,865] $[OsCl_n(H_2O)_{6-n}]^{(4-n)-}$[863,865] and $[OsI_5(H_2O)]^-$ [812,866] has been presented. Studies of the equilibria in equation (12) have been made (X = Cl, Br[863]).

$$[OsX_5(H_2O)]^- + OH^- \rightleftharpoons [OsX_5(OH)]^{2-} + H_2O \quad (12)$$

There are electronic spectral data on $[OsCl_5(H_2O)]^-$.[842,863] The species $OsCl_5(H_2O)$ is probably formed by oxidation of $[OsCl_5(H_2O)]^-$ by Cl_2^-; electronic spectra have been recorded.[867]

The salts of '$[OsX_5(OH)]^{2-}$' (X = Cl, Br) reported in the earlier literature[637] are almost certainly those of the binuclear symmetrically bridged μ-oxo complexes $[Os_2OX_{10}]^{4-}$ (see p. 594), but $[OsCl_5(OH)]^{2-}$ and possibly $[OsCl_4(OH)_2]^{2-}$ are probably present in aqueous solutions of $[Os_2OCl_{10}]^{4-}$.[639]

(b) Aqua and hydroxo complexes of mixed halo species. The equilibria between *cis*-$[OsCl_3I_2(H_2O)]^-$ and *cis*-$[OsCl_3I_2(OH)]^-$ have been studied.[863]

For the mixed halo species see under the appropriate substituting ligand (*e.g.* oxo halo complexes, p. 594; nitrido halo species, p. 563).

46.10 HYDROGEN AND HYDRIDES AS LIGANDS

Hydrido complexes have been dealt with already under the appropriate coligands (*e.g.* hydrido nitrosyls, p. 545; hydrido phosphines, pp. 570, 572; hydrido arsines, p. 576).

In tetrahydroborate and borane complexes the effective ligand is hydrogen so we deal with these small sections here.

46.10.1 Tetrahydroborate Complex

The tetrahydroborato complex $Os(BH_4)H_3\{P(cyclo\text{-}C_5H_9)_3\}_2$ has been made by reaction of $OsH_6\{P(cyclo\text{-}C_5H_9)_3O\}_2$ and the THF adduct of BH_3. The X-ray crystal structure shows it to be distorted pentagonal bipyramidal: the axial ligands are the phosphines (Os—P = 2.346(2) Å, the BH_4^- is bound by two bridging hydrogen atoms (Os—H = 1.90, B—H (bridge) = 1.31, Os—B = 2.30(1), B—H (terminal) = 1.09(7) Å), and the equatorial plane is completed by three terminal hydrido ligands (Os—H = 1.57 Å). At 90 °C there is rapid exchange of the bridging H atoms with the hydrido ligands bound to osmium.[868]

46.10.2 Borane Complex

The *closo*-type 11-vertex metalloborane $(PMe_2Ph)_2OsB_{10}H_8(OEt)_2$ will react with $MCl_2(PPh_3)_3$ (M = Os, Ru) to give the mixed-valence complexes $(PPh_3)_2ClMClOs(PMe_2Ph)B_{10}H_8(OEt)_2$. The Os or Ru atoms are bound exopolyhedrally to the initial metalloborane by two two-electron M $-H_\mu-$B links and an Os—Cl—M four-electron bridge.[869]

46.11 MIXED DONOR ATOM LIGANDS

46.11.1 Bidentate N—O Complexes

46.11.1.1 Benzamido ligand

The benzamidato complex $Os_2Cl_2(NHCOPh)_4$ is made from $Os_2(OAc)_4Cl_2$ and molten benzamide, and $Os_2Br_2(NHCOPh)_4$ from the chloro species and Br^-. The X-ray crystal structures show these to have 'lantern' structures with four bridging benzamido ligands and the halide ligands axial. Each has two closely related molecules in the unit cell with slightly different structures. For the chloro complex the mean distances are Os—Os = 2.367, Os—Cl = 2.491, Os—O = 1.99 and Os—N = 2.02 Å; for the bromo species the mean values are Os—Os = 2.384, Os—Br = 2.610, Os—O = 2.02 and Os—N = 1.93 Å.[870,871]

46.11.1.2 Hydroxybenzamido ligands

An interesting piece of recent research concerns the osmium complexes of 1,2-bis(3,5-dichloro-2-hydroxybenzamide)ethane (H_4chba-Et) and of 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene (H_4chba-dcb) which function as tetradentate tetraanions. They are difficult to oxidize and their amide functional groups tend to stabilize higher oxidation states of metals. The intention is to use complexes of these with osmium as specific oxidants; by controlling the ligands on the metal, control of oxidative properties may be achieved. Reaction of the ligand with *trans*-$K_2[OsO_2(OH)_4]$ gives *trans*-$K_2[OsO_2(\eta^4\text{-chba-Et})$ (characterized analytically, by ^{1}H NMR and by the observation of $\nu_{as}(OsO_2)$ at 820 cm^{-1} in the IR shifting to 788 cm^{-1} on ^{18}O substitution). The structures of the complexes $Os(\eta^4\text{-chba-Et})py_2$, made from pyridine and *trans*-$K_2[OsO_2(\eta^4\text{-chba-Et})]$, and $Os(\eta^4\text{-chba-dcb})$ bipy, made from $Os(\eta^4\text{-chba-dcb})(PPh_3)_2$ and bipyridyl, were established crystallographically.[872] For $K_2[OsO(\eta^4\text{-chba-Et})_2(OPPh_3)_2]$ see p. 594.

For aminocoumarin and aminopentenone complexes, see p. 569; for complexes with amino acids, see p. 583, and with alkaloids, p. 587.

46.11.2 Complexes of Miscellaneous Sulfur-Nitrogen Ligands

46.11.2.1 Sulfamato complexes

The salt $K_2[Os(NH_2SO_3)Cl_5]$ was made as yellow plates from reaction of $[OsCl_6]^{2-}$, $SnCl_2$ and sulfamic acid. The magnetic moment is 2.21 BM at room temperatures, and on the basis of the IR

spectrum it seems likely that the sulfamato ligand is N-bonded to the metal. Another species, $K_3[OsCl_6]\cdot NH_3SO_3$, not fully characterized, was also obtained. Refluxing of $[Os(NH_2SO_3)Cl_5]^{2-}$ in aqueous solution gave a very low yield of $K_3[Os_2NCl_8(H_2O)_2]$ and another nitrido complex, probably $K_5[Os_2NCl_{10}]$.[349]

46.11.2.2 2-Thioamidopyridine complexes

These, $[Os(N_2SC_6H_6)_3]Br_3$ ($\mu_{eff} = 1.71$ BM at room temperature),[873] and the diamagnetic 6-methyl-2-thioamidopyridine complex $Os(SN_2C_7H_8)_2Cl_2$,[874] are made from $[OsX_6]^{2-}$ and the ligands. Complexes of thiazolidine-2-thione ($S_2NC_3H_5$) with OsX_3 (X = Cl, Br) and the ligands, gives the complexes OsL_3X_3. IR and electronic spectra were measured, and the magnetic moments of the thiomorpholin-3-one complex are 1.9 (X = Cl) and 1.8 (X = Br) BM respectively.[718]

46.11.2.3 Miscellaneous sulfur–nitrogen complexes

These, for the most part, lack effective characterization.

The following have also been reported, made from the ligand and OsO_4, sometimes with HCl: $Os(C_7H_5N_2S)_3$ and $Os(C_7H_5N_2S)\cdot(C_7H_3N_2SH)Cl_2\cdot 2H_2O$ (from 2-mercaptobenzimidazole);[875] $Os(C_7H_4NSO)_3$ (from 2-mercaptobenzoxazole);[876] $(pyH)_6[OsO(S_3N_2C_2)_6]$ (from 2,5-dimercapto-1,3,4-thiadiazole and pyridine);[877] $Os(SN_2O_4C_{12}H_{10})(OH)_2$ and $OsO_2(SN_2O_4C_{12}H_{10})Cl_2$ (from 3,3′-diamino-4,4′-dihydroxyphenylsulfone);[878] $[OsO_2(SON_4C_9H_{12})_2]Cl_4$ (from 4-benzylamidothiosemicarbazide);[510] $Os(SNO)_2C_3H_6)_2$ (from cysteine);[544] $Os(SNO_2C_3H_7)_3\cdot L$ and $Os(SNO_3C_5H_9)_2\cdot L$ (from 1-methylimidazole (L) and cysteine or α-*N*-acetylonethylcysteine respectively);[544] $Os(SN_3O_6C_{10}H_{15})_2$ (from glutathione);[544] $OsO_2(SNOC_7H_6)_2$ (from thiosalicylamide).[879]

46.11.3 Complexes of Miscellaneous Sulfur–Oxygen Ligands

There are relatively few of these; as with many of the sulfur–nitrogen donor complexes, little more than the stoichiometries is known.

Thiomorpholin-3-one gives complexes of the type OsL_3X_3 with OsX_3 (X = Cl, Br); their magnetic moments are respectively 1.8 and 2.0 BM at room temperatures.[718] Osmium tetroxide reacts with α-mercaptopropionic acid in NaOH to give $Na_2[Os(OH)_2(OOCSCHMe)_2]$[880], and 'thiovanol' (3-mercapto-1,2-propanediol) gives allegedly tetra- and penta-meric species $[OsL_4]_4$ $[OsL_4]_5$ with OsO_4.[881] Some osmium-(III) and -(IV) complexes with 8-mercaptoquinolines have been reported. The ligands include 2,6-dimethyl-8-mercaptoquinoline,[882] 2,7-dimethyl-8-mercaptoquinoline[883] with osmium(III), 6-methyl-8-mercaptoquinoline[884] with osmium(IV), 5-fluoro- and 5-iodo-8-mercaptoquinolines[885] and 5-alkylthio-8-mercaptoquinoline[886] with osmium-(III) or -(VI). Two species which have been more fully characterized with this type of ligand are $Os(NSC_9H_6)_3$, made from $K_2[OsBr_6]$ and 8-mercaptoquinoline,[887] and $Os(NSC_9H_5Cl)_2$, prepared using 5-chloro-8-mercaptoquinoline.[888]

46.12 MULTIDENTATE MACROCYCLIC LIGANDS

46.12.1 Porphyrin Complexes

The porphyrin ligands impose an N_4 plane on their complexes and, by virtue of the extensive aromaticity of the ligand, are effective π acceptors. Thus it is that most of the osmium complexes are octahedral and of the form *trans*-Os^{II}(porphyrin)L_2 or -Os^{II}(porphyrin)LL'. Most of the work on osmium complexes has been carried out by Buchler and his collaborators using the octaethylporphyrin (OEP^{2-}) ligand. There are two reviews on the subject.[889,890]

We shall deal with complexes of OEP first, and then with those of other porphyrins.

(*i*) *Octaethylporphyrin (OEP) complexes*

(a) Osmium(II). Most of the known complexes involve osmium(II). The two commonest starting materials are Os(OEP)(CO)py, made from H_2(OEP) and $OsCl_3$ under CO in pyridine,[891] from OsO_4,

H_2(OEP), CO and pyridine,[892] or from $Os_3(CO)_{12}$, pyridine and the porphyrin[893] or the dinitrogen complex Os(OEP)(N_2)(THF), prepared from Os(OEP)O_2 and N_2H_4.[894] Many complexes of the form Os(OEP)L_2 have now been isolated (*e.g.* py, OMe, P(OMe)$_3$, NO (p. 551), THF, O (pp. 582, 594 and 595), MeCN, imidazole, 1-methylimidazole, NH_3, NMe_3[890]) and most are made from Os(OEP)(CO)Cl or Os (OEP)py_2 (the latter is prepared from the former by treatment with pyridine).[891]

There are ^{1}H NMR, electrochemical,[890] electronic[232,895] as well as mass spectral data[82] on many of these complexes. A rich resonance Raman spectrum of Os(OEP)py_2 has been measured; many of the porphyrin ligand fundamentals are resonance-enhanced.[896]

Iterative extended Hückel calculations have been carried out on a number of these complexes and used to interpret absorption and emission spectra of Os(OEP)py_2, Os(OEP)(CO)py, Os(OEP)(N_2)(THF) and Os(OEP)$\{P(OMe)_3\}_2$.[895]

(b) Osmium(III). Although no osmium(III) porphyrin complexes seem to have been isolated, electrochemical data indicate the existence of $[Os(OEP)L_2]^+$, made by electrooxidation of Os(OEP)L_2 (L = py, γ-picoline, piperidine, imidazole, 1-methylimidazole, NH_3, NMe_3, P(OMe)$_3$, MeCN). In some cases correlations between $E_{\frac{1}{2}}$ for this oxidation reaction and electronic spectral absorptions could be drawn.[890,897] Similar electrochemical data for Os(OEP)LL′ oxidized to $[Os(OEP)LL']^+$ shows $E_{\frac{1}{2}}$ values intermediate between those for $[Os(OEP)L_2]^+$ and $[Os(OEP)L'_2]^+$; analogies have been drawn between this and the cytochrome system.[897]

46.12.1.1 Osmium(IV)

Few examples are known. One which has been isolated is Os(OEP)Br_2, made from Os(OEP)(N_2)(THF) and CBr_4,[898] and Os(OEP)$(OMe)_2$ obtained from Os(OEP)O_2 and $SnCl_2$ in methanol.[894] In a recent report, reaction of Os(OEP)(CO)Cl with $CHCl_3$ or CCl_4 under photolysis at 365 nm gave Os(OEP)Cl_2. Quantum yields were measured.[899]

46.12.1.2 Osmium(VI)

For the osmyl species OsO_2(OEP) see p. 582 (an improved procedure for its preparation has recently been described[893]).

46.12.1.3 Dimeric complexes

The dimer $[Os(OEP)]_2$ is made by heating Os(OEP)py_2, and a mixed dimer OsRu$(OEP)_2$ is prepared in similar fashion by thermolysis of a mixture of Os(OEP)py_2, and Ru(OEP)py_2. It was suggested that M=M bonds are present in these species.[891]

46.12.1.4 Complexes with other porphyrins

Reaction of $K_2[OsCl_6]$[900] or $OsCl_3$[891] with meso(*p*-tolyl)porphyrin (H_2TTP) with CO in the presence of pyridine yields Os(TTP)(CO)py which with pyridine gives Os(TTP)py_2.[900] On heating this gives a dimer $[Os(TTP)]_2$ which presumably, like its OEP analogue, contains an Os=Os bond.[891]

A number of other complexes of the form Os(porphyrin)(CO)py can be obtained from $K_2[OsCl_6]$, the porphyrin and CO in pyridine, *e.g.* mesoporphyrin-IX dimethyl ester, mesoporphyrin-XI dianion (I) and mesotetraphenylporphyrin;[900] the complex with (I) can also be made from $Os_3(CO)_{12}$, pyridine and the porphyrin.[893]

46.12.2 Phthalocyanine Complexes

Rather surprisingly the phthalocyanine chemistry of osmium is far less developed than that of the porphyrins. Here we use Pc for $[C_{32}H_{16}N_8]^{2-}$.

46.12.2.1 Osmium(II)

The polymeric $[OsPc]_n$ has been made by reaction of OsO_4 with pyromellitic dianhydride or with

phthalic anhydride in the presence of ammonium molybdate.[901] An 'osmium phthalocyanine' is said to be formed by reaction of $(NH_4)_2[OsCl_6]$ and phthalonitrile.[902]

46.12.2.2 Osmium(III)

The complex $OsPcClC_6H_4(CN)_2$ is made from $(NH_4)_2[OsCl_6]$ and excess 1,2-dicyanobenzene at 360 °C, and is dark blue. It has a magnetic moment of 1.1 BM at room temperature.[903]

46.12.2.3 Osmium(IV)

The polymeric $[OsPc \cdot SO_4]_n$ has been made by reaction of OsO_4 and excess molten phthalonitrile followed by extraction with H_2SO_4. It is dark blue and diamagnetic;[904] it has however been suggested that it could be an osmyl complex, $OsO_2Pc \cdot C_6H_4(CN)_2$.[903,905] The ion $[Os(PcH)(HSO_4)_2]^+$ may be present in solutions of '$[OsPc \cdot SO_4]_n$' in H_2SO_4,[906,907] and $OsPcX_2$ has been very briefly mentioned (X = Cl, Br, I).[908]

46.12.2.4 Osmium(VI)

Reaction of OsO_4 and 1,2 dicyanobenzene at 180 °C gives the dark blue $OsO_2 \cdot Pc\{C_6H_4(CN)_2\}$ which is paramagnetic (μ_{eff} = 1.4 BM at 20 °C);[903] however, all other osmyl complexes reported (p. 581) are diamagnetic, so this could well be an osmium(IV) or even an osmium(III) species. Another osmyl species claimed is $OsO_2 \cdot Pc \cdot 3PhNH_2$, made from $OsO_2 \cdot Pc \cdot \{C_6H_4(CN)_2\}$ and aniline; no magnetic properties were reported for this.[903]

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47

Cobalt

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47.1 INTRODUCTION

47.1.1 General Scope

The coordination chemistry of cobalt can be summed up in three words: *synthesis*, *structure* and *reactivity*, with synthesis being the most important because it comes first. This chapter concentrates on synthetic aspects and its aim is to provide the reader with starting points to the preparation of cobalt complexes in addition to surveying their chemistry.

The chapter deals with complexes formed with groups IV (C, Si), V (N, P, As) and VI (O, S, Se) donor atoms with the following exceptions. Organocarbon chemistry including organocobalt(III) model systems for vitamin B_{12} have been considered by Kemmitt and Russell in the companion series

'Comprehensive Organometallic Chemistry';[1] only CN^-, CO_2 and CS_2 complexes are considered here. The extensive chemistry of cobalt with ammonia and saturated amines is dealt with by House, N-containing heterocyclics by Reedijk, and N macrocycles (porphyrins, corrins, phthalocyanines), polyaza macrocycles, and all-encompassing ligands (cryptands, crown ethers and sepulchrates) by Dolphin, Curtis, and Lehn and Mertes respectively in companion chapters in the present series. Similarly, the mixed O,N donor ligands including Schiff bases are dealt with by Randaccio, Calligaris and Bresciani Pahor.

47.1.2 Synthesis Reference Works

Table 1 lists useful general texts which may be consulted on preparative methods and recipes for cobalt complexes. Table 2 gives references and preparative procedures for some especially useful Co^{III} starting materials and complexes since these are critically important to most investigations; Table 3 gives a more detailed listing of preparations which are to be found in publications which can be relied on for their accuracy and reproducibility. Some comment is appropriate: preparations given in 'Inorganic Synthesis' and Brauer's 'Handbook of Preparative Inorganic Chemistry' can be relied on, but the comprehensive information given in the 1974 edition of Gmelin's 'Handbook of Inorganic Chemsitry' is non-critical in this respect.

47.1.3 Structural Reference Works

A structural index of cobalt complexes is inappropriate since this is readily available from standard data bases.[2] Specific articles and reviews dealing with structures or structurally related aspects are given in Table 4. Structures, where appropriate to the present chapter, are given in the text or in tables but no attempt has been made to be comprehensive.

47.1.4 Properties and Reactivity Reference Works

Table 5 gives references to recent general accounts or reviews of aspects of cobalt chemistry not specifically dealt with in this chapter. Other chapters in the present series also contain much detailed information.

47.2 CARBON LIGANDS

47.2.1 Carbon Dioxide

Whereas the highly basic Ir^I, Rh^I and Ni^0 complexes which are active in CO_2 fixation are monofunctional systems, bifunctional [Co(salen)M] complexes (M = K, Na) which bind CO_2

Table 1 Primary Reference Works: Preparations of Cobalt Complexes or Preparative Methods

Author/editor	*Title, reference*	*Comments*
A. Werner	'Neuere Anschauungen auf dem Gebiete der anorganischen Chemie', 4th edn., Freidrich Vieweg und Sohn, Brunswick, 1920	Earliest account of 'classical' Co^{III} chemistry
G. Brauer	'Handbook of Preparative Inorganic Chemistry', 2nd edn., Academic, New York, vol. 2, 1965	Preparations of several cobalt salts and complexes, *cf.* Table 3
Various (series)	'Inorganic Synthesis', McGraw-Hill, New York, vols. 1 (1939)–17 (1977); Wiley-Interscience, New York, vol. 18 (1978)–	Extensive source of primary preparations; checked, *cf.* Table 3 (complete vols. 1–22)
Gmelin	'Handbuch der Anorganischen Chemie', Springer-Verlag, Berlin; Kobalt, vol. 58, 8th edn.; new supplement series vols. 5–6, 1973	Comprehensive listing of all reported preparations; not checked for reliability
W. G. Palmer	'Experimental Inorganic Chemistry', Cambridge, New York, 1954	A few basic preparations; good early account
G. G. Schlessinger	'Inorganic Laboratory Preparations', Chemical Publishing Co., New York, 1962	A few useful preparations, methods
W. L. Jolly	'Preparative Inorganic Reactions', Interscience, New York, vol. 1, 1964	Preparation methods; a few recipes
M. Shibata	'Topics in Current Chemistry' series, Springer-Verlag, 1983, vol. 110	Co^{III} preparations; some recipes

Table 2 Particularly Useful Cobalt Complexes for Synthetic Work

Complex	*Ref.*	*Complex*	*Ref.*
Cobalt(I)		*Cobalt(III)*	
$[CoH(N_2)(PPh_3)_3]$	25	$K[Co(acac)_2(CN)_2]$	9
$[CoH\{P(OPh)_3\}_4]$	26	$[Co(S_2COEt)_3]$	10
		$Na_3[Co(NO_2)_6]$	24
Cobalt(II)		$[Co(CO_3)(NH_3)_4]NO_3$	11
$[Co(NCMe)_6](BF_4)_2$	1	$[Co(CO_3)(phen)_2]Cl\cdot 5H_2O$	12
$[Co(acac)_2]$	2	$[Co(DMGH)_2X(py)]$	13
$(Et_4N)_2[Co\{S_2C_2(CN)_2\}_2]$	3	*cis*-$[Co(NO_2)_2(en)_2]NO_2$, resolution	14
		trans-$[Co(Cl)_2(py)_4]Cl\cdot 6H_2O$	15
Cobalt(III)		$[Co(OSO_2CF_3)(NH_3)_5](CF_3SO_3)_2$	16, 23
$Na_3[Co(CO_3)_3]\cdot 3H_2O$	4	$[Co(CO_3)(NH_3)_5]ClO_4$	17
CoO(OH)	5	*trans*-$[Co(Cl)_2(en)_2]Cl\cdot H_2O$	18
$[Co(H)_3(PPh_3)_3]$	6	*cis*-$[Co(OSO_2CF_3)_2(en)_2](CF_3SO_3)$	16, 23
$K_3[Co(CN)_5I]$	7	$[Co(DMG)_2Br(Me_2S)]$	19
$Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$	8	(−)-$Na[Co(C_2O_4)_2en]$, resolution	20
(+)-Ag[Co(edta)], resolution	21	*fac*-$[Co(OSO_2CF_3)_3dien]$	23
$[Co(NH_3)_3(H_2O)_3]Cl_3$	23		

1. B. J. Hathaway, D. G. Holah and A. E. Underhill, *J. Chem. Soc.*, 1962, 2444; M. Shibata, *Top. Curr. Chem.*, 1983, **110**, 15.
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22. R. B. Hogel and L. F. Druding, *Inorg. Chem.*, 1970, **9**, 1496.
23. N. E. Dixon, W. G. Jackson, M. J. Lancaster, G. A. Lawrance and A. M. Sargeson, *Inorg. Chem.*, 1981, **20**, 470.
24. Ref. 5, p. 1541.
25. A. Sacco and M. Rossi, *Inorg. Synth.*, 1970, **12**, 18.
26. J. J. Levison and S. D. Robinson, *Inorg. Synth.*, 1972, **13**, 107.

reversibly have also been described (equation 1).[3,4] It appears that the alkali metal ion acts as a Lewis acid in a concerted acid–base attack on CO_2, with the basic Co^I centre as the other partner. The resultant diamagnetic red or red-brown adducts liberate 1 mol of CO_2 on treatment with acids and have been characterized by IR spectroscopy[3,4] and X-ray crystallography.[4] The solid complexes are, however, unstable in the absence of a CO_2 atmosphere. The structure of $[Co(Pr_2salen)(CO_2)(K)(THF)]_n$ shows that carbon dioxide is C bonded to the cobalt centre with each oxygen bonded to two different K^+ ions. The Co—C distance of 199 pm resembles that found for many alkyl derivatives of [Co(salen)] and the coordinated CO_2 is bent (O—C—O angle 135°) and has C—O distances of 122 and 124 pm. The overall geometry about cobalt is square pyramidal (CoN_2O_2C chromophore). Increased stability of the CO_2 adducts may result from the binding of bases such as pyridine in the vacant sixth position.[3]

$$[Co(salen)M] + CO_2 \rightleftharpoons [Co(salen)(CO_2)M] \quad (1)$$

Table 3 Preparations: Cobalt Compounds listed in Inorganic Synthesis (*e.g.* **16**, 33) and Brauer's 'Handbook of Preparative Inorganic Chemistry', vol. 2, 2nd edn., Academic, New York, 1966 (*e.g.* **B**, 1515)

Complex	*Ref.*
Cobalt(0)	
$[Co(PPh_3)_3NO]$	**16**, 33
Cobalt (I)	
$[CoH(dppe)_2]$	**20**, 208
$[Co\{P(OMe)_3\}_5](BPh_4)$	**20**, 208
$[CoH\{P(OPh)_3\}_4]$	**13**, 107
$[CoH\{PhP(OEt)_2\}_4]$	**13**, 118
$[CoI(NO)_2]_x$	**14**, 86
$[CoH(N_2)(PPh_3)_3]$	**12**, 12, 21
$[Co(NO)_2(PPh_3)_2]BPh_4$	**16**, 18
$[Co(NO)_2(dppe)]BPh_4$	**16**, 19
$[Co(NO)_2(Me_4en)]BPh_4$	**16**, 17
Cobalt(II)	
$[Co(acac)_2]$	**11**, 84
$[Co(acac)_2(H_2O)_2]$	**11**, 82
$[Co(hfacac)_2]$	**15**, 96
$Na[Co(hfacac)_3]$	**11**, 87
$[Co(acac)_2L]$ (L = en, phen, bipy, pic)	**11**, 85
$[Co(NO_2)_2(MequinO)_2]$	**13**, 206
$[Co(NO_2)_2(RpyO)_2]$	**13**, 204
trans-$[Co(DMG)_2(H_2O)_2]$	**11**, 64
$[Co\{(sacac)_2en\}]$	**16**, 227
$[Co(edda)(H_2O)_2]$	**18**, 100
$[\{Co(salen)\}_2(\mu\text{-}H_2O)]$	**3**, 196
$[Co(HBpyz)_2]$	**12**, 105
$[Co\{SeC(NH_2)_2\}_4]Y_2$ ($Y_2 = (ClO_4)_2$, SO_4)	**16**, 84
Cobalt(III)	
Co_3O_4, Co_3S_4	**B**, 1520, 1523
$CoO(OH)$	**B**, 1520
K_xCoO_2 ($x = 0.5$–1.0)	**22**, 58
Na_xCoO_2 ($x = 0.6$–1.0)	**22**, 56
CoP, CoP_3	**B**, 1530
CoN	**B**, 1529
oF_3	**3**, 175
$Co(NH_2)_3$	**B**, 1526
$CsCo(SO_4)_2 \cdot 12H_2O$	**10**, 61; **B**, 1524
$Co_2(SO_4)_3 \cdot 18H_2O$	**5**, 181
$CoFe_2O_4$	**9**, 154

Complex	*Ref.*
Cobalt(II)	
$CoCl_2$	**B**, 1515
$CoBr_2$; $CoBr_2 \cdot 6H_2O$	**B**, 1517
$CoI_2(\alpha, \beta)$	**B**, 1518
$CoI_2 \cdot 6H_2O$	**B**, 1518
$CoCO_3$	**6**, 189
Co_2N	**B**, 1529
$CoAl_2O_4$	**B**, 1525
$(Et_4N)_2CoCl_4$	**9**, 139
$(Et_4N)_2CoBr_4$	**9**, 140
$(Et_4N)_2CoI_4$	**9**, 140
K_2CoCl_4	**20**, 51
$(Ph_4P)_2Co(SPh)_4$	**21**, 24
$[Co(NO)(PPh_2Me)_2Cl_2]$	**16**, 29
$[Co(NO)(S_2CNMe_2)_2]$	**16**, 7
$R_2[Co\{S_2C_2(CN)_2\}_2]$ (R = Et_4N, Bu^n_4N, Ph_4P)	**13**, 190; **10**, 13, 17; **13**, 191
$(Ph_4P)_2[Co\{S_2C_2(CN)_2\}_2]_2$	**13**, 191
[Co(ketoimine)$_2$]	**11**, 76
$[CoCl_2(NH_2py)_2]$	**5**, 184
$[Co(NCS)_2(py)_4]$	**12**, 251
[Co(Bz$_2$macrocycleN$_4$)]	**18**, 46
$[CoBr(Me_2pyO[14]trienN_4)]Br \cdot H_2O$	**18**, 19
[Co(benzoporphine)]	**20**, 156
$[Co(NH_3)_6]Cl_2$	**8**, 191; **9**, 157; **B**, 1530
$[Co(C_{18}H_{30}N_{12})](BF_4)_2$ (encapsulating ligand)	**20**, 87
Cobalt(III)	
$(Bu^n_4N)[Co\{S_2C_2(CN)_2\}_2]$	**10**, 17
$[Co\{S_2P(OEt)_2\}_3]$	**6**, 142
$[Co(S_2COEt)_3]$	**10**, 45
$[Co(S_2CNEt_2)_3]$	**10**, 47
$[Co(S_2CSR)_3]$ (R = Me, Et)	**10**, 47
$K_5[\{Co(CN)_5\}_2(\mu\text{-}O_2)] \cdot H_2O$	**12**, 202
$[Co(H)_3(PPh_3)_3]$	**12**, 19
$[Co(NO)_2(dppe)_2]BPh_4$	**16**, 19
$K[Co(NO_2)_4(NH_3)_2]$	**9**, 170
asym,cis-$[Co(edda)(H_2O)_2]Cl$	**18**, 105
$Na[Co(edda)CO_3]$	**18**, 104

Table 3 (*continued*)

Complex	*Ref.*
Cobalt(III)	
$H_3[Co_4I_3O_{24}H_{12}]\cdot xH_2O$	**9**, 142
$Na_3[Co(CO_3)_3]\cdot 3H_2O$	**8**, 202
$Na_3[Co(HCO_3)_3(OH)_3]$	**8**, 203
$K_3[Co(C_2O_4)_3]$	**1**, 37
$K_3[Co(C_2O_4)_3]\cdot 3H_2O$, resolution	**8**, 208
$R_4[Co_2(C_2O_4)_2(OH)_2]\cdot xH_2O$ (R = Na, K)	**8**, 204
$[Co(acac)_3]$	**7**, 205
$[Co(acacNO_2)_3]$	**B**, 1541
$Na_3[Co(NO_2)_6]$	**B**, 1541
$K_3[Co(CN)_6]$	**2**, 225
$R_3[Co(CN)_6]$ (R = H, K, Na)	**6**, 189
$[Co(NO_2)_3(NH_3)_3]$	**6**, 180
$[Co(Cl)_2(NH_3)_3(H_2O)]Cl$	**7**, 211
$[Co(Cl)_3dien]$	**7**, 209
$[Co(NO_2)_3dien]$	**7**, 212
$[Co(NO_3)_3dien]$	**7**, 209
$[Co(NCS)_3dien]$	**7**, 208
$[Co(NCS)_2(OH)dien]$	**7**, 210
$[Co(NO_2)_2Cl(dien)]$	**B**, 1536
$[Co(Cl)_2(NH_3)_4]Cl$ (*cis, trans*)	**B**, 1535
cis-$[Co(CO_3)(NH_3)_4]_2SO_4\cdot 3H_2O$	**6**, 173
cis-$[Co(CO_3)(NH_3)_4]NO_3$	**18**, 70
cis-$[Co(NO_2)_2(NH_3)_4]NO_3$	**18**, 71
trans-$[Co(NO_2)_2(NH_3)_4]NO_3$	**18**, 83
cis-$[Co(H_2O)_2(NH_3)_4](ClO_4)_3$	**18**, 81
cis-$[Co(OH)(H_2O)(NH_3)_4]S_2O_6$	**6**, 178
cis-$[CoCl(H_2O)(NH_3)_4]Cl_2$	**18**, 88
$[\{Co(NH_3)_4\}_2(\mu\text{-}OH)_2](ClO_4)_2\cdot sH_2O$	**6**, 176
$[\{Co(NH_3)_4(OH)_2\}_3Co](SO_4)_3\cdot 4H_2O$	**14**, 70; **2**, 224
cis-$[Co(Cl)_2(en)_2]Cl\cdot H_2O$, resolution	**18**, 73; **13**, 232; **14**, 68
trans-$[Co(Cl)_2(en)_2]Y$ (Y = Cl, Br)	**21**, 121
cis-$[Co(Br)_2(en)_2]Br\cdot H_2O$	**9**, 165
trans-$[CoClBr(en)_2]NO_3$	**7**, 211
$[Co(NO_2)_2(NH_3)dien]Cl$	**18**, 21
trans-$[Co(Br)_2(Me_2pyO[14]trienN_4)]Br$	**20**, 111
trans-$[Co(Cl)_2([13]aneN_4)]Cl$	**20**, 112
trans-$[Co(Cl)_2([15]aneN_4)]Y$ (Y = Cl, ClO_4)	**20**, 113
trans-$[Co(Cl)_2([16]aneN_4)]ClO_4$	**18**, 14
trans-$[Co(Br)_2(meso\text{-}Me_6[14]aneN_4)]ClO_4$	**18**, 25
trans-$[Co(Br)_2(Me_4[14]tetraeneN_4)]Br$	**18**, 28
trans-$[Co(Br)_2(Me_2[14]dieneN_4)]ClO_4$	**20**, 141
trans-$[CoCN(H_2O)(cobalamine)]ClO_4$	
sym,cis-$K[Co(edda)(NO_2)_2]$, resolution	**18**, 101
$K[Co(edta)]\cdot 2H_2O$, resolution	**5**, 186; **18**, 100; **6**, 193
$Ba[Co(edta)]_2$	**5**, 186
$Na[Co(C_2O_4)_2en]$, resolution	**13**, 196
asym,cis-$[Co(edda)en]Cl$, resolution	**18**, 105
sym,cis-$[Co(edda)en]NO_3$, resolution	**18**, 109
$K[Co(Gly)_2(NO_2)_2]$	**9**, 173
cis-$[Co(OSO_2CF_3)_2(en)_2](CF_3SO_3)$	**22**, 105
cis-$[Co(NO_2)_2(en)_2]Y$ (Y = NO_2, Br), resolution	**6**, 192, **8**, 196; **4**, 178; **6**, 195; **14**, 72
trans-$[Co(NO_2)_2(en)_2]NO_3$	**4**, 177
cis-$[Co(SO_3)N_3(en)_2]$	**14**, 78
cis-$[Co(OH)(H_2O)(en)_2]S_2O_6$	**14**, 74
cis-$[CoCl(H_2O)(en)_2]Y_2$ (Y_2 = SO_4, $Br_2\cdot 2H_2O$)	**9**, 165
trans-$[CoCl(H_2O)(en)_2]Y_2$ (Y_2 = $S_2O_6\cdot H_2O$, $BrNO_3$, $SO_4\cdot 2H_2O$)	**21**, 125; **9**, 163
trans-$[CoBr(H_2O)(en)_2]S_2O_6\cdot H_2O$	**21**, 124
cis-$[CoBr(H_2O)(en)_2]Br_2\cdot H_2O$	**21**, 123
cis-$[Co(H_2O)_2(en)_2]Br_3$	**14**, 75
cis-$Na[Co(SO_3)_2(en)_2]\cdot NaNO_3$	**14**, 77
trans-$Na[Co(SO_3)_2(en)_2]\cdot 3H_2O$	**14**, 79
m r1$[CoCO_3(en)_2]Y$ (Y = Cl, Br)	**14**, 64
$[Co(C_2O_4)(en)_2]Cl$, resolution	**18**, 97
$[Co(acac)(en)_2]I_2$, resolution	**9**, 167
$[Co(O_2CCH_2S)(en)_2]ClO_4$	**21**, 21
$[\{Co(OH)_2(en)_2\}_2\{\mu\text{-}Co(H_2O)_2\}](SO_4)_2\cdot 7H_2O$	**8**, 199
$[\{Co(en)_2\}_2(\mu\text{-}OH)_2]Br_4\cdot 2H_2O$	**18**, 92
$[CoF(NH_3)_5](NO_3)_2$	**4**, 172
$[Co(NO_2)(NH_3)_5]Y_2$ (Y = Cl, NO_3)	**B**, 1534; **4**, 174
$[Co(NO_3)(NH_3)_5](NO_3)_2$	**4**, 174
$[CoCl(NH_3)_5]Cl_2$	**B**, 1532; **5**, 185; **6**, 182; **9**, 160
$[CoBr(NH_3)_5]Br_2$	**1**, 186
$[CoI(NH_3)_5](NO_3)_2$	**4**, 173
$[Co(H_2O)(NH_3)_5]Y_3$ (Y = Cl, Br)	**1**, 188; **9**, 160
$[Co(CO_3)(NH_3)_5]Y$ (Y = NO_3, $ClO_4\cdot H_2O$)	**17**, 152
$[Co(OAc)(NH_3)_5](NO_3)_2$	**4**, 175
$[CoNO(NH_3)_5]Cl_2$	**4**, 168; **5**, 185; **8**, 191
$[Co(ONO)(NH_3)_5]Cl_2$	**B**, 1535
$[Co(OReO_3)(NH_3)_5](ClO_4)_2$	**12**, 216
$[Co(OSO_2CF_3)(NH_3)_5](CF_3SO_3)_2$	**22**, 104
$[\{Co(NH_3)_5\}_2(\mu\text{-}O_2)](SO_4)_2\cdot 3H_2O$	**B**, 1540
$[\{Co(NH_3)_5\}_2(\mu\text{-}O_2)](NO_3)_4$	**12**, 198
$[\{Co(NH_3)_5\}_2(\mu\text{-}O_2)]Cl_5\cdot H_2O$	**12**, 200
$[\{Co(NH_3)_4\}_2(\mu\text{-}NH_2,OH)]Cl_4\cdot H_2O$	**12**, 210
	12, 203

trans-[$CoCl(DMG)_2py$] **11**, 62
trans-[$CoBr(DMG)_2(Me_2S)$] **20**, 128
trans-[$Co(Me)(DMG)_2py$] **11**, 65
trans-[$Co(Me)(DMG)_2H_2O$] **11**, 67
trans-[$CoBr(DMG)_2(Bu^tpy)$] **20**, 130
trans-[$Co(CH_2CH_2OEt)(DMG)_2(Bu^tpy)$] **20**, 131
trans-[$Co(Ph)(DMG)_2py$] **11**, 68
trans-[$Co(CH_2OEt)(DMG)_2(Bu^tpy)$] **20**, 132
cis-[$CoBr(NH_3)(en)_2]Br_2$, resolution **8**, 198; **16**, 93
cis-[$Co(CO_3)(NH_3)(en)_2]Br\cdot 0.5H_2O$ **17**, 152
trans-[$Co(CO_3)(NH_3)(en)_2]ClO_4$ **17**, 152
cis-[$Co(H_2O)(NH_3)(en)_2]Br_3\cdot H_2O$ **8**, 198
trans-[$Co(H_2O)(NH_3)(en)_2]Br_3$ **8**, 198
[$\{Co(en)_2\}(\mu\text{-}NH_2,O_2)](NO_3)_4$ **12**, 208
[$Co(SCH_2CH_2NH_2)(en)_2](ClO_4)_2$ **21**, 19
[$CoBr(tetren)]Br_2$ **9**, 176
α,β-sym-[$CoCO_3(tetren)]ClO_4\cdot 3H_2O$ **17**, 153

[$\{Co(NH_3)_4\}_2(\mu\text{-}NH_2,O_2)](NO_3)_4$ **12**, 206
[$\{Co(NH_3)_4\}_2(\mu\text{-}NH_2,Cl)]Cl_4\cdot 4H_2O$ **12**, 209
[$Co(NH_3)_6]Y_3$ (Y = OAc, Cl) **18**, 68
(Y = Cl) **9**, 157; **B**, 1531; **2**, 220
(Y = NO_3) **B**, 1531; **2**, 118
(Y = Br) **2**, 119
(Y = $FeCl_6$) **11**, 48
[$\{Co(NH_3)_5\}_2(\mu\text{-}NH_2)](ClO_4)_5\cdot H_2O$ **12**, 212
[$Co(Phbiguanide)_3]Cl_3\cdot 2.5H_2O$ **6**, 73
[$Co(en)_3]Cl_3$, resolution **2**, 221; **9**, 162; **B**, 1538; **6**, 185
[$Co(pn)_3]Y_3$ (Y = $MnCl_6$) **11**, 48
(Y = $FeCl_6$) **11**, 49
[$Co(amine)_{3,2}]Br_3$ (amine = en, pn, chxn, dien) **14**, 58
[Co(sepulchrate)]Cl_3 **20**, 86
[$Co(C_{18}H_{30}N_{12})](BF_4)_3$ **20**, 89
[$Co(BzO_2[12]hexeneN_3)_2]Br_3$ **18**, 34
[$Co\{(DMG)_3BF_2\}]BF_4$ **17**, 140

Table 4 Recent Reviews and Specialist Articles on Structural Aspects of Cobalt Complexes

Author	*Topic*	*Ref.*
R. G. Teller and R. Bau	Crystallographic studies of transition metal hydride complexes	*Struct. Bonding (Berlin)*, 1981, **44**, 1
D. L. Kepert	Stereochemistry of six-coordination	*Prog. Inorg. Chem.*, 1977, **23**, 1
R. R. Holmes	Five-coordinate structures	*Prog. Inorg. Chem.*, 1984, **32**, 119
P. L. Orioli	Stereochemistry of five-coordinate Co^{II} complexes	*Coord. Chem. Rev.*, 1971, **6**, 285
Y. Saito	Absolute stereochemistry of chelate complexes	*Top. Stereochem.*, 1978, **10**, 95
B. E. Douglas and Y. Saito	Stereochemistry of optically-active transition metal complexes	*ACS Symp. Ser.*, 1980, **119**
K. Toriumi and Y. Saito	Electron density distributions in inorganic compounds	*Adv. Inorg. Radiochem.*, 1983, **27**, 27
F. Valach, B. Koren, P. Sivy and M. Melnik	Crystal structure non-rigidity	*Struct. Bonding (Berlin)*, 1983, **55**, 101
G. R. Brubaker and D. W. Johnson	Molecular mechanics calculations and structure	*Coord. Chem. Rev.*, 1983, **51**
D. J. Hodgson	Structural and magnetic studies on bridged systems	*Prog. Inorg. Chem.*, 1975, **19**, 173
K. Bernauer	Stereochemical aspects	*Top. Curr. Chem.*, 1976, **65**, 1
R. Morassi, I. Bertini and L. Sacconi	Five-coordinate structures	*Coord. Chem. Rev.*, 1973, **343**, 402

Table 5 General Reference Works on Cobalt Complexes: Series Reports, Reviews and Books

Author/editor	*Topic*	*Ref.*
Series reports		
Various	'Inorganic Chemistry of the Transition Elements' (series); reviews of current cobalt literature (1970–76, terminated)	'Specialist Periodical Reports', the Chemical Society, London, vols. 1 (1970–71), 2 (1971–72), 3 (1972–73), 4 (1973–74), 5 (1974–75), 6 (1975–76)
R. W. Hay	Continuation of Specialist Periodical Reports on cobalt chemistry, current literature (1978–)	*Coord. Chem. Rev.*, 1981, **35**, 85 (1978–79), 1982, **41**, 191 (1979–80), 1984, **57**, 1 (1980–81)
D. W. A. Sharp (ed.)	Transition metal chemistry; review of literature (1967–73; not continued)	'MTP International Review of Science', ed. H. J. Emeléus, Butterworths–University Park Press; Series one, vol. 5 (1967–71); Series two, vol. 5 (1972–73)
M. L. Tobe (ed.)	Reaction mechanisms; review of literature (1967–73; not continued)	'MTP International Review of Science', ed. H. J. Emeléus, Butterworths–University Park Press, Series one, vol. 9 (1967–71); Series two, vol. 9 (1972–73)
A. G. Sykes (ed.)	'Inorganic Reaction Mechanisms'; review of current literature (covering cobalt complexes)	'Specialist Periodical Reports', the Chemical Society, London, vols. 1 (1969)–7 (1979)
Various	'Spectroscopic Properties of Inorganic and Organometallic Compounds'; review of current literature in NMR, NQR and vibrational spectroscopy	'Specialist Periodical Reports', the Chemical Society, London, vols. 1 (1967)–16 (1982)
Various	'Inorganic Biochemistry'; review of current literature; cobalamins and cobaloximes (McAuliffe); trace elements in animal nutrition (Arthur, Bremner, Chesters)	'Specialist Periodical Reports', the Chemical Society, London, vols. 1 (1977)–3 (1980)
A. G. Sykes (ed.)	'Advances in Inorganic and Bioinorganic Mechanisms'; series of reviews on current topics	Academic, London, vols. 1 (1982)–3 (1984)
A. G. Lappin	Mechanistic aspects of bioinorganic reactions in solution	'Inorganic Reaction Mechanisms', Chemical Society Special Periodic Departments, 1981, vol. 7, p. 303.
E. R. Hamner, R. D. W. Kemmitt and N. S. Sridhara	Review of 1976 literature (organometallic bias)	*J. Organomet. Chem.*, 1979, **167**, 135
Reviews and books		
R. G. Pearson	History of ligand substitution in Co^{III} complexes	*J. Chem. Educ.*, 1978, **55**, 720
G. A. Melson (ed.)	'Coordination Chemistry of Macrocyclic Compounds' (book)	Plenum, New York, 1979
M. des. Healy and A. J. Rest	Template synthesis of macrocycles	*Adv. Inorg. Radiochem.*, 1978, **21**, 1
R. E. Tapscott, J. D. Mather and T. F. Them	Isomerism in bidentate ligand complexes with asymmetric donor atoms	*Coord. Chem. Rev.*, 1979, **29**, 87
B. Bosnich and M. D. Fryzuk	Asymmetric synthesis as mediated by transition metal complexes	*Top. Stereochem.*, 1981, **12**, 119
N. M. N. Gowda, S. B. Naikara and G. K. N. Reddy	ClO_4^- complexes of transition metals	*Adv. Inorg. Radiochem.*, 1984, **28**, 265
A. G. Sykes and J. A. Weil	Binuclear complexes	*Prog. Inorg. Chem.*, 1970, **13**, 1
L. Banchi, A. Bencini, C. Benelli, D. Gatteschi and C. Zanchini	Spectral–structural correlations of high spin Co^{II} complexes	*Struct. Bonding (Berlin)*, 1982, **52**, 37

Table 5 (*continued*)

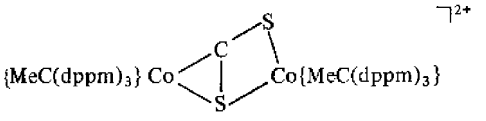
Author/editor	*Topic*	*Ref.*
C. Daul, C. W. Schlapfer and A. Von Zelewsky	Electronic structure of Co^{II} complexes with Schiff bases	*Struct. Bonding (Berlin)*, 1979, **36**, 129
M. L. H. Van Gaul and J. G. M. Van der Linden	Redox chemistry	*Coord. Chem. Rev.*, 1982, **47**, 41
Y. Yoshikawa and K. Yamasaki	Chromatography of Co^{III} complexes	*Coord. Chem. Rev.*, 1978, **28**, 205
S. F. Mason	MCD of tetrahedral Co^{II} complexes	*Struct. Bonding (Berlin)*, 1980, **39**, 63
A. Schweiger	ENDOR of Co^{II} complexes (organic ligands)	*Struct. Bonding (Berlin)*, 1982, **51**, 83
R. K. Harris and B. E. Mann	^{59}Co NMR (review)	'NMR and the Periodic Table', Academic, New York, 1977, p. 225
B. N. Figgis and J. Lewis	Magnetic properties	*Prog. Inorg. Chem.*, 1964, **6**, 37
A. P. B. Lever	Stereochemistry of Co^{II} complexes from visible–UV studies	'Inorganic Electronic Spectroscopy', Elsevier, New York, 1968, p. 317
B. R. McGarvey	Magnetism of Co^{II} complexes	*Transition Met. Chem.*, 1966, **3**, 176
A. G. Sykes and J. A. Weil	'Inorganic Reaction Mechanisms' (book)	Wiley, Chichester, 1970
A. M. Sargeson	Octahedral substitution; Mechanisms and reactive intermediates (Co^{III})	*Pure Appl. Chem.*, 1973, **33**, 527
N. M. Samus and A. V. Ablov	Mechanisms of substitution of *trans*-dioxime Co^{III} complexes	*Coord. Chem. Rev.*, 1979, **28**, 177
R. W. Hay	Substitution reactions of Co complexes	*Mech. Organomet. Inorg. React.*, 1984, **2**,
G. A. Lawrance and D. R. Stranks	$\Delta V^{\ddagger}$ and mechanism in coordination complexes	*Acc. Chem. Res.*, 1979, **12**, 403
D. A. Palmer and H. Kelm	$\Delta V^{\ddagger}$ for reactions of metal complexes	*Coord. Chem. Rev.*, 1981, **36**, 89
E. Zinato	Photochemistry of Co^{III} complexes	'Concepts of Inorganic Photochemistry', ed. A. W. Adamson and P. D. Fleischauer, Wiley-Interscience, New York, 1975, p. 143
A. Cox	Photochemistry of transition metal complexes	*Photochemistry*, 1979, **10**, 223
M. S. Wrighton	Photochemistry of transition metal complexes	*Top. Curr. Chem.* (series), 1976, **65**, 48
D. Dolphin (ed.)	'Vitamin B_{12}' (book)	vol 1 (Chemistry), vol. 2 (Biochemistry and Medicine), Wiley, Chichester, 1981
D. G. Brown	Vitamin B_{12} model systems	*Prog. Inorg. Chem.*, 1973, **18**, 177
A. W. Johnson	Vitamin B_{12}, retrospect and prospect	*Chem. Soc. Rev.*, 1980, **9**, 125
G. N. Schrauzer	Vitamin B_{12}	*Angew Chem., Int. Ed. Engl.*, 1976, **15**, 417
P. J. Toscano and L. G. Marzilli	B_{12} and related compounds; formation and cleavage of Co—C bonds	*Prog. Inorg. Chem.*, 1982, **31**, 105

R. H. Ables and D. Dolphin	Vitamin B_{12} coenzyme	*Acc. Chem. Res.*, 1976, **9**, 114
R. J. P. Williams	Metal ions in biological catalysis	*Pure Appl. Chem.*, 1982, **54**, 1889
I. Bertini and C. Luchinat	Co^{II} as a probe for carbonic anhydrase	*Acc. Chem. Res.*, 1983, **16**, 272
C. F. Meares and T. G. Wensel	Metal chelates as probes of biological systems	*Acc. Chem. Res.*, 1984, **17**, 202
R. S. Young	'Cobalt in Biology and Biochemistry' (book)	Academic, London, 1979
E. J. Underwood	'Trace Elements in Human and Animal Nutrition' (book, section on Co)	4th edn., Academic, London, 1977
E. Tsuchida and H. Nishide	Catalytic activity of polymer–metal complexes	*Adv. Polym. Sci.*, 1977, **24**, 1
J. E. Lyons	Transition metal catalysts for O_2 addition to organic substrates	'Aspects of Homogeneous Catalysis' (book); ed. R. Ugo, Reidel, Dordrecht, 1977, vol. 3, chap. 1

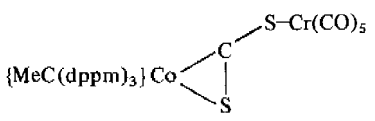
47.2.2 Carbon Disulfide

The tris (tertiary phosphine) ligand $MeC(dppm)_3$ forms both mono- and di-nuclear cobalt–carbon disulfide complexes.[5] The monomer $[Co\{MeC(dppm)_3\}(CS_2)]$ is formed by the direct reaction of $[Co_2(CO)_8]$ with $MeC(dppm)_3$ and CS_2, or by treating the binuclear Co^I complex $[\{MeC(dppm)_3\}Co]_2(\mu\text{-}CS_2)](BPh_4)_2$ with sodium naphthalenide or with $NaBH_4$ in the presence of excess CS_2. The monomer is an air-stable red solid ($\mu = 1.91$ BM) with the Co atom coordinated to the three phosphorus atoms of $MeC(dppm)_3$ and to CS_2 by a σ bond to C and a π bond to one C=S group. The S—C—S angle (133.8°) and the average length of the C—S bonds (166 pm) approach those found for uncoordinated CS_2 in the $^3A_2$ excited state (135.8°, 164 pm).[6]

The coordinated CS_2 group is electron rich at sulfur and is activated towards attack by electrophiles. Thus treatment of $[Co\{MeC(dppm)_3\}(CS_2)]$ with $[Co(H_2O)_6]^{2+}$ in the presence of $MeC(dppm)_3$ gives the diamagnetic dimer $[\{[MeC(dppm)_3]Co\}_2(\mu\text{-}CS_2)]^{2+}$, and the uncoordinated S atom displaces coordinated THF from $[Cr(CO)_5(THF)]$ and $[Mn(CO)_2(THF)Cp]$ to form $[\{MeC(dppm)_3\}Co(\mu\text{-}CS_2)Cr(CO)_5]$ and $[\{MeC(dppm)_3\}Co(\mu\text{-}CS_2)Mn(CO)_2Cp]$ respectively. Structural data for these binuclear complexes are given in Table 6. The linkage arrangement of the CS_2-bridged dimers is shown by (**1**) and (**2**). In both $[\{[MeC(dppm)_3]Co\}_2(CS_2)]^{2+}$ and $[\{MeC(dppm)_3\}Co(CS_2)Cr(CO)_5]$ the π C=S bond is retained and the bond lengths and angles in the $Co(CS_2)$ units differ little from those found in $[\{MeC(dppm)_3\}Co(CS_2)]$. Apparently π bonding of CS_2 to the Co atom in (**1**) does not greatly influence the σ-bonding capabilities of the sulfur atoms since the bond lengths of the two Co—S σ bonds are nearly identical (~230 pm).



(1)



(2)

With molecular oxygen $[\{MeC(dppm)_3\}Co(CS_2)]$ in THF solution forms the yellow-green dithiocarbonate complex $[Co\{MeC(dppm)_3\}(S_2CO)]$. Related reactions using elemental sulfur or selenium give the corresponding trithiocarbonato and selenodithiocarbonato complexes respectively.[7]

47.2.3 Cyanide

The chemistry of cobalt cyanide complexes has been extensively reviewed by Sharpe.[8]

47.2.3.1 Cobalt(−I) and cobalt(0)

The cyano complexes of cobalt(−I) are restricted to nitrosyl and carbonylnitrosyl mixed ligand complexes, all of which obey the 18-electron rule.

Dark-violet $K_3[Co(CN)_3(NO)]$ results from the action of KCN on $[Co(CO)_3(NO)]$ in liquid ammonia and the intermediate compounds $K[Co(CN)(CO)_2(NO)]$ and $K_2[Co(CN)_2(CO)(NO)]$ may be obtained when the reaction is carried out using stoichiometric ratios of the reactants.[9] The conversion of $[Co(NO)_2Br_2]$ to brown $Na[Co(CN)_2(NO)_2]$ by treatment with ethanolic NaCN has been described,[10] and similar preparations using $[Co(NO)_2BrL]$ reactants (L = PPh_3, $AsPh_3$, $SPPh_3$, $SePPh_3$) give the corresponding $Na_2[Co(CN)(NO)_2L]$ complexes.

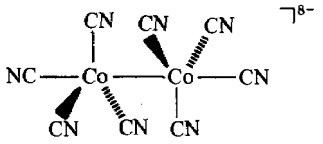
The reduction of $K_3[Co(CN)_6]$ by potassium in liquid ammonia affords the air-sensitive brown-violet complex $K_8[Co_2(CN)_8]$,[11] which is the only cyano complex of Co^0 so far described. On the

Table 6 Structures: Cobalt–Carbon Disulfide Complexes[a]

Complex	*Comments*
$[Co(CS_2)\{MeC(dppm)_3\}]$	η^2 linkage; Co—S(1) = 220.6 pm, Co—C = 188 pm; planar $CoCS_2$ fragment
$[\{[MeC(dppm)_3]Co\}_2(CS_2)](BPh_4)_2$	Bridging CS_2; Co(1)—CS(2) bound η^2; Co(2) bound via σ bond to each S atom; Co(1)—S(1) = 229 pm, Co(1)—C = 172 pm, Co(2)—S = 227, 231 pm; planar $Co(CS_2)Co$ fragment
$[\{MeC(dppm)_3\}Co(CS_2)Cr(CO)_5]$	Bridging CS_2, Co—CS(2) bound η^2; Cr octahedral; Cr—S(2) = 244 pm, Co—S(2) = 218 pm, Co—C = 187 pm

[a] C. Bianchini, C. Mealli, A. Meli, A. Orlandini and L. Sacconi, *Inorg. Chem.*, 1980, **19**, 2968.

basis of IR and Raman spectra bridging CN^- groups appear to be absent and the centrosymmetric structure of D_{3d} symmetry (**3**) has been assigned.[12]

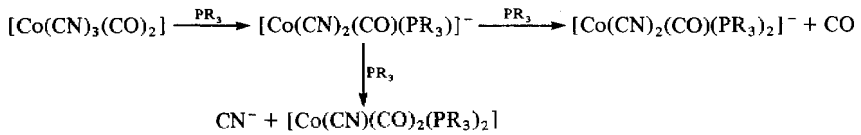


(3)

47.2.3.2 Cobalt(I)

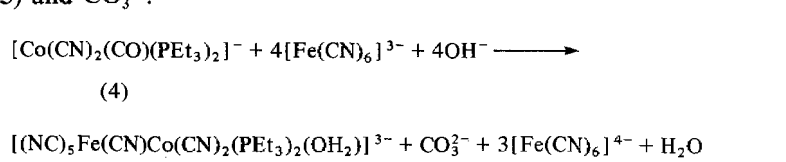
The pentacyanocobaltate(I) ion has been postulated as an intermediate in the electrochemical and chemical reductions of $[CoH(CN)_5]^{3-}$ as well as in the electrochemical reduction of $[Co(CN)_5]^{3-}$. Pulse radiolysis of solutions of $[Co(CN)_5]^{3-}$ produces $[Co(CN)_5]^{4-}$, observable as a transient intermediate which reacts with water to yield $[CoH(CN)_5]^{3-}$. The kinetics of these processes has been studied.[13] The isolation of $K_3[Co(CN)_4]$ as a yellow air-sensitive solid from the chemical reduction of $K_3[Co(CN)_6]$ has been reported but the product has not been fully characterized.[14]

Carbonylation of solutions of $K_3[CoH(CN)_5]$ yields $[Co(CN)_3(CO)_2]^{2-}$, however attempts to isolate pure salts of this species have been unsuccessful owing to its tendency to decompose and disproportionate.[15] On treatment of the product solutions with phosphines moderately stable five-coordinate Co^I complexes of the type $[Co(CN)(CO)_2(PR_3)_2]$, $[Co(CN)_2(CO)(PR_3)_2]^-$ and $[Co(CN)_2(CO)_2(PR_3)]^-$ are obtained (Scheme 1).[16] An alternative route to $[Co(CN)(CO)_2(PR_3)_2]$ complexes (PR_3 = PEt_2Ph, $PEtPh_2$, PPh_3) is provide by direct carbonylation of $[Co(CN)_2(PR_3)_2]$. In $C_2H_4Cl_2$ solution addition of CO gives $[Co(CN)_2(CO)(PR_3)_2]$ initially, which is then reduced by CO to the cobalt(I) product.[17]



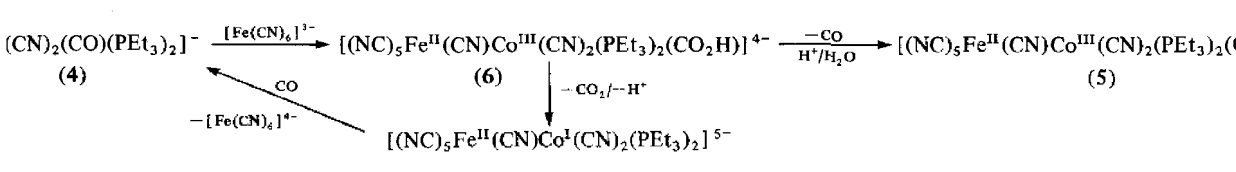
Scheme 1

Oxidation of $[Co(CN)_2(CO)(PEt_3)_2]^-$ (**4**) by $[Fe(CN)_6]^{3-}$ proceeds quantitatively in accordance with Scheme 2 to yield the cyanide-bridged iron(II)–cobalt(III) dimer $[(CN)_5Fe(CN)Co(CN)_2(PEt_3)_2(OH_2)]^{3-}$ (**5**) and CO_3^{2-}.



Scheme 2

Detailed studies of this reaction agree with the mechanism in Scheme 3.[18] The intermediate (**6**) is observable as a transient species (λ_{max} 500 nm, $\varepsilon = 5 \times 10^2$), which may decay by pH-dependent pathways to the final product (**5**), or to the intermediate cyano-bridged iron(II)–cobalt(I) dimer (**7**). The existence of (**7**) is inferred from trapping experiments with acrylonitrile (yielding stable $[Co(CN)_2(PEt_3)(CH_2{=}CHCN)]^-$), or allyl alcohol (yielding the π-allyl complex $[Co(CN)_2(PEt_3)_2(\eta\text{-}C_3H_5)]$. The observation that (**7**) is also trapped by CO provides a basis for the catalytic oxidation of CO to CO_2 (CO_3^{2-}) *via* the cycle (**4**) → (**6**) → (**7**) → (**4**).



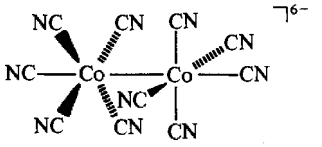
Scheme 3

Hydrazine reduction of $[Co(CN)_2(dpe)_2]$ affords the air-sensitive five-coordinate complex $[Co(CN)(dpe)_3]$.[19] This process involves displacement of coordinated cyanide ion accompanied by chelation of the dangling dpe ligand. One diphosphine ligand in the product is readily displaced by CO giving five-coordinate $[Co(CN)(CO)_2(dpe)]$.

47.2.3.3 Cobalt(II)

Light-brown precipitates of cobalt(II) cyanide containing varying amounts of bound water are obtained from addition of stoichiometric quantities of cyanide ion to aqueous solutions of cobalt(II) salts. On heating to 250 °C the hydrates lose water to give blue $\{Co(CN)_2\}_n$.[20] This form of cobalt cyanide possesses the ability to form inclusion compounds with a wide variety of small orgnaic molecules, and X-ray powder patterns indicate an open structure based on a face-centred cube with $a = 1012$ pm.[21] The structure was originally suggested to be related to that of Prussian blue, $KFe[Fe(CN)_6]$, with Co^{2+} replacing K^+ and Fe^{2+} and $[Co(CN)_6]^{4-}$ replacing $[Fe(CN)_6]^{4-}$. However, this structure would need to contain 12 formula units in the unit cell, which is incompatible with the observed crystal density (1.87 g cm^{-3}). Although similarities exist between the structure of $[Co(CN)_2]_n$ and those of both Prussian blue and $Co_3[Co(CN)_6]$, the nature of the differences remains uncertain.[8,20]

The olive-green $[Co(CN)_5]^{3-}$ ion is the predominant cobalt(II) cyanide species in deoxygenated aqueous solutions of cobalt(II) salts to which excess cyanide ion has been added. The pentacyanocobaltate(II) ion is paramagnetic and undergoes rapid exchange of bound CN^-.[22] UV–visible and ESR studies have been interpreted in terms of a purely five-coordinate structure (C_{4v} symmetry),[23] but the anion may be hexacoordinate with a weakly bound water molecule in the sixth position and with C_{4v} symmetry maintained.[24] Studies of the ion in solution are complicated by its tendency to dimerize to diamagnetic violet $[Co_2(CN)_{10}]^{6-}$, the structure of which has been characterized.[25] The dimer possesses D_{4d} symmetry with a Co—Co bond separation of 279.8 pm and with the two sets of equatorial cyanide ligands in staggered conformation (**8**).



(8)

A yellow form of the pentacyanocobaltate(II) ion has been observed in DMF solution. Various monomeric $(NR_4)_3[Co(CN)_5]$ complexes have been crystallized[26] and a structural study on one shows the anion to possess a truly five-coordinate square-pyramidal geometry.[27] Electron irradiation of solid $K_3[Co(CN)_6]$ gives a presumed pentacyanocobaltate(II) ion,[28] the visible spectrum of which is virtually identical with that of $[Co(CN)_5]^{3-}_{(aq)}$. The structural parallels between the green and yellow forms of $[Co(CN)_5]^{3-}$ and isoelectronic $[Co(CNR)_5]^{2+}$ ions indicate that all the green forms observed both in the solid state and in solution are weakly coordinated in the sixth axial position.

The existence of a tetracyanocobaltate(II) ion in aqueous solution has been inferred from studies at high dilution and a brown polymeric complex of composition $K_2[Co(CN)_4]$ has been isolated from solutions of $[Co(SCN)_2]$ and KCN in ammonia.[20] Recently, the monomeric air-sensitive complex $[(PPh_3)_2N]_2[Co(CN)_4]\cdot DMF$ has been crystallized from DMF solution.[29] The complex is essentially square planar but does feature a very weak axial interaction to a neighbouring DMF molecule (Co—O separation 264 pm). The $[Co(CN)_4]^{2-}$ anion appears to be the sole example of a square-planar low-spin ($\mu = 2.15$ BM) cobalt(II) complex containing solely unidentate ligands.

Of the various cobalt(II) cyanide complexes the reactions of $[Co(CN)_5]^{3-}$ have been the most widely studied. Oxidative addition is the characteristic reaction of the low-spin ion, and the driving force for reaction derives from the increase in stability achieved on passing from the 17-valence-electron configuration of the reactant to the closed-shell, 18-valence-electron configuration of the cobalt(III) product. These reactions have been reviewed.[30] Two-electron oxidizing agents with $[Co(CN)_5]^{3-}$ either give bridged $[(NC)_5Co(X)Co(CN)_5]^{6-}$ species (X = O_2,[31] *p*-benzoquinone,[32] C_2F_4,[33] C_2H_2,[34] SO_2,[35] $SnCl_2$[35]) or undergo reductive cleavage with formation of monomeric cobalt(III) products (equation 2, X—Y = H_2,[36] halogen,[37] ICN,[38] H_2O,[39] H_2O_2,[38] alkyl halide,[39] NH_2OH[38]). Except for the reaction of H_2 (and possibly H_2O) these processes occur through a

free-radical stepwise mechanism (Scheme 4).[38,39] For alkyl halides, the rate-determining step is halogen-atom abstraction and the alkyl radicals so produced may combine with $[Co(CN)_5]^{3-}$ giving organocobalt(III) products or may disproportionate to alkanes or alkenes. α,ω-Dihalides are dehalogenated.

$$2[Co(CN)_5]^{3-} + X{-}Y \longrightarrow [Co(CN)_5X]^{3-} + [Co(CN)_5Y]^{3-} \quad (2)$$

$$[Co(CN)_5]^{3-} + X{-}Y \xrightarrow{\text{slow}} [Co(CN)_5X]^{3-} + Y\cdot$$

$$[Co(CN)_5]^{3-} + Y\cdot \longrightarrow [Co(CN)_5Y]^{3-}$$

Scheme 4

Hydrogen absorption by aqueous solutions of $[Co(CN)_5]^{3-}$ was first reported by Iguchi in 1942.[40] H_2 uptake corresponds to 0.5 mol per mol Co and is accompanied by formation of the colourless hydrido complex $[CoH(CN)_5]^{5-}$.[41] The same product results from the reduction of $[Co(CN)_5]^{3-}$ electrolytically or by means of $NaBH_4$. Hydrogenation is reversible with $K = 10^5\,dm^3\,mol^{-1}$ at 25 °C (equation 3). The forward reaction follows third-order kinetics with rate = $k[Co(CN)_5^{3-}]^2[H_2]$. This is consistent with a mechanism involving rate-determining reaction of H_2 with $[Co_2(CN)_{10}]^{6-}$ since the latter exists in rapid equilibrium with $[Co(CN_5]^{3-}$.[30] The further observation that both $[CoH(CN)_5]^{3-}$ and $[CoD(CN)_5]^{3-}$ are produced when the hydrogenation is carried out in D_2O media has been claimed to support a mechanism involving heterolytic fission of H_2.[42] However, homolytic fission with subsequent Co—H/D_2O exchange would lead to the same result and this issue is unresolved.[43]

$$2[Co(CN)_5]^{3-} + H_2 \rightleftharpoons 2[CoH(CN)_5]^{3-} \quad (3)$$

Several low-spin cobalt(II) cyanide complexes containing tertiary or secondary phosphine ligands, and corresponding to the general formula $[Co(CN)_2P_3]$ have been prepared by halide–cyanide exchange (CN^--form anion resin) from tetrahedral $[CoX_2P_2]$ complexes (X = Cl, Br) and an excess of phosphine (Table 7).[44,45] With ditertiary phosphines the reaction gives either diphosphine-bridged binuclear complexes $[(P,P)(CN)_2Co(P,P)Co(CN)_2(P,P)]$ (P,P = dppp, dppb) or mononuclear complexes $[Co(CN)_2(P,P)_2]$ (P,P = dppe) in which one of the diphosphine ligands is monodentate. In all cases the reactions yield orange or red complexes which are five coordinate with a C_2P_3 donor set. In solution ($C_2H_4Cl_2$, benzene) they are frequently unstable and are decomposed by a dissociative process to yellow or green products presumed to be four coordinate.[45]

In many respects the reactions of the monomeric mixed phosphine–cyanide complexes parallel those of $[Co(CN)_5]^{3-}$. Thus, $[Co(CN)_2(dppe)_2]$ undergoes oxidative reactions with SO_2, $SnCl_2$, and alkyl and hydrogen halides, and forms a peroxo dimer on exposure to dioxygen. This latter species is unstable however and in methanol reacts with solvent giving CH_2O and $[Co(CN)_2(dppe)_2]^+$.[46] In $C_2H_4Cl_2$ and in the presence of dioxygen the dimer oxidizes solvent to CO_2 and this process is accompanied by formation of the zwitterionic complex $[(dppe)_2(NC)Co(CN)CoCl_3]$.[47]

Table 7 Five-coordinate Cobalt(II)–Phosphine Cyanide Complexes

Complex	*Comments*	*Ref.*
$[Co(CN)_2(PR_3)_3]$	Red or red-brown, PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, EPR	1
$[Co(CN)_2(PEt_2Ph)_3]$	Dark red, decomposes at 110–113 °C, μ = 2.0 BM, unstable in solution	2
$[Co(CN)_2(PEtPh_2)_3]$	Red, decomposes at 108–110 °C, μ = 2.0 BM	2
$[Co(CN)_2\{Ph_2P(CH_2)_nPPh_2\}_{1.5}]$	Pink-red, n = 3, 4; μ = 2.3–2.4 BM, possibly dimeric	2
$[Co(CN)\{Ph_2P(CH_2)_2PPh\}_2](ClO_4)$	Red-brown, decomposes at 257 °C, μ = 2.2 BM	3
$[Co(CN)_2(PHR_2)_3]$	Red or orange red, R = cyclohexyl, Ph; μ = 1.9–2.0 BM	4

1. R. S. Drago, J. R. Stahlbush, D. J. Kitko and J. Breese, *J. Am. Chem. Soc.*, 1980, **102**, 1884.
2. P. Rigo, M. Bressan and A. Turco, *Inorg. Chem.*, 1968, **7**, 1460.
3. P. Rigo and M. Bressan, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 527.
4. P. Rigo and A. Turco, *Coord. Chem. Rev.*, 1974, **13**, 133.

Table 8 Preparation and Properties of Cobalt(III)–Cyanide Complexes

Complex	*Preparation*	*Comments*	*Ref.*
$K_3[Co(CN)_6]$	$Co^{2+} + CN^- + O_2$; heat	λ_{max} = 312, 260 and 193 nm	1
$K_2[Co(CN)_5(H_2O)]$	$K_3[Co(CN)_6] + h\nu$	λ_{max} = 380 nm	2
$[Co(CN)_5(H_2O)]^{2-}$	$K_6[(CN)_5Co(O_2)Co(CN)_5] + H^+$		3
$[Co(CN)_5(H_2O)]^{2-}$	$[Co(CN)_5]^{3-} + OX$	$OX = H_2O_2$, $S_2O_8^{2-}$	3
$(Et_4N)_3[Co(CN)_5O_2]$	$[Co(CN)_5]^{3-} + O_2$ (DMF)		28
$K_3[Co(CN)_5X]$	$[Co(NH_3)_5X]^{2+} + CN^- + Co^{2+}$	$X^- = Cl^-$, Br^-, NO_2^-, N_3^-	5, 6, 10
$K_3[Co(CN)_5X]$	$[Co(CN)_5(H_2O)]^{2-} + X^-$	$X^- = N_3^-$, I^-, Br	4, 5
$K_3[Co(CN)_5(NCS)]$	$[Co(CN)_5(H_2O)]^{2-} + SCN^-$	λ_{max} = 363 (447)	8
$K_3[Co(CN)_5(SCN)]$	$[Co(NH_3)_5(NCS)]^{2+} + CN^- + Co^{2+}$	λ_{max} = 378 (191)	7, 8
$K_3[Co(CN)_5(NCSe)]$	$[Co(OAc)_2] + CN^- + K_2Hg(SeCN)_4$		23
$K_4[Co(CN)_5(SO_3)]$	$K_3[Co(CN)_5Br] + SO_3^{2-}$		10
$K_4[Co(CN)_5(S_2O_3)]$	$[Co(NH_3)_5(S_2O_3)]^+ + CN$	λ_{max} = 265 nm	9
$K_2[Co(CN)_5(NH_3)]$	$[(CN)_5Co(SO_2)Co(CN)_5]^{6-} + NH_3 + H_2O_2$		14
$K_3[Co(CN)_5(NCO)]$	$[Co(CN)_5\{OP(OEt)_3\}] + NCO^-$	λ_{max} = 366 nm	15
trans-$[Co(CN)_4(SO_3)_2]^{5-}$	$Co(OAc)_2 + SO_2 + CN^- + O_2$	λ_{max} = 377 nm	11
cis-$[Co(CN)_4(SO_3)_2]^{5-}$	$Na_3[Co(SO_3)_3] + CN^-$	λ_{max} = 351 nm	11, 12
cis-$[Co(CN)_4(N_2)]^-$	*trans*-$[Co(Cl)_2(NH_3)_2(en)]^+ + S_2O_3^{2-} + CN^-$	$(N)_2$ = en, tn	16
$Na[Co(CN)_4X_2]$	*trans*-$[Co(CN)_4(SO_3)_2]^{5-} + X$ + heat	X = PPh_3, $AsPh_3$	20
$[Co(CN)_3(NH_3)(en)]$	*trans*-$[Co(Cl)_2(NH_3)_2(en)]^+ + AgCN$	λ_{max} = 392 nm	18
cis-$[Co(CN)_3(NH_3)_3]$	$Na_2K_3[Co(CN)_4(SO_3)_2]$ + aqua regia	Orange, λ_{max} = 380 nm	
trans-$[Co(CN)_3(NH_3)_3]$	$[Co(NH_3)_6]^{3+} + CN^- + C$	Yellow, λ_{max} = 427, 374 nm	13
mer-$[Co(CN)_3(dien)]$	$[Co(dien)_2]^{3+} + CN^- + C$	λ_{max} = 378 nm	13
$K[Co(CN)_3Cp]$	$[Co(I)_2(CO)Cp] + KCN$	M.p. 210 °C	21
cis-$[Co(CN)_2(en)_2]Cl$	$Na[Co(S_2O_3)_2(en)_2] + CN^-$	Resolved, $[M]_D = +66°$	17
cis-$[Co(CN)_2(N_2)_2]^+$	*trans*-$[Co(CN)Cl(NH_3)_4]^+ + AgCN$	N_2 = en, pn, phen, bipy, $2NH_3$	18
trans-$[Co(CN)_2(N_2)_2]^+$	*trans*-$[Co(CN)Cl(NH_3)_4]^+ + CN^-$	N_2 = en, $2NH_3$	18
trans-$K[Co(CN)_2(DMGH)_2]$	Various	λ_{max} = 385 nm	18
cis-$K[Co(CN)_2(acac)_2]$	$[Co(acac)_3] + CN^- + C$	λ_{max} = 524, 534 nm	19
$[Co(CN)_2(PPh_3)Cp]$	$[Co(I)_2(PPh_3)Cp] + KCN$	M.p. 196 °C	21
$[Co(CN)(NH_3)_5]Cl_2$	$[Co(CN)(H_2O)(NH_3)_4]^{2+} + NH_3 + C$	Orange-yellow	22
cis-$[Co(CN)(X)(en)_2]^{n+}$	*cis*-$[CoCl(X)(en)_2]^{n+} + AgCN$	X = NO_2^-, SO_3^{2-}, H_2O	18
trans-$[Co(CN)(X)(en)_2]^+$	*trans*-$[CoCl(X)(en)_2]^+ + AgCN$	X = SO_3^{2-}	18
trans-$[Co(CN)(SO_3)(NH_3)_4]$	$Co^{2+} + NH_3 + S_2O_5 + CN^- + H_2O_2$	λ_{max} = 435, 326 nm	22
trans-$[Co(CN)(DMGH)_2(SO_3)]^{2-}$	*trans*-$[Co(CN)(SO_3)(NH_3)_4] + DMGH_2$	Orange-yellow	18
$K_6[(NC)_5Co(O_2)Co(CN)_5]\cdot 4H_2O$	$[Co(CN)_5]^{3-} + O_2$	Brown, λ_{max} = 327 nm	3
$K_5[(NC)_5Co(O_2)Co(CN)_5]\cdot 5H_2O$	$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+} + CN^-$	Magenta, λ_{max} = 485, 367, 312, 272 nm	24
$Ba_3[(NC)_5Co(NC)Fe(CN)_5]\cdot 16H_2O$	$[Co(CN)_5]^{3-} + [Fe(CN)_6]^{3-}$	λ_{max} = 390, 325 nm	3
$[(NC)_5Co(CN)Co(NH_3)_5]\cdot H_2O$	$[Co(NH_3)_5OH_2][Co(CN)_6]$ + heat	Orange, λ_{max} = 474, 313 nm	25
$[(NC)_5Co(NC)Co(NH_3)_5]\cdot H_2O$	$[(NH_3)_5Co(CN)]^{2+} + [(NC)_5CoOH_2]^{2-}$	Yellow, λ_{max} = 440, 343 nm	26
$[(NC)_5Co(SCN)Co(NH_3)_5]\cdot H_2O$	$[Co(CN)_5OH_2]^{2-} + [Co(NCS)(NH_3)_5]^{2+}$	Orange, λ_{max} = 482, 267 nm	27
$[(NC)_5Co(NCS)Co(NH_3)_5]\cdot H_2O$	$[Co(CN)_5OH_2]^{2-} + [Co(SCN)(NH_3)_5]^{2+}$	Pink, λ_{max} = 508, 282, 274 nm	27
$K_4[(NC)_4Co(NCS)(SCN)Co(CN)_4]\cdot 5H_2O$	$Co^{2+} + CN^- + K_2[Hg(SCN)_4]$	Brown	23

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47.2.3.4 Cobalt(III)

The preparation and properties of a number of cobalt(III)–cyano complexes are given in Table 8. Many reactions involving formation of cobalt(III)–CN bonds are catalyzed by cobalt(II) species. Adamson[37] first proposed that catalysis of cyanide substitution in $[CoX(NH_3)_5]^{2+}$ ions ($X = Br^-$, I^-) to form $[Co(CN)_5X]^{3-}$ involved the participation of the substitutionally labile $[Co(CN)_5]^{3-}$ (Scheme 5). Subsequent mechanistic studies have been interpreted in terms of inner-sphere electron transfer between $[Co(CN)_5]^{3-}$ and $[CoX(NH_3)_5]^{2+}$ through bridged $[(NC)_5CoXCo(NH_3)_5]^-$ intermediates ($X = Cl^-$, N_3^-, NCS^-, OH^-). For a number of other pentaamminecobalt(III) complexes, including those where $X = PO_4^{3-}$, RCO_2^-, CO_3^{2-}, SO_4^{2-} and NH_3, cyanide substitution, while still catalyzed by Co^{II}, follows a different stoichiometry (equation 4). These processes are believed to proceed *via* outer-sphere electron transfer between $[Co(CN)_6]^{4-}$ (presumed to exist in equilibrium with $[Co(CN)_5]^{3-}$) and the $[CoX(NH_3)_5]^{y+}$ reactant.[8,48] These latter reactions have no real preparative value however and the $[Co(CN)_6]^{3-}$ ion is usually prepared as its potassium salt by aerial oxidation of hot solutions of cobalt(II) salts containing excess KCN. The product is obtained as a pale-yellow crystalline solid, soluble in water but insoluble in common organic solvents. Its parent acid, $H_3[Co(CN)_6]\cdot 0.5H_2O$, is readily obtained by chromatography on acidic-form cation-exchange resin and may be used to prepare various other M^{n+} or quaternary ammonium salts.[49]

$$[Co(CN)_5]^{3-} + [CoX(NH_3)_5]^{2+} \longrightarrow [Co(CN)_5X]^{3-} + [Co(NH_3)_5]^{2+}$$

$$[Co(NH_3)_5]^{2+} + 5CN^- \longrightarrow [Co(CN)_5]^{3-} + 5NH_3$$

Scheme 5

$$[CoX(NH_3)_5]^{n+} + 6CN^- \longrightarrow [Co(CN)_6]^{3-} + X^{n-} + 5NH_3 \quad (4)$$

Strong acids, bases and oxidants leave $[Co(CN)_6]^{3-}$ unaffected and the only substitutions of preparative significance are photosolvation or photoanation. Reduction gives either Co^0– or Co^{II}–cyano complexes depending on conditions.[8]

The spectroscopy and photochemistry of the $[Co(CN)_6]^{3-}$ ion have been studied extensively and have been reviewed.[50] Bands at 312, 260 and 202 nm in the electronic spectrum of aqueous solutions are assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$ and CT transitions respectively,[51] and similar spectroscopic features are exhibited by solid-state samples.[52] Recent studies have identified a weak absorption band at ~390 nm as being associated with the singlet to triplet $^1A_{1g} \rightarrow {}^3T_{1g}$ transition.[53,54] Crystalline $K_3[Co(CN)_6]$ (and also *cis*-$K_3Na_2[Co(CN)_4(SO_3)_2]$ and *trans*-$Na_5[Co(CN)_4(SO_3)_2]$[55]) exhibits phosphorescence from the $^3T_{1g}$ excited state of the molecule at low temperatures,[56] and laser irradiation of $[Co(CN)_6]^{3-}$ in a glass matrix at 94 K gives rise to a transient spectrum ($t_{1/2} = 1.5 \times 10^{-5}$ s) in the 350 to 500 nm region assigned to absorption by this excited-state species.[54]

In aqueous solution $[Co(CN)_6]^{3-}$ undergoes efficient CN^- photoaquation (equation 5) with a wavelength-independent quantum yield ($\phi = 0.3$) irrespective of whether irradiation occurs in the 254–365 nm region,[57] corresponding to spin-allowed LF absorptions, or in the 405–436 nm region,[58] corresponding primarily to direct triplet excitation. The aquapentacyanocobaltate(III) ion is effectively the terminal product in these processes since it is practically photoinert with respect to further substitution of cyanide. A value of $\Delta V^{\ddagger}$ of $+1.3\,cm^3\,mol^{-1}$ has been reported for the reaction.[59]

$$[Co(CN)_6]^{3-} + H_2O \xrightarrow{h\nu} [Co(CN)_5(OH_2)]^{2-} + CN^- \quad (5)$$

Photolysis of aqueous solutions of $[Co(CN)_5X]^{n+}$ ($X = Cl^-$, Br^-, I^-, N_3^-, SCN^-, H_2O, NH_3) and $[Co(CN)_4(SO_3)Y]^{n-}$ ($Y = SO_3^{2-}$, OH^-, H_2O) in the LF region involves replacement by H_2O of the X and SO_3^{2-} ligands respectively. Unlike the photoreaction of $[Co(CN)_6]^{3-}$, photoaquation efficiencies depend on ionic strength and these reactions appear to occur through dissociative mechanisms involving five-coordinate intermediates. In contrast, photoaquation of $[Co(CN)_6]^{3-}$ is interpreted in terms of a photoactivated interchange mechanism between inner-sphere CN^- and an outer-sphere water molecule.[50] This photoactivated interchange has been shown[60] to be the primary step in the photoanation of $[Co(CN)_6]^{3-}$ by nucleophiles ($Y = I^-$, N_3^-) and photoproduction of $[Co(CN)_5Y]^{3-}$ occurs exclusively from the immediate product $[Co(CN)_5(H_2O)]^{2-}$ (Scheme 6). Irradiation of cobalt(III)–cyano complexes in the CT region results in photoredox processes in parallel with substitutions. The former are comparatively inefficient, presumably because of effective conversion mechanisms from CT to LF states. However, UV irradiation of *trans*-$[Co(CN)_4(SO_3)(H_2O)]^{3-}$,[61] $[Co(CN)_5(NO_2)]^{3-}$ [50] and $[Co(CN)_5(OH)]^{3-}$ [62] produces Co^{II} species, and oxidized acidoligand products have been detected during photolysis of $[Co(CN)_5X]^{3-}$ anions ($X = N_3^-$, I^-, SCN^-).[63,64]

$$[Co(CN)_6]^{3-} + H_2O \xrightarrow{h\nu} [Co(CN)_5(OH_2)]^{2-} + CN^-$$

$$[Co(CN)_5(OH_2)]^{2-} + Y^- \longrightarrow [Co(CN)_5Y]^{3-} + H_2O$$

Scheme 6

Early kinetic measurements on the thermal anation of $[Co(CN)_5(H_2O)]^{2-}$ by anionic nucleophiles ($Y = N_3^-$, SCN^-) indicated that substitution proceeded with a less-than-first-order dependence on [Y] and approached a limiting rate at high concentrations.[65] This, together with the substantial agreement between the limiting rates for the thiocyanate and azide systems and the apparent water-exchange rate on $[Co(CN)_5(H_2O)]^{2-}$, indicated that substitution occurred *via* a limiting dissociative mechanism involving five-coordinate $[Co(CN)_5]^{2-}$ as a reaction intermediate (Scheme 7).

$$[Co(CN)_5(OH_2)]^{2-} \rightleftharpoons [Co(CN)_5]^{2-} + H_2O$$

$$[Co(CN)_5]^{2-} + Y^- \longrightarrow [Co(CN)_5Y]^{3-}$$

Scheme 7

Similar kinetic behaviour is found for substitution of H_2O by CN^- in *trans*-$[Co(CN)_4(SO_3)(H_2O)]^{4-}$.[66] However, a reactive intermediate $[Co(CN)_4(SO_3)]^{3-}$ species generated by loss of H_2O from the coordination sphere need not, in this case, be five coordinate since the possibility exists for rearrangement to a configuration where SO_3^{2-} is bidentate (Section 47.7.4.3).

The reactions of $[Co(CN)_5(H_2O)]^{2-}$ with N_3^- [67,68] and SCN^- [68] have been reinvestigated and important differences found which indicate that the evidence in favour of limiting kinetics is not as clear as originally supposed. In particular, deviations from the simple second-order rate law for anation, rate $= k[Co(CN)_5(H_2O)^{2-}][Y^-]$, appear to be small and the question of reaction mechanism remains somewhat open at present. The effect of solvent on reaction between $[Co(CN)_5(H_2O)]^{2-}$ and N_3^- [69] and the small positive activation volumes for anation by Br^-, I^- and SCN^- [70] are indicative of a dissociative mechanism, but the existence of a long-lived five-coordinate intermediate has not been definitively established.

The thermal reaction between *trans*-$[Co(CN)_4(SO_3)_2]^{5-}$ and $^{13}CN^-$ in aqueous solution results in stereospecific incorporation of label to form *trans*-$[Co(^{13}CN)(CN)_4(SO_3)]^{4-}$, whereas when the reaction is carried out photochemically, labelled cyanide is randomly incorporated.[71] Photodissociative loss of SO_3^{2-} appears to lead to an electronically or vibrationally excited intermediate which has a chemistry quite distinct from the intermediate produced in the thermal reaction. Whatever its exact nature, the photoexcited intermediate has a short configurational lifetime and this causes random introduction of $^{13}CN^-$.

Structural data for cobalt(III)–cyano complexes are given in Table 9. Numerous studies have been carried out on hexacyanobaltates(III) and on Prussian blue analogues of the type $M_3[Co(CN)_6]_2 \cdot 12H_2O$. Various structural models have been proposed for the latter complexes and a discussion of these and the physical changes which occur on dehydration has been given by Beall.[72] In Co^{III} cyanide complexes the Co—C and C—N bond distances (typically 189 ± 2 and 115 ± 2 pm respectively) show little variation irrespective of whether the ligand is terminal or bridging. Better sensitivity to the coordination mode is shown by the stretch frequencies, ν_{CN}, which generally occur at a wavenumber 60–80 cm^{-1} higher for bridging cyanide ligands than for terminal. In a series of related cyanoaminecobalt(III) complexes the respective frequency ranges of 2190 ± 10 cm^{-1} and 2130 ± 10 cm^{-1} are characteristic of these two modes.

Structures have been reported for both the $[(NC)_5Co(CN)Co(NH_3)_5]$ and $[(NC)_5Co(NC)Co(NH_3)_5]$ linkage isomers as well as for $[Co(CN)(DMGH)_2(H_2O)]$ and its isostructural linkage isomer $[Co(NC)(DMGH)_2(H_2O)]$. The electronic spectra of the binuclear complexes do not correspond to those expected for an average environment of CN^- and NH_3 ligands on a single Co^{III} centre but rather to the sum of the spectra of the two cobalt(III) moieties. Similar spectral relationships are found for the thiocyanate-bridged dimers $[(NC)_5Co(SCN)Co(NH_3)_5]$ and $[(NC)_5Co(NCS)Co(NH_3)_5]$.[73] The isocyano complex $[Co(NC)(DMGH)_2(H_2O)]$ appears to be the only Co^{III} complex containing a monodentate isocyano ligand, and is prepared from the reaction of $[Co(DMGH)_2(NH_3)_2]$ with $[Ag(CN)_2]^-$ in aqueous solution.[74] The similar reaction with CN^- in the absence of silver ion yields the corresponding C-bonded isomer. $[Co(NC)(DMGH)_2(H_2O)]$ is hydrolytically stable but is converted to its linkage isomer on heating to 250 °C.

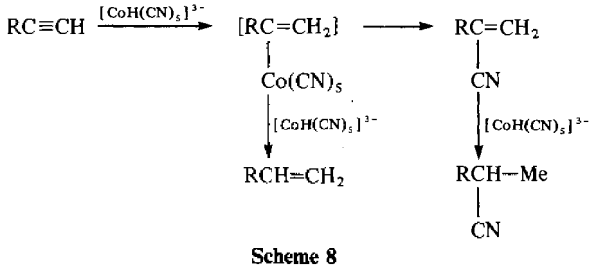
Table 9 Structures: Cobalt(III)–Cyano Complexes

Complex	*Co—C(CN)* (pm)	*C—N* (pm)	*Comments*	*Ref.*
$H_3[Co(CN)_6]$	189	109	X-Ray	1
$D_3[Co(CN)_6]$	188	115	Neutron diffraction, N—D—N bonds linking $[Co(CN)_6]^{3-}$ octahedra, ND = 260 pm	2
$Ag_3[Co(CN)_6]$	189	114	AgN = 206 pm, CNAg = 157.3°	3
$K_3[Co(CN)_6]$	188–190	113–117	X-Ray and neutron diffraction	4
$(MN_6)[Co(CN)_6]$	187	116	$(MN_6)^{3+} = [Cr(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$	5
$M_3[Co(CN)_6]_2 \cdot 12H_2O$	187–188	115–116	$M^{2+} = Co^{2+}$, Cd^{2+}, Mn^{2+}, X-ray and neutron diffraction	6
$K_3[Co(CN)_5(CF_2CF_2H)]$	193(ax), 189(eq)	—	CoCC = 119.7°, CoC(C_2F_4H) = 199 pm	8
$K_3[Co(CN)_5N_3] \cdot 2H_2O$	189	115	Linear N_3 group, CoNN = 116.3°	7
$K_6[(NC)_5CoC(R)=C(R)Co(CN)_5] \cdot 6H_2O$	192(ax), 190(eq)	—	R = CO_2Me, CoC = 207.6 pm	9
$[Co(CN)(NH_3)_5]X_2$	188–191	114	$X^- = Cl^-$, ClO_4^-	10
Δ-*cis*-$[Co(CN)_2(en)_2]Cl$	—	—	—	11
trans-$[Co(CN)(DMGH)_2(H_2O)]$	191	114	Isostructural with $[Co(NC)(DMGH)_2(H_2O)]$	12
$[Co_3(CN)_2(OH)(NO_2)_2(NH_3)_8](ClO_4)_3 \cdot 2H_2O$	190	113	Central Co with *cis* CN^- ligands and dibridged (OH, NO_2) to two $Co(NH_3)_4$ units	13
$[(NC)_5Co(CN)Co(NH_3)_5] \cdot H_2O$	189(eq), 189(*trans*), 189(br)	115(br)	CoNC = 159.8°, CoCN = 172.4°	14
$[(NC)_5Co(NC)Co(NH_3)_5] \cdot H_2O$	191(eq), 188(*trans*), 190(br)	112(br)	CoNC = 166.5°, CoCN = 165.6°	15
$[(NC)_5Co(SCN)Co(NH_3)_5] \cdot H_2O$	188	114	Linear SCN, CoSC = 101.1°, CoNC = 169.5°	16
$K_8[(NC)_5Co(O_2)Co(CN)_5](NO_3)_2 \cdot 4H_2O$	187–191	115	Peroxo OO = 145 pm, CoO = 199 pm, CoCo = 490 pm	17
$K_5[(NC)_5Co(O_2)Co(CN)_5] \cdot H_2O$	188(eq), 184(*trans*)	115–119	Superoxo OO = 126 pm, CoO = 194 pm, CoCo = 463 pm	18
$(Et_4N)_3[Co(CN)_5(O_2)] \cdot 5H_2O$	192	109–112	Superoxo OO = 124 pm, CoO = 191 pm	19

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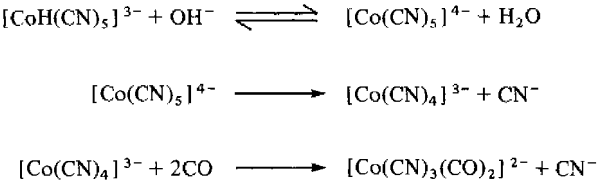
The $[CoH(CN)_5]^{3-}$ ion results from treatment of solutions of $[Co(CN)_5]^{3-}$ with H_2 (Section 47.2.3.3). The hydrido complex is somewhat unstable in solution and salts are obtained with difficulty, however $Cs_2Na[CoH(CN)_5]$ has been isolated as a pure colourless solid which displays $\nu_{CN} = 2113\,cm^{-1}$ and $\nu_{CoH} = 1840\,cm^{-1}$. Freshly prepared solutions of the ion have $\lambda_{max} = 305\,nm$ and a ^1H NMR signal 17.6 p.p.m. upfield from the H_2O resonance.[8]

The $[CoH(CN)_5]^{3-}$ ion has been used extensively as a catalyst in various homogeneous hydrogenations and reviews of the catalytic applications are available.[30,75,76] Under neutral conditions the classes of compounds reduced include conjugated dienes, styrenes, α,β-unsaturated acids (as either salts or esters) and aldehydes, 1,2-diketones and epoxides. Many of these reactions involve σ-complex formation and under favourable conditions stable organopentacyanobaltate(III) products may be isolated.[30] Simple alkenes and alkynes are not reduced but terminal alkynes incorporating an OH function are either selectively hydrocyanated to saturated secondary nitriles or reduced to alkenes (Scheme 8).[77] C_4 allylic alcohols are catalytically hydrogenolyzed to alkenes with the product distributions being highly dependent on reaction conditions.[77] Similar selectivities have been noted in the catalytic hydrogenation of conjugated dienes to monoalkenes.[30]

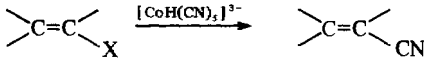


Scheme 8

Carbonylation of $[CoH(CN)_5]^{3-}$ in strongly alkaline media results in the formation of $[Co(CN)_3(CO)_2]^{2-}$ and the intermediacy of the short-lived tetracyanocobaltate(I) ion $[Co(CN)_4]^{3-}$ in this process has been inferred from mechanistic studies (Scheme 9).[15] Under very similar conditions $[CoH(CN)_5]^{3-}$ catalyzes the cyanation of vinyl halides to form α,β-unsaturated nitriles with retention of configuration (equation 6). Oxidative addition of vinyl halide to the intermediate $[Co(CN)_4]^{3-}$ ion is stereoselective and in the σ complex so produced reductive coupling of the vinyl and cyano ligands gives the stereoretentive organic product and regenerates $[Co(CN)_4]^{3-}$.[78]



Scheme 9



(6)

47.3 SILICON LIGANDS

47.3.1 Silyl Complexes

A few trialkylsilyl (SiR_3^-) complexes of cobalt are known and a recent account of the reactions of transition-metal trialkylsilanes is available.[79] The cobalt complexes are often prepared *via* oxidative addition of $HSiR_3$ to a low-valent carbonyl or dinitrogen complex (equation 7) or by elimination of H_2 from a cobalt hydride (equation 8). They are usually air sensitive, and unstable with respect to displacement of $HSiR_3$ on heating or on treatment with N_2, H_2 or CO, sometimes in a reversible manner. Deuteration (Scheme 10) provides a useful catalytic route to $DSiR_3$ systems through the intermediacy of the 16-electron $[CoD(PPh_3)_3]$ complex, and O-silylation to give $Si(OR)_4$ species (R = Me, Et) is possible at ambient temperatures *via* $[CoH_2\{Si(OEt)_3\}(PPh_3)_3]$ in the appropriate alcohol.[80]

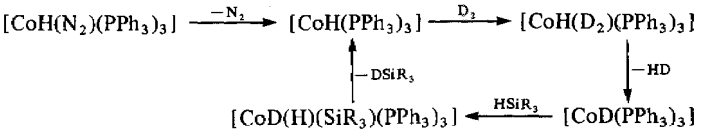
Table 10 Silyl Complexes of Cobalt

Complex	*Preparation*	*Comments*	*Ref.*
$[Co(SiR_3)(CO)_4]$	$[CoH(CO)_4]$ or $Co_2(CO)_8 + HSiR_3$	R = Me, Cl	1
$[CoH(SiCl_3)(CO)(Cp)]$	$[Co(CO)_2(Cp)] + HSiCl_3$; hexane, light, r.t.	Low yield; ν_{CO} 2045 cm^{-1}; ^1H, 23.3 p.p.m.	2
$[Co(H)_2(SiR_3)(PPh_3)_3]$ ($R_3 = F_3$, MeF_2, $(OEt)_3$)	$[CoH(N_2)(PPh_3)_3] + HSiR_3$; hexane	Yellow; ^1H, 24–25 p.p.m.; ν_H 1850–2040 cm^{-1}	3
$[Co(SiF_3)(CO)_n(PR_3)_{4-n}]$ ($R_3 = Me_2Ph$, Et_3, PPh_3, Bu^n_3)	$[Co(CO)_3(PR_3)]_2 + HSiF_3$; benzene, hexane; r.t.	Yellow, IR	4
	$[CoH(CO)_3(PPh_3)] + HSiF_3$; pentane, −95 °C		

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$$[CoH(N_2)(PPh_3)_3] + HSiR_3 \rightleftharpoons [Co(H)_2(SiR_3)(PPh_3)_3] + N_2 \quad (7)$$

$$[CoH(CO)_n(PR'_3)_{n-4}] + HSiR_3 \longrightarrow [Co(SiR_3)(CO)_n(P'R_3)_{n-4}] + H_2 \quad (8)$$



Scheme 10

Various substitutions are possible (equation 9)[81] and $[CoH(CO)_4]$ is known to catalyze the addition of $HSiMe_3$ to C_2H_4 at room temperature to give high yields of $SiMe_3Et$.[82] Treatment of $[Co(SiMe_3)(CO)_4]$ with ROH or NH_2R rapidly results in $SiMe_3OR$ or $SiMe_3(NR_2)$ species and $[CoH(CO)]_4$, while GeF_4 and $AsMe_2Cl$ generate $SiMe_3F$ and $SiMe_3Cl$.[82]

$$[Co(SiR_3)(CO)_2(dppe)] \xleftarrow{dppe} [Co(SiR_3)(CO)_4] \xrightarrow{PPh_3} [Co(SiR_3)(CO)_3(PPh_3)] \quad (9)$$

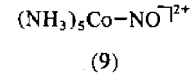
47.4 NITROGEN LIGANDS

47.4.1 Nitrosyl

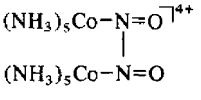
47.4.1.1 Synthesis

Phosphine complexes containing the NO ligand are considered in Section 47.5.2.3. Most remaining cobalt nitrosyls are simply prepared from the corresponding isolated or *in situ* Co^{II} complex and $NO_{(g)}$ (Table 11). General articles dealing with synthetic methods are available.[83–86] There appears to be no known synthesis *via* oxygen abstraction from coordinated ONO^-, NO_2^- or NO_3^-, or by oxidation of coordinated NH_3 or NH_2OH. Dimeric $[Co(NO)_2X]_2$ (X = Cl^-, Br^-) is a potential starting material for bis(nitrosyl) complexes, but few examples of its use outside the phosphine complexes (Table 34) exist. Most cobalt nitrosyls are diamagnetic with an 18-electron count if NO is considered a three-electron donor in the four- and five-coordinate systems and a one-electron donor in six-coordination; paramagnetic $[Co(NO)\{N(dppe)_3\}](BPh_4)$ (17-electron, tetrahedral) and $[Co(NO)Cl(das)_2](ClO_4)_2$ (17-electron, probably octahedral) are exceptions (Table 11).

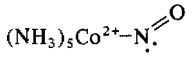
The chemistry of the reaction of NO with ammoniacial solutions of $Co^{2+}_{(aq)}$ has had a long and interesting history. As early as 1903, Sand and Genssler[87] demonstrated the existence of two isomeric forms of $[Co(NO)(NH_3)_5]X_2$, a black series (X = Cl^-, NO_3^-, IO_3^-) and a red series (X = Br^-, I^-, NO_3^-, SO_4^{2-}); the former liberated $NO_{(g)}$ rather readily in aqueous solution but the latter was far more stable, especially in dilute acid. Based on empirical evidence, Werner and Karrer[88] considered the black series to be monomeric, designated (**9**), and the red series to be dimeric with a hyponitro structure (**10**). Since that time the reported paramagnetism of the black series has been corrected (both are diamagnetic) but most investigators (and there have been a large number) considered Werner to be wrong and assigned the same or similar structure in the opposite sense. However Werner and Karrer were indeed correct (or nearly so) as the known structures (**11**) and (**12**) testify (Table 12).



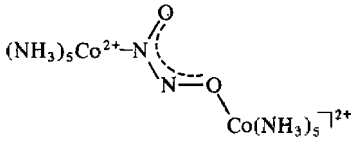
(9)



(10)



(11) black



(12) red

Table 11 Preparations: Cobalt–Nitrosyl Complexes (Non-phosphine Containing)

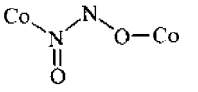
Complex	*Preparation*	*Comments*	*Ref.*
$[Co(NO)_2Cl]_2$	$CoCl_2$ + NEt_3; MeOH; NO	Black; diamagnetic; ν_{NO} 1866 cm^{-1}	13
$K_3[Co(NO)(CN)_3]$	$[Co(NO)(CO)_3]$ + KCN; liq. NH_3, 120 °C, 7 d	Violet; decomposes in H_2O; ν_{NO} 1485 cm^{-1}	14
$K_2[Co(NO)(CN)_2(CO)]$	As above, lower temp.	Red-brown; ν_{NO} 1645 cm^{-1}	14
$K[Co(NO)(CN)(CO)_2]$	$[Co(NO)(CO_3)]$ + KCN; MeOH	Red; ν_{NO} 1728 cm^{-1}	14, 15
$Na[Co(NO)_2(CN)_2]$	$[Co(NO)_2Br]_2$ + NaCN; EtOH, r.t.	Brown; ν_{NO} 1837, 1748 cm^{-1}	16
$[Co(NO)(CO)_2L]$ (L = PR_3, $P(OR)_3$, AsR_3, py, CNR)	$[Co(NO)(CO)_3]$ + L; THF, r.t.	Orange-red (mostly); ν_{NO} 1730–1770 cm^{-1}, kinetics	21
$[Co(NO)_2(S_3N)]$	$[Co_2(CO)_8]$ + S_4N_4; pentane, 2 h; NO	Violet (structure Table 12)	
[Co(NO)(acacen)]	$Co(OAc)_2 \cdot 4H_2O$ + NO + LH_2; MeOH, acetone, N_2	Black; diamagnetic; NMR; IR, ν_{NO} 1654 cm^{-1}	1
[Co(NO)(benacen)]	LH_2 + NO; acetone; $Co(OAc)_2 \cdot 4H_2O$, MeOH	Black; diamagnetic; NMR; IR, ν_{NO} 1635	1
Co(NO)(ONNO)]	[Co(ONNO)] + NO; CH_2Cl_2	Brown; diamagnetic; ν_{NO} 1663–1698 cm^{-1}	18
[Co(NO)(sacacen)]	$Co(OAc)_2 \cdot 4H_2O$ + LH_2 + NO; MeOH	Black; diamagnetic; ν_{NO} 1638 cm^{-1}	2
[Co(NO)(salen)]	$Co(OAc)_2 \cdot 4H_2O$ + LH_2 + NO; MeOH, acetone, N_2	Black; diamagnetic; ν_{NO} 1624 cm^{-1}	1, 3
$[Co(NO)(OClO_3)(en)_2](ClO_4)$	$Co(ClO_4)_2 \cdot 6H_2O$ + en; MeOH, N_2, NO	Red; ν_{NO} 1663 cm^{-1}	4
$[Co(NO)(Me_2dtc)_2]$	$[Co(NO)(en)_2](ClO_4)_2$ + NaL; MeOH, N_2	Dark green; ν_{NO} 1630 cm^{-1}	5
$[Co(NO)X(en)_2]ClO_4$	$[Co(NO)(OClO_3)(en)_2](ClO_4)$; acetone + LiX	Brown, red-brown; ν_{NO} 1611 cm^{-1}	4
$[Co(NO)X(das)_2]X$ (X = Cl, Br, I, NCS)	$[CoX_2(das)_2]$; MeOH + NO	Red-brown; ν_{NO} 1550–1570 cm^{-1}	4
$[Co(NO)(das)_2](ClO_4)_2$	$[Co(ClO_4)_2(das)_2]$; MeOH, NO	Red; ν_{NO} 1852 cm^{-1}	4
$[Co(NO)(DMGH)_2]$	$Co(OAc)_2 \cdot 4H_2O$ + NO + LH_2; MeOH	Black; ν_{NO} 1641 cm^{-1}	6
$[Co(NO)(big)_2(H_2O)]$ (big = biguanide, *N*-amidinothioureas)	$CoCl_2$ + NO + N_2 + bigH; 0 °C, 30 min	Violet; diamagnetic	22
$[Co(NO)(8\text{-quin})_2]$	$CoCl_2 \cdot 6H_2O$ + L + NO; MeOH	ν_{NO} 1650 cm^{-1}	7
$[Co(NO)\{N(dppe)_3\}]$	$[CoH\{N(dppe)_3\}]$ + NO; THF	Brown; ν_{NO} 1620 cm^{-1}; diamagnetic	11
$[Co(NO)\{N(dppe)_3\}](BPh_4)$	$[Co(NO)\{N(dppe)_3\}]$ + $NaBPh_4$; EtOH	Green; ν_{NO} 1680 cm^{-1}; μ = 1.98 BM; tetrahedral structure (Table 12)	11
$[Co(NO)Cl(das)_2](ClO_4)_2$	$[Co(NO)(das)_2](ClO_4)_2$ + Cl_2; MeOH	Green; ν_{NO} 1760 cm^{-1}; μ = 1.90 BM	12
$[Co(NO)X(bipy)_2]Y$ (X = Cl, I, NO_2; Y = ClO_4, PF_6)	$CoX_2 \cdot 6H_2O$ + bipy; EtOH, N_2, NO	Brown, yellow; ν_{NO}, 1642 cm^{-1}; oxidizes in air	19
$[Co(NO)(NH_3)_5]Y_2$ (Y = Cl, NO_3)	$CoY_2 \cdot 6H_2O$ + 0.88NH_4OH; NO; 0 °C, 45 min	Black (monomeric); diamagnetic; ν_{NO} 1170 cm^{-1}; (structure, Table 12)	8, 9
$[Co_2(N_2O_2)(NH_3)_{10}]Y_4$	CoY_2 + 0.88NH_4OH; NO, r.t., 2 h	Red (dimeric); diamagnetic; ν_{NO} 1040–1080 cm^{-1}; (structure, Table 12)	9, 10
$K_3[Co(NO)(CN)_5] \cdot 2H_2O$	'Black' $Co(NO)(NH_3)_5$ Cl_2 + KCN; 0 °C, aq.	Yellow; diamagnetic; ν_{NO} 1130, 1050, 980 cm^{-1}	17

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Table 12 Structures: Cobalt–Nitrosyl Complexes

Complex	*Structural details*	*Comments*	*Ref.*
		{CoNO}^{10} systems	
$[Co(NO)_2Cl]_2$	CoNO 176°; Co—NO 173, N—O 112 pm	Dist. tet., dimeric layered structure disordered	14
$[Co(NO)_2I]_n$	CoNO 168°; Co—NO 161, N—O 116 pm	Tet., infinite chains with bridging Co—I—Co	10
$[Co(NO)_2(ONO)]_n$	CoNO 167°; Co—NOO 198, Co—O 215, N—O 113 pm	Bridging CoNOCo (O above N)	11
$[Co(NO)_2(N_2C_5H_7)]_2$	CoNO 161.6, 173.5°; Co—NO 164.6, 168 pm	Dist. tet., dimeric units joined by 3,5-Me_2 pyrazolate ions; NO(ax) bent more than NO(eq)	27
$[Co(NO)(CO)_2(PPh_3)]$	Co—NO(CO) 172–176, Co—P 222.4 pm; PCoCP(NO), 104—106°	Tet., disordered CO, NO	17
$[Co(NO)(CO)(PPh_3)_2]$	Co—NO(CO) 172, Co—P 223 pm; PCoNO(CO) 103.5°, 108°	Tet., disordered CO, NO	17
$[Co(NO)(SO_2)(PPh_3)_2]$	CoNO 169°; Co—P 225–226, Co—NO 168 pm; PCoP 104.8°, PCoN 109–114°	Tet., bending of NO in plane of η^1-planar SO_2	28
$[Co(NO)(1\text{-}CN\text{-}2,6\text{-}Me_2C_6H_3)_3]$	CoNO 177.5°, CoCN 175.9°; Co—N 163, Co—C 184.6–186.5 pm; NCoC 115–120°	Dist. tet., linear NO, CNR coordination	18
$[Co(NO)(CO)_2(AsPh_3)]$	CoNO 177°; Co—NO 174, N—O 114 pm	Tet.	22
$[Co(NO)_2I(PPh_3)]$	CoNO, 163–165°; Co—NO 166, Co—I 257, Co—P 224, N—O, 115 pm	Dist. tet., nearly linear NO coordination (−170 °C study)	5
$[Co(NO)_2I(PPh_2R')]$ ($R' = CH_2CH_2P(O)Ph_2$)	CoNO uncertain; Co—NO 168, N—O 105, Co—P 226, Co—I 225 pm	Dist. tet., disordered NO	7
$[Co(NO)_2(sacsac)]$	CoNO 170°; Co—NO 165, N—O Tet.	12	
$[Co(NO)_2(S_3N)]$	CoNO, 166–167°; Co—N 165–166, N—O 113, 115 pm; NCoN, 112.1°	Dist. tet.	29
$[Co(NO)_2(dppe)](PF_6)$	CoNO, 174.4°; Co—NO 166, N—O 113 pm	Tet.	8
$[Co(NO)_2(PPh_3)_2](PF_6)$	CoNO, 171°; Co—NO 164, N—O 117; NCoN 136–7°	Dist. tet.	9
$[Co(NO)_2(PPh_3)_2](ClO_4)$	CoNO, 171°; Co—NO 166, N—O 115 pm	Dist. tet.	23
		{CoNO}^{9} systems	
$[Co(NO)\{N(dppe)_3\}](BPh_4)$	CoNO 165°; Co—NO 183, N—O 114 pm	Tet.; ν_{NO} 1680 cm^{-1}; μ = 1.98 BM; N^t not coordinated	24
		{CoNO}^{8} systems	
$[Co(NO)(Me_2dtc)_2]$	CoNO 127°; Co—NO 170, N—O 110 pm	Tet. pyr., disordered O in NO ligand	3
$[Co(NO)(Pr^i_2dtc)_2]$	CoNO 129°; Co—NO 171, N—O 111 pm	Tet. pyr., disordered O in NO ligand	4
$[Co(NO)(salen)]$	CoNO 127°; Co—NO 181, N—O 115.5 pm	Tet. pyr.	13
$[Co(NO)(acaen)]$	CoNO 124.4°; Co—NO 182 pm	Tet. pyr.	21
$[Co(NO)(benacaen)]$	CoNO 122.9°; Co—NO 183 pm	Tet. pyr.	21
$[Co(NO)(TPP)]$	CoNO < 128.5°; Co—NO 183, N—O > 110 pm	Sq. pyr. (C_{4v})	19
$[Co(NO)(Cl)_2(PPh_2Me)_2]$	CoNO 165°	Dist. trig. bipyr.; ν_{NO} 1750, 1650 cm^{-1}; equilibrium between bent and linear coordination in soln.	15

$[Co(NO)(das)_2](ClO_4)_2$	CoNO 179°; Co—NO 168, N—O 117 pm	Trig. bipyr.; ν_{NO} 1852 cm^{-1}	1
trans-$[Co(NO)(NCS)(das)_2](NCS)$	CoNO 135°; N—O 101, M—NO 185 pm	Oct.; ν_{NO} 1587 cm^{-1}	1
trans-$[Co(NO)(Cl)(en)_2](ClO_4)$	CoNO, 124.4°; M—NO 182, N—O 104,	Oct.; ν_{NO} 1611 cm^{-1}; long Co—Cl bond	2
trans-$[Co(NO)(OClO_3)(en)_2](ClO_4)$	CoNO 135–141° (or 122–123°); Co—NO 181, Co—OClO, 236, N—O 115 pm	Oct., may contain two disordered NO ligands	6
$[Co(NO)(NH_3)_5]Cl_2$	CoNO 119°; Co—N (*cis*) 198, Co—N (*trans*) 222, N—O 115.4, Co—NO 187 pm	Oct. (black), bent NO	16
$[Co(NH_3)_5NO]_2Br_{2.5}(NO_3)_{1.5}\cdot H_2O$	CoNO 121°, CoNN 117°, CoON 112°; Co—NO 192, Co—ON 187, Co—NH_3 192–197 pm	Oct. (red), bent hyponitrite ligand 	20
	(μ_2-NO) bridges		
$[\{Co(SNNS)\}_2(\mu_2\text{-}NO)](BF_4)$	CoNO 130°; Co—NO 180–182, N—O 121 pm	Oct.; ν_{NO} 1550 cm^{-1}; bridging thiolato (2) and NO	25
$[\{Co(C_5H_5)\}_2(\mu_2\text{-}NO)_2]$	CoNO 139.6°; Co—NO 182, N—O 119	No Co—Co bonding; diamagnetic	26
$[\{Co(C_5H_5)\}_2(\mu_2\text{-}NO)(\mu_2\text{-}CO)]$	CoNO 139.8°; Co—NO 183, N—O 120	No Co—Co bonding; μ = 1.86 BM	26

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Preparation of the black monomer is achieved at 0 °C after short reaction times; the red dimer is formed at ambient temperatures using longer reaction times (Table 11). Also the red dimer can be prepared from the black monomer and isomer and an intermediate hyponitrito monomer $[Co(N_2O_2)(NH_3)_5]^{2+}$ appears to be involved.[89] Miki and Ishimori[90] suggest that by using ammoniacal solutions which have been pre-exposed to the atmosphere a second hyponitrito isomer, assigned structure (**13**), can be formed. The isomer is less stable in solution giving rise to $[Co(NO_2)(NH_3)_5]^{2+}$ and $Co(OH)_3$ in boiling water and its thermal decomposition appears to differ from the others.[90,91] However structural clarification is necessary.

$$(NH_3)_5Co^{2+}—N{=}O—O{=}N—Co(NH_3)_5^{2+}$$

(13)

Treatment of black $[Co(NO)(NH_3)_5]Y_2$($Y = Cl^-$, NO_3^-) with KCN at 0 °C gives yellow $K_3[Co(NO)(CN)_5]\cdot H_2O$, which may well have a dimeric hyponitrito structure, although direct structural evidence is lacking.[92,93] IR data support a *cis* or skewed hyponitrito bridge and earlier claims that the same compound could be prepared from red $[Co(NO)(NH_3)_5]_2(SO_4)_2\cdot 2H_2O$ have been discounted.[93] Further treatment with CN^- leads to $N_2O_{(g)}$ (equation 10).

Several mixed carbonyl–nitrosyls having the 18-electron count have been prepared from $[Co(NO)(CO)_3]$ or $[Co(NO)_2Br]_2$ (Table 11). All are four coordinate and probably tetrahedral, although the low ν_{NO} for $K_3[Co(NO)(CN)_3]$ (1485 cm^{-1}) may imply square-planar coordination with a bent nitrosyl. Rates of substitution in poorly coordinating solvents (THF, xylene; equations 11 and 12) follow the rate expression $k_{obs} = k_1 + k_2[L]$, with k_1 and k_2 being attributed to dissociative paths involving the sovlent and ligand respectively.[94] For L—L chelates formation of the monodentate species is rate determining.[95]

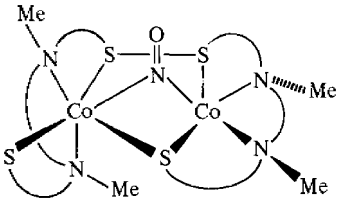
$$[Co(NO)(CN)_5]_2^{6-} + 2CN^- + 2H^+ \longrightarrow 2[Co(CN)_6]^{3-} + H_2O + N_2O \quad (10)$$

$$[Co(NO)(CO)_3] + L \longrightarrow [Co(NO)(CO)_2L] + CO_{(g)} \quad (11)$$

$$[Co(NO)(CO)_3] + L—L \longrightarrow [Co(NO)(CO)(L—L)] + 2CO_{(g)} \quad (12)$$

Oxidative addition of $NONO_2$ was suggested many years ago by Rossi and Sacco[96] for reaction (13) but ^{15}N experiments are necessary to confirm this. However Lippard and coworkers[97] have demonstrated NO^+ addition in the reaction of dimeric $[Co(SNNS)]_2$ (SNNS = $SCH_2CH_2N(Me)CH_2CH_2N(Me)CH_2CH_2S^-$) with $NOPF_6$. Here NO^+ adds across the $(\mu\text{-SR})_2$-bridging dimer to form the triply bridged diamagnetic Co^{III} complex (**14**; Table 12).

$$[Co(NO)(PPh_3)_3] + 7NO \longrightarrow [Co(NO)_2(NO_2)(PPh_3)] + 2OPPh_3 + N_2O + 0.5N_2 \quad (13)$$



(14)

Structures of two other μ_2-bridged nitrosyls $[\{Co(Cp)\}_2(\mu\text{-}NO)_2]$, $[\{Co(Cp)\}_2(\mu\text{-NO,CO})]$ are known (Table 12) and the preparation of $[\{Co(C_5R_5)\}_2(\mu\text{-}NO)_2]^{n+}$ (R = H, Me; n = 0, 1, 2) and $[\{Co(C_5Me_5)\}_2(\mu\text{-NO,CO})]^{n+}$ (n = 0, 1) from $[Co(CO)_2(C_5R_5)]$ and $NOPF_6$ in dichloromethane, and their electrochemistry, have recently been discussed by Connelly, Payne and Geiger.[98]

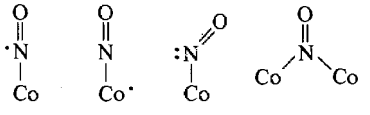
Reversibility in the coordination of NO to Co^{II} is not as widespread as it is with O_2, and this is supported by theory.[99] The Co—NO bond is stronger than the Co—O_2 bond, particularly in the absence of a sixth ligand, and with spin-pairing complete there is no driving force to form a Co—NO—Co dimer similar to that found with Co—O_2—Co complexes. Reversible coordination is however found in a few cases: in $[Co(NO)Cl(dipy)_2]^+$[100] and in some ill-defined [Co(NO)(amino acid)(base)] species.[101] Nitrosyl transfer from $[Co(NO)(DMGH)_2]$ to various electron-deficient Fe, Co, Ru and Rh complexes (*e.g.* to $[CoCl_2(PPh_3)_2]$,[102] to iron hemoproteins (*e.g.* hemoglobin),[103] and to O_2 leading to $[Co(NO_3)(DMGH)_2]$[104] may result from low concentrations of NO generated in equilibria such as (14) and (15) rather than from the direct addition of coordinated NO.

$$[Co(NO)(DMGH)_2] \rightleftharpoons [Co(DMGH)_2] + NO \quad (14)$$

$$[Co(NO)(DMGH)_2] + B \rightleftharpoons [Co(DMGH)_2B] + NO \quad (15)$$

47.4.1.2 Bonding and structure

A recent review on structural aspects is available,[105] and accounts of bonding have been given by Enemark and Feltham[106] and Mingos.[107] Three distinguishable coordination modes occur in transition metal nitrosyl: terminal linear (**15**) or (**16**), terminal bent (**17**), and bridging (**18**). These formally correspond to the coordination of NO and NO^+, NO^- and NO^- respectively. Terminal Co—ON coordination has not been found since N is the more basic end of the NO dipole, but it may be possible to form this isomer *via* reactions of Co=O or Co—O_2, or by appropriate cleavage of dimeric Co—N(O)NO—Co systems (see below). Some unusual bridging structures involving O and N coordination are known (Section 47.5.2.3).



(**15**) (**16**) (**17**) (**18**)

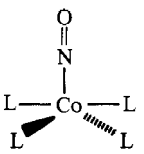
Low-oxidation-state cobalt complexes are invariably four or five coordinate with linear or nearly linear NO bonding. In these (**15**) is considered as NO coordinated to Co^{II} *via* a three-electron bond and (**16**) as NO^+ coordination to d^8 Co^I; the latter description is usually preferred although an overall molecular orbital is involved and individual oxidation states have no reality, and perhaps little usefulness. A general $\{MNO\}^n$ picture has been developed by Mingos[107] and by Enemark and Feltham[108] (n is the sum of electrons associated with the metal d orbitals and the π^*(NO) orbitals of NO groups), and a more specific $\{MNO\}^8$ scheme by Hoffmann and coworkers.[109] Larkworthy and coworkers have recently correlated ^{15}NO and ^{59}Co NMR shifts in five- and six-coordinate cobalt–nitrosyl complexes.[110] Shielding parameters decrease with decreasing MNO angle consistent with the argument that (as a general rule) bent nitrosyl is a weaker ligand than linear nitrosyl.

All known $[Co(NO)L_3]$ systems have close to tetrahedral symmetry (C_{3v}), with linear or nearly linear NO coordination (Table 12) consistent with a closed shell $\{CoNO\}^{10}$ configuration.[107,108,111] A square-planar structure should contain bent NO[108,109] but no example has yet been found. Fenske and coworkers have used extended MO calculations to predict acceptable ionization energies for $[Co(NO)(CO)_3]$,[112] and emphasize the relationship between isoelectronic CO and NO^+ by relating the electronic structure of $[Co(NO)(CO)_3]$ to symmetry lowering in $Ni(CO)_4$ and $Fe(CO)_5$. Evans and Zink use photochemical results to predict a bent NO in the excited state of $[Co(NO)(CO)_3]$.[113] Many four-coordinate systems contain two NO ligands with $[Co(NO)_2Cl]_2$ being tetrahedral and dimeric (Cl bridges), while $[Co(NO)_2I]_n$ is tetrahedral with infinite —I—Co—I— chains and no Co—Co bond (Table 12). Canadell and Eisenstein discuss factors influencing this choice of structure.[114] For tetrahedral monomeric $[M(NO)_2L_2]$ systems, Martin and Taylor have correlated M—N—O bending with the ON—M—NO angle; bending away of the O atoms accompanies larger NCoN angles while smaller angles are found when the nitrosyls point toward each other.[115] This is in agreement with theory,[106] and all $[Co(NO)_2L_2]$ structures are either close to the cross-over point (NCoN = 131 °) or the two nitrosyls point towards each other. However Kaduk and Ibers[116] point out that although available bonding schemes allow rationalization of known structural results, they are not yet able to predict confidently the ground state geometry or more detailed stereochemistry. The 'suck it and see' experimental approach is still of value.

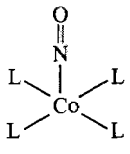
$[Co(NO)\{N(dppe)_3\}](BPh_4)$ has the $\{CoNO\}^9$ configuration and has a slightly distorted tetrahedral structure (Table 12) not unlike that found in high-spin $[CoCl\{N(dppe)_3\}](PF_6)$ (Table 40). The one unpaired electron (μ = 1.98 BM) lies predominantly in a metal-based orbital,[108] which is consistent with the considerable bending in the CoNO grouping (165 °).

For $\{CoNO\}^8$ systems the following conclusions arise.[109]

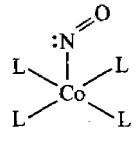
(i) for σ- and π-donating ligands a range of geometries is possible from a strongly bent square pyramid (**21**; C_s) to a less bent trigonal bipyramid (**19**; C_{2v}). A bent nitrosyl will tend to move its Co—N coordination axis in the direction of increased π overlap; in the square pyramid the bent structure (C_s) is favoured over the linear one (**20**; C_{4v}).



(19) C_{2v}



(20) C_{4v}

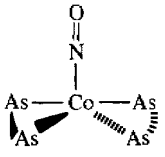


(21) C_s

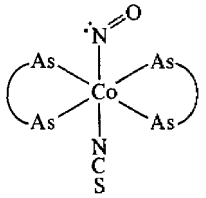
(ii) For π-acceptor ligands the trigonal bipyramid is favoured over the square pyramid with NO being equatorial (C_{2v}), and if a nitrosyl bends it will do so in the axial plane rather than in the equatorial plane.

(iii) Linear coordination is expected for axial coordination in a trigonal bipyramid and for basal coordination in the square pyramid. Geometrical deductions have also been made for mixed L systems.[109] Observed structures (Table 12) agree with these conclusions in most instances; thus $[Co(NO)(das)_2](ClO_4)_2$ is trigonal bipyramidal with linear NO coordination, $[Co(NO)(Me_2dtc)_2]$, $[Co(NO)(Pr^i_2dtc)_2]$ and [Co(NO)(salen)] are square pyramidal or tetragonal pyramidal with a bent NO, but $[Co(NO)Cl_2(PPh_2Me)_2]$ adopts an intermediate bent geometry with a stereochemistry of bending at variance with prediction. The second isomer found in the $[Co(NO)Cl_2(PPh_2Me)_2]$ system[117] has not been structurally defined but is thought to be a rotational isomer of the C_{4v} manifold rather than one of the more limiting geometries.[108]

No paramagnetic $\{CoNO\}^8$ systems have been found, but a dramatic change in stereochemistry accompanies the conversion of five-coordinate $[Co(NO)(das)_2](ClO_4)_2$ (**22**), to six-coordinate $[Co(NO)(NCS)(das)_2](ClO_4)$ (**23**).[118] The increased energy of the d_{z^2} orbital shifts the electron pair to the N atom, increasing the tendency to bend with NO^- coordination to Co^{III}.



(22) $\nu_{NO} = 1852\,cm^{-1}$
CoNO = 179°



(23) $\nu_{NO} = 1567\,cm^{-1}$
CoNO = 135°

Bent structures (**17**) and (**18**) are favoured for six-coordinate Co^{III} systems (CoNO, 120–130°; $\nu_{NO} \approx 1600\,cm^{-1}$) and are clearly distinguished from the others. Although often synthesized from d^7 Co^{II} complexes (or $Co^{2+}_{(aq)}$ + L) and $NO_{(g)}$, internal redox and coordination of NO^- is clearly indicated with the electron pair on N available for subsequent attack on electron-deficient species (*e.g.* O_2 or NO, see below). In the $\{MNO\}^8$ formalism the bending arises from the higher energy of the d_{z^2} metal-based orbital compared to $\pi^*(NO)$.[107] Noell and Morokuma[119] discuss this in some detail for $[Co(NO)(NH_3)_5]^{2+}$ and predict the observed eclipsing of an adjacent ammonia ligand (Table 12). The large structural *trans* effect in octahedral $\{MNO\}^8$ complexes is well recognized.[120] The *trans* Co—NH_3 bond in $[Co(NO)(NH_3)_5]^{2+}$ is some 24 pm longer than the *cis* Co—NH_3 bonds, and the large majority of bent Co^{III} systems have no *trans* ligand at all (Table 12).

Bridged μ-NO structures are found in a few instances (Table 12) and are in agreement with NO^- coordination and the absence of Co—Co bonding.

47.4.1.3 Reactivity

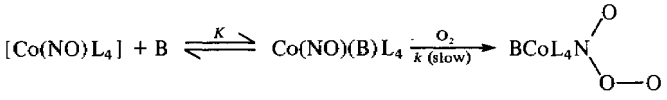
General accounts of the reactivity of coordinated nitrosyls are available.[106,121–124] A metal ion or metal complex is unable to generate the reactivity of ionic NO^+ towards nucleophiles (*i.e.* OH^-, RS^-, RHN^-) or of NO^- towards electrophiles (*i.e.* H^+, $PhCH_2X$), but it can present NO in a less reactive form under conditions inappropriate to the free ion. Thus linear coordination with $\nu_{NO} > 1886\,cm^{-1}$ may promote nucleophilic reactions at N, and bent coordination with the higher electron density on N ($\nu_{NO} < 1700\,cm^{-1}$) may promote electrophilic attack by H^+, O_2, NO and $PhCH_2Br$.[125] No cobalt nitrosyl is known to undergo nucleophilic attack on the nitrosyl group. Normally linear coordination is associated with four or five coordination and the nucleophile adds to the unsaturated metal instead. However a number of electrophilic reactions are known (Table 13). A recent discussion of these is recommended.[124]

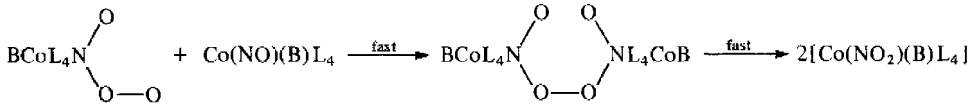
Table 13 Electrophilic Reactions of Cobalt–Nitrosyl Complexes

Complex	ν_{NO} (cm^{-1})	*Electrophile*	*Products*	*Ref.*
$[Co(NO)Br(diars)_2]^+$	1665	HBr	$[Co(HNO)\{Br(diars)_2\}]^{2+}$	1
[Co(NO)(salen)]	1624	O_2/py	$[Co(NO_2)(salen)py]$	2
[Co(NO)(acaen)]	1690	O_2/py	$[Co(NO_2)(acaen)py]$	2
[Co(NO)(sacsacen)]	1638	O_2/py	$[Co(NO_2)(sacsacen)py]$	2
$[Co(NO)(Me_2dtc)]$	1626	O_2/py	$[Co(NO_2)(Me_2dtc)py]$	2
$[Co(NO)(NH_3)_5]^{2+}$	1600	NO	$[Co_2(NH_3)_{10}(N_2O_2)]^{4+}$ (dimer) and/or $[Co(NH_3)_5OH]^{2+} + NO_2^- + N_2O$	8
$[Co(NO)(en)_2]^{2+}$	1660	O_2/MeCN	$[Co(NO_2)(en)_2(MeCN)]^{2+}$	2
cis-$[Co(NO)(en)_2(MeOH)]Cl_2$	1611	NO	*cis*-$[Co(NO_2)Cl(en)_2]Cl + N_2O$	5
$[Co(NO)(DMGH)_2(H_2O)]$	1641	O_2/py	$[Co(NO_3)(DMGH)_2py] + [Co(NO_2)(DMGH)_2py]$	3
$[Co(NO)(CO)_3]$	1806	NO	$[Co(N_3O_4)]_n$ (n = 2, polymer) + $[Co_4(NO)_8(NO_2)_3(N_2O_2)]$	7
$[Co(NO)(CO)_2X]^-$ (X = Br, I)	1767, 1712	$PhCH_2Br$	$PhCH{=}NOH + PhCH_2CO_2H$	4
$[Co(NO)(PPh_3)_3]$	1738	NO	$[Co(NO_2)(NO)_2(PPh_3)] + N_2O + N_2 + Ph_3PO$	5
$[Co(NO)(DMGH)_2(MeOH)]$	1640	NO/py	$[Co(NO_2)(DMGH)_2py]$	5
$[Co(NO)(8\text{-quin})_2]$	1650	NO	$NO[Co(NO_3)(NO_2)(8\text{-quin})_2]$	9

1. J. H. Enemark, R. D. Feltham, J. Rikker-Nappier and K. F. Bizot, *Inorg. Chem.*, 1975, **14**, 624.
2. S. G. Clarkson and F. Basolo, *Inorg. Chem.*, 1973, **12**, 1528.
3. W. C. Trogler and L. G. Marzilli, *Inorg. Chem.*, 1974, **13**, 1008.
4. M. Foa and L. Cassar, *J. Organomet. Chem.*, 1971, **30**, 123.
5. D. Gwost and K. G. Caulton, *Inorg. Chem.*, 1974, **13**, 414.
6. M. Rossi and A. Sacco, *Chem. Commun.*, 1971, 694.
7. R. Bau, I. H. Saberwal and A. B. Burg, *J. Am. Chem. Soc.*, 1971, **93**, 4926; C. E. Strouse and B. I. Swanson, *Chem. Commun.*, 1971, 55.
8. P. Gans, *J. Chem. Soc. (A)*, 1967, 943.
9. E. Miki, *Chem. Lett.*, 1980, 835.

Protonation is found with $[Co(NO)Br(das)_2]^+$, but it remains uncertain whether at N or O. Electrophilic attack by O_2 occurs with most uncharged tetragonal pyramidal five-coordinate systems (Table 13), but prior association with a base ligand such as pyridine appears necessary. The mechanism proposed by Clarkson and Basolo (Scheme 11) is probably general,[126] although neither intermediate has been identified. The function of B appears to be to make the N atom more nucleophilic by promoting the back-bonding component. However it has not been shown that coordinated NO_2 derives directly from coordinated NO, that exchange or reaction with uncoordinated NO is absent, and that only one of the O atoms in the product derives from O_2. Likewise the reaction with an excess of NO remains uncertain in detail although the major product is the same, *i.e.* the coordinated nitro group. In a recent ^{15}N study by Miki[127] on $[Co(NO)(8\text{-quin})_2]$ an 80% yield of $NO[Co(NO_2)(NO_3)(8\text{-quin})_2]$ was obtained (equation 16); liberated N_2O and coordinated NO_3^- derived exclusively from $NO_{(g)}$, while coordinated NO_2^- derived exclusively from coordinated NO. This supports a role for $N_2O_{2(g)}$ and eliminates homolytic N—O fission in an intermediate such as (**24**).

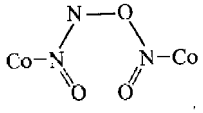




$$\text{rate} = \frac{kK[B][O_2][Co(NO)L_4]}{1 + K[B]}$$

Scheme 11

$$[Co(^{14}NO)(8\text{-quin})_2] + 8\,^{15}NO \longrightarrow {}^{15}NO[Co(^{14}NO_2)(^{15}NO_3)(8\text{-quin})_2] + 3\,^{15}N_2O \qquad (16)$$



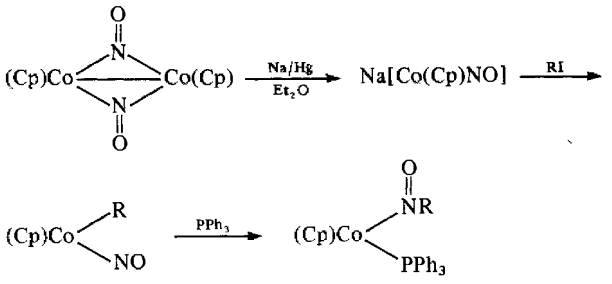
(24)

Further studies are required to support and extend these mechanistic aspects. Likewise ^{15}N tracer studies are needed to determine the source of coordinated NO_3^- in $[Co(NO_3)(DMGH)_2py]$ produced in the aerial oxidation of $[Co(NO)(DMGH)_2]$ in the presence of pyridine,[104] and to determine the source of N in N_2 and N_2O produced in the very unusual reduction of NO by NH_3 (or aliphatic amines) as catalyzed by *cis*- and *trans*-$[Co(NO_2)_2(en)_2]X$ ($X = NO_2^-$, NO_3^-).[128]

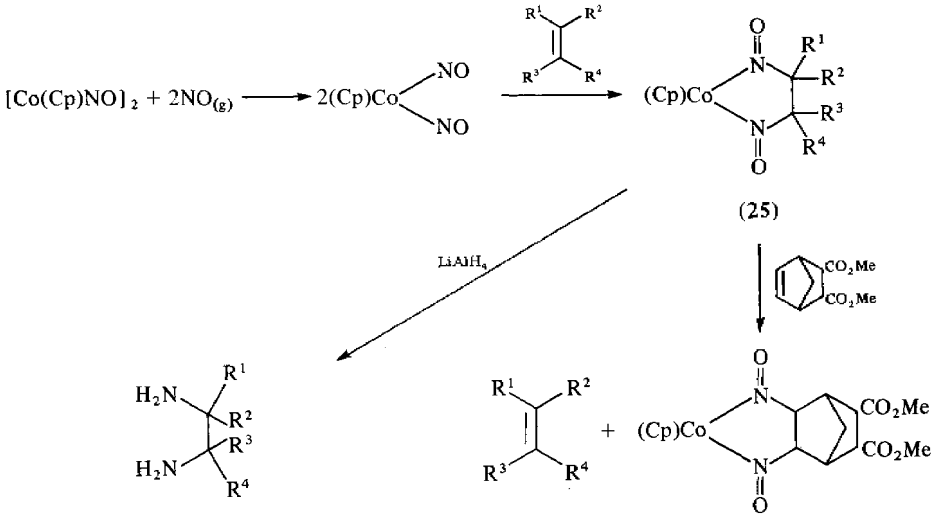
Bergmann and coworkers have used $[Co(Cp)(\mu\text{-}NO)]_2$ to investigate NO insertion into metal–carbon bonds (Scheme 12; crystal structure, R = Et),[129] and to study addition of coordinated NO to alkenes (Scheme 13).[130,131] The product dinitrosoalkene complex (**25**) can be reduced by $LiAlH_4$ to the primary diamine and can undergo both thermal and photochemical alkene exchange. The catalytic reduction of nitric oxide by amines to $N_2O_{(g)}$ and $N_{2(g)}$ has been found to occur in the presence of *cis*-$[Co(NO_2)_2(en)_2](NO_3)$ and other Co^{III} amines both in aqueous solution and in Y-type zeolites.[128,132] Co^{II} ions incorporated into Y-type zeolites are also effective catalysts in the presence of NH_3 and '$[Co(NO)_2(NH_3)]^{2+}$' has been proposed as a steady-state intermediate.[133] Likewise the catalytic reaction between NO and CO on the surface of Co_3O_4 generating N_2 and CO_2 has considerable interest in the control of nitrogen oxide emissions.[134] A general account of the use of cobalt nitrosyls in pollution control has been given recently by Pandey.[135]

47.4.2 Nitro (NO_2) and Nitrito (ONO)

$[Co(NO_2)(NH_3)_5]X_2$ and $[Co(ONO)(NH_3)_5]X_2$ represent the first examples of linkage isomerism in coordination chemsitry.[136–138] The former nitro isomer is yellow, the latter nitrito is orange, and



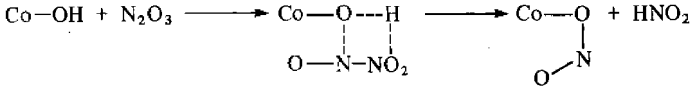
Scheme 12



Scheme 13

they are easily prepared.[139] Nitro complexes are usually formed *via* nitrito intermediates and heating a $Co—OH_2^{n+}$ complex with $NaNO_2$ at 60–80 °C in 0.01 M H^+ for 20 minutes is often sufficient to isomerize the latter. For systems where water exchange is rapid, direct displacement of coordinated H_2O by NO_2^- may occur. Some useful preparations are collected in Table 14. $Na_3[Co(NO_2)_6]$ is particularly useful in synthesis since the first four or five nitro groups can usually be displaced successively by other ligands, particularly chelating amines.

Co—ONO complexes are formed by addition of Co—OH to $N_2O_{3(aq)}$. Pearson, Henry, Bergmann and Basolo[140] first described the rate law, rate = $k[CoOH_2][HNO_2][NO_2^-]$, and van Eldik and coworkers have recently confirmed the second-order dependence on $[NO_2^-]_T$ over a wide pH range.[141] Murmann and Taube demonstrated retention of the Co—O bond by ^{18}O tracer methods (equation 17).[142] Other $Co—OH^{n+}$ systems behave similarly and the reaction is relatively fast at room temperature and maximizes at a pH between 3 and 5. Specifically labelled complexes (*e.g.* $Co—^{18}ONO$, $Co—ON^{18}O$) have recently been made.[143]



(17)

Structures of several $Co—NO_2^{n+}$ and $Co—ONO^{n+}$ complexes are known (Table 15, for examples). The $Co—NO_2$ group results in no major structural *trans* influence although Juranic and coworkers[144] report a 5 pm shortening in the $Co—NO_2$ bond when the *trans* ligand is carboxylate.

The $Co—NO_2$ bond is usually very robust and nitro complexes are well known for their stability in aqueous solution. A kinetic *trans* influence of the NO_2 group has not been clearly demonstrated. Hydrolysis is very slow in water but does occur (*cis,trans*-$[Co(en)_2(NO_2)_2]^+$ 3×10^{-8} s^{-1}, 25 °C);[145] heating in strong acids or in NaOH solution results in more rapid hydrolysis. Photolysis of the solid

Table 14 Preparations: Some Cobalt(III) Nitro (NO_2) and Nitrito (ONO) Complexes

Complex	*Preparations*	*Comments*	*Ref.*
Nitro complexes			
$Na_3[Co(NO_2)_6]$	$Co(NO_3)_2 \cdot 6H_2O + NaNO_2 + HOAc$; air, 30 min	Yellow; v. water sol.	9
$K_2[Co(NO_2)_5(NH_3)]$	$K_2[Co(CO_3)(NO_2)_3NH_3] + HOAc$	Yellow	11
trans-$K[Co(NO_2)_4(NH_3)_2]$ (NH_4^+ is Erdmann's salt)	$CoCl_2 \cdot 6H_2O + NaNO_2 + NH_4Cl + NH_4OH$; air oxidation	Yellow-brown	1, 11
$K[Co(NO_2)_4(en)]$	$Co(CO_3)_3^{3-} + NaNO_2 + NH_4Cl + en + NH_4OH$	Yellow	11
$[Co(NO_2)_3(NH_3)_3]$	$Co(CO_3) + HOAc + NaNO_2 + NH_4OH$; $H_2O_2 + C$ + heat	Yellow-brown; various isomers	2, 10
$K[Co(CO_3)(NO_2)_3(NH_3)]$	$Co(CO_3)_3^{3-} + NH_4Cl + NaNO_2$; warm HOAc	Orange-brown	11
$[Co(NO_2)_3(dien)]$	$Co(NO_3)_2 \cdot 6H_2O + NaNO_2 + NaOH + HOAc$; dien + O_2; pH 5–6	Yellow	3
cis-$[Co(NO_2)_2(NH_3)_4]NO_3$	$[Co(CO_3)(NH_3)_4]NO_3 + HNO_3 + NaNO_2$; heat	Yellow	4, 11
trans-$[Co(NO_2)_2(NH_3)_4]NO_3$	$CoCl_2 \cdot 6H_2O + NaNO_2 + NH_4Cl + NH_4OH$; air oxidation	Yellow-brown	4
cis-$[Co(NO_2)_2(en)_2]NO_3$	$K_3[Co(NO_2)_6]$ + en; 70 °C HNO_3; resolved using KSbOtart	Yellow; $[\alpha]_{589}$ 44° (Br)	6
trans-$[Co(NO_2)_2(en)_2]NO_3$	$Co(NO_3)_2 \cdot 6H_2O + NaNO_2 + en + HNO_3$; air, 20 min	Yellow	5
$K[Co(NO_2)_2(Gly)_2]$	$Co(OAc)_2 \cdot 4H_2O + GlyH + KOH + KNO_2$; air, 12 h	Brown	7
$[CoNO_2(NH_3)_5](NO_3)_2$	$[Co(CO_3)(NH_3)_5]NO_3 + HNO_3 + NaNO_2$; 15 min, r.t.	Yellow-brown; ε_{457} 96, ε_{324} 1720	8, 11, 14
α-$[Co(NO_2)_2(trien)]Cl$	$CoCl \cdot 6H_2O$ + trien HCl + $NaNO_2$; air, 0 °C	Yellow	12
Nitrito complexes			
$[Co(ONO)(NH_3)_5]X_2$ (X = Cl^-, ClO_4^-)	$[Co(OH_2)(NH_3)_5]X_3 + HX + NaNO_2$	Orange; ε_{491} 70.5, ε_{361} 259	13, 14
cis-$[Co(ONO)_2(en)_2]ClO_4$	$[CoCO_3(en)_2]ClO_4 + HClO_4$; $NaNO_2$, 0 °C	Orange; ε_{475} 140, ε_{328} 1443	15, 16, 17
trans-$[Co(ONO)_2(en)_2]ClO_4$	$[CoCO_3(en)_2]ClO_4 + HClO_4$; NaOH, 90 °C, 3 min; neut. $HClO_4 + NaNO_2$, 0 °C	Red-orange; ε_{515} (sh) 66.8	15, 18, 17
$(+)_D$-*cis*-$[Co(ONO)(NO_2)(en)_2]ClO_4$	$(+)_D$-$[CoCO_3(en)_2]ClO_4 \cdot 0.5H_2O$	$[M]_{589}^{20}$ 240°, $[M]_{436}^{20}$ 1430°	19
cis-$[Co(ONO)(NO_2)(en)_2]NO_3$	*cis*-$[Co(Cl)(NO_2)(en)_2]Cl + AgNO_3 + H_2O$; $NaNO_2$ pH 4.5, 15 °C, 20 min	Orange-tan	20
cis-$[Co(ONO)_2(NH_3)_4]X$ (X = NO_3^-, ClO_4^-)	$[CoCO_3(NH_3)_4]NO_3 + HNO_3$; $NaNO_2$, 5 °C, 10 min	Red; ε_{500} 92, ε_{356} 480	21, 15
cis-$[Co(OH_2)(ONO)(NH_3)_4](NO_3)_2$	$[CoCO_3(NH_3)_4]NO_3 + NaNO_2 + HNO_3$; 0–2 °C, 5 min	Carmine red	21
cis-, *trans*-$[Co(NH_3)(ONO)(en)_2](NO_3)_2$	$[Co(NH_3)(OH_2)(en)_2]^{2+} + NaNO_2$ (pH 4)	Synthesis of other complexes also reported	22
trans-$[Co(NCS)(ONO)(en)_2]X$	*trans*-$[Co(NCS)(OH_2)(en)_2](NO_3)_2 + NaNO_2$; r.t.	Orange-red; ε_{515} 145	23

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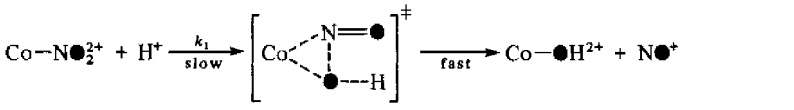
Table 15 Structures: Some Recent Nitro and Nitrito Cobalt(III) Complexes

Complex	*Crystal data*[a]	*Comments*	*Ref.*
cis-$[Co(NO_2)_2(tn)_2]Cl_2 \cdot H_2O$	*C2/c*, monoclinic; $CoN(O_2)$ 192, 194; CoN 198–200; NO 123; ONO 119°	Enantiomeric crystal; chair conformations of tn	1
α,β-$[Co(NO_2)(pydien)](ClO_4)_2$	*Cc*, monoclinic; $CoN(O_2)$ 210; CoN 194–198; NO 105; ONO 135°	Red crystals; prepared from μ-peroxo dimer; yellow (ONO) isomer available	2
mer-$[Co(NO_2)_3(dien)]$	*Pbca*, orthorhombic; $CoN(O_2)$ 191.6–199.7; CoN 194.6–195.0; NO 118–120; ONO 119–120°	Dist. oct. meridional coordination of dien	3
sym fac-$[Co(NO_2)_2(dien)(NH_3)]Cl$	$P2_1/n$, monoclinic; $CoN(O_2)$ 193–196; CON 195–198; NO 123–125; ONO 118–119°	Dist. oct. facial coordination of dien; one of less predominant isomers	4
$[Co(NO_2)(NH_3)_4]Cl_2$	*C2/c*, monoclinic; $CoN(O_2)$, 191; CoN 196–198; NO 123; CoNO 119.6°, ONO 120.8°	Oct; no significant *trans* effect	7
sym-A-$[Co(NO_2)_2(trien)]Cl_2 \cdot H_2O$	$P2_12_12_1$; $CoN(O_2)$ 191, 193; CoN 195–197; NCON 89.2°	Spontaneous resolution	8
cis-A-$[Co(NO_2)_2(en)_2]Cl$	$P2_1$; $CoN(O_2)$ 192.5; CoN, 196–198; NCoN 88.6°	Spontaneous resolution	8
trans-K$[Co(NO_2)_4(NH_3)_2]$	$P2_12_12_1$; $CoN(O_2)$ 193–197; CON 193, 195	*trans* NH_3	8
trans-$[Co(NCS)(ONO)(en)_2]X$ and *trans*-$[Co(NCS)(NO_2)(en)_2]X$ ($X = I^-$, ClO_4^-)	$P2_1$, monoclinic; low temp. data 245 K (I), 165 K (ClO_4); CO(O) 191.5, 187.5; $CoN(O_2)$ 189.7, 188.1	Solid state ONO → NO_2, and reverse photochemical isomerization studied by powder methods	5
$[Co(ONO)(NH_3)_5]Cl_2$	$P2_1nb$, orthorhombic; CoO, 192.7; CoN, 195–197°; NO 124.4; CoON, 131.3°; ONO 125.3°	Solid state isomerization and reverse photochemical process studied by powder methods	6

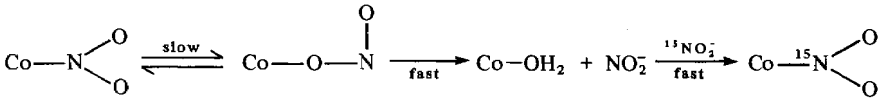
[a] Bond lengths in pm.

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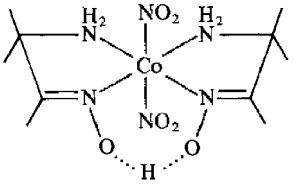
can result in complete isomerization[146] and this may prove a useful method for the complete removal of the nitro group. Acid hydrolysis of $[Co(NO_2)(NH_3)_5]^{2+}$ follows the rate law $k_{obs} = k(\text{antilog } H_0)$ (H_0 = Hammett acidity constant) and is very slow at ambient temperatures.[147] Jolly and coworkers showed many years ago that the O atom in the $[Co(NH_3)_5OH_2]^{3+}$ product derives from coordinated NO_2^- and suggested $Co—ONO^{2+}$ as a possible intermediate (equation 18).[148] The $[Co(NO_2)_4en]^-$ ion hydrolyzes more rapidly with $k_0 = 2.8 \times 10^{-4}\,s^{-1}$ and $k_H = 2.2 \times 10^{-2}\,mol^{-1}\,dm^3\,s^{-1}$ at 25 °C, $k_{obs} = k_0 + k_H[H^+]$; this reaction is reversible in weakly acidic solution.[149] Murmann and Rahmoeller in a recent elegant study demonstrated the independence of the rate of the NO_2^- exchange reaction of (**26**) on $[NO_2^-]$, solvent and added electrolytes by using ^{15}N- and ^{18}O-labelled NO_2^-;[150] (**26**) is especially labile, and the aqua–nitro complex is known to anate rapidly. The mechanism given by equation (19) probably holds in a general sense.



(18)

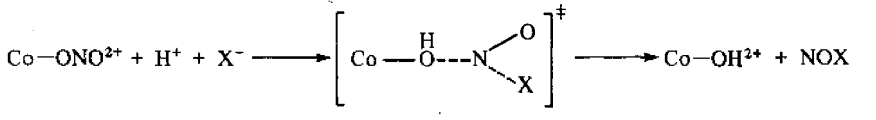


(19)



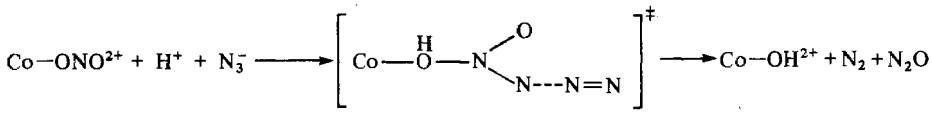
(**26**)

The Co—ONO bond is less robust and can be cleaved by mild acid (the reverse of its formation) but this appears to occur with O scrambling;[143,151] alternatively, it can be cleaved by the action of HN_3. Acid hydrolysis is markedly catalyzed by Cl^-, Br^-, I^- and SCN^- with major terms in the rate law being $k_{obs} = k_1[H^+] + k_2[H^+][X^-]$.[152] Thus the half-life for aquation of $[Co(ONO)(NH_3)_5]^{2+}$ in $HClO_4$ (0.1 mol dm^{-3}), $LiClO_4$ (0.9 mol dm^{-3}) is *ca.* 1 h at 25 °C, but with the same $HClO_4$ containing LiCl (0.9 mol dm^{-3}) it is *ca.* 1.5 min. A transition state (**27**; equation 20) is proposed.[152] Such Cl^- catalysis could possibly be used in conjunction with the photolytic isomerization of $Co—NO_2^{2+}$ to cause rapid hydrolysis of stable nitro species. The HN_3-promoted reaction has been extensively studied by Seel and coworkers.[152,153] The rate law takes the form $k_{obs} = k_1 + k_2[HN_3]$, where k_1 is the spontaneous isomerization rate (Table 16; $k_2 = 5.53 \times 10^{-3}$ and $2 \times 10^{-2}\,dm^3\,mol^{-1}\,s^{-1}$, 25 °C for $[Co(ONO)(NH_3)_5]^{2+}$[153] and *cis*-$[Co(ONO)_2(en)_2]^+$,[154] respectively). In this case N_3^- attack results in gaseous N_2 and N_2O products (equation 21). The lower $\Delta H^{\ddagger}$ for the assisted reaction (74 *vs.* 93 kJ mol^{-1}) means that isomerization can be prevented at low temperatures (~ 5 °C) by using reasonable N_3^- concentrations.



(20)

(**27**)



(21)

Present interest lies in the Co—ONO to $Co—NO_2$ interconversion. This is spontaneous in the forward direction (Co^{III} favours N and O coordination) and light catalyzed in the reverse. The solid-state reaction has been studied in some detail by Grenthe and Nordin.[155,156] These authors compared the structures of *trans*-$[Co(NCS)(ONO)(en)_2]X$ and *trans*-$[Co(NCS)(NO_2)(en)_2]X$ ($X = I^-$, ClO_4^-) and propose an intramolecular rotation in the Co—ONO plane for the spon-

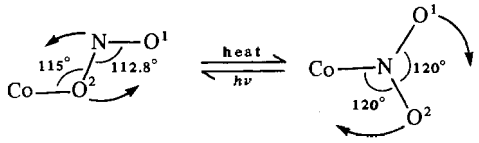
Table 16 Rate Data for the Isomerization $CoONO \rightarrow CoNO_2$

Complex	k (s^{-1})	*Comments*[a]	*Ref.*
cis-$[Co(ONO)(NO_2)(en)_2]^+$	7.5×10^{-4} (35 °C)	Same rate at $I = 0$ and in 1.0 M $NaNO_2$, 0.01 M HNO_2	1
$[Co(ONO)(NH_3)_5]^{2+}$	1.7×10^{-5} (20 °C)	$\Delta H^{\ddagger}$, 92; $\Delta S^{\ddagger}$, −21	2
$[Co(ONO)(NH_3)_5]Cl_2$	1.0×10^{-4} (58 °C)	Solid state (KBr disc) $\Delta H^{\ddagger}$, 109	2
$[Co(ONO)(NH_3)_5]^{2+}$	7.8×10^{-5} (25 °C)	$\Delta H^{\ddagger}$, 93; $\Delta S^{\ddagger}$, -10 ± 4, $\Delta V^{\ddagger}$, −6.5	4
$[Co(ONO)(NH_3)_5]^{2+}$	2.4×10^{-6} (25 °C)	Sulfolane solvent; $\Delta V^{\ddagger}$, -6.8 ± 0.7	3
$[Co(ONO)(NH_3)_5]^{2+}$	8×10^{-6} (25 °C)	DMF solvent; $\Delta H^{\ddagger}$, 93 ± 1; $\Delta S^{\ddagger}$, -29 ± 3	3
$[Co(ONO)(NH_3)_5]^{2+}$	2.5×10^{-5} (25 °C)	DMSO solvent; $\Delta V^{\ddagger}$, -3.6 ± 0.3; $\Delta H^{\ddagger}$ 98 ± 3; $\Delta S^{\ddagger}$, -4 ± 8	3
$[Co(ONO)(NH_3)_5]^{2+}$	$k_{Hg} = 1.16 \times 10^{-2}$ ($dm^3\,mol^{-1}\,s^{-1}$)	$k_{obs} = k + k_M[Mn^+]$	
$[Co(ONO)(NH_3)_5]^{2+}$	$k_{Ag^+} = 2.85 \times 10^{-4}$ ($dm^3\,mol^{-1}\,s^{-1}$)	$M^{n+} = Hg^{2+}$, Cd^{2+}, Ag^+	
$[Co(ONO)(NH_3)_5]^{2+}$	$k_{Cd^{2+}} = 4.4 \times 10^{-5}$ ($dm^3\,mol^{-1}\,s^{-1}$)	25 °C, $I = 1.0$	5
$[Co(ONO)(NH_3)_5]^{2+}$	$k_{OH} = 5.9 \times 10^{-3}$ ($dm^3\,mol^{-1}\,s^{-1}$)	$k_{obs} = k + k_{OH}[OH^-]$; $\Delta V^{\ddagger}$, +27	10
$[Co(ONO)(NH_3)_5](ClO_4)_2$	$k_{NH_3} = 8.1 \times 10^{-6}$ ($kg\,mol^{-1}\,s^{-1}$)	$k_{obs} = k[NH_4ClO_4]^{-1}$	9
cis-$[Co(ONO)_2(en)_2]^+$	8.0×10^{-4} (25 °C)	$\Delta H^{\ddagger}$, 65; $\Delta S^{\ddagger}$, −86; $\Delta V^{\ddagger}$, −5.6	6, 9
cis-$[Co(ONO)(NO_2)(en)_2]^+$	2.4×10^{-4} (25 °C)	$\Delta H^{\ddagger}$, 82; $\Delta S^{\ddagger}$, −39; $\Delta V^{\ddagger}$, −6.9	7
cis-$[Co(ONO)(NO_2)(en)_2]^+$	$k_{OH} \approx 4 \times 10^{-2}$ ($dm^3\,mol^{-1}\,s^{-1}$, 25 °C)	$k_{obs} = k + k_{OH}[OH^-]$; $\Delta V^{\ddagger}$, 19.7	6, 9
trans-$[Co(ONO)_2(en)_2]^+$	$8–10 \times 10^{-4}$ (35 °C)	$\Delta H^{\ddagger}$, 97; $\Delta V^{\ddagger}$ −3.6	7
trans-$[Co(ONO)_2(en)_2]^+$	$k_{OH} \approx 0.1$ ($dm^3\,mol^{-1}\,s^{-1}$, 25 °C)	$k_{obs} = k + k_{OH}[OH^-]$; $\Delta V^{\ddagger}$, 13.6	8
cis-$[Co(OH_2)(ONO)(NH_3)_4]^{2+}$	4×10^{-5} (30 °C)		8
cis-$[Co(ONO)_2(NH_3)_4]^+$	2.4×10^{-4} (25 °C)	$\Delta H^{\ddagger}$, 34	11
cis-$[Co(ONO)(NO_2)(NH_3)_4]^+$	1.0×10^{-4} (25 °C)		11
cis-$[Co(ONO)(NCS)(en)_2]^+$	8.1×10^{-4} (25 °C)	$\Delta H^{\ddagger}$, 81; $\Delta S^{\ddagger}$, −31	11
cis-$[Co(ONO)(CN)(en)_2]^+$	4.2×10^{-4} (25 °C)	$\Delta H^{\ddagger}$, 97; $\Delta S^{\ddagger}$, 15	11
cis-$[Co(ONO)(NH_3)(en)_2]^{2+}$	1.7×10^{-4} (25 °C)	$\Delta H^{\ddagger}$, 91; $\Delta S^{\ddagger}$, −13	11
trans-$[Co(ONO)(NH_3)(en)_2]^{2+}$	4.2×10^{-5} (25 °C)	$\Delta H^{\ddagger}$, 94; $\Delta S^{\ddagger}$, −13	11
cis-$[Co(ONO)(NH_3)(tn)_2]^{2+}$	1.4×10^{-4} (25 °C)		11
trans-$[Co(ONO)(NH_3)(cyclam)]^{2+}$	6×10^{-6} (25 °C)	$\Delta H^{\ddagger}$, 115; $\Delta S^{\ddagger}$, 40	11
mer-$[Co(ONO)(en)(dien)]^{2+}$	1.85×10^{-4} (25 °C)	$\Delta H^{\ddagger}$, 91; $\Delta S^{\ddagger}$, −10.5	11
fac-$[Co(ONO)(en)(dien)]^{2+}$	4.0×10^{-5} (25 °C)	$\Delta H^{\ddagger}$, 96; $\Delta S^{\ddagger}$, −7.4	11

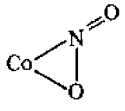
[a] $\Delta H^{\ddagger}$ in $kJ\,mol^{-1}$, $\Delta S^{\ddagger}$ in $J\,K^{-1}\,mol^{-1}$, $\Delta V^{\ddagger}$ in $cm^3\,mol^{-1}$.

1. R. G. Pearson, P. M. Henry, J. G. Bergmann and F. Basolo, *J. Am. Chem. Soc.*, 1954, **76**, 5921.
2. F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1962, **1**, 1.
3. W. G. Jackson, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *Aust. J. Chem.*, 1982, **35**, 1561.
4. M. Mares, D. A. Palmer and H. Kelm, *Inorg Chim. Acta*, 1978, **27**, 153.
5. W. G. Jackson, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *Inorg. Chem.*, 1980, **19**, 904.
6. F. Seel and D. Meyer, *Z. Anorg. Allg. Chem.*, 1974, **408**, 283.
7. W. Rindermann and R. van Eldik, *Inorg. Chim. Acta*, 1983, **68**, 35.
8. R. G. Yalman and T. Kuwana, *J. Phys. Chem.*, 1955, **59**, 298.
9. W. Rindermann, R. van Eldik and H. Kelm, *Inorg. Chim. Acta*, 1982, **61**, 173.
10. S. Balt, H. J. A. M. Kuipers and W. E. Renkema, *J. Chem. Soc., Dalton Trans.*, 1983, 1739.
11. K. Miyoshi, N. Katoda and H. Yoneda, *Inorg. Chem.*, 1983, **22**, 1839.

taneous reaction (equation 22).[155] An intermolecular process would involve at least a 400 pm movement of N in the crystal. Powder photography ($X = ClO_4^-$, 293 K) shows a gradual transformation indicating a homogeneous change (*i.e.* separate phases do not appear to coexist in the sample). Photochemical irradiation reverses the process (80% complete) with full retention of crystallinity and of structure. The authors conclude that minimal atomic and molecular movement occurs and that both processes are topochemical. A somewhat more complex solid-state reaction occurs with $[Co(ONO)(NH_3)_5]Cl_2$.[156] A fast spontaneous Co—ONO → Co—NO_2 change is followed by a slower and more substantial structural change to thermodynamically stable crystalline $[Co(NO_2)(NH_3)_5]Cl_2$ (monoclinic, C_2/c_1). The initial isomerization retains the original space group (orthorhombic, $P_{2_1}nb$) but ionic and intermolecular contacts apparently prevent a simple rotation in the Co—ONO plane in this case, and a more complex structural movement is necessary. The reverse photochemical reaction of the stable $[Co(NO_2)(NH_3)_5]Cl_2$ crystal gives a new crystalline modification of $[Co(ONO)(NH_3)_5]Cl_2$, which easily reverts to the original on standing. No ionic Cl^- is incorporated in these processes, and crystal dimensions again imply intramolecular reactions. Johnson and Pashman claim to have observed the 'transition state' complex involving bidentate species (A) in a low temperature photolytic study.[157]



(22)



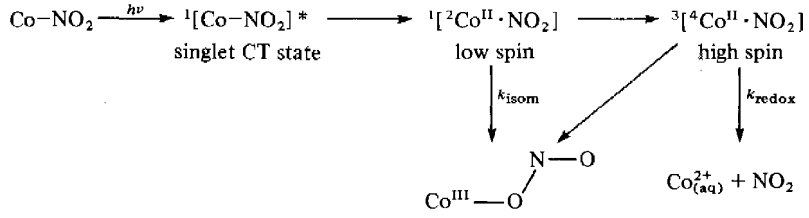
(A)

The solution chemistry of the Co—ONO to Co—NO_2 isomerization has now been widely studied, mostly with the pentaammine system. Basolo and coworkers initially showed the rate to be independent of added NO_2^- (Table 16) and the intramolecular nature was confirmed by ^{18}O-labelling studies.[142] Murmann earlier had shown that optically active $(+)_{589}$-*cis*-$[Co(NO_2)(ONO)(en)_2]^+$ isomerized with full retention of configuration[158] and this has been confirmed for the OH^--catalyzed reaction in a recent study.[143] The rate for the pentaammine complex has been recently measured in 16 solvents and the 100-fold variation (THF slowest, H_2O fastest) has been interpreted in terms of various solvent parameters; mild catalysis by F^-, AcO^- and NEt_3 is found in Me_2SO.[159] Hg^{2+}, Cd^{2+} and Ag^+ catalyze the reaction in water (Table 16) and in acetone (Zn^{2+} also), and the lack of competitive coordination by H_2O, AcO^- and NO_3^- for the induced path in water again point to a concerted intramolecular process.[159] The rate is also OH^- catalyzed (Table 16), $k_{obs} = k + k_{OH}[OH^-]$, and the large $\Delta V^{\ddagger}$ for k_{OH} ($27 \pm 1.4\,cm^3\,mol^{-1}$) points to the normal S_N1cb mechanism with a large $\Delta\bar{V}$ ($22\,cm^3\,mol^{-1}$) for ammine deprotonation.[143] A similar situation has been found with *cis*- and *trans*-$[Co(ONO)_2(en)_2]^+$ (Table 16).[160] The reaction has also been studied in $NH_{3(l)}$, where $k_{obs} = k[NH_4ClO_4]^{-1}$, indicating isomerization *via* $[Co(NH_2)(ONO)(NH_3)_4](ClO_4)$ (Table 16) and experiments using the specifically labelled *trans*-$^{15}NH_3$ complex show retention of geometrical configuration and the absence of competition for entry by NH_3.[161]

Oxygen scrambling has been demonstrated by Sargeson and coworkers using specifically labelled Co—^{17}ONO and Co—ON^{17}O pentaammine complexes.[151] Acid cleavage results in Co—$^{17}OH_2^{3+}$ from both reactants and this confirms the earlier 50% scrambling result obtained using ^{18}O-labelled complexes.[143] The spontaneous reaction gives a $k(O \rightarrow O)/k(O \rightarrow N)$ ratio of 1.2 indicating a slightly faster rate for the O to O interconversion. This is difficult to reconcile with the intramolecular rotation mechanism (equation 22) proposed for the solid-state reaction and suggests a more complex twist mechanism or momentary complete bond cleavage and re-entry of O and N.

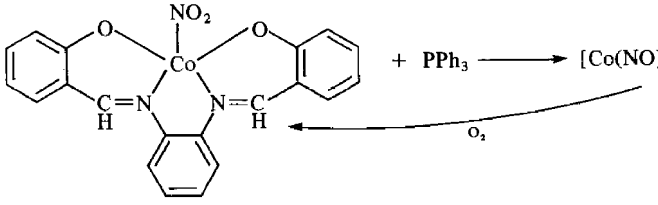
The solution photochemistry of Co—NO_2 leads to both redox decomposition (Co_{aq}^{2+}) and isomerization to Co—ONO ($[Co(NO_2)(NH_3)_5]^{2+}$,[162] *cis*-$[Co(NO_2)_2(en)_2]^+$[163]). The ratio of products is wavelength independent, indicating efficient mixing of reactive LMCT and LF singlet excited states.[164] A semiquantitative model has been described by Endicott.[165] The isomerization pathway is facilitated by increasing solvent viscosity suggesting that the redox process may come at a later stage.[166] A possible mechanism is given by Scheme 14. Scandola and colleagues report acetone

sensitization of both k_{redox} and k_{isom} by an energy-transfer process and have discussed the relative energetics in some detail.[167] No attempt has been made to see if the excited-state species compete for 'spectator' anions (*e.g.* ion-paired NO_3^-) but apparently $Co—OH_2^{3+}$ is not formed. In aerated acetonitrile O_2 acts as a scavenger forming a $Co^{III}—O_2^-$ adduct, while in the absence of O_2 another Co^{III} complex is formed.[168] There has been a report that photolysis of *cis*-$[Co(OC_2O_3)(NO_2)(en)_2]$ leads to *ca.* 10% chelated $[Co(O_2C_2O_2)(en)_2]^+$ as well as $Co^{2+}_{(aq)}$,[169] but whether this results from direct entry of the free carboxylate group in the excited state or from subsequent chelation in the aqua complex is not yet known.



Scheme 14

Unlike Co—NO complexes (Section 47.4.1.3), the reactivity of coordinated nitro and nitrito ligands toward electrophiles is not well explored. However Tovrog and his colleagues at Allied Chemical Corporation have recently shown that (**28**) catalytically oxidizes PPh_3 in a bimolecular transfer of O from coordinated NO_2 (equation 23),[170] and that (**28**) and the similar porphyrin complex $[Co(TPP)(py)(NO_2)]$ both catalyze the oxidation of primary and secondary alcohols to aldehydes and ketones in the presence of the Lewis acids $BF_3 \cdot H_2O$ or $LiPF_6$; non-radical pathways are proposed.[171] Internal redox in $[Co(NO_2)_2(bipy)_2]X$ also occurs on heating, with oxygen transfer, to give the Co^{II} complex $[Co(NO_3)X(bipy)_2]$ and NO ($X = Cl^-$, Br^-, I^-, ClO_3^-, ClO_4^-).[172]



(23)

(28)

47.4.3 Nitriles

47.4.3.1 Cobalt(III)

Cobalt(III) nitrile complexes are easily prepared *via* displacement of a poorly coordinating ligand such as $(MeO)_3PO$, $(EtO)_3PO$ or $CF_3SO_3^-$ by RCN. Thus treatment of $[Co(N_3)_x(NH_3)_{6-x}]^{(3-x)+}$ with NOX ($X = ClO_4^-$, BF_4^-, $OSO_2CF_3^-$) in $(EtO)_3PO$, followed by addition of the nitrile and warming, or addition of the nitrile to $[Co(amine)_x\{(MeO)_3PO\}_{6-x}](ClO_4)_3$ and warming, or dissolution of $[Co(amine)_x(OSO_2CF_3)_{6-x}](CF_3SO_3)_{x-3}$ ($x = 5, 4, 3$) in the appropriate nitrile and warming, leads to excellent yields (Table 17). Jordan, Sargeson and Taube were the first to use such methods,[173] and subsequent reports by Balahura,[174] Sargeson and coworkers[175] and Kupferschmidt and Jordan[188] are recommended for more recent preparations. Most nitrile complexes are stable in neutral to acidic aqueous solution, and have yellow-orange colours characteristic of amine complexes.

The reactivity of coordinated nitriles towards nucleophiles, and electrophiles when deprotonated, has been of major interest. Addition of OH^- to the nitrile carbon occurs readily in alkaline solution, $k_{obs} = k_{OH}[OH^-]$, and the rate is increased some 10^6–10^7 times by coordination (equation 24).[176,177] k_{OH} has values of 1–50 $mol^{-1}\,dm^3\,s^{-1}$ for R = alkyl[177] [*e.g.* 3.4 (Me); 35 ($CH{=}CH_2$)] and varies over a wider range for substituted benzonitriles following a Hammett relationship.[178] For 2-cyanobenzonitrile addition of one equivalent of OH^- is followed by intramolecular amidine formation on treatment with further alkali (**29**), or by rearrangement in acid and hydrolysis to the diamide (**31**), or cyclization to the alternative amidine isomer (**32**; Scheme 17).[179] The alkaline hydrolysis of the

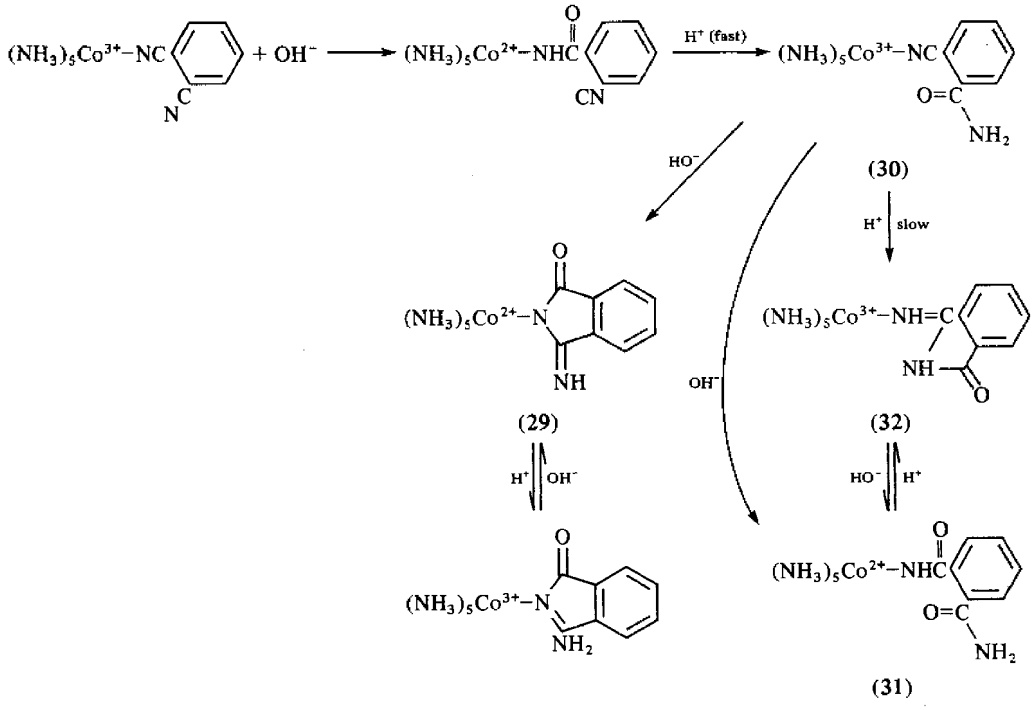
Table 17 Preparations of Nitrile Complexes of Cobalt(III)

Complex	*Nitrile*	*Properties*	*Ref.*
$[Co(NH_3)_5NCMe](ClO_4)_3$	Acetonitrile	$[CoN_3(NH_3)_5](ClO_4)_2 + NOClO_4$, MeCN; yellow-orange, ε_{467} 62.5	3, 7
cis-$[Co(en)_2(NCMe)_2](NO_3)(ClO_4)_2$	Acetonitrile	*cis*-$[Co(OSO_2CF_3)_2(en)_2](CF_3SO_3)_2$, MeCN, 2 h; yellow, ε_{456} 102	7
trans-$[Co(en)_2(NCMe)_2](ClO_4)_3$	Acetonitrile	*trans*-$[Co(N_3)_2(en)_2]ClO_4 + NOCF_3SO_3$; rexal. ε_{447} 69	7
$[Co(NH_3)_5NCNH_2](ClO_4)_3$	Cyanamide	$[Co(NH_3)_5OH_2](ClO_4)_3 + L$, $MeCONMe_2$; 1 h, 90 °C; orange, ε_{480} 74 (acid soln.); pK_1 4.2.	1
		$[Co(OSO_2CF_3)(NH_3)_5](CF_3SO_3)_2 + L$, sulfolane, r.t., 17 h, chrom.; ε_{480} 75.6	7
$[Co(NH_3)_5NCN(NH_2)_2](ClO_4)_3$	*N*-Cyanoguanidine	$[Co(NH_3)_5OH_2](ClO_4)_3 + L$, $OP(OMe)_3$, 1 h, 90 °C; orange, ε_{487} 116	1
		$[Co(OSO_2CF_3)(NH_3)_5](CF_3SO_3)_2 + L$, sulfolane, 20 °C; orange, ε_{486} 98.9 (acid soln.)	4
$[Co(NH_3)_5NCN(Me)_2](ClO_4)_3$	Me_2cyanamide	$[Co(NH_3)_5OP(OEt)_3](ClO_4)_3 + L$, 50 °C; yellow, ε_{470} 69	3
$[Co(NH_3)_5NCCHCH_2](ClO_4)_3$	Acrylonitrite	$[CoN_3(NH_3)_5](ClO_4)_2 + NOCF_3SO_3$, L, 40 °C, 24 h;	5
$[Co(NH_3)_5NCCH_2R](ClO_4)_3$	R = Ph, $CHCH_2$, NHCOMe, 5-norbornene-2-	$[Co(NH_3)_5OP(OMe)_3](ClO_4)_3 + L$, heat, chrom.	3
		$[Co(NH_3)_5OP(OEt)_3](ClO_4)_3 + L$, 50 °C; yellow-orange, ε_{465} 84	6
$[Co(NH_3)_5NCCH_2CN](ClO_4)_3$	Malonitrile	$[CoN_3(NH_3)_5](ClO_4)_2 + NOBF_4$, $OP(OEt)_3$, L, heat, 2 h, chrom.; yellow-orange, $\varepsilon_{466-472}$ 66–79	2
$[Co(NH_3)_5NCR](ClO_4)_3$	R = Ph, 3,4-CNPh, 3,4-HCOPh, py	$[Co(NH_3)_5OP(OMe)_3](ClO_4)_3 + L$, or	
$[Co(NH_3)_5NCR](ClO_4)_3$	R = CH_2CN, CH_2CO_2Et, CMe_2CO_2Et	$[CoN_3(NH_3)_5](BF_4)_2 + NOBF_4 + L$, $OP(OMe)_3$	

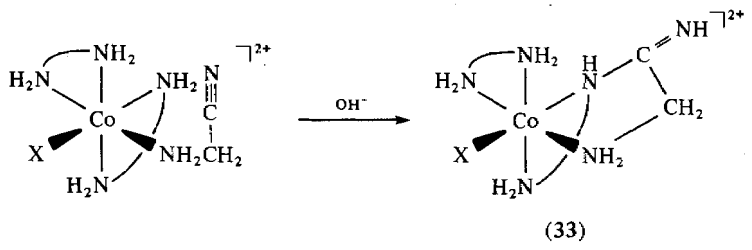
1. R. J. Balahura and R. B. Jordan, *J. Am. Chem. Soc.*, 1971, **93**, 625.
2. I. I. Creaser, J. MacB. Harrowfield, F. R. Keene and A. M. Sargeson, *J. Am. Chem. Soc.*, 1981, **103**, 3559.
3. R. B. Jordan, A. M. Sargeson and H. Taube, *Inorg. Chem.*, 1966, **5**, 1091.
4. N. E. Dixon, D. P. Fairlie, W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, 1983, **22**, 4038.
5. D. G. Butler, I. I. Creaser, S. F. Dyke and A. M. Sargeson, *Acta Chem. Scand., Ser. A*, 1978, **32**, 789.
6. R. J. Balahura, *Can. J. Chem.*, 1974, **52**, 1762.
7. N. E. Dixon, W. G. Jackson, M. L. Lancaster, G. A. Lawrance and A. M. Sargeson, *Inorg. Chem.*, 1981, **20**, 470.

coordinated 2-cyanobenzamide intermediate (**30**) is very fast ($k_{OH} = 5.8 \times 10^6 mol^{-1} dm^3 s^{-1}$ and assistance by the adjacent amide substituent is likely.[179]. Attack by deprotonated coordinated amine centres on nitrile groups of coordinated ligands occurs under mild alkaline conditions to form bidentate amidines (**33**; equation 25).[180] Attack by other nucleophiles such as CO_3^{2-} and CN^- are known,[181,182] with the latter being followed by successive additions of coordinated ammonia and CN^- with the tridentate bis(amidine)aminomethylmalonate complex (**34**) resulting (Scheme 18).[182]

$$(NH_3)_5Co^{3+}—N{\equiv}CR + OH^- \longrightarrow (NH_3)_5Co^{2+}—NHC(=O)R \qquad (24)$$

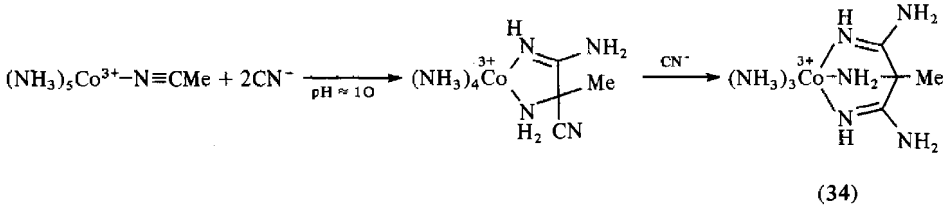


Scheme 17



(25)

(33)



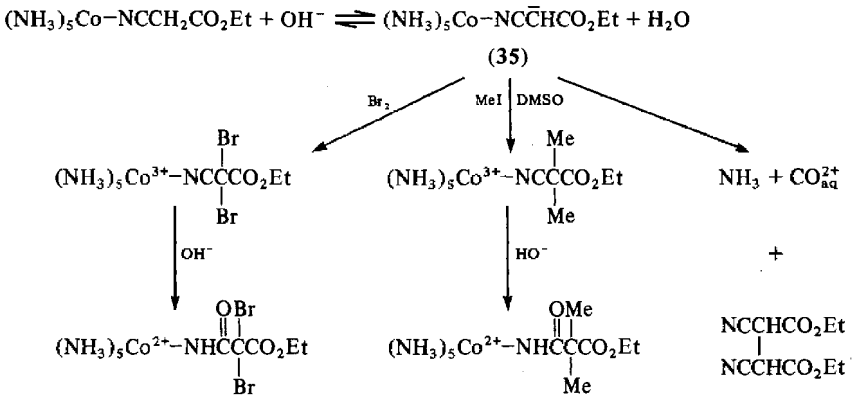
(34)

Scheme 18

Methylene groups adjacent to coordinated nitrile carbon are acidic (*e.g.* for R = CH_2CN, $pK_a = 5.7$) and rapidly undergo base-catalyzed proton exchange (for R = Me this is faster than hydrolysis), and addition of electrophiles other than H^+ to the resulting carbanion (**35**; Scheme 19).

In the absence of an added electrophile the anions undergo spontaneous electron transfer to the metal with release of $Co^{2+}_{(aq)}$ and the nitrile radical, which dimerizes. Alternatively, the coordinated radical anion induces polymerization of methacrylate, styrene, acrylonitrile and methylacrylonitrile monomers under mild non-aqueous conditions.[181]

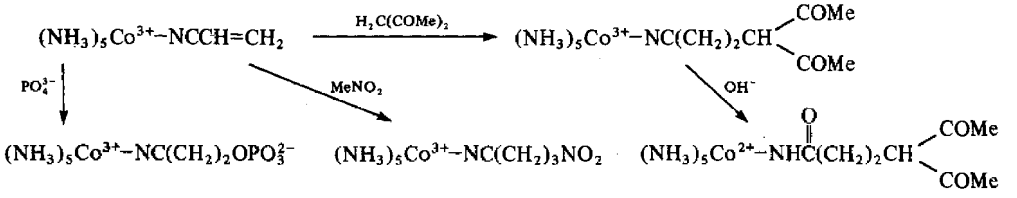
Reduction of coordinated nitrile to the parent amine can be accomplished with $NaBH_4$ in slightly



Scheme 19

alkaline aqueous solution (equation 26);[183] in acid solution, reduction results in the very rapid formation of $Co^{2+}_{(aq)}$ and Co^0. Adjacent double bonds are activated towards species possessing an acidic H atom. Thus coordinated acrylonitrile adds to acetylacetone, nitromethane and PO_4^{3-} to form saturated nitrile species (Scheme 20).[183]

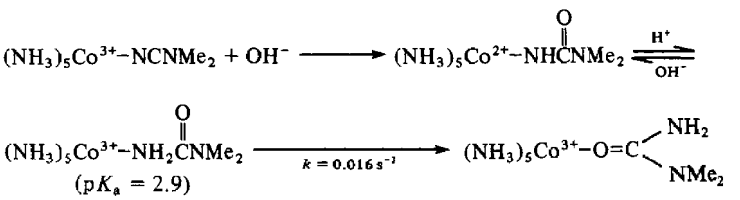
$$(NH_3)_5Co^{3+}—N{\equiv}CR \xrightarrow[pH \approx 9]{BH_4^-} (NH_3)_5Co^{3+}—NH_2CH_2R \qquad (26)$$



Scheme 20

Coordinated cyanamide does not add OH^- to form the N-bound urea complex since it deprotonates ($pK_a \approx 5.2$) to give the unreactive $[Co(NCNH)(NH_3)_5]^{2+}$ ion, but in acid it readily loses NH_4^+ to form N-coordinated cyanate (equation 27).[183] The analogous dimethylcyanamide complex cannot deprotonate and adds OH^- to form urea (Scheme 21),[185] but this does not proceed further to coordinated carbamic acid and $NHMe_2$ in a process analogous to that suggested for the function of Ni^{2+} in the metalloenzyme jack bean urease (which catalyzes the conversion of urea to these products),[186] nor does it lose $NHMe_2$ to form the cyanato complex as suggested by Balahura and Jordan for the similar urea derivatives (equation 28).[193] Alternatively, in acid solution the protonated urea rapidly isomerizes to the O-coordinated complex ($t_{1/2} \approx 40$ s, 25 °C; Scheme 21).[185] This isomer undergoes OH^--catalyzed hydrolysis at the metal rather than at acyl carbon, so the function of the metalloenzyme has not been duplicated in this system. A similar property is found for O-bound urea (equation 29).[187]

$$(NH_3)_5Co^{3+}—NCNH_2 + H_3O^+ \longrightarrow (NH_3)_5Co^{2+}—NCO + NH_4^+ + H^+ \qquad (27)$$



Scheme 21

$$(NH_3)_5Co^{3+}—OH_2 + RC(=O)NH_2 \longrightarrow (NH_3)_5Co^{3+}—NHC(=O)R + H_2O + H^+ \longrightarrow (NH_3)_5Co^{2+}—NCO + RH \quad (28)$$

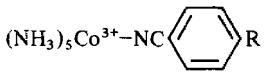
R = NH_2, OEt, $NHCH_3$, NHPh

$$(NH_3)_5Co^{3+}—O=C(NH_2)(NR_2) + OH^- \longrightarrow (NH_3)_5Co^{2+}—OH + H_2NC(=O)NR_2 \quad (29)$$

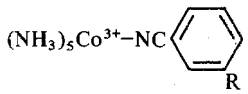
Pathways for reduction of Co^{III}—NCR complexes by M^{2+} reductants ($Cr^{2+} < Eu^{2+} < V^{2+} < [Ru(NH_3)_6]^{2+}$ in a rate sense) are a continuing source of interest.[188–190] Most coordinated nitriles (**36**; equation 30) reduce *via* an outer-sphere pathway (*i.e.* without specific prior attachment of the reductant), but an inner-sphere route becomes available when R = CH_2CO_2H, $CH_2CO_2^-$ in an appropriately substituted aryl species (**37**), especially with $Cr^{2+}_{(aq)}$ ($[Ru(NH_3)_6]^{2+}$ provides a marker rate for the outer-sphere reaction). Some representative data are given in Table 18. Reduction of the corresponding *m*-substituted derivatives (**38**) is some 10 times slower and appears to occur *via* the outer-sphere route.[190] Kupferschmidt and Jordan[188] point out the possibility of an outer-sphere mechanism when the oxidant and reductant can approach each other in flexible intermediates such as (**39**), but this is prevented in (**37**) species. The same authors[191] have come up with the interesting observation that the radical cation intermediate (**40**; equation 31) appears to react preferentially with Cr^{2+} to form $[(NH_3)_5CoNCCH_2Cr(OH_2)_5]^{5+}$ rather than undergo internal reduction to $Co^{2+}_{(aq)}$. This differs from that found with radical anion (**35**). Recently Anderes and Lavallee have shown that the Ru^{II}—Co^{III} dimer (**41**) is very inert ($k < 3 \times 10^{-6}\,s^{-1}$) to electron tunnelling through the insulating bicyclooctane bridge.[192]

$$(NH_3)_5Co^{3+}—NCR + Cr^{2+} \xrightarrow{H^+} Co^{2+}_{(aq)} + 5NH_4^+ + RCN + Cr(H_2O)_6^{3+} \quad (30)$$

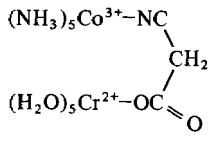
(**36**) R = alkyl, aryl, $(CH_2)_nX$ with X = CN, $CONH_2$, CO_2Me



(**37**) R = CO_2H, CN, COR



(**38**)

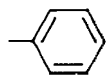
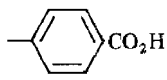
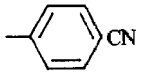
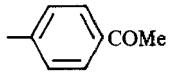
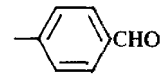


(**39**)

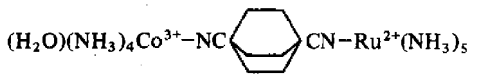
$$(NH_3)_5Co^{3+}—NCCH_2I + Cr^{2+} \longrightarrow (NH_3)_5Co^{3+}—NCCH_2\cdot + CrX^{2+} \xrightarrow{Cr^{2+}_{(aq)}} (NH_3)_5Co—NCCH_2—Cr(OH_2)_5^{5+} \quad (31)$$

(**40**)

Table 18 Rates of Reduction of $(NH_3)_5CoNCR^{3+}$ Complexes by $Cr^{2+}_{(aq)}$ (25 °C)

R (ref. 1)	k ($mol^{-1}\,dm^3\,s^{-1}$)	*R (ref. 2)*	k ($mol^{-1}\,dm^3\,s^{-1}$)
Me	0.94×10^{-2}		4.3×10^{-2}
$(CH_2)_2CN$	2.54×10^{-2}		0.29
CH_2CONH_2	2.61×10^{-2}		
CH_2CO_2Me	2.34×10^{-2}		0.93
$CH_2CO_2^-$	2.11×10^{2}		6×10^3
			2.5×10^5

1. W. C. Kupferschmidt and R. B. Jordan, *Inorg. Chem.*, 1981, **20**, 3469.
2. R. J. Balahura, W. C. Kupferschmidt and W. L. Purcell, *Inorg. Chem.*, 1983, **22**, 1456.



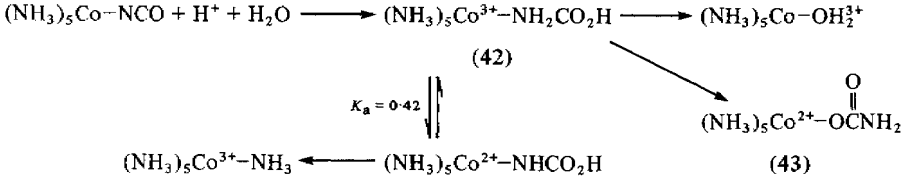
(41)

47.4.4 Cyanate, Thiocyanate and Selenocyanate

A review of the coordination chemistry of these ligands is available.[194]

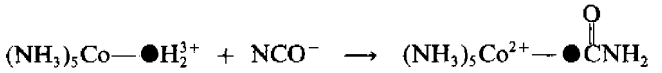
47.4.4.1 Cobalt(III)

Balahura and Jordan[193] first prepared $[Co(NCO)(NH_3)_5](ClO_4)_2$ by heating the aqua complex with urea or a substituted urea in trimethyl phosphate; dimethylacetamide as a solvent gives a better yield (Table 19). Coordination is *via* the N atom. The O-bound isomer has not been reported and is probably unstable to rapid isomerization. Other $CoNCO^{n+}$ complexes have been prepared from the aqua complex, and $K_3[Co(CN)_5(NCO)]$ from the $(EtO)_3PO$ complex (Table 19). $[Co(NCO)(NH_3)_5]^{2+}$ protonates and rapidly adds water to form the carbamic acid complex (**42**). This subsequently aquates, isomerizes to the O-bound carbamate (**43**), and forms $[Co(NH_3)_6]^{3+}$ depending on $[H^+]$ (Scheme 22).[195] Linhard and Flygare[196] showed that treating $[Co(NH_3)_5OH_2]^{3+}$ with NCO^- results in the O-bound carbamate complex (equation 32), and Sargeson and Taube showed that this occurred with retention of the Co—O bond.[197] Similar treatment of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ finally results in the carbonato chelate $[Co(O_2CO)(en)_2]^+$ *via* the chelated carbamate (Scheme 23).[197]

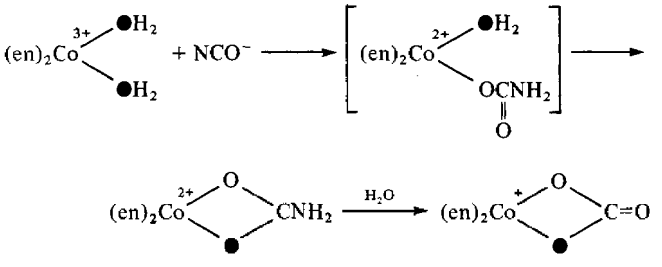


(42) (43)

Scheme 22



(32)



Scheme 23

Treatment (heating is usually required) of $Co—OH_2^{3+}$ with NCS^- results in the isothiocyanato complex $Co—NCS^{2+}$. These have been known since the beginnings of coordination chemistry and many syntheses are described in 'Inorganic Synthesis' (Table 3). Vinaixa and Ferrer have recently described the preparation of $[Co(NCS)(NH_3)_5]^{2+}$ as an undergraduate experiment in kinetics and preparative chemistry.[198] The Co—NCS group is linear or almost so with a Co—N bond length of ~195 pm; a similar bond length is found in amine complexes. Many crystal structures have been determined, and two recent studies on *trans*-$[Co(NCS)_2(NH_3)_4](OAc)$[199] and $(-)_{589}$-$[Co(NCS)_2(tn)_2]_2(Sb_2(+)tart_2)\cdot 4H_2O$[200] may be consulted for details. The Co—NCS bond is very robust, and most complexes are stable in acidic and alkaline solution for long periods of time.

Table 19 Cyanate, Thiocyanato and Selenocyanato Complexes of Cobalt(III)

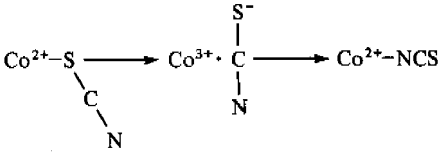
Complex	*Preparation*	*Properties*	*Ref.*
$[CoNCO(NH_3)_5](ClO_4)_2$	$[Co(NH_3)_5OH_2](ClO_4)_3 + (NH_2)_2CO$, $OP(OMe)_3$ (or $MeCONMe_2$), heat; $[Co(NH_3)_5OP(OEt)_3](ClO_4)_3 + Ph_4AsNCO$, DMSO, 12 h, RT	Orange-yellow; ε_{504}, 135	8, 9
$K_3[Co(CN)_5NCO]$	$K_3[Co(CN)_5N_3] + NOClO_4$, $OP(OEt)_3$, KNCO, MeOH	ε_{367}, 184	11
$[Co(SCN)(NH_3)_5]Cl_2 \cdot H_2O$	$[Co(NO_3)(NH_3)_5](ClO_4)_2 + OH^-$, 5 M NaSCN 30 s acid quench, chrom.	Violet; ε_{512}, 74	1
trans-$[Co(en)_2(SCN)(NH_3)]Cl_2 \cdot 2H_2O$	*trans*-$[Co(N_3)(NH_3)(en)_2]Cl_2 + H_2NO_2^+$, 10 M NaSCN, chrom.	Purple; ε_{520}, 66	2
$[Co(SCN)(DMGH)_2(B)]$ (B = py, pip)	$Co(OAc)_2 \cdot 4H_2O$ + NaNCS + $DMGH_2$ + B, EtOH recryst.	^1H NMR, IR	3
t-$[Co(SCN)(NH_3)(tren)](ClO_4)_2$	*t*-$[Co(tren)(N_3)(NH_3)](ClO_4)_2 + H_2NO_2^+$, 10 M NaSCN, chrom.	Purple	4
p-$[Co(SCN)(NH_3)(tren)]Br_2$	*p*-$[Co(N_3)(NH_3)(tren)](ClO_4)_2 + H_2NO_2^+$, 20 M NaSCN, chrom.	Brown	4
$K_3[Co(CN)_5SCN]$	$[Co(NCS)(NH_3)_5]SO_4$ + KCN + $Co(NO_3)_2$, H_2O, EtOH	Yellow-orange; ε_{378}, 191; ε_{265}, 17 000	5
$K_3[Co(CN)_5SeCN]$	$[Co(NCSe)(NH_3)_5]Br_2 + Co(OAc)_2$ + KCN, H_2O, EtOH	Brown; ε_{429}, 121	6
$(H_4N)_3[Co(CN)_5NCSe]$	Isomerization with time	ε_{358}, 484	6
$[Co(NCSe)(NH_3)_5]Br_2$	$[Co(NH_3)_5OP(OEt)_3](ClO_4)_3$ + NaSeCN, DMSO, heat, 80 °C, 1 h, NaBr, H_2O	Orange; ε_{493}, 162	7, 6
$[Co(SeCN)(DMGH)_2(B)]$	$Co(OAc)_2 \cdot 4H_2O + DMGH_2$ + KSeCN + B, H_2O, EtOH, 3 h, r.t., B	^1H NMR, ^{13}C NMR, IR	3

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Reversible coordination of heavy metals (Ag^+, Hg^{2+}, Tl^{3+}, Cu^{2+}, Fe^{3+}) can occur to form Co—NCS—M^{n+} species, with an orange to yellow colour change for $[Co(NH_3)_5(\mu\text{-NCS})Hg]^{4+}$.[201]

The thiocyanato linkage isomer Co—SCN^{2+} has been found in several complexes (Table 19). This grouping is bent about the S atom (105°) in $[Co(SCN)(NH_3)_5]Cl_2 \cdot H_2O$ with a Co—S bond length of 225–235 pm. No structural *trans* effect is observed.[202] For the labile $[Co(SCN)(Bu^tpy)(DMGH)_2]$ complex the Co—SCN isomer is favoured by protic solvents (MeOH) and aprotic solvents of low dielectric constant (C_6H_6, CH_2Cl_2), whereas the Co—NCS isomer predominantes in DMF and DMSO.[203] Gutterman and Gray[204] showed that $K_3[Co(CN)_5(NCS)]$ isomerizes to $K_3[Co(CN)_5(SCN)]$ when the solid is heated above 128 °C, whereas the Et_4N^+ salt does the reverse at ambient temperature over 3 d; in solution the S-bonded isomer is favoured by protic solvents, whereas low dielectric solvents (CH_2Cl_2, acetone, nitrobenzene) favour the N-bonded species.[205] $R_3[Co(CN)_5(SeCN)]$ (R = K, Bu^n) follows a similar cation behaviour in the solid and in solution. Rates of dissociation follow the order Co—SCN > Co—SeCN > Co—NCS > Co—NCSe in DMSO. It appears that hard cations (K^+, Cs^+, $MeNH_3^+$) favour S and Se coordination, while soft cations (Me_4N^+, $Bu^n_4N^+$) favour N coordination. Gutterman and Gray put forward a convincing argument for such variations based on polarization effects,[206] but H bonding of the solvent to the N end of NCS^- and Co—SCN seems to play a role.[205] Alkylcobaloximes react with NCX^- (X = Se, S, O) to form labile $[CoR(NCX/XCN)(DMGH)_2]^-$ systems which equilibrate rapidly in solution with a Co—XCN bonding preference Se ≫ S > O. This is in agreement with inert $[Co(XCN)(DMGH)_2(B)]$ systems (B = py, pip).[207]

$[Co(SCN)(NH_3)_5]^{2+}$ isomerizes spontaneously to $[Co(NCS)(NH_3)_5]^{2+}$ in aqueous solution and in the solid chloride salt,[202,208] but some 45% lattice $S^{14}CN^-$ is incorporated on heating $[Co(SCN)(NH_3)_5](S^{14}CN)_2$.[209] The similar isomerization of *t*-$[Co(SCN)(tren)(NH_3)]^{2+}$ in aqueous solution incorporates some $S^{14}CN^-$ into both the Co—SCN^{2+} reactant and Co—NCS^{2+} product[210] so that bond breaking rather than rotation about the ligand π system seems to be involved (equation 33). The reaction is also catalyzed by Hg^{2+},[211] Ag^+ and OH^-,[208] with Co—OH_2^{3+} or Co—OH^{2+} being formed in addition to Co—NCS^{2+}. For the Hg^{2+} and Ag^+ reaction NO_3^- competes for both the Co—NCS^{2+} and Co—OH_2^{3+} products,[210] whereas N_3^- is found to compete for only the Co—OH^{2+} product in the OH^--catalyzed reaction.[208] Some (~0.5%) intramolecular *trans*-Co—SCN^{2+} to *cis*-Co—NCS^{2+} isomerization has been found in the base hydrolysis of *trans*-$[Co(SCN)(NH_3)(en)_2]^{2+}$,[212] but no *t*-Co—$SCN^{2+}$ to *p*-Co—NCS^{2+} isomerization occurs with *t*-$[Co(SCN)(NH_3)(tren)]^{2+}$ under the same conditions and the earlier experiments needs to be re-examined.[210]



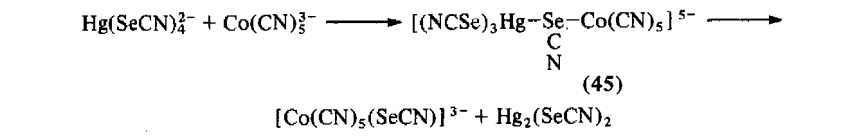
(33)

Electron transfer reactions mediated by $[Co(CN)_5]^{3-}$ proceed *via* attack on the adjacent S atom with the rate of reaction (34) being considerably faster than reaction (35), both leading to the S-bonded $[Co(CN)_5(SCN)]^{3-}$ isomer (**44**).[213] Similarly $[Co(CN)_5]^{3-}$ appears to react with $[Hg(SeCN)_4]^{2-}$ *via* the bridged species (**45**, Scheme 24).

$$(NH_3)_5Co^{2+}—SCN + Co(CN)_5^{3-} \longrightarrow Co^{2+} + 5NH_3 + [(NC)_5Co—SCN]^{3-} \quad (34)$$

(**44**)

$$(NH_3)_5Co^{2+}—NCS + Co(CN)_5^{3-} \longrightarrow Co^{2+} + 5NH_3 + [(NC)_5Co—SCN]^{3-} \quad (35)$$



(**45**)

Scheme 24

Bridged complexes containing NCX^- (X = O, S, Se) have been synthesized in both isomeric forms by treating ligand-inert $[Co(XCN)(DMGH)_2(py)]$ (X = S, Se) or $[Co(NCX)(DMGH)_2(py)]$ (X = O, S) with labile $[CoR(DMGH)_2(H_2O)]$ in the presence of an oxidizing agent such as CCl_3Br.[207] Remote attack is suggested (equation 36). The resulting dimer is prone to dissociation

with the rate increasing $CN^- > SCN^- > SeCN^- > NCS^- \gg NCO^-$.[207] Likewise, dimeric complexes $[(L)(DMGH)_2Co—XCN—Co(DMGH)_2XCN]$, involving L = $AsPh_4$, $SbPh_4$, $SbBu^n_4$, have been prepared for X = Se, S.[214]

$$[Co(NCS)(DMGH)_2(B)] + [CoR(DMGH)_2(OH_2)] \longrightarrow [(B)(DMGH)_2Co—NCS—Co(DMGH)_2R] + H_2O \quad (36)$$

47.4.5 Ureas, Amides and Peptides

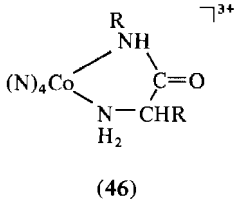
A general review of the coordinating ability of amides is available,[215] as is a more specific article dealing with the reactivity of coordinated esters, amides and peptides.[216]

47.4.5.1 Cobalt(III)

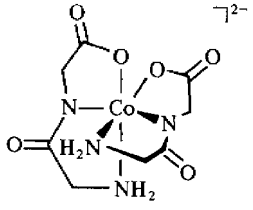
The O-bound urea complex $[Co(NH_3)_5\{OC(NH_2)_2\}](ClO_4)_3$ can be prepared from the aqua or trifluoromethylsulfonate complex (Table 94). It slowly aquates in dilute acid ($k = 4.0 \times 10^{-5}\,s^{-1}$, 25 °C) hydrolyzes in alkali ($k_{OH} = 15.3\,mol^{-1}\,dm^3\,s^{-1}$) largely with Co—O bond fission (equation 37).[187] The N-bound isomer $[Co(NH_3)_5\{NH_2CON(R)_2\}]^{3+}$ has been prepared (R = H, Me) but rapidly isomerizes to the O-bonded species in acid solution ($k_i = 1.6 \times 10^{-2}\,s^{-1}$).[185] A similar property holds for the N-coordinated carbamic acid complex $[Co(NH_3)_5(NH_2CO_2H)]^{3+}$ ($k_i = 8 \times 10^{-2}\,s^{-1}$).[195] Both these 3+ ions are reasonably acidic ($pK_a = 2.9$, -0.4 respectively) with the conjugate base forms being stable to isomerization. However $[Co(NH_3)_5(NHCO_2H)]^{2+}$ gives rise to $[Co(NH_3)_6]^{3+}$ and $CO_{2(g)}$ spontaneously;[195] $[Co(NH_3)_5(NHCONMe_2)]^{2+}$ does not result in $[Co(NH_3)_6]^{3+}$, CO_2 and $NHMe_2$.[185]

$$(NH_3)_5Co^{3+}—O=C(NH_2)(NH_2) \ (pK_a\ 13.2) + \bullet H^- \xrightarrow{97\%} (NH_3)_5Co—\bullet H^{2+} + (NH_2)_2CO$$
$$\xrightarrow{3\%} (NH_3)_5Co—OH^{2+} + (NH_2)_2C\bullet \quad (37)$$

The O-coordinated dimethylformamide and acetamide complexes are susceptible to slower OH^- attack at the carbonyl centre with significant retention of the Co—O bond, *e.g.* equation (38).[217] The reasons for this change in site of attack are not well understood. Likewise, O-chelated amides and peptides are very susceptible to OH^- attack with hydrolysis being accelerated 10^4–10^5 times by coordination.[216] This is the basis of the N-terminal cleavage of small peptide fragments first studied by Buckingham and Collman[218] and extended by others in recent times (equation 39).[219] N-coordinated amides (**46**) are inert to alkaline hydrolysis (they are in fact stabilized by the metal) and this deprotonated form is the preferred bonding mode for Co^{II} and Co^{III} systems in alkaline solution. Coordination results in immediate deprotonation for kinetically labile Co^{II} complexes near pH 10,[220] and protonation of the kinetically more robust Co^{III} complexes ($pK_a \approx 1$) results in the iminol tautomer (**48**), *e.g.* $[Co(Gly\text{-}GlyH)_2](ClO_4)$ (Table 21, crystal structure), rather than the N-bound amide. This protonated amide form slowly reverts to the O-bound amide in $[Co(NH)_3(Gly_4)]^{2+}$ ($k = 2.5 \times 10^{-5}\,s^{-1}$);[221] this property is probably a general one (equation 40).

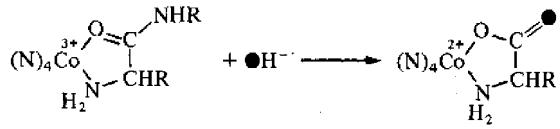


(46)

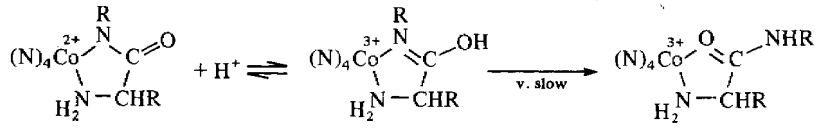


(47)

$$(NH_3)_5Co^{3+}—O=C(H)(NMe_2) + \bullet H^- \longrightarrow (NH_3)_5Co^{2+}—O\overset{\bullet}{C}H + HNMe_2 \quad (38)$$



(39)



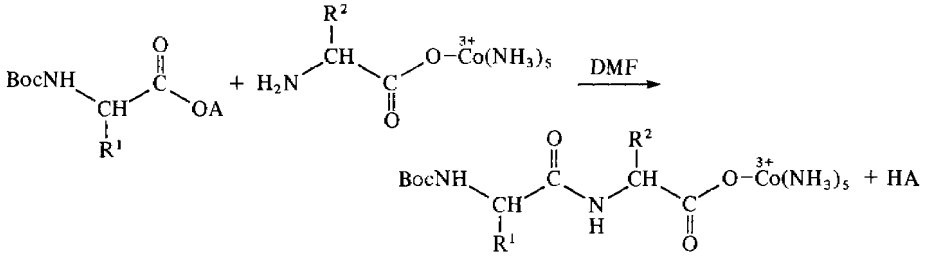
(40)

(48)

Preparations for some Co^{III} amide and peptide complexes are given in Table 20. In oxygen-free aqueous solutions $Co^{2+}_{(aq)}$ forms weak, pink complexes with peptides,[220] chelated *via* the terminal amino N and amide O atoms. Near pH 10 two equivalents of OH^- are consumed and the light-blue solutions containing $[Co(dipeptide)_2]^{2-}$ presumably have the meridional structure (**47**) shown by the analogous Ni^{II} complex.[222] The Co^{II} complexes adopt an electronic configuration of intermediate spin, $\mu \approx 4.1$ BM.[220] Co^{III} peptide complexes have been prepared by several routes and most have been reviewed by Gillard and coworkers.[223] These authors favour using CoO(OH) but Hawkins and his colleagues have used the peroxo decaammine dimer $[\{Co(NH_3)_5\}_2O_2](NO_3)_4$ with considerable success, particularly in preparing mixed ammine–peptide systems.[224] Gillard reports the partial resolution into optical enantiomers of $[Co(Gly\text{-}Gly)_2]^-$ and the separation of other [Co(AA—A′A′)$_2$]$^-$ diastereoisomers by chromatographic methods.[223] Some crystal structures are available (Table 21). The C-terminal methylene residue of $[Co(Gly\text{-}Gly)_2]^-$ undergoes proton exchange in alkali, and Gillard has shown that it reacts with HCHO and MeCHO in the presence of Na_2CO_3 forming $[Co(Gly\text{-}Ser)_2]^-$ and $[Co\{Gly\text{-}(R,S)Thr\}_2]^-$ respectively.[223]

The enhanced reactivity of chelated amino acid esters towards attack by other nucleophiles has been used to advantage in the sequential synthesis of small peptides equation (41).[225] Formation of the amide bond takes only seconds to minutes at room temperature in DMSO as solvent, and the peptide can be easily recovered by reducing the metal to the Co^{II} state. Recent studies have shown that the Λ and Δ diastereoisomeric reactants are selective in their couplings to (*R*) and (*S*) amino acid esters and that mutarotation at the asymmetric centre of the chelated ester reactant varies from 0–6%.[226] Isied and coworkers have described the use of the $Co(NH_3)_5^{3+}$ as a C-terminal protecting group for the sequential synthesis of peptides (equation 42).[227] This procedure has advantages over other methods in some cases.

$$\Lambda\text{-}[Co(AAOMe)(en)_2]^{3+} + A'A'OMe \longrightarrow \Lambda\text{-}[Co(AAA'A'OMe)(en)_2]^{3+} + MeOH \quad (41)$$



(42)

47.4.6 Pyridine, Pyrazine, Triazine and Purine

47.4.6.1 Cobalt(II)

Violet (octahedral, polymeric chain structure) and blue (tetrahedral, monomer) $[CoCl_2(py)_2]$ have been known for a very long time and an early paper by Gill, Nyholm and their colleagues is recommended as an informative starting point to the colours, magnetic properties and structural possibilities of the $[CoX_2(Rpy)_2]$ series (X = Cl, Br, I, NCS).[228] A recent paper by Darby and Vallarino discusses later work.[229] Preparation is easy: addition of an ethanolic solution of anhydrous CoX_2 (sometimes containing dimethoxypropane or triethyl orthoformate as a water scavenger) to a hot solution of the ligand results in blue (tetrahedral) or pink (octahedral) complexes depending on the ratios used. Equilibrium (43) is temperature,[230,231] pressure[231] and solvent[232,233] dependent with the tetrahedral form being stabilized by low pressures and high temperatures. Structures are known

Table 20 Preparations and Properties of Amide and Peptide Complexes of Cobalt(III)

Complex	*Preparation*	*Properties*	*Ref.*
$Na[Co(Gly\text{-}Gly)_2]$	$CoO(OH) + LH_2 + NaOH$; H_2O, r.t.	Red, ε_{520} 375	1, 2
$R[Co(AA\text{-}A'A')_2]$ (R = Li, Na; AA, A′A′ = gly, (*S*)-Phe, (*S*)-Ala)	$CoO(OH) + LH_2$; H_2O, r.t.; chrom. (G-10)	Red, $\varepsilon_{520\text{-}25}$ 365–420; resol., CD, ^{1}H NMR	2
$K[Co(AA\text{-}A'A')_2]$ (AA = Gly, β-Ala, (*S*)-Ala, (*S*)-Pro)	$CoCl_2 + LH_2 + NaOH$ (pH 9–9.5); H_2O, PbO_2, 40 °C, 1 h; chrom.	Ab. spectra; CD; resol.	3
$K[Co(Gly\text{-}Gly)\{(S)\text{-}Pro\text{-}Gly\}]$	As above; chrom. sep.	ε_{532} 363	3
$[Co(NH_3)_3(AA\text{-}A'A')]$ (AA-A′A′ = Gly-Gly; Gly-(*S*)-Ala; (*S*)-Ala-Gly; (*S*)-Ala-(*S*)Ala)	$CoCl_2 + L + NH_4OH$; H_2O, H_2O_2, warm	Red, ε_{489} 217 (Gly-Gly); ORD, CD	4
$[Co(NH_3)_2(AA\text{-}A'A'\text{-}A''A'')]\cdot xH_2O$ (AA = Gly, (*S*)-Ala, (*S*)-Leu, (*S*)-Phe, (*S*)-Tyr, (*S*)-His)	$\{[Co(NH_3)_5]_2O_2\}(NO_3)_4 + L + NH_4OH$; H_2O, 5 °C, 1.5 h; chrom.	Orange-red, ε_{456} 150; ^{1}H, ^{13}C NMR, CD	5, 6
(AA = Gly, (*S*)-Ala, β-Ala)	$[Co(NH_3)_5OH_2](ClO_4)_3 + L + NaOH$; DMSO, H_2O; 50 °C; chrom.	Vis–UV; ^{1}H NMR; CD	8
$[Co(NH_3)_3(Gly_4)]\cdot 2H_2O$	$\{[Co(NH_3)_5]_2O_2\}(NO_3)_4 + L + NH_4OH$; H_2O, pH ≈ 9, 5 °C, 1.5 h; chrom.	Orange, ^{1}H, ^{13}C NMR	7
$[Co(NH_3)_2(Gly_4)]\cdot 2H_2O$	As above; NH_4OH, pH ≈ 9; 40 °C, 20 h, chrom.	Orange, ε_{433} 215; ^{1}H, ^{13}C NMR	7
$NH_4[Co(NH_3)_2(AA)_4]\cdot xH_2O$	As above	^{1}H NMR, CD	8
$Ba[Co(Mida)(AA\text{-}A'A')]_2$ (AA, A′A′ = Gly, (*S*)-Ala, (*S*)-Leu, β-Ala)	$CoCl_2 + L + Mida$; H_2O, pH 9.5, PbO_2, 40 °C, 1 h; chrom.	Vis-UV; ^{1}H NMR, CD	9, 10
$K[Co(\beta\text{-}Ala\text{-}Gly)_2]\cdot H_2O$	$Co(NO_3)_2 + L + NaOH$; H_2O, pH 9.5, C, air, 12 h; chrom.	Vis-UV; ^{1}H NMR	9
$[Co(en)_2(GlyNHR)](NO_3)_2ClO_4$ (R = H, Me)	$[Co(en)_2(GlyNHR)Br](ClO_4)_2 + AgNO_3$; H_2O	Orange, ε_{487} 97 (H), 116 (Me)	11
$[Co(trien)(Gly\text{-}GlyOR)](ClO_4)_3$	$\beta_2[Co(trien)CO_3]ClO_4 + HClO_4 + L$; H_2P, pH 7–8, 1 h	Orange, ε_{478} 133–140	11

1. A. R. Manyak, C. B. Murphy and A. E. Martell, *Arch. Biochem. Biophys.*, 1955, **59**, 373.
2. L. V. Boas, C. A. Evans, R. D. Gillard, P. R. Mitchell and D. A. Phipps, *J. Chem. Soc., Dalton Trans.*, 1979, 583.
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11. D. A. Buckingham, C. E. Davis, D. M. Foster and A. M. Sargeson, *J. Am. Chem. Soc.*, 1970, **92**, 5571.

Table 21 Structures: Peptide Complexes of Cobalt(III)

Complex	*Structure*[a]	*Comments*	*Ref.*
$(NH_4)[Co(Gly\text{-}Gly)]\cdot 2H_2O$	CoO 185; CoN (amide) 192; $CoNH_2$ 200	Meridional coordination	1
$[Co(H_2O)_6][Co(Gly\text{-}Gly)_2]_2\cdot xH_2O$	CoO 193; CoN (amide) 187; $CoNH_2$ 196	As above	2
$Ba[Co(Gly\text{-}Gly)_2]_2\cdot nH_2O$ (n = 12–17) $[Co(Gly\text{-}GlyH)_2]ClO_4$	CoO 198; CoN (amide) 194; $CoNH_2$ 191	Protonated on amide O atom	2
$[Co(NH_3)_2\{(S)\text{-}Ala\text{-}Gly\text{-}Gly)\}]\cdot 2H_2O$	CoO 194.5, 197.6; CoN (amide) 184–188; CoN, 20.1, 193.9; $CoNH_3$ 195–197	Meridonal coordination *trans* NH_3; two independent molecules	3

[a] Bond lengths in pm.

1. R. D. Gillard, E. D. McKenzie, R. Mason and G. B. Robertson, *Nature (London)*, 1966, **209**, 1347.
2. M. T. Barnett, H. C. Freeman, D. A. Buckingham, I. Nan Hsu and D. van der Helm, *Chem. Commun.*, 1970, 367.
3. E. J. Evans, C. J. Hawkins, J. Rodgers and M. R. Snow, *Inorg. Chem.*, **22**, 34.

in many instances (Table 22) with little distortion form tetrahedral coordination but with tetragonal distortion and *trans* X ligands for the pink octahedral systems. The magnetic[234] and ESR[235] properties of the latter have been accurately accounted for using the angular overlap MO formalism. Establishment of successive equilibria (equations 44 and 45) have been investigated by T-jump and ^{15}N NMR methods ($k_3 = 3.1 \times 10^3\,mol^{-1}\,dm^3\,s^{-1}$,[236] $k_{-4} = 6.5 \times 10^6\,s^{-1}$)[237] and the $[CoBr_2(py)_3]$ intermediate has been detected in the bromide system.[238] Similarly $[CoCl_3(py)]^-$ can be formed by adding Bu^n_4NCl to $\{CoCl_2(py)_2]$[239] and has been isolated.[240]

$$[CoX_2(Rpy)_2] + 2Rpy \rightleftharpoons [CoX_2(Rpy)_4] \quad (43)$$
blue pink

$$[CoCl_2py_2] + py \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [CoCl_2py_3] \quad (44)$$

$$[CoCl_2py_3] + py \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [CoCl_2py_4] \quad (45)$$

Various carboxylate complexes of the type $[Co(O_2CR)_2py_2]$ are known and in general they adopt a distorted octahedral configuration with bidentate carboxyl and *trans* pyridine ligands.[241] *Cis–trans* equilibria in $[Co(O_2CCF_3)_2(Me_xpy)_2]$ have been studied by ^1H NMR line broadening as a function of temperature.[242] Oxidative decarbonylation of $Co_2(CO)_8$ occurs when it is treated with picolinic acid or 2,6-dipicolinic acid with $[Co_2(pic)_3(picH)_3][Co(CO)_4]\cdot 3H_2O$ and bright-purple polymeric $[Co(dipic)]_n$ being isolated from refluxing methanol.[249]

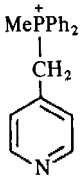
Pyrazine forms pink insoluble $[CoX_2(pyz)_2]$ and $[CoX_2(pyz)]$ complexes (X = Cl, Br, I), which are presumably polymeric and octahedral,[243] but monomeric tetrahedral units are possible with increased methyl substitution. No direct confirmation of bridging pyrazine has been found in these Co^{II} systems. Some orange-red 2-substituted carboxylate and carboxamide pyrazine complexes have been prepared[244] and a distorted octahedral geometry has been confirmed by O'Connor and Sinn, with chelated ligands (Table 22). No well-characterized pyridazine or pyrimidine complexes have been reported.

Pink $[CoX_2(trz)_2]$ and green $[CoX_2(trz)]$ complexes of 1,2,3-triazine are known[245] and bridging triazine is possible. Orange-coloured $[Co(purine)_2](ClO_4)_2\cdot 3H_2O$ has been isolated and a bridging role for at least one purine has been suggested,[246] but the structure of $[Co(OH_2)_4(adenine)_2]^{2+}$ with monodentate *trans* octahedral coordination *via* N-9 of the five-membered purine ring makes this unlikely (Table 25).

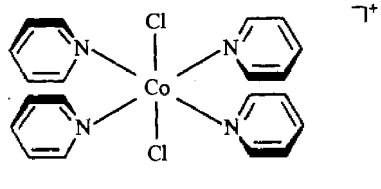
$[CoBr_3(L)]$ complexes containing the cationic ligands (**49**) and (**50**) have been reported[247] and many linear and branched ligand systems containing pyridine are known; a recent article by Martell and coworkers may be consulted for details.[248]



(49)



(50)



(51) $(-)^{CD}_{630}$-$[CoCl_2py_4]$ $[(-)_{589}$-HDBT]

Table 22 Structures: Six-membered N-Heterocyclic Complexes (Pyridine, Pyrazine, Bipyridyl, Phenanthroline and Terpyridyl)

Complex	*Comments*[a]	*Ref.*
Cobalt(I)		
$[Co(BH_4)terpy]$	Dist. tet. pyr.; CoN 181, 192.5; CoH 180; HCoH 73.6°; bidentate BH_4^-	1
$[Co(bipy)_3]Cl \cdot H_2O$	Oct.; CoN 211; NCoN 76.6°	2
Cobalt(II)		
$[Co(Cl)_2(py)_2]_x$ (violet)	Oct. (polymeric); two solid phases; Co—Cl—Co chains; CoN 214, 216; CoCl 249, 248	3, 4
$[Co(Br)_2(4\text{-}CHOpy)_4]$	Oct. (*trans* Br); CoBr 251, 269; CoN 219.4	5
$[Co(Cl)_2(4\text{-}Mepy)_2]$	Tet.; CoCl 223; CoN 203, 206	6
$[Co(NCS)_2(py)_4]$	Oct. (*trans* NCS); CoN_{py} 219.2, 221.4; CoN(CS) 208.4; CoNC(S) 155.9°	7
$[Co(NCS)_2(py)_4] \cdot 2CHI_3$	Oct. (*trans* NCS); CoN_{py} 218; CoN(CS) 210; CoNC(S) 174.7°	8
$[Co(Cl)_2(2\text{-}MeOpy)_2]$	Tet.; CoCl 222; CoN 206, 208; ClCoCl 113°; NCoN 114.5°	9
$[Co(4\text{-}Mepy)_4](PF_6)_2$	Dist. tet.; CoN 201; NCoN 113.8°, 101.2°	10
$[\{Co(NO_3)py_2\}_2(\mu\text{-}Cl)_2]$	Oct. (dimeric); Cl bridges; CoCl 236, 252; CoClCo 93.5°; bidentate NO_3	11
$[Co(3\text{-}Mepy)_4(H_2O)_2](ClO_4)_2$	Oct. (*trans* H_2O); CoN 217; CoO 212.4	12
$[Co(NCS)_2(4\text{-}vinylpy)_4]$	Oct. (*trans* NCS); CON_{py} 214.7–219.7; CoN(CS) 210, 205; CoNC(S) 166.4°, 173°	13
$[Co(H_2O)_4(2\text{-}NH_2COpy)_2]Cl_2 \cdot 2H_2O$	Dist. oct. (*trans* py); CoN 215.6; CoO 209	14
$[CoCl_2(PPhpy_2)] \cdot 0.5EtOH$	Dist. tet.; CoCl 222.1; CoN, 203.1; dipyridylphenylphosphine forms 6-membered chelate; ClCoCl 116.2°; NCoN 94.8°	15
$[CoCl(H_2O)(2\text{-}CHNPhpy)_2]NO_3 \cdot H_2O$	Oct.; CoCl 240; CoO 213.5; CoN 215, 219.7; five-membered chelate	16
$[Co(H_2O)_2\{pyz(CO_2)CO_2H\}_2]$	Dist. oct. (*trans* H_2O); CoN 210.9; CoO(H) 212.3; CoO(C) 205.7; NCoO 77.6; five-membered chelate	17
$[Co(H_2O)_2(pyzCO_2)_2]$	Dist. oct. (*trans* H_2O); CoN 210.2; CoO(H) 211.7; CoO(C) 209.3; NCoO 78.8°; five-membered chelate	17
$[CoCl_2(pyz)_2]_x$	Oct. (*trans* Cl); sheet-like structure with bridging pyz	23
$[CoCl_2(pySSpy)]$	Tet.; CoN 202.5, 205.5; CoCl 224, 225 (no coordination of disulfide)	20
$[Co(bipy)_3]Cl_2 \cdot 2H_2O \cdot EtOH$	Oct.; CoN 212.8; NCoN 76°	2
$[Co(phen)_3](ClO_4)_2 \cdot H_2O$	Dist. oct.; CoN 212.7; NCoN 78.1°	24
cis-$[Co(NCS)_2(bipy)_2]$	Dist. oct.; CoN(CS) 207; CoN 215; NCoN 75.5°; CoNC 162, 168°	25
$[Co(terpy)_2]Br_2 \cdot 3H_2O$	Dist. oct.; CoN 189, 210; NCoN 79.0°, planar tridentate (D_{2d})	18
$[Co(terpy)_2](NCS)_2 \cdot 2H_2O$	Dist. oct.; two phases, CoN 198, 212 and 195, 211–215	19
$[Co(NCO)_2(terpy)]$	Five-coordinate; tridentate planar, CoN 205.8, 214.6; NCO 160°	21
$[Co(Cl)_2(terpy)]$	Five-coordinate; CoN 209, 215	22
Cobalt(III)		
$[Co(CO_3)(py_2)_4]ClO_4 \cdot H_2O$	Oct.; CoN 197.4–200.4; CoO 189; OCoO 69.3°	26
$[Co(Cl)(py)(tren)][ZnCl_4] \cdot 0.5H_2O$	*p-Cis*, oct.; CoCl 227.6 CoN 198.7	30
$(-)_{546}$-*trans*-$[Co(NO_2)_2\{(-)_{589}bipip\}_2](d\text{-}BCS) \cdot 4H_2O$	Oct.; CoN(O) 194–195; CoN 199; NCoN 84–85	36
$[Co(CO_3)(phen)_2]Cl \cdot 3H_2O$	Oct.; CoN 192.8–194.5; CoO 188; OCoO 68.4°, NCoN 84°	27
$[Co(CO_3)(OH)(terpy)]$	Dist. oct.; CoN 185–195; CoO(H) 189.4; CoO 191.8; OCoO 68°; NCoN 81–84°	28
$[Co(Cl)_2(phen)_2]Cl \cdot 3H_2O$	*Cis*, oct.; CoCl, 223, 226; CoN 194–203	29
$(-)_D$-$[Co(bipy)_3][Fe(CN)_6] \cdot 8H_2O$	Oct.; CoN 193.2; NCoN 83.2°; Δ absolute configuration	31
$[Co(NO_3)(bipy)_2](NO_3)(OH) \cdot 4H_2O$	Oct.; bidentate NO_3; OCoO 69.9°; ONO, 111.2°; CoO 188.8; CoN 192.2, 193.6	32
$[Co(phen)_3](ClO_4)_3 \cdot 2H_2O$	Oct.; CoN 192–195; NCoN 84.4°	33
$[Co(CO_3)(bipy)_2]NO_3 \cdot 5H_2O$	Oct.; CoO 188.7; CoN 192.3, 193.0; OCoO 69.9°; NCoN 83.2°	34
$[Co(CO_3)(phen)_2]Br \cdot 4H_2O$	Oct.; CoO 188–189; CoN 191–194; OCoO 69.5°; NCoN 84.6°	34
cis-$[Co(Me)_2(bipy)_2](AlEt_4)$	Oct.; CoC 199–200; CoN 193–203; CCoC 89°	35
$(+)_{589}$-$[Co(en)_2(Me_2bipy)](ClO_4)_2Cl \cdot H_2O$	Oct.; Λ-absolute configuration; CoN 196–197	37

[a] Bond lengths are in pm.

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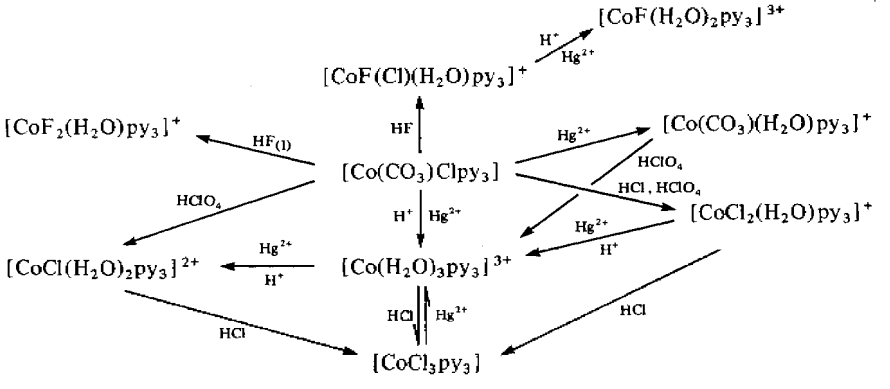
Table 22 (*continued*)

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Polymers containing the 4-vinylpyridine moiety complexed to cobalt(II) acetate have been used to catalyze the condensation of aldehydes with ketones. High yields of α,β-unsaturated ketones are formed at 80 °C in DMF.[250]

47.4.6.2 Cobalt(III)

Preparations of representative complexes are given in Table 23 and crystal structures in Table 22. Recent preparations of $[CoX_3(py)_3]^{n+}$ and $[CoX(py)_4]^+$ by Schaffer and his colleagues[251–253] have made available a wide range of complexes (Scheme 25). The solvolysis of *trans*-$[CoCl_2(Rpy)_4]^+$ has been studied in water–alcohol mixtures by Elgy and Wells who correlate activation parameters with changes in solvation structure of the transition state.[254] The well-known slow acid-catalyzed hydrolysis of bidentate carbonate in these systems has been studied in some detail by Harris and coworkers for $[Co(CO_3)(py)_4]^+$;[259] the immediate product is thought to be the *trans*-$[Co(OH_2)_2(py)_4]^{3+}$ ion. Utsuno claims to have isolated the asymmetric atropisomer (**51**) by treating *trans*-$[CoCl_2(py)_4]Cl\cdot 6H_2O$ with $(-)_{589}$-Hdibenzoyl tartrate.[255] A large number of mixed-ligand complexes containing oxalate, malonate or carboxylate in addition to pyridine are available, and a recent paper by Fujinami and his colleagues may be consulted for details.[256]



Scheme 25

Table 23 Preparations: Cobalt Complexes Containing Six-Membered N-Heterocyclic Ligands

Complex	*Preparation*	*Comments*	*Ref.*
Cobalt(0)			
$[Co(bipy)_3]$	$CoCl_2 \cdot THF + Li_2$bipy; THF, r.t.	Dark blue; $\mu = 2.23$ BM	3
$[Co(bipy)_2]$	Co + toluene, −196 °C; bipy, warm	Black-green; $\mu = 2.02$ BM	4
Cobalt (I)			
$[Co(bipy)_3]ClO_4$	$[Co(bipy)_3](ClO_4)_2 + bipy + NaBH_4$	Dark blue; 285 nm; ^1H NMR	1, 5
$[Co(phen)_3]ClO_4$	$[Co(phen)_3](ClO_4)_2 + NaBH_4$; EtOH–$H_2O$, −5 °C, vac.	Dark brown	2
Cobalt(III)			
trans-$[Co(Cl)_2(py)_4]Cl \cdot 6H_2O$	$CoCl_2$ + py + MeOH; heat, 15 min.; cool −40 °C, $Cl_{2(l)}$, <25 °C, 40 °C, 4 M HCl	Green; ε_{631} 43; ε_{505} 30	6, 10
trans-$[Co(F)_2(py)_4](ClO_4) \cdot 0.5H_2O$	*trans*-$[Co(Cl)_2(py)_4]Cl \cdot 6H_2O + HF_{(l)}$; −70 °C; $Hg(OAc)_2$; MeOH; 70% $HClO_4$	Red-purple; ε_{567} 27.5; ε_{479} 37.8	6
$[Co(F)_2(H_2O)(py)_3]ClO_4$	$[Co(CO_3)Cl(py)_3] + HF_{(l)}$	Purple; ε_{520} 40.5; ε_{381} 48	6
$[Co(CO_3)Cl(py)_3]$	$CoCl_2 \cdot 6H_2O + KHCO_3 + H_2O_2$; H_2O, 5 °C, py, 12 M HCl, 1 h; stand	Blue-violet; ε_{577} 50; ε_{409} 60	7
$[Co(CO_3)(py)_4]ClO_4 \cdot H_2O$	$[Co(CO_3)Cl(py)_3]$ + py + $Hg(ClO_4)_2$; 50 °C, 45 min; cool	Red; ε_{530} 172; ε_{379} 190	7
trans-$[Co(H_2O)_2(py)_4](ClO_4)_3 \cdot 4H_2O$	$[Co(CO_3)(py)_4]ClO_4 \cdot H_2O$ + 70% $HClO_4$	Brown; ε_{560} 44; ε_{490} 51; $pK_{a(1)}$ 1.37	7
mer-$[Co(Cl)_3(py)_3]$	$[Co(CO_3)Cl(py)_3]$ + 12 M HCl; r.t.	Green; ε_{640} 60.2; ε_{670} 57.7	8
mer-$[Co(H_2O)_3(py)_3](ClO_4)_3$	$[Co(CO_3)(H_2O)(py)_3]ClO_4$ + 12 M $HClO_4$	Purple; ε_{518} 52	8
cis-$K[Co(CO_3)_2(py)_2] \cdot 2H_2O$	$K_3[Co(CO_3)_3]$ + py; 25 °C, 100 h	Purple; ε_{561} 165; ε_{388} 232	9
$[Co(NH_3)_5pyz](ClO_4)_3$	$[Co(NH_3)_5DMSO](ClO_4)_3$ + pyz; DMSO 90 °C, 30 min.	Yellow-orange; ε_{473} 54	11
$[Co(terpy)_2]X_2 \cdot nH_2O$ (X = Cl, Br, NO_3, ClO_4)	CoX_2 + terpy; H_2O heat	Brown-red; ε_{654} 100; ε_{549} 450	12
$[Co(bipy)_3](ClO_4)_2$	$CoCl_2 \cdot 6H_2O$ + bipy; EtOH, heat	Orange; $\mu = 4.85$	13
$[Co(phen)_3](ClO_4)_2 \cdot H_2O$	$CoCl_2 \cdot 6H_2O$ + phen; EtOH	Orange-red	14
$[Co(CO_3)(bipy)_2]ClO_4$	$Na_3[Co(CO_3)_3] \cdot 3H_2O$ + bipy; H_2O, 8 h, $NaClO_4$ to hot soln.	Dark red; ε_{504} 116	15, 16
cis-$[Co(H_2O)_2(bipy)_2](ClO_4)_3 \cdot H_2O$	$[Co(CO_3)(bipy)_2]ClO_4 + HClO_4$; H_2O, 72 h	Orange-red; ε_{490} 60; $pK_{a(1)}$ 4.6; $pK_{a(2)}$ 7.0	15, 16
cis-$[Co(X)_2(bipy)_2]X$	$CoCl_2 \cdot 6H_2O$ + bipy; H_2O or MeOH; O_2 or X_2 oxidation	*cis* (purple) for X = Cl; ε_{538} 58 (*cis*)	17, 18
cis-$[Co(Cl)_2(phen)_2]Cl \cdot 3H_2O$	$CoCl_2$ + phen; MeOH, reflux; −60 °C, $Cl_{2(l)}$; 65 °C, 4 M HCl	Violet; ε_{542} 56.6	18
$[Co(CO_3)(phen)_2]ClO_4$	$[Co(Cl)_2(phen)_2]Cl + Na_2CO_3$	Dark red; ε_{509} 136	19, 23
$[Co(OH)(H_2O)(N—N)](ClO_4)_2$ (N—N = phen, bipy)	$[Co(Cl)_2(N—N)]Cl + Ag_2O$; H_2O pH ≈ 5, $NaClO_4$	Red-purple; ε_{505} 74; ε_{512} 74.5 [$(OH)_2$ complex]	18
$[Co(bipy)_3](ClO_4)_3 \cdot 2H_2O$	$CoCl_2 \cdot 6H_2O$ + bipy + H_2O_2; H_2O, $HClO_4$; resolution Na(+)-tart$^-$	Yellow, ε_{540} 71.5 $[\alpha]_{589}$ −263°	13, 25 20
$[Co(phen)_3](ClO_4)_3 \cdot Br_2 \cdot H_2O$	heat, $HClO_4$	Orange; ε_{455} 99.1(sh)	21, 25

$[Co(terpy)_2](ClO_4)_3 \cdot H_2O$	$CoCl_2 \cdot 6H_2O$ + terpy + Br_2; H_2O reflux; $HClO_4$	Yellow	21
$[Co(CO_3)(bipy)_2]NO_3 \cdot 5H_2O$	$Co(NO_3)_2 \cdot 6H_2O$ + bipy; H_2O, N_2; O_2	Red; ε_{503} 118	23
$[Co(R)_2(bipy)_2](AlEt_4)$ (R = Me, Et)	$Co(acac)_3$ + bipy + AlR_3; Et_2O, r.t.	Red; ^1H NMR; I.R.	24
$[Co(en)(phen)_2]Cl_3$	$[CoCl_2(phen)_2]Cl$ + en; EtOH, r.t.	Yellow	25
$[Co(O_2C_2O_2)(bipy)_2]I \cdot H_2O$	$K_3[Co(O_2C_2O_2)_3]$ + bipy; EtOH, H_2O, heat; NaI	Orange-yellow; ε_{498} 88; resolved	26
$K[Co(O_2C_2O_2)_2(bipy)]$	As above, isolate $[Co(O_2C_2O_2)_2(bipy)]$-$[Co(O_2C_2O_2)(bipy)_2] \cdot 4H_2O$; treat with KI then $Ba(OAc)_2$; then K_2SO_4	Purple; ε_{555} 145	26
$K[Co(CO_3)_2(bipy)] \cdot 2H_2O$	$Na_3Co(CO_3)_3$ + bipy; MeOH, r.t., 1 h.	ε_{562} 151; resolved using $(-)_{589}$-$[Co(NO_2)_2(en)_2](OAc)_2$	27
cis-$[Co(CN)_2(bipy)_2]Cl \cdot 4.5H_2O$	$[Co(bipy)_3]Cl_3$ + KCN; H_2 + H_2O + C; SP-C25 chrom.	ε_{385} 160	28

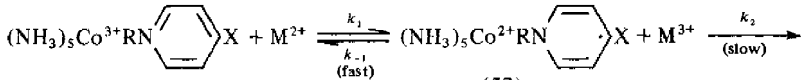
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The 2,6-dipicolinic acid complex $[Co(dipic)_2]^-$ has recently been used as a lipophilic oxidant to study electron transfer with cytochromes *c* and c_{551} and with the blue copper centre in stellacyanin, plastocyanin and azurin; penetration of the complex towards the metal centre of the protein is thought to aid electron transfer.[257,271]

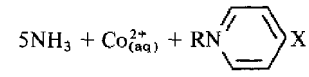
Pentaammine complexes may be easily prepared using readily replaceable trimethyl phosphate[173] or trifluromethanesulfonate[175] in $[Co(NH_3)_5L]^{3+,2+}$, using an inert solvent such as sulfolane or trimethyl phosphate. For N-heterocyclic donors, however, reaction (46) is perhaps most convenient since $[Co(NH_3)_5(DMSO)](ClO_4)_3$ is easier to prepare.[260] Chromatographic purification is recommended using ~4 M HCl as eluent. As an example, the work of Leopold and Haim on the preparation of 4,4′-bipyridyl complexes may be consulted.[261] It is likely that *cis*- and *trans*-$[Co(amine)_4(N\ heterocycle)_2]^{3+}$ can be prepared from the corresponding trifluoromethanesulfonate complex using sulfolane or HMPA as solvent.[175] A variety of nicotinamide complexes have recently been made *via* the 'old' method using $[Co(NH_3)_5(OH_2)](ClO_4)_3$ in aqueous solution.[258]

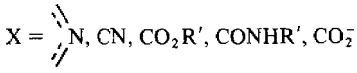
$$[Co(DMSO)(NH_3)_5]^{3+} + \text{N heterocycle} \xrightarrow[DMSO]{90\,^\circ C} [Co(\text{N heterocycle})(NH_3)_5]^{3+} + DMSO \quad (46)$$

Studies on the rates and mechanisms of reduction of $[Co(NH_3)_5L]^{3+}$ species, where L = pyridines, pyrazines, fused bipyridyls and bipyridyls containing ester, acid, nitrile and amide substituents, by metal reductants (Cr^{2+}, V^{2+}, Eu^{2+}) continue to be advanced by Gould and coworkers. For this class of reductants there is good evidence for rapid electron transfer to form a radical oxidant (**52**), with slower subsequent tunnelling of the electron to the Co^{III} centre (Scheme 26). A break in conjugation seriously slows down the k_2 step and sometimes the intermediate can be detected.[360] A representative paper by Gould may be consulted for details.[262] Reduction by $e^-_{(aq)}$, HO· and R· has also been extensively studied,[263,264] while Taube[265] and Haim[266] and their colleagues continue to study the rates of electron transfer in stable bridged species such as (**53**), and in ion pairs such as (**54**). Both adiabatic and non-adiabatic electron transfer appear possible. Marlin, Ryan and O'Halloran have generated the similar intermediate (**55**) and have followed its thermal and photoinduced reactions.[267] Weaver has studied reduction on Hg, Pt and Au surfaces.[268] Such investigations have considerable interest, both as regards understanding more about the barriers to electron transfer by combining theory and experiment and as a means of providing basic knowledge for biological electron transfer. A useful readable account of these studies up to 1975 is provided by Haim,[269] and Taube's small book 'Electron Transfer Reactions of Complex Ions in Solution' provides eloquent background.[270]

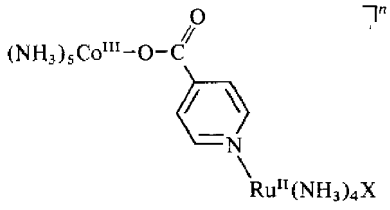


(52)

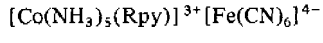




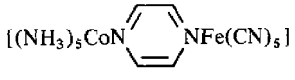
Scheme 26



(53)



(54)



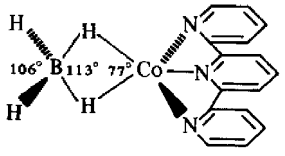
(55)

47.4.7 Phenanthroline, Bipyridyl and Terpyridyl

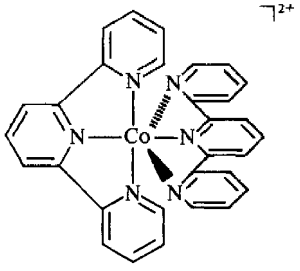
An early review article is available.[272]

47.4.7.1 *Cobalt(−1), cobalt(0) and cobalt(I)*

Low oxidation state complexes have been known for a long time. Vlĉek in 1957 isolated dark blue crystals of $[Co(bipy)_2](ClO_4)$ following $NaBH_4$ reduction of $[Co(bipy)_3](ClO_4)_3 \cdot 3H_2O$ in H_2O–EtOH and showed that the redox process was electrochemically reversible;[273] in the same year Waind and Martin correctly reported this complex as $[Co(bipy)_3](ClO_4)$.[284] Since then the redox chemistry of $[Co(bipy)_3]^{n+}$, $[Co(phen)_3]^{n+}$ and $[Co(terpy)_2]^{n+}$ has been extensively explored, and a crystal structure of $[Co(bipy)_3]Cl \cdot H_2O$ is available (Table 22). Some preparations are given in Table 23. A structure of the intermediate BH_4^- adduct (**56**) is also available (Table 22).



(56)



(57)

The redox chemistry (equations 47 and 48) is largely reversible in acetonitrile (0.1 M Et_4NClO_4)[274–276,282] and appears to be ligand based, although the expected tetragonal distortion is not particularly evident in the crystal structure of $[Co(bipy)_3]Cl \cdot H_2O$. Note the $2e^-$ change for the $[Co(phen)_3]^{+/-}$ process *vs.* the stepwise $1e^-$ changes for the $[Co(terpy)_2]^{+/0/-}$ system.

$$Co(N{-}N)_3^{3+} \overset{e^-}{\rightleftharpoons} Co(N{-}N)_3^{2+} \overset{e^-}{\rightleftharpoons} Co(N{-}N)_3^{+} \overset{2e^-}{\rightleftharpoons} Co(N{-}N)_3^{-} \qquad (47)$$

N—N	$E_{1/2}$ *vs. SCE* (V)	
phen[275]	+0.37	−0.95	−1.64
bipy[282]	+0.30	−0.97	−1.56

$$Co(terpy)_3^{3+} \overset{e^-}{\rightleftharpoons} Co(terpy)_3^{2+} \overset{e^-}{\rightleftharpoons} Co(terpy)_3^{+} \overset{e^-}{\rightleftharpoons} Co(terpy)_3^{0} \overset{e^-}{\rightleftharpoons} Co(terpy)_3^{-}$$

$E_{1/2}$ *vs. SCE* (V)[276] +0.28 −0.77 −1.65 −2.00 (48)

The high-spin character of $[Co(bipy)_3]^+$ ($\mu = 2.53$–2.89 BM)[277,278] and ^1H NMR[279] have been used as evidence for $\sigma_d \rightarrow \pi_{bipy}$ spin delocalization, and the near-UV[279] and near-IR[277] spectra are due to π–π^* transitions in the ligand resulting from this delocalization. Much of the additional electron density in these low-valent complexes clearly resides on the conjugated ligand[272] and the absence of similar reduced $[CoX_2(py)_4]^{n-}$ or $[Co(py)_6]^{+,0}$ species may result in part from conjugation. Apparently $[Co(bipy)_3]^+$ in water produces stoichiometric quantities of H_2 and $[Co(bipy)_3]^{2+}$[280] but the details appear to be complex.[281] The electrochemical properties of related tris{(2-pyridyl)amine}-cobalt(II) complexes have also been discussed.[285]

Metal-vapour-deposition methods have begun to provide new low-valent complexes of uncommon stoichiometry. The preparation of gram quantities of paramagnetic ($\mu = 2.02$ BM) $[Co(bipy)_2]$ has been reported and its reactions with Br_2, tetracyanoethylene and tetracyanoquinodimethane studied.[283] Electrochemically it behaves identically to $[Co(bipy)_3]^{2+}$ (equation 47).[283]

47.4.7.2 *Cobalt(II)*

Orange-brown $[Co(N{-}N)_3]^{2+}$ (N—N = bipy, phen) has been known since the days of Burstall and Nyholm,[286] and crystal structures are now available on salts of both (Table 22). They behave as typical high-spin Co^{II}. However $[Co(terpy)_2]X_2$ appears to be at the high to low spin cross-over with $X = Br^-$, NO_3^- having $\mu = 2.96$ BM, and $X = Cl^-$, ClO_4^- being high spin, $\mu = 4.49$, 4.65 BM (300 K).[287] Crystal structures for $X = Cl^-$ and NCS^- (intermediate spin, $\mu = 4.0$ BM; Table 22) suggest the difference, and an X-ray phase transition noted for the NCS complex results from a 10 pm decrease in the Co—N bond length to the central N of an appreciably ruffled tridentate (**57**).[288] A detailed magnetic and spectral (visible–UV, ESR) study suggests that intermolecular cooperative exchange between adjacent Co^{II} sites is a more likely model for spin exchange than

intramolecular thermal excitation.[289] $[Co(bipy)_3]^{2+}$ when trapped in a Y-zeolite matrix shows a similar spin equilibrium[290] although this behaviour is unknown in solid $[Co(bipy)_3]X_2$ salts or in aqueous solution.

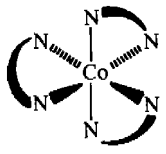
Distorted octahedral *cis*-$[CoX_2(N—N)]$ complexes are well known,[291] and a crystal structure for $X = NCS^-$ is available (Table 22). Very distorted five-coordinate $[CoX_2(terpy)]$ ($X = Cl^-$, NCO^-) is also known (Table 22). Akabori reports that pyrolysis of $(HN—NH)CoCl_4$ salts (N—N = phen, bipy) results in two phases of $[CoCl_2(N—N)]$, one of which is polymeric and octahedral and the other is tetrahedral and monomeric,[293] but such studies need structural clarification.

Watanabe and coworkers have described some Co^{II}–bipyridyl (phenanthroline) catalyzed Michael additions of nitromethane generalized by equation (49) but the catalyzing effect of the complex remains obscure.[292]

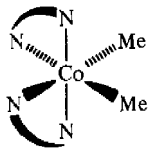
$$XCH{=}CHY + HZ \xrightarrow[DMF,\ r.t.]{Co(phen)_x^{2+}} \underset{Z}{XCHCH_2Y} \qquad (49)$$

47.4.7.3 Cobalt(III)

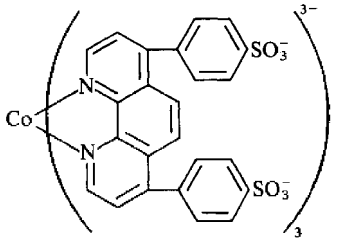
The orange-yellow $[Co(N—N)_3]^{3+}$ ions (N—N = bipy, phen) have been known for a long time (Table 23).[286] The considerable theoretical uncertainty as to their absolute configurations has now been resolved by a crystal structure of $(-)_{589}$-$[Co(bipy)_3][Fe(CN)_6]\cdot 8H_2O$, which has the Δ absolute configuration (**58**).[294] A similar configuration is likely for $(-)_{589}$-$[Co(phen)_3]^{3+}$, which is in agreement with oxidation of $[Co(phen)_3]^{2+}$ in the presence of $(-)_{589}$-malic acid for which evidence exists for Pfeiffer stabilization of the Λ absolute configuration.[295] These species undergo light and halide (I^-, Br^-) induced racemization,[296] and the process is also promoted by $[Co(N—N)_3]^{2+}$,[297] so solutions of the optically active ions should be carefully protected. Thermal racemization of $[Co(phen)_{3-x}(en)_x]X_3$ species ($x = 0$–2; $X = Cl^-$, Br^-, I^-) has been examined in the solid state.[311]



(58) Δ-$(-)_{589}$-$[Co(bipy)_3]^{3+}$



(59)



(60)

The preparation of $(+)_{589}$-$[Co(phen)_3]^{3+}$ by oxidation of the analogous $(+)_{589}$-$[Co(phen)_3]$ $[(+)SbOtart]_2$ complex (Table 23) illustrates the transient optical stability of the Co^{II} cation. The $[Co(phen)_3]^{2+}$ and $[Co(terpy)_2]^{2+}$ ions have been extensively used as stable reductants in outer-sphere redox studies. Recent theoretical[312] and practical[313,314] papers may be consulted for background. Considerable use is now being made of Co^{III}–phen systems in specific labelling of biological enzymes, notably those which have a reductive function. Holwerda, Gray and coworkers have characterized the penetrative ability of $[Co(phen)_3]^{3+}$ for oxidation by measuring the relative rates of reduction, *i.e.* $k[Co(phen)_3^{3+}]/k[Co(C_2O_4)_3^{3-}]$, for several metalloproteins.[315] This varies from 250 for Cu^I stellacyanin to 3.4×10^5 for $HIPIP_{red}$. The hydrophilic oxidants $[Fe(edta)]^{2-}$ and $[Co(C_2O_4)_3]^{3-}$ are considered not to penetrate the protein and are therefore used as marker oxidants. Sykes and coworkers have used $[Co(phen)_3]^{3+}$ and the 4,7-di(benzene-4′-sulfonate) derivative (**60**) in a number of such studies.[316–320] Comparisons are made with other oxidants including $[Fe(CN)_6]^{3-}$, $[Fe(edta)]^{2-}$ and $[Ru(NH_3)_5py]^{3+}$. Studies include reductions of the Fe^{II} heme protein cytochrome b_5 ($k_eK_b = 1.5 \times 10^3\ mol^{-1}\ dm^3\ s^{-1}$ for $[Co(phen)_3]^{3+}$) and some modified derivatives which suggest that the inorganic oxidant acts at a site close to Lys 27 on the right-hand side of the heme edge,[316] high-potential Fe–S protein from *Chromatium vinosum* $HIPIP_{red}$ ($k_eK_b = 2.8 \times 10^{-3}\ mol^{-1}\ dm^3\ s^{-1}$),[317] and the Cu^I proteins parsley plastocyanin PCu(I),[318,319] stellacyanin SCu(I), cytochrome c_2(II), and azurin from *Pseudomonas aeruginosa* ACu(I).[320] For some of these rate-limiting binding to the protein was observed and Table 24 contains some particular information for these. It is clear that although (**60**) binds more strongly it is a poorer oxidant in a kinetic sense since the electron transfer rate is very much reduced compared to $[Co(phen)_3]^{3+}$.

Table 24 Binding Constants (K_b) and Electron Transfer Rates (k_e) for Oxidation of Some Cu^I Metalloproteins[a]

Protein	*Oxidant*	K_b	k_e	k_eK_b
PCu(I)	$[Co(phen)_3]^{3+}$	167	17.9	3000
PCu(I)	$[Co(4,7\text{-DPSphen})_3]^{3-}$	4600	0.041	190
ACu(I)	$[Co(phen)_3]^{3+}$ (pH 9.1)	457	21.3	9700
	$[Co(4,7\text{-DPSphen})_3]^{3-}$	2750	0.21	580
$HIPIP_{red}$	$[Co(phen)_3]^{3+}$	–	–	2800
	$[Co(4,7\text{-DPSphen})_3]^{3-}$	3420	0.020	68
	$[Fe(CN)_6]^{3-}$	(< 10)	–	240

[a] K_b in $dm^3\,mol^{-1}$, k_e in s^{-1}.

Preparations of $[CoCl_2(N{-}N)]Cl$ species were pioneered by Jaeger and van Dijk (bipy) and Pfeiffer and Werdelmann (phen) many years ago but recent work is due to Ablov and Palade[298] and to Schaffer and coworkers.[299] A wide range of complexes is now available some of which are given in Table 23. It appears that green *trans*-$[CoX_2(N{-}N)]^+$ ions ($X = Cl^-$, Br^-) are unlikely despite many earlier claims,[299] and considerable doubt now exists about *trans*-$[Co(OH_2)(OH)(N{-}N)_2]^+$ species.[300] The *cis* configuration may be the only geometry possible sterically. Acid hydrolysis of $[CoCl_2(N{-}N)_2]^+$ is very slow compared to the saturated amine (*e.g.* ethylenediamine) counterparts and previous disagreements have been traced to catalytic impurities.[301] Acid hydrolysis of $[Co(CO_3)(N{-}N)_2]^+$ ions is also slow, $k = k_1\ [H^+] (k_1 = 1.5 \times 10^{-4}\,mol^{-1}\,dm^3\,s^{-1}$ (phen); $2.2 \times 10^{-4}\,mol^{-1}\,dm^3\,s^{-1}$ (bipy), 25 °C), with Co—O bond cleavage for the rate-controlling ring-opening process.[302] Alkaline hydrolysis however is fast[299,301] and must result from an alternative to the normal conjugate base mechanism (S_N1cb) found with saturated amine systems. The mixed chelates $[Co(C_2O_4)_2(N{-}N)]^-$ and $[Co(C_2O_4)(N{-}N)_2]^+$ have been prepared and resolved,[303] and their photochemical[304] and thermal[309] reduction has been studied. Other complexes containing amino acids,[305] ethylenediamine[306,307] and ammonia,[308] and CN^- [308] have been prepared in recent years; some have been resolved into optical enantiomers. The paper by Utsuno and coworkers[308] records ^{13}C resonances for a large number of systems and may be consulted for background references. Some interesting *cis*-dialkyl complexes, *cis*-$[Co(R)_2(bipy)_2](AlR_4)$,[310] have been made (equation 50), and a crystal structure has been reported on (**59**; Table 22). The intermediate $[Co(R)_2(acac)(bipy)]$ was also isolated. Complex (**59**) is stable in aqueous solution, but liberates CH_4 when treated with concentrated H_2SO_4; the chloride salt is even more stable in aqueous solution, however it is rapidly decomposed by UV light, liberating CH_4. ^1H NMR shows no exchange of alkyl groups in $[Co(Me)_2(bipy)_2](AlEt_4)$.[310]

$$[Co(acac)_3] + bipy + AlR_3 \xrightarrow{Et_2O} [Co(R)_2(bipy)_2](AlR_4) \quad (50)$$

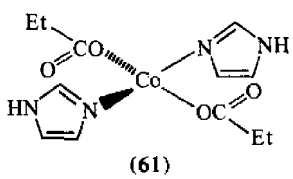
R = Me, Et (**59**)

Just as Co^{III}–phenanthroline complexes have been used in metalloprotein electron transfer studies (*vide supra*), Yount and coworkers have utilized $[CoCO_3(phen)_2]^+$ and $CoCl_2$ in the presence of phenanthroline to block the ATPase activity of myosin, and attachment to sulfhydryl groups near the active site is suggested.[321]

47.4.8 Imidazole, Pyrazole, Triazole and Tetrazole

47.4.8.1 Cobalt(II)

Co^{II} complexes of imidazole retain some interest as structural models for biological systems, notably carboxypeptidase A and thermolysin. Vallee and colleagues discuss this with special reference to MCD spectra,[322] and Hodgson discusses stereochemical aspects of purine and metal–nucleotide complexes for similar reasons.[323] Horrocks, Ishley and Whittle have recently described some $[Co(O_2CR)_2(im)_2]$ structural models, *e.g.* (**61**), which have physical properties similar to Co^{II}–substituted carboxypeptidase.[324]



(**61**)

Table 25 Structures: Five-membered N-Heterocyclic Complexes of Cobalt (II, III)

Complex	*Comments*[a]	*Ref.*
Cobalt(II)		
$[Co(imH)_2]_x$	Tet.; polymeric helical structure with bridging imidazolate anions; CoN 197–199; NCoN 104–117°	1
$[Co\{OC(O)Me\}_2(im)_2]$	Tet.; monodentate acetate; CON ≈ 200	2
$[CoCl_2(im)_2]$	Tet.; CoN 199; CoCl 224, 226; NCoN 105°; ClCoCl 111°	3
$[Co(CO_3)(OH_2)_2(im)_2]$	Oct.; *cis* OH_2, *trans* im; OCoO 61.2°; CoO_6 214.3; CoO(H) 216.6; CoN 211.2	4
$[Co(im)_6](O_2CMe)_2 \cdot 0.5H_2O$	Oct.; CoN 215; NCoN 90°	5
$[Co(im)_6](CO_3) \cdot 5H_2O$	Oct.; CoN 216, 218	6
$[Co(NO_3)(2Meim)_4]NO_3 \cdot 0.5EtOH$	Dist. oct.; bidentate NO_3; OCoO 56.8°; CoN 196, 210 (*trans* to O), 221, 225	7
$[Co(SiF_6)_2(N\text{-vinylim})_4]_x$	Dist. oct.;—F—Co—F—Si— chains, equatorial im; CoN 209.7; CoF 214.3	8
$[Co(o\text{-}NO_2PhO)(1\text{-}Meim)_2]$	Dist. oct.; bidentate *o*-nitrophenolate; *trans* Meim; CoN 208.7; CoO 197.2; CoO(NO) 221.9; OCoO 81.3°	9
$[Co(NO_3)_2\{2(SMe)Meim\}_2]$	Quasi-tet.; with bidentate NO_3 groups	10
$[Co(O_2CR)_2(R'im)_2]$ (R = Me, Et; R′ = H, 2Me, 2Et)	Dist. tet.; monodentate carboxylate; CoO, 196, 200.5; CoN 201; OCoO 105.1°, NCoN 108.6°	12, 1
$[Co(O_2CR)_2(2Meim)_2]$ (R = Me, Pr)	Dist. oct.; bidentate carboxylate; CoO 208.6–214.5; CoN 205.5–206.9; OCoO, 138.5°, 151.6°; NCoN, 98.2°, 98.8°	13
$[Co(NCS)_2(3,5\text{-}Me_2\text{-}1\text{-}Phpyrz)_2]$	Dist. tet.; NCoN 106–112°; CoN, 203; CoN(CS) 195; CoNC 177–178°	15
$[\{CoCl_2\}_2(\mu\text{-}Me_2pyrzl)]$	Tet.; bridging pyrazolyl; CoN 201; CoCl 224	14
$[\{Co(3,5\text{-}Me_2pyrz)_3\}(\mu\text{-}F)_2](BF_4)_2$	Trig. bipy.; dimeric with μ-F bridging; CoF_{ax} 214.6; CoF_{eq} 192.4; CoN_{ax} 204.2; CoN_{eq} 203.3; FCoF 81.2°; CoFCo 98.8°	11
$[CoCl_2(2\text{-}NH_2thiaz)_2]$	Tet.; CoN, 201; CoCl 226	16
$[CoCl_2(1,3\text{-}Bzthiaz)_2]$	Tet.; CoN 206; CoCl 223; ClCoCl 114.8°	17
$[\{Co(NCS)_2(4\text{-}Phtriz)\}_2(\mu\text{-}4\text{-}Phtriz)_3] \cdot xH_2O$	Oct.; dimeric; three triazole bridges; CoCo 390.7; CoN 210–212	18
$[Co(NCS)_2(triz)_2]_x$	Oct. (*trans* NCS); bridging triazoles CoN_2 218; CoN_4 212; CoN(CS) 208.2; NCoN 84–96°	19
$[\{Co(H_2O)_3\}_2\{\mu\text{-}(triz)_3\}_2Co](CF_3SO_3)_6$	Oct.; three triazole bridges to central Co^{2+}; structure on isomorphous Fe^{II} complex	20
$[\{Co(NCS)_2(Et_2triz)\}_2\{\mu\text{-}(NCS)(Et_2triz)_2\}Co]$	Oct. with two triazole and one NCS bridging units; structure on isomorphous Ni^{II} complex	21
$(adeH)_2[Co(H_2O)_4(ade)_2](SO_4)_2 \cdot 6H_2O$	Oct. (*trans* adenine); CoN 216.4; CoO 211.4, 207.3; coordination *via* N_9	22
$[CoCl_2(ade)]$	Tet.; CoN(1) 203; CoN(7) 204.7; CoCl	23
$[Co(H_2O)_5(5'\text{-}IMP)] \cdot 2H_2O$	Oct. (purine nucleotide); CoN(7) 216.2	27
$[Co(H_2O)_5(5'\text{-}GMP)]$	Oct. (purine nucleotide)	29
Cobalt(III)		
$[CoCl(adeH)(en)_2]Br \cdot H_2O$	Oct.; CoN(9) 194.9; CoN(C) 195, 197; CoCl 225.9	24
cis-$[CoCl(Me_2xant)(en)_2]ClO_4$	Oct.; CoN(7) 198.4; CoCl 222.5	25
trans-$[CoCl(Me_2xant)(en)_2]Cl \cdot 2H_2O$	Oct.; CoN(7) 195.6; CoCl 225.5	26
trans-$[Co(NO_2)(acac)_2(dAdO)]$	Oct.; CoN(7) 199	28
$[Co(xant)(DMGH)_2(Bu^n_3P)]$	Oct.; (*trans*) CoN(2) 199.9; CoP 228.5	35
cis-$[CoCl(im)(en)_2]Cl_2$	Oct.; *cis* Cl, im; CoN_{im} 194.5, CoN_{en} 196; CoCl 225.7	30
$[Co(4\text{-}NO_2imH)(NH_3)_5]Cl_2$	Oct.; imidazolate ligand; CoN_{im} 194.1, CoN_{cis} 197.2, CoN_{trans} 196.6	31
$[(NH_3)_5Co(\mu\text{-}imH)Cu(Me_5dien)](ClO_4)_4$	Oct. (Co) bridging imidazolate, CoN, 195.7–198.3; CoN_{im} 193.3; dist. sq. planar (Cu), CuN_{im} 195.4	32
$[Co(5\text{-}CNtetzH)(NH_3)_5](ClO_4)_2$	Oct. tetrazolate ligand; CoN_{tetz} 192; CoN 196–199 (N(2) coordination)	33
$[Co(5\text{-}NH_2tetzH)(NH_3)_4]Br_2$	Oct.; chelated (N-1, N-5) amidinotetrazolato ligand; CoN(1) 191, 194; CoN 195–198	33
$[Co(5\text{-}FtetzH)(DMGH)_2(Bu^n_3P)]$	Oct. (*trans*); CoN_2 197.9; CoP 226.3	34

[a] Bond lengths in pm.

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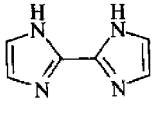
Table 25 (*continued*)

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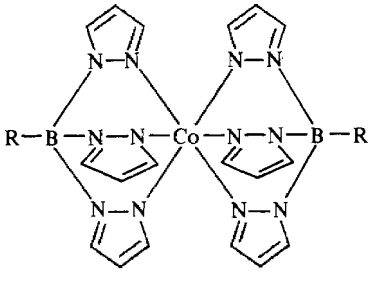
Martin and Edsall were the first to show that the colours and compositions of crystalline Co^{II}–imidazole complexes depend on the pH and conditions of preparation.[325] A general account of the properties of imidazole and histidine complexes is available,[326] and Table 25 lists some structures. Articles by Eilbeck[327] and coworkers and by Davis and Smith[328] may be consulted for preparative details. The complexes are usually easily prepared from the ligand and metal salt in hot ethanol or acetone. An equilibrium between pink (octahedral) and blue (tetrahedral) geometries is found with the unsubstituted ligand, *e.g.* equation 51,[329] and structures are available for each in various salts, as well as for polymeric tetrahedral $[Co(imH)_2]_x$ containing linear chains of bridging imidazolate anions (Table 25). Octahedral complexes containing bidentate NO_3^- or CO_3^{2-} are known (Tabel 25), and a paper by Freeman and coworkers may be consulted for spectral, structural, and magnetic properties of these.[330] Goodgame and coworkers also discuss spectral properties of octahedral and tetrahedral systems.[331] In every case a high-spin electronic configuration obtains with $\mu \approx 5.0$ BM for pink octahedral systems and 4.2–4.5 BM for blue tetrahedral $[CoX_2(im)_2]$ and $[Co(im)_4](ClO_4)_2$ complexes.[328] No structure of imidazole anion with side-on bonding (**64**) is available.

$$\underset{\text{blue, } > 140\,^\circ\text{C}}{[Co(imH)_4][Co(CO)_4]_2} + imH \rightleftharpoons \underset{\text{pink, } < 70\,^\circ\text{C}}{[Co(imH)_6][Co(CO)_4]_2} \qquad (51)$$

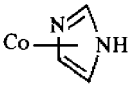
Preparative details and background information may be found in the following references: imidazole and substituted imidazoles,[327,332,333] thiazole,[327] benzothiazoles,[334] tetrazoles,[335] pyrazoles.[336] The ligand 2,2′-biimidazolyl (**62**) forms very weak complexes when compared to bipyridyl and phenanthroline but it can be deprotonated to form $[Co(L{-}H)_2]$ species.[337] The very stable complex (**63**) has been known for several years[338] and is characterized by having precise C_{3v} symmetry. White and Faller have pointed out that such a system is ideally suited as a paramagnetic NMR probe.[339] They prepared the R = 4-LiC_6H_4 derivative and have suggested how it might be attached to appropriate sites in target molecules.



(62)



(63) R = H, Ph, 4-BrPh, 4-LiPh



(64)

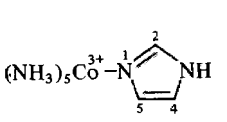
Table 26 Preparations: Cobalt(III) Complexes Containing Imidazole and Tetrazole

Complex	*Preparation*	*Properties*	*Ref.*
$[Co(imH)(NH_3)_5](ClO_4)_3$	$[Co(DMSO)(NH_3)_5](ClO_4)_3$ + im; DMSO 80 °C, 45 min; chrom.	Yellow; ε_{472} 61.5; ε_{334} 70.7	1
$[Co(RimH)(NH_3)_5]Cl_3$ (R = 4-Me, 5-Me, 2,5-Me_2)	$[Co(O_3SCF_3)(NH_3)_5](CF_3SO_3)_2$ + Rim; sulfolane, 85–90 °C	^{1}H NMR, vis–UV, pK_a	2
cis-$[CoCl(imH)(en)_2]Cl_2$	*trans*-$[Co(Cl)_2(en)_2]Cl$ + im; H_2O, MeOH	Red; ε_{520} 78.5; resolution, ORD, CD	3
$[Co(NH_3)_5(\mu\text{-imH})Ru(NH_3)_4(SO_4)](BF_4)_3$	$[Co(imH)(NH_3)_5](ClO_4)_3$ + $[Ru(NH_3)_4(OH_2)(SO_3)]$; aq. 0.1 M LiOH, Ar	ε_{460} 450 (sh); ε_{339} 4300	4
$[Co(5\text{-Rtetz})(NH_3)_5](BF_4)_2$	$[Co(NH_3)_5(H_2O)](ClO_4)_3$ + tetz$^-$; H_2O, 85–90 °C, 3 h; chrom.	Yellow; ε_{464} 64.8 (R = Me), N(2) isomers	5
$[Co(5\text{-Rtetz})(NH_3)_5]I_2$	$[Co(NCR)(NH_3)_5](ClO_4)_3$ + NaN_3; H_2O; pH 5, 15 min–2 h	Yellow; (N(1) isomer) ε_{473} 62	6

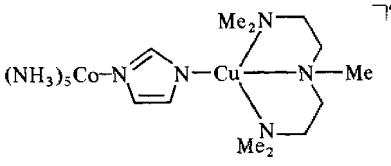
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47.4.8.2 Cobalt(III)

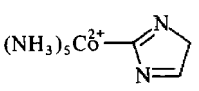
Several $[CoL(NH_3)_5]^{3+}$ and *cis*-$[CoL(X)(en)_2]^{2+}$ complexes have been prepared (Table 26) and some crystal structures are available (Table 25). Pentaammine complexes are easily made from $[Co(DMSO)(NH_3)_5](ClO_4)_3$, and there is no need to use a better leaving group.[340,341] The physical properties (^1H NMR, visible–UV, ^{13}C NMR, pK_a) for both systems (L = imH) have been comprehensively documented.[341,342] The acidity of the N_3 proton in (**65**) is enhanced by coordination and the imidazolate anion is readily accessible (pK_a 10.0 *vs.* 14.1 for imH). Several deprotonated bimetallic bridged species have been prepared and structure (**66**) has been put forward as a model for heterobiometallic protein centres.[343] The tetrazole complexes (**68**) exist predominantly in the anionic form (pK_a 1–2)[351] and preparation normally gives the N(2)-bonded form. However Ellis and Purcell[352] have prepared the N(1) isomer by reacting a coordinated nitrile with N_3^- ion at pH ~ 5 (equation 52). Properties of both isomers are available.[351]



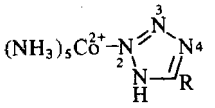
(65)



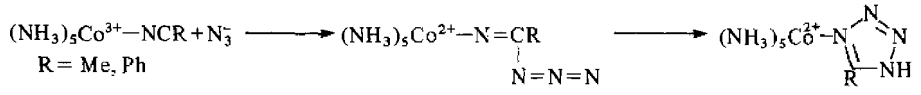
(66)



(67)



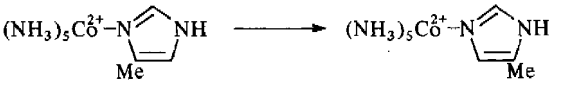
(68)



(52)

(69)

The C(2) proton in (**65**) does not exchange in alkaline aqueous solution in contrast to that of the uncoordinated ligand; the C(2)-bonded mode (**67**) has never been identified. Isomerization in the adjacent 5-Me-substituted complex (**70**) to the more stable 4-Me isomer (**71**; equation 53), occurs *via* the imidazolate anion ($pK_a = 10.46$, $k = 9.6 \times 10^{-4}\,s^{-1}$) although a limiting rate was never achieved;[334] a dissociative but intramolecular pathway *via* the π-bonded ligand (**64**) is preferred. Similar isomerization occurs with N(1)-coordinated 5-methyltetrazole with the protonated ligand now being some 100 times more reactive than its conjugate base (equation 54).[351] Rotation about the double bond similar to that found in Ru^{II} chemistry is more likely in this case. Some comparative intramolecular isomerization rates are given in Table 27.



(53)

(70) (71)

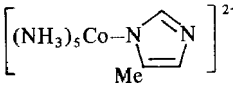
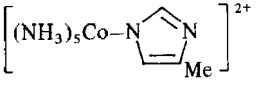
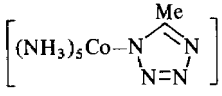
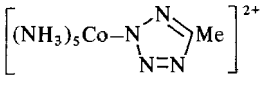
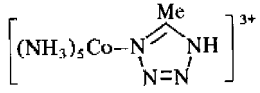
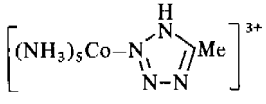


(54)

(74)

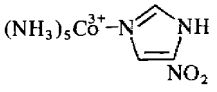
Mononitration of $[Co(NH_3)_5(im)]^{3+}$ occurs exclusively at the less-hindered C-4 site and the resulting complex (**72**) is very acidic, $pK_a = 1.66$.[345] Bromination occurs stepwise in acidic aqueous solution with the substitution pattern given by equation (55).[346] Rates of bromination follow the order $k_2 \gg k_3 > k_1$, which is the same as that found with the uncoordinated ligand. Electron transfer in systems (**73**) has been investigated by Isied[349] and Haim,[350] and Table 28 contains some comparative rate data. The imidazolate bridge provides the lowest energy pathway compared to other conjugated systems even though it is the poorest π-acceptor ligand. Szecsy and Haim[350] argue convincingly that the measured value represents k_1 (equation 56), and that subsequent dissociation, k_2, is more rapid. The insulating bis(4-pyridyl)ethane bridge is believed to prevent intraligand transfer and an outer-sphere mechanism is suggested in this case.[350] Reduction of the protonated tetrazole complex (**74**) by $Cr^{2+}_{(aq)}$ has been studied ($k = 19 \pm 2\,mol^{-1}\,dm^3\,s^{-1}$, 25 °C) and an inner-sphere mechanism with coordination of Cr^{II} to N-1 is suggested; the anion form is also reactive.[353] Reduction of $[Co(imH)(NH_3)_5]^{3+}$ by $e^-_{(aq)}$ and the HO· radical results in the diffusion-controlled

Table 27 Rate Data for Intramolecular Linkage Isomerization in Some Cobalt(III) Complexes

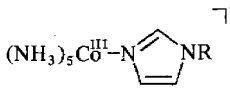
Reactant	*Product*	k (s^{-1}, 25 °C)	*Activation parameters* (kJ mol^{-1}; J K^{-1} mol^{-1})	*Ref.*
$[Co(ONO)(NH_3)_5]^{2+}$	$[Co(NO_2)(NH_3)_5]^{2+}$	8.2×10^{-3} (60 °C)	$\Delta H^{\ddagger}$ 95 ± 4; $\Delta S^{\ddagger}$ −4 ± 12 ($I = 1.0$)	1
			$\Delta H^{\ddagger}$ 92 ± 1; $\Delta S^{\ddagger}$ −17 ± 3 ($I = 0.1$)	2
$[Co(SCN)(NH_3)_5]^{2+}$	$[Co(NCS)(NH_3)_5]^{2+}$		$\Delta H^{\ddagger}$ 103 ± 1; $\Delta S^{\ddagger}$ −14 ± 3 ($I = 0.1$)	3
$[Co(NH_2SO_3)(NH_3)_5]^{2+}$	$[Co(OSO_2NH_2)(NH_3)_5]^{2+}$	1.1×10^{-3}	$\Delta H^{\ddagger}$ 103; $\Delta S^{\ddagger}$ 46 ($I = 1.0$)	4
$[Co(NH_2CONMe_2)(NH_3)_5]^{3+}$	$[Co\{OC(NH_2)(NMe_2)\}(NH_3)_5]^{3+}$	1.6×10^{-2}	$\Delta H^{\ddagger}$ 81; $\Delta S^{\ddagger}$ −8 ($I = 1.0$)	5
		9.6×10^{-4}	$\Delta H^{\ddagger}$ 140 ± 20; $\Delta S^{\ddagger}$ 70 ± 50	6
		2×10^{-6}	$\Delta H^{\ddagger}$ 110 ± 10; $\Delta S^{\ddagger}$ 11 ± 24	7
		3.1×10^{-4}	$\Delta H^{\ddagger}$ 60 ± 20; $\Delta S^{\ddagger}$ −100 ± 50	7

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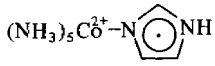
production of radical ion intermediates, *e.g.* (**75**), which slowly decay to $Co^{2+}_{(aq)}$ and free ligand ($k = 3 \times 10^3\ s^{-1}$, 25 °C).[354] The barrier to conjugated electron flow from the ligand to the metal is clearly quite high and mechanisms involving restricted overlap of the requisite π-ligand donor and σ-metal acceptor orbitals and an unfavourable equilibrium to form low-spin Co^{II} have been suggested.



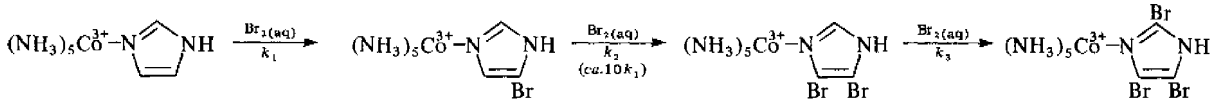
(72)



(73) R = $[Fe(CN)_5]^{3-}$, $[Ru(SO_3)(H_2O)(NH_3)_4]$

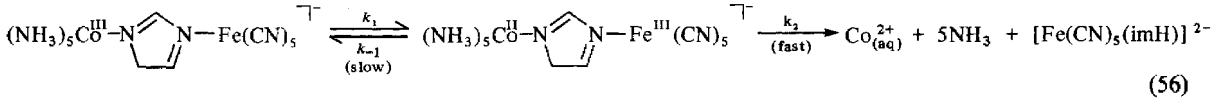


(75)



pK_a = 10.0 pK_a = 7.75 pK_a = 4.42 $pK_a \approx 2$–3

(55)



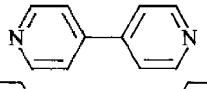
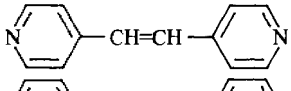
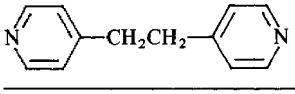
(56)

47.5 PHOSPHORUS LIGANDS

47.5.1 Phosphorus

The cubane-like $[CoCpP]_4$ unit containing tridentate P atoms has been investigated structurally and semi-theoretically by Dahl and coworkers.[355] This green-black diamagnetic complex has a tetragonally distorted Co_4P_4 core (**76**) with Co—Co bonding (250.4 pm) arising from the requirement to reach the 18-electron configuration. This molecule is related to the series $[P_3Co(CO)_3]$, $[P_2Co_2(CO)_6]$, $[PCo_3(CO)_9]$ in which $Co(CO)_3$ units successively replace a P atom from the structurally similar and electronically equivalent P_4 molecule. The structure of $[Co_2(CO)_5(PPh_3)(\mu\text{-}P_2)]$ (**77**) emphasizes this, while the $[Co_6(CO)_{14}(\mu\text{-}CO)_2P]^-$ anion (**78**) provides a good example of a clathrated phosphide atom (structures, Table 29). Sacconi and his colleagues in a number of reports have made use of the coordinated tricyclic P_3 unit in $[Co\{MeC(dppm)_3\}P_3]$ (**79**) to further coordinate other ML^{2+} units (M = Fe, Co, Ni; L = $MeC(dppm)_3$, $N(dppe)_3$, $MeC(depm)_3$) and to $Cr(CO)_5$

Table 28 Comparisons of Rates of Intramolecular Electron Transfer in $[(NH_3)_5Co^{III}L\text{-}Fe^{II}(CN)_5]^{0/-}$ and $[(NH_3)_5Co^{III}LRu^{II}(NH_3)_4(H_2O)(SO_3)]^{2+/3+}$ Systems (25°C)[1]

L	$k_e(s^{-1})^a$	$k_e(s^{-1})^b$
	6	0.165
	0.3	0.055
	4.4×10^{-2}	2.6×10^{-3}
	1.87×10^{-2}	1.4×10^{-3}
	1.0×10^{-3}	2.1×10^{-3}

[a] For Ru^{II}. [b] For Fe^{II}.

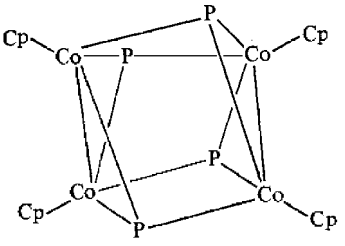
1. A. P. Szecsy and A. Haim, *J. Am. Chem. Soc.*, 1981, **103**, 1679 (correction for L = imidazolate anion).

Table 29 Preparation and Structures of Phosphorus-containing Cobalt Complexes

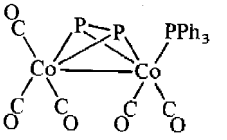
Complex	*Preparation*	*Properties, structure*	*Ref.*
$[CoP(Cp)]_4$	$[CoCp(CO)_2] + P_4$; toluene, reflux	Green-black; structure cubane-like, each P coordinated to three Co	8
$[Co_2(CO)_5(PPh_3)(\mu\text{-}P_2)]$	$Na[Co(CO)_4] + PCl_3$; THF, PPh_3; benzene, reflux	Structure, P_2 unit bonded at 90° to CoCo bond	7
$(PPh_4)[Co_6(CO)_{14}\{\mu\text{-}(CO)_2P\}]$	$Na[Co(CO)_4] + PCl_3$; THF	Structure, P atom coordinated to 6 Co atoms	6
$[Co\{MeC(dppm)_3\}P_3]$	$Co(BF_4)_2 \cdot 6H_2O + L + P_4$; BuOH	Yellow-orange; diamagnetic; structure, δ-P_3 units	1, 5
$[\{Co[Me(dppm)_3]\}(\mu\text{-}P_3)](BF_4)_2$	$Co(BF_4)_2 \cdot 6H_2O + L + P_4$; EtOH, THF, r.t., 1 h, N_2	μ = 2.02–2.20 BM	2
$[\{Co, Ni\{MeC(dppm)_3\}_2\}(\mu\text{-}P_3)](BF_4)_2 \cdot 2(Me)_2CO$	$[Co\{MeC(dppm)_3\}P_3] + NiBF_4 \cdot 6H_2O + L + NaBH_4$; EtOH, CH_2Cl_2, N_2	μ = 3.14 BM; structure, tribridging-P_3 unit	2
$[Co\{N(dppe)_3\}P_3] \cdot 0.5$ THF	$Co(BF_4)_2 \cdot 6H_2O + L + P_4$; THF, EtOH, 50 °C	Red, diamagnetic; structure, δ-P_3 unit	3
$[Co\{MeC(dppm)_3\}(\mu\text{-}P_3)\{MeC(depm)_3\}\text{-}Fe](PF_6)_2 \cdot CH_2Cl_2$	$[Co\{MeC(dpgm)_3\}P_3] + Fe(BF_4)_2$, $6H_2O + L$; EtOH, CH_2Cl_2, N_2	Blue; structure, tribridging δ-P_3 unit	4
$[Co\{MeC(dppm)_3\}(\mu\text{-}P_3)(Cr_2(CO)_{10}]$	$[Co\{MeC(dppm)_3\}P_3] + Cr(CO)_6$; THF; N_2, UV light, 4 h	Structure, two P atoms coordinated to two $Cr(CO)_5$ units	5
$[\{Co[MeC(dppm)_3](\mu\text{-}P_3)\}_2\{CuBr)_6] \cdot 2CH_2Cl_2$	$[Co\{MeC(dppm)_3\}P_3] + CuBr$; CH_2Cl_2, 30 °C, 3 h, N_2	Red-brown; μ-P_3 coordination to hexagonal $(CuBr)_6$ fragment	9

1. M. Di Vaira, C. A. Ghilardi, S. Midollini and L. Sacconi, *J. Am. Chem. Soc.*, 1928, **100**, 2550.
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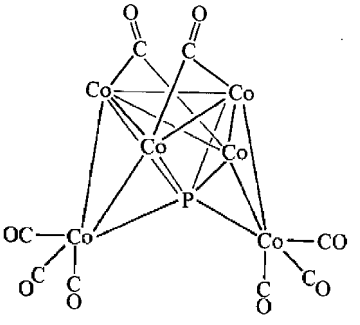
and CuBr units.[356,357,358] These provide good examples of 30-, 31- and 32-electron systems and each example is characterized by a crystal structure (Table 29). Similar δ-As_3 units are possible. Reduction with $NaBH_4$ allows the $[\{Co[MeC(dppm)_3]\}_2(\mu\text{-}P_3)](BPh_4)$ species to be isolated ($\mu = 3.13$ BM),[356] whereas oxidation at Pt generates the bright green diamagnetic $[\{Co[MeC(dppm)_3]\}_2(\mu\text{-}P_3)]^{3+}$ ion.[358] A two-electron reduction product is also reversibly formed at the Pt electrode.[359]



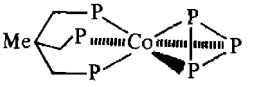
(76)



(77)



(78)



(79)

47.5.2 Phosphines

Large numbers of monodentate (PF_3, PR_3, PHR_2, a few PH_2R, and PH_3), bidentate ($NH_2(CH_2)_nPR_2$ and $R_2P(CH_2)_nPR_2$), tridentate and quadridentate (linear, branched) phosphine complexes are known. Much interest lies in their use to catalyze insertion, addition and elimination processes of industrial importance. Review articles covering 1977 are available.[361,362,363]

The σ-donor ability of phosphine ligands varies: $P(alkyl)_3 > P(aryl)_3 > P(OR)_3 > PX_3$ (X = halogen). Basicity ($pK_a(PMe_3) = 8.65$) is an important factor for Co^{III} and Co^{II} but the availability of filled π MOs on the metal for Co^0 and Co^I can modify bonding properties and stereochemsitry. Tollman has discussed the steric requirements of phosphine ligands.[364] Often this factor is of major importance in determining coordination number, stereochemistry and stability. Tollman's steric factor is defined in terms of the 'cone angle' subtended at the metal by the van der Waals' boundaries of the substituents on the P atom; small angles (*i.e.* H, Me and tied-back substituents) favour maximum coordination numbers and maximum stability. A list of cone angles is given in Table 30. Garrou has published a review discussing the use of ^{31}P NMR parameters in determining the chelating ability of phosphine ligands.[365]

Table 30 Minimum Cone Angles for Some P Ligands[1]

Ligand	*Angle* (°)	*Ligand*	*Angle* (°)
PH_3	87 ± 2	PBr_3	131 ± 2
$P(OCH_2)_3CMe$	101 ± 2	PEt_3	132 ± 4
PF_3	104 ± 2	PPh_3	145 ± 2
$P(OMe)_3$	107 ± 2	PPr^i_3	160 ± 10
$P(OEt)_3$	109 ± 2	PCy_3	179 ± 10
PMe_3	118 ± 4	PBu^t_3	182 ± 2
PCl_3	125 ± 2	PPh_3	184 ± 2
		$P(o\text{-tolyl})_3$	194 ± 6

1. C. A. Tollman, *J. Am. Chem. Soc.*, 1970, **92**, 2956.

Table 31 Preparations: Phosphine–Hydride Complexes

Complex	Preparation	Properties[a]	Ref.
$[HCo(PF_3)_4]$	$CoI_2 + PF_3$; Cu, H_2 (100 atm), 170 °C	Yellow liquid; diamagnetic; H^- acid of $Co(PF_3)_4^-$; ν_H 1973; ^1H, 20.7	1
$[CoH\{P(OEt)_3\}_4]$	$CoCl_2 + P(OEt)_3 + NaBH_4$; MeOH, N_2, −78 °C	Diamagnetic; soluble in non-polar solvents	2
$[CoH\{P(OPr^i)_3\}_4]$	$CoCl_2 + P(OPr^i)_3 + NaBH_4$; $C_2H_2(OMe)_2$, EtOH, 0 °C	Cream, diamagnetic; ν_H 1945	35
$[CoH\{P(OPh)_3\}_3(CO)]$	$[CoH\{P(OPh)_3\}_4] + CO$; toluene, 150 psi, 100 °C	White	32
$[CoH(N_2)(PPh_3)_4]$	$Co(acac)_3 + PPh_3 + AlR_3 + N_2$	Orange-red; ν_H not observed	4
$[CoH(N_2)\{P(OPr^i)_3\}_3]$	$[CoH_3\{P(OPr^i)_3\}_3] + N_2$; hexane	Near colourless (not isolated)	33
$[CoH(PMe_3)_4]$	$Co^{2+}_{(aq)} + PMe_3 + OH^- + Zn$; aq.	Yellow; ν_H, 1885, not acidic	5
$[Co(BH_4)(PPh_3)_2]$	$CoCl_2 + NaBH_4 + PPh_3$; EtOH, toluene	Green; $\mu \approx 1.2$	8
$[Co(BH_4)(PPh_3)_3]$	$CoX(PPh_3)_3$ (X = Cl, Br, I) + $NaBH_4$	$\mu = 2.71$; monodentate HBH_3^-	7
$[CoH(C_2H_4)(PMe_3)_3]$	$K[Co(C_2H_4)(PMe_3)_3] + H^+$	*Trans* H, P; trig. bipyr.	14
$[CoH(dppv)_2]$	$[CoBr_2(dppv)_2] + NaBH_4$; EtOH	Red; unstable; diamagnetic; ν_H 1885	16
$[CoH(dppe)_2]$	$[CoBr_2(dppe)_2] + NaBH_4$; EtOH	Red; soluble in organic solvents; diamagnetic; ν_H, 1885; unstable soln.	16
$[CoH\{P(dppe)_3\}]$	$Co(acac)_3 + (Bu)_2AlH$; Et_2O		17
	$CoCl_2 + L + NaBH_4$; DMF, reflux	Yellow; diamagnetic; ν_H 1780; air sensitive in CH_2Cl_2	21
$[CoH\{P(dppC_6H_4)_3\}]$	$Co(BF_4)_2 + L + NaBH_4$; DMF, EtOH, 60 °C	Brown-red, diamagnetic; ν_H 1880	24
$[CoH\{N(dppe)_3\}]$	$Co(BF_4)_2 \cdot 6H_2O + L + NaBH_4$; EtOH 50 °C	Red; diamagnetic; ν_H 1870, 1805 (THF adduct)	23
$[CoH(PEt_2R)_4]$ (R = Et, Ph)	$Co(C_8H_{12})(C_8H_{13}) + L + H_2$; benzene, MeCN	Yellow; diamagnetic	25
$[CoH\{P(OMe)_3\}_4]$	$CoCl_2 + L + NaBH_4$; $(MeO)_2C_2H_4$, 0 °C	Yellow; diamagnetic; ^1H 15.09	26
$[CoH\{P(OEt)_2Ph\}_4]$	$CoCl_2 + L + NaBH_4$; EtOH, 60–70 °C	Yellow-orange; diamagnetic; soluble in organic solvents; stable	27
$[CoH\{P(OPh)_3\}_4]$	$Co(NO_3)_2 \cdot 6H_2O + L + NaBH_4$; EtOH	Yellow; no ν_H; fluxional; stable	28
$[CoH\{P(OCH_2)_3CPr^i\}_4]$	$Co(NO_3)_2 \cdot 6H_2O + L + NaBH_4$; EtOH	White	29
$[CoH\{P(Oaryl)_3\}_3(MeCN)]$ (aryl = Ph, tolyl, Pr^iPh, PhPh)	$Co(C_8H_{12})(C_8H_{13}) + L + H_2$; MeCN, r.t.	Yellow; diamagnetic	25
$[Co(H)_2(PPh_3)_3]$	$Co(acac)_2 + PPh_3 + Et_2AlOEt + H_2$; Et_2O	Brown; stable; abs. N_2	12
$[CoH(PMe_3)_4]Cl$	$Co(PMe_3)_4 + HCl$	Fluxional 12-electron system; tet. with added H^-; ν_H 1935 (broad)	6
$[CoH(BH_4)(PCy_3)_2]$	$CoCl_2 + PCy_3 + NaBH_4$	Green; $\mu = 2.15$; dist. sq. pyr. structure (Table 32)	9
$[CoH(BH_3CN)(PPh_3)_3]$	$Co(ClO_4)_2 + PPh_3 + NaBH_3CN$; toluene, EtOH, N_2	Red, $\mu = 1.9$; unstable in soln.	9
$[Co(H)_3\{MeC(dppm)_3\}]BPh_4$	$Co(BF_4)_2 \cdot 6H_2O + L + NaBH_4$; Et_2O	Red; $\mu = 3.29$; stable as solid; ν_H 1700–2200	20
$[CoH\{P(OPh)_3\}_4]PF_6$	$[CoH\{P(OPh)_3\}_4] + Ph_3CPF_6$; CH_2Cl_2	Green; $\mu = 1.96$; no ν_H; unstable	30
$[CoH\{P(OR)_2Ph\}_4]PF_6$ (R = Me, Et)	As above	Green; $\mu = 2.1$–2.4; ν_H 1950; unstable	30
$[Co(H)_3\{P(OPr^i)_3\}_3]$	$[Co(\eta_3\text{-}C_3H_5)\{P(OPr^i_3)_3\}_3] + H_2$; Et_2O	Yellow-brown; diamagnetic	33
$[Co(H)_3(PEt_3)_3]$	$CoCl_2$, PEt_3, $NaBH_4$; EtOH, Ar, 0 °C	Yellow, soluble in benzene, THF; ν_H 1933, 1745	34
$[Co(H)_2\{P(OR)_3\}_4]PF_6$ (R = Me, Et, Pr^i)	$[CoH\{P(OR)_3\}_4] + TFA + NaPF_6$; ROH	White; diamagnetic	35
$Co(H)_3(PPh_3)_3$	$CoCl_2 + PPh_3 + NaBH_4$; EtOH	Yellow; sensitive to air; soluble in non-polar solvents; ν_H 1933, 1745	3
cis-$[Co(H)_2(PR_3)_4]ClO_4$ (R_3 = Me_3, $PhMe_2$, Ph_2H)	$Co(ClO_4)_2 \cdot 6H_2O + PR_3 + H_2$; Pr^iOH	Yellow; ν_H 1900–2000	11

$[CoH(PHR_2)_5](BF_4)_2$ (R_2 = Et_2, EtPh)	$Co(BF_4)_2 + PHR_2$; Pr^iOH	White; diamagnetic; ^1H 24.79	11, 16
trans-$[CoH(X)(PPh_2H)_4]ClO_4$	$Co(ClO_4)_2 \cdot 6H_2O + PPh_2H + HX$	No details; $\nu_H \approx 2000$	11
cis-$[Co(H)_2(PR_3)_2(bipy)]ClO_4$ (R = Bu^n, Pr, Et)	$[Co(bipy)(PR_3)(diene)]^+ + PR_3 + H_2$	Red-orange	13
$[Co(H)_2(dppe)_2]ClO_4$	$[CoH(dppe)_2] + 1.0\,M\,HClO_4$; EtOH, H_2O	Yellow; diamagnetic; ν_H 1940, 1985	18
$[CoH(Cl)(dppe)_2]BPh_4$	$[CoCl(dppe)_2]Cl + NaBH_4$; EtOH; HCl, hexane	Yellow; ν_H 1960	19
$[CoH\{P(OEt)_2Ph\}_4L](PF_6)_2$ (L = RCN, $P(OEt)_2Ph$)	$[CoH\{P(OEt)_2Ph\}_4]PF_6 + Fe(Cp)_2PF_6 + L$; CH_2Cl_2	Yellow; diamagnetic; ν_H 1968	31
trans-$[CoH(X)\{P(OEt)_2Ph\}_4]PF_6$ (X = Cl, Br, I)	$[CoH(H_2O)\{P(OEt)_2Ph\}_4]PF_6 + Fe(Cp)_2PF_6 + LiX$; MeOH	Yellow; diamagnetic; ν_H 1980	31
trans-$[CoH(MeCN)\{P(OEt)_2Ph\}_4](PF_6)_2$	$[CoH\{P(OEt)_2Ph\}_4]PF_6 + Fe(Cp)_2PF_6 + MeCN$; CH_2Cl_2	Yellow, diamagnetic; ν_H 1990; ^1H 29.23	31

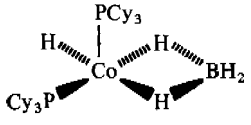
[a] IR data in cm^{-1}; NMR data in p.p.m; μ values in BM.

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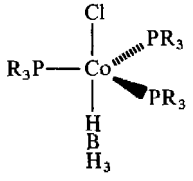
47.5.2.1 Hydrides

General articles concerning transition metal hydrides,[366] their crystallography,[368] and on the preparation and properties of borohydride complexes[369] are available. An overview on the use of $HCo(CO)_4$ and related cobalt hydrides as catalysts in the hydroformylation of alkenes is available.[367]

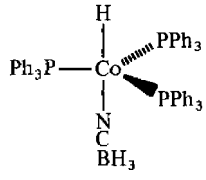
Complexes containing diamagnetic Co^I (five-coordinate) and Co^{III}, and paramagnetic Co^I (four-coordinate) and Co^{II} are easily prepared (Table 31). Several structures are available (Table 32). The Co—H bond is characteristically strong and normally cannot be titrated by strong bases. Exceptions are $[HCo(PF_3)_4]$, which is a very strong acid in aqueous solution, and $[HCo\{P(OMe)_3\}_4]$, which can be titrated by KH. Acid strength decreases rapidly $[HCo(PF_3)_4] > [HCo\{P(OR)_3\}_4] > [HCo(PR_3)_4]$. Alkyl and aryl phosphine hydrides have properties more in keeping with coordinated H^- (a 'super' halogen). Preparation often involves hydride transfer from BH_4^- to a $CoX(L)_x$ species generated from CoX_2 and L in alcoholic solution, *e.g.* equation (57). Species such as (**80**) and (**81**) are probable intermediates; (**80**) is known, and an analogue of (**81**) has been crystallized as (**82**; Table 32). Other methods of preparation include Zn or Cu reduction of $Co^{2+}_{(aq)}$ in alkaline solution, and the oxidative addition of H_2 or HX to $Co^{2+}_{(aq)}$ or to a low-valent complex (equations 58–61). To avoid the copreparation of dinitrogen complexes Ar should be used as the inert blanket.



(80)



(81)



(82)

$$CoCl_2 + PR_3 + NaBH_4 \longrightarrow [CoCl(PR_3)_3] \xrightarrow{NaBH_4} [Co(H)_3(PR_3)_2] \quad (57)$$

$$Co^{2+}_{(aq)} + PMe_3 + Zn \xrightarrow{OH^-} [CoH(PMe_3)_4]$$
$$cis\text{-}[Co(H)_2(PR_3)_4] \xleftarrow{H_2} Co^{2+}_{(aq)} + PR_3 \xrightarrow{HX} trans\text{-}[CoH(X)(PR_3)_4]^+ \quad (58)$$

$$[Co(dppv)_2]BF_4 + H_2 \longrightarrow [Co(H)_2(dppv)_2]^+ \quad (59)$$

$$[Co(PMe_3)_4] + HCl \longrightarrow [CoH(PMe_3)_4]Cl \quad (60)$$

$$K[Co(C_2H_4)(PMe_3)_3] + H^+ \longrightarrow [CoH(C_2H_4)(PMe_3)_3] \quad (61)$$

Phosphite ester complexes $[CoH\{P(OCH_2)_3CR'\}_4]$ (R′ = Me, Pr^i; tied-back substituents) and $[CoH\{P(OR)_3\}_4]$ (R = Me, Et, Pr^i, Ph) can be prepared in a similar fashion, and are yellow or white crystalline solids (Table 31). They are mostly diamagnetic and show less hydride character than $[CoH(PR_3)_4]$ due to the more electronegative phosphite ligand. They are not nearly as acidic as $[HCo(PF_3)_4]$ or $[HCo(CO)_4]$ but for R = Me, Et can be deprotonated by the very strong base KH (equation 62).[370]

$$[CoH\{P(OMe)_3\}_4] + KH \xrightarrow{THF} K[Co\{P(OMe)_3\}_4] + H_2 \quad (62)$$

Some properties of hydrido-phosphine complexes have been summarized.[366,371] For Co^I systems $\nu_H \approx 1870$–1900, for Co^{II} $\nu_H \approx 1930$, and for Co^{III} $\nu_H \approx 1950$–$2000\,cm^{-1}$; but sometimes ν_H is not observed. Often the hydride can be titrated with aqueous HCl, and complete decomposition in this manner has been used for analysis (equation 63), but this is not universal (Scheme 26).[372,373] D is retained in $[Co(D)_2(dppe)_2](ClO_4)$ on adding OH^-, and HD rather than D_2 is evolved on treatment with acids.[373] $[CoH(dppe)_2]$ reduces CCl_4 to $CHCl_3$[373] and $[Co(H)_2(PPh_3)_2]$ reduces 1-heptene to heptane,[374] but $[CoH(Cl)(dppe)_2]Cl$ oxidizes EtOH to acetaldehyde in alkaline solution (equation 64).[372] The interesting paramagnetic $[Co_2(H)_3\{MeC(dppe)_3\}_2](BPh_4)$ ($\mu = 3.29$ BM) is dimeric with three μ-H bridges (**83**; Scheme 27), and most (if not all) hydride complexes react with CO to give dimeric diamagnetic carbonyl systems (equations 65 and 66). The two *cis* hydrides in $[Co(H)_3(PPh_3)_3]$ can easily be eliminated by Y = CO or N_2 and the resulting Co^I complex has a distorted trigonal bipyramidal geometry with axial H and Y groups (equation 67).[376]

Table 32 Structures: Phosphine–Hydride Complexes

Complex	*Ligand*	*Structure*[a]	*Ref.*
$H[Co(PF_3)_4]$	PF_3	Dist. tet. (H not located); CoP 205(w); PCoP 101–118°	1
$[Co(H)(N_2)(PPh_3)_3]$	PPh_3	Dist. trig. bipyr. (two independent molecules); NN 101, 112–3; CON, 178, 183; CoH, 164–167	2
$[Co(H)(CO)(PPh_3)_3]$	PPh_3	Dist. trig. bipyr.; CoH 141 (150); CoC 170 (173); CoP 219, 214–217; CCoH, 173°	3
$[Co(H)(BH_4)(PCy_3)]$	$P(C_6H_{12})_3$	Dist. sq. pyr. (PCy_3, ax) bidentate H_2BH_2; CoP(ax) 222; CoH 134	4
$[Co(H)(NCBH_3)(PPh_3)_3]$	PPh_3	Dist. sq. pyr., CoH, 142; CoN 190.4 CoP(ax) 229	5
$[Co(H)\{P(dppC_6H_4)_3\}]$	$P(o\text{-}C_6H_4PPh_2)_3$	Trig. bipyr.; CoP(ax) 206; CoP 213; CoH 160	6
$[Co(H)\{P(dppe)_3\}]$	$P(CH_2CH_2PPh_2)_3$	Trig. bipyr.; CoP(ax) 209; CoP, 213; CoH 143	7
$[CoH\{P(dppe)_3\}]BF_4$	$P(CH_2CH_2PPh_2)_3$	Trig. bipyr.; CoP(ax) 216; CoP 221–223; CoH 153; PCoP 115–124°	8
$[Co(H)\{N(dppe)_3\}]$	$N(CH_2CH_2PPh_2)_3$	Trig. bipyr.; CoP 211–212; CoN 207; CoH, 145; PCoP 115.7–124.2°	9
$[Co(H)\{N(dppe)_3\}]\cdot THF$	$N(CH_2CH_2PPh_2)_3$	Trig. bipyr., more regular geometry; CoP 212; CoN 209; CoH 138; PCoP 120.0°	10

[a] Bond lengths in pm.

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$$2[CoH\{P(dppe)_3\}] + 4H^+ \longrightarrow 2Co^{2+}_{(aq)} + 2P(dppe)_3 + 3H_2 \quad (63)$$

$$[CoH(Cl)(dppe)_2]Cl + OEt^- \longrightarrow [CoCl(dppe)_2] + HOEt + Cl^- \xrightarrow{OEt^-}$$

$$[CoH(dppe)_2] + MeCHO + Cl^- \quad (64)$$

$$[Co(H)_3(PPh_3)_3] + CO \longrightarrow [Co_2(CO)_6(PPh_3)_2] \quad (65)$$

$$[Co(H)_2(PPh_3)_3] + CO \longrightarrow [Co_2(CO)_2(PPh_3)_6] \quad (66)$$

$$[Co(H)_3(PPh_3)_3] + Y \longrightarrow Ph_3P{-}Co(H)(PPh_3)_2(Y) + H_2 \quad (67)$$

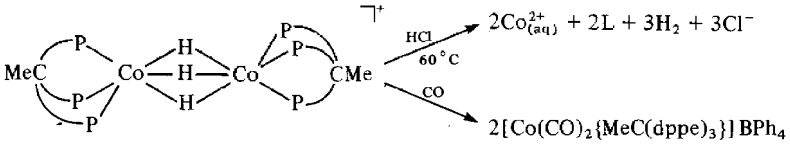
$[CoH(dppe)_2]$ (red) $+ HCl_{(g)} \longrightarrow [CoCl(dppe)_2]$ (brown) $+ H_2$

$[CoCl(dppe)_2] \xrightarrow{HCl} [CoH(Cl)(dppe)_2]Cl$ (green)

$[CoH(dppe)_2] \underset{OH^-}{\overset{HClO_{4(aq)}}{\rightleftharpoons}}$ red

$[Co(dppe)_2]ClO_4 \xrightarrow{H_2} [Co(H)_2(dppe)_2]ClO_4$ (yellow)

Scheme 26



(83)

Scheme 27

All $[CoH(PR_3)_4]$ complexes (R = F, alkyl, aryl, OR) have near C_{3v} microsymmetry with a distorted tetrahedral CoP_4 skeleton and H^- fluxionally disposed between tetrahedral faces. In solution $[HCo(PF_3)_4]$ shows a limiting ^{31}P spectrum (3:1 ratio of PF_3 groups) at $-160\,^{\circ}C$[377] and its solid state structure shows an almost tetrahedral CoP_4 unit (H^- not located) (Table 32).[378] Limiting slow exchange is not shown by $[CoH\{P(OR)_3\}_4]$ at $-140\,^{\circ}C$ (R = Me, Et, Pr^i),[379,380] $\Delta G^{\ddagger} < 25\,kJ\,mol^{-1}$, but $[CoH\{P(OEt)_2Ph\}_4]$ with the more bulky phosphonite ligand shows a temperature-dependent collapse of the symmetrical high field ^{31}P quintet, and its crystal structure shows H^- to be located on a distorted tetrahedral face (Table 32).[381] It is likely that the cone angle of the ligand is important in determining the coalescence temperture for these species. $[CoH\{P(OR)_3\}_4]$ complexes (R = Me, Et, Ph) readily add CO to form five-coordinate trigonal bipyramidal $[CoH(CO)\{P(OR)_3\}_3]$ (Table 31), and H–D exchange occurs in acid solution *via* the *cis*-$[CoH(D)\{P(OR)_3\}_4]^+$ intermediate. This species is relatively unstable but has been examined by ^1H NMR,[382] and has been isolated as the PF_6^- salt.[383]

Oxidation to give Co^{II} and Co^{III} hydride complexes has been achieved in a number of instances (Table 31). $[CoH\{P(OPh)_3\}_4]$ and $[CoH\{P(OR)_2Ph\}_4]$ (R = Me, Et) can be readily oxidized to the analogous Co^{II} cation using trityl salts, and green paramagnetic $[CoH\{P(OEt)_2Ph\}_4](PF_6)$ may be further oxidized in the presence of L = H_2O, RCN, $P(OEt)_2Ph$ to the Co^{III} complex *trans*-$[CoH(L)\{P(OEt)_2Ph\}_4](PF_6)_2$ (Scheme 28). *trans*-$[CoH(H_2O)\{P(OEt)_2Ph\}_4]PF_6$ is especially interesting as it appears to be the only phosphine complex containing both hydride and aqua ligands.[384]

$[CoH\{P(OEt)_2Ph\}_4] \xrightarrow{Ph_3C^+PF_6^-} [CoH\{P(OEt)_2Ph\}_4]PF_6 \xrightarrow{CCl_4}$ *trans*-$[CoH(Cl)\{P(OEt)_2Ph\}_4]PF$ (yellow, diamagnetic)

$[CoH\{P(OEt)_2Ph\}_4]PF_6 \xrightarrow{Fe(Cp)_2^+PF_6^-} [CoH\{P(OEt)_2Ph\}_4](PF_6)_2$ (L)

trans-$[CoH(L)\{P(OEt)_2Ph\}_4](PF_6)_2 \xrightarrow{CO} [Co(CO)\{P(OEt)_2Ph\}_4]PF_6$

trans-$[CoH(L)\{P(OEt)_2Ph\}_4](PF_6)_2 \xrightarrow[(L = H_2O\ only)]{LiX}$ *trans*-$[CoH(X)\{P(OEt)_2Ph\}_4]PF_6$ (yellow, diamagnetic; X = Cl^-, Br^-, I^-)

Scheme 28

Reductive elimination of H_2 occurs when $[Co(H)_2\{P(OR)_3\}_4]^+$ salts are treated with CO or $P(OR')_3$ and the reaction is not measurably reversible, $p(H_2) = 1$ atm (equation 68).[383] This contrasts with that found for isoelectronic $[Fe(H)_2\{P(OR)_3\}_4]$. Also, the hydrogen exchange reaction (69) occurs without H–D scrambling and both reactions have been interpreted in terms of a dissociative $[Co\{P(OR)_3\}_4]^+$ intermediate.[383]

$$[Co(H)_2\{P(OR)_3\}_4]^+ + L \longrightarrow [CoL\{P(OR)_3\}_4]^+ + H_2 \quad (68)$$

$$[Co(H)_2\{P(OR)_3\}_4]^+ + D_2 \longrightarrow [Co(D)_2\{P(OR)_3\}_4]^+ + H_2 \quad (69)$$

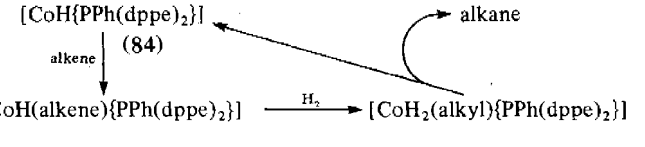
Ligand substitution rates in $[CoH\{P(OR)_3\}_4]$ have been studied by Muetterties and Hirsekorn who found that exchange is slow in non-polar solvents (benzene) taking 4–6 weeks at 100 °C (R = Me > Et > Ph; equation 70).[382] However in polar solvents it is faster, being 100 times faster in MeCN. A dissociative process to give $[CoH\{P(OR)_3\}_3]$ is suggested as being rate determining, but CO displacement is 10–100 times faster under the same conditions so that an associative process also appears to be possible. Conder and coworkers have shown that CO substitution is photocatalyzed with reaction (71) being complete within 20 minutes in CO-saturated tethyhydrofuran at ambient temperature; the reverse of reaction (71) was not photocatalyzed.[385]

$$\begin{array}{l} [CoH\{P(OR)_3\}_4] + P(OR')_3 \rightleftharpoons [CoH\{P(OR)_3\}_3\{P(OR')_3\}] + P(OR)_3 \\ \quad \text{CO} \downarrow \\ [CoH\{P(OR)_3\}_3CO] \xrightarrow{CO} [CoH\{P(OR)_3\}_2(CO)_2] \end{array} \quad (70)$$

$$[CoH\{P(OPh)_3\}_4] + CO \xrightarrow{h\nu} [CoH\{P(OPh)_3\}_3CO] + P(OPh)_3 \quad (71)$$

Cobalt hydrido phosphine and phosphite complexes can be useful catalysts in hydrogenations. Thorn and Hoffman[386] have discussed the MO consequences of hydride insertion into alkenes and its catalysis by d^8 metals. The requirement appears to be the ability to generate a vacant coordination site for the substrate. Thus the five-coordinate systems $[CoH(PR_3)_4]$ and $[CoH\{P(OR)_3\}_4]$ are rather sluggish, although laser excitation of $[CoH\{P(OEt)_2Ph\}_4]$ has been shown to generate a coordinatively unsaturated species, presumed to be $[CoH\{P(OEt)_2Ph\}_3]$ (ε_{580}(max), 17 000), which reacts rapidly with $P(OEt)_2Ph$ ($1.4 \times 10^8\ M^{-1}s^{-1}$) and 1-hexene ($1.1 \times 10^8\ M^{-1}s^{-1}$).[387,389] However $[CoH(N_2)(PPh_3)_3]$ is an excellent catalyst for alkene hydrogenation,[390] the dimerization of C_2H_4[391] and $MeCHCH_2$[392,288] and the isomerization of alkenes;[393] it readily loses N_2 in the presence of the alkene (equation 71). Likewise the stereochemically rigid $[Co(H)_3\{PhP(dppp)_2\}]$ and $[Co(H)_3\{PhP(dppe)_2\}]$ readily catalyze the hydrogenation of 1-octene *via* the initial loss of H_2 to form the reactive four-coordinate 16-electron intermediate (**84**), which coordinates alkene (Scheme 29),[394] whereas $[Co(H)_3(PPh_3)_3]$ generates the coordinatively unsaturated intermediate $[Co(H)_3(PPh_3)_2]$ by loss of PPh_3.[395] $[Co(H)_3\{P(OPr^i)_3\}_3]$ has likewise been shown to be an effective catalyst for the hydrogenation of both terminal and internal alkenes at 0 °C and $p(H_2) = 1$ atm, and selectively hydrogenates α,β-unsaturated ketones and amides *via* a reaction involving displacement of H_2 (equation 73).[406]

$$\underset{\text{yellow}}{[CoH(N_2)(PPh_3)_3]} + \text{alkene} \rightleftharpoons \underset{\text{red-brown}}{[CoH(\text{alkene})(PPh_3)_3]} + N_2 \quad (72)$$

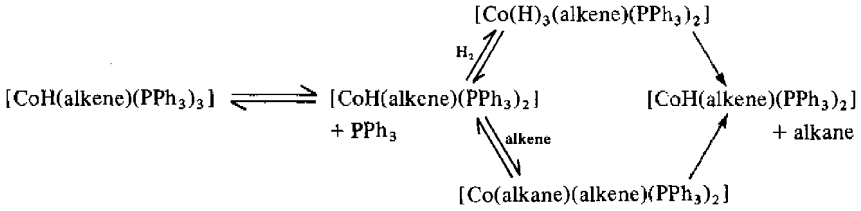


Scheme 29

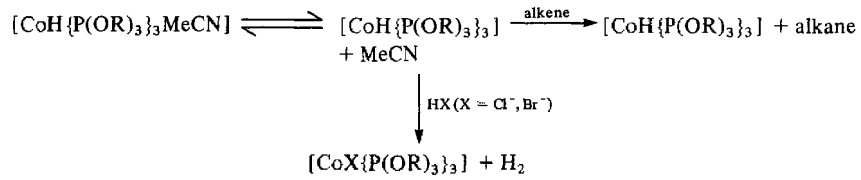
$$[Co(H)_3\{P(OPr^i)_3\}_3] + \text{alkene} \rightleftharpoons [CoH\{P(OPr^i)_3\}_3(\text{alkene})] + H_2 \quad (73)$$

Various kinetic studies on these processes have been carried out.[388,391,393,395,396] For example alkene hydrogenation in $[CoH(alkene)(PPh_3)_3]$ follows the rate law $k_{obs} = k[H_2][alkene][PPh_3]^{-1}$ and this has been interpreted in terms of a dual pathway originating from the coordinatively unsaturated $[CoH(alkene)(PPh_3)_2]$ intermediate (Scheme 30),[396] but other mechanisms are possible. Similarly

$[CoH\{P(OPh)_3\}_3MeCN]$ rapidly catalyzes the hydrogenation of 1-butene (no isomerization) and it reacts spontaneously with HX generating H_2;[397] facile dissociation of MeCN generating an unsaturated system is again likely (Scheme 31), since stable systems such as $[CoH\{P(OR)_3\}_4]$ are unreactive under similar conditions. Similarly $[CoH(N_2)(PPh_3)_3]$ reacts with HX, and will oxidize PPh_3 in the presence of air, presumably *via* the initial loss of N_2 and coordination of H^+ and O_2 respectively (equation 74). Likewise N_2O can be reduced to N_2 in the presence of PPh_3, which is oxidized to Ph_3PO.



Scheme 30



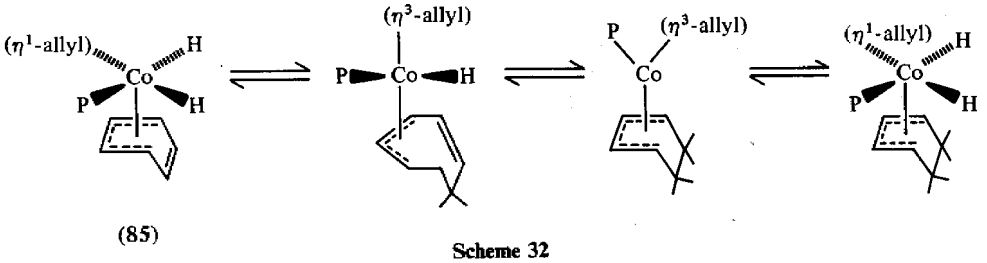
Scheme 31

$$[Co(X)_2(PPh_3)_2] + N_2 + H_2 + PPh_3 \xleftarrow{HX} [CoH(N_2)(PPh_3)_3] \xrightarrow[\text{catalytic}]{PPh_3} Ph_3P{=}O \qquad (74)$$

Hydride complexes have been shown to be present in the selective *cis* hydrogenation of arenes accidentally discovered by Muetterties and Hirsekorn in 1973.[398] Muetterties and coworkers have since shown in an impressive series of papers[399] that the parent catalyst $[Co\{P(OMe)_3\}_3(\eta^3\text{-}C_3H_5)]$ and a number of other π-allyl phosphite Co^I systems are possibly unique in their ability to hydrogenate aromatic hydrocarbons (room temperature, $p(H_2) = 1$ atm), and to a degree they are chemoselective. Requirements for catalysis include the ability to undergo rapid reversible $\eta^3 \rightleftharpoons \eta^1$ coordination of the allyl group (thereby generating vacant coordination sites on the metal) and the ability to undergo $Co^I \rightarrow Co^{III}$ oxidative addition of H_2. The catalyst prepares itself as given in equation (75)[400] followed by successive $\eta^1 \rightarrow \eta^3 \rightarrow \eta^1$ allyl changes which generate vacant coordination sites and allow the binding of the arene (Scheme 32). The initial reactive intermediate appears to be the strained η^4-arene (**85**), and by successive hydrogenation steps ($Co^{III} \rightarrow Co^{II} \rightarrow Co^I$) and oxidative additions of H_2 reduction takes place without the dissociation (or scrambling) of semireduced products (*i.e.* C_6H_6 gives $C_6H_6D_6$, and unreacted C_6H_6 essentially no D); however alkenes can compete for the final η^2-cyclohexene hydrogenation step (**86**; Scheme 33). The structure of $[Co(\eta^3\text{-cyclooctenyl})\{P(OMe)_3\}_3]$ (**87**) establishes its square-pyramidal geometry if the allyl is considered as a bidentate ligand; a similar structure is found for $[Co(\eta^3\text{-}C_3H_5)\{P(OMe)_3\}(CO)_2]$ and a somewhat more distorted structure for $[Co(\eta^3\text{-benzyl})\{P(OMe)_3\}_3]$ (**88**). A wide variety of benzene derivatives, cyclohexadienes and cyclohexenes are reduced but steric, electronic and acidic properties interfere (*e.g.* F, CN and NO_2 substituents deactivate); hydrogenation rates are low (one turnover per hour for C_6H_6) but the larger phosphite ligands improve this,[401,402,406] *e.g.* $[Co(H)_3\{P(OPr^i)_3\}_3]$ (equation 73). Janowicz and Bergman[403] provide evidence to support an alternative autocatalytic bimolecular pathway for the hydrogenation of Me in $[Co(PPh_3)(Me)_2(Cp)]$ (equation 76). If the $[Co(PPh_3)_2(Cp)]$ product is introduced at the beginning of the reaction (45 °C, benzene) the normal induction period disappears, and the inhibition in rate on adding PPh_3 implies a role for coordinatively unsaturated $[Co(Me)_2(Cp)]$ and $[Co(PPh_3)(Cp)]$. It is proposed that H_2 adds to the latter, which then reacts with the former.

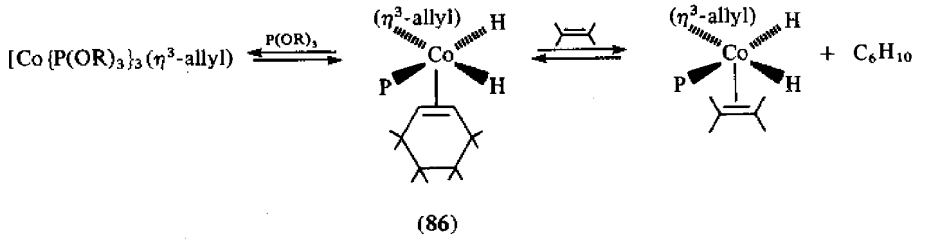
$$[Co\{P(OR)_3\}_3(\eta^3\text{-allyl})] \rightleftharpoons [Co\{P(OR)_3\}_3(\eta^1\text{-allyl})] \xrightleftharpoons{H_2} [Co\{P(OR)_3\}_3(H)_2(\eta^1\text{-allyl})] \qquad (75)$$

Mirbach and coworkers have investigated the use of $[CoH(CO)_3(PBu^n_3)]$ in catalyzing the formation of straight-chain aldehydes from propene and 1-octene (equation 77).[404] The catalyst is produced photochemically from $[Co(CO)_3(PBu^n_3)][Co(CO)_4]$, and the mild experimental conditions and polar solvents used (MeOH, 80 °C, 80 bar) make such ionic complexes useful alternatives to the



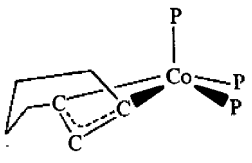
(85)

Scheme 32

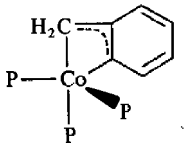


(86)

Scheme 33



(87)



(88)

$$[Co(PPh_3)(Me)_2Cp] + H_2 + PPh_3 \longrightarrow [Co(PPh_3)_2Cp] + 2CH_4 \quad (76)$$

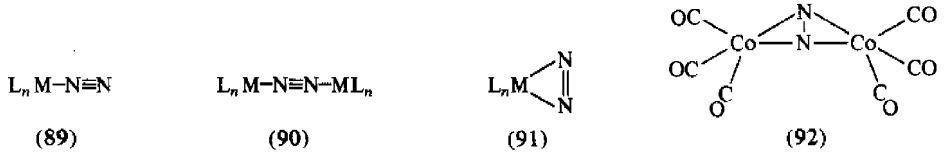
normal cobalt or rhodium carbonyl catalysts. Thus Murata and coworkers have shown that $[Co_2(CO)_8]$ in the presence of the ligand dppe catalyzes the hydroformylation of propene at 135 °C in a water gas shift process (equation 78).[405]

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CHO \quad (77)$$

$$MeCH{=}CH_2 + CO + H_2O \xrightarrow{\text{catalyst}} MeCH_2CH_2CHO \quad (78)$$

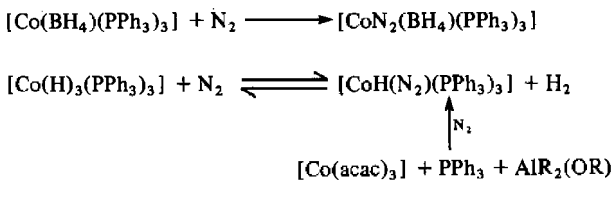
47.5.2.2 Dinitrogen

Dinitrogen usually coordinates in an end-on fashion, (**89**) or (**90**), and sometimes in a side-on π-bonded mode (**91**). Hoffmann and coworkers consider that side-on coordination to two metal centres such as (**92**) is possible,[407] and Yamabe and coworkers have also considered theoretical aspects in relation to possible reduction to hydrazine or ammonia.[408]



(89) (90) (91) (92)

Dinitrogen complexes can be prepared by the addition of N_2 to a Co hydride or borohydride complex, by reduction under N_2 of $CoCl_2$ or $[Co(acac)_3]$ using Mg or $R_2Al(OR)$ in the presence of PR_3 (R = Ph, Me), or by displacement of a coordinated alkene (Schemes 34 and 35; Table 33).



Scheme 34

Table 33 Preparations: Phosphine–Dinitrogen Complexes

Complex	*Preparation*	*Properties*	*Ref.*
$[Co(H)(N_2)(PPh_3)_3]$	$[CoH_3(PPh_3)_3] + N_2$	Orange-red; ν_{N_2} 2096 (structure Table 32);	1
	$[Co(acac)_3] + PPH_3 + AlR_3 + N_2$	ν_{N_2} 2096 (benzene)	2
$[Co(N_2)(BH_4)(PPh_3)_3]$	$[Co(PPh_3)_4(BH_4)] + N_2$; benzene, hexane	Yellow-brown; ν_{N_2} 2089, 2098	3
$[Mg(THF)_4][Co(N_2)(PMe_3)_3]_2$	$CoCl_2 + PMe_3 + Mg$; THF, N_2, 3 d, 20 °C	Orange; ν_{N_2} 2058; diamagnetic (structure Table 36)	4
$[Mg(THF)_2][Co(N_2)(PPh_2Et)_3]$	$[Co(acac)_3] + PPh_2Et + MgEt_2$; N_2, THF, 0 °C	Red-brown; ν_{N_2} 1835	6
$K[Co(N_2)(PMe_3)_3]$	$[CoCl(PMe_3)_3] + C_3H_6 + K$; THF, 24 h, 20 °C, then N_2	Orange; ν_{N_2}, 1868, 1843 (soln.) (structure Table 36)	5
$Na[Co(N_2)(PEt_2Ph)_3]$	$[Co(Cl)_2(PEt_2Ph)_2] + PEt_2Ph + Na$; THF, N_2, r.t.	Black; diamagnetic; ν_{N_2} 1840, 1875 (THF soln.)	7
$[\{Co(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$	As above, ratio 1:1:2	Dark brown; no ν_{N_2}; dimeric	7

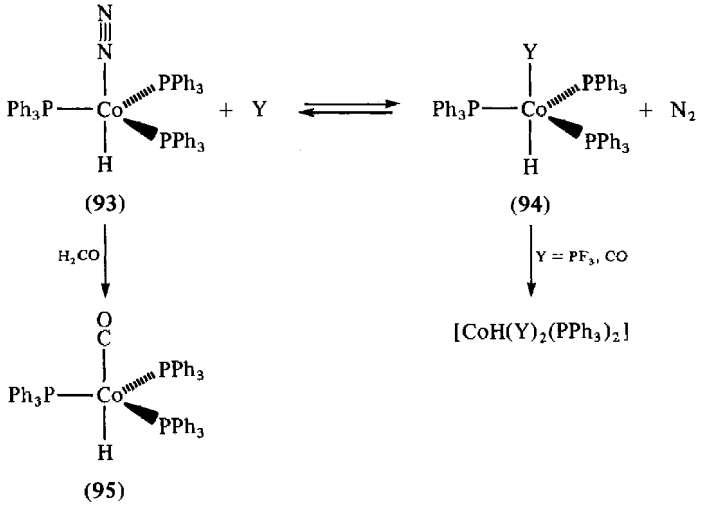
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$$CoCl_2 + PMe_3 + Mg + N_2 \longrightarrow [Mg(THF)_4][CoN_2(PMe_3)_3]_2 \xrightarrow{K/Et_2O}$$

$$K[CoN_2(PMe_3)_3] + C_3H_6 \longleftarrow K[Co(C_3H_6)(PMe_3)_3] + N_2$$

Scheme 35

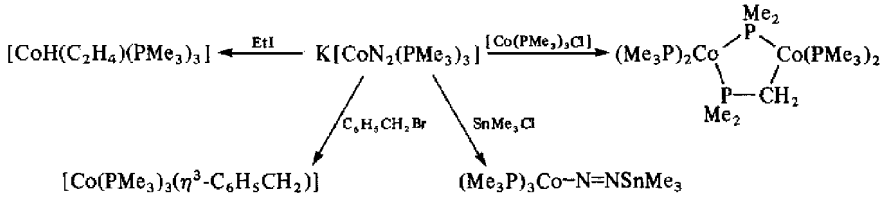
$[CoH(N_2)(PPh_3)_3]$ has been extensively studied;[409] it has the distorted trigonal-bipyramidal structure (**93**; Table 32). The end-on coordinated N_2 is reversibly displaced by H_2, C_2H_4 and NH_3, and is irreversibly displaced by CO and PF_3 with retention of geometry (**94**). It also reacts with formaldehyde to give the *trans* complex (**95**) (structure, Table 32).



$K[Co(N_2)(PMe_3)_3]$ and $[Mg(THF)_4][Co(N_2)(PMe_3)_3]_2$ are unstable in non-polar solvents giving rise to the paramagnetic $[Co(N_2)(PMe_3)_3]$ intermediate, and ultimately to Co, $[Co(PMe_3)_4]$ and N_2 (equation 79).[410] Structures are available (Table 35). Although the reduction of coordinated N_2 has not yet been demonstrated in these systems, end-on coordination occurs with the above cations stabilizing the linear $Co{=}N^{\delta+}{=}N^{\delta-}{-}{-}{-}M^{n+}$ array. Addition, or oxidative addition, to $[Co(N_2)(PMe_3)_3]^-$ is also known (Scheme 36).[411] Miura and Yamamoto report that coordinated N_2 in $[Mg(THF)_2][Co(N_2)(PR_3)_3]_2$ is converted to N_2H_4 and a small amount of NH_3 on hydrolysis.[412] Mason and Ibers report that the bridged N_2 dimer $\{[Co(PEt_2Ph)_3]_2(\mu\text{-}N_2)\}$ and $Na[Co(N_2)(PEt_2Ph)_3]$ react with dry CO_2 to give ill-defined Co—CO and $Co(CO_3)$ products *via* some sort of reductive disproportionation process.[413]

$$[CoN_2(PMe_3)_3]^- \xrightarrow{-e^-} [CoN_2(PMe_3)_3] \longrightarrow [Co(L)_2(PMe_3)_2] + PMe_3 + N_2 \qquad (79)$$

$$(L)_2 = (CO)_2, \text{ bipy, PhNNPh, PhCHCHPh}$$



Scheme 36

47.5.2.3 Nitrosyl

Non-phosphine-containing nitrosyl complexes are considered in Section 47.4.1.

$[Co(NO)(PR_3)_3]$ (R = Ph, alkyl, OEt) can be directly prepared from $CoX_2 \cdot 6H_2O$ salts ($X = Cl^-$, NO_3^-) and PR_3 under appropriate conditions (Table 34). A tetrahedral structure is inferred from IR and NMR evidence for these $\{CoNO\}^{10}$ diamagnetic systems, and is indeed found for

Table 34 Preparations: Phosphine–Nitrosyl Complexes

Complex	*Preparation*	*Properties*	*Ref.*
$[Co(NO)(PF_3)_3]$	$[Co(NO)_2Cl]_2 + PF_3 + Cu$; 70 °C, 300 atm	Red-brown liquid; diamagnetic; light sensitive; stable ν_{NO} 1844	1
$[Co(NO)(PR_3)_3]$ ($R_3 \neq Ph_3$, Bu^n_3)	$Co(NO_3)_2 \cdot 6H_2O + PR_3$; Pr^iOH	Red; diamagnetic; tet.; ν_{NO} 1640–1660	2
$[Co(NO)(PPh_3)_3]$	$[Co(NO)_2Cl]_2$ or $[Co(NO)_2X(PR_3)] + PPh_3$; Na/Ag, THF	Violet; diamagnetic	3, 5, 9
	$CoCl_2 \cdot 6H_2O + PPh_3 + p$-toluene–(Me,NO)sulfonamide + $NaBH_4$; MeOH		18
$[Co(NO)\{P(OPr^i)_3\}_3]$	$[Co\{P(OPr^i)_3\}_4] + NO$; THF	Brown; diamagnetic; ν_{NO} 1695	17
$[Co(NO)\{N(dppe)_3\}]BPh_4$	$[Co(NO)\{N(dppe)_3\}] + NaBPh_4$; EtOH	Green; ν_{NO} 1760; $\mu = 1.90$	17
$[Co(NO)\{N(dppe)_3\}]$	$[CoH\{N(dppe)_3\}] + NO$; THF	Brown; ν_{NO} 1620; diamagnetic	15
$[Co(NO)\{P(OEt)_2Ph\}_3]$	$[Co(NO)_2\{P(OEt)_2Ph\}_2]BPh_4 + L$; acetone	Red; ν_{NO} 1673	9
$[Co(NO)(Cl)_2(dppe)]$	$[Co(NO)_2(dppe)]Cl + dppe$; benzene	Brown; ν_{NO} 1676	4, 6, 16
$[Co(NO)(X)_2(PR_3)_2]$ (X = Cl, Br, I; R = Et, Bu^n, Ph)	$[Co(X)_2(PR_3)_2] + NO$; benzene	Dark brown, unstable in air	7
$[Co(NO)L(PPh_3)_2]$ (L = 1,4-napthaquinone, maleic anhydride, fumaronitrile)	$[Co(NO)(PPh_3)_3] + I_2$; THF	Brown-green, diamagnetic	5
	$[Co(NO)(PPh_3)_3]$ + alkene; Et_2O		11
$[Co(NO)(PR_3)SR']_2$	$[Co(NO)(CO)_2(PR_3)] + R'SH$	RS-bridged dimer	13
$[Co(NO)(dppe)_2]X_2$	$Co(NO_3)_2 \cdot 6H_2O + P(OR)_3 + NO$; EtOH	Pink, unstable in polar solvents; diamagnetic; linear CoNO (^{1}H NMR)	13, 15
$[Co(NO)\{P(OR)_3\}_4](BPh_4)_2$ (R = Me, Et)	$[Co(NO)\{P(OR)_3\}_4](BPh_4)_2 + LiX$; EtOH	Green-brown; unstable to disproportionation; diamagnetic	3, 8
$[Co(NO)X\{P(OR)_3\}_3]Y$ (X = Cl, Br, I; Y = BF_4, BPh_4)	$[Co(NO)_2X]_2 + PR_3$	Dark brown; diamagnetic	9
$[Co(NO)_2X(PR_3)]$ (R = Ph, Cy, Et; X = Cl, Br, I)	$[Co(NO)Cl(PPh_3)] + PPh_3$; EtOH, $NaClO_4$	Brown; diamagnetic (structure Table 36)	10
$[Co(NO)_2(PPh_3)_2]X$ (X = Cl, ClO_4, BPh_4, PF_6)	$[Co(NO)_2Cl]_2 + KPPh_2$	Ph_2P-bridged dimer	13
$[Co(NO)_2(PPh_2)]_2$	$[Co(NO)\{P(OR)_3\}_4]^{2+} + NO$		14
$[Co(NO)_2\{P(OR)_3\}_2]BPh_4$	$[Co(Cl)_2(dppv)_2]Cl + NaNO_2$; MeOH, N_2, reflux	Red; ν_{NO} 1800, 1858	9, 16
$[Co(NO)_2(dppv)]ClO_4$	$[Co(NO)_2Cl]_2 + dppe$; benzene	Red; ν_{NO} 1850, 1795	
$[Co(NO)_2(dppe)]Y$ (Y = Cl, ClO_4, BPh_4)	$CoCl_2 + L + NEt_3 + NO$; EtOH, $NaBPh_4$	Brown; ν_{NO} 1855	16
$[Co(NO)_2(PPh_3)_2]BPh_4$			

[a] IR data in cm^{-1}; μ values in BM.

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Table 35 Structures of Monodentate Phosphine Complexes

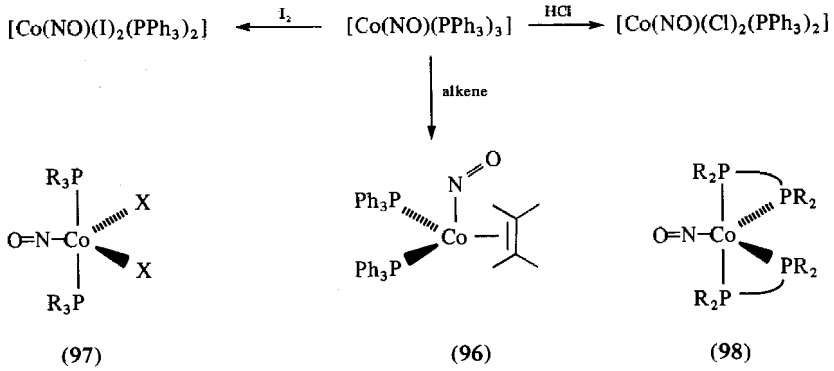
Complex	*Data*[a]	*Comments*	*Ref.*
$[Co(PPh_3)_2(NO)_2]PF_6$	CoN 164.5; CoP 226.6; MCoN 136.7°; CoNO 171°	Dist. tet., flattened towards planar	1
$[Mg(THF)_4][Co(N_2)(PMe_3)_3]_2$	CoN 172; NN 118; MgN 204; NNMg 158°	Dist. tet., long NN bond; N_2 evolved in low polarity solvents	3
$K[Co(N_2)(PMe_3)_3]$	NN 116–118; CoN 170–1; KN 276–293	Hexameric, linear Co—NN—K	4
$[Co(PPh_3)(CpZn)_2(Cp)]$	CoZn 229; CoP 212	Dist. tet., $CpZn^+$ ligands	8
$\{Li[Co(PMe_3)_3C_2H_4]\}_3$	CoLi 238; LiC 231–261; CoC 200	Dist. oct., trimeric with bridging Li	24
$[Co(NO)(CO)_2(PPh_3)]$	CoP 222; NCoC 111–116°	Dist. tet., Co and NO disordered	14
$[Co(NO)(CO)(PPh_3)_2]$	CoP 223; NCoC 120°	Dist. tet (as above)	14
$[Co_2(PPh_3)_2(NO)(SO_2)]$	CoS 202.1; CoN 168; CoNO 169	Dist. tet., planar $CoSO_2$	23
$[Co_2(PMe_3)_2(CO)_4(C_2H_2)]$	CoCo 246.4; CoCO 178; CoC 196	Dimeric, C_{2v} sym., bridging C_2H_2 unit	9
$[Co(PMe_3)_3(PhCCPh)]BPh_4$	CoCo 185.2; CoP 212.7, 221.2; CoC 126.5	Dist. tet., bonded to triple bond	26
$[Co_2(PMe_3)_4(\mu\text{-}OMe_2)(PMe_2CH_2)]$	P=CH_2 171; PCCo, 88°	Dist. tet., dimeric oxidation product of $[Co(N_2)(PMe_3)_3]^-$; bridging PMe_2, PMe_2CH_2	5
$[Co_2(PMe_3)_2(Me_2PCH_2PMe_2)_2PMe_2]$	CoCo 260.3; $CoPMe_2$ 214.4; CoPCo 74.8°	Dist. tet. pyr.; dimeric with diphosphine bridge; μ-PMe_2	20
$[Co(PPh_2Me)_2(NO)Cl_2]$	CoN 171; CoP 226; CoCl 226–229; CoNO 164.5°	Dist. trig. bipyr., NO (slightly bent) equatorial; another isomer detected in solid and soln.	6
$[Co(PMe_3)_3(Ph)(C_2H_4)]$	CoP 119–121; CoC(Ph) 200; CoC(ethylene) 204–5; PCoP 97.9°; PCoC(Ph) 81.6°; PCoC(Et) 92.6°	Dist. trig. bipyr., equatorial coplanar Ph, C_2H_4; axial PMe_3	7
$[Co\{P(OMe)_3\}_3(C_8H_8)]$	CoP 211–213; P(1)CoP 103.5–106.2°; PCoP, 97.4°	tet. pyr.; η^3-cyclooctenyl ligand spans base edge; catalyst for arene hydrogenation; axial $P(OMe)_3$	16
$[CoH(BH_4)(PCy_3)_2]$	CoP 222; CoH 135; PCoP 158°; CoH(**B**) 180, 187(ax)	Dist. sq. pyr., bidentate BH_4^-	10
$[Co(PMe_3)_3(MeCN)C_2H_4]BPh_4$	CoC 202.3, 203; CC 141; CON 191.3; CoP 217.5–224	Dist. trig. bipyr.; equatorial C_2H_4, MeCN	25
$[Co(PMe_3)_2(MeCN)PhCCPh]BPh_4$	CoC 197.7, 198.1; CC 126.7; CoN axial MeCN	Dist. trig. bipyr.; equatorial PhCCPh, axial MeCN	26
$[CoH(PPh_3)_3(NCBH_3)]$	CoH 142; CoN 190.4; CoP(ax) 229	Dist. sq. pyr. with H axial	11
$[Co(X)_2(PPh_3)_2]$ (X = Cl, Br)	CoX 221(Cl), 235(Br); CoP 238; XCoX 115(Cl), 117°(Br)	Tet., high spin	12
$[Co(PEt_3Ph)_2(mesityl)_2]$	CoP 223.4; CoC 199.4; CCoP 89.6°	Planar, low spin, apical sites blocked, *trans* PR_3	13
$[Co(Cl)_2(PMe_3)_3]$	CoCl 226, 238; CoP 221–224; PCoP 87–96°, 169°	Dist. trig. bipyr. Cl(eq)	15
$[Co(Br)_2(PPhF_2)_3]$	CoP(ax) 216; CoP(eq) 212; CoBr 237–8; BrCoBr 126°; P(1)CoP(2), 172.5°	Trig. bipyr., Br(eq)	17
$R[Co(Cl)_3(PPh_3)]$	CoCl 222–227; CoP 239; ClCoCl 113–116°; ClCoP, 103–105°	Tet.	19
$[Co_4(\mu_3\text{-}PPh)_4(PPh_3)]_4$	CoCo 257–258; CoCoCo 59.6–60.1°	Tet., Co_4 cluster with PPh-coordination on faces, terminal PPh_3; also Co_4^+ cluster	19
$[Co(Br)_2(PPh_2H)_3]$	CoBr 233, 254; CoP 220–223; BrCoBr 125.6; PCoP 175.9°	Trig. bipyr., Br(eq)	22
$\{CoCl(PMe_3)_4\}BF_4$	CoCl 231; CoP 225–229; PCoCl 84°; PCoP 86–97°, 167°	Dist. trig. bipyr., Br(eq)	15
$[Co_2(CN)_4(PMe_2Ph)_5(O_2)]$	CoP(ax) 229–230; CoP(eq) 220–224; CoC(t) 190–1; CoC(b) 185; CoN 195; CoO 189–191; CO 144	Co^{III} dimer from $Co(CN)_2^-$, $(PMe_2Ph)_3 + O_2$; bidentate O_2^{2-}	18
$[Co(Cl)_2(PPh_3)(Me_4EtCp)]$	CoP 229; CoCl 226, 229; CoC 209–214; ClCoCl 94	Dist. oct., Me_4EtCp occupies three coordination sites	21
		Octa. long trans bond to PPh; Co displaced 11.2 pm	2

$[CoCl(DMGH)_2(PC_y)]\cdot$toluene	CoP 236.9; CoCl 229.4	Oct., Co displaced 10 pm above dist. N_4 plane	2
$[Co(NO_2)(DMGH)_2(PPh_3)]$	$CoNO_2$ 198; CoP 239.2	Oct.	27
$[Co(Cl)(DMGH)_2(PBu_3)]$	CoCl 229.5; CoP 227.1; CoN 188.9	Oct.	28
$[Co(Cl)(DMGH)_2P(OMe)_3]$	CoCl 227.2; CoP 216.5; CoN 184–194	Oct.	28
$[Co(CH_2Br)(DMGH)_2(PPh_3)]$	CoP 239.9; CoC 199.8; PCoC 175°	Oct.	29
$[Co(CH_2CN)(DMGH)_2(PPh_3)]$	CoP 239.1; CoC 204.3; PCoC 177.7°	Oct.	29
$[Co(CH_2CMe_3)(DMGH)_2(PMe_3)]$	CoP 231.6; CoC 208.4; CCoP 173.7°; $CoCH_2C$ 130.2°	Oct.	30
$[Cp(Me)(DMGH)_2(PR'_3)]$ (R′ = Ph, OMe)	CoP 242.8, 226.8; CoC 203.3, 204.1	Oct.	31
$[Co(Pr^i)(DMGH)_2\{P(COH_2)_3CMe\}]$	CoP 227; CoC 212–3; PCoC 169.9°	Oct.	32

[a] Bond lengths in pm.

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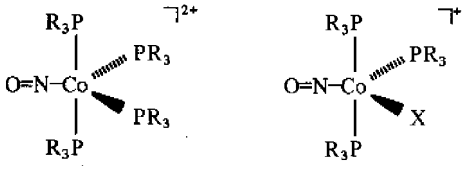
$[Co(NO)(PR_3)_{3-n}(CO)_n]$ ($n = 1,2$; Table 35). They undergo addition reactions to form five-coordinate $\{CoNO\}^8$ systems,[414] and alkene replacement to give (**96**), which may not be tetrahedral (Scheme 37).[415] Replacement of PPh_3 by SO_2 gives tetrahedral $[Co(NO)(SO_2)(PPh_3)_2]$ with coplanar Co—SO_2 and linear Co—NO coordination (structure, Table 35). The interesting paramagnetic $[Co(NO)\{N(dppe)_3\}](BPh_4)$ complex ($\mu = 1.98$ BM) also has the tetrahedral structure (Table 35) and this is one of the few examples of a paramagnetic nitrosyl complex.



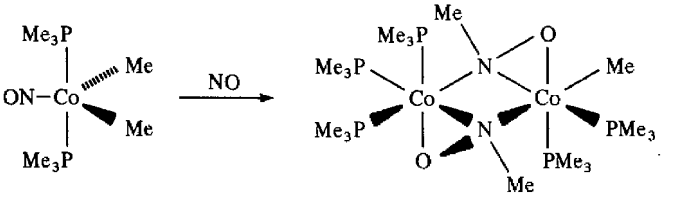
(97) (96) (98)

Scheme 37

Addition of NO to the high-spin tetrahedral Co^{II} species $[CoX_2(PR_3)_2]$ ($X = Cl^-, Br^-$; structure, Table 35) gives the $\{CoNO\}^8$ species (**97**), which for $R_3 = Ph_2Me$, $X = Cl^-$ (structure, Table 35, CoNO = 164.5°) appears to be close to the crossover between tetragonal pyramidal (C_s) with a bent CoNO and trigonal bipyramidal (C_{2v}) with linear CoNO. Thus (**98**) has been shown by ^{31}P NMR to be fluxional.[416] An analogue of (**97**) is (**101**), which is formed by addition of NO to $[Co(Me)_2(PMe_3)_3]$, but in this case the complex is unstable to further insertion into the Co—Me bond forming the bridged nitrosomethane Co^{III} complex (**102**; equation 80).[417] $[Co(NO)\{P(OR)_3\}_4]^{2+}$ (R = Me, Et; $P(OEt)_2Ph$) has been prepared from $CoX_2 \cdot 6H_2O$ (Table 34) and ^1H NMR at −60 °C supports equatorial coordination in a trigonal-bipyramidal cation (**99**).[418] No structures are apparently available on these systems. Further reaction with NO gives $[Co(NO)_2\{P(OR)_3\}_2]^+$, and CO and CNR can displace coordinated NO. Reduction to the 19-electron system $[Co(NO)\{P(OR)_3\}_4]^+$ results in loss of $P(OR)_3$ followed by further reduction to $[Co(NO)\{P(OR)_3\}_3]$. Likewise addition of NO to $[CoX\{P(OR)_3\}_4]^+$ or to $[Co(X)_2\{P(OR)_3\}_2]$, or of LiX (or HX) to $[Co(NO)\{P(OR)_3\}_4]^{2+}$ gives $[Co(NO)X\{P(OR)_3\}_3]^+$ (Table 34). IR (ν_{NO}, 1780–1800 cm^{-1}) and NMR evidence again support trigonal-bipyramidal equatorial coordination (**100**) with no evidence for a second isomer. Further reaction with NO gives $[Co(NO)_2\{P(OR)_3\}_2]$ and $[Co(NO)_2\{P(OR)_3\}]$ and reaction with I^-, PR_3, CO and CNR gives a variety of products.[419] Loss of halide occurs on reduction of $[Co(NO)X\{P(OR)_3\}]^+$ at platinum ($X = Cl^-, I^-$) with $[Co(NO)\{P(OR)_3\}_3]$ being formed; oxidation results in $[Co(NO)_2\{P(OR)_3\}_2]^+$ and $[Co(NO)_2X\{P(OR)_3\}_2]$ and species containing no nitrosyl ligand.[430]



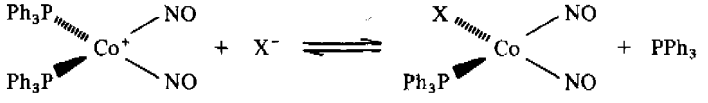
(99) (100)



(101) (102) (80)

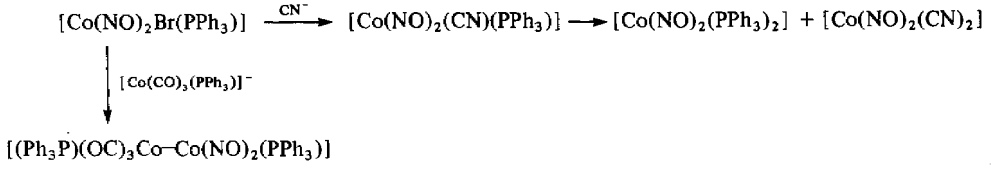
Hydrolysis and alcoholysis at the coordinated P atom have been found to occur with $[Co(NO)(PF_3)_3]$ giving $[Co(NO)(PF_3)_{3-n}(PF_2O)_n]^{n-}$ ($n = 1, 2$) and $[Co(NO)\{P(OR)_3\}_3]$ respectively,[420] and Sacco and his colleagues have shown that the nitrosyl ligand in $[Co(NO)(PPh_3)_3]$ can be transferred to a variety of Co^{II} and Ni^{II} phosphine complexes.[431]

Dinitrosyl–phosphine complexes can be prepared in a number of ways. Treatment of the diamagnetic halide-bridged dimer $[Co(NO)_2X]_2$ with PR_3 gives an equilibrium distribution of tetrahedral (**103**) and (**104**), with the former (structure, Table 35) being favoured by excess PR_3 and large non-coordinating counterions (ClO_4^-, BPh_4^-, PF_6^-) and the latter by excess halide ($X = Cl^-$, Br^-; equation 81). ^{59}Co NMR data for $[Co(NO)_2X(L)]$ have been interpreted in terms of decreasing π-acceptor power in the series $L = P(OR)_3 > P(NR_2) \sim P(alkyl)_3$.[421] Both (**103**) and (**104**) can be readily reduced by $NaBH_4$ to $[Co(NO)(PPh_3)_3]$, and heating $[Co(NO)_2(PPh_3)_2](ClO_4)$ with KNO_2 produces the nitrito complex $[Co(NO)_2(PPh_3)(ONO)]$. On the other hand Br^- in (**104**) can be displaced by other basic species such as CN^- and $[Co(CO)_3(PPh_3)]^-$ (Scheme 38).[422] $[Co(NO)_2(vpp)]^+$ has been prepared *via* internal redox in the unstable yellow-brown cobalt(III) intermediate $[Co(NO_2)_2(dppv)_2]^+$ (equation 82).[423] Treatment of $[Co(NO)_2X]_2$ ($X = Cl^-$, Br^-, I^-) with dppe results in products which depend on the amount of dppe used:[424] $[Co_2(X)_2(dppe)(NO)_4]$ containing possible bridging N_2O_2 (or dppe),[425] $[Co(NO)_2(dppe)]X$, and, in the presence of excess ligand, $[Co_2(NO)_2(dppe)_3]$ and $[Co(X)_2(dppe)(NO)]$. Treatment of $[Co(NO)_2(dppe)](PF_6)$ with Et_4NI in THF results in oxidation at one P centre and monodentate phosphine coordination (**105**).[426]

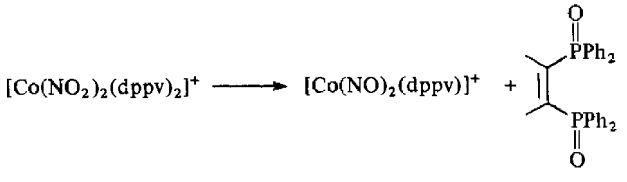


(81)

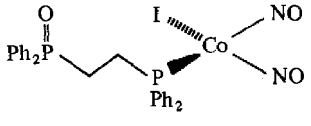
(103) (104)



Scheme 38



(82)



(105)

Major structural interest in $[Co(NO)_2(PPh_3)_2]^+$ lies in its nearly tetrahedral stereochemistry (Table 35; NCoN, 137.6°) and linear CoNO bond (171°); this is to be compared with its more distorted Rh^I (NRhN, 157.5°; RhNO, 158.9°) and Ir^I (154.2°, 163.5°) analogues.[427,428] The latter two complex ions undergo the potentially valuable redox reaction shown in equation (83), and the failure of the Co^I complex to do so is thought to arise from the more acidic character of the metal orbitals in the $\{Co(NO)_2\}^{10}$ framework. A tetrahedral structure is likewise found for $[Co(NO)_2(dppe)](PF_6)$ (Table 12) but there is some suggestion based on NMR evidence that both tetrahedral and square-planar structures exist for $[Co(NO)_2\{P(OR)_3\}_2]^+$ in solution.[419] Direct confirmation of this is required. Both reduction ($E_{1/2} \approx -0.4$ V, -1.5 V) and oxidation (~ 0.8 V) of $[Co(NO)_2\{P(OEt)_3\}_2]^+$ have been observed with the first reduction wave being reversible; impure paramagnetic $[Co(NO)_2\{P(OEt)_3\}_2]$ has been isolated, and there is IR evidence suggesting bending of the nitrosyl in this 19-electron system.[429]

$$[M(NO)_2(PPh_3)_2]^+ + 4CO \longrightarrow [M(CO)_3(PPh_3)_2]^+ + N_2O + CO_2 \quad (83)$$

47.5.2.4 *Monodentate phosphines*

(*i*) *Cobalt(−I)*

Yellow-orange diamagnetic $[Co(PMe_3)_4]^-$ is formed by the low-temperature reduction of $[Co(PMe_3)_4]$ (equation 84; Table 36) and equilibrium electron electron transfer may be involved.[432] This ion is almost certainly tetrahedral and is one of the strongest reducing agents known ($E^\circ = -2.5$ to -3 V). It is also a powerful nucleophile reacting with both inorganic (*e.g.* H^+) and organic electrophiles *via* an oxidative (possibly free radical) process.[432] Similar properties hold for alkene-substituted systems (Scheme 39), and this leads to the possibility of industrially important catalytic processes.[445] Semireduced $K_2[Co(C_2H_4)(PMe_3)_3]_4$ has been isolated and shown to be a convenient source of reducing power in organic solvents at room temperature.[477] A similar property holds with $Li[Co(C_2H_4)(PMe_3)_3]$ whose structure (Table 35) shows weak interactions with the metal and alkene in a distorted trimeric octahedral arrangement.

$$[Co(PMe_3)_4] \xrightarrow[-70\,^\circ C]{M} [Co(PMe_3)_4]^- \xrightarrow[-70\,^\circ C]{RCl} [CoR(PMe_3)_4] + Cl^- \quad (84)$$

M = Li, Na, K; R = H, alkyl

$$[Co(PMe_3)_3] + \text{alkene} \longrightarrow [Co(\text{alkene})(PMe_3)_3] \xrightarrow{K}$$

green, $\mu = 1.85$ BM

$$[Co(\text{alkene})(PMe_3)_3]^- \xrightarrow{RCl} \text{Me}_3\text{P}(\text{R})\text{Co}(\text{alkene})(\text{PMe}_3)_2$$

orange-brown

alkene = C_2H_4, C_3H_7, cyclopentene

Scheme 39

Unlike $[Co(PMe_3)_4]^-$ less basic $[Co(PF_3)_4]^-$ and $[Co\{P(OR)_3\}_4]^-$ can be prepared by deprotonation of the parent hydride (equation 85; Table 36). Such species also readily undergo oxidative addition reactions.[433] The hydrides $[HCo(PF_3)_4]$, $[HCo\{P(OMe)_3\}_4]$ and $[HCo(PMe_3)_4]$ can be considered as H^+ conjugate acids of d^{10} bases. However their acidity decreases dramatically in the above order with $[HCo(PF_3)_4]$ being easily titrated by most bases in aqueous solution; the latter two hydrides cannot be titrated with LiR or KH and are better considered as hydride complexes of Co^I (*cf.* Section 47.5.2.1). $Hg[Co\{P(OMe)_3\}_4]_2$ retains C_{3v} trigonal-bipyramidal symmetry even at 100 °C (it has a strong axial Co—Hg—Co framework) but the phosphite ligands are stereochemically fluxional among the remaining coordination sites ($E_a \approx 42$ kJ mol^{-1}).[434] Likewise $[HCo(PF_3)_4]$ is stereochemically non-rigid,[433] as is $[CoR(PMe_3)_4]$, R = H, Me (Section 47.5.2.1).

$$HCo\{P(OR)_3\}_4 + KH \xrightarrow{THF} K[Co\{P(OR)_3\}_4] + H_2 \quad (85)$$

R = Me, Et; colourless

(*ii*) *Cobalt(0)*

Reduction of Co^{II} halides with Na/Hg or Hg/Grignard (but not $NaBH_4$) in the presence of PR_3 under Ar (N_2 complexes are usually formed in the presence of N_2) forms dark-coloured paramagnetic C_{3v}-distorted $[Co(PR_3)_4]$ complexes (Table 36). The ESR spectrum of $[Co(PMe_3)_4]$ shows a well-resolved eight-line pattern characteristic of axial symmetry.[435] $[Co(PPh_3)_4]$ has apparently not been made but $[Co(PPh_2Me)_4]$ and $[Co(DBP)_4]$ have, so steric constraints may not be important. Intermediate paramagnetic '$Co(PR_3)_3$' species (PR_3 = PMe_3, DBP) have been observed and are synthetically useful (see below).

These 17-electron systems are excellent nucleophiles and undergo a variety of displacement, dimerization and oxidative addition reactions; $[Co(PMe_3)_4]$ is especially reactive (Scheme 40).[435]

Table 36 Preparations: Monodentate Phosphine Complexes

Complex	*Preparation*	*Properties*[a]	*Ref.*
Cobalt(−I)			
$M[Co(PMe_3)_4]$	$[Co(PMe_3)_4] + M$; Ar, THF	Yellow-orange; diamagnetic; very reactive nucleophile	1
(M = Li, Na, K)			
$[Mg(THF)_4][Co(PMe_3)_3N_2]_2$	$CoCl_2 + PMe_3 + Mg$; THF, N_2, 3 d, 20 °C	Orange-yellow; ν_{NN} 2068(s)	2
$K[Co\{P(OR)_3\}_4]$	$[HCo\{P(OR)_3\}_4] + KH$; THF	Colourless; rapidly gives $[Co(H)\{P(OR)_3\}_4]$ in H^+ media	3
(R = Me, Et)			
$K[Co(PF_3)_4]$	$[HCo(PF_3)_4] + K/Hg$; $E^c_{1/2}$	Colourless; diamagnetic	4
Cobalt(0)			
$[Co(PMe_3)_4]$	$CoCl_2 + PMe_3 + Mg$/THF (or Na/Hg); Ar	Brown; μ = 1.70; very reactive nucleophile	7
$[Co(PPh_2Me)_4]$	$[CoCl_2(PPh_2Me)_2] + PPh_2Me$	Brown-black; μ = 1.71	8
$[Co(DBP)_4]$	$CoCl_2 \cdot 6H_2O + DBP + NaBH_4$; boiling EtOH	Red-brown; diamagnetic; possibly dimeric	9
$[Co(C_2H_4)(PMe_3)_3]$	$[Co(PMe_3)_3] + C_2H_4$	μ = 1.85	12
$[Co(C_2H_4)(PPh_3)_3]$	Et_2O, ArCo(acac) + $Et_2Al(OEt)$ + PPh_3 + Et_2O, Ar[3], 0 °C	Orange; μ = 1.90	22
Cobalt(I)			
$[CoX(PPh_3)_3]$	$CoX_2 \cdot 6H_2O + PPh_3 + NaBH_4$; EtOH, N_2	Green (X = Cl); tet.	14, 9
(X = Cl, Br, I)	$[CoX_2(PPh_3)_2] + LiPPh_3$; THF		15
$[CoX(PMe_3)_3]$	$CoX_2 + PMe_3 + Na/Hg$; Et_2O	Blue-violet; μ = 3.1–3.4; tet.	9, 16
(X = Cl, Br, I)	$[Co(PMe_3)_4] + CoX_2 + PMe_3$		17
	$[Co(Me)(PMe_3)_4] + NH_4Cl$		18
$[CoX(PPhF_2)_4]$	$CoCl_2 + PPhF_2$		21
(X = Cl, Br)	$[CoBr_2(PPhF_2)_3] + PPhF_2$	Brown-orange; dimagnetic	22
$[Co(Me)(PPh_3)_3]$	$[Co(acac)_3] + Me_2Al(OEt) + PPh_3$; toluene, −5 °C	Orange; unstable giving CH_4	
$[Co(Me)(PPh_3)_2]$	$[Co(acac)_3] + Me_2Al(OEt) + PPh_3$; Et_2O, Ar, 0 °C, 4 h		7
$[Co(Me)(PMe_3)_4]$	$[CoCl(PMe_3)_3] + LiMe + PMe_3$; Et_2O, −78 °C	Diamagnetic	19
$[Co(PPh_3)_{2,1}(CNR')_{3,4}](PF_6)$	$[Co(PR_3)_2Cl_2] + RNC(N_2H_4)$; EtOH	Orange; diamagnetic; trig. bipyr. (^1H NMR, IR); fluxional	
(R′ = alkyl, aryl)	$[Co(CNR)_5]X + PPh_3$; CH_2Cl_2		
Cobalt(II)			
$[Co(X)_2(PMe_3)_2]$	$CoX_2 + PMe_3$; EtOH	Blue, red (X = NCS); μ = 3.9–4.4 (2.15, X = NCS); tet.	35
$[Co(X)_2(PR_3)_2]$	$CoX_2 + PR_3$; EtOH	Blue (Cl); blue-green (Br); brown (I); μ = 4.4–4.7	5
(X = Cl, Br, I; R = Et, Ph)	$CoX_2 + PPh_3$; NBu^n_4X; acetone	Blue (Br); green (I); μ = 4.5–4.6	23
$(NBu^n_4)[Co(X)_3(PPh_3)]$	$Co(NCS)_2 + PEt_3$; EtOH	Red-brown; μ = 2.21; dimeric; dissociates in CH_2Cl_2 soln.	36
(X = Cl, Br, I)	$CoX_2 + PCy_3$; EtOH	Blue-green; μ = 4.40	37
$[Co(NCS)_2(PEt_3)_2]$			
$[Co(X)_2(PCy_3)_2]$			
(X = Cl, Br, NCS)			

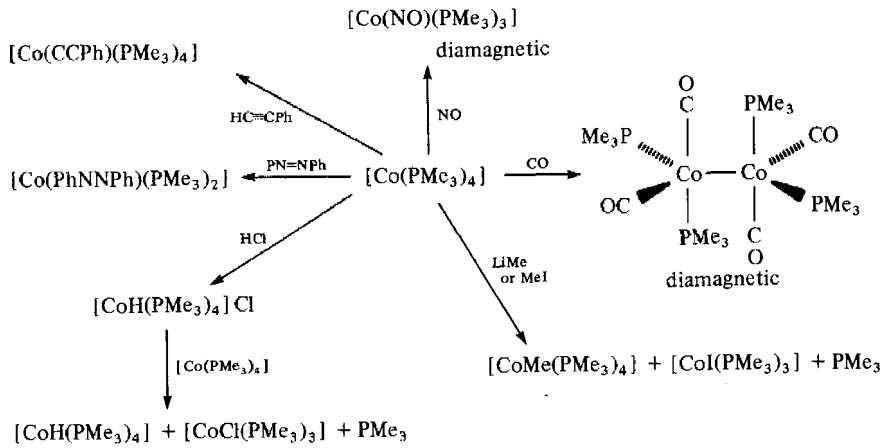
Table 36 (*continued*)

Complex	*Preparation*	*Properties*[a]	*Ref.*
trans-$[Co(aryl)_2(PR_3)_2]$ (aryl = mesityl, C_6Cl_5, 2-Menapth, 2-biphenylyl)	$[CoBr_2(PR_3)_2]$ + MgBr (aryl); benzene, −30 °C	Yellow; decomposes in hot C_6H_6 (structure Table 35)	6
$[Co(X)_2(CO)(PEt_3)_2]$ (X = Cl, Br, I)	$[CoX_2(PEt_3)_2]$ + CO; benzene	Brown; decomposes in air; ν_{CO} 1975–7	11
$[Co(X)_2(PMe_3)_3]$ (X = Cl, Br, I, Me)	$CoCl_2$ + PMe_3 ($LiCH_3$); Et_2O, −70–20 °C	Violet, orange-brown (X = Me); μ = 2.0–2.2	10
$[CoH(PMe_3)_4]Cl$	$Co(PMe_3)_4$ + HCl; Et_2O, −70 °C	Green-blue	10
$[Co(X)_2(PMe_2Ph)_3]$ (X = SCN, Cl, F, Br, CN)	CoX_2 + PMe_2Ph; CH_2Cl_2	Violet-green; low spin; ν_{SCN} 2095	13
$[Co(X)_2(PMe_3)_3]$ (X = Cl, Br, I)	CoX_2 + PMe_3; CH_2Cl_2, vac., −30 °C	Blue-violet; μ = 2.1–2.3	13, 35
$[Co(Br)_2(PHR_2)_4]$ (R = Ph, Cy, Et)	$CoBr_2$ + PHR_2; CH_2Cl_2,	Green; μ = 2.0; oct. in solid; dissociates in soln. to $[CoBr_2(PHR)_3]$	24
$[Co(X)_2(PHPh_2)_3]$ (X = Cl, Br)	No details	Red; μ = 2.43 (Br), 2.23 (I); sq. pyr. (structure, Table 35)	34
$[CoX(PMe_3)_4]BPh_4$	CoX_2 + PMe_3; EtOH, −30 °C	Green; μ = 2.1–2.4	35
Cobalt(III)			
$[CoCl_3(PR_3)_2]$ (R = Me, Et, Pr, Bu)	$[CoCl_2(PR_3)_2]$ + NOCl, −80°C	Violet-black crystals; $\mu \approx 3.02$; monomeric; dipole moment ≈ 0	25
mer-$[Co(Me)_3(PMe_3)_3]$	$[Co(acac)_3]$ + LiMe + PMe_3; Et_3I	Orange-brown; diamagnetic	26
trans-$Na[Co(CN)_4(PPh_4)_2]\cdot 3H_2O$	$Na_5[Co(CN)_4(SO_3)_2]$ + HOAc + PPh_3, 75–80 °C, 6 h	Yellow; visible–UV	27
cis,trans-$[Co(acac)_2(PR_3)_2]PF_6$ (R = Me, Ph)	$[Co(acac)_3]$ + PR_3 + C; EtOH, 25 °C, SP-Sephadex chrom.	Blue-violet (*trans*), red-brown (*cis*); ^1H and ^{13}C NMR, visble–UV	28
trans-$[Co(CN)_2(acac)(PR_3)_2]$	$K[Co(CN)_2(acac)_2]$ + PR_3; EtOH, alumina chrom.	Orange-yellow; ^1H and ^{13}C NMR, visible–UV	28
trans-$K(Co(CN)_4(PR_3)_2]$	$K_3[Co(CN)_5I]$ + PR_3; HOAc, 75 °C, 1 h	Yellow; ^1H and ^{13}C NMR, visible–UV	28
$K_2[Co(CN)_5(PPh_3)]\cdot 3H_2O$	$K_3[Co(CN)_5Br]$ + PPh_3; H_2O–HOAc, 75 °C, 6 h	Yellow, visible–UV	29
$[CoCl_3(PF_2Ph)_3]$	$CoCl_2$ + PF_2Ph_3; benzene, 20 °C	Diamagnetic; ε_{450} 3125 (Cl)	30
$[CoBr_3(PF_2Ph)_3]$		Disproportionates	
$[Co(DMGH)_2(PPh_3]R]$ (R = Ph, Me, Et)	$[CoCl(DMGH)_2PPh_3]$ + RMgX, THF	Vitamin B_{12} analogues; orange	31
$[Co(DMGH)_2(PR_3)Cl]$	$[Co(DMGH)_2(PPh_3)Cl]$ + PR_3; CH_2Cl_2, r.t.	Brown-purple, easily solvated; ^1H NMR, P–H chemical shifts, ^{13}C NMR	32
$[Co(DMGH)_2(PR_3)(H_2O)]NO_3$ (R = alkyl, aryl)			
$[\{Co(DMGH)_2(Me)\}_2$diphosphine]	$[Co(DMGH)_2(Me)(SMe_2)_2]$ + diphosphine; $CHCl_3$	*Syn* and *anti* isomers of unusual ligands	38
cis(N,P)-$[Co(acac)_2(NO_2)(PR_3)]$	$Na[Co(acac)_2(NO_2)_2]$ + PR_3; benzene–EtOH, 50 °C	Red-brown; ^1H NMR, visible–UV	33
trans(P,P)-$[Co(acac)(NO_2)_2(PMe_2Ph)]$ (R = Me, Ph, Bu)			

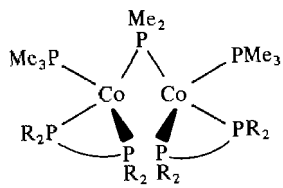
[a] IR data in cm^{-1}; μ values in BM.

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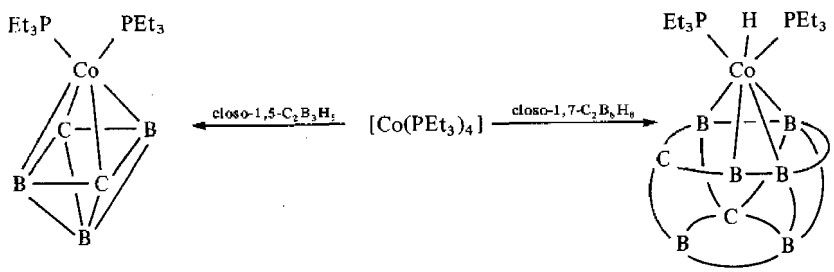
Addition of $Me_2PCH_2PMe_2$ in THF at room temperature leads to the red-brown paramagnetic dimer (**106**), which has an unusually short Co—Co bond (bond order 1.5; structure, Table 35) with each Co being formally at the 0.5 oxidation level. $[Co(PEt_3)_4]$ also adds to the B,C skeleton of *closo*-carbonates to form paramagnetic (**107**) and diamagnetic (**108**) clusters (equation 86).[436] Many uses for these electron-rich species will be found.



Scheme 40



(**106**)

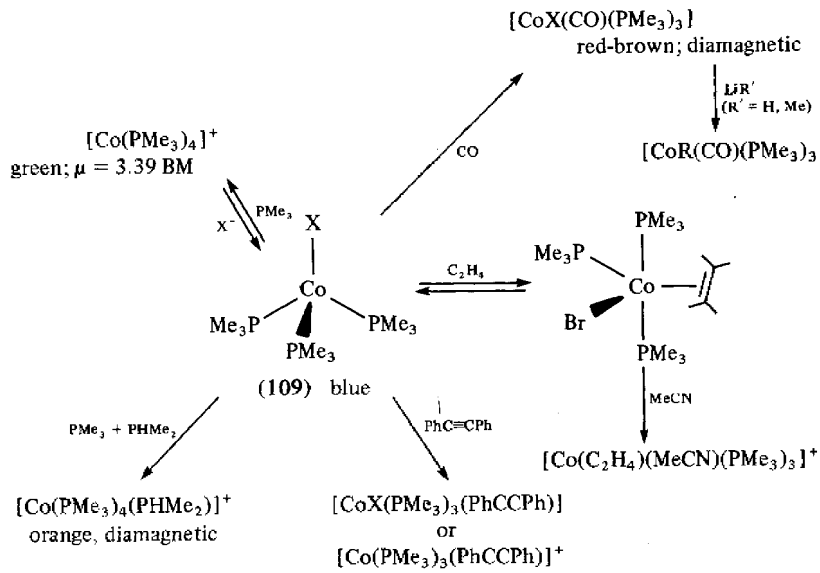


(**107**) (**108**) (86)

(iii) Cobalt(I)

Cautious reduction of CoX_2 in the presence of PR_3 or of $[Co(Cl)_2(PR_3)_2]$ at low temperature produces $[CoX(PR_3)_3]$ species (X = Cl^-, Br^-, I^-, O_2CMe ; Table 36). The four-coordinate 16-electron systems (**109**) are typically high spin (μ = 3.1–3.4 BM) and tetrahedral (probably C_{3v}) with high fluxional lability. With R = Ph or other aryl they are not very stable in solution (THF, CH_2Cl_2, C_6H_6) and oxidize readily to ill-defined products. With R = Me they are more stable and readily add electron pairs generating diamagnetic trigonal-bipyramidal systems (Scheme 41).[437] Addition of C_2H_4 to $[CoBr(PMe_3)_3]$ is reversible forming $[CoBr(C_2H_4)(PMe_3)_3]$ with equatorial Br and C_2H_4 ligands,[475] whereas treatment with PhCCPh leads to trigonal-bipyramidal $[CoBr(PhCCPh)(PPh_3)_3]$ in toluene and some tetrahedral $[Co(PhCCPh)(PPh_3)_3]Br$ in acetone;[476] a structure of the latter is available (Table 35). Addition of MeCN to these products results in $[Co(MeCN)(R)(PMe_3)_3]^+$ (R = C_2H_4, PhCCPh) with equatorial R (structures, Table 35). Displacement of Br^- and PMe_3 occurs readily in acetonitrile at −80 °C (equations 87 and 88).[475] $[CoCl(PPh_3)_3]$ and $[CoCl_2(PPh_3)_2]$ have been shown to be effective catalysts in the oxidation of cyclic $B_3H_8^-$ to $B_3H_7PPh_3$ (and lower

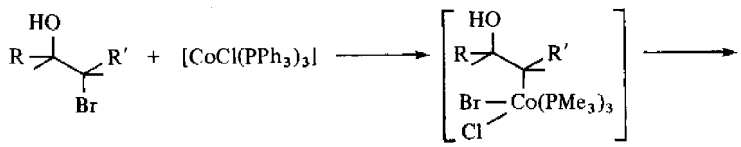
homologues) possibly *via* initial displacement of halide and chelation of borate, and for the oxidation of bromohydrins to ketones *via* a β-hydroxylalkyl cobalt(III) intermediate[439] in a manner reminiscent of the vitamin-B_{12}-catalyzed dehydration of 1,2-diols (equation 89). $[CoX(PPh_3)_3]$ ($X = Cl^-, Br^-, I^-$) also catalyzes the dimerization of ethylene to an isomeric mixture of butenes[440] and of methyl acrylate to dimethyl adipate;[441] Co^I complexes are again proposed as intermediates and are probably similar to those outlined by Klein.[442]



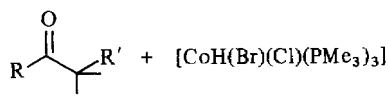
Scheme 41

$$[CoBr(PMe_3)_3] + MeCN \longrightarrow [Co(MeCN)_2(PMe_3)_3]^+ + Br^- + PMe_3 \quad (87)$$

$$[Co(PMe_3)_4]^+ + MeCN \longrightarrow [Co(MeCN)(PMe_3)_4]^+ + PMe_3 \quad (88)$$



(89)



Diamagnetic $[Co(Me)(PPh_3)_3]$ and the 14-electron $[Co(Me)(PPh_3)_2]$ can be prepared by treating $[Co(acac)_3]$ with Me_3Al or $Me_2Al(OEt)$ in toluene (Table 36). These electron-deficient compounds are rather unstable and readily transfer the Me group (equation 90). $[Co(Me)(PPh_3)_3]$ also catalyzes the aldol condensations of acetone (to give mesityl oxide) and of methyl ethyl ketone (to give isomers of hepten-5-ones)[443] and spontaneously evolves biphenyl and $PMePh_2$ in non-polar solvents (migration of Me from Co to P).[444] $[Co(Me)(PMe_3)_3]$ does not appear to exist.

$$[CoX(PPh_3)_3] + CH_4 \xleftarrow{HX} [CoMe(PPh_3)_3] \xrightarrow{PhC\equiv CPh} \underset{(cis\ +\ trans)}{\overset{Me}{\overset{|}{PhC}}=CHPh} \quad (90)$$

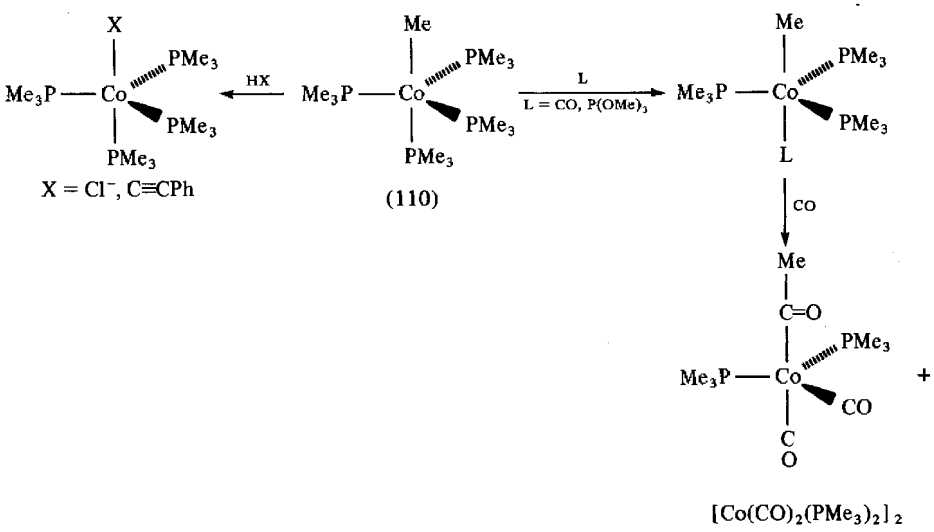
$[CoR\{(PMe)_3\}_4]$ species (R = H, alkyl) may be readily prepared by substitution on $[CoCl(PMe_3)_4]$ or by oxidative addition to $[Co(PMe_3)_4]^-$ (equations 91 and 92);[435,445] these 18-electron systems have a distorted trigonal bipyramidal geometry with axial R (**110**). ^1H and ^{31}P spectra demonstrate fluxional character at ambient temperatures with a coalescence temperature of −52 to −75 °C. With more bulky alkyl or aryl ligands, or phosphines, stereochemical rigidity in $[CoR(PR'_3)_4]$ is maintained to higher temperatures. The *trans* influence of axial R causes substitution by Y (CO, $P(OMe)_3$) to occur in the axial position, but with HX methane is liberated (Scheme 42).[435]

These systems offer promise for the insertion of alkenes (or CO) into M—H or M—C bonds. Klein and coworkers[442] have demonstrated reversibility in the system (**111**), (**112**) by observing complete deuteration *via* $[Co(D)(C_2H_4)(PMe_3)_3]$; 1-pentene is also converted into 2-pentene (*cis*:*trans* = 9:1). However methyl migration in $[Co(Me)(1\text{-pentene})(PMe_3)_3]$ was not observed but on warming solutions of $[Co(Ph)(C_2H_4)(PMe_3)_3]$ in C_2H_4 at 50 °C biphenyl is produced. Some mixed phosphine–isocyanide complexes of the type $[Co(PR_3)(RNC)_4]^+$ and $[Co(PR_3)_2(RNC)_3]^+$ with axial phosphine ligands have been prepared (Table 36) and their oxidation studied.[446,447] Some of the most interesting systems involve NO coordination; these are considered in Sections 47.4.1.2 and 47.5.2.3 but in the case of $[Co(Cl)_2(NO)(PPh_3)_2]$ there is good IR (1750 cm^{-1}, 1650 cm^{-1} NO stretches) and photoelectron evidence for the existence of both linear and bent CoNO isomers in both the solid and in solution.[448,117]

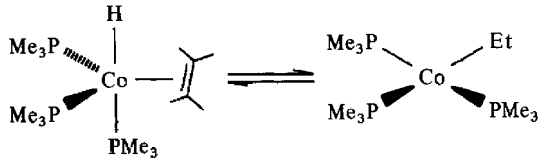
$$K[Co(PMe_3)_4] \xrightarrow[-70\,^\circ C]{RX} [CoR(PMe_3)_4] \xleftarrow{LiR} [CoX(PMe_3)_4] \qquad (91)$$

$$X = Cl^-, Br^-, I^-$$

$$[Co(C_2H_4)(PMe_3)_3]^- \xrightarrow[R = H, Me]{RCl} \text{yellow-orange} \xleftarrow[R = Me, Ph]{LiR} [Co(C_2H_4)Cl(PMe_3)_3] \qquad (92)$$



Scheme 42

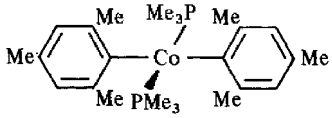


(iv) Cobalt(II)

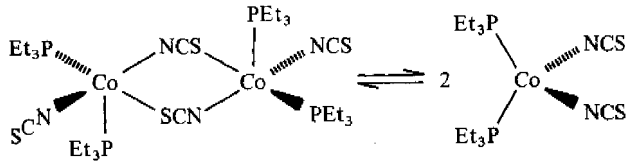
High-spin tetrahedral or pseudo-tetrahedral (C_{2v}) $[Co(X)_2(PR_3)_2]$ (R = alkyl, aryl; X = Cl^-, Br^-) complexes are easily prepared from CoX_2 and PR_3 in hot EtOH (Table 36). Addition of a large cation can lead to the isolation of the $[Co(X)_3(PR_3)]^-$ anion, and $[Co(X)(PMe_3)_4](BPh_4)$ has been isolated (Table 36). Crystal structures are available (Table 35). Care must be taken to avoid ligand oxidation, especially for R = aryl. $[Co(X)_2(PR_3)_2]$ and $(NBu^n_4)[Co(X)_3(PR_3)]$ have ESR and NMR characteristics consistent with a fast spin–lattice relaxation process ($T_1 \approx 6 \times 10^{13}\,s^{-1}$)[450] and use of

this has been made to study by NMR methods the ion pairing of large cations.[451] Temperature- and pressure-dependent shifts have been used to follow PPh_3 exchange in $[Co(Br)_2(PPh_3)_2]$ and the parameters $\Delta H^{\ddagger} = 32 \pm 2\,kJ\,mol^{-1}$, $\Delta S^{\ddagger} = -80 \pm 13\,J\,mol^{-1}\,K^{-1}$, $\Delta V^{\ddagger} = -12.1 \pm 0.6\,cm^3\,mol^{-1}$ have been interpreted in terms of an associative process *via* the known $[Co(X)_2(PR_3)_3]$ species.[452,453]

Complexes of the type $[Co(R)_2(PR_3)_2]$ appear to be stable only when R is an *o*-disubstituted or very bulky *o*-substituted aryl (R = alkyl are unknown) and their low spin ($\mu = 2.3$–2.7 BM) and zero dipole moment have been associated with the planar *trans* structure (**113**; Table 36) in which the two axial sites are blocked by the Me substituents. Gerloch has considered the theoretical aspects of bonding in these systems.[454] Another example of (**113**) may be low-spin $[Co(NCS)_2(PMe_3)_2]$ ($\mu = 2.15$ BM),[468] but $[Co(NCS)_2(PEt_3)_2]$ is dimeric in the solid with NCS bridges and exists in equilibrium with the high-spin tetrahedral monomer in CH_2Cl_2 solution (equation 93).



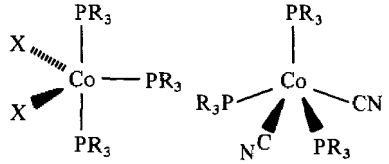
(113)



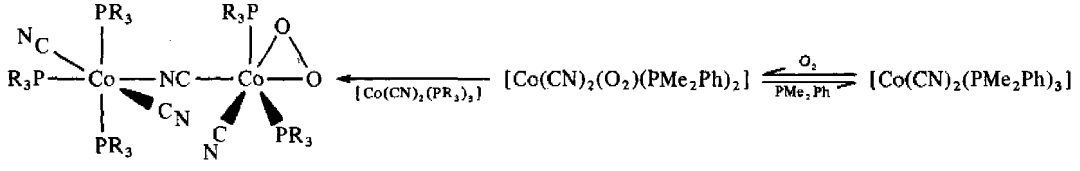
(93)

$\mu = 2.2$ BM $\qquad\qquad$ $\mu = 4.4$ BM

The 17-electron five-coordinate $[CoX_2(PR'_3)_3]$ systems (X = halide, Me; $R'_3 = Me_3$, Me_2Ph, HR^1R^2) are again easily prepared (Table 36), but with the exception of the PMe_3 complex partially dissociate to $[Co(X)_2(PR'_3)_2]$ in the absence of excess phosphine; steric effects are considered to be important.[455] These low-spin complexes have the trigonal bipyramidal structure (**114**) for X = halide, Me (structures, Table 35); $[CoH(PMe_3)_4]^+$ probably has a tetrahedral skeleton with an appended hydride (ν_H, 1935 cm^{-1}), and for X = CN^-, SCN^- the complexes have the tetragonal-pyramidal structure (**115**) with *trans* X groups (ESR).[456] The X = CN^-, SCN^- and F^- complexes absorb O_2 (reversibly at low temperature) releasing PR_3, and eventually form the Co^{II} dimer (**116**; Scheme 43).[437,457]



(114) $\qquad$ (115)



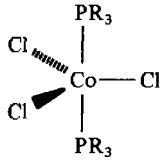
(116)

Scheme 43

Treatment of $CoBr_2$ with PHR_2 ($R_2 = Et_2$, EtPh, MePh) in the presence of $NaBPh_4$ results in low-spin light-green $[CoBr(PHR_2)_4](BPh_4)$, while octahedral $[Co(Br)_2(PHR_2)_4]$ is apparently formed in its absence.[455]

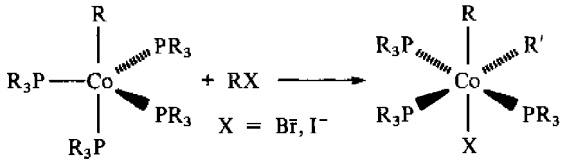
(v) *Cobalt(III)*

An increasing number of monodentate phosphine complexes of Co^{III} are becoming available (Table 36); few structures are known (Table 35). Many years ago Jensen[458] prepared the high-spin five-coordinate $[Co(X)_3(PR_3)_2]$ complexes ($\mu = 3.0$ BM; X = Cl^-, Br^-) and their monomeric nature and zero dipole moment imply a trigonal-bipyramidal structure (**117**). Oxidative addition of HX or RX to electron-deficient four-coordinate Co^I (equation 94) or to five-coordinate Co^I (**118**; equation 95) or to Co^{II} (equation 96) provides additional routes to octahedral Co^{III} systems of type (**119**; Table 36). The formation of the analogous hydrido–Co^{III} systems (Section 47.5.2.1) is often reversible (equations 97 and 98).



(117)

$$2[CoI(PMe_3)_3] + MeI \longrightarrow [CoI(Me)_2(PMe_3)_3] + [Co(I)_2(PMe_3)_3] \quad (94)$$



(118) (119) (95)

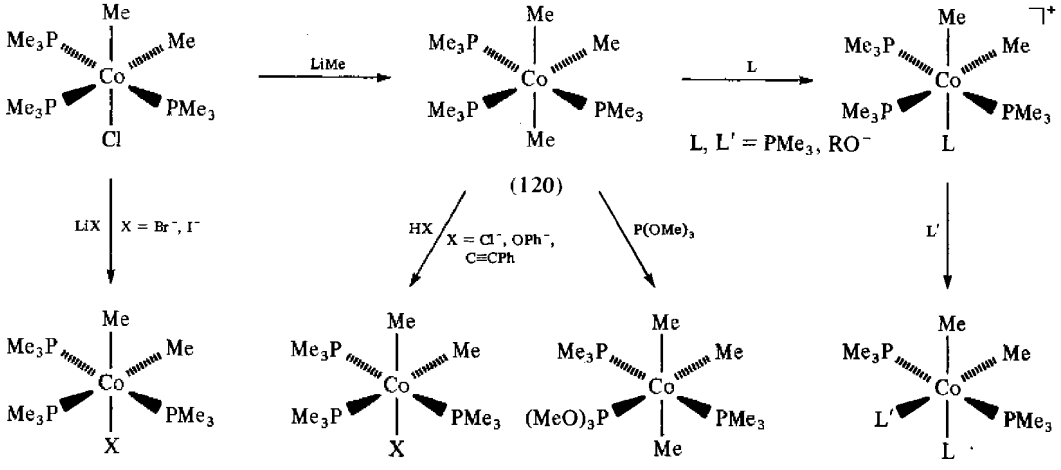
$$[Co(Me)_2(PMe_3)_3] + X_2 \xrightarrow[X=Br^-,I^-]{} [CoX(Me)_2(PMe_3)_3] \quad (96)$$

$$[CoH(PPh_3)_3] + H_2 \rightleftharpoons [CoH_3(PPh_3)_3] \quad (97)$$

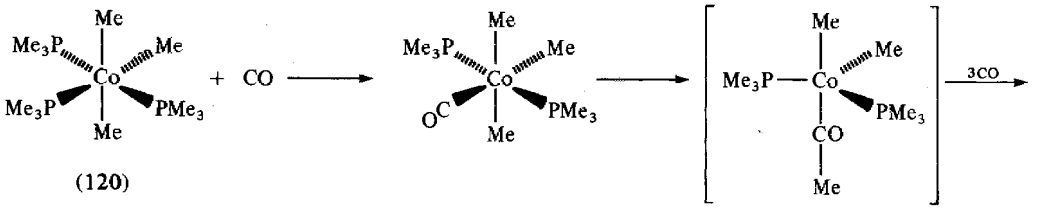
$$[Co(PHR_2)_5] + H^+ \rightleftharpoons [CoH(PHR_2)_5]^{2+} \quad (98)$$

red white

Subsequent substitutions in these systems are often regiospecific (Scheme 44).[459,460,461] Unlike the reductive elimination of *cis* hydrides in $[Co(H)_3(PPh_3)_3]$, ethane is not formed from *cis* Me groups in (**120**; Scheme 44), but for L = CO insertion into the Co—Me bond occurs with the release of acetone (Scheme 45); no intermediates have been observed.[459] Using the diphosphomethamide anion as an analogue of allyl an interesting bonding isomerization has been observed (**121** to **122**; Scheme 46).[462]



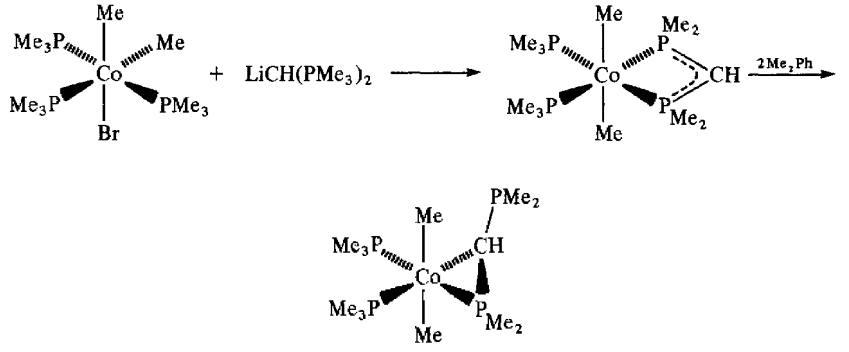
Scheme 44



(120)

$[Co(CO)_2(COMe)(PMe_3)_2] + Me_2CO$

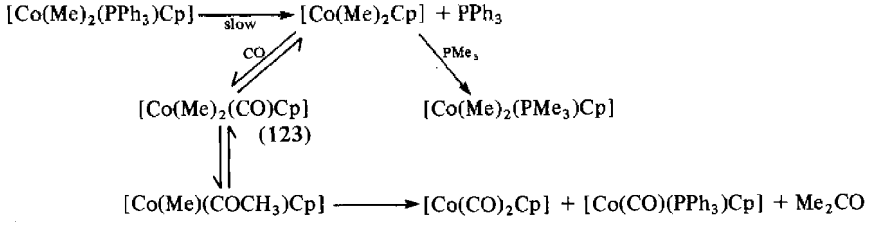
Scheme 45



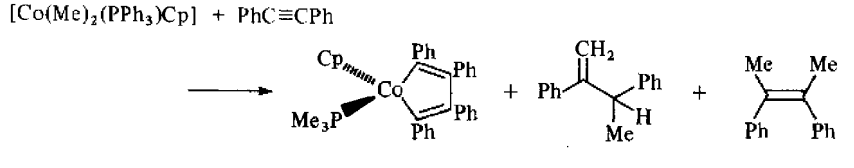
(122)

Scheme 46

Bergman and coworkers have investigated in some depth the $[Co(Me)_2(PPh_3)(Cp)]$ system, which provides low-temperature routes to carbonylation, hydroformylation and polymerization processes.[471–474] An overview of this work is available.[478] Methyl scrambling occurs between similar $[Co(Me)_2(PPh_3)(Cp)]$ units in THF at 60 °C and PPh_3 dissociation from one appears to be a prerequisite.[471] In another study this dissociation (Scheme 47) was shown to occur with $k = 4 \times 10^{-4}\,s^{-1}$ in toluene at 30 °C with the $[Co(Me)_2(Cp)]$ product reacting rapidly with PMe and CO. The latter product (**123**) gives rise to acetone without scrambling (intramolecular) in 0.05 M solution (some scrambling occurs at higher concentration).[472] Reactions with PhCCPh (dimerization, methyl migration; equation 99) and with C_2H_4 (equation 100) have also been investigated by Bergman in some depth extending earlier work by others and having some bearing on the chain-growth step in Ziegler–Natta polymerization.[472,473] The authors have also shown that the similarly substituted Co^{III} dialkyl complex (**124**) undergoes cyclopentadienyl exchange with the Co^{I} complex (**125**) in THF.[474] Equilibrium was reached (67%, **126**; 33%, **124**) within 48 h at 62 °C (equation 101). These Co^{I} bis(phosphine) complexes readily undergo phosphine exchange *via* dissociation to the unsaturated intermediate (**127**; equation 102).[475] For the PPh_3 complex $k = 1.15 \times 10^{-3}\,s^{-1}$ at −60 °C and the intermediate prefers PMe_3 to PPh_3 by a factor of about four over PPh_3.

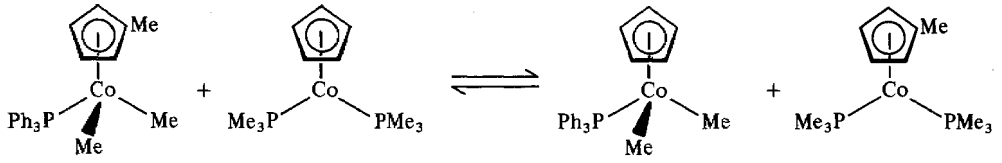


Scheme 47



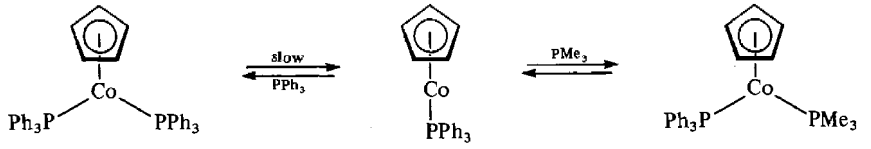
95% (99)

$$[Co(Me)_2(PPh_3)Cp] + CH_2{=}CH_2 \longrightarrow [Co(C_2H_4)(PPh_3)Cp] + CH_4 + MeCH{=}CH_2 \quad (100)$$



(101)

(124) (125) (126)

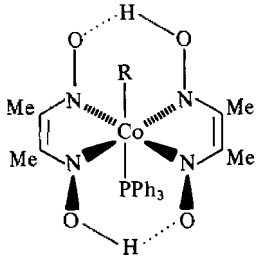


(102)

(127)

Shibata and coworkers[463,464] have used $[Co(acac)_3]$, $K[Co(CN)_2(acac)_2]$ and $K_3[Co(CN)_5I]$ to prepare a wide range of the more classical Co^{III} complexes: *cis*- and *trans*-$[Co(acac)_2(PR_3)_2]^+$, $[Co(CN)_2(acac)(PR_3)_2]$, and *trans*-$[Co(CN)_4(PR_3)_2]^-$ (R = alkyl, aryl; Table 36). They report ^1H, ^{31}P and visible–UV spectra and some simple reactions. *trans*-$[Co(acac)_2(PMe_2Ph)_2]^+$ aquates to blue-green *trans*-$[Co(acac)_2(PMe_2Ph)(H_2O)]^+$ in aqueous ethanol, and in the presence of charcoal it isomerizes to an equilibrium mixture containing mostly the *cis* isomer.

A number of vitamin B_{12} analogues containing dimethylglyoxime (**128**) have been prepared,[465] and ^1H and ^{13}C NMR spectra of $[Co(DMGH)_2(PR_3)R']^{0,+}$ (R′ = Cl^-, NO_3^-, CN^-, CH_2R^-, Ph^-, Me^-, $PO(OR)_2$, MeOH) have been correlated with the size and electronic properties of the phosphine. ^{13}C shifts are accounted for largely by through-bonding effects and ^1H shifts by spatial effects. The latter increase in the order oxygen donors < halides ≈ CN^- ≈ SR^- ≈ PR_3 < alkyl, aryl.[466] Dissociation of R′ occurs readily, and an equilibrium is often established in poor donor solvents. Randaccio and Bresciani-Pahor, and Marzilli and coworkers have carried out a series of structural characterizations in an attempt to correlate the structural *trans* effect of the phosphine ligand on the Co—C bond (Table 35).



(128) R = Me, Et, Ph

47.5.2.5 Bidentate phosphines

(*i*) *Cobalt(−I) and cobalt(0)*

A few low-valent complexes containing bidentate phosphines are known. Paramagnetic $[Co(dppe)_2]$ can be made by reducing $[Co(Br)_2(dppe)_2]$ with Na (Table 37); it is an excellent reducing agent, reducing Sn^{2+} to the metal and H_2 to $[CoH(dppe)_2]$.[479] Some exotic systems with poor σ donors such as (**129**; Scheme 48) are known. King and coworkers have shown that the $[Co_2\{MeN(PF_2)_2\}_3]$ structural unit containing a Co—Co bond (271–277 pm) is very stable. Stepwise substitution of terminal CO groups by other neutral Lewis bases[497] and by halogens[496] is possible (Scheme 48) as well as reduction to the radical anion and dianion.[498] Structures are known for several of these complexes (Table 38). Similar treatment of $[Co_2(CO)_8]$ with $MeN\{P(OMe)_2\}_2$ forms (**130**).[499]

Table 37 Preparations: Bidentate Phosphine Complexes

Complex	*Preparation*	*Properties*[a]	*Ref.*
Cobalt(0)			
$[Co(dppe)_2]$	$[CoBr_2(dppe)_2]$ + Na; benzene	Dark red; dipole moment 1.2	11
Cobalt(I)			
$[Co(dppv)_2](BPh_4)$	$[CoCl(PPh_3)_3]$ + dppv; benzene	Green; ε_{400} 3080	8, 10
$[Co(dppe)]Y$	$[CoBr(dppe)_2]$; EtOH, $NaClO_4$	Violet-black; ε_{434} 1710; ε_{563} 1190; ε_{720} 1040	12
($Y = ClO_4$, BPh_4)	$[CoBr_2(dppe)_2]$ + Na; benzene, r.t.	Brown; *ca.* 540 nm (sh)	12
$[Co(Br)(dppe)_2]$	$[Co(dppe)_2]$ + $[CoBr_2(dppe)_2]$; benzene, r.t. 15 min		13
$[Co(CN)(dppv)_2]$	$[Co(dppv)_2]ClO_4$; Dowex 1 × 4 (CN^-), CH_2Cl_2	Red; diamagnetic	14
$[Co(CN)(dppe)_2]$	$[Co(CN)_2(dppe)_2]$ + $N_2H_4 \cdot H_2O$; EtOH, reflux, N_2	Red; diamagnetic, air sensitive	
Cobalt(II)			
$[CoX(dppe)_2]Y$	$CoX_2 \cdot 6H_2O$ + L; hot Pr^iOH	Green (Cl, Br); brown (I); low spin, μ 1.9–2.3	1, 2
($Y = Cl$, Br, I, BPh_4, ClO_4	$CoX_2 \cdot 6H_2O$ + L; acetone, r.t.	Blue (Cl, Br, I); high spin, μ 4.4–4.5	1
$[Co(X)_2(dppe)]$	$CoX_2 \cdot 6H_2O$ + L; Pr^iOH	Blue (Cl, Br, I); green (I)	1
$[Co(X)_2(dppp)]$	CoX_2 + L; EtOH	Green (Cl, Br); μ 1.9–2.0	3
$[CoX(dmpp)_2](BPh_4)$	$CoX_2 \cdot 6H_2O$ + L; EtOH	Blue (Cl); green (Br); purple μ 4.3–4.4	4
$[Co(X)_2(dppm)]$	$CoX(ClO_4)$ + L; EtOH, CH_2Cl, reflux	Brown (Cl); red (Br, I); μ 2.1–2.3	4
$[CoX(dppm)_2]ClO_4$	Not detailed	X = Cl, Br, I	5
$[CoX(dppv)_2](BPh_4)$	Ref. 1	X = Cl, Br, I	8
$[CoX(dppv)_2](CoCl_3)$	CoY_2 + L (excess); hot EtOH	Planar (ESR) with $^2A_1$ ground state	6, 1
$[Co(dppe)_2]Y_2$			
($Y = ClO_4^-$, BPh_4^-, CoI_4^{2-})	[CoBr(dppe)]Br + L; Dowex 1×4 (CN^-)	Red-pink; μ 2.4; air sensitive; one monodentate dppe	7
$[Co(CN)_2(dppe)_2]$	$CoY_2 \cdot 6H_2O$ + L; acetone, N_2	Yellow	8
$[Co(dppv)_2]Y_2$	$CoBr_2 \cdot 6H_2O$ + *trans* L; EtOH, CH_2Cl_2	Green; $\mu = 4.4$; tet., polymeric	9
($Y = ClO_4^-$, BF_4^-)	$[Co(dppv)_2](ClO_4)_2$ + 2NaCN; MeOH	Red; $\mu = 2$	13
$[Co(Br)_2(t\text{-}dppv)]$	$[Co(CN)(dppe)_2]$ + $NaClO_4$ + O_2; EtOH, r.t.	Red-brown; $\mu = 2.20$	13
$[Co(CN)_2(dppv)_2]$			
$[Co(CN)(dppe)_2]ClO_4$			
Cobalt(III)			
trans-$[CoCl_2(dppv)_2]ClO_4$	$[CoCl(dppv)_2](CoCl_3)$ + Cl_2; CH_2Cl_2, r.t. (dark)	Green; *trans* from electronic spectrum	8
trans-$[CoBr_2(dppv)_2]ClO_4$	$[Co(CO_3)(dppv)_2]ClO_4$ + HBr, MeOH, reflux	Orange (yellow-green, −176 °C); red, 160 °C	8
$[Co(CO_3)(dppv)_2]ClO_4$	$[Co(Cl)_2(dppv)_2]ClO_4$ + Ag_2CO_3, MeOH, r.t.	Red-orange; *cis* chelate	8
$[Co(O_2)(dppv)_2]Y$	$[Co(dppv)_2]BF_4$ + O_2, CH_2Cl_2	Green-brown; diamagnetic trig. bipyramidal (structure Table 38); ε_{463} 1170; ε_{355} 1200; ε_{318} 25 500; ν_{O_2} 909	15, 7
($Y = ClO_4^-$, BF_4^-, BPh_4^-, PF_6^-)	$[Co(dppv)_2](BF_4)_2$ + O_2; MeOH, reflux		8
	$Co(BF_4)_2 \cdot 6H_2O$ + L + O_2; acetone		15, 7

Table 37 (*continued*)

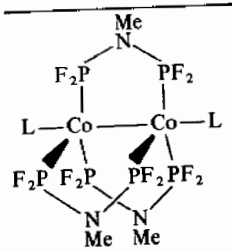
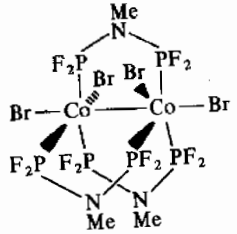
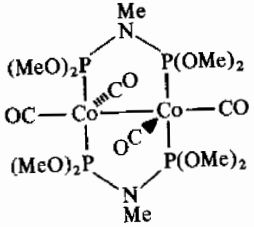
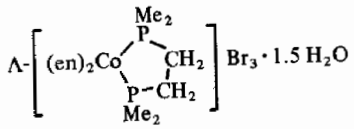
Complex	*Preparation*	*Properties*[a]	*Ref.*
$[Co(H)(CN)(dppv)_2]ClO_4$	$[Co(CN)(dppv)_2] + HClO_4$, EtOH	ν_{CN} 2110; ν_{COH} 1950	17
trans-$[Co(CN)_2(dppv)_2]ClO_4$	$[Co(dppv)_2]ClO_4$ + HCN (1 equiv.) $[Co(dppv)_2]ClO_4$ + HCN (excess)	Yellow; diamagnetic; ν_{CN} 2100	17
trans-$[Co(CN)_2(dppe)_2]ClO_4$	$[Co(dppv)_2(CN)_2] + 0.5O_2$	Yellow; diamagnetic; ν_{CN} 2113	16
trans-$[Co(CN)(dppe)_2(CN)]MCl_3$ (M = Co, Mn, Fe, Ni, Zn)	$[Co(dppe)_2(CN)_2] + O_2$, MeOH, r.t. $[Co(CN)_2(dppe)_2]ClO_4 + MX_2 + LiX$, hot MeOH	Green-yellow; isomorphous; tet. Co—CN—MCl_3 unit	16
trans-$[Co(X)_2(dmpp)_2]ClO_4$ ($X = Cl^-, Br^-, I^-$)	$CoX_2 + L + HX$ + air; EtOH, r.t. 6 h	Green (X = Cl, Br); violet (X = I)	3
trans-$[Co(Cl)_2(dmpe)_2]ClO_4$	$CoCl_2 \cdot 6H_2O + L$, MeOH, N_2; Cl_2 oxidation	Pale green; soluble in MeOH, EtOH; aquates in H_2O	8
$[Co(dmpe)_3](ClO_4)_3$	*trans*-$[Co(Cl)_2(dmpe)_2]ClO_4$ + dmpe, MeOH, N_2, 10 h, r.t.	Pale yellow; soluble in Me_2SO, insoluble in H_2O; decomposes in air. Reacts Br^- in MeOH to give $[CoBr_2(dmpe)_2]Br$; ε_{385} 933	8
$[Co(acac)_2(dppe)]PF_6$	$[Co(acac)_3] + L$, MeOH, Sephadex C25	Red; ^1H and ^{13}C NMR, visible–UV	19
cis-$[Co(CN)_2(acac)(dppe)]$	$K[Co(CN)_2(acac)_2] + L$, MeOH, 55 °C, 4 h	Orange; ^1H and ^{13}C NMR, visible–UV	19, 21
$K[Co(CN)_4(dppe)]$	$K_3[Co(CN)_5I] + L$, dioxane–H_2O, 75 °C, 7 h	Yellow; ^1H and ^{13}C NMR, visible–UV	19
fac-$[Co(dppe)_3]Br_3 \cdot 3H_2O$	*cis*-$[CoCl_2(en)_2]Cl + L$; DMF, r.t., chrom.	Yellow; optical isomers separated with $Na_2(Sbtart)_2$	26
$[Co(2,3,2\text{-tet})(admpe)]Br_3$	*trans*-$[Co(Cl)_2(2,3,2\text{-tet})]ClO_4 + L$, MeOH–$Me_2SO$, r.t., N_2	Red-orange; crystal *cis* β structure (Table 40)	20
trans-$[Co(CN)_2(acac)(admpe)]$	$K[Co(CN)_2(acac)_2] + L$, MeOH, 50 °C, chrom.	Orange; ^1H and ^{13}C NMR	21
trans-$[Co(Cl)_2(admpe)_2]Cl$	$CoCl_2 \cdot 6H_2O + L$, MeOH, r.t., chrom.	Blue-green	22
trans-$[Co(Cl)_2\{(R)abppe\}_2]ClO_4$		Green (crystal structure Table 40)	23
trans-$[Co(Cl)_2(adppe)_2]ClO_4$		Green (crystal structure Table 40)	23
$[Co(O—O)(adppe)_2]X$ (O—O = acac$^-$, CO_3^{2-}, $C_2O_4^{2-}$, $CH_2(CO_2)_2$)	*trans*-$[CoCl_2(adppe)_2]ClO_4 + (NH_4)_2(O—O)$; chrom.	Orange-red, *trans* (P,P) and *trans* (P,N) isomers, enantiomers resolved	23
$[Co(O—O)(en)(dppe)]X$	*trans*-$[CoCl_2(en)(dppe)]ClO_4$	^{13}C NMR, visible–UV	23
$[Co(en)_n(admpe)_{3-n}]Br_3$ ($n = 0, 1, 2$)	*cis*-$[CoCl_2(en)_2]Cl + L$, DMF, r.t., chrom.	Yellow; optical isomers separated	24
$[Co(en)_n(adppe)_{3-n}]Br_3$			24
$[Co(acac)_2(N—P)](PF_6)$, (BPh_4) (N—P = admpe = $NH_2CH_2CH_2P(CH_3)_2$; ddppe = $NH_2CH_2CH_2P(Ph)_2$; (*S*)adppp = $NH_2CH(CH_3)CH_2P(Ph)_2$; amppe = $NH_2CH_2CH_2P(Me)(Ph)$; (*R*)abppe = $NH_2CH_2CH_2P(Bu)(Ph)$	$Co(acac)_3$ + N—P + C; MeOH, r.t., chrom. Chiral N—P eluted with $Na_2(SbOtart)$	Optical isomers separated; ^1H and ^{13}C NMR, CD, visible UV	25

[a] IR data in cm^{-1}; μ values in BM.

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Table 38 Structures of Some Bidentate Phosphine Complexes

Complex	*Structural data*[a]	*Comments*	*Ref.*
	L = CO; $P_{2_1/n}$; CoCo 271.6	Dark purple; dist. trig. bipyr.; small bite angle of chelate	1
	L = PF_2NHMe; CoCo 276.9	Dark purple; as above	1
	L = PF_2NMe_2; CoCo 274.0	Dark violet; as above	2
	*C*2/*c* CoCo 271.7	As above	3
	$P2_1/c$; CoCC 269.8; CCoC 115.7, 96.6	Non-equivalent Co geometries; trig. bipyr., sq. pyr.	4
[CoCl(dppe)$_2$](SnCl$_3$)	CoCl 240; CoP 225–229; ClCoP 90–94°	Sq. pyr. (red)	10
[CoCl(dppe)$_2$](SnCl$_3$)·PhCl	CoCl 225; CoP 225–227; ClCoP 92°, 126–128°	Trig. bipyr. (green)	10
	*C*2; CoP 225–226, *trans* influence of P; CoN (*trans*) 203.2°; CoN (*cis*) 198.7; CoPC 108–109°; CoNC 109–110°; NCoN 84, 85°	$(+)_{589}$-Λ-configuration	5

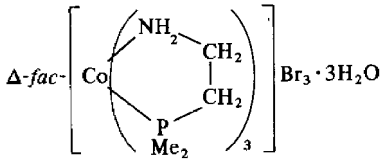
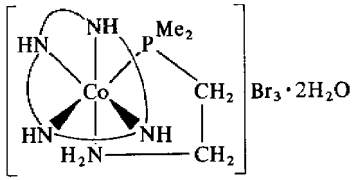
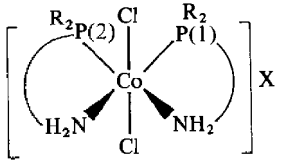
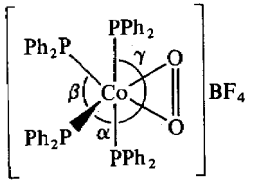
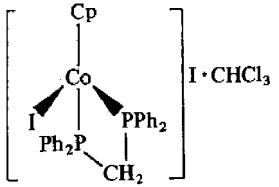
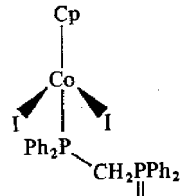
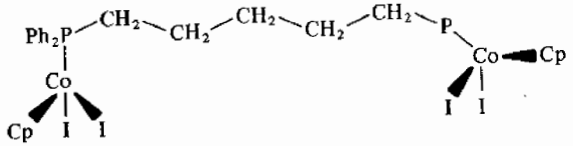
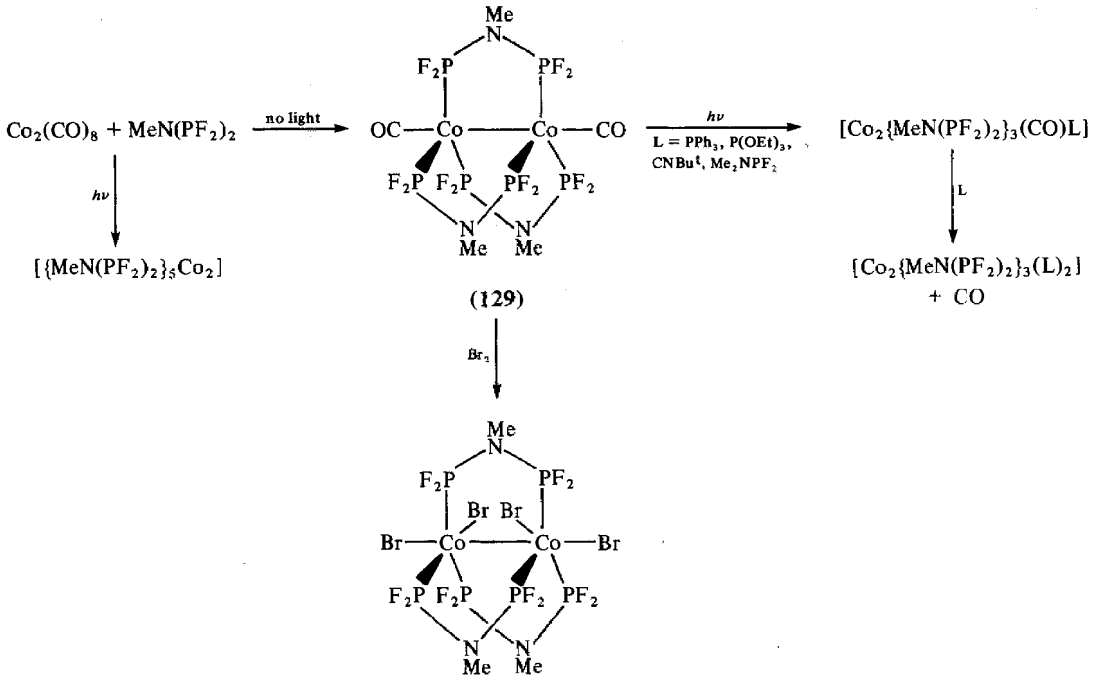
	$P2_12_12_1$; CoN 202–204; CoP 223–224; PCoN 83–86°	$(+)_{589}$-Δ-configuration	6
	$P2_1/a$; CoP 224.3; CoN (*trans*) 202.9; CoN (*cis*) 196–200	*Cis* β configuration of 2,3,2-tet; *trans* influence of P	7
 $R_2 = Ph_2$; $X = \frac{1}{2}CoCl_4$ $R_2 = (S)Bu, Ph$; $X = ClO_4$	*C*2/*C* (R = Ph) CoN 202–203; P(1)CoP(2) 103.1°; CoCl 224; CoP 225.4; CoN 203; NCoN 85.2°; NCoP 86.2° $P2_12_12$ (R = Bu, Ph); CoN 204–205; P(1)CoP(2) 99.4; CoCl 224; NCoN 87.8°; NCoP 85.9°	*Trans* (Cl,Cl) *cis* (P,P); (*S*) configuration on asymmetric P in (Bu, Ph) complexes	8
	$P2_1/C$; PCoP(α) 84°; PCoP(β) 102; PCoP(γ) 176°; OO 142; CoO 187, 190	Dist. trig. bipyr.; 'side-on' chelated O_2^{2-} (non-reversible coordination)	9
	I_4^-; PCoP 75.1°; ICoP 89–91°; ICoCp 122.3°; CoI 255.6; CoP 220–221.6; CoCp 169	Dist. tet.	11
	$P2_1/n$; ICoP 89°, 96.7°; ICoI 94.5°; ICoCp 120–122°; CoI 257.2–259.8; CoP 22.9; CoCp 170.4	Dist. tet.	11

Table 38 (*continued*)

Complex	*Structural data*[a]	*Comments*	*Ref.*
	$P2_1/C$; ICoP 92.1°, 93.3°; ICoI 94–95°; CpCoI 120–122°; CoI 258–260; CoP 223.1, 224; CoCp 170	Dist. tet. dimer	11

[a] Bond lengths in pm.

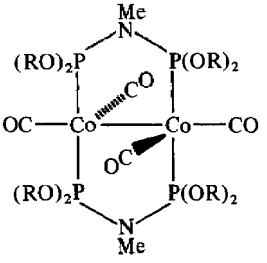
1. M. G. Newton, R. B. King, M. Chang, N. S. Pantaleo and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 1977, 531.
2. M. Chang, M. G. Newton, R. B. King and T. J. Lotz, *Inorg. Chim. Acta*, 1978, **28**, L153.
3. M. G. Newton, N. S. Pantaleo, R. B. King and T. J. Lotz, *J. Chem. Soc., Chem., Commun.*, 1978, 514.
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5. S. Ohba, U. Saito, T. Ohishi, K. Kashiwabara and J. Fujita, *Acta. Crystallogr., Sect. C*, 1983, **39**, 49.
6. I. Kinoshita, K. Kashiwabara, J. Fujita, K. Matsumoto and S. Ooi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2683; *Chem. Lett.*, 1980, 95.
7. T. Ohiski, K. Kashwabara, H. Ito and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1551.
8. I. Kinoshita, Y. Yokotu, K. Matsumoto, S. Ooi, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1067.
9. N. W. Terry, E. L. Amma and L. Vaska, *J. Am. Chem. Soc.*, 1972, **94**, 653.
10. J. K. Stalick, P. W. R. Corfield and D. W. Meek, *J. Am. Chem. Soc.*, 1972, **94**, 6194.
11. Q.-B. Bao, S. J. Landon, A. L. Rheingold, T. M. Haller and T. B. Brill, *Inorg. Chem.*, 1985, **24**, 900.



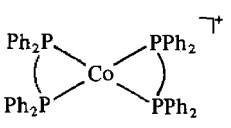
Scheme 48

(ii) Cobalt(I)

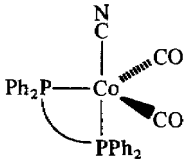
The dark $[Co(P—P)_2]ClO_4$ complexes (Table 37) (P—P = dppe, dppv) are diamagnetic and this, with their electronic spectra, suggests the uncommon planar structure (**131**) (planar structures are known for the analogous Rh and Ir complexes).[480] Being coordinatively unsaturated they readily add basic ligands and undergo oxidative addition (Scheme 49). Thus $[Co(dppv)_2](ClO_4)$ rapidly adds O_2 and H_2 (Section 47.5.2.5.ii; equation 106), NO, SO_2, and HCN to form octahedral Co^{III} systems.



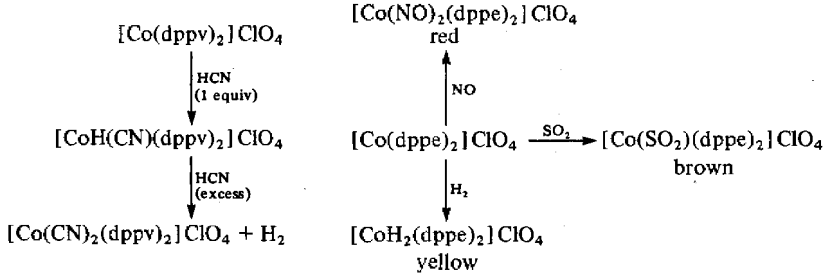
(130)



(131)



(132)



Scheme 49

Low-spin five-coordinate $[CoX(P—P)_2]$ ($X = Br^-$, CN^-; Table 37) probably have a square-pyramidal (C_{3v}) structure. For $X = Br^-$ the complex appears to be extensively dissociated into (**131**) in solution. These complexes readily undergo substitution and oxidative addition (equations 103 and 104).[481,482] The preparation of five-coordinate $[CoR(P—P)_2]$ species (R = alkyl, aryl) has not been reported, but $[Co(PMe_3)(dmpm)_2]Cl$ has been made and its disproportionation studied (equation 105).[483]

$$[CoBr(dppe)_2] + L \longrightarrow [Co(CO)(dppe)_2]Br \quad (103)$$

L = CO, PhCOCl; yellow

$$[CoH(CN)(dppv)_2]ClO_4 \xleftarrow{H_2} [Co(CN)(dppv)_2] \xrightarrow{CO} [Co(CO)_2(dppv)_2]ClO_4 \quad (104)$$

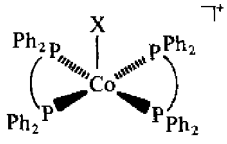
(**132**)

$$[Co(PMe_3)(dmpm)_2]Cl \xrightarrow{THF} [CoCl_2(PMe_3)(dmpm)] + [Co(PMe_3)(dmpm)_2]_2PMe_2 \quad (105)$$

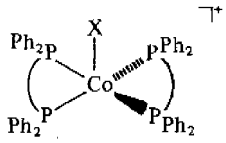
orange

(*iii*) *Cobalt(II)*

High-spin ($\mu = 4.4$ BM) $[Co(X)_2(P—P)]$ and low-spin five-coordinate ($\mu = 1.9$–2.3 BM) $[CoX(P—P)_2]^+$ are easily prepared (Table 37). The detailed structure of the former is uncertain but it appears to be pseudo tetrahedral, and does not contain CoX_4^{2-}.[484] $[CoX(P—P)_2]^+$ species are more robust and their magnetic moment indicates some orbital mixing. ESR studies show that $[CoX(P—P)_2]^+$ species with P—P = dppm, dppv have a different electronic ground state than those with P—P = dppe.[485] $[CoX(dppe)_2]^+$ adopts both square-pyramidal (**133**) and trigonal-bipyramidal (**134**) structures in the solid state, and an equilibrium between them (mostly **134**) is quickly established in solution; major spectral differences occur only at *ca.* 660 nm.[486] $[Co(NCS)_2(diphos)]$ ($\mu = 2.5$ BM) is reported to contain terminal isothiocyanate ligands and may be planar,[487] and $[Co(Cl)_2(diphos)_2]$ ($\mu = 1.97$ BM) is octahedral.[488] With $[Co(CN)_2(dppe)_2]$ (Table 37) it is proposed that both cyanides are coordinated with one dppe remaining monodentate, while with dppp and dppb dimeric $[Co(P—P)_{1.5}(CN)_2]_2$ units with bridging phosphine chelates have been suggested.[45] Considerable electronic and structural variation apparently exists in the paramagnetic ions with chelate ring flexibility probably making a significant contribution to the ground-state geometry.



(**133**) red



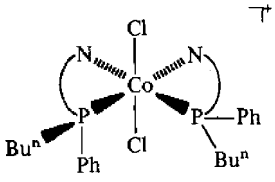
(**134**) green

$[Co(P—P)_2]^{2+}$ (P—P = dppe, dppv, diphos) has been prepared (Table 37) and although no structure has been reported, a planar geometry with a $^2A_1$ electronic ground state (unpaired electron in d_{z^2} orbital) is inferred from ESR studies.[489,490] Substitution into $[CoCl(dppe)_2]^+$ by the chelating ligands L = bipy, phen, 2,9-Me_2phen follows the rate law $k = k_1k_3[L]/(k_2 + k_3[L])$, which implies a dissociative process with a limiting rate for ring opening of $k_1 = 62.5\,s^{-1}$, 25 °C.[491] $[Co(dppv)_2](ClO_4)$ readily adds two equivalents of CN^- to form $[Co(CN)_2(dppv)_2]$, and $[Co(CN)_2(dppe)_2]$ is oxidized by half an equivalent of O_2 to diamagnetic $[Co(CN)_2(dppe)]ClO_4$. The latter complex induces unusual oxidation processes (Section 47.5.2.5.iv; Scheme 50).

(*iv*) *Cobalt(III)*

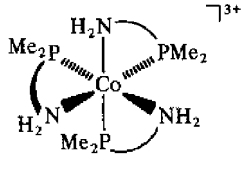
A large number of bidentate chelates of the type *trans*-$[CoX_2(P—P,N—P)_2]^+$ have been prepared by halogenation or air oxidation of $CoCl_2 \cdot 6H_2O$ in the presence of the phosphine, or by halogenation of a five-coordinate Co^{II} complex, *e.g.* $[CoCl(dppv)_2]^+$ (Table 37). *Cis* coordination must occur in $[Co(CO_3)(P—P)_2]^+$, but addition of acid results in isolation of only the *trans* diaqua product. The synthesis of *trans*-$[Co(Cl)_2(dppe)_2]^+$ by routine methods has not been successful but many *trans*-$[Co(Cl)_2(N—P)_2]^+$ systems have been prepared and the importance of steric crowding about the P atom is clearly shown by several crystal structures such as (**135**; Table 38).[492] The PCoP angle in (**135**) is extended (99°, 103°) and the NCoN angle reduced (85°, 88°) even allowing for the longer CoP

bond (225 pm) compared to CoN (202 pm). It is interesting that in structures (**135**), (**136**) and (**137**) (Table 38) the donor P atoms are mutually *cis*. Apparently the structural *trans* effect of P (Δ_r = 5–7 pm) results in a *trans* labilizing effect with the stronger bonding N donor being preferred in the *trans* position. This influence must outweigh the increased steric requirements that result. Steric problems are minimized using dmpe, and the tris complex $[Co(dmpe)_3]Br_3$ (**137**) has been prepared;[493] it is not very stable, is insoluble in water and has not been produced in optically active forms. It appears to be the only $[Co(P—P)_3]^{3+}$ chelate known.



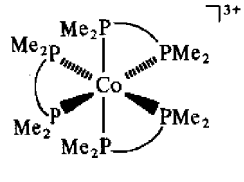
(135)

trans-$[CoCl_2\{(S)\text{-abppe}\}_2]^+$



(136)

Δ-*fac*-$[Co(adme)_3]^{3+}$

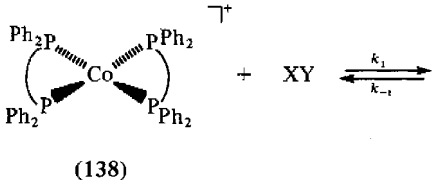


(137)

Δ, Λ-$[Co(dmpe)_3]^{3+}$

A variety of mixed (P—P), (N—P) chelates containing acac$^-$, CO_3^{2-}, $C_2O_4^{2-}$ and 2,3,2-tet have been prepared (Table 37); some have been resolved into optical enantiomers by conventional or chromatographic means (Table 37), and ^1H, ^{31}P, CD and electronic spectra have been reported. Metathesis of *trans*-$[Co(Cl)_2(P—P)_2](ClO_4)$ with NaX in methanol leads to other *trans*-$[Co(X)_2(P—P)_2]^+$ complexes (X = N_3^-, NCO^-, NCS^-, CN^-); however NO_2^- addition to *trans*-$[Co(Cl)_2(dppv)_2](ClO_4)$ results in the isolation of the unsaturated 14-electron complex $[Co(NO)_2(dppv)]$ and oxidized ligand.[423]

Complexes containing $R_2P(CH_2)_nPR_2$ (R = Ph, aryl) are unstable and have not been isolated, but diamagnetic $[Co(Cl)_2(diphos)_2](ClO_4)$ has (ε_{560}, 78).[488] Yellow *trans*-$[Co(CN)_2(P—P)_2](ClO_4)$ systems are easily formed *via* oxidation of $[Co(CN)_2(P—P)_2]$ or by addition of excess HCN to $[Co(P—P)_2](ClO_4)$. Oxidative addition of O_2, H_2 and HCN (1 equiv) to $[Co(dppv)_2](BF_4)$ (**138**) results in diamagnetic $[Co(Y_2)(dppv)_2](BF_4)$ (**139**; equation 106),[481,494] and for $Y_2 = O_2$ the side-on bonding mode of the peroxide moiety has been verified (Table 38).[495] Oxidative addition appears to occur only with planar diamagnetic d^8 systems; $[CoCl(PPh_3)_3]$, $[Co(dppe)_2]^+$ (both tetrahedral) and five-coordinate $[Co(CN)(dppv)_2]$ either do not react or slowly decompose to give the oxidized ligand (with O_2).



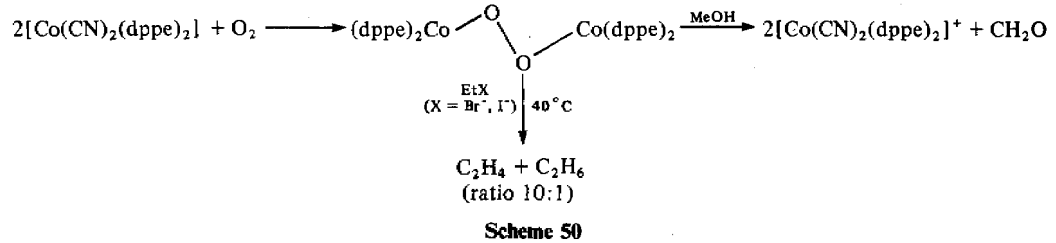
(106)

(138)

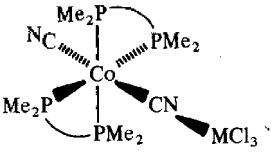
(139)

XY	k_1 ($mol^{-1}\ dm^3\ s^{-1}$)	*K*
O_2	1.7×10^4	$>10^9$
H_2	1.2×10^5	$>10^{10}$

Oxygenation of $[Co(CN)_2(dppe)_2]$ in MeOH or CH_2Cl_2 as solvent, or oxygenation in the presence of EtI, produces CH_2O, CO_2 and C_2H_4 respectively (Scheme 50). An unusually reactive peroxo Co^{III} dimer has been suggested as the important intermediate.[46] Also the cyano ligand has been shown to act as a bridging ligand to other divalent metals,[47] *e.g.* (**140**).



Scheme 50

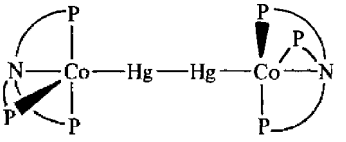


(140) M^{II} = Co, Mn, Fe, Ni, Zn

47.5.2.6 Tri- and multi-dentate phosphines

(i) Cobalt(−1) and cobalt(0)

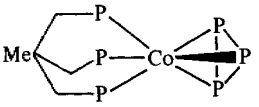
Reduction of $[CoCl(L)](BPh_4)$ (L = N(dppe)$_3$, P(dppe)$_3$) with Na/Hg in THF results in red-brown dimeric $[Co(L)]_2(Hg_2)$ species (**141**) in which Hg_2^{2+} is linearly coordinated between two Co^{-1} centres.[500] These unstable diamagnetic trigonal-bipyramidal complexes (structure, Table 40) react with CO and CO_2 at ambient temperatures in an apparent redox process (equation 107).[500]



(141)

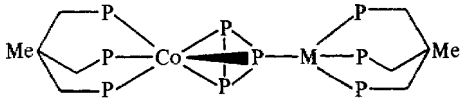
$$[Co(CO)\{N(dppe)_3\}]^+ + Hg \xleftarrow{CO} [Co\{N(dppe)_3\}]_2\text{-}\mu(Hg)_2 \xrightarrow{CO_2} [Co(CO)\{N(dppe)_3\}]^+ + Hg + CO_3^{2-} \quad (107)$$

Sacconi and coworkers[501,502] have prepared some interesting *cyclo*-P_3 ligand systems of the type $[Co(P_3)L]$ containing formally d^9 Co^0 by reacting $Co(BF_4)_2 \cdot 6H_2O$ with $MeC(CH_2PPh_2)_3$ or $N(CH_2CH_2PPh_2)_3$ in alcoholic THF (Table 39). The diamagnetic orange-yellow $[Co(P_3)\{MeC(dppm)_3\}]$ and red $[Co(P_3)\{N(dppe)_3\}]$ are stable as solids with the former being soluble and stable in THF, CH_2Cl_2 and nitroethane. Their structures (Table 40) show a staggered arrangement of the two tridentate P_3 chelates but with the Co atom lying closer to the phosphine-P_3 plane (**142**). The similar $[Co(P_2S)\{MeC(dppm)_3\}](BF_4)$ complex has recently been prepared from P_4S_3 and its structure (Table 40) closely resembles the others.[503]

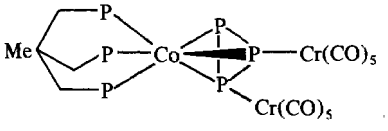


(142)

$[Co(P_3)\{MeC(dppm)_3\}]$ retains considerable basic character and is capable of donating electron pairs to other $[M\{MeC(dppm)_3\}]^{2+}$ units (**143**), $[M\{MeC(depm)_3\}]^{2+}$, or to one or more $Cr(CO)_5$ units, *e.g.* (**144**).[356,504,505] In all these complexes the *cyclo*-P_3 unit can be viewed as being linked to Co^0 *via* three localized electron-pair σ bonds; an MO framework involving all the sandwiched atoms is however likely.



(143) M = Ni, Co



(144)

Table 39 Preparations: Tri- and Multi-dentate Phosphine Complexes

Complex[a]	*Preparation*	*Properties*[b]	*Ref.*
Cobalt(−I)			
$[Co\{N(dppe)_3\}]_2(Hg_2)$	$[Co(Cl)L](BPh_4)$ + Na/Hg; THF 50 °C	Red; diamagnetic; decomposes in air (structure Table 40)	1
$[Co\{P(dppe)_3\}]_2(Hg_2)$		Orange-brown; air-stable, diamagnetic; soluble in organic solvents	1
Cobalt(0)			
$[Co(P_3)\{MeC(dppm)_3\}]$	$Co(BF_4)_2\cdot 6H_2O$ + L + P_4; THF, BuOH, 50 °C, N_2	Yellow-orange; air-stable, diamagnetic, soluble in organic solvents	2
$[Co(P_3)\{N(dppe)_3\}]\cdot THF$	$Co(BF_4)_2\cdot 6H_2O$ + L + P_4; THF, EtOH, N_2, 50 °C	Red; diamagnetic, insoluble in organic solvents	3
$[Co(CS_2)\{MeC(dppm)_3\}]$	$[Co_2(CO)_8]$ + L + CS_2; THF, EtOH	Red; air stable; unstable in soln.; $\mu = 1.91$	6
Cobalt(I)			
$[Co(P_2S)\{MeC(dppm)_3\}]BF_4$	$Co(BF_4)\cdot 6H_2O$ + L + P_4S_3; benzene, EtOH; reflux, N_2	Orange; air-stable; 1:1 elect. in CH_2Cl_2	4
$[\{Co[MeC(dppm)_3]\}_2(\mu\text{-}P_3)](BF_4)_2$	$Co(BF_4)_2\cdot 6H_2O$ + L + P_4; THF, EtOH, N_2, r.t.	$\mu = 2.0$–2.2; stable as solid, soln.	5
$[Co\{PhP(dppe)_2\}L_2]BF_4$ (L = CO, PR_3, $P(OMe)_3$)	$[CoH\{PhP(dppe)_2\}Co]$ + NH_4BF_4 + L; EtOH, heat	Red-yellow; diamagnetic; trig. bipyr.	26
$[Co\{PhP(dppp)_2\}L_2]BF_4$ (L = CO, PPh_2H, $P(OMe)_3$)	$[CoH\{PhP(dppp)_2\}CO]$ + NH_4BF_4 + L; EtOH, heat	Yellow-orange; diamagnetic; sq. pyr.	26
$[CoN(dppe)_3]BF_4$	$Co(BF_4)_2\cdot 6H_2O$ + L + $NaBH_4$; EtOH, acetone, N_2	Green; $\mu = 3.11$ (structure Table 40), trig. pyr. with vacant apical site	7
$[CoMeC(dppm)_3X]$ (X = Cl, Br, I)	CoX_2 + L + $NaBH_4$; CH_2Cl_2, EtOH, N_2	Red-orange; $\mu = 3.0$–3.1; air sensitive; tet.	8
$[Co\{P(C_6H_4PPh_2)_3\}X]$ (X = Cl, Br, I, NCS, H)	CoX_2 + L + $NaBH_4$; glycol, EtOH, N_2	Brown-violet; diamagnetic (structure Table 40, X = H); trig. bipy.	9
$[Co\{P(dppe)_3\}X]$	CoX_2 + L + $NaBH_4$; EtOH, CH_2Cl_2, N_2	Green (Cl, Br, I); red (NCS); orange (CN); air sensitive; diamagnetic (structure Table 40, X = H)	10
$[Co\{MeC(dppm)_3\}L(CO)BF_4]$ (L = CO, PPh_2H, $P(OMe)_3$, PEt_3)	$[CoH\{MeC(dppm)_3\}CO]$ + NH_4BF_4 + L; MeOH, heat	Orange; diamagnetic fluxional	26
$[Co\{N(dppe)_3\}X]$ (X = Cl, Br, I, CN, NCS, H)	CoX_2 + L + $NuBH_4$; DMF, N_2	Yellow (Cl), green (I); $\mu = 3{,}2$–3.3 (Cl, Br, I, NCS); diamagnetic (CN, H) (structure Table 40, X = H)	11
Cobalt(II)			
$[Co\{MeC(dppm)_3\}X]BPh_4$ (X = Cl, Br)	CoX_2 + L + $NaBPh_4$; Bu^nOH	Red-brown; dist. trig. bipyr. (spec.) dimeric with X bridges; $\mu = 1.70$ (Cl), 1.48 (Br)	12
$[Co\{MeC(dppm)_3\}OH]_2(BPh_4)_2$	$Co(BF_4)_2\cdot 6H_2O$ + L + $NaBPh_4$; Bu^nOH	Red-brown (structure Table 40); $\mu = 1.90$, antiferromagnetic dimeric	12

Table 39 (*continued*)

Complex[a]	*Preparation*	*Properties*[b]	*Ref.*
$[Co\{MeC(dppm)_3\}X]BPh_4$	$CoNO_3 + L + NaBPh_4$; Bu^nOH	Orange-brown; monomeric (structure Table 40); $\mu = 2.1$; bidentate X	12
$(X = O_2NO, O_2CCH_3$, acac)	$CoCl_2 + L$; EtOH	Orange-yellow; non-elect.; $\mu = 2.11$	13
$[Co\{MeP(dppe)_2\}Cl_2]$	$CoX_2 \cdot 6H_2O + L$; EtOH reflux, N_2	Orange-brown; variable dissociation in MeCN; $\mu = 2.01$; dist. sq. pyr. spec.	14
$[Co\{PhP(dppp)_2\}]X_2$	$CoCl_2 \cdot 6H_2O + L$; EtOH reflux	Orange; $\mu = 2.11$; soln. turns blue	15
$(X = Cl, Br, I)$	$CoCl_2 \cdot 6H_2O + L$; EtOH reflux	Brown; $\mu = 1.7$–2.1; dist. sq. pyr. (Table 40, X = Br)	18
$[Co\{PhP(dppe)_2\}Cl_2]$	$Co(BF_4)_2 \cdot 6H_2O + L + NaBPh_4$; EtOH, acetone		
$[Co\{P(dppe)_3\}X]PF_6$ or BF_4	$CoX_2 + L$; EtOH, CH_2Cl_2, $NaBPh_4$, N_2	Brown; $\mu = 1.95$–2.1; dist. sq. pyr.	18, 19
$(X = Cl, Br, OH, H_2O)$	$CoX_2 \cdot 6H_2O + L$; EtOH, reflux; NaY	Blue-black; red-brown (NO_3, NCS); $\mu = 1.9$–2.1 (structure Table 40, X = Cl, Y = BPh_4) brown; $\mu = 2.1$	20
$[Co(Pe)_4X]BPh_4$ or BF_4	$Co(BF_4)_2 \cdot 6H_2O + QP$; EtOH reflux		
$(X = Cl, Br, I, NCS)$	$CoX_2 + L + NaBPh_4$; EtOH, $Co(ClO_4)_2 \cdot 6H_2O + L$; EtOH, acetone	Magenta-brown (I); $\mu = 4.3$; orange-red (OH); brown (OH_2); $\mu = 4.25$–4.56	16, 17
$[Co\{P(C_6H_4PPh_2)_3\}X]Y$	$CoX_2 \cdot 6H_2O + L$; EtOH, acetone, $NaBPh_4$	$\mu = 4.1$–4.3; trig. bipyr. in solid and soln.	21
$(X = Cl, Br, I, NCS, OH, H_2O;$ $Y = ClO_4, BPh_4, BF_4)$	$MX_2 + L$; DMF, r.t.	Green; decomposes	23
$[CoX\{N(dppe)_3\}]Y$	$Co(OAc)_2 \cdot 4H_2O + L$; MeOH, reflux	Red-brown	24
$(X = Cl, Br, I, NCS, OH, H_2O)$	$CoX_2 + L$; Bu^nOH, hot	Blue-purple; $\mu = 3.8$–4.6; trig. bipyr. in solid; dissociates in soln.	25
$[CoX\{N[d(Cy)pe]_3\}]BPh_4$	$Co(NO_3)_2 \cdot 6H_2O + L$; benzene, EtOH	Yellow-green; $\mu = 4.28$	22
$(X = Cl, Br, I, NCS)$	$Co(ClO_4)_2 \cdot 6H_2O + L$; acetone	Red-brown; $\mu = 2.36$	22
$\{[CoN(dmpe)_3]_3\}(BF_4)_6$	Oxid. $[CoX\{P(C_6H_4PPh_2)_3\}]ClO_4 + X_2$; CCl_4, CH_2Cl_2	Red; diamagnetic; oct.	20
$[CoCl(3,3,3\text{-}NPPN)]BF_4$	Conc. soln. $[Co(NCS)_2(NNP)]$ in $CHCl_3$, CH_2Cl_2	Red-brown; diamagnetic	25
$[CoX_2\{Ph_2P(CH_2)_2N(R)(CH_2)_2NEt_2\}]$ $(R = H, Me; X = Cl, Br, I, NCS)$			
$[Co(NO_3)_2\{py(dppm)_2\}]$			
$[Co\{py(dppm)_2\}_2](ClO_4)_2$			
$[CoX_2\{P(C_6H_4PPh_2)_3\}]BPh_4$			
$(X = Cl, Br)$			
$[Co(NCS)_3(NNP)]$			
$(NNP = Ph_2P(CH_2)_2NH(CH_2)_2NEt_2)$			

[a] Ligand abbreviations: $PhP(dppe)_2 = PhP(CH_2CH_2PPh_2)_2$ $MeP(dppe)_2 = MeP(CH_2CH_2PPh_2)_2$; $P(dppe)_3 = P(CH_2CH_2PPh_2)_3$; $MeC(dppm)_3 = MeC(CH_2PPh_2)_3$; $(Pe)_4 = Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$; $P(C_6H_4PPh_2)_3 = P(C_6H_4PPh_2\text{-}o)_3$; $Ph_2P(C_6H_4PPh_2) = Ph_2P(C_6H_4PPh_2\text{-}o)$; $N[d(Cy)pe]_3 = N[CH_2CH_2P(cyclohexyl)_2]_3$; $P(py)_3 = P(2\text{-pyridyl})_3$.

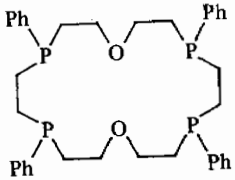
[b] μ values in BM.

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Table 40 Structures: Di- and Multi-dentate Phosphine Complexes

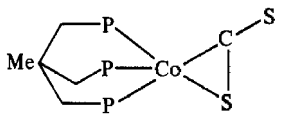
Complex	*Ligand*	*Structure*[a]	*Ref.*
Cobalt(−I)			
$[Co_2L_2Hg_2]$	$N(CH_2CH_2PPh_2)_3$	Trig. bipyr.; CoHg 243; HgHg 265; CoN 210; HgCoN 179.9°; dimeric with Hg_2^{2+} bridge	18
Cobalt(0)			
$[CoL(P_3)]$	$MeC(CH_2CH_2PPh_2)_3$	Dist. oct.; CoP 219; CoP_3 230	20
$[CoL(P_3)]$	$N(CH_2PPh_2)_3$	Dist. oct.; CoP 224–226; CoP_3 231–232	21
$[CoL(P_3)NiL](BPh_4)_2 \cdot$ acetone	$MeC(CH_2PPh_2)_3$	Dist. oct.; CoP 222–224; CoP_3 230	22
$[CoL(CS_2)]$	$MeC(CH_2PPh_2)_3$	Five-coordinate (π-CS_2); CoP 222–225; CoC 188; CoS 221; CSS 133.8°	23
$[CoL(P_3)[Fe\{MeC(depm)_3\}]]PF_6 \cdot CH_2Cl_2$	$MeC(CH_2PPh_2)_3$	Dist. oct.; CoP 220–222; CoP_3 227–230	24
Cobalt(I)			
[CoHL]	$P(o\text{-}C_6H_4PPh_2)_3$	Trig. bipyr., CoP(ax) 209; CoP 213; CoH 143	26
$[CoL]BF_4$	$N(CH_2CH_2PPh_2)_3$	Trig. pyr., CoP 225–227; CON 220.7; axial site vacant	1
$[CoL(P_2S)]BF_4$	$MeC(CH_2CH_2PPh_2)_3$	Dist. oct.; CoP 221; CoP_2S 227	17
Cobalt(II)			
$[CoL(CO)Br]BPh_4$	$MeC(CH_2CH_2PPh_2)_3$	Dist. sq. pyr.; CoBr 237; CoC 179; CoP 224–229	15
$[Co_3L_2Cl_6]$	$MeC(CH_2PPh_2)(CH_2CH_2PPh_2)$	Dist. tet. (trimer); CoCl 220, 223; CoP 235–239	25
$[Co_2L_2(OH)_2](BPh_4)_2 \cdot$ acetone	$MeC(CH_2PPh_2)_3$	Trig. bipyr., dimeric (OH bridges); CoP 224–229; CoX 191–199, CoCO 306	2
$[CoL(OAc)](BPh_4) \cdot$ acetone	$MeC(CH_2PPh_2)_3$	Sq. pyr.; CoP 221–228; CoX 200, 203	2
$[CoLBr]PF_6$	$[Ph_2P(CH_2)_2N(Me)(CH_2)]_2$	Sq. pyr.; CoP 222; CoBr(ax) 254; CoN 203	3
$[CoLCl]PF_6$	$[Ph_2P(CH_2)_2]_2N(CH_2)_2OMe$	Dist. trig. bipyr.; CoN 242; CoO 203; CoP 241–244; CoCl 225 [NCS complex sq. pyr. (low spin)]	4
$[CoLCl]PF_6$	$N(CH_2CH_2PPh_2)_3$	Tet. trig. bipyr.; high spin; CoN 268 (partial bonding)	5
$[CoLBr]PF_6 \cdot EtOH$	$N(CH_2CH_2PPh_2)_3$	Dist. trig. bipyr.; CoP 226–240; CoBr 236; high spin	6
[CoLI]I	$N(CH_2CH_2PPh_2)_3$	Dist. sq. pyr. (ap. P); CoP 223–228; CoI 258; CoN 212; low spin	19
$[CoLI]BPh_4$	$N(CH_2CH_2PPh_2)_3$	Dist. trig. bipyr.; CoP 235–237; CoI 247; CoN 272; high spin	6
$[CoLBr]PF_6$	$P(CH_2CH_2PPh_2)_3$	Dist. sq. pyr. (ap. P); CoP 216–229; CoBr 238; low spin	7
$[CoLCl]BPh_4$	$P(o\text{-}C_6H_4PPh_2)_3$	Dist. sq. pyr.; CoP 206 (ap), 226–232; CoCl 231	8
$[CoL(OH)]BF_4 \cdot EtOH$	$P(CH_2CH_2PPh_2)_3$	Dist. sq. pyr. (ap. P); CoP 213–229; CoO 187	9
$[CoL(H_2O)](BF_4)_2 \cdot$ acetone	$P(CH_2CH_2PPh_2)_3$	Dist. sq. pyr. (ap. P); CoP 215-231; CoO 210	9
[CoLI]I	$(Ph_2PCH_2CH_2)_2NCH_2CH_2NEt_2$	Dist. trig. bipyr.; CoP 242, 245; CoI 265; CoN 244, 218	10

$[CoL(NCS)_2]$	$Ph_2PCH_2CH_2NHCH_2CH_2NEt_2$	Dist. trig. bipyr.; CoP 232; CoN 210, 207; CoN(CS) 204, 192	11
$[CoL(NCS)_2]$	$Ph_2PCH_2CH_2N(Me)CH_2CH_2NEt_2$	Dist. trig. bipyr.; CoP 240; CoN 236, 214; CoN(CS) 214	11
$[CoL(NCS)_2]$	$Ph_2P(CH_2)_2NH(CH_2)_2NEt_2$	Low temp. form: dist. sq. pyr. (120 K); high temp. form: dist. trig. bipyr. (298 K)	12
$[CoLCl]BF_4 \cdot 0.8H_2O$	$NH_2(CH_2)_3P(Ph)(CH_2)_3P(Ph)(CH_2)_3NH_2$ (*meso*)	Sq. pyr. (Cl axial); CoN 204–2-5; CoP 219–218; CoCl 243; PCoP 89.5°; PCoN 92.7°; NCoN 86.4°	13
$[Co_3L_4](BF_4)_6$	$N(CH_2CH_2PMe_2)_3$	Trig. bipyr.; CoN 205; CoP 225–226; NCoP 177.3°; trimeric	14
$[CoL](BPh_4)_2$		Three structures known	16

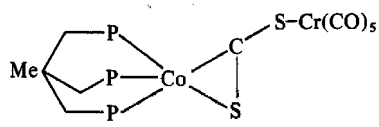
[a] Bond lengths in pm.

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Likewise an air-stable CS_2 adduct $[Co(CS_2)\{MeC(dppm)_3\}]$ can be prepared from $Co_2(CO)_8$ (Table 39). The Co atom is coordinated to the three P atoms and one π linkage to CS_2 (**145**).[505] This 17-electron system is capable of adding other electrophilic species such as $[Co\{MeC(dppm)_3\}]^{2+}$, $Cr(CO)_5$, $Mn(Cp)(CO)_2$, and structures on the former two are available, *e.g.* (**146**).[5]



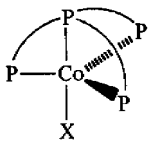
(145)



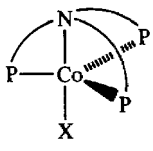
(146)

(ii) Cobalt(I)

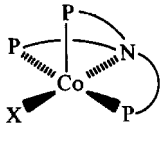
Several complexes with tripod ligands of the type $RC(P_3)$, $N(P_3)$ and $P(P_3)$ have been prepared (Table 39). With $RC(P_3)$ high-spin tetrahedral [Co(L)X] are formed; these are air sensitive and not very stable. With $P(P_3)$ the five-coordinate [Co(L)X] systems are trigonal bipyramidal (**147**) and low spin for all X (halides, NCS^-, CN^-, H^-, CO), but for $N(P_3)$ high-spin (μ = 3.2–3.3 BM) complexes occur with the more electronegative ligands ($X = Cl^-$, Br^-, I^-, NCS^-) and low-spin trigonal-bipyramidal structures for more nucleophilic X (CN^-, H^-, CO). Structures for high-spin $[Co\{N(P_3)\}X]$ are not available but it is likely that the symmetry is lifted from C_{3v} (**148**) towards C_{2v} (**149**). For the electronically identical d^8 Ni^{II} complexes (**148**) is found for all X in $[Ni\{N(P_3)\}X]^+$ but a cross-over to high-spin (**149**) occurs at about $[Ni(N_2P_2)X]^+$; for the lower-charged Co^I systems this cross-over apparently requires a higher ligand field. Sacconi has related the electronegativity and nucleophilic ability of ligands to spin-pairing energy and structure for d^7 and d^8 systems in an important publication.[506] Du Bois and Meek[522] have investigated the stereochemical properties of $[Co\{PhP(dppe)_2\}(CO)L]^+$, $[Co\{PhP(dppp)_2\}(CO)L]^+$ and $[Co\{MeC(dppm)_3\}(CO)L]^\bullet$ (L = CO, $P(OMe)_3$, PPh_2H, PPh_2Me, PEt_3, PPh_3) by ^{31}P NMR spectroscopy. $[Co\{PhP(dppe)_2\}(CO)L]^+$ has the rigid structure (**150**), whereas $[Co\{PhP(dppp)_2\}(CO)L]^+$ with the large chelate bite adopts the rigid structure (**151**) with L in the apical position (L = CO adopts structure **150**). $[Co\{MeC(dppm)_3\}(CO)L]^+$ on the other hand is fluxional at room temperature with rapid intramolecular switching of L and CO in the trigonal-bipyramidal structure (**150**); only $[Co\{MeC(dppm)_3\}(CO)\{P(OMe)_3\}]^+$ gives a limiting spectrum at $-100\,^\circ C$. Monodentate phosphine exchange with the free ligand is fast with $[Co\{PhP(dppp)_2\}(CO)(PPh_2H)]^+$, $[Co\{PhP(dppe)_2\}(CO)(PPh_3)]^+$ and $[Co\{MeC(dppm)_3\}(CO)(L)]^+$ ($L \neq P(OMe)_3$) *via* a dissociative process.



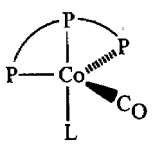
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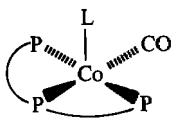
(148)



(149)



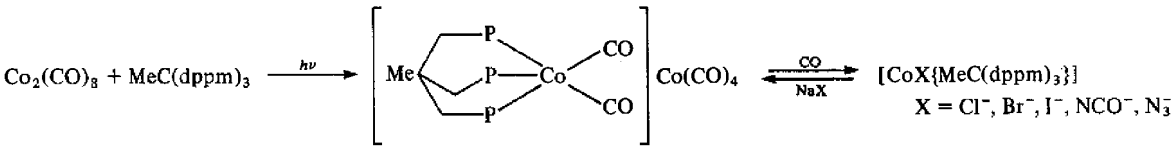
(150)



(151)

The above five-coordinate complexes can best be made *via* the hydride (equation 108), while treatment of $[Co\{MeC(dppm)_3\}(CO)_2][Co(CO)_4]$ with NaX leads to paramagnetic ($\mu \sim 3$ BM) tetrahedral $[Co(X)\{MeC(dppm)_3\}]$ (Scheme 51) whose reactions with CO, O_2 and phenanthroline have been reported.[507] Similar treatment of $[Co\{N(dppe)_3\}](BF_4)$, whose trigonal-bipyramidal structure has a vacant coordination site (see Table 40) with CO gives $[Co(CO)\{N(dppe)_3\}](BF_4)$.[508]

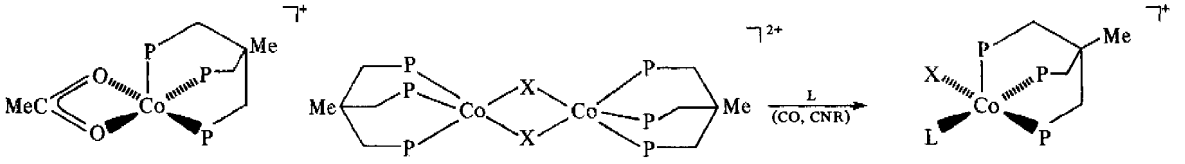
$$[CoH(CO)\{MeC(dppm)_3\}] + NH_4BF_4 + L \longrightarrow [CoL(CO)\{MeC(dppm)_3\}](BF_4) + H_2 + NH_3 \quad (108)$$



Scheme 51

(*iii*) *Cobalt(II)*

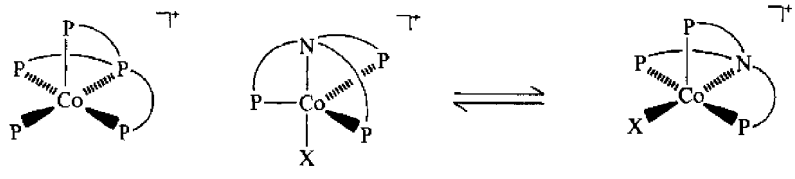
Branched P_3 donor ligands such as $MeC(dppm)_3$, $MeP(dppe)_2$, $PhP(dppe)_2$ and $PhP(dppp)_2$ form distorted square-pyramidal low-spin monomeric $[Co(X)_2(L)]$ ($X = Cl^-$, Br^-) or $[CoX(L)]^+$ ($X = NO_3^-$, AcO^-, $acac^-$) complexes, *e.g.* (**152**), or dimeric trigonal-bipyramidal systems $[CoX(L)]_2^{2+}$ (**153**) in which the low magnetic moment is believed to result from exchange coupling *via* the X bridges.[509] Table 39 gives some representative preparations. Monomeric $[Co(X)_2(L)]$ is sensitive towards O_2 and is inclined to dissociate to tetrahedral species in solution, whereas the dimeric systems are more stable.



(152) (153)

The stronger ligand field provided by P_4 donors results in low-spin ($\mu \approx 2.0$ BM) distorted trigonal-bipyramidal $[CoX(L)]^+$ systems for both linear and tripod donors with a decided square-pyramidal tendency, *e.g.* $[CoBr\{P(dppe)_3\}](PF_6)$ and $[CoCl\{P(dppC_6H_4)_3\}](BPh_4)$ (**154**). This switch from trigonal-bipyramidal (D_{3h}) to square-pyramidal (C_{4v}) geometry is expected for the d^7 configuration on increasing the ligand field. Venanzi and coworkers,[510] and Higginson, McAuliffe and Venanzi[511] have correlated such ligand-field effects with spectral and magnetic properties, and discuss the structural consequences in terms of static Jahn–Teller distortions. This distortion of C_{3v} microsymmetry is also expected on removing one electron from a diamagnetic d^8 Co^I complex and can be seen in the structures of $[CoH\{P(dppC_6H_4)_3\}]$ (trigonal bipyramidal) and $[CoCl\{P(dppC_6H_4)_3\}]BPh_4$ (square pyramidal).

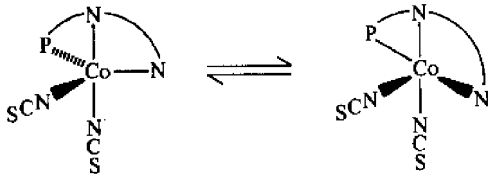
The intermediate-strength $N(dppe)_3$ ligand forms high-spin trigonal-bipyramidal $[CoX\{N(dppe)_3\}]^+$ (**155**) with $X = Cl^-$, Br^-, OH^-, H_2O, but low-spin distorted square-pyramidal structures (**156**) with the harder ligands NCS^-, I^-, and CN^-. An interesting situation exists with $[CoI\{N(dppe)_3\}]Y$, which is high spin with a distorted trigonal-bipyramidal structure for $Y = BPh_4^-$ in the solid state, but low spin with a distorted square-pyramidal structure for $Y = I^-$ (Table 40). This spin-state change is also seen in nitroethane solution for $Y = I^-$, where the visible spectrum shows a preference for the trigonal-bipyramidal structure at higher temperatures,[512] and for solid $[CoX\{N(dppe)_3\}](BPh_4)$ ($X = Cl^-$, Br^-), where increasing the pressure to 35 kbar gives spectra characteristic of low-spin square-pyramidal (**156**).[513] Di Vaira discusses these changes in MO terms,[514] but lattice forces must decide the issue at cross-over points which can be approached gradually from either side. With the more bulky $N\{CH_2CH_2P(Cy)_2\}_3$ ligand high-spin trigonal-bipyramidal $[CoX\{N(dCype)_3\}]Y$ species exist for $X = Cl^-$, Br^-, I^-, NCS^- in the solid state but when $Y = X = Cl^-$ partial ligand dissociation to form tetrahedral $[Co(Cl)_2P_2]$ occurs in nitroethane.[515] With more basic $N(CH_2CH_2PMe_2)_3$ trimeric $[\{CoN(dmpe)_3\}_3N(dmpe)_3](BF_4)_6$ has been isolated. This contains three trigonal-bipyramidal $CoN(dmpe)_3^{3+}$ units coordinated in axial positions to the P atoms of an additional $N(CH_2CH_2PMe_2)_3$ ligand.[516]



(154) (155) (156)

As further P donors are replaced by N the decreasing ligand field of the chelate favours high-spin trigonal-bipyramidal structures (Table 40). However steric consideration also play a part. Thus with the linear PNNP and NPPN ligands $Ph_2PCH_2CH_2N(Me)CH_2CH_2N(Me)CH_2CH_2PPh_2$ and *meso*-$H_2N(CH_2)_3P(Ph)(CH_2)_3P(Ph)(CH_2)_3NH_2$, low-spin square-pyramidal $[CoX(L)]Y$ ($Y = PF_6^-$, BF_4^-) are still favoured, but with the branched ligands $(Ph_2PCH_2CH_2)_2NCH_2CH_2NEt_2$ and $(Ph_2PCH_2CH_2)_2NCH_2CH_2OMe$ high-spin trigonal-bipyramidal $[CoX(L)]^+$ ions result (Table 40). The linear PNN tridentates $Ph_2PCH_2CH_2N(R)CH_2CH_2NEt_2$ (R = H, Me) form trigonal-bipyramidal $[Co(X)_2(L)]$ complexes in the solid state with some dissociation to tetrahedral species in

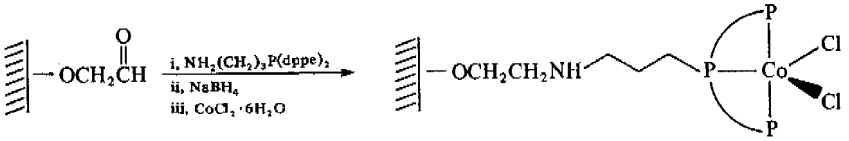
solution depending on R.[517] For X = NCS^-, R = H, an interesting temperature-dependent high–low spin equilibrium exists, which is accompanied by spectral (visible, IR) changes consistent with the structural forms (**157**) and (**158**) (equation 109). Structural studies at 120 K and at room temperature confirm this proposal.[518,519] Furthermore, the low-temperature form (**158**) appears to react with O_2 more rapidly than (**157**) with the ultimate formation of $[Co(NCS)_3L]$ containing Co^{III} and $[Co(NCS)_2(LO)]$ containing the oxidized ligand.[517] This agrees with the known reactivity of square-planar and square-pyramidal Co^{II} systems.



(109)

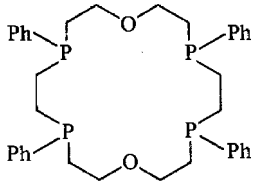
(**157**) μ = 4.32 BM, 418 K (**158**) μ = 2.16 BM, 79 K.

Uriarte and Meek have attached NPP and $NP(P_2)$ ligands to derivatized glass beads (equation 110),[520] and such hybrid polymer-supported catalysts offer advantages over homogeneous systems.



(110)

Co^{II} complexes of all five diastereoisomers of the phosphorus-containing crown ether (**159**) have been isolated[521] and crystal structures are available on three of them (*RS,RS,RS,RS,*(δ); *RSRS,SR,*(α); *RS,RS,SR,SR,*(β); Table 40). No enantiomeric systems have been separated. All five complexes are low spin (μ = 2.0–2.5 BM), consistent with planar coordination of the four P donors, but the ligand geometry determines how many oxygen atoms are coordinated. $[CoL_\beta](BPh_4)_2$ and $[CoL_\delta](BPh_4)_2$ are essentially octahedral with both O atoms coordinated in a *trans* arrangement, while $[CoL_\alpha](BPh_4)_2$ is square pyramidal with only one O bound. The $[CoL_\varepsilon]^{2+}$ ion containing the (*RS,SR,RS,SR*) diastereoisomer is also expected to be square pyramidal on spectral grounds, while L_γ = (*RS,SR,SR,RS*) gives $[CoCl(L_\gamma)]^+$ in which the fifth coordination site is occupied by Cl^-.[521] This is consistent with the chemistry of (N,P) and (all-N) macrocycles where the ligand geometry is largely responsible for determining the coordination stereochemistry.



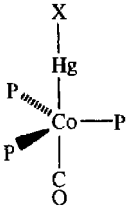
(**159**)

47.5.2.7 Phosphites, phosphonites and phosphinites

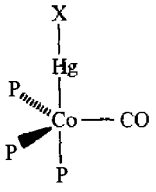
Hydride and dinitrogen complexes containing these ligands are considered in Sections 47.5.2.1 and 47.5.2.2. The electronegative OR substituent reduces σ-donor strength but increases electron delocalization from the metal, stabilizing low oxidation states. The cone angle for $P(OR)_3$ is smaller than for PR_3 (Table 30) but it may still be restrictive in the preparation of $[Co\{P(OR)_3\}_5]^+$ species with bulky R.[526] Weiss and Verkade have correlated ^{59}Co NMR shifts for a series of $[Co\{P(OR)_3\}_3\}_6]^{3+}$ complexes in terms of increasing ligand field with decreasing σ basicity or increasing phosphorus π acidity.[536]

(i) Cobalt(−1)

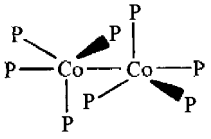
The $[Co\{P(OR)_3\}_4]^-$ ions have been produced by reaction of $[CoH\{P(OR)_3\}_4]$ with KH, by Na/Hg reduction of $CoCl_2$ in the presence of $P(OR)_3$, or electrochemically (Table 41). Rakowski and Muetterties have reported a very soluble $Na[Co\{P(OPr^i)_3\}_5]$ species which has two different ^1H resonances for $P(OPr^i)_3$ in the ratio of 4:1 and which does not rapidly exchange coordinated and free ligand.[406] A number of yellow-orange monomeric $[Co\{P(OPh)_3\}_4(HgX)]$ and $[Co\{P(OPh)_3\}_x(CO)_{4-x}(HgX)]$ species have been prepared from $[CoH\{P(OPh)_{3,4}\}(CO)_{1,0}]$ and HgX_2 with the latter having properties consistent with both axial (**160**) and equatorial (**161**) CO isomers.[535]



(160)

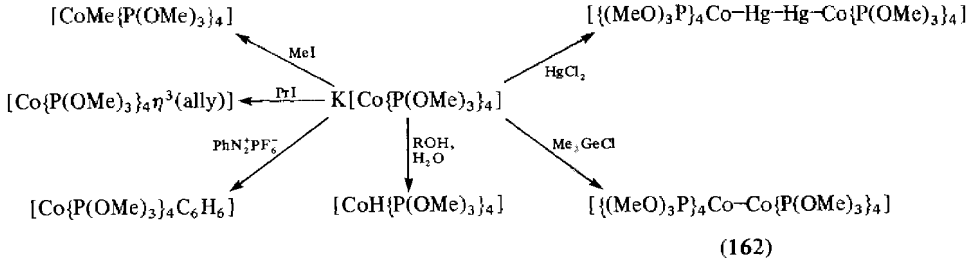


(161)



(162)

The chemistry of the d^{10}, presumably tetrahedral, $[Co\{P(OMe)_3\}_4]^-$ ion demonstrates some typical reactions with the products (Scheme 52) being in general more robust than their PR_3 analogues.[382]



(162)

Scheme 52

(ii) Cobalt(0)

Several paramagnetic $[Co\{P(OR)_3\}_4]$ complexes (R = Me, Et, Pr^i, Ph) have been prepared by the controlled reduction of $CoCl_2$ in the presence of excess $P(OR)_3$,[406] or by controlled electrochemical oxidation of $[Co\{P(OEt)_3\}_4]^-$ [527] or reduction of Co^{II} in the presence of excess $P(OR)_3$ (Table 41).[532,533] There appears to be some uncertainty in colour with Rakowski and Muetterties reporting orange-red $[Co\{P(OPr^i)_3\}_4]$ and Zecchin and coworkers white or pale yellow $[Co\{P(OR)_3\}_4]$ (R = Et, Pr^i, Ph). They are very sensitive to traces of moisture and O_2 and readily undergo ligand displacement in a good donor solvent such as acetonitrile (Scheme 53).[532] Dimeric $[Co_2\{P(OR)_3\}_8]$ (R = Me, Et, Pr^i) has been prepared by treating $K[Co\{P(OR)_3\}_4]$ with Me_3GeCl (Scheme 52),[382] or by reducing $CoCl_2$ with Na/Hg in the presence of $P(OPr^i)_3$ (Table 41),[534] and its structure (R = Me) shows a staggered arrangement of axially bridged trigonal bipyramids (**162**). This species is not formed by the radical dimerization of $[Co\{P(OR)_3\}_4]$ and the dimer does not dissociate to the monomer below 70 °C. Neither monomer nor dimer reacts with H_2 at ambient temperatures or abstracts H from solvent. Photolysis forms $[Co\{P(O)(OMe)_2\}\{P(OMe)_3\}_4]$, and photolysis in the presence of H_2 gives $[CoH\{P(OMe)_3\}_4]$.

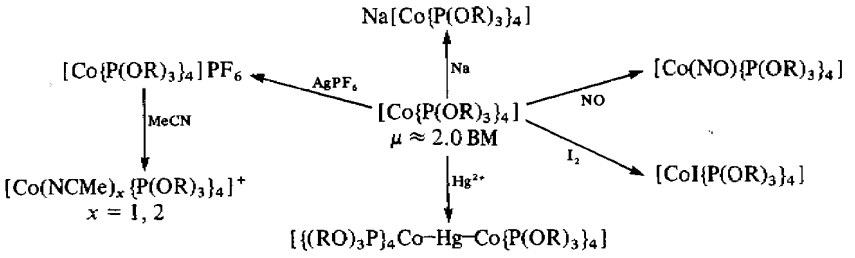
(iii) Cobalt(I)

Some $[CoCl\{P(OR)_3\}_3]$ complexes of tetrahedral symmetry are known ($\mu \approx 3$ BM; Table 41); these dissociate one $P(OR)_3$ ligand in solution. $[Co\{P(OR)_3\}_5]^+$ ions (R = Me, Et; $P(OCH_2)_3CMe$) are fluxional at room temperature but the A_2B_3 spectrum (^{31}P NMR) obtained at low temperature (−122 to −200 °C) establishes a trigonal-bipyramidal ground state (D_{3h} symmetry) with $\Delta G^{\ddagger}$

Table 41 Preparations: Phosphite, Phosphonite and Phosphinite Complexes

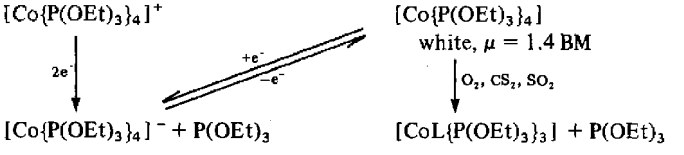
Complex	*Preparation*	*Properties*	*Ref.*
$[CoH\{P(OR)_3\}_4]$ (R = Me, Et)	$CoCl_2$ + L + $NaBH_4$; $(RO)_2C_2H_4$, 0 °C	Yellow; diamagnetic	4
$K[Co\{P(OR)_3\}_4]$ (R = Me, Et)	$[CoH\{P(OR)_3\}_4]$ + KH; THF, 65 °C, vac.	White; diamagnetic insoluble in inorganic solvents	4
$Na[Co\{P(OPr^i)_3\}_5]$	$CoCl_2$ + L; THF, Na/Hg	White; diamagnetic, two kinds of L	14
$Na[Co\{P(OPh)_3\}_4]$	CPE of $[Co\{P(OPh)_3\}_4]$ at −1.00 V; $C_2H_4(OMe)_2$, −30 °C	White	15
$[Co\{P(OEt)_3\}_4]$	CPE of $(Et_4N)[Co\{P(OEt)_3\}_4]$; MeCN	White; μ = 1.4 BM, v. reactive	8
$[Co\{P(OPr^i)_3\}_4]$	$CoCl_2$ + L + Na/Hg; THF	Orange-red; μ = 2.0 BM	14
$[Co\{P(OPh)_3\}_4]$	Co^{2+} + L + $NaClO_4$; MeCN; CPE at −1.10 V	Pale yellow	15
$[CoR\{P(OR)_3\}_4]$ (R = Me, Ph)	$K[Co\{P(OR)_3\}_4]$ + RI; THF	Yellow; diamagnetic	4
$[Co\{P(OPh)_3\}_x(CO)_{4-x}(HgX)]$ (X = Cl, Br, I; x = 4, 3, 2)	$[CoH\{P(OPh)\}_x(CO)_{4-x}]$ + HgX_2; acetone	Orange-yellow	16
$[CoCl\{P(OEt)_3\}_3]$	$[Co\{P(OEt)_3\}_5]Cl$; vac., 90 °C	Brown; μ = 3.15; tet	5
$[CoCl\{P(OPr^i)_3\}_3]$	$CoCl_2$ + Zn + L; THF	Purple; μ = 2.9 BM, soluble in non-polar solvents	14
$[Co\{P(OMe)_3\}_5]Y$ (Y = BF_4, BPh_4)	$Co(BF_4)_2 \cdot 6H_2O$ + L; acetone; $(MeO)_2CHEt$	Yellow; soluble in THF, DMF, acetone; insoluble in Et_2O, ROH, RH	1
$[Co\{P(OEt)_3\}_5]Y$ (Y = Cl, BPh_4)	$CoCl_2$ + L + NEt_3; EtOH, H_2O, r.t.	Yellow; diamagnetic	5
$[Co\{P(OCH_2)_3CMe\}]Y$ (Y = NO_3, ClO_4)	$Co(ClO_4)_2 \cdot 6H_2O$ + L; EtOH, 0 °C	Yellow; diamagnetic	2
$[Co\{P(OR)_3\}_5]BPh_4$ (R = Me, Et; $P(OCH_2)_3CMe$)	$[Co(C_8H_{12})(C_8H_{13})]$ + L; MeOH; MeCOCl, $NaBPh_4$	Yellow	6
$[Co(CO)_n\{P(OMe)_3\}_{5-n}]BPh_4$ (n = 0–3)	$Co_2(CO)_8$ + L; pentane	Yellow-white; diamagnetic	7
$[Co\{P(OR)_3\}_3(\eta^3\text{-}C_3H_5)]$ (R = Me, Et, Pr^i)	$K[Co\{P(OMe)_3\}_4]$ + PrI; THF, evap.	Orange; diamagnetic, fluxional	4, 13
$[Co\{P(OR)_3\}_3(\eta^3\text{-}C_8H_{13})]$ (R = Me, Et, Pr^i)	$[Co(C_8H_{12})(C_8H_{13})]$ + L; pentane, 16 h, evap.	Orange-brown; diamagnetic	12
$[Co\{C_2H_2(CO_2Et)_2\}\{P(OR)_3\}_3]$ (R = Me, Et, Pr^i)	$[Co(MeCN)_2\{C_2H_2(CO_2Et)_2\}_2]$ + $P(OR)_3$; toluene, N_2	Yellow; ethyl fumarate, maleic anhydriude (structure, Table 42)	17
$[CoX\{P(OEt)_2Ph\}_4]BPh_4$ (X = Cl, Br, I, NCS)	CoX_2 + L; EtOH, $NaBPh_4$	Green; μ = 2.0–2.3 BM; stable under N_2; soluble in organic solvents	9
$[Co(Cl)_2\{P(OEt)_nEt_{3-n}\}_2]$	$CoCl_2$ + 2L; benzene	Blue-green; μ = 4.23–4.66 BM	10
$[Co(Cl)_2\{P(OEt)_nEt_{3-n}\}_3]$	$CoCl_2$ + 3L; benzene	Green-black; μ = 2.03–2.48 BM; dissociates in benzene	10
$[Co\{P(OMe)_3\}_6]Y_3$ (Y = ClO_4, BF_4, BPh_4)	$Co(ClO_4)_2 \cdot 6H_2O$ + L; EtOAc; DMSO, H_2O	Colourless; diamagnetic; ε_{350} 200; ^1H and ^{59}Co NMR	3
$[Co\{P(OCH_2)_3CMe\}_6](ClO_4)_3$	$Co(ClO_4)_2 \cdot 6H_2O$ + L	Colourless; diamagnetic	2
cis-$[Co(NCS)_2\{P(OR)_3\}_4]BPh_4$ (R = Me, Et)	$Co(SCN)_2$ + L; MeOH, $NaBPh_4$	Yellow; diamagnetic	11
trans-$[Co(NCS)_2(L)_4]BPh_4$ (L = $P(OMe)_3$, $P(OMe)_2Ph$)	$[Co(NCS)(L)_4]BPh_4$ + NO; CH_2Cl_2	Red; diamagnetic (structure Table 42)	11

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Scheme 53

for intramolecular exchange of phosphite ligands > 40 kJ mol^{-1} (*vs.* < 20 kJ mol^{-1} for $[CoH\{P(OR)_3\}_4]$; Section 47.5.2.1).[526] Dissociation and intermolecular ligand exchange occur at higher temperatures. Oxidation of $[Co\{P(OR)_3\}_4]$ with $AgPF_6$ leads to $[Co\{P(OR)_3\}_4](PF_6)$ (R = Me, Et, Pr^i, Ph),[406] and the reverse reduction to Co^0 and Co^{-1} has been achieved electrochemically with the latter couple being reversible.[527] Preparation of $[Co\{P(OR)_3\}_5]Y$ can be achieved by disproportionation of Co^{2+} in the presence of $P(OR)_3$,[523] photolysis of $[Co(CO)\{P(OMe)_3\}_4]^+$ in the presence of $P(OMe)_3$,[524] and the displacement of cyclooctadiene from $Co(C_8H_{12})(C_8H_{13})$ using excess $P(OR)_3$ followed by the addition of one equivalent of acetyl chloride (Table 41).[525] Protonation of $[Co(Me)\{P(OMe)_3\}_4]$ leads to CH_4 *via* the intermediate hydride $[Co(H)(Me)\{P(OMe)_3\}_4]$ (equation 111).[383]



Scheme 54

$$[CoMe\{P(OMe)_3\}_4] + H^+ \longrightarrow [Co\{P(OMe)_3\}_4] + CH_4 \qquad (111)$$

(*iv*) *Cobalt(II)*

Five-coordinate low-spin Co^{II} species $[CoX\{P(OEt)_3\}_4]^+$ have been prepared (Table 41), but dissociation to tetrahedral $[CoX\{P(OEt)_3\}_3]^+$ occurs in solution.[528] Similarly low-spin $[Co(Cl)_2\{P(OEt)_nEt_{3-n}\}_3]$ have been prepared (n = 3, 2, 1; n = 3 in solution only; Table 41) and these dissociate one ligand in organic solvents (benzene, nitrobenzene) to form high-spin tetrahedral $[Co(Cl)_2\{P(OEt)_nEt_{3-n}\}_2]$ (equation 112). Stability constants suggest maximum stability with phosphinite and phosphonite ligands (n = 1, 2) and this has been rationalized in terms of increasing cone angle and decreasing σ-donor ability.[529] Both the high-spin four-coordinate and low-spin five-coordinate complexes react with O_2 in benzene solutions or as solids producing phosphine oxide products (equation 113). The rate for L = $P(OEt)_3$ is slower than that for the phosphonite and phosphinite complexes (0.038 *vs.* 0.36–0.68 dm^3 mol^{-1} s^{-1} for $P(OEt)_nEt_{3-n}$, n = 1–3) and a green $[Co(Cl)_2(L)_2(O_2)]$ intermediate has been investigated.[530]

$$[CoCl_2(L)_2] + L \rightleftharpoons [CoCl_2(L)_3] \qquad (112)$$

$$\mu = 4.2\text{–}4.7\,BM \qquad \mu = 2.0\text{–}2.5\,BM$$

$$[CoCl_2(L)_2] + O_2 \longrightarrow [CoCl_2(LO)_2] \qquad (113)$$

(*v*) *Cobalt(III)*

The few Co^{III} phosphite complexes that have been prepared (Table 41) have resulted from disproportionation reactions (equations 114, 115 and 116). Phosphite ester hydrolysis has been found to occur with *trans*-$[Co(DMGH)_2(Cl)\{P(OMe)_nPh_{3-n}\}]$ (n = 3, 2, 1) with the formation of the corresponding phosphonato complex anion *trans*-$[Co(DMGH)_2Cl\{P(O)(OMe)_{n-1}Ph_{3-n}\}]^-$. This most interesting reaction requires the presence of a nucleophilic agent such as halide (or a nitrogen

Table 42 Structures: Phosphite, Phosphinite and Phosphonite Complexes

Complex	*Structure*	*Data*[a]	*Ref.*
$[CoH\{P(OEt)_2Ph\}_4]$	Dist. trig. bipyr.; non-rigid in soln.	CoH 138; CoP 210–213; PCoH 173.5°; PCoP 98–124°	1
$[Co\{P(OMe)_3\}_4]$	Disordered; C_{3v} tet. framework		6
$[Co\{P(OMe)_3\}_4]_2Hg$	Trig. bipyr.; staggered CoP_4 units	CoHgCo 180°; $HgCoP_{ax}$ 178.9	6
$[Co\{P(OMe)_3\}_3(\eta^3\text{-}C_8H_{13})]$	sq. pyr.; π-allyl occupying basal sites	CoP_{ax} 213; CoP_{eq} 211; CoC-1(3) 212; CoC-2 196	3
$[Co\{P(OMe)_3\}_3(\eta^3\text{-}CH_2Ph)]$	Dist. trig. bipyr. with CH_2, P axial	CoP 211–213; $CoCH_2$ 203.6; CoC-2(3) 211.7–240.8	4
$[Co(CO)_2(PPh_3)(\eta^3\text{-}C_3H_5)]$	Dist. sq. pyr.; one CO axial	CoC_{ax} 178; CoC_{allyl} 209–212;	5
trans-$[Co(NCS)_2\{P(OEt)_3\}_4]BPh_4$	Oct.; *trans* NCS	CoN 184, 187; CoNC 176, 178°	2
$[Co(CNC_6H_4F)_3\{P(OMe)_3\}_2]BF_4$	Trig. bipyr.	CoP 213.7; CoC 183, 185; PCoP 89.4–90.3	7
$[Co\{C_2H_2(CO)_2O\}\{P(OMe)_3\}_3]$	Dist. tet. with coord. maleic anhydride	CoC 203.3; CoP 217.2; PCoP 99.4; PCoC 117.4	8

[a] Bond lengths in pm.

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2. G. Albertin, G. Pelizzi and E. Bordignon, *Inorg. Chem.*, 1983, **22**, 515.
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$$2Co^{2+}_{(aq)} + 11P(OMe)_3 \longrightarrow [Co\{P(OMe)_3\}_5]^+ + [Co\{P(OMe)_3\}_6]^{3+} \quad (114)$$

$$2Co(NCS)_2 + 9P(OMe)_3 \longrightarrow [Co\{P(OMe)_3\}_5]^+ + \textit{cis}\text{-}[Co(NCS)_2\{P(OMe)_3\}_4]^+ \quad (115)$$

$$2[Co(NCS)\{P(OMe)_3\}_4]^+ + NO \longrightarrow [Co(NO)_2\{P(OMe)_3\}_2]^+ + \textit{trans}\text{-}[Co(NCS)_2\{P(OMe)_3\}_4]^+ \quad (116)$$

heterocycle) which becomes alkylated in the process. An S_N2 displacement at the ester carbon centre of the coordinated phosphite has been proposed.[531]

47.5.2.8 Phosphates, cobalt(III)

The structures of several Co^{III}–phosphate complexes are known (Table 46), but their chemistry is not well understood and is not considered here.

(*i*) *Orthophosphates*

Preparations are given in Table 45 and structures in Table 46. Monodentate and bidentate coordination is very slow and occurs by water exchange at the metal (k_{ex}) rather than by attack of coordinated water or hydroxide at phosphorus(V). It is therefore expected that there will be some sort of correlation between k_{ex} and the rate of anation k_{an}. An ion-pair mechanism is likely in all cases, and rather large K_{ip} values and limiting kinetics have been observed (Scheme 55, Table 43). k_1 is some 10–10^2 times slower than k_{ex}, and this can be accounted for by unusually strong H bonding in the ion pair, and by orientation effects.[537] Other oxyanions behave similarly where substitution (*i.e.* oxygen exchange) at the metal is slow.

$$\underset{(cis + trans)}{[Co(HO)(H_2O)(en)_2]^{2+}} + HPO_4^{2-} \overset{K_{ip}}{\rightleftharpoons} \underset{(cis + trans)}{[Co(HO)(H_2O)(en)_2]^{2+}HPO_4^{2-}} \xrightarrow{k_1}$$

$$[Co(O_2PO_2)(en)_2]^+ + H_2O + OH^-$$

$$k_{an} = \frac{k_1K_{ip}[HPO_4^{2-}]}{1 + K_{ip}[HPO_4^{2-}]}$$

Scheme 55

Complex	Oxyanion	k_{an} ($mol^{-1} dm^3 s^{-1}$)	K_{ip} ($mol^{-1} dm^3$)	k_i (s^{-1})	Temperature (°C)	Ref.
$[Co(NH_3)_5OH_2]^{3+}$	$H_2PO_4^-$	2.1×10^{-6}	3	7×10^{-7}	25	1
		4.50×10^{-5}			50	17
		5.39×10^{-4}			70	17
(*cis* + *trans*)-$[Co(en)_2(OH)(OH_2)]^{2+}$	HPO_4^{2-}	7.4×10^{-2}	60	1.23×10^{-3}	47.9	2
α-$[Co(trien)(OH)(OH_2)]^{2+}$	$MeP(O_2H(OC_6H_4p\text{-}NO_2)$	1.6×10^{-2}			25	3
$[Co(tn)_2(OH)(OH_2)]^{2+}$	$MeP(O_2H)(OC_6H_4p\text{-}NO_2)$	2.3×10^{-2}			25	3
$[Co(tme)_2(OH)(OH_2)]^{2+}$	$MeP(O_2H)(OC_6H_4p\text{-}NO_2)$	~0.15			25	3
$[Co(NH_3)_5OH_2]^{3+}$	SO_4^{2-}	1.5×10^{-5}	11.2	1.3×10^{-6}	25	16
	HCO_2^-	5.9×10^{-4}	1.0	5.6×10^{-4}	70	4
	$MeCO_2^-$	8.7×10^{-4}	5.2	1.6×10^{-4}	70	5
	$EtCO_2^-$	8.6×10^{-4}	3.4	2.5×10^{-4}	70	6
	HC_2O_4	8.8×10^{-4}	1.8	4.9×10^{-4}	70	7
	C_2O_4	3.7×10^{-3}	9.2	4.0×10^{-4}	70	7
	$HO_2CCH_2CO_2^-$	6.9×10^{-4}	1.3	5.3×10^{-4}	70	8
	$^-O_2CCH_2CO_2^-$	4.0×10^{-3}	5.4	7.4×10^{-4}	70	8
cis-$[Co(en)_2(OH_2)_2]^{3+}$	$H_2C_2O_4$	5.9×10^{-5}	1.0	5.9×10^{-5}	50	9
	$HC_2O_4^-$	2.6×10^{-4}	4.4	5.8×10^{-5}	50	9
$[Co(en)_2(OH_2)(OH)]^{2+}$	$C_2O_4^{2-}$	7×10^{-3}	7.5	9.4×10^{-4}	25	11
				$\Delta V^{\ddagger} + 4.6$ ($cm^3\ mol^{-1}$)		
	$C_2O_4^{2-}$		5.5	7.2×10^{-4}	25	14
	$^-O_2CCH_2CO_2^-$		3.3	7.0×10^{-4}	25	15
	$^-O_2C(CH_2)_2CO_2^-$		2.8	6.8×10^{-4}	25	15
	$^-O_2C(CH_2)_6CO_2^-$		2.3	6.5×10^{-4}	25	15
cis-$[Co(en)_2(NH_3)(OH_2)]^{3+}$	$H_2C_2O_4$	5.2×10^{-3}	–	–	60	10
	$HC_2O_4^-$		1.5	2.3×10^{-4}	60	10
	$C_2O_4^{2-}$		5.8	1.96×10^{-4}	60	10
cis-$[Co(NH_3)_4(OH_2)_2]^{3+}$	$H_2C_2O_4$		0.52	4.2×10^{-4}	62	13
	$HC_2O_4^-$		5.3	4.2×10^{-4}	62	13
	$C_2O_4^{2-}$		6.6	5.13×10^{-4}	60	12
cis-$[Co(en)_2(NH_3)(OH_2)]^{3+}$	$HOC_6H_4CO_2^-$	1.5×10^{-4}	2.3	6.53×10^{-5}	60	

1. W. Schmidt and H. Taube, *Inorg. Chem.*, 1963, **2**, 698.
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3. R. A. Kenley, R. H. Fleming, R. M. Laine, D. S. Tse and J. S. Winterle, *Inorg. Chem.*, 1984, **23**, 1870.
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Hydrolysis of monodentate phosphate is also very slow and Co^{III}–OPO_3H_n species ($n = 3$–0) can be considered inert at room temperature (k_0, Table 44). As expected, hydrolysis occurs by substitution at the metal and without exchange into the phosphate (equation 117). Acid catalysis is interpreted in terms of aquation of the acid conjugate of the complexed phosphate (Table 44). $[Co\{OP(OH)_3\}(NH_3)_5]^{3+}$ ($pK_a \approx -0.7$) hydrolyzes some 10^2 times slower than $[Co\{OP(OMe)_3\}(NH_3)_5]^{3+}$, which suggests that protonation at the bound O atom is not important. Base hydrolysis is also very slow (Table 44), occurs *via* substitution at the metal, and an S_N1cb process is likely *via* prior deprotonation of an ammine ligand (equation 118).

$$[(NH_3)_5Co—OPO_3H]^+ + H_2● \xrightarrow{k_0} [(NH_3)_5Co—●H_2]^{3+} + HPO_4^{2-} \quad (117)$$

$$[(NH_3)_5Co—OPO_3] + ●H^- \xrightarrow{k_{OH}} [(NH_3)_5Co—●H]^{2+} + PO_4^{3-} \quad (118)$$

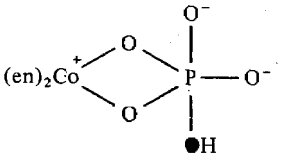
Ring opening in bidentate orthophosphate complexes is both fast and reversible. The inherent stability of chelate rings compared to their acyclic analogues is offset in this four-membered chelate by distortion at the tetrahedral P centre (98.7°), at octahedral Co^{III} (76°), and possibly by the close approach of Co to P. Strain is obvious in the crystal structure of $[Co(O_2PO_2)(en)_2]$ (Table 46). Lincoln and Stranks[538] carried out a careful study of the hydrolysis of this complex. In dilute acid (pH < 4) ring opening occurs *via* protonation and Co—O bond fission. In neutral and alkaline

Table 44 Rates of Aquation and Alkaline Hydrolysis of Some Cobalt(III)–Oxyanion Complexes

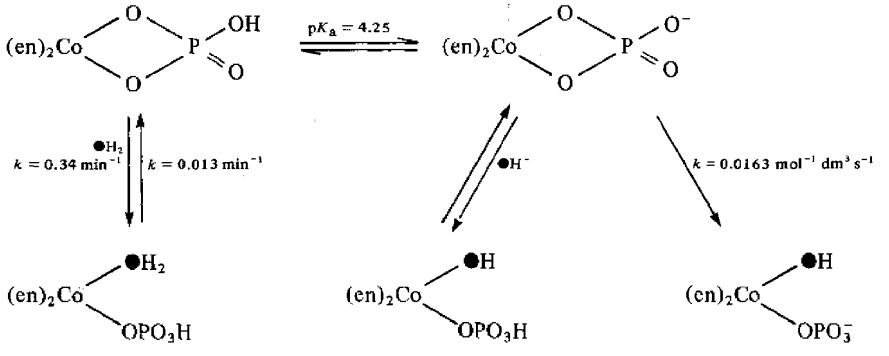
Complex	k_o (s^{-1})	k_{OH} ($mol^{-1}\,dm^3\,s^{-1}$)	*Ref.*
$[Co(OPO_3)(NH_3)_5]$	2×10^{-6} (60 °C)	4.0×10^{-4} (60 °C)	1, 2
$[Co(OPO_3H)(NH_3)_5]^+$	2×10^{-5} (60 °C)		4
	1.05×10^{-5} (60 °C)		1
$[Co(OPO_3H_2)(NH_3)_5]^{2+}$	2.6×10^{-7} (25 °C)		3
	1.6×10^{-5} (60 °C)		1, 4
$[Co(OPO_3H_3)(NH_3)_5]^{3+}$	1.5×10^{-4} (60 °C)		4
$[Co\{OP(OMe)_3\}(NH_3)_5]^{3+}$	$2.5(1.4) \times 10^{-4}$ (25 °C)	79	3, 6
$[Co\{OPO_2(O\text{-}p\text{-}NO_2C_6H_4)\}(NH_3)_5]^{2+}$		8.1×10^{-4} (25 °C, *ca.* 50% hydrolysis at Co)	8
$[Co(OPO_2OCOMe)(NH_3)_5]^+$		0.53 (25 °C); hydrolysis at acyl centre only	10
$[Co(OPO_2F)(NH_3)_5]^+$		3.3×10^{-3} (25 °C; *ca.* 50% hydrolysis at Co)	11
$[Co(OSO_3)(NH_3)_5]^+$	8.9×10^{-7}	4.9×10^{-2}	12, 13
	6.4×10^{-6} (H^+, 35 °C)		14
$[Co(SSO_3)(NH_3)_5]^+$	1.6×10^{-7}	6×10^{-5}	15
$[Co(OS_2O_2)(NH_3)_5)]^+$	4.3×10^{-4} (isom)	1.85×10^{-2} (53% isom)	16
cis-$[Co(OPO_3)(OH)(en)_2]^-$	3.3×10^{-5} (60 °C)	2×10^{-4} (60 °C)	2
		1.4×10^{-2} (25 °C)	5
cis-$[Co(OPO_3)(OH)(NH_3)_4]^-$	1.4×10^{-2} (60 °C)	7×10^{-3} (60 °C)	2
cis-$[Co(OPO_3)(OH)(cyclen)]^-$		2.7×10^{-2} (25 °C)	5
cis-$[Co(OPO_3H_2)(OH_2)(cyclen)]^{2+}$	5×10^{-4} (25 °C)		5
cis-$[Co(OPO_3H_3)(NH_3)(en)_2]^{3+}$	1.7×10^{-4} (70 °C)		7
trans-$[Co(OPO_3H_3)(NH_3)(en)_2]^{3+}$	1.65×10^{-4} (70 °C)		7
$[Co(O\text{-}p\text{-}NO_2C_6H_4)(O_2PO)(tn)_2]^+$	7×10^{-5} (25 °C)	5.1 (25 °C)	9
$[Co(OSO_3)(OH_2)(en)_2]^+$	3.3×10^{-4} (52 °C)		17
$[Co(OSO_3)(OH)(en)_2]$	4.1×10^{-2} (52 °C)	0.22 (25 °C)	17, 19
$[Co(O_2SO_2)(en)_2]^+$ (chelate)	7.3×10^{-5} (ring opening)	1.63×10^{-2} (25 °C)	17, 19
$[Co(OSSO_2)(en)_2]^+$ (chelate)	2.75×10^{-4} (ring opening)		18

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conditions some O—P bond cleavage was initially believed to occur (35–40%),[538] but recent ^{18}O and ^{17}O experiments have shown exclusive Co—O bond cleavage in 0.4 mol dm^{-3} NaOH[1216] and at pH ≈ 8.[1217] A phosphorane intermediate or transition state (**163**) is therefore not involved in this reaction.



(163)



Scheme 56

Scheme 56 gives the current state of affairs, and it is clear that the chelate is only stable in neutral to slightly alkaline conditions; in acidic solution (pH < 4) the monodentate form predominates. Similar chemistry obtains with [Co(O_2PO_2)(cyclen)].[539]

(ii) Orthophosphate esters and halides

Preparations are given in Table 45. Schmidt and Taube[540] pioneered the early work in this area by preparing and studying the hydrolysis of the $OP(OMe)_3$, $OP(OBu)_3$ and $^-O_2P(OMe)_2$, pentaammine complexes. The triesters (R = Me, Et, Bu^n) are not good ligands and are relatively easily displaced in aqueous solution (equation 119). They have also been used in poorly coordinating solvents to prepare other pentaammine complexes.[173] Recent studies[187] establish that both aquation (10^{-3} mol dm^{-3} HCl) and base hydrolysis (0.1 mol dm^{-3} OH^-) occur exclusively by substitution at Co rather than at P. A similar result is likely for all alkyl and aryl monodentate (or bidentate) phosphate esters unless the metal can force unusually large strain at the P centre. A rather more complex situation occurs with *p*-nitrophenylphosphate.[541] In 0.05–1.0 mol dm^{-3} OH^- about 50% hydrolysis at Co occurs (*p*-nitrophenylphosphate is released) but the remainder occurs *via* a phosphoamidate intermediate generated by attack of a deprotonated ammine ligand with release of *p*-NO_2PhOH (Scheme 57). Ultimately this path leads to free $NH_2PO_3^{2-}$ without incorportion of solvent label. It appears that a single Co^{III} centre cannot provide sufficient activation at P for attack at this centre, even when an excellent leaving group is provided. However, attachment of two oxygen atoms to form a four-membered chelate can provide sufficient activation to allow hydrolysis at P to occur (probably as a result of distortion of the OPO angle). With $[Co\{O_2PO(OC_6H_4NO_2)\}(en)_2]^+$ only hydrolysis at Co is observed but with $[Co\{O_2PO(OC_6H_4NO_2)\}(tn)_2]^+$ sufficient flexibility about Co^{III} results and about 35% hydrolysis at P is found (Scheme 58).[542] Production of the *p*-nitrophenolate ion in the pH range 6.5–13.5 follows the rate $k_{obs} = k_1 + k_2[OH^-]$ ($k_1 = 7 \times 10^{-5}$ s^{-1}, $k_2 = 5.1$ mol^{-1} dm^3 s^{-1}) and the initial fast release of *p*-nitrophenol (35% of total) is followed by a slower reaction presumably *via* leakage back from the monodentate complex. The same rate was found using excess *trans*-$[Co(OH)(tn)_2(H_2O)]^{2+}$ and $Na_2O_3POC_6H_4NO_2$ at pH 7.54, which implies complete coordination of the substrate, and the 100% production of *p*-nitrophenol in this case implies recycling of released ester. This study, which provides an acceleration of 10^4–10^9 (depending on pH) over hydrolysis of the uncoordinated ester, was not the first to report the Co^{III}–promoted hydrolysis of a phosphate ester but it does provide some important mechanistic detail.[543] Clearly bidentate attachment to a metal ion is a minimum requirement and this parallels organic chemistry where five-membered ring phosphate esters are remarkably reactive.[544] It also supports the associative nature of nucleophilic displacement at phosphorus(V) with accelerated reactions being found only when distortion of the ground state of the P centre (both electronic and steric) is provided.

Table 45 Preparations: Cobalt Phosphate, Phosphate Ester, Phosphonate and Phosphite Complexes

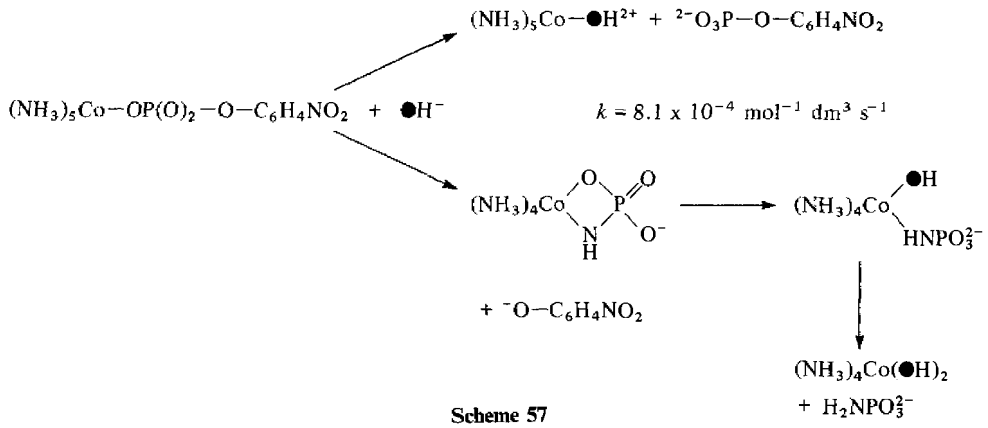
Complex	*Preparation*	*Properties*	*Ref.*
Monodentate			
$[Co(OPO_3)(NH_3)_5]\cdot xH_2O$ ($x = 2, 3$)	$[Co(H_2O)(NH_3)_5](ClO_4)_3$ + H_3PO_4/NaH_2PO_4, 70–80 °C, 1 h	ε_{524} 90; ε_{364} 74 (pH 8); pK_{a_1} 8.5(1+); pK_{a_2} 3.6(2+); pK_{a_3} −0.7(3+)	1 2
cis-$[Co(OPO_3H)(H_2O)(en)_2]ClO_4$	$[Co(O_2PO_2)(en)_2]$ + $HClO_4$	ε_{511} 108; ε_{366} 84; pK_{a_1} 9.4 (hydroxo monodentate); pK_{a2} 3.1(2+)	2
cis-$[Co(OPO_3H)(H_2O)(NH_3)_4]ClO_4\cdot 2H_2O$	$[Co(O_2PO_2)(NH_3)_4]$ + 0.5 M HCl_{aq} + $NaClO_4$; MeOH; 24 h	IR spectrum	3
cis-$[Co(OPO_3)(NH_3)(en)_2]$	*cis*-$[Co(en)_2(NH_3)(H_2O)]Br_3$ + NaH_2PO_4 + H_3PO_4; 70 °C 1h; chrom.	ε_{513} 112.5; ε_{362} 96.2; pK_{a_2} 3.2(2+); pK_{a_1} 7.85(1+)	4
trans-$[Co(OPO_3)(NH_3)(en)_2]$	*trans*-$[Co(en)_2(NH_3)(H_2O)](NO_3)_3$ + NaH_2PO_4 + H_3PO_4; to 70 °C; chrom.	ε_{521} 90.5; ε_{357} 76.5; pK_{a2} 3.0(2+); pK_{a1} 7.73(1+)	4
cis-$[Co\{OPO_2(OC_6H_4NO_2)\}(H_2O)(en)_2]ClO_4\cdot H_2O$	$[Co(en)_2(\mu\text{-}O_3POPh)]_2$ + CF_3SO_3H + HNO_3; chrom.	ε_{507} 103; pK_a 7.61	17
$[Co\{OP(O)_2OPh\}(NH_3)_5]Cl$	$[Co(OH_2)(NH_3)_5]ClO_4$ + Na_2PO_4Ph; 60–80 °C, 1 h, Dowex chrom.	ε_{518} 77.3; ε_{356} 61.1	6
$[Co\{OP(O)_2OCOMe\}(NH_3)_5]ClO_4$	$[Co(OPO_3)(NH_3)_5]$ + Ac_2O	ε_{518} 71.5; ε_{356} 56	7
$[Co\{NH_2P(O_2H)O\}(H_2O)(NH_3)_4]Cl_2$	$[Co\{OP(O)(OH)OC_6H_4NO_2\}(NH_3)_5]Cl$ + OH^-; 28 min, 25 °C	Probably N-bonded isomer	6
$[Co\{OP(O_2H)CH(Me)NH_3\}(NH_3)_5]^{2+}$	$[Co(CO_3)(NH_3)_5]NO_3$ + LH + H_2O; 50–60 °C, evap.	ε_{513} 61.3; ε_{353} 52.8; pK_a 3.2(3+)	8
$[Co\{OP(O)_2OC_6H_4OH\}(NH_3)_5]ClO_4$	$[Co(CO_3)(NH_3)_5]NO_3$ + $H_2PO_3(OC_6H_4OH)$ + H_2O; 65–70 °C, 1.5 h; SP-C25 chrom.	ε_{519} 67; pK_{a_1} 2.83; pK_a (OH) 7.75	9
$[Co\{OP(OMe)_3\}(NH_3)_5]X_3$ (X = ClO_4, BF_4, CF_3SO_3)	(1) $[Co(Br)(NH_3)_5]Br_2$ + $AgClO_4$; $OP(OMe)_3$ solvent	ε_{520} 46.3; ε_{347} 39.2	1
	(2) $[Co(N_3)(NH_3)_5](BF_4)_2$ + $NOBF_4$; $OP(OMe)_3$ solvent		13
$[Co\{OPO(OMe)_2\}(NH_3)_5]^{2+}$	$[Co(OH_2)(NH_3)_5](ClO_4)_3$ + $NaOPO(OMe)_2$ pH 1–3, aq. soln; 75 °C, 45 min. Dowex 50 W × 4 chrom.	ε_{517} 58.1; ε_{325} 48.3; not isolated	1
$[CoOP(O_2H)F(NH_3)_5]Cl_2$	$[CoN_3(NH_3)_5](ClO_4)_2$ + $NOCF_3SO_3$ + Na_2PO_3F; sulfolane, 50 °C, 3–4 d; SP-C25 chrom.	Purple, ^{19}F and ^{31}P NMR	15
$[Co\{OP(O_2H)H\}(NH_3)_5](ClO_4)_2$	$[Co(OH_2)(NH_3)_5](ClO_4)_3$ + Na_2HPO_3; aq, pH 4–5; 80 °C, 2 h; Dowex 50 W × 4 chrom.	^{31}P NMR; phosphito complex	16
Bidentate			
$[Co(O_2PH_2)_2]$	$Co(O_2CPh)_2$ + H_3PO_2; MeOH; anhydrous	Purple hypophosphite complex	14
$[Co(O_2PO_2)(NH_3)_4]$	$[Co(NH_3)_4(H_2O)_2]Cl_3$ + $(NH_4)_2HPO_4$; H_2O, 60 °C; NH_4OH, 24 h	IR spectrum	3
$[Co(O_2PO_2)(en)_2]\cdot H_2O$	*trans*-$[Co(Cl)_2(en)_2]ClO_4$ + Na_3PO_4, 60–70 °C, 5–6 h	ε_{529} 112; ε_{377} 98; pK_a 4.25	2
$[Co(O_2PO_2)(cyclen)]\cdot H_2O$	*cis*-$[Co(Br)_2(cyclen)]Br$ + Na_3PO_4; paste, 50 °C	ε_{530} 174; ε_{365} 140	5
$[Co\{O_2P(O)OC_6H_4NO_2\}(tn)_2]ClO_4$	*trans*-$[Co(Cl)_2(tn)_2]Cl$ + $Ag_2(O_3POC_6H_4NO_2)$, Me_2SO, 20 °C (dark)	Limited solubility in H_2O	10
$[Co\{O_2P(O)OC_6H_4NO_2\}(en)_2]Cl$	*trans*-$[Co(Cl)_2(en)_2]Cl$ + $Na_2O_3POC_6H_4NO_2$; paste, H_2O; 60 °C	Limited solubility in H_2O; aquates	5
Bridging			
$[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}HPO_4)Co(NH_3)_4](NO_3)_3\cdot H_2O$	$[Co_2(\mu\text{-}NH_2)(\mu\text{-}OH)(NH_3)_8]Cl_4$ + H_3PO_4; 40 °C, 1.5 h	ε_{538} 374; ε_{372} 553; pK_{a_1} 6.0(3+); pK_{a_2} 1.5(4+)	11
$[(en)_2Co(\mu\text{-}O_3POPh)_2Co(en)_2]X_2$ (X = Cl, CF_3SO_3)	*cis*-$[Co(Cl)_2(en)_2]Cl$ + $Ag_2(O_3POPh)$, Me_2SO, 80 °C, 70 min; SP-C25 (Na^+) chrom.	Red-violet; limited solubility in H_2O	12
$[(NH_3)_5Co(\mu\text{-}PO_4H)Co(NH_3)_5](ClO_4)_4$	$[Co(OPO_3)(NH_3)_5]$ + $[Co(NH_3)_5OH_2](ClO_4)_3$; H_2O, pH 2.5–3, 70 °C, 4 h	^{31}P NMR	16

Intramolecular hydrolysis by Co^{III}-coordinated hydroxide in *cis*-$[Co(OH)\{OPO_2(OC_6H_4NO_2)\}(en)_2]$ has also been demonstrated (Scheme 58a) and a phosphorane intermediate analogous to (**163**) is suggested.[1216] The advantages of metal-coordinated hydroxide over alkoxide in facilitating such cyclizations and hydrolyses are discussed in this report.

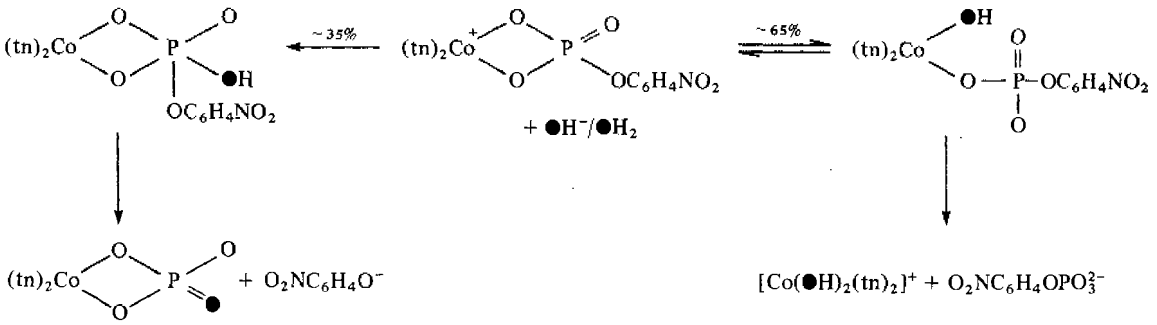
Table 45 (*continued*)

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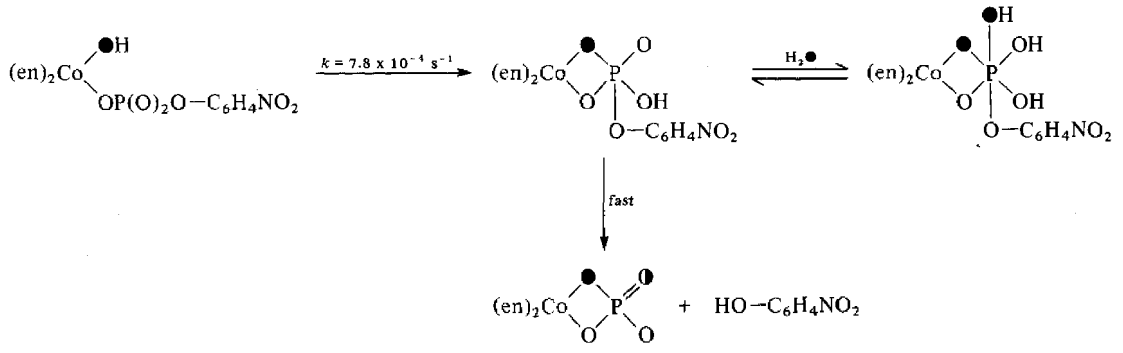
Intramolecular hydrolysis by Co^{III}-coordinated hydroxide in *cis*-[Co(OH){$OPO_2(OC_6H_4NO_2)$}$(en)_2$] has also been demonstrated (Scheme 58a) and a phosphorane intermediate analogous



Scheme 57

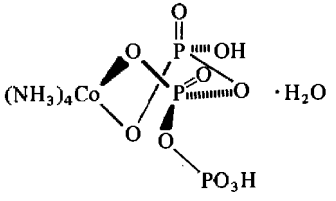
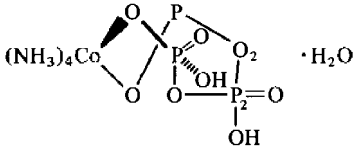
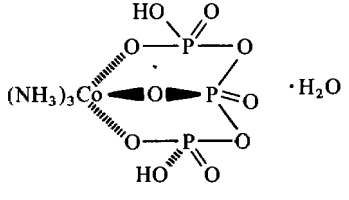
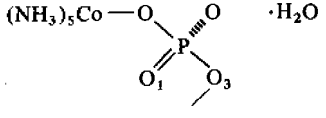


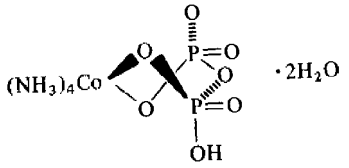
Scheme 58



Scheme 58a

Table 46 Structures: Cobalt Phosphate, Phosphonate, Phosphite, ADP and ATP Complexes

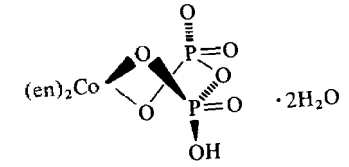
Complex	*Data*[a]	*Comments*	*Ref.*
$Co_3(PO_4)_2$	$P2_1/n$	Dist.; CoO_6, CoO_5 units	1
$Co_2(PO_4)Cl$	$C2/c$; CoO 194–224; CoCl 243.5–254.2	Dist.; CoO_4Cl_2 polyhedra with one face shared with two adjacent polyhedra; 3D network	16
$K_4Co(P_3O_9)_2 \cdot 7H_2O$	$Fm2m$; ionic structure	3D network of P_3O_9 rings linked by Co^{2+}, K^+	2
$Na[Co\{OPH(O)(OH)_3\}] \cdot H_2O$	$Pbca$; CoO 206–215	3D network; oct.; five O(P), one OH_2 donors; two O(P) bridges	3
$[Co(O_3PCH_2NH_3)_2(H_2O)_2]$	$P2_1/c$; CoO 210, 212; OPC 108.6 °C; OPO (bridge) 111.9 °	Dist. oct.; two OH_2 (*trans*); two $O(PO_2R)$, two bridging $O_2(POR)$ (*trans*); prep. from $CoCl_2 \cdot 6H_2O$ in aq. soln.	4
	$P2_1$; β,γ coord., six-membered chelate; OCoO 93.7 °; CoOP 129, 130 °; CoO 193, 194; H-bond between amine and oxygens	Derived from HIO_5 cleavage of $(NH_3)_4$CoATP; *S*-chirality at P (same as in Mg(ATP) substrate for PRPP synthetase)[b]	5, 8
	$P2_1/n$; α,γ coord., eight-membered chelate; H-bonds between ammines to β,γ oxygens OCoO 94.6 °; CoOP 140, 151 °; CoO 192, 193	Boat configuration (P-1 O-1 P-2 O-2 almost coplanar); many H-bonds; More folded P_3O_{10} structure than in β,γ isomer (above)	6
	$P4_2/mbc$; α,β,γ coord.; two six-membered chelates; OCoO 88.3, 92.9 °; CoO 192, 194	Two chelate rings are mirror images; phosphate units sharply folded.	7
	*Cc*; monodentate pyrophosphate; CoO 192; CoOP 139 °; PO_3P 131.3 ° (unconstrained)	Intramolecular H bonds between ammines and O-1, O-2	8



$P2_1/c$; six-membered chelate; OCoO 92.5°; CoOP 126, 127°; CoO 193.6, 193.9; H bonds between axial ammines and oxygens.

Distorted boat conformation with more packed chelate than in β,γ P_3O_{10} chelate

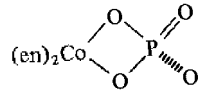
8



$P2_1/c$; six-membered chelate; OCoO 92.8°; CoOP 125, 127°; CoO 193, 195; H bonds between axial ammines and oxygens

Skew-boat conformation, stabilized by H bonding; similar bond lengths to ionic $P_2O_7^{4-}$

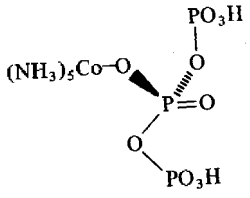
9



$P1$; two independent molecules in unit cell; OCoO 76.0°; CoO 194.8, 193.3; CoOP 92.5, 92.8°; OPO 98.7°

Constrained angles at Co, P in four-membered chelate; discrete $\Delta(\lambda\lambda)$, $\Lambda(\delta\delta)$ chains held together by H bonds

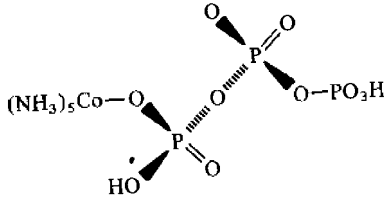
10



$P2_12_12_1$; β-coord. of $H_2P_3O_{10}^{3-}$ ligand; CoO 193.6

Two H bonds with ammines; extended phosphate chain

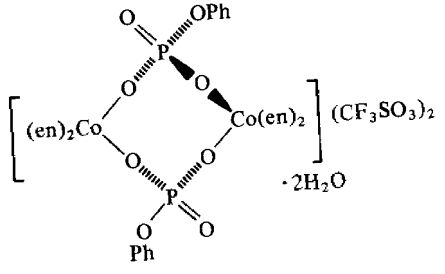
11



$P2_12_12_1$; γ-coord. of $H_2P_3O_{10}^{3-}$ ligand; CoO 191.2

No intramolecular H bonds; helical conformation of phosphate

11

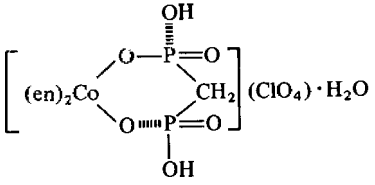
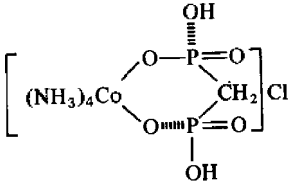
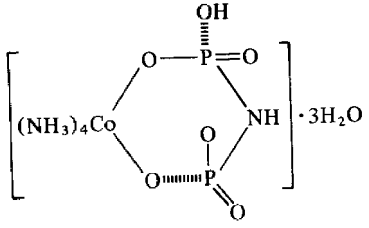
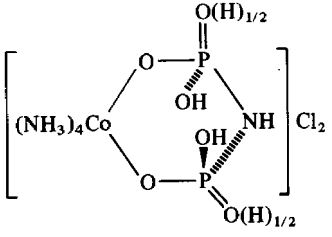


$P2_1/c$; bridging coord. of phosphate ester; CoO 192.2, 195.6; OCoO 94.1

meso (Δ,Λ) isomer formed from $[Co(en)_2Cl_2]ClO_4$ + Ag_2O_3POPh in Me_2SO

12

Table 46 (*continued*)

Complex	*Data*[a]	*Comments*	*Ref.*
	OCoO 94.3°; OPC 109.7°; CoO 193.1	Racemic crystal; no distortion about Co or P	13
	CoO 194; CoOP 131–137°; PO 152; OPC 111°	ATP analogue	14
	$P2_1/c$; OCoO 91.8°; CoO 1.91	Chair conformation; trianionic chelate	15
	$P2_12_12_1$; OCoO 94.4°; CoO 1.93–1.94	Boat-twist boat conformation; monoanionic chelate	15

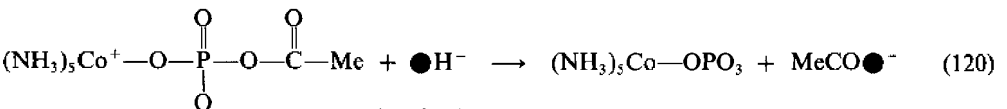
[a] Bond lengths in pm. [b] The *R,S* convention used here assumes the metal (Co, Mg) takes precedence over P and C in all situations.

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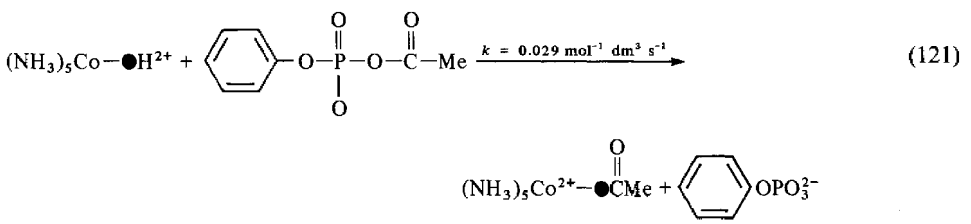
to (**163**) is suggested.[1216] The advantages of metal-coordinated hydroxide over alkoxide in facilitating such cyclizations and hydrolyses are discussed in this report.[1216]

$$(NH_3)_5Co{-}OP(OMe)_3^{3+} + \bullet H_2/\bullet H^- \longrightarrow (NH_3)_5Co{-}\bullet H_2^{3+}/\bullet H^{2+} + PO(OMe)_3 \quad (119)$$

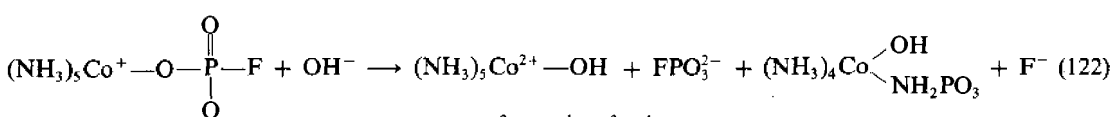
Ligands closely related to orthophosphate esters include acetylphosphate, acetylphenylphosphate and fluorophosphate. Alkaline hydrolysis of $[Co\{OP(O)_2OCOMe\}(NH_3)_5]^+$ occurs exclusively at the carbonyl centre, and the acceleration provided by cobalt(III) four atoms removed is minimal (10 times, equation 120).[546] This is a good comparative example of phosphoryl *versus* acyl hydrolysis, since an excellent leaving group at P is provided (AcO^-) and P is two atoms closer to the activating metal. Likewise the coordinated-hydroxide-promoted hydrolysis of acetylphenylphosphate occurs exclusively at C (equation 121), but the rate enhancement over solvolytic OH^- is in this case significant (10^2 for a 10 mM Co^{III} solution).[546] Hydrolysis at P does not occur even with O-bound monofluorophosphate, with *ca.* 50% hydrolysis occurring at Co^{III} and the remainder involving intramolecular attack of a coordinated amide ion (equation 122).[547] The latter path presumably involves a four-membered chelated amidate intermediate and an enhancement of *ca.* 10^{10} over hydrolysis of FPO_3^{2-} is calculated for this part. Attack by phosphate species such as is found in ADP and ATP synthetases is more difficult. Apparently heating $[Co\{OP(O_2H)F\}(NH_3)_5](ClO_4)_2$ with a solution of NaH_2PO_4 leads to some pyrophosphate complex $[Co(OP_2O_6H)(NH_3)_5]$ but the published details are not very clear.[548]



$$k = 0.53\,mol^{-1}\,dm^3\,s^{-1},\ 25\,^{\circ}C,\ I = 1.0\,M \quad (120)$$



(121)



(122)

$$k = 3.3 \times 10^{-3}\,mol^{-1}\,dm^3\,s^{-1}$$

(iii) Pyrophosphates, triphosphates, ADP and ATP

Preparations are listed in Table 47. Main interest lies in determining how metal ions catalyze the hydrolysis of ADP and ATP. ATP plays a crucial role in the energy metabolism of all living cells and divalent metal ions (Mg^{2+}, Mn^{2+} and Ca^{2+}) play an important role in these phosphoryl transfer processes.[549] Divalent metal ions such as Mg^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+} and Mn^{2+} provide only modest *in vitro* catalysis[550–554] and stronger, more specific coordination to phosphate units appears to be required by the enzyme. Co^{III} (and Cr^{III}) complexes of ADP and ATP have been shown to mimic many of the biological functions of the Mg^{2+} enzyme, and since the cobalt(III)–phosphate coordination remains intact, the specificity of alternative coordination sites, and the stereochemical requirements at phosphorus, have been elucidated in some cases.[555] Often the Co^{III}–enzyme species is biologically active and several enzymic functions of ATP have been examined in this manner.

$HP_2O_7^{3-}$ coordinates to Co^{III} either as a monodentate ligand (terminal O^-) or as a bidentate chelate (six-membered $^-O,O^-$). The complexes are easily made in aqueous solution (equation 123),[556] or by heating sparingly soluble $[Co(N)_{6-n}(H_2O)_{n-6}](HP_2O_7)$ (N = NH_3, en, tn) under a good vacuum at ~100 °C.[557] Chromatographic separation on Dowex or Sephadex anion–cation resins leads to pure species (Table 47). Crystal structures of $[Co\{OP(O)_2OPO_3H\}(NH_3)_5]\cdot H_2O$, $[Co\{O_2P_2O_4(OH)\}(NH_3)_4]\cdot 2H_2O$ and Δ,Λ-$[Co\{O_2P_2O_4(OH)\}(en)_2]\cdot 2H_2O$ are available (Table 46) with the six-membered chelates showing no apparent strain about the Co or P centres. The alternative four-membered ring isomer has not been identified and is unlikely to occur in an equilibrium sense because of chelate ring strain.

This lack of ring strain in the six-membered chelate stabilizes the system towards hydrolysis at

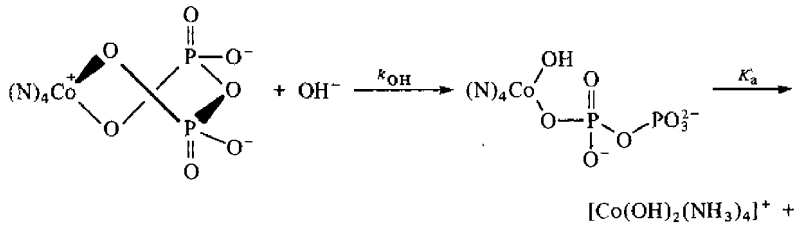
Table 47 Preparations: Di- and Tri-phosphate, Phosphate Ester, Phosphonate and Phosphonamate Complexes

Complex	*Preparation*	*Properties*	*Ref.*
$[Co(OP_2O_6H)(NH_3)_5]\cdot H_2O$	$[Co(CO_3)(NH_3)_5]NO_3$ + HCl; $K_4P_2O_7$, pH 3, 10 min, 80 °C; AG50W × 2 chrom.	Red; ε_{520} 70; ε_{358} 56 (pH 8)	1
$[Co(ADP)(NH_3)_5]$	As above + Na_2HADP, AG50W × 2 chrom.	Red soln.; ε_{518} 71; ε_{353} 59	1
$[Co(O_2P_2O_5H)(NH_3)_4]\cdot 2H_2O$	$[Co(CO_3)(NH_3)_4]NO_3$ + HCl; $K_4P_2O_7$ as above	Red-violet; ε_{522} 70.5; ε_{372} 55 (pH 8)	1
$[Co(ADP)(NH_3)_4]$	As above + Na_2HADP	Red soln.; ε_{517} 64; ε_{359} 68	1
$[Co(HATP)(NH_3)_4]$	As above + Na_2H_2ATP, AG50W × 2 chrom.	Red soln.; ε_{518} 68; ε_{366} 56	1
$[Co(ADP\text{-}\alpha S)(NH_3)_4]$	$[Co(CO_3)(NH_3)]NO_3$ + HCl + ADP S; pH 3; 80 °C, 5 min; Dowex 50W × 2 chrom.	ε_{542} 71 (O,S); ε_{522} 63 (O,O) coord.	2
$[Co(HATP)(NH_3)_3(H_2O)_x]$	Chrom.; ref. 1	Lavender solid; ε_{548} 77; ε_{372} 74	1, 3
$[Co(HATP)(NH_3)_2(H_2O)_x]$	Chrom.; ref. 1	Violet soln.; low yields	1
$[Co(O_2P_3O_8H_2)(NH_3)_4]\cdot H_2O$	$[Co(CO_3)(NH_3)_4]NO_3$ + HCl + $Na_5P_3O_{10}$, pH 3; 10 min, 80 °C; AGI-X2 chrom.	Red; largely β,γ isomer ε_{518} 67; ε_{366} 55 (pH 8); pK_{a_1} 2.2; pK_{a_2} 5.7	1, 4
$[Co(O_2P_2O_5H)(en)_2]\cdot 2H_2O$	*trans*-$[Co(Cl)_2(en)_2]Cl$ + $Na_2H_2P_2O_5$, 10 min, 80 °C; AG50W × 2 chrom.	Red; ε_{512} 106; ε_{369} 77 (pH 8)	1
$[Co(O_3P_3O_7H_2)(NH_3)_3]\cdot H_2O$	$[Co(Cl)_2(NH_3)_3(H_2O)]Cl$ + $Na_5P_3O_{10}$	Violet; α,β,γ-tridentate; ε_{561} 68; ε_{375} 64 (pH 8)	1
$[Co(en)_2\{O_2P(OH)CR(R')P(OH)O_2\}]ClO_4\cdot H_2O$ (R,R′ = H, Me, OH, Ph, NH_2, Cl, *etc.*)	$[Co(Cl)_2(en)_2]Cl$ + Na_2H_2L; aq. 70–80 °C, pH 7; Dowex 50W × 2 chrom.	Red; six-membered phosphonate chelate (structure Table 46)	5

1. R. D. Cornelius, P. A. Hart and W. W. Cleland, *Inorg. Chem.*, 1977, **16**, 2799.
2. I. Lin, A. Hsueh and D. Dunaway-Mariano, *Inorg. Chem.*, 1984, **23**, 1692.
3. S. H. McCaugherty and C. M. Grisham, *Inorg. Chem.*, 1982, **21**, 4133.
4. R. D. Cornelius, *Inorg. Chem.*, 1980, **19**, 1286.
5. S. S. Jurisson, J. J. Benedict, R. C. Elder, R. Whittle and E. Deutsch, *Inorg. Chem.*, 1983, **22**, 1332.

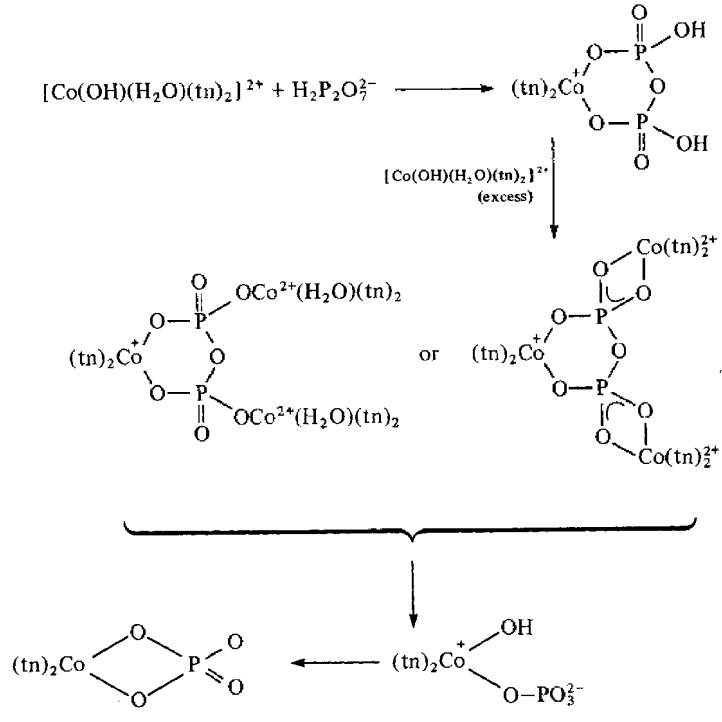
$$\underset{0.01\,M}{[Co(H_2O)_2(NH_3)_4]^{3+}} + \underset{0.01\,M}{H_2P_2O_7^{2-}} \xrightarrow[80\,^\circ C,\ 10\,min]{pH\,3} [Co(O_2P_2O_5H)] \qquad (123)$$

P, and for $(N)_4 = (NH_3)_4$, $(en)_2$, tren and $(tn)_2$ (equation 124), hydrolysis is unimportant over the wide range pH 3–14. At pH values above 11 hydrolysis at Co occurs with the ultimate release of unaffected (no O exchange) $P_2O_7^{4-}$. The monodentate intermediate appears to have some stability since it has been observed, but not isolated. For $(N)_4 = (NH_3)_4$ (equation 124), reduction to Co^{II} becomes an increasing problem at high pH.

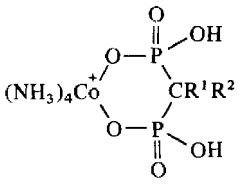


(124)

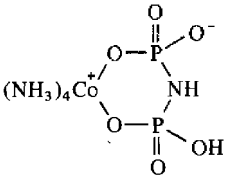
Using ^{31}P NMR in a semi-quantitative sense Hubner and Milburn[558] have shown that with the labile $(N)_4 = (tn)_2$ system multiple coordination to the $HP_2O_7^{3-}$ unit is possible when excess Co^{III} reagent is present. Then hydrolysis at P (probably stoichiometric rather than catalytic) ensues with a maximum rate at pH $\approx$ 7. This suggests $[Co(OH)(H_2O)(tn)_2]^{2+}$ is the reactive ingredient. At pH 5 ($[Co] = 0.3$, $[H_2P_2O_7^{2-}] = 0.1$ mol dm^{-3}) a half-time for $H_2PO_4^-$ production of about 1 h compared to 10 years for the uncoordinated ligand demonstrates the accelerating effect of the additional Co^{III} unit(s). Although no reactive species have been identified, Scheme 59 gives some of the possibilities. Crystal structures are available for the diphosphonate (PCP) and diphosphoamidate (PNP) analogues (**164**) and (**165**) (Table 46) and these have been used as probes for H transfer, Ca^{2+} binding, and cleavage patterns in phosphoryl transfer. Thus the potato enzyme apyrase catalyzes the hydrolysis of $[Co(PXP)(NH_3)_4]$ species (X = O, N) to give $[Co(OPO_3)_2(NH_3)_4]$ with the possible intermediacy of $[Co(OPO_3)(OPO_2NH_3)(NH_3)_4]$ in the case of X = N.[573]



Scheme 59

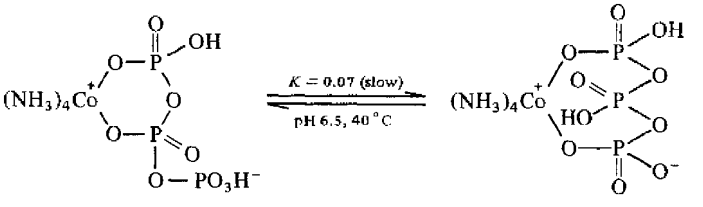


(164) R^1, R^2 = H, Me, OH, Bu^t, NH_2, Cl, NMe_2

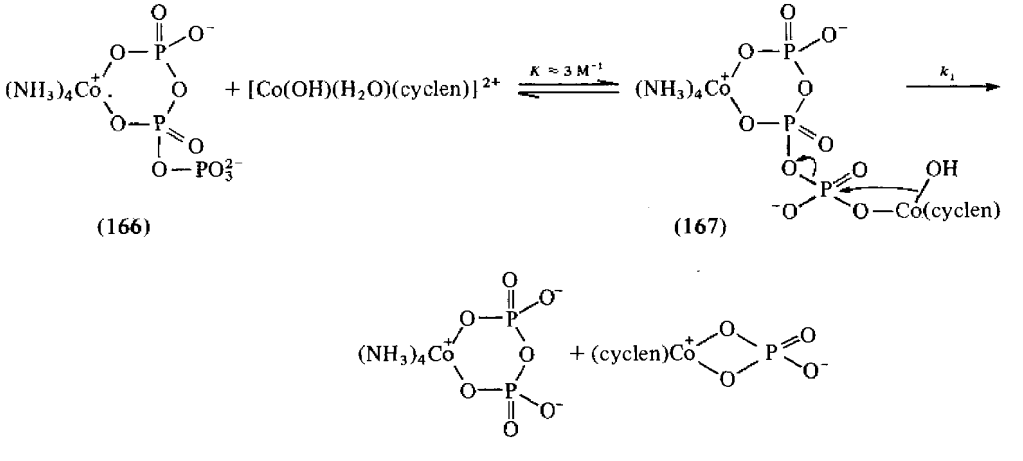


(165)

$H_2P_3O_{10}^{3-}$ can act as a monodentate (terminal O^-), bidentate (β,γ, six membered; α,γ, eight membered) and tridentate (α,β,γ, six membered) ligand system (crystal structures Table 46). The β,γ six-membered chelate is particularly interesting since it is the only structure to have an asymmetric P centre. Although prepared from $[Co(NH_3)_4(OH_2)_2]$ and $H_2P_3O_{10}^{3-}$ as a racemic mixture, the crystal structure was carried out on the isomer isolated from $[Co(ATP)(NH_3)_4]$ by periodate cleavage, and has the absolute (*S*) chirality. All structures (Table 46) indicate little or no strain at either Co or P, although sharply folded units are often involved. As with chelated $HP_2O_7^{3-}$ little or no accelerated hydrolysis at P occurs in the absence of additional metal activation and this appears to be independent of ring size (equation 125).[559,560,561] This is consistent with the absence of distortion at the tetrahedral P centres. Some accelerated hydrolysis at alkaline pH values results from the slower hydrolysis for the parent $P_3O_{10}^{5-}$ compared to the protonated species rather than from a significant increase in k_{obs} for the chelate. Table 48 gives some hydrolysis data for $[Co(O_2P_3O_8)(NH_3)_4]^{2-}$ and the β and γ isomers of $[Co(OP_3O_9)(NH_3)_4]^{2-}$. The presence of additional Co^{III} reagent significantly accelerates the reaction, especially with species having two available *cis* coordination sites.[562,563] The pH variation in k_{obs} has been interpreted as intramolecular hydrolysis by coordinated hydroxide in the bifunctionalized system (**167**; Scheme 60) and the derived rate $k_1 = 0.01\ s^{-1}$ represents an acceleration of $\sim 3 \times 10^4$ compared to the initial chelate (**166**) and 5×10^5 compared to $P_3O_{10}^{5-}$, so considerable activation has been achieved. $[Co(OH)_2(cyclen)]^+$ also initiates hydrolysis in monodentate β- and γ-$[Co(OP_3O_9)(NH_3)_5]^{2-}$ systems[564] (formation of PO_4^{3-} + $[Co(OP_2O_7)(NH_3)_5]^-$ is 50-fold faster for the β isomer) but the effect is considerably smaller and does not appear to show the same pH variation. None of the reactive intermediates have been isolated in these studies, or indeed clearly identified, so that considerable uncertainty remains as to details. However distortion about the P centre undergoing hydrolysis seems a necessary requirement, and it is likely that this can only be achieved in four-membered chelates.



(125)



(166) (167)

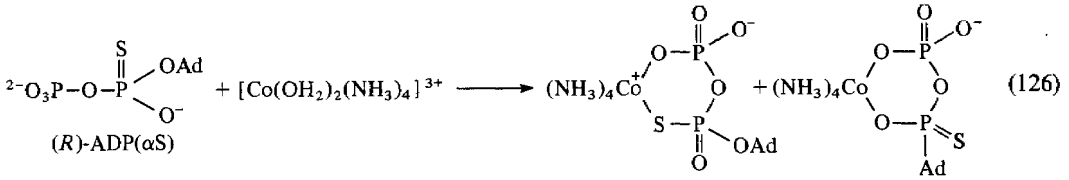
Scheme 60

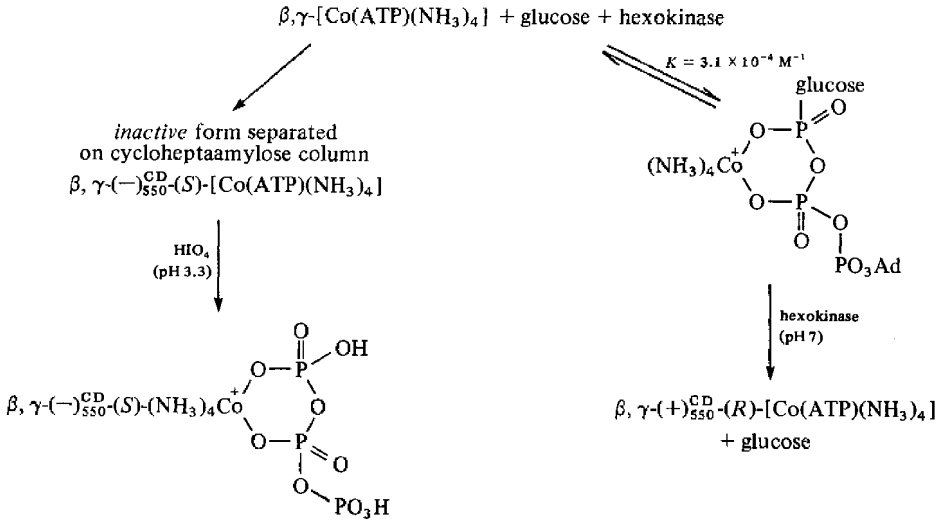
Table 48 Accelerated Hydrolysis at Phosphorus in β,γ-$[Co(NH_3)_4O_2P_3O_8]^{2-}$ [1]

Activating species[2]	*pH*	*Relative rate*	$10^5 k_{obs}(s^{-1})$
$P_3O_{10}^{5-}$ (free ligand)	6.0	1[3]	–
None	6.0	7	0.16
None	9.0	160	~0.3[4]
$[Co(teta)(H_2O)(OH)]^{2+}$	6.0	7	–
$[Co(Me_6dien)(H_2O)(OH)]^{2+}$	6.0	12	–
$[Co(NH_3)_5OH_2]^{3+}$	6.0	26	–
$[Co(NH_3)_4(H_2O)_2]^{3+}$	6.0	700	–
$[Co(cyclen)(H_2O)(OH)]^{2+}$	6.0	66	1.5
	7.0	–	6.2
	8.0	–	33
	8.5	–	50
	10.12	–	54

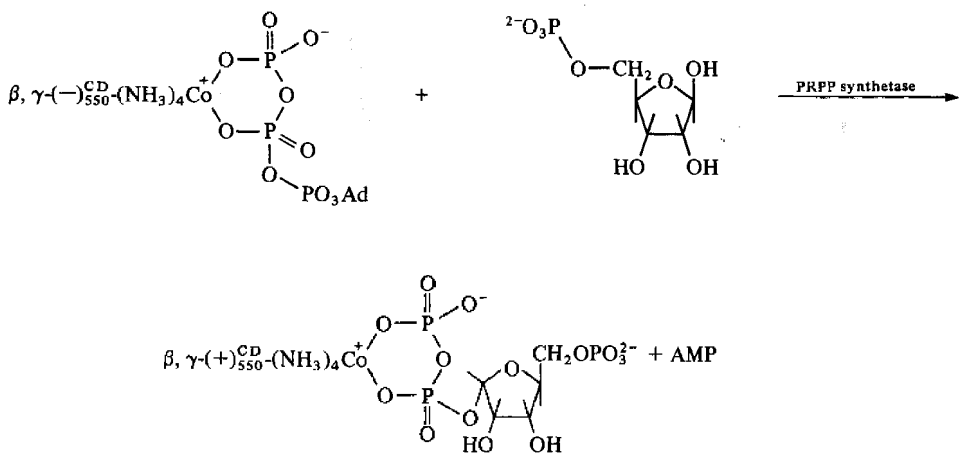
1. P. R. Norman and R. D. Cornelius, *J. Am. Chem. Soc.*, 1982, **104**, 2356.
2. $[Co(NH_3)_4O_2P_3O_8]^{2-}$ = 25 mM; [activating complex] = 20 mM.
3. At pH 6 $k_{hyd} = 2.3 \times 10^{-7}\ s^{-1}$ (40 °C).
4. For β-$[Co(NH_3)_5OP_3O_9]^{2-}$ $k_{obs} < 10^{-6}s^{-1}$ and for γ-$[Co(NH_3)_5OP_3O_9]^{2-}$ $k_{obs} < 10^{-8}\ s^{-1}$ (*i.e.* little or no acceleration over free ligand). T. P. Haromy, P. F. Gilletti, R. D. Cornelius and M. Sundaralingam, *J. Am. Chem. Soc.*, 1984, **106**, 2812.

Several complexes of the $[Co(HATP)(NH_3)_n]$ (n = 2, 3, 4) and $[Co(ADP)(NH_3)_n]$ (n = 4, 5) variety have been prepared and isolated (as solids or as aqueous solutions; Table 47). Spectral data (^1H and ^{31}P NMR, UV–visible) have been reported.[556] Likewise the diastereoisomeric ADP(αS) coordinates with a preference for (O,S) binding (equation 126).[565] No crystal structures are available, but the configuration of the inactive form of $[Co(HATP)(NH_3)_4]$, isolated from the yeast-hexokinase-mediated synthesis of glucose 6-phosphate ADP, has been characterized following periodate cleavage and a crystal structure on the resulting $[Co(O_2P_3O_8H_2)(NH_3)_4]$[566] is available (Table 46; Scheme 61). The (*S*) configuration at P requires the (*R*) diastereoisomer of β,γ-$[Co(HATP)(NH_3)_4]$ to be the active ingredient in the enzymic process.[567] This strongly implies similar β,γ coordination and an (*R*) configuration for MgATP. Likewise, phosphoribosyl-pyrophosphate (PRPP) synthetase specifically utilizes the β,γ-$(-)^{CD}_{550}$-(*S*)-$[Co(ATP)(NH_3)_4]$ diastereoisomer in the phosphorylation of ribose 5-phosphate[568] but in this case the phosphorylated ribose product containing the metal has the opposite CD from the starting material implying that inversion at P has occurred (Scheme 62). The (*R*)- and (*S*)-α,β-$[Co(ADP)(NH_3)_4]$ diastereoisomers have been separated on cycloheptaamylose[566] and assignments of configuration follow the above ATP complexes.



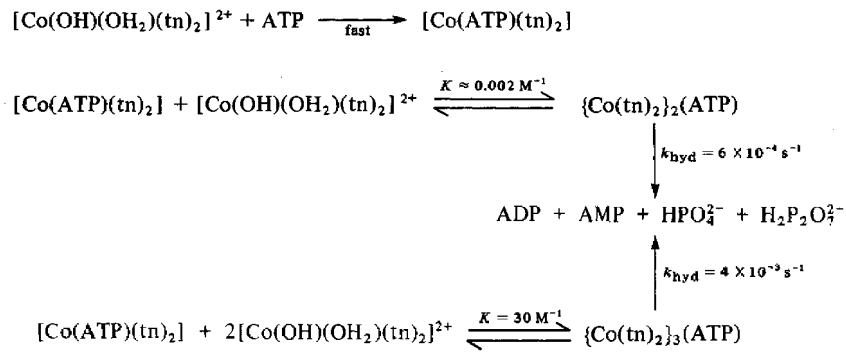


Scheme 61

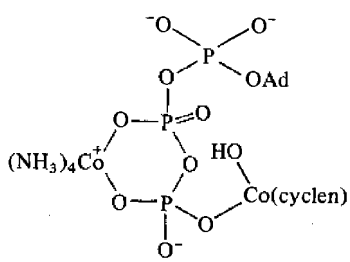


Scheme 62

As found with $H_2P_2O_7^{2-}$ and $H_2P_3O_{10}^{3-}$ hydrolysis of ATP and ADP can be accelerated by $[Co(OH)(OH_2)(N)_4]^{2+}$ species[570,571] and by the hydrolysis products of $[Co(Cl)_3(dien)]$.[572] The $(N)_4 = (tn)_2$ complex shows no acceleration for a 1:1 ratio, but the 2:1 metal:ATP mixture (0.1–0.01 mol dm^{-3} ATP) shows $\sim 10^5$ enhancement at pH 7. Scheme 63 summarizes these findings. At high pH hydrolysis of the Co^{III} complex predominates. $[Co(cyclen)(H_2O)_2]^{3+}$ also catalyzes the hydrolysis of $[Co(NH_3)_4(ATP)]^-$ at pH 8–9, and (**168**) has been claimed as the reactive species.[581] In all these studies however no intermediates have been positively identified, and the immediate products, coordinated or otherwise, also lack definition.



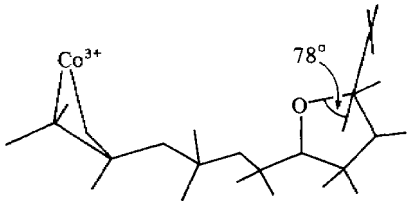
Scheme 63



(**168**)

Stable Co^{III} ADP and ATP complexes have been used as competitive inhibitors in a number of enzymic studies and some progress has been made at unravelling the requirements of the active sites. Steady-state kinetic studies show β,γ-$[Co(ATP)(NH_3)_4]$ to compete with MnATP for $(Na^+ + K^+)$, Mg^{2+} and Ca^{2+} ATPases derived from kidney medulla.[574] K_i values for β,γ-$[Co(ATP)(NH_3)_4]$ are similar to the K_m values for MnATP for both the $(Na^+ + K^+)$ and Mg^{2+} enzymes, and ^{31}P NMR shows that the Co^{III} complex acts as a substrate for the Mg^{2+} and Ca^{2+} systems. Likewise,

$(-)_{505}$-[Co(ATP)$(NH_3)_4$] and $(-)_{532}$-[Co(ADP)$(NH_3)_3(H_2O)$] compete with MgADP for the active site of creatine kinase although they are not as effective in this role as similar Cr^{III} species.[575] Werber and coworkers have used an uncertain Co(phen)ATP complex to probe the active ATPase site of the energy-releasing myosin enzyme.[376,377] A more recent publication suggests that the initial inhibitor may be a $Co^{II}(phen)_x$ species and that the site of inactivation is not the true active site of the enzyme.[578] The paramagnetic effects of enzyme-bound Mn^{2+} on the ^1H and ^{31}P T_1 relaxation rates of β,γ-[Co(ATP)$(NH_3)_4$] have been used to describe the active site of cAMP-dependent bovine-heart kinase.[579,580] β,γ-[Co(ATP)$(NH_3)_4$] competes with MgATP (and MnATP) for the nucleotide binding site in the enzyme and the T_1 data suggest that Mn^{2+} (attached to an adjacent inhibitory site) coordinates to either all three α,β,γ or the α,γ phosphates of β,γ-[Co(ATP)$(NH_3)_4$]; the latter possibility is favoured.[579] A decision on the two possible orientations of the adenosine ring about the glycosidic bond has been made possible by nuclear Overhauser studies, with the antiglycosidic structure shown by (**169**) being favoured.[580]



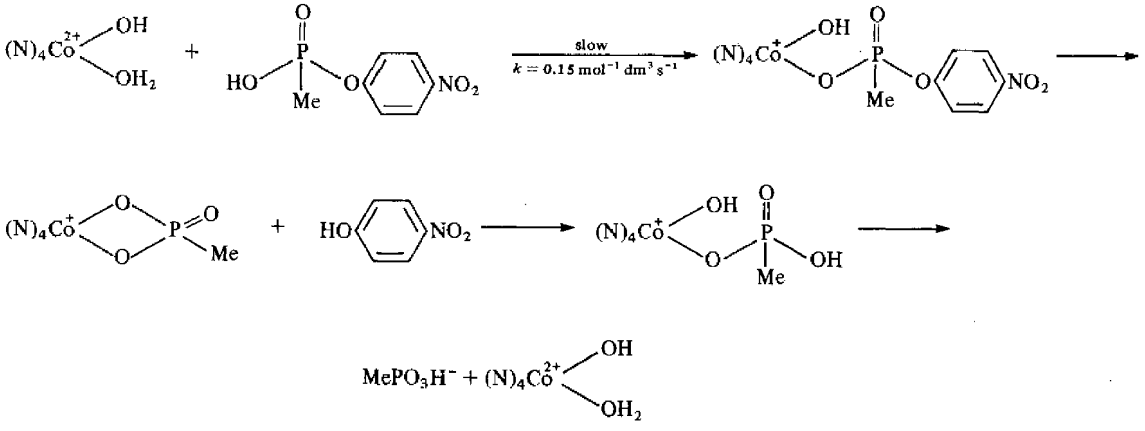
(**169**) Co(ATP)$(NH_3)_4$-bound protein kinase

(*iv*) *Phosphonates, phosphoamidates, phosphites and their esters*

Busch and Pennington have prepared the $[Co\{OP(O_2H)CH(Me)NH_3\}(NH_3)_5]^{2+}$ ion containing O-bound 1-aminoethylphosphoric acid, but it remains to be isolated and fully characterized.[582] The terminal amine group has a pK_a of 3.2 and the deprotonated complex acts as a bridge for intersphere electron transfer with $Cr^{2+}_{(aq)}$.[582] A series of diphosphonate chelates of type (**164**) have been prepared (Table 47) and fully characterized.[583] Crystal structures on the parent (R^1, R^2 = H) bis(ethylenediamine) and tetraammine complexes are available (Table 46). Complex (**164**) binds Ca^{2+} strongly (K varies from 4×10^3 to 2×10^6 mol dm^{-3}), particularly when R = OH, and this implies a similar role for radioactive ^{99m}Tc-bound pyrophosphonates and pyrophosphates, which are used as skeletal imaging reagents.[584]

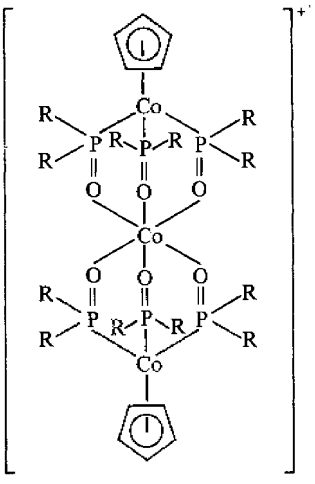
N-bound phosphoamidate in $[Co(NH_2PO_3H)(H_2O)(NH_3)_4]Cl_2$ has been prepared by treating O-bound $[Co\{OP(O_2H)PhNO_2\}(NH_3)_5]^{2+}$ with 3 mol dm^{-3} NaOH.[541] It is easily removed from the metal by treating with acid, but further characterization seems desirable; O,O-chelated amidates such as (**165**) have been prepared and a crystal structure is available (Table 46).

Several $[Co(OH)(OH_2)(N)_4]^{2+}$ systems catalyze the hydrolysis of *p*-nitrophenylmethylphosphonate (PMP) and its ethyl ester (EPMP) [$(N)_4$ = tme > tn > trien ≫ bipy], possibly *via* the sequence shown by Scheme 64 with rate-determining coordination of the ester.[584] This involves an acceleration of $> 10^4$ at pH 7.6 (1.5 mM complex) but none of the intermediates have been characterized. Recycling of the $[Co(OH)(OH_2)(N)_4]^{2+}$ reagent appears to be involved.



Scheme 64

Klaui has recently described the first clear example of a $^5T_2$ (high spin) $\rightleftharpoons$ $^1A_1$ (diamagnetic) spin equilibrium in an octahedral Co^{III} complex using the phosphito complex $[Co(OPR_2)_3Cp]$ (R = OR, Et) as a tridentate ligand.[585,586] Complex (**170**) has been isolated (ClO_4^- and PF_6^- salts) following electrochemical oxidation of the neutral Co^{II} complex. The six phosphite oxygens provide a ligand field about the central metal intermediate between H_2O (low spin) and F^- (CoF_6^{3-}, high spin) with the complexes being green and paramagnetic at elevated temperatures (μ = 4.1 BM, R = Et, 393 K) and yellow and diamagnetic below 200 K. The behaviour is reversible, occurs both in the solid and in solution, and is R dependent.[586] ^{31}P NMR studies show little solvent influence on the spin equilibrium, with $\Delta H^\circ = 24\,kJ\,mol^{-1}$, $\Delta S^\circ = 70\,J\,mol^{-1}\,K^{-1}$ in four different solvents.[587] It is concluded that inner-sphere electronic effects are responsible for the equilibrium position.

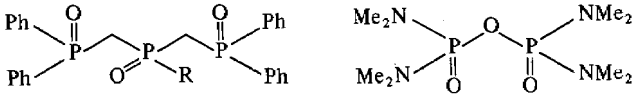


(170)

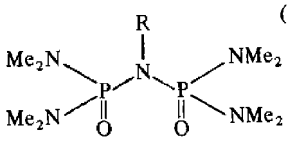
(*v*) *Phosphine oxides, phosphoramides and phosphinates*

These are largely restricted to Co^{II} and Co^{III}. The former are invariably tetrahedral and the latter octahedral, sometimes with ligand-induced distortion. An early paper by Goodgame and Cotton discusses some spectroscopic properties[588] and MCD spectra have been investigated by Kato and Akimoto.[589] A review covering recent chemistry is available.[590] Table 49 lists some structural information.

Co^{II} complexes containing phosphoramides ($O = P(NR^2)_3$)[591] iminophosphoranes ($RN = PPh_3$)[592] and phosphinates ($^-O_2PR^1R^2$)[593] are known, as are distorted octahedral complexes containing the neutral chelating ligands (**171**),[594] (**172**)[595] and (**173**).[596]



(171) (172)

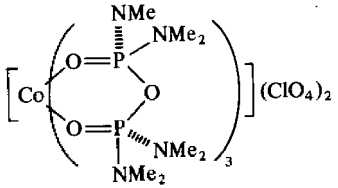


(173)

47.6 ARSENIC LIGANDS

The softer and larger As atom results in weaker coordination to all first-row transition elements. $As(OR)_3$ and AsX_3 (X = halogen) coordination to cobalt has not been well characterized. Arsines (AsR_3) form longer and weaker bonds with the σ-donor power decreasing in the order NR_3

Table 49 Structures: Some Phosphine Oxide Complexes of Cobalt(II)

Complex	*Structural data*[a]	*Comments*	*Ref.*
$[Co(NO_3)_2(OPMe_3)_2]$	CoO(P) 192–195; CoO(N) 215–223; POCo 133, 140°; ONO 115, 122°	Six-coordinate; bidentate O_2NO^-	1
$[Co(NO_3)_2(OPPh_3)_2]$	CoO(P) 199; CoO(N) 213, 217; POCo 158.5°; ONO 116.7, 120–123°; (N)OCoO(N) 58.3°	Dist. oct.	2
$[CoCl_2(OPPh_3)_2]$	CoCl, 220; CoO, 200; ClCoCl, 114°; OCoO 96.4°; CoOP 153	Dist. tet.	3
$[CoCl_2\{dppe(O_2)\}]$	CoCl 225; CoO 197; ClCoCl 114.7°; OCoO 102.2°; CoOP 148, 139°	Tet.; infinite chains of $CoCl_2$, oxidized dppe(O_2) ligand	4
$[CoCl_2(OPPh_2NHBz)_2]$	CoCl 223.5; CoO 192; ClCoCl 116.5°; OCoO 106.6°; CoOP 160.3°	Tet.; O bound	5
	CoO 208.5; OCoO 87.9°	Oct.	6

[a] Bond lengths in pm.

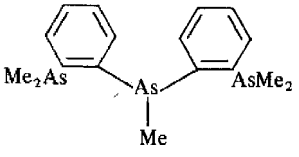
1. F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, 1963, **85**, 2402.
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(Co—L ≈ 200 pm), PR_3 (225), AsR_3 (233). Few low-oxidation-state complexes have been reported and no crystal structures. The alkyl-substituted arsines of Co^{II} are usually easily air-oxidized to Co^{III} complexes, but this is difficult with phenyl- and aryl-arsines. Further oxidation to Co^{IV} does not appear to be possible.

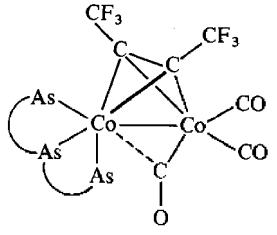
47.6.1 Cobalt(−I), Cobalt(0) and Cobalt(I)

$AsPh_3$ displaces alkene from $[Co(C_8H_{13})(C_8H_{12})]$ under H_2 to form $[HCoH(AsPh_3)_4]$, and under suitable conditions $[CoH(N_2)(AsPh_3)_3]$ and $[Co(H)_3(AsPh_3)_3]$ can be obtained.[598] Several Co^0 complexes containing CO and NO ligands in addition to AsR_3 are known. $[Co(NO)(L)_{1,2}(AsR_3)_{2,1}]$ and $[Co(NO)_2L(AsR_3)]$ are tetrahedral or close to tetrahedral with linear or nearly linear bonding of NO. Some preparations are given in Table 50 and structures in Table 51.

Several nominally Co^0 complexes containing chelated arsines are known and a recent study of the coordination of **(174)** to $[Co_2\{C_2\{CF_3\}_2\}(CO)_6]$ resulting in structure **(175)**[599] typifies organocobalt work in this area.

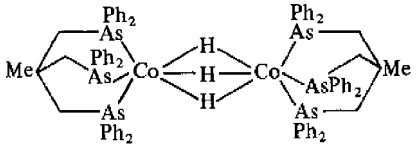


(174) ttas

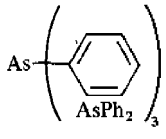


(175)

Diamagnetic $[Co\{MeC(dpam)_3\}(CO)_2](BPh_4)$ containing the tridentate arsine tris(diphenylarsinomethyl)ethane is formed on treating the paramagnetic Co^{II} dimer **(176)** with CO, and a similar five-coordinate complex $[Co\{As(dpap)_3\}(CO)](BPh_4)$ containing ligand **(177)** has been prepared from $[Co_2(CO)_8]$ (Table 50). Structures of these monomeric systems are not known.



(176)



(177)

47.6.2 Cobalt(II)

Unlike their phosphine analogues monotertiary arsines do not readily combine with simple Co^{II} halides. Anhydrous CoX_2 with $AsEt_3$ *in vacuo* forms unstable $[Co(X)_2(AsEt_3)_2]$ species,[600] and $[Co(I)_2(AsPh_3)_2]$ has been isolated from nitromethane solution.[601]

Bidentate arsines form more stable complexes and some preparations are given in Table 50. The electronic spectrum of red-brown $[Co(I)_2(dpav)]$ **(178)** is inconsistent with a tetrahedral geometry and it may be planar (μ = 2.9 BM), but $[Co(X)_2(dpae)]$ **(179)** (X = Cl^-, Br^-, I^-) is almost certainly tetrahedral.[487] The asymmetric phenyl analogue forms $[Co(mpae)_2](CoX_4)$ as the solid and a planar structure is possible for the cation (μ = 2.1 BM for the ClO_4^- salt).[602] Bis(diphenylarsino)methane forms green $[Co_3(dpam)_4I_6]$ of unknown structure and low stability. Four-coordinate planar structures for complexes $[Co(As—As)_2](ClO_4)_2$ have not been positively identified with the poorer aryl or vinyl As donors (see below) but dark green $[Co(dmav)_2](CoCl_4)$ is probably planar (μ = 2.6 BM for cation).[603] Attempts to prepare five-coordinate $[CoX(diars)_2]^+$ complexes (diars = **180**) have not been successful for X = Cl^-, Br^-, I^-, but for X = NCS^- excess ligand results in $[Co(NCS)(As—As)_2]^+$ (As—As = dpav, dpae), and using a 1:1 ratio of ligand to metal the non-electrolyte $[Co(NCS)_2(diars)_2]$ has been isolated which may be planar (μ = 2.6 BM).[487] Irradiation of a mixture of *cis* and *trans* bis(dimethylarsine)ethylene with CoX_2 results in $[CoX(dmav)_2]X$, which is five-coordinate; a 1:1 electrolyte in solution (X = Cl^-, Br^-, I^-), its magnetic moment in the solid state

Table 50 Preparations: Some Cobalt–Arsine Complexes

Complex	*Preparations*	*Properties*[a]	*Ref.*
Cobalt(0,I)			
$[Co(CO)_3(AsPh_3)_2][Co(CO)_4]$	$Co_2(CO)_8 + AsPh_3$; Et_2O, 0 °C	Brown	21
$[Co(NO)(CO)_2(AsPh_3)]$	$[Co(NO)(CO)_3] + AsPh_3$; C_6H_6, r.t.	Red-brown; ν_{CO} 2044, 1986; ν_{NO} 1765	15
$[Co(NO)(CO)(AsPh_3)_2]$	$[Co(NO)(CO)_2(AsPh_3)] + AsPh_3$; C_6H_6	Red-brown; ν_{CO} 1959; ν_{NO} 1722	15
$[Co(NO_2)(Br)(AsPh_3)]$	$[Co(NO)_2Br]_2 + AsPh_3$; THF, warm	Black; diamagnetic	16
$[Co(NO)_2(CN)(AsPh_3)]$	$[Co(NO)_2Br(AsPh_3)] + NaCN$; EtOH	ν_{CN} 2094; ν_{NO} 1857, 1792	17
$[Co(NO)_2(NCS)(AsPh_3)]$	$[Co(NO)_2(NCS)]_2 + AsPh_3$; r.t.	Black	18
$[Co(NO)_2(SPh)(AsPh_3)]$	$[Co(NO)_2(SPh)]_2 + AsPh$	Black-brown	18
trans-$[Co(NO)(AsPh_3)SEt]_2$	$[Co(NO)(CO)_2AsPh_3] + EtSH$; C_6H_6	Brown; ν_{NO} 1691; EtS^--bridged dimer	19
cis-$[Co(NO)(AsPh_3)SPh]_2$	$[Co(NO)(CO)_2AsPh_3] + PhSH$; MeOH	Black-brown; ν_{NO} 1718, 1692; RS^--bridged dimer	19
$[Co\{As(dpap)_3\}CO]Y$	$Co_2(CO)_8 + L$; THF, reflux, 15 min	Orange; diamagnetic	13
($Y = Co(CO)_4^-$, BPh_4^-)			
$[Co\{MeC(dpam)_3\}(CO)_2](BPh_4)$	$[Co_2(H)_3L_2](BPh_4) + CO$; CH_2Cl_2, heat	Red-orange; diamagnetic; 1:1 elect; ν_{CO} 2020, 1972	14
$[Co(CNPh)_3(AsPh_3)_2]ClO_4$	$[Co(CNPh)_5](ClO_4)_2 + AsPh_3$; CH_2Cl_2, 25 °C, 10 min	Deep red; ν_{CN} 2065; ^1H NMR, visible spectra	22
Cobalt(II)			
trans-$[Co(X)_2(das)_2]$	$CoX_2 + das$; EtOH	Yellow-brown; IR; magnetic data, $\mu = 2.0$–2.4; possible five-coord. in soln.; oct. in solid	1, 8
(X = Cl, Br, I, NCS, NO_3, ClO_4)			
$[Co(I)_2(dpav)]$	$CoI_2 + dpav$; EtOH	Red-brown; $\mu = 2.9$	6
$[Co(NCS)(dpav)_2]$	$Co(ClO_4)_2 + dpav + NaNCS$; EtOH	Brown; $\mu = 1.96$	6
$[CoX(dmav)_2]$	$CoX_2 + L$; EtOH + Et_2O + H_2O, N_2; irrad. UV, 8 h	Yellow-brown; $\mu = 1.9$–2.1; IR	7
(X = Cl, Br, I, NO_3)			
$[Co\{MeAs(dmap)_2\}](ClO_4)_2$	$Co(ClO_4)_2 + L$; acetone H_2O; boil, N_2, 1 h	Yellow-green; $\mu = 1.96$	11
$[Co_2\{MeC(dpap)_3\}_2(\mu\text{-}H_3)]$	$Co(BF_4)_2 \cdot 6H_2O + L$; BuOH, 0 °C, $NaBH_4$; $NaBPh_4$	Mauve; $\mu = 3.17$	14
Cobalt(III)			
trans-$Na[Co(CN)_4(AsPh_3)]$	$Na_5[Co(SO_3)_2CN_4] + AsPh_3$; HOAc, 75 °C, 10 h	Orange-yellow; diamagnetic	12
$[Co(das)_3](ClO_4)_3$	$Co(das)_2(OAc)_2$; EtOH, air, $NaClO_4$	Yellow; diamagnetic	10, 11
trans-$[Co(Cl)_2(das)_2]Cl$	$Co(OAc)_2 \cdot 4H_2O + das + HOAc$; EtOH, H_2O, air 1 min; HCl, 5 min	Green; ^1H NMR, IR, visible	2, 3, 9
$[Co(CO)_3(das)_2]ClO_4 \cdot CH_2Cl_2$	*trans*-$[Co(Cl)_2(das)_2]Cl + Li_2CO_3$; MeOH, heat	Orange, ^1H NMR, IR	2
cis-$[Co(Cl)_2(das)_2]Cl \cdot 0.5HCl \cdot 4H_2O$	$[Co(CO_3)(das)_2]^+$ soln. + HCl	Red; ^1H NMR, IR resolved (Δ,Λ)	2
trans-$[Co(Br)_2(dmav)_2]Br$	$CoBr_2 + dmav$; MeOH, 55 °C, air, 48 h	Green; *cis* spectra	4
trans-$[Co(NO)X(das)_2](ClO_4)$	*trans*-$[Co(X)_2(das)]$; MeOH + NO	Brown-red; IR spectral conditions, bent CoNO	5, 20
(X = Cl, Br, I, NCS, ClO_4)			
$[CoX_2(dmav)_2]X$	$[Co(X)_2(dmav)] + HCl$; EtOH boil, 1 h, air	Green; diamagnetic, IR spectrum	4, 7
(X = Cl, Br, NCS)			
$[Co(dmav)_3](BF_4)_3$	$Co(BF_4)_2 + L$; EtOH, N_2	Yellow; ε 24 400, 980(DMF)	7
$[CoX_3\{MeAs(dmap)_2\}]$	CoX_2 (or $Na_3[Co(NO_2)_6]$) + L + HX; EtOH, air	Black (I, Br) to red (NCS); diamag.	11
(X = Cl, Br, I, NCS, NO_2, NO_3)			
$[CoX_2\{As(dmap)_3\}]ClO_4$	$CoX_2 + LiClO_4 + L$; EtOH, N_2, air, overnight	Red (Cl, NCS), Brown (Br, I); diamagnetic; visible spectrum	23
(X = Cl, Br, I, NCS)			

α,β-*trans*-$[CoCl_2(RR,SS\text{-tetars})]Cl$	$CoCl_2 \cdot 6H_2O$ + L + HCl; MeOH, air, 3 h	Blue (α); resolved using (−) dibenzoyl (+) tartaric acid. red-brown (β); green (*trans*)	24 25
trans-$[CoH(X)(As—As)_2]ClO_4$	*cis*-$[CoCl_2(As—As)_2]Cl$ + HOAc; MeOH, N_2, $NaBH_4$	Brown; *trans* configuration, IR, ^1H NMR	26
$[(As—As)_2 = (das)_2$, tetars]			
trans-$[Co(R)_2(das)_2]ClO_4$ (R = H, Me)	*trans*-$[CoCl_2(das)_2]Cl + NaBH_4$; hot MeOH	Yellow-brown; *trans* configuration, IR, ^1H NMR	26
α,β-*trans*-$[Co(Cl)_2(qars)]Cl$	$Co(OAc)_2 \cdot 4H_2O$ + L; MeOH, Et_2O; air, 3 h, HCl	Brown-violet (α); ^1H NMR, visible eqm. data; green (*trans*)	27
α,β,*trans*-$[Co(X)_2(fars)]X$ (X = Cl, Br)	$Co(OAc)_2 \cdot 4H_2O$ + L; MeOH, Et_2O; air, 2 h, HX	Brown-green *trans* (Br); green (*trans*) (Cl)	27

[a] IR data in cm^{-1}; μ values in BM.

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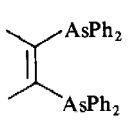
Table 51 Structures: Some Cobalt–Arsine Complexes

Complex	*Structural data*[a]	*Comments*	*Ref.*
Cobalt(II)			
$[Co(OClO_3)(OAsMePh_2)_4]ClO_4$	CaO(As) 202; OCoO 85–95°	Dist. tet. pyr.; four equiv. arsine oxide groups	1
trans-$[Co(OClO_3)_2(das)_2]$	CoAs 229–230; CoO(ClO_3) 280–330	Planar; two crystalline forms; with v. long CoO bonds in axial sites	2
$[Co_2(H)_3\{MeC(dpam)_3\}_2](BPh_4)$	CoCo 237.7; CoAs 232–237; CoH 157–184;	μ_3-bridged hydride dimer	6
Cobalt(III)			
trans-$[Co(Cl)_2(das)_2]ClO_4$	CoAs 234; CoCl 222; AsCoAs 88°	Oct.	3
trans-$[Co(Cl)_2(das)_2]Cl$	CoAs 233–4; CoCl 226; AsCoAs 88.6°	Oct.; isostructural with Ni^{III} complex	4
$[Co(NO)(das)_2](ClO_4)_2$	CoAs 233–236; AsCoAs 85° CoNO 178°; CoN 168	Trig. bipyr.; NO in eq. plane	5
trans-$[Co(NO)NCS(das)_2]NCS$	CoN(CS) 212; CoAs 234–235; AsCoAs 86°; NCoAs 85–92°	Oct.; *trans* NO, NCS	5
trans-$[CoCl\{As(OH)MePh\}(DMGH)_2]\cdot H_2O$	CoAs 231, 232; CoCl 228.6; CoN 190(av): AsO 176	Oct.; probably MePhAs(OH) coord.	7
$Co[Co\{As(O)MePH\}(DMGH)(DMG)]_2$	$Co^{II}O$ 208; CoP 230; CoAs 236; CoN 187–191; AsO 166	Oct.; *trans* CoAs bond with $As(O^-)$ bonded to central Co^{II} ion	8
Δ-$(+)_{546}$-*cis*β-$[Co(O_2)\{R,R\}$-tetars$\}]ClO_4$	CoO 186.7; CoAs 229–232; OO 142.4; OCoO 44.9°	Dist. oct.; side-on bonding of O_2^{2-}	9

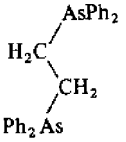
[a] Bond lengths in pm.

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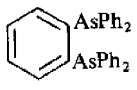
(μ = 1.96–2.16 BM) is consistent with pentacoordination.[603] $[CoX_2(das)_2]$ (das = **181**) is likely to be *trans* octahedral in the solid state although magnetic data are in the range found for five-coordinate Co^{II}.[604] The structure of $[Co(OClO_3)_2(das)_2]$ shows long bonds in the axial positions of a tetragonally distorted octahedraon (Table 51). In ionizing solvents such as nitromethane a planar geometry for $[Co(das)_2]^{2+}$ is possible, although Bosnich, Jackson and Lo suggest dimerization in acetonitrile.[606] The related ligand (**182**) forms green paramagnetic $[Co(nas)_3](CoCl_4)$ and yellow diamagnetic $[Co(nas)_3](ClO_4)_2$, and dimerization is possible for the latter and octahedral coordination for the former.[607] Reduction of $[Co(H_2O)_2(das)_2](ClO_4)_3$ with primary alcohols leads to the dimer (**183**), which is essentially diamagnetic (μ = 0.7 BM).[606]



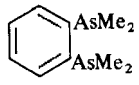
(178) dpav



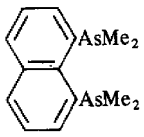
(179) dpae



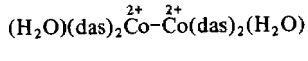
(180) diars



(181) das



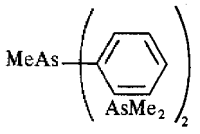
(182) nas



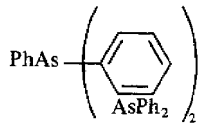
(183)

The branched ligand (**184**) forms unstable $[Co\{MeAs(dmap)_2\}_2]^{2+}$ salts with possibly the apical As remaining uncoordinated,[608] but no Co^{II} complexes have been reported with the softer ligand (**185**) (the apical phosphine analogue $PhP(dmap)_2$ forms square-pyramidal $[CoCl_2\{PhP(dmap)_2\}]$,

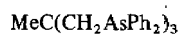
Section 47.5.2.6.iii). Reduction of $Co(BF_4)_2$ with $NaBH_4$ in the presence of (**186**) forms the mauve μ_3-hydrido-bridged dimer (**176**)[375] (structure Table 51), which reacts with HCl or CO generating 3 mol of H_2 and Co^{2+} or $[Co\{MeC(dpam)_3\}(CO)_2](BPh_4)$ respectively.



(184)



(185)



(186)

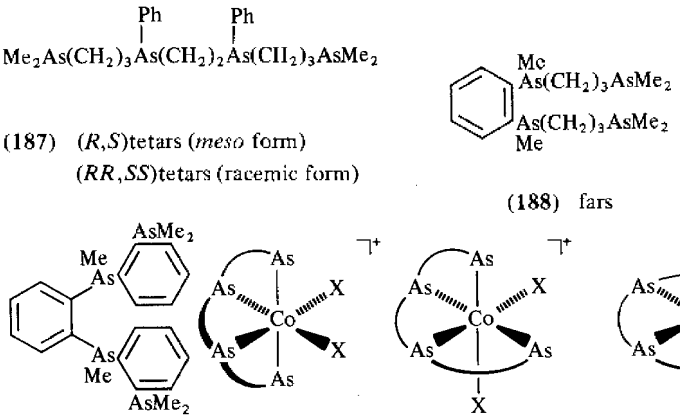
47.6.3 Cobalt(III)

Few monotertiary arsine complexes are known for Co^{III}. Displacement of *trans* sulfito groups from $Na_5[Co(CN)_4(SO_3)_2]$ gives $Na[Co(CN)_4(AsPh_3)_2]$, which presumably also has the *trans* configuration.[609] Some $[CoY(DMGH)_2(AsR_3)]$ cobaloximes are also known (R = Me, Ph; Y = Cl^-, $SnPh_3^-$)[610] as are some σ-bonded $R^1R^2As^-$ and $R^1R^2(O)As$ complexes (see below).

Bidentate diarsines are more common and Nyholm many years ago reported the preparation of several *trans*-$[CoX_2(das)_2]^+$ complexes by air oxidation of the corresponding Co^{II} systems (X = Cl^-, Br^-, I^-, NCS^-).[611] He also isolated $[Co(das)_3](ClO_4)_3$. Subsequently, the *cis*-$[CoX_2(das)_2]^+$ isomer was prepared, initially following treatment of *trans*-$[CoI_2(das)_2]I$ with Ag^+,[612] and later *via* $[Co(CO_3)(das)_2]ClO_4$.[613] In this later work Bosnich and coworkers resolved *cis*-$[Co(Cl)_2(das)_2]^+$ using (+)-arsenyltatrate and showed optical retention in various substitutions with H_2O, CO_3^{2-}, NO_3^-, NO_2^- and $C_2O_4^{2-}$. Racemization in dry MeOH occurs with some 80% conversion to the *trans* isomer.[613] Some preparations are given in Table 50 and crystal structures in Table 51. The green *trans* complexes are usually tetragonally distorted in the solid state but the *trans* configuration is thermodynamically favoured in solution. Peloso and Dolcetti have followed rates of substitution (Cl^- exchange, NCS^-) and isomerization for *cis*- and *trans*-$[Co(Cl)_2(das)_2]^+$,[614] and Jackson, McLaren and Bosnich report an interpretation of their CD spectra.[615] Some unusual self-induced catalytic substitution and racemization processes have also been reported and solutions should be protected from the light.[613] The *cis*-diaqua, hydroxyaqua, and dihyroxy ions do not racemize rapidly although water and hydroxide exchange occurs within hours at 25 °C.[613] Green, presumably *trans*, $[Co(X)_2(dmav)_2]X$ complexes have also been prepared, as has $[Co(dmav)_3](BF_4)_3$ (Table 50). Bubbling NO through methanol solutions of *trans*-$[Co(X)_2(das)_2]X$ results in *trans*-$[CoX(NO)(das)_2](ClO_4)$ and trigonal-bipyramidal $[Co(NO)(das)_2](ClO_4)$ (Table 50), and Brant and Feltham have recently correlated their photoelectron spectra with those of other Co and Fe nitrosyls. A linear correlation between ν_{NO} and the N 1*s* binding energy was demonstrated as well as insensitivity of the As 3*d* binding energy to the other ligands.[616]

A number of multidentate arsine complexes have been prepared by air oxidation of the corresponding Co^{II} complexes (Table 50). Perhaps the most interesting work in this area is that of Bosnich and his colleagues using the quadridentates (**187**), (**188**) and (**189**); all contain two central chiral As atoms. Air oxidation of $CoCl_2$ in acidified MeOH in the presence of (**187**) gives five $[Co(Cl)_2(tetars)]Cl$ isomers, three containing the racemic (*RR,SS*) ligand and two the *meso* (*RS*) form.[617] Resolution of α-$[Co(Cl)_2(RR,SS\text{-tetars})]^+$ followed by reduction using KCN gives the optically-active (*SS*) ligand, which is optically stable and stereospecific in its subsequent coordination to Co^{III}. However an interesting and unexplained halide-induced racemization process was found for the complexes in acetonitrile. Metathesis leads to a wide range of complexes (X = CO_3^{2-}, H_2O, Br^-, NO_2^-, NCS^-, CN^-, N_3^-) with retention at the chiral As centres but with changes in stereochemistry between isomers (**190**), (**191**) and (**192**).[618] The *meso* ligand prefers the *trans* structure (**192**) but the racemic ligand exists in all three forms. A rationalization of their CD spectra has also been reported.[619] Reduction of α-$[Co(Cl)_2(RR,SS\text{-tetars})]Cl$ with $NaBH_4$ in MeOH–H_2O mixtures produces a yellow solution which absorbs O_2 forming β-$[Co(O_2)(RR,SS\text{-tetars})](ClO_4)$ containing side-on-bonded dioxygen (**204**; Table 51). A similar property holds for *trans*-$[Co(Cl)_2(R,S\text{-tetars})]Cl$ and *trans*-$[Co(Cl)_2(das)_2]Cl$. If the solutions are kept acidic hydrido complexes *trans*-$[CoH(Cl)(As—As)_2](ClO_4)$ are formed (**193**; Scheme 65). Use of excess $NaBH_4$ at pH 8 leads to almost white $[Co(H)_2(das)_2](ClO_4)$, which slowly absorbs O_2 in the solid forming pink $[Co(O_2)(das)_2](ClO_4)$ (**194**).[620] Likewise treatment with MeI results in (**195**). The *trans*-labilizing effect of hydride is seen in the very facile exchange of aqua ligand in $[CoH(H_2O)(das)_2]^{2+}$.[620] A similar study using fars (**188**) and qars (**189**) has given the *meso* and optically active ligands and

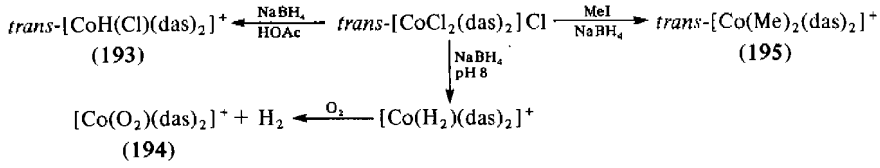
interconversions similar to the above are possible.[621] The (*RR,SS*) qars ligand forms only the α stereochemistry (**190**) due to the rigid ligand backbone but fars gives α, β- and *trans* complexes. Reduction of *trans*-[Co(Br)$_2$(*RR,SS*-fars)]Br with $NaBH_4$ in basic solution and subsequent O_2 absorption forms [Co(*RR,SS*-fars)O_2]$^+$, while in acidic solution *trans*-[CoH(Br)(*RR,SS*-fars)]$^+$ is formed. A stable dihydride [Co(H)$_2$(*RR,SS*-qars)](ClO_4) was also isolated.[621]



(187) (*R,S*)tetars (*meso* form)
(*RR,SS*)tetars (racemic form)

(188) fars

(189) qars (190) α (191) β (192) *trans*



Scheme 65

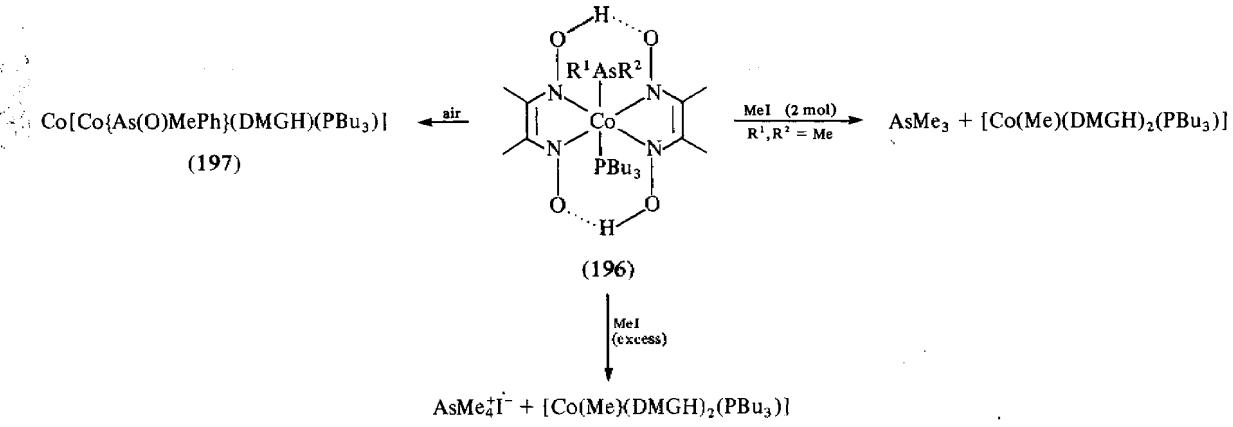
Few mechanistic studies on ligand replacement have been reported. Nanda and Tobe many years ago studied the displacement of Cl^- by $Y = Br^-$, NCS^- in [Co(Cl)$_3${MeAs(dmap)}], and the independence of rate on the nature and concentration of Y^- suggested rate-limiting dissociation. Also it appears that [CoX(solv)(As—As)$_2$]$^{2+}$ species rapidly undergo anation by X^- (halide, pseudohalide). The rate is very much faster than for the corresponding amine complexes.

Some interesting σ-bonded $R_2(OH)As$ complexes containing As^{III} result from treating [Co(DMGH)$_2$] with Ph_2AsCl or MePhAsCl in methanol, and a structure on [CoCl{As(OH)MePh}-(DMGH)$_2$]·H_2O (Table 51) establishes a Co^{III}—As bond.[623] Treatment of Co^I cobaloximes with R^1R^2AsX (X = Cl, I) leads to $R^1R^2As^-$ coordination. Thus addition of [Co(DMGH)$_2$py]$^-$ to $AsMe_2Cl$ and [Co(DMGH)$_2$(Bu^{t}py)]$^-$ to $AsMe_2I$ in methanol gives a product which approximates to [Co(DMGH)$_2$($AsMe_2$)·MeOH. This is thought to be polymeric with $AsMe_2$ bridges.[624] Using [Co(DMGH)$_2$(PBu^n_3)]$^-$ as the nucleophile R^1R^2AsCl forms green solutions (R^1, R^2 = Me, Ph) thought to be (**196**), which air oxidize to (**197**; Scheme 66). A crystal structure (Table 51) shows two [Co(DMGH)(PBu^n_3){As(O)MePh}] units joined to a central Co^{II} ion.[624] Complex (**196**) also reacts with MeI, or [Co(DMGH)$_2$(py)Me], to form $AsMe_3$ (Scheme 66), and this is seen as a possible model for the aerobic biological methylation of arsenic.

47.6.4 Arsenates

Comparisons with phosphate (and other oxyanions) can be made with reference to Section 47.5.2.8.(i).

Substitution at As^V is much faster than that at P^V due to its more polarizable nature and readiness to expand its covalency from four to five or six. Thus O exchange in $AsO_4H_n^{(3-n)-}$ is considerably faster than in P analogues and this is paralleled by their ability to react with $CoOH_2^{n+}$ species with displacement at As rather than at the metal. The reaction given by equation (127) is reasonably fast in the forward direction ($k_f = 5 \times 10^{-3}\ s^{-1}$ in 0.1 mol dm^{-3} arsenate, pH 6)[597] and when assumptions are made concerning ion pairing the rate for displacement at As within the ion pair is somewhat faster (*ca.* 10 times) than that for the unassisted O exchange in $HAsO_4^{2-}$ (k_{ex}; Table 74). Proton

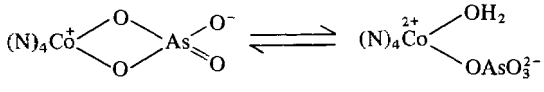


Scheme 66

transfers in a transition state of type (**253**) have been proposed with the lower reactivity of $H_2AsO_4^-$ being attributed to the smaller ion-pairing constant.[597] The reverse hydrolysis reaction (k_{hyd}; Table 74) is fastest with $[Co(OAsO_3H_3)(NH_3)_5]^{2+}$ ($pK_a \approx 3.3$), and an acid-catalyzed route *via* $[Co(OAsO_2H_3)(NH_3)_5]^{3+}$ ($pK_a \approx -0.5$) is also available. The more basic complexes are relatively stable in aqueous solution. Comparison of k_{hyd} and k_{ex} (Table 74) shows that the CoO—AsO_3H_n bond is more inert than the HO—AsO_3H_n bond.

$$[(NH_3)_5CoOH_2]^{3+} + [HAsO_4]^{2-} \underset{k_{hyd}}{\overset{k_f}{\rightleftharpoons}} [(NH_3)_5CoOAsO_3H]^{+} + H_2O \qquad (127)$$

The chelate form of arsenate (equation 128) has not been clearly identified. It is more likely than phosphate to dissociate to the monodentate form in aqueous solution.



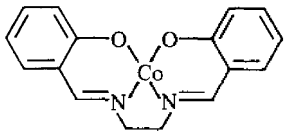
(128)

47.7 OXYGEN LIGANDS

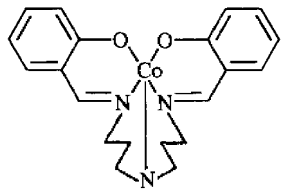
47.7.1 Superoxo and Peroxo

Cobalt–dioxygen chemistry has its origins with Fremy[625] who, in 1852, reported that the exposure of ammoniacal solutions of cobalt(II) salts to air resulted in the formation of brown 'oxo-cobaltiates'. However, it was not until 1898 that these cobalt–dioxygen complexes were correctly formulated by Werner and Mylius as containing the $[(NH_3)_4Co(O_2)Co(NH_3)_4]^{4+}$ cation.[626] In the late 1930s Tsumaki[627] observed that solid samples of the cobalt(II)–Schiff-base complex [Co(salen)] possessed the capacity to bind dioxygen reversibly. This discovery prompted a widespread and continuing interest in the oxygen-carrying ability of cobalt chelates. Much of the early work in this area concerned solid state cobalt(II)–Schiff-base systems, in particular the square-planar complexes derived from [Co(salen)] (**198**) and the trigonal-bipyramidal complexes derived from [Co(salpr)] (**199**). Both types of compound can be prepared in active and inactive forms, with dioxygen-carrying ability being dependent on purification procedures and the methods of preparation employed. Calvin and his coworkers prepared, characterized and tested for dioxygen-carrying properties a total of 57 Co–Schiff-base complexes[628] and many more were examined by Diehl.[629] Compounds of type (**198**) bind 1 mol of O_2/mol of Co while those of type (**199**) bind 0.5 mol O_2/mol of Co. Oxygenation can be reversed either by heating or by evacuation, however after many oxygenation–deoxygenation cycles dioxygen-carrying ability decreases. In the solid state [Co(3-Fsalen)] deteriorates to ~60% of its original activity after 1500 cycles,[630] and this deterioration is linked to irreversible oxidation or to strain imposed on the crystal leading to inactive modifications. In non-aqueous solution oxygen uptake by both the type (**198**) and (**199**) chelates was complicated by problems of irreversibility and the failure of the complexes to appreciably oxygenate under oxygen pressures sufficient to cause oxygenation in the solid state.[631] A significant development came with the discovery of Burk, Hearon, Caroline and Schade[632] that the cobalt(II)–amino-acid complex

[Co(his)$_2$] combined reversibly with dioxygen in aqueous solution. This was an important result, for [Co(his)$_2$] was the first synthetic compound to undergo reversible oxygenation in aqueous solution and it was evident that oxygenation was a general rather than an isolated phenomenon. This early chemistry of cobalt–dioxygen complexes has been reviewed.[630,633–635]

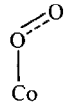


(198)

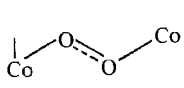


(199)

It is now recognized that cobalt dioxygen complexes may be classified according to their molecular geometries and electronic distributions into four related categories. These structural classes were originally proposed by Vaska[636] in his general review on dioxygen–metal complexes and allow the cobalt systems to be viewed as either superoxo (types Ia and Ib) or peroxo complexes (types IIa and IIb) of cobalt(III). This formalism is supported by the collective experimental evidence for cobalt–dioxygen adducts, which indicates that binding of O_2 to cobalt involves considerable electron transfer from the metal to the coordinated dioxygen moiety. Unlike the situation with chromium– and iron–O_2 adducts the degree of electron transfer, and consequently the nature of the bonding in the cobalt–dioxygen complexes, is relatively clear.



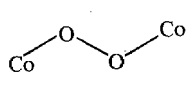
(Ia)



(Ib)



(IIa)



(IIb)

One of the best measures of the degree of charge transfer to dioxygen is the stretching frequency ν_{O_2}, and selected data for cobalt–dioxygen complexes are given in Table 52. Several early assignments of ν_{O_2} are known to be incorrect but the increasing use of isotopic substitution ($^{18}O_2/^{16}O_2$) and Raman and resonance-Raman techniques has now eliminated many of the problems and ambiguities associated with the measurements. The frequency ranges 1075–1195 cm^{-1} and 790–932 cm^{-1} are widely recognized as diagnostic for superoxo and peroxo complexes respectively[636] and virtually all stable cobalt–dioxygen adducts are found to have stretch frequencies lying in one or the other of these ranges. The unstable complexes formed between cobalt(II) porphyrins and O_2 doped into Ar matrices have recently been shown[637,638] to have ν_{O_2} values ($\sim$ 1280 cm^{-1}) significantly greater than the upper limit of the superoxo range.

Single-crystal X-ray structures have now been determined for a large number of cobalt–dioxygen complexes and comparisons of the observed O—O bond lengths with those of superoxide anion or peroxide dianion (O—O separation = 128 pm, KO_2; 149 pm, Na_2O_2) also form a reliable guide to classification.

Recent reviews on the chemistry of metal–dioxygen complexes with particular relevance to cobalt systems include a number dealing with general properties,[636,639–641] binuclear superoxo and peroxo complexes,[642,643] reversible oxygenation,[644–646] complex stability,[647,648] catalytic oxidation[649,650] and electronic[651] and EPR[652] spectral properties.

47.7.1.1 η^1 Superoxo

The 1:1 dioxygen adducts of cobalt(II) complexes containing tetradentate ligands have been widely studied. In these systems dioxygen binding requires the presence of a Lewis base in the coordination site *trans* to the dioxygen moiety, which gives rise to six-coordinate adducts. Complexes of this type include those with Schiff bases, porphyrinato and various other macrocyclic ligands. Other ligand types are also suitable however. Certain pentadentate ligands provide the additional donor atom to eliminate the need for an external Lewis base, and a stable six-coordinate cobalt–dioxygen adduct containing solely unidentate ligands has been reported,[26] five-coordinate

Table 52 Stretching Frequencies in Cobalt–Dioxygen Complexes

Compound	$\nu(^{16}O_2)$ (cm^{-1})	$\nu(^{18}O_2)$ (cm^{-1})	*Comments*	*Ref.*
Peroxo complexes				
$[Co_2(CN)_4(Me_2PhP)_5(O_2)]$	881	–	IR, nujol	1
$[\{(NH_3)_5Co\}_2(O_2)]Cl_4 \cdot H_2O$	824	–	Raman, cryst.	2
$K_6[\{(NC)_5Co\}_2(O_2)] \cdot H_2O$	805	–	Raman, cryst.	2
$Na[\{(NH_3)_4Co\}_2(NH_2)(O_2)](ClO_4)_4$	834	–	Raman, cryst.	2
Superoxo complexes				
$[CoHb(O_2)]$	1122, 1153	1066, 1095	Res. Raman, H_2O	3
$[CoMb(O_2)]$	1122, 1153	1066, 1095	Res. Raman, H_2O	3
$[Co(OEP)(O_2)]$	1275	1202	Res. Raman, Ar matrix	4
$[Co(TPP)(O_2)]$	1278	1209	Res. Raman, Ar matrix	5
$[Co(TTP)(1\text{-Meim})(O_2)]$	1142	1071	IR, CH_2Cl_2	6
$[Co(Cap)(1\text{-Meim})(O_2)]$	1176	1084	IR, CH_2Cl_2	6
$[Co(TpivPP)(1\text{-Meim})(O_2)]$	1150	1077	IR, nujol	7
$[Co(TPP)(py)(O_2)]$	1144	1084	Res. Raman, CH_2Cl_2	8
$[Co(salen)(O_2)]$	1011	943	Res. Raman, cryst.	9
$[Co(salen)(py)(O_2)]$	888	833	Res. Raman, cryst.	10
$[Co(acacen)(B)(O_2)]$	1123–1195	–	IR, nujol, B = py, 4-Mepy, 4-NH_2py, 4-CNpy	11
$[\{(NH_3)_5Co\}_2(O_2)]Cl_5 \cdot H_2O$	1122	–	Raman, cryst.	2
$K_5[\{(NC)_5Co\}_2(O_2)] \cdot H_2O$	1099	–	Raman, cryst.	2
$[\{(NH_3)_4Co\}_2(NH_2)(O_2)]Cl_4 \cdot 3H_2O$	1075	–	Raman, cryst.	2

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cobalt(II)–trisphosphine complexes bind dioxygen but dissociate a phosphine ligand in the process to form five-coordinate terminally bound dioxygen complexes.[456]

In many systems there is a marked tendency for μ-peroxo dimer formation (Scheme 67) but the 1:1 adducts may be stabilized by the use of polar solvents and by bulky groups in the ligand which hinder the dimerization step. They may also be stabilized kinetically by use of low temperatures, however bases with the ability to hydrogen bond will accelerate dimerization[653] and σ basicity is also important. Detailed discussions of the factors influencing stability are available.[644,646]

$$(B)(L_4)Co + O_2 \underset{}{\overset{K_{O_2}}{\rightleftharpoons}} (B)(L_4)Co(O_2)$$

$$(B)(L_4)Co(O_2) + Co(L_4)(B) \xrightarrow{k} (B)(L_4)Co(O_2)Co(L_4)(B)$$

Scheme 67

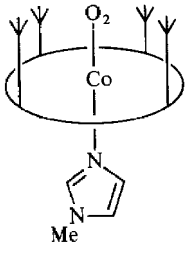
Table 53 gives a list of a number of cobalt(III)–superoxo complexes which have been isolated as crystalline solids. There is a marked preponderance of complexes of the type $[Co(SB)(B)(O_2)]$ (SB = Schiff base). The base adducts of simple Co^{II} porphyrins have low affinities for dioxygen at room temperature and consequently their 1:1 adducts with O_2 are not isolable. In contrast, exposure of a solid sample of Collman's picket fence porphyrin system [Co(TpivPP)(*N*-Meim)] to 1 atm of dioxygen for 24 h produces [Co(TpivPP)(*N*-Meim)(O_2)] (**200**).[654] The pivalamido pickets in this compound exercise control of solvation about the coordinated dioxygen moiety and the stability is comparable with that of $CoMbO_2$,[655] where the globin protein environment performs the same function.

Virtually all water-soluble cobalt dioxygen complexes are binuclear but $(NR_4)_3[Co(CN)_5(O_2)]$ (R = Et, Pr^n) complexes may be obtained following the reaction of O_2 with $[Co(CN)_5]^{3-}$ in DMF

Table 53 Crystalline Monomeric Cobalt(III)–Superoxo Complexes

Complex	*B*	*Colour*	*Comments*	*Ref.*
[Co(acacen)(B)(O_2)]	DMF	Black	μ_{eff} = 2.22 BM	3
	Py	Red-brown	μ_{eff} = 1.89 BM	3
	4-Mepy	Carmine	μ_{eff} = 1.54 BM	3
	4-CNpy	Red-black	μ_{eff} = 1.71 BM	3
	4-NH_2py	Brown	μ_{eff} = 1.49 BM	3
[Co(3-MeOsalen)(B)(O_2)]	Py	Red-brown	μ_{eff} = 1.65 BM	4
[Co(3-MeOsaltmen)(B)(O_2)]	H_2O	Red	–	5
[Co(3-Fsaltmen)(B)(O_2)]	1-Meim	Burgundy	–	12
[Co(3-Bu^{t}salen)(B)(O_2)]	Py		–	7
[Co(saltmen)(B)(O_2)]	Bzim	Dark red	–	6
[Co(*N*-Mesalpr)(O_2)][Co(*N*-Mesalpr)]	–	Black	μ_{eff} = 3.26 BM	8
[Co(J-en)(B)(O_2)]	Py	Black	λ_{max} = 525 nm (CH_2Cl_2)	2, 9
[Co(J-pn)(B)(O_2)]	Py	Purple	λ_{max} = 525 nm (CH_2Cl_2)	2
[Co(2-Xacacen)(B)(O_2)]	Py	Dark red	X = Cl, λ_{max} = 370 nm (CH_2Cl_2)	1
	Py	Orange	X = succNH, λ_{max} = 355, 525 nm (CH_2Cl_2)	1
[Co(2-Xbzacen)(B)(O_2)]	Py	Orange	X = succNH, λ_{max} = 360, 525 nm (CH_2Cl_2)	1
[Co(bzacen)(B)(O_2)]	Py, PPh_3	–	–	10
[Co(salpen)(O_2)]	–	Black-purple	λ_{max} = 560 nm (CH_2Cl_2)	11
$[NR_4]_3$[Co(CN_5)(O_2)]	–	Red-brown	R = Et, Pr^n	13
[Co(Cl)(*s*-Me_2en)$_2$(O_2)]	–	Dark brown	λ_{max} = 330 nm (EtOH/MeOH)	14
[Co(TpivPP)(B)(O_2)]	1-Meim	–	λ_{max} = 412, 549 nm (toluene); μ_{eff} = 2.54 BM	15, 16

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(200)

solution,[26] and oxygenation of ethanolic solutions of *cis*-[$Co(Cl)_2$(*s*-Me_2en)$_2$] gives *cis*-[CoCl(*s*-Me_2en)$_2$(O_2)]$^+$ isolated as its PF_6^- or ClO_4^- salt.[656] That the monomeric rather than the dimeric complexes are obtained appears to be due to the influence of solvent in the first case and to steric hindrance in the ligand in the second. The five-coordinate Co^{II}–Schiff-base complexes [Co(salpr)] and [Co(*N*-Mesalpr)] differ only by substitution of H for Me at the axial nitrogen atom, yet on oxygenation in non-polar solvents the former gives a stable μ-peroxo dimer, [{Co(salpr)}$_2$(O_2)],[657] while the latter gives the unusual superoxo complex [Co(*N*-Mesalpr)(O_2)]·[Co(*N*-Mesalpr)].[658] Clearly, the balance between formation of the mononuclear and binuclear complexes is delicate.

Structural studies on the monomeric dioxygen complexes have often been hampered by solid-state disorder or excessively high thermal motion of the coordinated dioxygen moiety. Despite these problems a number of structures have been reported (Table 54) and with one exception the O—O bond distances all lie within the relatively narrow range 124 to 135 pm. Both the O—O bond lengths and the Co—O—O bond angles (range 117° to 153°) are consistent with the formulation of these 1:1 adducts as cobalt(III)–superoxo complexes. The variation in the Co—O—O bond angles has been attributed to packing forces.[644]

Magnetic susceptibility measurements on $[Co(L_4)(B)(O_2)]$ complexes correspond to the presence of one unpaired electron and EPR spectra exhibit a well-defined eight-line ^{59}Co hyperfine spectrum with a peak separation of ~12 G. Studies using $^{17}O_2$-labelled [Co(bzacen)(py)(O_2)] show the two oxygen atoms to be non-equivalent in the solid state and in frozen solution,[659] but equivalent in fluid solution.[660,661] The equivalence may be due to a rapid equilibrium between two bent conformations: $Co—(O_AO_B) \rightleftharpoons Co—(O_BO_A)$. These experiments also showed the electron to be localized essentially on dioxygen. The commonly held view that there is a formal transfer of an electron from the cobalt metal centre to a dioxygen π^* orbital in the cobalt–dioxygen adducts ($Co^{III}—O_2^-$) has been challenged by Tovrog, Kitko and Drago.[662] On the basis of EPR experiments they suggest that on combination of a Co^{II} complex with dioxygen only partial transfer occurs, with the degree of transfer being dependent on the ligand environment about the metal. For a series of cobalt(II) complexes containing a range of different ligand types they estimate between 0.1 and 0.8 electrons transferred to the coordinated dioxygen fragment. The proposed alternative bonding interaction involves the spin pairing of unpaired electron in an antibonding orbital of O_2 with an unpaired electron in a d_{z^2} orbital on cobalt(II).[663] That the unpaired electron in the adducts resides in an oxygen π^* orbital is not in dispute. Smith and Pilbrow[652] have discussed the merits of this proposal, but have concluded from a recent analysis of the EPR spectra of several cobalt–dioxygen complexes that electron transfer cannot be estimated reliably at present.[664] The results of EPR studies on a wide range of η^1 cobalt–dioxygen complexes, including $CoHbO_2$, $CoMbO_2$ and the dioxygen adduct of vitamin B_{12r}, have been summarized in recent reviews.[644,652]

Several η^1 cobalt–dioxygen adducts have been studied theoretically. These investigations include studies on $[Co(Cl)_4(B)(O_2)]$ systems (B = none, NH_3, py, im) by Boca[665] and the construction of Walsh diagrams by Teo and Li[666] for the interaction of O_2 with the fragments $[Co(CN)_5]^{3-}$ and $[Co(PH_3)_4]^+$. Calculations on [Co(acacen)(B)(O_2)] (B = none, H_2O, CN^-, CO, im) by Veillard and

Table 54 Structures: Mononuclear Cobalt(III)–Superoxo Complexes

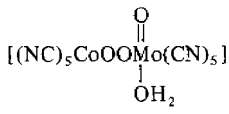
Compound	*O—O* (pm)	*Co—O* (pm)	*Co—O—O* (°)	*Comments*	*Ref.*
[Co(bzacen)(py)(O_2)]	126	186	126	High thermal motion of O_2	1
[Co(acacen)(py)(O_2)]	–	195	–	O_2 disordered, −40 °C	2
[Co(salpeen)(O_2)]·MeCN	106	190	134	O_2 irresolvably disordered	3
[Co(3-Bu^{t}salen)(py)(O_2)]	135	187	116	C_2H_4 bridge disordered	8
[Co(3-MeOsaltmen)(H_2O)(O_2)]·dme	125	188	117	O_2 two-fold disordered	4
[Co(saltmen)(Bzim)(O_2)]	128	189	120	–	6
$[Et_4N]_3[Co(CN)_5(O_2)]\cdot 5H_2O$	124	190	153	O_2 two-fold disordered	7
[Co(3-Bu^{t}saltmen)(Bzim)(O_2)]	127	187	117	At −152 °C and room temp.	9
[Co(*N*-Mesalpr)(O_2)]	135	188	133	O_2 two-fold disordered	10
[Co(3-Fsaltmen)(*N*-Meim)(O_2)]·2ac	130	188	117	At −171 °C	5

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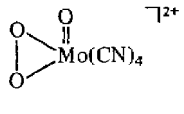
coworkers[667] show the bent η^1 geometry to be more stable than the η^2 by 190–340 kJ mol^{-1} depending on **B**, and also preferred over the linear η^1 arrangement. In agreement with the related calculations of Fantucci and Valenti on [Co(acacen)(NH_3)(O_2)][668] the unpaired electron is found to be localized essentially in a π_g^* orbital of dioxygen. Veillard's calculations[667] also show a relationship between the σ-donor ability of the axial ligand **B**, the ease of oxidation of cobalt(II) to cobalt(III), and the ease of oxygenation.

Qualitative support for this result comes from the observation by Carter, Rillema and Basolo[669] that for a number of complexes of the type [Co(SB)(B)] (SB = Schiff base) a linear correlation exists between log K_{O_2} (K_{O_2} = [Co(SB)(B)(O_2)]/[Co(SB)(B)]pO_2) and the oxidation potential cobalt(II) to cobalt(III). The correlation holds both for variation in B within the [Co(bzacen)(B)] series and for variation in the Schiff base within the [Co(SB)(py)] series, thus giving a measure of the effects of axial and in-plane ligands on the stability of the [Co(SB)(B)(O_2)] adducts. Basolo[669] suggested the correlations exist because the oxidation potentials provide a measure of the charge density on the cobalt centre. The greater the charge density on Co the greater will be the electron transfer from cobalt to dioxygen, and consequently the more stable the dioxygen complexes. The correlation between K_{O_2} and the base strength of axial phosphine ligands in [Co(porphyrin)(PR_3)] complexes[670] also relates to the amount of electron density at the cobalt metal centre. An analogous correlation relating electronic effects arising from substitution in the in-plane ligand to the dioxygen-binding ability of [Co(porphyrin)(py)] complexes has been described by Walker, Beroiz and Kadish.[671]

The reduction of $[Co(CN)_5(O_2)]^{3-}$ by Mo^V species in aqueous solution produces the bimetallomer (**201**), which is slowly decomposed in organic solvents to the η^2-Mo(O_2) species (**202**).[672] Tracer studies using $^{18}O_2$ show however that the peroxo bridge in (**202**) does not derive from $[Co(CN)_5(O_2)]^{3-}$.[673]



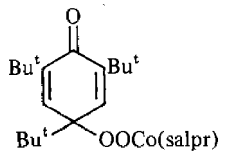
(201)



(202)

Kumar and Endicott[673] have examined the one-electron oxidation–reduction of [Co([14]aneN$_4$)-(H_2O)(O_2)]$^{2+}$ in aqueous solution. Reduction competes successfully with dimerization in this system and even mildly reducing metal ions such as Fe^{2+} react *via* an inner-sphere process. Presumably this pathway is preferred owing to the large free-energy changes associated with formation of the μ-peroxo adducts. With Fe^{2+} the adduct is observable as a transient CoOOFe species, which decays to Fe^{3+} and unspecified cobalt products.

The coordination of O_2 to Co^{II} centres not only enhances the basicity of the dioxygen fragment but also increases its tendency to undergo free-radical reactions. The radical nature of η^1 cobalt–dioxygen complexes is now well established and is particularly demonstrated through their participation in hydrogen-abstraction reactions. The autooxidation of phenols to the corresponding *p*-quinones and diphenoquinones catalyzed by cobalt(II) complexes provides the best example. Nishinaga[675] has demonstrated that the dioxygen complex [Co(salpr)(O_2)] activates 2,4,6-tri-*t*-butylphenol *via* hydrogen abstraction by following the simultaneous decrease in the Co—O_2 EPR signal and appearance of the phenoxy radical signal. The product of the reaction of [Co(salpr)] with the radical has since been isolated and found to have the structure (**203**).[649] Similar H-atom abstractions are observed for [Co(salen)(py)O_2)] and the dioxygen adduct of vitamin B_{12r} with 1,4-dihydroxybenzene, and with *N,N'*-tetramethyl-*p*-phenylene.[676] Drago and coworkers have also examined the oxidation of phenols catalyzed by cobalt(II)–Schiff base complexes[677,678] and report a high selectivity toward *p*-quinone production over solution analogues when the complex is bound to a polymer support.[678] A further illustration of the radical character of the η^1 Co—O_2 complexes has been given by the reaction of [Co(*N*-Mesalpr)(O_2)] with the spin trap 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) to form a stable Co—O—O—DMPO spin adduct.[679]



(203)

The role of cobalt–dioxygen complexes in autooxidations other than phenol oxidation is less certain, and ostensibly similar reactions appear to follow radically different pathways. Thus, in the oxidation of thiols to disulfide catalyzed by Co^{II} species catalysis by the phthalocyanine complex $[Co^{II}(TSPc)]^{4-}$ apparently proceeds *via* a Co^{I} intermediate and without participation of Co—O_2 species,[680] whereas catalysis by $[Co^{II}(TPP)]$ appears to involve initial formation of an η^1 cobalt–dioxygen complex from which O_2^- is displaced by thiolate.[681] Several reviews giving extensive coverage to oxidations catalyzed by cobalt(II) complexes are available.[649,650,682,683]

There have been a number of reports describing the formation of η^1 cobalt–dioxygen complexes by reactions not involving oxygenation of cobalt(II) chelates. Ligand substitution at the axial positions of the cobalt(III) complex aquacobalamin (vitamin B_{12a}) is sufficiently rapid to allow coordination of electrochemically generated O_2^- ion in DMF solution.[684] The product displays an EPR spectrum identical with that of the dioxygen adduct of the Co^{II} complex vitamin B_{12r}. Condensation of $[Co(CO)_4]$, produced from the thermal dissociation of $[Co_2(CO)_8]$, and O_2 at 77 K produces $[Co(CO)_4(O_2)]$,[685] which has the EPR characteristics of an η^1 cobalt–dioxygen adduct. The same product is reported from the cocondensation of Co atoms with CO/O_2 mixtures at 10–12 K.[686] Simic and Hoffman[687] have found that O_2^- adds to both $[Co(4,11\text{-dieneN}_4)(H_2O)_2]^{2+}$ and $[Co(1,3,8,10\text{-tetraeneN}_4)(H_2O)_2]^{2+}$ in aqueous solution to produce transient species displaying intense charge transfer bands. The spectra do not correspond to Co^{I} or Co^{III} complexes, excluding O_2^- as a simple electron transfer agent. It is concluded that O_2^- adds to the Co^{II} centre at a labile axial site.

47.7.1.2 η^1:η^1 Superoxo

The only μ-superoxo complexes to have been characterized are those which contain cobalt. They are readily prepared by treatment of the corresponding μ-peroxo complexes with strong oxidants. Thompson and Wilmarth[688] observed that MnO_4^-, HOCl, Br_2, BrO_3^- and NO_3^- are all effective oxidants toward $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{3+}$ in acidic solution whereas Fe^{3+}, H_2O_2, Ag^+ and $Cr_2O_7^{2-}$ are not. In other systems Cl_2, PbO_2, persulfate and Ce^{IV} in nitric acid solution have also effected oxidation.[642] A number of well-characterized μ-superoxo cobalt(III) complexes are listed in Table 55. There are no reports of μ-superoxo complexes containing Schiff base ligands and all that are known contain either terminal amine or cyano groups.

The μ-superoxo cobalt(III) complexes are usually green light-sensitive compounds and their measured magnetic susceptibilities ($\mu \approx 1.6$ BM) correspond to the presence of one unpaired electron. Werner[689] originally formulated the complexes as containing a peroxide group briding Co^{III} and Co^{IV} centres, however the equivalence of the two metal atoms has been demonstrated by EPR experiments. Room temperature EPR spectra of both the single-bridged μ-superoxo[690,691] and μ-amido-μ-superoxo[690,692] ions are well-defined isotropic spectra consisting of 15 lines with $A_{iso} \sim 10$ G. This is the expected spectrum for two magnetically equivalent cobalt nuclei with the unpaired electron residing primarily on the dioxygen bridge. A theoretical study of $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$ using SCCC methods[693] is in agreement with this result.

Several structural studies on the μ-superoxocobalt(III) complexes have been undertaken (Table 56) and the observed O—O bond lengths (range 124 to 135 pm) also support the structural formalism $Co^{III}(O_2^{2-})Co^{III}$. Recently, Raman spectroscopy has allowed the determination of O—O stretching frequencies for a number of single-bridged superoxo complexes.[694,695] As is the case for the corresponding μ-peroxo species, this vibration is IR inactive, presumably because the molecular symmetry is such that dipole changes due to this vibration are small. A general discussion of the Raman and IR spectra of μ-superoxocobalt(III) complexes has been given[694] and values of ν_{O_2} appear in Table 52.

The purple salt $[(NH_3)_5Co(O_2)(NH_3)_5][(NC)_5Co(O_2)Co(CN)_5]$ has been prepared[690] and is stable in the solid state, whereas $[(NH_3)_5Co(O_2)Co(NH_3)_5](ClO_4)_5$ decomposes with loss of oxygen within 2 to 3 d at room temperature.[696] In acidic solution $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$ and the doubly bridged $[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{4+}$ ion decompose by pH independent paths to yield Co^{III} and Co^{II} species in equal amounts. These processes appear to be simple aquations at cobalt(III), following which the leaving group is further decomposed.

Valentine and Valentine[698] found that irradiation of the LMCT bands of $[(NH_3)_5Co(O_2)$-$Co(NH_3)_5]^{5+}$ and $[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{4+}$ gives efficient decomposition into 1:1:1 mixtures of $[Co(NH_3)_5(H_2O)]^{3+}$, $Co^{2+}_{(aq)}$ and O_2 independent of the temperature, acidity or ionic strength of the solutions. Attempts to trap electronically-excited intermediates gave negative results and the quantum yields fall sharply if the ammine ligands are replaced by chelating amines such as tetren.[699]

Table 55 Water Soluble Cobalt(III) Peroxo and Superoxo Complexes

Complex	Preparation	Comments	Ref.
Monobridged, peroxo			
$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$	$Co^{2+} + NH_{3(aq)} + O_2$	Dark brown; stable in 2–6 M $NH_{3(aq)}$	2
$[(en)_2(NH_3)Co(O_2)Co(NH_3)(en)_2]^{4+}$	$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$ + en	Brown; λ = 550 nm (sh)	3
$[(trien)(NH_3)Co(O_2)Co(NH_3)(trien)]^{4+}$	$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$ + trien	Brown; λ = 562 nm (sh)	3
$[(dien)(NH_3)_2Co(O_2)Co(NH_3)_2(dien)]^{4+}$	$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$ + dien	Brown; λ = 537 nm (sh)	3
$[(dien)(en)Co(O_2)Co(en)(dien)]^{4+}$	Co^{2+} + en + dien + O_2	Dark brown; λ = 420 nm (sh)	6
$[(tren)(NH_3)Co(O_2)Co(NH_3)(tren)]^{4+}$	Co^{2+} + tren + NH_3 + O_2	Brown; λ = 500 nm (sh)	6
$[(tren)(py)Co(O_2)Co(py)(tren)]^{4+}$	Co^{2+} + tren + py + O_2	Orange-brown	
$[(tetren)Co(O_2)Co(tetren)]^{4+}$	$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$ + tetren	Brown	9
$[(pydpt)Co(O_2)Co(pydpt)]^{4+}$	$[Co(pydpt)]I_2 + O_2$	Brown	4
$[([14]aneN_4)(X)Co(O_2)Co(X)([14]aneN_4)]^{n+}$	Co^{2+} + $[14]aneN_4$ + X + O_2	X = NCS^-, Cl^-, NO_2^-, H_2O	4
$[([14]aneN_4)(N_3)Co(O_2)Co(N_3)([14]aneN_4)]^{2+}$	$[([14]aneN_4)(H_2O)Co(O_2)Co(H_2O)([14]aneN_4)]^{4+} + N_3^-$	Brown; λ_{max} = 550, 440 nm	4
$[(en)_2(X)Co(O_2)Co(X)(en)_2]^{2+}$	$[(en)_2(NH_3)Co(O_2)Co(NH_3)(en)_2]^{4+}$ + X	X = NCS^-, NO_2^-; red-brown	8
$[(his)Co(O_2)Co(his)]\cdot 3H_2O$	Co^{2+} + hisHCl + OH + O_2	Brown; λ_{max} = 385 nm	1
$[(NC)_5Co(O_2)Co(CN)_5]^{6-}$	$[Co(CN)_5]^{3-} + O_2$	λ_{max} = 489, 370, 327 nm (1 M NaOH)	5, 16
		–	10
$[(tn)(ditn)Co(O_2)Co(ditn)(tn)]^{4+}$	Co^{2+} + ditn + tn + O_2	–	10
$[(tn)(dien)Co(O_2)Co(dien)(tn)]^{4+}$	Co^{2+} + dien + tn + O_2	–	7
$[(NH_3)_5Co(O_2H)Co(NH_3)_5]^{5+}$	$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+} + H^+$	Red; hydroperoxo	
Dibridged, peroxo			
$[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{3+}$	$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+} + OH^-$	Dark brown; λ_{max} = 595 (sh), 336 nm	7
$[(en)_2Co(\mu\text{-}OH,O_2)Co(en)_2]^{3+}$	$Co(ClO_4)_2$ + en + O_2	λ_{max} = 335 (~ 550)	13, 12
$[(N_2)_2Co(\mu\text{-}NH_2,O_2)Co(N_2)_2]^{3+}$	$[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{3+} + N_2$	N_2 = phen, bipy	11
$[(tren)Co(\mu\text{-}OH,O_2)Co(tren)]^{3+}$	Co^{2+} + tren + O_2, pH 10.5	Resolved	6, 12
$[(tren)Co(\mu\text{-}OH,O_2)Co(tren)]^{3+}$	Co^{2+} + tren + O_2, pH 10.5	λ_{max} = 500, 350 nm	12
$[(trien)Co(\mu\text{-}OH,O_2)Co(trien)]^{3+}$	α- or *β-cis*-$[Co(trien)(H_2O)_2]^{3+} + H_2O_3$	Product configuration *α-cis* or *β-cis* on both centres	13
$[(en)_2Co(\mu\text{-}en,O_2)Co(en)_2]^{4+}$	$Co(ClO_4)_2$ + en + O_2	λ_{max} = 360 (2590), 370 nm (123)	6
$[(tren)Co(\mu\text{-}NH_2,O_2)Co(tren)]^{3+}$	$[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{3+}$ + tren	λ_{max} = 484, 325 nm	14
$[(tren)Co(\mu\text{-}tren,O_2)Co(tren)]^{4+}$	$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$ + tren	–	7
$[(en)_2Co(\mu\text{-}NH_2,O_2H)Co(en)_2]^{4+}$	$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{3+} + H^+$	Red; λ_{max} = 491 nm; μ-hydroperoxo	12
$[(trien)Co(\mu\text{-}NH_2,O_2)Co(trien)]^{3+}$	$[(trien)Co(\mu\text{-}OH,O_2)Co(trien)]^{3+} + NH_{3(aq)}$	–	2
$[(NH_3)_4Co(\mu\text{-}NH_2,O_2H)Co(NH_3)_4]^{4+}$	$[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{3+} + H^+$	Red; μ-hydroperoxo	
Monobridged, superoxo			
$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$	Peroxo + $S_2O_8^{2-}$	λ_{max} = 670, 480 nm	15
$[(en)_2(NH_3)Co(O_2)Co(NH_3)(en)_2]^{5+}$	Peroxo + Cl_2^-	λ_{max} = 693, 471 nm; μ = 2.02 BM	3
$[(trien)(NH_3)Co(O_2)Co(NH_3)(trien)]^{5+}$	Peroxo + Cl_2	λ_{max} = 706, 409 nm; μ = 1.89 BM	3
$[(dien)(NH_3)_2Co(O_2)Co(NH_3)_2(dien)]^{5+}$	Peroxo + Cl_2	λ_{max} = 707, 468 nm; μ = 1.97 BM	3
		λ_{max} = 706, 427 nm; μ = 1.89 BM	3

$[(tetren)Co(O_2)Co(tetren)]^{5+}$	Peroxo + Cl_2	λ_{max} = 704, 468 nm; μ = 1.86 BM	3
$[(en)_2(NO_2)Co(O_2)Co(NO_2)(en)_2]^{3+}$	Peroxo + Cl_2	–	8
$[(NC)_5Co(O_2)Co(CN)_5]^{5-}$	Peroxo + HOBr	Red; λ_{max} = 485.5, 360 nm	16
$[Co_2(CN)_6(en)_2(O_2)]^{-}$	Peroxo + Cl_2	Purple	8
Superoxo, dibridged			
$[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{4+}$	Peroxo + HNO_3	λ_{max} = 700 (306), 475 nm (368)	17
$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+}$	Peroxo + Ce^{IV}	λ_{max} = 682 (230), 479 (274), 311 nm (3540); μ = 1.39 BM	13
$[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2]^{4+}$	Peroxo + $HNO_3/HClO_4$	Resolved, CD	11
$[(bipy)Co(\mu\text{-}NH_2,O_2)Co(bipy)]^{4+}$	Peroxo + $HNO_3/HClO_4$	Resolved, CD	11
$[(tren)Co(\mu\text{-}NH_2,O_2)Co(tren)]^{4+}$	Peroxo + Cl_2	λ_{max} = 730, 468, 300 nm	6
$[(NC)_4Co(\mu\text{-}NH_2,O_2)Co(CN)_4]^{4-}$	$[(NH_3)_5Co(O_2)(NH_3)_5]^{4+} + CN^-$	λ_{max} = 519, 394 nm	15
$[(L\text{-}pn)_2Co(\mu\text{-}NH_2,O_2)Co(L\text{-}pn)_2]^{4+}$	Peroxo + HNO_3	λ_{max} = 694, 469 nm	18
Superoxo, tribridged			
$[(NH_3)_3Co(\mu\text{-}NH_2,OH,O_2)Co(NH_3)_3]^{3+}$	$[(NH_3)_3ClCo(\mu\text{-}NH_2,O_2)CoCl(NH_3)_3]^{2+} + AgNO_3$	λ_{max} = 730, ~450 nm	17

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Table 56 Structures: Dimeric Cobalt(III)–Superoxo Complexes

Compound	*O—O* (pm)	*Co—O* (pm)	*Co—O—O* (°)	*Ref.*
Monobridged				
$[\{Co(NH_3)_5\}_2(O_2)](NO_3)_5$	132	190	117	1
$[\{Co(NH_3)_5\}_2(O_2)](SO_4)(HSO_4)_3$	131	189	118	3
$[\{Co(NH_3)_5\}_2(O_2)](NO_3)_2(Cl)_3$	129	191	118	4
$K_5[\{Co(CN)_5\}_2(O_2)]\cdot H_2O$	129, 144	192, 194	121, 122	2
Dibridged				
$[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$	132	187	121	5
$[(en)_2Co(OH)(O_2)Co(en)_2](NO_3)_4\cdot H_2O$	134	187	120	6
$[(en)_2Co(NH_2)(O_2)Co(en)_2](NO_3)_4\cdot H_2O$	135	189	119	7

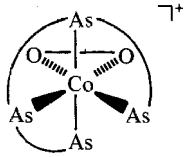
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Photolysis of $[(NC)_5Co(O_2)Co(CN)_5]^{5-}$ gives $[Co(CN)_5(OH_2)]^{2-}$, O_2 and H_2O_2[698] with quantum yields being dependent on the wavelength of excitation.[700] Superoxide ion appears to be generated in the primary photolysis step.

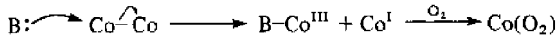
Kinetic data have been reported for reduction of μ-superoxo complexes by Fe^{2+},[701] Mo^{V},[702] Co^{II}[703] and Ru^{II} complexes,[704] and V^{2+}, Cr^{2+} and Eu^{2+}.[705] These processes involve outer-sphere electron transfer and in some cases[703,706] the Marcus theory has been applied to the rate constants obtained. Electron transfer quenching of the excited state of $[Ru(bipy)_3]^{2+}$ by various μ-superoxo cobalt(III) complexes leads to production of $[Ru(bipy)_3]^{3+}$ and the corresponding μ-peroxo species.[706]

47.7.1.3 η^2 Peroxo

Few examples of this type are known and all appear to be formed irreversibly. Oxygenation of the planar Co^{I} complex $[Co(vpp)_2](BF_4)$ either in the solid state or in solution gives $[Co(vpp)(O_2)](BF_4)$, which shares with $[Co(bzacen)(py)(O_2)]$[707] the distinction of being the first monomeric cobalt–dioxygen complex to be structurally characterized.[495] Bosnich[708] found that the similar reaction of O_2 with the Co^{I} species produced by BH_4^- reduction of *cis*-α-[Co(Cl)$_2$(*R,R*:*S,S*-tetars)]$^+$ gave red *cis*-β-[Co(*R,R*:*S,S*-tetars)(O_2)]$^+$ for which a structural study[709] has also confirmed the η^2-bonded mode of the dioxygen moiety (**204**). This complex is also produced exclusively when an equilibrium mixture of the *cis*-α and *cis*-β isomers of [Co(*R,R*:*S,S*-tetars)$(H_2O)_2]^{3+}$ in water is treated with H_2O_2. This specificity appears to arise through Co^{II}–catalyzed isomeric equilibration of the products since the H_2O_2 reaction is far faster than the *cis*-α- to *cis*-β-diaqua isomerization. The corresponding reaction with *cis*-[Co(diars)$_2(H_2O)_2]^{3+}$ gives *cis*-[Co(diars)$_2(O_2)]^+$, which is also formed quantitatively when *cis*-[Co(H)$_2$(diars)$_2$](ClO$_4$) in neutral methanol solution is exposed to dioxygen. Bosnich[708] reports an alternative method of preparing η^2-dioxygen adducts *via* the base-induced cleavage of Co—Co bonds in dimers of the type *trans,trans*-[(X)(As$_4$)Co—Co(As$_4$)(X)]$^{4+}$ (X = H_2O or MeCN; As$_4$ = (diars)$_2$, *R,S*-tetars, *R,R*-tetars). The yields are always less than 50% and the reactions involve heterolytic cleavage of the Co—Co bonds to produce Co^{III} complexes and the O_2 sensitive Co^{I} species (Scheme 68).

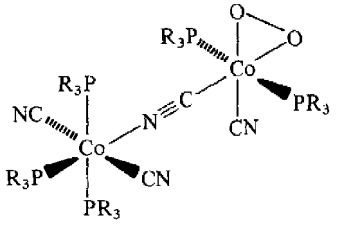


(204)



Scheme 68

Under certain conditions two one-electron-donor Co^{II} centres can interact with dioxygen as if they were a single two-electron donor. This occurs in the formation of $[Co_2(CN)_4(PMe_2Ph)_5(O_2)]$ (**205**) from the reaction of dioxygen with $[Co(CN)_2(PMe_2Ph)_3]$.[457] In this case the binuclear complex arises from a cyanide-bridged inner-sphere electron-transfer reaction between $[Co(CN)_2(PMe_2Ph)_3]$ and the immediate O_2-substituted product $[Co(CN)_2(PMe_2Ph)_2(O_2)]$. The formal oxidation states of the final product thus correspond to $Co^{III}NCCo^{III}(O_2^{2-})$. All the η^2-dioxygen adducts are kinetically robust, which is surprising in view of the small bite angles ($OCoO \approx 45°$) reported for these species (Table 57).



(205)

47.7.1.4 η^1:η^1 Peroxo

The reaction of cobalt(II) complexes with dioxygen in aqueous solution normally produces diamagnetic μ-peroxocobalt(III) complexes, and isotopic labelling shows the peroxo bridge to be derived entirely from the O_2 used in the preparation.[710] Formation of the dimer is preceded by formation of a monomeric superoxo species (Scheme 69), which may be stabilized by steric hindrance in the ligand. Generally the kinetic and/or energy balance favours the dimer. The ligands include simple monodentates (H_2O, NH_3, CN^-, NO_2^-, halide), aminocarboxylates, polyamines and various macrocycles.

$$[(L_5)Co]^{n+} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(L_5)Co(O_2)]^{n+}$$

$$[(L_5)Co(O_2)]^{n+} + [Co(L_5)]^{n+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(L_5)Co(O_2)Co(L_5)]^{2n+}$$

Scheme 69

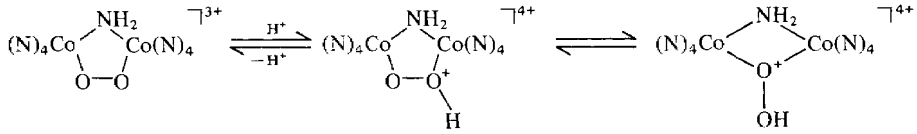
Under basic conditions acidic ligands (H_2O, NH_3) *cis* to the peroxo group can be deprotonated to form dibridged μ-(OH,O_2) or μ-(NH_2,O_2) species. The effect of the second bridge is to stabilize the peroxo dimer toward dissociation. However, while the amido bridge is stable in acidic solution the μ-hydroxo bridge is readily cleaved. Ethylenediamine[711] and tren[712] dibridged μ-peroxo species have also been reported. The one-electron oxidation of the usually brown μ-peroxo cobalt(III) complexes with strong oxidants such as Ce^{IV}, Cl_2 or $S_2O_8^{2-}$ affords green paramagnetic μ-superoxo complexes. Table 55 gives details of the preparation of water-soluble μ-peroxo and μ-superoxo complexes where these have been isolated as crystalline solids. Ligand exchange on many of the μ-peroxo complexes is rapid and the facile substitution of monodentate ligands frequently provides an alternative to direct oxygenation as a synthetic route, *e.g.* equation (128).

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{4+} + 2\text{dien} \longrightarrow [(NH_3)_2(\text{dien})Co(O_2)Co(\text{dien})(NH_3)_2]^{4+} + 6NH_3 \quad (128)$$

It has recently been shown that the rates of substitution of NH_3 ligands in $[\{(en)_2(NH_3)Co\}_2(O_2)]^{4+}$ [713] and dioxygen exchange in $[\{(tren)(MeNH_2)Co\}_2(O_2)]^{4+}$ [714] are identical with the pH-independent rates of decomposition of these complexes to cobalt(II) species and dioxygen. Similarly, the rates of formation of μ-hydroxo bridges, following loss of amine ligand, in $[\{(tren)(NH_3)Co\}_2(O_2)]^{4+}$,[715] $[\{(en)_2(NH_3)Co\}_2(O_2)]^{4+}$ [713] and $[\{(tren)(MeNH_2)Co\}_2(O_2)]^{4+}$ [714] are found to be identical with the rates of decomposition of the complexes to cobalt(II) and O_2. Thus the fast ligand-exchange rates observed for the μ-peroxo complexes arise from the lability of the cobalt(II) species produced *via* Scheme 69.

Not all singly bridged μ-peroxo complexes decompose as indicated by the reverse pathways of Scheme 69. It has long been known that in acidic solution $[\{(NC)_5Co\}_2(O_2)]^{6-}$ is cleaved quantitatively to $[Co(CN)_5(H_2O)]^{2-}$ and hydrogen peroxide,[31] and a number of other μ-peroxo complexes behave similarly. Also, in acidic media *trans*-$[\{(SCN)([14]aneN_4\}Co)_2(O_2)]^{2+}$ is quantitatively converted to *trans*-$[Co(SCN)_2([14]aneN_4)]^+$ in the presence of SCN^- in a process which produces H_2O_2.[716] Solutions of $[\{(H_2O)([14]aneN_4)Co\}_2(O_2)]^{4+}$ possess both oxidizing and reducing properties[717] and it is probable that H_2O_2 formation in this reaction is due to an outer-sphere electron transfer between the oxidizing Co^{III}—(O_2) and reducing Co^{II} species produced in the first step of peroxo-dimer decomposition.

Concentrated solutions of strong acids protonate the peroxo bridge to produce red μ-hydroperoxo complexes. Protonation of $[(N_4)Co(\mu\text{-}NH_2,O_2)Co(N_4)]^{3+}$ ions $[(N_4) = (NH_3)_4, (en)_2$; Scheme 70] initially gives the orange intermediate (**206**), which slowly isomerizes to the red isomer (**207**).[710,718] Crystallographic studies on (**207**) for $(N_4) = (en)_2$[719] confirm the end-on coordination mode for the hydroperoxo group and give the O—O bond distance as 142 pm. The three bonds to the bridging oxygen atom are not coplanar.

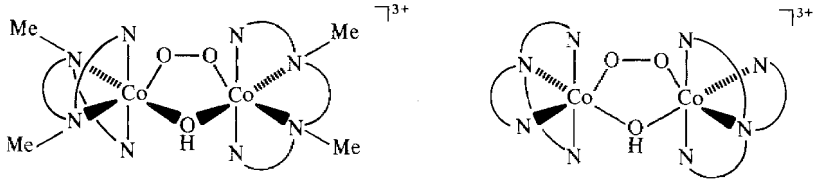


(206) (207)

Scheme 70

Zehnder and Fallab[720] have demonstrated peroxo bridge formation *via* anation of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ with H_2O_2. Reaction at pH 4.8 initially gives the hydroperoxo complex *cis*-$[Co(OOH)(en)_2(H_2O)]^{2+}$, which at higher pH reacts with $[Co(OH)(en)_2(H_2O)]^{2+}$ to yield racemic $[(en)_2Co(\mu\text{-}OH,O_2)Co(en)_2]^{3+}$. Crystal structures of the dibridged species are available for the *meso*[721] and racemic[722] forms.

The question regarding isomer distributions in μ-peroxo complexes containing multidentate ligands has been addressed by Fallab and coworkers. In the formation of $[(trien)Co(\mu\text{-}OH,O_2)Co(trien)]^{3+}$ eight chemically distinct isomers are possible of which three are observed.[723] Methylation at the secondary nitrogens of the trien ligand destablizes isomers with the β configuration and oxygenation of $[Co(Me_2trien)(H_2O)_2]^{2+}$ in alkaline solution gives the dibridged complex (**208**)[723] with an α,α configuration. Three achiral isomers of $[(tren)Co(\mu\text{-}OH,O_2)Co(tren)]^{3+}$ are possible, however only (**209**) is formed by oxygenation of $[Co(tren)(OH_2)]^{2+}$.[724]



(208) (209)

The electronic spectra of μ-peroxo cobalt(III) complexes are dominated by LMCT transitions from filled $\pi^*(O_2^{2-})$ orbitals to empty Co^{III} $d\sigma^*$ orbitals, giving rise to intense broad bands in the near UV region.[725] Ligand field bands often appear as poorly defined shoulders on the rising UV absorption but are resolved for certain [14]aneN$_4$ complexes.[716] The monobridged μ-peroxo dimers often exhibit two band maxima at ~ 320 and 380 nm, whereas the dibridged complexes $[\mu\text{-}(OH,O_2)$, $\mu\text{-}(NH_2,O_2)]$ display one intense band at 360 nm with a shoulder at higher energies. These features arise from splitting of the $\pi^*(O_2^{2-})$ level and are related to the planarity of the $Co(O_2)Co$ unit.[651] Electronic[716] and ^{59}Co NMR[726] spectral studies indicate that the μ-peroxo group possesses normal spectrochemical properties for an oxygen donor ligand bound to Co^{III}.

Selected structural data for μ-peroxo cobalt(III) complexes are included in Table 57. Orbital diagrams constructed for Co—O—O bonds in $N_4Co(O_2)CoN_4$ species show that *trans* bent bonds are the most stable[727] and this is what is observed for the monobridged complexes. Dibridging forces the μ-peroxo group to adopt a skewed *cis* geometry except in cases (*e.g.* $[(tren)Co(\mu\text{-}tren,O_2)Co$-

Table 57 Structures: Monomeric and Dimeric Cobalt(III)–Peroxo Complexes

Compound	*O—O* (pm)	*Co—O* (pm)	*Co—O—O* (°)	*Ref.*
Monomeric				
$[Co(vpp)_2(O_2)](BF_4)$	142	189	–	1
$[Co_2(Me_2PhP)_5(CN)_4(O_2)]\cdot 0.5C_6H_6$	144	190	44.6 (O—Co—O)	2
cis-β-[Co(*R*,*R*-tetars)(O_2)](ClO_4)	142	186	44.9 (O—Co—O)	3
Dimeric, monobridged				
$[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2\cdot 4H_2O$	147	188	113	4
$[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_4\cdot 2H_2O$	147	189	111	5
[(pydpt)Co(O_2)Co(pydpt)]$I_4\cdot 3H_2O$	146	189	115	6
[(en)(dien)Co(O_2)Co(dien)(en)]$(ClO_4)_4$	149	190	110	7
$[(NO_2)(en)_2Co(O_2)Co(en)_2(NO_2)](NO_3)_2\cdot 4H_2O$	153	189	110	8
[(tetren)Co(O_2)Co(tetren)]$(S_2O_6)(NO_3)_2\cdot 4H_2O$	149	192	112	9
$[(NH_3)_5Co(O_2)Co(NH_3)_5](SCN)_4$	147	188	111	10
$K_8[(NC)_5Co(O_2)Co(CN)_5](NO_3)_2\cdot 4H_2O$	145	199	119	11
[{Co(3-Fsalen)}$_2$$(H_2O)(O_2)]_2\cdot$pip$\cdot 2CHCl_3$	131	193, 200	118	21
[{Co(salen)(pip)}$_2$$(O_2)]\cdot\frac{1}{3}pip\cdot\frac{2}{3}$ac	138	191	120	22
[{Co(salpr)}$_2$$(O_2)]\cdot$toluene	145	193	119	23
[{Co(salen)(dmf)}$_2$$(O_2)$]	134	191	120	24
Dimeric, dibridged				
[(tren)Co(OH)(O_2)Co(tren)]$(ClO_4)_3\cdot H_2O$	146	186	112	13
[(dmtad)Co(OH)(O_2)Co(dmtad)]$(ClO_4)_3\cdot 2H_2O$	143	189	107	14
$[(en)_2Co(NH_2)(O_2)Co(en)_2](SCN)_3\cdot H_2O$	146	187	110	15
[(tren)Co(tren)(O_2)Co(tren)]$(ClO_4)_4\cdot 2H_2O$	149	188	116	16
$[(en)_2Co(NH_2)(O_2H)Co(en)_2](NO_3)_4\cdot H_2O$	142	192	111, 119	17
$[(en)_2Co(OH)(O_2)Co(en)_2]I_3\cdot 4.5H_2O$	145	174, 184	116, 110	18
$[(en)_2Co(OH)(O_2)Co(en)_2](S_2O_6)(NO_3)\cdot 2H_2O$	147	186	110	19
$[(en)_2Co(OH)(O_2)Co(en)_2](NO_3)_3AgNO_3\cdot H_2O$	143	188	111	20

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(tren)]$^{4+}$) where the additional bridging ligand possesses sufficient conformational flexibility to allow the *trans* structure. The O—O bond lengths (mean 147 pm) are comparable with that found for ionic peroxide in Na_2O_2 (149 pm).[728] In the solid-state structures hydrogen-bonding effects, packing forces and the nature of the counterion play a role in determining the planarity of the Co—O—O—Co unit.[644,729]

Rate studies on the oxygenations of cobalt(II) complexes in aqueous solution are numerous. According to Scheme 69, and assuming a steady state in $L_5Co(O_2)$, production of the μ-peroxo complex follows equation (129), which for $k_2[CoL_5] \gg k_1$ reduces to equation (130) and k_1 is obtained directly. At ambient concentrations of O_2 this is generally the case, implying that for most Co^{II} complexes formation of the monomeric L_5CoO_2 species is rate determining under these conditions. Values of the rate constant k_1 (Table 58) mainly lie in the relatively narrow range 10^3 to 10^5 dm^3 mol^{-1} s^{-1} at 25 °C irrespective of the nature of the ligands on the Co^{II} reactant. This

constancy appears to arise, at least in part, from a mechanism dominated by water exchange; however the oxygenation rates are slower than the estimated rates of water exchange at Co^{II} centres by a factor of $\sim 10^3$, and the data indicate that there is a strict orientation requirement of the O_2 moiety in the substitution process. It is of some interest to find that the low-spin $[Co([14]aneN_4)(OH_2)_2]^{2+}$ and high-spin $[Co([15]aneN_4)(OH_2)_2]^{2+}$ ions combine with O_2 at comparable rates.[730] Since reaction of the latter complex requires a change in spin multiplicity, the intrinsic barrier to adduct formation appears not to be sensitive to the spin state of the Co^{II} reactant.

$$d[L_5Co(O_2)CoL_5]/dt = k_1k_2[CoL_5]^2[O_2]/(k_{-1} + k_2[CoL_5]) \quad (129)$$

$$d[L_5Co(O_2)CoL_5]/dt = k_1[CoL_5][O_2] \quad (130)$$

A recent kinetic study has monitored oxygenation of the primary Co^{II} photoproduct produced following flash photolysis of *cis*-$[Co(NO_2)_2(en_2]^+$ in air-saturated acetonitrile solution.[731]

Hyde and Sykes[732] have carried out a detailed study of the Cr^{II} reduction of $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{3+}$. The reaction proceeds in five identifiable stages; the first involving inner-sphere attack by Cr^{2+} on the peroxo bridge to give a Cr^{III}—$(O_2)^{2-}$—Co^{III} species. The stepwise reduction is complicated, with isomerization and decomposition being involved in the intermediate stages before final Cr^{2+} reduction of the Co^{III} centre. The Fe^{2+} reduction of $[(N_4)Co(\mu\text{-}OH,O_2)Co(N_4)]^{3+}$ ions in acidic solution is slower than hydrolysis of the OH bridge, and the previously reported Fe^{2+} reduction of the doubly bridged species[733] has been shown to be in error.[734]

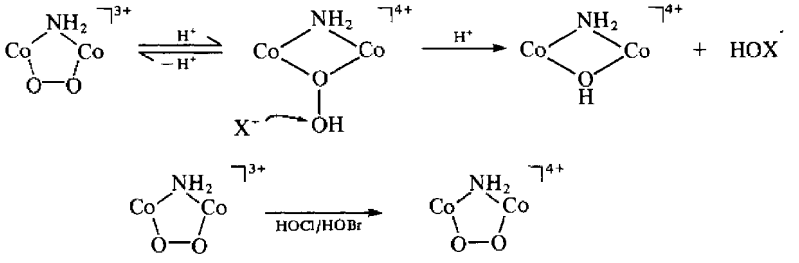
Fallab[735] has shown that reaction of I^- with $[(en)_2Co(\mu\text{-}OH,O_2)Co(en)_2]^{3+}$ gives $[Co(en)_2(OH_2)]^{3+}$ and I_2 in acidic solution. Hydrolysis of the OH bridging group is followed by I^- attack on the mono-bridged species. The latter process is related to that occurring when I^- reacts with $[(N_4)Co(\mu\text{-}NH_2,O_2)Co(N_4)]^{3+}$ ions to produce $[(N_4)Co(\mu\text{-}NH_2,OH)Co(N_4)]^{4+}$ species,[736] and to the Cl^-- or Br^--catalyzed disproportionation of the μ-amido-μ-peroxo complexes to produce the correspond-

Table 58 Rate Constants for Oxygenation of Co^{II} Complexes in Water at 25 °C

Complex	k_1 ($M^{-1}s^{-1}$)	*Ref.*
$[Co(tren)(H_2O)]^{2+}$	2.2×10^2	1
$[Co([14]aneN_4)(H_2O)_2]^{2+}$	5×10^5	2
$[Co([15]aneN_4)(H_2O)_2]^{2+}$	3.8×10^3	2
$[Co(NH_3)_5(H_2O)]^{2+}$	2.5×10^4	3
$[Co(en)_2(H_2O)_2]^{2+}$	4.7×10^5	4
$[Co(dien)_2]^{2+}$	1.2×10^3	4
$[Co(trien)(H_2O)_2]^{2+}$	2.5×10^4	5
$[Co(OH)(trien)(H_2O)]^{+}$	2.8×10^5	5
[Co(L-his)]	3.5×10^3	6
$[Co(gly\text{-}gly)]^{2-}$	1.0×10^4	7
$[Co(cys)_3]^{-}$	2.0×10^5	8
$[Co(sdtma)(H_2O)_2]^{+}$	3×10^3	9
$[Co(udtma)(H_2O)_2]^{+}$	1.4×10^4	9
$[Co(sedda)(H_2O)_2]$	25	10
$[Co(uedda)(H_2O)_2]$	22	10
$[Co(terpy)(phen)(H_2O)]^{2+}$	8.5×10^5	11
$[Co(terpy)(bipy)(H_2O)]^{2+}$	1.0×10^6	11

1. H. Macke, *Helv. Chim. Acta*, 1981, **64**, 1579.
2. C. L. Wong, J. A. Switzer, K. P. Balakrishnan and J. F. Endicott, *J. Am. Chem. Soc.*, 1980, **102**, 5511.
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9. G. McLendon, D. T. MacMillan, M. Hariharan and A. E. Martell, *Inorg. Chem.*, 1975, **14**, 2322.
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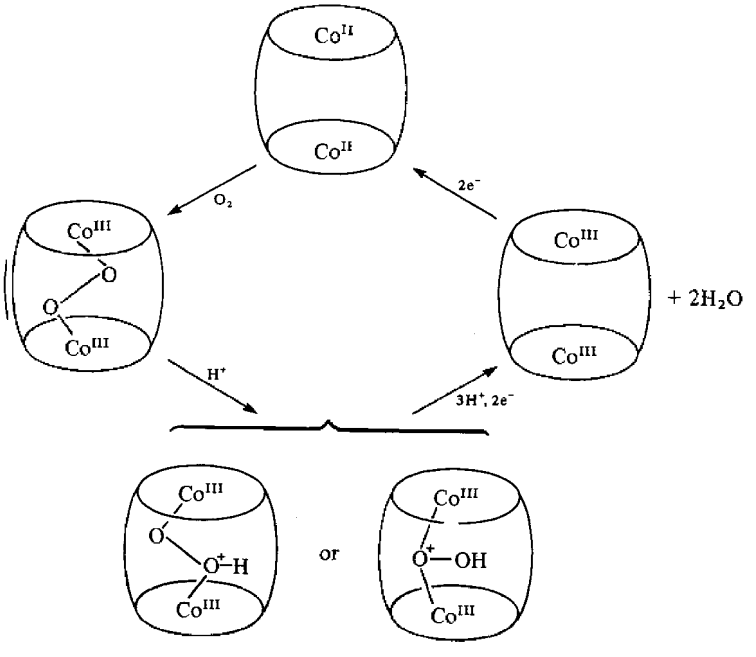
ing μ-amido-μ-hydroxo and μ-amido-μ-superoxo species.[737] In those systems it is likely that the reactive form of the complex is the hydroperoxo species, which undergoes initial attack by halide ion at the non-bridging oxygen atom (Scheme 71). Sulfite and nitrite ions with $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{3+}$ give respectively $[(en)_2Co(\mu\text{-}NH_2,SO_4)Co(en)_2]^{3+}$ and $[(en)_2Co(\mu\text{-}NH_2,NO_2)Co(en)_2]^{4+}$.[738]



Scheme 71

Reduction potentials for μ-superoxo/μ-peroxo–cobalt(III) couples have recently been obtained by cyclic voltammetry.[739,740] Decomposition or dissociation of one or the other of the components of the couple, which frustrated measurements by other techniques, may be overcome by the use of fast scan rates. Protonation of the μ-peroxo group stabilizes the complex and $E^{\ominus}$ values are pH dependent below pH 3. A similar stabilization on protonation of the peroxo bridge has been noted in the Cr^{2+}-, V^{2+}- and Eu^{2+}-promoted reduction[705] of the $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$ ion. The protonated species has $K_a \sim 10\,dm^3\,mol^{-1}$ at 25 °C.[705]

Dimeric cobalt porphyrins linked at the porphyrin periphery to provide a cofacial configuration, and capable of forming μ-bridged oxygen adducts, have been reported.[742,743] Chang[742] demonstrated that peroxo-bridge formation occurred on exposure of a dicobalt porphyrin to dioxygen and that the μ-peroxo complex was readily oxidized to the corresponding μ-superoxo species. More recently, Collman's group[743] has investigated electroreducing properties of a number of dicobalt porphyrins bound to graphite electrodes in acidic aqueous solution. Electroreduction of O_2 to H_2O_2 or H_2O is observed in all cases with the mode of catalytic activity being dependent on the degree of separation of the two Co centres. One possible mechanism for the four-electron reduction of dioxygen to water in this system is shown in (Scheme 72), but it should be emphasized that bridging dioxygen species have not been directly observed in this process.



Scheme 72

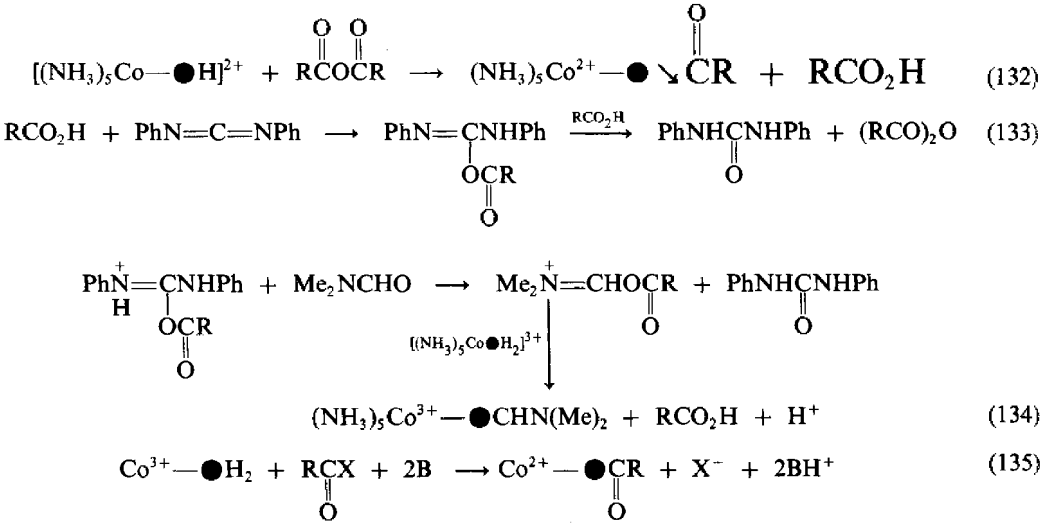
47.7.2 Carboxylates

47.7.2.1 Synthesis, cobalt(III)

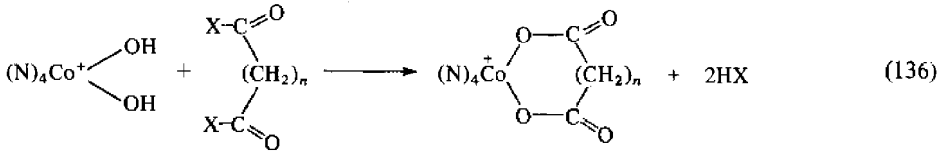
Until recently the heating of Co—OH_2^{n+} species with RCO_2H or RCO_2Na in neutral aqueous solution, first used by Gibbs and Genth,[744] was the recognized method of preparation. Gould,[745–747] following earlier work by Sebra and Taube,[74] prepared numerous $[Co(OCOR)(NH_3)_5]^{2+}$ ions by this method (equation 131). Some improvement is possible using $[Co(DMF)(NH_3)_5](ClO_4)_3$ or $[Co(DMSO)(NH_3)_5](ClO_4)_3$ in DMF or DMSO, by using $[Co(OH_2)(NH_3)_5](ClO_4)_3$ in ethylene glycol, and by using $[Co(OCO_2)(NH_3)_5](NO_3)$ in diglyme[746] or methanol.[747] The Ag^+-induced removal of Cl^- from $[CoCl(NH_3)_5]Cl_2$ or *cis*-$[Co(Cl)_2(en)_2](ClO_4)$ in MeOH at room temperature[750,751] is another possibility but is not recommended.

$$[Co(OH_2)_{6-x}(amine)_x]^{3+} + RCO_2^- \longrightarrow [Co(OCOR)_{6-x}(amine)_x]^{(3-x)+} + (6-x)H_2O \quad (131)$$

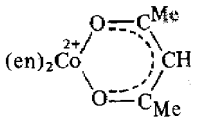
The new method, rediscovered by Jackman, Scott and Portman,[752] originates with Werner who prepared $[Co(OCOR)(NH_3)_5](NO_3)_2$ (R = Me, Et) using a heterogeneous mixture of solid $[Co(OH)(NH_3)_5](NO_3)_2$ and the appropriate anhydride (equation 132).[753] Jackman and coworkers use non-aqueous conditions and have extended the reaction to include a large number of acid anhydrides, with the hydroxo complex being generated *in situ* by adding the sterically hindered base $N(Me)_2Bz$.[754] The rate law for reaction (132) in aqueous solution takes the form $k_{obs} = kK_a[Co]_T/(K_a + [H^+])$, which is consistent with Co—OH^{2+} being the reactive species (K_a = acidity constant for Co—OH_2^{3+}). The reaction is normally quite fast ($k = 3.1\,mol^{-1}\,dm^3\,s^{-1}$ for R = Et, 25 °C $I = 1.0$) and ^{18}O tracer experiments confirm that the oxygen atom in the coordinated carboxylate derives from the hydroxo ligand.[755] The difficulty with using aqueous solutions in a preparative sense is the ready hydrolysis of many anhydrides. In non-aqueous solvents (DMF, DMSO, $(MeO)_3PO$) the anhydride can often be generated *in situ* from the parent acid (equation 133), but in DMF it is important to generate the Co—OH species before adding RCO_2H (*i.e.* add the sterically hindered base before adding RCO_2H) otherwise Co—DMF^{3+} is formed in rather large amounts (equation 134).[756] Such side reactions can also be fast and occur *via* nucleophilic attack of Co—OH at the unsaturated C centre.[757] This new preparative method has general utility since any acyl compound with a good leaving group can be used (equation 135). This probably includes dicarboxylic acid species (monodentate or bidentate) but such preparations (equation 136) have not been examined in detail. However chelated acetylacetonate (**210**) has been prepared in this manner.[758] The recent preparations of *cis*- and *trans*-$[Co(NO_2)(OC_2O_3)(en)_2]$ uses displacement of the aqua ligand by $C_2O_4^{2-}$.[169]



$X = Cl^-, PhO^-, p\text{-}NO_2C_6H_4O^-, RCO_2^-$; B = NEt_3, or similar non-nucleophilic base



$X = Cl^-, p\text{-}NO_2C_6H_4O^-$



(210)

47.7.2.2 Monocarboxylates

(*i*) *Formato, cobalt(I)*

The reaction of CO_2 with $[CoH(N_2)(PPh_3)_3]$ or $[Co(H)_3(PPh_3)_3]$ in benzene containing excess phosphine leads to the green formato complex $[Co(O_2CH)(PPh_3)_3]$.[409] In the absence of excess ligand only brown $[Co(CO)(PPh_3)_3]$ and a cobalt(II) formate species, which converts to $Co(HCOO)_2 \cdot 2H_2O$ on exposure to moist air, are formed. Attempts to insert CO_2 into the Co—H bonds of $[CoH(dppe)_2]$ and $[CoH(dppv)_2]$ lead to poorly defined products which release CO_2 on treatment with H_2SO_4 and which do not contain coordinated formate.[759] By contrast, $[CoH(N_2)(RR'_2P)_3]$ and $[Co(H)_3(RR'_2P)_3]$ (R = Et, R′ = Ph; R = Ph, R′ = Et) both give formate complexes on treatment with CO_2. These are less stable than the corresponding PPh_3 complexes but few experimental details are available. $[CoH(PMe_2Ph)_4]$ does not react with CO_2 in the solid state but in benzene solution it takes up CO_2 reversibly to give $[Co(O_2CH)(PMe_2Ph)_3]$.[760] This has antisymmetric and symmetric vibrations of the CoOCHO group at 1610 and 1360 cm^{-1}. A general scheme for the insertion of CO_2 into Co—H bonds involving initial formation of cobalt–carbon dioxide adducts has been proposed (Scheme 73).[760]

$$[CoH(L)_4] + CO_2 \rightleftharpoons [CoH(CO_2)(L)_3] + L$$

$$[CoH(CO_2)(L)_3] \rightleftharpoons [Co(OCHO)(L)_3]$$

Scheme 73

(*ii*) *Formato, cobalt(III)*

$[Co(O_2CH)(NH_3)_5](ClO_4)_2$ containing O-bonded formate has been prepared *via* $[Co(OH_2)(NH_3)_5](ClO_4)_3$ (pink, ε_{500} 69.6),[761] but it can undoubtedly be made *via* $[Co(OH)(NH_3)_5]^{2+}$ and MeO_2CH (equation 135), or by using $[Co(DMSO)(NH_3)_5](ClO_4)_3$ and NaO_2CH. The carbonyl O undergoes H^+-catalyzed exchange, $k = 6.2 \times 10^{-5}$ mol^{-1} dm^3 s^{-1},[762] but the complex is quite stable in aqueous solution (Table 59). The *cis*-$[Co(O_2CH)(H_2O)(en)_2]^{2+}$ ion has been reported in aqueous solution (λ_{max} 300, 500 nm).[761]

Major interest lies in the oxidation of Co^{III}—OC(O)H species to CO_2, its use in electron transfer, and its photochemistry. Candlin and Halpern showed that oxidation by MnO_4^- (1.0–0.1 mol dm^{-3} H^+, ~0 °C) followed the rate law $k_{obs} = k[MnO_4^-]$ ($k = 2.5 \times 10^{-2}$ mol^{-1} dm^3 s^{-1}) but with the $[Co(NH_3)_5(OH_2)]^{3+}$ product showing an additional $[MnO_4^-]$ dependence over the less abundant $Co^{2+}_{(aq)}$ product (ratio ≈ 3.5 in 10^{-2} mol dm^{-3} MnO_4^-).[763] This was interpreted in terms of Scheme 74 with the primary act being H atom abstraction to give the formate radical anion (**211**). Presumably the k_2 path leads to Co^{III}—O=C=O or Co^{III}—CO_2, which rapidly aquates. More recently Brezniak and Hoffman generated (but did not directly observe) the same radical intermediate (**211**) using pulse radiolysis methods with H atom abstraction by HO· and H·.[764] Only $Co^{2+}_{(aq)}$ was observed in this study ($k \sim 2 \times 10^9$ mol^{-1} dm^3 s^{-1}) and using an estimate of $k_3 > 10^6$ s^{-1} for the electron-tunnelling process (equation 137) they estimate k_2 of Scheme 74 as $> 3 \times 10^8$ mol^{-1} dm^3 s^{-1}. Clearly the CO_2^- radical coordinated to Co^{III} is a powerful reducing agent. Photolysis at 254 nm also leads to $Co^{2+}_{(aq)}$ and CO_2 (also H_2 by a secondary process),[761] and a long-lived intermediate, assigned as the C-bonded formato isomer (**212**; Scheme 75), has been characterized.[765] This species is attributed to a pathway involving ligand excitation (Scheme 75) and has a $pK_a = 2.6$. It is much more stable than the radical anion, existing for at least one minute in acidic solution but more rapidly decaying at pH 5 (~50 s^{-1}).[765]

Table 59 Rate Data for Aquation and Base Hydrolysis of Some Carboxylate Cobalt(III) Complexes

Complex	*Ligand*	k^0_{aq} (s^{-1})	k_{OH} ($mol^{-1}dm^3s^{-1}$); k'_{OH} ($mol^{-2}dm^6s^{-1}$)[a]	*Ref.*
$[CoX(NH_3)_5]^{n+}$	HCO_2^-	5.8×10^{-4}	–	13
	$MeCO_2^-$	3.0×10^{-7}, 40 °C	–	1
	$MeCO_2H$	1.2×10^{-4}, 40 °C	(K_a 0.65)	1
	$(MeO)C_6H_4CO_2^-$	1.3×10^{-5}	–	1
	$(MeO)C_6H_4CO_2H$	2.7×10^{-4}	(K_a 0.14)	1
	$C_2O_4^{2-}$	1.1×10^{-6}, 40 °C	2.45×10^{-4} (k_{OH}) 6.1×10^{-5} (k'_{OH})	1, 5
	$HC_2O_4^-$	6.3×10^{-6}	(K_a 116)	1
	$HO_2CCH_2CO_2^-$	2.9×10^{-7}, 40 °C	–	1
	$M^{2+}O_2CCO_2^-$	1.5×10^{-5} (Zn^{2+}), 60 °C	–	2
		2.0×10^{-5} (Ni^{2+}), 60 °C	–	–
		1.5×10^{-5} (Co^{2+}), 60 °C	–	–
		1.0×10^{-4} (Cu^{2+}), 60 °C	–	–
	$HC_2O_4^-$	2.2×10^{-8}, 25 °C	–	7
	$C_2O_4^{2-}$	1.5×10^{-8}, 25 °C	–	7
	$HO_2C(CH_2)_2CO_2^-$	1.0×10^{-7}, 40 °C	–	1
	$HO_2C(CHOH)_2CO_2^-$	5.0×10^{-7}, 40 °C	–	1
	$HO_2CC_6H_4CO_2^-$	1.0×10^{-7}, 40 °C	–	1
	$HOC_6H_4CO_2^-$	4.6×10^{-6}, 70 °C	–	12
$[CoX(NH_3)(en)_2]^{n+}$	$C_2O_4^{2-}$	$< 1.0 \times 10^{-6}$, 60 °C	2.75×10^{-3}, 30 °C	9
	$HC_2O_4^-$	4.9×10^{-6}, 60 °C	–	9
	$HC_2O_4^- + H^+$	8×10^{-6}, 60 °C ($mol^{-1}dm^3s^{-1}$)	–	9
	$HOC_6H_4CO_2^-$ (also derivatives)	1.66×10^{-6}, 60 °C	–	10
	$^-OC_6H_4CO_2^-$ (also derivatives)	1.39×10^{-4}, 30.4 °C	1.13×10^{-3}, 30.4 °C	11
$[CoX(NH_3)(trien)]^{n+}$	$C_2O_4^{2-}$	–	2.95×10^{-2} (k_{OH}), 30 °C	8
	$^-OC_6H_4CO_2^-$	–	3.56×10^{-3} (k_{OH}), 30 °C	8
trans-$[CoX(OH)(en)_2]$	$C_2O_4^{2-}$	–	6.5×10^{-4} (k_{OH})	3
cis-$[CoX(OH)(en)_2]$	$C_2O_4^{2-}$	–	6.3×10^{-3} (k_{OH})	4
$[Co(O_2C_2O_2)(en)_2]^+$	Chelated $C_2O_4^{2-}$	–	6.2×10^{-5} (k'_{OH})	6

[a] At 25 °C.

1. D. Smith, M. F. Amira, P. D. Abdullah and C. B. Monk, *J. Chem. Soc., Dalton Trans.*, 1983, 337.
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10. A. C. Dash and B. Mohanty, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1179.
11. A. C. Dash and R. K. Nanda, *J. Inorg. Nucl. Chem.*, 1978, **40**, 309.
12. A. C. Dash and R. K. Nanda, *Inorg. Chem.*, 1973, **12**, 2024.
13. W. E. Jones, R. B. Jordan and T. W. Swaddle, *Inorg. Chem.*, 1969, **8**, 2504.

$$(NH_3)_5Co^{2+}\text{–}\overset{O}{\overset{\|}{O}}CH + MnO_4^- \xrightarrow[\text{(slow)}]{k} (NH_3)_5Co^{2+}\text{–}O\dot{C}{=}O + HMnO_4^- \quad (211)$$

$$(NH_3)_5Co^{2+}\text{–}O\dot{C}{=}O \xrightarrow{k_1 \geq 10^6\ s^{-1}} Co^{2+} + CO_2 + 5NH_3$$

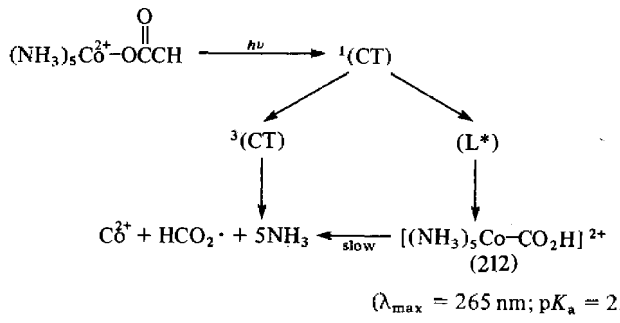
$$(NH_3)_5Co^{2+}\text{–}O\dot{C}{=}O \xrightarrow{k_2[MnO_4^-]} (NH_3)_5Co^{3+}\text{–}OH_2 + CO_2$$

Scheme 74

$$[(NH_3)_5Co^{III}\text{—}O\dot{C}{=}O]^{2+} \xrightarrow{k_3} [(NH_3)_5Co^{II}\text{—}OC{=}O]^{2+} \quad (137)$$

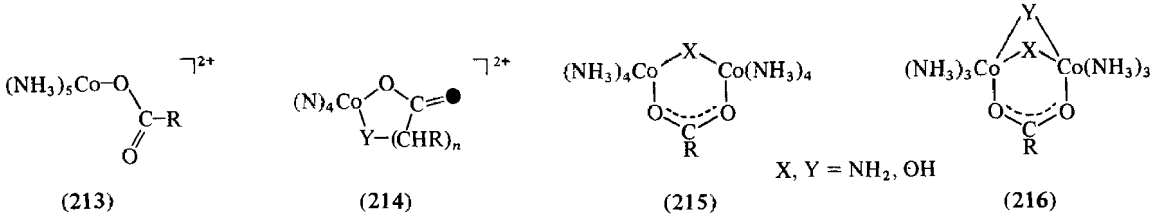
(*iii*) *Alkyl and aryl monocarboxylates, cobalt(III)*

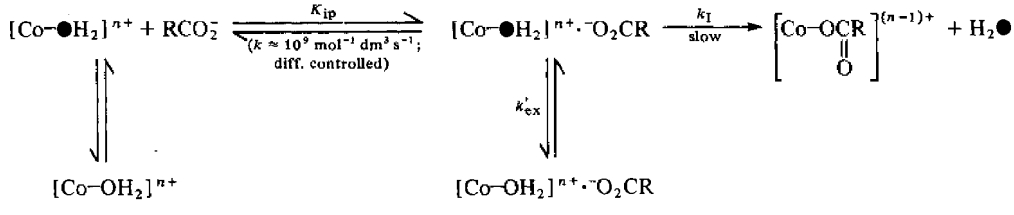
Both monomeric (**213**), chelated (**214**) and bridged dimeric (**215**) and (**216**) complexes are known. The latter were first prepared by Werner[689] and in the last decade have received some attention in relation to remote attack and outer-sphere electron transfer (see below). The monomeric complexes



Scheme 75

(**213**) are very abundant and simple to prepare (Section 47.7.2.1). Formation *via* anation of Co—OH_2^{n+} by RCO_2H or RCO_2^- is slow and occurs *via* displacement of coordinated water (Scheme 76). Table 43 contains some recent kinetic data and extensive compilations are to be found elsewhere.[772,773] Saturation kinetics are often encountered, $k_{obs} = k_I K_{ip}[RCO_2^-]/(1 + K_{ip}[RCO_2^-])$, with rate-determining substitution from within the ion pair (the alternative possibility of non-reactivity of the ion pair would be counter productive).[771] A dissociative mechanism is implied since k_I bears some resemblance to the water-exchange rate and has never been known to exceed it, but whether a totally dissociative process is involved within the ion pair with the five-coordinate intermediate existing long enough for unfavourably positioned ions to reorient themselves is not known.

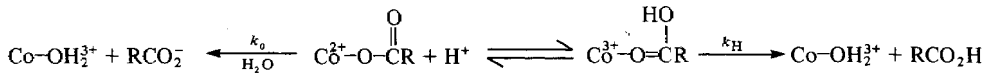




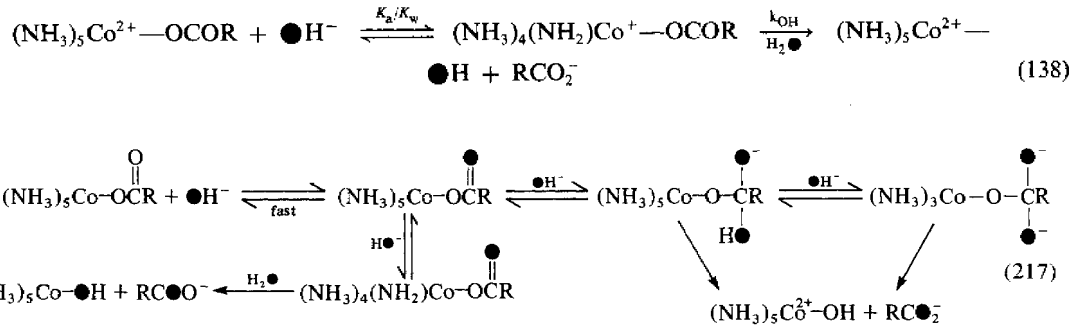
Scheme 76

The reverse hydrolysis in acidic to neutral solution often follows the rate law $k_{obs} = k_0 + k_H[H^+]$ and the reaction is again very slow; usually such studies are carried out at elevated temperatures. Table 59 contains some relevant data and extensive compilations are available.[772,773] k_H is regarded as solvolysis of the protonated substrate (Scheme 77) and represents the reverse of the anation by RCO_2H. Acid-catalyzed O exchange into the coordinated acyl function is generally slower than hydrolysis except for electronegative R (H, CF_3, CO_2H) where it is faster.[762] However, Jackman and coworkers have found intramolecular scrambling between the O atoms in $[Co\{OC(O)Me\}(NH_3)_5]Y_2$ both in solid and in solution.[757] In the solid it is about one-third complete in 90 d at 23 °C, and is two-thirds complete after 15 min at 50 °C in aqueous solution. It is not known whether this process is H^+- or OH^--catalyzed[774] and it may well resemble Co—SCN/Co—NCS isomerization (Section 47.4.4.1). O scrambling has not been observed in chelate complexes of type (**214**), probably because rotation about the acyl function is now more difficult. Alkaline hydrolysis is also slow, but is faster than acid hydrolysis; it follows the rate law $k_{obs} = k_{OH}[OH^-]$ in most complexes (Table 59). An S_N1cb mechanism is generally accepted with aquation of the amine-deprotonated conjugate and cleavage of the Co—O bond (equation 138).[772,773] For some electronegative R (CF_3, CCl_3, $CHCl_2$, CO_2^-) $k_{obs} = k_{OH}[OH^-] + k'_{OH}[OH^-]^2$ with OH^- attack at the acyl function and both Co—O and CoO—C bond cleavage, the latter *via* the deprotonated addition intermediate (**217**; Scheme

78).[774–776] OH^--catalyzed exchange of carbonyl oxygen is generally slower than alkaline hydrolysis for most alkyl groups with monodentate systems,[777] but for the above electronegative species it is comparable.[774,775]



Scheme 77



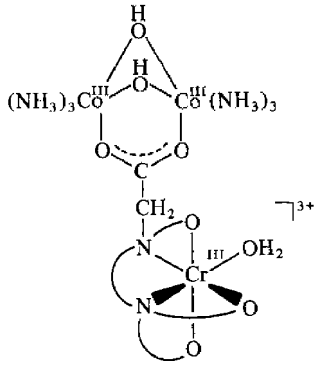
(138)

(217)

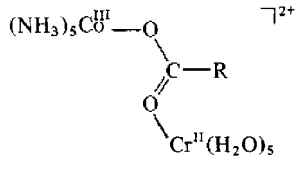
Scheme 78

The bridged complexes (**215**) and (**216**) are generally prepared from μ-(OH) species (Table 60).[781] Thus the rate law for the formation of $[\{Co(NH_3)_4\}_2(\mu\text{-}NH_2,O_2CMe)]^{4+}$ in the $[H^+]$ range 0.1–1.5 takes the form $k_{obs} = (k_1 + k_2[H^+])[MeCO_2H]$ with $k_1 = 1.4 \times 10^{-6}\,mol^{-1}\,dm^3\,s^{-1}$, $k_2 = 6.5 \times 10^{-6}\,mol^{-2}\,dm^6\,s^{-1}$ at 25 °C.[768] Initial anation at one Co^{III} centre is considered to be rate determining with rapid subsequent bridging. Protonation of the bridging μ-(OH) also plays a part. The reverse hydrolysis is also H^+-catalyzed and is somewhat slower.[768] Recently the novel $Co_2^{III}Cr^{III}$ complex (**218**) has been reported[767] and obvious extensions are possible.

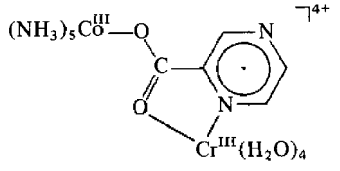
Carboxylate–Co^{III} systems have been extensively used to study electron transfer. Taube and Gould pioneered this work and have remained major contributors.[270,748] A recent review by Pennington is recommended,[769] and articles by Haim (bridged activated complexes), Meyer (excited state), Sutin (theory), Endicott (structural and photochemical probes), Ford, Wink and DiBenedetto (photochemical), Espenson (free radical) and Creutz (mixed valence complexes) in a volume dedicated to Taube[770] provides up-to-date background. Inner-sphere paths using a Cr^{2+} reductant probably proceed *via* an intermediate such as (**219**), while if R contains a coordination centre then radical intermediates such as (**220**) have been observed.[778] The same or similar reduced-ligand intermediates have also been directly generated *via* pulse-radiolysis studies.[779,780] With bridged carboxylates (**216**), an outer-sphere mechanism is more likely since both oxygens are already coordinated but if R contains an available coordination site then bridged intermediates are again observed and are probably the reactive entity.[360] Other reductants, such as the photoexcited $[Ru(bipy)_3^*]^{2+}$ species, are thought to act by both outer-sphere and ligand-reduced inner-sphere mechanisms.[782]



(218)



(219)



(220)

Table 60 Preparations: Some Bridged Monocarboxylate and Dicarboxylate Cobalt(III) Complexes

Complex	*Ligand*	*Preparation*	*Properties*	*Ref.*
Monodentate				
$[CoL(NH_3)_5](ClO_4)_2$	$C_2O_4H^-$	$[Co(OH_2)(NH_3)_5](ClO_4)_3 + NaHC_2O_4$; heat, neutral to pH 8	Red; ε_{505} 73	21
$[CoL(NH_3)_5]ClO_4$	$C_2O_4^{2-}$	As above	Red; ε_{505} 76	21
$[CoL(NH_3)_5](ClO_4)_2$	$CH_2(CO_2^-)_2$	As above	Red; ε_{505} 75	22
$[CoL(NH_3)_5](ClO_4)_2$	$(CH_2CO_2^-)_2$	As above	Red; ε_{505} 68	
$[CoL(NH_3)_5](ClO_4)_2$	$C_6H_4(CO_2^-)_2$	As above	Red; ε_{505} 79	22
$[CoL(NH_3)_5](ClO_4)_2$	$(CHCO_2^-)_2$	As above (fumarate)	Red; ε_{502} 75	23
$[CoL(NH_3)_5](ClO_4)_2$	$(CHCO_2^-)_2$	As above (maleate)	Red; ε_{502} 77	24
Bridged				
$[\{Co(NH_3)_5\}_2(\mu\text{-L})](ClO_4)_4$	All of above	$[Co(NH_3)_5L](ClO_4)_2 + [Co(NH_3)_5H_2O](ClO_4)_3$; pH 4, 70–75 °C, 2–3 h, chrom.	Red; ε_{505} 150–170	25
$[\{(NH_3)_4Co\}_2(\mu\text{-}NH_2,L)]Y_4$	HCO_2^-	μ-(NH_2,Cl) + 50% RCO_2H; 50 °C, 30–50 min	Red; IR; ε_{517} 353 (H); 368 (Me)	28
(Y = Cl^-, ClO_4^-)	$MeCO_2^-$			
$[\{(NH_3)_3Co\}_2\{\mu\text{-}(OH)_2,L\}](ClO_4)_3$	$PhCO_2^-$	μ-$(OH)_3$ + RCO_2H; 65 °C, 10–15 min.	Red; IR; ε_{524} ~110	29
$[\{(NH_3)_3Co\}_2\{\mu\text{-}(OH)_2,L\}](ClO_4)_3$	$HOC_6H_4CO_2^-$	As above		
$[\{(NH_3)_3Co\}_2\{\mu\text{-}(OH)_2,L\}](ClO_4)_3$	$^-O_2CC_6H_4CO_2^-$	As above		
$[\{(NH_3)_3Co\}_2\{\mu\text{-}(OH)_2,L\}](ClO_4)_3$	$^-O_2CCH(OH)CH_2CO_2^-$	As above		
$[\{(NH_3)_3Co\}_2\{\mu\text{-}(OH)_2,L\}](ClO_4)_3$	HCO_2^-, $MeCO_2^-$	μ-$(OH)_3$ + RCO_2H; 60 °C, 30 min	Red; ε_{522} 111	30
$[\{(NH_3)_3Co\}_2\{\mu\text{-}(OH)_2,L\}](ClO_4)_3$	$[Cr(edta)(H_2O)]$	μ-$(OH)_3$ + $[Cr(edta)(H_2O)]$; 65 °C, 15 min.	Violet; ε_{534}	31
$[\{(NH_3)_4Co\}_2\{\mu\text{-}NH_2,L)](NO_3)_3$	SO_4^{2-}	μ-(NH_2,O_2) + SO_2; 0.1 M HNO_3	Red	32
$[\{(NH_3)_4Co\}_2(\mu\text{-}NH_2,L)]Cl_4$	$C_2O_4^{2-}$	μ-(NH_2,Cl) + $H_2C_2O_4$; 50 °C, 35 min	Red; ε_{517} 370	19
$[\{(NH_3)_3Co\}_2(\mu\text{-}NH_2,OH,L)](ClO_4)_3$	$C_2O_4^{2-}$	μ-(NH_2,OH) + $H_2C_2O_4$; 50 °C, 1 h	Red	20
Chelates				
$K_3[Co(L)_3]$	$C_2O_4^{2-}$	$CoCO_3 + H_2C_2O_4 + K_2C_2O_4$; 40 °C, PhO_2	Green; sensitive to light	1
K_3-Δ,Λ-$[Co(L)_3]\cdot 3H_2O$	$C_2O_4^{2-}$	Resolved using $(-)_{589}$-$[Ni(phen_3)]^{2+}$	Racemizes in soln. 24 h; some oxalate exchange (crystal structure, Table 61)	2, 3
$K_4[Co(L)_2(OH)]_2$ (Durrant's salt)	$C_2O_4^{2-}$	$Co(OAc)_2 + K_2C_2O_4 + H_2O_2$; 55 °C	Green; sensitive to light, heat, alkaline soln.	4
cis-$[CoL(en)_2]Cl\cdot H_2O$	$C_2O_4^{2-}$	$Co(OAc)_2$ + en + $H_2C_2O_4$ + PbO_2; 80 °C, 30 min	Red; ε_{500} 113; ε_{360} 143	5, 6
Δ,Λ-$[CoL(en)_2]Br\cdot H_2O$	$C_2O_4^{2-}$	Resolved using $Ag_2\{(+)\text{-tart}\}$	$[\alpha]_{589}$ 820°	5
$Na[Co(L)_2(en)]$	$C_2O_4^{2-}$	$Co(OAc)_2 + K_2C_2O_4$ + en·2HCl + PbO_2; 80 °C, $Na_2C_2O_4$	Red-purple; ε_{540} 95; ε_{384} 172	6
Na-Δ,Λ-$[Co(L)_2(en)]\cdot H_2O$	$C_2O_4^{2-}$	Resolved using $(+)_{546}$-$[Co(NO_2)_2(en)_2]Br$	$[\alpha]_{589}$ 500°	6, 7

Table 60 (*continued*)

Complex	*Ligand*	*Preparation*	*Properties*	*Ref.*
$K_3[Co(NO_2)_2(L)_2]\cdot H_2O$	$C_2O_4^{2-}$	$CoCl_2 + K_2C_2O_4 + KHCO_3$; H_2O_2 40–50 °C; KNO_2; 40–50 °C, 2 h	Red; unstable in soln.	26
cis,trans-K(Li)[Co(L)$_2$(py)$_2$]·xH$_2$O	$C_2O_4^{2-}$	$K_3[Co(L)_3]$ + py + C; 60 °C, 2 h	Pink (*trans*); violet (*cis*)	27
$[CoL(NH_3)_4]ClO_4\cdot H_2O$	$C_2O_4^{2-}$	$[Co(CO_3)(NH_3)_4]NO_3 + H_2C_2O_4$	Red	10
$K[Co(CO)_3L(NH_3)_2]\cdot H_2O$	$C_2O_4^{2-}$	$Na_3[Co(CO_3)_3] + (NH_4)_2C_2O_4$	Purple	11
cis-$(NH_4)[Co(L)_2(NH_3)_2]\cdot H_2O$	$C_2O_4^{2-}$	$K[Co(CO_3)L(NH_3)] + H_2C_2O_4$	Red-purple; ε_{556} 110	11
$K[Co(CO_3)L(en)]\cdot H_2O$	$C_2O_4^{2-}$	$Na_3[Co(CO_3)_3] + (enH)_2C_2O_4$	Red-purple	11
$[Co(L)(en)_2]NO_3$	$CH_2(CO_2^-)_2$	$[Co(CO_3)(en)_2]NO_3 + Na_2mal$	Red; ε_{360} 103	8
$K[Co(L)_2(en)]\cdot H_2O$	$CH_2(CO_2^-)_2$	$Co(OAc)_2 + K_2CH_2(CO_2)_2 + (enH)_2[CH_2(CO_2)_2] + PbO_2$; 75 °C	Purple-red	6
K-Δ,Λ-$[Co(L)_2(en)]\cdot 2H_2O$	$CH_2(CO_2)_2$	Resolved using $(-)_{546}$-*trans*-$[Co(Cl)_2(en)_2]Cl$ + NaHsal; pH 7.5, > 90 °C	Red; ε_{516} 170; ε_{330} 2490	8
Δ,Λ-$[Co(L)(en)_2]NO_3$	$^-OC_6H_4CO_2^-$	Resolved using Brcamp. sulfonate	$[\alpha]_{589}$ 2540	8
β-[CoL(trien)]Cl·H$_2$O	$^-OC_6H_4CO_2^-$	*β*-$[Co(Cl)_2(trien)]Cl + H_2sal$; pH 10–11, heat	ε_{530} 270(β_1); ε_{520} 270(β_2); ^1H, ^{13}C NMR	9
$[CoL(bipy)_2]Cl$	$^-OC_6H_4CO_2^-$	*cis*-$[Co(Cl)_2(bipy)]Cl + H_2sal$	Red-brown	12
$[Co\{(R)\text{-tart}\}(NH_3)_4]ClO_4$	(*R*)-$[CH(OH)CO_2^-]_2$	$[Co(CO_3)(NH_3)_4] + H_2tart$; r.t.	Red; ε_{513} 80; $\Delta\varepsilon_{554}$ +0.35	13, 14
Λ-$[Co\{(R)\text{-tart}\}(en)_2]ClO_4$	(*R*)-$[CH(OH)CO_2^-]_2$	$[Co(CO_3)(en)_2]Cl + H_2tart$; heat, 4 h	Red; ε_{508} 118; $\Delta\varepsilon_{526}$ +1.79; stereospecific synthesis	14
$[Co\{(R)\text{-tart}\}(phen)_2]ClO_4\cdot 3.5H_2O$	(*R*)-$[CH(OH)CO_2^-]_2$	$[Co(CO_3)(phen)_2]Cl + H_2tart$; dark, 7 d; chrom.	Red; ε_{520} 130; CD, ^1H NMR; light	15, 16 17
$[Co\{(R,S)\text{-tart}\}(phen)_2](ClO_4)\cdot 3H_2O$	(*R,S*)-$[CH(OH)CO_2^-]_2$	$[Co(Cl)_2(phen)_2]Cl + H_2tart$; 60 °C, 0.5 h; chrom.	Red; ε_{252} 125; CD	18
$[Co\{(S)\text{-mal}\}(phen)_2]ClO_4\cdot 3.5H_2O$	(*S*)-$[^-O_2CCH_2CH(OH)CO_2^-]$	$[Co(CO_3)(phen)_2]Cl + H_2$ mol; dark, 3 d	Red; ε_{517} 130; CD, ^1H NMR; light sensitive	17, 18

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Table 61 Some Recent Structures of Carboxylate–Co^{III} Systems

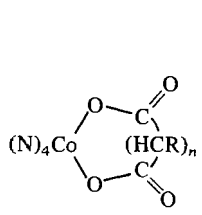
Complex	*Data*[a]	*Comments*	*Ref.*
trans-$[Co(CF_3CO_2)_2(Me_4en)_2](CF_3CO_2)$	*C*2/*c*; CoO 193.6; CoN 196.2; NCoN 82.9°	*trans* configuration of carboxylates	20
$K(+)_{589}$-$[Ni(phen)_3](-)_{589}[Co(C_2O_4)_3]\cdot 2H_2O$	$P2_13$; CoO 190, 195; OCoO 84.3, 93.4°	$\Lambda(-)_{589}$ configuration	1
$KCa(+)_{589}$-$[Co(S_2C_2O_2)_3]\cdot 4H_2O$	$P2_11_11$; CoS 223–226; SCoS 89.3–89.9°	$\Lambda(+)_{589}$ configuration, long CoS bonds; small trigonal distances	2
$(+)_{589}$-$[Co(en)_2(C_2O_4)](H\text{-}+\text{-tart})\cdot H_2O$	$P2_1$; CoN 192–196; CoO 194, 188; OCoO 86°	Λ configuration	3
$(-)_{589}$-$[Co(en)_2(C_2O_4)](H\text{-}+\text{-tart})\cdot 2H_2O$	$P2_12_12_1$; CoN 194–196; CoO 192; OCoO 85–7°	Λ configuration	4
$(+)_{589}$-$[Co\{S\text{-2-pyCH(Me)NH}_2\}(C_2O_4)](ClO_4)$	*C*2; CoN 193; CoO 190; OCoO 86.6°	Λ configuration	5
$(-)_{589}$-β-$[Co(R,R\text{-peatn})(C_2O_4)](ClO_4)$	$P2_1$; CoN 192–196; CoO 189, 191; OCoO 85°	*cis* β configuration of *R*,*R*-2pyCH(Me)NH$(CH_2)_3$NHCH(Me)2py	6
$(+)_{589}$-β-$[Co(S,S\text{-peatn})(C_2O_4)](ClO_4)\cdot H_2O$	$P2_1$; CoN 193–194; CoO 192; OCoO 85.6°	*cis* β configuration	7
cis-β-$[Co(S,S\text{-pyht})(C_2O_4)](ClO_4)$	$P2_1$; CoN 195–200; CoO 192; OCoO 85°	Λ configuration (*S*,*R*,*R*,*S*)	8
$(+)_{546}$-β-$[Co(S,S,S,S\text{-3}'',2,3''\text{-tet})(C_2O_4)]Br\cdot 3H_2O$	$P2_1$; CoN 197–199.6; CoO 190; OCoO 84.3°	Λ configuration; chair conformation of six-membered chelates	9
trans-$[Co(en)_2(OH_2)(C_2O_4)](CF_3SO_3)\cdot 2H_2O$	$P2_1/C$; CoN 194–196; CoO(C_2O_3) 189	Monodentate coord. *via* one O atom; *trans* water	10
$[Co\{2,4(Me)_2tn\}_2(C_2O_4)](ClO_4)$	$P\bar{1}$; CoN 195–197; CoO 192; OCoO 84.8°	–	11
$[Co\{2,4(NH_2)_2butyrato\}]Br\cdot 1.7H_2O$	$C222_1$; CoN 194, 197; CoO 189	*trans* O	12
$Li[Co\{R,S\text{-en(disuccinato)}\}]\cdot 3H_2O$	$P2_1/C$; CoN 189–190; CoO 189–190	Dimeric; one O from adjacent complex anion	13
$(-)^{CD}_{500}$-$[Co(S,S\text{-epro})(R\text{-pipec})]$	$P3_1$; CoN 194–205; CoO 191–194	Δ *sym* configuration	14
$[Co(en)_2(tart)Co(en)_2(tart)]Na(ClO_4)_3\cdot 5H_2O$	$P2_12_12_1$; CoN 191–200; CoO 189, 192	Dimeric; tridentate tart; Λ-*cis*,*trans* configuration about Co	15
$(+)_{546}$-$Na[Co(en)(O_2CCH_2CO_2)]\cdot 2H_2O$	$P2_12_12_1$	Δ-$(+)_{546}$ configuration	16
$(-)_{546}$-$K[Co(tda)]\cdot 2H_2O$	$B22_12$; CoN 196.6; CoO 190, 186; OCoN 84.3, 87.9°	Λ configuration when related to $\Lambda(+)_{589}$ $Co(en)_3^{3+}$	17
β-$[Co(trien)(citrato)]\cdot 5H_2O$	$P\bar{1}$; CoO(H) 195; CoO 188; CoN 193–196	Carboxyl, hydroxyl coord. five-membered chelate	18
$(-)_{546}$-*asym*-$[Co(edda)(R\text{-pn})]Cl\cdot H_2O$	$P2_1$; CoO 190, 191; CoN 194–195	Δ configuration	19

[a] Bond lengths in pm.

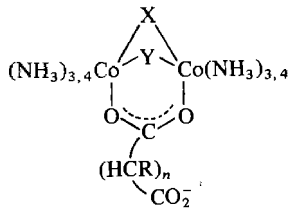
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47.7.2.3 Dicarboxylates, cobalt(III)

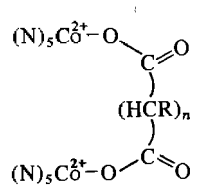
As well as regular monodentate complexes (**213**), R = $(CH_2)_nCO_2H$, two types of chelate have been prepared (**221**) and (**222**), and one other bidentate (**223**). Some preparations are given in Table 60 and some structures in Table 61. The extended dimeric complexes (**223**) were first reported by Duff[804] and his method has been recently improved and extended to include a number of symmetrical systems,[805] but asymmetric or heterometal complexes are possible. Sykes and coworkers have prepared μ-bridged chelated oxalato complexes of type (**226**) but also including (**224**) and (**225**) (X, Y = NH_2, OH).[806] Wieghardt has made similar complexes with other dicarboxylic acids[807] and Nishide and Saito some related oxalato and carbonato complexes containing 2-aminopropanol.[808] Complex (**226**) aquates slowly to the ring-opened species $[(NH_3)_5CoOCOCOOCo(NH_3)_4(H_2O)]^{4+}$ in 1.0 mol dm^{-3} $HClO_4$, and this is representative of others.



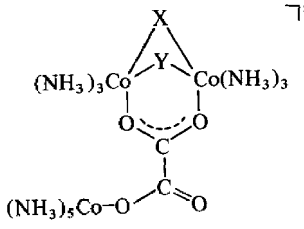
(221)



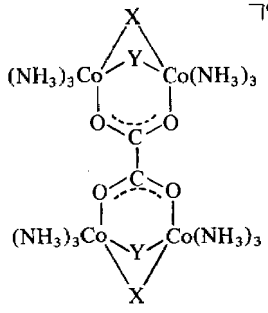
(222)



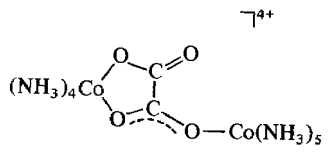
(223)



(224)



(225)

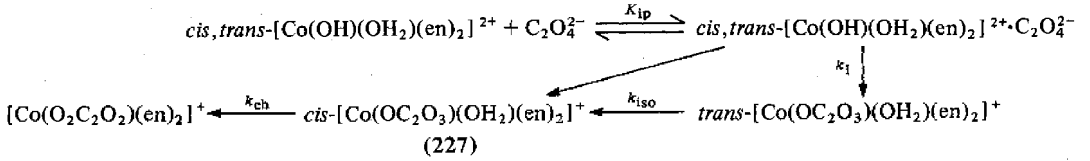


(226)

Simple bidentate chelates (**221**) have been extensively studied. Their formation *via* anation of *cis*-$Co(OH_2)_2^{n+}$ systems is slow (Table 60), but saturation rates consistent with the intervention of ion pairs (Scheme 76) are observed, especially with $C_2O_4^{2-}$.[783] Both monodentate and bidentate coordination are possible. With $[Co(OH_2)(N)_5]^{3+}$ and oxalate $[Co(OC_2O_3H)(N)_5]^{2+}$ is formed [(N)$_5$ = $(NH_3)_5$,[784] $(en)_2(NH_3)$].[785] With *cis*-$[Co(OH_2)_2(N)_4]^{3+}$ the chelate $[Co\{O_2C_2(CH_2)_n\}(NH_3)_4]^+$ is the final outcome but intermediate monodentate carboxylates $[Co\{OCO(CH_2)_nCO_2\}(N)_4(OH_2)]^+$ become increasingly stable as the subsequent chelation step slows down. This occurs with increasing ring size ($n > 1$) and steric requirement.[792] With $H_2C_2O_4$ and $HC_2O_4^-$ biphasic kinetics are not observed however (*cis*-$[Co(H_2O)_2(en)_2]^{3+}$,[786,787] *cis*-$[Co(OH_2)_2(NH_3)_4]^{3+}$,[788] pH < 1) and $[Co(O_2C_2O_2)(N)_4]^+$ appears to be the only observed product (equation 139). In 2.0 mol dm^{-3} H^+ marked catalysis by NO_3^- has been found,[787,789,790] but this is not apparent with $[Co(OH_2)(N)_5]^{3+}$. The effect is not understood and marked H^+ catalysis is also involved.[791] Possible decomposition products such as HNO_2, N_2O_3 or $H_2NO_2^+$ may be formed under the acid conditions and elevated temperatures (50–70 °C) or the water-exchange rate (k_{ex}, k'_{ex}; Scheme 76) may be increased by the presence of nitrate species. A biphasic reaction is however found with $C_2O_4^{2-}$ in the pH range 3–7 ($[Co(OH)(H_2O)(en)_2]^{2+}$,[793] *cis*-$[Co(H_2O)_2(NH_3)_4]^{3+}$).[794] For $[Co(OH)(H_2O)(en)_2]^{2+}$ water exchange has been increased significantly over that for $[Co(H_2O)_2(en)_2]^{3+}$ and the resulting increased anation rate for both *cis* and *trans* reactants leads to *cis*- and *trans*-$[Co(OC_2O_3)(OH_2)(en)_2]^+$ intermediates (Scheme 79).[793] These intermediates have been recovered and studied independently with the *trans* isomer isomerizing to *cis* ($k_{iso} = 8 \times 10^{-6}\,s^{-1}$) before chelating ($k_{ch} = 4.6 \times 10^{-5}\,s^{-1}$).[795] An ^{18}O tracer study has shown that chelation in the *cis* monodentate (**227**) proceeds partly (~30–40%) *via* attack by coordinated water, while *cis*-$[Co(OC_2O_3)(OH)(en)_2]$ reacts entirely by this path (equation 140).[796] Under acidic conditions (pH < 2) the cyclization of *cis*-$[Co(OC_2O_3H)(en)_2]^{2+}$ has increased three-fold over that at pH 5 and

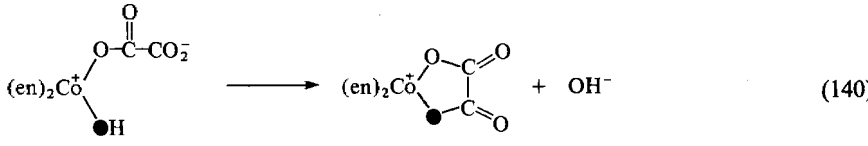
the reaction is also believed to occur exclusively *via* intramolecular oxygen exchange at the carboxyl centre rather than at the metal (equation 141).[796]

$$[Co(OH_2)_2(N)_4]^{3+} + H_2C_2O_4/HC_2O_4^- \overset{K_{ip}}{\rightleftharpoons} [Co(OH_2)_2(N)_4]^{3+}\cdot H_2C_2O_4/HC_2O_4^- \xrightarrow[slow]{k_1} [Co(O_2C_2O_2)(N)_4]^+ + 2H_2O + 2H^+ \quad (139)$$

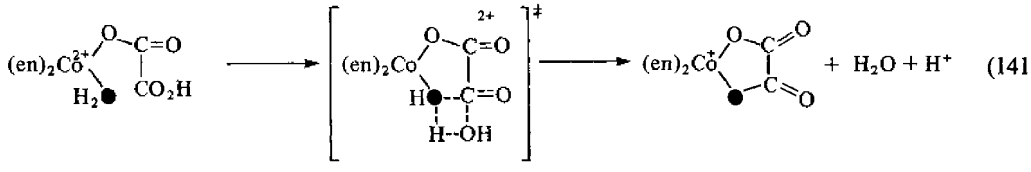


(227)

Scheme 79



(140)



(141)

Both monodentate and chelated oxalato complexes undergo H^+- and OH^--catalyzed exchange of O atoms. For $[Co(OC_2O_3/H)(NH_3)_5]^{+,2+}$ this is faster (H^+) or comparable (OH^-) with hydrolysis of the complex, while for $[Co(O_2C_2O_2)(en)_2]^+$ the two exocyclic O atoms exchange much faster than chelate ring opening. Some O-exchange data are given in (Table 62).

Hydrolysis of chelated oxalate and malonate is very slow and both systems can be considered inert at ambient temperatures. There is no report of H^+- or M^{n+}-catalyzed ring opening; there is no easy point of attachment of the catalyst in such systems. Acid hydrolysis of monodentate complexes at elevated temperatures (Table 59) often follows the rate law $k_{obs} = k_1 + k_2[H^+]$ with k_2 corresponding to hydrolysis of $[Co\{OC(O)(CH_2)_nCO_2H\}(N)_5]^{2+}$. The acid-catalyzed pathway becomes less important with increasing n.[797,798] Metal ions (Fe^{3+}, Al^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}) catalyze the reaction in the same manner by coordinating to the free carboxylate function.[799,803] Dash and Harris have studied this initial rapid binding of Fe^{3+} species to $[Co(OC_2O_3)(NH_3)_5]^+$.[800]

Alkaline hydrolysis is somewhat faster and generally follows the rate law $k_{obs} = k_{OH}[OH^-] + k'_{OH}[OH^-]^2$, although sometimes k'_{OH} is not observed (Table 59). For $[Co(OC_2O_3)(NH_3)_5]^+$, k_{OH} corresponds to Co—O and k'_{OH} to C—O bond cleavage.[776] Dash and

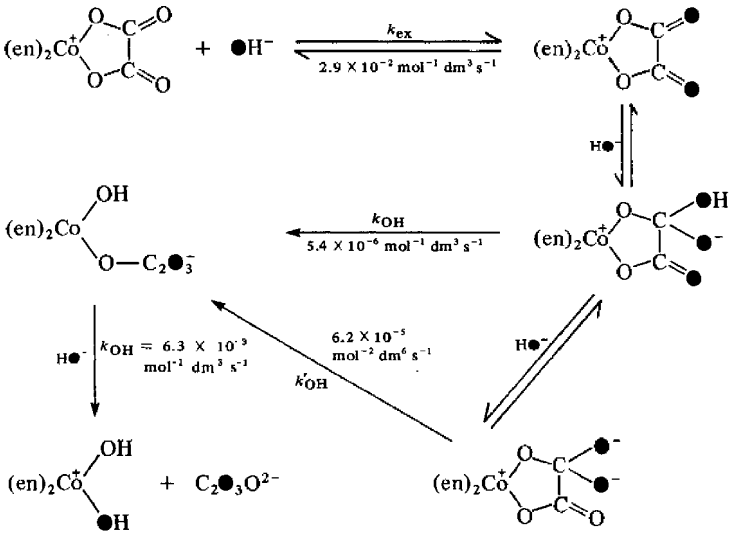
Table 62 ^{18}O-Exchange Data for Oxalato Complexes

Complex	*Exchangeable O*[a]	*Rate, rate law*	*Ref.*
$[Co\{OC(O)CO_2H\}(NH_3)_5]^{2+}$	$[Co\{OC(O^*)CO_2H\}(NH_3)_5]^{2+}$	$k_{obs} = k_H[H^+]$; $k_H = 4.5 \times 10^{-4}$ mol^{-1} dm^3 s^{-1}, 25 °C	1
	$[Co\{OC(O)CO_2^*H\}(NH_3)_5]^{2+}$	$k_{obs} = k_H$; $k_H = 2.1 \times 10^{-5}$ s^{-1}	1
	$[Co\{O^*C(O)CO_2H\}(NH_3)_5]^{2+}$	Very slow; uncertain	1
$[Co\{OC(O)CO_2\}(NH_3)_5]^+$	$[Co\{O^*C(O^*)CO_2\}(NH_3)_5]^+$	$k_{obs} = k_{OH}[OH^-]$; $k_{OH} = 4 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}, 25 °C	2, 3
$[Co(O_2C_2O_2)(en)_2]^+$	$[Co(O_2C_2O_2^*)(en)_2]^+$	$k_{obs} = k_H[H^+]$; $k_H = 2.3 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}, 25 °C	1
	$[Co(O_2C_2O_2^*)(en)_2]^+$	$k_{obs} = k_{OH}[OH^-]$; $k_{OH} = 2.9 \times 10^{-2}$ mol^{-1} dm^3 s^{-1}, 25 °C	4

[a] Exchangeable O indicated by asterisk.

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4. G. Miskelly, C. R. Clark and D. A. Buckingham, *J. Am. Chem. Soc.*, 1986, **108**, 5202.

coworkers have carried out a number of kinetic studies.[801] For chelated $[Co(O_2C_2O_2)(en)_2]^+$, Andrade and Taube showed that close to three O atoms had exchanged on complete alkaline hydrolysis[775] and recent studies by Buckingham and coworkers have demonstrated that two of these exchange rapidly in the chelate before hydrolysis, and that both the k_{OH} and k'_{OH} paths for chelate cleavage occur with substantial (60% and 100% respectively) C—O bond fission (Scheme 80). The subsequent hydrolysis of the monodentate *cis* hydroxo product occurs entirely *via* Co—O bond cleavage.[796] Similar mechanisms have been suggested for the alkaline hydrolysis of other chelated dicarboxylate complexes.[802]



Scheme 80

The photochemistry of Co^{III} oxalate complexes was studied and reviewed at an early stage.[809] Thermally unstable green $K_3[Co(O_2C_2O_2)_3]$ and $K[Co(O_2C_2O_2)_2en]$ undergo photoredox decay both in solution and in the solid with the $C_2O_4^-$ radical being a major product (Scheme 81). An intermediate bidentate oxalate radical coordinated to high-spin Co^{II} (**228**) has been identified.[813] Endicott and coworkers have shown by studying the photolysis of monodentate $[Co(OC_2O_3)(NH_3)_5]^+$ and chelated $[Co(O_2C_2O_2)(en)_2]^+$ that an additional pathway exists (Scheme 82) whereby excitation results in heterocyclic C—C cleavage and the formation of CO_2 and a C-bonded formato complex of Co^{III} (**229**);[812] this latter species spontaneously decays *via* internal electron transfer to $Co^{2+}_{(aq)}$ and $\cdot CO_2H$ or CO_2^- radicals. More stable Co^{II} products are formed in the photolysis of $[Co(O_2C_2O_2)(N—N)_2]X$ (N—N = phen, bipy), with $[Co(O_2C_2O_2)(N—N)_2]$ and $[Co(X)_2(N—N)_2]$ being identified.[810] Some MO calculations on these latter systems have been described.[811]

$$[Co(O_2C_2O_2)_3]^{3-} \underset{}{\overset{h\nu}{\rightleftharpoons}} \underset{(228)}{[Co^{II}(O_2C_2O_2\cdot)(O_2C_2O_2)_2]^{3-}} \longrightarrow [Co(O_2C_2O_2)_2]^{2-} + C_2O_4^-$$

$$[Co(O_2C_2O_2)_3]^{3-} + C_2O_4^- \longrightarrow [Co(O_2C_2O_2)_2]^{2-} + C_2O_4^{2-} + 2CO_2$$

Scheme 81

$$[Co(O_2C_2O_2)(en)_2]^+ \xrightarrow{h\nu} \underset{(229)\quad pK_a = 2.6}{[Co(CO_2H)(H_2O)(en)_2]^{2+}} + CO_2 \xrightarrow{slow} Co^{2+}_{(aq)} + CO_2H + 2en$$

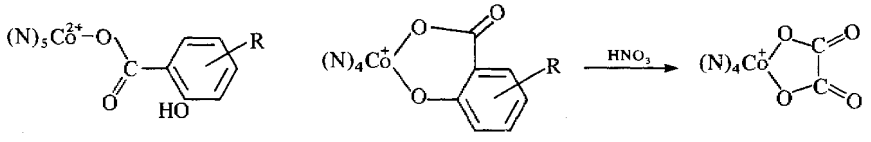
Scheme 82

47.7.2.4 Hydroxycarboxylates: cobalt(III)

(*i*) *Salicylate*

The formation and hydrolysis of monodentate salicylate complexes (**230**) parallels other carboxylates (Tables 60 and 59, respectively). Metal-ion-accelerated hydrolysis (Fe^{3+} species,[814]

Al^{3+}[815]) is also found, and a pathway *via* the phenolate anion ($pK_a \sim 11.2$) exists for both aquation and alkaline hydrolysis.[816] Chelated salicylates (**231**) are known [$(N)_4 = (NH_3)_4$, $(en)_2$, β-(trien)] and $[Co(sal)(en)_2]^+$ has been resolved into enantiomeric forms (Table 60). These chelates are very stable in aqueous solution and hydrolysis is very difficult. O-exchange studies do not appear to have been carried out. Garbett and Gillard have noted an interesting oxidation–decarboxylation of $(-)_{589}$-$[Co(sal)(en)_2]^+$ in concentrated HNO_3 in which the five-membered oxalate chelate (**232**) is formed in ~90% yield together with picric acid.[817] Nitration of the chelate precedes ring oxidation and Yamamoto and coworkers have carried out an extensive study on the green nitro product first noted by Morgan and Smith.[818] Green $[Co(5\text{-}NO_2sal)(N)_4]^{2+}$ is paramagnetic ($\mu = 1.6$–1.9 BM) and appears to be formed during the nitration since similar treatment of authentic orange $[Co(5\text{-}NO_2sal)(NH_3)_4]^+$ does not appear to lead to the paramagnetic species.[819] Yamamoto has investigated a number of such systems [$(N)_4 = (NH_3)_4$, $(en)_2$, (trien), $(phen)_2$] and has shown that the related nitroso species $[Co(5\text{-}NOsal)(NH_3)_4]^+$ and its brown paramagnetic oxidation product $[Co(5\text{-}NOsal)(NH_3)_4]^{2+}$ are not formed as intermediates in the nitration process.[817,820] Photoelectron spectroscopy indicates substantial ligand as opposed to metal oxidation.[820,821]

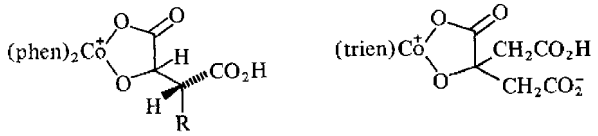


(230) (231) (232)

(*ii*) *Tartrate, malate and citrate*

Some preparations using these hydroxy acids are given in Table 60 and some structures are listed in Table 61.

An early report[822] of the stereospecific reaction between (*R*)(+)-tartaric or (*R*)(+)-malic acid and $[Co(CO_3)(phen)_2]Cl$ at ambient temperature has been refuted and both Δ- and Λ-$[Co\{(R)L\}(phen)_2]^+$ ions (**233**) are formed.[823,824] The distribution ratio $\Delta(R)/\Lambda(R) = 0.38$ for the (*R*)-tartrate complex. Using $[Co(Cl)_2(phen)_2]Cl$ at 60 °C and Na(+)-tartrate the ratio is 0.70, but thermodynamic distributions remain unknown. Δ(*R*) and Λ(*R*) diastereoisomers of both acids have recently been isolated and characterized by CD and 360 MHz ^1H NMR.[825] The reaction of *meso*-tartaric acid results in four diastereoisomeric possibilities (depending on which asymmetric carbon is in the chelate ring) and all four have been separated ($\Delta(S)R$:$\Lambda(S)R$:$\Delta(R)S$:$\Lambda(R)S$ = 26:24:27:23).[824] From these results it appears likely that the reported stereospecific reaction of $[Co(CO_3)(en)_2]Cl$ with (*S*)(−)-tartaric acid resulting in only Λ-$[Co\{(S)tart\}(en)_2]Cl$[826] is in error. The reaction of sodium citrate with $[Co(Cl)_2(trien)]Cl$ also leads to a preference for the five-membered chelate involving the hydroxyl group (**234**) as has recently been shown by a crystal structure of β-$[Co(cit)(trien)]\cdot 5H_2O$.[827]



(233) R = OH [(*R*)-tart]
R = H [(*R*)-mal]

(234)

47.7.2.5 Tridentates and quadridentates, cobalt(III)

Variations in ligand type and geometrical configuration provide an almost endless array of possibilities, and far too many to consider here. Bernauer[828] considers such possibilities and some recent preparations are given in Table 63, and crystal structures in Table 61.

Main interest centres on correlating alterations in stereochemistry with CD and ^1H NMR spectra, and $[Co(edda)XY]^{n+}$ systems figure prominently in this regard. An early review is available[829] and a selected study[830] may be consulted. $Na[Co(edda)(CO_3)]$ serves as a good starting material for many

Table 63 Preparations: Recent Quadridentate and Tridentate Carboxylate–Cobalt(III) Complexes

Complex	*Ligand*	*Preparation, properties*	*Ref.*
Δ-[Co(NO_3){(*S*)-ven}(H_2O)], Δ-[Co{(*S*)-ven}en]ClO_4	(*S*)-[$^-O_2CCH(CHMe_2)NH(CH_2)_2CH(CHMe_2)CO_2^-$]	$CoCO_3$ + H_2ven + C + HNO_3; 60 °C, H_2O_2; chrom. *cis* α > *cis* β; ^{1}H, ^{13}C NMR; Δ-configuration	1
[CoX_2(adao)] (X = Cl^-, NO_2^-, H_2O)	$NH_2(CH_2)_2NH(CH_2)_2NHCH_2CO_2^-$	$Na_3Co(NO_2)_6$ + Hadao; 50–60 °C, α, β configurations; ^{1}H NMR	2
[CoXY(adao)](ClO_4) (X, Y = Cl^-, py, H_2O, NH_3, NO_2^-)	As above	As above, *fac*, *mer* isomers, ^{1}H NMR	3
[CoY(aeida)]Cl (Y = gly^-, *meso*-bn)	$(^-O_2CCH_2)_2N(CH_2)_2NH_2$	[$Co(NO_2)_2$(aeida)]·2H_2O + HOAc; glyH; Y = *meso*-bn resolved; ^{1}H NMR, CD; geometric isomers	6
[CoY(dtma)]Cl (Y = gly^-, ala^-, pn)	$^-O_2CCH_2N(CH_2CH_2NH_2)_2$	*fac*-(*N*)-[CoCl(H_2O)(dtma)]Cl, H_2O + NY; 70 °C chrom.; geometric isomers; ^{1}H NMR, CD	7
K-*sym*,*cis*-[$Co(NO_2)_2$(edda)]	$O_2CCH_2NH(CH_2)_2NHCH_2CO_2^-$	$CoCO_3$ + H_2edda; KNO_2 + O_2 + C; 12 h, r.t.; red-brown, resolved using $(-)_{589}$-[$Co(O_2C_2O_2)(en)_2$]Br; $\Delta\varepsilon_{496}$ 2.50	8
Na-*asym*-[$Co(CO_3)$(edda)]	As above	$Na_3Co(CO_3)_3$ + H_2 edda + HCl	9
asym,*cis*-[$Co(H_2O)_2$(edda)]Cl	As above	Na[$Co(CO_3)$(edda)] + HCl	9
asym,*cis*-[Co(edda)en]Cl	As above	[Co(edda)(H_2O)$_2$]Cl + en; resolved using Ag(BrcamphSO$_3$); $\Delta\varepsilon_{485}$ 2.24	9
sym-[Co(edda)en](NO_3)	As above	$CoCO_3$ + H_2edda + HNO_3 + O_2 + C; 8 h, r.t.; resolved using Ag_2(tart) + H_2(tart); $\Delta\varepsilon_{532}$ 4.46	9
K-*sym*-[$Co(C_2O_4)$(edda)]	As above	$CoCO_3$ + H_2edda + $K_2C_2O_4$ + $H_2C_2O_4$; C, air, 17 h; resolved using $(+)_{546}$-[$Co(O_2C_2O_2)(en)_2$]I	11

		$CoCl_2 \cdot 6H_2O + H_2mida + PbO_2$; pH 3.5–4.0; chrom.; resolved optical forms; *asym, fac* isomers	4
	$MeN(CH_2CO_2^-)_2$	As above; CD	4
$K[Co(mida)_2]$		As above; ^1H, CD isomerization, racemization studies; *asym,fac, sym,fac* isomers	5
	$EtN(CH_2CO_2^-)_2$	Red violet; $CoCl_2 \cdot 6H_2O + H_2ida +$ KOH; H_2O_2; $\sim 0\,^\circ C$	10
$K[Co(eida)_2]$	$RN(CH_2O_2^-)_2$	Yellow-brown; as above; $80\,^\circ C$	10
$K[Co(ida)(Rida)]$ (R = Me, Et)			
	$HN(CH_2CO_2^-)_2$		
asym,fac-$K[Co(ida)_2]$	As above		
sym,fac-$K[Co(ida)_2]$			

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Table 64 Preparations: Some Sexidentate and Quinquedentate Carboxylate Complexes of Cobalt(III)

Complex	*Preparation*	*Properties*	*Ref.*
Sexidentates			
$M[Co(edta)]\cdot xH_2O$ ($M = K$, $x = 2$; $M = Na$, $x = 4$)	$CoX_2 + MOAc + M_2H_2edta + C + H_2O_2$; r.t., air	Red-violet; ε_{537} 326	1, 2
$(\pm)_{546}$-$K[Co(edta)]\cdot 3H_2O$	Resolved using $(+)_{589}$-$[Co(en)_3]Cl_3$	$[\alpha]_{589}$ 150°	1
	Resolved using $(+)_{589}$-$[Co(en)_2(NO_2)_2]Br$	$[\alpha]_{589}$ 150°	3
	Resolved using $(-)_{589}$-$[Co(O_2C_2O_2)(en)_2]Br$	$[\alpha]_{546}$ 1000°	4
$K[Co(tdta)]\cdot 2H_2O$	$Co(OAc)_2\cdot 4H_2O + H_4tdta + KOAc + C + H_2O_2$; r.t. air, 50 h	Red-violet; IR, visible–UV	5
$(\pm)_{546}$-$K[Co(tdta)]\cdot 2H_2O$	Resolved using $(+)_{589}$-$[Co(NO_2)_2(en)_2]_2Br$ and $Ag[Co(tdta)]\cdot H_2O$	$[\alpha]_{546}$ 1500°; CD, ORD; ^1H NMR	6
$K[Co\{(R,S)\text{-pdta}\}]\cdot 2H_2O$	$Co(OAc)_2\cdot 4H_2O + H_4pdta + KOAc + C + H_2O_2$; 42 h, r.t.	Purple	7
$(+)_{546}$-$K[Co\{(R)\text{-pdta}\}]$	Resolved using $(+)_{589}$-$[Co(NO_2)_2(en)_2]_2(SO)_4$, 60 °C, $Ba[Co\{(R,S)pdta\}]_2$	$[\alpha]_{546}$ 1000°	8
$K[Co\{R,S\text{-cdta}\}]\cdot 3H_2O$	$Co(OAc)_2\cdot 4H_2O + H_4cdta + KOAc + C + H_2O_2$; r.t., 2 h	Red-violet	8
$(+)_{546}$-$Ba[Co\{(R)\text{-cdta}\}]_2$	Resolved using $(-)_{589}$-$[Co(en)_2(NO_2)_2]Br$	$[\alpha]_{546}$ 900°	8
$K[Co(bdta)]\cdot 3H_2O$	$Co(OAc)_2\cdot 4H_2O + H_4ndta$, $KOAc + PbO_2$; 50 °C, EtOH	Blue; ^1H NMR; ε_{581} 130	9
$K[Co(eddda)]\cdot 2H_2O$	$CoCl_2\cdot 6H_2O + KOAc + H_4eddda + H_2O_2$; 90 °C	Purple; ε_{540} 290	17
	$Ag[Co(eddda)]$ resolved using $(-)_{546}$-$[Co(O_2C_2O_2)(en)_2]Br$	$\Delta\varepsilon_{543}$ ±2.2	17
$Na[Co(edpa)]\cdot 2H_2O$	$Na_3Co(CO_3)_3 + Na_2H_2edpa$; 4 h, 40 °C	Violet; ε_{528} 332	18
$(-)_{576}$-$Na[Co\{(S,S)\text{-edds}\}]\cdot H_2O$	$Na_3Co(CO_3)_3 + H_4(S,S)edds + C$	Stereospecific	19
$(-)_{546}$-$Na[Co\{(S)\text{eddams}\}]\cdot H_2O$		Stereospecific	21
$K[Co(Hedta)Cl]\cdot 2H_2O$	$K[Co(edta)] + conc.\ HCl$	Blue	10
$(\pm)_{546}$-$K_2[Co(edta)Cl]\cdot 3H_2O$	Resolved using $(+)_{589}$-$[Co(en)_2(NO_2)_2]Br$	$[\alpha]_{546}$ 700°; ε_{584} 250	10
$Na[Co(Hedta)Br]\cdot H_2O$	$K[Co(edta)] + conc.\ HBr$	Blue-green; ε_{595} 218	11
$(\pm)_{546}$-$Na_2[Co(edta)Br]\cdot 4H_2O$	Resolved using $(+)_{589}$-$[Co(NO_2)_2(en)_2]Br$	$[\alpha]_{546}$ 700°; ε_{571} 293	10
$Na[Co(Hedta)(NO_2)]\cdot 2H_2O$	$Na_3Co(NO_2)_6 + Na_2H_2edta$; 50–90 °C	Violet-brown	10
$(\pm)_{546}$-$Na_2[Co(edta)(NO_2)]\cdot 3H_2O$	Resolved using $(+)_{589}$-$[Co(NO_2)_2(en)_2]Br$	$[\alpha]_{546}$ 700°; ε_{584} 116; ε_{499} 236	10
$Na_2[Co(edta)(OH)]\cdot 3H_2O$		Blue	12
$[Co(edta)(NO_2)Co(NH_3)_5]ClO_4\cdot 3H_2O$	$Na[Co(edta)(NO_2)] + [Co(NH_3)_5(OH_2)](ClO_4)_3$; 75–80 °C, 1 h; chrom.	Brown; ε_{582} 144; ε_{500} 337	22
$K[Co\{R,S\text{-Hpdta}\}Cl]$	$K[Co\{(R,S)\text{-pdta}\}] + conc.\ HCl$	Blue	8, 13
$(+)_{546}$-$K[Co\{(S)\text{-Hpdta}\}Cl]\cdot 2H_2O$	Resolved using $(+)_{589}$-$[Co(NO_2)_2(en)_2]Cl$	$[\alpha]_{546}$ 800°	8
$Na[Co\{(R,S)\text{-Hpdta}\}(NO_2)]\cdot H_2O$	$Na_3Co(NO_2)_6 + Na_2H_2pdta + KOAc + C + H_2O_2$	Mauve	8, 13
$(-)_{546}$-$Na[Co\{(S)\text{-Hpdta}\}(NO_2)]\cdot 2H_2O$	Resolved using $(+)_{589}$-$[Co(NO_2)_2(en)_2]Cl$	$[\alpha]_{546}$ 850°	8
$Na[Co\{(R,S)\text{-Hpdta}\}Br]\cdot H_2O$	$CoBr_2\cdot 6H_2O + pdta + Br_2$; 0 °C, 4 h	Blue-green	13
$Na_2[Co\{(R,S)\text{-pdta}\}OH]\cdot 4H_2O$	Co^{II} complex + NaOH + H_2O_2; 0 °C, 3 h	Blue	13
$K[Co\{(R,S)\text{-Hedta}\}Cl]\cdot 2.5HCl$	$K[Co\{(R,S)\text{-cdta}\}] + conc.\ HCl$	Purple-blue; ε_{585} 229	11
$Na[Co(Meedtra)(NO_2)]$	$Na_3Co(NO_2)_6 + Meedtra$; 50–85 °C	Red; ^1H NMR	14, 20
	Resolved using $(-)_{546}$-$[Co(O_2C_2O_2)(en)_2]Br$	$\Delta\varepsilon_{517}$ 0.4; ε_{585} 90; ε_{493} 182	14

K[Co(Heedtra)X] ($X = Cl^-$, Br^-, NO_2^-)	$CoCl_2 \cdot 6H_2O$ + Heedtra + Cl_2 (or Br_2); 0 °C, 12 h	Purple (Cl), ε_{578} 210; brick red (NO_2); blue-green (Br), ε_{588} 241; resolved using $(+)_{546}$-$[Co(O_2C_2O_2)(en)_2]Br$	15, 14
$[Co(edtra)H_2O] \cdot 1.5H_2O$	$Co(NO_3)_2 \cdot 6H_2O$ + edtra + H_2O_2 + C; 3 d; chrom.	—	
K[Co(edtra)X] ($X = NO_2^-$, ONO^-)	$[Co(edtra)H_2O]$ + $NaNO_2$ + HOAc; chrom.		16
$K[Co(edtra)Cl] \cdot 0.5H_2O$	$[Co(edtra)H_2O]$ + NaCl + HCl; chrom.	Brick red (NO_2), ε_{585} 78; purple (ONO, ε_{562} 186	16
$K[Co(Me_2edtra)(NO_2)] \cdot H_2O$	$Na_3[Co(NO_2)_6]$ + Me_2edtra; 50 °C, chrom.	Blue, ε_{573} 226	16
		Brick-red, ^1H NMR	20

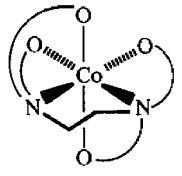
[a] Ligand abbreviations: ethylenediaminetetraacetate, edta; (*R,S*)-1,2-propylenediaminetetraacetate, (*R,S*)-pdta; (*R,S*)-1,2-*trans*-cyclohexanediaminetetraacetate, (*R,S*)-cdta; 1,3-trimethylenediaminetetraacetate, tdta; 1,4-butanediaminetetraacetate, bdta; *N*-methylethylenediaminetriacetate, Meedtra; ethylenediaminetriacetate, edtra; *N*-hydroxyethylethylenediaminetriacetate, Heedtra; *N*-hydroxypropylethylenediaminetriacetate, Hpedtra; ethylenediaminediacetate, edda; ethylenediaminediacetatedi-3-propionate, eddda; ethylenediaminediacetatedi-2-propionate, edpa; ethylenediamine (*S,S*)-disuccinate, edds; ethylenediaminediacetate(S)-succinate, eddams; 2,2-dimethylethylenediaminetriacetate, Me_2edtra.

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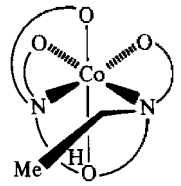
complexes.[831] The potential tri- and quadri-dentate hydroxy acids (malic, tartaric and citric) show bidentate chelation and are considered in Section 47.7.2.4.(ii).

47.7.2.6 Quinquedentates and sexidentates, cobalt(III)

Brintzinger, Thiele and Muller appear to have been the first to prepare a sexidentate polycarboxylate cobalt(III) complex when they reported $Na[Co(edta)]\cdot 4H_2O$.[832] The sexidentate nature of the ligand was confirmed by a crystal structure of $NH_4[Co(edta)]\cdot 2H_2O$.[833] Busch and Bailar first reported the resolution of $[Co(edta)]^-$ into its enantiomeric forms[834] and its absolute configuration (**235**) was assigned by comparisons with $K(+)_{546}$-[Co{(*R*)pdta}] (**236**) (the (*R*)-methyl substituent prefers the equatorial disposition)[835] and by its reaction with ethylenediamine, which leads to a preponderance of Λ-$(+)_{589}$-$[Co(en)_3]^{3+}$.[836] Such stereospecific effects have been discussed by Sargeson.[837] Subsequently other methods of preparation and resolution have become available and these are collected in Table 64. A crystal structure of $(-)_{546}$-$K[Co(edta)]\cdot 2H_2O$ has confirmed its enantiomeric configuration as (**235**).[838] Koine and Tanigaki report the isolation, resolution and 400 MHz ^1H NMR spectrum of $(-)_{546}$-[Co{(*R*)pdta}]$^-$ containing the axial (*R*)-methyl orientation and confirm that it is present to only 0.1% at equilibrium.[839] Similar stereospecific effects are found with [Co{(*R*,*R*)-cdta}]$^-$ containing *trans*-1,2-cyclohexanediaminetetraacetate;[835,837] oxidation of Co^{II} with H_2O_2 in the presence of excess ligand leads to a 1:2 Co^{III}:cdta complex of unknown structure.[840] Lengthening the $N—(CH_2)_n—N$ chain to $n = 4$ gives $[Co(bdta)]^-$ (Table 64) but no suitable oxidizing agent has been found for $n = 6$.[841] Proton assignments in the ^1H NMR spectrum of $[Co(edta)]^-$ have recently been confirmed by Overhauser enhancement studies.[862]



(235) $(+)_{546}$-$[Co(edta)]^-$



(236) $(+)_{546}$-[Co{(*R*)-pdta}]$^-$

An early general account of the properties and some reactions of $[Co(Y)]^-$ (Y^{4-} = edta, pdta, cdta) has been given by Garvan,[842] and Bernauer[843] has discussed more recent stereospecific effects of related sexidentates. ^1H NMR assignments and proton exchange data are available.[844] Some reversible E° values and stability constants have been reported by Ogino and Ogino[845] and are given in Table 65. A good parallel exists between the stability of the Co^{II} and Co^{III} complexes.

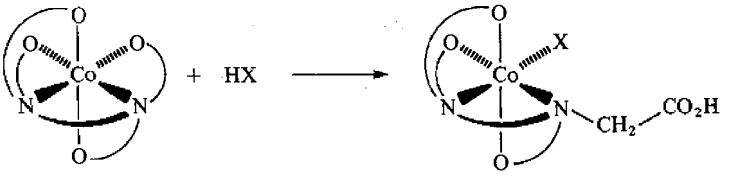
The crystal structures of $NH_4[Co(edta)]\cdot 2H_2O$[833] and $(-)_{546}K[Co(tdta)]\cdot 2H_2O$[838] imply that equatorially placed acetate arms are more strained than axial ones and can be displaced to form quinquedentate complexes (**237**) containing a free carboxylic acid $[CoX(HY)]^-$ or carboxylate $[CoX(Y)]^{2-}$ residue (equation 142). Preparations exist for X = Cl^-, Br^-, NO_2^-, H_2O, OH^- (Table 64) and extension is obviously possible. Schwarzenbach[846] first reported the preparation of the quinquedentate complexes and the uncertainty in the geometrical purity of $[CoBr(Hedta)]^-$ has now been traced to the use of $CoCl_2\cdot 6H_2O$ as starting material.[847] Some have been resolved into optical isomers in their own right (Table 64) but reaction (142) occurs largely (75%; Y = edta; X = Cl^-),

Table 65 Redox and Stability Constant Data for Some Co^{II}/Co^{III} Polycarboxylate Complexes[a]

Couple	E° (mv)[b]	$\log K_{Co^{II}Y}$	$\log K_{Co^{III}Y}$
$[Co(edta)]^{-/2-}$	0.374	16.03	40.92
$[Co(tdta)]^{-/2-}$	0.295	15.39	41.70
$[Co(bdta)]^{-/2-}$	0.547[c]	15.58	37.6
$[Co(pdta)]^{-/2-}$	0.367	17.40	42.4
$[Co(m\text{-}bdta)]^{-/2-}$	0.339	16.9	42.4
$[Co(cdta)]^{-/2-}$	0.356	18.73	43.9
$[Co(Heedtra)(H_2O)]^{0/-}$	0.507	14.8	37.5

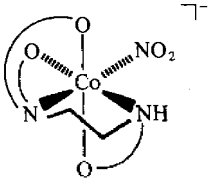
[a] Data taken from H. Ogino and K. Ogino, *Inorg. Chem.*, 1983, **22**, 2208.
[b] *vs.* hydrogen electrode; 0.1 mol dm^{-3} $NaClO_4$.
[c] 1.0 mol dm^{-3} $NaClO_4$.

or completely (Y = pdta, cdta) with retention of absolute configuration. The exclusive disengagement of one equatorial acetate arm is suported by ^{1}H and ^{13}C NMR data[848,849] and by a structure on $K[Co(NO_2)(Hedtra)]\cdot 1.5H_2O$ (**238**).[850] However the reactions of $(+)_{546}$-$[Co(edta)]^-$ and $(-)_{546}$-$[CoX(edta)]^{2-}$ (X = Cl^-, Br^-) of the same absolute configuration with ethylenediamine to give an excess of $\Delta(-)_{589}$-$[Co(en)_3]^{3+}$,[851] and the similar reactions of $(-)_{546}$-$[Co\{(S)pdta\}]^-$ with ethylenediamine to give $\Lambda(+)_{589}$-$[Co(en)_3]^{3+}$, and with (*R*,*S*)-propylenediamine to give $\Lambda(+)_{589}$-$[Co\{(S)\text{-}pn\}_3]^{3+}$,[852] suggest that a rather specific complete unravelling occurs.[861]



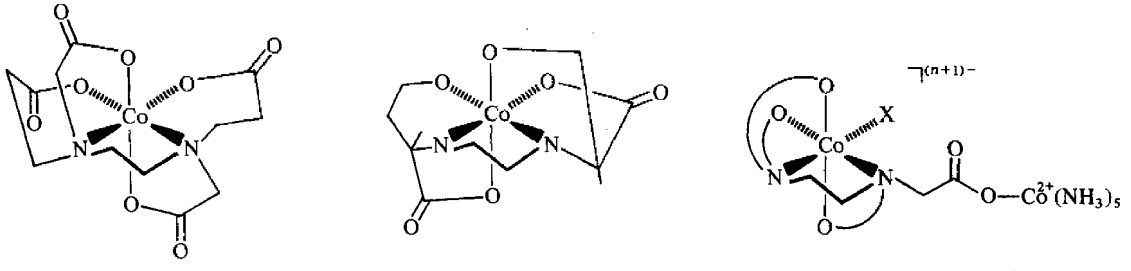
(142)

$(+)_{546}$-$[Co(Y)]^-$ (237) $(-)_{546}$-$[Co(HY)X]^-$



(238)

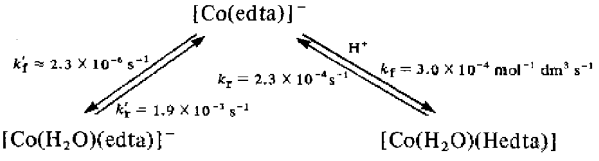
Including two six-membered chelates as in (**239**) appears to position these in the equatorial plane,[853] and a similar result is found in the crystal structure of the ethylenediaminedisuccinic acid (edds) complex (**240**).[854] Removal of these less-strained equatorial chelates to form quinquedentate complexes (equation 142) appears to be difficult. Substitution of methyl groups on two of the acetate arms seems to force these into axial positions.[855] The free acetate arms of $[CoX(edta)]^{n-}$ (X = H_2O, NH_3, NO_2^-) can coordinate to other metal ions and (**241**) has been prepared.



(239) Δ-$[Co(eddda)]^-$ (240) Λ-$[Co\{(S,S)\text{-}edds\}]^-$ (241)

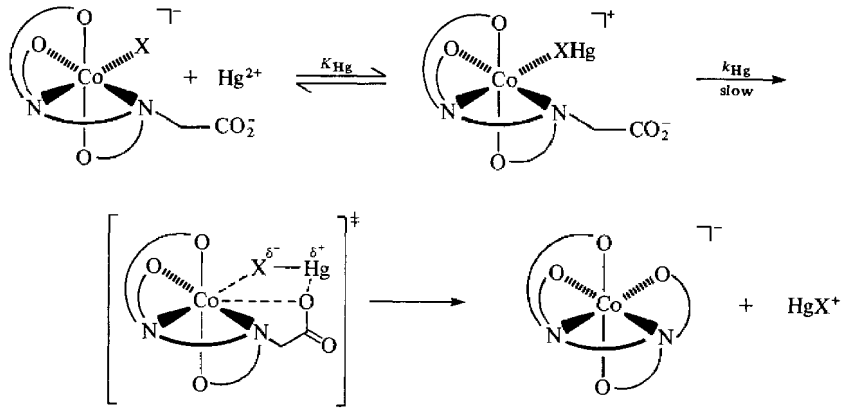
Higginson and coworkers[856] have investigated the rates and equilibria of ring closure and have shown that protonation of the acetate arm (pK_a = 3.1) results in considerable stabilization of the quinquedentate chelate (> 50% in 1.0 mol dm^{-3} H^+). A related equilibrium is found with the *N*-hydroxyethyl derivative.[857] The faster chelation rate for the anion (k_r') compared to the protonated carboxylic acid (k_r; Scheme 83) was considered to demonstrate anchimeric assistance in removing the coordinated water molecule. However the corresponding rates for $[Co(H_2O)(cdta)]^-$ and $[Co(H_2O)(Hcdta)]$ are 7×10^{-4} s^{-1} and 1.6×10^{-2} s^{-1},[857] which is contrary to the above interpretation; a change in mechanism is possible. Some relevant data are given in Table 66. Spontaneous halide removal from $[CoX(HY)]^-$ and $[CoX(Y)]^{2-}$ (X = Cl^-, Br^-) in aqueous solution is slower than chelation of the aqua complex so that a decision as to whether the immediate product is $[Co(H_2O)(Y)]^-$ or $[Co(Y)]^-$ cannot be made. However studies by Wilkins and coworkers using quinquedentates which do not contain a free carboxylate arm and hence must form $[Co(H_2O)(Y)]$ suggest that the sexidentate $[Co(Y)]^-$ is the immediate product in the aquation with loss of X^- being assisted by the carboxylate arm in some fashion (Table 66).[858] Many M^{2+} and some M^{3+} ions catalyze the removal of Cl^-, and for Hg^{2+} and Ag^+ the induced reactions lead directly to

the coordinated carboxylate with full retention of configuration (*i.e.* $[Co(H_2O)(Y)]^-$ is not formed). Higginson and coworkers relate the relative abilities of M^{2+} (M^{3+}) to bind the carboxylate and coordinated halide in $[CoX(Y)]^{2-}$ with assistance from both being considered important (Scheme 84).[859,860] With Hg^{2+} and several M^{3+} ions (In^{3+}, Sc^{3+}, La^{3+}) limiting rates of reaction were observed with K_{Hg} being independent of protonation of the carboxylate residue but with k_{Hg} being considerably faster for the anion. This suggests strong binding to chloride in an equilibrium sense but with assistance in its subsequent removal by carboxylate.



25 °C, $I = 0.1$ mol dm^{-3}

Scheme 83



Scheme 84

Table 66 Rates of Ring Closure and Loss of Halide for Some Quinquedentate Polycarboxylate Cobalt(III) Complexes

Complex	k (s^{-1})	*Comments*	*Ref.*
$[Co(Hedta)H_2O]$	2.3×10^{-4}	$pK_a = 3.1$; reversible reaction, $K_e = 0.78\ mol^{-1}\ dm^3$	1
$[Co(edta)H_2O]^-$	1.9×10^{-3}	$pK_a = 8.1$; poorly reversible, $K_e = 830$	1
$[Co(edta)OH]^{2-}$	4.3×10^{-5}	–	1
$[Co(Hcdta)H_2O]$	1.6×10^{-2}	$pK_a \approx 1$; unusually fast	2
$[Co(cdta)H_2O]^-$	7.0×10^{-4}	–	2
$[Co(Hpdta)H_2O]$	2.7×10^{-4}	–	3
$[Co(pdta)H_2O]^-$	2.0×10^{-3}	–	3
$[Co(pdta)OH]^{2-}$	2.5×10^{-4}	–	3
$[Co(Heedtra)H_2O]$	1.9×10^{-5}	$pK_a = 7.94$; very reversible, $K_e = 5.8 \times 10^{-2}$	4
$[Co(Heedtra)OH]$	3.3×10^{-5}	Poorly reversible, $K_e = 35$	4
$[Co(Hedta)Cl]^-$	3×10^{-6}	Very slow	1
$[Co(edta)Cl]^{2-}$	3×10^{-6}	No apparent assistance	1
$[Co(edta)Br]^{2-}$	2×10^{-5}	–	2
$[Co(Hcdta)Cl]^-$	1.5×10^{-4}	$pK_a = 2.8$	2
$[Co(cdta)Cl]^{2-}$	7×10^{-5}	–	2
$[Co(Hpdta)Cl]^-$	4×10^{-6}	–	3
$[Co(Hpdta)Br]^-$	1.2×10^{-5}	–	3
$[Co(Heedtra)Cl]^-$	1×10^{-6}	Loss of Cl^-	5
$[Co(Heedtra)Br]^-$	5×10^{-6}	Loss of Br^-	5
$[Co(Meedtra)Cl]^-$	2.8×10^{-7}	Loss of Cl^-	2
$[Co(Meedtra)Br]^-$	2.1×10^{-6}	Loss of Br^-	2

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Rates and mechanisms for the reduction of $[Co(edta)]^-$, $[Co(H_2O)(Hedta)]$, $[CoX(edta)]^{2-}$, $[Co(edta)(NH_3)_5]^-$ and $[Co(NH_3)_5\{Co(edta)(H_2O)\}]^{2+}$ by Cr^{2+}, Fe^{2+}, $Fe(CN)_6^{4-}$, $Ru(NH_3)_6^{2+}$ and Ti^{3+} have been investigated by many research workers and an article by Pennington[769] is recommended for background reading. Recent studies by Ogino and coworkers[866,867,868] and by Marec and Orhanovic[869] are also relevant.

The photochemistry of $[Co(edta)]^-$ and $[CoX(Hedta)]^-$ has been investigated by Natarajan and Endicott.[864] Besides a small amount of photoaquation the limiting yields of Co^{2+}_{aq} and CO_2 differ ($\phi_{Co} = 0.025, 0.14$) but for the quinquedentate complex ϕ_{Co} is nearly independent of X ($X = Cl^-$, Br^-, NO_2^-) over the excitation range 300 nm $> \lambda \geqslant$ 229 nm. This suggests a rapid thermal equilibration between singlet excited states with rate-determining competitive formation of products and unreactive reactant states of lower energy.[865]

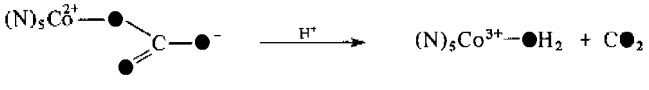
47.7.3 Carbonate

47.7.3.1 Cobalt(II)

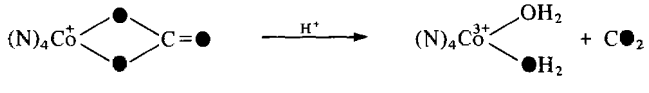
Few well-defined Co^{II}–carbonate complexes are known. The two structures given in Table 68 are probably representative of chelated and monodentate carbonate. $K_2[Co(CO_3)_2(H_2O)_4]$ crystallizes as rose-coloured plates from warm solutions of Co^{II} salts in the presence of K_2CO_3[870] and contains *trans* monodentate carbonate. Bidentate carbonate in $[Co(CO_3)(H_2O)_2(imH)_2]$ appears to exert a measurable structural *trans* influence on the *trans* water molecules (CoO, 216.6 pm *vs.* 209.4 in $Co(H_2O)_6^{2+}$)[330] and a similar effect is found in Co^{III}–carbonato complexes. Violet crystals of $[Co(CO_3)(H_2O)_2(NHpy_2)]$ have been isolated on reacting $Na_3[Co(CO_3)_3]$ with 2,2′-bipyridylamine and presumably contain chelated carbonate (IR; $\mu = 5.23$ BM).[871]

47.7.3.2 Cobalt(III)

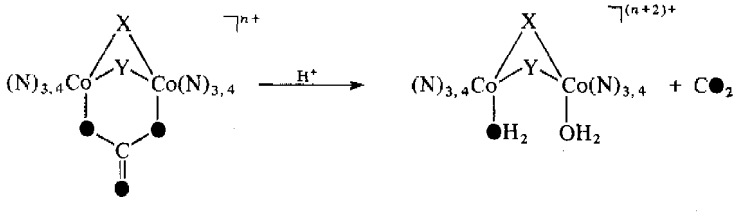
Cobalt(III)–carbonato complexes provide a very useful starting point for the preparation of other cobalt(III) complexes so that high yield synthetic methods are of great practical importance. Table 67 lists preparations for the major structural types **(241)**–**(244)** and variations for substituted or related ligand systems are based on these. Recent reviews covering the wider aspects of transition metal carbonates are available.[872–874]



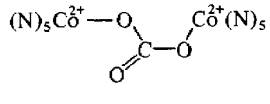
(241) (143)



(242) (144)



(243) (145)



(244)

Table 67 Some Recent Preparations of Carbonato Cobalt(III) Complexes

Complex	*Preparation*	*Properties*	*Ref.*
Monodentate			
$[Co(OCO_2)(NH_3)_5]NO_3 \cdot 1.5H_2O$	$Co(NO_3)_2 + (NH_4)_2CO_3 + NH_4OH$; air, r.t., 24 h	Red; ε_{505} 94; ε_{237} 13 800	33
cis-$[Co(CO_3)(NH_3)(en)_2]ClO_4$	*cis*-$[Co(OH)(NH_3)(en)_2]^{2+} + CO_2$	Red	34
trans-$[Co(CO_3)(NH_3)(en)_2]ClO_4$	*trans*-$[Co(OH)(NH_3)(en)_2]^{2+} + CO_2$	Red	34
α,β-$[Co(CO_3)(tetren)]ClO_4 \cdot 3H_2O$	α,β-$[Co(OH)(tetren)]^{2+} + CO_2$	Red	34
trans-$[Co(CO_3)Cl(en)_2] \cdot H_2O$	*trans*-$[Co(OH)Cl(en)_2]^{2+} + CO_2$	Blue; ε_{578} 74	35
Bridging monodentate			
$[(NH_3)_5CoOC(O)OCo(NH_3)_5](SO_4)_2 \cdot 4H_2O$	$[Co(OH_2)(NH_3)_5]I_3 + (NH_4)_2SO_4 + CO_2 + Ag_2CO_3$; 0 °C, 2 h	Red; v. soluble; ε_{505} 138; ε_{350} 152	1
Bridging-μ-bidentate			
$[(NH_3)_3Co\{\mu\text{-}(OH)_2,CO_3\}Co(NH_3)_3]SO_4 \cdot 5H_2O$	$CoSO_4 \cdot 7H_2O + (NH_4)_2CO_3 + NH_4OH$; 0°C O_2, 24 h	Red; crystal structure	2
$[(S\text{-pra})_2Co(\mu\text{-}OH,CO_3)Co(S\text{-pra})_2]$	$Co(CO_3)_3^{3-}$ + *S*-praH; heat, 60 °C, 2 h; chrom.	Hygroscopic; uncertain	3
$[(S\text{-pra})_2Co(\mu\text{-}CO_3)_2Co(S\text{-pra})_2]$	As above	As above	3
Chelated			
$Na_3[Co(CO_3)_3] \cdot 3H_2O$	$Co(NO_3)_2 + NaHCO_3 + H_2O_2$; 0 °C, 1 h	Olive-green; ε_{635} 155; ε_{440} 166	4
	Resolved using $(+)_{589}$-$[Co(en)_3]^{3+}$	Optically v. unstable	5
cis-$K[Co(CO_3)_2(NH_3)_2]$	$[Co(CO_3)_3]^{3-} + (NH_4)_2CO_3$; resolved	Blue-violet; ε_{575} 174, ε_{395} 258; racemizes with $t_{1/2}$ 3 min	6
cis-$K[Co(CO_3)_2(py)_2] \cdot 2H_2O$	$[Co(CO_3)_3]^{3-}$ + py; 100 h, 25 °C	Purple; ε_{561} 165; ε_{388} 232	7
$K[Co(CO_3)_2en] \cdot H_2O$	$[Co(CO_3)_3]^{3-} + (enH)_2CO_3$; 40 °C, 2 h; chrom.	Blue-black; ε_{567} 154; ε_{394} 164	8
$K_3[Co(CO_3)_2(NO_2)_2] \cdot H_2O$	$[Co(CO_3)_3]^{3-} + KNO_2$; 0 °C, 3–4 h	Violet-red; ε_{548} 220	9, 10
$(+)_{589}$-$[Co(en)_3][Co(CO_3)_2(CN)_2] \cdot H_2O$	$[Co(CO_3)_3]^{3-}$ + 2KCN; r.t.	ε_{546} 92; ε_{444} 108	11
$K[Co(CO_3)_2Y]$ (Y = phen, bipy)	$[Co(CO_3)_3]^{3-}$ + L; EtOH, r.t., Y = bipy resolved using $(-)_{589}$-$[Co(NO_2)_2(en)_2](OAc)$, Y = phen with $(-)_{589}$-$[Co(C_2O_4)(en)_2]OAc$	ε_{562} 152 (bipy, phen); racemizes with $t_{1/2}$ 7 h in aq. soln. $\Delta\varepsilon = 5.93$ (bipy), 7.72 (phen)	12
trans-$K[Co(CO_3)_2(py)_2] \cdot 3H_2O$	–	Purple; ε_{549}, 100	15
$K_3[Co(CO_3)(NO_2)_4] \cdot H_2O$	$Co(CO_3)_3^{3-} + KNO_2$; 0 °C, 1 h; HOAc, 3–4 h	Orange	10
$K_3[Co(CO_3)(CN)_2(C_2O_4)]$	$[Co(CO_3)_2(CN)_2]^{3-} + H_2C_2O_4$	ε_{535} 80; ε_{435} 118	11
$K[Co(CO_3)(gly)_2] \cdot H_2O$	$Co(CO_3)_3^{3-}$ + glyH; 60 °C, 3 h	Red-violet	13
$[Co(CO_3)(NH_3)_4]X$	$Co(CO_3)_3^{3-} + NH_4OH$; heat	Red; ε_{520} 104	14
$[Co(CO_3)(en)_2]X$ (X = Cl^-, Br^-)	$CoCl_2$ + 2en + CO_2 + H_2O_2; 0–35 °C, resolved using $Na[Co(C_2O_4)_2(en)]$	Red; ε_{512} 133; ε_{360} 124 $[\alpha]_{589}$ 1250° (X = I)	16 17
$K[Co(CO_3)(edda)]$	$Na_3Co(CO_3)_3 + H_2edda$	Violet; ε_{565} 114 (sym); ε_{533} 234 (asym)	18
$[Co(CO_3)(Y)_2]Cl \cdot 3H_2O$ (Y = bipy, phen)	$Co(CO_3)_3^{3-}$ + 2Y; 20–35 °C	Red; ε_{503} 118, $\varepsilon_{380} \sim 250$ (bipy); ε_{509} 136, $\varepsilon_{565} \sim 200$ (phen); crystal structure	19
$[Co(CO_3)(py)_4](ClO_4) \cdot H_2O$	$[Co(CO_3)Cl(py)_3] + Hg(py)_2(ClO_4)_2$ + py; 50 °C, 45 min	Red; ε_{530} 170; ε_{378} 189	20
cis-$[Co(CO_3)(NH_3)_2(en)]Cl \cdot H_2O$	$K[Co(CO_3)_2(en)] + NH_4OH + NH_4Cl$; 50 °C; chrom; resolved.	Red; ε_{504} 125, ε_{347} 148	37
trans-$[Co(CO_3)(NH_3)_2(en)]Cl \cdot H_2O$	*cis*-$[Co(Cl)_2(NH_3)_2(en)]Cl + Ag_2CO_3$; dark	Red; ε_{512} 95; ε_{356} 103	21
cis-$[Co(CO_3)(NH_3)_2(bipy)]Cl \cdot 2H_2O$	$K[Co(CO_3)_2(NH_3)_2] + bipy + HClO_4$; p*K* 5.5, 0 °C; r.t., chrom., resolved with Na(+) [Co(edta)]	Red	37
cis-$K[Co(CO_3)(gly)_2] \cdot H_2O$	$CoCl_2 + H_2O_2 + KHCO_3$ + glyH; 60–65 °C, 3 h	ε_{556} 147; ε_{391} 163	22
$[Co(CO_3)(tren)]ClO_4 \cdot H_2O$	$CoCl_2$ + tren 3HCl + $NaHCO_3$ + PbO_2; 25–70 °C + $AgClO_4$	Red; ε_{504} 130; ε_{354} 110	23
sym-$[Co(CO_3)(trien)](ClO_4)$	α-$[Co(Cl)_2(trien)]Cl + NaHCO_3$; evap. r.t. + $NaClO_4$	Red; ε_{503} 124; resolved, $[\alpha]_{589}$ 1230°	24
asym-$[Co(CO_3)(trien)](ClO_4)$	$[Co(Cl)_2(trien)]Cl + Li_2CO_3$; heat	Red; ε_{503} 180; resolved, $[\alpha]_{589}$ 770°	24
$[Co(CO_3)(cyclen)]Cl \cdot 2H_2O$	$[Co(Cl)_2(cyclen)]Cl + Li_2CO_3$; 80 °C, 6 h	Red; ε_{530} 280	25

Table 67 (*continued*)

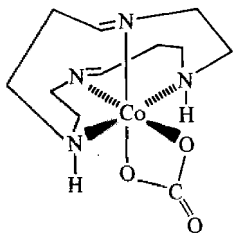
$[Co(CO_3)(cyclam)]Cl$	$Na_3[Co(CO_3)_3]$ + cyclam 3.5HCl	Red; ε_{520} 204; ε_{365} 140	26
$[Co(CO_3)([15,16]aneN_4)](ClO_4)$	$[Co(X)_2([15,16]aneN_4)]X$ ($X = Cl^-$, Br^-) + Li_2CO_3	Red; ε_{528} 138 (15); ε_{540} 146 (16)	27
$[Co(CO_3)$; (*trans*[14]diene$)](ClO_4)$	$Na_3[Co(CO_3)_3]$ + L; heat	Red; ε_{500} 121; ε_{350} 135	36, 38
$[Co(CO_3)(3,2,3\text{-tet})](ClO_4)$	*trans*-$[Co(Cl)_2(3,2,3\text{-tet})]ClO_4$ + Na_2CO_3; heat, 30 min	Red; ε_{520} 127; ε_{360} 125	28
$[Co(CO_3)(tetb)](ClO_4)$	$Na_3[Co(CO_3)_3]$ + tetb; heat, pH 8	Purple; ε_{554} 200 (α); ε_{551} 184 (β)	29
$[Co(CO_3)(diars)_2]Y$	*trans*-$[Co(Cl)_2$diars$]Cl$ + Li_2CO_3; MeOH, H_2O; 15 min, heat	Orange, resolved using $NaAsO(tart)_2$ $[\alpha]_{546}$ 880°	30
$[Co(CO_3)(tetars)](ClO_4)$	$[Co(Cl)_2(tetars)]Cl$ + Na_2CO_3; MeOH, H_2O, 80 °C	Red; *sym* and *asym* isomers; both resolved	31
asym-$[Co(CO_3)\{(R,S)\text{-qars}\}](ClO_4)$	*trans*-$[Co(Cl)_2(qars)]Cl$ + Li_2CO_3; heat, 20 min	Red	32
asym-$[Co(CO_3)\{(R,S)\text{-fars}\}]$	*trans*-$[Co(Br)_2(fars)]Br$ + Na_2CO_3; 10 min, heat	Red	32

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The usefulness of cobalt(III)–carbonato complexes derives from their acid lability, with CO_2 and the Co^{III}–aqua complex being rapidly generated in most cases (equations 143, 144 and 145), with full retention of geometric and optical configuration. The coordinated water molecule can then be replaced by the ligand of choice. In non-aqueous solvents the cleavage pattern (equations 143, 144 and 145) would predict an easy route to $[Co(solv)(H_2O)(N)_4]^{3+}$ systems, and if finely divided $[Co(CO_3)(N)_4]X$ ($N_4 = (NH_3)_4$, $(en)_2$) is suspended in dry acetone and concentrated HX added ($X = Cl^-$, Br^-, $CF_3SO_3^-$), $[CoX(OH_2)(N)_4]X_2$ results. However dissolution in concentrated HX invariably results in largely $[Co(X)_2(N)_4]X$.

$Na_3[Co(CO_3)_3]$,[876] or the $[Co(CO_3)_3]^{3-}$ ion prepared *in situ*, has been extensively used for prepar-

ing $[Co(CO_3)_2(AB)]^{n-}$ complexes, and from these, mixed $[Co(CO_3)(AB)(A'B')]$ systems, especially where AB, A'B' are bidentate ligands such as oxalate, amino acids, phen, bipy and related chelating diamines. Shibata and colleagues have been largely responsible for developing this area and a recent account of their work is available.[877] The green $[Co(CO_3)_3]^{3-}$ ion has been resolved into its optical forms but racemizes rapidly,[878] and it is only moderately stable between pH 8 and 10 in the presence of 0.1–1.0 mol dm^{-3} HCO_3^-;[879] it is best prepared and used immediately. Many of the $[Co(CO_3)(AB)_2]^+$ and $[Co(CO_3)(macrocycle)]^+$ systems can be prepared directly from $CoCl_2$ or $Co(OAc)_2$ and the ligand and $NaHCO_3$, others from $[Co(X)_2(AB)_2]^+$ or $[Co(X)_2(macrocycle)]X$, where X = Cl^-, Br^-, using Ag_2CO_3, and still others by oxidation of the Co^{II} complexes in the presence of CO_2 (Table 67). For the macrocycles cyclam,[880,881] [15 or 16]aneN_4,[882] *trans*[14]dieneN_4[883] and tet b,[884] $[Co(CO_3)(macrocycle)]^+$ is particularly valuable since bidentate carbonate requires adjacent *cis* coordination sites and this forces a strained stereospecific geometry on the macrocycle, *e.g.* (**245**). This forced configuration is retained on removing the carbonate moiety in acid solution. This property is valuable since it can present a Co^{III} centre to potential ligands in an alternative configuration and it might be useful in the investigation of biological active sites.



(**245**) $[Co(CO_3)\{trans(S,R)[14]dieneN_4\}]^+$

Monodentate systems $[Co(OCO)_2(N)_5]^{n+}$ are easily formed by saturating an aqueous solution of the aqua complex with CO_2 at pH ≈ 6. Under such conditions maximum concentrations of dissolved CO_2 occur and many $[Co(OH_2)(N)_5]^{n+}$ complexes have pK_a values in this range. It is the complexed hydroxo conjugate which is the reactive species (equation **146**)[875] and if the pK_a is a little higher (*i.e.* the complex is somewhat less acidic) then the reaction is a little slower under any pH condition. The reaction of HCO_3^- and CO_3^{2-} (pH 8–10) is very slow by comparison and can generally be disregarded for those complexes which have slow water exchange rates. But contributions by such species have been found.[886] The rate law takes these factors into consideration and some rate constants corresponding to equation (**146**) are given in Table 69. A recognizable Brönsted relationship exists between $\log k$ and the pK_a of the $Co—OH_2^{n+}$ complex,[885] and the β value of ~0.15 suggests control by the properties of $CO_{2(aq)}$ rather than by the nucleophilic ability of coordinated hydroxide. A $\Delta V^{\ddagger}$ study gives a value of $-10.1 \pm 0.6\,cm^3\,mol^{-1}$ for the pentaammine system and this has been interpreted in terms of significant bond formation in the transition state.[887]

$$[(N)_5Co—\bullet H]^{2+} + CO_{2(aq)} \xrightarrow{k} [(N)_5Co—\bullet \searrow CO_2]^+ + H^+ \qquad (146)$$

Four basic structural types have been found: monodentate (**241**), bridging monodentate (**244**), bridging μ-bidentate (**243**) and the four-membered chelate (**242**). Some structures are given in Table 68. Koshy and Dasgupta have recently reinvestigated the preparation of (**244**) $[(N)_5 = (NH_3)_5]$[888] but its very rapid hydrolysis to $[Co(OCO_2H)(NH_3)_5]^+$ and $[Co(OH_2)(NH_3)_5]^{2+}$ still leaves some doubt as to its structure. Churchill and colleagues have described the structure of μ-bridged $[\{(NH_3)_3Co\}_2\{\mu\text{-}(OH)_2CO_3\}]SO_4 \cdot 5H_2O$ together with preliminary data on its acid hydrolysis and reconstitution.[889] The cleavage patterns for the two structural types (**243**) and (**244**) have not been described in any detail.

Monodentate complexes (**241**) are well characterized (Table 67) but only one structure, that of $[Co(OCO_2)(NH_3)_5]Br \cdot H_2O$, is available (Table 68). Considerable unsaturation into the coordinated O atom is suggested by the similar C—O bond lengths. These complexes undergo rapid acid-catalyzed decarboxylation (reverse of equation 146) and some rate data are given in Table 69. Acyl–O bond cleavage has been established for $[Co(OCO_2H)(NH_3)_5]^{2+}$,[890] and the rapidity of the reactions makes this certain in a general sense. Bidentate (**242**) shows some 10 pm longer bond lengths for C—O in the chelate ring with 68–70° angles at the metal (Table 68), which indicates considerable strain. Acid catalysis follows the rate law $k_{obs} = k_0 + k_1[H^+]$ with k_0 and k_1 values of $1–8 \times 10^{-4}\,s^{-1}$ and $0.1–1\,mol^{-1}\,dm^3\,s^{-1}$ respectively for tetraammine systems and $\sim 10^{-5}\,s^{-1}$ and $10^{-4}–10^{-5}\,mol^{-1}\,dm^3\,s^{-1}$ for the aromatic amines py, phen, bipy.[874] Note the very much slower k_1 values for the complexes containing aromatic amines. ^{18}O tracer experiments have established

Table 68 Crystal Structures of Carbonato Complexes

Complex	*Structural data*[a]	*Comments*	*Ref.*
Co^{II}			
trans-$K_2[Co\{(CO)_3\}_2(H_2O)_4]$	$P2_1/n$; CoO 207; OC 128–129; (H_2O)CoO 87.8°; OCO 119–120°	Co^{II} complex, *trans* monodentate OCO_2^{3-}	1
$[Co(CO_3)(OH_2)_3(imH)_2]$	*A*2/*a*; CoO 214; OC 130; OCoO 61.2°	*cis*$(OH_2)_2$; *trans*$(imH)_2$ bidentate	18
Co^{III}			
$[Co(CO_3)(NH_3)_5]Br\cdot H_2O$	$Pna2_1$; CoO 193; OC 131–120; OCO 117, 123, 118°	Monodentate	2
$[Co(CO_3)(NH_3)_4]Br$	*Pcmn*; CoO 190.5; OC 113.6, 123.7; OCoO 70.5°	Bidentate	3
$[Co(CO_3)(py)_4]ClO_4\cdot H_2O$	$P2_1/c$; CoO 189; OC 132, 133, 122; OCoO 69.3°	Bidentate	4
$[Co(CO_3)(en)_2]I\cdot 2H_2O(Cl)$	*C*2/*c*; CoO 191; OC 130.6(2), 123; OCoO 68.2°	Bidentate	5
$[Co(CO_3)(en)_2]ClO_4$	CoO 192; OC 132(2), 122; OCoO 68.8°	Bidentate	6
$[Co(CO_3)(phen)_2]Cl\cdot 3H_2O$	$P2_1/c$; CoO 188; OC 133, 128, 120; OCoO 69.4°	Bidentate	7
$[Co(CO_3)(phen)_2]Br\cdot 4H_2O$	*C*2/*c*; CoO 189; OC 131, 133, 121; OCoO, 69.3°	Bidentate	8
$[Co(CO_3)(bipy)_2]NO_3\cdot 5H_2O$	*C*2/*c*; CoO 188.7; OC 131, 124; OCoO 69.9°	Bidentate	9
$Na[Co(CO_3)(pren)]\cdot 3H_2O$	$P2_1$; CoO 191; CoO 131, 132, 123; OCo© 69.1°	Bidentate	10
$K[Co(CO_3)\{(R)\text{-val}\}]\cdot 2H_2O$	$P2_12_12_1$; CoO 191; OC 126, 133, 129	Λ(+), *cis*(N), *cis*(O) configuration	11
$(+)_{589}$-$[Co(CO_3)(cyclen)]ClO_4\cdot H_2O$	$P2_12_12_1$; CoO 192; OC 131, 132, 122; OCoO 68.4°	Bidentate	12
$(+)_{589}$-$[Co(CO_3)(3,8\text{-}Me_2\text{trien})]ClO_4$	$P2_12_12_1$; CoO 192; OC 131, 130, 124; OCoO 68.6°	Bidentate	13
$[Co(CO_3)(terpy)(OH)]\cdot 4H_2O$	$P\bar{1}$; CoO 192; OC 129, 129, 126; OCoO 68.0°	Bidentate	14
$[(NH_3)_4Co(\mu\text{-}OH,NH_2)Co(CO_3)_2]I_2\cdot H_2O$	$P2_1/c$; CoO 192; OC 131(2), 124; OCoO 68.5°	Bidentate	15
$[(NH_3)_3Co\{\mu\text{-}(OH)_2,CO_3\}Co(NH_3)_3]SO_4\cdot 5H_2O$	$P\bar{1}$; CoO 190; OC 129–130, 126	μ-bridging	16
$[Co(CO_3)(ms\text{-}bn)_2]I\cdot H_2O$	$P2_12_12_1$; CoO 191–192; CoN 194–197; OCoO 68.8°	μ-bridging	17

[a] Bond lengths in pm.

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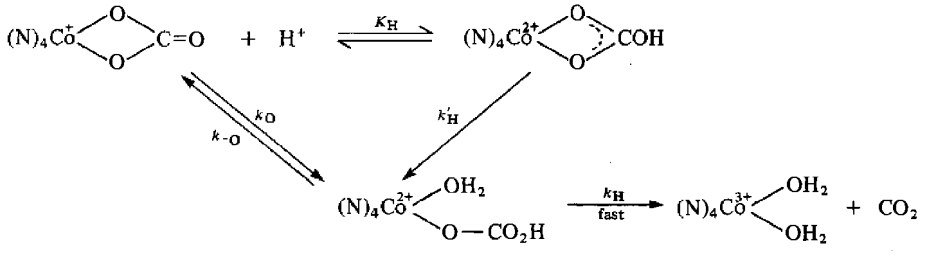
Co—O bond cleavage for k_1 in $[Co(CO_3)(NH_3)_4]^+$ (Scheme 85)[892] followed by faster O—CO_2H hydrolysis of the monodentate (Table 69). In strongly acidic solutions k_1 can exceed k_H for the monodentate with a limiting rate (k'_H in Scheme 85) being approached. In this case the monodentate is observed as an intermediate.[896] The reverse ring closure for $[Co(OCO_2)(OH_2)(N)_4]^+$ is fast ($k_{-0} = 0.02$–$0.1\ s^{-1}$, Scheme 85). For $[Co(CO_3)_2(en)]^-$ and $[Co(CO_3)_2(py)_2]^-$ loss of the first carbonate chelate is very fast and rate data are only available for the intermediate $[Co(CO_3)(H_2O)_2(N)_2]^+$ species [$(N)_2$ = en,[897] $(py)_2$[898]].

Table 69 Rates of $CO_{2(aq)}$ Uptake and Release for Some Monondentate Cobalt(III) Carbonato Complexes[a]

Complex	$pK_{(aq)}$	k ($mol^{-1}dm^3s^{-1}$)	*pK*	k_H (s^{-1})	*Ref.*
$[Co(OCO_2H)(NH_3)_5]^{2+}$	6.6	220 ± 40 $\Delta V^{\ddagger} -10.1 cm^3 mol^{-1}$	6.7, 6.4	1.10, 1.25 $\Delta V^{\ddagger} +6.8 cm^3 mol^{-1}$	1, 2 13
α,β-*S*-$[Co(OCO_2H)(tetren)]^{2+}$	6.3	166 ± 15	6.4	0.28 ± 0.03	4
$[Co(OCO_2H)(OH_2)(tren)]^{2+}$	5.3 (pK_1) 7.9 (pK_2)	44 ± 2 170 ± 10	5.9	1.5, 1.2	5, 6
cis-$[Co(OCO_2H)(OH_2)(en)_2]^{2+}$	6.1	225 ± 15	5.8	0.37	3
trans-$[Co(OCO_2H)(OH_2)(en)_2]^{2+}$	–	–	5.6	2.1 ± 0.1	3
cis-$[Co(OCO_2H)(NH_2)(en)_2]^{2+}$	–	–	6.7	0.60 ± 0.02	7
trans-$[Co(OCO_2H)(NH_3)(en)_2]^{2+}$	–	–	6.3	0.66 ± 0.02	7
trans-$[Co(OCO_2H)Cl(en)_2]^{+}$	–	–	6.5	1.02 ± 0.05	8
cis-$[Co(OCO_2H)(OH_2)(cyclam)]^{+}$	4.9 8.0	57 ± 4 196 ± 24	–	–	9
trans-$[Co(OCO_2H)(OH_2)(cyclam)]^{+}$	2.9 7.2	37 ± 0.1 70 ± 0.2	–	–	9
trans-$[Co(OCO_2H)(CN)(NH_3)_4]^{+}$	7.6	338 ± 32	6.9	0.38 ± 0.01	10
$[Co(OCO_2H)(OH_2)(nta)]^{-}$	–	–	–	57	11
sym-$[Co(OCO_2H)(OH_2)(edda)]$	–	–	–	55	12
asym-$[Co(OCO_2H)(OH_2)(edda)]$	–	–	–	2.3	12

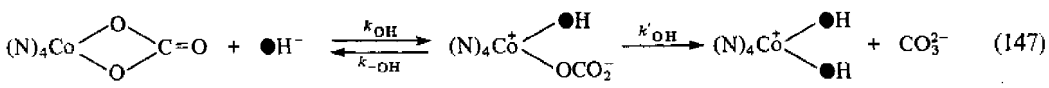
[a] For reaction $(R)_5CoOH^{n+} + CO_{2(aq)} \overset{k}{\rightleftharpoons} (R)_5CoOCO_2H^{n+}$, where $pK_{(aq)}$ relates to $(R)_5CoOH_2^{(n+1)}$ and pK to $(R)_5CoOCO_2H^{n+}$

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Scheme 85

Under alkaline conditions pathways first order in $[OH^-]$ become available for both ring opening and subsequent hydrolysis of the monodentate carbonate intermediate (equation 147). Both reactions are quite slow ($k_{OH} = 3.6 \times 10^{-3} mol^{-1} dm^3 s^{-1}$, $k'_{OH} = 8.2 \times 10^{-6} mol^{-1} dm^3 s^{-1}$ for $[Co(CO_3)(tren)]^+$).[893] Both reactions involve Co—O cleavage for $(N)_4 = (en)_2$ and probably occur *via* S_N1cb cleavage in the deprotonated amine base conjugate.[894] Endicott and coworkers have discussed this reaction in some detail[895] and Dasgupta and Sadler report a recent example using $[Co(CO_3)(cyclam)]^+$.[903] The reverse cyclization is also very slow under alkaline conditions ($k_{-OH} = 6.5 \times 10^{-5} s^{-1}$ for $(N)_4 = (en)_2$) and the ring-opened form (**246**) is stabilized for $[OH^-] > 0.01 mol dm^{-3}$. Carbonate exchange in monodentate (**241**) and chelate (**242**) systems therefore nearly always occurs *via* hydrolysis and Co^{III}–hydroxo attack on solvated CO_2. Dobbins and Harris have discussed this for chelate systems[899] and Francis and Jordan for $[Co(OCO_2)(NH_3)_5]^+$.[900] However, displacement of carbonate in $[Co(CO_3)_3]^{3-}$ by pyridine, diamines and SO_3^{2-} is thought to occur both directly as well as *via* $[Co(CO_3)_2(H_2O)(OCO_2H)]^{2-}$ species.[901,902]



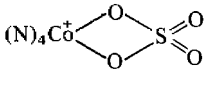
(147)

47.7.4 Oxyanions of Cobalt(III)

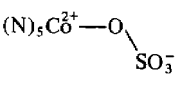
47.7.4.1 Sulfate, selenate and tellurate

The group oxidation state anions SO_4^{2-}, SeO_4^{2-} and $TeO_2(OH)_4^{2-}$ show an increasing tendency to polymerize with SO_4^{2-} being relatively inert to oxygen exchange and dimerization, while $TeO_2(OH)_4^{2-}$ rather easily dimerizes to $Te_2O_6(OH)_4^{4-}$.[904] The racemic chelate $[Co\{O_2Te(OH)_4\}(en)_2]^+$ also rapidly equilibrates to the dimer $[Co(en)_2\{O_2Te(OH)_4O_2\}(en)_2Co]^{2+}$ in aqueous solution and tetrameric $[\{Co(en)_2\}_2(O_4TeO_2TeO_4)\{(en)_2Co\}_2]Cl_4$ has also been isolated.[905] This increasing tendency to raise the valence of the non-metal by substitution with other oxy species increases the possibility of Co^{III}—OH_2 or Co^{III}—OH attack. Some preparations are listed in Table 70.

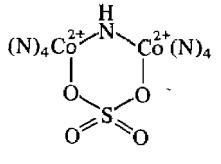
SO_4^{2-} coordinates in three structural modifications (**247**), (**248**) and (**249**) with the chelate (**247**) being unstable towards pH-independent ring opening [$(N)_4 = (en)_2$, $k = 7.3 \times 10^{-5}\,s^{-1}$].[906] The monodentate (**248**) is quite stable but undergoes slow aquation, $k_{obs} = k_1 + k_2[H^+]$, and base hydrolysis (Table 44). Ring opening and hydrolysis almost certainly occur without S—O bond cleavage.[907] Formation of monodentate sulfato complexes $[Co(OSO_3)(NH_3)_5]^+$ and $[Co(OSO_3)(H_2O)(en)_2]^+$ is also very slow (Table 43) and assumes a rate independent of $[SO_4^{2-}]$ above 0.02 mol dm^{-3} indicative of strong ion pairing.[908,909] Bridged species (**249**) are easily formed by bubbling SO_2 through a solution of the μ-superoxo dimer $[(N)_4Co\{\mu\text{-}(O_2,NH_2)\}Co(N)_4]^{4+}$ [$(N)_4 = (NH_3)_4$, $(en)_2$] with oxidation at S and reduction at O occurring rapidly.[910] A corresponding μ-selenato complex can be formed in a similar manner using SeO_2 but the reaction is slower.[911] Selenate analogous of (**247**) and (**248**) appear to be unknown. As mentioned above the preparation of the Te^{VI} chelate $[Co\{O_2Te(OH)_4\}(en)_2]Cl\cdot H_2O$ corresponding to (**247**) has been reported and it has been resolved into its optical enantiomers.[905]



(247)



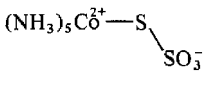
(248)



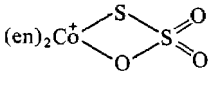
(249)

47.7.4.2 Thiosulfate

Some interesting chemistry is now available on the mono sulfur analogue of sulfate, the thiosulfate ion. Both S- and O-bound isomers of $[Co(S_2O_3)(NH_3)_5]^+$ are known, and a structure on the former (Table 72) confirms it, *i.e.* (**250**), as the stable form. Preparations are given in Table 70. The O-bound isomer has been observed as a minor product (*ca.* 3%) in the alkaline hydrolysis of $[Co(OSO_2R)(NH_3)_5]^{2+}$ (R = Me, CF_3) in 1.0 M $Na_2S_2O_3$.[947] It rather rapidly isomerized intramolecularly in solution to the *S*-bound isomer ($t_{1/2} \approx 27$ min). The O,S chelate (**251**) has been prepared by Deutsch and coworkers but is unstable towards hydrolysis to monodentate *trans*-$[Co(SSO_3)(OH_2)(en)_2]^+$.[948] Such hydrolysis is some four times faster than that for the sulfato chelate $[Co(O_2SO_2)(en)_2]^+$, which suggests a small *trans* influence for the coordinated sulfur (*cf.* Section 47.8.5). Oxidation of *cis*-$[Co(SSO_3)_2(en)_2]^-$ with an excess of I_2 leads to *trans*-$[Co\{S(S)SO_3\}(OH_2)(en)_2]^+$ containing the stabilized disulfane monosulfonate anion (**252**), possibly *via* an unstable tetrathionate intermediate (equation 148). The product was isolated as *trans*-$[Co\{S(S)SO_3\}Cl(en)_2]$ and shows *trans* labilizing effects.[949] Stoichiometric oxidation of *trans*-$[Co(SSO_3)_2(en)_2]^-$ using I_3^- gives *trans*-$[Co(SSO_3)(H_2O)(en)_2]^+$, and anation of this ion with NCS^-, NO_2^-, NCO^-, Cl^- and $C_2O_4^{2-}$ is fast, consistent with the kinetic *trans* labilizing order SO_3^{2-} > RSO_2^- > SSO_3^{2-} (*cf.* Section 47.8.5).[950,951] Aquation of the resulting *trans*-$[Co(SSO_3)(Y)(en)_2]$ is also fast.



(250)

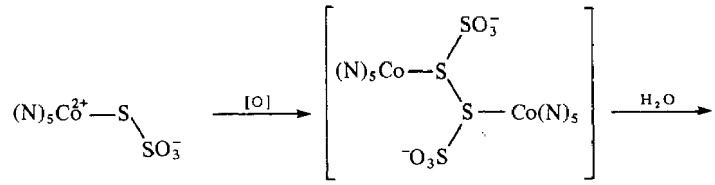


(251)

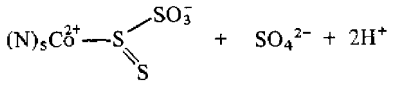
Table 70 Preparations: Some O-bonded Oxyanion Complexes Containing S, Se, Te, As and Re

Complex	*Preparation*	*Comments*	*Ref.*
$[Co(OSO_2)(NH_3)_5]^+$	$[Co(OH_2)(NH_3)_5](ClO_4)_2 + Na_2S_2O_5$; pH 5.5	Red. soln. (not isolated); ε_{518} ~88; ε_{330} ~2100; decomp. to Co^{II} in soln and solid	1
$[Co(OSO_2)(OH_2)(tren)]^+$	$[Co(OH_2)_2(tren)]^{3+} + Na_2S_2O_5$; pH ~ 6	Orange soln. (not isolated); ε_{510} 136; ε_{325} 1825	6
α,β-$[Co(OSO_2)(tetren)]^+$	$[CoOH_2(tetren)]^{3+} + Na_2S_2O_5$, pH ~ 5.5	Red-brown soln. (not isolated); ε_{510} 150; ε_{330} 1928	7
$[Co(OAsO_3)(NH_3)_5]$	$[Co(CO_3)(NH_3)_5](NO_3) + HClO_4 + NaHAsO_4$; pH 6.5, 40 °C, 35 min	Red; pK_2 3.90; pK_1 8.20	5
$[Co(O_2AsO_2)(NH_3)_4]$ (chelate)	$[Co(CO_3)(NH_3)_4](NO_3) + HClO_4 + (NH_4)_2HAsO_4$; 40 °C, 30 min	Violet	5
$[Co(OSeO_2)(NH_3)_5]$	$[Co(OH_2)(NH_3)_5](ClO_4)_3 + Na_2SeO_3$; 70 °C min	Red-purple; ε_{519} 62	2
$[Co(O_2ScO)(en)_2](ClO_4)\cdot H_2O$ (chelate)	*cis*-$[Co(H_2O)(OH)(en)_2](ClO_4)_2 + Na_2SeO_3$; 60 °C 10 min	Crimson; ε_{510} 155; ε_{360} 142	2
cis,trans-$[Co(OSeO_2)(OH_2)(en_2](ClO_4)\cdot H_2O$	*cis*- or *trans*-$[Co(H_2O)(OH)(en)_2](ClO_4)_2 + H_2SeO_3$	Mauve (*cis*); blue-green (*trans*); ε_{532} 100 (*cis*); ε_{590} 50 (*trans*)	2
$[Co(O_2Te)(OH)_4(en)_2]Cl\cdot 3H_2O$ (chelate)	$[Co(CO_3)(en)_2]_2SO_4 + Te(OH)_6$; 55 °C, 1 h	Red; ε_{521} 117; ε_{324} 85 optically active complexes separated	3
$[Co(OReO_3)(NH_3)_5]X_2$ (X = Cl^-, NO_3^-, ClO_4^-)	$[CoOH_2(NH_3)_5](ReO_3)_3$; 95–130 °C, 10^{-3} mm, 2–5 h	Purple; ε_{530} 63.5	4
$[Co(OClO)(NH_3)_5](NO_3)_2$	$Co(NO_3)_2 + NH_4NO_3 + NH_4OH + ClO_2$; $NaClO_2 + HClO_4$, 0 °C	ε_{515} 87; ε_{358} 2320	8
$[Co(OClO_3)(NH_3)_5](ClO_4)_2$	$[CoN_3(NH_3)_5](ClO_4)_2 + NO + NO_2 + HClO_4$ (70%); 2 h	Pink, aquates rapidly in soln. ($t_{1/2} \approx 7$ s)	9
$[Co(SSO_3)(NH_3)_5](ClO_4)\cdot H_2O$	$Co(NO_3)_2 + NH_4NO_3 + Na_2S_2O_3 + NH_4OH$; air, 20 °C; chrom.	Pink; $\varepsilon_{512.5}$ 69.9; ε_{289} 14 130	10
cis-$[Co(OSO_3)(H_2O)(en)_2](ClO_4)$	*trans*-$[Co(Cl)_2(en)_2]Cl + H_2SO_4$; warm; $H_2O + LiClO_4$	Purple; ε_{500} 105	11
trans-$[Co(S_2O_3)(Y)(en)_2]$ (Y = NCS^-, NO_2^-, NCO^-, Cl^-, $C_2O_4^{2-}$)	*trans*-$[Co(S_2O_3)(OH_2)(en)_2]^+ + NaY$; 30 min, r.t.; chrom	Labile Y;	14, 15
$[Co(O_2SO_2)(en)_2]Br$ (chelate)	*cis*-$[Co(OSO_3)(H_2O)(en)_2]Br$; 110 °C, 24 h	Purple-red; ε_{505} 107	11
$[Co(OSSO_2)(en)_2](ClO_4)$ (chelate)	*trans*-$[Co(SSO_3)(OH_2)(en)_2]^+$; chrom., dehydrate	Red; ε_{530} 144; ε_{276} 12 100	12
cis,trans-$Na[Co(SSO_3)_2(en)_2]$	*cis*-$[CoCl_2(en)_2]Cl + (NH_4)_2S_2O_3$; DMSO + H_2O, 70 °C, 30 min.; chrom.	Green (*trans*); ε_{596} (sh) 611; ε_{544} 85	13, 14
	$CoCl_2\cdot 6H_2O + Na_2S_2O_3 + en$; 0.8 M HOAc, < 10 °C; air (*trans* isomer)	Brown-violet (*cis*); ε_{545} 166; ε_{283} 15 850	13

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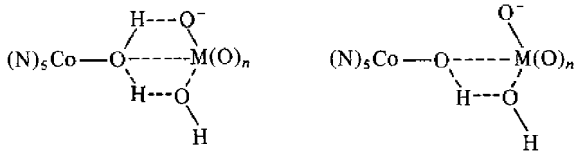
(148)



(252)

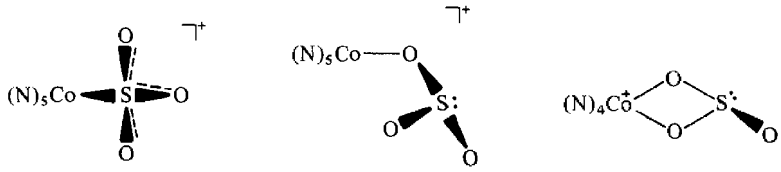
47.7.4.3 Sulfite and selenite

The lower oxidation state group IV anions SO_3^{2-} and SeO_3^{2-} rapidly undergo substitution and oxygen exchange and associative interchange processes involving expansion of covalency are attractive routes to their metal complexes.[912] Coordination is often much faster than the unassisted water exchange at the metal, and proton transfer and bond making in associated transition states of the type (**253**) and (**254**) are important for Co^{III}.



(253) (254)

Tetrahedral SO_3^{2-} is known to coordinate to Co^{III} in three ways (**255**), (**256**) and (**257**), although structures are only confirmed for (**255**; Table 72). Preparations to some O-bonded complexes are given in Table 70 and some S-bonded systems in Table 71. Since SO_3^{2-} can be removed by treatment with hot concentrated acid, S-bonded complexes (**255**) can sometimes be useful in synthesis but reduction to $Co^{2+}_{(aq)}$ is often a competing problem.[913] They are reasonably stable in alkali. Baldwin many years ago prepared orange-brown $[Co(O_2SO)(en)_2]X$ ($X = Cl^-, ClO_4^-, NO_3^-$) and on the basis of molecular weight and IR data represented them as chelates (**257**).[914] More recently some phenanthroline and bipyridyl complexes of similar constitution have been prepared (Table 71). The chelate structure has not been confirmed but Baldwin's observations suggest that it is quite robust.



(255) (256) (257)

The O-bonded isomer (**256**) has been examined recently by Harris and his colleagues[915,916] and can be easily prepared by the addition of the aqua complex to $Na_2S_2O_5$ or $NaHSO_3$ solutions at pH ~ 5–6 (Table 71). These species are much less stable, undergoing reduction to Co^{II} or hydrolyzing in acid solution (pH < 5), and isomerizing to the S-bound isomer in alkali. Addition of $SO_{2(aq)}$ to Co^{III}—OH is fast at pH ≈ 5 where the concentration of the two reactants is maximized. Compared to the reaction with $CO_{2(aq)}$ reaction (149) is some 10^6 times faster. Some kinetic data are collected in Table 73. The resulting red-brown products (Table 70) are typical of other O-bound group VI anions, and a recent ^{17}O experiment verifies the source of the O atom.[917] The reverse hydrolysis is subject to H^+ catalysis as required by equation (149; Table 74). For the pentaammine system reduction to Co^{II} also occurs at pH < 5 but the O-bound isomer is stable in alkaline solution and apparently isomerizes to $[Co(SO_3)(NH_3)]^+$; this latter aspect has not been described in much

Table 71 Preparations: Some S-Bonded Sulfito, Sulfinato Complexes of Cobalt(III) (Monodentate)

Complex	*Preparation*	*Properties*	*Ref.*
α,β-$[Co(SO_3)(tetren)](ClO_4)\cdot H_2O$	$[CoOH_2(tetren)](ClO_4)_3 + Na_2S_2O_5$; r.t.	Orange-yellow; ε_{444} 236, ε_{281} 16900	11
$[Co(SO_3)(phen)_2]Cl$ (chelate)	*cis*-$[CoCl_2(phen)_2]Cl + Na_2SO_3$; water bath conc.	Orange; IR characteristic of bidentate	10
$[Co(SO_3)(en)_2](ClO_4)$ (chelate)	*trans*-$[Co(Cl)_2(en)_2]Cl + Na_2SO_3$; evap., 6 weeks	Orange-brown; ε_{530} (sh) 90, ε_{430} 120	9
$[Co(SO_3)(NH_3)_5]Cl\cdot H_2O$	$[Co(OH_2)(NH_3)_5]Cl_3 + Na_2S_2O_5 + NH_4OH$; 40–60 °C	Brown; ε_{457} 148; ε_{278} 17800	2, 3
trans-$[Co(SO_3)(OH_2)(NH_3)_4]Cl$	$[Co(SO_3)(NH_3)_5]Cl + HCl$ (conc); 30 min	Yellow-brown; ε_{473} 120; ε_{273} 6460	2, 3
cis-$NH_4[Co(SO_3)_2(NH_3)_4]\cdot 3H_2O$	$CoCl_2\cdot 6H_2O + (NH_4)_2CO_3 + NH_4OH$; air, 8 h; $NaHSO_3$, air, 4 min	Brown; ε_{452} 200; ε_{264} 20000	6
trans-$Na[Co(SO_3)_2(NH_3)_4]\cdot 2H_2O$	*trans*-$[Co(SO_3)(H_2O)(NH_3)_4]Cl + Na_2SO_3$; MeOH	Yellow; ε_{430} (sh) 490; ε_{295} 29500	4
cis-$Na_2[Co(SO_3)_2(en)_2]ClO_4\cdot 3H_2O$	$Co(NO_3)_2\cdot 6H_2O + Na_2SO_3 + enHNO_3$; air, 1 h	Brown-yellow; ε_{440} 251, resolved using $(+)_{589}$-$[Co(C_2O_4)(en)_2]I$	5, 9
trans-$Na[Co(SO_3)_2(en)_2]\cdot 3H_2O$	*cis*-$[Co(SO_3)(N_3)(en)_2] + Na_2SO_3$; boil 3 min	Yellow; ε_{433} 417	12
$Na_2[Co(SO_3)_2(tren)]ClO_4\cdot H_2O$	$[Co(H_2O)_2(tren)](ClO_4)_3 + Na_2S_2O_5$; pH 8	Yellow; ε_{450} 250; $\varepsilon_{300} \sim 16000$	5, 9
$Na[Co(SO_3)(DMGH)_2(OH_2)]$	$[Co(DMGH)_2Cl(OH_2)] + Na_2SO_3$; 50 °C, 10 min	Red-brown; ε_{460} 304; ε_{325} 5450	8
$[Co\{S(O_2)C_6H_4R\}(NH_3)_5](ClO_4)_2$ (R = H, Me)	$[Co(OH_2)(NH_3)_5](ClO_4)_3 + NaSO_2C_6H_4R$; DMSO, 60 °C, 1 h	Yellow-brown; ε_{465} 204(H); 221(Me)	1 7

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Table 72 Structures of Some Cobalt(III) Sulfito (S) Complexes

Complex	*Structural data; trans effect*[a]	*Kinetic trans lability ($\log k_h$); comments*	*Ref.*
$[CoSO_3(NH_3)_5]_2(SO_3)$ (also Cl·H_2O salt)	CoS 221.8; SO 148; CoN (*trans*) 205.5; CoN (*cis*) 196.6; Δr 8.9	−1.98	1a, 7
trans-$[Co(SO_3)H_2O(en)_2](ClO_4)\cdot H_2O$	CoS 218.1; CoO (*trans*) 203.7; CoN (*cis*) 194.2	2.4	2a, b
trans-$[Co(SO_3)(NCS)(en)_2]$	CoS 220.3; CoN (*trans*) 197.4, CoN (*cis*) 196.2	−0.8	3, 2b
trans-$[Co(SO_3)(im)(en)_2]ClO_4\cdot 2H_2O$	CoS 222.3; CoN (*trans*) 200.8, CoN (*cis*) 196.3; Δr 4.5	−1.5	4, 2b
cis-$NH_4[Co(SO_3)_2(NH_3)_4]\cdot 3H_2O$	CoS 222; CoN (*trans*) 199.3, 202.3; CoN (*cis*) 197.0; Δr 5.3, 2.3	−0.82	5a, b
cis-$Na_2[Co(SO_3)_2(en)_2](ClO_4)\cdot H_2O$	CoS 220.6, 223.3: CoN (*trans*) 201.5, 200.3; CoN (*cis*) 196.4, 195.9; Δr 4.4, 5.1	–	6
trans-$Na[Co(SO_3)_2(en)_2]\cdot 3H_2O$	CoS 226.7; SO 148.9 (av); CoN (*trans*) 195.8 (av)	V. long Co—S bonds	8
trans-$[Co(SO_3)Cl(en)_2]\cdot H_2O$	CoS 220.5; SO 148; CoCl 237.7; CoN (*trans*) 196	V. long Co—Cl bond	9
trans-$[Co(SO_3)(NH_3)(en)_2](ClO_4)$	CoS 222.7; SO 147.5; CoN (*trans*) 207.0; CoN (*cis*) 196; Δr 11	V. long Co—NH_3 bond	10
$[Co\{S(O)_2C_6H_4Me\}(NH_3)_5](ClO_4)_2\cdot H_2O$	CoS 223; SO 147; CoN (*trans*) 202.3; CoN (*cis*) 196.5; Δr 5.8; CoSC 112.90°	–	7
$[Co(SSO_3)(NH_3)_5]Cl\cdot H_2O$	CoS 228.7; SS 204.8; SO 146; CoN (*trans*) 198.6; CoN (*cis*) 196.7; Δr 1.9; CoSS 110°	–	11

[a] Data in pm.

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detail.[915] The α,β-$[Co(OSO_2)(tetren)]^+$ ion is more stable toward reduction and isomerizes to α,β-$[Co(SO_3)(tetren)]^+$ at a pH-independent rate (pH 6–7.5, $2.7 \times 10^{-4}\,s^{-1}$, 25 °C). This is some 10^3 times faster than the related isomerization of O-chelated sulfinate in $[Co(cystO_2)(en)_2]^{2+}$ (Section 47.8.2.2.iii). The resulting S-bound isomer undergoes slow hydrolysis in alkali, $k_{OH} = 8.15 \times 10^{-5}\,mol^{-1}\,dm^3\,s^{-1}$.[916] $[Co(OSO_2)(OH_2)(tren)]^+$ reduces to Co^{II} in the pH range 2.9–5.4 ($k_{OH} \approx 1.0 \times 10^{-3}\,s^{-1}$) but adds a second SO_3^{2-} ligand in the pH range 7.2–8.9 to form $[Co(SO_3)_2(tren)]^-$.[918] Unlike $[Co(NO_2)(NH_3)_5]^{2+}$ and S-bound $[Co(cysO_2)(en)_2]^+$, $[Co(SO_3)(NH_3)_5]^+$ shows no signs of photoisomerization.[919]

$$(NH_3)_5Co^{2+}—\overset{\diagup}{\bullet}H + SO_{2(aq)} \underset{k_{hyd}}{\overset{k_f}{\rightleftharpoons}} (NH_3)_5Co^{2+}—\bullet\!\!<^{O}_{SO_2^-} + H^+ \qquad (149)$$

The direct reaction of Co^{III}—OH_2 or Co^{III}—OH species with SO_3^{2-}, as distinct from the above reaction with $SO_{2(aq)}$, is not well documented but appears to be moderately fast. Stranks and coworkers[920] many years ago found that *trans*-$[Co(OH)(OH_2)(en)_2]^{2+}$ reacts with SO_3^{2-} to form *trans*-$[Co(SO_3)_2(en)_2]^-$ within one second at pH 7.5, which is faster than expected for substitution at the metal centre, and Spitzer and van Eldik[919] have recently discussed the relatively fast reaction of $[Co(OH)(NH_3)_5]^{2+}$ with SO_3^{2-} at pH 9–10 to form *trans*-$[Co(SO_3)_2(NH_3)_4]^-$ (Table 71). It is very likely that these reactions occur by the addition of coordinated water or hydroxide to the sulfur atom of SO_3^{2-} with subsequent isomerization of O-bound sulfite to the favoured S-bound isomer (equation 150).

Crimson-red selenito complexes are formed within milliseconds by the addition of $CoOH_2^{n+}$ species to Na_2SeO_3 at pH values between 3 and 6.[921–923] Bidentate chelates of type (**247**) do not

Table 73 Rate Data for Addition of $CoOH_2^{n+}/CoOH^{(n-1)+}$ to SO_2 and CO_2, and the H^+-catalyzed Hydrolysis of $CoOSO_2^{(n-2)+}$ and $CoOCO_2^{(n-2)+}$

Complex	*Reactant*	k ($mol^{-1}dm^3s^{-1}$)	*Complex*	k (s^{-1})	*Ref.*
$[Co(OH)(NH_3)_5]^{2+}$	SO_2	4.7×10^8	$[Co(OSO_2H)(NH_3)_5]^{2+}$	1.0×10^3	1
	CO_2	2.2×10^2	$[Co(OCO_2H)(NH_3)_5]^{2+}$	1.10	2, 3
cis-$[Co(OH)(OH_2)(en)_2]^{2+}$	SO_2	1.0×10^8	*cis*-$[Co(OSO_2H)(OH_2)(en)_2]^{2+}$	6.0×10^3	4, 7
	CO_2	2.8×10^2	*cis*-$[Co(OCO_2H)(OH_2)(en)_2]^{2+}$	0.45	5, 6
$[Co(H_2O)_2(tren)]^{2+}$	SO_2	9×10^6	$[Co(OSO_2H)(OH_2)(tren)]^{2+}$	3.8×10^3	7
$[Co(OH)(OH_2)(tren)]^{2+}$	SO_2	5.3×10^7	–	–	7
$[Co(OH)_2(tren)]^{2+}$	SO_2	2.4×10^9	–	–	7
$[Co(OH)(OH_2)(tren)]^{2+}$	CO_2	44	$[Co(OCO_2H)(OH_2)(tren)]^{2+}$	1.19	8, 9
α,β-$[Co(OH)(tetren)]^{2+}$	SO_2	3.3×10^8	$[Co(OSO_2H)(tetren)]^{2+}$	1.1×10^3	10

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$$(N)_5Co^{3+}—OH_2 + SO_3^{2-} \longrightarrow (N)_5Co^{2+}—O(SO_2^-) \xrightarrow{fast} (N)_5Co^{+}—SO_3 \qquad (150)$$

coexist with the monodentate (**248**) at equilibrium and equilibrium constants for formation of the monodentate are such that the monodentate is stabilized in solutions above pH 3. Rate data have been interpreted in terms of addition of $CoOH_2^{3+}$ and $CoOH^{2+}$ to $HSeO_3^-$ (Table 74) and for the aqua complexes rate saturation can be attributed to ion pairing.[921] The fast rate for $CoOH_2^{3+}$ is attributed to efficient proton transfer to selenite oxygen in the associative transition state (**253**). The reaction of SeO_3^{2-} is some 15–24 times slower if OH^- is considered the leaving group on Se. Dimeric selenite species become important contributors to the reaction at pH > 7.[923]

It is well known that S-bonded SO_3^{2-} complexes (**255**) labilize monodentate ligands *trans* to them in octahedral coordination. Thus Siebert and Wittke showed that $[Co(SO_3)(NH_3)_5]^+$ could be prepared and purified only in solutions containing an excess of $NH_{3(aq)}$, otherwise *trans*-$[Co(SO_3)(OH_2)(NH_3)_4]^+$ was isolated.[924] This *trans* labilizing effect is also discussed in Section 47.8.5. It is found in the reactions of $[Co(SO_3)(NH_3)_5]^+$,[925,926,930] *trans*-$[Co(SO_3)(H_2O)(en)_2]^+$,[927] *trans*-$[Co(SO_3)X(DMGH)_2]^{0,+}$,[928,929,931] and with *trans*-$[Co(SO_3)(CN)_4(OH_2)]^{3-}$.[66,932] The large body of evidence suggests that SO_3^{2-} promotes an S_N1(lim) displacement mechanism with complete dissociation of the *trans* group prior to interaction with the incoming ligand, especially with *trans*-$[Co(SO_3)(CN)_4(OH_2)]^{3-}$ (Scheme 86). The alternative dissociative interchange process with saturation of the rate being attributed to saturation within a preformed ion pair (Scheme 87) is possible for cationic systems with the rate variation being ascribed largely to variation in K_{ip}.[927] However the S_N1(lim) mechanism seems certain for $[Co(SO_3)(CN)_4(OH_2)]^{3-}$ where ion pairing with Y^{n-} should not cloud the issue and where k_1 is independent of the concentrations and identity of Y^{n-} over a wide range of entering groups (SO_3^{2-}, CN^-, NCS^-, NH_3, py; $k_1 \approx 2.5 \pm 0.5\,s^{-1}$; $\Delta H^{\ddagger}$ 92.4 kJ mol^{-1}, $\Delta S^{\ddagger}$ 73 J $mol^{-1}K^{-1}$).[932] Wilmarth's contributions to this area have now been suitably acknowledged.[933] Perhaps the $[Co(SO_3)(CN)_4]^{3-}$ intermediate is stabilized as the chelated octahedral ion (**258**). Such a species would allow the solvent cage to reach or approach the equilibrated state, but its subsequent preference for other ligand donors over H_2O, *e.g.* 140 (NH_3), 340 (py), remains a mystery. Studies such as these establish the dissociative influence of coordinated SO_3^{2-}, whereas the similar influence of coordinated CN^- is now open to question.[67] Farrell and Murray report the possibility of O entry in the reaction of $[Co(SO_3)(OH_2)(en)_2]^+$ with SO_3^{2-} at pH 7.1 with the $[Co(OSO_2)(SO_3)(en)_2]^-$ product rearranging subsequently to $[Co(SO_3)_2(en)_2]^-$.[934]

$$[Co(SO_3)(CN)_4(OH_2)]^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(SO_3)(CN)_4]^{3-} + H_2O$$

$$[Co(SO_3)(CN)_4]^{3-} + Y^- \xrightarrow{k_2} [Co(SO_3)(CN)_4Y]^{4-}$$

Scheme 86

Table 74 Rate Data for Addition of Co—OH_2 and Co—OH to Oxyanions and the Reverse Hydrolysis

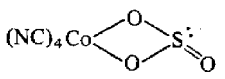
Reactant	*Anion*	k_f ($mol^{-1}\,dm^3\,s^{-1}$)	*Product*	*Catalyst*	k_{hyd} (s^{-1}; $mol^{-1}\,dm^3\,s^{-1}$)	k_{ex}[a] (s^{-1})	k_{ex}^b ($mol^{-1}\,dm^3\,s^{-1}$)	*Ref.*
$[Co(NH_3)_5OH_2]^{3+}$	$H_2AsO_4^-$	0.012	$[Co(NH_3)_5OAsO_3H_2]^{2+}$	H^+	0.67	7.8×10^{-4}	–	1
	$HAsO_4^{2-}$	0.11	$[Co(NH_3)_5OAsO_3H_2]^{2+}$	–	4.1×10^{-4}	.	–	1
		–	$[Co(NH_3)_5OAsO_3H]^+$	–	2.9×10^{-5}	1.9×10^{-4}	–	1
	ReO_4^{2-}	–	$[Co(NH_3)_5OReO_3]^{2+}$	H^+	1.22	–	–	2
		–	$[Co(NH_3)_5OReO_3]^{2+}$	–	3.1×10^{-4}	–	–	2
		–	$[Co(NH_3)_5OReO_3]^{2+}$	OH^-	2.9×10^4	–	–	2
		–	$[Co(NH_3)_5OReO_3]^{2+}$	H^+	2.3×10^6	–	–	3
	$HMoO_4^-$	3.2×10^5	$[Co(NH_3)_5OMoO_3]^+$	–	0.2	–	–	3
$[Co(NH_3)_5OH]^{2+}$	$HMoO_4^-$	6.6×10^4	$[Co(NH_3)_5OMoO_3]^+$	–	–	0.33	2.22 (OH^-)	
	MoO_4^{2-}	–		–	–	6.5×10^3	–	4
$[Co(en)_2(OH_2)_2]^{3+}$	HIO_3^-	1.44×10^4	$[Co(en)_2(OH_2)OIO_2]^{2+}$	H^+	1.21×10^4	–	–	5
$[Co(NH_3)_5OH_2]^{2+}$	$HSeO_3^-$	147	$[Co(NH_3)_5OSeO_2H]^{2+}$	–	0.28	–	–	10
$[Co(NH_3)_5OH]^{2+}$	$HSeO_3^-$	8		.	–	–	–	10
	$H_2(SeO_3)_2^{2-}$	20		–		–	.	10
	$H(SeO_3)_2^{3-}$	20		–	–	–	–	10
	SeO_3^{2-}	~2 (pH 10)		–	–	..	–	6
	SO_3^{2-}	0.2 (40 °C)	$[Co(NH_3)_5OSO_2]^+$	H^+	5.2×10^{-2} (loss of 3×10^{-3} *trans* NH_3)			6
		–				–	–	2
	ReO_4^{2-}	–	$[Co(NH_3)_5OReO_3]^{2+}$	H^+	1.22	–	–	2
		–		–	3.12×10^{-4}	–	–	2
		–		OH^-	2.89×10^4	$[H^+]$, $[H^+]^2$ paths	2.15×10^{-3} (OH^-)	2
		–		H^+	$\sim 1.7 \times 10^{-3}$ (5 °C)	–	–	9
$[Co(NH_3)_5OH_2]^{3+}$	$HCrO_4^-$	~1 (5 °C)	$[Co(NH_3)_5OCrO_3]^+$	–	0.57	–	–	7
$[Co(en)_2(OH)(H_2O)]^{2+}$	HWO_4^-	1.03×10^7	$[Co(en)_2(OH)OWO_3]$	–	–	–	–	7
$[Co(en)_2(OH)_2]^+$	HWO_4^-	3.22×10^7		–	–	0.44	273 (OH^-)	
	WO_4^{2-}			–	–	fast	–	5
cis-$[Co(tn)_2(H_2O)_2]^{3+}$	$HSeO_3^-$	290	*cis*-$[Co(tn)_2(OH_2)OSeO_2H]^{2+}$	.	0.20	–	–	5
trans-$[Co(tn)_2(H_2O)_2]^{3+}$	$HSeO_3^-$	1030	*trans*-$[Co(en)_2(OH_2)OSeO_2H]^{2+}$	pK_a 4.55	1.1	–	–	10
cis-$[Co(en)_2(OH)(H_2O)]^{2+}$	$HSeO_3^-$	4	*cis*-$[Co(en)(OH_2)OSeO_2H]^{2+}$	pK_a 4.35	0.18	–	–	10
	$H_2(SeO_3)_2^{2-}$	110		–	–	–	–	10
	$H(SeO_3)_2^{3-}$	110		.	–	–	–	8
$[Co(CN)_5OH_2]^{2-}$	$HSeO_3^-$	47		–	–	–	..	

[a] Unassisted H_2O exchange. [b] Catalyzed paths.

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3. R. S. Taylor, *Inorg. Chem.*, 1977, **16**, 116.
4. R. K. Wharton, R. S. Taylor and A. G. Sykes, *Inorg. Chem.*, 1975, **14**, 33.
5. A. D. Fowless and D. R. Stranks, *Inorg. Chem.*, 1977, **16**, 1276.
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$$[Co(SO_3)(en)_2(OH_2)]^+ + Y^- \overset{K_{ip}}{\rightleftharpoons} [Co(SO_3)(en)_2(OH_2)]^+ \cdot Y^- \xrightarrow{k} [Co(SO_3)(en)_2Y] + H_2O$$

Scheme 87



(258)

47.7.4.4 Chromate, molybdate and tungstate

A relatively rapid red–orange colour change accompanies the addition of Na_2CrO_4 to $[Co(NH_3)_5(OH_2)]^{3+}$ in acid solution and this can be attributed to equilibrium (151). Equilibrium studies indicate the existence of a very stable ion pair $[Co(NH_3)_5(OH_2)]^{3+} \cdot CrO_4^{2-}$ in addition to the inner-sphere complex (**256**) ($K_c = k_f/k_{hyd} = 3.07 \times 10^5$) and limited kinetic data indicate a rate first order in both Cr^{VI} and $[H^+]$ (Table 74).[935] Hydrolysis of $[Co(OCrO_3)(NH_3)_5]^+$ is reasonably rapid ($t_{1/2} < 7$ min, 5 °C). Early reports on the preparations of chelate complexes $[Co(O_2MO_2)(NH_3)_4]X$ and monodentate $[Co(OMO_3)(NH_3)_5]X$ need to be reexamined. It is likely that the fast rate of oxygen exchange at M (Cr,[936] Mo,[937,938] W[939]) makes the chelates (**247**) unstable with respect to the monodentate $[Co(OMO_3)(H_2O)(NH_3)_4]^+$ and these complexes need to be isolated and carefully characterized.

$$(NH_3)_5Co^{3+}—OH_2 + HCrO_4^- \underset{k_{hyd}}{\overset{k_f}{\rightleftharpoons}} (NH_3)_5Co^+—OCrO_3 + H_3O^+ \quad (151)$$

(256)

Anation of $[Co(OH)(NH_3)_5]^{2+}$ by MoO_4^{2-} in the pH range 7.1–8.0 is in the stopped-flow range indicating rapid oxygen displacement at Mo^{VI}.[940] Rate data have been interpreted in terms of $[Co(OH_2)(NH_3)_5]^{3+}$ and $[Co(OH)(NH_3)_5]^{2+}$ reacting with $HMoO_4^-$ (Table 74) even though the pK_a of the latter is 3.53. Both reactions are faster than water exchange (k_{ex}) although slower than substitution by anionic species at $HMoO_4^-$. Reaction (152) is reversible ($K = 475\,mol^{-1}\,dm^{-3}$) with the acid-catalyzed path being the reverse of $HMoO_4^{2-}$ addition. It is clear that exchange of Co^{III}-coordinated molybdate is reasonably fast.

$$(NH_3)_5Co^{3+}—OH_2 + MoO_4^{2-} \underset{k_{hyd}}{\overset{k_f}{\rightleftharpoons}} (NH_3)_5Co^+—OMoO_3 + H_2O \quad (152)$$

Subsititution by $[Co(OH)_{2,1}(OH_2)_{0,1}(en)_2]^{+,2+}$ into WO_4^{2-} in the pH range 8.0–9.0 is in the stopped-flow range indicating a very fast attack by Co—OH or Co—OH_2 at W^{VI}.[941] Rate data given in Table 74 are for substitution into HWO_4^- even though its $pK_a = 3.5$. The alternative of $[Co(H_2O)_2(en)_2]^{3+}$ and $[Co(OH)(H_2O)(en)_2]^{2+}$ reacting with WO_4^{2-} gives forward rates (6.60×10^2 and $2.8 \times 10^4\,mol^{-1}\,dm\,s^{-1}$), which suggest exchange within the ion pair in excess of 66 and $560\,s^{-1}$. These values are very much faster than the unassisted water exchange rate ($0.44\,s^{-1}$) and an associative interchange process (see **253**) is again likely.

47.7.4.5 Iodate, perrhenate, chlorite and perchlorate

O exchange into IO_3^-, ReO_4^- and ClO_2^- is fast and their cobalt(III) complexes are formed by the addition of Co—OH_2 to the group VII centre. The immediate red–purple colour change which accompanies the addition of $NaIO_3$ to $[Co(OH_2)_2(en)_2]^{3+}$ must be followed by relaxation methods.[942] Both the forward and reverse reactions (equation 153) are acid catalyzed ($[H^+] = 0.03$–$0.005\,mol\,dm^{-3}$) and have been interpreted in terms of addition of coordinated water to HIO_3 (Table 74). Using a value of $0.3\,mol^{-1}\,dm^3$ for the association constant, the formation rate within the associated reactant (**253**) is $5 \times 10^4\,s^{-1}$, which is almost 10 times faster than unassisted water exchange into HIO_3. Clearly IO_3^- exchange on Co^{III} is very fast and it has not been possible

to isolate solid iodate complexes.[943] Early reports in the literature of isolated cobalt(III) complexes containing IO_3^-, BrO_3^- and ClO_3^- are probably erroneous.

$$(en)_2(H_2O)Co^{3+}—OH_2 + HIO_3 \underset{k_{hyd}}{\overset{k_f}{\rightleftharpoons}} (en)_2(H_2O)Co^{2+}—OIO_2 + H_3O^+ \quad (153)$$

Addition of perrhenate to $CoOH_2^{n+}$ or $CoOH^{(n-1)+}$ complexes has not been studied in detail but heating $[Co(OH_2)(NH_3)_5](ReO_4)_3$ results in displacement of coordinated water (Table 70). Both $[H^+]$ and $[OH^-]$ paths for O—Re bond cleavage in $[Co(OReO_3)(NH_3)_5]^{2+}$ exist (Table 74) and these processes are strongly catalyzed by acetic acid and by acetate and biphthalate ions.[944]

The chlorito complex $[Co(OClO)(NH_3)_5](NO_3)_2$ has been prepared by ClO_2 oxidation of Co^{II} in the presence of ammonia (Table 70); it is stable for considerable periods when protected from light.[945] The reverse reaction is acid catalyzed. Attempts to prepare a chlorato complex by oxidation were unsuccessful. Reduction using Fe^{2+}, HSO_3^-, or VO^{2+} results in substantial retention of the Co—O bond (equation 154), but oxidation with $Co^{3+}_{(aq)}$ results in some 66% Co—O bond cleavage.[945]

$$[(NH_3)_5CoO—ClO]^{2+} + SO_3H^- + 2H^+ \longrightarrow [(NH_3)_5CoOH_2]^{3+} + HSO_4^- + Cl^- \quad (154)$$

Few cobalt complexes exist containing coordinated tetrahedral perchlorate, and those which do show weak coordination. Table 75 gives some structural data. Early reports on the isolation of $[Co(OClO_3)(NH_3)_5](ClO_4)_2$ are erroneous but Sargeson and coworkers have prepared it as pink crystals by nitrosation of $[CoN_3(NH_3)_5](ClO_4)_2$ in concentrated $HClO_4$.[946] Coordinated perchlorate is rapidly displaced by water in aqueous solution ($t_{1/2} \approx 7$ s) and cobalt in any oxidation state prefers almost any other donor atom over perchlorate oxygen.

47.7.4.6 Polyoxyanions of Nb^V, Mo^{VI}, W^{VI} and I^{VII}

Some interesting chemical and structural patterns are beginning to emerge in the coordination of cobalt with oxyanions of these elements. Together with V^V, Ta^V and Cr^{VI} the simple oxyanions readily condense to form structural units based on MO_6 octahedra by sharing an edge or a trigonal face.[952,953] CoO_6 or CoO_4 units fit into these polyhedra as integral parts and the high group valence often stabilizes Co^{III} octahedra. The structural unit is often large but is robust and many have been known for a long time. Some preparations are given in Table 76 and structures in Table 77.

Several Co^{III} complexes containing the $Nb_6O_{19}^{8-}$ unit have been prepared (Table 76). $Nb_6O_{19}^{8-}$ (**259**) consists of six NbO_6 octahedra condensed by edge sharing and one of the triangular faces coordinates as a tridentate to form *fac*-$[Co(Nb_6O_{19})L_3]^{3-}$ complexes. $K_7[Co(Nb_6O_{19})(CO_3)(NH_3)]$ has been prepared from $K[Co(CO_3)_2(NH_3)_2]$ and has been used to coordinate (*S*)-aspartate, glycinate, (*S*)-valinate and (*S*)-alaninate, with the last two being resolved into enantiomeric forms.[954] When

Table 75 Structures of Cobalt Complexes Containing ClO_4^-

Complex	*Structural data*[a]	*Comments*	*Ref.*
$[Co(OClO_3)(CNPh)_5](ClO_4)\cdot 0.5(CH_2Cl)_2$	*P*2,*C*; CoC 195, 184 (av); $CoO(ClO_3)$ 259	Sq. pyr.; green form, v. long Co—O bond into basal site	1
$[Co(OClO_3)(OAsMePh_2)_4](ClO_4)$	*P*4/*n*; $CoO(AsR_3)$ 202; OCoO 85–95°, CoOCl 130°; $CoO(ClO_3)$ 210	Dist. sq. pyr.; disordered oxygens in coord. ClO_4^-	2
trans-$[Co(OClO_3)_2\{S(Me)CH_2CH_2S(Me)\}_2]$	*P*2,*C*; CoS 229; CoO 234; SCoS 88.1°; SCoO 88°	Dist. oct.; *trans* ClO_4; *meso* (*RS*) dithioether	3
trans-$[Co(OClO_3)(NO)(en)_2](ClO_4)$	*P*2/*C*; CoN 197 (av); $CoO(ClO_3)$ 236; NCoN 93°, 85°	Dist. oct.; long Co—O bond	4
trans-$[Co(OClO_3)_2(diars)_2]$	*P*2/*C*; CoAs 229–230; CoO 280–330	Planar with v. long bonds to axial ClO_4^-; oxygens not located	5

[a] Bond lengths in pm.

1. F. A. Jurnak, D. G. Greig and K. L. Raymond, *Inorg. Chem.*, 1975, **14**, 2585.
2. P. Pauling, G. B. Robertson and G. A. Rodley, *Nature (London)*, 1965, **207**, 73.
3. F. A. Cotton and D. L. Weaver, *J. Am. Chem. Soc.*, 1965, **87**, 4189.
4. P. L. Johnson, J. H. Enemark, R. D. Feltham and K. B. Swedo, *Inorg. Chem.*, 1976, **15**, 2989.
5. F. W. B. Einstein and G. A. Rodley, *J. Inorg. Nucl. Chem.*, 1967, **29**, 347.

Table 76 Preparations: Cobalt(III) Complexes Containing Polyoxyantions of Nb^{V}, Mo^{VI}, W^{VI} and I^{VII}

Complex	*Preparation*	*Properties*	*Ref.*
$K_7[Co(Nb_6O_{19})(CO_3)(NH_3)]$	$K[Co(CO_3)_2(NH_3)_2] + K_7HNb_6O_{19}\cdot 13H_2O + KOH$; pH 10.6	Green; useful starting material	1
$Na_5[Co(Nb_6O_{19})(dien)]$	*mer*-$[Co(Cl)_3dien] + Na_7HNb_6O_{19}\cdot 15_2O + NaOH$; conc. heat, MeOH, cool	Purple; ε_{550} 63	1
$Na_5[Co(Nb_6O_{19})(OH_2)en]$	*trans*-$[Co(Cl)_2(en)_2]Cl + Na_7HNb_6O_{19}\cdot 15H_2O$; boiling H_2O, NaOH	Green-blue; ε_{600} 64; ε_{408} 51	2
$H_3[Co_4I_3O_{12}(OH)_{12}]\cdot 3H_2O$	$CoCl_2\cdot 6H_2O + NaIO_4 + NaOH$; NaOCl; Dowex 50 ($H^+$)	Green; very stable	7
$H_3[Co_4I_3O_{18}(en)_3]\cdot 5H_2O$	$H_3[Co_4I_3O_{24}H_{12}]\cdot 8H_2O$ + 98% en; 55 °C, 3 h	Red-brown; ε_{555} 400	3
$H_3[Co_4I_3O_{18}(NH_3)_6]\cdot 9.5H_2O$	$H_3[Co_4I_3O_{24}H_{12}]\cdot 8H_2O + NH_{3(l)}$; 30 h, r.t.	Red-brown; ε_{588} 350	3
$Na_4[Co_4I_3O_{18}(OH_2)_4\{(S)\text{-ala}\}]\cdot 8H_2O$	$H_3[Co_4I_3O_{24}H_{12}]\cdot 8H_2O$ + (*S*)-alanine; H_2O, 65 °C, 10 h	Green; ε_{580} 370 resolved on Sephadex	3
$(NH_4)_3[CoMo_6O_{18}(OH)_6]\cdot 12H_2O$	$Co^{2+}_{(aq)} + Mo_7O_{24}^{6-} + Br_2$	Green; ε_{605} 20	4
$(NH_4)_6[Co_2Mo_{10}O_{34}(OH)_4]\cdot 7H_2O$	$[CoMo_6O_{18}(OH)_6]^{3-} + C$; H_2O, heat	Green; ε_{605} 90 resolved using $(+)_{589}$-$[Co(en)_3]^{3+}$	5
$K_4H[CoW_{12}O_{40}]\cdot 20H_2O$	$[CoW_{12}O_{40}]^{6-}$; 2 M H_2SO_4, $K_2S_2O_8$, boil	Yellow	6

1. Y. Hosokawa, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3175.
2. C. M. Flynn and G. D. Stucky, *Inorg. Chem.*, 1969, **8**, 178.
3. T. Ama, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 2145.
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5. H. T. Evans and J. S. Showell, *J. Am. Chem. Soc.*, 1969, **91**, 6881; T. Ama, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 2654.
6. L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, 1956, **78**, 4503.
7. C. J. Nyman and R. A. Plane, *J. Am. Chem. Soc.*, 1961, **83**, 2617.

Table 77 Structures: Cobalt Complexes of Polyoxyanions

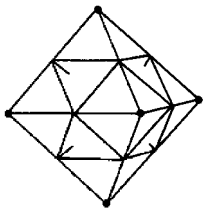
Complex	*Structural data*[a]	*Ref.*
$(NH_4)_6[Co_2Mo_{10}O_{34}(OH)_4]\cdot 7H_2O$	Dimeric CoO_6 joined by two μ-(O) bridges; CoO 189, 190–195; bidentate O_2MoO_4 units	1
$(NH_4)_{23}[Co_2(NH_4)(H_2O)_2As_4W_{40}O_{140}]\cdot nH_2O$	Four AsW_9O_{23}, four WO_6; two Co^{II} in external sites	2
$K_5[CoW_{12}O_{40}]\cdot 20H_2O$	Dist. CoO_4 tetrahedron surrounded by WO_6 octahedra; CoO 188	4
$Li(H_2O)_2H[Co_4I_3O_{12}(OH)_{12}]\cdot 3H_2O$	Co^{3+} at centre of planar hexagon with alternate Co^{3+} and I^{7+} at vertices; CoO_6 octahedra	3

[a] Bond lengths in pm.

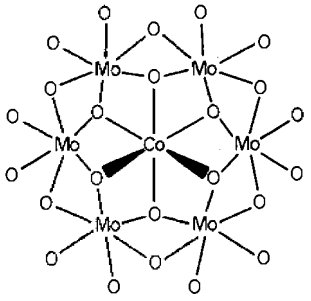
1. H. T. Evans and J. S. Showell, *J. Am. Chem. Soc.*, 1969, **91**, 6881.
2. F. Robert, M. Legrie, G. Herve, A. Teze and Y. Jeannin, *Inorg. Chem.*, 1980, **19**, 1746.
3. L. Lebioda, M. Ciecharowicz-Rutkowska, L. C. W. Baker and J. Grochowski, *Acta Crystallogr., Sect. B*, 1980, **36**, 2530.
4. L. C. W. Baker, in 'Advances in the Chemistry of the Coordination Compounds', ed. S. Kirschner, Macmillan, New York, 1961, p. 608.

solutions of $Co^{2+}_{(aq)}$ are mixed with the stable $Mo_7O_{24}^{6-}$ ion in the presence of an oxidizing agent such as Br_2 the central Mo^{VI} atom is replaced by Co^{III} and the remarkably stable, emerald-green $[Co\{Mo_6O_{18}(OH)_6\}]^{3-}$ ion results (Table 76). Its structure is presumably the same as that of the analogous Cr^{III} species[955] (**260**) with four-membered chelates surrounding a Co^{III} centre in a symmetric configuration. Treating (**260**) with activated charcoal or Raney nickel forms the racemic dimeric unit (**261**)[956] and this has been resolved into its enantiomeric forms using $(+)_{589}$-$[Co(en)_3]^{3+}$.[957] Heteropoly complexes based on IO_6^{5-} units have been surveyed[958] and the structure of $[Co_4I_3O_{24}H_{12}]^{3-}$ (**262**; Table 77) shows a central CoO_6 octahedron surrounded by alternating CoO_6 and IO_6 octahedra. The three terminal Co^{III} centres contain *cis*-aqua ligands, which can be readily replaced by NH_3, ethylenediamine or amino acids (Table 76). The $[Co_4I_3O_{18}(OH_2)_4\{(S)ala\}]^{4-}$ ion has been separated into its diastereoisomeric forms by chromatography on Sephadex.[959]

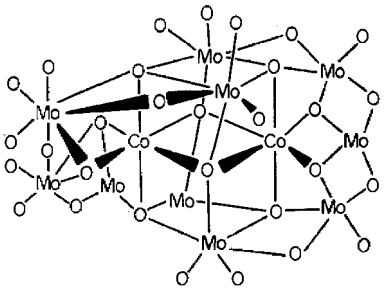
The $[CoW_{12}O_{40}]^{5-}$ ion has the classic 'Keggin' structure with a central tetrahedrally situated Co^{III} atom surrounded by four W_3O_{12} clusters making up an almost regular cubo-octahedron (**263**).[953] This unit is structurally very stable, does not undergo rapid O exchange at pH 1–2,[960] and can be used as an outer-sphere electron transfer oxidant in both inorganic[961] and organic[965] reactions.



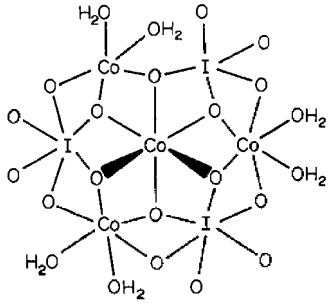
(259) $Nb_6O_{19}^{8-}$



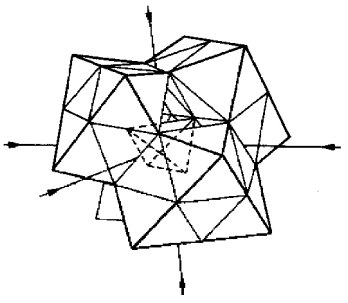
(260) $Co(Mo_6O_{24})^{9-}$



(261) $[Co_2(Mo_{10}O_{38})]^{10-}$



(262) $[Co_4I_3O_{24}H_{12}]^{3-}$



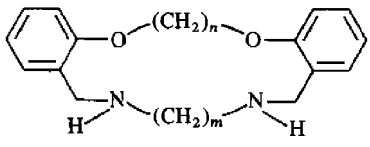
(263) $[CoW_{12}O_{40}]^{5-}$

Recent oxidations to be studied include those of *p*-methoxytoluene,[962] glutathione[963] and cysteine and related mercapto acids.[964]

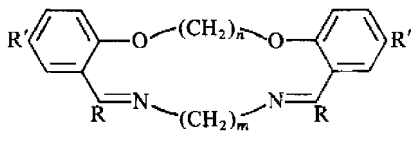
47.7.5 Ethers, Cobalt(II)

Well-defined crystalline complexes possessing cobalt(II)–ether oxygen bonds are comparatively rare. There are no authenticated examples of monodentate ether complexes. Light blue or lavender adducts of cobalt(II) halides with 1,4-dioxane are formulated as containing six-coordinate cobalt(II) and bridging dioxane ligands[966] but have not been fully characterized. Only one example of bidentate ether oxygen coordination has been reported. Addition of $SOCl_2$ to a solution of $Co(CF_3COO)_2$ in 2-dimethoxyethane (dme) gives the red trimeric complex $[Co_3(Cl)(SO_4)(CF_3COO)_3(dme)_3]$ in which dme acts as a chelating group and the remaining ligands bridge octahedral metal centres.[967] Octahedral coordination is also found in the dimeric complex $[Co(Cl)(diglyme)]_2(SbCl_6)_2$ (diglyme = triethyleneglycol dimethyl ether), where the chlorides act as bridging ligands and the coordination sphere of each metal is completed by binding of one molecule of the tetradentate polyether.[968]

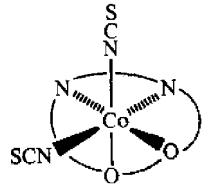
Lindoy and coworkers[969,970] have reported cobalt(II) complexes of various 14- to 17-membered macrocycles with O_2N_2 donor sets. For ligands of type (**264**) high spin $[CoX_2(macrocycle)]$ complexes (X = Cl^-, Br^-, NCS^-) are octahedral for 15- and 16-membered ring systems, but tetrahedral and without Co—O (ether) bonds for the 17-membered ligand. The complexes $[CoX_2(macrocycle)]$ of the ligand (**265**; R = R′ = H; $n = 2$; $m = 3$) have been isolated as orange and purple isomers for X = NCS^-. IR studies indicate thiocyanate to be N bound in both species and a crystal structure on the purple isomer confirms a six-coordinate geometry in which the quadridentate is folded about the Co atom giving a *β-cis* configuration (**266**).



(264)



(265)



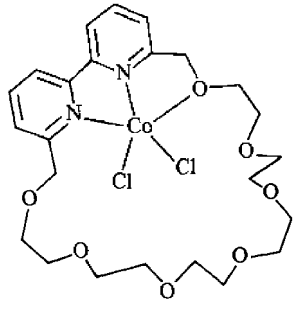
(266)

Table 78 Structural Data for Cobalt(II)–Ether Complexes

Complex	*Ligand type*	*Comments*	*Ref.*
$[Co_2(\mu\text{-}Cl)_2L_2](SbCl_6)_2$	O_4 tetradentate	Oct.; CoO 211.5 to 213.6 pm	1
$[Co_3(\mu_3\text{-}Cl)(\mu_3\text{-}SO_4)(\mu\text{-}CF_3COO)_3L_3]$	O_2 bidentate	Oct.; CoO 214 pm	2
$[Co(Cl)_2L]$	N_2O_6 macrocyclic	Trig. bipyr.; N_2OCl_2 donor set; CoO 231.9 pm	3
$[CoL][CoCl_4]$	N_2O_5 macrobicyclic	Pent. bipyr.; N_2O_5 donor set; CoO 209.6 to 221.9 pm	4
$[Co(NO_3)_2L]$	O_4 macrocyclic	Seven-coordinate; CoO (ether) 216 to 221 pm; NO_3^- mono and bidentate	5
$[Co(H_2O)_2L](NO_3)_2$	O_5 macrocyclic	Pent. bipyr.; CoO (ether) 213.1 to 234.7 pm; H_2O ligands axial	5
$[CoClL](PF_6)$	NOP_2 tripodal	Trig. bipyr.	6
$[Co(NCS)_2L]$	N_2O_2 macrocyclic	Dist. oct.; CoO 217–233 pm	7

1. A. J. Kinneging, W. J. Vermin and S. Gorter, *Acta. Crystallogr., Sect. B*, 1982, **38**, 1824.
2. J. Estienne and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 1972, 862.
3. G. R. Newkome, D. P. Kohli and F. Fronczek, *J. Chem. Soc., Chem. Commun.*, 1980, 9.
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6. P. Dapporto, G. Fallani and L. Sacconi, *J. Coord. Chem.*, 1971, **1**, 269.
7. L. G. Armstrong, L. F. Lindoy, M. McPartlin, G. M. Mockler and P. A. Tasker, *Inorg. Chem.*, 1977, **16**, 1665.

There are now several structural studies on cobalt(II) crown ether and cryptand complexes (Table 78), which show the coordination mode to be markedly sensitive to the macrocycle cavity diameter. Both 12-crown-4 and 15-crown-5 (cavity diameters 120–150 pm and 170–220 pm respectively) can include Co^{2+} ions to form structures in which every ether oxygen atom is bound to the metal.[971] In contrast Co—O (ether) bonding is destabilized in the larger 18-crown-6 and dicyclohexyl-18-crown-6 polyethers. In the blue complexes obtained from the reaction of these compounds with $CoCl_2$ the role of the cyclic polyether is to solvate discrete $[Co(H_2O)_6]^{2+}$ cations and $[CoCl_4]^{2-}$ anions and there are no direct Co—O (ether) bonds.[972,973] A similar effect is seen in the Co^{II} complex of a 27-membered-ring macrocycle where the pentacoordinate structure (**267**) features only one long Co—O (ether) bond.[974]



(267)

47.8 SULFUR LIGANDS

47.8.1 Sulfides and Disulfides

Monomeric cobalt complexes containing SH^- or S^{2-} as ligands are comparatively rare since there is a tendency toward formation of binary sulfides. Di Vaira, Midollini and Sacconi[975] showed that tri(tertiary phosphines), when used as coligands, are capable of stabilizing Co—S bonds and were able to prepare the five-coordinate complexes $[Co(SH)\{P(dppe)_3\}](BPh_4)$ and $[Co(SH)\{N(dppe)_3\}](BPh_4)$. These species are low spin with trigonal-bipyramidal geometries, and with the sulfur atom in an axial position. Treatment of $[Co(SH)\{N(dppe)_3\}](BPh_4)$ with NaOEt produces the diamagnetic complex $[\{N(dppe)_3\}Co(\mu\text{-}S)Co\{N(dppe)_3\}]$ which features a linear Co—S—Co bridge and tetrahedral sp_3 coordination about each Co atom. Diamagnetism in this complex appears to arise through superexchange coupling of two d^8 metal centres.[976]

Binuclear ions containing only disulfide as a bridging ligand are also rare but oxidation of $[Co(CN)_5]^{3-}$ by elemental sulfur leads to $[(NC)_5Co(S_2)Co(CN)_5]^{6-}$, isolated as its potassium salt, and the same species is formed on treatment of $[Co(CN)_5(OH)]^{3-}$ or $[(NC)_5Co(O_2)Co(CN)_5]^{6-}$ with H_2S. The selenium analogue $[(NC)_5Co(Se_2)Co(CN)_5]^{6-}$ has also been reported.[977] A recent study[978] suggests that the bridging disulfide ligand in $[(NC)_5Co(S_2)Co(CN)_5]^{6-}$ is slowly oxidized on exposure to air to thiosulfite (SSO_2^{2-}) but the preparation appears to suffer from problems of poor reproducibility. A crystal structure of $K_6[(CN)_5Co(SSO_2)Co(CN)_5]$ characterizes the product as containing a μ-(thiosulfito-*S*,*S*′) unit indicating that oxidation of the sulfide bridge does not involve Co—S rupture.

Both sulfide and disulfide are more commonly encountered as bridging ligands in cobalt clusters. There are few systematic syntheses. For example, $[Co_2(CO)_8]$ reacts at room temperature with CS_2 either neat or in the presence of hydrocarbon solvents to form $[Co_3(S)(CO)_9]$, $[Co_6(C)(S)_2(CO)_{12}]$ and at least three other sulfur-containing derivatives in addition to sulfur-free species such as $[Co_3(C)(CO)_9]$.[979] Similarly, $[Co_2(CO)_8]$ with elemental sulfur in hydrocarbon solvent gives $[Co_3(S)(CO)_9]$, $[Co_4(S)_2(CO)_{10}]$, $[Co_6(S)_8(CO)_6]$ and $[Co_6(S)_4(CO)_{14}]$,[980] with the product distribution dependent on the reaction conditions. Details of several cluster preparations are given in Table 79 and structural data in Table 80.

Single crystal EPR studies of paramagnetic $[Co_3(X)(CO)_9]$ species (**268**; X = S, Se) diluted in the diamagnetic $[FeCO_2(X)(CO)_9]$ analogues[981] demonstrate that the unpaired electron in (**268**) resides in an antibonding orbital. The antibonding nature of the HOMO is also demonstrated by the lengthening of the M—M bonds in (**268**) relative to those in $[FeCo_2(X)(CO)_9]$ species, which contain one electron less.[982] The effect of electron occupancy of antibonding orbitals on Co—Co bond

Table 79 Preprations and Properties of Cobalt–Sulfide Clusters

Compound	*Preparation*	*Comments*	*Ref.*
$[Co_3S(CO)_9]$	$[Co_2(CO)_8]$ + PhSH + CO, 0 °C	Black; air sensitive	1
$[FeCo_2S(CO)_9]$	$[Fe_2S(CO)_6]$ + $[Co(CO)_8]$, hexane	Dark violet; air stable; m.p. 107–112 °C	2
$[(\eta^5\text{-Cp})_3Co_3S_2]$	$(Bu^tN)_2S$ + $[(\eta^5\text{-Cp})Co(CO)_2]$	Black; μ_{eff} = 2.83 BM	3
$[(\eta^5\text{-Cp})_3Co_3S(CO)]$	$(Bu^tN)_2S$ + $[(\eta^5\text{-Cp})Co(CO)_2]$	Black; diamagnetic	3
$[(\eta^5\text{-Cp})_3Co_3S_2]^+$	$[(\eta^5\text{-Cp})_3Co_3S_2]$ + I_2	Black; μ_{eff} = 1.95	4
$[Co_4S_2(CO)_{10}]$	$[Co_2(CO)_8]$ + S, heptane, 30 °C	Red-brown	5
$[(\eta^5\text{-Cp})_4Co_4S_6]$	$[(\eta^5\text{-Cp})Co(CO)_2]$ + S, hexane	Black; air stable; diamagnetic	6
$[(\eta^5\text{-Cp})_4Co_4S_4]$	$[(\eta^5\text{-Cp})_4Co_4S_6]$ + PPh_3, toluene, reflux	Red-black	7
$[(\eta^5\text{-Cp})_4Co_4S_4]^+$	$[(\eta^5\text{-Cp})_4Co_4S_4]$ + $AgPF_6$, CH_2Cl_2/MeOH	μ_{eff} = 1.73 BM	7
$[Co_6S_4(CO)_{14}]$	$[Co_2(CO)_8]$ + S, hexane	Black; air sensitive	8
$[Co_6C(S)_2(CO)_{12}]$	$[Co_2(CO)_8]$ + CS_2, hexane, r.t.	Dark green; air stable	9
$[Co_6S(SEt)_4(CO)_{11}]$	$[Co_2(CO)_8]$ + EtSH, hexane	–	10
$[Co_6S_8(PEt_3)_6]^+$	$CoCl_2$ + PEt_3 + H_2S, acetone/EtOH	Dark brown; air stable; μ_{eff} = 2.15 BM	11
$[Co_6S_8(PEt_3)_6]$	$[Co_6O_8(PEt_3)_6]$ + sodium naphthalenide	Deep brown; diamagnetic	14
$[Co_3S(S_2\text{-}o\text{-xyl})_3]$	CO^{2+} + $Na_2(S_2\text{-}o\text{-xyl})$ + Li_2S	Black; air sensitive; μ^{Co} = 1.93–2.09 BM	13
$[(\eta^5\text{-Cp})_3Co_3S(CNR)]$	$[(\eta^5\text{-Cp})Co(CO)(PPh_3)]$ + RNCS	Black; air stable; R = Me, Ph, C_6H_{11}	15
$[Co_8S_6(SPh)_8]^{4-}$	$[Co_4(SPh)_{10}]^{2-}$ + HS^-, acetone	Black; air sensitive; μ^{Co} = 1.56 BM	12
$[Co_8S_6(SPh)_8]^{5-}$	$[Co_8S_6(SPh)_8]^{4-}$ + sodium naphthalenide	Black; air sensitive; μ^{Co} = 1.35 BM	12
$[Co_6S_8(CO)_6]\cdot 3S_8$	$[Co_2(CO)_8]$ + S + CO, petroleum ether, 40 °C	Air stable	16

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Table 80 Structures: Cobalt–Sulfide Clusters

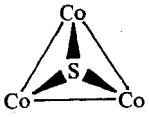
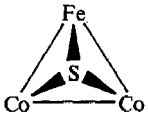
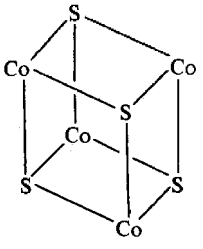
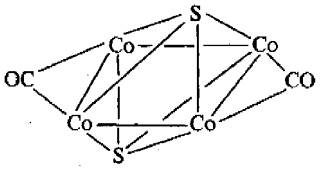
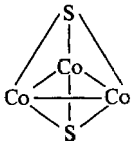
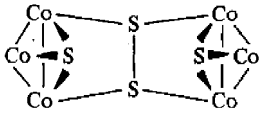
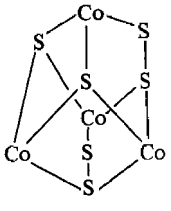
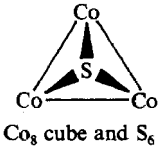
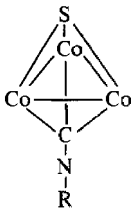
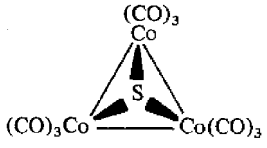
Complex	*Core structure*	*Comments*	*Ref.*
$[Co_3S(CO)_9]$		CoCo = 265 pm; CoS = 213 pm	1
$[FeCo_2S(CO)_9]$		MM = 255 pm; MS = 216 pm	2
$[(\eta^5\text{-Cp})_4Co_4S_4]^{n+}$		Cubane-like, CoCo = 324–334 pm; CoS = 230 pm (n = 0); CoCo = 317, 331 pm; CoS = 221 pm (n = 1)	3
$[Co_4S_2(CO)_{10}]$		Rectangular bipyramid; CoCo = 248 and 260 pm; apical S atom 137 pm above the Co_4 plane	4
$[(\eta^5\text{-Cp})_3Co_3S_2]^{n+}$		Trigonal bipyramid; CoCo = 269 pm (n = 0); 259 pm (n = 1)	5
$[Co_6S_4(CO)_{14}]$		Two Co_3 (μ-S) units linked by disulfide bridge; CoCo = 246–254 pm; SS = 204 pm	6
$[(\eta^5\text{-Cp})_4Co_4S_6]$		SS = 203, 204 pm; CoS = 219–223 pm	7
$[Co_6S(SEt)_4(CO)_{11}]$	$Co_3(\mu\text{-SEt})(\mu\text{-CO})_2$ unit linked by three (μ-SEt) bridges to the Co atoms of a $Co_3(\mu\text{-S})$ fragment	–	8
$[Co_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$		Distorted tetrahedral CoS_4 units; CoCo = 281 pm; CoS = 232 pm(b), 224 pm(t)	9
$[Co_8S_6(SPh)_8]^{4-/5-}$	Concentric Co_8 cube and S_6 octahedron	Distorted tetrahedral CoS_4 units; CoCo = 266 pm (4−), 267 pm (5−)	10
$[Co_6S_8(CO)_6]$	Concentric S_8 cube and Co_6 octahedron	CoCo = 288 pm; CoS = 228 pm	11
$[Co_6S_8(PEt_3)]^{n+}$	Concentric S_8 cube and Co_6 octahedron	CoCo = 279 pm; CoS = 223 pm (n = 1); CoCo = 281 pm; CoS = 223 pm (n = 0)	12

Table 80 (*continued*)

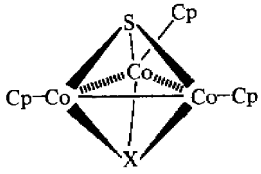
Complex	*Core structure*	*Comments*	*Ref.*
$[(\eta^5\text{-Cp})_3Co_3S(CNR)]$		R = C_6H_{11}; CoCo = 249–251 pm; CoS = 211 pm; CoC = 188–206 pm	13

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11. G. Gervasio, R. Rossetti and P. L. Stanghelli, *Inorg. Chim. Acta*, 1984, **83**, L9.
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13. J. Fortune, A. R. Manning and F. S. Stevens, *J. Chem. Soc., Chem. Commun.*, 1983, 1071.

lengths is also seen in the family of clusters $[Co_3(S)(X)(Cp)]^{n+}$ (**269**; X = CO, *n* = 0; X = S, *n* = 1; X = S, *n* = 0).[983] Approximate MO calculations using Fenske–Hall procedures have been carried out on these systems.[984]

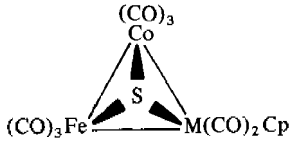


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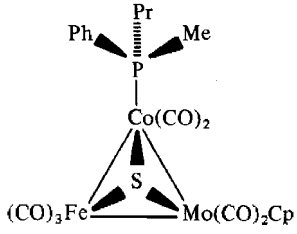


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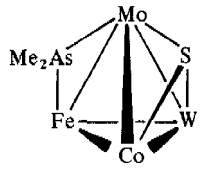
Vahrenkamp[985] first synthesized the chiral tetrahedrane type clusters (**270**), which have been resolved for M = Mo *via* the diastereoisomeric phosphane (**271**),[986] and a directed synthesis[987] has achieved the construction of the μ_3-S-bridged tetranuclear CoFeMoW cluster (**272**).



(270) M = Mo, W, Cr



(271)



(272)

A chemistry of cobalt–sulfide–thiolate molecular clusters comparable with that of iron systems has also begun to emerge. Treatment of $[Co_4(\mu\text{-SPh})_6(SPh)_4]^{2-}$ with HS^- in acetone affords the octanuclear cluster $[Co_8(\mu_4\text{-S})_6(SPh)_8]^{4-}$ isolated as its $Pr^n_4N^+$ salt.[988] In MeCN solution the complex is red-purple with intense sulfur-core charge transfer bands which obscure the Co^{II} *d–d* transitions. This behaviour contrasts with that of both mono- and poly-nuclear cobalt^{II}-thiolate complexes, which all display LMCT bands below 440 nm and have well-developed ν_2 and ν_3 features. The $[Co_8(\mu_4\text{-}S_6)]^{4+}$ core sustains reversible one-electron oxidation and reduction ($E_{1/2} = -0.54$, -1.18 V, MeCN) and chemical reduction with sodium acenaphthylenide in THF gives $[Co_8(\mu_4$-

$S_6)(SPh)_6]^{5-}$, which has also been structurally characterized (Table 80). A similar Co_8S_6 core unit is found in the synthetic mineral pentlandite, Co_9S_8.[989]

In systems containing cobalt(II) salts, sulfide and thiolate substitution of the bidentate S_2-*o*-xyl^{2-} ligand (S_2-*o*-xyl^{2-} = *o*-xylene-α,α'-dithiolate) for monofunctional thiolate directs cluster assembly away from the Co_8S_6 core and toward the $Co_3(\mu_3\text{-S})$ unit. A high yield preparation (50%) of the complex $(Et_4N)_2[Co_3(\mu_3\text{-S})(S_2\text{-}o\text{-xyl})_3]$ has been reported[990] and structural studies[990,991] show the pyramidal $Co_3(\mu_3\text{-S})$ unit to be unsupported by additional metal–sulfur bonding. The solution properties of the complex (^{1}H NMR, UV–visible spectra and magnetic moments) are consistent with magnetically coupled tetrahedral CoS_4 chromophores.

Structural studies on $[Co_6(\mu_3\text{-S})_8(CO)_6]\cdot 3S_8$[992] and $[Co_6(\mu_3\text{-S})_8(PEt_3)_6](BPh_4)$[993] show the cluster components to consist of Co_6 octahedra encapsulated in S_8 cubes. This geometry is the inverse of that found for $[Co_8(\mu_4\text{-S})_6]^{4+/3+}$ cores, where Co_8 cubes are circumscribed by S_6 octahedra.

47.8.2 Thiolates, Sulfenates and Sulfinates

A useful review of the stereodynamic possibilities for inversion at chiral and prochiral sulfur (and Se, Te) in metal complexes is available.[994]

47.8.2.1 Low oxidation states of cobalt

Structural data for Co—SR complexes are given in Table 81; selected data for Co—S—Co systems are included in Table 80.

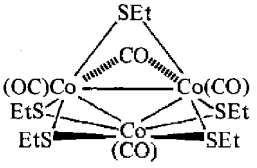
Klumpp, Marko and Bor[980] described the synthesis of presumed $[Co_4(SEt)_7(CO)_5]$ and $[Co_4(SEt)_3(CO)_7]$ from the reaction of $[Co_2(CO)_8]$ with EtSH in hexane. However subsequent X-ray structures by Wei and Dahl[995,996] have shown the products to be $[Co_3(SEt)_5(CO)_4]$ (**273**) and

Table 81 Structures: Cobalt(II)–Thiolate Complexes

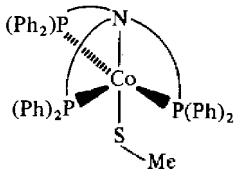
Complex	*Comments*	*Ref.*
$(Pr^n_4N)[Co(SC_{10}H_{13})_3(NCMe)]$	Monomeric, tetrahedral CoS_3N; CoS = 228 pm, CoN = 204 pm	1
$[Co(Cl)_2(SC_5H_4N)_2]$	Monomeric, distorted tetrahedral CoS_2Cl_2; CoS = 232 pm, CoCl = 227 pm	2
$[Co(SC_4H_6N_2)_4](ClO_4)$	Monomeric, tetrahedral CoS_4; CoS = 230 pm	3
$(Me_4N)_2[Co_2(S_2\text{-}o\text{-xyl})_3]$	Dimeric, $Co_2(\mu\text{-S})_2$ core; CoCo = 279 pm, $CoS_{b,t}$ = 230 pm	4
$(Ph_4N)_2[Co(SPh)_4]$	Monomeric, distorted tetrahedral CoS_4; CoS = 232–234 pm	5
syn- and *anti*-$[Co_2(SEt)_6]^{2-}$	Dimeric, $Co_2(\mu\text{-S})_2$ core; CoCo = 305 pm (*anti*), 302 pm (*syn*); CoS_b = 235–238 pm, CoS_t = 226–229 pm	6
$(Me_4N)_2[Co_4(SPh)_{10}]$	$Co_4(\mu\text{-S})_6$ core; CoCo = 387 pm, CoS_b = 232 pm, CoS_t = 226 pm	7
$[Co_3(SEt)_5(CO)_4]$	$Co_3(\mu\text{-SEt})_5(\mu\text{-CO})$ core; CoCo = 255 pm, CoS = 220–223 pm	8
$[Co_4(SEt)_8(CO)_4]$	$Co_4(\mu\text{-SEt})_8$ core; each pair of Co atoms joined by two briding SEt groups; CoS = 224–229 pm; minimum CoCo = 250 pm	9
$[Co_5(SEt)_5(CO)_{10}]$	A $Co_3(\mu\text{-SEt})_2(\mu\text{-CO})_2(CO)_3$ fragment connected by two (μ_3-SEt) bridges to a $Co_2(\mu\text{-SEt})(\mu\text{-CO})(CO)_4$ residue	10

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9. C. H. Wei, L. Marko, G. Bor and L. F. Dahl, *J. Am. Chem. Soc.*, 1973, **95**, 4840.
10. C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, 1968, **90**, 3969.

$[Co_6S(SEt)_4(CO)_{11}]$ respectively (Table 80). In the absence of solvent $[Co_2(CO)_8]$ and EtSH form $[Co_5(SEt)_5(CO)_{10}]$[997] for which a crystal structure is also available.[998] In these cobalt–carbonyl–thiolate systems the S atoms doubly or triply bridge metal centres and there appears to be no examples where RS^- functions as a monodentate ligand.



(273)



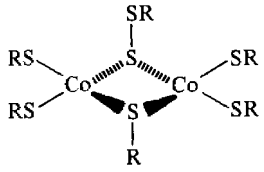
(274)

Early attempts to prepare Co^{II}—SR complexes by the reaction of RS^- (R = Et, Pr^i, Bu^t, Ph) with cobalt(II) salts in ethanolic solution produced only poorly characterized coordination polymers.[999] Subsequently, Sacconi and coworkers[975] isolated stable monomeric methylthio complexes $[Co(SMe)(L)](BPh)_4$ (L = $N(dppe)_3$, $P(dppe)_3$) by reacting the tetradentate ligand with Co^{II} in the presence of MeSH. A crystal structure of low-spin $[Co(SMe)\{N(dppe)_3\}](BPh_4)$ shows the expected trigonal-bipyramidal geometry (**274**). Dance[1000] showed that the equilibria of Scheme 88 are established in MeCN, and that tetrahedral $[Co(SPh)_4]^{2-}$ and the molecular cluster $[Co_4(\mu\text{-}SPh)_6(SPh)_4]^{2-}$ could be crystallized by treatment with R_4N^+ salts. Alternatively, $(Ph_4P)_2[Co(SPh)_4]$ can be obtained by reacting $[Co(S_2COEt)_3]$ with KSPh and Ph_4PCl.[1001]

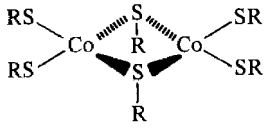
$$Co^{2+} + 4PhS^- \rightleftharpoons Co(SPh)_4^{2-} \rightleftharpoons [(\mu\text{-}PhS)_2\{Co(SPh)_2\}_2]^{2-} \rightleftharpoons [Co_4(\mu\text{-}SPh)_6(SPh)_4]^{2-}$$

Scheme 88

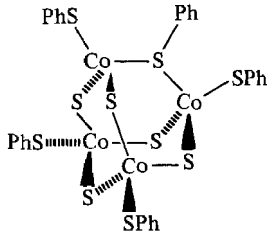
The $[(\mu\text{-}RS)_2\{Co(SR)_2\}_2]^{2-}$ anion, anticipated but not isolated in the thiophenolate systems, has now been obtained in both *anti* (**275**) and *syn* (**276**) forms for R = Et.[1002] Salts of $[Co(SEt)_4]^{2-}$, $[Co_4(\mu\text{-}SEt)_6(SEt)_4]^{2-}$ and $[Co_4(\mu\text{-}SPh)_6(Cl)_2(SPh)]^{2-}$ have also been isolated.[1000,1002] The adamantane-like core in $[Co_4(\mu\text{-}SPh)_6(SPh)_4]^{2-}$ (**277**) is maintained by bridging thiolate ligands rather than by direct Co—Co bonding, and the bridges are thermodynamically stable; added halides (Cl^-, Br^-) displace terminal rather than bridging PhS^- and the core is not disrupted in donor solvents (H_2O, py, DMSO). Bridging thiolate gives rise to a characteristic MCD spectrum for the ν_3 transition and this property has been utilized in the assignment of ligational modes (*b* or *t*) to RS^- in Co^{II} complexes of cysteine peptides and for Co^{II}-substituted metallothioneins.[1003]



(275)

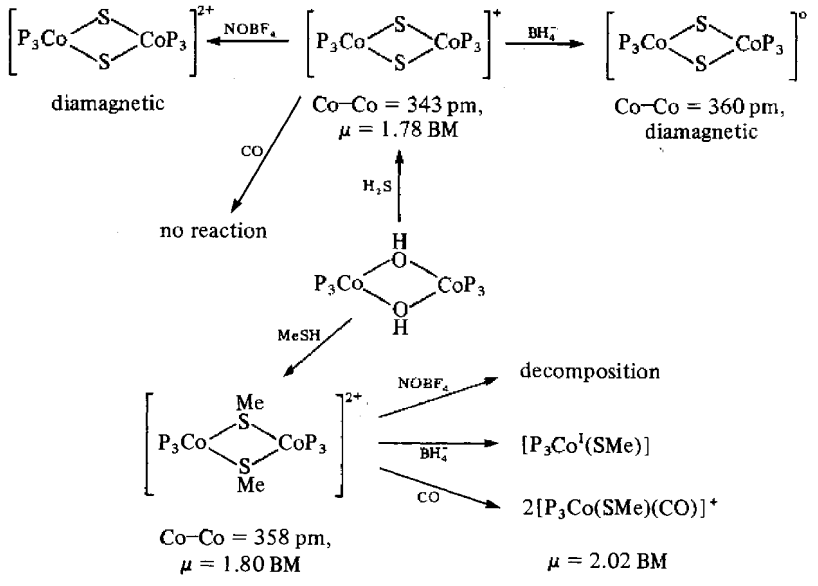


(276)



(277)

The reaction of $[\{MeC(dppm)_3\}_2Co_2(\mu\text{-}OH)_2](BPh_4)_2$ with MeSH in acetone in the presence of air produces the thiolate-bridged species $[\{MeC(dppm)_3\}Co_2(\mu\text{-}SMe)_2](BPh_4)$. Replacement of MeSH with H_2S in the reaction results in $[\{MeC(dppm)_3\}_2Co_2(\mu\text{-}S)_2](BPh_4)$. The redox and substitution chemistry of these systems has been examined in some detail and considerable crystallographic data are available.[1004] Some of these aspects are summarized in Scheme 89, where P_3 = $MeC(dppm)_3$. A feature of the dinuclear species is the planar nature of the Co_2S_2 unit and the insensitivity of the Co—Co separation on the formal oxidation state. In contrast to the stability of the μ-sulfido dimer the $[Co_2(\mu\text{-}SMe)_2]^{2+}$ structure does not survive reducing or oxidizing conditions, and ligand substitution by CO leads to monomeric products.



Scheme 89

No sulfenate complexes of low-valent cobalt appear to be known but some sulfinate systems have been described. Treatment of $Na[Co(CO)_3(PPh_3)]$ with CF_3SO_2Cl gives stable monomeric $[Co(SO_2CF_3)(CO)_3(PPh_3)]$ in which $CF_3SO_2^-$ acts as a monodentate S donor.[1005] Blue tetrahedral $(PPh_4)_2[Co(O_2SR)_4]$, formed on treating $(PPh_4)[CoCl_4]$ with RSO_2Ag salts (R = Me, Ph, *p*-MePh), is hydrolyzed in water to octahedral (usually rose-red) $[Co(O_2SR)_4(H_2O)_2]$.[1006] The stereochemistry of these six-coordinate species is uncertain but IR studies indicate bidentate *O,O′* sulfinate, and their limited solubility in water and organic solvents is consistent with polymeric structures.[1007] An alternative route to their preparation involves the addition of NaO_2SR salts to solutions of cobalt(II) halides.[1007,1008]

Prolonged acetone extraction of $[Co(bipy)_3](O_2SR)_2$ (R = *p*-MePh) results in the formation of $[Co(O_2SR)_2(bipy)_2]$ linkage isomers involving O- and S-bonded monodentate sulfinate.[1009] The yellow S-bonded isomer is difficult to isolate (8%) owing to its tendency to decompose in the solid, but like the orange O-bonded form it displays spectral and magnetic properties consistent with an octahedral high-spin configuration.

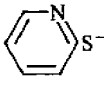
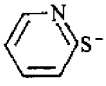
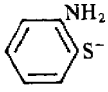
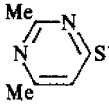
47.8.2.2 Cobalt(III)

A general account of the work of Sargeson's group up to 1979 is available[1010] as is an account of the oxidation of coordinated thiolate by Deutsch's group.[1011] X-Ray photoelectron spectroscopy provides a useful tool for determining the oxidation of coordinated sulfur by comparing $S2p_{3/2}$ binding energies with authentic systems.[1012]

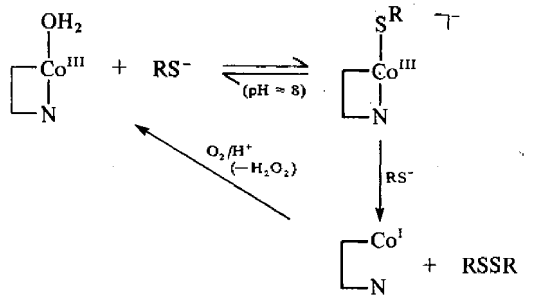
(*i*) *Monodentate systems*

Authentic monodentate thiolate complexes of Co^{III} amines are unknown. Treatment of Co^{II} salts or Co^{III} amines with alkene- or arene-thiols, especially in the presence of air, should be avoided. Disproportionation and reduction of the Co^{III} complex and polymerization and oxidation of the thiol occurs. An intractable mess usually results. Thiolate complexes of cobaloximes and cobalamines are however well known. Treatment of $[Co(DMGH)_2py(Cl)]$ with a stoichiometric amount of NaOH and RSH (R = Me, Et) results in dark-green $[Co(DMGH)_2py(RS)]$ and similar treatment of the Co^{II} dimer $[Co(DMGH)_2py]_2$ with PhSH results in black $[Co(DMGH)_2py(PhS)]$ (Table 82). Solutions of $[Co(DMGH)_2py(RS)]$ are sensitive to air and in the presence of alkali decompose to RSSR and a mixture of cobaloxime(I) and [Co(DMGH)(OH)py]. In the presence of air cobaloximes and cobalamines catalyze thiol oxidation (Scheme 90),[1013] and visible light has been shown to sproduce $H_{2(g)}$ catalytically when $[Co(DMGH)_2py(PhS)]$ is irradiated in the presence of excess PhSH (Scheme 91).[1014]

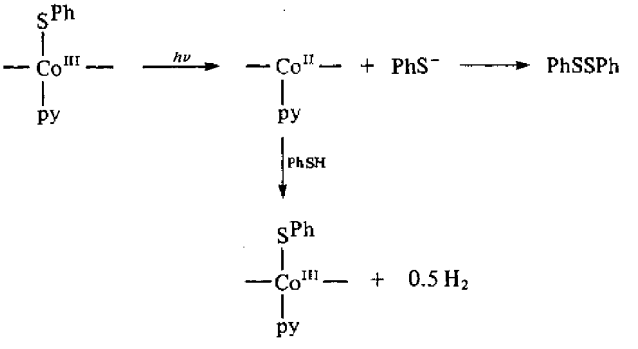
Table 82 Preparations: Monodentate and Bidentate Thiolate Chelates of Cobalt(III) (Not Containing Mixed Ligand Systems)

Complex	*Ligand*	*Preparation*	*Ref.*
Monodentate			
$[Co(DMGH)_2py(PhS)]$	PhS^-	$[Co(DMG)_2py]_2$; MeOH, r.t.	13
$[Co(DMGH)_2py(RS)]$	RS^- (R = Me, Et)	$CoCl_2 \cdot 6H_2O + DMGH_2 + py +$ NaOH; 0.5 h, r.t.	13
Bidentate			
$H_4[Co(tga)_2(OH)]_2$ (brown, uncertain)	$^-O_2CCH_2S^-$	$CoSO_4$, pH 7–8, O_2 (0.25 mol equiv.)	1
$[Co(tga)_2(H_2O)_2]$ (brown soln.)	$^-O_2CCH_2S^-$	$CoSO_4$, pH 8, air, r.t.	3
$Na_3[Co(tga)_3] \cdot 6H_2O$ (green)	$^-O_2CCH_2S^-$	$Na_3[Co(CO_3)_3]$, warm, 30 min	5
$[Co(Ettga)_3]$	$EtOCOCH_2S^-$		
$[Co(PhNHtga)_3] \cdot 4H_2O$	$PhNHCOCH_2S^-$		10
$H[Co(cys)_2(H_2O)_2]$ (brown, *cis*, uncertain)	$NH_2CH(CO_2^-)CH_2S^-$	$CoSO_4$, pH 8, air, r.t., conc. HCl	2
$Na[Co(cys)_2(H_2O)_2]$	$NH_2CH(CO_2^-)CH_2S^-$	$[Co(NH_3)_6]Cl_3$, 60–70 °C, 2 h, conc. HCl	2
$(N,S)[Co(cys)_3]^{3-}$ (green soln.)		$[Co(NH_3)_6]Cl_3$, N_2, pH ~ 2, 20–50 °C	3, 4
$K_3(+)_{400}$-$(N,S)[Co(cys)_3] \cdot 6H_2O$		$[Co(NH_3)_6]Cl_3$, N_2, KOH, 70 °C, 3 h	6
$(S,O)[Co(cys)_3] \cdot nH_2O$ (red, unconfirmed)		$CoSO_4$, pH ~ 6, air, r.t., 1 h	3
$(S,O)[Co(cys)_3] \cdot 2H_2O$ (red)		$CoCl_2 \cdot NaOAc$, pH 5.1, air, r.t., 12 h, conc. HCl	4
$Na_3[Co(cys)_3] \cdot 6H_2O$ (green solid, red soln.)		As above; NaOH	4
$(+)_{400}$-$(N,S)[Co(Mecys)_3]$ (blue-green)	$NH_2CH(CO_2Me)CH_2S^-$	$Na_3Co(CO_3)_3$, 95 °C, 1 h	7
$[Co(cyst)_2(H_2O)_2]^+$ (brown soln., uncertain)	$NH_2CH_2CH_2S^-$	$CoSO_4$, pH 8, air, r.t.	3
$[Co(cyst)_3]$ (green soln., blue-green solid)		$CoSO_4$, pH ~ 11.5, r.t.	3
		$Na_3Co(CO_3)_3$, 95 °C, 1 h	7
		$Co(NH_3)_6Cl_3$, pH ~ 10.5, N_2, 50 °C, 24 h	4
$Na_3[Co(edt)_3] \cdot 3H_2O$ (black ppt.)	$^-SCH_2CH_2S^-$	$Na_3Co(CO_3)_3$, warm, 30 min	5
$[Co(pyt)_3]$ (brown)		CoO(OH), H_2O, EtOH	8
$[Co(pyt)_{3-n}(en)_n]^{n+}$ (n = 1, 2)		$Co(ClO_4)_2$ + en + $(L)_2$; EtOH; n = 1 (green); n = 2 (brown), resolved	8
$Co(atp)_2$			11
$[Co(Me_2pymt)_3]$ (green)		$Co(ClO_4)_2$; acetone, warm	12

1. L. Michaelis and M. P. Schubert, *J. Am. Chem. Soc.*, 1930, **52**, 4418; R. G. Neville and G. Gorin, *ibid.*, 1956, **78**, 4893 (K^+ salt).
2. R. G. Neville and G. Gorin, *J. Am. Chem. Soc.*, 1956, **78**, 4891.
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4. G. Gorin, J. E. Spessard and G. A. Wessler, *J. Am. Chem. Soc.*, 1959, **81**, 3193.
5. H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, 1968, **82**, 5031.
6. L. S. Dollimore and R. D. Gillard, *J. Chem. Soc., Dalton Trans.*, 1973, 933.
7. M. Kita, K. Yamanari and Y. Shimura, *Chem. Lett.*, 1980, 275; *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2873.
8. M. Kita, K. Yamanari and Y. Shimura, *Chem. Lett.*, 1983, 141.
9. M. Schubert, *J. Am. Chem. Soc.*, 1932, **54**, 4077.
10. T. Bersin, *Z. Anal. Chem.*, 1931, **85**, 428; R. N. Misra and S. S. G. Sirear, *J. Indian Chem.*, 1955, **32**, 127.
11. W. Hieber and R. Bruck, *Z. Anorg. Allg. Chem.*, 1952, **269**, 13, 28.
12. B. A. Cartwright, D. M. L. Goodgame, I. Jeeves, P. O. Langguth, Jr. and A. C. Skapski, *Inorg. Chim. Acta*, 1977, **24**, L45.
13. G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, 1967, **89**, 3607.



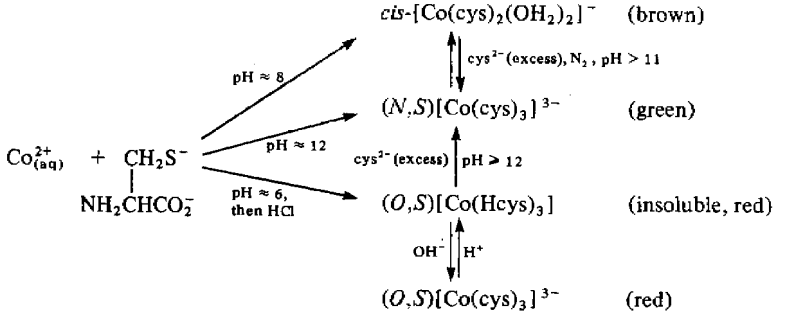
Scheme 90



Scheme 91

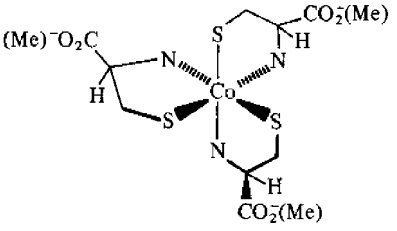
(*ii*) *Tris(bidentate) chelates*

The chemistry of bidentate thiols containing five- and six-membered chelates is now quite extensive. Table 82 summarizes some preparations. There is an interesting history to these complexes and some uncertainty still remains. Harris seems to be the first to have investigated cobalt—thiolate systems,[1015] and Michaelis and Schubert used Co^{II} salts in strongly alkaline aqueous media in the presence of air to prepare solutions of uncertain Co^{III} complexes containing cysteine and thioglycolic acid.[1016,1017,1018] Schubert then isolated dark-brown, green and red complexes[1019] and these were described in detail by Neville and Gorin,[1020,1021] sometimes with internal disagreements but with obvious difficult in reproducing the earlier work. The preparations and interconversions are outlined in Scheme 92 and should be reexamined in the absence of atmospheric oxygen since we now know that oxidation of thiolate sulfur both prior and subsequent to coordination is relatively easy. However green (N,S) and red(O,S) coordination of cysteine seems certain with the latter $Na_3[Co(cys)_3]\cdot 6H_2O$ complex in alkaline solution having an identical absorption spectrum to $[Co(O_2CCH_2CH_2S)_3]^{3-}$. The use of the Co^{III} reagents $Na_3[Co(CO_3)_3]\cdot 3H_2O$, $[Co(NH_3)_6]Cl_3$ and CoO(OH) in an N_2 atmosphere gives better yields of green or blue-green $[Co(cys)_3]^{3-}$, $[Co(tga)_3]^{3-}$ and $[Co(cyst)_3]$ (cyst = $NH_2CH_2CH_2S^-$; Table 82). With (*R*)-cysteine or its *O*-methyl ester[1024] the *fac*-(*N*,*S*)-Δ configuration of $[Co\{(R)\text{-cys}\}_3]^{3-}$ (**278**) appears to be formed stereospecifically with equatorially oriented uncoordinated carboxylate functions. The Δ absolute configuration about



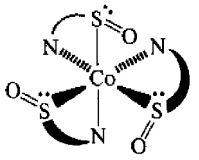
Scheme 92

Co^{III} has been confirmed by comparing CD spectra[1022,1024] with that for resolved Λ-[Co(cyst)$_3$] whose absolute configuration is known from a structure (**279**) of its semi-oxidized [Co(cystO)$_3$]·(+)-tartaric acid mixed salt.[1025] Using Λ-[Co(en)$_3$]Br$_3$ as starting material partially resolved Λ-[Co(cyst)$_3$] has been prepared[1024] and it may be possible to extend this type of synthesis to other optically-active tris(N,S) systems. These green and blue-green complexes (Table 82) have been assigned the symmetrical *fac*-(N,S) geometry with the exception of brown [Co(pyt)$_3$] (pyt = pyridine-2-thiolate) which has been assigned the *mer*-(N,S) configuration on the basis of its more complex ^{13}C spectrum.[1026]



(278)

Δ-*fac*(*N*,*S*)-(+)$_{400}$-[Co{(*R*)-cys}$_3$]$^{3-}$

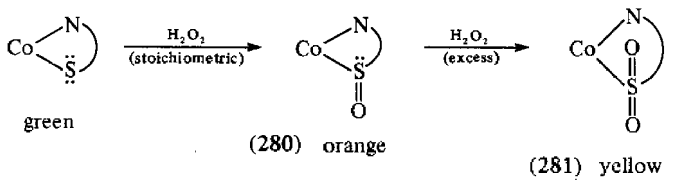


(279)

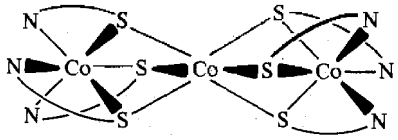
Λ-*fac*(*N*,*S*)-(+)$_{500}$-[Co(cystO)$_3$]

Such tris(N,S) chelates appear to be only moderately stable in neutral aqueous solution with [Co(cys)$_3$]$^{3-}$ being stable only at pH > 11 in the presence of excess cysteine; the oxidized sulfenate and sulfinate chelates are more stable (see below). Reexamination of brown *cis*-[Co(cys)$_2$(OH$_2$)$_2$]$^-$, the dimer [H$_2$Co(tga)(OH)]$_2$, black insoluble Na$_3$[Co(edt)$_3$]·3H$_2$O and green Na$_3$[Co(tga)$_3$]·6H$_2$O (Table 82) seems warranted. The tris(penicillamine) complex does not appear to have been made. Little is known about their optical and configurational stability, and no ligand replacement studies appear to have been undertaken. Heber and coworkers report the preparation of [Co(SCH=CHS)$_2$(PR$_3$)] (R = Ph, Bu, OPh) containing apparently Co^{IV},[1027] and the diamagnetic thioether complex [Co(SCH=CHSR)$_3$] (R = Me, Et, Bu),[1028] but further study to confirm their composition and to determine their structure is necessary.

Oxidation of coordinated thiolate to the sulfenic (**280**) and sulfinic (**281**) acid chelates can be readily achieved and the accompanying green–orange–yellow colour change is very striking (equation 155); it was used over 50 years ago by Michaelis and Yamaguchi as a sensitive test for H_2O_2[1016] and it was first correctly described by Schubert.[1019] The oxidized forms are much more stable and structural characterization has largely been done using them. Oxidation occurs without breaking the Co—S bond and the semi-oxidized sulfenate is asymmetric on sulfur (*i.e.* coordinated thiolate is prochiral). Four diastereoisomeric possibilities therefore exist for a single Δ-*fac*-(N,S)[Co(N—S)$_3$] configuration and steric arguments suggest oxidation will occur preferentially at the equatorial lone pair. Oxidation of Δ-[Co(cys)$_3$]$^{3-}$ is said to form only the Δ-(*S*,*S*,*S*) and Δ-(*R*,*S*,*S*)-[Co(cysO)$_3$]$^{3-}$ possibilities with the latter subsequently mutarotating to the former.[1024] This selectivity agrees with the chromatography of Δ-[Co{(*R*)MecysO}$_3$] where only one isomer is observed,[1024] and with the structure of Λ-(*R*,*R*,*R*)-[Co(cystO)$_3$]·C$_4$H$_6$O$_6$·H$_2$O,[1025] but it places the oxygen atom over an adjacent chelate ring rather than between chelates (**279**). Further investigations of this stereospecific or stereoselective effect would be useful. No similar studies appear to have been carried out on the oxidation products of Na$_3$[(tga)$_3$]. Few quantitative data are available on the rates and rate laws for oxidation. Qualitatively it is known that it is difficult to stop it at the tris(sulfenato) stage.[1024] Oxidation using non-oxygen-transferring agents (V^V, Ce^{IV}, HNO$_3$, Co^{3+}_{aq}) usually produces a disulfide. This remains coordinated if more than one electron is transferred (*cf.* Section 47.8.4) but it can be released to the solvent *via* an internal redox process with formation of Co^{II} and free ligand. Deutsch and coworkers have examined these aspects in some detail and a general account of this work is available.[1011] Oxidation of [Co(cyst)$_3$] using HNO$_3$ produces (**282**) and internal electron transfer in a semi-oxidized intermediate is proposed (Scheme 93).[1061]



green (280) orange (281) yellow (155)



(282)

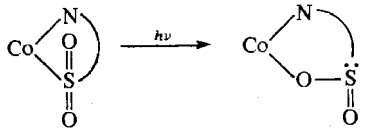
$$[Co(cyst)_3] + ox \longrightarrow [Co(cyst)_2(cyst^+)] + red \xrightarrow[\text{internal electron transfer}]{H^+} Co^{II} + cyst + cyst\text{-}cyst$$

$$Co^{II} + 2[Co(cyst)_3] \longrightarrow [\{Co(cyst)_3\}_2\mu_6(Co^{II})]^{2+} \xrightarrow{\text{oxidation}} [\{Co(cyst)_3\}_2\mu_6(Co^{III})]^{3+}$$

(282)

Scheme 93

Dollimore and Gillard observed a yellow (406 nm) to red (490 nm) colour change on standing solid K_3-$\Delta(+)_{400}$[Co{(*R*)cysO_2}$_3$], or an aqueous solution of it, in bright sunlight.[1022,1023] This is likely to result from isomerization to the O-bound sulfinato complex (**283**) containing the six-membered chelate (equation 156).[1029] This O-bound sulfinate is now asymmetric on sulfur leading to further isomers, and inversion at S is synchronous with the exchange between coordinated oxygens. The unknown five-membered (N,O)carboxylate-bound chelate may be more stable in this case with release of the oxidized sulfur donor. No corresponding photolytic study has been reported for the sulfenate chelate, and it is not known if the isomerization given by equation (156) is thermally reversible.



(156)

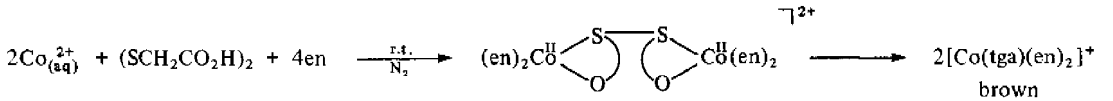
(283)

The $\Delta(+)_{400}$-[Co{(*R*)cysO_2}$_3$]$^{3-}$ anion forms sparingly soluble yellow salts with a number of 3+ cations[1019] and Dollimore and Gillard[1022] have shown it to be an excellent resolving agent for a wide variety of Co^{III}, Cr^{III} and Rh^{III} complexes.

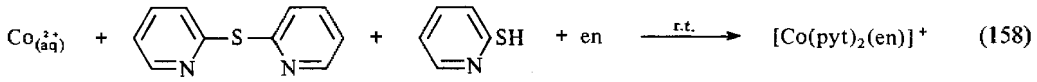
(*ii*) *Mixed bidentate chelates*

The mixed bidentate thiolato complexes $[Co(N—S)(en)_2]^{2+,1+}$ and $[Co(O—S)(en)_2]^+$ have received considerable attention over the last decade. Having only one coordinated S atom they provide ideal starting points for investigating the spectral and structural properties of different oxidation states of sulfur as well as for studying the reactivity of coordinated sulfur. Originally poor yields of these complexes were obtained by treating *trans*-[Co(Cl)$_2$(en)$_2$]Cl with (*R*)-cysteine, cysteamine and thioglycolic acid in aqueous alkaline solution[1030–1032] but Lane and Bennett[1033] discovered that oxidation of $Co^{2+}_{(aq)}$ using the disulfide of the thiol in the absence of air gave excellent yields (equation 157). This stoichiometry provides the basis of the modern method for preparing these complexes (Table 83). Some minor modification is necessary for aromatic thiols. The Cr^{III} analogues can be made in an identical manner.[1034] The excellent yield probably derives from internal redox within a Co^{II}–disulfide intermediate (**284**), although such a species has never been observed. The bidentate nature of the ligand probably stabilizes (**284**) and no successful preparations have been reported using disulfides which lack this capacity. The method also appears to be applicable to $[Co(N—S)_2(en)]^+$ and $[Co(O—S)_2(en)]^-$ chelates, and green $[Co(pyt)_2(en)](ClO_4)$ has been prepared using a mixture of the disulfide (1 mol equiv) and thiol (2 mol equiv) in ethanol (equation 158).[1035] A *trans*-(*S*) structure has been proposed. This particular complex is unstable in hot aqueous solution giving rise to $[Co(pyt)_3]$, but the preparative method can probably be extended to other systems. With (*R*)-cysteine the thermodynamically least stable diastereoisomer Λ-(*N*,*S*)[Co{(*R*)cys}(en)$_2$]-

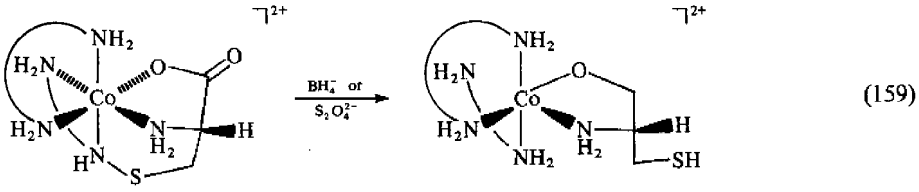
(ClO_4) crystallizes in 96% yield in a second-order asymmetric manner. The solution actually contains the equilibrium mixture $\Delta(R):\Lambda(R) = 7:3$.[1036] Both $Co^{2+}_{(aq)}$ and OH^- effect rapid mutarotation about the metal in this complex but not about the chiral carbon. With (*S*)-penicillamine a similar equilibrium obtains ($\Lambda:\Delta[Co\{(S)pen\}(en)_2]^{2+} = 7:3$) but preferential crystallization does not occur.[1037] X-Ray structures confirm equatorial and axial dangling carboxylate functions in Λ-$[Co\{(R)cys\}(en)_2](ClO_4)$ and Δ-$[Co\{(R)cys\}(en)_2](ClO_4)\cdot H_2O$ respectively.[1037] (N,S) bonding seems to be preferred in (N,S,O) systems (cysteine, penicillamine) but (N,O)$[Co\{(R)cys\}(en)_2]^{2+}$ has been prepared by reduction of the tridentate sulfenamide complex (**285**; equation 159).[1038] This (N,O) chelate lacks the extended charge transfer absorptions in the near UV characteristic of thiolate coordination.



(157)



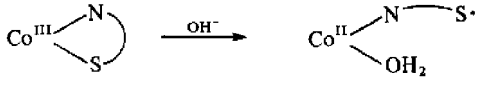
(158)



(159)

(285)

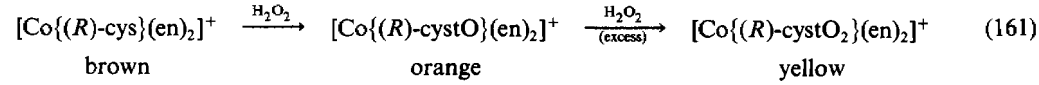
Thiolate sulfur in $[Co(cyst)(en)_2]^{2+}$ can be protonated in strong acid without dissociation from the metal[1039] but all thiolate chelates seem to be unstable in strongly alkaline solutions undergoing slow thermal reduction *via* an inner-sphere electron-transfer process (equation 160).[1056]



(160)

Spectral and structural data are given in Table 84 and Table 85 and methods of resolving enantiomeric systems in Table 86. Photodecomposition ot $Co^{2+}_{(aq)}$ occurs without photoaquation and is wavelength independent.[1049]

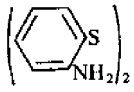
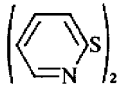
Oxidation to coordinated sulfenate and sulfinate (equation 161) was first reported by Sloan and Krueger[1040] who isolated the orange sulfenate and yellow sulfinate as their perchlorate salts. Similar oxidized products have now been isolated for several systems; these are given in Table 87. Generally the sulfenate complexes aquate or decompose slowly in neutral aqueous solution and the reaction is acid catalyzed. They also decompose to unknown products in strongly alkaline conditions. Reversible O-protonation occurs in acid ($pK_a \approx -1$) without mutarotation at S (see below). The sulfinate complexes are more stable in neutral and acid solution but they also decompose in alkali. One mole equivalent of oxidizing agent generates the sulfenate exclusively with excess reagent and longer times being necessary to form the sulfinate (this differs from the tris(thiolate) systems, Section 47.8.2.2.ii). Stabilization of sulfenate S is not found in uncoordinated sulfenic acids. Lydon and Deutsch have discussed these properties in a general article.[1043]



(161)

Two-electron oxidizing reagents are the best ($S_2O_8^{2-}$, Br_2, NaOCl, MnO_4^-, H_2O_2) and the reaction of H_2O_2 follows a two-term rate law, $k_{obs} = k_1[H_2O_2] + k_2[H_2O_2][H^+]$, with k_2 being interpreted as attack by $H_3O_2^+$; this term is important only when $[H^+] > 0.1\,mol\,dm^{-3}$. Comparative data are given in Table 88. A similar situation holds for $S_2O_8^{2-}$. Coordinated thiolate is about as nucleophilic as NCS^- and the reduced nucleophilicity of coordinated sulfenate is probably why it is stabilized relative to organic sulfenates. The ligand field strength of sulfur increases with formal oxidation

Table 83 Preparations: Mixed Chelate Complexes Containing Bidentate Thiolates

Disulfide	*Preparative conditions*	*Product*	*Ref.*	*Crystal structure (cf. Table 85)*
$(SCH_2CO_2H)_2$	$CoClO_4$, aq, N_2, r.t.	$[Co(tga)(en)_2]ClO_4$ (brown)	1, 8	Yes
$(SCH_2CH_2NH_2)_2$	$CoClO_4$, aq, N_2, r.t.	$[Co(cyst)(en)_2](ClO_4)_2$	2, 8	
$[SCH_2CH(CO_2H)NH_2]_2$	$CoCl_2$, aq, N_2, pH 9, r.t.	$[Co(cys)(en)_2]ClO_4$	3	Yes
	$Co(ClO_4)_2$, aq, N_2, r.t.	Λ-[Co{(*R*)-cys}$(en)_2$](ClO_4) (asymmetric synthesis)	4	Yes
$[SC(Me)_2CH(CO_2H)NH_2]_2$	$Co(ClO_4)_2$, aq, N_2, r.t.	30% Δ-[Co{(*S*)-pen}$(en)_2$]$(ClO_4)_2$ 70% Λ-[Co{(*S*)-pen}$(en)_2$]$S_2O_6 \cdot 2H_2O$	5	No
	$Co(ClO_4)_2$, THF/H_2O, r.t.	$[Co(atp)(en)_2](ClO_4)_2$ (green brown)	6	Yes
	$Co(ClO_4)_2$, aq EtOH, 50°C	$[Co(pyt)(en)_2](ClO_4)_2$, resolved	7	No
	$[Co(Cl)_2(tren)]Cl$	*t*-$[Co(tga)(tren)](ClO_4)$	9	No
	$[Co(Cl)_2(tren)]Cl$	$(+)_{589}$-*t*-[Co{$O_2CCH(Me)S$}(tren)](ClO_4)	9	No
	$[Co(Cl)_2(tren)]Cl$	*t*- and *p*-$[Co(cyst)(tren)](ClO_4)_2$	10	No

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Table 84 UV–Visible Spectral Data for Sulfur-Bonded Co^{III} Complexes [nm (ε)]

Thiolato (RS⁻)				
$[Co(cys)_3]^{3-}$ (green)	582 (269)		444 (568)	279 (1640)
$[Co(cyst)_3]$ (green)	570 (568)		434 (1240)	
$[Co(cysH)_3]\cdot 2H_2O$ (red)		510 (24 700)	417 (8400)	270 (9800)
				225 (8300)
$H_3[Co(O_2CCH_2CH_2S)_3]$ (red)		510 (22 600)	415 (6400)	270 (8200)
$[Co(cys)(en)_2]^+$	600 sh (37)	483 (126)		283 (11 700)
$[Co(cyst)(en)_2]^{2+}$	600 sh (44)	482 (142)		282 (13 800)
$[Co(NH_2C_6H_4S)(en)_2]^{2+}$	580 sh (80)	470 sh (170)	400 (240), 350 sh (300)	279 (19 400)
				260 (14 600)
$[Co(tga)(en)_2]^+$		518 (152)		282 (11 700)
$[Co\{O_2CCH(Me)S\}(en)_2]^+$		515 (149)		280 (12 600)
$[Co\{O_2CC(Me)_2S\}(en)_2]^+$		514 (153)		282 (10 900)
Sulfenato (RSO⁻)				
$[Co(cysO)(en)_2]^+$		480 (600)	371 (5800)	287 (3750)
$[Co(cystO)(en)_2]^{2+}$		470 (500)	365 (6700)	287 (3750)
$[Co(NH_2C_6H_4SO)(en)_2]^{2+}$		475 sh (800)	375 (6000)	285 (4400)
$[Co(tgaO)(en)_2]^+$		493 (350)	360 (6000)	285 (3000)
$[Co\{O_2CCH(Me)SO\}(en)_2]^+$		480 (390)	357 (6000)	287 (3500)
Sulfinato (RSO_2^-)				
$[Co(cystO_2)(en)_2]^{2+}$			432 (220)	288 (14 200)
$[Co(NH_2C_6H_4SO_2)(en)_2]^{2+}$			430 (250)	285 (13 400)
$[Co(cysO_2)(en)_2]^+$			430 (190)	287 (11 900)
$[Co(tgaO_2)(en)_2]^+$			448 (435)	294 (10 200)
Thioether (R_2S)				
$[Co(cystMe)(en)_2]^{3+}$		487 (177)		282 (8380)
				257 (4140)
$[Co(tgaMe)(en)_2]^{2+}$		499 (168)		280 (7300)
				270 (7210)
Disulfide (RSSR)				
$[Co(cystSMe)(en)_2]^{3+}$		489 (149)		343 (1710), 278 (7550)
				319 (1340)
$[Co(tgaSMe)(en)_2]^{2+}$		501 (161)	340 (1640)	285 (7680)

Table 85 Structural Data for Sulfur Chelates

Complex	*Structural data* (pm)	*Ref.*
Thiolate		
$[Co(tga)(en)_2]Cl\cdot H_2O$	CoS 224.3; *trans* CoN 200.5; Δ*r* 4.3	1
$[Co(cyst)(en)_2](SCN)_2$	CoS 222.6; *trans* CoN 200.1; Δ*r* 4.1	1
Λ-$[Co\{(R)$-cys$\}(en)_2](ClO_4)$	CoS 223.4; *trans* CoN 202.4; Δ*r* 4.9	3
Δ-$[Co\{(R)$-cys$\}(en)_2](ClO_4)\cdot H_2O$	CoS 225.2; *trans* CoN 201.1; Δ*r* 3.9	3
$[Co(NH_2C_6H_4S)(en)_2]Cl(ClO_4)$	CoS 224.6; *trans* CoN 201.1; Δ*r* 4.4	4
$[Co(Me_2pymt)_3]\cdot$acetone	CoS 225.9; CoN 197.4; SCoN 72.5°	11
$K[Co\{(S)$-pen$\}\{(R)$-pen$\}]\cdot 2H_2O$	CoS 222.2, 222.9; CoN 192.2, 198.3; CoO 197.1, 194.2	13
$[Co\{(R)$-pen$\}(dien)]Cl\cdot H_2O$	CoS 225.5; *trans* CoN 200.7; Δ*r* 4.6	14
Thioether		
$[Co(cystMe)(en)_2][Fe(CN)_6]\cdot 4H_2O$	CoS 226.7; Δ*r* 0	5
$[Co(tgaCH_2Ph)(en)_2](SCN)_2$	CoS 227.4; Δ*r* 2.0	5
Λ(*S*)-$[Co\{(R)$-cysMe$\}(en)_2](NCS)_2$	Cambridge Crystallographic Data Centre	6
$[Co\{[cyst(CHCON)Et]COCH_2\}(en)_2(ClO_4)_3$	CoS 227.6; CoN 195–198; Δ*r* 0	7
$[Co\{(R)$-cysMe$\}_2](ClO_4)\cdot H_2O$	CoS 227.1; CoO 190.6; CoN 194.6; XCoY 83.8–98.9°	12
$[Co\{[(R)$-cysMe$]_2$en$\}](ClO_4)$	CoS 225.7, 226.4; *trans* (O) isomer	16
Disulfide		
$[Co(cystSEt)(en)_2](ClO_4)_3$	CoS 227.2; SS 203.3; Δ*r* 1	9
$[Co\{S[SC(Me)_2CO_2H]C(Me)_2CO_2\}(en)_2](ClO_4)_2\cdot 2H_2O$	CoS 226.0; SS 205.2; Δ*r* 0	10
$[Co(en)_2(cys)]_2(ClO_4)_4\cdot 6H_2O$	SS 203.2	15
Metal bridged thiolates		
$\{\Lambda(S)$-$[Co(en)_2(tga)]\}_2Ag](ClO_4)_3$	CoS 224.7; Δ*r* 1.4; AgS 237	8
Δ,Λ-$[Co(en)_2(cyst)]_2[Cu(MeCN)_2](ClO_4)_6\cdot 2H_2O$	CoS 227.3; CuS 240.6, 234.2; SCuS 97°	17
$[\{Co(cyst)_3\}_2\mu_6(Co)]_2(SO_4)Cl_4$	CoCo 285.7; Co_tS 223.8; Co_cS 226.2; CoN 199.6; SCo_tN 88.3°; Co_tSCo_c 78.8°	18

Table 85 (*continued*)

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Table 86 Resolutions: Bidentate Sulfur Chelates

Complex	*Method*	*Ref.*
$K_3\Delta(+)_{400}$-[Co{(*R*)-cys}$_3$]	Spontaneous (stereospecific)	1
$K_3\Delta(+)_{400}$-[Co{(*R*)-Mecys}$_3$]	Spontaneous (stereospecific)	2
$(+)^{CD}_{500}$-[Co(cystO)$_3$]	(+)-H_4 tart	9
[Co(tga)(en)$_2$]Cl	Sb_2-(+)-tart$_2^{2-}$	3
[Co(pyt)(en)$_2$](ClO_4)$_2$	Sb_2-(+)-tart$_2^{2-}$	4
[Co{(*R*)-cys}(cn)$_2$](ClO_4)	Biorad-AG-50W × 4 (Na^+), 0.4 NaCl	5
Λ-[Co{(*R*)-cys}(en)$_2$](ClO_4)	Spontaneous (asymmetric synthesis)	7
[Co(tgaMe)(en)$_2$]Cl_2	Ag_2(+-tart)	3
[Co(cyst)(en)$_2$]Cl_2·H_2O	Sb_2-(+)-tart$_2^{2-}$	3
[Co(cystMe)(en)$_2$]Cl_3·H_2O	Sb_2-(+)-tart$_2^{2-}$	3
[Co{(*R*)-cysMe}(en)$_2$](ClO_4)$_2$	Dowex 50W × 2	6
[Co{(*S*)-pen}(en)$_2$](ClO_4)$_2$	Dowex 50W × 2 (Na^+)	8
[Co(cystO)(en)$_2$]$^{2+}$	Sephadex C-25, 0.1 M, Sb_2-(+)-tart^{2-}	10
p-[Co(cystO)(tren)](ClO_4)$_2$	(+)-Tart^{2-} [resolved on S(O)]	10
t-[Co(cystO)(tren)]$^{2+}$	0.1 M Sb_2-(+)-tart^{2-} [resolved on S(O)]	10

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state, thiolate(II) < sulfenate(IV) < sulfinate(VI); $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions at 470–520 nm (brown), 470–490 (orange) and 430–440 (yellow) (Table 84).

Metal sulfenates are formally analogous to organic sulfoxides being asymmetric at S; the [Co(N—SO)(en)$_2$]$^{n+}$ systems are therefore diastereoisomeric. Oxidation of Λ-[Co{(*R*)cys}(en)$_2$]$^+$ occurs preferentially at the axial lone pair (**286**),[1036] probably because the prochiral centre is more accessible to H_2O_2 and the carboxylic acid substituent of cysteine prefers to be equatorial. But oxidation is not stereospecific with Λ(*S*):Λ(*R*) ≈ 2.5 for the 1+ reactant (at pH ≈ 5) and 1.3 for the 2+ reactant (at pH < 2). More sterically hindered oxidizing agents increase this ratio.[1036] The more rapid further oxidation of the remaining axial lone pair in Λ(*R*)-[Co{(*R*)cysO}(en)$_2$]$^+$ compared to the slower oxidation of the equatorial lone pair in Λ(*S*)-[Co{(*R*)cysO}(en)$_2$]$^+$ supports this idea.[1041] However the structure of Δ(*S*)-[Co(cystO)(en)$_2$](SCN)$_2$ (**287**; Table 87) clearly shows that oxidation in this complex has occurred at the equatorial site. The specificity in this latter system has not been detailed.[1042] Equatorial oxidation is also found with [Co(cyst)$_3$] (Section 47.8.2.2.ii), so some flexibility is possible. The *p*- and *t*-[Co(cystO)(tren)]$^{2+}$ ions having S^{IV} as the only centre of asymmetry have been resolved into their (*R*) and (*S*) enantiomers (**288**) and (**289**).[1045] This is the first reported resolution of enantiomeric sulfenate complexes in which coordinated sulfur is the only source of asymmetry.

Table 87 Preparation and Structures of Oxidation Products of Chelated Thiolates

Complex	*Preparation*	*Structure,[a] comments*	*Ref.*
$[Co(cystO_2)(en)_2](NO_3)(ClO_4)$ (red-brown)	50 °C, H_2O_2, $HClO_4$	*trans* CoN 202.7; Δr 4.9; $CoS(O_2R)$ 219.1	1
$\Delta(R),\Lambda(S)$-$[Co(en)_2\{cyst(O)Me\}]I_3 \cdot H_2O$ (red)	MeI, Me_2SO, 20 °C, 12 h	Rearranges from S- to O-bonded sulfoxide; CoO 190.6; SO 152.4; CoN 195–6	10
$[Co(cysO)(en)_2](ClO_4)_2$ (orange)	r.t., 1.1 equiv. H_2O_2; 1 h	–	2
$[Co(cysO_2)(en)_2](ClO_4)_2$ (yellow)	r.t., excess H_2O_2; 12 h	–	2
$\Lambda(S)$-$[Co\{(R)$-$cysO\}(en)_2](ClO_4)_2$	r.t., 1 equiv. H_2O_2	COS(OR) 223; *trans* CoN 203.6; Δr (S)	3
$\Delta(S)$-$[Co(cystO)(en)_2](SCN)_2$ (red-brown)	1 equiv. H_2O_2	COS(OR) 225.3; Δr 7.2; *trans* CoN 204.8	4
$[Co(tgaO)(en)_2](ClO_4)$ (orange)	1 equiv. H_2O_2, chrom.	Not very stable	4
$\Lambda(R,R,R)$-*fac*-$[Co(cystO)_3] \cdot d$-$C_3H_6O_6 \cdot H_2O$ (orange-red)	1 equiv. H_2O_2, < 5 °C	CoSO 225; CoN 201.2	5
$t(R)$- and $t(S)$-$[Co(cystO)(tren)](ClO_4)_2$	1 equiv. H_2O_2; separate $t(R)$, $t(S)$ using SP-C25 (0.1 M) Sb_2-(+)-$tart^{2-}$); separate $p(R)$, $p(S)$ from (+)-$tart^{2-}$ salt	Resolved on Co—S(O)R	6
$p(R)$- and $p(S)$-$[Co(cystO)(tren)](ClO_4)_2$			6
$[Co(cystNH_2)(en)_2](ClO_4)_2(C_2O_4) \cdot 0.5H_2O$	NH_2OSO_3H	CoS 225; CoN 196–199; Δr 0.0	7
$\{[Co(en)_2(cyst)]_2I\}(NO_3)_5 \cdot 4H_2O$	I_2 or I-N <O	CoN 198; Δr 0.0	8
$(-)_{589}$-*t*-$[Co\{O_2CCH(Me)S(Me)(tren)\}](ClO_4)_2$	MeI	–	9
$(+)_{589}$-*t*-$[Co\{O_2CCH(Me)S(O)_2(tren)\}](ClO_4)$	H_2O_2	–	9

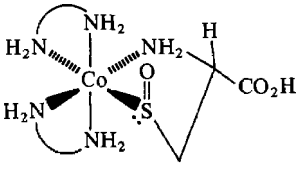
[a] Bond length data in pm.

1. B. A. Lange, K. Libson, E. Deutsch and R. C. Elder, *Inorg. Chem.*, 1976, **12**, 2985.
2. C. P. Sloan and J. H. Krueger, *Inorg. Chem.*, 1975, **14**, 1481.
3. W. G. Jackson, A. M. Sargeson and P. O. Whimp, *J. Chem. Soc., Chem. Commun.*, 1976, 934.
4. I. K. Adzamli, K. Libson, L. D. Lydon, R. C. Elder and E. Deutsch, *Inorg. Chem.*, 1979, **18**, 303.
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7. M. S. Reynolds, J. D. Oliver, J. M. Cassel, D. L. Nosco, M. Noon and E. Deutsch, *Inorg. Chem.*, 1983, **22**, 3632.
8. D. L. Nosco, M. J. Heeg, M. D. Glick, R. C. Elder and E. Deutsch, *J. Am. Chem. Soc.*, 1980, **102**, 7784.
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10. G. J. Gainsford, W. G. Jackson and A. M. Sargeson, *J. Am. Chem. Soc.*, 1982, **104**, 137.

Table 88 Rate Data (at 25 °C) for Oxidation of Coordinated Thiolate by H_2O_2 (see text)

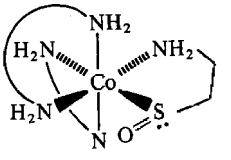
Complex	k_1($mol^{-1}\,dm^3\,s^{-1}$)	*Ref.*
$[Co(en)_2\{NH_2CH(CO_2H)CH_2S\}]^{2+}$	0.24	1
$[Co(en)_2\{NH_2CH(CO_2)CH_2S\}]^{+}$	0.36	1
$[Co(en)_2\{NH_2CH(CO_2)CH_2S\}]^{+} + S_2O_8^{2-}$	9.9 (I = 0.513, 19.9°)	3
$[Co(en)_2(NH_2CH_2CH_2S)]^{2+}$	0.85	1
	3.2	4
$[Co(en)_2\{(S)NH_2CH(CO_2)C(Me)_2S\}]^{+}$	0.14	1
$[Co(en)_2\{NH_2CH_2CH_2S(O)\}]^{2+}$	0.34×10^{-3}	2
$[Co(en)_2(O_2CCH_2S)]^{+}$	2.5	4
$[Co(en)_2\{O_2CCH(Me)S\}]^{+}$	2.2	4
$[Co(en)_2\{O_2CC(Me)_2S\}]^{+}$	0.52	4

1. D. L. Herting, C. P. Sloan, A. W. Cabral and J. H. Krueger, *Inorg. Chem.*, 1978, **17**, 1649.
2. I. K. Adzamli, K. Libson, J. D. Lydon, R. C. Elder and E. Deutsch, *Inorg. Chem.*, 1979, **18**, 303.
3. O. Vollarova and J. Benko, *J. Chem. Soc., Dalton Trans.*, 1983, 2359.
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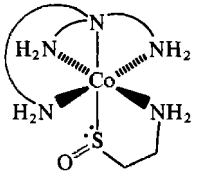
(286)

Λ(*S*)-[Co{(*R*)-HcysO}(en)$_2$]$^{2+}$



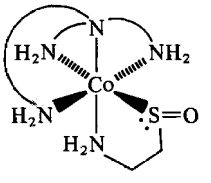
(287)

Δ(*S*)-[Co(cystO)(en)$_2$]$^{2+}$



(288)

t(*R*)-[Co(cystO)(tren)]$^{2+}$

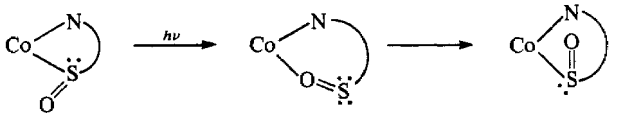


(289)

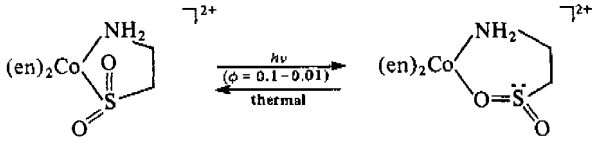
p(*S*)-[Co(cystO)(tren)]$^{2+}$

Mutarotation at coordinated sulfenate S is slow, which is analogous to the situation with organic thiols. Introduction of the S=O group imparts a high resistance to inversion. Racemization in *p*-(*S*)-$[Co(cystO)(tren)]^{2+}$ occurs at the rate $9.92 \times 10^{-5}\,s^{-1}$ (30 °C; pH independent) and the *t*-(*S*) isomer is some 80 times slower.[1045] Other diastereoisomeric sulfenate systems have also been shown to be optically very stable. Protonation to form Co—S(OH)R ($pK_a \approx 0$) does not alter this, but addition of alkali does with mutarotation of Λ(*S*)-$[Co\{(R)cysO\}(en)_2]^{+}$ being rapid at both S and Co in 0.1 mol dm^{-3} OH^- (but not at C). This may occur *via* a labile Co^{II}—SO(R) intermediate.[1036]

Mutarotation at S is also reported to be catalyzed by light,[1041] possibly *via* an O-bound sulfenate intermediate (equation 162). Adamson and coworkers report that photodecomposition to $Co^{2+}_{(aq)}$ is the final outcome.[1049] For sulfinate complexes donor S to O isomerization occurs[1029,1049] and red O-bound (N,O)$[Co(cystO_2)(en)_2](ClO_4)_2 \cdot H_2O$ has been isolated.[1029] This process (equation 163; *hν* 350–450 nm) is thermally reversible ($t_{1/2} \approx 600$ h, r.t.) but which O atom is involved, axial or equatorial, is not known. The O-bound form is now asymmetric, and some specificity might be expected.

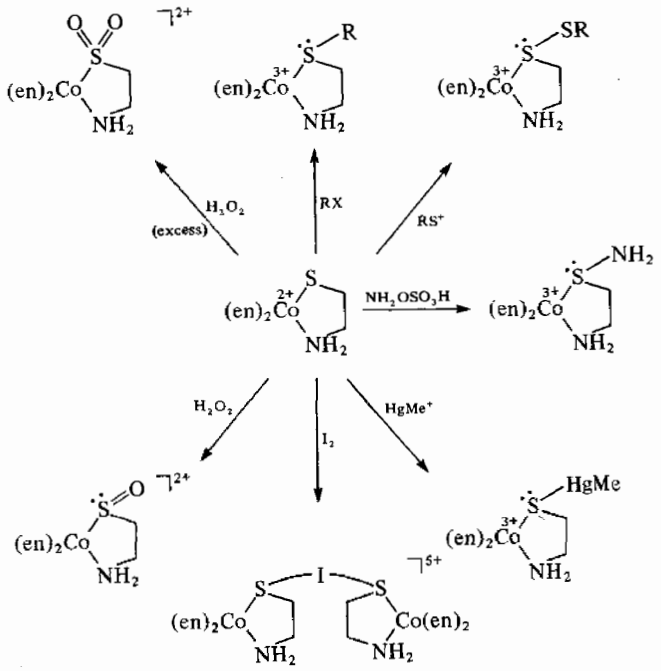


(162)

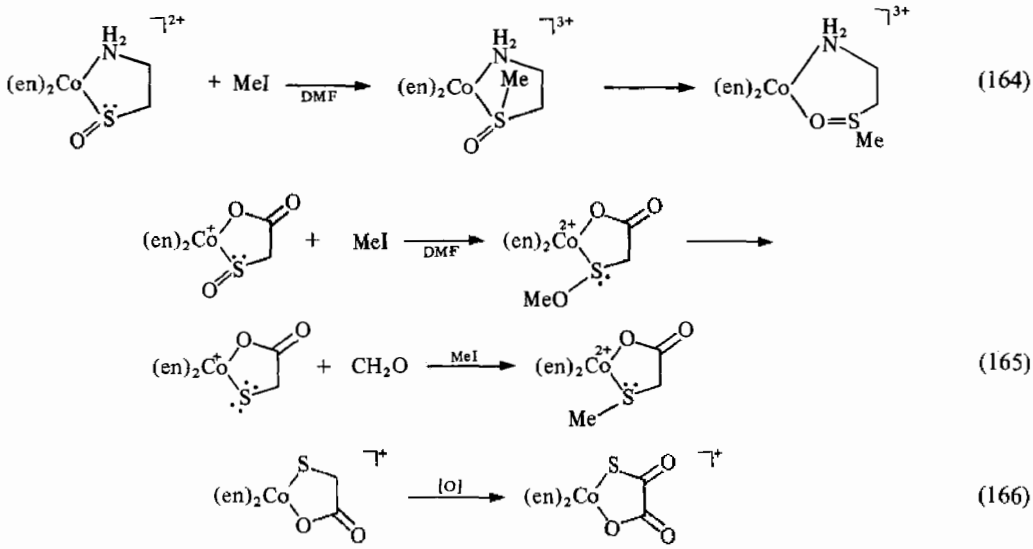


(163)

Root and Deutsch discuss other oxidations of coordinated thiolate[1059] and Scheme 94 outlines some of these. Nucleophilicity towards MeI is similar to that of uncoordinated RSH or RSR. Some crystal structures of the oxidized products are given in Table 87. The reactivity of sulfenic acids is masked by coordination to the metal and these complexes are reasonbly stable in neutral or weakly acidic solutions, but strong acid gives mostly $Co^{2+}_{(aq)}$. Unlike organic sulfoxides (which preferentially O-alkylate and then slowly rearrange to the sulfoxonium ion R_3SO^+) only S-methylation is observed when $[Co(cystO)(en)_2]^{2+}$ is treated with MeI (it may however initially occur at O).[1044] This product then isomerizes to the O-bound isomer (equation 164). Both processes occur with full retention of configuration at S and Co and the six-membered ring is apparently more stable than the five-membered chelate. Treatment of $[Co(tgaO)(en)_2]^+$ with MeI however gives rise to the thioether $[Co(tgaMe)(en)_2]^{2+}$ rather than the sulfoxide possibly *via* disproportionation of the intermediate *O*-methyl ester to the thiolate and formaldehyde (equation 165), the process being activated by the acidic α-carbon centre.[1043,1044] Other oxidants may react to give oxidation at the adjacent C atom rather than at coordinated S. Thus treatment of $[Co(tga)(en)_2]^+$ with *N*-chlorosuccinimide[1057] or acetic anhydride[1058] in DMF or DMSO leads to the monothiooxalate chelate (**290**; equation 166).



Scheme 94



(164)

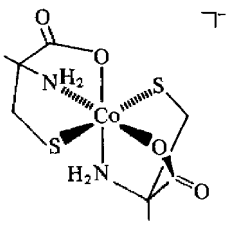
(165)

(166)

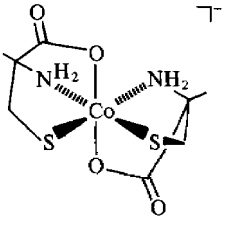
(290)

(*iv*) *Tridentate, quadridentate and sexidentate chelates*

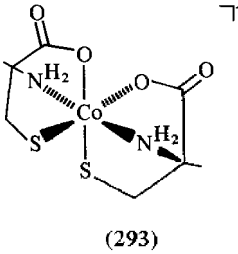
The (S,O,N) tridentate ligands (*R*)-cysteine, (*R*)-methionine and (*R*)-penicillamine coordinate stereospecifically but often give several geometric isomers of $[Co\{(R)L\}_2]^{-,+}$. Table 89 lists some preparations and Table 85 some structures. All three isomers (**291**), (**292**) and (**293**) of $[Co\{(R)cys\}_2]^-$ have been isolated and their visible and CD and ^1H NMR spectra compared.[1046,1047] Isomerization to a common equilibrium slowly occurs in aqueous solution. Treatment of *trans*(*N*)-$[Co\{(S)pen\}_2]^-$ with Me_2SO_4 in aqueous solution results in all three geometric thioether complexes $[Co\{(S)penMe\}_2]Br$,[1047] whereas similar treatment of the three $[Co\{(S)pen\}(dien)]^+$ isomers appears to proceed with geometric integrity.[1048] ^1H NMR also suggests that methylation at the asymmetric S atom is stereospecific. The isolation of the tridentate $[Co\{(R)cys\}_2]^-$ has not been reported (*cf.* Section 47.8.2.2.ii for $[Co\{(R)cys\}_3]^{3-}$). Some mixed-ligand complexes are included in Table 89. The quadridentate ligand $HS(CH_2)_2N(Me)CH_2CH_2N(Me)(CH_2)_2SH$ forms two $[Co(eddt)(en)]^+$ isomers (**294**) and (**295**), and a crystal structure establishes stereospecific coordination of the sexidentate thioether ligand *N*,*N*′-ethylenebis{(*R*)-cysteine-Me} (**296**; Table 89).



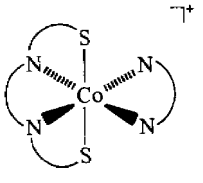
(291)
(*R*)-*trans*(S)



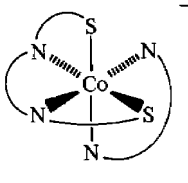
(292)
(*R*)-*trans*(O)



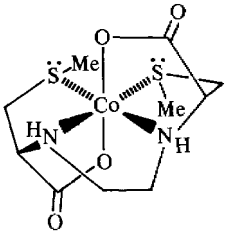
(293)
(*R*)-*trans*(N)



(294)



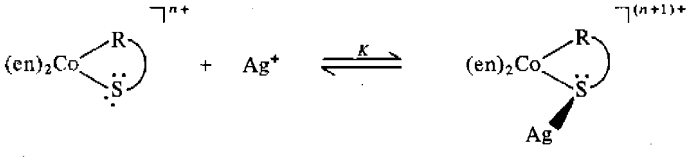
(295)



(296)

(*v*) *Metal binding to coordinated thiolate*

Soft metals such as Ag^+, Cu^+ and $MeHg^+$ coordinate to $Co^{III}SR^{n+}$ complexes and uncoordinated thioethers with about equal ease. Thus it seems that Co^{III} and R^+ have similar effects on the binding power of RS^-, reducing it by about 10^{10} (Table 90; equation 167). This property has implications for electron transfer since ligation of coordinated thiol to a second metal centre is probably the first step in inner-sphere electron transfer. Data given in Table 90 demonstrate that Co^{III}—SR^{n+} retains some Lewis basicity towards soft metals. These studies have utilized $[Co(R—S)(en)_2]^{+,2+}$ systems (R—S = cyst, tga)[1050] but the metals Fe^{III},[1051,1052] Ru^{III}[1052] and Co^{III}[1053] also form very stable $[Co(cyst)_3]_2M^{3+}$ cations *via* bonding to the trigonal faces of two $Co(cyst)_3$ octahedra,[1052] and Zn^{II}, Cu^{II} and Cd^{II} form $\{[Co(cyst)_3]_2M\}MBr_4$ species which are thought to involve μ-Br bridges.[1053] Resonance Raman studies show two strong absorptions which have been assigned to the somewhat weakened stretching and bending modes of the $Co(cyst)_3$ moiety,[1054] and oxidation by H_2O_2 appears to be modified by the presence of the second metal.[1060] The prochiral S centre generates two diastereoisomeric possibilities in a CoS(R)M product. Structure (**297**; Table 85) shows the axial lone pair to be more nucleophilic generating $\Lambda(S),\Lambda(S)$ and $\Delta(R),\Delta(R)$ dimers. The Ag^+ ion lies on a two-fold symmetry axis and the dimer unit is chiral with two units existing in the crystal related by a centre of inversion. Both lone pairs are involved in the binding of Cu^I (structure **298**; Table 85). This red-brown dimer has been suggested as a model for ESR-silent type 3 copper in multicopper oxidases.[1055]

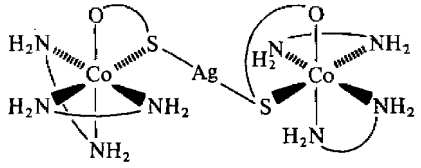


(167)

Table 89 Preparations: Some Tri-, Quadri- and Sexi-dentate Thiolate and Thioether Chelates of Cobalt(III)

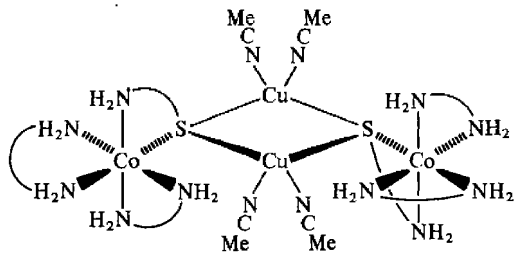
Complex	*Ligand*	*Preparation*	*Ref.*
$K[Co\{(S)\text{-pen}\}_2]\cdot nH_2O$	$NH_2CH(CO_2^-)C(Me)_2S^-$	$CoCl_2\cdot 6H_2O$, H_2O, pH 7, 6 h. Brown [*trans* (N)] and green [*trans* (O)] isomers isolated	1
$K[Co\{(S)\text{-pen}\}\{(R)\text{-pen}\}]\cdot 2H_2O$		$Co(NO_3)_2$, H_2O, pH 7	2
$[Co(dien)\{(R)\text{-pen}\}]Cl$		$[Co(dien)Cl_3] + AgNO_3$; H_2O, N_2; chrom; three brown isomers	3
$[Co\{(S)\text{-met}\}_2](ClO_4)$	$NH_2CY(CO_2^-)CH_2CH_2SCH_3$	$CoCl_2\cdot 6H_2O$, H_2O, 70 °C, charcoal; PbO_2, chrom.; three isomers	4
$[Co\{(S)\text{-met}\}\{(R,S)\text{-asp}\}]$		$CoCl_2\cdot 6H_2O$, H_2O, pH 8; charcoal, PbO_2, 65 °C; chrom.	6
$Co[\{(R)\text{-cysMe}\}\{(R,S)\text{-asp}\}]$	$NH_2CH(CO_2^-)CH_2SMe$	$CoCl_2\cdot 6H_2O$, H_2O, pH 8; charcoal, PbO_2, 65 °C; chrom.	6
$[Co\{(R)\text{-cysMe}\}_2](ClO_4)$		$CoCl_2\cdot 6H_2O$, H_2O, 70 °C, charcoal; PbO_2 20 min; chrom; three isomers	1
$[Co\{(S)\text{-penMe}\}_2]Br$	$NH_2CH(CO_2^-)C(Me)_2SMe$	$K[Co\{(S)\text{-pen}\}_2]$, $H_2O + Me_2SO_4$ chrom.; three isomers	1
$[Co(NH_3)_3\{(R)\text{-penMe}\}](ClO_4)_2$		$[Co(NH_3)_6]Cl_3$; H_2O; pH 2.5, charcoal, 40 °C, 16 min, chrom.; $MeSO_4$, chrom.	5
$[Co(dien)\{(R)\text{-penMe}\}]Cl_2$		$[Co(dien)\{(R)\text{-pen}\}]Cl + Me_2SO_4$, H_2O, chrom.	5
$[Co(dpt)_2]Cl\cdot H_2O$	$(NH_2CH_2)_2CHS^-$	$[Co(NH_3)_6]Cl_3 + OH^-$, 90 °C; chrom., two isomers, resolution of *cis*-(*S*)	7
$[Co(en)(eddt)](ClO_4)$	$[^-S(CH_2)_2N(Me)CH_2]_2$	$[Co(en)_3]Cl_3 + OH^-$; 2 h, r.t. chrom., two isomers	7
$[Co\{(R)\text{-cysMe}\}_2(en)](ClO_4)$	$[CH_2NCH(CO_2^-)CH_2SMe]_2$	$CoCl_2\cdot 6H_2O$; PbO_2, 70 °C, 20 min; chrom.	8

1. K. Okamoto, W. Wakayama, H. Einaga, S. Yamada and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 165.
2. H. M. Helis, P. de Meester and D. J. Hodgson, *J. Am. Chem. Soc.*, 1977, **99**, 3309.
3. K. Okamoto, K. Wakayama, H. Einaga, M. Ohmasa and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3473.
4. J. Hidaka, S. Yamada and Y. Shimura, *Chem. Lett.*, 1974, 1487.
5. K. Wakayama, K. Okamoto, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1995.
6. T. Isago, K. Igi and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 407.
7. K. Yamanari, N. Takeshita, T. Komorita and Y. Shimura, *Chem. Lett.*, 1981, 861.
8. K. Okamoto, T. Isago, M. Ohmasa and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1077.



(297)

$\{\{\Lambda(S)\text{-}[Co(en)_2(tga-)]\}_2Ag\}^{3+}$



(298)

$\Delta\Lambda\text{-}\{[Co(cyst)(en)_2][Cu(NCMe)_2]_2\}^{6+}$

Table 90 Equilibrium Constants for Ag^+ and $MeHg^+$ Binding to Thiolate (RS^-) and Thioether (RSR) Sulfur[1,2]

Species	K ($dm^3\,mol^{-1}$)
$HOCH_2CH_2SAg$	1.6×10^{13}
$(HOCH_2CH_2)_2SAg^+$	3.4×10^{3}
$[Co(cystAg)(en)_2]^{3+}$	4.0×10^{4}
$[Co(tgaAg)(en)_2]^{2+}$	4.8×10^{4}
$(HOCH_2CH_2)_2SAg^+ S(CH_2CH_2OH)_2$	1.9×10^{2}
$[Co(en)_2(tga)]^{2+} Ag^+ [(tga)(en)_2Co]^{2+}$	1.3×10^{3}
$HOCH_2CH_2SHgMe$	1.3×10^{16}
$[Co(cystHgMe)(en)_2]^{3+}$	4.6×10^{4}
$[Co(tgaHgMe)(en)_2]^{2+}$	3.3×10^{5}
$[Co(en)_2(cyst)]^{2+} HgMe^+ [(cyst)(en)_2Co]^{2+}$	5.3×10^{2}

[1] In water at 25 °C

[2] M. J. Heeg, R. C. Elder and E. Deutsch, *Inorg. Chem.*, 1979, **18**, 2036.

47.8.3 Thioethers

The coordination chemistry of thio-, seleno- and telluro-ethers in transition metal complexes has recently been reviewed in detail.[1094]

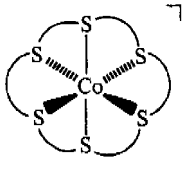
47.8.3.1 Cobalt(II)

Co^{II} is generally regarded as forming only weak bonds to thioether sulfur. This is indicated by the absence of complexes containing monodentate thioether and by only a few reports dealing with bidentate thioether complexes. The latter are of the $[Co(X)_2\{RS(CH_2)_2SR\}_2]$ type (R = Me, Et, Pr; $X = Cl^-, Br^-, I^-, NCS^-$)[1062,1063] and they display spectral and magnetic properties consistent with a *trans* octahedral geometry. This has been verified for $[Co(ClO_4)_2\{MeS(CH_2)_2SMe\}_2]$, which incidently was the first complex containing coordinated perchlorate to be structurally characterized (Table 75).[1064] Its magnetic properties resemble Co^{II} in a square-planar environment due to the weak coordination of ClO_4^- and have been interpreted in terms of a doublet–quartet equilibrium.[1063]

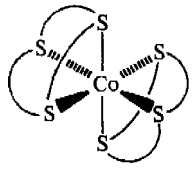
Various mixed-donor bidentate systems have been investigated. N—S bidentates generally form high-spin octahedral $[Co(X)_2(N—S)_2]$ complexes but increasing ligand bulk can result in tetrahedral $[Co(X)_2(N—S)]$. Ligands investigated include 2-(methylthio)aniline (mta),[1065] 2-[(methylthio)methyl]aniline (mtma),[1066] 2-{(methylthio)methyl}pyridine (mtmp)[1067] and *trans*-2-(ethylthio)cyclopentylamine (etcp).[1068] Tris complexes containing these ligands are rare but $[Co(mtmp)_3](ClO_4)_2$ has been reported.[1067]

The structure of *trans*-$[Co(Cl)_2\{HO(CH_2)_2S(CH_2)_2OH\}_2]$ shows the potentially tridentate thioether acting as a bidentate with normal Co—O bonds (207 pm) but long Co—S bonds (251 pm).[1069] Structural studies have also been carried out on high-spin Co^{II} complexes of alkylthioacetate ($RSCH_2COO^-$) ligands.[1070,1071] With Ph_2P(2-MeSPh) and $Ph_2P(CH_2)_3S(CH_2)_3S(CH_2)_3PPh_2$ low-spin five-coordinate $[CoX(P—S)_2]^+$ and $[CoX(PSSP)]^+$ have been characterized by magnetic and spectral studies.[604,1072] Similar complexes exist with the related As—P and Se—P ligands. The NSN tridentate $Me_2N(CH_2)_2S(CH_2)_2S(CH_2)_2NMe_2$ (Me_4daes) forms high-spin (μ = 4.4–4.5 BM) five-coordinate $[Co(X)_2(Me_4daes)]$ complexes ($X = Cl^-, Br^-, I^-$) and visible spectra indicate trigonal bipyramidal structures in the solids.[1073] This geometry also occurs with $[CoBr(Bu^t\text{-}NS_3)]PF_6$ ($Bu^t\text{-}NS_3 = N(CH_2CH_2SBu^t)_3$). All three sulfur atoms lie in the equatorial plane with the Co atom displaced 35 pm toward the apical bromine (Co—S, 238 pm).[1074]

Cobalt(II) complexes of polythioethers include those of 1,2-bis-(*o*-methylthiophenylthio)ethane,[1075] and the macrocyclic ligands 1,4,7-trithiacyclononane ([9]aneS$_3$)[1076] and 1,4,7,10,13,16-hexathiacyclooctadecane ([18]aneS$_6$).[1077] The structure of $[Co([18]aneS_6)](picrate)_2$ shows the cobalt atom in a distorted octahedral environment with each three-sulfur segment coordinated facially to give the *meso* geometry (**299**). Facial coordination of the trithia ligands is also found in the tetragonally distorted CoS_6 complex $[Co([9]aneS_3)_2](BF_4)_2$ (**300**),[1076] but here $Co—S_{eq} > Co—S_{ax}$, whereas the reverse occurs with $[Co([18]aneS_6)](picrate)_2$.[1077] The low spin ($\mu$ = 1.8 BM) of the latter complex is unusual since thioether donors are normally regarded as relatively weak-field ligands. However this is the only $Co(SR)_6^{2+}$ system for which magnetic and ESR data have been reported.



(299)

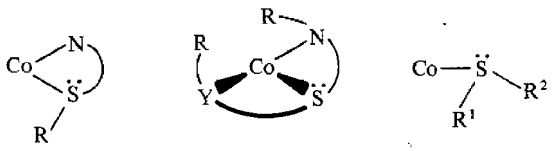


(300)

47.8.3.2 Thioethers, sulfoxides and sulfones, cobalt(III)

Thioether complexes are mostly of the bidentate (**301**) or multidentate (**302**) type. Monodentate systems (**303**) are rare but are known (equation 167a),[1078] and in such cases they provide useful starting materials since the thioether ligand is easily displaced.

$$Co(NO_3)_2 + 2DMGH_2 + NaBr + Me_2S \xrightarrow[EtOH,\ heat]{O_2} \underset{\text{brown}}{trans\text{-}[CoBr(Me_2S)(DMGH)_2]} \quad (167a)$$



(301) (302) (303)

Coordinated thioether S is often asymmetric. In (**302**) the asymmetry is frozen by the configuration of the attached chelate rings but in (**301**) it is not and inversion is fast. Conventional resolution *via* diastereoisomeric salts has never been substantiated for a purely enantiomeric Co—SR^1R^{2n+} system devoid of other chirality. ^{13}C and ^1H studies on diastereoisomeric systems[1079] however show that inversion rates are normally of the order $0.1–10\,s^{-1}$, which makes coordinated thioethers decidedly more configurationally labile than organic sulfonium salts. The effects of asymmetry in (**302**) are readily seen in diastereoisomeric systems where the lone pair on S is often stereospecifically orientated. It usually directs stereochemical change and ligand replacement processes.

(*i*) *Bidentates*

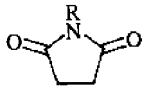
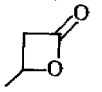
Kolhari and Busch were the first to describe the alkylation of Co^{III}—SR when they treated (N,S)[Co(cys)$(en)_2$]I with MeI in aqueous methanol.[1030] However they incorrectly described the product as (N,O)[Co(cysMe)$(en)_2$]I_2 containing carboxylate rather than thioether coordination. The (N,S) and (N,O) chelates have subsequently been clearly distinguished (equations 168 and 169), and the methylation reaction gives the (N,S) isomer with retention of the Co—S bond.[1080] Deutsch and coworkers in a comprehensive investigation of alkylating reagents describe the versatility of this reaction.[1081,1082] Some of this information is collected in Table 91. Primary and secondary alkyl groups, activated double bonds, carbocations, and strained groups have been added. Alkylation of $[Co(cyst)(en)_2]^{2+}$ with methyl vinyl ketone is first order in both reactants and in $[H^+]$, consistent with the mechanism given by equation (170).[1082] Where crystal structures are available (Table 85) they show alkylation occurs stereospecifically at the axial lone pair with the R group directed between adjacent ethylenediamine chelates,* *e.g.* (**304**). Subsequent mutarotation does not usually occur.

$$\Lambda\text{-}(N,S)[Co\{(R)\text{-cys}\}(en)_2]ClO_4 + MeI \xrightarrow{DMSO} \underset{\text{brown}}{\Lambda\text{-}(N,S)[Co\{(R)\text{-cysMe}\}(en)_2](ClO_4)_2} \quad (168)$$

$$cis\text{-}[Co(DMSO)_2(en)_2](ClO_4)_3 + (R)\text{-HcysMe} \xrightarrow{DMSO} \underset{\text{orange}}{\Delta,\Lambda\text{-}(N,O)[Co\{(R)\text{-cysMe}\}(en)_2](ClO_4)_2} \quad (169)$$

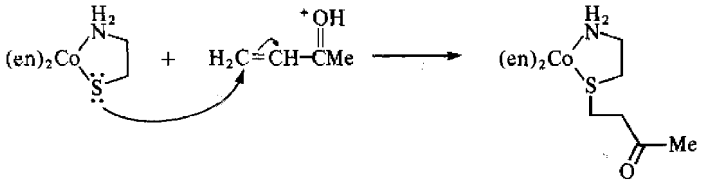
Bidentate thioether complexes are reasonably stable in neutral and acidic aqueous solutions but readily hydrolyze in alkali, and the process appears to be reversible. Oxidation to the sulfoxide is difficult but once thioether S is dissociated from the metal becomes relatively easy (Scheme 95).

Table 91 Preparations: Thioether Complexes [Co$(en)_2$(cystR)]$(ClO_4)_3$

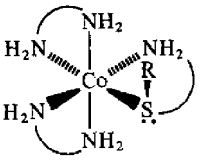
R	*Reagent, conditions*	*Ref.*
Me, CH_2R^1 (where R^1 is almost anything)	RX (X = Cl, Br, I); DMF; r.t.	1
$(CH_2)_2CO_2H$, $(CH_2)_2CONH_2$, $(CH_2)_2COMe$ $(CH_2)_2CHO$, $(CH_2)_2CN$, $CHCHCO_2H$, $CH(CO_2H)CH_2CO_2H$, $CHCONHCOCH_2$, $CHCON(Me)COCH_2$, $CHCON(CH_2Me)COCH_2$, $CHCON(Ph)COCH_2$	 or alkene, r.t., 6 M $HClO_4$ 0.5–2 h, chrom.	2
Me, Et, Bu^t	ROH, $MeSO_3H$, r.t., 0–1 week	2
$CH(Me)CH_2CO_2H$	 DMF, $BF_3{\cdot}OEt_2$, r.t., 4 d	2

1. R. C. Elder, G. J. Kennard, M. D. Payne and E. Deutsch, *Inorg. Chem.*, 1978, **17**, 1296.
2. L. Roecker, M. H. Dickman, D. L. Nosco, R. J. Doedens and E. Deutsch, *Inorg. Chem.*, 1983, **22**, 2022.

*The IUPAC designation (*S*) or (*R*) at sulfur depends on the nature of the substituent. When R = H, Me, Et, the Λ-[Co$(NH_2\text{-SR})(en)_2]^{3+}$ complex takes the (*R*) configuration but for heavier substituents (*e.g.* O, S) the configuration is (*S*). For the sake of consistency with the sulfenate and disulfide complexes we will designate the substituent as taking precedence in all cases, *i.e.* (*S*) for all substituents.



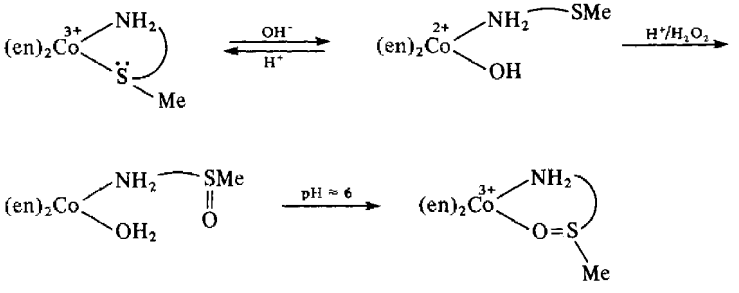
(170)



(304)

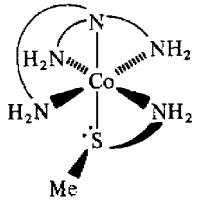
$\Lambda(S)$-$[Co(H_2N{-}SR)(en)_2]^{3+}$

Subsequent coordination now ocurs *via* the O atom, probably with displacement of coordinated water. This chemistry resembles that of organic sulfonium salts (R_3S^+) and thioethers.



Scheme 95

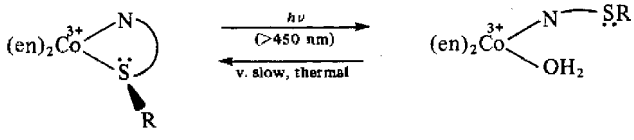
Inversion at Co^{III}—SR^1R^2 is fast (0.1–10 s^{-1}) but diastereoisomeric systems have been detected by ^1H and ^{13}C NMR spectroscopy. Thus (**305**) shows clearly resolved signals of the tren ligand arising from the chiral thioether.[1079] Also the related *t*-(N,S)[Co{(*R*)cys}(tren)]$^{3+}$ chelate shows immediate ^1H-NMR spectral changes on deprotonation of the dangling equatorial carboxylate arising from rapid (< 5 s) mutarotation of the (*R*)S(*R*)C, (*S*)S(*R*)C diastereoisomeric mixture. Thus inversion appears to be 10^5–10^7 times more rapid than for uncoordinated sulfonium salts, a result in keeping with other M—SR^1R^2 systems.[1083]



(305)

t-[Co(cystMe)(tren)]$^{3+}$

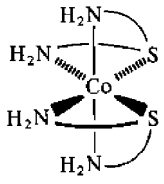
Photolysis in the ligand field region leads to photoaquation (equation 171), while irradiation in the charge-transfer region leads to some reduction to $Co^{2+}_{(aq)}$.[1049] The thioether S atom in [Co$(RSCH_2CH_2NH_2)(en)_2]^{3+}$ (R = alkyl, aryl) has been shown to act as a lead-in centre for inner-sphere reduction of the metal by $Cr^{2+}_{(aq)}$, with more bulky R slowing down the rate and carboxylate substituents increasing the rate by chelating to the reductant.[1097]



(171)

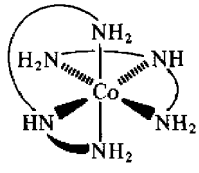
(*ii*) *Multidentates*

Preparations and structures are given in Tables 92 and 93 respectively. Bridging thioether (**302**) prefers the bent configuration with adjacent chelate rings in different planes. Thus $[Co(daes)_2]^{3+}$ adopts only the *u-fac* configuration (**306**), whereas the analogous all N system prefers the *mer* geometry (**307**). Similarly, $[Co(X)_2(eee)]^{n+}$ is *s-cis* (**308**) for X = Cl^-, Br^-, NO_2^-, NCS^-, $C_2O_4^{2-}$, bipy, as is $[Co(Cl)_2(tet)]^+$, while $[Co(X)_2(ete)]^{n+}$ prefers the *u-cis* geometry (**309**) but does adopt *trans* (**310**) for X = Cl^- (60% *u-cis*, 40% *trans* at equilibrium).[1084] The corresponding all-N complexes $[Co(Cl)_2(trien)]^+$, $[Co(Cl)_2(3,2,3\text{-tet})]^+$ and $[Co(Cl)_2(2,3,2\text{-tet})]^+$ adopt *s-cis*, *u-cis* and *trans,trans*, and *trans* configurations respectively. This stabilization of the bent geometry at S is not well understood but may be connected with its larger size. The reader is referred to a recent article by Abel, Bhargava and Orrell on such aspects.[994] In (**308**) the lone pair on S is stereospecifically orientated and only $\Lambda(R,R)$ and $\Delta(S,S)$ configurations obtained, but for (**309**) and (**310**) the planar S may be (*R*) or (*S*). This can direct subsequent stereochemical change.[1084,1085] Thus inversion at S must occur for the stereochemical change (**309**) *R,S* to (**308**) *R,R*, and (**310**) *R,R* gives stereospecific (**309**)-$\Lambda(R,R)$ and (**308**)-$\Lambda(R,R)$ products if the asymmetry at S is maintained. Little is known about such processes compared to the well-documented chemistry for coordinated N. Worrell and colleagues have synthesized several thioether chelates in order to study the effects of the long Co—S bonds on inner-sphere electron transfer reactions *via trans* ligands.[1089,1090] The cations (**311**) and (**312**) show increased rates of reduction by $Fe^{2+}_{(aq)}$ compared to their all N analogues.[1090,1096] One recent study[1086] serves to highlight the ease of inversion at thioether S and suggests that the restriction of geometrical configuration resultant upon retention at S is not as certain here as it is in N multidentates. The ready interconversion of the optically active brown (**313**) and green (**314**) isomers of [Co{1,10-bis(salicylideneamino)-4,7-dithiadecane}]$^+$ (equation 172), can be accomplished *via* a trigonal twist process with simultaneous inversion at both chiral S centres. The alternative possibility of retention at S would require a complex series of edge displacements and predicts the opposite absolute configuration about the metal. Rapid (0.1–10 s^{-1}) inversion at coordinated S allows for flexible rearrangement in such multidentates. The structure of (**313**; Table 93) contains the very unusual planar thioether ligand.



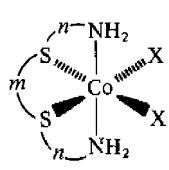
(306)

Λ-*asym,fac*-(+)$_{589}$-$[Co(daes)_2]^{3+}$



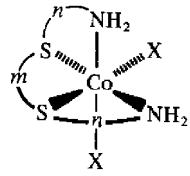
(307)

mer-$[Co(dien)_2]^{3+}$



(308)

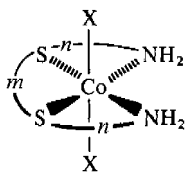
Λ-*sym,cis* or *cis*-α
blue, X = Cl^-



(309)

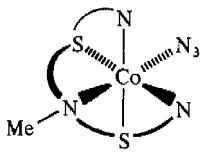
Δ-*asym,cis* or *cis*-β
red-violet, X = Cl^-

$n = m = 2$ (eee)
$n = m = 3$ (ete)
$n = 3, m = 2$ (tet)



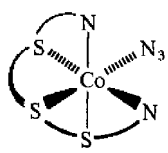
(310)

trans
green, X = Cl^-



(311)

$[CoN_3(NSNSN)]^{2+}$



(312)

$[CoN_3(eee)]^{2+}$

Cyclic 14- and 15-membered tetrathioether ligands (**315**) and (**316**) also form $[CoX_2(S_4)]^+$ complexes with (**315**) preferring the *cis* geometry and (**316**) being *trans* with planar S donors (Table 92). *cis*-$[CoCl_2(ttp)]^+$ undergoes normal metathetical reactions to form *cis*-$[CoX_2(ttp)]^+$ species but *trans*-$[CoCl_2(ttx)]^+$ decomposes readily in hot water to give Co^{2+}_{aq}.[1095]

Complex	Preparation	Properties	Ref.
fac-[Co(X)$_3$(daes)] (X = NO_2^-, Cl^-)	$CoCl_2$ + L·2HCl + $NaNO_2$; MeOH, air, 15 min	Yellow-orange (NO_2); green (Cl) (structure Table 93)	1
asym,fac-[Co(daes)$_2$]Y_3 (Y = Cl^-, Br^-, ClO_4^-)	$[Co(NH_3)_6]Cl_3$ + L·2HCl + LiOH; charcoal, H_2O, 95 °C, 2 h	Orange; same isomer by different methods; resolved using (+)-AsO(tart)$^-$	2
fac-[Co{(*R*)-cmtp}$(NH_3)_3$]Cl	$[Co(NO_3)_3(NH_3)_3]$ + L; H_2O, 50 °C, 1 h, chrom.	Red-violet; two isomers; ^{13}C NMR	9
sym,cis-[CoX_2(eee)]Y (X = NO_2^-, Cl^-, Br^-, NCS^-, N_3^-; X_2 = CO_3^{2-})	$CoCl_2 \cdot 6H_2O$ + L + HCl; MeOH, 50 °C, air, $NaNO_2$	Orange (NO_2); blue (Cl); ^{1}H NMR; IR; resolved using (−)-[Co(en)$(C_2O_4)_2]^-$; CD, ORD	3, 4, 5
[Co(Cl)$_2$(ete)](ClO_4)	$Co(OAc)_2 \cdot 4H_2O$ + $NaNO_2$ + L + HCl; MeOH, 2 h, 0 °C; HCl	Green (*trans*) ε_{630} 58; red-violet (*asym,cis*) ε_{537} 246	5
[Co(Cl)$_2$(tet)]	$Co(OAc)_2 \cdot 4H_2O$ + $NaNO_2$ + L + HCl; MeOH, 2 h, 0 °C, HCl	Blue (*sym,cis*); red-violet (*asym,cis*)	5
asym,cis-[Co(Cl)(NO_2)(ete)](ClO_4)	[Co$(NO_2)_2$(ete)]Cl + HCl	Red; Cl *trans* to S (structure Table 93); ^{1}H NMR; IR; ε_{522} 378	6
asym,cis-[Co(CO_3)(ete)](ClO_4)	[CoCl(NO_2)(ete)]Cl + $(NH_4)_2CO_3$; heat, 15 min	Red-purple (useful for synthesis); ^{1}H NMR; IR; ε_{524} 387	6
sym,cis-[Co(Cl)$_2${(*R,S*)-epe}]Cl	$CoCl_2 \cdot 6H_2O$ + L·2HCl; MeOH; air + LiOH, 35–40 °C, air	Blue; resolved using (+)-SbO (tart), stereospecific; ε_{610} 313; other complexes, X = Br, 0.5CO_3	7
sym,cis-[Co(Cl)$_2${(*S,S*)-pep}]ClO_4	$CoCl_2 \cdot 6H_2O$ + L; MeOH, air; HCl	Blue; two isomers (*exo* 65%, *endo* 35%)	8
[CoX{ecee}]Y_2 (X = Cl^-, Br^-, NO_2^-, NCS^-)	$CoCl_2 \cdot 6H_2O$ + L; MeOH, air, HCl	Violet (Cl); α,α structure	10
[CoX{NSN(Me)SN}]Y_2 (X = Cl^-, Br^-, N_3^-, NO_2^-, N_3^-, NCS^-)	$CoCl_2 \cdot 6H_2O$ + L; MeOH, air, HCl	Violet (Cl); α,α structure	11
[Co(atch)](ClO_4)$_3$	$Co(OAc)_2$ + L + C; H_2O, O_2, 2 h, chrom.	Red; ε_{484} 708; ^{1}H NMR; resolved using (+)-SbO(tart)	12
[Co(ten)](Cl)$_2$(ClO_4)	$Co(OAc)_2$ + L; MeOH, O_2, 5 h; chrom.	Red; ε_{484} 574; ^{1}H NMR; resolved using chrom.	13
[Co(azacapten)](ClO_4)$_3$	[Co(ten)$(Cl)_2$](ClO_4) + Li_2CO_3 + NH_4OH + HCHO; H_2O, 1 h, chrom.	Red; ε_{489} 831; ^{1}H NMR; resolved using chrom. (structure Table 93)	13
cis-[Co(Cl)$_2$(ttp)](ClO_4)	$Co(ClO_4)_2 \cdot 6H_2O$ + L + LiCl; $MeNO_2$, 5 h	Red-violet; ε_{535} 654	14
trans-[$CoCl_2$(ttx)](ClO_4)	$Co(ClO_4)_2 \cdot 6H_2O$ + L + LiCl; $MeNO_2$, r.t.	Green; ε_{630} 69	14

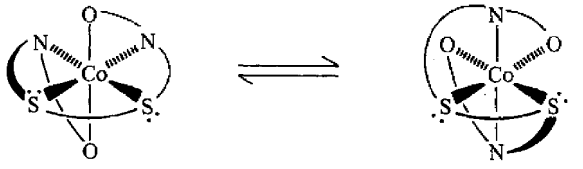
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Table 93 Structures: Multidentate Thioether–Cobalt(III) Complexes

Complex	*Structural data*[a]	*Comments*	*Ref.*
fac-[Co(Cl)$_3$(daes)]	CoS 221.6; CoCl 227–8; CoN 193.3, 195.9; SCoCl 175–6°; CSC 102–7°	Bent configuration at S; no *trans* Δ*r*	1
$(-)_{589}$-*asym,fac*-[Co(daes)$_2$]Cl$_3$·2H$_2$O	CoS 224.4, 224.8; CoN 197–9; SCoS 19.2°C; CSC 102.2°	Bent configuration at S; no *trans* Δ*r*	2
asym,cis-[Co(Cl)(NO$_2$)(ete)]Cl	CoS 222–4; CoN 196–9; CoCl 227; CoN(O$_2$) 209	Cl *trans* to S	3
Δ-*trans*(*S,O*)-[Co{(*S*)-aehc}gly](ClO$_4$)	CoS 222.3	(*R*) configuration for asymmetric S atom	4
[Co(ONSSNO)]I (two isomers)	CoS 224–5; CoO 189–190; CoN 194–6	Brown isomer (NSSN planar); green (two forms NSSN bent, planar)	5
[Co(azacapten)](S$_2$O$_6$)$_{1.5}$·4H$_2$O	CoS 217–224; CoN 194–198	Sexidentate, encapsulated	6
$(+)_{510}$-[Co(azacapten)](ZnCl$_4$)Cl	CoS 222.6; CoN 200.9	Optically active complex	6
[CoCl(eeee)]Cl(ClO$_4$)	CoS 223–4; CoCl 226.8; CoN 196.8, 197.8	Racemate; all-bent configuration	7

[a] Bond lengths in pm.

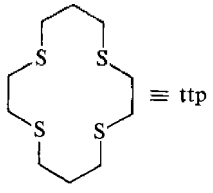
1. G. Baumann, L. G. Marzilli, C. L. Nix and B. Rubin, *Inorg. Chim. Acta*, 1983, **77**, L35.
2. A. Hammershoi, E. Larsen and S. Larsen, *Acta Chem. Scand., Ser. A*, 1978, **32**, 501.
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6. L. R. Gahan, T. W. Humbley, A. M. Sargeson and M. R. Snow, *Inorg. Chem.*, 1982, **21**, 2699.
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(172)

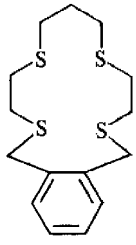
(313) $(+)_{589}$-(*S,S*)-[Co(ONSSNO)]$^+$ brown

(314) $(-)_{589}$-(*R,R*)-[Co(ONSSNO)]$^+$ green



≡ ttp

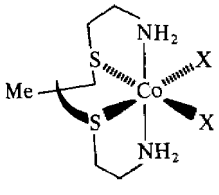
(315)



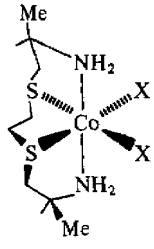
≡ ttx

(316)

Steric or conformational restraints imposed by substituents on the ligand can impose stereoselectivity or can enforce some stereospecificity. Thus (*R*)-epe stereospecifically forms (**317**) with the methyl group equatorial rather than axial,[1087] and (*S,S*)-pep also prefers (65%) the Λ configuration (**318**) with the methyl groups adjacent to X.[1088] In both systems the configuration about Co and S

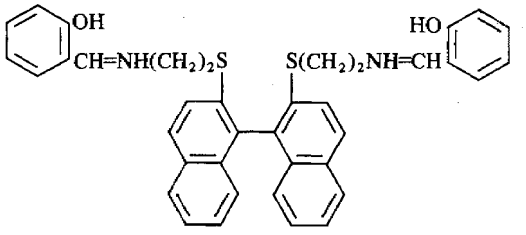


(317) Λ-(*R,R*)-[CoX$_2${(*R*)-epe}]$^+$

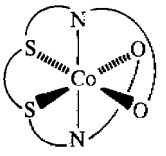


(318) Λ-(*R,R*)-[CoX$_2${(*S,S*)-pep}]$^+$

is maintained in various displacements of X. Gahan and O'Connor have used the optically-active binaphthyl fragment (**319**) to stereospecifically form the cobalt sexidentate (**320**) in which the two S donors have the (*S*) configuration.[1091]



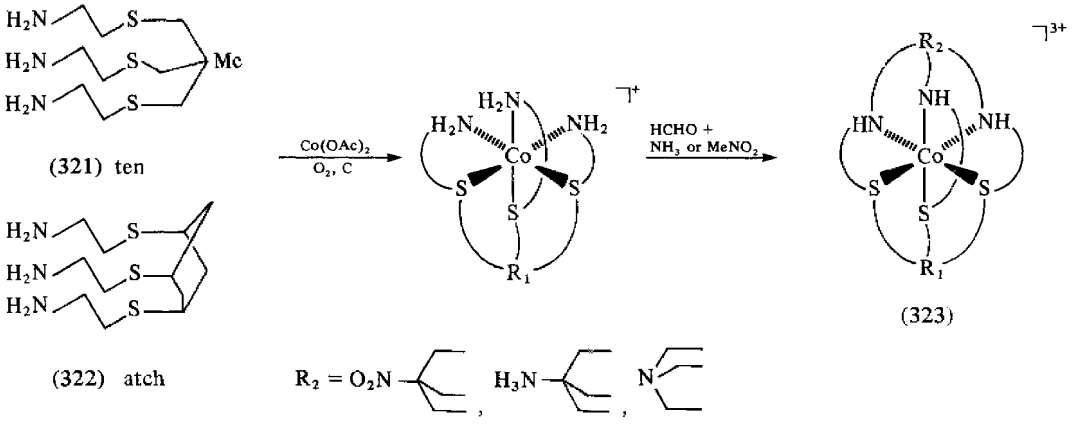
(319)



(320)

Λ-(+)$_{546}$-[Co{(*S*,*S*)-nmep}]$^+$

Sargeson and coworkers have synthesized a number of thioether cryptate sexidentates including (**321**)[1092] and (**322**)[1093] condensing the appropriate trithiol with aziridine. The trigonally positioned amine groups in their Co^{III} complexes (Table 92) have been capped by condensation with HCHO and an appropriate nucleopile to form the totally encapsulated complexes (**323**; Scheme 96). These have been resolved into their optical enantiomers which can be reduced to the chiral Co^{II} chelates and reoxidized by O_2 with full retention of chirality. Indeed it is very difficult to remove the metal from within the cage under any condition.

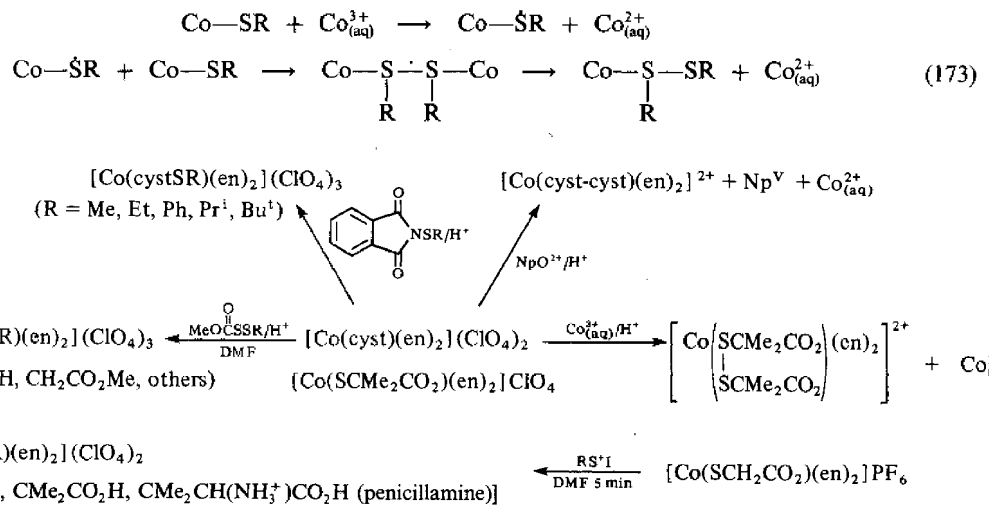


Scheme 96

47.8.4 Disulfides (RSSR), Cobalt(III)

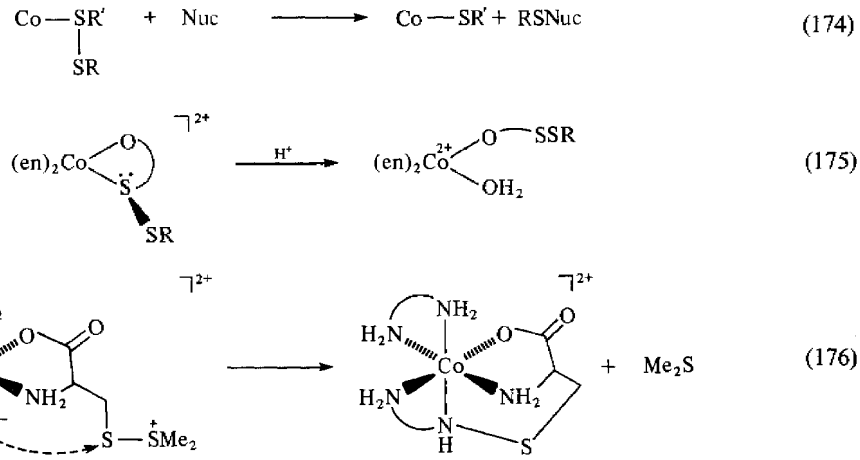
Interest in these systems stems largely from the influence of metals on the thiolate–disulfide redox couple found in blue copper proteins. The synthesis of Co^{III} disulfides has been largely due to Deutsch and coworkers.[1098] Single-electron oxidation of Co^{III}—SR^{n+} by Np^{IV}, $Co^{3+}_{(aq)}$, or $Fe^{3+}_{(aq)}$ leads to symmetrical disulfides containing only one coordinated S atom. The reaction (equation 173) is generally fast and is considered to proceed *via* a free radical mechanism. Unsymmetrical disulfides may be generated using potent RS^+ species such as *N*-thiophthalimides, sulfonyl iodides, and methoxycarbonyl alkyl disulfides, with the latter being possibly the most useful because of their generality and ease of preparation. The reactions proceed *via* bimolecular attack of the coordinated thiolate on RS^+Y^-; examples are given in Scheme 97. The coordinated S atom is asymmetric in the product (**323**; equation 173) and structural studies (Table 85) suggest that with diastereoisomeric systems only the axial lone pair is used with the added SR group being located between chelate rings, that is the thioalkylation is probably stereospecific at coordinated S. However, there is no information on the optical stability of the coordinated disulfide. Electronegativity arguments would place RS^+ somewhere between R^+ and O^{2-}, and whereas Co^{III}–thioether systems invert fairly rapidly (*cf.* Section 47.8.3.2.i). Co^{III} sulfenates are optically stable. Mutarotation or racemization at Co^{III}–disulfide probably lies somewhere in between.

Coordinated disulfides are very susceptible to nucleophilic cleavage and this is often an obstacle to their preparation. Nucleophiles such as OH^- and RSH cause rapid regeneration of the Co^{III} thiol



Scheme 97

except when the S—S bond is protected by bulky groups (equation 174). Thus when R = Bu^t and $C(Me)_2CO_2H$, the $[Co(tga\text{-}SR)(en)_2]^{2+}$ complex is reasonably stable and hydrolysis of the Co—S bond now becomes a competitive process.[1098] The S—S bond is more inert in acidic solution but hydrolysis of the Co—S bond occurs (equation 175). The susceptibility of the S—S bond to nucleophilic attack is displayed by the intramolecular formation of a coordinated sulfonamide *via* a sequence of reactions including that with the solvent DMSO (equation 176).[1099] The last step in this process involves attack of deprotonated coordinated ethylenediamine on the activated disulfide.



47.8.5 *Trans* Effect of Coordinated Sulfur

Sulfur ligands have a tendency to labilize groups *trans* to them in octahedral cobalt(III) complexes. In recent years structural and NMR evidence has been correlated with rates of substitution to justify semiquantitatively the statement that a longer than normal bond represents a weaker bond in a kinetic sense; that is ground-state destabilization is a major factor influencing rates of substitution. Recent publications in this area may be consulted for details.[426,927,1100] Crystal structure data (Table 72) clearly show longer *trans*-NH_3 bonds compared to *cis*-NH_3 in S-bonded SO_3^{2-} complexes and this is extended and correlated (Scheme 98).[1081] For SO_3^{2-} and $S(O)_2R^-$ complexes rates of replacements of the *trans* ligand have been correlated with this lengthening in both amine[426,927] and dimethylglyoxime[1100,1101] complexes. Such studies assume a purely dissociative reaction, with loss of *trans*-L (k_1 for loss of NH_3 in equation 177) being a measure of the observed rate. This gives $k(SO_3^{2-})/k\{S(O)_2R^-\} \approx 150$ corresponding to a Δr of ~ 3 pm. A comparison of the type $k(SO_3^{2-})/k(NH_3$ or $H_2O)$ is more difficult, but Yandell and Tomkins[927] estimate a value of $\sim 10^8$ corresponding to $\Delta r = 9$–10 pm. SO_3^{2-} is not the best *trans*-labilizing ligand in octahedral Co^{III}

chemistry and, although structural evidence is lacking, the extended kinetic *trans* effect given by Scheme 99 has been obtained from dimethylglyoxime complexes with labilization of *trans*-MeOH.[1100]

$$SO_3^{2-} > S(O)_2R^- \geqslant S(O)R^- > SR^- > SSO_3^{2-} \approx S(R)R \approx S(SR)R$$

Oxidation state of sulfur	IV	II	0	−II	−II	−II	−I
Δr (pm) = (*trans* Co–N bond length) − (*cis* Co–N bond length)	9	≈6	5–7	≈4	≈1	1–0	1–0

Scheme 98

$$[Co(SO_3)(NH_3)_5]^+ \xrightarrow[\text{slow}]{k_1} [Co(SO_3)(NH_3)_4]^+ + NH_{3(aq)} \xrightarrow[\text{fast}]{Y^-} \textit{trans}\text{-}[Co(SO_3)Y(NH_3)_4] \quad (177)$$

$$CH_3^- > C_6H_5^- > SO_3^{2-} > (MeO)_2P(O)^- > RS(O)_2^-$$

Δk_1 (equation 177)	900	300	100	50	1

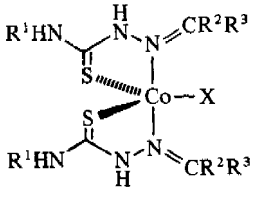
Scheme 99

The absence of a structural effect for SSO_3^{2-}, S(R)R and S(SR)R is consistent with a lack of formal negative charge on the coordinated S atom. This results in a decreased σ-donor ability and a longer Co—S bond, with the *trans* Co—N bond returning to its normal value of ~195 pm (Table 85). However anation of *trans*-$[Co(SSO_3)(H_2O)(en)_2]^+$ is some 10^4 times faster than anation of similar amine complexes[950] demonstrating that kinetic effects are more sensitive than structural ones.

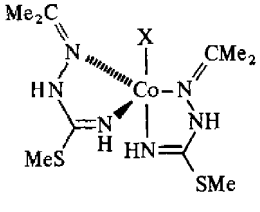
Deutsch and coworkers have used a simple harmonic oscillator model to relate the kinetic effects (as measured by activation enthalpies) to the energy necessary to stretch the *trans* N bond, $\Delta H^{\ddagger}S(O)_2R^- - \Delta H^{\ddagger}(SO_3^{2-}) = k^1\{(r^{\ddagger} - r\{S(O)R_2^-\})^2 - (r^{\ddagger} - r(SO_3^{2-})^2\}$, which gives $r^{\ddagger} = 320$ pm for the transition-state complex.[426] This represents a stretching of some 120 pm. This value may be used to estimate $\Delta H^{\ddagger}$ for other (perhaps hypothetical) dissociation processes. More general articles on the *trans* effect emphasizing its structural and electronic aspects are available.[1102–1104]

47.8.6 Thiosemicarbazones, Cobalt(II)

A variety of CoX_2L_2 complexes have been prepared[1105,1106] where L = $R^1NHCSNHN{=}C(R^2)(R^3)$ and X = Cl^-, Br^-, I^-. When R^2 and R^3 are alkyl, the ligand is (S,N) bidentate and the complexes are five coordinate with a trigonal-bipyramidal stereochemistry (**324**). However if R^2 and/or R^3 are aryl, they are tetrahedral with S_2X_2 donor arrangements. Structures are known for both five-coordinate $[CoXL_2]X$ (L = $H_2NCSNHN{=}C(Me)_2$, X = Cl^-;[1107] L = $PhNHCSNHN{=}C(Me)_2$, X = Br^-)[1106] and four-coordinate $[Co(I)_2L_2]$ [L = $H_2NCSNHN{=}C(Ph)(Me)$] systems.[1108] Structural investigations on the cobalt(II) complexes of acetone *S*-methylthiosemicarbazone have shown that the ligand is an (N,N) bidentate and that both five-coordinate[1109,1110] (**325**) and octahedral geometries obtain.[1111]



(324)

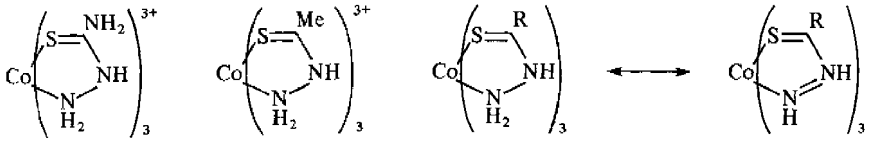


(325)

47.8.7 Thiosemicarbazides, Cobalt(III)

Tris complexes of $H_2NCSNHNH_2$ (Htsc) were first reported by Jensen and Rancke-Madsen,[1112] and Sadykova and coworkers investigated complex formation using various Co^{II} salts in aqueous solution. They found that the cation formed was in fact $[Co(Htsc)_3]^{3+}$ (**326**).[1113] Samus and Ablov[1114]

separated the violet (ε_{429} 414) facial and green (ε_{420} 1900) meridional isomers and Sun and Harris[1115] resolved both with the $(+)_{589}$-SbOtartrate anion and assigned geometric structures from comparisons of electronic spectra and absolute configurations from CD and ORD measurements. Gabel and Larsen[1116] have likewise prepared and resolved the tris(thioacethydrazide) complex $[Co(Htah)_3]^{3+}$ (**327**), and on the basis of a single methyl ^1H NMR signal have assigned it as the *fac* isomer. The complexes can be easily deprotonated (pK_a = 4.77, 6.17, 7.53 for *fac*-$[Co(Htsc)]^{3+}$; 1.4, 3.17, 4.63 for *fac*-$[Co(Htah)_3]^{3+}$) to give the neutral species (**328**), but *fac* to *mer* isomerization then slowly occurs, which on addition of acid results in *mer*-$[Co(Htsc)_3]^{3+}$. This isomer slowly reconverts to the more stable *fac*-$[Co(Htsc)_3]^{3+}$ ion with inversion of configuration.[1115,1116]

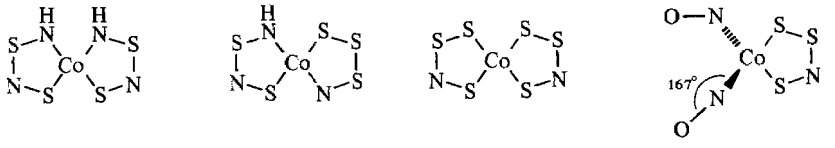


(326) (327) (328)

47.8.8 Thionitro and Thionitrosyl

Addition of $(NSCl)_3$ to $[CoH\{P(OPh)_3\}_4]$ dissolved in THF under argon forms the green thionitrosyl $[Co(NS)(Cl)_2\{P(OPh)_3\}_2]$, which on exposure to oxygen changes to yellow-green $[Co(NSO)(Cl)_2\{P(OPh)_3\}_2]$ containing the thionitro monoanion.[1117] This reaction resembles the oxidation of coordinated nitrosyl to coordinated nitro (Section 47.4.1.3) and the thionitro group is presumably coordinated as Co—N(S)O. A crystal structure of $[Co(NSF)_6](AsF_6)_2$ is available and demonstrates Co—N bonding.[1118]

The reaction of $CoCl_2$ with S_4N_4 in refluxing MeOH under N_2 produces a mixture of $[Co(S_2N_2H)_2]$ (**329**), $[Co(S_2N_2H)(S_3N)]$ (**330**) and $[Co(S_3N)_2]$ (**331**), which have been separated by preparative TLC and crystallized as dark black solids.[1119] Subsequent attempts to prepare $[Co(S_3N)_2]$ by the direct reaction of $CoBr_2$ with $(PPN)(S_3N)$ met with only limited success.[1120] IR assignments support bidentate (S,S) coordination with *cis* square-planar geometries.[1119] The reaction of $[Co_2(CO)_8]$ with S_4N_4 in deoxygeneated benzene gives a black explosive solid formulated either as polymeric $[Co_2(CO)(N_4S_4)]$[1121] or as $[CoN_4S_4]$.[1122] The absence of obvious Co—S stretch frequencies infers Co—N bonding of the N_4S_4 unit. Treatment with refluxing acetone gives $[Co(S_2N_2H)_2]$, while nitrosation in pentane leads to readily sublimable violet $[Co(NO)_2(S_3N)]$.[1123] The IR spectrum of this latter complex shows two NO stretching absorptions (1836, 1778 cm^{-1}) characteristic of a pseudotetrahedral geometry and this has been confirmed by its structure (**332**; Table 12).



(329) (330) (331) (332)

47.8.9 Sulfamates, Sulfonamides and Isothiocyanates, Cobalt(III)

Preparations are given in Table 94. The N-bound sulfamate complex $[Co(NH_2SO_3)(NH_3)_5]^{2+}$ (pK_a, 5.83) is easily made but it spontaneously isomerizes in aqueous acid to the O-bound isomer $[Co(OSO_2NH_3)_5]^{2+}$,[1125] ($pK_a \approx 13.1$), which itself aquates primarily by an acid-catalyzed path, $k = k_1 + k_2[H^+]$ (equation 178). In alkaline solution both the N-bound sulfamate and its conjugate base undergo OH^--catalyzed hydrolysis (equation 179), with the latter reaction being very slow.[1126] The O-bound isomer is more reactive under the same conditions (k_{OH} = 20 $mol^{-1}\,dm^3\,s^{-1}$).[907] The protonated sulfamide complexes $[Co(NH_2SO_2NHR)(NH_3)_5]^{3+}$ aquate more rapidly ($k = 1.3 \times 10^{-2}\,s^{-1}$, R = H; $k > 0.11\,s^{-1}$, R = *p*-MeC_6H_4) but their acidity, $pK_a = -0.24$ (R = H), makes this apparent only in acid solutions; the basic forms appear to be quite stable.[1126] Their reduction by $Cr^{2+}_{(aq)}$ in acid solution is considered to occur *via* a bridged outer-sphere intermediate.[1127]

Table 94 Preparations: Sulfamate, Sulfamide, Sulfonamides, Ureas, Carbamates of Cobalt(III)

Complex	*Ligand*	*Preparation, properties*	*Ref.*
$[Co(NH_2SO_3)(NH_3)_5](ClO_4)_2$	Sulfamate	$[Co(OCO_2)(NH_3)_5](NO_3) + NH_2SO_3H$; aq, pH 2.6, 4 weeks, r.t.; yellow; ε_{488} 60.2, ε_{345} 49.6; pK_a 5.83; $k_{OH} = 1.0 \times 10^{-2}\,mol^{-1}\,dm^3\,s^{-1}$	7
$[Co(NHSO_2NH_2)(NH_3)_5](Br)(ClO_4)$	Sulfamide	$[Co(OSO_2CF_3)(NH_3)_5](CF_3SO_3)_2 + L$ + 2,6-lutidine; acetone, 14 h, r.t.; red; ε_{501} 78	8
$[Co(NHSO_2R)(NH_3)_5](ClO_4)_2$	Toluenesulfonamides	$[Co(NH_3)_5OH_2](ClO_4)_3 + MeCONMe_2 + L$ + 2,6-lutidine; heat 6 h; chrom.	8
$[Co\{SC(O)NHPh\}(NH_3)_5](ClO_4)_2$	Phenyl thiocarbamate	$[Co(NH_3)_5OH_2](ClO_4)_3 + L + Me_2BzN$; DMF, 2 h, r.t., chrom.; red-brown; ε_{510} 98.6, ε_{262} 24 200	6
$[Co\{OC(NH_2)_2\}(NH_3)_5](ClO_4)_3$	Urea	$[Co(NH_3)_5OH_2](ClO_4)_3 + L$; Me_2CONH_2, 0.75 h, 90 °C; pink; ε_{514} 67.4. $[Co(OSO_2CF_3)(NH_3)_5](CF_3SO_3)_2 + L$; sulfolane, r.t., 75 min; ε_{517} 79	1, 3 5
$[Co\{OC(O)NH_2\}(NH_3)_5](ClO_4)_2$	Carbamate	$[Co(NH_3)_5OH_2](ClO_4)_3 + NaNCO$	2, 3
$[Co\{OC(NH_2)N(Me)_2\}(NH_3)_5]_2(S_2O_6)_3 \cdot 3H_2O$	*N,N*-Dimethyl urea	Isomerization of $[Co\{NHC(O)N(Me)_2\}(NH_3)_5](CF_2SO_3)_2$; pH 2; pink, ε_{523} 93.5	4
$[Co\{OC(H)N(Me)_2\}(NH_3)_5](CF_3SO_3)_3$	DMF	$[Co(OSO_2CF_3)(NH_3)_5](CF_3SO_3)_2$ in DMF; 15 min; r.t., ether; red; ε_{506} 78	5

1. R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 1964, **3**, 1561.
2. A. M. Sargeson and H. Taube, *Inorg. Chem.*, 1966, **5**, 1094.
3. R. J. Balahura and R. B. Jordan, *J. Am. Chem. Soc.*, 1971, **93**, 625.
4. N. E. Dixon, D. P. Fairlie, W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, 1983. **22**, 4038.
5. N. E. Dixon, W. G. Jackson, M. J. Lancaster, G. A. Lawrence and A. M. Sargeson, *Inorg. Chem.*, 1981, **20**, 470.
6. R. J. Balahura, G. Ferguson, L. Ecott and R. Y. Siew, *J. Chem. Soc., Dalton Trans.*, 1082, 747.
7. E. Sushynski, A. Van Roodselaar and R. B. Jordan, *Inorg. Chem.*, 1972, **11**, 1887.
8. J. L. Laird and R. B. Jordan, *Inorg. Chem.*, 1982, **21**, 855.

$$[(NH_3)_5Co{-}NH_2SO_3]^{2+} \underset{k=1.1\times10^{-3}\,s^{-1}}{\rightleftharpoons} [(NH_3)_5Co{-}OSO_2NH_2]^{2+} \xrightarrow{k_2=3.0\times10^{-5}\,mol^{-1}\,dm^3\,s^{-1}}$$
$$[(NH_3)_5Co{-}OH_2]^{2+} + NH_2SO_3H \quad (178)$$

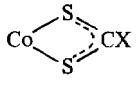
$$[(NH_3)_5Co{-}NH_2SO_3]^{2+} \underset{(pk_a=5.83)}{\overset{OH^-}{\rightleftharpoons}} [(NH_3)_5Co{-}NHSO_3]^{+}$$
$$(k_{OH} = 0.01\,mol^{-1}\,dm^3\,s^{-1}) \searrow^{OH^-} \qquad HO^- \swarrow (k_{OH} = 2.5\times10^{-7}\,mol^{-1}\,dm^3\,s^{-1}) \quad (179)$$
$$[(NH_3)_5Co{-}OH]^{2+} + NH_2SO_3^-$$

Treatment of phenyl isothiocyanate with $[Co(OH_2)(NH_3)_5](ClO_4)_3$ in the presence of a base leads to the S-bound isomer rather than the O-bound form (Table 94). The latter is possibly formed as an intermediate (equation 180).[1124]

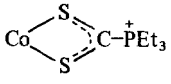
$$[(NH_3)_5Co{-}OH]^{2+} + S{=}C{=}NPh \xrightarrow{slow} [(NH_3)_5Co{-}O(C{=}S)NHPh]^{2+} \longrightarrow [(NH_3)_5Co{-}S(C{=}O)NHPh]^{2+} \quad (180)$$

47.8.10 1,1-Dithioacids and 1,1-Dithiolates

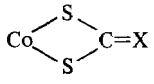
General articles and reviews are available.[1128–1131] Dithioacid complexes are of the type **(333)**, where X is alkyl or aryl (dithiocarboxylates), NR_2 (dithiocarbamates), OR (xanthates) and SR (thioxanthates). The $CS_2 \cdot PEt_3$ adduct **(334)** is also of this type although it acts as a zwitterion in its coordination. These systems are formally monoanion chelating agents. The 1,1-dithiolates **(335)**, where X = CR_2 (alkyl, aryl), NR (dithiocarbimates), S^- (trithiocarbonate), O^- (dithiocarbonate), are dianion chelating agents.



(333)



(334)



(335)

47.8.10.1 1,1-Dithioacid complexes

Preparations are given in Tables 95 and 97 and structures in Table 96. Alkali metal salts of 1,1-dithioacids can be easily prepared by addition of the appropriate nucleophile to the electrophilic carbon of CS_2 (equations 181–184).[1128,1132]

$$CS_2 + HR_2N + NaOH \longrightarrow R_2N{-}(C{=}S){-}S^- + H_2O \quad (181)$$

dithiocarbamates

$$CS_2 + ROH + NaOH \longrightarrow RO{-}(C{=}S){-}S^- + H_2O \quad (182)$$

xanthates

$$CS_2 + EtSH + NaH \longrightarrow EtS{-}(C{=}S){-}S^- \quad (183)$$

ethylthioxanthate

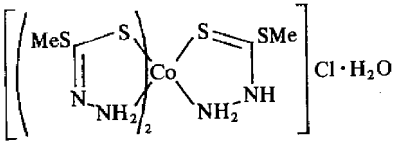
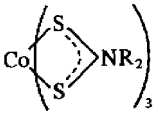
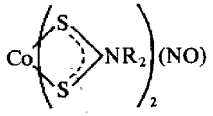
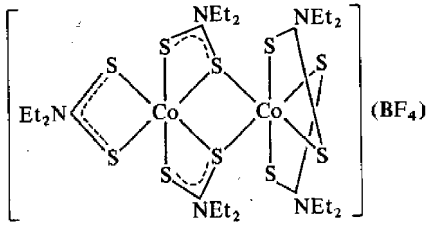
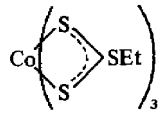
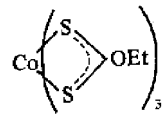
$$CS_2 + PEt_3 \longrightarrow Et_3\overset{+}{P}{-}(C{=}S){-}S^- \quad (184)$$

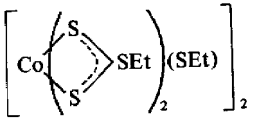
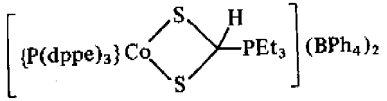
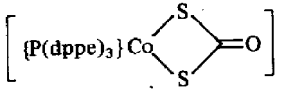
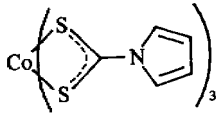
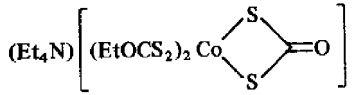
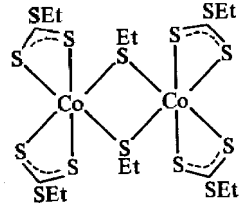
triethylphosphine dithiolate

Complex	Preparation	Properties	Ref.
Cobalt(II)			
$[Co(S_2CNR_2)_2]$	$CoCl_2$, NaR_2dtc, H_2O	Green; μ = 1.60–2.0 BM; $\varepsilon_{625-640}$ 490 (sh)	3
(R =  ; X = CH_2, S, NMe)			
Cobalt(III)			
$[Co(S_2CNR_2)_3]$	$CoCl_2$, NaR_2dtc, H_2O	Green-brown; diamagnetic; $\varepsilon_{650-660}$ 430, ε_{475} 650	1, 2
(R = Me, Et, py, Bu^n, Bz, pyr)			
$\Delta(+)_{546}$-$[Co(S_2CNR_2)_3]$	$(+)_{546}$-K[Co(edta)], $(+)_{546}$-K[Co{(−)-PDTA}], H_2O, NaR_2dtc	Green; asymmetric synthesis, $\Delta(+)_{546}$ compound preferred (> 60%)	2
(R = Me, Et, Bu^n, pyr, Ph, Bz, Pr^i, Bu^i)			
$[Co(S_2CN$  $)_3]$	$[Co(NH_3)_6]Cl_3$ + NaRdtc; DMSO, H_2O, r.t., C, 6 h	Green; diamagnetic; ε_{627} 500; R = $(S)CO_2^-$ compound resolved	5, 14
(R = CH(Me)Ph)	$Co(ClO_4)_2$, NaR_2dtc; H_2O, r.t., asymmetric synthesis	Green, $\Lambda(+)_{658}(S,S,S)$, $\Delta\varepsilon$ +2.04; ε_{643} 460; $\Delta(-)_{658}(S,S,S)$, $\Delta\varepsilon$ −1.07; ε_{660} 465	6
$\Lambda(S,S,S)$-$[Co(S_2CNHR)_3]$	$[Co(R_2dtc)_3]$, $Et_2O{\cdot}BF_3$; O_2, C_6H_6	Green-brown; diamagnetic; $\varepsilon_{610-620}$ 1260, ε_{410} 15 850	4
(R = CH(Me)Ph)			
$[Co_2(S_2CNR_2)_5]BF_4$	$[Co_2(S_2CNR_2)_5]BF_4$, KR'_2dtc; CH_2Cl_2, chrom.	Green-brown; diamagnetic, mixed systems	4
$[Co(S_2CNR_2)_2(S_2CNR'_2)]$	L—L = $acac^-$, $sacsac^-$, CS_2O^{2-}	Substitution reaction	10, 11
$[Co(S_2CNR_2)_2(L—L)]$	L—L = en, R_2en, R_4en, dithiooxamides	Substitution reaction	10, 11
$[Co(S_2CNR_2)_2(L—L)]BF_4$	$CoCl_2{\cdot}6H_2O$ + NH_4L; MeOH	Olive-green; diamagnetic; ε_{418} 7590	15
$[Co(SSeCNEt_2)_3]$	$CoCl_2$ + KROxant + $KHCO_3$; r.t.	Green; ε_{621} 326, ε_{478} 451; resolved using (−)-$PhEtNH_2Cl$; CD, MCD	13
$[Co(S_2COR)_3]$	$CoCl_2$ + KROxant; H_2O, MeOH + HOAc, H_2O_2; H_2O, 0 °C		
(R = Me, Et, Bu^n, Pr^i, cyclohexyl)			
$[Co(S_2CSR)_3]$	$CoCl_2$ + KRSxant; r.t., $KHCO_3$, H_2O_2. $Co(NO_3)_2$ + NaEtSxant, $FeCl_3$; THF, H_2O, chrom.	Green; diamagnetic; ε_{630} 1000, ε_{390} 40 000	9
$[Co(S_2CMe)_3]$	$CoCl_2{\cdot}6H_2O$ + LH; EtOH	Green; diamagnetic; ε_{595} 200; ^1H NMR 2.63 p.p.m.	12
$[Co(S_2CPh)_3]$	$CoCl_2$ + NaS_2CPh; H_2O	Red-brown; ε_{625} 200; ^1H NMR; electrochem.	16, 17

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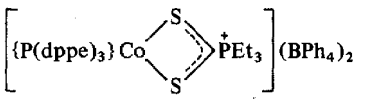
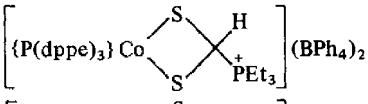
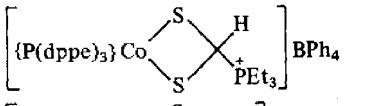
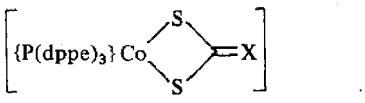
Table 96 Structures: Some 1,1-Dithioacid Complexes of Cobalt

Complex	*Geometry*	*Structural data*				*Ref.*
		Co—S (pm)	*SCoS* (°)	*S—C* (pm)	*C—X* (pm)	
	Oct.	221	–	–	–	13
 (R = Me, Et, morpholine, H)	Dist. oct.	227	76.4	171	132	1
 (R = Me, Pr^i)	Tet. pyr.	226.3	76.9	121.5	131	2
	Dist. oct. (Δ,Λ pairs)	226.6 233.3	77.6 86	– –	– –	3
	Dist. oct.	226.6	76.2	170	172	4
	Dist. oct.	227.7	76.1	167	136	5

	Dimer, SEt bridges	–	–	–	–	7
	Dist. sq. pyr. (disulfide Co^{III} complex)	220 217	79	180	186	8
	Dist. sq. pyr.	225	75.5	170	127	9
	Dist. oct.	226.7	76.3	167.5	139	6
	Dist. oct.	225 228.5	77.1 76.0, 76.3	177 168	120 133–4	10
	Dist. oct. (centrosymmetric)	224.2 (b) 225.0 (b) 226 228(t)	84.5 94.3	(Co—Co 332.1 pm)		11
$[Co_2(SEt)_2(S_2CSEt)(S_2CNEt_2)_3]$	Dist. oct. dimer	Disordered dtc and Sxant ligands		(Co—Co 335.0 pm)		12

1. (a) T. Brennan and I. Bernal, *J. Phys. Chem.*, 1969, **73**, 443; B. Merlino, *Acta Crystallogr., Sect. B*, 1968, **24**, 1441 (R = Et); (b) H. Iwasaki and K. Kobaysashi, *Acta Crystallogr., Sect. B*, 1980, **36**, 1657 (R = Me); (c) C. L. Raston, A. H. Whitew and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1975, 2429 (R = H); (d) R. J. Butcher and E. Sinn, *J. Am. Chem. Soc.*, 1976, **98**, 2440 (R = morpholine).
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Table 97 Preparation and Properties of Trialkyl Phosphine Dithioacid Complexes

Complex	*Preparation*	*Properties*	*Ref.*
	$Co(BF_4)_2$, P(dppe)$_3$, Et_3PCS_2, EtOH/CH_2Cl_2, BPh_4^- (rapid)	Brown; μ = 1.95 BM; λ_{max} 475 nm	1
	$Co(BF_4)_2$, P(dppe)$_3$, Et_3PCS_2, EtOH/CH_2Cl_2, 2 h, r.t.; *or* I_2 oxidation of Co^{II} complex	Red-brown; diamagnetic; λ_{max} 685 nm	1
	$NaBH_4$ redn. of Co^{III} complex, EtOH/CH_2Cl_2	Orange-brown; μ = 2.02 BM; ε_{485} 1260	1
	X = S, O, e; addn. of S_8, O_2, Na, Co^{II} complex	Red/yellow-green; μ = 2.10, 1.97 BM: ε_{480} 1820, ε_{425} 4150	2

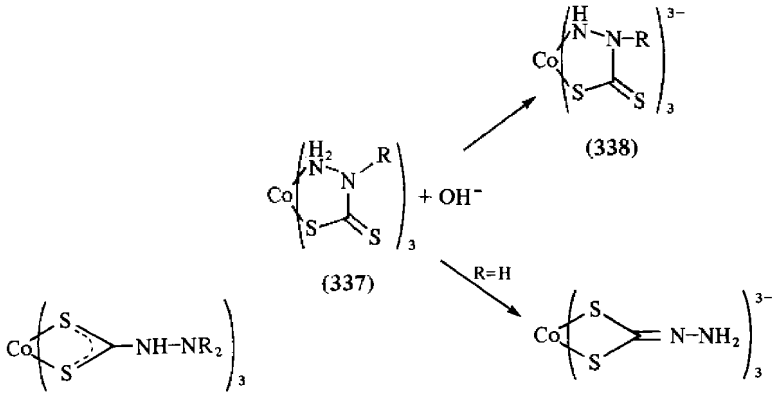
1. C. Bianchini, A. Meli and A. Orlandini, *Inorg. Chem.*, 1982, **21**, 4161.
2. C. Bianchini, A. Meli and A. Orlandini, *Inorg. Chem.*, 1982, **21**, 4166.

(*i*) *Dithiocarboxylates*

Both Co^{II} and Co^{III} complexes are known (Table 95). The dark-green or red-brown diamagnetic $[Co(S_2CR)_3]$ systems[1148,1149] appear to contain bidentate (S,S) coordination, although no structures are available and they have not been resolved into enantiomeric forms. This differs from monodentate coordination for their all-O analogues. The electrochemical reduction of the tris(dithiobenzoate) system has been studied.[1149]

(*ii*) *Dithiocarbamates and thioselenocarbamates*

Dithiocarbamic acid itself and its alkali metal salts are unstable towards hydrolysis but metal chelates are known and a structure of $[Co(S_2CNH_2)_3]$ is available (Table 96). This complex is probably unstable towards hydrolysis giving $[Co(S_2CO)_3]^{3-}$. Salts of dithiocarbamates derived from primary amines are also unstable under alkaline conditions, although N(3)-substituted dithiocarbazic acid forms green tris(S,S) chelates (**336**).[1133] The similar N(3)-unsubstituted acids form (N,S) chelates (**337**) which can be deprotonated when R = H with possible isomerization to the (S,S) dithiocarbimate chelate (**339**).[1133] The (N,S) chelate (**338**) has been positively identified by a crystal structure of its *S*-methyl ester, R = H (Table 96).[1134]



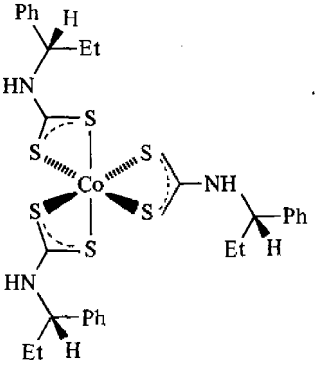
(336) R = Me, Ph (337) (338) (339)

Ammonium salts of diseleno- and thioseleno-diethylcarbamic acid have been made and Heber and coworkers have reported the preparation of olive-green, diamagnetic $[Co(SeSCNEt_2)_3]$ and mention $[Co(Se_2CNEt_2)_3]$.[1157]

Tris(dialkyldithiocarbamate)Co^{III} complexes can be easily prepared in water using $Na^+R_2dtc^-$ and $CoCl_2$ in the presence of O_2,[1135] or by oxidation of Co^{II} using the disulfide dimer; the former method is preferable (equation 185). Representative examples are given in Table 95. A very large number of these green or green-brown, neutral water-insoluble complexes have been prepared. Normally the diamagnetic tris Co^{III} chelate results even when O_2 is rigorously excluded but a few $Co(R_2dtc)_2$ have been reported when R is large (Table 95). These Co^{II} species are paramagnetic with one unpaired electron and probably have a square planar structure. Their stability is surprising and must reside in steric factors; no structural information is available.

$$CoCl_2 + Na^+R_2NCS_2^- \xrightarrow{O_2} [Co(S_2CNR_2)_3] \longleftarrow CoCl_2 + R_2NC(=S)SC(=S)NR_2 \qquad (185)$$

O'Connor and coworkers have synthesized several optically-active $[Co(R_2dtc)_3]$ complexes using $(+)_{546}$-K[Co(edta)] or $(+)_{546}$-K[Co{(−)pdta}] as the asymmetric cobalt source.[1135] The latter gives $(+)_{546}$ species for all R (assigned Δ-$[Co(R_2dtc)_3]$), while the former gives $(+)_{546}$ for R = Me, Et, Bu^n, pyrr, Ph, Bz, and $(-)_{546}$ for R = Pr^i, Bu^i. Recrystallization results in considerable racemization[1135] and this has been followed in a number of solvents over the temperature range 50–70 °C.[1151] ^1H NMR studies confirm a rapid intramolecular process at 170 °C in $C_6D_5NO_2$.[1137] A $\Delta V^‡$ study has been interpreted in terms of a trigonal-twist mechanism without bond breaking for R = pyrr ($\Delta V^‡$, 9.8 $cm^3 mol^{-1}$ in ethanol) and one-ended dissociation for R = Ph ($\Delta V^‡$, −2 to −9.3 $cm^3 mol^{-1}$ in several solvents).[1136] Woon and O'Connor have prepared the optically-active (*S*)-2-carboxypyrrolidine derivative, which in its deprotonted form is water soluble.[1156] This was resolved on DEAE cellulose into its $(+)_{546}$-Δ(*SSS*) and $(-)_{546}$-Λ forms and CD spectra were used to assign configurations. Similarly, Haines and Chan have used optically-active *S*(−)-1-phenylethylamine to prepare $(+)_{660}$-[Co{(*S*)PhEtdtc}$_3$] *via* a second-order asymmetric procedure.[1138] The $(-)_{660}$ diastereoisomer is apparently also formed but is more soluble in water and mutarotates to the $(+)_{660}$ isomer which slowly precipitates. The latter is assigned the Λ configuration (**340**) and ^1H NMR shows only one sharp doublet at 1.49 p.p.m. for the methyl group. When dissolved in non-polar solvents (CH_2Cl_2, CS_2, C_6H_6) this isomer apparently mutarotates completely to the Δ-$(-)_{660}$-[Co{(*S*)PhEtdtc}$_3$] diastereoisomer (Me doublet, 1.44 p.p.m.). Enantiomeric results were obtained using the (*R*)-(+)-PhEtdtc ligand. Rate constants for inversion ($2.1 \times 10^{-4} s^{-1}$ (CH_2Cl_2), $8.5 \times 10^{-5} s^{-1}$ (CS_2) at 25 °C) and activation parameters [$\Delta H^‡$ 80 kJ mol^{-1}, $\Delta S^‡$ −39 J $K^{-1} mol^{-1}$ (CH_2Cl_2)] are in general agreement with other studies. Kida and his colleagues have found that $[Co(en)_3]^{3+}$ reacts with dithiocarbamates (R = Et, C_2H_4OH) in aqueous alkaline solution in the presence of light.[1152] Substitution is quite rapid (3 h in room light at ambient temperatures is sufficient) and quantum yields are in excess of 1.0. A primary photoredox process followed by a chain reaction involving Co^{II} species is proposed.[1152]



(**340**)
Λ-$(-)_{660}$-[Co{(*S*)-PhEtdtc}$_3$]

Several crystal structures of $[Co(R_2dtc)_3]$ complexes are available (Table 96) and they all show a distorted octahedral geometry with a bite angle of ~76° at the metal. There is no suggestion of distortion towards a trigonal prismatic structure. For R = H there is some suggestion of electron redistribution within the ligand but this may result from H bonding in the lattice. Much of the early structural work was aimed at verifying a zwitterionic component to the bonding (*i.e.* [Co($S_2C{=}NR_2$)]) and this appears to have been partly realized (*cf.* Section 47.8.10.2.i).

Gahan and O'Connor have noted rapid photoracemization of $[Co(R_2dtc)_3]$ when solutions in organic solvents are exposed to sunlight.[1151] Light of wavelength less than 400 nm appears to be necessary and the process is very rapid in $CHBr_3$. No decomposition occurs and preliminary flash photolysis studies indicate a transient intermediate with $\lambda_{max} = 500$ nm. This optical instability contrasts with the apparent reluctance of $[Co(R_2dtc)_3]$ and $[Co(R_2'dtc)_3]$ to exchange ligands in nitrobenzene when heated at 195 °C for several hours[1139] and with the inability of $[Co(Et_2dtc)_3]$ to react with the $[Co(SEt)(S_2CSEt)]_2$ dimer in refluxing $CHCl_3$.[1145] However, it has been reported that $[Co(Et_2dtc)_3]$ and $[Co(S_2CSEt)_3]$ form $[Co(Et_2dtc)_2(S_2CSEt)]$ on refluxing in $CHCl_3$ for 10 minutes.[1140] Clearly these ligand exchange processes need to be reexamined.

Early uncertainty in the redox chemistry of $[Co(R_2dtc)_3]$ has now been resolved.[1141,1142] BF_3 oxidation leads to $[Co_2(R_2dtc)_5]^+$ dimers containing Co^{III} rather than a Co^{IV} species. Here a $Co(R_2dtc)_3$ unit is *cis* chelated to a second $Co(R_2dtc)_2^+$ fragment of opposite chirality *via* sulfide bridges (Table 96). These bridges form longer and less robust bonds to the metal and the dimer can be easily cleaved with the incorporation of acetylacetone, dithioacetylacetone, ^-S_2COR and ^-S_2CNR to form unsymmetrical tris chelates (equation 186; Table 95). Also, neutral ligands such as ethylenediamine and its *N*-alkyl derivatives, and several dithiooxamides (equation 187) result in well-defined mixed chelates (Table 95). These products are diamagnetic and appear to be monomers. Some kinetic data are available.[1154,1155]

$$[Co_2(R_2dtc)_5]BF_4 + Y{-}Y^- \longrightarrow [Co(R_2dtc)_3] + [Co(R_2dtc)_2(Y{-}Y)] \quad (186)$$

$$[Co_2(R_2dtc)_5]BF_4 + R_2NC(=S)C(=S)NR_2 \longrightarrow [Co(R_2dtc)_3] + \left[(Et_2dtc)_2Co\begin{smallmatrix} S & NR_2 \\ S & NR_2 \end{smallmatrix}\right]BF_4 \quad (187)$$

Oxidation to the formally cobalt(IV) species $[Co(R_2dtc)_3]^+$ is difficult ($E^\circ = 0.96$ V (cyclohexyl), 1.22 V (benzyl), acetone solvent) but at Pt in CH_2Cl_2 it is electrochemically and chemically reversible with controlled potential electrolysis resulting in monomeric $[Co(Cy_2dtc)_3]^+$ ($\lambda_{max} \approx 410$ nm).[1142] However attempts to isolate this complex were unsuccessful with the $[Co_2(Cy_2dtc)_5]^+$ dimer being the only product. These E° values suggest a Co^{III}-oxidized ligand formalism and the monomer is apparently unstable. The first one-electron reduction to give $[Co(R_2dtc)_3]^-$ is also not easy ($E_{1/2} = -0.80$ V (benzyl), -1.13 V (cyclohexyl), acetone solvent) but shows considerable chemical reversibility at Pt and Hg in acetone[1142] or DMSO.[1153] Further reduction leads to Co^0 (equation 188). Both the electrochemistry and the stability of the oxidized and reduced species are sensitive to the nature of the R group, the solvent and the redox procedure.[1142]

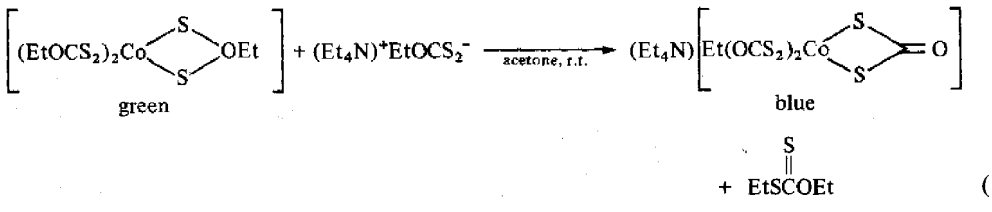
$$Co(R_2dtc)_3 + e^- \longleftrightarrow Co(R_2dtc)_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(R_2dtc)_2 + R_2dtc^- \xrightarrow{2e^-} Co + 2R_2dtc^- \quad (188)$$

(*iii*) *Xanthates and thioxanthates*

There are suggestions that the early preparations of Compin and Delepine[1143] give rise to impure products. $[Co(S_2COR)_3]$ can be prepared from either $[Co(CO_3)_3]^{3-}$ (equation 189), or $[Co(NH_3)_6]^{3+}$ (equation 190; Table 95), with recrystallization of the green water-insoluble products from an organic solvent. Care is needed since dealkylation is easy in the presence of an excess of ligand anion.[1146] This presumably occurs *via* nucleophilic attack at O (equation 191). The structure of the resulting $(Et_4N)[Co(S_2COEt)_2(S_2CO)]$ complex shows short Co—S and C—O bonds in the dianionic dithiocarbonate chelate (Table 96) indicating substantial 1,1-dithiolate character. By using 2-sulfonatoethyl xanthate Hansen and Harnung have resolved the resulting $[Co(S_2COC_2H_4SO_3)_3]^{3-}$ anion (Table 95) and have assigned charge transfer and ligand field absorptions using CD and MCD spectra.[1150] This appears to be the only example of separated enantiomers.

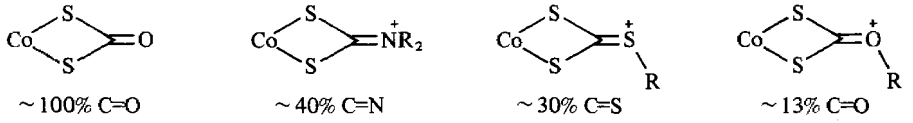
$$[Co(CO_3)_3]^{3-} + 3ROCS_2^- \longrightarrow [Co(S_2COR)_3] + 3CO_3^{2-} \quad (189)$$

$$[Co(NH_3)_6]Cl_3 + 3K^+ROCS_2^- \xrightarrow{0\text{-}5\,^\circ C} [Co(NH_3)_6](ROCS_2)_3 \xrightarrow{60\,^\circ C} [Co(S_2COR)_3] + 6NH_3 \quad (190)$$



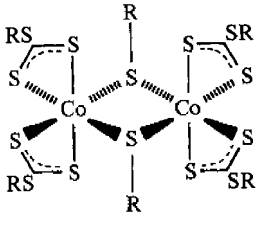
(191)

The above method using $[Co(CO_3)_3]^{3-}$ can also be used to prepare the tris(thioxanthates) $[Co(S_2CSR)_3]$ but these can also be made from Co^{II} salts and $Na^+RSCS_2^-$ provided a little $FeCl_3$ is present to prevent dimerization (Table 95). Crystal structures of $[Co(S_2COEt)_3]$ and $[Co(S_2CSEt)_3]$ (Table 97) show a resemblance to that of $[Co(Et_2dtc)_3]$ with a 76° bite angle at the metal and similar bond lengths within the four-membered chelates. The more electronegative *exo* O and S atoms (when compared to N in the dithiocarbamates) have been rationalized in terms of less zwitterionic character (Scheme 100).



Scheme 100

Green water-insoluble $[Co(S_2CSR)_3]$ are diamagnetic and rather unstable to heat, eliminating CS_2 in organic solvents giving brown thiolate-bridged diamagnetic dimers (**341**).[1144] The sulfide bridges adopt a symmetrical anticonfiguration (Table 97) and it has so far not been possible to isolate asymmetric systems using mixed-ligand or mixed-metal reactants. Preparation *via* Co^{II} salts in the absence of $FeCl_3$ leads largely to the dimer (except for R = Bu^t). The terminal thioxanthate ligands undergo stepwise nucleophilic displacement at C when $NHEt_2$ is used, resulting in mixed dithiocarbamate–thioxanthate dimers (equation 192).[1145] A similar reaction occurs with $[Co(S_2CSMe)\{MeC(dppm)_3\}](BPh_4)$.[1161]



(341)

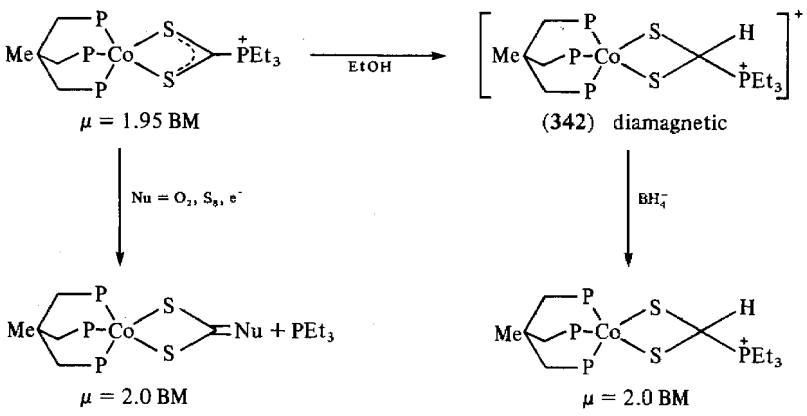
$$[Co(SEt)(S_2CSEt)_2]_2 + NHEt_2 \xrightarrow[CHCl_3]{heat} [Co(SEt)(S_2CNEt_2)_n(S_2CSEt)_{2-n}]_2 \quad (192)$$
$$2n = 1\text{–}3$$

The $[Co(S_2CSR)_3]$ monomer undergoes reversible reduction ($E \approx -0.80$ to -1.0 V in CH_2Cl_2) but irreversible oxidation ($E \approx 1.5$ V). The $[Co(SR)(S_2CSR)_2]_2$ dimer undergoes irreversible reduction ($E \approx -1.0$ V) and oxidation ($E \approx 1.4$–1.6 V).[1144]

(*iv*) *Trialkylphosphine dithioacids*

Immediate addition of BPh_4^- to a solution of $MeC(dppm)_3$, S_2CPEt_3 and $Co^{2+}_{(aq)}$ in ethanol results in the crystallization of brown five-coordinate $[Co(S_2CPEt_3)(MeC(dppm)_3)](BPh_4)_2$[1147] (Table 97). However if the solution is left to stand or if it is refluxed, internal redox occurs and the red-brown distorted square-pyramidal Co^{III} complex (**342**) containing the reduced ligand is obtained (structure, Table 96; Scheme 101). This process may occur *via* H^- abstraction from the solvent followed by oxidation at the metal, or by H atom abstraction by the Co^{III} radical anion. Complex (**342**) may be reduced by BH_4^- to an orange-brown Co^{II} complex containing the reduced ligand (Scheme 101). Other nucleophiles also add readily to the C atom of the initial Co^{II} complex (Nu = O_2, S_8, e^-) with

displacement of PEt_3, forming S_2CO^{2-} (structure, Table 96), S_2CS^{2-} and π-CS_2 chelates respectively. As the authors[1147] point out this chemistry provides a useful synthetic route to a variety of 1,1-dithiolato systems and to a potential source of metal-activated CS_2 (Nu = e^-).



Scheme 101

47.8.10.2 1,1-Dithiolate complexes

A general account of this area is available.[1158] These complexes include di- and tri-thiocarbonates (OCS_2^{2-}, SCS_2^{2-}), unsaturated alkene systems ($R_2C{=}CS_2^{2-}$), and dithiocarbimates ($RN{=}CS_2^{2-}$). K_2CS_3 can be prepared as a yellow solid by adding CS_2 to an alcoholic solution of KOH which has been saturated with H_2S,[1159] and as a solution in DMF by adding KOH to CS_2.[1160] Relatively few cobalt complexes of these localized dithiols are known (Table 98).

(i) Di- and tri-thiocarbontes, cobalt(III)

Cleavage of the C—P bond in $[Co\{S_2CP(Et)_3\}\{MeC(dppm)_3\}](BF_4)_2$ by O_2 and S_8 has already been noted (Scheme 101). The resulting $[Co(S_2CO)\{MeC(dppm)_3\}]$ and

Table 98 Preparations: Some 1,1-Dithiolate Complexes of Cobalt

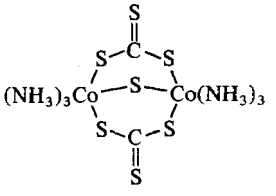
Complex	*Preparation*	*Properties*	*Ref.*
Cobalt(II)			
$[Co\{MeC(dppm)_3\}(S_2CO)]$	$[Co\{MeC(dppm)_3\}\{S_2CP(Et)_3\}](BF_4)_2$, NaOEt, O_2; EtOH	Yellow-green (structure Table 96)	6
$[Co\{MeC(dppm)_3\}(S_2CS)]$	$[Co\{MeC(dppm)_3\}\{S_2CP(Et)_3\}](BF_4)_2$, NaOEt, S_8, EtOH	Green; μ = 2.09 BM	6
$(Et_4N)_2[Co(S_2CC_6H_4)_2]$	$CoBr_2 + Na_2L + Et_4NBr$; MeCN, −70 °C; 1 h, r.t.	Brown; μ = 2.55 BM; ESR; IR	7
Cobalt(III)			
$(Ph_4P)_3[Co(S_2CS)_3]$	$Na_3Co(NO_2)_6 + K_2CS_3$ (soln.); H_2O, 30 min; $(Ph)_4PCl$	Olive green; diamagnetic; ε_{667} 517; ε_{454} 93 000	1
$(Bu^n_4N)_3[Co\{S_2CC(N)_2\}_3]$	$Na_3Co(CO_3)_3\cdot 3H_2O + Na_2L$; MeOH, heat, 15 min; Bu^n_4NBr	Green-gold; diamagnetic; ε_{667} 517; ε_{402} 36 000	2
$(Me_3PhN)_3[Co\{S_2CC(CO_2R)_2\}_3]\cdot 2H_2O$		Diamagnetic; $E_{1/2}$(oxid) 0.14 V	3
$(Ph_2I)_3[Co\{S_2CC(CN)_2\}_3]$	$Na_3Co(CO_3)_3\cdot 3H_2O + L^{2-}$; H_2O, steam bath, 15 min; Ph_2ICl	Green; heating causes Ph transfer to S	4
$(Ph_4P)_3[Co(mnt)_2(S_2CX)]$ (X = $C(CN)_2$, $C(CN)CO_2Et$, $C(CN)CONH_2$, $CHNO_2$, NCN)	$(Ph_4P_3)[Co(mnt)_2]_2 + K_2L$; DMF, N_2; Na_2SO_3	Brown; ESR; IR; electrochem.	5

1. A. Muller, P. Christophliemk, I. Tossidis and C. K. Jorgensen, *Z. Anorg. Allg. Chem.*, 1973, **401**, 274.
2. B. G. Werden, E. Billig and H. B. Gray, *Inorg. Chem.*, 1966, **5**, 78.
3. D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301.
4. K. K. Ramaswamy and R. A. Krause, *Inorg. Chem.*, 1970, **9**, 2649.
5. J. A. McCleverty, D. G. Orchard and K. Smith, *J. Chem. Soc. (A)*, 1971, 707.
6. C. Bianchini, A. Meli and A. Orlandini, *Inorg. Chem.*, 1982, **21**, 4166.
7. B. J. Kalbacher and R. D. Bereman, *Inorg. Chem.*, 1973, **12**, 2297.

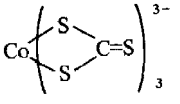
$[Co(S_2CS)\{MeC(dppm)_3\}]$ complexes[1147] are five coordinate and a crystal structure of the former (Table 96) shows a distorted square-pyramidal P_3S_2 donor set. As with the π-CS_2 complexes (Section 47.2.2) the uncoordinated S atom in $[Co(S_2CS)\{MeC(dppm)_3\}]$ is nucleophilic and will displace halide ion from alkyl halides or weakly bound ligands from organometallic derivatives. This gives thioxanthate (*e.g.* $[Co(S_2CSMe)(\{MeC(dppm)_3\})]^+$) and CS_3-bridged binuclear (*e.g.* $[\{MeC(dppm)_3\}Co(\mu\text{-}CS_3)Cr(CO)_5]$) complexes respectively.

(*ii*) *Di- and tri-thiocarbonates, cobalt(III)*

Olive-green $[Co(S_2CS)_3]^{3-}$ has been prepared and isolated (Table 98) and a brown-green complex of composition $[Co_2(C_2S_7)(NH_3)_6]$ precipitates from ammoniacal $CoSO_4$ when treated with Na_2CS_3.[1162] IR data for the latter have been interpreted in terms of structure (**343**),[1163] and $[Co(S_2CS)_3]^{3-}$ (**344**) probably contains the bidentate S_6 donor set although it is less stable than the unstable all-oxygen analogue $[Co(CO_3)_3]^{3-}$ (Section 47.7.3.2).



(343)



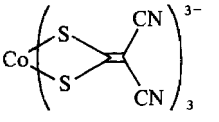
(344)

(*iii*) *Alkenedithiolates and dithiocarbimates*

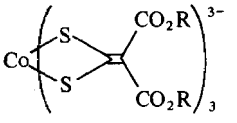
The preparation and properties of known cobalt(II) and cobalt(III) complexes are given in Table 98. The dithiocyclopentadienyl anion is a resonance hybrid and the low spin (μ = 2.55 BM) and ESR of (**345**) suggest a distorted planar structure. The 1,1 analogue of maleonitriledithiolate (**346**) has reduced electron delocalization and McCleverty and his colleagues have investigated the electrochemistry of the mixed $[Co\{S_2C_2(CN)_2\}_2(S_2C{=}X)]^{3-}$ system.[1164] Only one-electron oxidation is possible in CH_2Cl_2 at Pt (equation 193), and chemical oxidation with I_2 has resulted in the isolation of $(Ph_4P)_2[Co\{S_2C_2(CN)_2\}(S_2C{=}X)]$ (X = $CHNO_2$, $C(CN)CO_2Et$). Likewise diamagnetic (**347**) can be reversibly oxidized ($E_{1/2}$ = 0.14 V).[1165] The dithiocarbazic acid anion $[Co(S_2C{=}NNH_2)_3]^{3-}$ has been discussed in Section 47.8.10.1. (i) and the corresponding nitrile $[Co(S_2C{=}NCN)_3]^{3-}$ has been isolated (Table 98).



(345)



(346)



(347)

$$[Co\{S_2C_2(CN)_2\}_2(S_2C{=}X)]^{3-} \underset{E_{1/2}=0.02 \text{ to } -0.11\,V}{\longleftrightarrow} [Co\{S_2C_2(CN)_2\}_2(S_2C{=}X)]^{2-} + e^- \quad (193)$$

47.8.10.3 Thiophosphinates and selenophosphinates

These ligands can be easily made (equations 194 and 195), but obviously extreme care is necessary with the Se compound.[1174,1175]

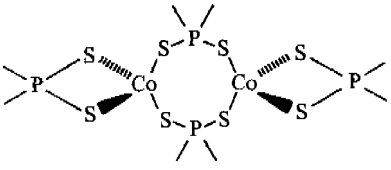
$$P_2S_5 + 4EtOH \xrightarrow[N_2,\ heat]{} 2(EtO)_2PS_2H + H_2S \quad (194)$$

$$PPh_2Cl + S_8 \longrightarrow Ph_2PSCl \xrightarrow{NaHS} Ph_2PS_2^-Na^+ \quad (195)$$

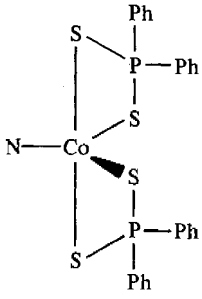
(i) Cobalt(II)

The synthesis of $[Co(S_2PR_2)_2]$ (R = alkyl, aryl, OEt, CF_3) involves addition of the sodium or ammonium salt of the ligand to solutions of Co^{II} halides, or the reaction of Co metal with the acid ligand (R = F, CF_3; Table 99).[1166,1168,1169] $[Co\{S_2P(OEt)_2\}_2]$ has also been made by photoreduction of the Co^{III} complex (equation 196).[1179] Although many of these tetrahedral species are quite soluble in organic solvents, this is not the case for R = Me, Ph, and the former complex at least is polymeric in the solid state.[1169] In contrast the structure of $[Co(S_2PEt_2)_2]_2$ consists of dimeric units (**348**).[1169] Benzene solutions of this complex appear to be associated into larger polymeric units with retention of tetrahedral geometry about the metal. Attempts to prepare $[Co(S_2PMe_2)_2]$ in aqueous solution lead to $[Co(S_2PMe_2)(SOPMe_2)]$ but with other dialkyldithiophosphinates this substitution of O for S is not stoichiometric. Monomeric $[Co(S_2PR_2)_2]$ is stabilized towards oxidation at the metal by the formation of trigonal-bipyramidal five-coordinate (**349**) and octahedral adducts with unidentate amines and phosphines (Table 99).[1170,1171] Dimeric structures such as (**350**) are also known.[1172]

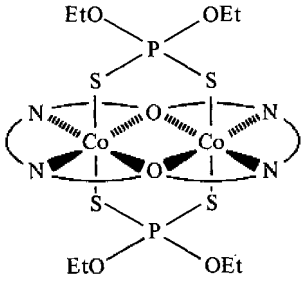
$$2[Co\{S_2P(OEt)_2\}_3] \longrightarrow [Co\{S_2P(OEt)_2\}_2] + (EtO)_2P(S)—S—S—P(S)(OEt)_2 \quad (196)$$



(348)



(349)



(350)

Table 99 Preparations: Some 1,1-Dithio- and Diseleno-phosphinate Complexes of Cobalt

Complex	*Preparation*	*Properties*	*Ref.*
Cobalt(II)			
$[Co(S_2PF_2)_2]$	$Co + HS_2PF_2$ (−80 °C)	Green; volatile; m.p. 44–44.5 °C; μ = 6.1 BM	1
$[Co(NO)_2(S_2PF_2)]$	$[Co(S_2PF_2)_2] + NO_{(g)}$ (0 °C)	Brown; m.p. 64–66 °C; ν_{NO} = 1797, 1869 cm^{-1}	1
$[Co\{S_2P(F)Et\}_2]$	$Co + HS_2P(F)Et$	Green; decomposes on storage	2
$[Co\{S_2P(Me)_2\}_2]$	$CoX_2 + HS_2PMe_2$	Green; air stable; μ = 4.38 BM	3
$[Co\{S_2P(OEt)_2\}_2]$	$CoCl_2 \cdot 6H_2O$ + $NaS_2P(OEt)_2$	Blue; μ = 5.49 BM	3
$[Co(Se_2PPh_2)_2]$	$CoCl + NaSe_2PPh_2$	Green; μ = 4.75	4
$[Co(S_2PPh_2)_2$(quinoline)]	$[Co(S_2PPh_2)_2]$ + quinoline; H_2O·rexal·$CHCl_3$	Turquoise; trig. bipyr. structure (CoS_{ax} 263, CoS_{eq} 232, CoN 203 pm); μ = 4.69 BM	5
$[Co\{S_2P(OR)_2\}(L)]$ (R = Me, Et; L = PPh_3, benzothiazole, benzim, pip, pyz)	$CoCl_2 \cdot 6H_2O$ + L; benzene, H_2O $CoCl \cdot 6H_2O$ + L; benzene	Mostly five-coordinate; trig. bipyr. structure (R = Me, L = PPh_3)	6
Cobalt(III)			
$[Co(S_2PPh_2)_3]$	$Na_3Co(NO_2)_6 + NaS_2PPh_2$; EtOH	Brown; diamagnetic, ε_{769} 600; ε_{450} 93 000	7
$[Co\{Se_2P(OEt)_2\}_3]$	$CoCl_2 \cdot 6H_2O$ + L; EtOH, 60 °C, N_2	Red; trig. dist. oct.	8
$[Co\{S_2P(OEt)_2\}_3]$	$CoCl_2 \cdot 6H_2O$ + L; EtOH	Olive-green; diamagnetic	9

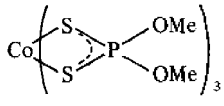
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Cobalt(II) complexes of the mixed thiophosphinic and selenophosphinic ligands R_2PXY^- (X = S, Se; Y = S, Se, O) were first investigated by Kuchen and coworkers,[1166,1167] and Calligaris and his group describe the structure of polymeric $[Co(SOPPh_2)_2]_n$ as chains of alternate single- and triply-bridging Ph_2PSO units coordinated to distorted tetrahedral Co atoms.[1173] Their preparation is similar to the dithiophosphinate complexes (Table 99) and polymerization in solution appears to be extensive.[1173,1167] They are susceptible to hydrolysis and oxidation but can normally be stored for extended periods in sealed tubes.

The preparation and spectral properties of $[Co(Se_2PPh_2)_2]$ have been reported[1174] and $[Co\{Se(O)PEt_2\}_2]$ has been described.[1167] Both are rather unstable.

(*ii*) *Cobalt(III)*

Dark green $[Co\{S_2P(OR)_2\}_3]$ can be prepared from the ligand and CoF_3[1175] or by oxidation of $[Co\{S_2P(OR)_2\}_2]$ with H_2O_2 (Table 99).[1176] The analogous Se complex forms red crystals having a distorted octahedral stereochemistry.[1177] Indigo-coloured (**351**; Scheme 102) reacts with diphenylphosphine[1178,1150] and diphenylarsine[1178] chelates in acetone or CH_2Cl_2 in two stages with the second stage involving transfer of a methyl group to the released $(MeO)_2PS_2^-$ nucleophile.[1150]



(351)

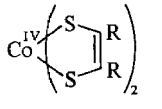
$$+ Ph_2PCH_2CH_2PPh_2 \longrightarrow [Co(dppe)(S_2P(OMe)_2]^+ + (MeO)_2PS_2^- \xrightarrow{(MeO)_2PS_2^-}$$

$$[Co(dppe)\{S_2P(OMe)_2\}\{S_2P(O)(OMe_2\}] + (MeO)_2P(S)SMe$$

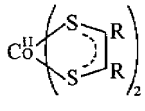
Scheme 102

47.8.11 1,2-Dithiolates

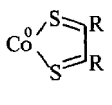
Well-documented articles and reviews are available.[1129,1180–1184] These ligands form five-membered chelates with most metals. Early interests lay in the difficulty in assigning a formal oxidation state to the metal (**352**)–(**354**), the discovery of the rare trigonal-prismatic structure for several neutral tris complexes (but not for Co) in some facile one- and two-electron transfer reactions, and in some unusual five- and six-coordinate adducts, including some with bonding to saturated carbon. No monodentate 1,2-dithiolate system is known and the *trans* configuration (**355**) has not been described. No attempted oxidation of *trans* dithiol–metal complexes has been described and it might be expected that (**355**) would be quite stable with rotation about the C—C bond occurring only in one tautomer.



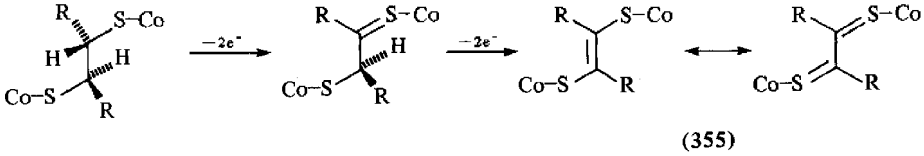
(352) dithiolate



(353) dithiene



(354) dithiolene

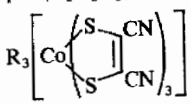
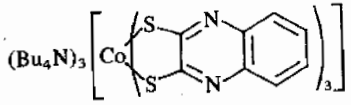
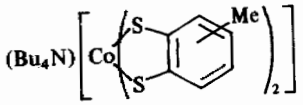
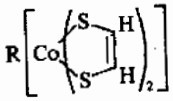
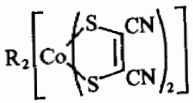
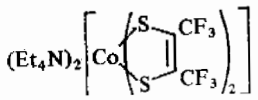


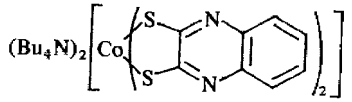
(197)

(355)

Cobalt forms diamagnetic $[Co(S_2C_2R_2)_3]^{3-}$, a series of monomeric square planar $[Co(S_2C_2R_2)_2]^{n-}$ ions (n = 1–3) and square-pyramidal dimeric $[Co(S_2C_2R_2)_2]_2^{n-}$ species (n = 0–2). All are highly coloured, indicating extensive electron delocalization, and all are reasonably labile both in a geometric sense and towards the displacement of one or more dithiolate ligands by other chelating groups. The square planar $[Co(S_2C_2R_2)_2]^-$ ion adds both monodentate and bidentate ligands forming five- and six-coordinate complexes. Their lability, wide range of oxidation states, and the rather rare square-planar $[Co(S_2C_2R_2)_2]^-$ ion distinguishes these complexes.

Table 100 Preparations and Properties of 1,2-Dithiolene Complexes

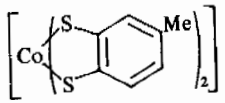
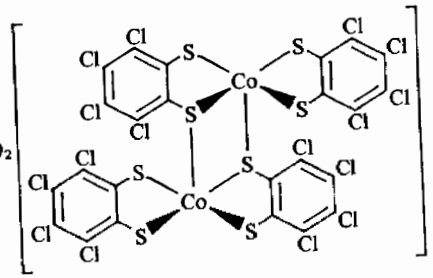
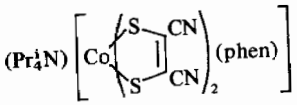
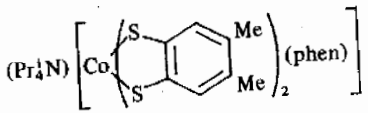
Complex	*Anion*	*Preparation*	*Properties*[a]	*Ref.*
$[Co(S_2C_2R_2)_3]^{3-}$ ions				
	$[Co(mnt)_3]^{3-}$	Na_2mnt, $Na_3Co(CO_3)_3 \cdot 3H_2O$ or $[Co(NH_3)_5Br]Br_2$; EtOH or H_2O (solvent); heat	Green; λ_{max} 665–670 (1100), 460 (6800); diamagnetic	1
(R = Ph_4As, Ph_4P, Pr_4N)				
	$[Co(qdt)_3]^{3-}$	NaOMe, H_2qdt, $Na_3Co(CO_3)_3 \cdot 3H_2O$, MeOH (solvent), r.t.	Orange; λ_{max} 600, 500; $E_{1/2}$, −0.56 (DMSO), decomp.; diamagnetic	2
$[Co(S_2C_2R_2)_2]^{1-,2-}$ ions				
	$[Co(tdt)_2]^-$	KOEt, H_2tdt, $CoCl_2 \cdot 6H_2O$, EtOH (solvent)	Blue; μ 3.47; λ_{max} 660 (16600); $E_{1/2}$, −0.95 (DMSO)	3
	$[Co(dt)_2]^-$	NaOMe, H_2dt, $CoCl_2 \cdot 6H_2O$, 0 °C	Black; λ_{max} 730 (1500), 628 (1100); $E_{1/2}$, −0.93 (DMSO); μ 2.7–2.9	4
(R = Et_4N, Ph_4As)				
	$[Co(mnt)_2]^{2-}$	Na_2mnt; $CoCl_2$ or $Co(OAc)_2$; EtOH–H_2O (solvent); $N_{2(g)}$ or Na_2SO_3	Black (solid), red (soln.); μ 2.16; $E_{1/2}$, −1.83 (THF)	5, 7
(R = Ph_4As, Bu_4N, Ph_4P, Et_4N)				
	$[Co(tfdt)_2]^{2-}$	Redn. $Co(tdt)_2^-$ with Na in THF	Orange; μ 2.06	6

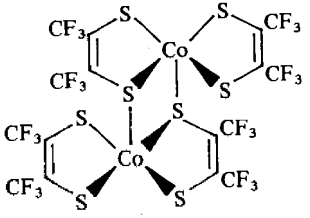
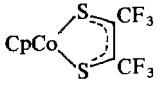
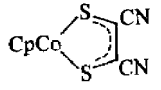
	$[Co(qdt)_2]^{2-}$	H_2qdt, $CoCl_2 \cdot 6H_2O$, NaOMe, $N_{2(g)}$, MeOH–EtOH (solvent)	Black; μ 2.40; λ_{max} 835 (295)	2
$[Co(S_2C_2R_2)_2]^{0,1-,2-}$ ions				
$R_2[Co\{S_2C_2(CN)_2\}_2]_2$	$[Co(mnt)_2]_2^{2-}$ (dimer)	I_2 or $[Ni(tfdt)_2]$ oxidation of $R_2[Co(mnt)_2]$	Green-brown; diamagnetic; λ_{max} 780 (3700), 715 (1200); $E_{1/2}$, +1.08 (CH_2Cl_2)	7
$(Et_4N)_2[Co\{S_2C_2(CF_3)_2\}_2]_2$	$[Co(tfdt)_2]_2^{2-}$ (dimer)	$[Co(tfdt)_2]$ in acetone–DMF, r.t.	Green-brown; diamagnetic; $E_{1/2}$ +0.50 (CH_2Cl_2)	6
$[Co\{S_2C_2(CF_3)_2\}_2]_2$	$[Co(tfdt)_2]_2$ (dimer)	$[Co_2(CO)_8]$ in *n*-pentane, H_2 fdt, $N_{2(g)}$, reflux	Black; diamagnetic; $E_{1/2}$ 0.535 V (MeCN)	6
$[Co\{S_2C_2(Ph)_2\}_2]_2$	$[Co(bdt)_2]_2$ (dimer)	P_4S_{10} + benzoin, $CoCl_2 \cdot 6H_2O$, H_2O, steam bath	Black (red soln.); diamagnetic	8
$(Et_4N)[Co\{S_2C_2(CF_3)_2\}_2]_2$	$[Co(tfdt)_2]_2^-$ (dimer)	$(Et_4N)_2[Co(tfdt)_2]_2$ + 0.5 mol equiv. $[Co(tfdt)_2]_2$	μ = 1.91; $\langle g \rangle$ = 2.043	9

[a] λ_{max} values in nm; $E_{1/2}$ values in V; μ values in BM.

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Table 101 Structures: Cobalt–1,2-Dithiolene Complexes

Complex	*Type*	*Structural data* (pm)					*Ref.*
		Co—S	*Co—S′ (dimer)*	*Co—Co*	*S—C*	*C—C*	
$(Bu^n_4N)_2$ 	Square planar	216.1	–	–	172.3	134	1
(Ph_3MeAs) 	Square planar	216.6	–	–	177	137	2
$(Bu^n_4N)_2$ 	Square pyramidal	218.5	240.4	309.9	176	141	3
(Pr^i_4N) 	Octahedral	224.7 221.2	–	–	172	134	4
(Pr^i_4N) 	Octahedral	225.3 221.5	–	–	176	141	4

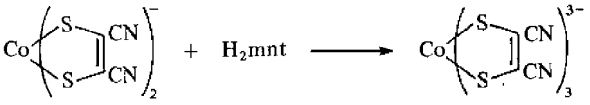
	Square pyramidal	216.1	238.2	278.1	169.4	139	3
	Cp and CoS_2C_2 planes at right angles	208	–	–	174	148	5
	Cp and CoS_2C_2 planes at right angles	211.7	–	–	–	136.4	6

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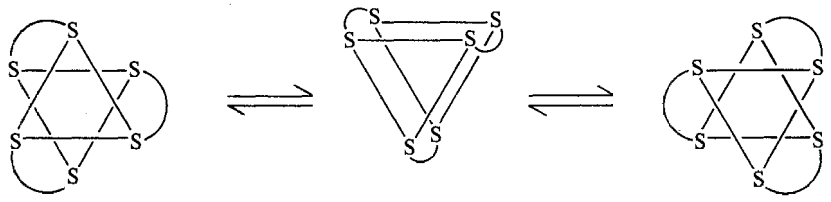
47.8.11.1 Tris(1,2-dithiolates)

Representative preparations are given in Table 100 and structural information in Table 101.

Diamagnetic $[Co(S_2C_2R_2)_3]^{3-}$ can be prepared from $Na_3[Co(CO_3)_3]$ or $[CoBr(NH_3)_5]^{2+}$ by heating with $Na_2S_2C_2R_2$ in water or alcohol or by adding excess ligand to the more stable square-planar monoanion (**356**; equation 198). $[Co(S_2C_2R_2)_3]^{3-}$ tends to dissociate to $[Co(S_2C_2R_2)_2]^-$ in the absence of excess ligand and to $[Co(S_2C_2R_2)_2]^{2-}$ in sunlight. It is probably octahedral, although no structure is available; $(Ph_4As)_3[Co\{S_2C_2(CN)_2\}_3]$ is isomorphous with the Cr^{III} complex, and the analogous Fe^{IV} complex is octahedral. In general the more reduced or negatively charge $[M(S_2C_2R_2)_3]^{n-}$ systems appear to be octahedral while the oxidized or neutral systems (*e.g.* of Re^{IV}, V^{VI}, Mo^{VI}) have the uncommon trigonal-prismatic structure (**357**; equation 199), possibly because the dithiolene structure would prefer to be *trans*, *e.g.* (**355**). $[V\{S_2C_2(CN)_2\}_3]^{2-}$ adopts an intermediate distorted geometry. Attempts to resolve $[Co(S_2C_2R_2)_3]^{3-}$ into its enantiomers have failed and the suggestion is that the trigonal-prismatic geometry (**357**) provides a low-energy pathway to intramolecular racemization (equation 199).[1185] Spectrally, however, these complexes resemble $[Co(thiooxalato)_3]^{3-}$, which has been resolved. The reduction potential, $E_{1/2} \approx -0.6$ V, suggests considerable reductive stability in neutral solution but the reduced $[Co(S_2C_2R_2)_3]^{4-}$ ion rapidly dissociates to $[Co(S_2C_2R_2)_2]^{2-}$ and free ligand. Oxidation is unknown although likely. Compared to the more common O- and N-donor octahedral chelates $[Co(S_2C_2R_2)_3]^{3-}$ is rather labile.



(356) green-brown (198)



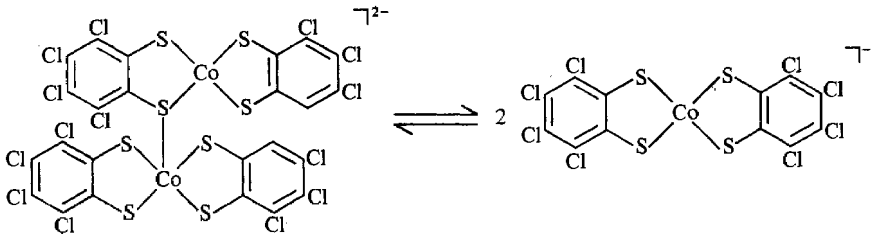
Λ-$[Co(S_2C_2R_2)_3]^{3-}$ (357) Δ-$[Co(S_2C_2R_2)_3]^{3-}$ (199)

47.8.11.2 Bis(dithiolates)

The $[Co(S_2C_2R_2)_2]^-$ ion can be prepared by the stoichiometric addition of $Na_2S_2C_2R_2$ to $CoCl_2 \cdot 6H_2O$ in EtOH or MeOH, or by the careful oxidation (*e.g.* I_2) of $[Co(S_2C_2R_2)_2]^{2-}$ (Table 100). This ion is chemically more robust than $[Co(S_2C_2R_2)_3]^{3-}$, although dimerization does occur and is usually rapid and reversible (equation 200). The equilibrium position depends on substituents with electron-withdrawing groups (CF_3, Ph, CN) stabilizing the dimer, and R = H, *p*-MeC_6H_4, giving monomeric products. Thus $[Co(p\text{-}MeC_6H_4dithiolate)_2]$ is monomeric and square planar both as a solid and in non-coordinating solvents, while the tetrachlorobenzene derivative $[Co(S_2C_6Cl_4)_2]_2^{2-}$ is diamagnetic and dimeric with a square-pyramidal geometry in the solid. In THF solution the latter dissociates to give the full spin-triplet ($S = 1$) ground state monomer (equation 201). Structures of both the square-planar monomer and square-pyramidal dimer (Table 101) show similar bond lengths to Co in the bridges and in the chelate rings with no Co–Co interaction. With $[Co\{S_2C_2(CF_3)_2\}]_2$ Co is 37 pm out of the basal plane of the square pyramid. The monomer unit has two unpaired electrons, the dimer is diamagnetic. Reversible oxidation (R = CF_3, Ph) is possible (equation 202), and the intermediate product $(Et_4N)[Co\{S_2C_2(CF_3)_2\}_2]_2$ has been isolated ($\mu = 1.91$ BM, Table 100). The fully oxidized $[Co(S_2C_2R_2)_2]_2$ systems (R = CF_3, Ph) are diamagnetic and adopt a square-pyramidal geometry (**358**), presumably because this allows the pairing up of spins in the semi-oxidized ligands. Thus both the electronic nature of the substituent and the oxidation state of the complex as a whole appear to control the structure and magnetic behaviour.

The tendency of $[Co(S_2C_2R_2)_2]^-$ to dimerize is paralleled by its ability to add additional ligands, those systems with electron-withdrawing substituents (R = CN, CF_3, halogenated phenyl) forming

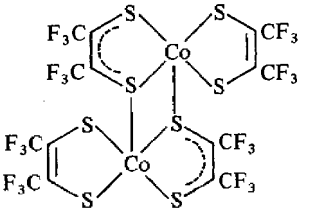
$$2[Co(S_2C_2R_2)_2]^- \rightleftharpoons [Co(S_2C_2R_2)_2]_2^{2-} \quad (200)$$



(201)

$$[Co(S_2C_2R_2)_2]_2^{2-} \underset{E_{1/2}\,0.5\,V}{\overset{-e^-}{\rightleftharpoons}} [Co(S_2C_2R_2)_2]^- \underset{E_{1/2}\,1.24\,V}{\overset{-e^-}{\rightleftharpoons}} [Co(S_2C_2R_2)_2] \quad (202)$$

$(CH_2Cl_2, Ag/AgI)$

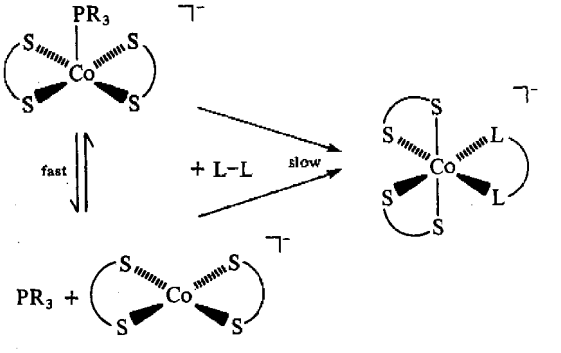


(358)

stable five- and six-coordinate systems but the others doing so only with difficulty (Table 102). Ligand addition is both fast and reversible. Addition to the square-planar monomer (**359**; equation 203) is rate determining (L = PPh_3, $AsPh_3$, py, phen).[1186,1187] With L = phen the process is two stage with chelation and stereochemical rearrangement following formation of the five-coordinate square pyramid. Subsequent reaction of $[Co(S_2C_2R_2)_2L]^-$ with chelating ligands such as phen, mnt^{2-}, bipy appears to occur *via* both associative and dissociative routes (Scheme 103). Green or tan five-coordinate $(Bu_4N)[Co\{S_2C_2(CN)_2\}_2L]$ (L = pip, morph) and six-coordinate $(Bu_4N)[Co\{S_2C_2(CN)_2\}_2L_2]$ (L = py, imH, NH_3, $BuNH_2$, $PhNH_2$) are representative of these systems.[1188] Crystal structures of two L = phen complexes (Table 101) show typical octahedral stereochemistries and these six-coordinate systems are spin paired and diamagnetic. The five-coordinate $[Co\{S_2C_2(CN)_2\}_2L]^-$ ion appears to be on the borderline between spin-triplet ($S = 1$) and diamagnetic ground states although there seems to be some uncertainty on this point.[1188,1189] The monodentate six-coordinate systems may adopt *cis* (preferred) and/or *trans* geometries.

$$[Co(S_2C_2R_2)_2]_2^{2-} \overset{fast}{\rightleftharpoons} 2[Co(S_2C_2R_2)_2]^- \overset{+L\ slow}{\rightleftharpoons} 2[Co(S_2C_2R_2)_2L]^- \quad (203)$$

(**359**)



Scheme 103

Ligand addition to the fully oxidized diamagnetic dimer $[Co(S_2C_2R_2)_2]_2$ (R = CF_3, Ph) cleaves the bridge forming spin-triplet $[Co(S_2C_2R_2)_2L]$ monomers of presumed square-pyramidal geometry (equation 204). These may be considered as Co^{IV} dithiolates or as Co^{III} complexes containing the

Table 102 Adducts of $[Co(S_2C_2R_2)_2]_2^{2-}$ and $[Co(S_2C_2R_2)_2]_2$

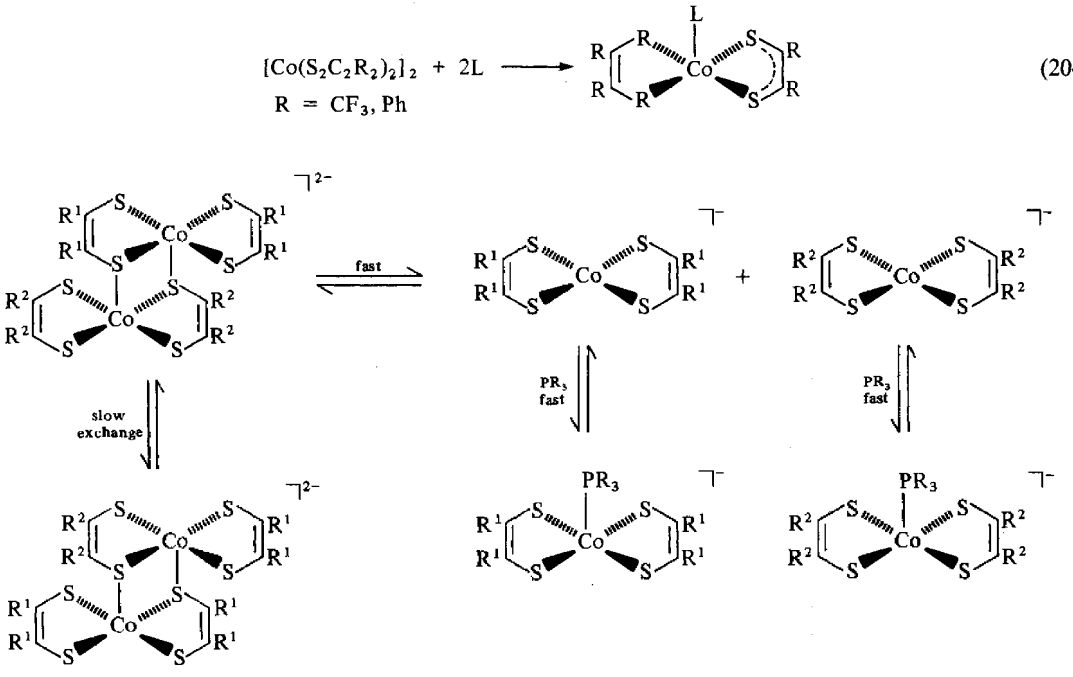
Reactant	*Solvent*	*Study*	*Ligand, L*	*Product*	*Ref.*
$[Co\{S_2C_2(CN)_2\}_2]_2^{2-}$, $[Co\{(S_2C_6H_3(Me)\}_2]^-$	Acetone	Preparation, kinetic, electronic	py, PPh_3, $AsPh_3$, phen, diarsine	$[Co(S_2C_2R_2)_2L]^-$, $[Co(S_2C_2R_2)_2L_2]^-$, $[Co(S_2C_2R_2)_2(L—L)]^-$	1
$[Co\{S_2C_2(CN)_2\}_2PPh_3]^-$	MeOH	Kinetic	en, bipy, phen, mnt^{2-}, $P(OPh)_3$	$[Co(mnt)_2(L—L)]^-$	3
$[Co\{S_2C_2(CN)_2\}_2(L—L)]^-$ (L—L = phen, bipy, en, mnt^{2-})	MeOH	Kinetic	PBu_3, PPh_3	$[Co(mnt)_2PR_3]^-$	2
$[Co(S_2C_2R_2)_2]_2^{2-}$ (R = CN, CF_3)	CH_2Cl_2	Kinetic, L exchange, polarographic	PPh_3, $AsPh_3$	$[Co(S_2C_2R_2)_2L]^-$	4
$[Co(S_2C_6Cl_4)_2]_2^{2-}$	THF	Preparation, properties	phen, PPh_3	$(Bu_4N)[Co(S_2C_6Cl_4)_2(PPh_3)]$, $(Bu_4N)[Co(S_2C_6Cl_4)_2(phen)]$	6
$[Co\{S_2C_2(CN)_2\}_2]_2^{2-}$	Acetone, CH_2Cl	Preparation, properties	pip, morph, py, NH_3, NH_2R, im	$[Co(mnt)_2L]^-$, $[Co(mnt)_2(L)_2]^-$	7
$[Co\{S_2C_2(Ph)_2\}_2]_2$	Acetone	Preparation, properties	PR_3, $P(OEt)_3$	$[Co\{S_2C_2(Ph)_2\}_2L]$, *cis*-$[Co\{S_2C_2(Ph)_2\}_2L_2]$	5
$[Co\{S_2C_2(CF_3)_2\}_2]_2^{2-}$, $[Co\{S_2C_2(CF_3)_2\}_2]_2$	Pentane, CH_2Cl_2	Preparation, properties	PPh_3, $AsPh_3$	$[Co\{S_2C_2(CF_3)_2\}_2L]^-$, $[Co\{S_2C_2(CF_3)_2\}_2L]$	8

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2. M. Hynes, D. A. Sweigart and D. G. DeWit, *Inorg. Chem.*, 1971, **10**, 1963.
3. D. A. Sweigart and D. G. DeWit, *Inorg. Chem.*, 1970, **9**, 1582.
4. A. L. Balch, *Inorg. Chem.*, 1971, **10**, 388.
5. G. N. Schrauzer, V. P. Mayweg, H. W. Finck and W. Heinrich, *J. Am. Chem. Soc.*, 1966, **88**, 4604; A. D. Troitskaya, Y. V. Yablokova, A. V. Ryzhmanova, A. I. Razumov and P. A. Gurevich, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1972, **17**, 2776.
6. M. J. Baker-Hawkes, E. Billig and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88**, 4870.
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oxidized ligand (more likely). Ligand exchange studies using mixtures of the reduced dimers $[Co(S_2C_2R_2)_2]_2^{2-}$ have shown[1190] that the monomer–dimer equilibrium is rapidly set up, that ligand exchange at the metal is slow (several hours) and probably occurs intramolecularly within the mixed dimer, and that dithiolate exchange does not occur in the five-coordinate system formed on adding L (Scheme 104).

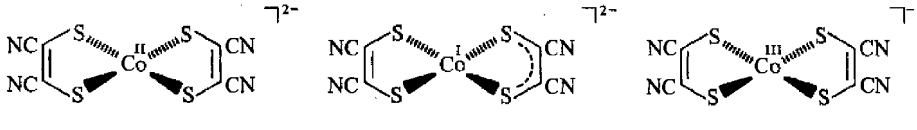
$$[Co(S_2C_2R_2)_2]_2 + 2L \longrightarrow \quad (204)$$

$R = CF_3, Ph$



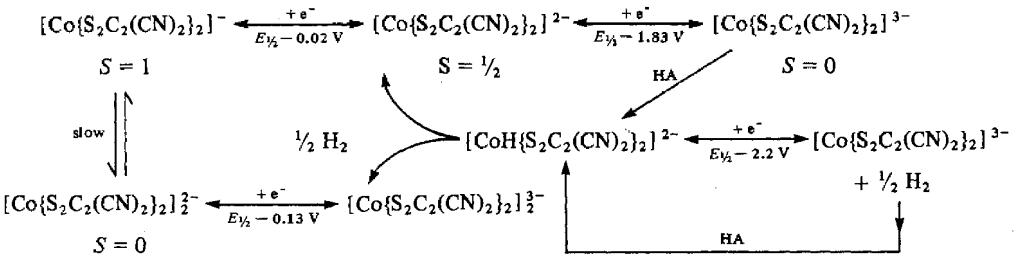
Scheme 104

The fully reduced monomeric anion $[Co(S_2C_2R_2)_2]^{2-}$ can be prepared from $CoCl_2 \cdot 6H_2O$ or $Co(OAc)_2 \cdot 6H_2O$ and $Na_2S_2C_2R_2$ in alcohol providing air is excluded (Table 100). Solutions are orange to red, the solids are paramagnetic with one unpaired electron and the structures are square planar. The complexes do not appear to dimerize and show a marked reluctance to add additional ligands except when the latter is a good π acceptor (*e.g.* $(Ph_4P)_2[Co\{S_2C_2(CN)_2(NO)\}]$ has been isolated). The photochemical oxidation of $[Co\{S_2C_2(CN)_2\}_2]^{2-}$ has been reported to be strongly wavelength dependent.[1191] The electronic structure of square planar $[Co(S_2C_2R_2)_2]^{2-}$ formed part of the considerable debate in the 1960s as to the extent of electron delocalization in the 1,2-dithiolene complexes, *i.e.* is $[Co\{S_2C_2(CN)_2\}_2]^{2-}$ d^7 Co^{II} with two dianionic dithiolate ligands (**360**) or is it spin-paired Co^{I} with an odd-electron dithiene radical anion (**361**).[1192,1193] The general consensus now seems to be that (**360**) is more correct with the odd electron being largely metal based but with some ligand character.[1182] The intense colour is consistent with extensive electron delocalization. Likewise MO calculations on the oxidized $[Co(S_2C_2R_2)_2]^{-}$ ion conclude that the two unpaired electrons are also largely metal based[1194] making these species examples of very rare square-planar paramagnetic d^6 Co^{III} (**362**) (*cf.* discussion above).



(360) (361) (362)

Electrochemical oxidation of $[Co\{S_2C_2(CN)_2\}_2]^{2-}$ in THF produces initially monomeric $[Co\{S_2C_2(CN)_2\}_2]^{-}$, which quickly dimerizes to $[Co\{S_2C_2(CN_2\}_2]_2^{2-}$ (Scheme 105). In DMSO this subsequent dimerization is only slight.[1187] Further reduction to $[Co\{S_2C_2(CN)_2\}_2]^{3-}$ is possible and weak acids are reduced to H_2 by this ion. A metal-based protonation mechanism (Scheme 105) has been proposed.[1197]



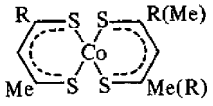
Scheme 105

Attempts to alkylate on sulfur in $[Co\{S_2C_2(CN)_2\}_2]^{2-,1-}$ have been unsuccessful. Reaction of MeI in THF with the former leads to decomposition while the latter appears to be unreactive.[1196]

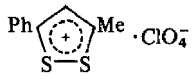
47.8.12 1,3-Dithiolenes

The syntheses and general properties of 1,3-dithiolene transition metal complexes have been discussed in a recent review.[1198]

Martin and Stewart[1199] first described the preparation of the deep-violet complex $[Co(SacSac)_2]$ (**363**; R = Me) from the reaction of $CoCl_2$ with acetylacetone (acacH) and H_2S. A similar synthesis[1200] where CF_3acac is substituted for acac yields $[Co(CF_3SacSac)_2]$ (**363**; R = CF_3). The preparation of $[Co(PhSacSac)_2]$ *via* BH_4^- reduction of the dithiolium salt (**364**) in the presence of $CoCl_2$ has also been reported.[1201]



(363)



(364)

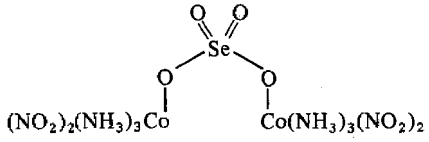
The magnetic properties of $[Co(SacSac)_2]$ (μ = 2.35 BM, 290 K; 2.30 BM, 112 K)[1198] are consistent with the known square-planar geometry in which the Co atom is precisely coplanar with the four S donor atoms.[1202] Low-spin five-coordinate base adducts $[Co(SacSac)_2B]$ (B = py, piperazine, $BiPh_3$, $SbPh_3$, $AsPh_3$, PPh_3) have been reported,[1203,1204] and oxidative addition of amines (phen, bipy) gives octahedral Co^{III} complexes $[Co(SacSac)_2(N{-}N)]^+$.[1205] With nitric oxide $[Co(SacSac)_2]$ yields two nitrosyls; dark brown, weakly paramagnetic $[Co(SacSac)_2(NO)]$ and red-brown, diamagnetic $[Co(SacSac)(NO)_2]$. The mononitrosyl is unstable in solution and disproportionates to the dinitrosyl and $[Co(SacSac)_3]$.[1206] A crystal structure of tetrahedral $[Co(SacSac)(NO)_2]$ is available.[115]

Dark-brown $[Co(SacSac)_3]$ is prepared by aerial oxidation of solutions of $[Co(SacSac)_2]$ in the presence of acetylacetone and H_2S.[1207] The initial product is $[Co(SacSac)_2(Sacac)]$ which converts to $[Co(SacSac)_3]$ under forcing conditions.

47.9 SELENIUM LIGANDS

47.9.1 Selenate and Selenite

These have been discussed together with oxyanions (Section 47.7.4), specifically SeO_4^{2-} (Section 47.7.4.1) and SeO_3^{2-} (Section 47.7.4.3). An early report on the preparation of (**365**)[1208] requires further confirmation.



(365)

47.9.2 Selenolate, Selenenate and Seleninate

47.9.2.1 Cobalt(II)

Pink-violet seleninato complexes $[Co(O_2SePhX)_2(H_2O)_2]$ (X = H, *m*-, *p*-Cl, *m*-, *p*-Br, *p*-Me, *p*-NO_2) can be obtained by the addition of cobalt(II) salts to aqueous solutions of substituted benzeneseleninato anions;[1209] IR studies indicate that the arylseleninato groups are (O,O) chelated to the metal. Reaction with N,N-bidentate ligands (phen, bipy) gives octahedral orange-yellow $[Co(O_2SeArX)_2(N,N)_2]$ species in which the $RSeO_2^-$ groups are bonded *via* a single oxygen donor.[1210]

47.9.2.2 Cobalt(III)

Co(III)—Se chemistry is in its infancy. Only a few compounds are known and those which are have been prepared *via* the oxidative Bennett approach[1033] using the diselenide and Co^{II} (equation 205, Table 103). Deutsch and coworkers were the first to make selenolate complexes.[1211] Generally they resemble their S counterparts, with H_2O_2 oxidation to the orange-yellow selenenato ($^-Se(O)R$) and seleninato ($^-Se(O)_2R$) complexes being even easier, and methylation with Me_2SO_4 in water giving selenoether Co—Se(Me)R complexes (Table 103).[1212] The structural *trans* effect of Co—SeR is somewhat greater than Co—SR (Δr = 6.3 *vs.* 4.1 pm) and all Co—Se complexes show intense charge-transfer spectra tailing into the visible.[1211,1212] The O atom in Co—Se(O)R is more basic than the corresponding oxygen atom in Co—S(O)R ($pK_a \approx 4$ *vs.* ≈ -1).[1213] This is in keeping with a longer Co—Se bond compared to Co—S (~236 pm *vs.* 224 pm).

$$2Co(ClO_4)_2 + 5en + (H_3N^+CH_2CH_2Se)_2SO_4^{2-} \xrightarrow[N_2,\ r.t.,\ H_2O]{} 2[Co(cystSe)(en)_2](ClO_4)_2 \quad (205)$$

One important difference from S is in the isomerization from Co—$Se(O_2)$R bonding to Co—OSe(O)R on standing an aqueous solution of $[Co(cystSeO_2)(en)_2](NO_3)_2$ for 1 d in a refrigerator.[1213] The structure of the resulting spontaneously resolved $\Delta(S)$-$(-)^{CD}_{500}$-$[Co\{cystSeO(O)\}(en)_2](NO_3)_2$ complex (**366**) gives the (*S*) configuration on Se with the *exo* O atom over an ethylenediamine ring.[1214] The longer Co—Se bond makes dissociation from the metal easier and this fact will probably limit the coordination chemistry of Se with Co. The lower energy of the ligand field absorption compared to S analogues (~10 nm shifts in the 490–500 nm absorption) is in keeping with this view. The corresponding sulfinate complex requires strong light for isomerization from S to O coordination (*cf.* Section 47.8.2.2.iii).

The Se atom becomes asymmetric on oxidation to Co—Se(O)R or on methylation to Co—Se(Me)R. Comparisons of CD spectra suggest that Se in Λ-$[Co\{cystSe(O)\}(en)_2]^{2+}$ takes on the

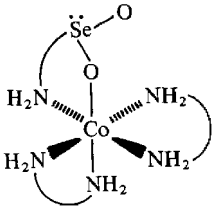
Table 103 Selenium Complexes

Complex	*Preparations, properties structures*[b]	*Ref.*
$[Co(cystSe)(en)_2](ClO_4)_2$, $[Co(cystSe)(en)_2](NO_3)_2$[a]	$(H_3N^+CH_2CH_2Se)_2SO_4^{2-}$, N_2, r.t., H_2O; CoSe 237.8, *trans* CoN 203.4, Δr 6.3; ε_{490} 170, ε_{297} 18 500	1
$[Co(tgaSe)(en)_2](ClO_4)$[a]	$(HO_2CCH_2Se)_2$, N_2, r.t., H_2; CoSe 235.5, *trans* CoN 200.6, Δr 4.0; ε_{520} 150, ε_{295} 17 000	1, 5
Λ-$(+)^{CD}_{500}$-$[Co(cystSe)(en)_2](NO_3)_2$	Ref. 1; resolved, K_2(Sb-+-tart)$_2$	2
$\Lambda(R)$-$(+)^{CD}_{500}$-$[Co\{cystSeO(O)\}(en)_2](ClO_4)_2$ (orange-yellow)	1 mol equiv. H_2O_2, r.t., 15 min	2
Λ-$(+)^{CD}_{500}$-$[Co\{cystSe(O_2)\}(en)_2](ClO_4)_2$	Excess 5% H_2O_2, $HClO_4$, 30 min	2
Λ-(S)-$(+)^{CD}_{500}$-$[Co\{cystSe(Me)\}(en)_2](ClO_4)_2$ (orange-red)	Me_2SO_4, overnight, A-25 Sephadex	2
$\Delta(S)$-$(-)^{CD}_{500}$-$[Co\{cystSeO(O)\}(en)_2](NO_3)_2$[a]	O-bound seleninate; spontaneous resolution; SeO 145.6, 147.6	3
p-$[Co(cystSe)(tren)](ClO_4)_2$	–	4
t-$[Co(cystSe)(tren)]ZnCl_4 \cdot 2H_2O$	–	4
p-$[Co\{cystSe(Me)\}(tren)]Cl_3 \cdot 2.5H_2O$ (orange)	MeI, DMSO	4
t-$[Co\{cystSe(Me)\}(tren)]Br_3 \cdot H_2O$ (orange)	MeI, DMSO	4

[a] Crystal structures. [b] Bond lengths in pm.

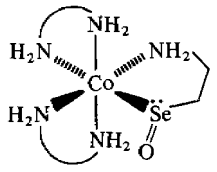
1. C. A. Stein, P. E. Ellis, R. C. Elder and E. Deutsch, *Inorg. Chem.*, 1976, **15**, 1618.
2. T. Konno, K. Okamoto and J. Hidaka, *Chem. Lett.*, 1982, 535.
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5. R. C. Elder, K. Burkett and E. Deutsch, *Acta Crystallogr., Sect. B*, 1979, **35**, 164.

equatorial (*R*) configuration (**367**) but this remains unconfirmed.[1213] ^1H and ^{13}C spectra suggest the opposite Λ(*S*) configuration* for the selenoether, and a stereospecific product.[1210] The long Co—Se bond should allow greater flexibility in this respect. Protonation at the O atom in Λ(*R*)-[Co{cysSe(O)}$(en)_2$]$^{2+}$ is easy ($pK_a \approx 4$) and appears to result in mutarotation at Se possibly *via* ready dissociation from the metal. Unlike thioether sulfur where racemization or mutarotation is reasonably fast ($0.1–10\ s^{-1}$) the two optical Se isomers, (*S*)- and (*R*)-*t*-[Co{cystSe(Me)}(tren)]$^{2+}$ (**368**) have been separated on SP-Sephadex.[1215] The mutarotation rate, $\sim 2 \times 10^{-4}\ s^{-1}$, demonstrates that inversion at Se is much slower than at S. The similar *p* complex could not be resolved chromatographically and it appears that the analogous *p*-(*R*)-[Co{cystSe(O)}(tren)]$^{2+}$ complex (**369**) racemizes some 50 times faster than its *t* congener. This may result from the greater lability of the Co—Se bond, or from differing rates of inversion at the metal. Photolysis of Co—SeR complexes leads to photoreduction at all wavelengths.



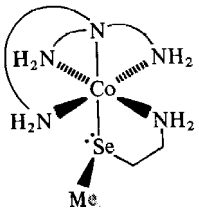
(**366**)

Δ(*S*)-(−)$^{CD}_{500}$-[Co{cystSeO(O)}$(en)_2$]$^{2+}$



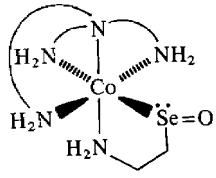
(**367**)

Λ(*R*)-(+)$^{CD}_{500}$-[Co{cystSe(O)}$(en)_2$]$^{2+}$



(**368**)

t(*S*)-[Co(cystSeMe)(tren)]$^{2+}$



(**369**)

p(*R*)-[Co{cystSe(O)}(tren)]$^{2+}$

47.10 REFERENCES

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Rhodium

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48.1 INTRODUCTION

Rhodium, as befits an element of the platinum metal sextet, occurs mainly as a minor constituent of platinum group metal ores. Thus, it occurs as a component of the ore deposits at Sudbury, Ontario, in the Merensky reef at Rustenberg in the Republic of South Africa, and in the platinum metals' ore deposits in the Ural range of the USSR. The major production centers are the Urals and South Africa, since the Sudbury ores in particular have a very low rhodium content. Minor deposits of the metal ores which contain some rhodium also occur in British Columbia, the United States of America, Columbia, Spain, Borneo and Australia. Nevertheless, rhodium is an exceedingly rare element with an abundance in the earth's crust of some 10^{-9}%.

The element was first isolated by Wollaston in 1804 who obtained it from crude platinum. The crude platinum was of Spanish origin and Wollaston complained of the mercury added by the Spaniards in an attempt to remove the gold from the material.[1]

Within a decade the first rhodium complex, $[RhCl(NH_3)_5]Cl_2$, had been prepared by Vauquelin.[2] Later this complex was studied by Claus whose name is often associated with the salt.[3] The naming of a complex after a later worker in the field has since become something of a tradition in rhodium chemistry.

The stereochemistry of rhodium(III) complexes was established by Werner who prepared the cation $[Rh(en)_3]^{3+}$ and resolved the racemate *via* its (+)-3-nitrocamphorate or (+)-tartrate salts.[4]

However, progress in rhodium complex chemistry was slow, and it was not until the early 1940s that Dwyer and Nyholm[5,6] prepared further examples of rhodium complexes. These included the

tertiary arsine complexes, which were later to exert such an important influence on the direction rhodium chemistry would take.

Again rhodium chemistry languished for two decades. In the 1960s four disparate lines of research suddenly burgeoned, making the chemistry of the element one of the most active research areas of the past two decades.

The kinetic and thermodynamic studies on the octahedral rhodium(III) complexes[7] suddenly gained momentum. This field was later to give rise to the important discovery of the photosensitivity of rhodium complexes.[8]

A totally new field of rhodium chemistry was opened up by the discovery of the remarkable catalytic properties of $[RhCl(PPh_3)_3]$ by Wilkinson's school.[9,10] This important complex has stimulated a rapid expansion in the chemistry of the lower oxidation state complexes. Much of this interest has, inevitably, spilled over into the organometalic chemistry of the element and is thus outside the scope of this chapter.

The facile changes of oxidation state exhibited by rhodium complex catalysts pointed the way to the employment of rhodium complexes in the photochemical decomposition of water.[11]

The interest in the lower valence states of rhodium also led to the synthesis of the rhodium(II) carboxylates,[12] which, although shown to be diamagnetic, excited little interest until the end of that momentous decade when an X-ray crystal structure revealed the source of the diamagnetism to be their rhodium—rhodium bonds.[13]

However, the rapid pace of rhodium chemistry has not been fully reflected in the review literature. The two extant English language reference works have been well overtaken by events.[14,15] There is an invaluable compendium of the early work by Griffith,[16] and a new edition of Gmelin's handbook has been published very recently.[17] However, apart from these last two books and the ever increasing space devoted to the chemistry of the element in undergraduate texts there has been no systematic attempt to review the chemistry of this element apart from its organometallic compounds, which form the subject of the companion series.[18]

To some extent this situation has been rectified by a number of reviews of more limited range. Among these are the review by Robinson on the rhodium(II) carboxylates,[19] and the reviews on the chemistry of $[RhCl(PPh_3)_3]$[20] and $[RhH(CO)(PPh_3)_3]$.[21] The tertiary phosphine, arsine and stibine complexes of the element have also been covered in two reviews of these ligands' complexes with the transition elements.[22]

Apart from catalytic reactions in organic and industrial chemistry there are few practical applications of rhodium complexes. Recently some interest has been shown in the use of rhodium(II) carboxylates in chemotherapy. Generally it appears that the rhodium(II) complexes are less effective than those of platinum(II),[23] although they also appear to induce less unwelcome side effects than do the platinum(II) complexes. They may have some promise as radiation sensitizers, although this is more probably due to the high atomic number of rhodium than any specific pharmaceutical properties.

As might be expected, the lipophilicity increases with increasing chain length of the carboxylato ligands' alkyl group. This increases the body burden of rhodium, which in turn increases both the toxicity and antitumor activity of the rhodium complex. However, it has been stated that too great an increase in the chain length (*i.e.* beyond the pentanoate) reduces the therapeutic properties.[24] It seems that optimal properties are shown by the butyrate.[25,26]

The mode of action of the carboxylates is, as yet, uncertain. It is believed that acetate is mainly decomposed in the liver. The labelled acetate produces $^{14}CO_2$, but only 5% of the rhodium is eliminated in the urine in the first 24 hours after administration.[27] The acetate, propionate[28] and butyrate[29] inhibit DNA and RNA syntheses. This has been demonstrated for the butyrate by *in vivo* studies on Erlich tumor cells in mice. It is possible that rhodium(II) acetate owes its antineoplastic activity to its inhibition of the enzymatic deamination of arabinosylcytosine. The latter is an antineoplastic agent in its own right, and it has been suggested that its joint administration with rhodium(II) acetate might prove efficacious.[30]

The complexes of rhodium will primarily be considered in order of increasing oxidation state. However, complexes in which the oxidation state of the metal is uncertain (*e.g.* nitrosyls) or dinuclear complexes of mixed oxidation state will be dealt with last.

The complexes will be assigned to sections according to the number of neutral ligands they contain. Polydentate ligands will, for the purposes of assignation, be considered to be equivalent to the number of donor atoms. However, polydentate ligands' complexes will normally be considered after those of similar monodentate ligands. For example, discussion of the properties of $[Rh(NH_3)_6]^{3+}$ will precede that of the reactions of $[Rh(en)_3]^{3+}$. Mononuclear complexes will precede bridged complexes. Within these classes the donor atom will determine the order to citation and

within each of these sub-classes the anionic ligand will then determine the order. Polyatomic anions will be cited in the order appropriate to their central atom. The final determinant of precedence will be increasing relative molar mass, which can generally be equated with complexity of the ligand set. For example *mer*-$[RhCl_3(PMe_3)_3]$ will be discussed before *mer*-$[RhCl_3(PPr_3)_3]$, which in turn will be followed by *mer*-$[RhCl_3(PPr^i_3)_3]$. To this end, invoking the complexity criterion, PR_3 complexes will, for example, precede $PR'R_2$ complexes. All complexes will be included at the first opportunity. Thus, $[RhCl_5(H_2O)]^{2-}$ would be considered to be the complex of an oxygen ligand rather than of five chloro ligands.

This order will be adhered to except where its slavish implementation would lead to extensive cross referencing and unnecessary duplication of material. The bald order will be supplemented by sundry reaction schemes since, historically, many areas of rhodium chemistry have been developed by preparing derivatives of some dozen or so key complexes, and it would be unwise to discard this aspect of the subject.

48.2 RHODIUM(−I) COMPLEXES

With one exception the only non-carbonyl complexes in this oxidation state are those of the $[Rh(PF_3)_4]^-$ ion. Complexes of this ligand were reviewed by Nixon in 1970.[31]

The salts of this ion, which is presumably tetrahedral like the isoelectronic anion $[Co(CO)_4]^-$, can be obtained by neutralizing $[RhH(PF_3)_4]$ with bases (equation 1).[32]

$$[RhH(PF_3)_4] + py \longrightarrow (pyH)[Rh(PF_3)_4] \quad (1)$$

The potassium salt can be prepared by reducing $[Rh_2(PF_3)_8]$ with potassium amalgam (equation 2),[32–35] or by allowing the latter reagent to react with the hydridorhodium(I) complex (equation 3).[32,35]

$$[Rh_2(PF_3)_8] + 2K/Hg \longrightarrow 2K[Rh(PF_3)_4] \quad (2)$$

$$[RhH(PF_3)_4] + 2K/Hg \longrightarrow 2K[Rh(PF_3)_4] + H_2 + Hg \quad (3)$$

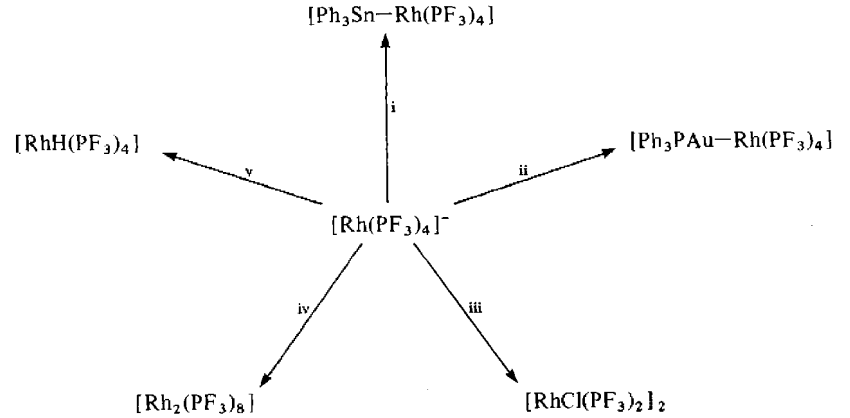
The dimeric chloro complex $[RhCl(PF_3)_2]_2$ can be similarly reduced.[36]

Large cations form isolable salts of the $[Rh(PF_3)_4]^-$ anion (equations 4 and 5).[32]

$$[Rh(PF_3)_4] + [Fe(phen)_3]^{2+} \longrightarrow [Fe(phen)_3][Rh(PF_3)_4]_2 \quad (4)$$

$$[RhH(PF_3)_4] + [Co(Cp)_2]^+ \longrightarrow [Co(Cp)_2][Rh(PF_3)_4] \quad (5)$$

The reactions of the $[Rh(PF_3)_4]^-$ anion are showing in Scheme 1. The most noteworthy reactions include the formation of metal–metal bonds with tin[33,36] and gold.[33] Other $[L_nM—Rh(PF_3)_4]$ complexes can be prepared by different routes (see Section 48.10.3). The anion is oxidized by $SnCl_4$, $TlCl_3$ or $[RhCl(PF_3)_2]_2$.[33]



i, Ph_3SnCl;[36] ii, $[Ph_3PAuCl]$;[33] iii, $TlCl_3$ or $SnCl_4$;[33] iv, $[RhCl(PF_3)_2]_2 + PF_3$;[33] v, 50% H_2SO_4[34]

Scheme 1 Reactions of $[Rh(PF_3)_4]^-$

The only other non-carbonyl rhodium(−I) complex that has been isolated is the closely related $[Rh(PF_2NMe_2)_4]^-$. The potassium salt can be obtained by reducing $[RhCl(PF_2NMe_2)_3]$ with potassium amalgam.[37]

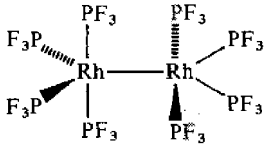
48.3 RHODIUM(0) COMPLEXES

48.3.1 $[Rh_2(PF_3)_8]$

This complex can be prepared by allowing PF_3 to react with anhydrous rhodium trichloride and copper powder under severe conditions (equation 6).[34,35]

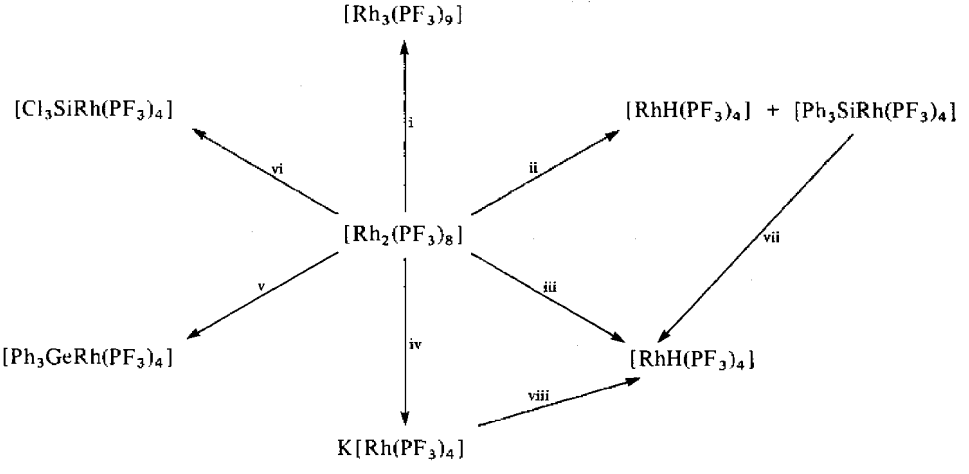
$$RhCl_3 + 6Cu + 8PF_3 \xrightarrow[150°C]{250\,atm} [Rh_2(PF_3)_4]_2 + 6CuCl \quad (6)$$

A more convenient preparation is to oxidize $K[Rh(PF_3)_4]$ with $[RhCl(PF_3)_2]_2$ (Scheme 1, Section 48.2 above).[33] The diamagnetic, orange-red crystals of the product melt at 92.5°C.[35] The dimeric formulation (**1**) is consistent with its diamagnetism, and with the ^{19}F and ^{31}P NMR spectra recorded at temperatures below −15°C.[33,38] Poor crystal quality prevents the solid state structure being determined.[38]



(1)

The rhodium(0) complex reacts instantaneously with hydrogen and abstracts it from several hydrides (Scheme 2). On heating $[Rh_2(PF_3)_8]$ to 170°C, it decomposes forming $[Rh_3(PF_3)_9]$. The trimer has been characterized by mass spectrometry, but there is the possibility it may be the mixed Rh^I/Rh^0 species $[Rh_3(PF_2)(PF_3)_8]$.[33]



i, 170°C;[33] ii, Ph_3SiH;[33] iii, H_2;[33] iv, K/Hg;[34] v, Ph_3GeH;[33] vi, $SiHCl_3$;[33] vii, H_2;[33] viii, 50% H_2SO_4[34]

Scheme 2 Reactions of $[Rh_2(PF_3)_8]$

48.3.2 $[Rh(PPh_3)_n]$ Complexes

Pale green $[Rh(PPh_3)_4]_2$ can be prepared by the polarographic reduction of $[RhCl(PPh_3)_3]$ in acetonitrile. The product is believed to be dimeric since it is diamagnetic. Attempts to demonstrate the presence of an Rh—H bond in the material failed.[39,40] The complex can also be prepared by electrochemically reducing solutions of $RhCl_3 \cdot 3H_2O$ in the presence of triphenylphosphine.[40]

There is a patent claiming that magnesium amalgam reduced $[RhCl(PPh_3)_3]$ to $[Rh(PPh_3)_2]_2$.[41] However, since the high field ^1H NMR spectra of these complexes have not been obtained, there

must be some doubt as to their authenticity. They may be hydridorhodium(I) complexes or even *o*-metallated rhodium(I) complexes.

48.3.3 [Rh(diphos)$_2$]

The ionic complex [Rh(diphos)$_2$]Cl can be reduced electrochemically in a variety of solvents to form the reactive species [Rh(diphos)$_2$]. The usual fate of this species is to abstract a hydrogen atom from the solvent and form [RhH(diphos)$_2$].[42] There is one instance where attack on the electrolyte, [Bu$_4$N][ClO$_4$], has been observed.[43] Another school disputes this mechanism of [RhH(diphos)$_2$] formation, and rightly questions the validity of deuterium labelling experiments which use alkaline mixtures of H_2O and D_2O.[44]

48.4 RHODIUM(I) COMPLEXES

48.4.1 Anionic Complexes

Rhodium does not readily form anionic complexes in its lower oxidation states, probably because π-acid ligands are usually required to disperse the electron density from the metal in neutral or even cationic complexes. It is not surprising, therefore, that the few examples of rhodium(I) anionic complexes contain powerful π-acid ligands.

The $[RhCl(SnCl_3)_2]_2^{4-}$ anion can be obtained by allowing $[SnCl_3]^-$ — to reduce rhodium trichloride (equation 7). The tetramethylammonium salt has been isolated.

$$2RhCl_3 + 6[SnCl_3]^- \xrightarrow{3M\ HCl} [RhCl(SnCl_3)_2]_2^{4-} + 2[SnCl_5]^- \quad (7)$$

Tetramethylammonium chloride cleaves the dimeric complex $[RhCl(PF_3)_2]_2$ and forms $[Me_4N][RhCl_2(PF_3)_2]$.[36]

48.4.2 [RhXL$_2$] Complexes

There are three principal types of complex which share this stoichiometry. The first consists of authentic three-coordinate complexes containing three monodentate ligands. The second type comprises complexes of mononegative bidentate anions. In the last type rhodium achieves four coordination by forming bridged species of general formula $[RhXL_2]_2$. Complexes where one of the neutral ligands is untypically bidentate are discussed in Section 48.4.2.4.

48.4.2.1 Three-coordinate complexes

These complexes (see Table 1) are formed by very bulky, electron-donating tertiary phosphine ligands since even relatively large ligands of this type from $RhXL_3$ complexes (*e.g.* $[RhCl(PPh_3)_3]$). Electron-withdrawing ligands give rise to halo-bridged complexes, for example $[RhCl\{P(C_6F_5)_3\}_2]_2$. There has been considerable interest in the synthesis and properties of such three-coordinate complexes since they are isolable analogs of the important catalytic intermediate $[RhCl(PPh_3)_2]$.

Bis(tricyclohexylphosphine) complexes are probably the most accessible and hence widely inves-

Table 1 Physical Properties of $[RhXL_2]$ Complexes

Complex	*Color*	*M.p.* (°C)	*Ref.*
$[RuH(PPr^i_3)_2]$	Orange	80[a]	55
$[RhH(PBu^t_3)_2]$	Dark brown	160[a]	55
$[Rh\{N(SiMe_3)_2\}(PPh_3)_2]$	Green	128–30	58, 59
$[RhF(PCy_3)_2]$	Red	—	46
$[RhCl(PCy_3)_2]$	Lilac	—	46
$[RhBr(PCy_3)_2]$	Lilac	—	46
$[RhI(PCy_3)_2]$	Lilac	—	46

[a] With decomposition.

tigated three-coordinate complexes. Numerous PCy_3 complexes can be prepared from $[RhF(C_8H_{14})_2]_n$ (equation 8).[46,47]

$$[RhF(cod)]_2 + 4PCy_3 \longrightarrow 2[RhF(PCy_3)_2] \xrightarrow{NaX} [RhX(PCy_3)_2] \quad (8)$$
$$X = Cl, Br, I, N_3$$

The bromo and iodo complexes can also be prepared from $[RhCl(C_8H_{14})_2]_2$.[47] The ^{31}P NMR spectrum shows $[RhCl(PCy_3)_2]$ to be in equilibrium with $[RhCl(PCy_3)_2]_2$.[46]

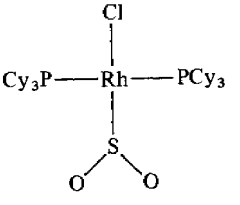
The bis(tricyclohexylphosphine) complexes are 14-electron species and are highly reactive. They are easily oxidized by air,[48] and even decompose when stored in an inert atmosphere. However, they will readily coordinate an additional small ligand. Many of these small ligands bind through carbon and are, therefore, outside the scope of this review. Both dinitrogen[46,49] and sulfur dioxide form adducts (equations 9 and 10).[50]

$$[RhX(PCy_3)_2] + N_2 \xrightarrow[25°C]{C_6H_6} [RhX(PCy_3)_2N_2] \quad (9)$$
$$X = Cl, Br, I$$

$$[RhCl(PCy_3)_2] + SO_2 \longrightarrow [RhCl(SO_2)(PCy_3)_2] \quad (10)$$

The fluoro complex does not react with dinitrogen, but the degree of reactivity increases with the atomic number of the halo ligand.

The sulfur dioxide complex (**2**) has been shown to contain an S-bound sulfur dioxide ligand.[51]



(2)

The $RhXL_2$ complexes can also be prepared by expelling one neutral ligand from $RhXL_3$ complexes. Tricoordinate or weakly solvated square planar complexes are known to exist in solution,[52,53] but unsolvated examples have seldom been isolated. The phenolate complex $[Rh(OPh)(PPh_3)_2]$ can be prepared by recrystallizing the tris(triphenylphosphine) complex from toluene, but it may be dimeric with anion bridges.[54] The best examples of this method of preparation are those of $[RhHL_2]$ complexes. These three-coordinate hydrido complexes are obtained due to the high *trans* effect of the hydrido ligand labilizing the third neutral ligand in the four-coordinate precursor. Several $[RhH(PR_3)_2]$ complexes can be obtained from the dinitrogen complexes $[RhH(N_2)(PR_3)_3]$.[55,56] The corresponding PCy_3 complex can be obtained by decomposing *trans*-$[RhHN_2(PCy_3)_2]$ at 60°C (equation 11).[55]

$$[RhH(N_2)(PR_3)_2] \longrightarrow [RhH(PR_3)_2] + N_2 \quad (11)$$
$$R_3 = Bu^t_3,[54,55]\ Bu^t_2Ph[54]$$

At lower temperatures dinitrogen coordinates to $[RhH(PCy_3)_2]$ forming the four-coordinate mononuclear complex $[RhH(N_2)(PCy_3)_2]$.[46,47,49,55,56]

Less commonly, three-coordinate complexes can be obtained containing a large anion. The yellow three-coordinate complex $[Rh\{N{=}C(CF_3)_2\}(PPh_3)_2]$ can be prepared by allowing $[Me_3Sn\{N{=}C(CF_3)_2\}]$ to react with $[RhCl(PPh_3)_3]$.[57] Poorer yields are obtained when $[LiN{=}C(CF_3)_2]$ is used. Presumably the anion is bound solely through nitrogen as it is in $[Rh\{N{=}C(CF_3)_2\}\{C(NMeCH_2)_2\}(PPh_3)_2]$ whose structure has been determined by X-ray crystallography.[58]

The green bis(trimethylsilyl)amido complex can be prepared by allowing $[RhCl(PPh_3)_3]$ to react with $LiN(SiMe_3)_2$ in THF.[59] It will be noted that neither of these anions can undergo β-hydride abstraction reactions that destroy simpler amido complexes.

48.4.2.2 Complexes containing bidentate anions

The pentan-2,4-dionato (acac) complexes may be prepared either by cleaving dinuclear pentan-2,4-dionato complexes with tertiary phosphines,[60,61] or by displacing the halo ligands in bridged, triphenyl phosphite or $PF_2(NEt_2)$ complexes (equations 12–16).[61,62]

$$[Rh(acac)(C_2H_4)_2]_2 + 4PR_3 \longrightarrow 2[Rh(acac)(PR_3)_2] + 4C_2H_4 \quad (12)$$

$R_3 = Ph_3, Ph_2Me$[60]

$$[Rh(acac)(C_8H_{14})_2]_2 + 4PR_3 \longrightarrow 2[Rh(acac)(PR_3)_2] + 4C_8H_{14} \quad (13)$$

$R_3 = PF_2NEt_2, PF(NMe_2)_2$[61]

$$[Rh(acac)(CO)_2] + 2PR_3 \longrightarrow [Rh(acac)(PR_3)_2] + 2CO \quad (14)$$

$R_3 = PF_2NEt_2, P(NMe_2)_3$[61]

$$[RhX\{P(OPh)_3\}_2]_2 + 2acacH \longrightarrow 2[Rh(acac)\{P(OPh)_3\}_2] \quad (15)$$

X = Cl, Br[62]

$$[RhCl(PF_2NEt_2)_2]_2 + 2acacH \longrightarrow 2[Rh(acac)(PF_2NEt_2)_2] \quad (16)$$

Closely similar is the preparation of the *N*-methylsalicylaldiminato complexes (equation 17).[63]

$$[RhCl(C_2H_4)_2]_2 + 2Tl(SalNMe) + 4PR_3 \xrightarrow{Et_2O} 2[Rh(SalNMe)(PR_3)_2] + 2TlCl + 4C_2H_4 \quad (17)$$

$R_3 = Ph_3, Ph_2Me$[63]

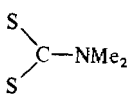
Orange crystals of the trifluoroacetato complex $[Rh(O_2CCF_3)\{P(OMe)_3\}_2]$ can be obtained if the trimeric hydrido complex $[RhH\{P(OMe)_3\}_2]_3$ is allowed to react with CF_3CO_2H in diethyl ether.[64]

Generally, however, this class of complex is the preserve of the disulfur anion. If $[RhCl(PPh_3)_3]$ is allowed to react with ammonium dialkyldithiophosphinates or diaryldithiophosphates in benzene, the products are $[Rh(S_2PCy_2)(PPh_3)_2]$ and $[Rh\{S_2P(OPh)_2\}(PPh_3)_2]$ respectively (equation 18).[65]

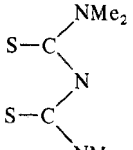
$$[RhCl(PPh_3)_3] + NH_4S_2PR_2 \longrightarrow [Rh(S_2PR_2)(PPh_3)_2] + PPh_3 + NH_4Cl \quad (18)$$

R = Cy, OPh[65]

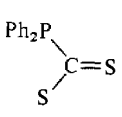
Other di- or mono-thioanions (**3**)–(**8**) form complexes.[66] The secondary phosphinethiol $MeCH(SH)CH_2PHPh$ also displaces the chloro and one triphenylphosphine ligand from $[RhCl(PPh_3)_3]$ when it is dissolved in aqueous ethanolic ammonia.[67] The structures of these complexes have been inferred from their ^1H and ^{31}P NMR spectra.



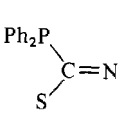
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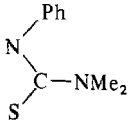
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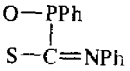
(5)



(6)



(7)



(8)

48.4.2.3 Bridged complexes

These complexes can be prepared from phosphorus ligands that are themselves substituted by electron-withdrawing groups. It is often beneficial, however, to employ a low ratio of phosphorus ligand to rhodium since in several instances excess ligand cleaves the halo bridges and forms four-coordinate monomeric complexes. Table 2 lists those complexes of this structure that have been isolated.

Many of the complexes can be prepared by displacing ethylene from Cramer's compound (equation 19). However, it is more difficult to displace all the cycloocta-1,5-diene from $[RhCl(cod)]_2$ (equation 20); unless excess ligand is used an intermediate cyclooctadiene complex is formed.[77]

Table 2 Physical Properties of $[RhXL_2]_2$ Complexes

X	*L*	*Color*	*M.p.* (°C)	*Ref.*
Cl	PPh_3	Salmon	—	68
SCN	PPh_3	—	—	69
Cl	$P(p\text{-}C_6H_4Me)_3$	Beige	240–43[a]	70
Cl	(**9**)	Red-brown	153	71
Cl	(**10**)	Orange-brown	151–53	71
Cl	PPh_2R^b	Dark red	Oil	72
Cl	$P(C_6F_5)_3$	Green	216–18	73, 74
Cl	$PPh_2(C_6F_5)$	Dark red	175–85	74
Br	$PPh_2(C_6F_5)$	Dark red	180–85	74
Cl	$PPh_2(C_6Cl_5)$	—	300	75
Br	$PPh_2(C_6Cl_5)$	—	300	75
Cl	$PPh(C_6F_5)_2$	Dark red	219–21	74
Br	$PPh(C_6F_5)_2$	Purple-black	190–93	74
Cl	$P(OMe)_3$	Yellow	205	76
H	$P(OPr^i)_3$	Green	123[a]	64
Cl	$P(OPh)_3$	Yellow	—	62, 77
Br	$P(OPh)_3$	Yellow	—	62, 77
SCN	$P(p\text{-}OC_6H_4Me)_3$	Yellow	150–75	78
PF_2	PF_3	—	140	32
Cl	PF_3	Red	70	33, 34, 79, 80
Br	PF_3	Red	61–62	79
I	PF_3	Dark red	62–63	79
Cl	PF_2CCl_3	Orange	118–19	80
Cl	PF_2NMe_2	Yellow	112–13	61, 81
Cl	PF_2NEt_2	Yellow	103–04	82
I	PF_2NEt_2	Yellow	—	61
Cl	$PF_2(OPr)$	Orange	Oil	76
Cl	$SPPh_3$	Brown	300	83, 84
Cl	$PF_3 + Ph_2N_2$	—	—	85

[a] With decomposition. [b] $R = (MeSiO)_2MeSiCH_2CH_2$.

$$[RhCl(C_2H_4)_2]_2 + 4L \longrightarrow [RhClL_2]_2 + 4C_2H_4 \quad (19)$$

$$L = P(p\text{-}C_6H_4Me)_3,^{70}\ PPh_2CH_2CH_2SiMe(OMe)_2,^{72}\ PF_2NMe_2,^{81}\ PF_2NEt_2^{82}$$

$$[RhCl(C_8H_{12})]_2 + 4L \longrightarrow [RhClL_2]_2 + 2C_8H_{12} \quad (20)$$

$$L = P(OMe)_3,^{76}\ P(OPh)_3,^{62}\ PF_2(OPr)^{76}$$

The enthalpies of these exothermic reactions have been determined for chloro, bromo and iodo species.[86] Other complexes that have been obtained from the cyclooctadiene complex include $[RhCl(PF_3)_2]_2$,[36] $[RhCl\{P(OMe)_3\}_2]_2$ and $[RhCl\{PF_2(OPr)\}_2]_2$.[76]

It is even more difficult to prepare $[RhClL_2]_2$ complexes from $[RhCl(CO)_2]_2$ (equation 21). Only the stronger π-acid ligands are capable of totally displacing the carbonyl ligands of the starting material. The triphenyl phosphite[78] and PF_3 complexes[79] can be made in this way.

$$[RhCl(CO)_2]_2 + 4L \longrightarrow [RhClL_2]_2 + 4CO \quad (21)$$

$$L = PF_3,^{79}\ P(OPh)_3,\ P(p\text{-}OC_6H_4Me)_3,\ P(p\text{-}OC_6H_4Cl)_3^{78}$$

The mixed ligand complex $[Rh_2Cl_2(PF_3)_2(PhN_2Ph)_2]$ was prepared by equilibrating the two dimeric complexes (equation 22).[85]

$$[RhCl(PF_3)_2]_2 + [RhCl(PhN_2Ph)_2]_2 \longrightarrow 2[RhCl(PF_3)(PhN_2Ph)]_2 \quad (22)$$

The complexes can also be prepared from other monomeric rhodium(I) complexes. Both the triphenylphosphine and the tri(*p*-tolyl)phosphine complexes can be prepared by refluxing solutions of the appropriate $[RhCl(PAr_3)_3]$ complex in an inert atmosphere (equation 23).[68,70] Alternatively one ligand of an $[RhXL_3]$ complex can be oxidized (equation 24).[87,88]

$$2[RhCl(PAr_3)_3] \rightleftharpoons [RhCl(PAr_3)_2]_2 + 2PAr_3 \quad (23)$$

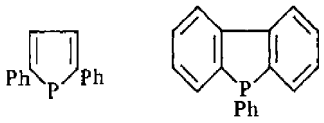
$$Ar = Ph,^{68}\ p\text{-}C_6H_4Me^{70}$$

$$2[RhCl(CO)(PPh_3)_2] + Bu^tOOH \longrightarrow [RhCl(PPh_3)_2]_2 + 2Ph_3PO \quad (24)$$

Finally several complexes can be prepared by utilizing the ligand to reduce hydrated rhodium trichloride in homogeneous solution (equation 25).[71,73–75,83,84]

$$2RhCl_3 \cdot 3H_2O + 6L \xrightarrow{EtOH} [RhClL_2]_2 + 2LO \quad (25)$$

L = (9), (10),[71] $P(C_6F_5)_3$,[73,74] $PPh_2(C_6F_5)$,[74] $PPh_2(C_6Cl_5)$[75]



(9) (10)

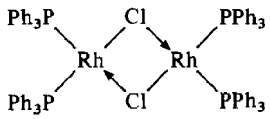
The kinetics of the formation of $[RhCl(PPh_3)_2]_2$ from $[RhCl(PPh_3)_3]$ have been studied.[91,92] The dimeric complex has the planar structure (11); this is similar to that found for $[RhCl(cod)]_2$, but differs from the folded structure adopted by $[RhCl(CO)_2]_2$.[93] Details of the far IR spectra, which indicate similar halo-bridged structures are collected in Table 3.

Of all the complexes detailed above, those containing fluorine-substituted ligands have been the most studied. Their ^{31}P NMR spectra are summarized in Table 4.

The dimeric complexes can undergo bridge cleavage, neutral ligand exchange, or anionic ligand exchange when allowed to react with suitable reagents. Again the reactions of $[RhCl(PF_3)_2]_2$ have been most widely studied. These reactions are summarized in Scheme 3.

Triphenyl phosphite complexes undergo several of the reactions of the PF_3 complexes and, unlike the latter, are cleaved by treatment with excess ligand (equation 26). In the presence of a non-complexing anion the chloro ligand is displaced.[62]

Excess triphenyl phosphite will convert $[RhCl\{P(C_6F_5)_3\}_2]_2$ to the triphenyl phosphite complex (equation 27). Triphenylphosphine reacts similarly.[73,74]



(11)

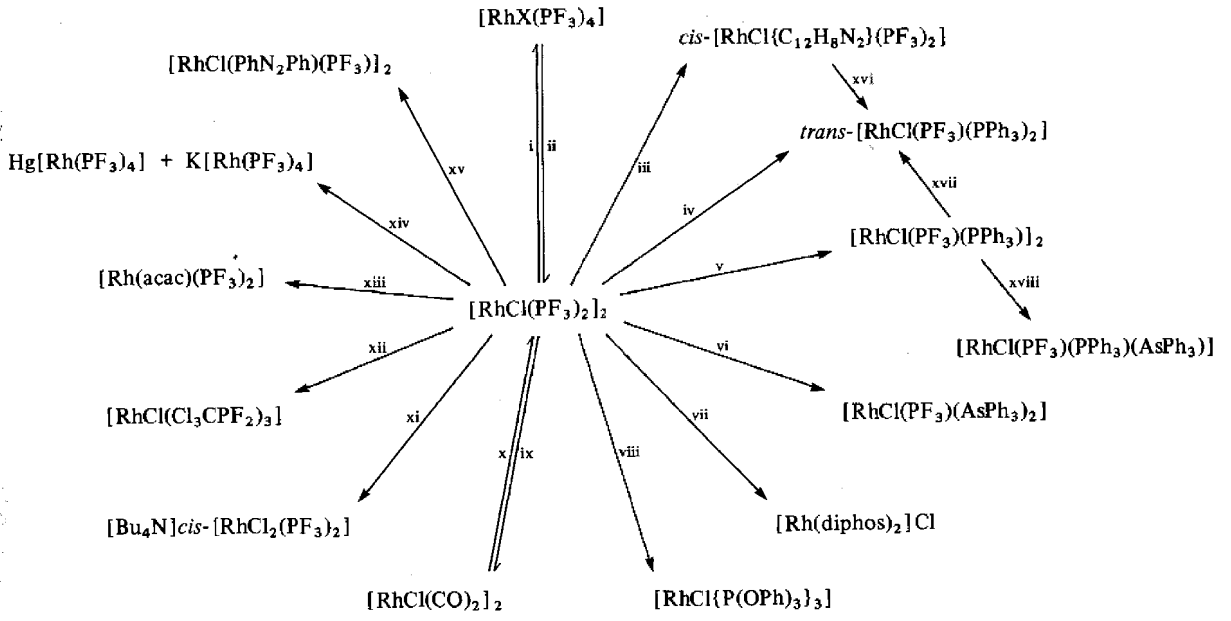
Table 3 Rh—Cl Stretch Frequencies in $[RhClL_2]_2$ Complexes

Complex	ν_{Rh-Cl} (cm^{-1})	*Ref.*
$[RhCl(PPh_3)_2]_2$	303	94
$[RhCl\{PPh_2(C_6F_5)\}_2]_2$	294	73
$[RhCl\{PPh(C_6F_5)_2\}_2]_2$	304	73
$[RhCl\{P(C_6F_5)_3\}_2]_2$	306	73
$[RhCl\{PPh_2(C_6Cl_5)\}_2]_2$	283	73

Table 4 NMR Spectra of Rhodium(I) Trifluorophosphine Complexes

Complex	*Solvent*	*Frequency* (MHz)	*φF* (p.p.m.)	*J (P–F)* (Hz)	*J (Rh–F)* (Hz)	*Ref.*
trans-$[RhCl(PF_3)(PPh_3)_2]$	$CHCl_3$	56.47	+16.0	—	—	89
trans-$[RhBr(PF_3)(PPh_3)_2]$	$CHCl_3$	56.47	+17.7	—	—	89
trans-$[RhCl(PF_3)(AsPh_3)_2]$	C_6H_6	56.47	+15.2	—	—	89
trans-$[RhCl(PF_3)(PPh_3)(AsPh_3)]$	$CHCl_3$	56.47	+13.9	—	—	89
trans-$[RhCl(PF_3)P(NMe_2)_3]_2$	$CHCl_3$	56.47	+15.6	—	—	89
$[RhCl(PF_3)_2]_2$	C_6H_6	56.47	+17.2	1340	31.6	33
$[RhCl(PF_3)_2]_2$	C_6H_6	94.1	+17.1	1311[b]	31.5	79
$[RhBr(PF_3)_2]_2$	C_6H_6	94.1	+15.9	1309[b]	31.5	79
$[RhI(PF_3)_2]_2$	C_6H_6	94.1	+14.2	1316[b]	31	79
$[Rh(acac)(PF_3)_2]$	C_6H_6	56.47	+20.5	a	29.8	33

[a] $^1J_{P-F} = 1322$ Hz, $^3J_{P-F} = -4$ Hz.
[b] $^1J_{P-F} + {}^2J_{P-F'}$.



i, $+PF_3$, $-120°C$;[89] ii, $-PF_3$, 27°C;[89] iii, C_6H_6, benzo[*c*]cinnoline, 80°C;[90] iv, PPh_3;[36,79,80,89] v, PPh_3;[89] vi, $AsPh_3$;[89] vii, diphos;[89] viii, $P(OPh)_3$, *i*-C_5H_{12};[89] ix, CO;[78] x, excess PF_3;[78] xi, $[Bu_4N]Cl$;[36] xii, Cl_3CPF_2;[79,80] xiii, Tl(acac);[36] xiv, K/Hg;[36] xv, $[RhCl(PhN_2Ph)_2]_2$;[85] xvi, PPh_3, 25°C;[90] xvii, excess PPh_3;[89] xviii, $AsPh_3$[89]

Scheme 3 Reaction of $[RhCl(PF_3)_2]_2$

$$[RhX\{P(OPh)_3\}_2]_2 + 2P(OPh)_3 \longrightarrow 2[RhX\{P(OPh)_3\}_3] \quad (26)$$

$$X = Cl, Br^{62}$$

$$[RhCl\{P(C_6F_5)_3\}_2]_2 + 6L \longrightarrow 2[RhClL_3] + 4P(C_6F_5)_3 \quad (27)$$

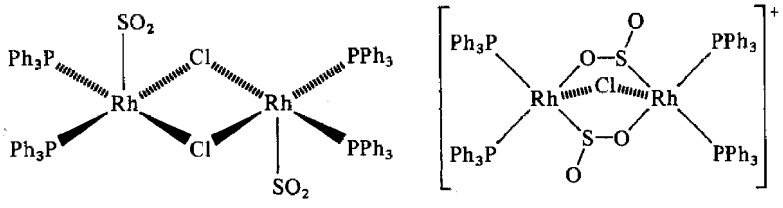
$$L = P(OPh)_3,^{73}\ PPh_3^{74}$$

The chloro ligands of $[RhCl\{P(OPh)_3\}_2]_2$ can also be displaced by pentan-2,4-dione.[62,77]

The dialkylamidodifluorophosphine complexes are also cleaved when allowed to react with excess ligand. However, these reactions are easily reversed.

The yellow dimethylamidophosphine complex is also cleaved by triphenylphosphine and reduced by potassium amalgam.[37]

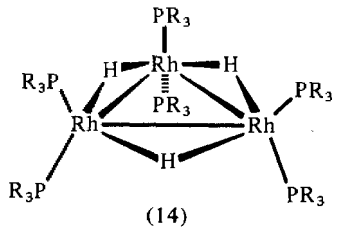
The triphenylphosphine dimer is not very soluble, and this together with its ready reaction with oxygen has deterred investigations of its chemical properties. Whilst liquid sulfur dioxide cleaves the molecule and forms $[RhCl(SO_2)(PPh_3)_2]$,[96] solutions of SO_2 in ethanol/chloroform yield the centrosymmetric dimer (**12**),[97] whose structure has been determined by X-ray crystallography.[98] Closely similar to this complex is the cation (**13**) which can be prepared by passing sulfur dioxide into a methanolic solution of $[RhCl(cod)]_2$, $NaClO_4$ and PPh_3. The orange perchlorate salt has had its structure determined by X-ray crystallography.[99]



(12) (13)

The allyl complex $[Rh(\eta^3\text{-}C_3H_5)(cod)]$ reacts with trialkyl phosphites to form $[RhHL_2]_n$ complexes. The dimeric triisopropyl phosphite complex has already been mentioned. Trimethyl and triethyl phosphite, however, form trimeric products.[64,100] The structure of the trimethyl phosphite complex (**14**) has been determined by X-ray crystallography.[100–102]

Finally there is a report of an ill-characterized benzothiazole complex $[RhCl(C_7H_5NS)_2]_2$. The benzothiazole ligands may be N-bound.[103]



(14)

48.4.2.4 [RhX(LL)] complexes

There are a few analogs of the bridged complexes described above which contain bidentate neutral ligands in place of the four monodentate neutral ligands.

They may be prepared by careful displacement of cycloocta-1,5-diene ligands from $[RhX(cod)]_2$ (equation 29).[104,105] Other complexes have been prepared by removing the single cyclooctadiene ligand from $[RhCl(LL)(cod)]_2$ complexes by hydrogenation (equation 30).[106]

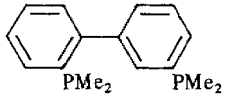
$$[Rh(PPh_2)(cod)]_2 + 2LL \longrightarrow [Rh(PPh_2)LL]_2 + C_8H_{12} \quad (28)$$

LL = $Ph_2PCH_2PPh_2$, diphos, $Ph_2P(CH_2)_3PPh_2$, $Ph_2P(CH_2)_2AsPh_2$[104]

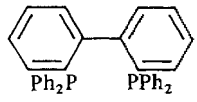
$$[RhCl(cod)]_2 + (\mathbf{15}) \xrightarrow{C_6H_6} [RhCl(\mathbf{15})]_2 + 2C_8H_{12} \quad (29)$$

$$[RhLL(cod)]Cl + H_2 \longrightarrow [RhClLL]_2 + C_8H_{14} \quad (30)$$

LL = diphos, (**16**), diop[106]



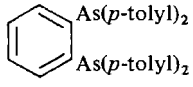
(15)



(16)

When the diarsine ligand (**17**) is allowed to react with rhodium trichloride in refluxing DMF, the bridged complex $[RhCl(\mathbf{17})]_2$ is formed (equation 31).[107]

$$RhCl_3 \cdot 3H_2O + (\mathbf{17}) \xrightarrow[\text{reflux}]{DMF} [RhCl(\mathbf{17})]_2 \quad (31)$$



(17)

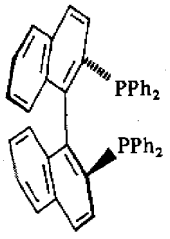
The complexes prepared by hydrogenation of their cyclooctadiene precursors may be solvated ionic monomers. This type of complex is formed if the anion is non-coordinating. For example, complexes of the ligand (**18**) can be obtained containing two methanol ligands (equation 32). However, the unsolvated complex $[Rh_2(\mathbf{18})_2][ClO_4]_2$ is the minor product in the reaction. It seems quite likely that this complex contains an η^6-phenyl group, as has been demonstrated for the corresponding diphos complex.[108,109]

$$10[Rh(\mathbf{18})(nbd)]ClO_4 + 20H_2 \xrightarrow{MeOH} 8[Rh(\mathbf{18})(MeOH)_2]ClO_4 + [Rh(\mathbf{18})]_2[ClO_4]_2 + 10C_7H_{12} \quad (32)$$

Recently, hydrogenation of the η^3-allyl complex $[Rh\{C_2H_4P_2(OR)_4\}(\eta^3\text{-}C_4H_7)]$ (R = Me, Et, Pr^i) has yielded $[RhH\{C_2H_4P_2(OR)_4\}]_n$ complexes (R = Me, Et, $n = 4$; R = Pr^i, $n = 2$) (equation 33).[110]

$$[Rh\{(RO)_2P(CH_2)_2P(OR)_2\}(\eta^3\text{-}C_4H_7)] \xrightarrow[C_7H_8]{H_2\ 3\,atm} [RhH\{(RO)_2P(CH_2)_2P(OR)_2\}]_n \quad (33)$$

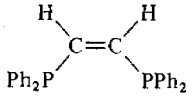
If the anion is bidentate then bidentate neutral ligands form [RhX(LL)] complexes. Strangely, only one example of such a complex is known. The orange 5-methyl-8-hydroxyquinolinato complex



(18)

can be prepared if its rhodium(I) dicarbonyl complex is allowed to react with the unsaturated ditertiary phosphine (**19**) (equation 34).

$$[Rh(C_{10}H_8NO)(CO)_2] + (\mathbf{19}) \longrightarrow [Rh(C_{10}H_8NO)(\mathbf{19})] + 2CO \quad (34)$$



(19)

The ^{31}P NMR spectrum shows $^{1}J_{Rh-P} = 160$ Hz.[111]

48.4.3 [$RhXL_3$] Complexes

This is the most populous class of rhodium(I) complex. Interest in this type of complex has undoubtedly been inspired by the important catalytic applications of [$RhCl(PPh_3)_3$].[10,20] All complexes of this stoichiometry are 16-electron compounds and are formally coordinately unsaturated. However, for steric reasons they do not readily add a fifth ligand and pentacoordinate rhodium(I) complexes are rare. Many of the complexes undergo important oxidative addition reactions. The rhodium(III) products from these reactions are described in Section 48.6.

Isolable complexes of this stoichiometry are listed in Table 5.

Table 5 Physical Properties of [$RhXL_3$] Complexes

X	*L*	*Color*	*M.p.* (°C)	*Ref.*
Cl	$PHPh_2$	Yellow-brown	173–75	112
Cl	$PHCy_2$	Yellow	193	113
Cl	PMe_3	Red	205–10	114–116
H	PEt_3	Red	Oil	117
Cl	PEt_3	Red-brown	185–95	114
Cl	PPr_3	Brown	120–30	114
H	PPr^i_3	Pale yellow	45	117
Cl	PPr^i_3	Brown	30–35	114
H	PPh_3	Orange	—	118
CN	PPh_3	Orange	100–02	69, 119
$SnCl_3$	PPh_3	Dark red	128–29	120–122
$SnBr_3$	PPh_3	Bright red	—	122
NCO	PPh_3	Yellow	—	123
N_3	PPh_3	—	—	124
OH	PPh_3	—	—	125
OPh	PPh_3	Red-brown	—	54, 126
OCN	PPh_3	Orange	100–03	69, 123
O_2CMe	PPh_3	Orange	207–08	127, 128
O_2CEt	PPh_3	Orange	—	127
O_2CPr	PPh_3	Orange	—	121
$O_2CC_5H_{11}$	PPh_3	—	—	121
O_2CCH_2Cl	PPh_3	—	—	121
O_2CPh	PPh_3	—	—	121, 129
p-$O_2CC_6H_4NO_2$	PPh_3	Orange	—	127
p-$O_2CC_6H_4Cl$	PPh_3	Orange	—	127
O_2CCF_3	PPh_3	Orange	233–35	130
O_2CCF_2Cl	PPh_3	Orange	136–38	121
$O_2CC_2F_5$	PPh_3	Orange	236–37	121, 130

Table 5 (*Continued*)

X	*L*	*Color*	*M.p.* (°C)	*Ref.*
$O_2CC_6F_5$	PPh_3	Orange	159–61[b]	130
F	PPh_3	—	—	47
Cl	PPh_3	Orange	130[a]	131
Cl	PPh_3	Red	158[a]	68, 131, 132
Br	PPh_3	Orange	130[a]	68, 131, 132
I	PPh_3	Red-brown	116[a]	68, 131
Cl	$P(p\text{-}C_6H_4Me)_3$	Beige	178–83	70
Cl	(**9**)	Brown	140–43	71
H	(**10**)	Orange-red	179–80	133
Cl	(**10**)	Orange-red	154–55	71
Cl	$P(p\text{-}C_6H_4OMe)_3$	Orange	—	134
Cl	$P(p\text{-}C_6H_4F)_3$	Orange	—	135
Cl	$P(p\text{-}C_6H_4Cl)_3$	Orange	—	134
Cl	PMe_2Ph	Brown-red	170–75	114
Cl	$PMe_2(1\text{-Np})$	Orange	185–95	136
Cl	PPh_2Me	Yellow	—	118
Cl	$PPh_2C_7H_{15}$	Orange	—	137
Cl	$PPh_2C_{16}H_{33}$	Orange	—	137
Cl	$PPh_2(m\text{-}C_6H_4SO_3Na)$	Orange[c]	230–50	138
Cl	PPh_2R[b]	Dark red	Oil	72
Cl	$PPh(C_5H_{10}N)_2$	Orange	82	139
Cl	$PPh(C_5H_{10}N)_2$	Red	82	139
Cl	$PPh(C_4H_8NO)_2$	Orange	104–06	139
Cl	$P(OPh)_3$	Yellow	170–80	62, 73, 77, 78, 89
Br	$P(OPh)_3$	Yellow	—	62, 77
I	$P(OPh)_3$	Yellow	—	78
SCN	$P(p\text{-}OC_6H_4Me)_3$	Yellow	—	78
Cl	$P(p\text{-}OC_6H_4Me)_3$	Yellow	—	78
SCN	$P(p\text{-}OC_6H_4Cl)_3$	Yellow	—	78
Cl	$P(p\text{-}OC_6H_4Cl)_3$	Yellow	183–86	78
I	$P(p\text{-}OC_6H_4Cl)_3$	Orange	135–36	78
Cl	$PF(NMe_2)_2$	Yellow	92–94	61
Cl	$PF_2(CCl_3)$	—	—	81
Cl	$PF_2(NMe_2)$	Yellow	135–39	37, 61, 81, 85
Cl	$AsPh_3$	Brown	150–55[a]	140, 141
Cl	$AsPh_2Et$	Orange	197–200	142
Br	$AsPh_2Et$	Orange-red	192–96	142
Cl	$SbPh_3$	Purple	170	140, 141, 143
Cl	$SPPh_3$	—	—	84

[a] With decomposition. [b] R = $(MeSiO)_2MeSiCH_2CH_2$. [c] Ethanol hemisolvate.

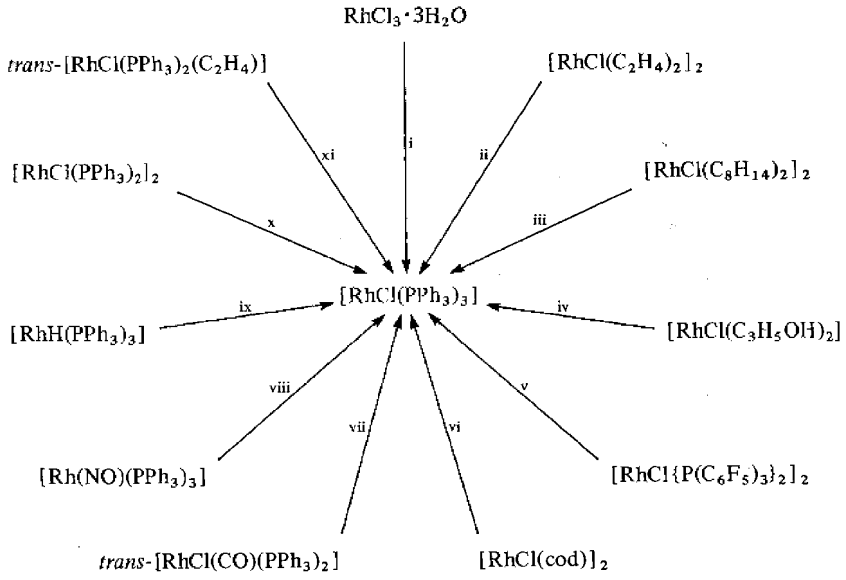
The neutral ligands usually possess some π-bonding capacity and it is rare, even in complexes containing two different neutral ligands, for a purely σ-bonding neutral ligand to coordinate to rhodium.

The anionic ligand can be virtually any uninegative ion. Anions of low coordinating power, however, do not form complexes of this stoichiometry and structure. There is an ionic perchlorate complex $[Rh(PPh_3)_3]ClO_4$ in which the cation is 'T' shaped.[144] It has been calculated that a cation of this structure lies near an energy minimum.[145] Two ionic PMe_3 complexes are also known.[146]

The complexes can be prepared by a wide variety of routes. The important complex $[RhCl(PPh_3)_3]$ has probably received the most attention, and preparations of this complex are shown in Scheme 4.

The main preparative routes to other complexes of this class usually involve the displacement of less firmly bound ligands from other rhodium(I) complexes (equations 35 and 36). This method has proved popular in catalytic studies since it enables the catalyst to be prepared *in situ* and obviates the necessity of isolating the catalytic complex.

A limited range of tertiary phosphine complexes can be prepared by reducing hydrated rhodium trichloride with the ligand itself (equation 37). Triarylphosphines containing electron-withdrawing substituents do not form monomeric complexes. Tris(perfluorophenyl)phosphine, for example, forms a dimeric complex (equation 25), and even heating the latter compound with neat ligand in a Carius tube for 24 hours does not form a mononuclear complex.[74] Under other conditions certain other tertiary phosphines can form a wide range of products which embraces rhodium(III), rhodium(II), and hydrido or carbonyl complexes.



i, $6PPh_3$, N_2, EtOH, reflux;[68,132] ii, PPh_3, N_2, MeOH;[147,148] iii, PPh_3;[139] iv, PPh_3, EtOH, reflux;[141] v, PPh_3, C_6H_6, reflux;[73,74] vi, excess PPh_3;[149] vii, PPh_3, $PhCH_2Cl$, reflux;[150] viii, $[NiCl_2(PPh_3)_2]$, C_6H_6/Me_2CO, 50°C;[151] xi, $HgCl_2$, PPh_3, N_2, C_6H_6, reflux;[152] x, PPh_3, C_6H_6;[68] xi, PPh_3, C_6H_6[68]

Scheme 4 Preparations of $[RhCl(PPh_3)_3]$

$$L = PHPh_2,^{112}\ P(p\text{-}C_6H_4Me)_3,^{70}\ PPh_2Me,^{118}\ PPh_2Et,^{135}\ PPh_2(CH_2)_2SiCl_3,\ PPh_2(CH_2)_8SiCl_3,$$
$$PPh_2(CH_2)_2SiMe(OMe)_2,^{72}\ PPh(C_4H_8NO)_2,\ PPh(C_5H_{10}N)_2,^{139}\ \mathbf{(9)},\ \mathbf{(10)},^{71}\ PF_2NMe_2,^{37}$$
$$PF_2NEt_2,^{82}\ AsPh_3,^{140}\ SbPh_3^{140,143}$$

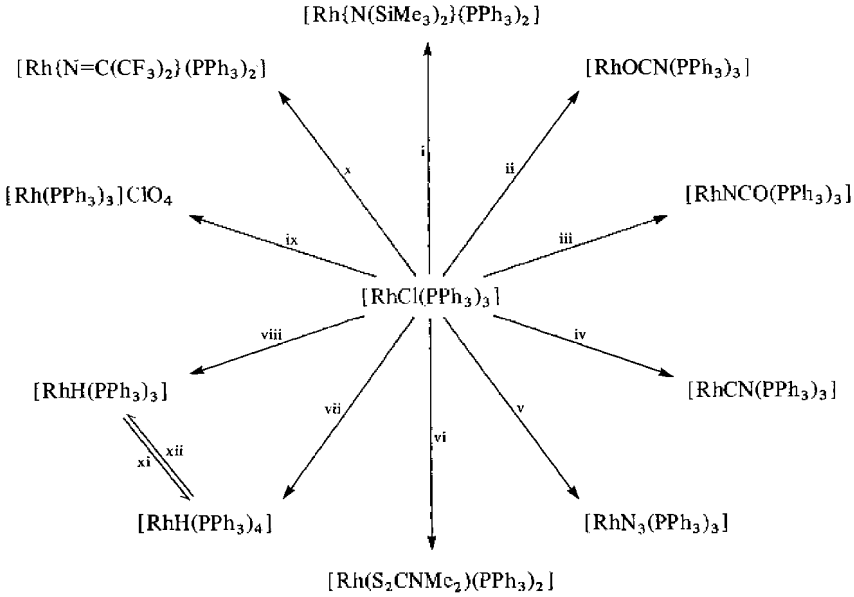
$$[RhCl(C_8H_{14})_2]_2 + 6L \longrightarrow 2[RhClL_3] + 4C_8H_{14} \quad (36)$$

$$L = P(p\text{-}C_6H_4OMe)_3,\ P(p\text{-}C_6H_4Cl)_3,^{134}\ PPh(C_4H_8NO)_2,\ PPh(C_5H_{10}N)_2,^{139}\ PF(NMe_2)_2^{61}$$

$$RhCl_3\cdot 3H_2O + \text{excess } L \longrightarrow [RhClL_3] \quad (37)$$

$$L = P(p\text{-}C_6H_4F)_3,^{135}\ AsEtPh_2,^{142}\ SPPh_3^{84}$$

Many other triphenylphosphine complexes of this stoichiometry can be prepared by anion metathesis of $[RhCl(PPh_3)_3]$. Some of these reactions are illustrated in Scheme 5.



i, $LiN(SiMe_3)_2$, THF;[59] ii, $[Ph_4As][NCO]$, EtOH;[123] iii, $[Ph_4As][NCO]$, MeCN;[123] iv, Dowex resin (CN form), CH_2Cl_2/EtOH;[69,119] v, $[Et_4N]N_3$;[124] vi, NaS_2CNMe_2;[66] vii, $NaBH_4$, EtOH;[153] viii, $NaBH_4$, PPh_3, EtOH;[153] ix, $TlClO_4$, Me_2CO;[144] x, $LiN{=}C(CF_3)_2$;[57] xi, PPh_3;[153] xii, PPh_3[153]

Table 6 IR Spectra of Carboxylatorhodium(I) Complexes

Complex	ν_{COO}^{a} (cm^{-1})	ν_{COO}^{b} (cm^{-1})	$\Delta\nu$ (cm^{-1})	*Ref.*
$[Rh(O_2CMe)(PPh_3)_3]$	1598	1373	225	127
$[Rh(O_2CEt)(PPh_3)_3]$	1597	1379	218	127
$[Rh(O_2CPr)(PPh_3)_3]$	—	1383	—	121
$[Rh(O_2CC_5H_{11})(PPh_3)_3]$	—	1389	—	121
$[Rh(O_2CPh)(PPh_3)_3]$	1590	1355	235	121
$[Rh(O_2CCH_2Cl)(PPh_3)_3]$	1644	1405	239	121
$[Rh(O_2CF_3)(PPh_3)_3]$	1673	1418	255	121, 130
$[Rh(O_2CCF_2Cl)(PPh_3)_3]$	1673	—	—	121
$[Rh(O_2CC_2F_5)(PPh_3)_3]$	1685	—	—	121, 130
$[Rh(p\text{-}O_2CC_6H_4Cl)(PPh_3)_3]$	1600	1350	250	127
$[Rh(p\text{-}O_2CC_6H_4NO_2)(PPh_3)_3]$	1580	1371	209	127

[a] Asymmetric. [b] Symmetric.

The hydrido complex $RhH(PPh_3)_3$ is also a good starting point for preparing other complexes. Upon treatment with acids it eliminates hydrogen and forms an $[RhX(PPh_3)_3]$ complex (equation 38).

$$[RhH(PPh_3)_n] + HX \longrightarrow [RhX(PPh_3)_3] + H_2 \quad (38)$$

$n = 3, 4$; X = OPh,[54,126] O_2CMe,[127,128,154] O_2CEt, $p\text{-}O_2CC_6H_4NO_2$, $p\text{-}O_2CC_6H_4Cl$[127]

The carboxylato complexes (Table 6; equation 39) can also be prepared from the uncharacterized dimeric rhodium(II) species obtained by treating rhodium(II) acetate with HBF_4.[121]

$$\{Rh_2^{4+}\} + LiO_2CR + PPh_3 \longrightarrow [Rh(O_2CR)(PPh_3)_3] \quad (39)$$

R = Me, Et, Pr, C_5H_{11}, Ph, CH_2Cl, $CClF_2$, CF_3, C_2F_5

If rhodium(III) acetate were known, it would be possible to believe the patent claim that $[Rh(O_2CMe)(PPh_3)_3]$ can be prepared from it.[155]

Chlorotris(triphenylphosphine)rhodium(I) is also the precursor of numerous chloro complexes which may be obtained by exchanging PPh_3 for other ligands. The main use of this reaction, however, is to prepare $[RhXL_2L']$ complexes (see Section 48.4.3.1 below). The triphenylphosphine substitution reactions of $[RhCl(PPh_3)_3]$ are shown in Scheme 6.

The hydrido complex, $[RhH(PPh_3)_3]$, is obtained in a number of anion exchange reactions of $[RhCl(PPh_3)_3]$ due to hydride abstraction from the anions (equation 40).

$$[RhCl(PPh_3)_3] + MX \longrightarrow [RhH(PPh_3)_3] \quad (40)$$

MX = $NaBH_4$,[153] $AlPr^i_3$,[54,118] $LiNHPr^i$,[160] $LiNMe_2$, $LiNPr^i_2$,[161] KOH/EtOH[152]

The trialkyl or triaryl phosphite complexes are more accessible than those of tertiary phosphines. The phosphite ligands complex strongly to rhodium, and easily displace alkene,[161] alkadiene[77,162] and even carbonyl[78] ligands from $[RhCl(CO)_2]_2$ (equations 41 and 42), a displacement that cannot be achieved by tertiary phosphines. Indeed, even tertiary phosphine ligands themselves can be displaced by the phosphite ligands (equation 43).[162] The phosphite complexes can also be prepared by cleaving $[RhX\{P(OR)_3\}_2]_2$ complexes with additional ligand (equation 26).

$$[RhCl(C_8H_{12})]_2 + 6L \longrightarrow 2[RhClL_3] + 2C_8H_{12} \quad (41)$$

L = $P(OMe)_3$,[76] $P(OPh)_3$[62,77]

$$[RhCl(CO)_2]_2 + 6P(OR)_3 \longrightarrow 2[RhCl\{P(OR)_3\}_3] + 4CO \quad (42)$$

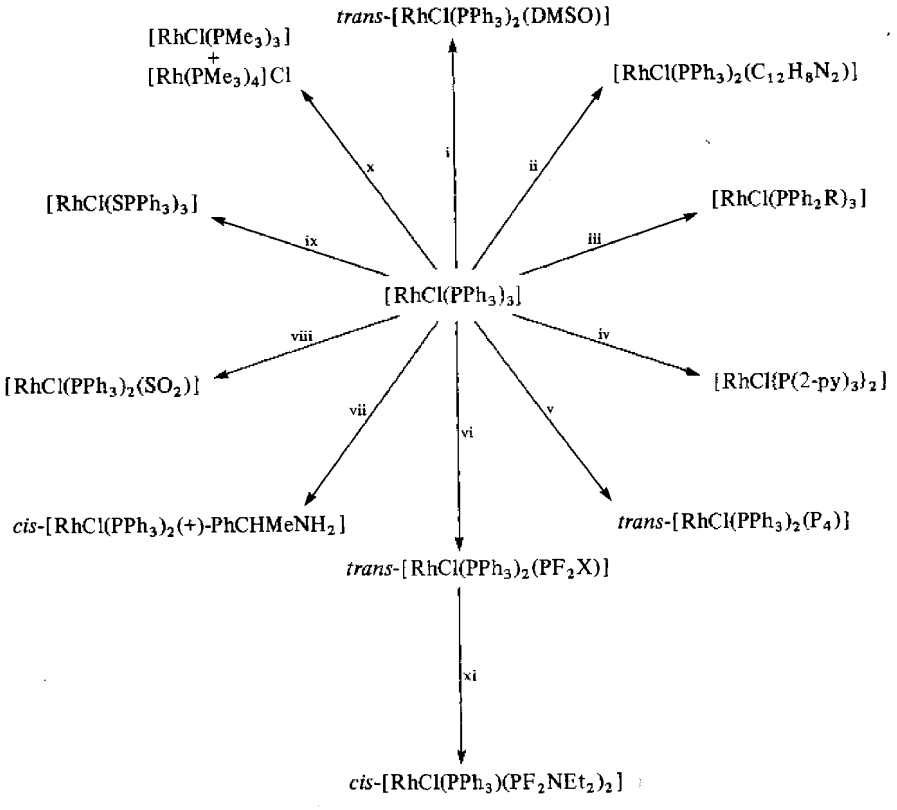
R = Ph, $p\text{-}C_6H_4Me$, $p\text{-}C_6H_4Cl$[78]

$$[RhCl(CO)(ZPh_3)_2] + \text{excess } P(p\text{-}OC_6H_4Cl)_3 \longrightarrow [RhCl\{P(p\text{-}OC_6H_4Cl)_3\}_3] + 2ZPh_3 + CO \quad (43)$$

Z = P, As, Sb[162]

By contrast tertiary arsine and stibine ligands do not displace alkadiene ligands[163] and are only able to displace weakly bound alkene[140,143] or allyl[141] ligands from other rhodium(I) complexes.

Few of the $[RhXL_3]$ complexes have had their physical properties investigated in great detail. As



i, DMSO, 100°C;[156] ii, benzo[*c*]cinnoline, C_6H_6;[90] iii, PPh_2R (R = C_7H_{15}, $C_{16}H_{33}$,[137] *m*-$C_6H_4SO_3Na$);[138] iv, P(2-py)$_3$, C_6H_6, 25°C;[157] v, P_4, CH_2Cl_2, −78°C;[158] vi, PF_2X (X = F,[80,89] CCl_3,[80] NMe_2, NEt_2[82]); vii, (+)-PhCHMeNH$_2$;[159] viii, $SO_{2(g)}$, C_6H_{14};[96] ix, $SPPh_3$;[84] x, PMe_3, C_6H_{14};[116] xi, PF_2NEt_2[80]

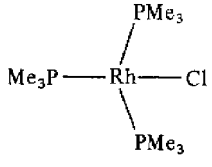
Scheme 6 Triphenylphosphine substitution reactions of [RhCl(PPh$_3$)$_3$]

in the case of their chemical properties nearly all interest has been focussed on the commercially and catalytically important [RhCl(PPh$_3$)$_3$].

A few of the complexes have had their structures determined by X-ray crystallography. Both the red[164,165] and orange[165] isomers of [RhCl(PPh$_3$)$_3$] have been investigated, as has [Rh(O$_2$CPh)(PPh$_3$)$_3$].[129,166] The latter compound was probably investigated because of its unusual preparation (equation 44).[129]

$$[RhPh(PPh_3)_3] + CO_2 \longrightarrow [Rh(O_2CPh)(PPh_3)_3] \quad (44)$$

The structures of the tris(triphenylphosphine) complexes are somewhat distorted from a true square planar arrangement of ligands. However, the structure of [RhCl(PMe$_3$)$_3$] (**20**) also deviates significantly from square planar geometry and this is unlikely to arise from interligand repulsions.[116] As might be expected, the large PPh$_3$ ligands of [RhH(PPh$_3$)$_3$] encroach severely upon the small hydrido ligand which has not been accurately located.[167]



(**20**)

The structure of [RhBr(PPh$_3$)$_3$] has been investigated by the relatively untried technique of X-ray absorption. It was concluded that its RhBrP$_3$ core was similar to the RhClP$_3$ cores of the chloro complexes.[168] The deviations of the cores from orthogonality are also indicated by the ^{31}P NMR study of solid [RhCl(PPh$_3$)$_3$]. The spectrum is complicated due to the many side bands caused by the ^{31}P chemical shift anisotropy, but is sufficiently well resolved to detect the inequivalence of the two *trans* PPh$_3$ ligands.[169]

The solution chemistry of $[RhCl(PPh_3)_3]$ has been dominated by the catalytically engendered interest in the dissociation of triphenylphosphine from the complex. The degree of dissociation has proved difficult to determine. Early results were erroneous due to aerial oxidation of the solutions,[68,131] and anaerobic isopeistic methods failed to provide an answer due to the slow precipitation of $\{RhCl(PPh_3)_2\}_2$.[170] However, more recent experiments in which oxygen has been rigorously excluded have shown the degree of dissociation in unadulterated solutions to be small.[171–173] The exchange of PPh_3 with $P(p\text{-}C_6H_4Me)_3$ has been shown to proceed by a dissociative mechanism.[174]

Data from the ^{31}P NMR spectra of some $[RhXL_3]$ complexes are collected in Table 7. The ^{103}Rh NMR spectrum of $RhCl(PPh_3)_3$ has also been obtained. In addition to the coupling constants recorded in Table 7 the additional coupling constant $^3J[P(1)\text{–}Rh\text{–}P(2)]$ was evaluated as -38 Hz.[176] The NMR data have been used in Hückel molecular orbital calculations for some $[RhCl(PR_3)_3]$ species.[177]

The X-ray emission spectrum of $[RhCl(PPh_3)_3]$ has been recorded.[178] However, X-ray photoelectron spectroscopy is claimed to show that the complex is 40% contaminated with a dioxygen rhodium(III) species.[179] This seems highly unlikely since two independent X-ray crystal structure determinations have been made.

The thermal decomposition of $[RhCl(PPh_3)_3]$ has been investigated twice. The first investigation revealed that the complex reacted with oxygen between 100 and 165°C, but decomposed in a helium atmosphere at 210°C.[180] The second proposed that biaryls were formed when $[RhCl(PPh_3)_3]$ and its congeners were heated above 140°C.[181]

48.4.3.1 [RhXL$_2$L′] complexes

The $[RhXL_2L']$ complexes exist in two isomeric forms. The *trans* complexes are listed in Table 8, and the few *cis* complexes in Table 9.

The *trans* complexes predominate since L′ is usually smaller than L and the *trans* disposition of the L ligands is of lower energy than the *cis* arrangement. The complexes can be prepared by a few general routes. The first of these involves cleaving $[RhXL_2]_2$ complexes with L′ or the addition of L′ to the three coordinate, monomeric complexes $[RhXL_2]$ (equation 46). In another method (equation 47), one neutral ligand is displaced from $[RhXL_3]$ complexes by L′ (see Scheme 6 for displacement of triphenylphosphine ligands from $[RhCl(PPh_3)_3]$).

$$[RhXL_2]_2 + 2L' \longrightarrow 2[RhXL_2L'] \quad (45)$$

X = Cl, L = PF_3, L′ = PPh_3,[34] L = PF_2NEt_2, L′ = PPh_3;[82] X = Cl, Br, I, L = PPh_3, L′ = $SO_{2(l)}$[96]

$$[RhX(PCy_3)_2] + N_2 \longrightarrow [RhX(PCy_3)_2(N_2)] \quad (46)$$

X = Cl, Br, I[46]

$$[RhXL_3] + L' \longrightarrow [RhXL_2L'] + L \quad (47)$$

X = Cl, L = $P(m\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4Me)_3$, $AsPh_3$, L′ = P_4;[156] X = Br, L = PPh_3, L′ = PF_3;[89] X = Br, I, L = PPh_3, L′ = DMSO[156]

Table 7 ^{31}P NMR Data for some $[RhX(PR_3)_3]$ Complexes

Complex	*∂P(1)* (p.p.m.)	*∂P(2)*[c] (p.p.m.)	*J[Rh–P(1)]* (Hz)	*J[Rh–P(2)]* (Hz)	*J[P(1)–P(2)]* (Hz)	*Ref.*
$[RhCl(PMe_3)_3]$	—	—	131[d]	180[d]	—	
$[RhH(PPh_3)_3]$	−35.9	−41.5	145[d]	172[d]	25[d]	
$[RhCl(PPh_3)_3]$	−31.5	−48.0	−142	−189	−38	
$[RhBr(PPh_3)_3]$	−29.8	−46.8	−141	−192	−37	
$[RhI(PPh_3)_3]$	−27.1	−43.2	−139	−194	−36	
$[RhCl\{P(p\text{-}C_6H_4Me)_3\}_3]$	−30.2	−46.2	143[d]	189[d]	38[d]	
$[RhCl(PPh_2R)_3]$[a]	−28.3	−42.7	140[d]	187[d]	39[d]	
$[RhCl(PPh_2R')_3]$[b]	−29.8	−45.0	140[d]	188[d]	40[d]	

[a] R = $(CH_2)_2SiCl_3$. [b] R′ = $(CH_2)_8SiCl_3$. [c] P(2) denotes the phosphorus atom *trans* to the anionic ligands. [d] Sign not determined.

Table 8 Physical Properties of $[RhXL_2L']$ Complexes

L	*L'*	*X*	*Color*	*M.p.* (°C)	*Ref.*
PPr^i_3	N_2	H	—	—	55
PPr^i_3	N_2	Cl	Yellow	—	182, 183
PPr^i_3	SO_2	Cl	—	—	51
PBu^t_3	N_2	H	Yellow	0[a]	55
PPh_3	N_2	Cl	Yellow	—	184
PPh_3	P_4	Cl	—	171–73	158
PPh_3	PF_3	Cl	Yellow	—	34, 89
PPh_3	PF_3	Br	—	—	89
PPh_3	$PF_2(CCl_3)$	Cl	Yellow	163–68	80
PPh_3	PF_2NMe_2	Cl	—	—	37
PPh_3	PF_2NEt_2	Cl	Yellow	194[a]	82
PPh_3	SO_2	Cl	—	—	96
PPh_3	SO_2	Br	—	—	96
PPh_3	SO_2	I	—	—	96
PPh_3	DMSO	Cl	Yellow	—	156
PPh_3	DMSO	Br	Yellow	—	156
PPh_3	DMSO	I	Yellow	—	156
PCy_3	N_2	H	—	—	55
PCy_3	N_2	Cl	—	—	46
PCy_3	N_2	Br	—	—	46
PCy_3	N_2	I	—	—	46
PCy_3	SO_2	Cl	—	—	51
$P(m\text{-}C_6H_4Me)_3$	P_4	Cl	—	110–15	158
$P(p\text{-}C_6H_4Me)_3$	P_4	Cl	—	132–34	158
$PPhBu^t_2$	N_2	H	—	—	55
$AsPh_3$	P_4	Cl	—	104–06	158
$AsPh_3$	PF_3	Cl	—	—	89

[a] With decomposition.

Table 9 Physical Properties of *cis*-$[RhClL_2L']$ Complexes

L	*L'*	*Color*	*M.p.* (°C)	*Ref.*
PPh_3	$C_{12}H_8N_2$	Yellow-orange	113–15[a]	90
PF_3	$C_{12}H_8N_2$	Yellow	140–45[a]	90
PF_2NMe_2	PPh_3	—	—	37
PF_2NEt_2	PPh_3	Lemon yellow	123–24[a]	82

[a] With decomposition.

Less commonly, treatment of the dimeric complexes with excess ligand both cleaves the dimers and displaces one of the original neutral ligands (equation 48). Some dinitrogen complexes can be prepared in a single reaction from hydrated rhodium trichloride (equation 49). Other dinitrogen complexes can be prepared by displacing cyclooctene from $[RhCl(C_8H_{14})_2]_2$ with PPr^i_3 under nitrogen (equation 50).[183] The most ingeneous preparation of a dinitrogen complex is the low temperature reaction of [*trans*-$RhCl(CO)(PPh_3)_2$] with butanoyl azide (equation 51).[184]

$$[RhClL'_2]_2 + 4L \longrightarrow 2[RhClL_2L'] + 2L' \quad (48)$$

$$L' = PF_3,\ L = PPh_3,\ AsPh_3{}^{89}$$

$$RhCl_3 \cdot 3H_2O + \text{excess } PR_3 \xrightarrow[THF]{Na/Hg,\ N_2} [RhH(PR_2)_2(N_2)] \quad (49)$$

$$R_3 = Bu^t_3,{}^{55}\ PhBu^t_2{}^{55,185}$$

$$[RhCl(C_8H_{14})_2]_2 + 4PPr^i_3 \xrightarrow{N_2} 2[RhCl(N_2)(PPr^i_3)_2] + 4C_8H_{14} \quad (50)$$

$$\textit{trans}\text{-}[RhCl(CO)(PPh_3)_2] + PrCON_3 \longrightarrow [RhCl(N_2)(PPh_3)_2] \quad (51)$$

Tetrakis(trimethylphosphine)rhodium(I) chloride loses two trimethylphosphine ligands when allowed to react with PPh_3 at elevated temperatures (equation 52). The ionic compound also undergoes a more complex reaction with benzene and sodium. In this a trimethylphosphine ligand is converted to a PMe_2Ph ligand (equation 53).[186] The geometry adopted by both these complexes

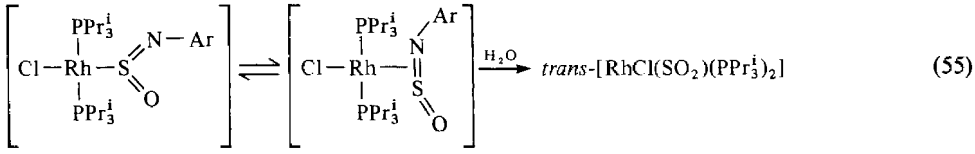
is unknown. When $[RhCl(PPh_3)_3]$ is allowed to react in refluxing benzene with 1-aryltetrazoline-5-thiones (equation 54), two PPh_3 ligands are replaced by two thione molecules. These are believed to be S-bonded, but again information on the geometry around rhodium is lacking.[187] Similar remarks apply to the geometry of $[RhCl(PPh_3)_2(MeCN)]$[188] and $[RhCl(PPh_3)_2SnCH(SiMe_3)_2]$.[189]

$$[Rh(PMe_3)_4]Cl + PPh_3 \xrightarrow[\text{reflux}]{C_7H_8/THF} \textit{trans}\text{-}[RhCl(PMe_3)_2(PPh_3)] + 2PMe_3 \quad (52)$$

$$[Rh(PMe_3)_4]Cl + Na \xrightarrow{C_6H_6} [RhCl(PMe_3)_2(PMe_2Ph)] \quad (53)$$

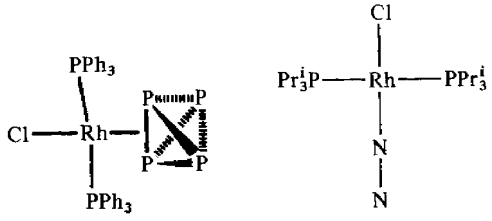
$$[RhCl(PPh_3)_3] + ArN_3NHCS \xrightarrow[\text{reflux}]{C_6H_6} [RhCl(PPh_3)(ArN_3NHCS)_2] + 2PPh_3 \quad (54)$$

By a similar reaction to that shown in equation (50), the unusual complex $[RhCl(PPr^i_3)_2(p\text{-}MeC_6H_4NSO)]$ can be prepared. In the solid state the ligand is S-bound but isomerization to a μ-bonded species occurs in solution. The latter compound is hydrolyzed by water to a sulfur dioxide complex (equation 55).[190]



(55)

Other complexes whose crystal structures have been determined include the tetraphosphorus complex (**21**),[191] and the dinitrogen complex (**22**).[182] The latter complex was originally believed to contain a sideways-on dinitrogen ligand;[183] however, once corrections were made for disorder and anisotropy of the dinitrogen ligand, the more usual end-on coordination was proposed.[182]



(21) (22)

The hydrido dinitrogen complexes, whilst failing to fulfill the modern alchemists' dream of a catalyst for the low temperature low pressure ammonia synthesis, have been thoroughly investigated and some of their spectroscopic properties are listed in Table 10.

Bidentate ligands very seldom form related complexes of the type [RhXL(LL)], possibly because one of the bidentate ligand's donor atoms must be *trans* to a tertiary phosphine, a factor that also accounts for the small number of [*cis*-$RhXL_2L'$] complexes known. A rare example of a complex containing a bidentate ligand is provided by the orange complex (**23**), which can be obtained from $[RhCl(PPh_3)_3]$ (Scheme 6).[157]

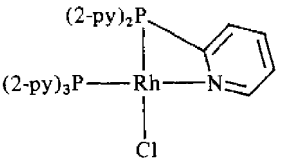
There are also a few dimeric complexes containing a bridging bidentate ligand. Particularly noteworthy are the binuclear dinitrogen complexes $[\{RhH(PR_3)_2\}_2N_2]$ (R = Pr^i,[55] Cy[55,56]).

Finally it should be noted that there are a few ionic $[RhL_3]X$ complexes besides $[Rh(PPh_3)_3](ClO_4)$

Table 10 ^{1}H NMR and IR Data for $[RhHL_3]$ Complexes

Complex	τ_{Rh-H}	ν_{Rh-H} (cm^{-1})	ν_{N-N} (cm^{-1})	*Ref.*
$[RhH(PEt_3)_3]$	17.9	1928	—	117
$[RhH(PPh_3)_3]$	18.3	2020	—	54, 118
$[RhH(N_2)(PPr^i_3)_2]$	23.2	1962[a]	2140[a]	55
$[RhH(N_2)(PBu^i_3)_2]$	—	2063	2145	55
$[RhH(N_2)(PCy_3)_2]$	23.0	1950	2130	55
$[RhH(N_2)(PPhBu^i_2)_2]$	23	1977	2155	55

[a] Hexane solution, all other IR spectra from Nujol mulls.



(23)

mentioned above.[144] Surprisingly these contain the smallest tertiary phosphine, PMe_3, rather than very large ligands whose bulk might be expected to favor three-coordinate cations. Even more surprisingly the complexes have been obtained directly from $[Rh(PMe_3)_4]Cl$ rather than $[RhCl(PMe_3)_3]$ (equation 56).[116,146]

$$[Rh(PMe_3)_4]Cl + KX \longrightarrow [Rh(PMe_3)_3]X + PMe_3 + KCl \quad (56)$$

$$X = BPh_4, PF_6^{116,146}$$

48.4.4 $[RhXL_4]$ Complexes

48.4.4.1 $[RhHL_4]$ complexes

There are three limiting forms of structure for hydrido complexes of this stoichiometry: trigonal bipyramidal, square pyramidal and monocapped tetrahedra. The structure of a given complex is difficult to classify since, in addition to the hydrido ligand being difficult to locate by X-ray crystallography, many of the complexes suffer radiolytic damage during data collection. This damage reduces the quantity and accuracy of the data available. However, examination of the structure of the rhodium ligand core gives a clue to the overall structure.

Similar difficulties occur in attempts to study solution structures by NMR spectrometry. Here ligand exchange is the problem. A further difficulty in ^1H NMR spectrometry is the multiple splitting of the hydride resonance by both ^{103}Rh and ^{31}P nuclei in the molecule. The ultimate example is found in $[RhH(PF_3)_4]$ where every nucleus in the molecule has a non-integral spin. It has been calculated that the hydrido resonance should be split into 130 peaks![192]

In the solid state $[RhH(PPh_3)_4]$[193] and the isomorphous $[RhH(PPh_3)_3(AsPh_3)]$[118] have been shown to have monocapped tetrahedral structures, and $[RhH(PPh_3)_3(PF_3)]$[194] is a trigonal bipyramidal species. It has been stated that the solution structures, at low temperatures, of $[RhH(PF_3)_4]$ and $[RhH\{P(OEt)_3\}_4]$,[195] and $[RhH\{P(OCH_2)_3CPr\}_4]$[196] are all monocapped tetrahedra. However, these three complexes clearly exhibit fluxional behavior in solution and pass through intermediate structures which can be represented as distorted trigonal bipyramids.[195,197] This stereochemical non-rigidity may account for their J(Rh–H) values of 9–9.5 Hz,[195] which may be compared with the coupling constant of the square pyramidal complex $[RhH(PPh_2Me)_4]$ of 7 Hz[118] (see below). Nevertheless, it has been found that the ^1H NMR spectrum of $RhH(PPh_3)_4$ (J(Rh–H) = 0 Hz) is similar (see Table 11) to that of the known trigonal bipyramidal species $[RhH(CO)(PPh_3)_3]$ (J(Rh–H) = 0.8 Hz). The ^1H NMR spectrum of $[RhH(PPh_2Me)_4]$ shows only the *cis* P–H coupling of 18 Hz, without any *trans* P–H coupling being observed. Additionally, J(Rh–P) is 7 Hz, which implies that $[RhH(PPh_2Me)_4]$ is square pyramidal in solution.[118] The triaryl phosphite complexes

Table 11 IR and ^1H NMR Spectra of $[RhHL_4]$ Complexes

Complex	τ_{Rh-H}	J_{Rh-H} (Hz)	ν_{Rh-H} (Hz)	*Ref.*
$[RhH(PF_3)_4]$	19.9	5.8[a]	1992[b]	197
$[RhH(PPh_3)_4]$	20.6	*ca.*0.0[c]	2140[d]	118, 204
$[RhH(PPh_2Me)_4]$	22.1	7.0[e]	—	118
$[RhH(\mathbf{10})_4]$	20.6	—	2070	133
$[RhH(PPh_3)_3(AsPh_3)]$	—	—	2180, 2125	213
$[RhH(PPh_3)(AsPh_3)_3]$	—	—	2140	204
$[RhH\{PPh(OEt)_2\}_4]$	21.12	9.5[f]	—	195
$[RhH\{P(OEt)_3\}_4]$	22.89	9[g]	—	195
$[RhH\{P(OAr)_3\}_4]$	—	*ca.*8[h]	—	198
$[RhH\{P(OCH_2)_3CPr^n\}_4]$	21.06	8.82[i]	—	196

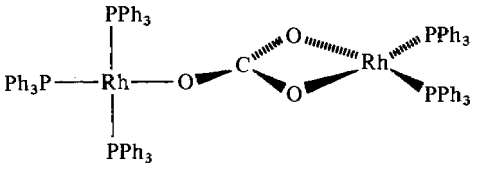
[a] J_{P-H} 57.4 Hz, J_{F-H} 16.6 Hz. [b] ν_{Rh-D} 1431 cm^{-1}. [c] Ref. 118. [d] ν_{Rh-D} 1548 cm^{-1}. [e] $J_{P(cis)-H}$ 18.0 Hz. [f] J_{P-H} 35 Hz. [g] J_{P-H} 27.5 Hz. [h] J_{P-H} *ca.* 45 Hz. [i] J_{P-H} 44.12 Hz.

$[RhH\{P(OAr)_3\}_4]$ have similar coupling constants and are probably also square pyramidal in solution.

One of the more important complexes in this class is $[RhH(PPh_3)_4]$. It can be prepared from a variety of starting materials (Scheme 7).

The four PPh_3 ligands form a tetrahedron around rhodium. The hydrido ligand could not be located by X-ray crystallography.[193]

The complex is very reactive; the hydrido ligand can be replaced by other anionic ligands (Scheme 8) and the lability of the triphenylphosphine ligands allows other complexes of this stoichiometry to be prepared. The most interesting product from these reactions is the dirhodium carbonato complex (**24**). This is the product when $[RhH(PPh_3)_4]$ is allowed to react with carbon dioxide in toluene at 25°C.[205] Originally the product was thought to be a CO_2 complex,[206] but X-ray crystallography showed it to be (**24**).[205] The additional oxygen atom may arise from traces of moisture or oxygen in the gas stream. ^{31}P NMR studies on benzene solutions of (**24**) imply that the dimeric structure is retained in solution.



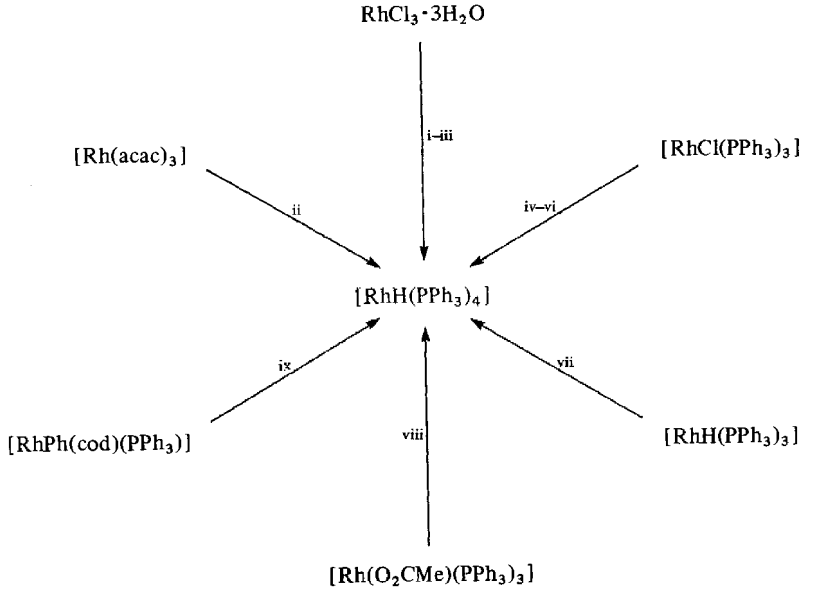
(24)

The action of PF_3 and hydrogen at high temperatures and pressures upon mixtures of anhydrous rhodium trichloride and copper forms (equation 57) the colorless liquid $[RhH(PF_3)_4]$ (b.p. 89°C/725 torr).[32,35,208] The liquid decomposes slowly at 20°C to form $[Rh(PF_2)(PF_3)_3]_2$, but on heating to 140°C it decomposes to rhodium metal.[32] The hydrido complex can also be formed by the action of strong acids on the potassium salt $K[Rh(PF_3)_4]$ (equation 58).[34]

$$RhCl_3/Cu + PF_3 + H_2 \xrightarrow[70°C]{200\ atm} [RhH(PF_3)_4] \quad (57)$$

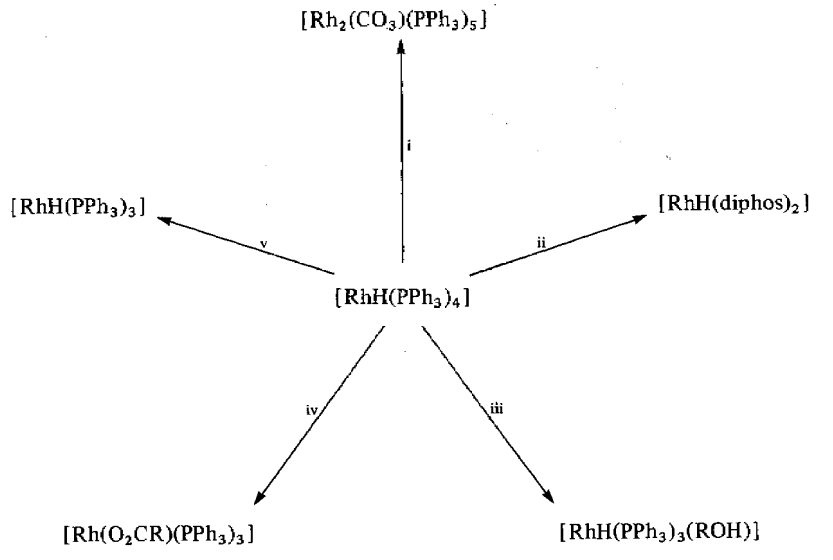
$$K[Rh(PF_3)_4] + H_2SO_4 \longrightarrow [RhH(PF_3)_4] \quad (58)$$

The complex behaves as a strong acid (Scheme 9). The deuterio complex can be prepared by treating the hydrido complex with D_2SO_4.[32] The exchange of hydrogen is much easier than in the case of $[RhH(PPh_3)_4]$ which only exchanges very slowly with deuterium gas (equation 59).[209]



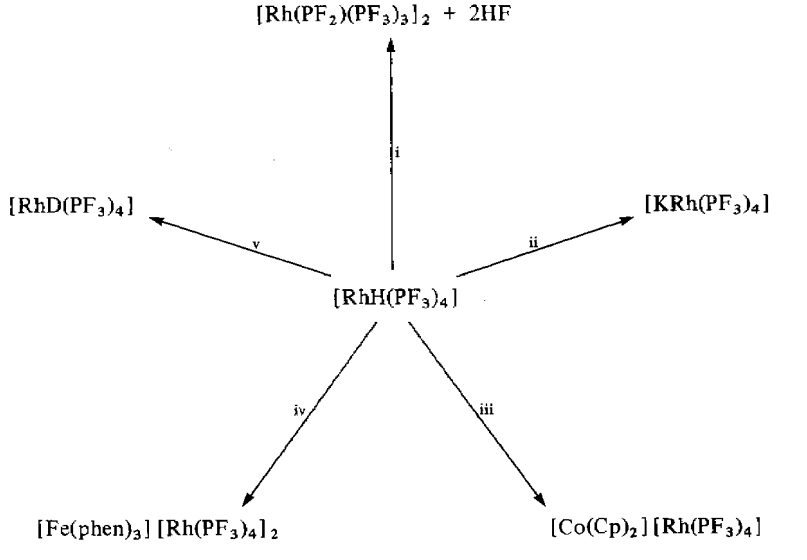
i, $NaBH_4$, PPh_3, EtOH;[198,199] ii, Et_3Al, PPh_3;[200] iii, EtOH/KOH, reflux;[201,202] iv, $NaBH_4$, PPh_3;[153] v, N_2H_4, PPh_3, C_6H_6/EtOH, H_2, reflux;[118] vi, $NaOPr^i$, PPh_3, Pr^iOH;[125] vii, PPh_3;[118,153] viii, H_2, PPh_3, C_6H_6;[203] ix, H_2, PPh_3[204]

Scheme 7 Preparations of $[RhH(PPh_3)_4]$



i, CO_2, C_7H_8, 25°C;[205] ii, diphos;[200] iii, ROH;[207] iv, RCO_2H;[127,128,130,154] v, $-PPh_3$[118,153]

Scheme 8 Reactions of $[RhH(PPh_3)_4]$



i, slow, 25°C;[32] ii, K/Hg, Et_2O, 20°C;[35] iii, $[Co(Cp)_2]^+$;[32] iv, $[Fe(phen)_3]^{2+}$;[32] v, D_2SO_4[32]

Scheme 9 Reactions of $[RhH(PF_3)_4]$

$$[RhH(PPh_3)_4] + D_2 \xrightarrow{C_6H_6} [RhD(PPh_3)_4] + HD \quad (59)$$

The next most important complexes of this type are trialkyl or triaryl phosphite complexes. These are best prepared by allowing the ligands to react with $[RhH(CO)(PPh_3)_3]$ (equations 60 and 61).

$$[RhH(CO)(PPh_3)_3] + 4PX_3 \longrightarrow [RhH(PX_3)_4] + 3PPh_3 + CO \quad (60)$$

$$X_3 = Et_3,[197] Ph_3,[210] Ar_3,[198] PrC(CH_2O)_3[196]$$

$$[RhCl\{PPh(OEt)_2\}_4] + PPh(OEt)_2 \xrightarrow[EtOH]{NaBH_4,\ Ar} [RhH\{PPh(OEt)_2\}_4] \quad (61)$$

Little is known of their chemical properties. If the electrochemical reduction of $[RhH\{P(OPh)_3\}_4]$ is essayed, loss of a phosphite ligand occurs before reduction to $[RhH\{P(OPh)_3\}_3]^-$ takes place. The anionic complex is unstable and *o*-metallates, eliminating hydrogen.[211]

Apart from $[RhH(PPh_2Me)_4]$, which can be prepared from $[RhCl(PPh_2Me)_3]$ by treating it with hydrazine (equation 63),[118] and $[RhH(PMe_3)_4]$, which is prepared by reducing the rhodium(III) complex $[RhH_2(PMe_3)_4]Cl$ with sodium amalgam (equation 62),[186] the remaining example of this type of complex is the dibenzophosphole complex $[RhH(\mathbf{10})_4]$ (equation 64). The last complex dissociates readily in solution (equation 65).[52,133,212]

$$[RhH_2(PMe_3)_4]Cl \xrightarrow[THF,\ 25°C]{Na/Hg} [RhH(PMe_3)_4] \quad (62)$$

$$[RhCl(PPh_2Me)_3] + PPh_2Me \xrightarrow[EtOH/C_6H_6]{N_2H_4,\ H_2,\ 80°C} [RhH(PPh_2Me)_4] \quad (63)$$

$$RhCl_3 \cdot 3H_2O + (\mathbf{10}) \xrightarrow{NaBH_4} [RhH(\mathbf{10})_4] \quad (64)$$

$$[RhH(\mathbf{10})_4] \rightleftharpoons [RhH(\mathbf{10})_3] + (\mathbf{10}) \quad (65)$$

The one complex of this stoichiometry not to have a set of four phosphorus ligands is $[RhH(PPh_3)_3(AsPh_3)]$. This can be prepared by allowing $AsPh_3$ to react with $[RhH(PPh_3)_3]$ (equation 66). It has been shown to be isomorphous with $[RhH(PPh_3)_4]$. Phosphorus and arsenic randomly occupy the coordination sites.[213] The corresponding tris(triphenylarsine) complex can be prepared from $[RhPh(cod)(PPh_3)]$ (equation 67).[204]

$$[RhH(PPh_3)_3] + AsPh_3 \longrightarrow [RhH(PPh_3)_3(AsPh_3)] \quad (66)$$

$$[RhPh(cod)(PPh_3)] + AsPh_3 + H_2 \longrightarrow [RhH(AsPh_3)_3(PPh_3)] \quad (67)$$

48.4.4.2 Other [RhXL$_4$] complexes

Very few complexes of this type are known. Some $[RhX(PF_3)_4]$ complexes can be prepared from $[RhX(PF_3)_2]_2$ but these readily lose PF_3 on warming to room temperature.[89] The complexes containing PF_2NR_2 ligands are slightly more stable. The complexes $[RhCl(PF_2NMe_2)_4]$, $[RhCl(PF_2NEt_2)_4]$, and $[RhI(PF_2NEt_2)_4]$ have been isolated. Their decomposition temperatures have been reported to be 79, 28, and 58°C respectively. The difluorodimethylaminophosphine complex is yellow and the others orange. They have been prepared by addition of excess ligand to various dimeric rhodium(I) complexes (equations 68–70).[61]

$$[RhCl(CO)_2]_2 + \text{excess } PF_2NMe_2 \xrightarrow{-78°C} [RhCl(PF_2NMe_2)_4] \quad (68)$$

$$[RhCl(PF_2NEt_2)_2]_2 + \text{excess } PF_2NEt_2 \xrightarrow{-78°C} [RhCl(PF_2NEt_2)_4] \quad (69)$$

$$[RhI(cod)]_2 + PF_2NEt_2 \longrightarrow [RhI(PF_2NEt_2)_4] \quad (70)$$

The yellow diethyl phenylphosphonite complex is also known. It can be prepared directly from hydrated rhodium trichloride (equation 71).[195]

$$RhCl_3 \cdot 3H_2O + NaBH_4 + \text{excess } PPh(OEt)_2 \xrightarrow{EtOH} [RhCl\{PPh(OEt)_2\}_4] \quad (71)$$

48.4.4.3 [RhH(LL)$_2$] complexes

Despite the isolation of numerous $[RhHL_4]$ complexes only two of the corresponding complexes containing bidentate ligands have been prepared. The first complex $[RhH(diphos)_2]$ may be prepared by the displacement of neutral ligands from $[RhH(PPh_3)_4]$ (equation 72),[200] or by allowing the chloride salt to react with $[BH_4]^-$ (equation 73). This reaction is reversed when the hydrido complex is dissolved in carbon tetrachloride. The deuterio complex can be prepared similarly from $Li[AlD_4]$. The hydrido complex eliminates hydrogen when allowed to react with $HClO_4$ (equation 74).[214]

$$[RhH(PPh_3)_4] + 2diphos \longrightarrow [RhH(diphos)_2] + 4PPh_3 \quad (72)$$

$$[Rh(diphos)_2]Cl \underset{CCl_4}{\overset{NaBH_4,\ N_2,\ EtOH}{\rightleftharpoons}} [RhH(diphos)_2] \quad (73)$$

$$[RhH(diphos)_2] + HClO_4 \longrightarrow [Rh(diphos)_2]ClO_4 + H_2 \quad (74)$$

The hydrido complex is formed as an intermediate in the electrochemical reduction of [Rh(diphos)$_2$]Cl,[42] but is itself oxidized in the system (equation 75).[215]

$$[Rh(diphos)_2]Cl \xrightarrow[MeCN]{e^-} [Rh(diphos)_2]^0 \xrightarrow{MeCN} [RhH(diphos)_2] \xrightarrow{-e^-} [RhH(diphos)_2]^+ \xrightarrow{-H_2} [Rh(diphos)_2]^+ \quad (75)$$

The light orange hydrido complex melts with decomposition at 280°C. Since the hydrido ligand is coordinated to rhodium (ν_{Rh-H} 1902 cm^{-1}, ν_{Rh-D} 1465 cm^{-1}), the complex is coordinatively saturated and exhibits poor catalytic properties.

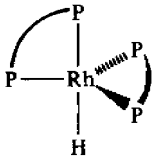
The second complex of this type has been prepared directly from hydrated rhodium trichloride (equation 76).[216] Later work has shown that the addition of formaldehyde is superfluous.[217] An alternative preparation uses $[BH_4]^-$ as the reducing agent (equation 77).[218]

$$RhCl_3 \cdot 3H_2O + (+)\text{-diop} \xrightarrow[HCHO_{(aq)}]{KOH/EtOH} [RhH\{(+)\text{-diop}\}_2] \quad (76)$$

$$RhCl_3 \cdot 3H_2O + (+)\text{-diop} \xrightarrow{NaBH_4} [RhH\{(+)\text{-diop}\}_2] \quad (77)$$

The yellow complex decomposes at 210°C. Upon recrystallization from dichloromethane the monosolvate is formed which melts at 185°C. In solution the complex exhibits fluxional behavior. The high field ^{1}H NMR spectrum shows the hydride resonance to be composed of a quintet of doublets centered at $\tau \approx 28.4$. In benzene solution $[\alpha]_D^{25} = -3.4°$.[218]

In the solid state $\nu_{Rh-H} = 2040\,cm^{-1}$.[218] X-Ray crystallography shows the complex to have the trigonal bipyramid structure (**25**).[219]



(25)

48.4.5 [RhL$_4$]X Complexes

48.4.5.1 Complexes containing monodentate ligands

There are comparatively few complexes of this type, which, given the populous nature of the related [Rh(LL)$_2$]X class (see Section 48.4.5.2 below), seems a little strange. However, the small bite of the bidentate ligands causes fewer steric problems than the accommodation of four large, monodentate ligands around the central rhodium atom. As a consequence, isolable complexes of this stoichiometry usually contain small or medium sized neutral ligands (see Table 12).

The complexes can be prepared from other ionic rhodium(I) complexes (equation 78)[221] or, in the presence of non-coordinating anions, they can be prepared by allowing excess neutral ligand to react with other rhodium(I) complexes (equation 79).[220,222]

$$[Rh(PPh_3)_2(cod)]PF_6 + PR_3 \longrightarrow [Rh(PR_3)_4]PF_6 \quad (78)$$

R_3 = Ph_2Me, Me_2Ph, $Ph(OMe)_2$[221]

$$[RhCl(PPh_3)_3] + PHPh_2 \xrightarrow[50°C,\ MeOH]{X^-} [Rh(PHPh_2)_4]X \quad (79)$$

X = BF_4, PF_6, ClO_4[221]

In general, the complexes are stable and unreactive. Their simple ^{31}P NMR spectra are unchanged upon addition of free ligand, showing the inert nature of the complexes. Their main reactions are

Table 12 Physical Properties of $[RhL_4]X$ Complexes

L	*X*	*Color*	*M.p.* (°C)	*Ref.*
$PHEt_2$	BPh_4	Yellow	147[a]	113
PHEtPh	ClO_4	Yellow	156[a]	113
$PHPh_2$	BF_4	Yellow	210–20[a]	220
$PHPh_2$	PF_6	Yellow	180–85[a]	220
$PHPh_2$	ClO_4	Yellow	150[c]	220
PHPhCy	ClO_4	Yellow	196[a]	113
$PHCy_2$	ClO_4	Yellow	193[a]	113
PMe_3	Cl	Lemon yellow	—	116, 146
PBu_3	BPh_4	Brown	—	76
PPh_2Me	PF_6	Red-orange	179–80	221, 222
PPh_2Me	ClO_4	Red-brown	—	222
PMe_2Ph	PF_6	Red-brown	124–30	221, 222
PMe_2Ph	ClO_4	Orange	—	222
$PPh_2(OMe)$	PF_6	Yellow	175–76[b]	222
$PPh(OMe)_2$	PF_6	Yellow	177	221, 222
$PPh(OMe)_2$	SbF_6	Yellow	177	222
$P(OPh)_3$	BPh_4	Yellow	—	76
$P(OPh)_3$	ClO_4	Yellow	—	76

[a] With decomposition. [b] CH_2Cl_2 solvate. [c] Explodes.

oxidative addition. The complexes prepared by way of equation (78) oxidatively add molecular hydrogen, in contrast to the complexes of secondary phosphines, which are unreactive even at high hydrogen pressures.[220]

Tetrakis(trimethylphosphine)rhodium(I) is more reactive, but tends to lose a PMe_3 ligand readily (see equations 52, 53 and 56).

48.4.5.2 Complexes containing bidentate ligands

A very large number of complexes of this stoichiometry have been prepared. Isolable complexes are listed in Table 13. Like the analogs containing monodentate ligands, the cations are somewhat inert and many of their reactions involve anion exchange.

The most accessible complex appears to be $[Rh(diphos)_2]Cl$ which can be obtained from a variety of starting materials (Scheme 10). The ligand will reduce rhodium(III) chloride or displace other ligands from many rhodium(I) complexes. Unlike tertiary monophosphines it will totally displace carbon monoxide from $[RhCl(CO)_2]_2$ (equation 80). It does, however, require excess ligand to bring about the reaction.[214,233] Less diphos forms an unstable carbonyl complex,[233] which slowly disproportionates (equation 81).[244]

$$[RhCl(CO)_2]_2 + 2\text{diphos} \longrightarrow 2[RhCl(CO)(\text{diphos})] + 2CO \quad (80)$$

$$4[RhCl(CO)(\text{diphos})] \xrightarrow{1\ \text{week}} 2[Rh(\text{diphos})_2]Cl + [RhCl(CO)_2]_2 \quad (81)$$

The other complexes are prepared similarly by utilizing the power of the bidentate ligands to displace (equations 82 and 83) monodentate ligands from rhodium's coordination sphere.

$$[RhCl(cod)]_2 + 4LL \longrightarrow 2[Rh(LL)_2]Cl + 2cod \quad (82)$$

LL = $PhMePCH_2CH_2PPhMe$, *cis*-$(Ph_2P)CH{=}CH(PPh_2)$, diars, *cis*-$(Ph_2As)CH{=}CH(AsPh_2)$[226]

$$[RhCl(C_8H_{14})_2]_2 + 4LL \longrightarrow 2[Rh(LL)_2]Cl + 4C_8H_{14} \quad (83)$$

LL = $(Ph_2P)_2CH_2$, $(Ph_2P)CH_2CH_2CH_2(PPh_2)$, $(Ph_2P)(CH_2)_4(PPh_2)$, (+)-diop[224]

Other ionic complexes which have a non-complexing anion can be prepared from chloro complexes and an inorganic salt of the anion (equations 84 and 85).

$$[RhCl(cod)]_2 + 4LL + 2MX \longrightarrow 2[Rh(LL)_2]X + 2cod + 2MCl \quad (84)$$

MX = $NaBPh_4$, LL = $(Ph_2P)_2NCH_2CO_2Me$, $(Ph_2P)_2NCHPr^iCO_2Me$,[236] $Ph_2PCH_2CH_2SEt$,[242]

$Ph_2PCH_2CH_2SPh$[242,243]; MX = NH_4PF_6, LL = $(Bu^tCH_2)_2PCH_2CH_2P(CH_2Bu^t)_2$[235];

MX = $AgPF_6$, LL = $(\eta^5\text{-}C_5H_4AsPh_2)_2Fe$, $PhMePCH_2CH_2PPhMe$, *cis*-$Ph_2AsCH{=}CHAsPh_2$, diars[230]

Table 13 Physical Properties of $[Rh(LL)_2]X$ Complexes

LL	*X*	*Color*	*M.p.* (°C)	*Ref.*
$(Ph_2P)_2CH_2$	BF_4	Orange	124[d]	223, 224
$(Ph_2P)_2CH_2$	Cl	Yellow	97[d]	224
$(Ph_2P)_2CHMe$	BF_4	—	—	223
cis-$\{(Ph_2P)CH\}_2$	BPh_4	Yellow	—	225, 226, 227
cis-$\{(Ph_2P)CH\}_2$	BF_4	—	—	226
cis-$\{(Ph_2P)CH\}_2$	PF_6	—	—	226
cis-$\{(Ph_2P)CH\}_2$	Cl[a]	Yellow	225[d]	225, 226
$\{(Me_2P)CH_2\}_2$	I	—	—	227
$\{(PhMeP)CH_2\}_2$	Cl	Yellow	240–50[d]	228, 229
$\{(PhMeP)CH_2\}_2$	BPh_4	—	—	226
$\{(PhMeP)CH_2\}_2$	BF_4	—	—	226
$\{(PhMeP)CH_2\}_2$	PF_6	Yellow	—	226, 230
diphos	BPh_4	Pale yellow	246	65, 214
diphos	BF_4	Pale orange	273–76	223, 224
diphos	$(MeC_6H_4)_2N_3$	Pale yellow	264–70	264–70
231				
diphos	$SnCl_3$	—	—	232
diphos	$SnClBr_2$	—	—	232
diphos	PF_6	—	265[d]	233, 234
diphos	S_2PCy_2	Yellow	—	65
diphos	$S_2P(OPh)_2$	Yellow	—	65
diphos	Cl	Yellow	215	141, 214
diphos	ClO_4	Yellow	282	214
$\{(Bu^tCH_2P)CH_2\}_2$	PF_6	Yellow	221–27	235
$(Ph_2P)_2(CH_2)_3$	BF_4	Pale orange	180[d]	224
$(Ph_2P)_2(CH_2)_3$	Cl	Yellow	162–65[d]	224
$(Ph_2P)_2(CH_2)_4$	BF_4	Red	169–73[d]	224
$(Ph_2P)_2(CH_2)_4$	Cl	Yellow	108[d]	224
$(Ph_2P)_2NCH_2CO_2Me$	BPh_4	Yellow	206–09	236
$(Ph_2P)_2NCHMeCO_2Me$	$RhCl_2(CO)_2$	Yellow	204	236
$(Ph_2P)_2NCHPr^iCO_2Me$	BPh_4	Yellow	203–04	236
$\{(Ph_2P)CH_2\}_2O$	BF_4	Yellow	225[d]	225
(−)-diop	BPh_4	Yellow	—	237
(+)-diop	BF_4	Pale orange	174–77[d]	224
(+)-diop	Cl	Yellow	79[d]	224
cis-$\{(Ph_2As)CH\}_2$	BPh_4	—	—	226
cis-$\{(Ph_2As)CH\}_2$	BF_4	—	—	226
cis-$\{(Ph_2As)CH\}_2$	BF_4[b]	Orange	238[d]	238
cis-$\{(Ph_2As)CH\}_2$	PF_6	Yellow	—	226, 230
cis-$\{(Ph_2As)CH\}_2$	Cl	—	—	226, 239
$\{(PhMeAs)CH_2\}_2$	Cl	—	—	240
$\{(Ph_2As)CH_2\}_2$	BPh_4	Yellow	—	65
$\{(Ph_2As)CH_2\}_2$	S_2PCy_2	Yellow	—	65
$\{(Ph_2As)CH_2\}_2$	$S_2P(OPh)_2$	Yellow	—	65
diars	BPh_4	—	—	226
diars	BF_4	—	—	226
diars	PF_6	—	—	226
diars	Cl	—	—	226
(26)	Cl[c]	—	—	107
(27)	PF_6	Golden brown	—	241
$Ph_2P(CH_2)_2SMe$	BF_4	Yellow	—	242
$Ph_2P(CH_2)_2SEt$	BPh_4	Yellow	—	242
$Ph_2P(CH_2)_2SEt$	BF_4	Yellow	—	242
$Ph_2P(CH_2)_2SPh$	BPh_4	Yellow	—	242, 243
$Ph_2P(CH_2)_2SPh$	BF_4	Yellow	—	242

[a] CH_2Cl_2 solvate. [b] MeOH solvate. [c] Monohydrate. [d] With decomposition.

$$[RhCl(C_8H_{14})_2]_2 + 4LL + 2MX \longrightarrow 2[Rh(LL)_2]X + 4C_8H_{14} + 2MCl \quad (85)$$

$$MX = NaBF_4,\ LL = (Ph_2P)_2CH_2,\ (Ph_2P)_2CHMe,\ diphos,\ Ph_2PCH_2CH_2CH_2PPh_2$$[223]

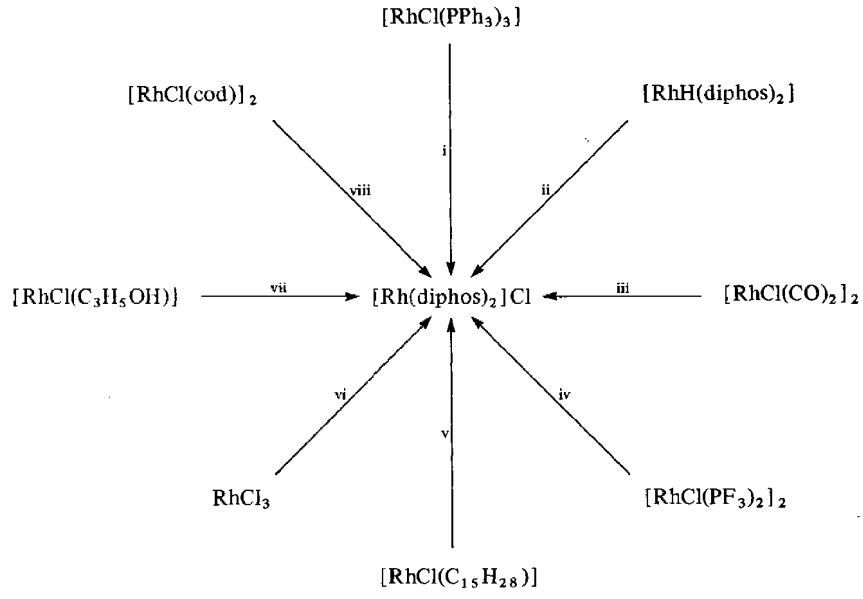
$$[RhCl(nbd)]_2 + 4(-)\text{-diop} + 2NaBPh_4 \longrightarrow 2[Rh\{(-)\text{-diop}\}_2]BPh_4 + 2NaCl \quad (86)$$

$$[RhCl(CO)_2]_2 + 4cis\text{-}Ph_2AsCH{=}CHAsPh_2 + 2NaBF_4 \longrightarrow \quad (87)$$

$$2[Rh(cis\text{-}Ph_2AsCH{=}CHAsPh_2)_2]BF_4 + 4CO + 2NaCl$$

$$[Rh(cod)(acac)] + Ph_3CBF_4 + 2Ph_2P(CH_2)_2SR \longrightarrow [Rh\{Ph_2P(CH_2)_2SR\}_2]BF_4 \quad (88)$$

$$R = Me,\ Et,\ Ph$$[242]



i, diphos, C_6H_6[228]; ii, CCl_4[214]; iii, diphos[233,244]; iv, diphos, C_6H_6[89]; v, diphos[247]; vi, diphos, 200–270°C[245]; vii, diphos, EtOH, 78°C[141]; viii, 2diphos, H_2/CO[246]

Scheme 10 Preparative reactions of $[Rh(diphos)_2]Cl$

$$[Rh(LL)_2]Cl + MX \longrightarrow [Rh(LL)_2]X + MCl \quad (89)$$

MX = $AgBF_4$, LL = $(Ph_2P)_2CH_2$, $Ph_2PCH_2CH_2CH_2PPh_2$, $Ph_2P(CH_2)_4PPh_2$, (+)-diop;[224]

MX = $NaBPh_4$, $NaBF_4$, $LiPF_6$, LL = $PhMePCH_2CH_2PPhMe$, *cis*-$(Ph_2P)CH{=}CH(PPh_2)$, *cis*-$(Ph_2As)CH{=}CH(AsPh_2)$, diars[226]

Although $(Bu^tCH_2)_2P(CH_2)_2P(CH_2Bu^t)_2$ forms a typical $[Rh(LL)_2]^+$ complex when allowed to react with $[RhCl(cod)]_2$ and NH_4PF_6 (equation 84),[234] the closely related ditertiary phosphine $Bu^t_2P(CH_2)_3PBu^t_2$ forms complexes which contain hydrido ligands or the diphosphine bound additionally to rhodium through carbon.[248,249]

Apart from anion exchange reactions the complexes are inert. One of the few reagents to bring about a change in the coordination sphere is sulfur dioxide which coordinates to rhodium without displacement of a bidentate ligand. However, the product is not well characterized and the crystals contain clathrated sulfur dioxide.[250]

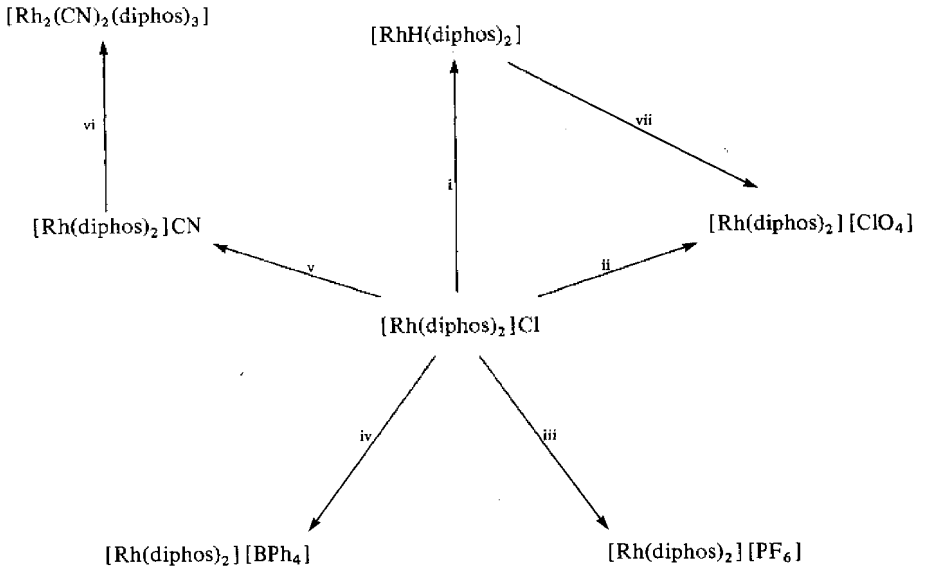
If $[Rh(diphos)_2]Cl$ is allowed to react with an anion exchange resin in the cyanide form, the corresponding cyanide complex (ν_{C-N} 2089 cm^{-1}) is formed. Upon dissolution of the product in benzene a diphos ligand is lost and $[Rh_2(CN)_2(diphos)_3]$ is formed.[119] The dinuclear product probably contains a bridging diphos ligand (*cf.* $[Cu_2(N_3)_2(diphos)_3]$[251]). These reactions and the anion exchange reactions of $[Rh(diphos)_2]Cl$ are shown in Scheme 10a.

By way of contrast, the unsaturated ditertiary phosphine complex $[Rh\{cis\text{-}(Ph_2P)CH{=}CH(PPh_2)\}_2]ClO_4$ forms a five-coordinate cyano complex (ν_{C-N} 2070 cm^{-1}) when allowed to react with an anion exchange resin.[252]

The structure of $[Rh(diphos)_2]ClO_4$ has been determined. X-Ray crystallography showed the RhP_4 core to be planar, but the aliphatic carbon atoms of the ligands do not lie in this plane.[253]

The electronic spectra of several of the complexes have been studied and attempts have been made to correlate the absorption bands with the energy levels of proposed molecular orbital diagrams.[254,255] An Rh–P coupling constant of 133 Hz has been observed in the ^{31}P NMR spectrum of $[Rh(diphos)_2]^+$.[256]

Many complexes of this type (*e.g.* $[Rh\{(HOCH_2)CH(PPh_2)CH_2PPh_2\}_2][BF_4]$[257]) have been prepared *in situ* and used as homogeneous catalytic hydrogenation catalysts, but have never been fully characterized.



i, $NaBH_4$, N_2, EtOH or $LiAlH_4$, N_2, THF;[214] ii, $NaClO_4$, EtOH;[214] iii, $K[PF_6]$, MeOH;[233] iv, $NaBPh_4$, EtOH;[214] v, Dowex resin (cyanide form), CH_2Cl_2;[119] vi, C_6H_6;[119] vii, $+HClO_4$, $-H_2$[214]

Scheme 10(a) Reactions of $[Rh(diphos)_2]Cl$

48.4.6 $[RhL_5]X$ Complexes

In this type of complex rhodium(I) achieves its maximum coordination number with neutral ligands. As might be expected, very few complexes of this type are known. The isolable examples are unstable and easily lose neutral ligands. The complexes so far isolated contain five trialkyl phosphite ligands. These ligands have high π-acidity but are poor σ-donors. All six $[Rh\{P(OR)_3\}_5]X$ complexes are white. They ionize in acetone solution. Their physical properties are shown in Table 14.

The salts have been prepared by adding excess trialkyl phosphite to $[RhCl(cod)]_2$ in the presence of an inorganic salt of a non-complexing anion (equation 90).

$$[RhCl(cod)]_2 + \text{excess } P(OR)_3 + 2MX \longrightarrow 2[Rh\{P(OR)_3\}_5]X + 2cod + 2MCl \quad (90)$$

$$R = Me, Et, Bu^i, Bu^n, MX = NaBPh_4; R = Me, MX = NH_4PF_6; P(OR)_3 = P(OCH_2)_3CMe, MX = NaBPh_4$$[222]

The ^1H NMR spectra of the complexes show the ligands to be labile. There is the further possibility that the cation is fluxional, having trigonal bipyramid and square pyramid configurations as limiting forms.

The ligands can be displaced by alkenes, and the trimethyl and triethyl phosphite complexes lose three ligands from the cation to yield η^6-tetraphenylborato complexes. In the case of the $P(OMe)_3$ complex the reaction can be reversed by adding excess $P(OMe)_3$ (equations 91a and 91b).[222]

Table 14 Physical Properties of $[RhL_5]X$ Complexes

Complex	*M.p.* (°C)	*Conductance* (S)	*Ref.*
$[Rh\{P(OMe)_3\}_5][BPh_4]$	—	73	222
$[Rh\{P(OMe)_3\}_5][PF_6]$	94–96	122	222
$[Rh\{P(OEt)_3\}_5][BPh_4]$	89–93	90	222
$[Rh\{P(OBu^n)_3\}_5][BPh_4]$	Oil	—	222
$[Rh\{P(OBu^i)_3\}_5][BPh_4]$	114–16	83	222
$[Rh\{P(OCH_2)_3CMe\}_5][BPh_4]$	178	92	222

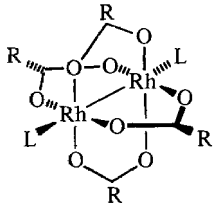
[a] Determined on *ca.* 10^{-3} M acetone solutions.

$$[Rh\{P(OEt)_3\}_5]BPh_4 \xrightarrow{-P(OEt)_3} [Rh(BPh_4)\{P(OEt)_3\}_2] \quad (91a)$$

$$[Rh\{P(OMe)_3\}_5]BPh_4 \underset{P(OMe)_3}{\overset{P(OMe)_3}{\rightleftharpoons}} [Rh(BPh_4)\{P(OMe)_3\}_2] \quad (91b)$$

48.5 RHODIUM(II) COMPLEXES

Despite the vast number of cobalt(II) complexes known, the dipositive oxidation state is rare for rhodium. The bulk of the rhodium(II) complexes known are dimeric, the classic examples being the diamagnetic carboxylato complexes that adopt the classic lantern structure (**26**). However, even the aqua complex is dimeric so the bridging carboxylato ligands are not essential for the formation of the rhodium–rhodium bond.



(26)

Rhodium(II) complexes with tertiary arsines were erroneously reported over 40 years ago. These complexes were, with the advent of NMR spectrometry, later proved to be hydridorhodium(III) complexes. Nevertheless, the only stable isolable monomeric rhodium(II) complexes are those containing tertiary phosphine and other similar group VB ligands.

A further difference between rhodium(II) and cobalt(II) complexes becomes apparent from a study of the monomeric complexes. Whereas virtually all cobalt(II) complexes are high spin d^7 species, with the exception of $[Co(CN)_5]^{3-}$ and related species, the rhodium(II) complexes are all low spin complexes. Thus, because of the lack of spin reorientation required in forming a low spin rhodium(III) complex, they are excellent reducing agents. The stability of the rhodium–rhodium bond in the dimers prevents their facile oxidation.

Because of the great differences in behavior between the few monomeric complexes and the dimeric complexes, this section is divided principally into two parts.

48.5.1 Monomeric Complexes

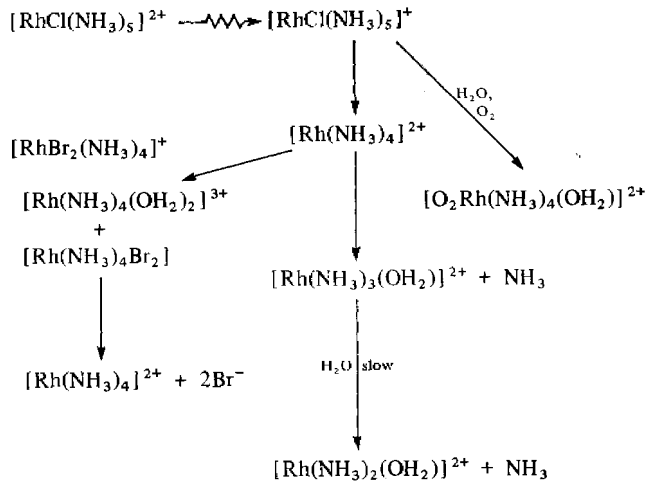
Few monomeric rhodium(II) complexes, other than those stabilized by group VB ligands, have anything but a transient existence. Whilst the former can be prepared by reduction of rhodium(III) salts with the group VB ligand, the latter are generated by photolytic or radiolytic methods. The short lifetimes of these species have occasionally been extended by trapping them within a crystal lattice.

It has been demonstrated that $RhBr_3$-doped AgBr crystals give rise to Rh^{2+} centers upon exposure to light. These rhodium(II) centers become more stable with decreasing temperatures and at 35 K it was shown that the low spin Rh^{II} center was in a D_{4h} environment.[258] However, it was believed that the D_{4h} symmetry observed for photolytically generated Rh^{2+} centers in LiH or LiD lattices was an artifact of site symmetry.[259] It is reasonable to assume less than ideal geometry for a $t_{2g}^6 e_g^1$ ion since Jahn–Teller effects will be prominent for such an electronic configuration and a static Jahn–Teller effect has been observed for Rh^{2+} in a CaO matrix at 4.2 K.[260]

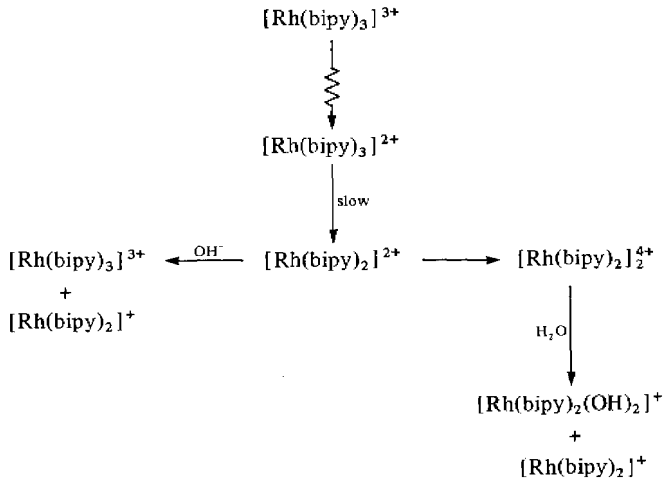
Gamma irradiation of Rh^{3+}-doped NH_4Cl crystals again gives rise to Rh^{2+} centers of D_{4h} symmetry. In this system further reduction to Rh^0 was also observed.[261] Pulse radiolysis has proved to be a powerful tool for the investigation of the behavior of rhodium(II) species in aqueous solution. Various reducing agents in the system can bring about the reduction of rhodium(III) complexes besides the ubiquitous solvated electron.[262]

Both $[RhCl(NH_3)_5]^+$ generated from $[RhCl(NH_3)_5]^{2+}$, and $[Rh(bipy)_3]^{2+}$ generated from $[Rh(bipy)_3]^{3+}$, have been studied. The former (Scheme 11) shows that Jahn–Teller effects persist in the solution chemistry of rhodium(II).[263] The principal reactions of the latter (Scheme 12) involve disproportionation to Rh^I and Rh^{III}.[262,264]

The complexes described in this section contain either (i) tertiary phosphines or stibines in



Scheme 11 Generation and reactions of $[RhCl(NH_3)_5]^+$



Scheme 12 Generation and reactions of $[Rh(bipy)_3]^{2+}$

conjunction with halo ligands, or (ii) bidentate tertiary monophosphine ligands. They are clearly different in nature from the $[Rh_2(O_2CR)_4(ZX_3)_2]$ (Z = P, As, Sb) complexes, which are best regarded as derivatives of carboxylatorhodium(II) complexes (Table 14a).

Table 14a Physical Properties of Rhodium(II) Complexes Containing Tertiary Phosphines and Stibines

Complex	*Color*	*M.p.* (°C)	*Ref.*
$[RhCl_2(PCy_3)_2]$	Red-brown	—	267
$[RhBr_2(PCy_3)_2]$	Green	—	267
[*cis*-$RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2$]	Purple	—	265
[*trans*-$RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2$]	Blue-green	—	265
[*trans*-$RhCl_2(PBu^t_2Me)_2$]	Purple	170–200	268, 269
[*trans*-$RhCl_2(PBu^t_2Et)_2$]	Green	165–75	268, 269
[*trans*-$RhCl_2(PBu^t_2Pr)_2$]	Green	175–95	268, 269
$[RhCl_2\{PBu^t_2(C{\equiv}CPh)\}_2]$	Red	140–45	270
[*trans*-$RhCl_2(PBu^t_2R)_2$][a]	Green	201–07[b]	272
[*trans*-$Rh\{PBu^t_2(o\text{-}C_6H_4O)\}_2$]	Dark blue	350	273
$[RhCl_2\{Bu^t_2P(CH_2)_2CO_2Et\}]$	Blue	145–47	275
$[RhCl_2\{Bu^t_2P(CH_2)_3CO_2Et\}]$	Green	90–96	275
$[RhCl_2(diphos)]$	Gray-green	—	277
$[RhCl_2\{Sb(o\text{-}C_6H_4Me)_3\}]$	Red-brown	—	278
$[RhBr_2\{Sb(o\text{-}C_6H_4Me)_3\}]$	Red-brown	—	278

[a] R = $—CH_2(2\text{-}Me\text{-}5\text{-}OMeC_6H_3)$. [b] With decomposition.

48.5.1.1 *Tertiary phosphine complexes*

Many large tertiary phosphines fail to reduce hydrated rhodium trichloride and form rhodium(I) complexes. Under mild conditions they usually reduce the salt to paramagnetic rhodium(II) complexes. This was first discovered when $P(o\text{-}C_6H_4Me)_3$ was employed, as in equation (92).[265]

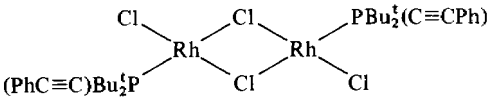
$$RhCl_3 \cdot 3H_2O + P(o\text{-}C_6H_4Me)_3 \xrightarrow[EtOH]{0°C} RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2 \quad (92)$$

The blue-green complex is paramagnetic ($\mu = 2.3$ BM) and has a single band due to $\nu_{Rh\text{-}Cl}$ in its far IR spectrum. Accordingly it has been assigned the *trans* configuration. If the preparative reaction is carried out at 0°C, or if CH_2Cl_2 solutions of the blue-green complex are evaporated *in vacuo*, purple crystals of a less stable and less well characterized isomer are obtained. The purple isomer is also paramagnetic (see Table 14b for magnetic and IR spectral data).

If these preparations are carried out at high temperatures, or if either of the above complexes is heated, *o*-metallation occurs. No reduction to rhodium(I) complexes was observed [265,266] It has been claimed that the attempted borohydride reduction of the dichloro complex in ethanol forms the unstable diamagnetic rhodium(II) complex $[RhH(BH_4)\{P(o\text{-}C_6H_4Me)_3\}]$.[212]

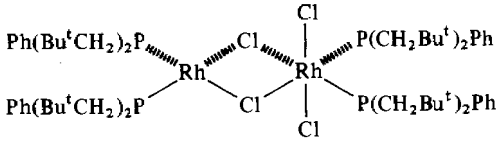
The large steric requirements of the tricyclohexylphosphine ligand are presumably responsible for the isolation of $[RhX_2(PCy_3)_2]$ (X = Cl, Br) complexes under mild conditions. Both the red-brown chloro complex and the green bromo complex are paramagnetic.[267]

The ligands PBu^t_2R (R = Me, Et, Pr) also yield *trans*-rhodium(II) complexes when allowed to react with ethanolic solutions of $RhCl_3 \cdot 3H_2O$. If the reaction is carried out above 25°C *o*-metallation does not occur, instead $[RhHCl_2(PBu^t_2R)_2]$ complexes are formed.[268,269] The closely related alkynylphosphine ligand $PBu^t_2(C{\equiv}CPh)$ also forms a hydridorhodium(III) complex when allowed to react with hydrated rhodium trichloride. Upon dissolution in chloroform, however, the red rhodium(III) hydrido complex decomposes and forms the orange binuclear rhodium(II) complex (**27**).[270]

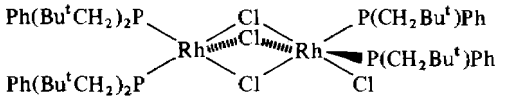


(27)

Tri(neopentyl)phosphine and phenyldi(neopentyl)phosphine also form complexes of this stoichiometry. However, these complexes are apparently diamagnetic. In their ^{1}H NMR spectra the resonances of the *t*-butyl groups are well defined. Accordingly they have been formulated as mixed Rh^I/Rh^{III} complexes. They may adopt either structure (**28**) or (**29**).[271]



(28)



(29)

Table 14b Magnetic Properties and Far-IR Spectra of Rhodium(II) Complexes of Tertiary Phosphines and Stibines

Complex	μ(BM)[b]	ν_{Rh-X}(cm^{-1})	*Ref.*
$[RhCl_2(PCy_3)_2]$	2.24	354, 343	267
$[RhBr_2(PCy_3)_2]$	2.24	288, 270	267
[*cis*-$RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2$]	2.0	—	265
[*trans*-$RhCl_2\{P(o\text{-}C_6H_4Me)_3\}_2$]	2.3	351	265
[*trans*-$RhCl_2(PBu^t_2Me)_2$]	1.15	352, 348	268, 269
[*trans*-$RhCl_2(PBu^t_2Et)_2$]	P	334, 360	268, 269
[*trans*-$RhCl_2(PBu^t_2Pr)_2$]	P	—	268, 269
$[RhCl_2\{PBu^t_2(C{\equiv}CPh)\}_2]$	P	295	270
$[RhCl_2(PBu^t_2R)_2]$[a]	P	349, 342	272
$[RhCl_2\{Bu^t_2P(CH_2)_2CO_2Et\}]$	P	352	275
$[RhCl_2\{Bu^t_2P(CH_2)_3CO_2Et\}]$	P	358	275
[$RhCl_2$(diphos)]	P	262	277
$[RhCl_2\{Sb(o\text{-}C_6H_4Me)_3\}]$	D	340	278

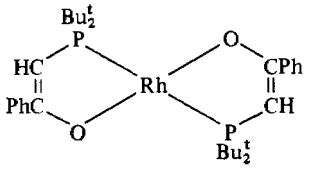
[a] R = —CH_2(2-Me-5-OMeC$_6$H$_3$). [b] P, paramagnetic; D, diamagnetic.

Emerald green crystals of *trans*-$[RhCl_2(PR_3)_2]$ can be obtained from the tertiary phosphine and hydrated rhodium trichloride at room temperature. The NMR spectrum is degraded and multiple peaks from ν_{Rh-Cl} in the far IR spectrum suggest that the product is a *trans* rhodium(II) complex.[272]

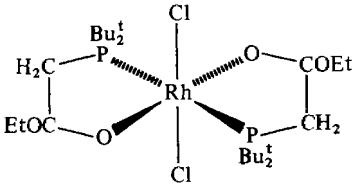
The closely related ligand, $PBu^t_2(o\text{-}C_6H_4OMe)$, also forms a paramagnetic rhodium(II) complex. However, in the reaction the ligand is demethylated, and the product has a totally different structure to the halo complexes so far described in this section.[273]

A similar reaction takes place between $RhCl_3 \cdot 3H_2O$ and the keto phosphine $PBu^t_2(CH_2COPh)$, except that a rhodium(III) complex is first formed containing the phosphaenolate. In the presence of sodium methoxide this rhodium(III) complex is reduced to the paramagnetic rhodium(II) species (**30**).[274]

The carbethoxy tertiary phosphine $Bu^t_2P(CH_2)_nCO_2Et$ ($n = 1$) forms an octahedral, cationic rhodium(III) complex (**31**), in which the carbonyl group coordinates to rhodium. Homologous ligands ($n = 2$, 3) from four-coordinate rhodium(II) complexes in which the ligands are only phosphorus bound.[275]



(30)



(31)

Although hydrated rhodium(II) propionate merely has its axial aqua ligands replaced when it is allowed to react with PPh_3, both the formate and acetate form orange mononuclear complexes under mild conditions.[276]

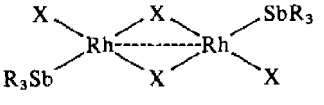
If diphos is allowed to react with the η^3-2-methallyl complex $[RhCl_2(\eta^3\text{-}C_3H_4Me)]$ in the presence of hydrogen the gray-green complex $[RhCl_2(diphos)]$ is formed.[277]

48.5.1.2 Tertiary arsine complexes

There are no tertiary arsine complexes of rhodium(II). Early reports of such complexes are erroneous.[5,6] The complexes have been shown to be hydridorhodium(III) species.

48.5.1.3 Tertiary stibine complexes

Rhodium(III) halides form $[RhX_2\{Sb(o\text{-}C_6H_4Me)_3\}]$ complexes when allowed to react with tri(*o*-tolyl)stibine. Despite their stoichiometry and diamagnetism there is no evidence for their being either *o*-metallated or hydridorhodium(III) complexes. It is believed they have the planar dimeric structure (**32**). Intramolecular interactions in such dimers could account for their diamagnetism and the non-equivalence of the methyl protons in their ^1H NMR spectrum.[278]



(32)

48.5.2 Dimeric Complexes

In 1960, Chernayev and co-workers reported that refluxing $[RhCl_6]^{3-}$ in aqueous formic acid leads to a stable, dark green compound.[279] Despite its initial formulation as a Rh^I formate, a formulation quickly retracted[280] when an X-ray study of the acetate analog showed it to be dimeric,[281] this dark green material is generally acknowledged to be the first well-characterized complex containing the Rh_2^{4+} moiety. Since then, interest in the structures, the metal–metal and metal–ligand bonding, and the reactions (*e.g.* substitutions, electrochemistry, chemotherapy, catalytic properties) of these complex has caused an explosion of research activity. These complexes

contain what is now generally recognized as a Rh—Rh single bond, and most, but not all, contain four ligands which span the Rh—Rh bond. They will be considered according to the type of bridging ligands, followed by brief discussions of the bonding and reactions of these complexes. Numerous excellent reviews have appeared recently and while overlap is unavoidable, the discussion here concentrates on work presented since their appearance.[282–286]

48.5.2.1 Synthesis and structure

(*i*) *Oxo-bridged dimers*

The prototypical Rh^{II} dimer is $[Rh_2(O_2CMe)_4]$ and is readily prepared by refluxing $RhCl_3 \cdot 3H_2O$ and $(Na^+/H^+)O_2CMe$ in ethanol, a mildly reducing solvent (equation 93).[287,288] Recrystallization of the dark green precipitate from methanol gives the dimethanol adduct, $[Rh_2(O_2CMe)_4(MeOH)_2]$, which forms the parent $[Rh_2(O_2CMe)_4]$ when heated to 100°C for 30 min. Yields as high as 85% (based on initial $RhCl_3$) have been reported.[289]

$$RhCl_3 \cdot 3H_2O + (Na^+/H^+)(O_2CMe^-) \xrightarrow{EtOH} [Rh_2(O_2CMe)_4] \quad (93)$$

The dimeric Rh^{II} acetates, readily soluble in a wide variety of solvents, are air-stable Lewis acids which readily form 1:1 and 1:2 adducts with many Lewis bases. They generally display two visible absorption bands at ~600 and ~450 nm. The 450 nm band is reasonably unaffected by adduct formation, while the position and intensity of the low energy band is extremely sensitive to the number and nature of the axially bonded ligands; two other characteristic transitions in the UV region near 250 and 220 nm are also axial-ligand dependent.[290,291] (Spectral assignments are discussed in Section 48.5.2.2.) The thermal stability of $[Rh_2(O_2CMe)_4L_2]$ is dependent on the nature of the adduct L, and on the nature of the carboxylate bridges.[292–294]

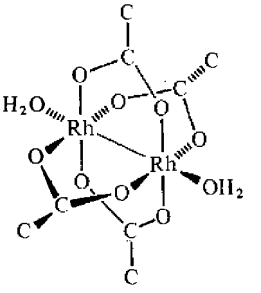
Much of our current understanding of $[Rh_2(O_2CMe)_4L_2]$ complexes comes from numerous single crystal X-ray structures. Table 15 lists, in order of increasing Rh—Rh bond length, the Rh—Rh and average Rh—L bond lengths for the tetraacetate complexes whose X-ray structures have been reported. The Rh—Rh bond is short and remarkably invariant within this series, with less than 0.08 Å difference between the longest and shortest examples. The structure of the dihydrate (**33**)[297] is representative of the structure of all of these tetracarboxylato species. The $[Rh_2(O_2CMe)_4]$ core has approximately D_{4h} symmetry, with the Lewis base adducts H_2O in (**33**) coordinated to the sites *trans* to the Rh—Rh bond. There is little evidence of strain, as the average bond angles (*e.g.*

Table 15 Bond Lengths (Å) for $[Rh_2(O_2CMe)_4L_2]$

L	*Rh—Rh*	*Rh—L*	*Comments*	*Ref.*
MeOH	2.377	2.286	—	295
MeCN	2.384(1)	2.254(7)	—	296
H_2O	2.3855(5)	2.310(3)	—	297
4-CNpy	2.393(1)	2.243(4)	One MeCN in lattice	282
Caffeine[a]	2.395(1)	2.315(9)	—	298
Cl	2.3959(6)	2.585(9)	As $[C(NH_2)_3]^+$ salt	299
Cl	2.397(1)	2.601(1)	As Li^+ salt	300
py	2.3963(2)	2.227(3)	—	301
$PhCH_2SH$	2.4020(3)	2.551(2)	—	302
$NH(Et)_2$	2.4020(7)	2.301(5)	—	303
PhSH	2.4024(7)	2.548(1)	—	299
AAMP[a]	2.404(1)	2.292(9)	One-dimensional polymer	304
$(Me)_2SO$	2.406(1)	2.451(2)	S atom coordination	305
7-Azaindole	2.408	2.243	—	b
Theophylline[a]	2.412(6)	2.23(3)	—	300
PhN(H)C(OMe)S	2.4121(4)	2.556(2)	S atom coordination	301
Tetrahydrofuran	2.413(1)	2.517(1)	—	305
CO	2.4193(3)	2.091(3)	—	303, 306
PF_3	2.4215(6)	2.340(2)	—	306
MeNC	2.4333(4)	2.158(5)	—	299
$P(OPh)_3$	2.4434(6)	2.412(1)	One toluene in lattice	307
PPh_3	2.4505(2)	2.4771(5)	—	307
$(NO)(NO_2)$	2.4537(4)	1.933(4)	L—NO	303
		2.010(4)	$L—NO_2$ (N coordinated)	
$P(OMe)_3$	2.4556(3)	2.437(1)	—	306

[a] See (**36**). [b] Cited (ref. 93a) in ref. 282.

Rh—Rh—O_{eq}, 88.07°; Rh—O—C, 119.50°; Rh—Rh—O_{ax}, 176.03°) suggest a comfortable fit of the acetates around the Rh_2^{4+} moiety.[297] The softness of the Rh^{II} center is apparent, as both DMSO and PhN(H)C(OMe)S are sulfur bonded, and the nitrite ion is bonded through the nitrogen atom (Table 15). The binding to the axial sites is relatively weak, and long Rh—L bond lengths are a general feature of these tetracarboxylate dimers; for example, in $[Rh_2(O_2CMe)_4(H_2O)_2]$, the Rh—OH_2 axial bonds are 0.27 Å longer than the Rh—O_{eq} bonds from the acetate bridges.



(33)

The readily prepared $[Rh_2(O_2CMe)_4]$ is the starting point for the synthesis of many other oxo-bridged Rh^{II} dimers. While the mechanisms of these reactions are not known, a carboxylate exchange must occur, as heating $[Rh_2(O_2CMe)_4]$ in an excess of the desired carboxylate, usually in the protonated form, generally leads to virtually quantitative conversion to the substituted carboxylate (equation 94). Substituted carboxylate dimers have also been prepared by refluxing ethanolic solutions of $RhCl_3 \cdot 3H_2O$ with the desired carboxylate, analogous to equation (93). As shown in Table 16, X-ray studies have shown that there is still little variety in the Rh—Rh bond length, and excluding the phosphate-bridged species, the difference between the shortest and longest Rh—Rh bond in this series is only 0.031 Å.

$$[Rh_2(O_2CMe)_4] + 4HO_2CR \longrightarrow [Rh_2(O_2CR)_4] + 4HO_2CMe \quad (94)$$

While X-ray structures have not been reported, numerous $[Rh_2(Q)_4L_2]$ complexes have been reported with a variety of bridging ligands.[282,283,286] Recent examples include complexes where Q is the conjugate base of glutaric acid $[^-O_2C(CH_2)_3COOH]$, α-propionic acid,[318] or mandelic acid (with L = H_2O, NH_3, N_2H_4, thiourea, DMSO, $PhNH_2$);[319] the CD spectrum of the tetramandelate $[Rh_2(L\text{-}(+)\text{-}O_2CC(OH)HPh)_4(H_2O)_2]$ has been reported.[320] Reaction of $RhCl_3 \cdot 3H_2O$ with ethanolic solutions of sodium cinnamate (*trans*-PhCH=CHCOO$^-$ Na^+) leads to $[Rh_2(\text{cinnamate})_4]$, which forms 1:2 adducts with DMF, MeCN and pyridine when dissolved in these solvents.[321]

Cotton recently reported the single crystal X-ray structures of two $[Rh_2(O_2CR)_4L_2]$ complexes, where R is a bulky hydrocarbon (R = 1-adamantane or 2-(PhC_6H_4).[308] The structures show little

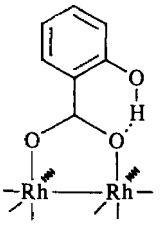
Table 16 Bond Lengths (Å) for some Rh_2^{II} Oxo-bridged Dimers

Complex	*Rh—Rh*	*Rh—L*	*Comments*	*Ref.*
$[Rh_2(O_2C\text{-}1\text{-adamantane})_4(MeOH)_2] \cdot 5MeOH$	2.371(2)	2.296(9)	—	308
$[Rh_2\{O_2CCMe_3\}_4(H_2O)_2]$	2.371(1)	2.295(2)	—	305
$[Rh_2(O_2CH)_4(H_2O)]$	2.38	2.45	Only one H_2O adduct	309
$[Rh_2\{O_2C(CH_2)_2NH_3\}_4(H_2O)_2](ClO_4)_4 \cdot 4H_2O$	2.386(3)	2.33(1)	—	310, 311
$[Rh_2(O_2CEt)_4(DDA)]_n$[a]	2.387(1)	2.324(6)	Zigzag chains with DDA bridges	312
$[Rh_2(2\text{-BPC})_4(MeCN)_2] \cdot 3C_6H_6$[b]	2.396(1)	2.233(3)	—	308
$[Rh_2(O_2CEt)_4(7\text{-azaindole})_2]$[a]	2.403(1)	2.275(6)	—	312
$[Rh_2(O_2CEt)_4(PHZ)]_n$[a]	2.409(1)	2.362(4)	Linear chains with PHZ bridges	312
$[Rh_2(O_2CEt)_4(\text{acridine})_2]$[a]	2.417(1)	2.413(3)	—	312
$[Rh_2(O_2CEt)_4(Me_2SO)_2]$	2.407(1)	2.449(1)	S atom coordination	313
$[Rh_2(O_2CC_6H_4OH)_4(EtOH)(H_2O)]$	2.385(2)	2.30(1)	Rh—O(H)Et	314
		2.30(1)	Rh—OH_2	
$Cs_4[Rh_2(O_2CO)_4(H_2O)_2]_2 \cdot 6H_2O$	2.378(1)	2.344(5)	—	315
$Cs_4Na_2[Rh_2(O_2CO)_4Cl_2] \cdot 8H_2O$	2.380(2)	2.601(3)	—	315
$[Rh_2(O_2CPh)_4(py)_2]$	2.402(1)	2.237(2)	—	316
$[Rh_2\{O_2P(OH)_2\}_4(H_2O)_2]$	2.485(1)	2.29(1)	Phosphate bridges	317

[a] See (35). [b] 2-BPC = 2-biphenylcarboxylate.

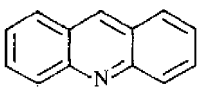
evidence of steric crowding, as the bulky groups are far from each other at the tips of the bridges. When R = CPh_3, a mixed bridged species $[Rh_2(O_2CMe)_2\{O_2CCPh_3\}_2(MeCN)_2]$ forms (see Section 48.5.2.1.iii).

The salicylate ion (sal = o-$O_2CC_6H_4OH^-$) forms, *via* a bridge-exchange with $[Rh_2(O_2CMe)_4]$, complexes of the form $[Rh_2(sal)_4L_2]$ (L = NH_3, py, aniline, en, urea, $MeC(S)NH_2$ and N_2H_4).[322] Reaction of salicylate with $RhCl_3 \cdot 3H_2O$ in aqueous EtOH, followed by recrystallization of the solid product from absolute ethanol, leads to the interesting diadduct species $[Rh_2(sal)_4(C_2H_5OH)(H_2O)]$, which has been characterized by a structural study.[314] Bonding to the Rh_2 core is through the carboxyl oxygens, the phenyl rings are coplanar with the Rh—Rh bond, and three of the salicylate hydroxyl groups face toward one end of the dimer. This 3,1 geometry is presumed to be sterically determined, as the ethanol is bonded to the Rh at the end of the complex with the three hydroxyl groups, while the water is coordinated at the more open end; there is evidence of hydrogen bonding between the phenyl hydroxides and the bridging carboxyl oxygens as in (**34**).[312]

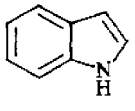


(34)

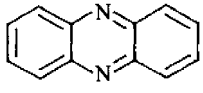
Steric crowding is more evident when bulky ligands occupy the axial sites. Cotton has presented[312] the single crystal X-ray structures of $[Rh(O_2CEt)_4(L)_n]$ (**35**; L = acridine (ACR), 7-azadine (AZA), phenazine (PHZ), or 2,3,5,6-tetramethyl-*p*-phenylenediamine (DDA); n = 1 or 2). For L = ACR or AZA (monobasic ligands), n = 2 and the normal coordination geometry occurs, consisting of discrete dimeric units with an ACR or an AZA bonded to each end of the Rh_2 core. In contrast, the dibasic ligands (L = PHZ or DDA) serve as bridges between Rh_2 units, and complexes of the stoichiometry [Rh(prop)$_4$L] are formed. For L = PHZ, almost linear chains occur (the Rh—Rh—N angle is *ca.* 174°), while the approximately tetrahedral amine of the DDA results in zigzag chains of —[Rh—Rh]—DDA—[Rh—Rh]—DDA—[Rh—Rh]—.[312]



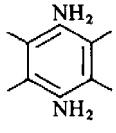
ACR = acridine



AZA = 7-azaindole



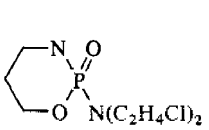
PHZ = phenazine



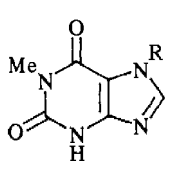
DDA = 2,3,5,6-tetramethyl-*p*-phenylenediamine

(35)

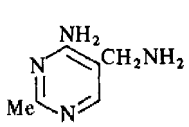
Interest in the antitumor properties of $[Rh_2(O_2CMe)_4]$ has led to studies of adduct formation with bases of biological importance. Cyclophosphamide (**36a**) does not generally coordinate with metal systems, but adducts of the form $[Rh_2(O_2CR)_4L_2]$ (R = Me, Et, Pr; L = cyclophosphamide) have been reported[323] although the nature of the phosphamide—Rh bond is not clear. Single crystal X-ray structures of $[Rh_2(O_2CMe)_4L_2]$ (L = theophylline, caffeine; **36b**) show they have the normal Rh^{II} dimeric structure.[298] The surprising feature of the theophylline complex is that bonding to the theophylline is through N(9), rather than the N(7) generally observed for other theophylline–metal complexes. It is suggested that the repulsion between the carbonyl oxygen at C(6) and the bridging carboxyls of $[Rh_2(O_2CMe)_4]$ hinders axial coordination at the N(7) site. Coordination through N(9) is also observed for the caffeine complex, where the methyl group prevents coordination at N(7).[298] Coordination at N(9) and at C(8) are observed in Cu^{II}–caffeine complexes,[324,325] and C(8) coordination is observed in the $[Ru^{III}(caffeine)(NH_3)_3Cl_2]^+$ ion.[326]



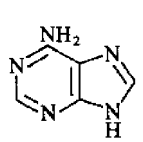
(36a) cyclophosphamide



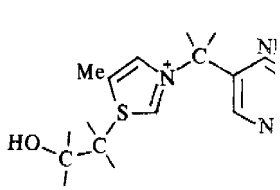
(36b) theophylline, R = H
caffeine, R = Me



(36c) AAMP



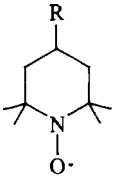
(36d) adenine



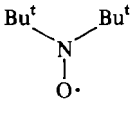
(36e) thiamine

Aoki has shown that AAMP (4-amino-5-aminomethyl-2-methylpyrimidine; **36c**) reacts with $[Rh_2(O_2CMe)_4]$ to form the 1:1 adduct $[Rh_2(O_2CMe)_4(AAMP)]\cdot 3.5\,H_2O$, a one-dimensional polymer reminiscent of the DDA complexes.[304] Coordination to the Rh_2 units is through the N(1) and the amino group from N(5), and does not involve the basic N(3) site. The bonding is end to end, with two amine nitrogens [from N(5)] bonded at each end of the same Rh_2 unit, and two pyrimidine N(1) atoms bonded at either end of the next unit; this can be represented as: $--N^1)$—[Rh—Rh]—$(N^1—N^5)$—[Rh—Rh]—$(N^5—N^1)$—[Rh—Rh]—$(N^1--$. Lack of binding by N(3) is attributed to steric crowding induced by the carboxylate oxygens, and suggests why $[Rh_2(O_2CMe)_4]$ does not react with polycytidlic acid bases, where the N(3) ring nitrogen is flanked by bulky carbonyl and amino groups; it also led Aoki to suggest that $[Rh_2(O_2CMe)_4]$ could develop into a useful probe for estimating the adenine (**36d**) containing regions of nuclei acids, as it should bind adenine much more strongly than the other nucleic acid bases. Aoki also reports the preparation of $[Rh_2(O_2CMe)_4(thiamine)(H_2O)]Y$ (**36e**; $Y = NO_3^-$, PF_6^-, BF_4^-, ClO_4^-); the electronic spectrum of this cation suggests the thiamine is N bonded to the Rh, with N(1) favored over N(3) for the same steric reason.[304]

Use of fluorinated carboxylates as bridges between Rh^{II} centers began with a report from Drago's group of the ESR spectrum of the 1:1 adduct of $[Rh_2(O_2CCF_3)_4]$ and 2,2,6,6-tetramethylpiperidine *N*-oxide (Tempol; **37a**).[327] Not surprisingly, the electron-withdrawing bridges enhance the Lewis acidity of the Rh centers. Numerous perfluorinated carboxylate dimers have been structurally characterized (Table 17), and while the variation in Rh—Rh bond lengths is a bit longer than that observed for the unfluorinated carboxylates, the total range is still small (0.086 Å). The increased acidity of the Rh centers is evident, as such weak bases as dimethyl sulfone (the first example of a structurally confined sulfone complex)[328] and nitroxide radicals (**37b**)[330,332] form structurally characterized adducts. Unless the axial ligands are similar, it is inappropriate to compare the structures of fluorinated and unfluorinated carboxylate-bridged complexes, but for the H_2O and alcohol adducts, the complexes with the electron-withdrawing bridges have marginally longer Rh—Rh, and shorter Rh—O_{ax} bonds.



(**37a**) Tempo, R = H
Tempol, R = OH



(**37b**) t-butyl nitroxide

The electron-withdrawing fluorides also seem to harden the Rh centers. For the soft phosphine and phosphate adducts, fluorinated bridges have the opposite effect on the Rh—L_{ax} bond lengths, as the Rh—P bonds are longer with the fluorinated bridges than with the electron-donating hydrocarbon substituents. More dramatic evidence of the effect of the electronegative bridges comes from studies of the potentially ambidentate DMSO adducts. Numerous DMSO adducts of unfluorinated tetracarboxylates have been reported[290,291,293,305,313,314,334–337] and the electronic and IR spectra of these orange complexes suggest sulfur coordination. In contrast, the DMSO adduct of $[Rh_2(O_2CCF_3)_4]$ is blue. Structural studies of $[Rh_2(O_2CR)_4(DMSO)_2]$ (R = Me, Et, CF_3) have confirmed the ambidentate nature of DMSO, as it is S-bonded in the unfluorinated complexes,[305,313] but is O-bonded when R = CF_3.[313] An interesting 'structural isotope effect' is observed in the

Table 17 Bond Lengths (Å) for Perfluorinated Complexes of the Form $[Rh_2(O_2CR)_4L_2]$[a]

L	*Rh—Rh*	*Rh—L*	*Comments*	*Ref.*
Me_2SO_2	2.400(1)	2.287(3)	Oxygen-coordinated sulfone	328
EtOH	2.403(6)	2.27(1)	—	329
Tempol[b]	2.405(1)	2.240(3)	4-OH coordination of Tempol	330
$(CD_3)_2SO$	2.408(1)	2.248(3)	O coordination of d^6-DMSO	331
H_2O	2.409(1)	2.243(2)	Two *t*-butyl nitroxides in lattice	330
Tempo[b]	2.417(1)	2.220(2)	Oxy coordination of Tempo	332
Me_2SO	2.420(1)	2.240(3)	O coordination of DMSO	313, 331
Tempo[b,c]	2.424(1)	2.238(5)	Oxy coordination of Tempo	332
$P(OPh)_3$	2.470(1)	2.422(2)	—	333
PPh_3	2.486(1)	2.494(1)	—	333

[a] Unless otherwise stated, R = CF_3. [b] See (**37**) for radical structures. [c] R = C_3F_7.

structures of $[Rh_2(O_2CCF_3)_4(L)_2]$ (L = Me_2SO or $(CD_3)_2SO$), as these complexes crystallize in different space groups, and the deuterated adduct has a surprisingly shorter Rh—Rh bond (0.012 Å). Such large packing modifications upon substitution of D for H are unusual, and may reflect the effect of the smaller size of the CD_3 group.[331]

Other sulfur-bonding adducts of the Rh_2^{4+} core have been reported for thiols,[338] thioethers,[305,335] alkyl sulfides,[291,293,336] thiourea derivatives,[339–341] and benzothiadiazole.[342] Reaction of NCX^- (X = S, Se) with $[Rh_2(O_2CMe)_4]$ is reported to lead to the anionic 1:1 adduct $[Rh_2(O_2CMe)_4(NCX)]^-$.[343] A structure has not been reported, but based on analytical data, one-dimensional chains with bridging NCX^- anions were proposed.[343]

The nitroxyl radical adducts (Table 17) are dramatic evidence of the increased acidity of Rh centers when encased by the fluorinated bridges. Hendrickson did variable temperature magnetic studies on $[Rh_2(O_2CR)_4(Tempo)_2]$ (R = CF_3, Pr, Ph) and $[Rh_2(O_2CCF_3)_4(Tempol)_2]$.[332] For the Tempo biradicals, an 'astonishingly large antiferromagnetic exchange interaction' between the biradical centers was observed. At 342 K, the magnetic moment is 1.06 BM, but by 80 K the complexes are essentialy diamagnetic; the fact that the biradical centers are *ca.* 6.8 Å apart makes this exchange all the more unusual. (The *J* values are 2–3 orders of magnitude greater than those observed for the tetrafluorocarboxylate dimer of molybdenum.) The significance of this biradical coupling to our understanding of the bonding in Rh^{II} dimers is discussed in Section 48.5.2.2.

Dirhodiumtetracarboxylates with N-donor adducts have been reported for numerous monodentate and bidentate bases, varying in complexity from ammonia through nucleic acids and adenine nucleosides and nucleotides; Table 18 lists references for studies on such N-donating adducts. The structures of a variety of these complexes have been determined (*vide supra*), and while the range of Rh—Rh bond distances is greatest for N-donating bases, the range is still only 0.067 Å.[282] Straightforward correlations between the Rh—Rh bond length and a specific property of the axial ligands have not yet appeared.

Carbon-bonded adducts include cyanide ions[356] and isocyanides.[357] The structure of $[Rh_2(O_2CMe)_4(MeNC)_2]$ is reported to confirm the formation of an axial Rh—C bond.[299] Interest in the CO adduct has been sparked by the question of whether σ or π bonding is involved in the Rh—L_{ax} bond. A structural study shows that in $[Rh_2(O_2CMe)_4(CO)_2]$ the CO is linearly bonded through the carbon atom, and that the C—O bond is 0.03 Å *longer* than in free carbon monoxide.[352] This is difficult to understand, as several groups have reported that a small (between 39 and 60 cm^{-1}) *decrease* in the $\nu_{C\ O}$ stretching frequency occurs upon coordination to the Rh_2^{4+} moiety.[335,352,358,359] The different experimental conditions used in the spectroscopic studies may account for the different C—O stretching frequencies, but it is difficult to rationalize the apparent contradiction in the IR and structural information.

Bridging by carbonate, sulfate and dihydrogenphosphate (O_2CR, for R = O^{2-}, SO_2^{2-} or $P(OH)_2^-$) have also been observed in dirhodium(II) complexes. The first report of a carbonate-bridged species came from Chernyaev's group,[360] and Wilson and Taube later prepared $[Rh(CO_3)_4]^{4-}$ by the reaction of aqueous carbonate with the unbridged dimer $[Rh_2(H_2O)_{10}]^{4+}$ (abbreviated as $Rh_{2(aq)}^{4+}$).[289] The similarity in the electrochemical properties of the carbonate and the acetate complexes led Taube to propose a carbonate-bridged dimeric structure, which was confirmed by structural studies on the diaqua and dichloro adducts (Table 16).[315] Bicarbonate-bridged complexes (R = OH^-) have been reported,[289,361] but have not been confirmed by structural studies. Taube also noted that the mobility of $Rh_{2(aq)}^{4+}$ on a cation-exchange column was markedly increased when sulfuric acid was used

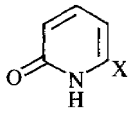
Table 18 Studies Dealing with N-coordinated Adducts of $[Rh_2(O_2CR)_4]$

Type of compound	*Refs.*	*Type of compound*	*Refs.*
NH_3 or N_2H_4	290, 291, 336 340, 341	Aromatic amines	312, 351, 340
		Nitriles	291, 299, 308,
Aliphatic/cyclic amines	290, 291, 303, 335, 336, 345		334, 335
		Nitric oxide	291, 352
Pyridine	281, 290, 291, 301,	Peptides	438
	334–336, 340,	Guanidine	344, 353
	344–347	Imidazole	354, 438
		Nitro	344
		Caffeine	298
Other heterocyclic amines	291, 308, 312, 335,	Amino acids	354, 355
	341, 345,	Adenosine derivatives	350
	347–351, 438		

as the eluant;[364] elution of $Rh_{2(aq)}^{4+}$ with $(NH_4)_2SO_4$ led to the isolation of the presumably sulfato-bridged $(NH_4)_4[Rh_2(SO_4)_4]\cdot 4.5H_2O$. The diaqua adduct $[Rh_2(SO_4)_4(H_2O)_2]^{4-}$, isolated as the Cs^+ salt, can also be prepared by heating $[Rh_2(O_2CR)_4]$ (R = H or Me) in sulfuric acid.[363] A variety of $H_2PO_4^-$-bridged species have been reported,[319,364,365] and structural studies on $[Rh_2(H_2PO_4)_4(H_2O)_2]$ confirm the standard dioxo-bridged Rh core, but with an unusually long Rh—Rh bond.[317]

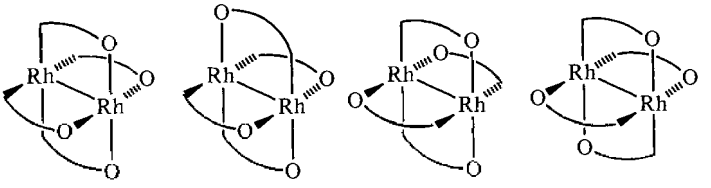
(*ii*) *Asymmetrically bridged dimers*

The dimers discussed so far have been bridged by four identical oxo ligands, with D_{4h} symmetry of the primary coordination sphere. Following work with Cr and W, a new class of Rh^{II} dimers with substituted 2-oxypyridine bridges (**38**) has been developed. These oxypyridines are prototypes for the bridging ligands with two different coordinating sites, considered in this section. This ligand asymmetry introduces the possibility of geometric isomerization in the tetrabridged dimer; as shown in (**39**), the four possible isomers can be labelled the 4,0 (C_{4v}), 3,1 (C_s), 2,2-*trans* (D_{2d}), and 2,2-*cis* (C_s) isomers. Examples of all four of these forms have now been characterized.



(**38**)

mhp = 6-methyl-2-oxypyridine, X = Me
chp = 6-chloro-2-oxypyridine, X = Cl
fhp = 6-fluoro-2-oxypyridine, X = F



4,0 3,1 2,2-*trans* 2,2-*cis*

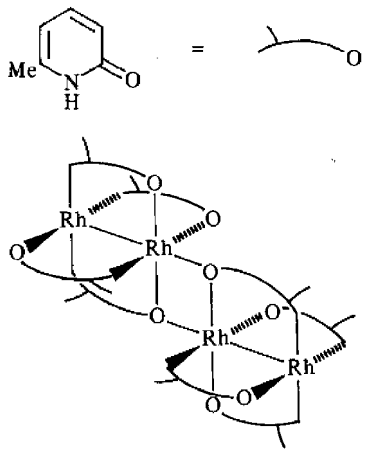
(**39**)

Synthesis of oxypyridine-bridged dimers can be achieved by the direct reaction of $RhCl_3\cdot 3H_2O$ with the appropriate ligand in a mildly reducing solvent, as in equation (93), or by bridge exchange (equation 94), with the ubiquitous $[Rh_2(O_2CMe)_4]$ as the common starting material. Data from structural studies on a variety of asymmetrically-bridged dimers are presented in Table 19. Initial studies of $[Rh_2(Q)_4]$ (Q = mhp or chp) showed that as with the Cr adducts steric crowding of the pyridine methyl groups hinders coordination at the axial sites, and the complex adopts the 2,2-*trans* geometry.[366,367] The 1:1 adducts of imidazole, acetonitrile and Hmhp with $[Rh_2(mhp)_4]$, and the imidazole adduct of $[Rh_2(chp)_4]$ have been structurally characterized, and all adopt the 3,1 geometry.[368,369] With three methyl groups around one end of the molecule, the Lewis base is able to bond at the less-crowded end. Synthesis of $[Rh_2(mhp)_4(Hmhp)]$, by reaction of $[Rh_2(O_2CMe)_4(MeOH)_2]$ with Na(Hmhp), also generates a tetrameric complex, $[Rh_2(mhp)_4]_2\cdot 2CH_2Cl_2$. This tetramer consists of two $[Rh_2(mhp)_4]$ units, each in a 3,1 geometry, with the open ends joined by two Rh—O bonds between the Rh (at the open end of each dimer), and an oxygen from one of the bridging oxypyridines.[369] This structure is represented in (**40**). The 12.65 MHz ^{103}Rh NMR spectrum (in CD_2Cl_2/CH_2Cl_2 at ~300 K) had a single resonance at 5745 p.p.m. for $[Rh_2(mhp)_4]$, while the tetramer had a pair of doublets (split by 35 Hz) centered at 7644 and 4322 p.p.m., consistent with the presence of two sets of inequivalent Rh atoms.[373]

Table 19 Bond Lengths (Å) of Some Rh^{II} Dimers with Four Identical, Asymmetric Bridges

Complex	*Rh—Rh*	*Rh—L*	*Comments*	*Ref.*
$[Rh_2(mhp)_4]$	2.359(1)	—	2,2-*trans* geometry	366, 367
$[Rh_2(mhp)_4]\cdot H_2O$	2.365(1)	—	2,2-*trans* geometry	368
$[Rh_2(mhp)_4]_2\cdot 2CH_2Cl_2$	2.369(1)	2.236(3)	mhp bridges 2 Rh_2 groups	369
$[Rh_2(mhp)_4(MeCN)]$	2.372(1)	2.152(7)	3,1 geometry	368
$[Rh_2(mhp)_4(Hmhp)]\cdot 0.5C_7H_8$	2.383(1)	2.195(4)	3,1 geometry	369
$[Rh_2(mhp)_4(imidazole)]\cdot 0.5MeCN$	2.384(1)	2.144(4)	3,1 geometry	368
$[Rh_2(OSCMe)_4(MeC(S)OH)_2]$	2.550(3)	2.521(5)	—	370
$[Rh_2(chp)_4]$	2.379(1)	—	2,2-*trans* geometry	368
$[Rh_2(chp)_4(imidazole)]\cdot 3H_2O$	2.385(1)	2.129(9)	3,1 geometry	368
$[Rh_2(fhp)_4(Me_2SO)]$	2.410(1)	2.332(3)	4-0 geometry, S-bonded DMSO	371
$[Rh_2(TFA)_4(py)_2]^a$	2.472	2.29	2,2-*cis* geometry	369

[a] TFA = conjugates base of trifluoroacetamide = $CF_3C(O)NH^-$.



(40)

The complexity of the tetramer's structure convincingly demonstrates the power of single crystal X-ray studies as a primary analytical tool. Perhaps an even more dramatic recommendation comes from the three imidazole adducts listed in Table 19, as imidazole was not a reagent used in their syntheses. The dimers were all prepared from a solid melt of $[Rh_2(O_2CMe)_4]$ + Hmhp (or Hchp) under argon, and the resulting solids were recrystallized from various solvents. The imidazole was identified by assigning atomic scattering parameters for either N or C to the different atoms in the ring; the only configuration with reasonable thermal ellipsoids was that of imidazole. The authors do not speculate (in print) about the source of the imidazole, and invite rational suggestions as to its origin.[368]

The 4,0 geometry is observed for $[Rh_2(fhp)_4(DMSO)]$ (**38**; X = F).[371] As observed with the Cr, Mo and W analogs,[374] the four fluorine atoms form a square around one end of the Rh_2 core, with a short F—F distance of 2.925 Å. The DMSO is S-bonded, with an unusually short Rh—S bond (2.332 Å *vs.* 2.449 Å for $[Rh_2(O_2C)_4(DMSO)_2]$).

Bear and co-workers have recently presented several reports on the chemistry of $[Rh_2(tfaa)_4]$, where tfaa is $CF_3C(O)NH^-$, the conjugate base of trifluoroacetamide.[372,375,376] The tfaa bridge can be considered to be a trifluoroacetate with a coordinated oxygen replaced by an isoelectric NH group, and represents the first N—O bidentate bridges of Rh_2 not based on the oxypyridine system. Similar to the carboxylate-bridged dimers in gross structure and adduct formation the tfaa dimers display some distinctive properties. Reaction of $[Rh_2(mhp)_4]$ with Htfaa leads to a mixture of products, separable into four bands by HPLC. The approximate distribution of Rh in the four bands as 4%, 94%, 2% and < 1%; NMR analysis of the first 4% band suggests the 3,1 isomer of $[Rh_2(tfaa)_4]$. Structural studies of the bis(pyridine) adduct of the second band showed it had the 2,2-*cis* geometry with a relatively long Rh—Rh bond.[372] (This structural study was marred by an unidentified 'mysterious' diatomic molecule, which occupied ~ 15% of the axial sites.) An analogous bridge-exchange of $[Rh_2(O_2CMe)_4]$ with *N*-phenylacetamide (MeCONHPh), also leads to four HPLC separable products. NMR analysis suggests that the four products correspond to the four geometric isomers (**39**) of $[Rh_2(PhNOCMe)_4]$, with the predominant product being the 3,1 isomer.[376] Much of the work with $[Rh_2(tfaa)_4]$ and its adducts centers on its interesting electrochemical properties, which are discussed in Section 48.5.2.3.(ii).

Bridge exchanges between $[Rh_2(O_2CMe)_4]$ and 2,4-dithiouracil (dtu)[377] or thiobenzoic acid (tbz)[378] generate the diamagnetic complexes $[Rh_2(Q)_4(L)_2]$ (L = H_2O for Q = ttu; L = py, thiourea, DMSO or DMF when Q = tbz). IR analysis indicates that a dtu nitrogen is deprotonated upon coordination, and that the dtu exhibits N and S bonding to the Rh_2 core, although a specific geometry is not suggested. Reaction of $RhCl_3 \cdot 3H_2O$ with 5,5′-thiodisalicylic acid in acid (pH 1) solution is reported to give an ill-characterized, paramagnetic (μ = 2.60 BM) brown complex of stoichiometry $[Rh(C_{14}H_8O_6S) \cdot 4H_2O]$.[379]

(*iii*) *Mixed-bridge dimers*

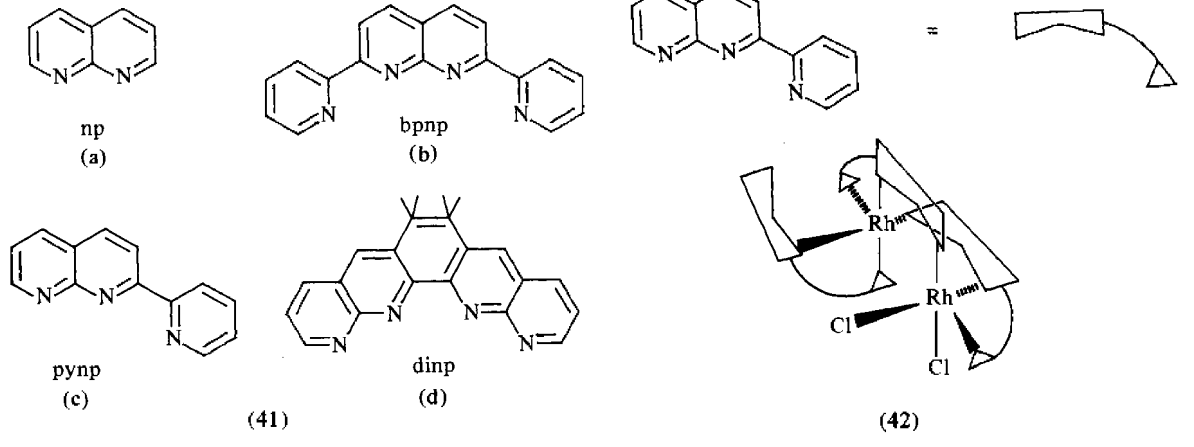
Recently, Rh^{II} dimers with more than one type of bridging ligand in the same complex have been characterized; these will be considered along with a few complexes with less than four bridging

ligands. Reaction of the Rh^{I} dimer $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$ (DPM = bis(diphenylarsino)methane = $Ph_2AsCH_2AsPh_2$) with HA ($A^- = Cl^-$, SO_3Ph^-, Me^-, BF_4^-) does not cause the expected oxidative addition, but leads to $[Rh_2Cl_2(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2(A)]$.[380] The single crystal X-ray structure of the HCl adduct, $[Rh_2Cl_3(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2]$ shows it to have two mutually *trans* bridging DPM ligands; the mutually *trans* H and the CO also serve as bridges, and the IR bands (ν_{CO} between 1748 and 1818 cm^{-1} and ν_{Rh-H} between 1230 and 1267 cm^{-1}) suggest that all of these complexes have structures similar to the trichloro complex. The Rh—Rh distance (2.7464 Å) is long, but still within the bonding range. This complex is unique among Rh^{II} dimers in several ways, as it has three different bridging ligands, and has three axial ligands (Cl^-), two at one end and the third at the other end of the dimer.[380] Oxidative addition across the Rh^{I}—Rh^{I} core (a transannular oxidative addition) does occur when I_2 reacts with $[Rh^{I}_2(CO)_2Cl_2(DPM)_2]$, generating the (DPM)-bridged Rh^{II} dimer, $[Rh(CO)_2Cl_2I_2(DPM)_2]$.[381] Similar reactions have led to the diamagnetic dimers, $[Rh_2(CNR)_4(X_2)(DPM)_2]$ (X = I, Br),[382] and $[Rh_2(CNR)_4(Ph_2AsCH_2AsPh_2)I_2]$, and $[Rh(CNR)_4(DPM)_2(SCF_3)_2]$.[383]

Mixed-bridge complexes based on a bridging carboxylate frame have been obtained from the products of the bridge exchange between $[Rh_2(O_2CMe)_4]$ and Hmhp.[368] Five different complexes apparently crystallized from this single brew (*vide supra*), and two of them were $[Rh_2(O_2CMe)_2(mhp)_2(im)]$ and $[Rh_2(O_2CMe)_2(mhp)_2(im)]\cdot 2CH_2Cl_2$. Both complexes exhibit mutually *trans* acetates and oxypyridines, with both pyridine-methyl groups pointing toward the same end of the dimer; the imidazole is coordinated to the other, more open, end. As with the $[Rh_2(mhp)_4(im)]$ (*vide supra*) the source of the imidazole is unknown.[368] All five members of the series $[Rh_2(O_2CMe)_n(NH(O)CMe)_{4-n}]$ ($n = 0, 1, 2, 3, 4$) have been prepared *via* bridge exchange between $[Rh_2(O_2CMe)_4]$ and $MeC(O)NH^-$.[384] The five complexes were separated by HPLC, but the exact geometric structure of the substituted species was not determined.

In their studies of $[Rh_2(O_2CR)_4]$ with bulky R groups, Cotton and Thompson noted that the bridge exchange between $[Rh_2(O_2CMe)_4]$ and $Ph_3CCO_2^-$ generates $[Rh_2(O_2CMe)_2(O_2CCPh_3)_2(MeCN)_2]$.[308] Other bulky substituents (R = 2-PhC_6H_4 or 1-adamantane) replaced all four acetate bridges, and it is not clear why the reaction with triphenylcarboxylate stops after the replacement of only two acetates. (Kinetic studies of acetate replacement by trifluoroacetate in $[Rh_2(O_2CMe)_4]$ indicate that the reaction slows markedly after replacement of two acetate bridges,[385] so a kinetic factor may be involved.) Steric crowding cannot be important, as $[Rh_2(O_2CMe)_2(O_2CCPh_3)_2(MeCN)_2]$ has the *cis* configuration, and there is adequate room for two additional triphenylcarboxylate bridges. Cotton points to a stacking of the phenyl groups from adjacent bridges as a possible contribution to the stability of the *cis* geometry.[308]

A new series of mixed-bridge dimers, recently characterized by Ford and his group, are based on a 1,8-naphthyridine frame (**41**).[386–388] Upon mixing the crescent-shaped bpnp with $[Rh_2(O_2CMe)_4]$ (in acidic methanol under argon in the presence of NH_4PF_6), substitution of one acetate bridge occurs, and the 'croissant complex' $[Rh_2(O_2CMe)_3(bpnp)]PF_6$ can be isolated. A single-crystal X-ray study (Table 20) reveals that the bpnp acts as a bridge, through the 1,8-naphthyridine nitrogens, allowing the pendant pyridines to bond to the axial sites at either end of the Rh_2 core. Other complexes in this series include $[Rh_2(O_2CMe)_3(L)]^+$ (L = dinp or pynp), $[Rh_2(np)_4]Cl_4$, $[Rh_2(O_2CMe)_2(pynp)_2]^{2+}$,[387] and $[Rh_2(pym)_3Cl_2](PF_6)_2$.[384] NMR analysis of $[Rh_2(O_2CMe)_2(pynp)_2]^{2+}$ indicates that the acetates and the pynp bridges have a mutually *cis* geometry.[387] A single-crystal X-ray study of $[Rh_2(pynp)_3Cl_2](PF_6)_2$ revealed its unusual geometry, represented in



(41) (42)

Table 20 Bond Lengths (Å) of some Miscellaneous Rh^{II} Dimers

Complex	*Rh—Rh*	*Rh—L*	*Comments*	*Ref.*
Mixed bridges				
$[Rh_2(mhp)_2(O_2CMe)_2(im)]$	2.388(2)	2.17(1)	*Trans* configuration	368
$[Rh_2(mhp)_2(O_2CMe)_2(im)]\cdot 2CH_2Cl_2$	2.388(1)	2.133(7)	*Trans* configuration	368
$[Rh_2(O_2CCPh_3)_2(O_2CMe)_2(MeCN)_2]$	2.388(2)	2.19(1)	*Cis* configuration, with a toluene of crystallization	308
$[Rh_2(O_2CMe)_3(bpnp)]$	2.405(2)	2.196(16)	Axial nitrogens from bpnp bridge	386, 387
$[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(DPM)_2Cl_3]$	2.7464(7)	2.358(2) 2.393(2) 2.462(2)	*Trans* phosphines, with three terminal chlorides	380
Two bridges				
$[Rh_2(pymp)_2Cl_2](PF_6)_2\cdot MeCN$	2.5668(7)	2.175(15)	Axial nitrogens from pymp bridges	388
$[Rh_2(phen)_2(O_2CH)_2Cl_2]$	2.576	2.506	—	385
$[Rh(DMG)_2(O_2CMe)_2(PPh_3)]\cdot H_2O$	2.618(5)	2.485(9)	Eclipsed DMG groups	390
No bridging ligands				
$[Rh_2(C_{22}H_{22}N_4)_2]\cdot 3C_6H_6$[a]	2.625(2)	—	—	391
$[Rh_2(p\text{-}MeC_6H_4NC)_8I_2](PF_6)_2$	2.785(2)	2.735(1)	—	392
$[Rh_2(DMG)_4(PPh_3)_2]\cdot PrOH\cdot H_2O$	2.936(2)	2.438(4)	—	393
Nitrile bridges				
$[Rh_2\{CN(CH_2)_3NC\}_4Cl_2]\cdot 8H_2O$	2.837(1)	2.447(1)	Long Rh—Rh bond	394
An oxidized complex (Rh_2^{5+})				
$[Rh_2(O_2CMe)_4(H_2O)_2]ClO_4$	2.317	2.22	Oxidation decreases both Rh—Rh and Rh—OH_2 distances	395, 396

[a] $C_{22}H_{22}N_4$ = 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinate (a macrocyclic dianion); im = imidazole; mhp = 2-oxy-6-methylpyridine; DPM = bis(diphenylphosphino)methane; bpnp = 2,7-bis(2-pyridyl)-1,8-naphthyridine (**41b**); pymp = 2-(2-pyridyl)-1,8-naphthyridine (**41c**).

(**42**), as it has only two bridging ligands. The pyridines pendant to the pynp bridges act as the axial donors, while the other pynp acts as a non-bridging bidentate ligand; the two chlorides bond in equatorial positions to the other Rh atom.[388] The two naphthyridine-bridged complexes characterized to date have longer Rh—Rh bonds than observed for the purely acetate-bridged complexes, but the length is still within the range of a Rh—Rh single bond.

Two other complexes with only two bridging ligands have been characterized by X-ray studies. $[Rh_2(O_2CH)_2(phen)_2]Cl_2$ is a 1:2 electrolyte in aqueous solution, suggesting that the chlorides are not axially bonded, or that they are readily labilized in aqueous solution.[389] This bis(bridge) complex has a Rh—Rh bond (2.576 Å) which is *ca.* 0.2 Å longer than that observed for the tetracarboxylate-bridged dimers, but is comparable to the 2.618 Å observed for the other bis(bridge) complex, $[Rh_2(O_2CMe)_2(DMG)_2(PPh_3)_2]$.[390]

While its structure has not been determined, the first well-characterized bis(bridge) complex was characterized by Ugo and co-workers, who noted that the reaction of $[Rh_2(O_2CMe)_4(H_2O)_2]$ with acac, trifluoroacetylacetone, or hfacac (Q) gives complexes of the form $[Rh_2(O_2CMe)_2(Q)_2]\,(H_2O)_2$. Adducts with py, 2-methylpyridine and 2-chloropyridine were characterized, and analysis of electronic and IR spectra, and the ^1H and ^{31}P NMR led Ugo to propose bridging acetates, with the acacs each chelated to a single metal.[397] Mixed acetate/salicylate,[398] acetate/phosphate[399] and formate/bipy[400] complexes have also been reported, but the nature of the bridging has not been determined.

(*iv*) *Dimers without bridging ligands*

Several claims could be supported for the first preparation of a Rh^{II} dimer with only the Rh—Rh bond to hold the dimer together. In 1961 Martin and co-workers reported that sodium amalgam reduction of $[Rh(bipy)_2Cl_2]X$ ($X = NO_3^-$, ClO_4^-) leads to red-violet solids with the stoichiometry $[Rh(bipy)_2Cl(X)]_2\cdot 4H_2O$ ($X = NO_3^-$, ClO_4^-).[401] They are diamagnetic, and were presumed to be chloro-bridged dimers; the preponderance of Rh^{II}—Rh^{II} bonds discovered since 1961, and the lack of halogen-bridged dimers, suggests that this work should be reinvestigated. In 1967, Shchepinov and co-workers used BH_4^- to reduce $[Rh(DMG)_2Cl_2]^+$ in the presence of PPh_3, generating $[Rh_2(DMG)_4(PPh_3)_2]$, a diamagnetic, air-stable solid.[402] Shchepinov's suggestion that $[Rh_2(DMG)_4(PPh_3)_2]$ contained a Rh—Rh bond was confirmed in a structural study, which found a long (2.936 Å) Rh—Rh bond, the longest Rh^{II}—Rh^{II} bond yet determined.[393] The nearly planar bidentate DMG ligands are staggered on the two Rh atoms, and are bent towards each other and away from the axial PPh_3 ligands; steric repulsions between the DMG ligands are thought to be responsible for the long Rh—Rh bond.[393] Keller and Seibold prepared $[Rh_2(DMG)_4]$ by reacting

HDMG with $[Rh_2(O_2CMe)_4]$, an interesting bridge → no bridge conversion.[403] Complexes with DMG derivatives, and the py and THF adducts, were prepared by this same route.[404] An X-ray photoelectron study of several DMG-containing Rh^{II} and Rh^{III} complexes has been reported.[405]

Soon after the preparation of $[Rh_2(DMG)_4(PPh_3)_2]$, Maspero and Taube reported that $Cr^{2+}_{(aq)}$ reduces $[Rh(H_2O)_5Cl]^{2+}$ to give a species with cation exchange behavior which implied a charge greater than 3+ (equation 95).[362] This complex was formulated as the $[Rh_2(H_2O)_{10}]^{4+}$ dimer [λ_{max} at 630 (ε39.8), 412 (59.1) and 250 nm (10 600)]. Attempts to isolate a solid with a variety of anions (PF_6^-, BF_4^-, BPh_4^-, $B_{10}H_{10}^{2-}$, $B_{12}Cl_{12}^{2-}$ and $[Fe(CN)_6]^{4-}$) failed, and halide-catalyzed disproportionation to Rh^{I} and Rh^{III} also interfered. A solid salt of this important cation has not yet been reported. The complex is reported to be 'slightly paramagnetic', which led Taube to suggest that the dimers are in equilibrium with the paramagnetic monomer.[362] Ziolkowski later suggested that the paramagnetism may result if the HOMOs are two degenerate π^* orbitals populated by two unpaired electrons,[406] and a study of the magnetic susceptibility of a variety of tetraacetate-bridged dimers also showed that a small temperature independent paramagnetism (μ_{eff} near 0.5 BM) was a common feature of these Rh^{II} dimers.[407]

$$2[Rh(H_2O)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow [Cr(H_2O)_5Cl]^{2+} + [Rh_2(H_2O)_{10}]^{4+} \quad (95)$$

Reduction of [Rh(OEP)Cl] (OEP = octaethylporphyrin) with $H_{2(g)}$ leads to the Rh^{III} hydride [Rh(OEP)H], which, when heated in benzene or oxidized with O_2, forms the brown diamagnetic $[Rh_2(OEP)_2]$ (equation 96).[408,409] The OEP ligand is a rigidly planar cyclic dianion, so ligand bridging is impossible. The dimer undergoes a variety of reactions with substituted hydrocarbons, leading to complexes with Rh^{III}—C bonds (Section 48.5.2.3.iii).

$$2[Rh(OEP)Cl] + H_2 \longrightarrow 2[Rh(OEP)(H)] \begin{cases} \xrightarrow{\frac{1}{2}O_2} [Rh_2(OEP)_2] + H_2O \\ \xrightarrow{\Delta,\ C_6H_6} [Rh_2(OEP)_2] + H_2 \end{cases} \quad (96)$$

During studies on a series of Rh^{I} isonitriles, Olmstead and Balch found that a series of dimeric Rh^{II}–isonitrile complexes could be generated by the reaction of appropriate Rh^{I} and Rh^{III} complexes (equation 97).[410] This reaction was found to be quite general (for X = I, R = Me, Bu^n, Ph, C_6H_{11}; and R = C_6H_{11} for X = Cl), but not universal, as no reaction is observed if R = Bu^t and X = Br or I. A halogen-bridged dimer would require little atomic motion, but IR analysis supports a Rh—Rh bond, with axial halides.[410] Support for this proposed structure came when it was shown that analogous compounds can be prepared by the transannular oxidative addition of monomeric $[Rh(p\text{-}MeC_6H_4NC)_4]PF_6$,[392] or dimeric $[Rh_2(bridge)_4]^{2+}$ (bridge = 1,3-diisocyanopropane).[411] Irradiation of $[Rh_2(bridge)_4]^{2+}$ in conc. HCl causes H_2 formation and the generation of a similar dimer $[Rh_2(bridge)_4Cl_2]^{2+}$.[394] A single-crystal X-ray structure confirmed the traditional Rh—Rh bonded structure, with short non-bonded interactions between eclipsed C—N groups on adjacent Rh atoms contributing to the length of the Rh—Rh bond (2.837 Å).[394] Another (presumably bridged dimer) has been prepared by the two-electron electrochemical oxidation of $[Rh_2(dimen)_4]^{2+}$ (dimen = 1,8-diisocyanomenthane). In the presence of axially coordinated Cl^-, oxidation occurs at low potentials, and in the presence of PF_6^- (in MeCN or CH_2Cl_2) a yellow salt, identified as $[Rh_2(dimen)_2Cl_2](PF_6)_2$, has been isolated.[412]

$$[Rh(RNC)_4]^+ + [Rh(RNC)_4X_2]^+ \rightleftharpoons [Rh_2(RNC)_8X_2]^{2+} \quad (97)$$

While studying Schiff base complexes of Rh^{III} (see Section 48.6.4.1 for a discussion of structures), West and co-workers reported that if $RhCl_3 \cdot 3H_2O$ or $[Rhpy_4Cl_2]Cl$ (in pyridine) is mixed with methanol solutions of *N,N'*-ethylenebis(salicylideneiminate) (H_2salen) and a reducing agent (Zn dust), a diamagnetic, pale yellow solid, formulated as [Rh(salen)py], forms.[413] This complex remains ill characterized, and while it displays an uncharacteristic chemical inertness, West suggested that it may be an unbridged Rh^{II} dimer, analogous to the bis(DMG) complexes.[413] Reaction of equimolar mixtures of $[Rh(CO)_2Cl_2]_2$, salenH_2 and a base (Et_3N or $NaHCO_3$) in refluxing methanol leads to a weakly paramagnetic (μ_{eff} = 0.90 BM) material formulated as Rh(salen).[414] The corresponding Schiff bases with 1,2-propylene (salpn) and *o*-phenylene (saloph) chains between the two salicylideneiminato groups also form 1:1 complexes with Rh, but both $[Rh(salpn)]_2$ and $[Rh(saloph)]_2$ are diamagnetic, suggesting that they are undissociated dimers, while $[Rh(salen)]_2$ is in equilibrium with its monomeric form. All three react with O_2 in air to give paramagnetic oxygen adducts (*e.g.* $[Rh(salen)O_2]$), formulated as hyperoxo Rh^{III} species.[414]

The O_2 oxidation of $[Rh(CO)_2Cl_2]_2$ in dimethylacetamide ($Me_2NC(O)Me$ = DMA) in the

presence of LiCl and Ph_4As^+ leads to a solid identified as $(Ph_4As)_2[Rh_2Cl_6(DMA)_2]$.[415] The solid has a low magnetic moment ($\mu = 0.95$ BM), and is a 2:1 electrolyte in DMA, although in $CHCl_3$ its molecular weight is *ca.* 23% lower than expected. Further oxidation leads to $[Rh_2Cl_9]^{3-}$, a characterized anion in which two pyramidally distorted $RhCl_6$ octahedra share an octahedral face (Section 48.6.7). This led to the proposal that the two Rh atoms in $[Rh_2Cl_6(DMA)_2]^{2-}$ are bridged by a pair of chloride atoms (two $[RhCl_4(DMA)]$ square pyramids sharing a basal edge).[415] If true, this is a unique Rh^{II} dimer; an alternate structure with a Rh—Rh bond is not difficult to imagine.

48.5.2.2 Bonding and electronic structure in Rh^{II} dimers

Two related features of Rh_2^{4+} dimers of obvious interest are the metal—metal bond, and the range of colors displayed by various adducts. The colors range from blue to green for oxygen donors, red to orange for nitrogen and sulfur donors, and red to yellow for phosphorus donors. The spectra generally consist of two relatively weak (ε 200–300) transitions centered near 600 nm (Band I) and 450 nm (Band II). The position of Band I is very dependent on the number and nature of axially bound ligands, while Band II is virtually invariant to the presence or absence of numerous ligands. Two intense bands (Band III near 250 nm and Band IV near 220 nm with $\varepsilon > 10\,000$) occur in the UV. These two bands undergo a ligand-dependent red shift as the axial ligands become more tightly bonded. Structural studies have shown that the Rh—Rh bond length varies by more than 0.5 Å, from 2.371 to 2.936 Å (see Table 17 and 21). To understand the spectra and structural features of these complexes clearly requires an understanding of their electronic structure. Few areas in rhodium chemistry have received such heated discussion, and while a consensus seems to have emerged on the Rh—Rh bond order, questions remain to be resolved.

The original report (in 1962) on the structure of $[Rh_2(O_2CMe)_4(H_2O)_2]$[281] suggested a Rh—Rh single bond; the Rh—Rh bond length (2.45 Å) and the observed diamagnetism could be rationalized with such a formulation. In 1970, Martin used extended Hückel calculations to arrive at an electronic configuration for the Rh_2 core ($14\,e^-$) of $\pi^4, \sigma^2, \delta^2, \delta^{*2}, \pi^{*4}$,[290] supporting the single bond hypothesis. The axial-ligand dependent absorption (Band I, 600 nm) was assigned as a $\pi^* \rightarrow \sigma^*$ (Rh_2^{4+}) transition. Band II, relatively unaffected by axial ligands, was assigned as a $\pi \rightarrow (\delta, \sigma^*)$ or $\pi \rightarrow (\delta^*, \sigma^*)$ transition, again within the Rh_2 core.

Just before Martin's extended Hückel analysis, Cotton and co-workers suggested that the manifold of occupied frontier orbitals included two non-bonding orbitals which were essentially the $5s$ and $5p_z$ orbitals of the Rh atoms (the Rh–Rh axis generally defines the z-axis). This led to a $14\,e^-$ core configuration of $\sigma^2, \pi^4, \delta^2, \sigma_n^2, \sigma_n'^2, \delta^{*2}$, with two empty π^* and an empty σ^* orbitals, and a Rh—Rh triple bond.[393,416,417] This configuration also accounted for the diamagnetism, and was soon supported by a reevaluation of the Rh—Rh bond length in $[Rh_2(O_2CMe)_4(H_2O)_2]$. The new value, 2.3855 Å,[297] was *ca.* 0.065 Å shorter than the earlier reported length,[281] and more than 0.5 Å shorter than the only other Rh—Rh bond length known at the time (2.936 Å in $[Rh_2(DMG)_4(PPh_3)_2]$).[390] An estimate of the Rh^{II} covalent radius (1.40–1.45 Å)[418] set a 'rather firm lower limit of 2.80 Å' for the Rh^{II}—Rh^{II} single bond.[297,393] Any bond which is 15% shorter than the minimum single bond length must be considered a serious candidate for a multiple bond.

The triple bond formulation did not receive theoretical support, however, as in 1978 Norman and Kolari presented their SCF–X^α–SW calculations on $[Rh_2(O_2CH)_4]$ and $[Rh_2(O_2CH)_4(H_2O)_2]$.[419] Their calculations indicate that the non-bonding $5s$ and $5p_z$ Rh-centered orbitals, important in Cotton's analysis, are at high energy and remain unoccupied. Their 14-electron core is $\sigma^2, \pi^4, \delta^2, \pi^{*4}, \delta^{*2}$ with only the σ^* unoccupied; this represents a single, σ bond, as predicted by Martin.[290] The electronic transitions were assigned as: Band I, $\pi^* \rightarrow \sigma^*$ (within the Rh_2 core); Band II, $\pi^* \rightarrow \sigma^*$ (Rh—O_{eq}); Band III, $\sigma \rightarrow \sigma^*$ (Rh_2); and Band IV, $\sigma(L) \rightarrow \sigma^*$, in reasonable agreement with Martin's earlier assignment.[290] Norman notes that the electronic spectra for the unbridged $Rh_{2(aq)}^{4+}$, and the bridged $[Rh_2(CO_3)_4]^{4-}$ and $[Rh(SO_4)_4]^{4-}$ ions are very similar to the spectra of the carboxylate-bridged dimers, and suggests analogous electronic configurations for the ions.[419]

When water molecules are brought in along the Rh–Rh axis, Norman's analysis indicates that there is very little π interaction with the metal, and that the π and δ MOs of the metal–metal bond are virtually unperturbed by the presence of the H_2O. As for σ bonding, within a_{1g} symmetry axial binding by water stabilizes both the Rh—OH_2 σ-bonding and antibonding orbitals so that both are fully occupied, and virtually no net bonding results. In a_{2u} symmetry, the Rh—Rh bond destabilizes the Rh—Rh σ^* orbital, lessening its interaction with the σ orbitals on the water. This nicely accounts for the observations that the metal–axial-ligand bonds are significantly weaker than normal in these Rh_2^{4+} dimers, and that the stronger the metal–metal bond (that is the higher in energy the Rh—Rh

σ^* orbital) the weaker the metal–axial-ligand bond. Thus, there is a mutual interaction, as the presence of axial ligands weakens the Rh—Rh bond, while the Rh—Rh bond weakens the Rh–axial-ligand bond.[419]

This analysis also accounts for the observed changes in the electronic spectra. Axial ligands strongly influence the energy of the Rh—Rh σ^* orbital, so the energy of Band I [$\pi^* \rightarrow \sigma^*$ (Rh_2)] would be expected to be dependent on the number and nature of the axial ligands. Band II ($\sim$450 nm) was assigned to the $\pi^* \rightarrow \sigma^*$ (Rh—O_{eq}), which is virtually unaffected by the presence or absence of axial ligands. The axial-ligand dependency and the greater intensity of Bands III and IV are consistent with their assignment as $\sigma \rightarrow \sigma^*$ transitions. These spectral assignments were supported by a single crystal polarized absorption study.[420]

In 1981, Nakatsuji *et al.* presented the results of an *ab initio* SCF study on [$Rh_2(O_2CH)_4$], various adducts, and the corresponding cations.[421] While their proposed electronic configuration was not exactly the same as that suggested by Norman and Kolari, they did agree that a Rh—Rh single bond of σ symmetry exists in these dimers. Their analysis showed just how sensitive the electronic configuration is to the nature of the axial ligands, for when there are no axial ligands, or when L = H_2O or NH_3, they put the electronic configuration of the 14-electron core (for [$Rh_2(O_2CH)_4(L)_2$] at π^4, δ^2, π^{*4}, δ^{*2}, σ^2); when L = PH_3, the ordering of the two lowest levels in the Rh_2 core reverses with the net result still being a single σ bond. This analysis was extended to the monocation radical dimer,[422] and the calculations are consistent with ionization of an electron from the HOMO σ orbital, leading to a cation with the unpaired electron in an orbital of σ symmetry. This assignment is supported by ESR studies.[423,424]

The differences caused by axial coordination by P, *vs.* bonding by either N or O, was also explored in an SCF–X^α–SW molecular orbital calculation by Bursten and Cotton.[425] These studies are of special interest, as Drago has presented several studies (*vide infra*) which imply the importance of π back bonding in phosphine adduct formation. Neither the X^α calculations of Cotton[425] nor the *ab initio* calculations of Nakatsuji[421,422] supports the existence of any significant amount of π bonding, as the only effective Rh—P bonding is through the Rh d_{z^2} orbital, and is thus of σ symmetry. The ESR spectra on [$Rh_2(O_2CR)_4(PX_3)_2$]$^+$ cations also imply the dominance of Rh—P σ bonds.

Gray and co-workers have recently presented a single-crystal polarized spectral analysis for [$Rh_2(O_2CMe)_4(H_2O)_2$] and for $Li_2[Rh_2(O_2CMe)_4Cl_2]\cdot 8H_2O$, and propose new assignments for the visible absorptions.[300] Both complexes showed similar spectra, with Band I split into two electric-dipole-allowed transitions near 650 (*z*-polarized) and 600 nm (*x,y*-polarized). The 650 band was assigned to a $\delta^*(Rh_2) \rightarrow \sigma^*$(Rh—O) band, while the band at *ca.* 600 nm was assigned as $\pi^*(Rh_2) \rightarrow \sigma^*$(Rh—O). Weak but structured transitions ($\varepsilon \approx$ 10–20) between 800 and 650 nm are assigned to the spin-forbidden components of these δ^*, $\pi^* \rightarrow \sigma^*$(Rh—O) transitions. The assignment of Band I as a $Rh_2 \rightarrow$ Rh—O transition, rather than the previously assigned Rh_2 core transition,[290,419,420] is based on the *x,y*-polarization of the major 600 nm band and the 300 cm^{-1} vibrational spacing, which corresponds to a Rh—O, not a Rh—Rh, stretch. The reasons for the sensitivity of Band I to axial ligands is not as straightforward as in the previous assignment, and is proposed to be due to axial-ligand-induced variations in the energy of the occupied π^* orbital. Band II is assigned to π(Rh—O) $\rightarrow \sigma^*$(Rh—O). Isotropic (solution) spectra were then used to assign the two UV bands to the $\sigma(Rh_2) \rightarrow \sigma^*(Rh_2)$ and σ(Rh—L) $\rightarrow \sigma^*(Rh_2)$.[300]

Use of vibronic spacing for electronic band assignment depends on knowledge of stretching frequencies, and estimates of the Rh—Rh stretching frequency in Rh_2^{II} carboxylates have varied: 155 cm^{-1} for [$Rh_2(O_2CMe)_4$][426], 170 cm^{-1} for [$Rh_2(O_2CMe)_4(MeOH)_2$][427] and between 288 and 351 cm^{-1} for a variety of carboxylates, with 320 cm^{-1} assigned to the Rh—Rh stretch in the diaquatetraacetate dimer.[428] In light of work with Ru_2 tetracarboxylate dimers (with significantly shorter metal–metal bonds)[429] and the value of 184 cm^{-1} for the Rh—Rh stretch in [$Rh_2(mhp)_4$],[430] Gray questions the 288–351 cm^{-1} range proposed by Oldham[428] and suggests that a range of 150–170 cm^{-1} is more resonable.[300] Gray then makes the interesting observation that this is the same region as the Rh—Rh stretch in [$Rh_2(bridge)_4X_2$]$^{2+}$, which has a Rh—Rh bond $\sim$0.4 Å longer than the tetracarboxylate complexes. This represents an unusual, but explicable, breakdown of Badger's rule, which correlates a given bond length with the cube root of its force constant.[431] (It is ironic that in the same manuscript Gray invokes Badger's rule to dispute the 288–351 cm^{-1} assignments of Rh—Rh stretching frequencies.[300])

Electronic transitions in [$Rh_2(O_2CMe)_4L_2$], and in its cation radical, have been qualitatively interpreted in terms of a molecular orbital model which assumes that metal–ligand interactions are larger than intermetallic interactions.[432] The intense near UV bands (Bands III and IV) are assigned to intermetallic $\sigma \rightarrow \sigma^*$ transitions; the bonding model qualitatively accounts for the observed red shift as ligand σ-donating ability increases. This is in agreement with the assignments of Gray *et al.*[300]

Table 21 Proposed Models for the Rh—Rh Bond in Rh^{II} Tetracarboxylate Dimers

Proposer (Ref.)	*Method used*	*Rh—Rh bond order*	*Molecular orbitals ordering*
Dubicki, Martin (290)	Extended Hückel	1	$\pi^4\sigma^2\delta^2\delta^{*2}\pi^{*4}$
Cotton *et al.* (416, 417)	Qualitative MO and empirical arguments	3	$\sigma^2\pi^4\delta^2\sigma_n^2\sigma'^2_n\delta^{*2}$
Norman, Kolari (419)	SCF–X^α–SW	1	$\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$
Nakatsuji *et al.* (421)	*Ab initio*–SCF	1	If L = H_2O, NH_3, or no L $\pi^4\delta^2\pi^{*4}\delta^{*2}\sigma^2$ If L = PH_3 $\sigma^2\pi^4\pi^{*4}\delta^{*2}\sigma^2$
Nakatsuji *et al.* (423)	*Ab initio*–HF	—	For cation radical, if L = H_2O, NH_3 $\sigma^2\pi^4\pi^{*4}\delta^{*2}\sigma^1$ For cation radical, if no L singly occupied δ^*

and Norman and Kolari.[419] For the cation radical, however, the corresponding transition does not show the same ligand dependency, leading Kawamura[423,424] to suggest that the odd electron in the cation radical is not accommodated in the Rh—Rh σ bond, directly contradicting the conclusions reached by Nakatsuji.[421,422]

To summarize the current position on the Rh—Rh bond, the 'triple-bond windmill'[368] seems to have stopped spinning, and workers in the area seem to have reached a consensus, and refer to a Rh—Rh single bond. Agreement ends at that point however, as generally accepted electronic configurations and spectral assignments have not yet emerged, and will doubtless remain a contested and stimulating subject for some time. Table 21 summarizes the conclusions reached by the major theoretical studies on Rh^{II}–Rh^{II} systems.

The nature of the bond between Rh and an axially coordinated ligand (L_{ax}) has also been debated in recent years. There is no argument that axial Rh—L bonds are significantly weaker and longer than bonds to the equatorial bridges, and that the ligands at axial sites are more readily replaced than the bridging ligands. The strong *trans* effect (and influence) of the Rh—Rh bond is often invoked to account for these observations.[282] Debate has centered around whether the Rh—L_{ax} bond involves σ or π bonding.

The opening salvo came from Drago and coworkers, who studied the thermodynamics of the formation of the 1:1 and 2:1 adducts of eight different bases with [Rh(buty)$_4$] (buty = $C_3H_7CO_2^-$) in benzene solution (equation 98).[359] They found K_1 was approximately three orders of magnitude larger than K_2; if uncoupled, statistical arguments would have $K_1 = 4K_2$.[359] Despite the differences between K_1 and K_2, $\Delta H_1 \approx \Delta H_2$, implying a large entropy effect. Drago suggested that [Rh_2(buty)$_4$] forms 2:1 adducts with benzene when dissolved in that solvent, but that coordination of an added base to one end causes the release of both benzenes (equation 99); the large entropy increase of this step contributes to the first equilibrium constant. Also noting that in benzene solution both acetonitrile and carbon monoxide form adducts with a decrese in C—N and C—O stretching frequencies respectively, Drago suggested that extensive π back-bonding must be involved in the Rh—L_{ax} bonding. The simplified MO diagram (Figure 1) shows that π bonding lowers the π^* level, and increases the energy of the $\pi^* \rightarrow \sigma^*$ transition. The presence of π back-bonding was supported by an analysis of the reduction potentials of the oxidation products $[Rh_2(buty)_4L_n]^+$ (n = 0, 1, 2)[359] and by a similar thermodynamic study in CH_2Cl_2, a non-coordinating solvent.[433]

$$[Rh_2(buty)_4] \underset{-L}{\overset{K_1}{\rightleftharpoons}} [Rh_2(buty)_4L] \underset{-L}{\overset{K_2}{\rightleftharpoons}} [Rh_2(buty)_4L_2] \quad (98)$$

$$[Rh_2(buty)_4] \overset{C_6H_6}{\rightleftharpoons} [Rh_2(buty)_4(C_6H_6)_2] \overset{L}{\rightleftharpoons} [Rh_2(buty)_4L] + 2C_6H_6 \quad (99)$$

Bursten and Cotton then presented the results of an X^α–SW molecular orbital calculation on $[Rh_2(O_2CH)_4(PH_3)_2]$ in which they found no evidence of Rh → P back-bonding, and commented that the 'evidence on the occurrence of π-bonding is neither extensive nor straightforward'.[425] Other theoretical studies have implied that Rh—L_{ax} bonding is predominantly σ.[421,422] The X-ray photoelectron spectra of [$Rh_2(O_2CMe)_4$] and its 1:1 adduct with 4-cyanopyridine show that the adduct displays lower binding energies (Rh $3d_{5/2}$ and Rh $3p_{1/2}$) than the parent complex. If extensive back-bonding to the 4-cyanopyridine existed, a decrease in electron density of the Rh_2 core (and an increase in binding energies) would be expected; this was interpreted to point to the dominance of

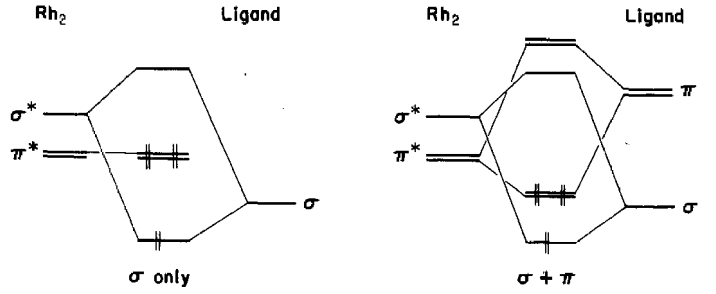


Figure 1 Simplified MO diagram for adducts of $[Rh(buty)_4]$ with bases in benzene solution

σ effects over any π back-bonding.[434] (Interestingly, the two Rh^{II} centers were indistinguishable in the 1:1 adduct with 4-cyanopyridine.)

Drago has presented additional thermodynamic arguments and a comparison between Rh_2^{4+} and Mo_2^{4+} systems to support the position that for some ligands, the admittedly weak Rh—L_{ax} bond can have a significant π component.[435-437] A recent ESR study of a variety of 1:1 and 2:1 adducts of the oxidized $[Rh_2(buty)_4L]^+$ ion led to the suggestion that the ordering of the filled molecular orbitals depends on the nature of the axial ligands, and that for the 2:1 phosphine adducts the HOMO is singly degenerate (presumably a σ^* orbital), while for the 1:1 phosphine adducts, or for complexes with weak donors, the HOMO is the doubly degenerate π^* level.[437]

The debate over the importance of π bonding of axially coordinated ligands has not yet been resolved, but the case for the existence of some π interaction seems to be growing. For example, Bear and coworkers determined the equilibrium constants for the 1:1 and 2:1 adducts of $[Rh_2(O_2CMe)_4]$ with a variety of di- and tri-peptides, substituted pyridines and imidazole, and found that the stability of the L—Rh bond does not correlate with the base strength of the entering ligand; this led Bear to suggest that more than σ bonding is involved, and that π bonding must be crucial.[438] Ironically, a recent study of the thermodynamics of the formation of 1:1 adducts between $[Rh_2(O_2CCF_3)_4]$ and 11 different alkenes found that the K_{form} values (between 6.1 for styrene and 578 for 2-methylpropane) do not correlate with association constants between these alkenes and more traditional π donors such as Rh^I, Pd^{II}, Pt^{II} and Ag^I.[439] Activation by the electron-withdrawing fluoroacetates is necessary, as no reaction is observed between alkenes and $[Rh_2(O_2CMe)_4]$, suggesting that back-donation from the Rh—Rh system may not have a dominant influence on Rh—L_{ax} stability. The case for π bonding is supported by the large antiferromagnetic exchange interaction between radical centers in $[Rh(O_2CR)_4(Tempo)_2]$ (R = CF_3, Pr, C_6F_5) which was rationalized in terms of a strong π interaction between the Rh and the axial radicals.[332] (The Mo—Mo π^* orbitals would be empty in the Mo analog, making such a π interaction impossible, consistent with the negligible antiferromagnetic exchange observed in $[Mo(O_2CCF_3)_4(Tempo)_2]$.[332]

48.5.2.3 Reactivity of Rh^{II} dimers

The reactivity of Rh^{II} dimers cannot be divided cleanly into substitution and redox processes, as the presence of the very stable +1 and +3 oxidation states means that processes which might be expected to cause substitution can lead to redox processes.

(*i*) *Substitutions at Rh^{II} dimers*

The most obvious reaction of Rh^{II} dimers is the formation of adducts by ligand substitution in the axial sites. An outline of the various bases which have been reported to coordinate to the Rh_2 core is given in Section 48.5.2.1. Numerous studies concerning the kinetics and thermodynamics of axial substitutions have been presented.[335,348,349,440-443] In general, adduct formation occurs in two kinetically separable steps at rates which suggest that the Rh—Rh bond has a strong *trans*-labilizing influence. The stability of the adducts is dependent on the nature of the bridging ligands, and Bear and co-workers have shown that for the reactions of $[Rh_2Q_4]$ (Q = acetate, propionate and methoxyacetate) with a variety of ligands, both K and k values follow the order propionate > acetate > Me-acetate.[436-438] This order was rationalized in terms of a desolvation effect of the bridging groups, and parallels the order observed in antitumor studies. The lability of the axial

site led Bear to use $[Rh_2(benzoate)_4]$ suspended in squalene as the stationary stage in GLC columns, which were used to separate alkene mixtures and various ethers, ketones and esters.[444] A multi-temperature study of the ^1H, ^{13}C, ^{31}P and ^{103}Rh NMR of the trimethyl phosphite (TMP) adducts of $[Rh_2(O_2CMe)_4]$ was able to detect the 1:1 and 2:1 adducts, and found rapid TMP exchange at 298 K.[445]

Few kinetic studies on bridge substitutions have been presented, but studies of the reaction of CF_3COOH with $[Rh_2(O_2CMe)_4]$ showed that the relative rates of bridge exchange is 80:40:2:1.[446] The geometry of the unisolated $[Rh_2(O_2CMe)_2(O_2CCF_3)_2]$ was not determined, but it is interesting to note that after substitution of the first two fluorinated bridges, the rate of further exchange slows dramatically.

There is no characteristic reaction in acidic solution, as the reaction depends on the nature of the conjugate base of the acid used. Bridge exchange is observed in carboxylic, thiocarboxylic, sulfuric and orthophosphoric acids, while arenesulfinic acids (RSO_2H) cause oxidation to $Rh(RSO_2)_3$ species.[447] Hydrochloric and hydrobromic acids cause disproportionation to Rh metal and RhX_3.[448,449] The potential bridge, dipicolinic acid, reacts with $[Rh_2(O_2CMe)_4]$, generating a structurally uncharacterized material identified as $Rh(dpc)\cdot 3H_2O$.[450] An early report[287] indicating that reaction of $[Rh_2(O_2CMe)_4]$ with perchloric, trifluoromethylsulfonic or fluoroboric acids leads to $Rh^{4+}_{2(aq)}$, was later questioned by Taube[451] and Pinnavaia[452] who showed that the products are $[Rh_2(O_2CMe)_3]^+$ and $[Rh_2(O_2CMe)_2]^{2+}$. In acetonitrile solutions of CF_3SO_3H or $HBF_4\cdot Et_2O$ (both strong, non-complexing acids), $[Rh_2(O_2CPr)_4]$ loses butyric acid and generates the cationic $[Rh_2(O_2CPr)_2]^{2+}$ dimer, although acetonitriles are presumably coordinated. The product gives no ESR signal, implying negligible amounts of monomeric radicals, but attempts to precipitate the dication with sulfide ion leads to black, intractable solids.[453]

In the presence of oxidizing agents the bridged dimers show surprising stability as $[Rh_2(O_2CMe)_4]$ does not react with O_2, but does react with ozone to form the trimeric $[Rh_3(\mu\text{-}O)(O_2CMe)_6(H_2O)_3]^+$.[454] A structural study of the perchlorate salt shows a central oxygen atom surrounded by a triangle of Rh atoms,[455] and is discussed in Section 48.5.2.4. Oxidation to $[Rh_2(O_2CMe)_4]^+$ has been reported with Cl_2, PbO_2 and Ce^{4+}, while basic peroxide and persulfate oxidations lead to Rh^{III} species.[451]

In the presence of H_2, the unbridged $Rh^{4+}_{2(aq)}$ is reduced to Rh metal, and the strongly reducing environment of H_2 over a THF solution containing PMe_3 and Na(Hg) causes the decomposition of $[Rh_2(O_2CMe)_4]$.[456] Low pressure CO leads to the formation of a labile CO adduct,[299,306,359] but under extreme conditions (up to 300 atm and 120°C) reduction to $Rh_6(CO)_{16}$ occurs.[358]

In a fluoroboric acid/methanol solution, PPh_3 reduces $[Rh_2(O_2CMe)_4]$ to $[Rh(PPh_3)_3(BF_4)]$,[457] while oxidation occurs in the presence of PMe_3, yielding *fac*-$[Rh(PMe_3)_3(H)(O_2CMe)_2]$.[458] In the presence of $P(Me)_3$, Grignards react with $[Rh_2(O_2CMe)_4]$ to generate monomeric Rh^{III} alkyls and Rh^{I} σ aryls.[457]

Little is known of the reactivity of the $Rh^{4+}_{2(aq)}$ ion, although Ziolkowski and Taube point out that it is probably labile, as it can be prepared by the Cr^{2+} reduction of $[Rh(NH_3)_5Cl]^{2+}$. No ammonia is retained in the primary coordination sphere of the resulting Rh^{II} dimer.[459] The dimer reacts with dihalogens (X_2) to give $[Rh(H_2O)_5X]^{2+}$ (X = Cl, Br, I),[362,460] and with O_2 to give $[Rh(H_2O)_6]^{3+}$ with a green transient, identified as the peroxo-bridged dimer $[(H_2O)_5Rh—O_2—Rh(H_2O)_5]^{4+}$.[459]

(*ii*) *Electrochemistry of Rh^{II} dimers*

The lack of Rh^{II} complexes generated from the reduction of Rh^{III} species was noted by Taube in 1968[362] and in his recent review Felthouse notes that electrochemical studies of other metal–metal bonded systems have been 'a fertile area for study... although relatively few studies have been reported on dirhodium(II) compounds.'[282] That is rapidly changing, as Rh^{II}_2 electrochemistry has become a vigorously pursued research area.

Wilson and Taube first reported that while $Rh^{2+}_{2(aq)}$ is not oxidizable by cyclic voltammetry, the tetraacetato-, tetracarbonato- and tetrasulfato-bridged dimers undergo reversible one-electron oxidations at 1.225 V, 1.022 V (in *p*-toluenesulfonic acid solution), and 1.112 V (0.2 M H_2SO_4) *versus* NHE respectively.[289] Oxidation of $[Rh_2(O_2CMe)_4]$ at a bright Pt electrode in 1.0 M $HClO_4$ leads to $[Rh_2(O_2CMe)_4]^+$, and the precipitation of uncharacterized solids $[Rh_2(O_2CMe)_5]$ and $[Rh_2(O_2CMe)_4Cl]$.[461] ESR and IR spectra of $[Rh_2(O_2CMe)_4]^+$ showed (within the time of the experiments) that the two Rh nuclei had identical electronic environments,[461] suggesting a $[Rh^{2.5}]_2$ formulation rather than $[Rh^{II}—Rh^{III}]$. This was supported by the X-ray photoelectron spectroscopy, which

showed a single binding energy for the Rh $3d_{5/2}$ orbitals (310.1 eV) in $[Rh_2(O_2CMe)_4]^+$, implying identical Rh atoms within the time scale of the XPS experiment.[434]

Bear and coworkers have shown that a reversible, one-electron oxidation is a general phenomenon for numerous $[Rh_2(O_2CR)_4]$ complexes (R = $C(Me)_3$, C_5H_9, Pr, Et, Me, $PhCH_2$, $MeOCH_2$, $PhOCH_2$, MeCHCl), but not when R = CF_3.[462] The oxidation potential is dependent on the nature of R, as dimers with electron-donating bridges (R = $C(Me)_3$, C_5H_9) are oxidized near 0.90 V (*versus* SCE in DMF solution) but *ca.* 1.28 V is needed to oxidize the complex with the electronegative R = MeCHCl bridge; oxidation was not observed (up to 1.7 V) for R = CF_3.[462] None of these complexes showed a second oxidation wave (up to 1.7 V), but all were irreversibly reduced (between −1.04 and −1.68 V); further electron absorption was observed, leading to uncharacterized reduction products. Again, the reduction potentials are dependent on the nature of the bridge, with complexes containing electron-withdrawing bridges the easiest to reduce. Bear showed[462] that the half-wave potentials (both oxidation and reduction) could be linearly correlated to the polar substitution parameters of Taft.[463] Bridges which effectively withdraw electron density from the Rh_2 core stabilize the higher oxidation state, making reduction of $[Rh_2(O_2CR)_4]$ easier and oxidation more difficult, while the electron-donating bridges stabilize the lower oxidation state, and the opposite trend in oxidation potentials is observed.[462] A more recent study of the one-electron oxidation of $[Rh_2(Q)_4]$ (Q = pivolate, butyrate, acetate, benzoate, methoxyacetate and chloroacetate) also found a LFER between $E_{\frac{1}{2}}$ and the Taft polar substituent parameters. Similar relationships were also observed for several 1:1 and 2:1 axially substituted adducts.[464]

Bear,[462] Bottomley[464] and Drago[359] have noted that the oxidation potential of $[Rh_2(O_2CR)_4L_2]$ is also sensitive to the nature of the axial ligands (L), and that axial coordination reduces the oxidation potential of the dimer. Increases in the σ donor strength (as mesured by pK_{BH^+}) of the axially bonded ligand should destabilize the d_{z^2} molecular orbital, leading to the observed cathodic shift in oxidation potential. Adduct stabilization of the cation was supported by estimates of the equilibrium constants for the reactions shown in equations (98), for L = py, and (100) as K_1 and K_2 (8.20 and 4.38) were three orders of magnitude less than for the analogous reactions involving the cation ($K_1^+ \approx 11$, and $K_2^+ \approx 8$).[464] The electrochemical reactions observed for $[Rh_2Q_4]$ can be summarized in equation (101).

$$[Rh_2(buty)_4]^+ \underset{-L}{\overset{K_1^+}{\rightleftharpoons}} [Rh_2(buty)_4L]^+ \underset{-L}{\overset{K_2^+}{\rightleftharpoons}} [Rh_2(buty)_4L_2]^+ \qquad (100)$$

$$[Rh_2Q_4]^+ \overset{1e^-}{\rightleftharpoons} [Rh_2Q_4] \overset{1e^-}{\rightleftharpoons} [Rh_2Q_4]^- \overset{ne^-}{\rightleftharpoons} \text{products?} \qquad (101)$$

Cannon and co-workers have used stopped-flow techniques to study the kinetics and thermodynamics of axial substitutions at $[Rh_2(O_2CMe)_4]^+$.[485] Their results are summarized in Table 22. The monoadduct $[Rh_2(O_2CMe)_4Br]$ was detected by rapid scanning stopped-flow spectrophotometry, with λ_{max} between 520 and 530, and between 790 and 800 nm. Oxidation of $[Rh_2(O_2CMe)_4]$ by Cl_2 (reaction 5 in Table 22) is independent of $[H^+]$ and $[Cl^-]$, indicating that Cl_2 (not HOCl or OCl^-) is the actual oxidizing agent.[465] Rates of reduction of $[Rh_2(O_2CMe)_4]^+$ with cationic reductants (to hinder the inner-sphere path) vary between 10.7 $M^{-1}s^{-1}$ with Fe^{2+}, to 6.0×10^4 $M^{-1}s^{-1}$ for Ce^{4+}.[466] Marcus analysis of these electron transfer rates allowed Cannon to estimate the rate of self-exchange between $[Rh_2(O_2CMe)_4]$ and $[Rh_2(O_2CMe)_4]^+$ (equation 102) at $k = 16\,M^{-1}s^{-1}$.[466]

$$[Rh_2(O_2CMe)_4] + [Rh_2(O_2CMe)_4]^+ \rightleftharpoons [Rh_2(O_2CMe)_4]^+ + [Rh_2(O_2CMe)_4] \qquad (102)$$

Bear, Kadish and co-workers have led a recent burst of activity centered on the electrochemical behavior of Rh^{II} dimers bridged by trifluoroacetamide (tfaa = $HN(O)CCF_3$). First prepared *via* bridge exchange[375] with $[Rh_2(O_2CMe)_4]$, $[Rh_2(tfaa)_4]$ undergoes one-electron oxidation between +0.91 V and +1.08 V (*vs.* SCE) in a variety of non-aqueous solvents.[375,467] The oxidations are reversible in $MeNO_2$, RCN (R = Ph, Me, Pr), acetone, THF and DMF, but are not reversible in

Table 22 Kinetic and Thermodynamic Parameters (From ref. 465)

Reaction	k_f ($M^{-1}s^{-1}$)	k_{rev} (s^{-1})	K
$[Rh_2(O_2CMe)_4]^+ + Cl^- \rightleftharpoons [Rh_2(O_2CMe)_4Cl]$	$4.7(\pm 1.6) \times 10^3$	60 ± 14	80
$[Rh_2(O_2CMe)_4]^+ + Br^- \rightleftharpoons [Rh_2(O_2CMe)_4Br]$	$16.4(\pm 0.5) \times 10^3$	18 ± 3	890
$[Rh_2(O_2CMe)_4Br] + Br^- \rightleftharpoons [Rh_2(O_2CMe)_4Br_2]^-$	—	—	150
$[Rh_2(O_2CMe)_4Br_2]^- \rightleftharpoons [Rh_2(O_2CMe)_4]^+ + Br_2^-$	6.0×10^2	—	—
$[Rh_2(O_2CMe)_4] + Cl_2 \rightleftharpoons [Rh_2(O_2CMe)_4]^+ + Cl_2^-$	120	—	—

py or MeCN/py solutions; in py, the K_{form} of $[Rh_2(tfaa)_4(py)]$ is *ca.* 250, implying that the irreversibility is due to a rapid reaction of the oxidized 1:1 py adduct, although 'the exact nature of the irreversibility has not been identified'.[467] Unlike the acetate-bridged dimers, the tfaa dimers are not reduced at potentials as low as -1.9 V. Electrochemical oxidation of $[Rh_2\{NH(O)CCF_3\}_4]$ contrasts with the behavior of the trifluoroacetate analog, which could not be oxidized electrochemically. The generalization—electron-withdrawing bridges destabilize the cationic species, making the oxidation potential more positive, while electron-donating bridges make oxidation less difficult—applies here, as the effect of the electron-donating nitrogen offsets the electron-withdrawing effects of the CF_3 group. The net effect is that the oxidation behavior of $[Rh_2(tfaa)_4]$ compares to that of $[Rh_2(O_2CEt)_4]$.[467]

This generalization was further explored in a study of the electrochemistry of the five dimers $[Rh_2(O_2CMe)_n(HN(O)CMe)_{4-n}]$ ($n = 0$, 1, 2, 3, 4).[384,468] Prepared by bridge exchange with $[Rh_2(O_2CMe)_4]$ and separated by HPLC, the oxidation potentials vary linearly with the number of amidate ligands. In acetonitrile solution the oxidation potential of $[Rh_2(O_2CMe)_4]$ is $+1.19$ V (*vs.* SCE), and is reduced by 0.25 ± 0.04 V for each amidate ligand which replaces an acetate; oxidation of $[Rh_2\{NH(O)CMe\}_4]$ occurs at 0.15 V.[384] All of the oxidations are reversible (or 'quasi-reversible'), and a second oxidation wave was observed for $[Rh_2(O_2CMe)\{NH(O)CMe\}_3]$ and $[Rh_2\{NH(O)CMe\}_4]$ at 1.65 and 1.41 V respectively. Study of the mixed acetate–amidate complexes (where $n = 0$ and 1) in the presence of various axial ligands and in different solvent systems supports the existence of a π interaction between the Rh_2 core and potential π acceptors such as DMSO and PPh_3. The sensitivity of the orbital structure to the nature of the bridging ligands is emphasized by the observation that the nature of the HOMO changes as n goes from 0 ($[Rh_2(O_2CMe)_4]$) to 1 ($[Rh_2(O_2CMe)_3\{NH(O)CMe\}]$).[368]

The effects of *N*-substituted phenyl groups has also been explored in electrochemical studies of $[Rh_2\{PhN(O)CMe\}_4]$.[376,469] Bridge exchange from $[Rh_2(O_2CMe)_4]$ followed by HPLC separation leads to a green isomer, identified by NMR analysis as the 3:1 isomer (see Section 48.5.2.1.ii), and a blue isomer, a 1:1 water adduct of unknown geometry. Both complexes undergo two reversible one-electron oxidations. The oxidations ($+0.55$ and $+1.65$ V (*vs.* SCE) for the blue isomer; $+0.53$ and $+1.63$ V for the green form) are separable in CH_2Cl_2, MeCN and PrCN, and the two-electron oxidation product is stable within the time of the cyclic voltammetry experiment, although a slow reaction to Rh^{III} products occurs. This suggests the interesting possibility that with very electron-donating bridges, stable Rh_2^{III} species might be prepared.[469]

(*iii*) *Miscellaneous reactions of Rh^{II} dimers*

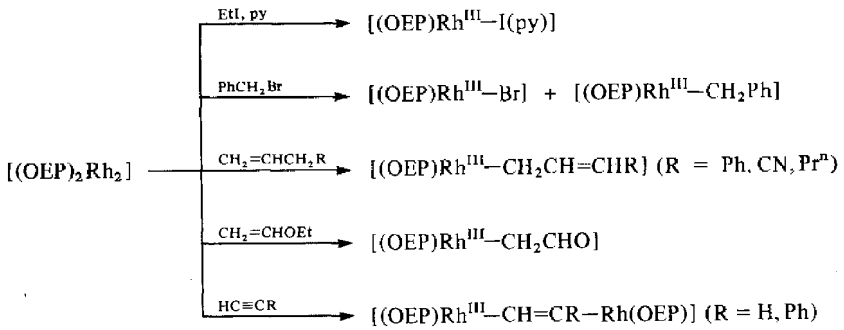
One obvious reaction of Rh^{II} dimers which has been little explored is the cleavage of the Rh—Rh bond. Taube suggested that the slight paramagnetism of $Rh_{2(aq)}^{4+}$ may be due to the dimer $\rightleftharpoons$ 2(monomer) equilibrium,[362] but the small paramagnetism (μ_{eff} near 0.5 BM) of tetraacetatodirhodium(II) complexes,[407] where Rh—Rh bond cleavage is unlikely, led Taube to suggest[289] that the paramagnetism of $Rh_{2(aq)}^{4+}$ is due to some other phenomenon. Espenson has shown that flash or continuous photolysis (visible irradiation) of $[Rh_2(DMG)_4(PPh_3)_2]$ homolytically cleaves the Rh—Rh bond, generating the $[Rh(DMG)_2PPh_3]$ radical monomer.[470] This monomer may play an important role in $FeCl_3$ oxidation of $[Rh_2(DMG)_4(PPh_3)_2]$ (equation 103) as the reaction is first order in $[Rh_2^{4+}]$ and zero order in $[Fe^{3+}]$ ($\Delta H^{\ddagger} = 85.6 \pm 2.6$ kJ mol^{-1}, $\Delta S^{\ddagger} = 19.2 \pm 7.7$ J K^{-1} mol^{-1}), implying that the reaction proceeds *via* rate-determining cleavage of the Rh—Rh bond, followed by rapid oxidation of the resulting radical monomers.[470] For the reaction (dimer) $\rightleftharpoons$ 2(monomer), Espenson estimated that $K \approx 1.5 \times 10^{-10}$, with $\Delta H^{\circ} \approx 86$ kJ mol^{-1} and $\Delta S^{\circ} \approx 100$ J K^{-1} mol^{-1}. Ignoring solvent effects, this ΔH° value is an estimate of the Rh—Rh bond dissociation energy when the Rh—Rh bond distance is 2.97 Å; in Rh metal, the Rh—Rh bond is 2.68 Å long, with a bond energy of 93 kJ mol^{-1}.[471]

$$[Rh_2(DMG)_4(PPh_3)_2] + 2FeCl_3 \longrightarrow 2[Rh(DMG)_2(PPh_3)Cl] + 2FeCl_2 \qquad (103)$$

There are scattered reports of the catalytic activity of Rh^{II} dimers, although this field is dominated by the thoroughly studied catalytic activity of Rh^{I} monomers. Rempel and coworkers investigated the $[Rh_2(O_2CMe)_4]$-catalyzed hydrogenation of terminal alkenes, substituted ethylenes and ethylene in DMF solution,[472] and found that only one of the Rh atoms is involved in the reaction, which is proposed to proceed *via* a hydride complex. Hydrogenation activity has been reported for $[Rh_2(phen)_2(O_2CMe)_2Cl_2]$,[389] and Rh^{II} (and Pd^{II}) carboxylates efficiently catalyze the cyclopropane

tion of alkenes by diazoesters.[473] A more thorough discussion of the catalytic activity of Rh^{II} dimers is in the companion series.[17]

The unbridged $[Rh_2(OEP)_2]$ undergoes a variety of reactions with substituted hydrocarbons in which the Rh—Rh bond is cleaved, and organometallic Rh^{III} complexes are formed. Several such reactions are represented in Scheme 13.[409] These reactions are intimately tied to reactions of Rh^{III} OEP complexes, discussed in Section 48.6.2.7.



Scheme 13

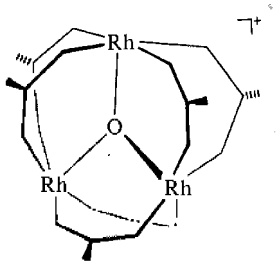
Interest in the chemistry of tetracarboxylate Rh^{II} dimers has doubtless been spurred by the observation that $[Rh_2(O_2CMe)_4]$ has shown antitumor activity against L1210 leukemia and Ehrlich ascites tumors in mice.[385,474–478] The rate of formation and the stability of 1:1 adducts in $[Rh_2(Q)_4]$ follows the order Q = propionate > Q = acetate > Q = methyl acetate, paralleling their antitumor activity.[441–443] Preliminary screening of the cyclophosphamide adducts of the tetrapropionate and tetrabutyrate dimers indicate that the complexes are inactive.[323]

48.5.2.4 Miscellaneous polynuclear complexes of Rh^{II}

Coordination complexes with more than two Rh^{II} are relatively rare. Numerous Rh-bridged (bridge = 1,3-diisocyanopropane) polynuclear species, and other organometallic clusters, involving Cp, CO (often as bridges), and phosphine ligands have been characterized. These have been efficiently reviewed by Felthouse[282] and are outside the scope of this report. Haines has reported the structure of a unique dimer containing Rh^{II}, $[Rh_2(CO)(L)_2Cl_2]\cdot 2CHCl_3$ (L = $(PhO)_2PN(Et)$-$P(OPh)_2$— a neutral symmetric diphosphorus bridge),[479] which nicely evades classification. One of the Rh atoms is in a square planar environment, coordinated to two mutually *cis* phosphite bridges, a CO and the other Rh atom; it has bond lengths and a coordination geometry characteristic of Rh^0. The other Rh is five coordinate, being bonded to two mutually *cis* phosphite bridges, two *cis* chlorines, and the other Rh atom. Its geometry and bond distance are characteristic of Rh^{II}. The Rh^0—Rh^{II} bond distance of 2.661 Å is well within the range observed for the more traditional Rh^{II} dimers.

An interesting compound, prepared by the ozonization of $[Rh_2(O_2CMe)_4]$, and formulated as $[Rh_3(O)(O_2CMe)_6(H_2O)_3]ClO_4$ was reported by Wilkinson and coworkers.[454] On the basis of electronic, IR and NMR spectra, they proposed a Rh_3O core; such M_3O cores were then known for Cr,[480] Mn,[481] Fe[480a,482] and Ru.[483] The same trimer was also prepared by reacting $RhCl_3\cdot 3H_2O$ with AgO_2CMe, and was shown to be isomorphous with the Cr analog.[484] A single crystal X-ray structure confirmed the presence of the planar Rh_3O core with the Rh atoms in an almost equilateral triangle around the central O atom (**43**).[455] While formally a Rh^{III} trimer, assuming a central O^{2-}, it is instructive to compare this structure to the numerous structures of Rh^{II} dimers discussed in Section 48.5.2.1. Each Rh pair in the trimer is bridged by two acetate groups, but the average Rh—Rh distance (3.33 Å) precludes the possibility of strong Rh—Rh interaction. The average distance between the Rh and the O atom of the bridging acetates (2.020 Å) is similar (even a bit shorter) than that observed in $[Rh_2(O_2CMe)_4(H_2O)_2]$ (2.039 Å[297]) despite a Rh—Rh distance which is almost 1 Å longer in the trimer. This is dramatic evidence that the acetate is a most accommodating bridge,[303] and that the C—O—Rh bond is flexible, expanding from *ca.* 119.5° in the dimer to *ca.* 132° in the trimer. Such clear evidence of flexibility confounds the problem of explaining why the Rh—Rh bond is so consistently short in the tetracarboxylate dimers, as the carboxylate bridges do not appear to be all that constraining. The average Rh—OH_2 distance in the trimer (*ca.* 2.13) is significantly

shorter (*ca.* 0.18 Å) than the Rh—O_{ax} distance in $[Rh_2(O_2CMe)_4(H_2O)_2]$, or in any of these axially bonded dimers. In the trimer, the Rh—OH_2 bond is not *trans* to a Rh—Rh bond, while the characteristically long Rh—O bonds in the dimers are directly *trans* to a Rh—Rh bond, clearly illustrating the often-cited *trans* influence of the Rh—Rh bond.



(43)

48.6 RHODIUM(III) COMPLEXES

48.6.1 Group IV Ligands

48.6.1.1 Cyano complexes

The hexacyanorhodate(III) anion was first prepared by the fusion of $[Rh(NH_3)_5Cl]Cl_2$ with KCN,[485] and Schmidtke prepared it by reacting $RhCl_3 \cdot 3H_2O$ with a five-fold excess of CN^-; aqueous KCN workup of the resulting '$Rh(CN)_3 \cdot 3H_2O$' leads to $K_3[Rh(CN)_6]$.[486] Wilkinson and co-workers reported that the reaction of an aqueous solution of CN^- with $[Rh(CO)_2Cl]_2$ leads to $[Rh(CN)_4(H)(H_2O)]^{2-}$,[487] but Jewsbury later identified the product as $[Rh(CN)_5(H)]^{3-}$.[488] An intermediate in this reaction was said to be polymeric $[Rh(CO)_2CN]_n$,[487] while Jewsbury later spoke of $[Rh(CO)_2(CN)Cl]^-$, *trans*-$[Rh(CO)_2(CN)_2]^-$ and $[Rh(CO)(CN)_3]^{2-}$ as intermediates in the same reaction.[488] A stopped-flow kinetic study of the reaction of CN^- with $[Rh(CO)_2Cl]_2$ indicated that successive CN^- substitutions lead to the tetracyanorhodate(I) anion, $[Rh(CN)_4]^{3-}$, which then undergoes oxidative addition with HCN to give $[Rh(CN)_5(H)]^{3-}$.[489] In the presence of MeI, pentacyanoalkylrhodium complexes are formed.[489]

The $[Rh(CN)_5(H)]^{3-}$ anion forms adducts with O_2, NO_2 and C_2F_4, although the nature of the oxygen adduct has been disputed.[487,490] Reaction of *trans*-$[Rh(py)_4Cl_2]Cl$ with excess KCN in boiling water gives a yellow solid, identified as the first mixed cyano complex of Rh^{III}, $[Rhpy_2(CN)_2Cl] \cdot 2H_2O$. Its insolubility in a variety of solvents and its IR spectrum suggest that it is a cyano-bridged dimer.[491]

Gray and co-workers showed that photolysis (254 nm) of $[M(CN)_6]^{3-}$ (M = Rh, Ir) in acidic aqueous solution leads directly to $[Rh(CN)_5(H_2O)]^{2-}$, and even extended photolysis leads to the loss of only one CN^-.[492] Thermal anation of the resulting aquapentacyanorhodate(III) anion provides a convenient synthetic path to $[Rh(CN)_5X]^{n-}$ (X = Cl^-, Br^-, I^-, OH^- and NCMe). The electronic spectra of the resulting complexes are given in Table 23; the spectrum of the $[Rh(CN)_6]^{3-}$ ion has

Table 23 Electronic Spectra of some Cyano Complexes of Rh^{III} (from Ref. 492)

Complex	λ_{max} (nm)(ε)	*Assignment*
$K_3[Rh(CN)_6]$	260sh (170)	$^1A_{1g} \rightarrow (^3T_{1g}, {}^3T_{2g})^a$
	225 (555)	$^1A_{1g} \rightarrow {}^1T_{1g}$
$K_2[Rh(CN)_5NCMe]$	245 (550)	$^1A_{1g} \rightarrow {}^1E^a$
$[Rh(CN)_5H_2O]^{2-}$	265 (605)	$^1A_{1g} \rightarrow {}^1E^a$
$[Rh(CN)_5OH]^{3-}$	258 (500)	$^1A_{1g} \rightarrow {}^1E^a$
$K_3[Rh(CN)_5Cl]$	277 (425)	$^1A_{1g} \rightarrow {}^1E^a$
$K_3[Rh(CN)_5Br]$	278 (402)	$^1A_{1g} \rightarrow {}^1E^a$
	237sh (1700)	π-LMCT
	205 (24 000)	σ-LMCT
$K_3[Rh(CN)_5I]$	313 (1500)	$^1A_{1g} \rightarrow {}^1E^a$
	258 (4200)	π-LMCT
	220 (42 000)	σ-LMCT

[a] Also assigned[494] to $[Rh(CN)_5(H_2O)]^{2-}$ contamination.

been the source of some controversy.[486,493-495] Schmidtke[486] originally assigned the 225 nm band to the spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition, and the weak shoulder at 260 nm to the spin-forbidden $^1A_{1g} \rightarrow ({}^3T_{1g}, {}^3T_{2g})$ transition. Gray and co-workers agreed[494] with the 225 nm band assignment, but suggested that the ill-defined shoulder near 260 nm, as well as the 325 nm (initially thought to be the $^1A_{1g} \rightarrow {}^1T$ band[494]), is due to contamination by the $[Rh(CN)_5(H_2O)]^{2-}$ ion.[492]

48.6.1.2 Miscellaneous group IV complexes

Acyl chlorides oxidatively add to $[RhCl(L)_3]$ (L = PMe_2Ph) to generate $[RhCl_2(COR)L_3]$ (R = Me or Et).[496] In the absence of oxygen, reaction of $[RhCl_2(COR)L_3]$ with NH_4PF_6 gives a square pyramidal Rh^{II} acyl salt $[RhCl(COR)L_3][PF_6]$ with an apical acetyl group.[496] In the presence of oxygen, however, the same conditions lead to a dirhodium, triply-chloro-bridged acetyl Rh^{III} cation $[Rh_2Cl_3(COR)_2L_4]PF_6$.[497] A single-crystal X-ray structure of this dimer shows both rhodiums to be octahedrally coordinated by three shared chlorides, two phosphines and the carbon atom of the acetyl group. The *trans* influence of the acyl group is apparent, as the Rh—Cl bond distance for the Cl *trans* to the acyl group is significantly longer (about 0.2 Å) than those *trans* to the phosphines. The long (3.328 Å) Rh—Rh distance suggests there is no metal–metal bond. A mechanism for the formation of the dimer, involving the dimerization of an unisolated $[RhCl(L)_2(Me)(CO)]^+$ ion, is proposed.[497]

The $SnCl_3^-$ moiety acts as a monoanionic ligand toward Rh^{III}, forming complexes with Rh—Sn bonds. Following the method of Kimura *et al.*,[498] $Cs_3[RhCl_4(SnCl_3)_2]$ and $(Me_4N)_3[RhX_n(SnX_3)_{6-n}]$ (X = Cl, Br; n = 1, 2, 3) have been prepared and characterized by conductivities, far IR spectra (Rh—Sn stretches found near 210 cm^{-1}), ^{119}Sn Mössbauer spectroscopy and by their reactions with water and iron(III) ion.[499] All of the complexes are diamagnetic, and SnX_3^- shows a strong *trans*-labilizing effect. Mössbauer spectra show a significant decrease in the density of the 5*s* electrons at the Sn^{II} atoms, suggesting σ donation to the Rh center, while the quadrupole splitting suggests the SnX_3^- ligand is also a π acceptor.[499] The three anions $[RhCl_{6-m}(SnCl_3)_m]^{3-}$ (m = 1, 2 or 3), have been studied by ^{119}Sn NMR spectroscopy. The ^{117}Sn satellite peak intensity is directly related to the number of coordinated tin atoms, and these satellites also reveal that fast intramolecular scrambling of the ligand occurs.[500] Reaction of these Rh^{III} complexes with a six-fold excess of Sn^{II} leads to a Rh^I complex with five Sn^{II} ligands.

The reaction of DMF with HCl solutions of $RhCl_3 \cdot 3H_2O$ in the presence of excess $SnCl_2$ leads to a Rh^{III} complex with one hydrido ligand, and four equivalent (by ^{119}Sn NMR) $SnCl_2$DMF ligands. Occupancy of the sixth coordination site is uncertain.[501] An X-ray analysis of blue-violet crystals of the composition $[RhL_6][Rh(SnCl_3)_4(SnCl_4)][SnCl_6] \cdot 4H_2O$ (L = NH_3 or 0.5 en) has been presented;[502] such salts have been used as hydrogenation or alcohol dehydrogenation catalysts. An X-ray analysis of $Cs_4[RhSn_6F_{19}(H_2O)_6]$ has shown that the structure consists of Cs^+ ions, H_2O molecules and $[Rh\{SnF_2(H_2O)_2\}_2[Sn_4F_{15}\}]^-$ anions.[503] The Rh atom is coordinated to the six Sn atoms, with the two mutually *cis* $SnF_2(H_2O)_2$ groups, and a tetradentate Sn_4F_{15} group held together by fluoride bridges between the 4 Sn atoms.

48.6.2 Nitrogen Ligands

48.6.2.1 Monodentate amines

(*i*) *Pentaammine complexes*

Complexes of the form $[Rh(NH_3)_5X]^{n+}$ have been studied and restudied for many years, and the work continues. Firmly bonded to the Rh^{III}, the five ammines are thermally quite inert, leaving the sixth site for ligand substitution studies. Numerous thermodynamic and kinetic studies of ligand substitutions have been reported and the reactivity at the sixth site is generally, but not always, between Co and Ir. Ligands at the sixth site are often susceptible to photoinduced substitution, but not to redox processes, making $[Rh(NH_3)_5X]^{n+}$ complexes popular candidates for photochemical studies.

(*a*) *Synthesis and characterization.* The starting material for this family of complexes is almost always the yellow $[Rh(NH_3)_5Cl]Cl_2$, initially prepared by Vauquelin[2] and Claus[3] but most modern references are to the methods of Johnson and Basolo[504] or Wilkinson and co-workers.[505] The former

is adapted from the method of Lebedinski,[506] and involves the direct reaction of $RhCl_3 \cdot 3H_2O$ with $(NH_4)_2CO_3/NH_4Cl$ in aqueous solution (equation 104). This leads to chloride salts of the chloropentaammine and dichlorotetraammine cations, but these are easily separated as $[Rh(NH_3)_5Cl]Cl_2$ is insoluble in cold water, while the dichlorotetraammine is quite soluble.[504] The latter synthesis takes advantage of the ability of reducing agents to catalyze substitutions at Rh^{III} centers (Section 48.6.2.5.iii), as an aqueous ethanolic solution of $RhCl_3 \cdot 3H_2O$ reacts rapidly with aqueous NH_3 to generate, in 80% yields, pure $[Rh(NH_3)_5Cl]Cl_2$.[505]

$$RhCl_3 \cdot 3H_2O + (NH_4)_2CO_3/NH_4Cl \xrightarrow[\Delta]{H_2O} [Rh(NH_3)_5Cl]Cl_2 + [Rh(NH_3)_4Cl_2]Cl \qquad (104)$$

Generation of other pentaammines $[Rh(NH_3)_5X]^{n+}$ generally involves simply heating an aqueous solution containing $[Rh(NH_3)_5Cl]^{2+}$ and an excess of X. Direct substitution of the chloride, without significant ammine labilization, is the rule, although a claim has been made that heating solid $[Rh(NH_3)_5Cl]Cl_2$ to 296°C causes ammine labilization, cleanly yielding $[Rh(NH_3)_4Cl_2]Cl$.[507] This was later questioned, as significant decomposition, yielding Rh metal and N_2 gas, was also observed under these harsh conditions.[508]

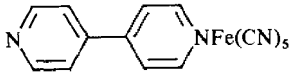
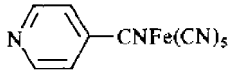
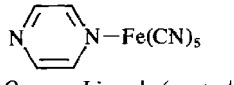
The chloride is readily removed by boiling a solution of $[Rh(NH_3)_5Cl]Cl_2$ with Ag^+ (usually as the nitrate or perchlorate salt), generating $[Rh(NH_3)_5(H_2O)]^{3+}$ and the easily removed AgCl; the aquapentaamminerhodium(III) cation can then be isolated, if desired, as the perchlorate salt.[509] The coordinated water is weakly acidic (cited pK_a values range from 6.14[510] to 6.24 in 0.47 M $NaClO_4$,[511] to 6.93 in 1.0 M $NaClO_4$[512]), and the free energy, enthalpy and entropy of neutralization are similar to those for the Co^{III} analog.[513] Replacement of the coordinated water proceeds more readily than removal of the chloride (the mechanisms of such direct anations are discussed below). The coordinated oxygen atom is also a reaction site in itself, and some of the apparent anations involve oxygen attack, and do not involve cleavage of the Rh—O bond (*e.g.* reaction with CO_2 to yield CO_3^{2-},[514,515] SO_2 to yield SO_3^{2-},[516] NO_2^-[517] and acetate[518]). These reactions are also discussed below.

A variety of ligands have occupied the sixth site of the pentaamminerhodium(III) moiety. The electronic absorption spectra for many of the resulting complexes are recorded in Table 24. Some of the more unusual and/or useful ligands merit mention here. Reduction of $[Rh(NH_3)_5Cl]^{2+}$ with BH_4^-[536] has been reported to yield the monohydrido complex $[Rh(NH_3)_5H]^{2+}$, although later reports say that reduction with Zn in ammonia is a more convenient preparative route.[505,541] The hydride ligand has a strong *trans*-labilizing effect, so the hydridopentaamminerhodium(III) cation is a convenient starting material for the synthesis of a variety of complexes, as both H^- and NH_3 labilization can be effected.[542]

Table 24 Electronic Spectra of Some $[Rh(NH_3)_5X]^{n+}$ Complexes

X	λ_{max}(nm)(ε)	*Ref.*
Nitrogen Ligands (neutral ligands)		
NH_3	306 (135)	519
	307 (135), 256 (105)	520
	305 (131), 256 (94)	521
NH_2Cl	395 (225), 258sh (304), 210sh (2416)	522
NH_2OH	299 (150), 250 (171)	523
$NH_2C(O)NH_2$	315 (152), 259 (112)	521
$NH_2C(O)Ph$	235 (12 900)	524
$NH_2C(O)Me$	308 (157), 256 (143)	525
$NH_2C(O)OH$	314 (154), 259 (122)	520
Imidazole	305, 250	526
	304 (146), 250sh (153)	527
NCMe	301 (158), 253 (126)	528
$NCCH{=}CH_2$	300 (380), 210 (8300)	528
$NCC(Me){=}CH_2$	301 (190), 213 (8300)	528
NCPh	301sh (324), 282sh (1400), 275 (1700), 268sh (1660), 245 (16 000), 234 (20 400)	528
NC(*o*-C_6H_4F)	305sh (316), 288sh (2450), 281 (2570), 243 (14 500), 235 (18 200)	528
NC(*m*-C_6H_4F)	300sh (275), 288 (1700), 265 (813), 237 (8400)	528
$NCCH_2Ph$	299 (221), 266 (294), 262 (368), 256 (422), 251 (389), 247 (350)	529
$NCCH{=}CHPh$	300 (183), 267 (208), 263 (276), 257 (341), 251 (311), 247 (271)	529
$NCCH_2$(2-MeC_6H_4)	310 (310), 290 (2100), 284 (2200), 247 (1300), 237 (16 000)	529

Table 24 (*Continued*)

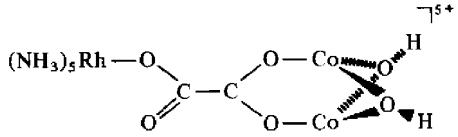
X	λ_{max}(nm)(ε)	*Ref.*
$NCCH_2(4\text{-}MeOC_6H_4)$	300 (249), 279 (1200), 273 (1400), 226 (9300)	529
$NCCH{=}CH(4\text{-}OHC_6H_4)$	307 (143), 280 (460), 274 (520), 223 (2500)	529
4-Mepy	302 (170), 256 (2500)	529
3-Clpy	302 (170), 272 (2930)	529
Pyridine	302 (160), 259 (2700)	529
Anionic Ligands		
NO_2^-	296 (330)	519
	295, 245	526
NCO^-	323 (276), 269 (160)	520
NCS^-	318 (474)	531
N_3^-	251 (6569)	522
	251 (5200)	532
	251 (6760)	533
Imidazolato	310, 252	526
	307 (166), 252.5 (216)	527
$NHC(O)NH_2^-$	318 (158), 259 (153)	521
$NHC(O)CH_3^-$	313 (164), 259 (153)	525
$NHC(O)Ph^-$	240 (7700)	524
	481 (5400)	534
	400 ($\approx$4500)	534
	571 (8200)	534
Oxygen Ligands (neutral ligands)		
H_2O	312 (105), 261 (89)	519
	312 (108), 261 (91)	531
	314 (112), 261 (101)	535
	314 (112)	514
	315 (105), 262 (95)	532
	315 (106), 263 (95)	512
	316, 267	536
	316 (105), 264 (94)	537
	314 (107), 262 (92.7)	511
$O{=}C(NH_2)_2$	330 (163), 266 (114)	521
$OC(NH_2)(NMe_2)$	324, 258	526
Anionic Ligands		
OH^-	319 (130), 277 (119)	512
	319 (132)	514
	321 (124)	519
	319, 277	526
$HC(O)O^-$	322, 266	526
$MeC(O)O^-$	322, 259	526
$MeCH_2C(O)O^-$	322 (156), 265 (125)	538
$NH_2C(O)O^-$	324 (145), 260 (100)	521
$HC_2O_4^-$	322 (159)	537
$OSO_2CF_3^-$	333 (103), 267 (84)	539
CO_3^{2-}	325 (178)	514
SO_3^{2-}	258 (2100)	516
Miscellaneous Anionic Ligands		
H^-	310 (120)	536
	312 (108), 261 (91)	531
Cl^-	347 (101), 276 (106)	511
	349 (100), 274 (103)	519
	344 (104), 274 (113)	531
Br^-	359 (122)	519
	424sh (29), 360 (125)	531
I^-	388 (230)	519
	419 (219), 381sh (230), 276 (3690)	531
CN^-	287 (146), 246 (139)	540

The conjugate base of trifluoromethanesulfonic acid, $OSO_2CF_3^-$, nicknamed 'Triflate', is becoming a popular ligand as it is an excellent leaving group. If $[Rh(NH_3)_5Cl]Cl_2$ is heated (90–110°C) in neat trifluoromethanesulfonic acid, the chloride-free solid, identified as $[Rh(NH_3)_5(OSO_2CF_3)](OSO_2CF_3)_2$, is generated. The ^1H NMR spectrum shows two peaks in a 4:1 ratio (3.16 p.p.m. *vs.* 3-(trimethylsilyl)propanesulfonate for the *cis* protons, and 2.90 p.p.m. for the *trans* protons), and the electronic spectrum (Table 24) suggests that the triflate ligand exerts a weak ligand field.[539] Its uses as a leaving group were demonstrated by Taube and co-workers,[543] who reacted $[Rh(NH_3)_5(OSO_2CF_3)]^{2+}$ with $[Os(NH_3)_5(pyrazine)]^{3+}$, and isolated the pyrazine-bridged $[(NH_3)_5Rh(pyrazine)Os(NH_3)_5]Cl_6$. Triflate's versatility was shown by Jackman and co-workers,[544,545] who reacted a DMF solution of $[Rh(NH_3)_5(OSO_2CF_3)]^{2+}$ with acetic anhydride in the presence of *N,N*-dimethylbenzylamine (DMB). The resulting acetylation, forming acetatopentaamminerhodium(III), is thought to proceed in two steps, with the basic DMB initially reacting with the triflate ligand, to generate the hydroxo complex, which then rapidly reacts with the acetic anhydride to form the acetatopentaamminerhodium(III) cation.

The hexaammine can be prepared by heating $[Rh(NH_3)_5Cl]Cl_2$ dissolved in concentrated aqueous ammonia in a sealed tube at 100°C for several days.[519,546,547] Detailed IR studies of the deuterated hexaammine,[548] and of $[Rh(NH_3)_6]^{3+}$ as the GaF_6^{3-}, ScF_6^{3-}[549] and MnF_6^{3-}[550] salts provide evidence of significant hydrogen bonding between the ammine hydrogens and the hexafluorometalate anions. Emission studies of crystalline powders of $[Rh(NH_3)_6][Rh(CN)_6]$, and the deuterated analog, suggest that the luminescent $^3T_{1g}$ excited state exhibits Jahn–Teller distortions.[551] An alternative route to the hexaammine involves the acid hydrolysis of $[Rh(NH_3)_5(NCO)]^{2+}$;[520] the details of this reaction and the synthesis of a series of organonitrilepentaammineRh(III) complexes are discussed below.[528]

Photolysis of $[Rh(NH_3)_5(N_3)]^{2+}$ can be used to generate $[Rh(NH_3)_5(NH_2Cl)]^{3+}$, or the NH_2OH analog;[522,523] the proposed mechanisms are discussed in Section 48.6.2.3.

One of the more unusual pentaamminerhodium(III) complexes was reported by Wieghardt,[552] who reacted the monodentate oxalatopentaamminerhodium(III) cation with $[Co_2(\mu\text{-}OH)_3(NH_3)_6]^{3+}$ to generate the $[Co_2Rh]^{5+}$ trimer, isolated as the bromide salt (**44**). IR spectra in the C—O stretching region for several oxalatopentaamminerhodium(III) complexes, and the deuterated analogs, are also recorded.[552]



(44)

The ^1H NMR spectra of a variety of $[Rh(NH_3)_5X]^{n+}$ ions dissolved in concentrated H_2SO_4 show only one ammine proton peak, at −3.82, −4.13, −3.78 and −3.65 p.p.m. (*vs.* external TMS) for $X = NH_3$, HSO_4^-, Cl^- and Br^- respectively.[547] The Ir analogs also have only one ammine resonance, but the Co species display two peaks in the expected 4:1 ratio. Neither intraligand nor proton exchange with the solvent could be used to explain the missing peaks; the magnitude of the 'diamagnetic' and 'paramagnetic' shielding in the heavier metals was cited to account for the single peak in the Rh and Ir cases. This is not a universal phenomenon, however, as other $[Rh(NH_3)_5X]^{n+}$ complexes do show two ammine peaks in the expected 4:1 ratio.[539]

(b) Reactions of $[Rh(NH_3)_5X]^{n+}$. The aquation and anation of $[Rh(NH_3)_5X]^{n+}$ in acidic aqueous solution (equation 105), was first studied by Lamb[553] who used conductance changes to monitor the 'interconversion of acido and aqua rhodium complexes', for the chloro and bromopentaammine-rhodium(III) cations. He found that both aquation and anation are first-order in $[Rh^{III}]$, and that the hydrolysis is accelerated by the presence of OH^-. The forward form of equation (105) (aquation) has since been studied for $X = Cl^-$,[554,556] Br^-, I^-,[531,556] OH_2,[557–559] SO_4^{2-},[560] NO_3^-[561] and N_3^-.[562] Representative results for the aquation of various pentaammine salts are given in Table 25. For aquations of halides or nitrate ions, rate expressions which are first-order in [Rh] and zero-order in $[H^+]$ are found. Poë[531] gives a detailed discussion of the thermodynamic, kinetic and intrinsic-kinetic *trans* effects, and compares the aquation and anation of $[Rh(NH_3)_5X]^{2+}$ (X = Cl, Br and I) with the $[Rh(en)_2XY]^+$ system. When $X = SO_4^{2-}$, a two-term rate expression was observed

$$[Rh(NH_3)_5X]^{n+} + H_2O \overset{H^+}{\rightleftharpoons} [Rh(NH_3)_5H_2O]^{3+} + X^{(3-n)-} \qquad (105)$$

Table 25 Kinetic Parameters for the Aquation of $[Rh(NH_3)_5X]^{n+}$ in Acidic Aqueous Solution

$$[Rh(NH_3)_5X]^{n+} + H_2O \rightarrow [Rh(NH_3)_5H_2O]^{3+} + X$$

X	*T* (°C)	*k* (s^{-1})	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}\,mol^{-1}$)	*Comments*	*Ref.*
Cl^-	50	1.13×10^{-6}	101 ± 1.3	-46.4 ± 3	$\mu = 0.2\,M$	531
	60	8.8×10^{-6}	94.4	—	—	556
	77	2.27×10^{-5}	102	—	$\Delta H^\circ = -14.6$; $\Delta S^\circ = -113$	554
Br^-	50	1.00×10^{-6}	103 ± 0.8	-41.4 ± 2.5	$\mu = 0.2\,M$	531
	60	5.4×10^{-6}	105	—	—	516
I^-	50	2.4×10^{-7}	109.6 ± 0.8	-32.6 ± 3	$\mu = 0.2\,M$	531
	60	2.51×10^{-6}	114	—	—	556
H_2O	25	1.07×10^{-5}	100 ± 1.3	-12.5	—	557
	25	1.07×10^{-5}	101	-2.7	—	558
	—	—	103 ± 1.3	$+3.3 \pm 4.6$	$\Delta V^* = -4.1 \pm 0.4\,cm^3\,mol^{-1}$	563
SO_4^{2-}	25	$k = 1.6 \times 10^{-5}$	89.5	-55.6	Rate $= k + k_H[H^+]$	560
		$k_H = 1.1 \times 10^{-5}$	119	$+38$		
NO_3^-	25	1.23×10^{-5}	97.5	-12.5	—	561
$ONO^-(NO_2^-)$	—	—	65.7 (68.6)	—	Aqueous H_2SO_4 solutions	564
$MeCO_2^-$	53.8	$k_H = 2.0 \times 10^{-4}$	96	-17	—	518
		$k_{obs} = 2.0 \times 10^{-5}$	—	—	$k_{obs} = k_{H_2O} + k_H[H^+]$	
$Me_3CCO_2^-$	68.6	$k_H = 3.3 \times 10^{-4}$	96	-25	—	518
		$k_{obs} = 3.2 \times 10^{-5}$	—	—	$k_{obs} = k_{H_2O} + k_H[H^+]$	
$CF_3CO_2^-$	64	$k_{obs} = 3.3 \times 10^{-5}$	105	-25	k_H very small	518
$O{=}C(NH_2)_2$	25	4.0×10^{-5}	—	—	Oxygen-bonded urea	521

(rate $= k_1 + k_2[H^+]$), implying significant acid catalysis as well as the normal, first-order aquation.[560]

The reverse of equation (105), the anation of aquapentaamminerhodium(III), has also been extensively studied. After Lamb's initial observations,[553] the first detailed study was reported by Poë and co-workers (for $X = Cl^-$, Br^-, I^- and NCS^-),[531] but was quickly followed by anation studies for $X = Cl^-$,[531,555,565] Br^- and SO_4^{2-},[565] propionate,[538] oxalate,[535] NO_3^- and $MeCOO^-$.[566] The results are summarized in Table 26. Interpretation of the kinetic results is complicated by unavoidable interference from ion-pairing, and while some differences exist, most systems showed: (a) ΔS^* values near zero; (b) rates which are less than, or comparable to, the rates of water exchange; and (c) rates which depend on the ionic strength and the nature of the nucleophile. The general consensus of these workers is that anation of pentaamminerhodium(III) complexes is associative in nature, and while not purely associative, the anations, and by implication the aquations, are probably more associative than the analogous reactions of $[Co(NH_3)_5(H_2O)]^{3+}$; the I_a designation is the most commonly used description. In the oxalate system, vanEldik points to the very negative values for ΔS^* (Table 26), the similarity in rates of anation by $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$, and their relative unreactivity

Table 26 Kinetic Parameters for the Anation $[Rh(NH_3)_5(H_2O)]^{3+} + X^{n-} \rightarrow [Rh(NH_3)_5X]^{(3-n)-} + H_2O$

X	*T* (°C)	*k* ($M^{-1}s^{-1}$)	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}\,mol^{-1}$)	*Comments*	*Ref.*
Cl^-	50	2.01×10^{-4}	107 ± 2.1	$+13 \pm 4$	$\mu = 0.2\,M$	531
	65	4.2×10^{-3}	—	—	4.0 M $NaClO_4$	565
	—	—	—	—	$\Delta V^* = 3.0 \pm 0.7\,cm^3\,mol^{-1}$	567
Br^-	50	1.44×10^{-4}	106 ± 1.3	$+8.4 \pm 4.2$	$\mu = 0.2\,M$	531
	65	7.9×10^{-3}	—	—	4.0 M $NaClO_4$	565
I^-	50	1.15×10^{-4}	102 ± 0.8	-4.2	$\mu = 0.2\,M$	531
NCS^-	50	1.19×10^{-4}	99.6	-13 ± 4.2	$\mu = 0.2\,M$	531
SO_4^{2-}	65	1.7×10^{-3}	—	—	4.0 M $NaClO_4$	565
N_3^-	65	5.97×10^{-2}	96.2	-20.0 ± 0.1	—	566
$MeCO_2^-$	60	1.83×10^{-2}	107 ± 2.1	$+4.85 \pm 1.3$	—	566
$EtCO_2H$	60	1.75×10^{-5}	89.1	-71 ± 4	—	538
$EtCO_2^-$	60	3.67×10^{-4}	92.9	-33 ± 4	*k* in s^{-1}	538
$H_2C_2O_4$	60	1.5×10^{-4}	35 ± 2.1	-213 ± 4.2	$\mu = 1.0\,M$	537
$HC_2O_4^-$	60	1.4×10^{-4}	56.1 ± 2.9	-142 ± 8.4	$\mu = 1.0\,M$; *k* in s^{-1}	537
$C_2O_4^{2-}$	60	1.2×10^{-4}	54.4 ± 2.1	-138 ± 4.2	$\mu = 1.0\,M$; *k* in s^{-1}	537
CO_2	25	$4.9 \pm 1.2 \times 10^2$	71 ± 4.2	$+50 \pm 12.6$	No Rh—O cleavage; $7 < pH < 9.9$	514
					$\Delta V^* = -4.7 \pm 0.8\,cm^3\,mol^{-1}$	535
SO_2	25	1.8×10^8	—	—	No Rh—O bond cleavage	516

Table 27 The Partial Molar Volume ($\bar{V}°$), the Volume of Activation (ΔV^*) and the Partial Molar Volume of the Transition State ($\Delta\bar{V}°$) during H_2O Exchange at $[M(NH_3)_5H_2O]^{3+}$ (in $cm^3\,mol^{-1}$) (from ref. 568)

M	$\bar{V}°$	ΔV^*	$\Delta\bar{V}^*$
Co	70.9	1.2	72.1
Rh	77.2	−4.1	73.1
Ir	77.3	−3.2	74.1
Cr	81.3	−5.8	75.5

when compared to anation by halides, sulfate, azide, *etc.*, to argue that a different mechanism (he suggests I_d) is operating during oxalate anation.[537]

A powerful technique for exploring the mechanisms of such ligand replacements is the determination of the volume of activation, ΔV^*, by monitoring the effect of pressure on the reaction rate. Swaddle first reported the ΔV^* for the water exchange of aquapentaamminerhodium(III) had a negative value ($-4.1 \pm 0.4\,cm^3\,mol^{-1}$),[563] comparable to values determined for aqua exchange at aquapentaamminechromium(III) ($-5.8\,cm^3\,mol^{-1}$) or hexaaquachromium(III) ($-9.3\,cm^3\,mol^{-1}$); such anations of Cr^{III} centers are generally thought to react *via* an associative path. The contrast to the more dissociative $[Co(NH_3)_5(H_2O)]^{3+}$ was also sharp ($\Delta V^* = +1.2\,cm^3\,mol^{-1}$), further supporting the idea that substitutions at Rh^{III} centers are more associative than those at Co^{III} (Table 27).

The effects of pressure on the kinetics of the anation of aquapentaamminerhodium(III) by Cl^- were also studied by vanEldik *et al.*[567] They assumed an ion-pairing mechanism, represented in equation (106), but could not determine K_x under the high ionic strength conditions used. They concluded that the value of K_x was 'immeasurably small', and discounted the importance of ion-pairing during the anation of aquapentaamminerhodium(III) under high ionic strength conditions. (vanEldik commented on the difficulty in distinguishing between I_a and I_d mechanisms on the basis of kinetic interpretations. At low ionic strengths, one can determine the value of K_x, but will not have enough nucleophile present to determine k; but with high ionic strengths, k, but not K_x, can be determined.) A positive ΔV^* ($+3.0 \pm 0.7\,cm^3\,mol^{-1}$) was found, similar to the values found for Co^{III} anations, but much more positive than the NCS^- anation of aquapentaamminechromium(III) ($-4.9\,cm^3\,mol^{-1}$). For the rhodium system, vanEldik disagreed with Swaddle's earlier conclusion,[563] and spoke of a 'dissociatively activated transition state'.[527]

$$[L_5RhH_2O]^{3+} + Cl^- \overset{K_x}{\rightleftharpoons} \{[L_5RhH_2O]\cdot Cl^-\}^{2+} \overset{k}{\rightleftharpoons} [L_5RhCl]^{2+} + H_2O \qquad (106)$$

Swaddle has determined the partial molar volumes[568] and reexamined the effects of pressure on the water exchange of $[M(NH_3)_5(H_2O)]^{3+}$ (M = Co, Rh, Ir and Cr).[569] The partial molar volume of the transition state, ($\Delta\bar{V}^*$) was defined to be the difference between the volume of activation and the partial molar volume of the ground state ($\Delta\bar{V}^* = \Delta V^* - \Delta\bar{V}°$). While earlier studies[563] showed that the volume of activation (ΔV^*) did vary as the central metal changed, the partial molar volume of the transition state ($\Delta\bar{V}^*$) is quite insensitive to the nature of the central metal (Table 27). Swaddle concludes that 'contrary to intuition. . . the transition states of a series of aqua exchange reactions must resemble one another surprisingly closely, regardless of detailed mechanism'.[569]

Pavelich has taken a different approach to kinetic studies of aquapentaamminerhodium(III) anations, and argues that the common practice of doing kinetic studies at high ionic strength is invalid, as ion pairing with the 'inert' electrolytes (typically perchlorates) confuses the interpretation of the results. He has presented a study of Cl^- anation of aquapentaamminerhodium(III) at low ionic strength, with the only anion added to the solution being the anating ligand. Ion-pairing was treated by potentiometric and spectral data, and was combined with kinetic data on the formation of $[Rh(NH_3)_5Cl]^{2+}$. A complex modeling analysis (to fit idealized *A*, *I* and *D* mechanisms) was used and Pavelich concluded that the reaction could most effectively be modeled assuming an interchange (*I*) path.[570] The activation parameters cited in Table 26 are based on that assumption.

It is fair to conclude that the mechanism of substitutions in acidic solution of $[Rh(NH_3)_5X]^{n+}$ has not yet been settled. The recent trend has been to question the earlier assignment of an I_a process, and to just refer to it as an interchange *I*, with less credence given to experimentally verifiable differences between I_a and I_d mechanisms.

The Hg^{2+} ion induces aquation of $[Rh(NH_3)_5X]^{2+}$ (X = Cl, Br and I) and numerous kinetic studies have been presented.[572–577] The mechanisms represented in equation (107) appear to occur;

the rate of aquapentaammine formation is proportional to $[Hg^{2+}]$ for X = Cl and Br, but approaches a constant value for X = I.[573] The $[Rh(NH_3)_5I—Hg]^{4+}$ intermediate has been detected (λ_{max} at 370 nm), and the K_{form} of this intermediate at 11.4 °C is 225 ± 16.[572] At that temperature, the Hg^{2+}-induced aquation is about seven orders of magnitude faster than the spontaneous aquation, and the rate constant for the dissociation of $[Rh(NH_3)_5I—Hg]^{4+}$ is $1.26 \times 10^{10} \exp(-66\,500 \pm 5000)/RT$ (at 25 °C, $k = 2.75 \times 10^{-2}\,s^{-1}$).[573] The enthalpy of activation for the Hg^{2+}-induced aquation of the bromopentaammine complex is 32 kJ mol^{-1} lower than for the spontaneous aquation.[574] The ΔV^* is negligible (-1.0 ± 0.4 cm^3 mol^{-1}) for the Hg^{2+}-induced aquation of $[M(NH_3)_5X]^{2+}$ (M = Co, Rh, Ir; X = Cl, Br, I), suggesting that the rate-determining step is not purely dissociative, but better described as an interchange.[575,576] A $t_{2g}^5 e_g^1$ configuration for the Rh^{III} center has been suggested for the $[Rh(NH_3)_5X—Hg]^{4+}$ intermediate.[573] A full kinetic study of the Hg^{2+}-induced aquation of *trans*-$[Rh(NH_3)_4Cl_2]^+$ has also been presented;[577] the rate of release of the first chloride is significantly greater than for the second chloride.

$$[L_5RhX]^{2+} + Hg^{2+} \overset{K}{\rightleftharpoons} [L_5Rh—X—Hg]^{4+} \xrightarrow{k} [L_5Rh]^{3+} + HgX^+ \xrightarrow[H_2O]{\text{fast}} [L_5RhH_2O]^{3+} \quad (107)$$

Lamb[553] first noted that OH^- ion accelerates the hydrolysis of $[Rh(NH_3)_5Cl]^{2+}$, but the increase is not as dramatic as observed for Co^{III} complexes. Kinetic studies have revealed a rate law of the form: $k_{obs} = k_{aq} + k_{OH}[OH^-]$ for the hydrolysis of $[Rh(NH_3)_5X]^{n+}$ for X = Cl^-, Br^-, I^-,[578] SO_4^{2-},[560] NO_3^-[561] and N_3^-.[533] Isokinetic plots (E_a plotted as a function of log A) are linear for halopentaammine complexes, but the data from the base hydrolysis of $[Rh(NH_3)_5N_3]^{2+}$ are well off the line, for both Rh^{III} and Co^{III} pentaammines, suggesting the azido complexes have some unspecified 'distinguishing feature' in their mechanisms.[533] For carboxylato complexes (X = RCO_2^-), a three-term equation is needed to account for the kinetic results: $k_{obs} = k_2[OH^-] + k_3[OH^-]^2$. The third-order path (second order in $[OH^-]$) was attributed to a path involving OH^- attack of the coordinated acetate.[579] For most systems, the base-catalyzed reaction is presumed to proceed *via* the well-known dissociative conjugate-base mechanism, S_N1CB. Palmer reported that the pressure dependence of the rates of base hydrolysis of $[Rh(NH_3)_5X]^{2+}$ (X = Cl^-, Br^-, I^-, NO_3^-) are consistent with an I_d model for X = Cl and Br, although he questions the utility of trying to draw fine distinctions between I_a and I_d steps. For X = I^- the volume data suggested some ion-pairing between the I^- and the coordinatively unsaturated conjugate base, $[Rh(NH_3)_4(NH_2)]^{2+}$, while for X = NO_3^- an I mechanism was favored.[580] Table 28 summarizes some of the kinetic parameters determined for the base hydrolysis of pentaammine complexes of Rh^{III}.

The kinetics of substitutions at pentaamminerhodium(III) in ammonia solutions have been studied by Balt and Jelsma.[581–583] For the two-step reaction represented in equation (108), they invoke an associative conjugate-base mechanism (S_N2CB) as the reaction appears more associative than the Co analog.[582] A major study of the ammoniation of $[Rh(NH_3)_5X]^{2+}$ (for X = Br^- or NO_3^-) revealed a two-term rate expression, $k_{obs} = k_s + k_b[NH_4^+]^{-1}$, with ΔS^* values for the rate-determining step which are *ca.* 420 J K^{-1} mol^{-1} less than for the Co analogs, again suggesting a mechanism more associative than for Co.[583] For $[Rh(NH_3)_5(NO_2)]^{2+}$, the hydrolysis follows the pattern observed for the Co^{III} analogs, with NH_3 being released in acidic solution, and NO_2^- being released in base. This was interpreted in terms of the kinetic *trans* effect of the nitrite ion.[581] Balt concludes that the acid reaction (ammine loss) 'proceeds *via* the same mechanism in the Co^{III} and Rh^{III} complexes (*i.e.* dissociative interchange), whereas aquation with loss of NO_2^- is probably more associative for Rh^{III}.[581]

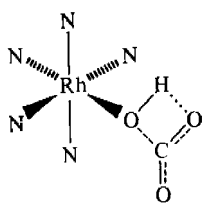
$$[Rh(NH_3)_4(OH)_2]^+ \xrightarrow[NH_{3(aq)}]{68–80\,^\circ C} [Rh(NH_3)_5OH]^{2+} \xrightarrow{112–142\,^\circ C} [Rh(NH_3)_6]^{3+} \quad (108)$$

Several of the apparent aquations and anations at the pentaamminerhodium(III) moiety have been shown to be reactions of the coordinated ligands, and do not involve cleavage of the rhodium–ligand bond. The aquation of $[Rh(NH_3)_5(RCOO)]^{2+}$ (RCOO = Ac^-, Bu^tCOO^- or CF_3COO^-) has a two-term kinetic expression, characteristic of a reaction proceeding *via* an uncatalyzed and a catalyzed path, $k_{obs} = k_{aq} + k_H[H^+]$.[518] Indirect evidence suggests that in the acid-catalyzed reaction (but not the uncatalyzed path), carbon–oxygen cleavage leads to the final aquapentaammine-rhodium(III) product.[518] More detailed kinetic studies of the uptake of CO_2[514] and SO_2[516] by aquapentaamminerhodium(III) have been presented. The reactive species in both cases is the hydroxopentaammine complex, and as shown in Table 29, the rates of decarboxylation of $[M(NH_3)_5(CO_3)]^+$ are very rapid, and virtually invariant for M = Co, Rh or Ir.[514] This mechanism is supported by volume of activation studies,[535] which also suggest that both C—O bond formation

Table 28 Kinetic Parameters for Base Hydrolysis of $[Rh(NH_3)_5X]^{n+}$

X	*T* (°C)	*k* ($M^{-1}s^{-1}$)	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}mol^{-1}$)	*Comments*	*Ref.*
Cl^-	40	4.93×10^{-4}	115	+66	$\mu = 0.1$ M	556
	40	4.18×10^{-3}	119	+25	Calculated to $\mu = 0$	578
	—	—	—	—	$\Delta V^* = 19.3\,cm^3\,mol^{-1}$	580
Br^-	40	5.77×10^{-4}	124	+93	$\mu = 0.1$ M	556
	40	3.98×10^{-3}	128	+33	Calculated to $\mu = 0$	578
	—	—	—	—	$\Delta V^* = 20.2\,cm^3\,mol^{-1}$	580
I^-	40	1.65×10^{-4}	134	+114	$\mu = 0.1$ M	556
	50	5.25×10^{-3}	137	+42	Calculated to $\mu = 0$	578
	—	—	—	—	$\Delta V^* = 20.4\,cm^3\,mol^{-1}$	580
NO_3^-	40	1.61×10^{-1}	116 ± 2	118 ± 7	$\Delta V^* = 22.3\,cm^3\,mol^{-1}$	580
	25	1.8×10^{-2}	115 ± 1	109 ± 5	—	561
SO_4^{2-}	25	1.3×10^{-3}	102 ± 2	42.8	—	560
N_3^-	78	4.76×10^{-4}	144.8 ± 1.3	—	—	533
NO_2^-	—	—	168 ± 4	+121 ± 9	Aqueous ammonia solution	581
OH^-	60	No reaction	—	—	$t_{1/2} > 150$ h	557
$CF_3CO_2^-$	25	$k_1 = 1.0 \times 10^{-4}$	75.3	−54	Rate = $k_1[OH^-] + k_2[OH^-]^2$	579
		$k_2 = 2.9 \times 10^{-1}$	31.4	−151	*k* in $M^{-2}s^{-1}$	
$CCl_3CO_2^-$	25	$k_1 = 3.0 \times 10^{-4}$	110.5	+58		579
		$k_2 = 1.5 \times 10^{-2}$	35.1	−163	*k* in $M^{-2}s^{-1}$	
$CHF_2CO_2^-$	25	$k_1 = 5 \times 10^{-5}$	126	+92	As K_a of acid decreases,	579
		$k_2 = 6.5 \times 10^{-3}$	43.9	−134	k_1 and k_2 decrease	
$CH_2FCO_2^-$	25	$k_1 = 4.1 \times 10^{-4}$	133	+109	—	579
		$k_2 = 1.6 \times 10^{-2}$	79.9	−71	*k* in $M^{-2}s^{-1}$	
HCO_2^-	45	$k_1 = 1.3 \times 10^{-4}$	139	+117	—	579
		$k_2 = 2.1 \times 10^{-4}$	107	+8	—	
$MeCO_2^-$	55.7	$k_1 = 3.3 \times 10^{-4}$	133	92	—	579
		k_2 too small to be detected				
NC—H	25	1.0 ± 0.1	—	—	Yields $[(NH_3)_5RhNHC(O)Me]^{3+}$	525
NCC_6H_5	25	4.7	—	—	Yields $[(NH_3)_5RhNHC(O)Ph]^{3+}$	524
$O{=}C(NH_2)_2$	25	6.0×10^{-2}	—	—	Oxygen-bonded urea	521

uptake, and C—O bond cleavage during decarboxylation are approximately 50% complete in the transition state. This suggests a transition state represented by (**45**).[535]



(**45**)

The classic example of an apparent aquation/anation which does not involve cleavage of a metal–ligand bond involves the $[M(NH_3)_5NO_2]^{2+}$ ion. First reported (for M = Rh^{III}, Ir^{III} and Pt^{IV}) by Basolo and Johnson,[517] the rate of formation of $[Rh(NH_3)_5NO_2]^{2+}$ from $[Rh(NH_3)_5H_2O]^{3+}$ followed the rate expression: rate = $k[[Rh(NH_3)_5H_2O]^{2+}][NO_2^-][HNO_2]$. Such kinetic behavior is reminiscent of the nitrosation of amines, and suggests a mechanism involving NO^+ attack at the coordinated hydroxyl oxygen (equation 109–111), followed by intramolecular linkage isomerization of the resulting nitrito complex (equation 112) to the stable N-bonded nitropentaammine-

Table 29 Parameters for the Decarboxylation of $[M(NH_3)_5CO_3]^+$ (25°C, $\mu = 0.5$ M) (from ref. 514)

$$[M(NH_3)_5CO_3]^+ + H^+ \overset{K_c}{\rightleftharpoons} [M(NH_3)_5(CO_3H)]^{2+} \overset{k}{\rightleftharpoons} [M(NH_3)_5OH]^{2+} + CO_2$$

M	$k\,(s^{-1})$	K_c (M)	ΔH_k^* ($kJ\,mol^{-1}$)	ΔS_k^* ($J\,K^{-1}mol^{-1}$)
Co	1.10 ± 0.05	2.0 ± 0.1	70.3 ± 0.8	−8 ± 4
Rh	1.13 ± 0.06	1.1 ± 0.1	71.1 ± 2.1	−4 ± 4
Ir	1.45 ± 0.07	1.6 ± 0.1	79.5 ± 2.1	+25 ± 4

rhodium(III).[517] Aquation in acid solution of both the nitro and nitritopentaamminerhodium(III) complexes are consistent with this mechanism.[564] The nitro complex is hydrolyzed by the loss of NO^+ ion from the transition state, and the entering water is not involved in the transition state. Aquation of the nitrito complex is less straightforward, and reacts *via* a mechanism involving both mono- and di-protonated species. Results with Rh parallel the results for other pentaammine complexes (Cr, Ir and Co), confirming that these reactions do not involve cleavage of the metal —ligand bond.[564]

$$[(NH_3)_5Rh\text{-}H_2O]^{3+} \rightleftharpoons [(NH_3)_5RhOH]^{2+} + H^+ \quad (109)$$

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \quad (110)$$

$$[(NH_3)_5Rh{-}OH]^{2+} + N_2O_3 \longrightarrow \left[(NH_3)_5Rh{-}\overset{H}{O}{-}\overset{+}{N}{-}O \;\; NO_2^-\right]^{2+} \longrightarrow [(NH_3)_5Rh{-}ONO]^{2+} + HNO_2 \quad (111)$$

$$[Rh(NH_3)_5{-}ONO]^{2+} \longrightarrow [Rh(NH_3)_5{-}NO_2]^{2+} \quad (112)$$

The spontaneous isomerization from the nitrito (—ONO) to the nitro ($-NO_2$) pentaammine-rhodium(III) complex has been well studied, and compared to the isomerizations of the analogous Co, Ir and Cr complexes. Isomerization was shown to occur in both the solid state and, about an order of magnitude more rapidly, in aqueous solution.[517] The volume of activation (ΔV^*) in aqueous solution is comparable for $[M(NH_3)_5ONO]^{2+}$ (M = Co, Ir and Rh, $\Delta V^* = -6.7$, -5.9 and $-7.4 \pm 4\,cm^3\,mol^{-1}$ respectively), which is consistent with the anticipated intramolecular isomerization.[584] The linkage isomerization is catalyzed by OH^-,[585] and by Hg^{2+}.[586] In alkaline solution, the linkage isomerization of nitritopentaamminerhodium(III) obeys the rate expression: rate = $k_s + k_{OH}[OH^-]$, and at 25°C, $k_s = 9.6 \pm 0.2 \times 10^{-4}\,s^{-1}$, $k_{OH} = 7.6 \pm 0.2 \times 10^{-3}\,M^{-1}\,s^{-1}$, $\Delta H_s^* = 85 \pm 2.5\,kJ\,mol^{-1}$, $\Delta H_{OH}^* = 96 \pm 2\,kJ\,mol^{-1}$, $\Delta S_s^* = -18 \pm 9\,J\,K^{-1}\,mol^{-1}$ and $\Delta S_{OH}^* = +38 \pm 6\,J\,K^{-1}\,mol^{-1}$.[585] For both the spontaneous and base-catalyzed paths, the rates of isomerization for the three pentaammines follow the order Rh > Co > Ir; for the base-catalyzed path the reaction rates are of the order 278:217:1, while for the spontaneous path (k_s), the relative rate constants are 32:2.3:1. The greater reactivity of the Rh complex, attributed to a lower ΔH^* for both the spontaneous and base-catalyzed paths, contrasts sharply with the order generally observed for the aquation of d^6 pentaammines. For example, for M = Co, Rh and Ir, the aquation of $[M(NH_3)_5Br]^{2+}$ in acidic solution occurs with relative rate constants of 4:1:0.001.[587] The ordering is not always Co > Rh ≫ Ir, however, as the rates of water exchange in aquapentaammine complexes in the Rh triad have relative rates of 0.53:1:0.0059,[559] and the relative rates of acid aquation of the $[M(NH_3)_5(CO_3)]^+$ ions are 1:1:0.02.[518]

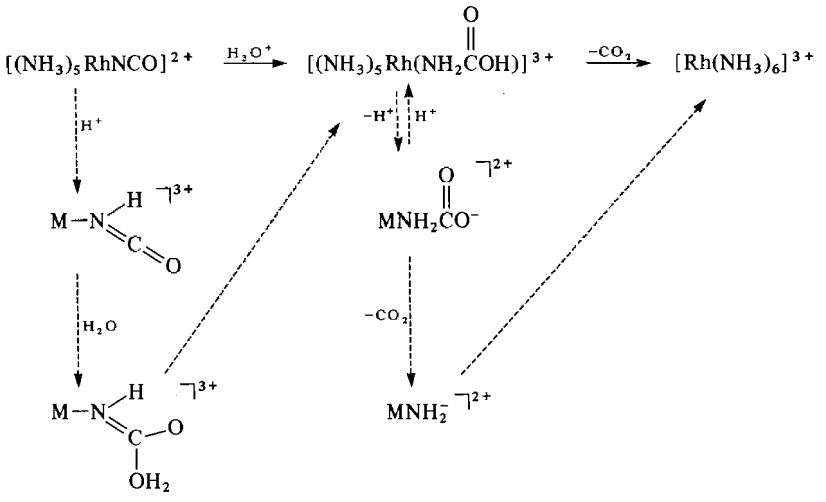
Linkage isomerization has also been observed in the $[Rh(NH_3)_5(urea)]^{3+}$ ion.[521] The direct substitution of urea into $[Rh(NH_3)_5(OSO_2CF_3)]^{2+}$ in sulfolane solution leads to $[Rh(NH_3)_5(urea)]_2(S_2O_6)_3 \cdot 3H_2O$, with both N- and O-bonded ureas. Recrystallization leads to the pure O-bonded isomer. The pK_a of the N- and O-bonded isomers are 13.19 and 13.67, respectively, compared to a pK_a of about 14 for free urea. The ^1H NMR suggests that the N-bonded form is in the imidol, not the amide form (**46**). In alkaline solution, the O form isomerizes to give the deprotonated N-bonded ureapentaammine complex and $[Rh(NH_3)_5OH]^{2+}$. In acidic solution, both the N- and O-bonded forms lead to $[Rh(NH_3)_5H_2O]^{3+}$ and $[Rh(NH_3)_6]^{3+}$, with the latter complex coming from a $[Rh(NH_3)_5NCO]^{2+}$ intermediate (*vide infra*). The isomerizations and the hydrolyses of both the N- and O-bonded urea complexes showed spontaneous and base-catalyzed paths. As with the Co^{III} analog, there was no evidence for the 'substantial production of $[Rh(NH_3)_5(OOCNH_2)]^{2+}$'; formamide is the product of urease-catalyzed hydrolysis of urea, and apparently the Rh^{III} does not polarize the C—O bond to the extent of the Ni^{2+} in the urease. Formation of the hexaammine does represent a 30 000 fold increase in the rate of urea hydrolysis, and is presumed to proceed through a Rh—NCO intermediate.[521]

$$\underset{\text{imidol form}}{[(NH_3)_5Rh{-}\overset{H}{N}{=}\overset{OH}{C}{-}NH_2]^{3+}} \qquad \underset{\text{amide form}}{[(NH_3)_5Rh{-}NH_2{-}\overset{O}{\overset{\|}{C}}{-}NH_2]^{3+}}$$

(46)

This last reaction, the hydrolysis of coordinated nitriles, has been extensively studied by Ford and co-workers; acidic hydrolysis of $[Rh(NH_3)_5NCO]^{2+}$ has been used as an alternate route to the hexaammine (equation 113).[520] The reaction was shown to go through a carbamic acid intermediate, which was isolated and characterized. The kinetic study of the hexaammine formation was complicated by the presence of these two consecutive reactions, and by two different reaction paths. The mechanism proposed for the hydrolysis of the coordinated cyanate is shown in Scheme 14; at low acid concentrations (0.005 to 0.025 M) the rate determining step is H_2O attack of the protonated species leading to a rate expression which is first-order in $[H^+]$: rate $= k_1[Rh][H^+]$. At higher acid concentrations (0.2 to 1.0 M), decomposition of the carbamic acid complex is rate determining, and a more complex rate law is observed: rate $= k_0[Rh] + k_{-1}[Rh][H^+]^{-1}$. At 25°C, $k_1 = 0.62\,M^{-1}s^{-1}$ (almost four times as reactive as the Co analog, and an order of magnitude faster than the Ru analog), $k_0 = 2.1 \times 10^{-3}\,s^{-1}$, $k_{-1} = 9.6 \times 10^{-4}\,M\,s^{-1}$.[522]

$$[Rh(NH_3)_5(NCO)]^{2+} + H_3O^+ \longrightarrow [Rh(NH_3)_6]^{3+} + CO_2 \qquad (113)$$



Scheme 14

In basic solution, however, the hydrolysis of benzonitrilepentaamminerhodium(III) ion (equation 114) is two orders of magnitude slower than the Ru^{III} analog, yet still represents a major rate enhancement (about six orders of magnitude) over the rate of hydrolysis of the free ligand. For the free ligand and the benzonitrilepentaammine complexes of Ir^{III}, Rh^{III}, Co^{III} and Ru^{III}, the relative rate constants are $1, 2.9 \times 10^5, 6.5 \times 10^6, 2.5 \times 10^6$ and 2.8×10^8 respectively.[524,525] The reaction is first-order in both [Rh complex] and $[OH^-]$. The intermediate amino complex can be protonated, but only at low pH, as its pK_b is 11.8.[524]

$$[(NH_3)_5Rh{-}N{\equiv}CPh]^{3+} + OH \longrightarrow [(NH_3)_5Rh{-}\underset{\text{amido form}}{\overset{H}{N}}{-}\overset{O}{C}Ph]^{2+} \qquad (114)$$

A kinetic study of the nitrous-acid-induced aquation of $[Rh(NH_3)_5N_3]^{2+}$ indicated that the reaction cannot be interpreted in terms of a single reaction mechanism.[588] The results suggest the mechanism proposed for the Co analog. As shown in equations (115)–(119), a series of nitrous acid preequilibria is followed by attack at the coordinated azide with $\{Rh(NH_3)_5N_3, NO\}^{3+}$ proposed as a likely intermediate. The $[Rh(NH_3)_5N_3]^{2+}$ ion is a factor of four less reactive than the Co analog,[526] and at least an order of magnitude less reactive than HN_3.[589]

$$H^+ + HNO_2 \rightleftharpoons NO^+ + H_2O \qquad (115)$$

$$H^+ + HNO_2 \rightleftharpoons H_2NO_2^+ \qquad (116)$$

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \qquad (117)$$

$$[Rh(NH_3)_5N_3]^{2+} + H_2NO_2^+ \longrightarrow [Rh(NH_3)_5H_2O]^{3+} + N_2O + N_2 \qquad (118)$$

$$[Rh(NH_3)_5N_3]^{2+} + N_2O_3 \longrightarrow [Rh(NH_3)_5H_2O]^{3+} + N_2O + N_2 + NO_2^- \qquad (119)$$

The electrochemical reduction of $[Rh(NH_3)_5OH]^{2+}$ has been studied in buffered ammoniacal solutions, and leads to a hydroperoxo species (equation 120).[590] Using a DME, $E_{\frac{1}{2}}^0 = -1.10$ V (*vs.* saturated calomel), but below pH 9.4, the pH dependence of the reduction potential led to the conclusion that a rapid proton uptake (presumably to give the aquapentaammine ion) occurs before electron transfer could occur. Gross electrolysis (−1.19 V, Hg cathode) leads to $[Rh(NH_3)_5H]^{2+}$, although a Rh^I intermediate is thought to be involved. Curtis *et al.* measured the reduction potentials of a large number of $[Rh(NH_3)_5X]^{n+}$ complexes in 0.1 M $NaClO_4$ solution and irreversible reductions occurred between −0.86 and −1.45 V.[591] Despite several references to apparent correlations between reduction potentials and numerous other physical properties of coordination complexes, Curtis could find no correlation between the reduction potentials and absorption spectra, ^1H NMR, or rates of aquation or base hydrolysis. The reduction potentials for the complexes studied are given in Table 30. Generally, the Rh^{III} complexes are *ca.* 0.8 ± 0.1 V more difficult to reduce than their Co analogs, and about 0.7 V easier to reduce than the corresponding Ir complexes. Early reports of some correlation between reduction potential and the wavelength of maximum *d–d* absorption[592,593] were assumed to be based on limited data as no such correlation could be found in this huge study involving dozens of pentaammine complexes of Co^{III}, Rh^{III} and Ir^{III}.[591] When carefully considered, the lack of such correlation is really not surprising, and is carefully rationalized by Curtis *et al.*

$$[Rh(NH_3)_5OH]^{2+} + O_2 \xrightarrow[NH_3/NH_4^+]{e^-} [Rh(NH_3)_4(OH)(O_2H)]^+ \quad (120)$$

(*ii*) *Other monodentate amine complexes*

The ubiquitous NH_3 ligand also forms a variety of tetraammine complexes, $[Rh(NH_3)_4XY]^{n+}$, but the chemistry of these complexes is closely related to that of the bis(ethylenediamine) analogs and relevant references will be included there. The acid dissociation constants for $[Rh(NH_3)_4(H_2O)X]^{n+}$ (X = NH_3, H_2O, OH^-, Cl^-, or Br^-; Table 31) have been determined from potentiometric titrations; the acidity of the coordinated H_2O can be rationalized in terms of electrostatic and σ and π bonding effects.[512] Heating solid *cis*-$[Rh(NH_3)_4(OH)(H_2O)]S_2O_6$ at 120°C for 15 hours leads to 'thermal deaquation' (equation 121) and the formation (after recrystallization from NH_4Br solution) of the bis(hydroxo) bridged salt, $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]Br_4$,[595] which is isomorphous with the well known Co^{III} and Cr^{III} analogs. The electronic spectra of these complexes, and other monodentate amine complexes not covered in the pentaammine section (Section 48.6.2.1.i), are given in Table 32.

$$cis\text{-}[Rh(NH_3)_4(OH)(H_2O)]S_2O_6 \xrightarrow{120°C,\ Br^-} [(NH_3)_4Rh(OH)_2Rh(NH_3)_4]Br_4 + 2H_2O \quad (121)$$

Monodentate amines other than NH_3 also form complexes with Rh^{III}. Edwards and co-workers prepared and characterized 12 complexes of the form $[Rh(Az)_3X_3]$, $[Rh(Az)_4X_2]^+$, $[Rh(Az)_5X]^{2+}$, $[Rh(Az)_6]^{3+}$, $[Rh(NH_3)_5Az]^{3+}$ and $[Rh(Az)_3(H_2O)_2(OH)]^{2+}$, where Az = aziridine (azacyclopropane), $NH(C_2H_4)$, and X = halide.[596] Prepared by the direct reaction of $RhCl_3 \cdot 3H_2O$ with aziridine, these complexes are similar to the well-studied ammine complexes; the aziridine acts as a typical monodentate ligand, halide aquation occurs in aqueous solution, and Br^- substitution of coordinated Cl^- was noted. Reaction of $[Rh(Az)_4Cl_2]^+$ with I^- causes reduction to $[Rh(Az)_3I]$, and HCl does not open the aziridine ring, suggesting that coordination to the Rh^{III} stabilizes the three-membered aziridine ring, presumably by saturating the N atom, and hindering the standard

Table 30 Reduction Potentials of some $[Rh(NH_3)_5X]^{n+}$ Complexes (*vs.* SCE) (from ref. 591)

X	E_{red}	X	E_{red}
Nitrogen ligands		*Oxygen ligands*	
NH_3	−1.12	H_2O	−0.96
$NH_2C(O)NH_2$	−1.24	OH^-	−1.02
Imidazole	−1.10	$HC(O)NMe_2$	−0.94
NCMe	−0.95	$O{=}C(NH_2)_2$	−0.86
Imidazolate	−1.17	HCO_2^-	−1.06
NCO^-	−1.14	$NH_2CO_2^-$	−1.09
NO_2^-	−1.33		
$NH_2C(O)NH^-$	−1.45	*Halide ligand*	
$MeC(O)NH^-$	−1.35	Co^-	−0.96

Table 31 pK Values for Some Rh^{III} Amine Complexes

Complex	pK_1	pK_2	*Conditions*	*Ref.*
cis-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	6.40	8.32	25°C, 1.0 M $NaClO_4$	512
trans-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	4.92	8.26	25°C, 1.0 M $NaClO_4$	512
cis-$[Rh(NH_3)_4(Cl)(H_2O)]^{2+}$	7.84	—	25°C, 1.0 M $NaClO_4$	512
trans-$[Rh(NH_3)_4(Cl)(H_2O)]^{2+}$	6.75	—	25°C, 1.0 M $NaClO_4$	512
cis-$[Rh(NH_3)_4(Br)(H_2O)]^{2+}$	7.89	—	25°C, 1.0 M $NaClO_4$	512
trans-$[Rh(NH_3)_4(Br)(H_2O)]^{2+}$	6.87	—	25°C, 1.0 M $NaClO_4$	512
cis-$[Rh(NH_3)_4(CN)(H_2O)]^{2+}$	6.8	—		
trans-$[Rh(NH_3)_4(CN)(H_2O)]^{2+}$	7.8	—		
$[Rh(NH_2Me)_5H_2O]^{3+}$	6.10	—	22°C, 0.047 M $NaClO_4$	511
$[Rh(NH_3)_5H_2O]^{3+}$	6.63	—	9.4°C, $\mu \approx 0.2$ M	531
	6.27	—	15°C, $\mu = 0.06$ M	594
	6.40	—	15°C, $\mu = 0.12$ M	594
	6.53	—	22°C, 0.047 M $NaClO_4$	511
	6.93	—	25°C, 1.0 M $NaClO_4$	512
	6.24	—	35°C, $\mu \approx 0.2$ M	531
$[Rh(NH_3)_5(NH_2COMe)]^{3+}$	3.3	—	1.0 M ClO_4^-	525
$[Rh(NH_3)_5(HN_2COPh)]^{3+}$	2.2	—	1.0 M ClO_4^-	524
$[Rh(NH_3)_5(imidazole)]^{3+}$	9.97	—	$\mu = 0.1$	527

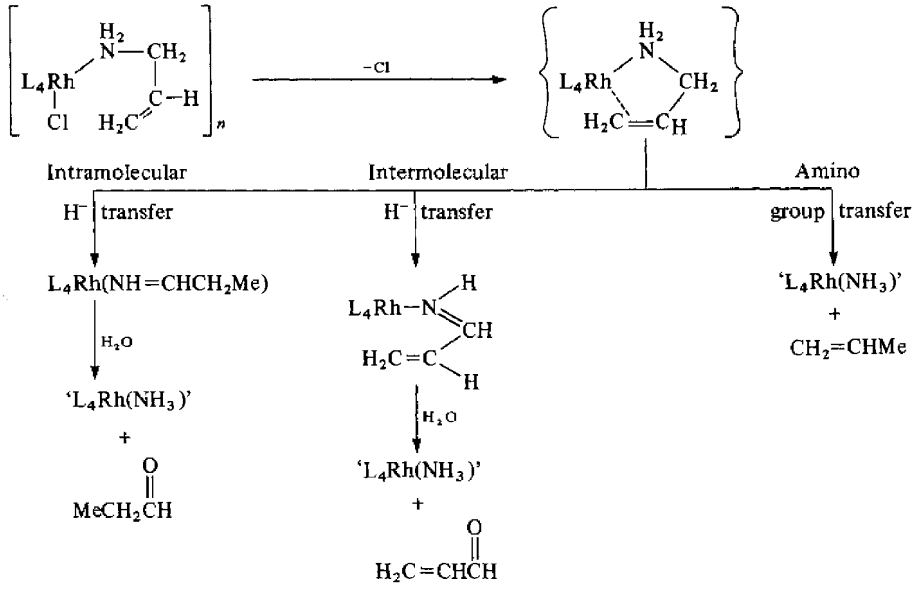
Table 32 Electronic Spectra of some Monodentate Amine Complexes of Rh^{III}

Compound	λ_{max} (nm) (ε)	*Ref.*
$[Rh(NH_2Me)_5Cl]^{2+}$	357 (122), 284 (144)	511
$[Rh(NH_2Me)_5H_2O]^{3+}$	321 (164), 269 (150)	594
$[RhAz_3Cl_3]$	394 (180), 326 (115), 223 (9800)	596
$[RhAz_4Cl_2]Cl$	417 (250), 340 (250), 287 (410), 223 (9700)	596
$[RhAz_4Cl_2]Br$	415 (170), 336 (170), 284 (400), 225 (3900)	596
$[RhAz_4Cl_2]I$	417 (400), 336 (400), 288 (616), 228 (16 100)	596
$[RhAz_5Cl]Cl_2$	410 (230), 330 (340), 289 (460), 221 (6300)	596
$[RhAz_3Br_3]$	418, 283, 223	596
$[RhAz_4Br_2]Br$	290, 225	596
$[RhAz_4I_2]I$	488, 358, 281, 221	596
$[Rh(NH_3)_5Az]Cl_3$	324 (370), 219 (940)	596
cis-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	326 (107), 268 (91)	595
cis-$[Rh(NH_3)_4(OH)_2]^{+}$	335 (122), 281 (118)	595
$[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]^{4+}$	331.5 (523)	595
trans-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	392 (54.3), 286 (124.6)	577
trans-$[Rh(NH_3)_4(H_2O)CN]^{2+}$	296 (160), 253 (138)	540
trans-$[Rh(NH_3)_4(OH)CN]^{+}$	295 (184), 260 (192)	540
trans-$[Rh(NH_3)_4(Cl)CN]^{+}$	302 (171), 259 (142)	540
cis-$[Rh(NH_3)_4(H_2O)CN]^{2+}$	291 (119), 251 (133)	540
cis-$[Rh(NH_3)_4(OH)CN]^{+}$	305 (142), 266sh (191)	540
cis-$[Rh(NH_3)_4(Cl)CN]^{+}$	366 (~109), 262 (~166)	540

ring-opening reactions. The electronic spectra (Table 32) are difficult to interpret, as no information on the geometric configuration of these complexes is given; an unusual feature is suggested, as a band identified as the spin-forbidden $^1A_{1g} \rightarrow {}^3T_{2g}$ transition, previously observed for $[RhCl_6]^{3-}$, $[Rh(C_2O_4)_3]^{3-}$ and $[Rh(NH_3)_5Br]^{2+}$,[597] is also observed for $[Rh(Az)_3Cl_3]$ and $[Rh(Az)_4I_2]I$ (488 nm). All the aziridine complexes showed strong intraligand transitions (217–227 nm), and IR peaks (850–890 cm^{-1}), confirming that the aziridine ring is intact. The molar absorption constants for several of these complexes were reported to increase upon dilution, but no explanation for this phenomenon was suggested.[596]

A series of monomeric and chloro-bridged oligomeric (or perhaps polymeric) allylamine complexes $[RhCl_3L_n]$ ($L = H_2NCH_2CH{=}CH_2$; $n = 1, 2, 3$) have been characterized (for $n = 1$ a coordinated H_2O is also present) and have been shown to undergo a variety of inter- and intra-molecular reactions.[598] As shown in Scheme 15, the reactions are thought to begin by a breakdown of the chloro bridges, followed by coordination of the unsaturated C=C moiety of the allylamine, H

transfer, and rapid collapse to the final products. (The organic products were identified by GLC, but the exact nature of the Rh^{III} product was not indicated.) Coordination to the Rh^{III} has no effect on the stretching frequency of the C=C double bond of the allylamine, showing that they are N-bonded. Analogous complexes with the saturated *n*-propylamine were prepared: $[RhCl_3L'_n]$ (n = 1, 2, 3) and $[RhL'_5Cl]Cl_2$ (L' = $H_2NCH_2CH_2Me$); while similar to the allyl complexes, the saturated ligands do not undergo the reactions represented in Scheme 15.[598]



Scheme 15

Swaddle has studied the H^+- and OH^--induced aquation of $[Rh(NH_2R)_5Cl]^{2+}$ (R = H or Me), and found, contrary to expectations, that $[Rh(NH_2Me)_5(H_2O)]^{3+}$ is more acidic (pK_a = 6.10) than the pentaammine complex (Table 31), suggesting that methylamine is a poorer electron-donor than ammonia.[511] Methyl substitution of the amine only slightly retards the acid hydrolysis of $[Rh(NH_2R)_5Cl]^{2+}$; the difference is in the ΔS^* term ($-50.2\,J\,K^{-1}\,mol^{-1}$ for R = Me *vs.* $-44\,J\,K^{-1}\,mol^{-1}$ for the pentaammine) not the ΔH^* (101.9 kJ mol^{-1} for R = Me *vs.* 102 kJ mol^{-1} for the pentaammine). In addition, the change in ΔS^* upon methyl substitution is opposite to the change observed for the analogous Co^{III} system, further supporting the assignment of an I_d mechanism for the aquation of Co^{III} amines in acidic aqueous solution, and a more associative (I_a) path for the Rh^{III} analogs. In contrast, methyl substitution accelerates the OH^- induced aquation of $[Rh(NH_2R)_5Cl]^{2+}$ by a factor of 29, consistent with a dissociative rate-determing step which is accelerated by steric crowding. The S_N1CB (or D_{CB}) mechanism is suggested.[511]

48.6.2.2 Bidentate aliphatic amines

(*i*) *$[Rh(en)_3]^{3+}$*

Werner first reported that the $[Rh(en)_3]Cl_3$ salt results when hydrated ethylenediamine reacts with $Na_3[RhCl_6]$,[4] and Jaeger showed that it could be formed when 50% en/H_2O reacts with $RhCl_3\cdot 3H_2O$.[599,600] Wilkinson and co-workers,[601] and Gasbol,[602] have taken advantage of the catalytic properties of ethanol to prepare $[Rh(en)_3]^{3+}$ by reacting $RhCl_3\cdot 3H_2O$ with ethylenediamine in aqueous ethanol, and Watt has used the direct reaction of 98% ethylenediamine with solid $RhCl_3\cdot 3H_2O$ with some success.[603] The electronic spectrum has been reported by a variety of workers,[601,602,604–606] and is consistent with a RhN_6 chromophore (Section 48.6.2.2.ii; Table 35). Werner resolved it as the 3-nitro-(+)-camphor and (+)-tartrate salt,[4] and the tartrate resolution has been repeated.[602,606] The (−)-$[Rh(en)_3]^{3+}$ ion is isostructural with (+)-$[Co(en)_3]^{3+}$ and (+)-$[Cr(en)_3]^{3+}$ and has the Λ configuration.[610]

Several researchers have used ^1H NMR to analyze configurational interactions of the ethylenediamine bidentates in $[Rh(en)_3]^{3+}$.[611–615] Hawkins noted[612] that the non-equivalence of protons in such tris(ethylenediamine) complexes is not necessarily due to conformational differences, for even if

Table 33 Population of Δ-$[Rh(en)_3]^{3+}$ Conformers (from ref. 615)

Ring configuration	*Name*	*Mole fractions* 0.15 M Δ-$[Rh(en)_3]^{3+}$	0.3 M PO_4^{3-} Δ-$[Rh(en)_3]^{3+}$
λλλ	A	8	45
λλδ, λδλ, δλλ	B	92	55
λδδ, δλδ, ββλ	C	0	0
δδδ	D	0	0

rapid configurational changes occur between σ and λ forms, the four C–H groups in a given ethylenediamine ring are still inequivalent, leading to an AA′BB′ ^1H NMR pattern. The ^1H NMR spectra of $[Rh(en)_3]X_3$ (X = Cl^-, I^- or ClO_4^-) have virtually identical chemical shifts and band widths (for both the methylene and amine bands), and the spectra are virtually unchanged between 4 and 82°C, indicating rapid conformational averaging. As observed with $[Co(en)_3]^{3+}$,[613,614] ion pairing to multiply-charged oxyanions is directional, and conformational ordering effects can be observed for D_2O solutions of $[Rh(en)_3]^{3+}$ in the presence of phosphate, selenate and selenite ions.[613] These changes were interpreted to imply directional association favoring the (*lel*) ring configuration, an assignment supported by the similarity of the spectra of $[Co(en)_3]^{3+}$ and $[Rh(en)_3]^{3+}$ in the hydrogen-bonding solvent, trifluoroacetic acid.[613] A thorough conformational analysis of $[Rh(en)_3]Cl_3$ (D_2O solutions with a 220 MHz ^1H NMR) disputed this assignment, however,[615] as the expected AA′BB′ pattern was found to be slightly perturbed by the stronger coupling to the low field proton; spectra were interpreted in terms of a conformationally labile ethylenediamine system which gave an AA′BB′X spectrum. Analysis of the molecular conformation population is represented in Table 33. Theoretical considerations and analogy to $[Co(en)_3]^{3+}$ ion suggest that configurations A and B would have approximately equal populations, yet the B configuration (*lls*) dominates, and is presumed to be the lowest energy configuration for Δ-$[Rh(en)_3]^{3+}$. In the presence of phosphate ions, directional association favors the A configuration (*'lll'*), and at 0.3 M PO_4^{3-} the A and B configurations are almost equally populated.[615]

Petersen and co-workers used ^{13}C NMR to study configurational changes in $[Rh(en)_3]^{3+}$ and $[Rh(en)_2XY]^{n+}$ (*vide infra*), and observing only one ^{13}C resonance for $[Rh(en)_3]^{3+}$ (46.35 p.p.m. *vs.* TMS), also concluded that ring configurational changes are fast on the NMR time scale.[607]

Little chemistry of $[Rh(en)_3]^{3+}$ has been presented, as it is thermally inert, although Watt and co-workers have reported on the products formed upon deprotonation of $[Rh(en)_3]^{3+}$ by KNH_2.[603,616–618] Deprotonation occurs as represented in equation (122), and all three products (x = 1, 2 or 3) have been characterized by IR analysis.[603] Reaction of $[Rh(en)_3]^{3+}$ with five equivalents of KNH_2 (25°C, 5 days) reportedly leads to dark green crystals of a paramagnetic (μ_{eff} = 1.5 ± 0.1 BM) solid identified as K[Rh(en − 2H)(en − H)$_2$].[616] Reaction of this material with water regenerates $[Rh(en)_3]^{3+}$, and quantitative reduction to Rh metal and the IR spectrum show that K[Rh(en − 2H)(en − H)$_2$] is a Rh^{III} complex without a Rh—H linkage. Watt concludes that the 'origin of paramagnetism remains obscure'.[616] Deprotonation of $[Rh(dien)_2]$ with amide ion has also been shown to lead to the doubly deprotonated [Rh(dien − H)$_2$]I, a diamagnetic H_2O-sensitive solid.[617] Further deprotonation leads to a pyrophoric solid (presumed to be [Rh(dien − H)-(dien − 2H)]), and an ill-characterized species assumed to be the hexadeprotonated $[Rh(dien - 3H)_2]^{3-}$.[617]

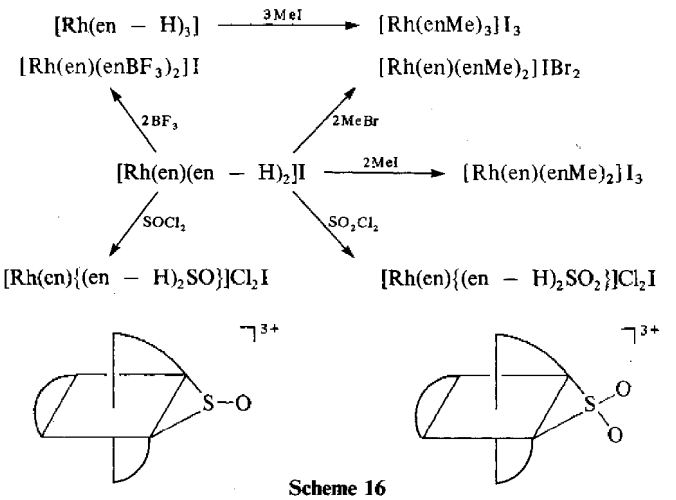
$$[Rh(en)_3]I_3 + xKNH_2 \longrightarrow [Rh(en - H)_x(en)_{3-x}]I_{(3-x)} + xNH_3 + xKI \quad (122)$$

$$x = 1, 2 \text{ or } 3$$

The deprotonated tris(ethylenediamine) complexes are, not unexpectedly, nucleophilic. The pale yellow doubly deprotonated complex [Rh(en − H)$_2$(en)]I acts as a nucleophile toward MeI, MeBr, $SOCl_2$, SO_2Cl_2, and triply deprotonated [Rh(en − H)$_3$] is electrophilically attacked by MeI (Scheme 16).[618] The methylated species are air and H_2O stable, but while air stable, the BF_3 and SO_2Cl_2 adducts hydrolyze rapidly. The low S—O stretching frequencies observed led to the suggested bonding configurations shown in Scheme 16, with the sulfur atoms bonded to two amine nitrogens.[618]

(*ii*) *$[Rh(en)_2XY]^{n+}$ complexes*

Basolo and Johnson opened the now extensive field of bis(ethylenediamine)Rh^{III} chemistry with a major study[619] of complexes of the form $[Rh(A)_4ClX]^{n+}$ (A_4 = $(NH_3)_4$, $(en)_2$, (*meso*-bn)$_2$, (±-bn)$_2$,



Scheme 16

(C,C,C',C'-tetramethylen)$_2$, tren or trien). The general synthetic route requires reaction of $RhCl_3 \cdot 3H_2O$ with a stoichiometric amount of the hydrochloride salt of the appropriate amine, followed by the gradual addition of a stoichiometric amount of NaOH to the refluxing solution. As part of this study, *cis* and *trans* isomers of $[Rh(en)_2X_2]^+$ (X = Cl, Br, I, NO_2 or N_3) as well as $[Rh(en)_2ClY]^{n+}$ (Y = SCN^-, NO_2^- or NH_3) were prepared and characterized by UV/visible and IR spectroscopy, with geometric assignments made on the basis of optical resolution (for the *cis* form), absorption spectra, and base-catalyzed hydrolysis of the *cis* complexes.[619] Reaction of *trans*-$[Rh(en)_2X_2]^+$ with BH_4^- was shown to lead to the monohydride (with retention of the *trans* geometry),[620] and the large *trans* effect of the H^- ion led to *trans*-$[Rh(en)_2H_2]^+$. Vibrational IR and Raman spectra for a variety of $[Rh(en)_2XY]^{n+}$ complexes showed that the Rh—N stretch occurs at 555–575 cm^{-1}, with N—Rh—N deformations at about 250 cm^{-1} and the Rh—X stretch (X = Cl, Br or I) between 150 and 350 cm^{-1}.[621] Conductivities (in DMSO solution) of *cis*- and *trans*-$[Rh(en)_2Cl_2]Cl$, as well as some *cis* dichlorobis(substituted diamine) complexes are similar to those for the Cr^{III} and Co^{III} analogs, and are characteristic of 1:1 salts.[622] The $[Rh(en)_2(H_2O)_2]^{3+}$ ions are weak diprotic acids, with the *trans* isomer an order of magnitude more acidic than the *cis* form (Table 34).

Direct synthesis of the *trans* form of $[Rh(en)_2XY]^{n+}$ is generally easier than that of the *cis* isomer, but the *cis* configuration can be ensured by bonding a bidentate to the two non-ethylenediamine coordination sites. The $[Rh(en)_2ox]NO_3$ salt was prepared by refluxing an aqueous solution of *cis*-$[Rh(en)_2Cl_2]NO_3$ with Na_2ox for 2.5 h.[629] In the presence of trace amounts of BH_4^- (at pH 4.7), a refluxing solution of either *cis*- or *trans*-$[Rh(en)_2Cl_2]^+$ reacts with ox^{2-} within seconds to form $[Rh(en)_2ox]^+$.[630,631] This BH_4^- catalyzed substitution (with *trans* to *cis* isomerization) was shown to be a general route to $[Rh(en)_2AA]^{n+}$ complexes (for AA = en, ox^{2-}, gly^-, ala^-, $malonate^{2-}$).[630–635] Reaction of the $[Rh(en)_2ox]^+$ with various anions in strongly acidic solution was then developed as a convenient route to *cis*-$[Rh(en)_2X_2]^+$ ions (X = Cl, Br, NO_2).[632] The electronic spectra of a rich variety of $[Rh(en)_2XY]^{n+}$ ions are recorded in Table 35, and depending upon the position of the charge-transfer bands, generally consist of two spin-allowed *d–d* transitions (descended from $^1A_1 \rightarrow {}^1T_1(O_h)$ and the higher energy $^1A_1 \rightarrow {}^1T_2$ transitions). The spin-forbidden $^1A_1 \rightarrow {}^3T_1$ transition has been observed in *trans*-$[Rh(en)_2Cl_2]ClO_4$ at −189°C as a very weak shoulder at 469 nm.[644]

Resolution of *cis*-$[Rh(en)_2XY]^{n+}$ has been effected by numerous workers; Basolo isolated $(-)_{535}$-$[Rh(en)_2Cl_2]^+$ as the bromocamphor-π-sulfonate (BCS) salt.[619] Gillard separated $(+)_{589}$-$[Rh(en)_2(C_2O_4)]^+$ ion (initially as the (+)-$[Co(EDTA)]^-$ salt), and found it to be isomorphous with

Table 34 Acid Dissociation Values for $[Rh(en)_2(H_2O)_2]^{3+}$

Complex	pK_1	pK_2	*T*(°C)	*Medium*	*Ref.*
trans-$[Rh(en)_2(H_2O)_2]^{3+}$	4.43	7.81	~20	0.20 M $NaNO_3$	623
	4.73	7.64	26.4	1.0 M $NaClO_4$	624
	4.33	7.72	25	0.5 M $NaClO_4$	625
	4.47	7.91	25.0	1.0 M $NaClO_4$	626
cis-$[Rh(en)_2(H_2O)_2]^{3+}$	5.82	7.98	25	0.01 M $NaClO_4$	627
	6.09	8.08	25	0.5 M $NaClO_4$	627
	6.34	8.24	25.0	1.0 M $NaClO_4$	627

Table 35 Electronic Spectra for $[Rh(en)_2XY]^{n+}$

Complex	*Counterion*	λ_{max} (nm) (ε)	*Ref.*
trans-$[Rh(en)_2Cl_2]^+$	NO_3^-	406 (83), 286 (134)	607
	NO_3^-	406 (75), 286 (130)	619
	Cl^-	406 (79.4), 312sh (79), 289 (123), 242sh (1585), 206 (40 000)	633
	ClO_4^-	406 (84), 286 (130), 240 (1350), 206 (38 900)	621
		407 (75), 286 (125)	634
		407 (82.5), 287 (126.4)	624
		410 (82), 289 (121), 240sh (1700), 297 (39 600)	635
		407 (82.5), 287 (120)	625
cis-$[Rh(en)_2Cl_2]^+$	NO_3^-	352 (147), 295 (189)	607
		352 (155), 295 (180)	619
	ClO_4^-	352 (203), 295 (205)	607
	Cl^-	394sh (100), 352 (191), 295 (186), 238(sh) (1000)	633
		350 (195), 296 (202)	636
		352 (194), 295 (189)	631
trans-$[Rh(en)_2Br_2]^+$	NO_3^-	429 (115), 327sh (91), 278 (2570), 234 (37 000)	633
		425 (100), 276 (1800)	619
		425 (100)	620
	ClO_4^-	425 (120), 276 (3000), 231 (~31 000)	634
		431 (115), 277 (2900), 234 (37 800)	635
		429 (120), 276 (3000)	637
		425 (120), 276 (3000)	634
cis-$[Rh(en)_2Br_2]^+$	Br^-	435sh (79.4), 368 (240), 278sh (1000)	633
		362 (210), 276sh (900)	619
		363 (260), 280sh (900)	636
		366 (255), ~280sh (980)	631
	NO_3^-	367 (258)	637
trans-$[Rh(en)_2I_2]^+$	I^-	465 (263), 340 (24 500), 270 (49 000), 223 (30 000)	633
		462 (260), 341 (10 000), 269 (30 000), 222 (20 000)	619
	ClO_4^-	467 (271), 342 (16 000), *ca.* 270	636, 653
		462 (322), 339 (2178), 269 (45 450), 220sh (~16 820)	621
		462 (260), 340 (14 300), 269 (31 000), 222 (20 000)	638
cis-$[Rh(en)_2I_2]^+$	I^-	444sh (447), 375 (955), 290 (4677), 225 (44 700)	633
		375 (1200)	635
trans-$[Rh(en)_2ClBr]^+$	ClO_4^-	486sh (~18), 419 (94), 270 (1590), 222 (31 700)	621
		486sh (~10), 413 (95), 262 (~1600)	634
trans-$[Rh(en)_2BrI]^+$	ClO_4^-	455 (260), 311 (7500), 253 (41 500)	638
	ClO_4^-	488 (162), 453 (172), 310 (4540), 253 (25 700), 226 (17 600)	621
trans-$[Rh(en)_2ClI]^+$	ClO_4^-	440 (154), 300 (4350), 242 (38 500)	638
		490 (260), 440 (160), 301 (4300), 241 (38 300)	639
trans-$[Rh(en)_2ClI]^+$		486 (243), 440 (151), 298 (3870), 242 (38 100)	621
trans-$[Rh(en)_2ClN_3]^+$	ClO_4^-	377 (560), 263 (9600)	638
trans-$[Rh(en)_2BrN_3]^+$	ClO_4^-	388 (580), 272 (15 100)	638
trans-$[Rh(en)_2IN_3]^+$	ClO_4^-	408, 292	638
trans-$[Rh(en)_2(Cl)(OH_2)]^{2+}$	ClO_4^-	383 (46), 283 (143)	621
		386 (55), 282 (147)	607
		350–380 (26); 280 (73)	640
		384 (56), 283 (143)	640
trans-$[Rh(en)_2(Cl)(OH)]^+$	ClO_4^-	363 (123), 285 (172)	621
		~360 (52), 280 (76)	640
		370 (94), 293 (134)	635
		367 (94), 285 (129)	641
		372 (102), 289 (111)	642
cis-$[Rh(en)_2(OH_2)Cl]^{2+}$	ClO_4^-	325, 285	607
trans-$[Rh(en)_2(Br)(OH_2)]^{2+}$	ClO_4^-	470 (32), 405 (55), 280 (520), 235 (5260)	621
		~465 (26), ~395 (48)	640
		465sh (31), 396 (58), 252sh (603)	641

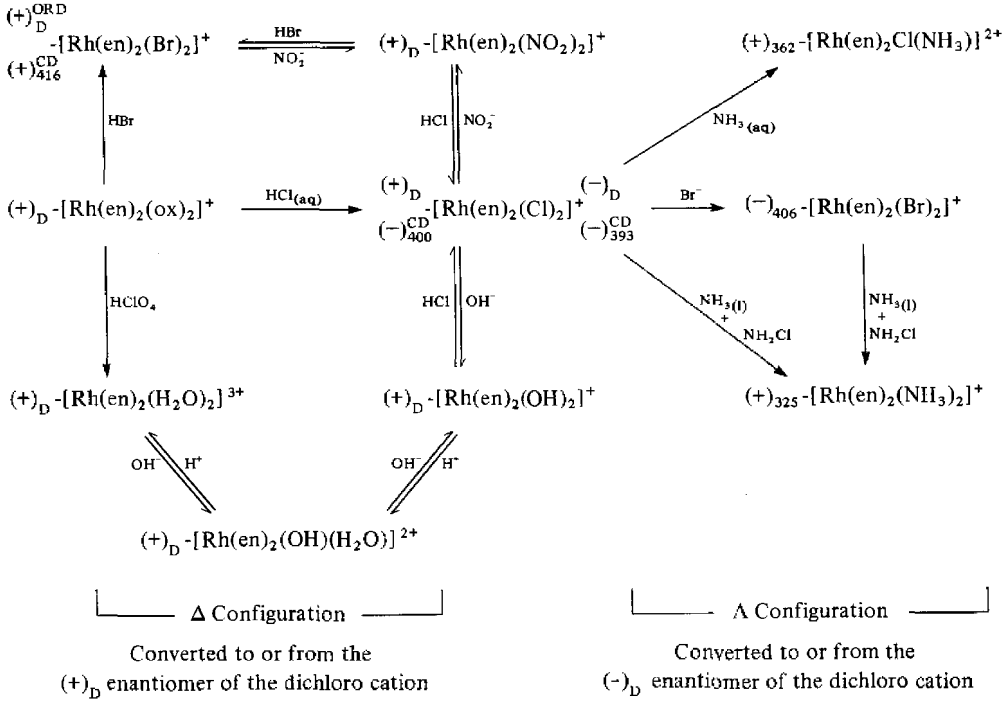
Table 35 (*Continued*)

Complex	*Counterion*	λ_{max} (nm) (ε)	*Ref.*
cis-$[Rh(en)_2(Br)(H_2O)]^{2+}$	ClO_4^-	358 (133)	637
	NO_3^-	357 (175)	637
trans-$[Rh(en)_2(Br)(OH)]^+$	ClO_4^-	370 (138), 275sh (1066)	621
		370 (103), 290sh (~200)	640
		376 (105), 290sh (148)	635
		373 (109), 295sh (146)	641
trans-$[Rh(en)_2(I)(OH_2)]^{2+}$	ClO_4^-	476 (150), ~410, 332sh (~760), 300sh (~1240), 270sh (~2030)	621
		475 (95), 300 (1000)	640
		480 (263), 298 (1417)	641
trans-$[Rh(en)_2(I)(OH)]^-$	ClO_4^-	445 (149), 391sh (~120), 338 (1195), 270 (6072)	621
		450–400 (71), 270 (2150)	640
		440sh (175), 397 (196)	641
trans-$[Rh(en)_2(NH_3)_2]^{3+}$	ClO_4^-	300 (182), 252 (166)	633
cis-$[Rh(en)_2(NH_3)_2]^{3+}$	ClO_4^-	302 (204), 254 (158)	633
trans-$[Rh(en)_2(NH_3)(OH_2)]^{3+}$	ClO_4^-, NO_3^-	302 (120), 259 (122)	621
trans-$[Rh(en)_2(NH_3)Cl]^{2+}$	NO_3^-	342 (80), 275 (113)	607
		342 (95), 275 (120)	619
		345 (105), 275 (132)	633
cis-$[Rh(en)_2(NH_3)Cl]^{2+}$	NO_3^-	342 (150), 276 (195)	619
		344 (151), 276 (182)	633
trans-$[Rh(en)_2(NH_3)Br]^{2+}$	NO_3^-	355 (117), 286sh (158), 244 (912)	633
		357 (116)	637
trans-$[Rh(en)_2(NH_3)I]^{2+}$	I^-	391 (347), 333sh (~479), 276 (4170), 227 (49 000)	633
cis-$[Rh(en)_2(en-H)Cl]^{3+}$	Cl^-	345 (140), 274 (239)	632
trans-$[Rh(en)_2(Cl)(OCO_2)]$	—	376 (118)	641
trans-$[Rh(en)_2(Br)(OCO_2)]$	—	384 (141)	641
trans-$[Rh(en)_2(I)(OCO_2)]$	—	456 (232), 415 (216)	641
trans-$[Rh(en)_2(OCO_2)(OH_2)]^+$	ClO_4^-	345 (101)	625
trans-$[Rh(en)_2(OCO_2)(OH)]$	—	346 (121)	625
trans-$[Rh(en)_2(OCO_2)_2]^-$	—	347 (146)	625
cis-$[Rh(en)_2(OH_2)(OCO_2)]^+$	ClO_4^-	332 (224)	627
cis-$[Rh(en)_2(OCO_2)]^+$	ClO_4^-	327 (312)	627
trans-$[Rh(en)_2(OH_2)_2]^{3+}$	pH = 2	342 (66), 272 (125)	621
		342 (64), 262 (148)	623
		351 (61.6), 274 (130)	624
		350 (60), 274 (130)	625
		351 (58.4), 274 (130)	626
trans-$[Rh(en)_2(OH)(OH_2)]^{2+}$	pH = 6	337 (88), 270 (158)	623
		343 (89), 282 (154)	625
		344 (87), 284 (149)	626
trans-$[Rh(en)_2(OH)_2]^+$		338 (136), 290 (136)	621
	pH = 11	336 (94), 289 (154)	623
		346 (98), 297 (130)	635
		344 (99), 296 (134)	625
		344 (97), 295 (132)	626
cis-$[Rh(en)_2(OH_2)_2]^{3+}$	ClO_4^-	318 (174), 271 (148)	627
		314 (184)	636
		318 (175), 271 (137)	626
cis-$[Rh(en)_2(OH_2)(OH)]^{2+}$	ClO_4^-	323 (199), 283sh (155)	627
		327	636
		323 (203), 280sh (161)	626
cis-$[Rh(en)_2(OH)_2]^+$	ClO_4^-	329 (184), 280 (179)	627
		330 (189)	636
		329 (179), 278.5 (171)	626
trans-$[Rh(en)_2(NO_2)_2]^+$	NO_3^-	330sh (590), 255sh (2400)	619
cis-$[Rh(en)_2(NO_2)_2]^+$	NO_3^-	290 (660), 245sh (3500)	619
trans-$[Rh(en)_2(NCS)Cl]^+$	NCS^-	363 (340)	619
trans-$[Rh(en)_2(N_3)_2]^+$	Cl^-	375 (780), 282 (12 000)	619
trans-$[Rh(en)_2NO_2Cl]^+$	NO_3^-	310sh (310), 255–265sh (860)	619
trans-$[Rh(en)_2H_2]^+$	NO_3^-	340 (250), 290 (500)	620
trans-$[Rh(en)_2(H)Cl]^+$	NO_3^-	365 (84)	620
trans-$[Rh(en)_2(H)Br]^+$	NO_3^-	371 (160)	620
trans-$[Rh(en)_2(H)I]^+$	NO_3^-	385 (220)	620
trans-$[Rh(en)_2(H)(OH)]^+$	NO_3^-	295 (323), 257 (272)	675

Table 35 (*Continued*)

Complex	*Counterion*	λ_{max} (nm) (ε)	*Ref.*
	[Rh(en)$_2$(bidentate)]$^{n+}$ complexes		
$[Rh(en)_3]^{3+}$	NO_3^-	301 (238), 255 (191)	610
		301 (243), 255 (194)	607
		306 (251), 257 (246)	606
		300 (250)	608
		350sh, 296 (244), 253 (195)	609
$[Rh(en)_2C_2O_4]^+$	ClO_4^-	325 (260)	659
		325 (270)	630
		325.5 (253)	631
$[Rh(en)_2(gly)]I_2$	—	316 (250), 268 (286)	643
$[Rh(en)_2(S\text{-ala})]I_2$	—	316 (330), 270 (335)	643
$[Rh(en)_2(S\text{-val})]I_2$	—	316 (298), 268 (350)	643
$[Rh(en)_2(S\text{-leu})]I_2$	—	316 (286), 265 (363)	643
$[Rh(en)_2(S\text{-ser})]I_2$	—	316 (335), 266 (350)	643
$[Rh(en)_2(2S,3R\text{-thr})]I_2$	—	316 (320), 266 (355)	643
$[Rh(en)_2(S\text{-met})]I_2$	—	317 (285), 265 (430)	643
$[Rh(en)(enMe)_2]I_3$	—	345 (300), 270 (900)	618
$[Rh(enMe)_2]I_3$	—	352 (700), 276 (1800)	618
$[Rh(en)\{(en-H)_2SO\}]Cl_2I$	—	450sh (150), 348 (500), 288 (900)	618
$[Rh(en)\{(en-H)_2SO_2\}]Cl_2I$	—	455 (280), 297 (500)	618
$[(en)_2Rh(OH)_2Rh(en)_2]^{4+}$	ClO_4^-, Br^-	331 (530)	628
$[(en)_2(H_2O)Rh(OH)Rh(en)_2(H_2O)]^{5+}$	ClO_4^-	329 (590), 273 (553)	628

$(-)_{589}$-$[Co(en)_2(ox)][(+)[Co(EDTA)]$, implying the L (now called the Δ) configuration for $(+)_{589}$-$[Rh(en)_2ox]^+$.[636] The $(+)_{589}$-$[Rh(en)_2(NO_2)_2]^+$ ion was also separated by the same technique. Spontaneous resolution can be observed if a solution containing $(+)$-$[Rh(en)_2ox]^+$ is added to a saturated solution of racemic $[Rh(en)_2ox]Cl$, as $(+)_{589}$-$[Rh(en)_2ox]Cl$ precipitates; a solution of $(-)_{589}$-$[Co(en)_2ox]^+$ can also be used to initiate the precipitation of $(+)_{589}$-$[Rh(en)_2ox]Cl$.[636] Bailar[633] also generated $(-)_{589}$-$[Rh(en)_2Cl_2]^+$ as the BCS salt, and showed that ammoniations (in liquid and aqueous ammonia) also occur with retention of configuration. Such substitution studies (summarized in Scheme 17), and a comparison of the electronic and CD spectra with their Co analogs has allowed the assignment of absolute configuration for a variety of *cis*-$[Rh(en)_2XY]^{n+}$ ions (Table 36).



Scheme 17

Table 36 Electronic and Optical Spectra of *cis*-$[Rh(en)_2XY]^+$ Complexes (Less Soluble Diastereomer)

Compound	*Electronic* λ_{max}(nm) (ε)	*ORD*[a] $[\alpha]_D^o$	*Circular dichroism* λ	$(\Delta\varepsilon)_{max}$	*Absolute configuration*	*Ref.*
$[Rh(en)_3]^{3+}$	300 (250)	(+)	320	−2.01	Δ	608
			288	+0.09		
	306 (251)	−79	320	+2.0	Λ	605
			287	−0.1		
	257 (246)		258	+0.8		
$[Rh(en)_2Cl_2]^+$	—	—	446	−0.10	Λ	633
	394 (100)		394	−0.52		
	352 (191)		345	+0.33		
	295 (186)		304	+0.72		
	350 (195)	(+)	400	+0.54	Δ	636
	296 (202)		307	−0.82		
$[Rh(en)_2Br_2]^+$	—	—	467	−0.15	Λ	633
	435 (79)		406	−0.62		
	368 (240)		350	+0.62		
	278sh (1.0×10^3)		303	+0.20		
	—	(+)	480	−0.17		
	363 (260)		416	+0.28	Δ	636
			353	−0.47		
	280(sh) (900)		310	−0.15		
$[Rh(en)_2(NH_3)_2]^{3+}$	302 (204)	—	325	+0.48	Λ	633
			293	−0.06		
	254 (158)		266	+0.20		
$[Rh(en)_2(NH_3)Cl]^{2+}$	344 (151)	—	362	+0.51	Λ	633
			291	+0.77		
	276 (182)		~263	+0.2		
$[Rh(en)_2(ox)]^+$	325 (270)	(+)	348	−2.88	Δ	636
			260	−1.25		
$[Rh(en)_2(NO_2)_2]^+$	290sh (660)	(+)	300	−0.8	Δ	636
	245sh (3500)					
$[Rh(en)_2(H_2O)_2]^{3+}$	314 (184)	(+)	314	−0.63	Δ	636
$[Rh(en)_2(H_2O)(OH)]^{2+}$	327	(+)	320	−0.99	Δ	636
$[Rh(en)_2(OH)_2]^+$	330 (189)	(+)	410	+0.03	Δ	636
			335	−0.38		
	276 (189)		272	−0.29		
$[Rh(en)_2gly]I_2$	316 (250)	+39	335	−2.31	Λ	643
	268 (286)		260	−0.38		
$[Rh(en)_2(S\text{-ala})]I_2$	316 (330)	+37	335	−2.31	Λ	643
	270 (286)		265	−0.59		
$[Rh(en)_2(S\text{-val})]I_2$	316 (298)	+36	335	−2.34	Λ	643
	268 (350)		265	−0.61		
$[Rh(en)_2(S\text{-leu})]I_2$	316 (286)	+35	335	−2.35	Λ	643
	265 (363)		265	−0.62		
$[Rh(en)_2(S\text{-ser})]I_2$	316 (335)	+37	335	−2.36	Λ	643
	266 (350)		265	−0.51		
$[Rh(en)_2\{(2S,3R)\text{-thr}\}]I_2$	316 (320)	+36	335	−2.37	Λ	643
	266 (335)		265	−0.49		
$[Rh(en)_2(S\text{-met})]I_2$	317 (285)	+27	342	−1.64	Λ	643
			293	−0.16		
			260	−0.09		

[a] Rotation, at D line of sodium, or the sign of the rotation at listed wavelength. [b] Absolute configurations based on the helical model proposed by IUPAC.[645]

Amino acid complexes of Rh^{III} are relatively rare,[646] but some $[Rh(en)_2(AB)]^{n+}$ complexes (AB = glycino, alanino, (−)-leucine, (−)-methionine, (−)-valine, (−)-phenylalanine, (−)-tyrosine) have been prepared by reacting equimolar mixtures of *cis* or *trans*-$[Rh(en)_2Cl_2]^+$, OH^- and the appropriate amino acid in an ethanol/water (1/3) solution.[647] In the absence of the reducing ethanol, no reaction is observed; the preparation of the gly and ala complexes using BH_4^- catalysis has been reported.[630] Resolution of such cations, and a comparison of their CD spectra with $(-)_{589}$-$[Rh(en)_3]^{3+}$ (with the Λ configuration) implies that all the $(-)_{589}$-$[Rh(en)_2AB]^+$ ions also have the Λ configuration.[643] The electronic and CD spectra of the methionine complexes suggest that the methionine is bonded through the N and O atoms.[643]

While electronic, IR and ^1H NMR spectra have been used to assign isomeric form for $[Rh(en)_2XY]^{n+}$ ions, ^{13}C NMR has recently been used to unambiguously assign their geometries.[607,648] The ^{13}C chemical shifts for several such compounds are given in Table 37. The *cis* species show more complex spectra than the *trans* isomers, and the ^{13}C signal in *trans*-$[Rh(en)_2XY]^{n+}$ is

Table 37 ^{13}C Chemical Shifts of some $[Rh(en)_2XY]^{n+}$ Complexes (from ref. 607)

Compound	*δ* (p.p.m.)	*Compound*	*δ* (p.p.m.)
$[Rh(en)_3]^{3+}$	46.36	*cis*-$[Rh(en)_2Cl_2]^+$	47.25 46.15
trans-$[Rh(en)_2Cl_2]^+$	45.68	*cis*-$[Rh(en)_2(H_2O)Cl]^{2+}$	47.78 47.07 45.98 45.20
trans-$[Rh(en)_2(H_2O)Cl]^{2+}$	45.75	*cis*-$[Rh(en)_2(NH_3)Cl]^{2+}$	47.07 46.27 45.81 (double intensity)
trans-$[Rh(en)_2(NH_3)Cl]^{2+}$	45.64	*cis*-$[Rh(en)_2(enH)Cl]^{3+}$	47.15 46.56 45.99 45.94 43.30 49.59 (broad)

relatively independent of the nature of the non-amine ligands, while it is quite sensitive to the nature of X and Y in *cis*-$[Rh(en)_2XY]^{n+}$ ions.[607] Few X-ray structures of these well-characterized ethylenediamine complexes have been reported, but an interesting geometry is displayed by the $HgCl_2$ adduct of *cis*-$[Rh(en)_2Cl_2]Cl$. It has a layered structure with each Hg atom in an environment of six Cl atoms, two each from the adjacent *cis*-$[Rh(en)_2Cl_2]^+$ moieties.[649]

Numerous studies on the substitutions at various $[Rh(en)_2XY]^{n+}$ complexes (equation 123) have been reported. Basolo and co-workers[555] presented a kinetic study of a large variety of $[Rh(N)_4Cl_2]^+$ complexes (*cis* and *trans* complexes for $N_4 = (en)_2$, $(tetrameen)_2$, $(C_2O_4)_2$; *trans* complexes for $N_4 = (NH_3)_4$, $(m\text{-bn})_2$, $(\pm\text{-bn})_2$; and *cis*-$[Rh(trien)Cl_2]^+$, and $[Rh(NH_3)_5Cl]^{2+}$). As with the Co^{III} analogs, the nature and concentration of the incoming nucleophile has little effect on the rate of Cl^- release; for example, the rate constant for Cl^- release from *trans*-$[Rh(en)_2Cl_2]^+$ is between 4.0 and 5.2 ($\times 10^{-5}\,s^{-1}$) for anation by OH^-, NO_2^-, I^-, $^{36}Cl^-$, NH_3 and thiourea.[555] Unlike Co^{III}, however, the Rh^{III} complexes display rates of chloride release which are insensitive to the total charge on the complex, not dramatically catalyzed by hydroxide ions, and which appear to be completely stereoretentive. Basolo suggested that the mechanism for these substitutions is probably more associative than the dissociative route proposed for the Co^{III} analogs, and that a seven-coordinate Rh^{III} intermediate may be involved.

$$trans\text{-}[Rh(en)_2XY]^{n+} + Z^- \longrightarrow trans\text{-}[Rh(en)_2XZ]^{n+} + Y^- \qquad (123)$$

Z = Cl, Br, I; X, Y = halide, H_2O, OH^-, or NH_3

Poë and co-workers have extensively studied the thermodynamics, kinetics and the *trans* effect in the reactivity of such complexes.[623,634,635,638,640,650,653] The thermodynamics of the successive anations of $[Rh(en)_2X(H_2O)]^{n+}$ by halogens suggests that the Rh center is a marginally soft acid, and that its softness is increased by the coordination of a soft base (such as I^-) in a position *trans* to the reaction site; a halide ligand weakens the metal–ligand bond *trans* to itself, and an I^- causes a more dramatic weakening than a Br^-, which has more effect than a coordinated Cl^-.[634,638–640] The spectrophotometrically obtained thermodynamic parameters are summarized in Table 38.

The kinetic parameters for reactions in acidic solution are consistent with the thermodynamic results, and they suggest the *trans*-labilizing series: $I^- > Br^- > Cl^- \approx NH_3 > H_2O$ (Table

Table 38 Thermodynamic Parameters for Halogen Substitutions (Anations and Aquations) of *trans*-$[Rh(en)_2XY]^+$

Starting complex	*Reactant*		*Rh product*	*K*	*ΔH°* (kJ mol^{-1})	*Ref.*
			Anations (at 90°C)			
$[Rh(en)_2Cl_2]^+$	+ Br^-	⇌	$[Rh(en)_2ClBr]^+$	1.9[a]	~0 ± 2.5	634
$[Rh(en)_2Cl_2]^+$	+ I^-	⇌	$[Rh(en)_2ClI]^+$	7.0	−3.8 ± 7.9	638
$[Rh(en)_2ClBr]^+$	+ Br^-	⇌	$[Rh(en)_2Br_2]^+$	0.8[a]	~0 ± 2.5	634
$[Rh(en)_2ClBr]^+$	+ I^-	⇌	$[Rh(en)_2ClI]^+$	—	−0.4 ± 3.3[b]	638
$[Rh(en)_2ClBr]^+$	+ I^-	⇌	$[Rh(en)_2BrI]^+$	—	−10.9 ± 3.3[b]	638
$[Rh(en)_2ClI]^+$	+ I^-	⇌	$[Rh(en)_2I_2]^+$	2.2	−26 ± 1.7	638
$[Rh(en)_2ClI]^+$	+ Br^-	⇌	$[Rh(en)_2BrI]^+$	—	−11.7 ± 2.1[b]	638
$[Rh(en)_2Br_2]^+$	+ I^-	⇌	$[Rh(en)_2BrI]^+$	7.0	−10.9 ± 1.7	638
$[Rh(en)_2BrI]^+$	+ I^-	⇌	$[Rh(en)_2I_2]^+$	1.9	−14.2 ± 1.3	638
			Aquations (K values at 50°C)			
$[Rh(en)_2Cl_2]^+$	+ H_2O	⇌	$[Rh(en)_2Cl(H_2O)]^{2+}$	0.0020	−2.5 ± 1.7	640
$[Rh(en)_2ClBr]^+$	+ H_2O	⇌	$[Rh(en)_2Cl(H_2O)]^{2+}$	0.0006	+13.4 ± 1.7	640
$[Rh(en)_2ClBr]^+$	+ H_2O	⇌	$[Rh(en)_2Br(H_2O)]^{2+}$	0.0006	+5.0 ± 2.9	640
$[Rh(en)_2ClI]^+$	+ H_2O	⇌	$[Rh(en)_2I(H_2O)]^{2+}$	0.0010	+6.7 ± 2.1	640
$[Rh(en)_2BrI]^+$	+ H_2O	⇌	$[Rh(en)_2I(H_2O)]^{2+}$	0.0006	+18.8 ± 1.3	640
$[Rh(en)_2I_2]^+$	+ H_2O	⇌	$[Rh(en)_2I(H_2O)]^{2+}$	0.0002	+29.7 ± 2.1	640
$[Rh(en)_2(OH)I]^+$	+ H_2O	⇌	$[Rh(en)_2(OH)H_2O]^{2+}$	0.002	+17.1 ± 0.8	639

[a] At 85°C. [b] 'Indirectly determined' parameter.

Table 39 Kinetic Parameters for the Anations

trans-$[Rh(en)_2(H_2O)L]^{2+}$ + X^- ⟶ *trans*-$[Rh(en)_2(L)X]^+$ + H_2O

Trans ligand (L)	*Anating ligand (X^-)*	k^a ($M^{-1}s^{-1}$)	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}mol^{-1}$)	*Ref.*
Cl	Cl	7.2×10^{-4}	106 ± 1.3	21.8 ± 4.2	640
Cl	Br	6.2×10^{-4}	102 ± 1.3	8.4 ± 4.6	640
Br	Cl	6.8×10^{-3}	92.0 ± 2.1	2.1 ± 6.3	640
Br	Br	5.3×10^{-3}	93.3 ± 1.3	1.7 ± 4.2	640
I	Cl	8.5×10^{-1}	81.6 ± 1.7	2.5 ± 5.0	640
I	Br	7.4×10^{-1}	77.8 ± 1.3	-5.9 ± 4.6	640
I	I	5.8×10^{-1}	75.3 ± 1.3	1.26 ± 4.6	640
NH_3	Cl	3.4×10^{-4}	105.2 ± 0.8	13.8 ± 2.6	623
OH	I	7.3×10^{-3}	99.6 ± 0.6	21.8 ± 2.0	623
H_2O	Br	1.5×10^{-4}	133.8 ± 0.9	95.6 ± 2.6	623

[a] At 50°C.

39).[623,640,650,651] Poë reminds us that to realistically compare the kinetic *trans* effect of different ligands, one cannot just consider kinetic parameters, but can only compare reactions in which the thermodynamic driving forces are the same; comparisons of ΔH^* (the kinetic term) with the thermodynamic ΔH° can be used to derive a kinetic *trans*-effect series.[651]

Table 40 demonstrates what little effect the incoming nucleophile has on the reaction rate, as well as the large role played by the *trans* ligand. (The rate of halide anation[650] was subsequently taken to be identical to that of direct aquation,[635,639,640,653] although specific data on aquations are not presented.) When the anating ligand has a high kinetic *trans* effect, such as I^-, no evidence of an intermediate aquahalo complex is observed, and the anations proceed directly, with retention of isosbestic points, to the diiodo complex.[650] The similarity of the anation activation parameters to those for the analogous reactions of the pentaammine complexes supports the associative model.[531] Substitutions at *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ appear unique. However, as the large entropy of activation suggests, a different mechanism (presumably a more dissociative one) operates for this complex.[640] [Chloride anation of $[Rh(H_2O)_6]^{3+}$ is also thought to involve a dissociative mechanism (*vide infra*).[654]] For the anation of *trans*-$[Rh(en)_2XI]^+$ (X = Cl or Br), an interesting catalyzed reaction was noted,[640] but not pursued.

Basolo[555] noted that reactions of Rh^{III} amine complexes were not dramatically accelerated by hydroxide ion, but did show that substitutions in base do follow the standard $k_{obs} = k_1 + k_2[OH^-]$ format, with k_1 representing the first-order aquation observed in acidic solution, and k_2 representing the second-order base-catalyzed path. Poë has studied the kinetics of the base hydrolysis of a variety of *trans*-$[Rh(en)_2XY]^{n+}$ complexes (Table 41). Studies on the base hydrolyses of *trans*-$[Rh(en)_2(OH)X]^+$ (X = Cl, Br, I) showed that the coordinated hydroxide has an intrinsic kinetic *trans* effect comparable to that of Cl^- but that its position in a thermodynamic *trans* effect series is much higher.[635] For *trans*-$[Rh(en)_2X_2]^+$ (X = Cl, Br), virtually complete *trans* → *cis* isomerization occurs upon hydrolysis in base, and *ca.* 50% isomerization is observed when X = I.[653] No such

Table 40 Kinetic Parameters for the Substitution

$[Rh(en)_2XL]^{n+}$ + Y ⟶ $[Rh(en)_2XY]^{n+}$ + L

Trans ligand (X)	*Leaving ligand (L)*	*Entering ligand (Y)*	k^a ($M^{-1}s^{-1}$)	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}mol^{-1}$)	*Ref.*
Cl	Cl	I	1.39×10^{-6}	104 ± 2.5	-35.6 ± 7.9	651
Cl	Br	Cl	3.34×10^{-7}	115.6 ± 0.5	-12.1 ± 4.6	651
Br	Br	I	5.19×10^{-6}	104 ± 0.63	24.7 ± 2.1	651
Br	Br	CN	5.45×10^{-6}	108 ± 0.84	12.6 ± 2.5	651
Br	Br	F	7.25×10^{-6}	106 ± 0.1	18.0 ± 6.3	651
Br	Cl	Br	3.94×10^{-6}	97.0 ± 2.0	-49.0 ± 6.3	651
I	Cl	Br	8.16×10^{-4}	87.2 ± 1.1	-35 ± 3.3	651
I	Cl	I	8.84×10^{-4}	91.3 ± 1.1	-22 ± 3.8	651
I	Br	Cl	4.36×10^{-4}	96.7 ± 1.3	-10.9 ± 3.3	651
I	Br	I	5.24×10^{-4}	96.1 ± 1.3	-11.3 ± 1.3	651
I	I	X[b]	1.2×10^{-4}	107 ± 3.1	$+10 \pm 12.6$	651
OH	I	H_2O	1.2×10^{-3}	117 ± 0.67	22.3 ± 2.0	639
OH	H_2O	I	7.3×10^{-4}	99.6 ± 0.63	$+21.8 \pm 2.0$	639

[a] At 50°C. [b] Data are an average for reactions when entering ligand is either Cl^- or Br^-.

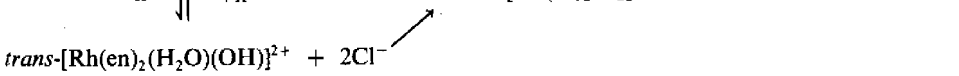
Table 41 Kinetic Parameters for the Base Hydrolysis of *trans*-$[Rh(en)_2XY]^{n+}$

Starting complex	k_1^a (s^{-1})	ΔH_1^* ($kJ\,mol^{-1}$)	ΔS_1^* ($J\,K^{-1}\,mol^{-1}$)	k_2^a ($M^{-1}s^{-1}$)	ΔH_2^* ($kJ\,mol^{-1}$)	ΔS_2^* ($J\,K^{-1}\,mol^{-1}$)	*Ref.*
$[Rh(en)_2Cl_2]^+$	5.53×10^{-6}	109 ± 2.6	-21.5 ± 7.7	3.85×10^{-6}	146.7 ± 5.9	87.9 ± 17.3	653
	—	103 ± 1	-38 ± 4	—	—	—	650
$[Rh(en)_2Br_2]^+$	1.79×10^{-5}	107.9 ± 1.4	-13.4 ± 4	1.68×10^{-5}	140 ± 7	84.8 ± 7.7	653
	—	105 ± 1	-21 ± 4	—	—	—	650
$[Rh(en)_2I_2]^+$	3.84×10^{-4}	102 ± 0.5	-5.6 ± 1.6	1.81×10^{-4}	130 ± 3	73.9 ± 9.0	653
	—	105 ± 1	$+4 \pm 4$	—	—	—	650
$[Rh(en)_2(OH)Cl]^+$	4.7×10^{-5}	105 ± 0.63	-2.8 ± 1.9	1.87×10^{-5}	108 ± 2.9	-2 ± 8.8	635
$[Rh(en)_2(OH)Br]^+$	4.7×10^{-5}	109 ± 0.79	8.0 ± 2.4	1.50×10^{-5}	105 ± 5.4	-13 ± 16	635

[a] At 50°C.

isomerization is observed upon base hydrolysis of the halohydroxy complexes.[635] It has been suggested[555,655] that an acidic N—H group must be coordinated *trans* to the reaction site in order for k_2 (the OH^- dependent term) to be significant, but *trans*-$[Rh(en)_2Cl(py)]^{2+}$ has a significant $[OH^-]$ dependent term, as do the *trans*-$[Rh(en)_2XY]^{n+}$ ions (Table 41).

Pavelich[624] has presented a thorough study of the chloride anation of *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ (equation 124), which implies that the conjugate base form (*trans*-$[Rh(en)_2(OH)(H_2O)]^{2+}$) is much more reactive than had previously been thought. Between $[H^+]$ values of 0.02 M to 0.2 M, the observed rate is strongly, and linearly, proportional to $[H^+]^{-1}$. Presumably due to the strong *trans*-labilizing influence of the coordinated hydroxide, the aquahydroxo complex is calculated to be at least three orders of magnitude more reactive than the diaqua ion. Pavelich calculated that at a pH of 1.7 ($[H^+]^{-1} = 50\,M^{-1}$), less than 1% of the complex is deprotonated, but that 95% of the anation still proceeds through this reactive aquahydroxo complex. Addition of the second chloride is 20 times faster still, presumably due to the *trans* influence of the coordinated chloride, so only the dichloro product is observed. The rate of chloride anation is not linearly dependent on $[Cl^-]$. This non-linearity was also observed by Poë for bromide anations of the same complex[623] and is presumed to be due to ion-pairing to both the diaqua (3+) and aquahydroxo (2+) cations. Analysis of this deviation from linearity in the Cl^- system could not be fitted to an interchange stoichiometric mechanism rate law, but could be fitted to a dissociative stoichiometric mechanism rate law. Interestingly, the data were similar to Poë's, but Pavelich reaches the opposite conclusion, and suggests that *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$, and its conjugate base, react *via* a dissociative mechanism.[624]



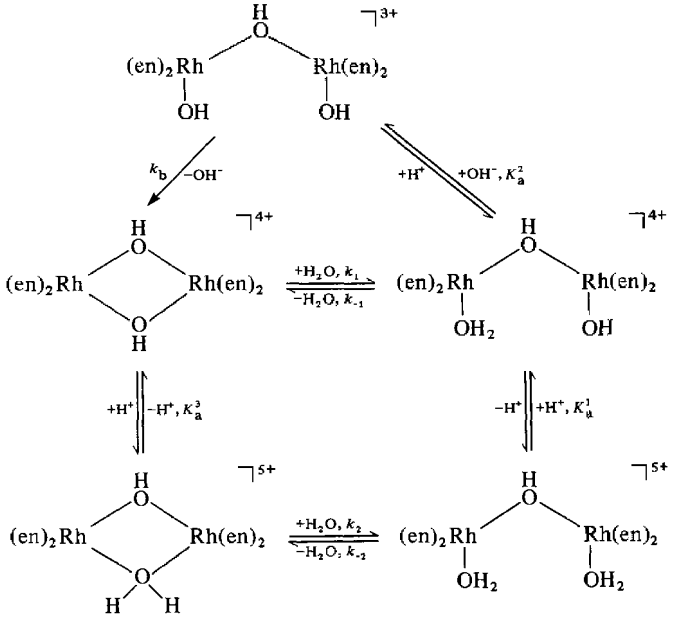
(124)

Pavelich also points out that there may be valid chemical reasons for the variety of different mechanisms which have been postulated for seemingly straightforward substitutions at Rh^{III} centers. Associative interchanges have been proposed for the pentaammine cations (Section 48.6.2.1.i). Both associative and dissociative interchanges have been proposed for the $[Rh(en)_2XY]^{n+}$ series, and dissociative interchanges, as well as purely dissociative paths, have been proposed for the hexaqua and hexachloro species (Sections 48.6.5.1 and 48.6.7). Such variation in mechanism suggests that the inert ligands have a profound effect on the substitution mechanism of a given rhodium complex. Pavelich speculates that when Rh^{III} is compared to Co^{III}, the increased polarizability of the Rh center (or perhaps its softness) makes it more susceptible to electronic changes induced by the innocent ligands, so that while a wide range of Co^{III} or Cr^{III} complexes may display similar substitution mechanisms, differing mechanisms can be expected for the analogous Rh^{III} or Ir^{III} complexes.[624]

Following from their work on the reactions of pentaammine complexes in liquid ammonia[581–583], Balt and Jelsma studied the kinetics of the ammoniation of some dihalobis(ethylenediamine)-rhodium(III) complexes.[656] While *trans*-$[Rh(en)_2Cl_2]^+$ proved 'too stable toward ammoniation to be studied', the *cis* isomer and *trans*-$[Rh(en)_2I_2]^+$ were both sufficiently reactive. Both cations react in two distinct steps to form $[Rh(en)_2(NH_3)_2]^{3+}$; substitution of the dichloro species goes with retention of the *cis* configuration, while the geometric configuration of the $[Rh(en)_2(NH_3)_2]^{3+}$ formed from the diiodo ion was not determined. In excess NH_4ClO_4, both displayed the rate expression observed in the pentaammine studies: $k_{obs} = k_s + k_b[NH_4^+]^{-1}$. For these complexes, k_s, the rate constant for the 'spontaneous' reaction, is *ca.* 0 for both reactions, and $k_b = k_1 K_{CB}$, where k_1 is the

constant for the rate-determining step, and K_{CB} is the equilibrium constant for the acid–base preequilibrium. (When no NH_4ClO_4 is added, an unusual rate expression is obtained: $k_{obs} = k_1(K_{CB})^{\frac{1}{2}}[Rh]^{-\frac{1}{2}}$.) As observed for the pentaammine complexes, the ΔS^* for base hydrolysis is lower for Rh^{III} than for the Co^{III} analogs, consistent with a more associative conjugate-base mechanism for the Rh complexes.[656]

There are few examples of acid-catalyzed substitutions of $[Rh(en)_2XY]^{n+}$ complexes; attempts to detect H^+-catalyzed aquation of *trans*-$[Rh(en)_2(NO_2)_2]^+$ were unsuccessful.[657] Hancock and co-workers found acid-catalyzed substitutions in a kinetic study of the dinuclear diol, Δ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2]^{4+}$.[628] The synthesis, 'thermal deaquation' and structure of this ion are analogous to $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]^{4+}$,[595] and the Δ,Λ configuration of the ethylenediamine complex is inferred from X-ray powder patterns, which show it to be isomorphous with the well-characterized Co^{III} and Cr^{III} analogs.[658] In aqueous solution, a ring opening/closing equilibrium is established, as represented in Scheme 18, with rate and equilibrium constant values given in Table 42. The Rh^{III} system is similar to the analogous Cr^{III} system, except that Rh^{III} displays acid catalysis (as does the Co complex). The similarity in ΔH^* and ΔS^* for the k_{-1} and k_{-2} paths suggests that similar mechanisms are operating in the two reactions, and since the nucleophiles are so different (OH^- and OH_2, respectively), it is argued that a dissociative mechanism seems likely. The two pK_a values of the diaquamonool differ by seven orders of magnitude ($pK_a^1 = 2.37$ and $pK_a^2 = 9.13$), too large a difference to be rationalized on the basis of charge considerations (note pK_a values in Tables 31 and 34), and Hancock suggests that the aquahydroxomonool is stabilized by intramolecular hydrogen bonding, as represented in (**47**).[628] A base-catalyzed path was also observed, but it only becomes significant at pH values above 9.5.

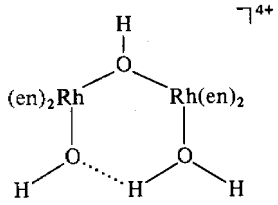


Scheme 18

Table 42 Parameters for the Equilibration of $[(en)_2Rh(OH)_2Rh(en)_2]^{4+}$ (ref. 628)[a]

Kinetic parameters		
Spontaneous path		
$k_1 = 4.6(1) \times 10^{-4}\,s^{-1}$		$k_{-1} = 4.1(1) \times 10^{-5}\,s^{-1}$
$\Delta H_1^* = 86(3)\,kJ\,mol^{-1}$		$\Delta H_{-1}^* = 101\,kJ\,mol^{-1}$
$\Delta S_1^* = -19(8)\,J\,K^{-1}\,mol^{-1}$		$\Delta S_{-1}^* = 9(9)\,J\,K^{-1}\,mol^{-1}$
Acid path		
$k_2/K_{a3} = 0.134(3)\,M^{-1}\,s^{-1}$		$k_{-2} = 5.1 \times 10^{-5}\,s^{-1}$
$\Delta H^* - \Delta H^\circ = 0.134(3)\,M^{-1}\,s^{-1}$		$\Delta H_{-2}^* = 100\,kJ\,mol^{-1}$
$\Delta S^* - \Delta S^\circ = -68(7)\,J\,K^{-1}\,mol^{-1}$		$\Delta S_{-2}^* = 9(9)\,J\,K^{-1}\,mol^{-1}$
Base path (0.1 M NaOH)		
$k_b = 2.10(2) \times 10^{-3}\,s^{-1}$		
Thermodynamic parameters		
$pK_a^1 = 2.372(7)$	$\Delta H^\circ = 28(4)\,kJ\,mol^{-1}$	$\Delta S^\circ = 49(13)\,J\,K^{-1}\,mol^{-1}$
$pK_a^2 = 9.128(7)$	—	—
$K_1 = 11.2(5)$	$\Delta H^\circ = -14(3)\,kJ\,mol^{-1}$	$\Delta S^\circ = -28(8)\,J\,K^{-1}\,mol^{-1}$

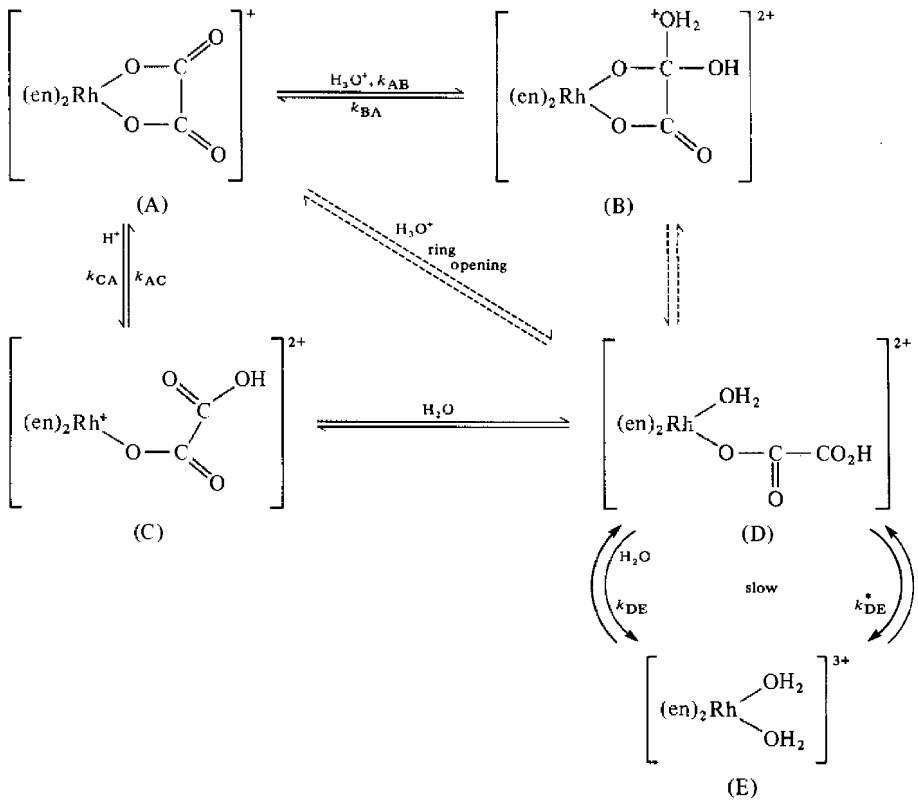
[a] 25°C, $\mu = 1.0$ M $(Na,H)ClO_4$, see Scheme 18 for labeled reactions.



(47)

Acid-catalyzed aquations were also observed in a major kinetic study of $[Rh(en)_2(ox)]^+$.[659] The overall reaction studied is given in equation (125), which belies the complexity of the system. All four of the oxalate oxygen atoms exchange with the solvent, but at two kinetically distinct rates. The reactions involved are summarized in Scheme 19, which assumes that there is no direct exchange between an 'inner' oxygen (coordinated to the Rh), and the solvent; an 'inner' oxygen must become an 'outer' oxygen before exchange can occur. There are three possible acid-catalyzed paths for outer oxygen/solvent exchange: two which involve a ring opening step (A → D → A or A → B → D → A, and A → C → A), and one which does not require ring opening (A → B → A). A two-term rate law expression, $k = k_2[H^+] + k_3[H^+]^2$ is needed to describe the reaction shown in equation (125).

$$[Rh(en)_2(ox)]^+ + 2H_3O^+ \rightleftharpoons \textit{cis}\text{-}[Rh(en)_2(H_2O)_2]^{3+} + H_2ox \qquad (125)$$



Scheme 19

Comparison of the kinetic parameters for the reactions in Scheme 19 to those for the analogous reactions of the anionic $[Rh(ox)_3]^{3-}$ (Section 48.6.5.2) is instructive.[660–662] The kinetic parameters (Table 43) for the exchange of the outer oxygens are similar for the two systems, implying that the net charge on the complex has little influence on the kinetics of that step. For the tris(oxalato) complex, the inner/outer oxygen exchange is always slower than the exchange of the outer oxygens with the solvent; in contrast, the rates of inner/outer interchange and outer/solvent exchange are similar for $[Rh(en)_2(ox)]^+$, and reach a crossover point at about 60°C. The faster inner/outer exchange in the latter system is presumably due to the more favourable ΔS^* values (Table 43). In both systems, acid hydrolysis of the oxalato ligand is much slower than the inner/outer exchange at any temperature. For the tris(oxalato) anion aquation proceeds to completion, while with

Table 43 Kinetic Parameters for Oxygen-exchange Processes at 25°C

Complex	*Process*	k ($M^{-1}s^{-1}$)	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}mol^{-1}$)	*Ref.*
$[Rh(en)_2(ox)]^+$	Outer-oxygen–solvent exchange	3.5×10^{-5}	71.5 ± 1.3	-90.4 ± 4.2	659
	Inner/outer oxygen exchange	1.0×10^{-5}	109 ± 4.2	$+24 \pm 17$	659
	Acid hydrolysis	$k_2 = 1.08 \times 10^{-6}$	101 ± 8.4	-21 ± 25	659
	$(k = k_2[H^+] + k_3[H^+]^2)$	$k_3 = 3.0 \times 10^{-6}$ ($M^{-2}s^{-1}$)	75.3 ± 10	-97.9 ± 8	
$[Rh(ox)_3]^{3-}$	Outer-oxygen–solvent exchange	9.2×10^{-5}	70.7 ± 8.4	-83.7 ± 25	660
	Inner/outer oxygen exchange	1.83×10^{-6}	97.9 ± 8.4	-26 ± 25	660
	Acid hydrolysis	$k_2 = 2.5 \times 10^{-8}$	107 ± 8.4	-33 ± 25	660
	$(k = k_2[H^+] + k_3[H^+]^2)$	$k_3 = 1.49 \times 10^{-7}$ ($M^{-2}s^{-1}$)	108 ± 8.4	-12 ± 25	

$[Rh(en)_2(ox)]^+$ equilibrium is established after about 70–75% of the oxalate is aquated, presumably due to the coulombic attraction between ox^{2-} (or Hox^-) and the cationic ethylenediamine complex.[659]

A thorough analysis of the complex kinetics for this system is inappropriate here, and despite the lack of direct evidence for the intermediates in Scheme 19, the predicted acid dependence was observed. (Interestingly, aquation of the analogous $[Co(en)_2(ox)]^+$ ion is not acid catalyzed.[663]) A relative ordering of the reaction rates gives: (a) $k_{CA} \gg k_{BA} > k_{AB} > k_{AC} > k_{DE} \approx k^*_{DE}$; and (b) $k_{CA} \gg k_{CD} > k_{DC} > k_{DE}$.

The chemistry of aqueous solutions of CO_2 in the presence of aquated transition metal complexes has been extensively studied by a group of researchers led by Harris, Palmer and vanEldik, and they have presented extensive kinetic studies on the carboxylation and decarboxylation of a variety of bis(ethylenediamine)carbonato complexes of Rh^{III}.[625,627,641] The decarboxylation of $[Rh(en)_2(CO_3)]^+$ (bidentate carbonate), occurs according to the two-term rate expression $k_{obs} = k_0 + k_1[H^+]$. The kinetic parameters for this reaction are given in Table 44, and the reaction is presumed to occur *via* the route represented in equations (126)–(128). The rapid decarboxylation of the intermediate ion *cis*-$[Rh(en)_2(CO_3H)(H_2O)]^+$ was independently studied, as was the rate of CO_2 uptake by *cis*-$[Rh(en)_2(OH)(H_2O)]^{2+}$ and *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$; the relevant parameters are also given in Table 44. The ΔH^* values for the carboxylation and the decarboxylation of the monodentate carbonate complexes are atypically low for substitutions at Rh^{III} centers, suggesting that these reactions do not involve the cleavage of a Rh—O bond; carboxylation must involve electrophilic attack of the CO_2 at the oxygen atom of the coordinated hydroxo group.[627] The markedly slower rate, and the higher

$$cis\text{-}[Rh(en)_2CO_3]^+ + H_2O \xrightarrow{k_{obs}} cis\text{-}[Rh(en)_2(H_2O)(OCO_2)]^+ \quad (126)$$

$$k_{obs} = (k_0 + k_1[H^+])$$

$$cis\text{-}[Rh(en)_2(H_2O)(OCO_2)]^+ + H^+ \rightleftharpoons cis\text{-}[Rh(en)_2(H_2O)(OCO_2H)]^{2+} \quad (127)$$

$$cis\text{-}[Rh(en)_2(H_2O)(OCO_2H)]^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} cis\text{-}[Rh(en)_2(H_2O)(OH)]^{2+} + CO_2 \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \quad (128)$$

$$cis\text{-}[Rh(en)_2(OH)_2]^+ \xrightarrow{CO_2,\,k_3} cis\text{-}[Rh(en)_2(OH)(OCO_2)]$$

Table 44 Kinetic Parameters for the Decarboxylation of *cis*-$[Rh(en)_2(OCO_2)X]^{n+}$ (from ref. 627)

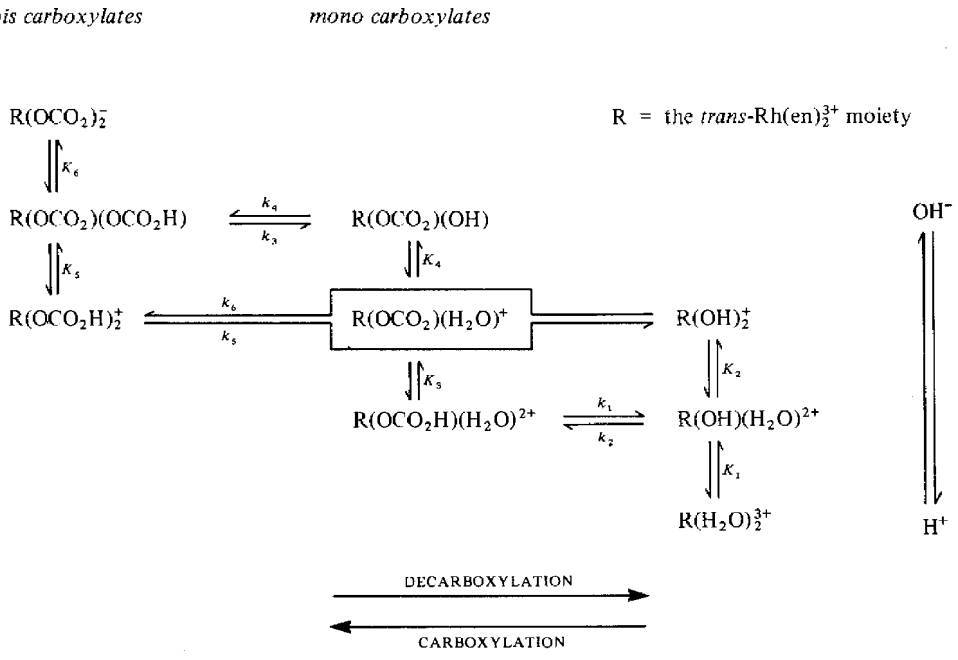
Process	k (25°C)[a]	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}mol^{-1}$)
Ring opening (k_{obs})	$k_0 = 9.33 \times 10^{-4}\,s^{-1}$	95.4 ± 6.3	-21 ± 21
	$k_1 = 1.00 \times 10^{-5}\,M^{-1}s^{-1}$	105 ± 15	8 ± 46
Decarboxylation of protonated form	$k_2 = 7.2 \times 10^{-1}\,M^{-1}\,s^{-1}$	81.2 ± 1.3	24.3 ± 8.3
CO_2 uptake by aquahydroxo ion	$k_{-2} = 69 \pm 18\,M^{-1}s^{-1}$	66.5 ± 2.1	16.3 ± 6
CO_2 uptake by dihydroxo ion	$k_3 = 215 \pm 29\,M^{-1}s^{-1}$	61.1 ± 0.8	4.6 ± 2.9

[a] Rate constant labels given in equations (126)–(128).

ΔH^* values for the decarboxylation of the bidentate carbonate, imply that the first, rate-determining step in this reaction must involve cleavage of a Rh—O bond as the carbonate ring is opened, and rapid decarboxylation of the monodentate complex can then occur with only C—O bond cleavage.

The *trans* carbonato complexes, *trans*-$[Rh(en)_2(OCO_2)(H_2O)]^+$ and *trans*-$[Rh(en)_2(OCO_2)_2]^-$ were also characterized, and the kinetics of their formation and decarboxylation studied.[625] Scheme 20 represents the complex reaction pattern observed. In the absence of added carbonate, decarboxylation of the monocarbonato complex has a rate expression of the form $k_{obs} = k_1[H^+]/([H^+] + K_3)$ (Scheme 20). Decarboxylation of the bis(carbonato) complex is unusual in that the researchers could find no evidence of an intermediate monocarbonato complex, and concluded that both carbonate ions are lost simultaneously (presumably as $2CO_2$). To support this supposition, they noted that at pH 8.82, CO_2 uptake by *trans*-$[Rh(en)_2(OH)_2]^+$ is proportional to $[CO_2]^2$. The *trans* geometry was maintained throughout these reactions, and the general pattern observed for the *cis* complexes,[627] *i.e.* rapid carboxylation of the Rh—OH^- or decarboxylation of the Rh—OCO_2H moieties, also held for the *trans* complexes.[621] This work was extended to include the kinetics of the formation and decarboxylations of the neutral $[Rh(en)_2(X)(OCO_2)]$ complexes (X = Cl, Br, I), so the effect of changing the ligand *trans* to the reactive site could be monitored.[641] These complexes displayed kinetic rate expressions similar to the *trans* aquacarbonato ions,[625] and a simpler reaction sequence, represented in equations (129) and (130), was observed. The pK_a of *trans*-$[Rh(en)_2(X)(H_2O)]^{2+}$ increases in the order Cl < Br < I, which can be considered as the order of increasing effectiveness for weakening the Rh—O bond, and hence strengthening the O—H bond; as expected, the first-order rate constant for decarboxylation decreases in the order Cl > Br > I. Summarizing the results given in Table 45, the ability of various ligands to labilize a *trans* bicarbonate decreases in the order: $H_2O > OCO_2H^- > OCO_2^{2-} > Cl^- > Br^- \approx NH_3 > I^-$ (the listing for NH_3 is from the *cis* series of complexes — Table 44). A graph of log k_1 *vs.* pK_a for a variety of M—CO_3 complexes shows a strong correlation between the acidity of the parent species and the rate of decarboxylation.

The rate of CO_2 uptake by *trans*-$[Rh(en)_2(X)(H_2O)]^{n+}$ increases in the order X = Cl < Br < I, which is reflected in a steady increase in ΔH^* and ΔS^* (Table 46). When compared with the rates of CO_2 uptake by a variety of aquated metal complexes (including complexes of Cu^{II}, Zn^{II}, Cr^{III}, and Ir^{III}) a clear correlation exists between the pK_a of the coordinated water and the rate of CO_2 uptake.



Scheme 20

$$trans\text{-}[Rh(en)_2(X)(H_2O)]^{2+} \rightleftharpoons trans\text{-}[Rh(en)_2(X)(OH)]^+ + H^+ \quad (129)$$

$$CO_2 + trans\text{-}[Rh(en)_2(X)(OH)]^+ \rightleftharpoons trans\text{-}[Rh(en)_2(X)(OCO_2H)]^+ \rightleftharpoons trans\text{-}[Rh(en)_2(X)(OCO_2)] + H^+ \quad (130)$$

Table 45 Kinetic Parameters for the Decarboxylations of *trans*-$[Rh(en)_2(X)(OCO_2H)]^{n+}$

trans-$[Rh(en)_2(X)(OCO_2H)]^{n+} \longrightarrow$ *trans*-$[Rh(en)_2(X)(OH)]^{n+} + CO_2$

Trans ligand (X)	*k* (25°C) (s^{-1})	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}\,mol^{-1}$)	pK_a	*Ref.*
Cl	1.26 ± 0.04	72.8 ± 2.1	−0.4 ± 6.7	6.36 ± 0.01	641
Br	1.12 ± 0.03	76.1 ± 0.8	+10.9 ± 3.3	6.42 ± 0.05	641
I	0.55 ± 0.04	72.0 ± 1.2	−9.6 ± 1.2	6.58 ± 0.01	641
H_2O	2.92 ± 0.08	45.6 ± 0.4	−82.0 ± 1.7	—	625
CO_3	1.3 ± 0.1	—	—	—	625
CO_3H	2.26 ± 0.05	68.2 ± 0.8	−8.8 ± 3.3	—	625

Table 46 Kinetic Parameters for the Carboxylation of *trans*-$[Rh(en)_2(X)(OH)]^{n+}$

trans-$[Rh(en)_2(X)(OH)]^{n+} + CO_2 \longrightarrow$ *trans*-$[Rh(en)_2(X)(OCO_2H)]^{n+}$

Trans ligand (X)	*k* (25°C) ($M^{-1}\,s^{-1}$)	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}\,mol^{-1}$)	*Ref.*
Cl	260 ± 12	52.3 ± 5.4	−22 ± 18	641
Br	395 ± 33	63.2 ± 4.6	+16 ± 16	641
I	422 ± 43	73.6 ± 3.3	+50 ± 11	641
H_2O	81 ± 3	54.0 ± 3.8	−23 ± 13	625
CO_3	330 ± 80	64.4 ± 2.9	+19 ± 10	625
OH	1.4 (± 0.2) × 10^{-4} ($M^{-2}\,s^{-1}$)	68.2 ± 3.8	+69 ± 13	625

Thus the rate of uptake does not depend on the nature of the metal, but depends on the nucleophilicity of the bound hydroxide ion, which correlates well with the strength of the O—H bond in the conjugate acid. Isokinetic plots (ΔH^* *vs.* ΔS^*) show parallel lines for CO_2 uptake and decarboxylation, confirming that these complexes share a common mechanism which does not involve cleavage of a metal–ligand bond.[641]

(*iii*) *Other aliphatic bidentate complexes*

The synthesis and reactivities of substituted aliphatic bidentate complexes are similar to the reactions of analogous ethylenediamine complexes. Basolo and co-workers prepared[619] and studied the rates of chloride aquation[555] of a variety of *trans*-$[Rh(NN)_2Cl_2]^+$ complexes (NN = *meso*-bn, where bn = 2,3-diaminobutane; (±)-bn, and tetrameen—both *cis* and *trans* isomers); the rate of chloride release is not dramatically dependent on the nature of the aliphatic amine ligand.

Hancock used the BH_4^--catalyzed path to generate $[Rh(tn)_2(ox)]^+$ (tn = 1,3-diaminopropane), and then showed that substitutions at both *trans*- and *cis*-$[Rh(tn)_2X_2]^+$ occur with retention of geometry (Scheme 21).[664] A kinetic study of the bromide anation and base hydrolysis of *trans*-$[Rh(tn)_2Cl_2]^+$ showed that the alkaline reaction displays the familiar $k_{obs} = k_1 + k_2[OH^-]$ rate expression;[665] the large entropy of activation for the OH^- dependent step ($\Delta S^* = 109 \pm 30\,J\,K^{-1}\,mol^{-1}$ *vs.* $71 \pm 5\,J\,K^{-1}\,mol^{-1}$ for the ethylenediamine analog) was noted, and an S_N1CB path was suggested.[664] When compared to the bromide anation of *trans*-$[Rh(en)_2Cl_2]^+$, the effect of the six-membered ring on the reaction rate is negligible.[665] The *cis* and *trans*-$[Rh(tn)_2(H_2O)_2]^{3+}$ ions have been prepared by Ag^+-induced release of the Cl^- ligands,[666] and these complex ions have electronic spectra and pK_a values (Table 47) comparable to their ethylenediamine analogs.

$$RhCl_3\cdot 3H_2O \longrightarrow \textit{trans}\text{-}[Rh(tn)_2Cl_2]^+ \xrightarrow[\Delta]{Br^-} \textit{trans}\text{-}[Rh(tn)_2Br_2]^+$$

$$\textit{trans}\text{-}[Rh(tn)_2Cl_2]^+ \xleftarrow{HCl} \textit{cis}\text{-}[Rh(tn)_2ox]^+ \xrightarrow{HBr} \textit{cis}\text{-}[Rh(tn)_2Br_2]^+$$

(ox^{2-} or BH_4^- from *cis*-$[Rh(tn)_2ox]^+$)

Scheme 21

Table 47 Electronic Spectra and pK_a Values for 1,3-Diaminopropane (tn) Complexes of Rh^{III}

Complex	λ_{max}(nm)(ε)	pK_1	*Media (at 25°C)*	*Ref.*
trans-$[Rh(tn)_2(H_2O)_2]^{3+}$	357 (60), 274 (171)	4.39	0.9 M $NaClO_4$, 0.1 M $HClO_4$	666
trans-$[Rh(tn)_2(H_2O)(OH)]^{2+}$	348 (88), 283 (179)	8.20	1.0 M $NaClO_4$	666
trans-$[Rh(tn)_2(OH)_2]^{+}$	351 (97), 294 (150)	—	0.96 M $NaClO_4$, 0.04 M NaOH	666
cis-$[Rh(tn)_2(H_2O)_2]^{3+}$	325 (123), 270 (147)	6.15	0.9 M $NaClO_4$, 0.1 M $HClO_4$	666
cis-$[Rh(tn)_2(H_2O)(OH)]^{2+}$	325 (134), 270 (135)	8.20	1.0 M $NaClO_4$	666
cis-$[Rh(tn)_2(OH)_2]^{+}$	330 (135), 279 (130)	—	0.96 M $NaClO_4$, 0.04 M NaOH	666
trans-$[Rh(tn)_2(H_2O)Cl]^{2+}$	395 (55), 282 (164)	6.39	10^{-3} M $HClO_4$	667
cis-$[Rh(tn)_2(H_2O)Cl]^{2+}$	342 (116), 281 (131)	7.53	10^{-3} M $HClO_4$	667
trans-$[Rh(tn)_2(OH)Cl]^{+}$	374 (96), 288 (151)	—	0.1 M NaOH, 0.9 M $NaClO_4$	667
cis-$[Rh(tn)_2(OH)Cl]^{+}$	343 (121), 279 (106)	—	0.1 M NaOH, 0.9 M $NaClO_4$	667
trans-$[Rh(tn)_2(H_2O)Br]^{2+}$	410 (59), 475 (36)	6.46	10^{-3} M $HClO_4$	667
cis-$[Rh(tn)_2(H_2O)Br]^{2+}$	358 (128)	7.51	10^{-3} M $HClO_4$	667
trans-$[Rh(tn)_2(OH)Br]^{+}$	385 (112), 284 (170)	—	0.1 M NaOH, 0.9 M $NaClO_4$	667
cis-$[Rh(tn)_2(OH)Br]^{+}$	354 (130)	—	0.1 M NaOH, 0.9 M $NaClO_4$	667
trans-$[Rh(tn)_2Cl_2]^{+}$	418 (80), ~315sh (~85), 289 (136)		—	664
cis-$[Rh(tn)_2Cl_2]^{+}$	~387sh (~89), 353 (123), 293 (125)		—	664
trans-$[Rh(tn)_2Br_2]^{+}$	441 (119), ~342sh (~58), 281 (3170)		—	664
cis-$[Rh(tn)_2Br_2]^{+}$	~405sh (~125), 368 (158), ~278sh (1140)		—	664
$[Rh(tn)_2(ox)]^{+}$	329 (172)		—	664

The ^{15}N NMR (natural abundance) spectra of some Rh^{III} complexes with alkyldiamine and aza aromatic ligands display nitrogen resonances *ca.* 20 p.p.m. upfield from the free ligand for the alkyl complexes, and about 100 p.p.m. upfield for the aza aromatic ligands.[668] This large shift is presumed to be due to the influence of low-lying excited states of the ligands themselves and not to any unusual property of the complexes. No correlation of the chemical shift with the position of the ligands in the spectrochemical series could be found, and non-bonded magnetic interactions are presumed to be involved. Diastereoisomerism was observed for $[Rh(1,2\text{-diaminopropane})_3]^{3+}$, and evidence of two different ligand conformations for the complex ion was also observed.[668]

A variety of substituted ethylenediamine complexes have been resolved, and their ORD, CD and electronic spectra reported (Table 48), with assignments of absolute configurations based on a comparison of their CD spectrum with the CD spectrum of $[Rh(en)_3]^{3+}$.[606] Complexes containing the optically active (*R*)-1,2-propanediamine and (*R*,*R*)-2,3-butanediamine ligands, in which the ligands are locked in the λ configuration by the bulky methyl groups, have also been resolved.[608,669] For $[Rh\{(R)\text{-pn}\}Cl_4]^{-}$ and *trans*-$[Rh\{(R)\text{-pn}\}_2Cl_2]^{+}$, the optical activity must arise from the assymmetry induced by the conformation of the optically active ligand; the effect appears to be additive in these complexes with one and two chiral ligands respectively (Table 48). The Δ configuration is also assigned[670] to the stable form (k,k,k) of $(+)_D$-$[Rh(1,2\text{-diaminocyclohexane})_3]^{3+}$.[671,672] The $[Rh\{(\pm)\text{-bn}\}_3]^{3+}$ ion (bn = 2,3-diaminobutane) has been prepared,[673] and all four diastereomers have been isolated and characterized by ^{13}C NMR.[674] The NMR spectrum of the λ,λ,λ form does not exhibit the broadened methyl group resonance observed for the Co analog, even though the X-ray structure (as the Br^- salt) shows a decreased intraring methyl group contact distance.[674]

48.6.2.3 Photochemistry of monodentate and bidentate amine complexes

The past 15 years have been exciting times for the study of Rh^{III} photochemistry. Photochemical reviews and texts of the late 1960s and early 1970s[676–678] hardly mention Rh^{III}, but as transition metal photochemistry grew in the 1970s, monographs and reviews chronicle the growth of Rh^{III} photochemistry.[679–684] The stability of the 3+ oxidation state and the inaccessibility of Rh^{II} or Rh^{IV}, the stereorigidity and inertness toward substitution of most Rh^{III} complexes in solution, and the photosensitivity of many Rh^{III} amines combined to make Rh^{III} photochemistry the most active Rh^{III} research area of the past 15 years. In general, the photochemistry of non-ammine complexes is discussed in the sections dealing with the specific compounds, but the amount of work presented on the photochemistry of simple monodentate and bidentate amine complexes requires this separate discussion.

Table 48 Electronic and CD Spectra of some Rh^{III} Complexes

Compound	*Electronic* λ_{max} (nm) (ε)	*ORD* $[\alpha]_D^c$	λ	*CD* $\Delta\varepsilon_{max}$	*Absolute configuration*	*Ref.*
$[Rh(en)_3]^{3+}$	306 (251)	−79	320	+2.0	Λ	606
			287	−0.1		
	257 (246)		258	+0.8		
	300 (250)	—	320	−2.01	Δ	608
			288	+0.09		
$[Rh\{(R)\text{-pn}\}_3]^{3+}$	303 (252)	+154	323	−0.72	Δ	606
			290	+1.25		
	255 (215)		253	−0.5		
	300 (270)	+162	320	−2.12	Δ	608
			286	+0.61		
$[Rh\{(R,R)\text{-bn}\}_3]^{3+}$	300 (270)	+175	320	−2.31	Δ	608
			286	+0.61		
trans-$[Rh\{(R)\text{-pn}\}_2Cl_2]^+$	405(75)	+158	405	+0.76	—	608
			315	−0.11		
	285 (120)		270	+0.57		608
trans-$[Rh\{(R,R)\text{-bn}\}_2Cl_2]^+$	405 (75)	+170	405	−0.12	—	608
			315	−0.12		
	285 (120)		270	+0.57		
$[Rh\{(R)\text{-pn}\}Cl_4]^-$	430 (70)	+188	432	+0.44	—	608
			370	−0.07		
	350 (80)		320	+0.26		
$[Rh\{(R,R)\text{-bn}\}Cl_4]^-$	430 (70)	+198	432	+0.46	—	608
			370	−0.08		
	350 (82)		320	+0.29		

(*i*) *The excited state*

Electronic excitation of a low-spin, d^6 Rh^{III} amine shifts electron density to a metal-dominated orbital (e_g) of σ symmetry, which is antibonding with respect to the Rh—ligand bonds. This electron density can come from either a t_{2g} orbital of π symmetry (ligand field excitation) or from a ligand-dominated orbital (ligand to metal charge transfer, or LMCT, excitation). Reduction or oxidation of Rh^{III} amines is difficult, so charge-transfer states are generally higher in energy than ligand field states and, for most complexes, they play little part in Rh^{III} photochemistry. With some exceptions, the quantum yield for photosubstitutions is independent of irradiation wavelength, suggesting that intersystem crossing to the lowest ligand field state occurs with unitary efficiency.[685] Photophysical studies have confirmed that luminescence from Rh^{III} amine complexes generally occurs from the lowest energy ligand field triplet state.[609,686–691] Consistent with rapid population of the ligand field states, the rates of intersystem crossing are extremely rapid and have been estimated to be in the range of $5 \times 10^9\,s^{-1}$ (for $[Rh(NH_3)_5Br]^{2+}$)[692] to $5 \times 10^{11}\,s^{-1}$ (for *cis*-$[Rh(bipy)_2Cl_2]^+$).[693] These findings all point to the generalization that the photochemistry of a Rh^{III} complex can be considered to be the chemistry of its lowest energy ligand field excited state.

Even in rigid media at reduced temperatures, the lifetimes of the luminescing states are short, implying that the thermally equilibrated excited states are extremely reactive.[609,688–691] With nanosecond and subnanosecond laser systems, the luminescence lifetimes under photochemically relevant conditions (fluid solution near room temperature) can now be measured.[692–703] (Emission quantum yields are extremely weak under these conditions, and luminescence quantum efficiencies are estimated to be in the 10^{-6} to 10^{-7} range.[692]) For $[Rh(L)_5X]^{2+}$ (X = Cl or Br, L = NH_3 or ND_3) and *cis*- and *trans*-$[Rh(en)_2Cl_2]^+$, the luminescent states have lifetimes in the range of 1–50 ns. These studies directly support the standard model, in which reactive and non-reactive paths compete for the transient excited state. For example, the rate of deactivation of $[Rh(ND_3)_5X]^{2+}$ is about half that of the undeuterated ions, consistent with the increased photochemical reactivity observed for the deuterated species.[694] It is interesting to note that for $[Rh(cyclam)(CN)_2]^+$, the lifetime of the luminescing state under comparable conditions (326.1 K, 0.001 M aqueous HNO_3 solution) is 2.0 μs, about three orders of magnitude longer than for the less constrained amine complexes.[700] This longevity is presumed to be due to the absence of a reactive decay mode.

The nature of the photoreactive state, as opposed to the luminescing state, is still the source of some debate, as states other than the lowest triplet have been proposed to be important. Evidence that an excited singlet may be involved comes from time-resolved studies of the luminescence of some haloammine complexes, where a weak fluorescence, with a lifetime of about 100 ps, was

observed.[692] A nearby quintet state has also been mentioned[695,701] and Endicott has questioned whether one should even consider this photochemistry to be the reaction of a distinct electronic excited state.[704] He suggests that the photoinduced substitutions and isomerizations may be considered hot ground state processes, with the photoinduced substitutions and isomerizations, not observed upon thermal excitation, resulting when the relaxation trajectory of the distorted excited state goes to a thermally inaccessible region of the ground state free energy surface. Perhaps, he argues, one should focus on understanding the full ground state surface, not the excited state surfaces.[704]

(*ii*) *Photochemistry of* $[Rh(NH_3)_5X]^{n+}$ *ions*

Whatever the nature of the photoreactive state, photolysis of a Rh^{III} amine leads to increased electron density in the metal-centered, σ^* e_g orbitals. Ligand labilization (especially of strongly σ-donating ligands), and subsequent solvolysis, is the anticipated (and observed) reaction. Photoinduced substitutions have now been reported for a large number of Rh^{III} amines, and some of the results are summarized in Table 49.

The first quantitative photochemical study of a Rh^{III} amine was reported by Moggi,[8] who noted that both 254 nm (LMCT) and 365 nm (ligand field) excitation of $[Rh(NH_3)_5Cl]^{2+}$ caused chloride labilization (equation 131). Other early reports include Basolo's study of the photoinduced stereoretentive halide aquation from $[M(en)_2X_2]^+$ (M = Rh, Ir; X = Cl, Br, I),[725] and Broomhead's observation of chloride aquation from $[RhCl_2(phen)_2]^+$.[726] While halide labilization dominates upon photolysis of $[Rh(NH_3)_5Cl]^{2+}$, both bromo and ammine loss occur upon photolysis of the bromo analog (equation 132)[685,707] and ammine is labilized from the iodo analog (equation 133).[708] Biacetyl sensitization of the bromo complex quenches the biacetyl phosphorescence, but not the fluorescence,[707] consistent with a photoreactive triplet state.

$$[Rh(NH_3)_5Cl]^{2+} + H_2O \xrightarrow{h\nu} [Rh(NH_3)_5H_2O]^{3+} + Cl^- \quad (131)$$

$$[Rh(NH_3)_5Br]^{2+} + H_2O \xrightarrow{h\nu} \begin{matrix} [Rh(NH_3)_5H_2O]^{3+} + Br^- \\ trans\text{-}[Rh(NH_3)_4(H_2O)Br]^{2+} + NH_3 \end{matrix} \quad (132)$$

$$[Rh(NH_3)_5I]^{2+} + H_2O \xrightarrow{h\nu} [Rh(NH_3)_4(H_2O)I]^{2+} + NH_3 \quad (133)$$

The photochemical behavior of the $[Rh(NH_3)_5I]^{2+}$ (and *trans*-$[Rh(NH_3)_4I_2]^+$) is unusual, as the quantum yield of ammine labilization decreases as the energy of the irradiating source increases. The quantum yield varies from 0.2 at 254 nm (LMCT region) to 0.9 upon ligand field excitation at 470 nm.[708] In the presence of excess I^- ion, flash photolysis of the LMCT region of $[Rh(NH_3)_5I]^{2+}$ leads to the readily recognizable I_2^- radical anion, suggesting that a redox process, involving the release of I atoms, is involved when the charge transfer state is populated. No I_2^- ions were detectable upon ligand field excitation, and throughout the ligand field region (385–470 nm) the quantum yield of ammine release is constant (0.85). These observations suggest that there are at least two paths to the same overall reaction (equation 133), and the lower quantum yield upon direct LMCT implies that the redox path is not as efficient as the ligand field path, and that energy transfer, from the LMCT state to the extremely reactive ligand field state, is inefficient. A mechanism for the CT path, involving a redox step (equation 134), a complexation (equation 135), and recombination steps (equations 136 and 137) was proposed.[727]

$$[Rh(NH_3)_5I]^{2+} \xrightarrow{h\nu} [Rh(NH_3)_4]^{2+} + NH_3 + I \quad (134)$$

$$I + I^- \longrightarrow I_2^- \quad (135)$$

$$[Rh(NH_3)_4]^{2+} + I + H_2O \longrightarrow [Rh(NH_3)_4(H_2O)I]^{2+} \quad (136)$$

$$[Rh(NH_3)_4]^{2+} + I_2^- \longrightarrow trans\text{-}[Rh(NH_3)_4I_2]^+ \quad (137)$$

Photoinduced ammonium ion release from $[Rh(NH_3)_5I]^{2+}$ absorbed into zeolite Y was studied to monitor the effects of an ion's environment on the photochemical behavior. The same photoreaction occurs in both media, but the quantum yield is reduced by almost a factor of 5 (to 0.18) in hydrated zeolite Y. This was presumed to be due to the steric hindrance of the zeolite walls, which hinder the access of solvent water to the photoexchange site. Consistent with this model, the quantum yield decreases still further (to 0.13) in 'partially dehydrated' zeolite Y.[728]

Table 49 Quantum Yields for Monodentate and Bidentate Amine Complexes of Rh^{III}

Complex	λ_{irr} (nm)	*Reaction or Rh product*	ϕ	*Comments*	*Ref.*
		$[Rh(NH_3)_5X]^{n+}$			
$[Rh(NH_3)_6]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.075	pH 3	705
$[Rh(ND_3)_6]^{3+}$	313	$[Rh(ND_3)_5(D_2O)]^{3+}$	0.15	pD 3 (D_2O)	705
$[Rh(NH_3)_5Cl]^{2+}$	366	(a) $[Rh(NH_3)_5(H_2O)]^{3+}$	0.18	pH 2–4 ($HClO_4$)	698
		(b) NH_3 release	0.02		
	358	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.13		706
			0.16		707
			0.14		8
$[Rh(NH_3)_5Cl]^{2+}$	366	Cl^- release	0.15	Acidic solution	702
		NH_3 release	0.04		
$[Rh(ND_3)_5(Cl)]^{2+}$	366	(a) $[Rh(ND_3)_5(H_2O)]^{3+}$	0.28	In $HClO_4/H_2O$	698
		(b) ND_3 release	$\leqslant 0.05$	Path (a) dominates	
	350	(a) $[Rh(NH_3)_5(H_2O)]^{3+}$	0.16	pH 2	685
		(b) $[Rh(NH_3)_4(H_2O)Cl]^{2+}$	$\leqslant 10^{-3}$		
	366	(a) $[Rh(NH_3)_5DMF]^{3+}$	0.004	In DMF solution	699
		(b) $[Rh(NH_3)_4Cl(DMF)]^{2+}$	0.070	Path (b) is favored	
	366	(a) $[Rh(NH_3)_5FMA]^{3+}$	0.057	In FMA solution	699
		(b) $[Rh(NH_3)_4Cl(FMA)]^{2+}$	< 0.011	Path (a) is favored	
$[Rh(NH_3)_5Br]^{2+}$	360	(a) $[Rh(NH_3)_5(H_2O)]^{3+}$	0.019		707
		(b) $[Rh(NH_3)_4Br(H_2O)]^{2+}$	0.18		
	366	(a) Br^- release	$\leqslant 0.02$	pH ≈ 3 ($HClO_4$)	698
		(b) NH_3 release	0.18	Path (b) dominates	
$[Rh(ND_3)_5Br]^{2+}$	366	(a) Br^- release	$\leqslant 0.03$	pH ≈ 3, $HClO_4$	698
		(b) NH_3 release	0.26	Path (b) dominates	
$[Rh(NH_3)_5I]^{2+}$	470	*trans*-$[Rh(NH_3)_4I(H_2O)]^{2+}$	0.85	pH 2	685
	385	*trans*-$[Rh(NH_3)_4I(H_2O)]^{2+}$	0.82		685
		$[Rh(NH_3)_5(H_2O)]^{3+}$	0.01		
	254	*trans*-$[Rh(NH_3)_4I(H_2O)]^{2+}$	0.43	pH 1–3	708
$[Rh(NH_3)_5(H_2O)]^{3+}$	313	$[Rh(NH_3)_5(H_2{}^{18}O)]^{3+}$	0.43	pH 4 in $H_2{}^{18}O$	709
		$[Rh(NH_3)_5(H_2O)(H_2{}^{18}O)]^{3+}$	0.001		
$[Rh(NH_3)_5(OH)]^{2+}$	350	Negligible photochemistry	—		710
$[Rh(NH_3)_5(SO_4)]^{+}$	313	$[Rh(NH_3)_5H_2O]^{3+}$	0.31	pH 2–3 ($HClO_4$), 14°C	711
$[Rh(NH_3)_5(NCS)]^{2+}$	460	Not determined	0.00018		704
$[Rh(NH_3)_5(N_3)]^{2+}$	350	$[Rh(NH_3)_5(NH_2Cl)]^{3+}$	0.03	HCl, NaCl (0.7 M)	522, 704
$[Rh(NH_3)_5(NH_2Cl)]^{3+}$	350	$[Rh(NH_3)_5Cl]^{2+}$	$\leqslant 0.187$	HCl, NaCl (0.7 M)	522
$[Rh(NH_3)_5(CN)]^{2+}$	313, 334	*cis*-$[Rh(NH_3)_4(H_2O)CN]^{2+}$	0.09	0.10 M $HClO_4$	712
$[Rh(NH_3)_5(bzn)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.31	pH 3 ($HClO_4$)[a]	713
$[Rh(NH_3)_5(bzyln)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.49	pH 3 ($HClO_4$)[a]	713
$[Rh(NH_3)_5(hcn)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.34	pH 3 ($HClO_4$)[a]	713
$[Rh(NH_3)_5(2\text{-}Mebzn)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.34	pH 3 ($HClO_4$)[a]	713
$[Rh(NH_3)_5(4\text{-}MeObzyln)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.24	pH 3 ($HClO_4$)[a]	713
$[Rh(NH_3)_5(4\text{-}HOhcn)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.27	pH 3 ($HClO_4$)[a]	713
$[Rh(NH_3)_5(N{=}CMe)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.47		714
$[Rh(NH_3)_5(bzn)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.35	pH 2–4 ($HClO_4$)	714
$[Rh(ND_3)_5(bzn)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.40	pH 2–4 ($HClO_4$)	714
$[Rh(NH_3)_5(MeCN)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.47	pH 2–4 ($HClO_4$), 25°C	714
		NH_3 release	$< 2 \times 10^{-3}$		
$[Rh(NH_3)_5(py)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.137	pH 2–3 ($HClO_4$)	714
$[Rh(NH_3)_5(4\text{-}Mepy)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.091	pH 2–3 ($HClO_4$)	714
$[Rh(NH_3)_5(3\text{-}Clpy)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.341	pH 2–3 ($HClO_4$)	714
$[Rh(NH_3)_5(py\text{-}d_5)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.16	pH 2–3 ($HClO_4$)	714
$[Rh(ND_3)_5(py)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.20	pH 2–3 ($HClO_4$)	714
$[Rh(ND_3)_5(py\text{-}d_5)]^{3+}$	313	$[Rh(NH_3)_5(H_2O)]^{3+}$	0.225	pH 2–3 ($HClO_4$)	714
		$[Rh(NH_3)_4(X)_2]^{n+}$			
trans-$[Rh(NH_3)_4(Cl)_2]^{+}$	407	*trans*-$[Rh(NH_3)_4(Cl)H_2O]^{2+}$	0.31	pH 3	706
	312–436	*trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.113	pH 0.3, $\mu = 1.0$	716
		cis-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.031		
cis-$[Rh(NH_3)_4Cl_2]^{+}$	365	*trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.33	pH 3	717
	365	*trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.34	pH 3–5, 25°C	718
	366	*cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.063	25°C	719
		trans-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.328		
		NH_3 release	0.013		
trans-$[Rh(NH_3)_4(Br)_2]^{+}$	405	*trans*-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	0.01	pH 3–5, 25°C	718
		NH_3 release	0.002		718
trans-$[Rh(NH_3)_4(I)_2]^{+}$	470	*trans*-$[Rh(NH_3)_4I(H_2O)]^{2+}$	0.48	pH 2, $HClO_4$	718
cis-$[Rh(NH_3)_4(Br)_2]^{+}$	365	*trans*-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	0.24	pH 3–5	718
		NH_3 release	0.06		718
trans-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	350	*cis*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	0.012	pH 0–2	710
cis-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	350	*trans*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	0.072	pH 0–2	710
trans-$[Rh(NH_3)_4(OH)_2]^{+}$	350	Negligible photochemistry	—		710
cis-$[Rh(NH_3)_4(OH)_2]^{+}$	350	Negligible photochemistry	—		710
		$[Rh(NH_3)_4XY]^{n+}$ ($X = H_2O$ or OH^-)			
trans-$[Rh(NH_3)_4H_2O(OH)]^{2+}$	350	*cis*-$[Rh(NH_3)_4(OH)(H_2O)]^{2+}$	0.59	pH 6.5	710
	365	Cl^- substitution	< 0.01	pH 3–5	710
		NH_3 release	< 0.001		
		Isomerization	< 0.02		
cis-$[Rh(NH_3)_4H_2O(OH)]^{2+}$	350	*trans*-$[Rh(NH_3)_4(OH)H_2O]^{2+}$	—	pH 7.4	710

Table 49 (*Continued*)

Complex	λ_{irr} (nm)	*Reaction or Rh product*	ϕ	*Comments*	*Ref.*
trans-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	365	Negligible photochemistry	—		710, 718
trans-$[Rh(NH_3)_4(H_2^*O)Cl]^{2+}$	366	*trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.33	pH 0.3, $\mu = 1.0$	719
		cis-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.064		
cis-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	365	*trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.46	pH 3–5	710, 718
		Cl^- release	< 0.01		
		NH_3 release	< 0.001		
cis-$[Rh(NH_3)_4(H_2^*O)Cl]^{2+}$	366	*cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	0.12	pH 0.3, $\mu = 1.0$	719
trans-$[Rh(NH_3)_4(OH)Cl]^+$	366	*cis*-$[Rh(NH_3)_4(OH)_2]^+$	0.21	pH 9.5–13	642
trans-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	365	Negligible photochemistry	—	pH 3–5	714, 718
		NH_3 release	0.001		
		Isomerization	< 0.01		
	365	NH_3 release	≈ 0.003	$\phi_{Br} < 0.01$	718
cis-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	365	*trans*-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	0.50	pH 3–5, 25°C	710, 718
		NH_3 substitution	≈ 0.006		
		Br^- substitution	< 0.01		
trans-$[Rh(NH_3)_4(OH)Cl]^+$	365	*cis*-$[Rh(NH_3)_4(OH_2)]^+$	0.21	pH 9–14	710
cis-$[Rh(NH_3)_4(OH)Cl]^+$	365	Not determined	≈ 0.02	pH 9–13	710
trans-$[Rh(NH_3)_4(OH)Br]^+$	365	*cis*-$[Rh(NH_3)_4(OH_2)]^+$	0.33	pH 9–14	710
cis-$[Rh(NH_3)_4(OH)Br]^+$	365	Not determined	≈ 0.02	pH 9–13	710
trans-$[Rh(NH_3)_4(H_2O)CN]^{2+}$	313, 334	*cis*-$[Rh(NH_3)_4(H_2O)]^{2+}$	0.52	0.001 M $HClO_4$	712
		[Rh(NN)$_2$(X)$_2$]$^+$			
$[Rh(en)_3]^{3+}$	313	*cis*-$[Rh(en)_2(en-H)Cl]^{3+}$	0.040	1 M Cl^-, pH 1–8	720
trans-$[Rh(en)_2(Cl)_2]^{2+}$	405	*trans*-$[Rh(en)_2(H_2O)Cl]^{2+}$	0.061	0.014 M $HClO_4$	721
	407	*trans*-$[Rh(en)_2(H_2O)Cl]^{2+}$	0.057		706
	254	*trans*-$[Rh(en)_2(H_2O)Cl]^{2+}$	0.12	'Natural pH'	722
	LF	*trans*-$[Rh(en)_2(H_2O)Cl]^{2+}$	0.08	'Natural pH'	722
	254	Cl^- release	0.030		715
cis-$[Rh(en)_2(Cl)_2]^+$	365	*trans*-$[Rh(en)_2(H_2O)Cl]^{2+}$	0.43	0.014 M $HClO_4$	721
	254	Cl^- release	0.056		715
trans-$[Rh(en)_2(Br)_2]^+$	405	*trans*-$[Rh(en)_2(H_2O)Br]^{2+}$	0.062	pH 2–5	637
	254	*trans*-$[Rh(en)_2(H_2O)Br]^{2+}$	0.054		715
	254	*trans*-$[Rh(en)_2(H_2O)Br]^{2+}$	0.12	'Natural pH'	722
	LF	*trans*-$[Rh(en)_2(H_2O)Br]^{2+}$	0.07	'Natural pH'	722
	254	Br^- release	0.054		715
cis-$[Rh(en)_2(Br)_2]^+$	365	*trans*-$[Rh(en)_2(H_2O)Br]^{2+}$	0.37	pH 2–5	637
trans-$[Rh(en)_2(I)_2]^+$	LF	*trans*-$[Rh(en)_2(H_2O)I]^{2+}$	0.20	'Natural pH'	722
	254	*trans*-$[Rh(en)_2(H_2O)I]^{2+}$	0.27	'Natural pH'	722
	436	*trans*-$[Rh(en)_2(H_2O)I]^{2+}$	0.33	pH 2–5 ($HClO_4$)	723
	254	I^- release	0.23		715
cis-$[Rh(en)_2(I)_2]^+$	366	*trans*-$[Rh(en)_2(H_2O)I]^{2+}$	≈ 0.034	pH 2–5 ($HClO_4$)	723
trans-$[Rh(en)_2(H_2O)_2]^{3+}$	334	*cis*-$[Rh(en)_2(H_2O)_2]^{3+}$	< 0.002	pH 1	626
cis-$[Rh(en)_2(H_2O)_2]^{3+}$	334	*trans*-$[Rh(en)_2(H_2O)_2]^{3+}$	0.27	pH 0–2	626
cis- or *trans*-$[Rh(en)_2(OH)]^+$	334	Isomerization	< 0.002	pH 12.6	626
trans-$[Rh(tn)_2(H_2O)_2]^{3+}$	334	*cis*-$[Rh(tn)_2(H_2O)_2]^{3+}$	0.28	pH 1.0	724
cis-$[Rh(tn)_2(H_2O)_2]^{3+}$	334	*trans*-$[Rh(tn)_2(H_2O)_2]^{3+}$	0.09		724
$[Rh(en)_2(OH)_2]^+$	254–336	No detectable photochemistry for either isomer			716
		[Rh(en)$_2$XY]$^{n+}$			
trans-$[Rh(en)_2(H_2O)Br]^{2+}$	405	No detectable photoreaction			637
cis-$[Rh(en)_2(H_2O)Br]^{2+}$	365	*trans*-$[Rh(en)_2(H_2O)Br]^{2+}$	0.95	$\phi_{Br} < 10^{-2}$	637
trans-$[Rh(en)_2(H_2O)OH]^{2+}$	312, 334	*cis*-$[Rh(en)_2(H_2O)OH]^{2+}$	0.61	pH 6.1–6.2	626
cis-$[Rh(en)_2(H_2O)OH]^{2+}$	334	*trans*-$[Rh(en)_2(H_2O)OH)]^{2+}$	0.05	pH 8.25–8.48	626
trans-$[Rh(en)_2(NH_3)Cl]^{2+}$	365	*trans*-$[Rh(en)_2(NH_3)H_2O]^{3+}$	0.062	0.014 M $HClO_4$	721
cis-$[Rh(en)_2(NH_3)Cl]^{2+}$	365	*cis*-$[Rh(en)(NH_3)H_2O]^{3+}$	0.145	0.014 M $HClO_4$	721
trans-$[Rh(en)_2(NH_3)Br]^{2+}$	365	*trans*-$[Rh(en)_2(H_2O)Br]^{2+}$	0.16	pH 2–5	637
		Br^- release	$< 10^{-3}$		
cis-$[Rh(en)_2(NH_3)Br]^{2+}$	365	*cis*-$[Rh(en)_2(NH_3)H_2O]^{3+}$	≈ 0.054		637
		trans-$[Rh(en)_2(H_2O)Br]^{2+}$	≈ 0.006		
trans-$[Rh(en)_2(NH_3)I]^{2+}$	405	*trans*-$[Rh(en)_2(H_2O)I]^{2+}$	≈ 0.034	pH 2–5 ($HClO_4$)	723
		cis-$[Rh(en)_2(NH_3)H_2O]^{3+}$	≈ 1.006	pH 2–5 ($HClO_4$)	723
trans-$[Rh(tn)_2(H_2O)(OH)]^{2+}$	334, 366	*cis*-$[Rh(tn)_2(H_2O)(OH)]^{2+}$	1.0	pH 5.5–6.3	723
cis-$[Rh(tn)_2(H_2O)(OH)]^{2+}$	334, 336	*trans*-$[Rh(tn)_2(H_2O)(OH)]^{2+}$	0.033	pH 8.35–8.52	724
trans-$[Rh(tn)_2(H_2O)Cl]^{2+}$	313–436	*cis*-$[Rh(tn)_2(H_2O)Cl]^{2+}$	0.059		667
cis-$[Rh(tn)_2(H_2O)Cl]^{2+}$	313–436	*trans*-$[Rh(tn)_2(H_2O)Cl]^{2+}$	0.538		667
trans-$[Rh(tn)_2(H_2O)Br]^{2+}$	366–436	*cis*-$[Rh(tn)_2(H_2O)Br]^{2+}$	0.026		667
cis-$[Rh(tn)_2(H_2O)Br]^{2+}$	366–436	*trans*-$[Rh(tn)_2(H_2O)Br]^{2+}$	0.55		667

[a] ϕ for NH_3 release $< 10^{-2}$.

One ammine is released upon ligand field excitation of $[Rh(NH_3)_6]^{3+}$, and the deuterated analog is twice as photosensitive.[694,705] The temperature dependence of the quantum yield led to the proposal that temperature independent weak coupling and temperature dependent strong coupling mechanisms were competitive paths for the non-radiative deactivation of the excited state.[705] Another RhN_6^{3+} chromophore, $[Rh(en)_3]^{3+}$, undergoes an inefficient ring opening/anation when photolyzed in the presence of Cl^- (equation 138).[720] Between pH 0 and 8, the quantum yield is pH independent,

and in basic solution, the deprotonated $[Rh(en)_2(monoen)Cl]^{2+}$ forms. Anation by Cl^- must be necessary to prevent ethylenediamine ring closure, as no photochemical reaction is observed in the absence of added Cl^-. Photoanation was also observed upon photolysis of $[Rh(NH_3)_5(H_2O)]^{3+}$ in the presence of Cl^- or Br^-.[709] The direct photolysis of ion pairs (*e.g.* $\{[Rh(NH_3)_5(H_2O)]^{3+}, Cl^-\}$) is evident in that the anation quantum yield is directly proportional to halide concentration. Photoinduced water exchange for $[Rh(NH_3)_5(H_2O)]^{3+}$ is efficient ($\phi = 0.47$), but little photoexchange was observed from the hydroxo complex, $[Rh(NH_3)_5OH]^{2+}$ ($\phi < 0.01$).[709]

$$[Rh(en)_3]^{3+} + HCl \xrightarrow{h\nu} [Rh(en)_2(enH)Cl]^{3+} \quad (138)$$

The ability to measure luminescence lifetimes in fluid solution at ambient temperatures has allowed a much clearer picture of the events which lead to photoinduced substitutions. A recent flurry of activity, led by Ford and Skibsted, has allowed the determination of rate constants for aquations, as well as for radiative and non-radiative decay modes from photoproduced excited states.[667,697,703] For $[Rh(NH_3)_5X]^{2+}$ (X = Cl, Br) and *cis*- and *trans*-$[Rh(NH_3)_4XY]^{n+}$ (X = Cl^-, Br^-, H_2O; Y = X, H_2O, OH^-) the rate constants for aquation of the excited states (at 25 °C) range between 6×10^6 to $3.1 \times 10^8\ s^{-1}$,[703] which represents an increase of 13–15 orders of magnitude over the rates of analogous reactions of the ground state complexes. For closely related complexes, the rate of labilization of X generally follows the order $H_2O > Cl^- > Br^- > I^-$, perhaps, Ford suggests, due to the relative abilities of these ligands to form π-bonds with the $t_{2g}^5 e_g^1$ ($\pi^5\sigma^1$) excited states. The influence of Y on the rate of release of Cl^- or Br^- follows the approximate order *cis* X > *trans* $OH^- \approx$ *trans* X > $NH_3 \approx$ *cis* OH^-.[703] The rate of halide release is reversed in *cis*- and *trans*-$[Rh(tn)_2X_2]^+$ (X = Cl, Br) however, as the rate of aquation (and of non-radiative decay) is greater for the bromo than for the chloro complexes.[667] The $[Rh(tn)_2Br_2]^+$ excited states also display rates of aquation and non-radiative decay at least an order of magnitude greater than for the dibromotetraammines. These effects are thought to be due to crowding in the inner coordination sphere by the bulky Br and tn ligands.

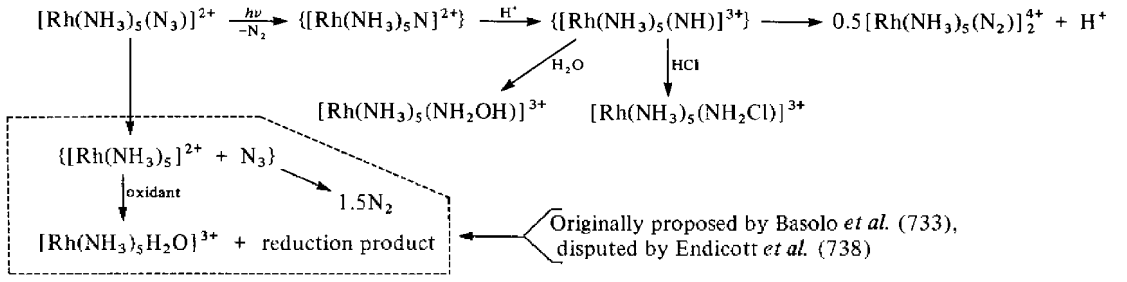
Hydroxide ion quenches luminescence from $[Rh(NH_3)_5X]^{2+}$ (X = Cl, Br), and reduces, but does not eliminate, the ligand labilizations.[707] For $[Rh(NH_3)_5Br]^{2+}$, ammine labilization is sharply reduced, but Br^- loss is unaffected by the presence of OH^-, leading Adamson to suggest that the two photoreactions originate from two distinct excited states; one which is luminescent, releases NH_3 and is quenched by hydroxide, and a second, non-luminescent state which releases Br^- and is not affected by OH^-.[695] Such a two-excited-state model, orginally proposed by Endicott[707] to account for ammine and bromide release from $[Rh(NH_3)_5Br]^{2+}$, contrasts sharply with the generally held view that Rh^{III} photochemistry originates from a single low-lying excited state (or several states in equilibrium with each other). Hydroxide also quenches NH_3 release from $[Rh(NH_3)_5I]^{2+}$, but increases the efficiency of I^- release by a factor of 5.[702] Ford argues that the enhanced reactivity of I^- is more readily rationalized if the OH^- ion is not considered an 'innocent quencher', but as a reactant which chemically interacts with the photoproduced excited state. A proton transfer, to generate $\{[Rh(NH_3)_4(NH_2)X]^+\}^*$, which is comparable to the reactive intermediate proposed in the S_N1CB reaction of the ground state, is suggested.[702] The reactivity patterns of this new excited species would be unrelated to that of the normal excited state (present in acidic solution), accounting for hydroxide's ability to affect two reaction paths differently, without invoking a distinct excited state species for each reaction.

The solvent cage can also influence photochemical reactivity, as studies with $[Rh(NH_3)_5Cl]^{2+}$ in various solvents showed that the identity of the photolabilized ligand, and the rates of radiative, non-radiative and reactive deactivations are solvent dependent. In polar media such as water and formamide, photoinduced Cl^- release dominates, but in less polar media (DMF, DMSO and MeOH), less capable of solvating the resulting Cl^- and Rh^{3+} ions, ammine substitution dominates.[699,730]

Ford and co-workers have also studied the luminescence and photochemistry of a variety of $[Rh(NH_3)_5L]^{3+}$ ions, where L is py, a substituted pyridine or an organonitrile.[713,714] While both ligand field and π–π transitions are apparent in the absorbance spectra, luminescence originates from only the ligand field state. Despite the similarity of the ligand field absorption spectra for all the nitrile complexes, the luminescence spectra depend on the nature of L, and as the energy of the emission band decreases, the quantum yield for nitrile labilization increases. The variation in quantum yield as a function of wavelength again indicates that energy transfer from ligand centered π–π^* states to ligand field states does not occur with unitary efficiency, but the lack of luminescence from the π–π^* states suggests that other, non-radiative paths are available for the normally fluorescence ligands upon coordination to the Rh^{III}.[713]

The photochemical reactivity of $[Rh(NH_3)_5(N_3)]^{2+}$ has proven especially interesting, for HCl solutions of the azidopentaammine ion undergo a ligand-centered reaction, releasing N_2 gas, and generating the chloramine complex (equation 139).[731] Minor products include $[Rh(NH_3)_6]^{3+}$, $[Rh(NH_3)_5(NH_2OH)]^{3+}$ and $[Rh(NH_3)_5(H_2O)]^{3+}$, and the ratio of products depends on the solution conditions and wavelength of irradiation. A coordinated nitrene mechanism, similar to that proposed for the thermal decomposition of Ru^{III}[732] and Ir^{III}[733] azides was proposed,[734] and is represented in Scheme 22. The nitrene intermediate is a soft Lewis acid, and when scavenged by Cl^-, the chloramine is formed; the hydroxylamine results from reaction with H_2O or ClO_4^-. The $[Rh(NH_3)_5(H_2O)]^{3+}$ photoproduct was presumed to result from a redox process involving the formation of transient $[Rh(NH_3)_5]^{2+}$ and the azide radical.[729] (It is interesting to note that only the nitrene path was detected upon photolysis of $[Ir(NH_3)_5(N_3)]^{2+}$,[735] and the azide radical/redox path has been noted for the Co^{III} analog,[736] so a combination of these two paths for the Rh^{III} analog seemed a logical conclusion.) Flash photolysis studies detected a transient N_2^{2-}-linked dimer, $[(NH_3)_5Rh—N—N—Rh(NH_3)_5]^{4+}$,[737] further supporting the nitrene mechanism, but did not find any photoproduced azide radical,[738] calling into question the redox path to $[Rh(NH_3)_5(H_2O)]^{3+}$. Zink suggested[739] photoinduced heterolytic cleavage of the terminal N—N bond in the Rh—N—N—N moiety, releasing N^- to the solution (which would be rapidly attacked by water or HCl to generate NH_2OH or NH_2Cl), and forming the instantly aquated $[Rh(NH_3)_5(N_2)]^{3+}$. While nicely accounting for the aquapentaammine product, Endicott and co-workers showed that virtually no NH_2OH, NH_2Cl, N_3 radical or N_3^- ion was generated in the photolyzed solution. While it seems an anticlimax, they concluded that the nitrene path is the only path available to $[Rh(NH_3)_5(N_3)]^{2+}$, and that the mysterious $[Rh(NH_3)_5H_2O]^{3+}$ must be formed from secondary photolysis of the hydroxylamine or chloramine primary photoproducts.[522]

$$[Rh(NH_3)_5(N_3)]^{2+} + HCl \xrightarrow{H^+,\ h\nu} [Rh(NH_3)_5(NH_2Cl)]^{3+} + N_2 \qquad (139)$$



Scheme 22

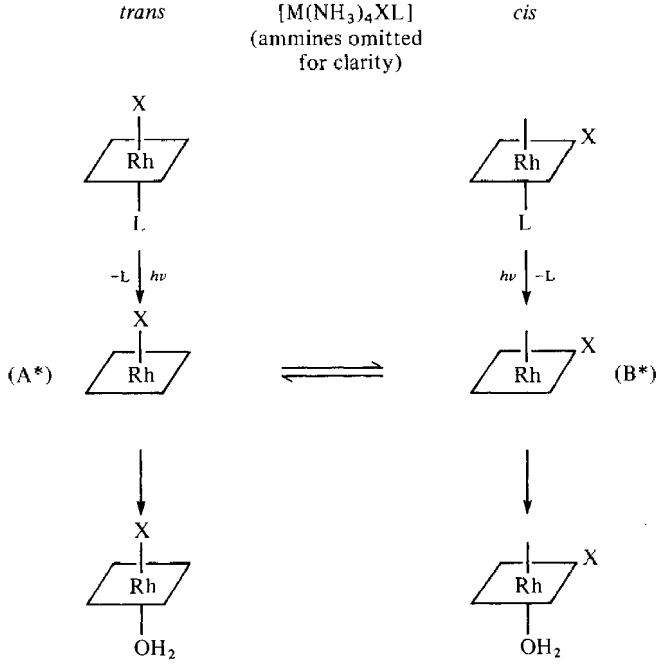
(*iii*) *Stereochemical consequences and mechanism*

The study of Rh^{III} photochemistry has been stimulated by numerous models which attempt to predict which of six ligands around an octahedrally coordinated metal center will be labilized upon ligand field photolysis. They range from sets of simple empirical rules to molecular-orbital-based theoretical studies,[740–744] and the success of Vanquickenborne's version[743] has made it the current standard. With some exceptions (*e.g.* the nitrene route for the azido complex,[733] the redox chemistry of the iodo,[727] and the effects of various solvents on the chloropentaammine ion[699]) the photochemistry of the $[Rh(NH_3)_5X]^{n+}$ ions discussed in the previous section generally follow Vanquickenborne's model. One recent test of this model used the strong *trans*-labilizing influence of the cyanide ligand to generate *trans*-$[Rh(NH_3)_4(*NH_3)CN]^{2+}$ from the reaction of *trans*-$[Rh(NH_3)_4(CN)Cl]^+$ with $^{15}NH_3$.[626] According to virtually all the models, photolysis of $[Rh(NH_3)_5CN]^{2+}$ should lead to labilization of an ammine in the plane *cis* to the coordinated CN^-, and photolysis (at 254 and 313 nm) does lead to *cis*-$[Rh(NH_3)_4(H_2O)CN]^{2+}$. Virtually all (96% upon 313 nm irradiation) of the photoreleased ammine was unlabeled, confirming that photolysis of this complex leads to regiospecific labilization of an ammine in the equatorial plane.[745]

An interesting challenge to Vanquickenborne's model of regiospecific labilization has been presented by Muir and co-workers,[746] who studied the photoinduced amine aquation from complexes of the form *trans*-$[RhL_4Cl_2]^+$ where L is a heterocyclic amine (pyrazine, pyrazole, pyridine, imidazole, and substituted analogs). Unlike the ammine and ethylenediamine analogs, where chloride loss dominates, both amine and chloride are stereoretentively labilized from these com-

plexes, and the fraction of the reactive decay leading to amine labilization increases with the pK_B of the free amine. An appealingly simple argument suggests that the weaker the amine base, the poorer a σ donor it will be, and the more likely it is to be labilized in the photoproduced excited state.[746]

As it became clear that isomerization often accompanies photoinduced substitution, attempts to predict the stereochemical course of a given photochemical reaction also appeared, with the most successful being that of Vanquickenborne and Ceulemans.[747] In this model, represented in Scheme 23, the photoproduced excited state is presumed to undergo a dissociative loss of the photolabilized ligand, leaving a five-coordinate species in a square pyramidal (SP) geometry. This intermediate is then presumed to undero unimolecular rearrangement to its lowest energy structure, which for d^6 metals is the SP configuration (the trigonal bipyramid arrangement was also considered, and is found to be the stabler geometry in d^3, but not d^6, systems). For a $\{[Rh(NH_3)_4X]^{n+}\}^*$ species, two geometric isomers are possible for the SP configuration, and angular overlap calculations indicate that the stabler species will have the weaker σ-donating ligand in the apical site. (That is, if X is a weaker σ donor than NH_3, excited state A* should be the dominant excited state, while if X is the stronger σ donor, B* should prevail.) Nucleophilic attack, usually by solvent water, at the vacant coordination site of the equilibrated excited state complex completes the photoinduced aquation.



Scheme 23

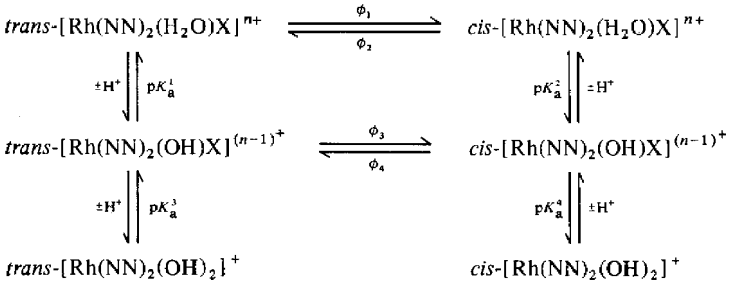
This model has been tested in numerous studies by Ford (and his even more numerous coworkers), and it has a remarkable record.[747–749] Photoaquation/isomerization studies have been presented for *cis*-$[Rh(NH_3)_4XY]^{n+}$ (X = Cl, Br; Y = H_2O, X),[718] *trans*-$[Rh(NH_3)_4(OH)Y]^+$ (Y = Cl, Br, OH),[642,710] *cis*-$[Rh(NH_3)_4Cl_2]^+$,[717] *trans*-$[Rh(NH_3)_4(CN)Z]^{n+}$ (Z = NH_3, OH),[712] *cis*- and *trans*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$,[750] and *cis*- and *trans*-$[Rh(en)_2XY]^{n+}$ (X = Cl, Br, I; Y = NH_3, H_2O or X).[637,721,723] In each case, the stereochemical consequences of photolysis are consistent with Vanquickenborne's model. In the study of *cis*-$[Rh(NH_3)_4Cl_2]^+$,[718] the HNO_2-induced aquation of *cis*-$[Rh(NH_3)_4(N_3)Cl]^+$ (which should also generate a $[Rh(NH_3)_4Cl]^{2+}$ species, but in the ground electronic state) was shown to be stereoretentive, yielding *cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$. This implies that the photoinduced *cis* $\rightleftharpoons$ *trans* isomerization is an excited state process.[718]

Skibsted and co-workers have recently presented several studies which rigorously test these stereochemical models. Complexes of the form *cis*- and *trans*-$[Rh(NN)_2XY]^{n+}$, (NN = en or tn (1,3-diaminopropane); X = H_2O, OH; Y = H_2O, OH), plus *cis* and *trans*-$[Rh(tn)_2(H_2O)Z]^{2+}$ (Z = Cl, Br), display similar photochemistries: (a) *cis* to *trans* isomerization dominates for the diaqua and aquachloro ions (in which the H_2O or halide, poorer σ donors than en, occupy the axial site in the SP (square planar) intermediate); (b) *trans* to *cis* photoisomerization dominates for the hydroxoaqua species, as the OH^- ion is a better σ donor than the en nitrogens, and hence occupies an equatorial site; and (c) no photochemistry is observed for the dihydroxo ions.[626,667,724] These results are summarized in Scheme 24 and Table 50.

Table 50 Quantum Yields and pK_a Values for some $[Rh(NN)_2X_2]^{n+}$ Complexes[a]

NN	*X*	ϕ_1	ϕ_2	ϕ_3	ϕ_4	pK_a^1	pK_a^2	pK_a^3	pK_a^4	*Ref.*
en	H_2O	< 0.002	0.27	0.61	0.048	4.47	6.34	7.91	8.24	626
tn	H_2O	0.10	0.29	1.0	0.033	4.39	6.15	8.20	8.20	724
tn	Cl	0.058	0.538	—	—	6.39	7.53	—	—	667
tn	Br	0.025	0.55	—	—	6.46	7.51	—	—	667
en	Br	< 0.001	0.95	—	—	—	—	—	—	637
$2NH_3$	Cl	0.064	0.523	b	b	—	—	—	—	716

[a] Numbers for quantum yields and pK_a values refer to Scheme 24. [b] Photolysis leads to halide labilization.[706]



Scheme 24

The excited state intermediates proposed in the Vanquickenborne model[747] are coordinatively unsaturated and usually cationic, and should be powerful Lewis acids immersed in a strongly nucleophilic aqueous environment. Despite this, they are presumed to exist long enough to reach thermal equilibrium, with the stereochemistries of the final products independent of the labilized ligand. This hypothesis has recently been tested,[716,719] as photolysis of *cis*- and *trans*-$[Rh(NH_3)_4Cl_2]^+$, and *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ should all lead to the same five-coordinate $\{[Rh(NH_3)_4Cl]^{2+}\}^*$ intermediate, and should therefore all lead to the same photochemical product. Careful reinvestigation of the photochemistry of the *trans*-$[Rh(NH_3)_4Cl_2]^+$,[716] the two *cis* complexes,[719] and a new study of *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ [716] showed that in all four cases the photoproduct is the same mixture of $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ isomers (17% *cis* and 83% *trans*; Figure 2). This strongly supports Vanquickenborne's stereochemical model for d^6 systems[747] and suggests that the substitutional photochemistry of these Rh^{III} amines may indeed proceed *via* a purely dissociative mechanism, with a five-coordinate intermediate sufficiently stable to undergo unimolecular isomerization and reach thermal equilibrium between two similar SP structures.

The limiting dissociative mechanism is also supported by studies of the effects of pressure on the photoinduced aquation of *cis*- and *trans*-$[Rh(NH_3)_4X_2]^+$, *cis*-$[Rh(NH_3)_4(H_2O)X]^{2+}$ (X = Cl, Br), *trans*-$[Rh(NH_3)_4(OH)Cl]^+$,[751] $[Rh(L)_5X]^{2+}$ (L = NH_3, ND_3; X = Cl, Br),[752] and $[Rh(NH_3)_5X]^{n+}$ (X = NH_3, I^-, SO_4^{2-}).[711] In the tetraammine series, the volume of activation of photoinduced aquation varies between -8.8 and $+9.3\,cm^3\,mol^{-1}$; in the pentaammine series halide loss has a negative volume of activation (between -10.3 and $-4.2\,cm^3\,mol^{-1}$), while ammine loss has a positive ΔV^* ($+3.4$ to $+12.7\,cm^3\,mol^{-1}$). The effect of pressure on the photochemistry of $[Rh(NH_3)_5Cl]^{2+}$ in formamide, DMF or DMSO allowed an estimation of the volumes of activations for Cl^- labilization, NH_3 labilization, luminescent and non-radiative deactivation paths.[753] Com-

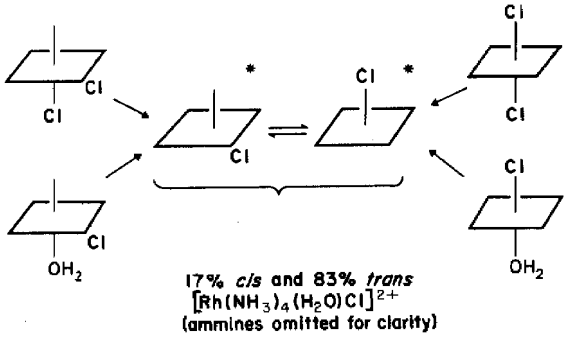
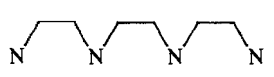


Figure 2 Photolysis of $[Rh(NH_3)_4Cl_2]^+$ and $[Rh(NH_3)_4(H_2O)Cl]$

parison of ΔV^* values for reactive and non-reactive paths led to the suggestion of a strong coupling between the two processes.[752] After accounting for the expanded volume of the ligand field excited state, vanEldik and coworkers state that 'a collection of circumstantial evidence points to a limiting dissociative mechanism for the ligand field photosubstitution reactions of rhodium(III) haloammine complexes in aqueous solution'.[753]

48.6.2.4 Polydentate aliphatic amine complexes

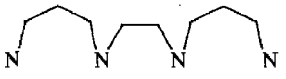
Aliphatic amines with three or more amine functions which form complexes with Rh^{III} are represented in (**48**). These can be subdivided into linear (trien, 2,3,2-tet, *etc.*), branched (tren) and cyclic (cyclam, cyclen, *etc.*) amines, and will be discussed in that order.



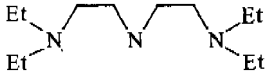
(48a) trien



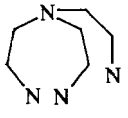
(48b) 2,3,2-tet



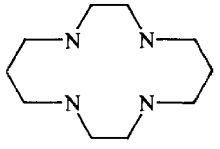
(48c) 3,2,3-tet



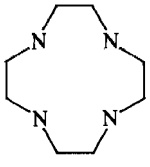
(48d) 1,1,7,7-tetraethyldien



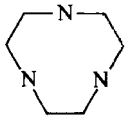
(48e) tren



(48f) cyclam

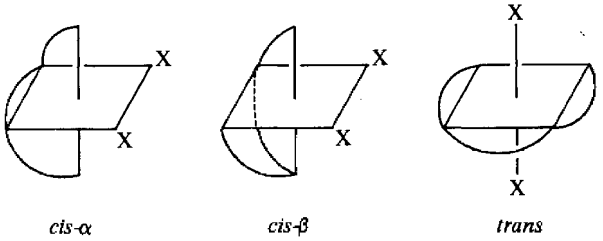


(48g) cyclen



(48h) [9]aneN$_3$

Two general synthetic paths to Rh^{III} polyamine complexes have emerged: extension of the procedure for the synthesis of $[Rh(en)_2X_2]^+$ [619] (reaction of $RhCl_3 \cdot 3H_2O$ or $[RhCl_6]^{3-}$ with the HCl salt of the appropriate amine), or the reaction of *trans*-$[Rhpy_4Cl_2]^+$ with the appropriate amine.[754] The $[Rh(trien)Cl_2]^+$ ion was first prepared by Basolo and Johnson[619] and later by Gillard and Wilkinson.[755] Three geometric isomers are possible for octahedral complexes with linear tetradentates (**49**), and while isomeric assignment was not made in these initial studies, later work showed



cis-α *cis*-β *trans*

(**49**)

Table 51 Electronic Spectra of some Polyamine Complexes of Rh^{III}

Complex	λ_{max} (nm) (ε)	*Ref.*
cis-α-$[Rh(trien)Cl_2]Cl \cdot H_2O$	352 (240), 288 (210)	756
cis-β-$[Rh(trien)Cl_2]Cl \cdot 2H_2O$	350 (270), 300 (290)	756
trans-$[Rh(trien)Cl_2]ClO_4$	406 (128), 286 (490)	756
cis-α-$[Rh(trien)Br_2]^+$	366 (306), 280sh (1330)	756
cis-α-$[Rh(trien)(N_3)_2]^+$	335sh (1130), 257 (12 700)	756
cis-α-$[Rh(trien)I_2]^+$	370 (1100), 295 (4600)	756
cis-α-$[Rh(trien)Cl(NCS)]^+$	~325, ~300	756
cis-$[Rh(trien)(H)Cl]^+$	300 (108), 255sh (140), 218 (~30 000)	757
trans-$[Rh(2,3,2\text{-tet})Cl_2]^+$	410, 293	754
cis-β-$[Rh(2,3,2\text{-tet})Cl_2]^+$	348 (218), 295 (241)	758
trans-*R*,*R*-$[Rh(3,2,3\text{-tet})Cl_2]^+$	417 (~75), ~300 (~190)	759
$[Rh(tren)Cl_2]NO_3$	352 (155), 295 (180)	619
$[Rh(tren)Cl_2]Cl$	364 (321), 292 (330)	760
$[Rh(tren)C_2O_4]ClO_4 \cdot H_2O$	328 (290)	761
$[Rh(tren)(N_3)_2]Cl$	357 (320)	761
$[Rh(tren)(NO_2)_2]NO_3$	295 (800)	761
$[Rh(tren)I_2]I$	395sh (1350)	761
$[Rh(tren)Br_2]Br \cdot 0.5H_2O$	382 (260)	761
$[Rh(tren)(H_2O)_2]^{3+}$	325, 272	762
$[Rh(tren)(OH)_2]^+$	332, 274	762
α-$[Rh(tren)Cl(H_2O)]^{2+}$	345, 287	762
β-$[Rh(tren)Cl(H_2O)]^{2+}$	335, 282	762
α-$[Rh(tren)Br(H_2O)]^{2+}$	345	762
β-$[Rh(tren)Br(H_2O)]^{2+}$	357	762

that the *cis*-α isomer had been prepared. Several examples of $[Rh(trien)X_2]^+$ ($X = Cl^-$, Br^-, I^- and N_3^-) have been prepared and the *cis*-α, *cis*-β and unstable *trans* isomers have been separated and identified on the basis of IR and UV/visible spectra (Table 51).[756] Reaction of $[Rh(trien)Cl_2]^+$ (presumably the *cis* isomer) with BH_4^- leads to a brown solution, said to contain the monohydrido *cis*-$[Rh(trien)Cl(H)]^+$; analysis of the *d*–*d* bands suggested that H^- belongs just above F^- in the spectrochemical series.[757]

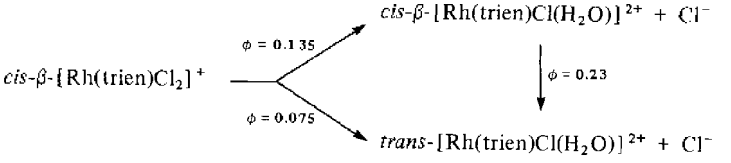
Kinetic studies of the aquation[619,763] and anation[756] of *cis*-α- and *cis*-β-$[Rh(trien)Cl_2]^+$ and of *cis*-β-$[Rh(2,3,2\text{-tet})Cl_2]^+$[763] have shown that, in the absence of light, substitutions occur with retention of amine configuration, and between 60–80 °C, the aquation rate constants are within an order of magnitude, with the most reactive *cis*-β-$[Rh(trien)Cl_2]^+$, aquating about eight times as rapidly as the least reactive, *cis*-α-$[Rh(trien)Cl_2]^+$. Activation parameters for these reactions, and reactions of other aliphatic polyamine Rh^{III} complexes, are given in Table 52. Photolysis of *cis*-β-$[Rh(trien)Cl_2]^+$ and *cis*-β-$[Rh(2,3,2\text{-tet})Cl_2]^+$ causes efficient release and isomerization, yielding a mixture of *cis*-β- and *trans*-aquachloro products (equations 140 and 141).[758] The *cis*-α-$[Rh(trien)Cl_2]^+$ ion, however, is at least three orders of magnitude less photoreactive than either *cis*-β complex, as no photoinduced reaction could be observed, even after extended photolyses.[758] A similar reactivity pattern was noticed for the *cis* isomers of $[Co(trien)Cl_2]^+$, and steric constraints, induced by the configuration of the trien, were invoked to rationalize the photoinertness of *cis*-α-$[M(trien)Cl_2]^+$ (M = Co or Rh).[766] (Interestingly, the *cis*-α-$[Cr(trien)Cl_2]^+$ ion is quite photosensitive.[767]) A summation of the photochemical reactivity of aliphatic polyamine Rh^{III} complexes is given in Table 53.

Table 52 Activation Parameters for Reactions of some Aliphatic Polyamines of Rh^{III}

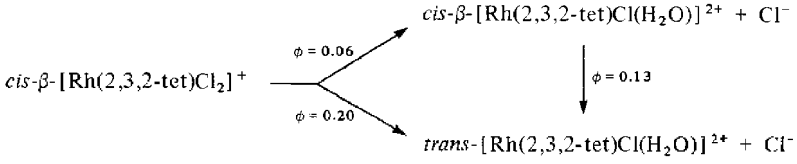
Starting material	*Reaction*	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}\,mol^{-1}$)	*Ref.*
cis-α-$[Rh(trien)Cl_2]^+$	Aquation	88	−71	763
cis-β-$[Rh(trien)Cl_2]^+$	Aquation	67	−113	763
cis-β-$[Rh(2,3,2\text{-tet})Cl_2]^+$	Aquation	82	−84	763
$[Rh(tren)Cl_2]^+$	Cl aquation	106	+24	764
β-$[Rh(tren)Cl(H_2O)]^{2+}$	Cl aquation	122	+65	764
$[Rh(tren)Br_2]^+$	Br aquation	105	+20	764
β-$[Rh(tren)Br(H_2O)]^{2+}$	Br aquation	108	+17	764
α-$[Rh(tren)Cl(H_2O)]^{2+}$	Cl aquation	147	+110	764
α-$[Rh(tren)Br(H_2O)]^{2+}$	Br aquation	153	+133	764
$[Rh_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)([9]aneN_3)_2]^{2+}$	Decarboxylation	63	−106	765

Table 53 Photochemical Behavior of some Aliphatic Polyamine Complexes of Rh^{III}

Complex	*Conditions*	*Products(s)*	ϕ	*Ref.*
cis-α-$[Rh(trien)Cl_2]^+$	0.1 N H_2SO_4	$[Rh(trien)Cl(H_2O)]^{2+}$	$< 10^{-4}$	655
cis-β-$[Rh(trien)Cl_2]^+$	0.1 N H_2SO_4	$[Rh(trien)Cl(H_2O)]^{2+}$, 65% *cis*-β, 35% *trans*	0.21	758
cis-α-$[Rh(trien)Cl(H_2O)]^{2+}$	0.1 N H_2SO_4	—	$< 10^{-4}$	758
cis-β-$[Rh(trien)Cl(H_2O)]^{2+}$	0.1 N H_2SO_4	*trans*-$[Rh(trien)Cl(H_2O)]^{2+}$	0.22	758
trans-$[Rh(cyclam)Cl_2]^+$	10% MeCN	*trans*-$[Rh(cyclam)Cl(H_2O)]^{2+}$	0.011	768
cis-$[Rh(cyclam)Cl_2]^+$	10% MeCN	*cis*-$[Rh(cyclam)Cl(H_2O)]^{2+}$	0.37	768
trans-$[Rh(cyclam)Br_2]^+$	10% MeCN	*trans*-$[Rh(cyclam)Br(H_2O)]^{2+}$	0.03	768
cis-$[Rh(cyclam)Br_2]^+$	10% MeCN	*cis*-$[Rh(cyclam)Br(H_2O)]^{2+}$	0.32	768
trans-$[Rh(cyclam)I_2]^+$	10% MeCN	*trans*-$[Rh(cyclam)I(H_2O)]^{2+}$	0.15	768
cis-β-$[Rh(2,3,2\text{-tet})Cl_2]^+$	pH 1	*cis*-$[Rh(2,3,2\text{-tet})Cl(H_2O)]^{2+}$, 77% *trans*, 23% *cis*-β	0.26	763
cis-β-$[Rh(2,3,2\text{-tet})Cl(H_2O)]^{2+}$	pH 1	*trans*-$[Rh(2,3,2\text{-tet})Cl(H_2O)]^{2+}$	0.13	763
$[Rh(tren)Cl_2]^+$	pH 1	α-$[Rh(tren)Cl(H_2O)]^{2+}$	0.09	762
$[Rh(tren)Br_2]^+$	pH 1	α-$[Rh(tren)Br(H_2O)]^{2+}$	0.22	764
α-$[Rh(tren)Cl(H_2O)]^{2+}$	pH 1	$[Rh(tren)(H_2O)_2]^{3+}$	0.10	762
α-$[Rh(tren)Br(H_2O)]^{2+}$	pH 1	$[Rh(tren)(H_2O)_2]^{3+}$	0.17	764
β-$[Rh(tren)Cl(H_2O)]^{2+}$	pH 1	Negligible photoreaction	$< 10^{-4}$	762
β-$[Rh(tren)Br(H_2O)]^{2+}$	pH 1	Negligible photoreaction	$< 10^{-4}$	764

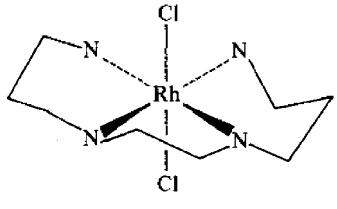


(140)



(141)

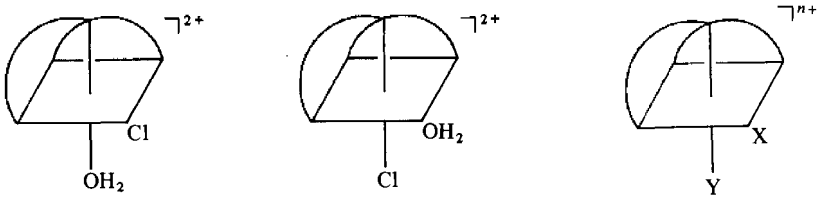
The stereochemistry of six-coordinte Co^{III} and Rh^{III} complexes with the 3,2,3-tet ligand (**48c**) was thoroughly studied by Bosnich and co-workers.[769] As shown in (**50**), if the six-membered rings are both in a chair conformation, the *trans*-$[Rh(3,2,3\text{-tet})Cl_2]^+$ ion is asymmetric due to the conformation of the five-membered, central ring. Bosnich resolved this ion and studied the solvent-induced changes in the CD spectra, which were attributed to solvation effects, and not to changes of ring configuration.[759,769] The single crystal X-ray structure of $[Rh(1,1,7,7\text{-tetraethyldien})(N_3)_3]$ shows it to be monomeric, with a distorted octahedron, and the substituted dien in a *mer* configuration.[770]



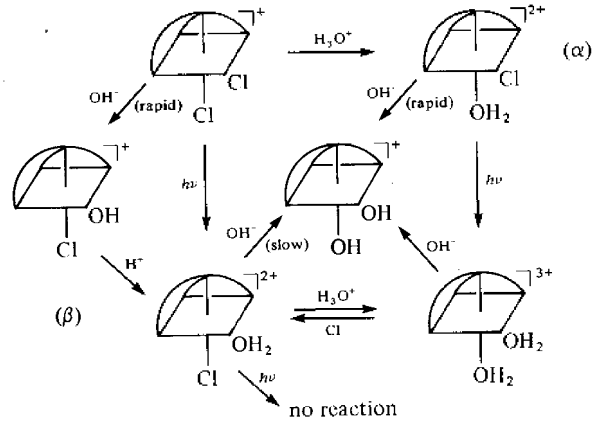
(50)

The branched isomer of trien, β,β′,β″-triaminotriethylamine (tren **48e**) can act as a tetradentate toward Rh^{III}, or, as the trihydrochloric acid salt $[(tren3H)^{3+}3Cl^-]$, it can act as a trivalent cation for the precipitation of $[RhCl_3X_3]^{3-}$ (X = Cl, Br, I) and $[RhBr_6]^{3-}$.[771] First reported by Basolo,[619] the aquation kinetics of $[Rh(tren)Cl_2]^+$ were later studied by Madan.[772] Ligand field photolysis of $[Rh(tren)Cl_2]^+$ also causes chloride loss, but the photo and thermally produced $[Rh(tren)Cl(H_2O)]^{2+}$

ions are distinct.[762] It was proposed that the thermal and photochemical reactions produced the two geometric isomers of $[Rh(tren)Cl(H_2O)]^{2+}$ (**51**). Base hydrolysis of $[Rh(tren)Cl_2]^+$ leads to the same isomer produced photochemically,[761] and it has been proposed that this is the α isomer (**51**). Mechanistic arguments, based on the hydrophilic nature of the site *trans* to the tertiary amine, were used to suggest that aquation in acidic aqueous solution (presumably *via* the I_a path), leads to the β isomer. A summary of the reactions of some $[Rh(tren)XY]^{n+}$ complexes is given in Scheme 25. For complexes of the form represented in (**52**), associative processes (aquations, anations) tend to occur at coordination site Y, while dissociative processes (base hydrolysis, photoinduced substitutions) lead to substitutions at site X. Consistent with this model, kinetic studies of the acid hydrolysis of α- and β-$[Rh(tren)X(H_2O)]^{2+}$ show that loss of a halide from site Y involves a small entropy of activation, while aquation of site X involves large positive values of ΔS^* (Table 52).[764]



(51)



Scheme 25

The Rh^{III} complexes containing the 14-membered cyclic tetramine, 1,4,8,11-tetraazatetradecane (cyclam, **48f**), have been extensively studied by Bounsall and Koprich.[773] When the free cyclam ligand is reacted with $RhCl_3 \cdot 3H_2O$ in aqueous solution the dominant product is *cis*-$[Rh(cyclam)Cl_2]Cl$; when the same reaction is run in methanol, the *trans* isomer predominates. Both *cis* and *trans* isomers of a variety of $[Rh(cyclam)XY]^{n+}$ (X and Y = halides, pseudohalides, H_2O, OH^-) have been prepared by direct substitution of the ligand by refluxing the cyclam complex in an aqueous solution of the desired anion.[764,773] With the exception of *cis*-$[Rh(cyclam)I_2]^+$, which isomerizes to the *trans* form when heated, substitutions at $[Rh(cyclam)XY]^{n+}$ occur with retention of geometric configuration.[773] The electronic spectra of a variety of $[Rh(cyclam)XY]^{n+}$ ions, and of other cyclic polyamine Rh^{III} complexes, are recorded in Table 54. Analysis of the IR spectra indicated that the NCS^- ligands are N-bonded, as are the NO_2^- ligands. The *cis* complexes offer an unusual opportunity to study the *trans* bond-weakening effect in a series of closely analogous compounds, as there is a Rh—N bond *trans* to a different ligand in each *cis* complex. Analysis of Rh—N stretching frequencies indicated that the *trans* bond-weakening series is $NO_2^- > I^- > Br^- > Cl^- \approx N_3^-$ > amine N > NCS^-. Photolysis of *trans*-$[Rh(cyclam)X_2]^+$ and the *cis*-dichloro cation causes stereoretentive halide aquation (Table 53).[768] The electrical resistances of compressed samples of *cis*-$[Rh(cyclam)Cl_2](TCNQ)$ (TCNQ = the monoanion of tetracyanoquinoline) are 32 times that of the *trans* isomer.[778] For the more constrained tetramine 1,4,7,10-tetraazacyclodecane (cyclen; **48g**) only the *cis*-$[Rh(cyclen)Cl_2]^+$ ion has been characterized (as the dihydrate of the chloride salt).[775]

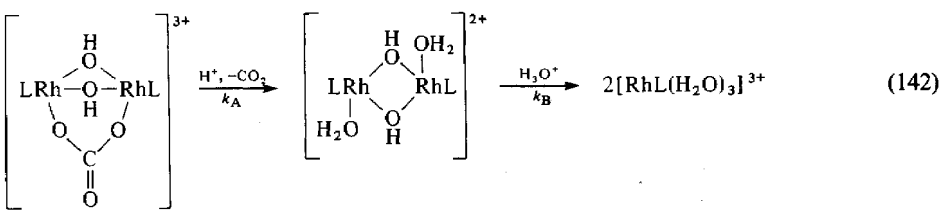
The coordination chemistry of the cyclic triamine 1,4,7-triazacyclononane ([9]aneN$_3$; **48h**) has been studied by Wieghardt *et al.* and has proven to be a rich area. In aqueous solution, [9]aneN$_3$

Table 54 Electronic Spectra of some Cyclic Polyaminerhodium(III) Complexes

Complex	λ_{max} (nm) (ε)	*Complex*	λ_{max} (nm) (ε)
XY	*[Rh(cyclam)XY]*$^{n+}$	*XY*	*[Rh(cyclam)XY]*$^{n+}$
cis-Cl_2^+	354 (223), 299 (308), 207 (33900)	*trans*-$ClBr^+$	418 (89), 312sh (95), 260sh (1950), 221 (32700)
trans-Cl_2^+	406 (78), 310sh (80), 242sh (3300), 204 (37100)	*trans*-ClI^+	493 (230), 445sh (138), 308 (3620), 245 (31300)
cis-Br_2^+	367 (243), 309 (871)		
trans-Br_2^+	429 (97.3), 285 (2520), 235 (34600)	*trans*-$Cl(N_3)^+$	382 (697), 270 (9390), 207 (23000)
cis-I_2^+	407 (1210), 295sh (5300), 260sh (17500), 228 (38400)	*trans*-$Cl(NCS)^+$	368 (340), 252 (8080)
		trans-BrI^+	497 (151), 459 (152), 321 (6200), 256 (33900)
trans-I_2^+	515sh (64), 466 (204), 353 (13100), 275 (34500), 226 (22800)	*trans*-$Br(N_3)^+$	393 (698), 281 (11900), 214 (21400)
cis-$(N_3)_2^+$	339sh (1250), 262 (11800)	*trans*-$Br(NCS)^+$	368 (355), 262 (8980)
trans-$(N_3)_2^+$	377 (892), 286 (12700), 208 (27100)	*trans*-$I(N_3)^+$	465sh (283), 417 (654), 300 (10100), 280sh (8970), 225 (20900)
cis-$(NO_2)_2^+$	293sh (1030)		
trans-$(NO_2)_2^+$	320sh (535), 260sh (2100), 213 (30800)	*trans*-$I(NCS)^+$	434 (393), 412 (413), 296 (4220), 274 (5660), 224 (30600)
cis-$(NCS)_2^+$	322 (1110), 244 (3630)		
trans-$(NCS)_2^+$	377 (882), 258 (3330)	*trans*-$(N_3)(NCS)^+$	352 (861), 270 (7330)
trans-$Cl(OH)^+$	363 (101), 276 (180)	*trans*-$(OH)_2^+$	341 (101), 277 (163)
trans-$Cl(H_2O)^{2+}$	385 (55), 296sh (101), 242sh (4420)	*trans*-$(H_2O)_2^{3+}$	352 (65)
		cis-$(OH)_2^+$	331 (226), 278 (202)
trans-$Br(OH)^+$	373 (113), 277sh (384)	*cis*-$(H_2O)_2^{3+}$	296 (249), 251 (230)
trans-$Br(H_2O)^{2+}$	468 (37), 403 (63), 310sh (106), 204 (25600)	*cis*-$(CN)_2^+$	281 (465), 218 (1830)[c]
		trans-$(CN)_2^+$	267 (270), 218 (1620)[c]
		cis-[Rh(cyclen)Cl_2]$^+$	365 (535), 302 (430)[d]
trans-$I(OH)^+$	443 (153), 393 (158), 275 (5330), 230 (26300)	$[Rh(sep)]^{3+}$	296 (309), 244sh[e]
		$[Rh(diNO_2sar)_3]Cl_3$	297 (553), 252 (347)[e]
		$[Rh(diAMsarH_2)_3]$-$Cl_5 \cdot 3.5H_2O$	299 (511), 251 (360)[e]
trans-$I(H_2O)^{2+}$	494 (222), 341sh (763), 301sh (1290), 271 (2240), 230 (24400)	$[Rh(L)_2]Br_3 \cdot 5H_2O$[b]	294 (265), 249 (316)[f]
		$[Rh_2(L)_2(\mu\text{-}OH)_2(H_2O)_2](ClO_4)_4$	340 (670)[f]
		$[Rh_2(L)_2(\mu\text{-}OH)_3](ClO_4)_3$	340 (437)[f]
trans-$N_3(OH)^+$	357 (525), 256 (6320)	$[Rh_2(L)_2(\mu\text{-}OH)_2(\mu\text{-}Ac)](ClO_4)_3$	337 (418)[f]
trans-$N_3(H_2O)^{2+}$	420sh (79), 363 (715), 261 (5640)	$[Rh_2(L)_2(\mu\text{-}OH)_2(OH)_2](ClO_4)_2$	340 (495)[f]
		$[Rh_2(L)_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]^{2+}$	343 (430)[f]
cis-$(OH)(H_2O)^{2+}$	328 (251), 291 (192)	$[Rh(L)(H_2O)_3]^{3+}$	340 (250), 280 (90)[g]
trans-$(OH)(H_2O)^{2+}$	342 (118), 274 (222)		

[a] [Rh(cyclam)XY]$^{n+}$ spectra from ref. 733. [b] L = ([9]aneN$_3$). [c] From ref. 774. [d] From ref. 775. [e] From ref. 776. [f] From ref. 777. [g] From ref. 765.

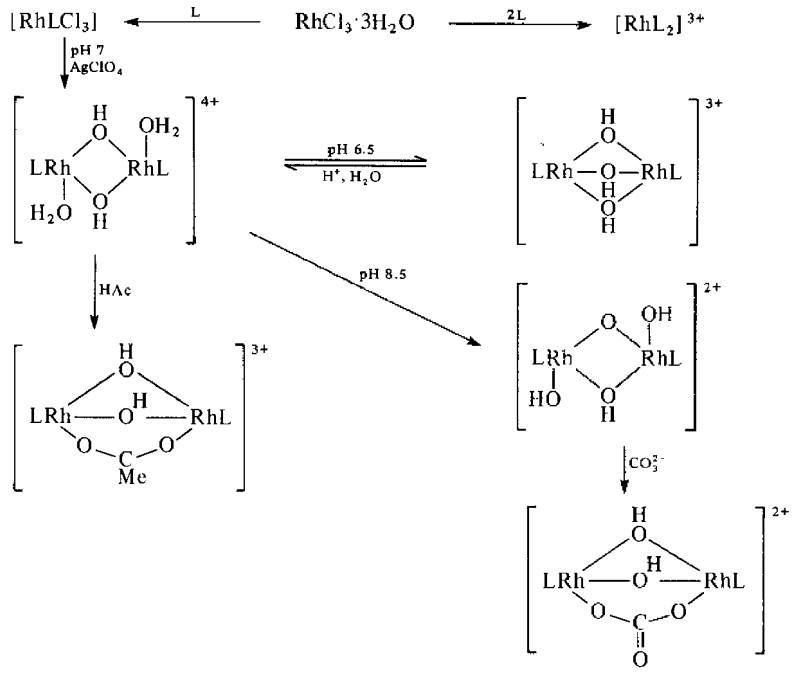
is a tridentate ligand, and a series of doubly and triply bridged hydroxo, carbonato and acetato dimers have been characterized.[775,777,779] As summarized in Scheme 26, $[Rh_2([9]aneN_3)_2(H_2O)_2(\mu\text{-}OH)_2]^{4+}$ is deprotonated at pH values above 8.5 and the resulting conjugate base reacts with carbonate to give a carbonato-bridged dimer.[775,779] A kinetic study of the decarboxylation (equation 142) has shown that both reactions exhibit an acidic dependence.[775] The X-ray structure of the diaquadi-μ-hydroxo tetravalent cation (as the perchlorate salt) confirmed the di-μ-hydroxo geometry.[779] Reaction of $RhCl_3 \cdot 3H_2O$ in ethanol with a methanolic solution of the *N,N′,N″*-trimethyl substituted version of this cyclic triamine (Me_3[9]aneN$_3$) leads to a yellow solid, which, if refluxed in an alkaline perchlorate solution, gives yellow crystals of $[Rh_2(Me_3[9]aneN_3)_2(\mu\text{-}OH)_3](ClO_4)_3$. A preliminary X-ray structure of these crystals confirms the triply bridged hydroxo geometry, and gives an Rh—Rh distance of about 2.96 Å.[777]



(142)

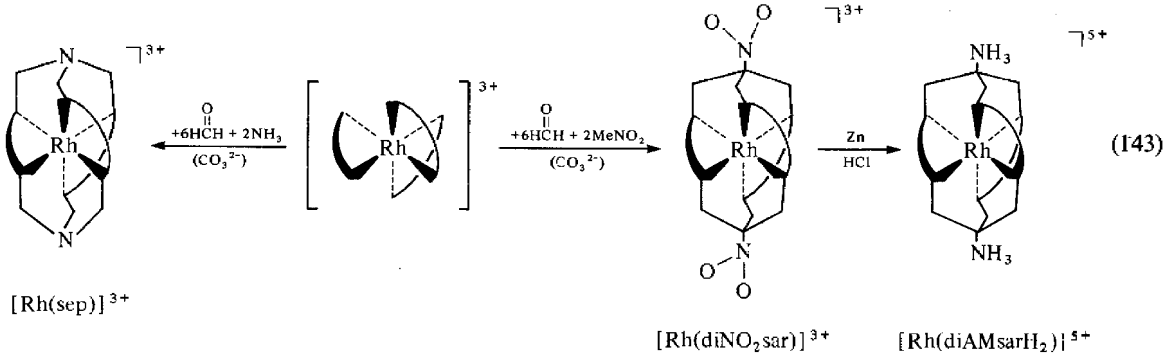
L = [9]aneN$_3$

Sargeson and co-workers have synthesized, characterized and studied the chemistry of a variety of remarkable macrocyclic amine complexes of Rh^{III}, in which the rhodium is virtually isolated



Scheme 26

within a cage defined by a six-coordinate aliphatic amine.[767] The syntheses are summarized in equation (143). Reaction of $[Rh(en)_3]^{3+}$ with six equivalents of formaldehyde and two equivalents of ammonia in an alkaline (carbonate) aqueous solution leads to the basic cage complex $[Rh(sep)]^{3+}$. If nitromethane is used instead of ammonia, the $[Rh(diNO_2sar)]^{3+}$ ion is formed; the nitrosyl functions can be reduced to amines with Zn/HCl. The compounds were characterized by UV/visible, IR and ^1H, ^{13}C and ^{103}Rh NMR; the electronic spectra are similar to that of the $[Rh(en)_3]^{3+}$ parent, and the ^1H decoupled ^{13}C NMR shows resonances for two sets of six equivalent methylenes, consistent with D_3 symmetry.



(143)

The effect of the cage on the one-electron reduction of the metal center has been studied in detail. Electrochemical reduction to $[Rh(sep)]^{2+}$ was observed at -1.8 V (*vs.* Ag/AgCl/0.1 M LiCl) in acetone solution, but not in water; reduction is reversible, but further reduction to Rh metal does occur at -2.2 V. The Rh^{II} thus formed is moderately stable, with a half-life of *ca.* 15 ms at 20 °C. As rapid as this decay of the Rh^{II} cage complex may seem, the one-electron reduction of Rh^{III} complexes is normally not reversible, and the Rh^{II} cages do not dimerize, disproportionate or undergo further reduction to the Rh^{I} complex. (While the Rh^{II} state is stabilized by the cage, the photoproduced ^3T excited state of $[Rh(sep)]^{3+}$ decays an order of magnitude more rapidly than the analogous state of $[Rh(NH_3)_6]^{3+}$; $t_{1/2} = 2.8$ μs and 27 μs, respectively.) Pulse radiolysis of $[Rh(sep)]^{3+}$ showed pseudo-first order quenching of the solvated electron ($k = 1.4 \times 10^{10}\ M^{-1}s^{-1}$ at 25 °C), producing $[Rh(sep)]^{2+}$. The authors also comment on the remarkably regiospecific nature of the synthesis of $[Rh(sep)]^{3+}$, as 11 molecules must condense to form the 14-membered ring macrocycle,

and this reaction can reach 90% yields. If chiral $[Rh(en)_3]^{3+}$ is used, the resulting cage is also chiral.[765]

48.6.2.5 N-heterocycle complexes

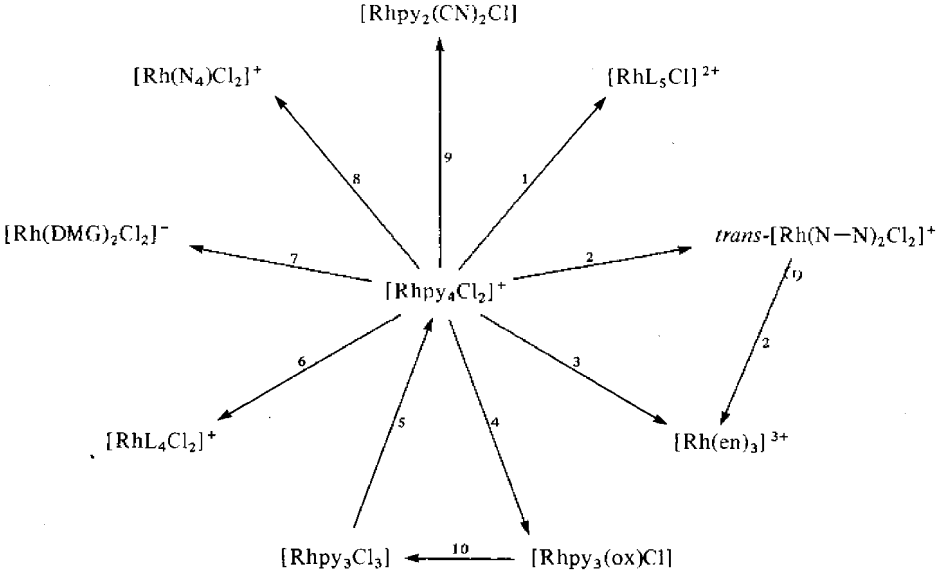
(*i*) *Pyridine complexes*

Numerous Rh^{III} complexes containing coordinated pyridine and substituted pyridines are known, but this area is dominated by the chemistry of the *trans*-$[Rhpy_4Cl_2]^+$ cation. First characterized by Jørgensen,[780] its chemistry has been studied extensively by Gillard, Wilkinson and co-workers, and it has served as the parent for a host of derivatives.

Attempts to replace the two chlorides by pyridine have been unsuccessful, and the hexapyridinerhodium(III) cation is unknown, although there are several reports of unsuccessful attempts to prepare it.[781] Reaction of *trans*-$[Rhpy_4Cl_2]^+$ in refluxing pyridine leads to *fac*- and *mer*-$[Rhpy_3Cl_3]$; the addition of ethanol leads to a pink residue identified as a chloro-bridged polymer $[Rhpy_2Cl_3]$.[781] Reaction of *trans*-$[Rhpy_4Cl_2]^+$ with Ag^+ (to remove Cl^-) presumably yields $[Rhpy_4(H_2O)_2]^{3+}$, but this material does not pick up even one additional pyridine when refluxed in neat pyridine for four days![781] Early claims for $[Rhpy_6]X_2$ and $[Rhpy_5X]X$ (X = Cl or Br)[782] were later shown to be due to the ubiquitous *trans*-$[Rhpy_4X_2]X$.[781,783]

The standard preparation of *trans*-$[Rhpy_4Cl_2]^+$ is due to Delépine,[784,785] who noticed that reaction of pyridine with $[RhCl_6]^{3-}$ leads to mixtures of $[Rhpy_3Cl_3]$ isomers, but that in the presence of primary or secondary alcohols, *trans*-$[Rhpy_4Cl_2]Cl$ is formed. (The role of the alcohol in this reaction is discussed in more detail in Section 48.6.2.5.iii.) Far IR spectra (pyridine ring vibrations, Rh—N and Rh—Cl stretches) of the *fac* and *mer* isomers of $[Rhpy_3Cl_3]$ confirmed the earlier isomer assignment.[786]

The *trans*-$[Rhpy_4Cl_2]^+$ ion is a convenient starting material, as the pyridines are readily replaced by other donors. Jørgensen's observation[787] that $[Rh(NH_3)_5Cl]Cl_2$ could be recrystallized from boiling pyridine, while NH_3 substitution of py in *trans*-$[Rhpy_4Cl_2]^+$ is facile, has been confirmed.[781] The lability of the pyridine ligands was emphasized in a recent secondary ion mass spectroscopy (SIMS) study of solid *trans*-$[Rhpy_4Cl_2]Cl \cdot 5H_2O$, which indicated that successive pyridine labilization occurred (the ions $[Rhpy_nCl_2]^+$ for $n = 4$, 3, 2 and 1 were detected), while Cl^- was not lost from the parent; no evidence of $[Rhpy_4Cl]^+$ could be detected.[788] Representative examples of the reactions of *trans*-$[Rhpy_4Cl_2]^+$ are given in Scheme 27 and Table 55. Pyridine volatility makes it an exceptionally convenient leaving group, as labilized pyridines can be steam distilled from the reaction flask. The neutral $[Rhpy_3(ox)X]$ complexes (presumably *mer*, X = Cl or Br) display an unusual synergistic solubility, as they are insoluble in both H_2O and pyridine, but are relatively soluble in mixtures of the two solvents, reaching a maximum solubility in 1:1 mixtures of the solvents.[791]



Scheme 27

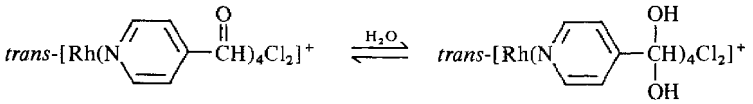
Table 55 Conditions for Reactions Cited in Scheme 27

Reaction	*Reactants*	*Ref.*
1	L = NH_3	789
	L = *N*-methylimidazole	790
2	N—N = en, pn	791
	N—N = phen	792
3	Excess ethylenediamine	601
4	Aqueous oxalate	793
5	Refluxing pyridine	781
6	L = substituted pyridine	781
7	Dimethylglyoxime	601
8	N_4 = trien, 2,3,2-tet	754, 790
	N_4 = 3,2,3-tet	769
9	Aqueous CN^-	794
10	Conc. HCl	791

An extensive number of substituted pyridine analogs of *trans*-$[Rhpy_4Cl_2]^+$ have been prepared *via* the path illustrated in equation (144). For the same reaction, if L = NH_3 or *N*-methylimidazole (miz), pentaamine complexes result. The $[Rh(miz)_4Cl_2]^+$ ion can be prepared by Cl^- anation of $[Rh(miz)_5Cl]^{2+}$ in refluxing aqueous ethanol (pH 3). No reaction is observed for L = α-picoline, 2,4-lutidine or 2-aminopyridine, probably due to steric hindrance. The electronic spectra for all of the $[RhL_4X_2]^+$ ions showed peaks at 409 and 439 nm (±2 nm). Water adds, reversibly, to *trans*-[Rh(4-formylpyridine)$_4$Cl$_2$]$^+$ as shown in equation (145); the analogous 3-formylpyridine complex is unreactive, and may be recovered unchanged from boiling water.[795]

$$RhX_3 \cdot 3H_2O + 4L \xrightarrow[\text{in } H_2O]{30\%\ EtOH} [RhL_4X_2]X \xrightarrow[H_2O]{HY} [RhL_4X_2]Y \qquad (144)$$

L = 3- or 4-substituted pyridine, 3,5-disubstituted pyridine, isoquinoline, pyrimidine, pyrazole or thiazole; X = Cl, Br (and I for L = py); Y = univalent anion



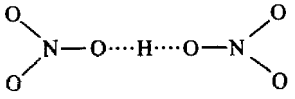
(145)

Halide substitution at *trans*-$[Rhpy_4Cl_2]^+$ is possible, but refluxing *trans*-$[Rhpy_4Cl_2]^+$ in HBr solution (4 M) does not lead to $[Rhpy_4Br_2]^+$, but *trans*-$[Rhpy_4Cl_2](H_5O_2)Br_2$. An unusual fluoride-assisted hydrolysis of *trans*-$[Rhpy_4X_2]^+$ (X = Cl, Br) rapidly leads to $[Rhpy_4X(OH)]^+$. Azide ion readily replaces Cl^- (and py) in $[Rhpy_4Cl_2]^+$, and the compounds $[Rhpy_n(N_3)_{6-n}]^{(n-3)+}$ (n = 2, 3, 4) have been prepared.[795] Thiocyanate does not react with $[Rhpy_4Cl_2]^+$, but NCO^- and NO_2^- each react to give incompletely characterized non-electrolytes.[795]

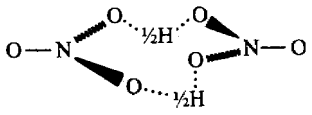
Photolysis (436 and 254 nm) leads to both halide and py labilization from *trans*-$[Rhpy_4X_2]^+$ (X = Cl, Br).[796] The efficiencies of Cl^- and py release are comparable (upon *d–d* excitation at 436 nm), but are uncharacteristically low for photoinduced Rh—Cl bond cleavage. Bromide release dominates over py release upon 254 nm excitation of *trans*-$[Rhpy_4Br_2]^+$. The photoreactions are presumed to proceed with retention of geometry.[796]

The *trans*-$[Rhpy_4Br_2]^+$ ion has been the cationic host to an interesting bit of chemistry concerning the $(HN_2O_6)^-$ anion. The salt was first formulated as $[Rhpy_4Br_2](NO_3)(HNO_3)$ by Poulenc,[797] and it was later proposed, on the basis of a broad IR band near 800 cm^{-1}, that the hydrogen dinitrate anion contains a symmetric H bond.[798] Thermogravimetric and differential thermal analysis showed that a molecule of nitric acid is released at *ca.* 200 °C.[799] A single-crystal X-ray analysis of *trans*-$[Rhpy_4Cl_2][H(NO_3)_2]$ showed that the hydrogen dinitrate anion has two nitrates arranged such that four oxygens (two from each nitrate) form a slightly distorted tetrahedron, with the mean O—O distance about 3.06 Å. The hydrogen atom was not found, but was presumed to be near the center of gravity of the oxygen tetrahedron.[800] The $[As(Ph)_4][H(NO_3)_2]$ salt also contains the hydrogen dinitrate anion, but in this case there is a linear, very short (O—O distance of 2.45 Å) hydrogen bond (**53a**); the anion of the Cs^+ salt has a structure similar to that of the $[Rhpy_4Cl_2]^+$ salt.[801] A neutron diffraction study[802] of *trans*-$[Rhpy_4Cl_2][H(NO_3)_2]$ revealed a disordered structure; the NO_3 moieties form a distorted tetrahedron of oxygen atoms, similar (but not identical) to that observed in the X-ray study,[800] where the hydrogen atoms are disordered between the two closest oxygen atoms (**53b**). The two sites are occupied with equal probability, so that the two non-coplanar nitrate groups may be considered to be bridged by two equivalent H bonds; the O—H—O moiety is bent with a

bond angle near 167.5°. The hydrogen dinitrate ion may, in fact, be a common ion in nitric acid solution, as Gillard and co-workers have prepared and analyzed the IR spectra of a variety of *trans*-$[Rhpy_4Cl_2]^+$ analogs which all contain the $[H(NO_3)_2]^-$ anion.[803] The *trans*-$[Rhpy_4Br_2]Br \cdot HBr \cdot 2H_2O$ crystalline salt has been proposed to contain the $(H_5O_2)^+$ cation with a symmetric O···H···O hydrogen bond between two H_2O moieties.



(53a)



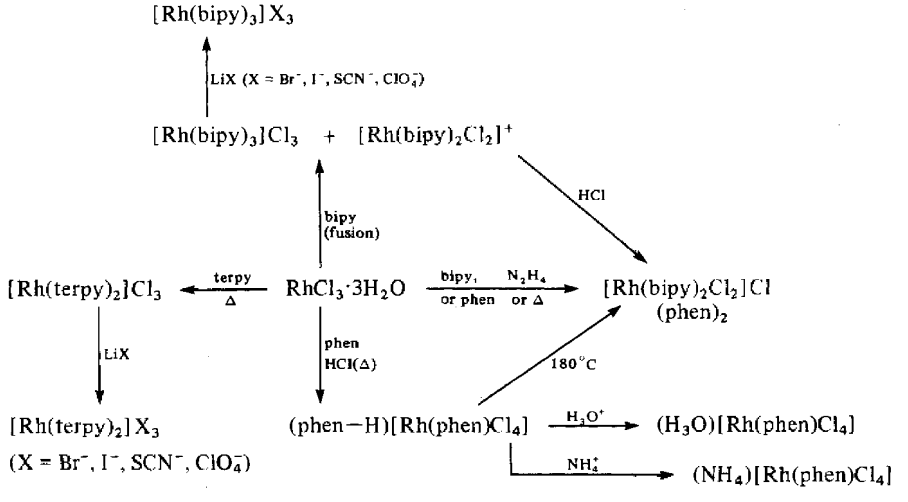
(53b)

Perhaps the most unusual, and potentially important, property of these pyridine–Rh^{III} complexes is their antibacterial activity. The activity is increased by substituting Br for Cl in the *trans*-$[Rhpy_4X_2]^+$ cation, and by adding lipophilic groups to the py ligand (*e.g.* Mepy, Etpy) and is decreased by adding polar groups (*e.g.* HOpy or H_2Npy). The activity seems specific to the *trans*-$[ML_4X_2]^+$ cation (M = Rh, but not Co or Ir; X = Cl, L = py or substituted py, but not NH_3 or $\frac{1}{2}$en).[804]

(*ii*) *Polypyridine complexes*

While not yet as extensive as the chemistry reported for bipy and phen complexes of ruthenium, the chemistry of rhodium polypyridine complexes (especially their excited states) has generated much recent interest. The claim of Lehn and co-workers[805] that excited states of $[Rh(bipy)_3]^{3+}$ are involved in the photoinduced generation of $H_{2(g)}$ from water has sparked renewed efforts to understand the rich excited state chemistry of these complexes.

Synthesis of polypyridine complexes of Rh^{III} generally involves replacing halide ligands with the chelated polypyridyls; fusion of $RhCl_3 \cdot 3H_2O$ and bipy is reported to yield $[Rh(bipy)_3]Cl_3$, and workup of the resulting solid in aqueous nitric acid gives an unreliable yield of $[Rh(bipy)_2Cl_2]$-NO_3.[806] More convenient and reliable syntheses take advantage of the catalytic properties of mild reducing agents (see Section 48.6.2.4.iii) as the reaction of $RhCl_3 \cdot 3H_2O$ with bipy (or phen) in ethanol/2-methoxyethanol solution,[601] or in ethanol with catalytic amounts of hydrazine,[792] gives $[Rh(LL)_2Cl_2]^+$ (or $[Rh(phen)_2Cl_2]^+$) in high yields. An uncatalyzed reaction of $[RhX_6]^{3-}$ (X = Cl, Br) with phen leads to the monosubstituted $[Rh(phen)X_4]^-$ anion, as the $(Hphen)^+$ salt, which can be further substituted to give $[Rh(phen)_2X_2]^+$;[807,808] the chloride form of the latter complex has been resolved on a cellulose column.[807] Mixed complexes of the series $[Rh(bipy)_n(phen)_{3-n}]^{3+}$ (n = 0–3), have been prepared by Crosby and Elfring by bipy or phen substitutions of both chlorides in $[Rh(N{-}{-}N)_2Cl_2]^+$ (N—N = bipy or phen).[809] Scheme 28 summarizes some synthetic paths for the various polypyridine complexes of Rh^{III}.



Scheme 28

The assignment of the geometric configuration for $[Rh(bipy)_2X_2]^+$ (and the phen analog) has been error prone and confusing, as electronic spectra,[601] acid adduct formation,[810] IR and Raman spectra,[808,811,812] ^1H NMR,[808] proposed mechanism of formation,[813,814] and X-ray powder patterns[815] have all been used to make (often conflicting) geometric assignments. It is now clear that these complexes, $[Rh(N—N)_2X_2]^+$ where (N—N) = bipy, phen or methyl or halo-substituted analogs; X = Cl, Br, I, all share the *cis* geometry. The *trans* configuration is unknown for these polypyridyl complexes, while the *cis* configuration is unknown for the monodentate pyridine analogs $[Rhpy_4X_2]^+$. Like the pyridine complexes, bis(bipy) complexes form acid adducts, and thermogravimetric analysis of $[Rh(bipy)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$, implies that the anion should be formulated as $[(H_5O_2)^+(2Cl^-)]^-$.[799]

Recent interest in Rh polypyridyl complexes has centered on the behavior of their excited states; this is an active and complicated research area, and our understanding is less than complete. Discussion here will proceed as follows: (a) the photochemical properties; (b) the chemistry of the reduced polypyridyl complexes; and (c) the role of Rh^{III} polypyridyls as electron-transfer agents in the quenching of photoproduced excited states of $[Ru(bipy)_3]^{3+}$, and the photogeneration of H_2 from water.

In aqueous solution at room temperature, *cis*-$[Rh(N—N)_2X_2]^+$ (N—N = bipy or phen, X = Cl, Br, I) display deceptively simple photochemistry. Upon irradiation between 254 and 436 nm, all undergo stereoretentive halide loss, with the primary photoproduct being the corresponding $[Rh(N—N)_2X(H_2O)]^{2+}$ complex; minor Rh—N bond cleavage also occurs.[796] Halide release quantum yields are about an order of magnitude lower than those generally observed for haloamines of Rh^{III}. In a rigid environment at reduced temperature, these complexes luminesce, and on the basis of lifetime measurements, a heavy-atom perturbation effect, and the large Stokes shifts, the luminescence has been assigned as a spin-forbidden phosphorescence.[816] This assignment was confirmed in a study of the luminescence at 77 K in an alcohol glass matrix (ethanol–methanol, 4:1), in which intrinsic lifetimes, radiative rate constants, and quenching rate constants were determined. The intersystem crossing efficiency to the emitting triplet (a ligand-centered π–π^* state) was found to be 'within 30% of unity', and a semi-empirical spin–orbit-coupling model was used to predict the intrinsic lifetimes of the excited states.[817] DeArmond and Hillis have reported the absorption and emission spectra for several polypyridyl complexes of Rh^{III} (room temperature and at 77 K in ethylene glycol–water 1:1, or ethanol–methanol 5:1 glasses); their spectral results are given in Table 56.[818] The tris(bipy) and tris(phen) complexes show structured emission in the same region as the free ligands, implying that the luminescence is from a ligand-localized π–π^* state, as suggested by Crosby.[820] The bis(bipy) and bis(phen) cations showed broad, structureless emissions at low energy (with short lifetimes), consistent with Crosby's assignment of a d–d,[816] $^3T_1 \rightarrow {}^1A_1$ phosphorescence.[818] The intensity of the ligand-localized phosphorescence again suggests that the intersystem crossing efficiency for the tris-chelated complexes is near unity, but the lower intensity for the bis-chelated complexes suggests that population of the metal-centered $^3T_1$ state is less efficient.[818] Emission from these Rh complexes is generally more efficient than from the Ir analogs.

Emission from the ligand-localized π–π^* state of the tris-chelated complexes was further studied by Crosby, who prepared and showed that the luminescence (77 K, ethanol–methanol 4:1 glasses) from $[Rh(bipy)_n(phen)_{3-n}]^{3+}$ (n = 0–3), displayed long lifetimes (41, 24, 16 and 2.5 ms for n = 0, 1,

Table 56 Absorption and Emission Spectra of some $[Rh(N—N)_2Cl_2]^+$ Complexes (77 K)[818]

Complex	*Absorption spectra* λ_{max} (nm) (ε)	*Emission* λ_{max} (nm)	*Lifetime* (s)
$[Rh(phen)_3]Cl_3$	351 (3080), 334 (4180), 314 (10 400), 304 (20 200), 459sh, 450, 279 (75 500)	555sh, 481	4.84×10^{-2}
$[Rh(bipy)_3]Cl_3$	321 (38 300), 307 (36 300), 242 (40 500)	521sh, 510, 483, 450	2.21×10^{-3}
cis-$[Rh(phen)_2Cl_2]Cl$	385sh (98), 355 (3410), 337 (3480), 321sh (5130), 298sh (21 100), 275 (65 400)	709	4.15×10^{-5}
cis-$[Rh(bipy)_2Cl_2]Cl$	382 (108), 342sh (2460), 313 (28 800), 302 (24 000)	704	4.73×10^{-5}
trans-$[Rh(py)_4Cl_2]Cl$	465 (~3), 403 (81.5), 268 (8340), 262 (12 500), 257 (13 600)	649	5.2×10^{-4}
$[Rh(en)_3]Cl_3$	350sh, 296 (244), 253 (195)	588	2.1×10^{-5}
$[Rh(en)_2Cl_2]Cl$	469sh (~1.5), 400 (82.2), 284 (123)	690	1.5×10^{-5}

2 and 3, respectively), consistent with phosphorescence from a $^3(\pi-\pi^*)$ excited state.[809] For $n = 0$ and 3, exponential decay of the phosphorescence was observed, but the mixed chelates ($n = 1$ and 2) showed non-exponential behavior. Crosby concludes that intraligand interaction is small in these complexes in both ground and excited states, and that the virtually isolated, ligand-localized, excited states decay independently, the apparent non-exponential decay resulting from the simultaneous, and unrelated, exponential decays from bipy- and phen-centered excited states. Supporting this model, Crosby notes that the absorption spectra of $[Rh(bipy)(phen)_2]^{3+}$ and $[Rh(bipy)_2(phen)]^{3+}$ are virtually indistinguishable from the spectra of appropriate mixtures of the tris(bipy) and tris(phen) complexes.[809]

A study of $[Rh(phen)_3]^{3+}$ confirmed that emission comes from a $^3(\pi-\pi^*)$ state.[819] No emission was observed in fluid solution, but a long-lived excited state occurs in DMF at room temperature, as 290 nm irradiation of $[Rh(phen)_3]^{3+}$ causes the characteristic 780 nm phosphorescence of $*[Cr(CN)_6]^{3-}$ (equation 146). The Sterm–Volmer constant of $3.0 \times 10^3\ M^{-1}$ implies a lower limit for the excited state lifetime of *ca.* 0.30 ms. Sensitization of biacetyl, and the oxidation of diphenylamine (in acetonitrile) and of 1,3,5-trimethoxybenzene are also observed for $*[Rh(phen)_3]^{3+}$, implying that the $^3(\pi-\pi^*)$ state of $*[Rh(phen)_3]^{3+}$ is a powerful oxidant. A potential of 2.00 V is calculated for the $*[Rh(phen)_3]^{3+}/[Rh(phen)_3]^{3+}$ couple,[819] making the excited state of $[Rh(bipy)_3]^{3+}$ a better oxidant than the Ru^{II}, Cr^{III} or Os^{II} analogs.

$$*[Rh(phen)_3]^{3+} + [Cr(CN)_6]^{3-} \longrightarrow [Rh(phen)_3]^{3+} + *[Cr(CN)_6]^{3-} \xrightarrow[\text{phosphorescence}]{780\text{ nm}} [Cr(CN)_6]^{3-} \quad (146)$$

In contrast, emission from $[Rh(bipy)_2X_2]^+$ is from a metal-centered, $^3(d-d)$ state. The various low-lying excited states for $[Rh(bipy)_2Cl_2]^+$ are represented in Figure 3, with initial excitation into the $^1(\pi-\pi^*)$ ligand state followed by relaxation and eventual phosphorescence from the $^3(d-d)$ state. The rise times for phosphoresence were reported to be 350–630 ns in room temperature solution and at 77 K,[820] but these values were later found to be artifacts of the detection system.[821] The emitting $^3(d-d)$ states of $[Rh(bipy)_2X_2]^+$ absorb at 580 (X = Cl) and 550 nm (X = Br), and the lifetimes of their transient absorptions (measured by time-resolved absorption spectroscopy in air-saturated ethanol–methanol (4:1) solution at room temperature) were found to be 84 ns (X = Cl) and 54 ns (X = Br).[821] (If the solutions are deoxygenated, the lifetimes increase by about a factor of five.) The presumed relaxation path is represented in equation (147), with the rate of internal conversion (IC) $\approx 4 \times 10^{11}\ s^{-1}$, followed by intersystem crossing (ISC), localized within the *d*-manifold, with the rate constant *ca.* 8×10^{11}.[821]

$$^1(\pi-\pi^*) \xrightarrow{IC} {}^1(d-d) \xrightarrow{ISC} {}^3(d-d) \quad (147)$$

A recent study[822] of the effect of steric interactions on the luminescence of 2,2′-bipyridyl complexes of Rh^{III} found luminescence from both ligand and metal-centered orbitals of $[Rh(dmbpy)_3]^{3+}$ (dmbpy = 3,3′-dimethyl-2,2′-bipyridyl). At 77 K the metal-centered luminescence dominates, but in fluid solution the ligand-centered emission is enhanced. As in the unsubstituted analogs, ligand-centered luminescence dominates under all conditions for $[Rh(dmbpy)_2Cl_2]^+$. Luminescence from fluid solutions of $[Rh(phen)_3]^{3+}$ and $[Rh(bipy)_3]^{3+}$ is consistent with the 77 K behavior,[816] as ligand-centered emission is observed.[822]

Closely tied to the photochemistry of these complexes is their behavior in the presence of reducing agents. Reduction of $[Rh(bipy)_3]^{3+}$ with BH_4^- or Zn amalgam was reported to yield $[Rh(bipy)_2]^+$.[401]

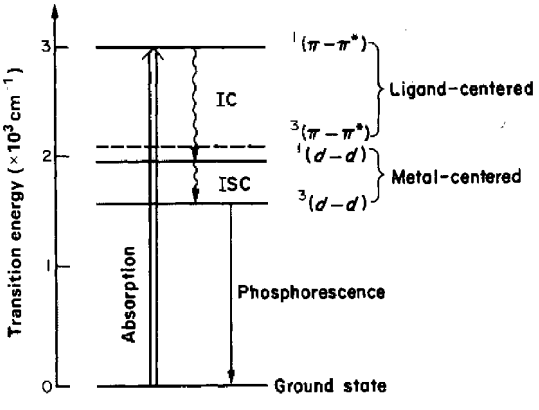
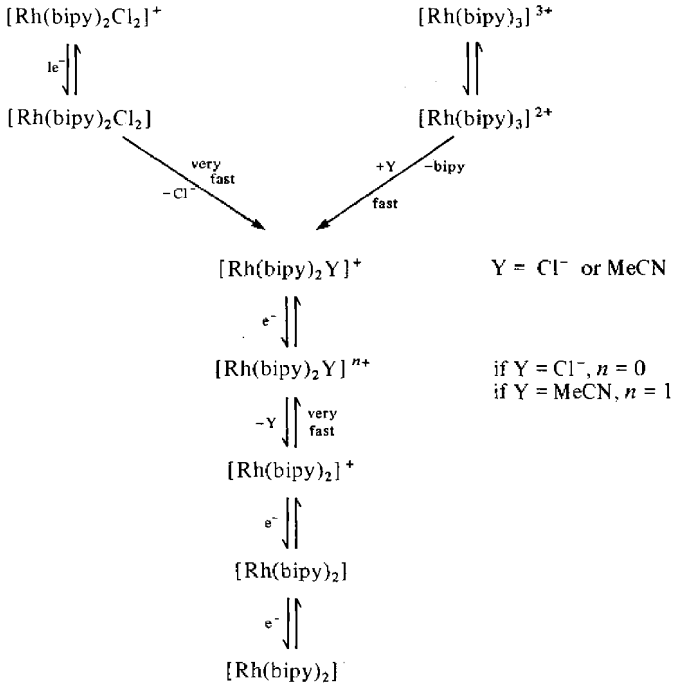


Figure 3 Low-lying excited states of $[Rh(bipy)_2Cl_2]^+$

The kinetics of the reduction of $[Rh(bipy)_2Cl_2]^+$ in alkaline aqueous ethanol (under H_2) revealed a two stage process: an initial induction period, during which time Rh^I species formed, and a faster, autocatalytic region. The kinetics could be fit to the expression: $d[Rh^I]/dt = k[Rh^{III}]^2[Rh^I]$. The reaction rate was retarded by the addition of excess bipy, suggesting the suppression of a dissociation equilibrium, and the rate constant varies with $[OH^-]$, but not with $[Cl^-]$. A five-step mechanism for the autocatalytic process was proposed, involving the formation (*via* an unspecified mechanism) of $[Rh(bipy)_2]^+$, followed by the oxidative-addition of H_2 to $[Rh(bipy)_2]^+$, and chloro-bridged dimeric and trimeric intermediates.[823]

The electrochemical reduction of $[Rh(bipy)_2Cl_2]^+$ and $[Rh(bipy)_3]^{3+}$ in room temperature acetonitrile solutions has been studied by DeArmond and co-workers and is represented in Scheme 29. For both complexes, they claim that the initial one-electron reduction is followed by a 'moderately' fast elimination of a ligand (Cl^- or bipy); if the cyclic voltammetry scans are sufficiently rapid, this reduction is reversible.[824] After ligand labilization, the two paths merge, and there is evidence for two additional one-electron reductions, leading to $[Rh(bipy)_2]$ and $[Rh(bipy)_2]^-$.



Scheme 29

Studies of the reaction of $[Rh(bipy)_3]^{3+}$ with radiation-generated reducing radicals ($e^-_{(aq)}$, $CO_2^{\cdot}$ and Me_2COH) have shown that, however appealing, this relatively simple picture is incomplete.[825] These strong one-electron reductants quantitatively and rapidly ($k = 10^9$–$10^{10}\,M^{-1}s^{-1}$) generate $[Rh(bipy)_3]^{2+}$. This ion has the following properties: (a) it has an absorption maximum at 485 nm ($\varepsilon = 1000$); (b) it slowly loses bipy ($k = 0.45 \pm 0.05\,s^{-1}$ at pH 3–10); (c) it is extremely air-sensitive, and reacts with O_2 ($k = 4.9 \times 10^8\,M^{-1}s^{-1}$); (d) in alkaline solution, $[Rh(bipy)_3]^{2+}$ disproportionates (equation 148), giving the red-violet $[Rh(bipy)_2]^+$ ion and the starting complex; and (e) in very alkaline solutions (pH > 10), $[Rh(bipy)_3]^{2+}$ reduces $[Rh(bipy)_3]^{3+}$, resulting in a redox-catalyzed chain of ligand labilizations.

$$[Rh(bipy)_3]^{2+} + [Rh(bipy)_2]^{2+} \rightleftharpoons \underset{\text{(red-violet)}}{[Rh(bipy)_2]^+} + [Rh(bipy)_3]^{3+} \quad (148)$$

The two-electron reduction product, initially identified as '$[Rh(bipy)_2]^+$' is a most mercurial species, and Hoffman has identified four forms. (a) A red-violet, soluble form [λ_{max} at 518 nm (9500)] identified as $[Rh(bipy)_2(OH)_n]^{(1-n)+}$. This may be dimeric, with OH^- bridges. In neutral solution, the maximum absorbance shifts to 415 nm with a shoulder near 470 nm. (b) A violet, insoluble form, identified as $[Rh(bipy)_2X]$, for $X = Cl^-$, ClO_4^-, *etc.* (c) A transient green form, observed when the red-violet species is acidified. This is presumably $[Rh(bipy)_2(H_2O)_n]^+$. (d) A colorless species formed in acidic solution, which is presumed to be a Rh^{III} hydride, *e.g.* $[Rh(bipy)_2(H)]^{2+}$.

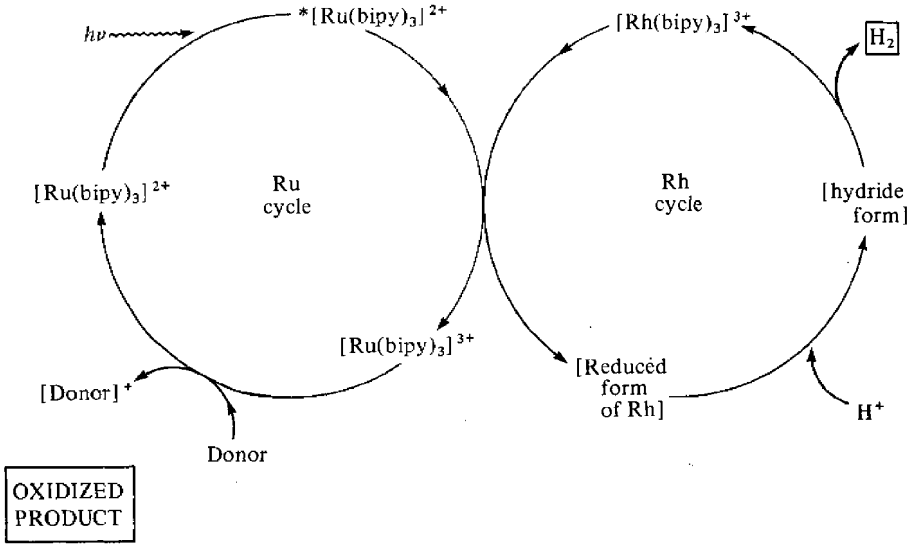
At 'natural pH' (around 5), reduction of $[Rh(bipy)_3]^{3+}$ with these radicals leads to H_2, with an efficiency of about 25%. The dihydrogen precursor is presumed to be the colorless RH^{III}–hydride for $[Rh(bipy)_2]^+$ is stable in an O_2 free environment, and at pH 10 a suspension of $[Rh(bipy)_2]ClO_4$ is stable for at least three months, and does not produce any dihydrogen.[825]

The reaction of radiolytically generated α-hydroxyalkyl radicals ($RR'\dot{C}OH$; R,R′ = H or Me) with $[Rh(phen)_3]^{3+}$ has also been studied, with the emphasis being on the fate of the radicals; equation (149) represents the observed process.[826] An earlier ESR study of such reactions in ethanol glasses found a metal-containing radical for the $[Rh(phen)_3]^{3+}$ system, but not when the starting complex was $[Rh(bipy)_3]^{3+}$.[827]

$$[Rh(phen)_3]^{3+} + RR'\dot{C}OH \xrightarrow{k_a} \text{adduct} \longrightarrow \text{products} \xrightarrow{k} [Rh(phen)_3]^{2+} + R\overset{\overset{O}{\|}}{C}R' \quad (149)$$

The importance of the reduced forms of $[Rh(bipy)_3]^{3+}$ is due to the fact that Rh^{III} polypyridyl complexes oxidatively quench the excited state formed upon visible light irradiation of $[Ru(bipy)_3]^{2+}$ (equation 150). Interest in this redox quenching dramatically increased when Lehn and co-workers demonstrated that aqueous solutions containing $[Ru(bipy)_3]^{2+}$, $RhCl_3 \cdot 3H_2O$, K_2PtCl_6 (or K_2PtCl_4), bipy and triethanolamine (TEOA) generated H_2 when the Ru complex was irradiated.[805] The role of the rhodium in this reaction has been the source of much discussion, as reduced forms of $[Rh(bipy)_3]^{3+}$ are thought to be the precursors to H_2 formation. In a detailed analysis of the mechanism of the H_2 generation, Lehn suggests that there are two catalytic cycles: the $[Ru(bipy)_3]^{2+}$ cycle and the $[Rh(bipy)_3]^{3+}$ cycle.[828] He conjectures that the $[Rh(bipy)_3]^{3+}$ serves as a 'relay species', which mediates water reduction by intermediate storage of electrons. This process is thought to involve a series of one-electron transfers, involving $[Rh(bipy)_2]^+$ and hydrido(bipy)rhodium species. A simplified representation of the relationship of the two catalytic cycles is shown in Scheme 30. Formation of H_2 requires two electrons, but the electrochemical experiments of DeArmond[824] showed that in acetonitrile the first two reduction potentials for $[Rh(bipy)_3]^{3+}$ are close (−0.86 and −1.00 V), so that formation of the ubiquitous $[Rh(bipy)_2]^+$ is facile.

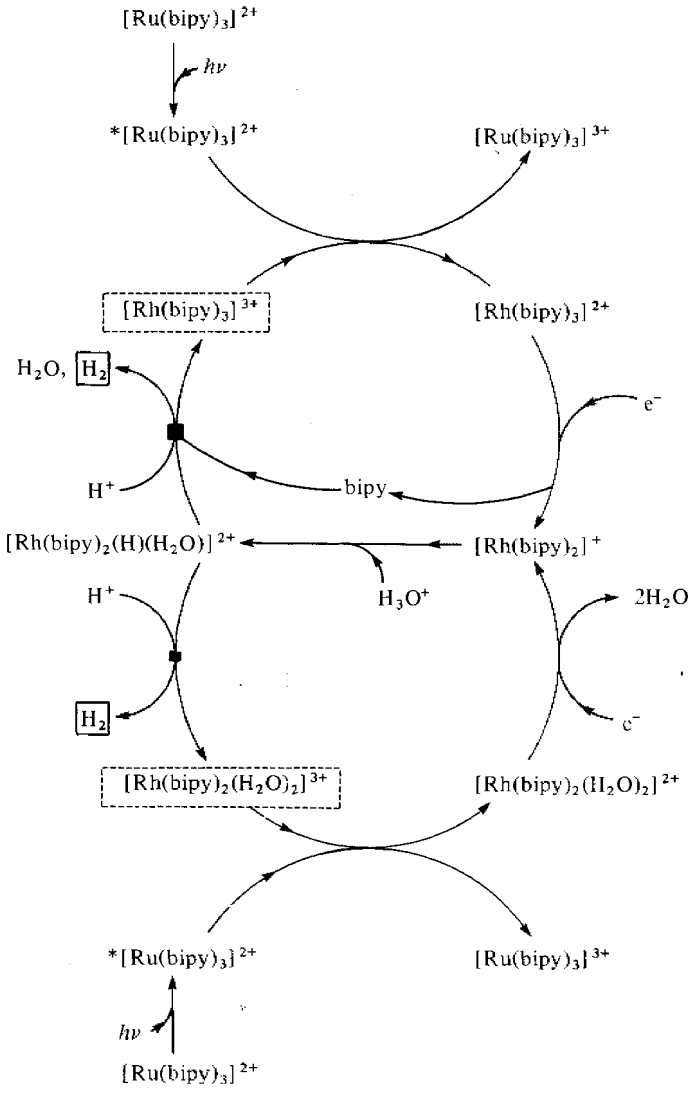
$$*[Ru(bipy)_3]^{2+} + [Rh(bipy)_3]^{3+} \longrightarrow [Ru(bipy)_3]^{3+} + [Rh(bipy)_3]^{2+} \quad (150)$$



Scheme 30

Lehn notes that photolysis of alkaline (pH > 10) solutions of $[Ru(bipy)_3]^{2+}$ in the presence of $[Rh(bipy)_3]^{3+}$ and TEOA (but no Pt) leads to the formation of the 520 nm peak characteristic of $[Rh(bipy)_2]^+$, suggesting that two-electron reduction is possible in this non-complementary system. They conclude that there are at least two paths possible within the Rh cycle, each involving a hydridorhodium(III) species formed *via* the oxidative-addition of H_3O^+ (or H_2O) to $[Rh(bipy)_2]^+$ (equation 151). The two possible paths within the Rh catalytic cycle are presented in Scheme 31.

Other workers have attempted to make sense of this complex set of reactions, and much of the work has concentrated on the nature of the transient $[Rh(bipy)_3]^{2+}$, which is assumed to be the



$$[Rh(bipy)_2]^+ + H_3O^+ \rightleftharpoons [Rh(bipy)_2(H)(H_2O)]^{2+} \overset{H^+}{\underset{OH^-}{\rightleftharpoons}} \quad (151)$$

$$[Rh(bipy)_2(H)(OH)]^+ \rightleftharpoons [Rh(bipy)_2]^+ + H_2O$$

Scheme 31

primary product upon quenching the Ru excited state. No H_2 is generated in the absence of Pt salts, and it has been shown that the Pt prevents the disproportionation of the $[Rh(bipy)_3]^{2+}$ (into Rh^{III} and Rh^{I} species).[829] A detailed study of the electrochemistry and quenching ability of a variety of RhL_3^{3+} ions (L = bipy, 4,4′-Me_2bipy, phen, 5-Clphen, 5-Brphen, 5-Phphen, 5-Mephen, 5,6-Me_2phen and 4,7-Me_2phen) as well as $[Rh(terpy)_2]^{3+}$ showed that all of these cations oxidatively quench the photoproduced $*[Ru(bipy)_3]^{2+}$ (equation 150). Detailed study of quenching by the $[Rh(4,4'\text{-}Me_2phen)_3]^{3+}$ ion suggested that the electron-transfer during the quenching is a facile and endergonic process.[830] Creutz and Sutin showed that a strong correlation exists between reduction potentials obtained in acetonitrile (where the one-electron reduction is quasi-reversible)[824] and those estimated in aqueous solution, implying that data collected in acetonitrile can be used to estimate aqueous behavior. They also argued against DeArmond's interpretation (Scheme 29), and reversed their earlier conclusion,[829] and concluded that the irritating irreversibility of the reduction of $[Rh(bipy)_3]^{3+}$ is due to rapid ligand labilization from the two-electron reduction product (equations 152–154); they estimate that $k_f \approx 5 \times 10^4 s^{-1}$ in H_2O at 25 °C. Pointing to the exceedingly rapid self-exchange between $[RhL_3]^{3+}$ and $[RhL_3]^{2+}$ ($> 10^9 M^{-1} s^{-1}$), they also suggest that the immediate quenching product is not a Rh^{II} species. Rather, they suggest that ligand reduction occurs, generat-

ing a species more appropriately designated as $[Rh^{III}L_2(L^-)]^{2+}$. They recognize a few inconsistencies in this designation, and comment that our current view of the immediate quenching product $[RhL_3]^{2+}$ contains some anomalies which need to be corrected.[830] A more detailed discussion of this interesting ion is presented elsewhere.[831]

$$[Rh(bipy)_3]^{3+} + e^- \longrightarrow [Rh(bipy)_3]^{2+} \quad (152)$$

$$[Rh(bipy)_3]^{2+} + e^- \longrightarrow [Rh(bipy)_3]^{+} \quad (153)$$

$$[Rh(bipy)_3]^{+} \xrightarrow{k_r} [Rh(bipy)_2]^{+} + bipy \quad (154)$$

The current status of our understanding in this area has been succinctly summarized by Hoffman, who commented that '. . .reduction of $[Rh(bipy)_3]^{3+}$ in aqueous solution yields a very rich chemistry. . . Both $[Rh(bipy)_3]^{2+}$ and $[Rh(bipy)_2]^{+}$ are involved in highly complex interlocking ligand-labilization, acid–base, redox, and aggregation reactions'.[825]

(*iii*) *Catalysis of substitutions at Rh^{III}*

Pyridine complexes of Rh^{III} have played a central role in the still poorly understood area of catalyzed substitutions at Rh^{III} centers. Delépine first noted that the consecutive substitution of $[RhCl_6]^{3-}$ by pyridine leads to the neutral, and insoluble, $[Rhpy_3Cl_3]$, but that if the aqueous solvent includes some alcohol, pyridine substitution continues and *trans*-$[Rhpy_4Cl_2]^+$ is the final product (equation 155).[784] Delépine showed that primary alcohols all had comparable effects on the rate of formation of $[Rhpy_4Cl_2]^+$, and that secondary alcohols were less active than primary alcohols.[785] Tertiary alcohols proved to be totally inactive, as are ether, dioxane or acetone. Poulenc had also reported that ethanol catalyzed substitutions at Rh^{III} centers.[793]

$$[RhCl_6]^{3-} \xrightarrow{+py,\ -Cl^-} [Rh(py)_3Cl_3]_{(s)} \xrightarrow[alcohol]{py} [Rh(py)_4Cl_2]Cl \quad (155)$$

Interest in this area was stimulated by a report from Basolo and co-workers,[832] who discussed possible mechanisms for the catalysis. They showed that the alcohols are true catalysts and are not consumed in the reaction (despite the detection of trace amounts of acetaldehyde as a reaction product), and that the substitutions could be catalyzed by a variety of reducing agents (*e.g.* Sn^{II}, BH_4^-, N_2H_4, H_3PO_2). The Co^{II} ion and the $[Rh_2OAc_4]$ dimer are both inactive, and while $[Rh(CO)Cl(PPh_3)_2]$ and $[Rh(CO)(SCN)(PPh_3)_2]$ are inactive, the dimer $[Rh(CO)_2Cl]_2$ is an extremely active catalyst. Kinetic studies were hampered by the evanescence of the catalyst, but Basolo did conclude that the reaction is first-order in Rh and catalyst, zero-order in pyridine (if in excess), and that Cl^- (as well as NO_3^- and ClO_4^-) inhibit the formation of *trans*-$[Rhpy_4Cl_2]^+$. In the presence of soft ligands, alkaline solutions of $RhCl_3 \cdot 3H_2O$ can be reduced to the Rh^I state by alcohols.[833] Basolo concluded that the Delépine catalyst involves a Rh^I species, and suggested a mechanism analogous to Pt^{II} catalysis of substitutions at Pt^{IV} centers (equations 156–158).[834,835]

$$[RhCl_5(H_2O)]^{2-} \xrightarrow{reductant} Rh^I \quad (156)$$

$$Rh^I + 4py \longrightarrow [Rh(py)_4]^+ \quad (157)$$

$$H_2O + [Rhpy_4]^+ + [RhCl_5(H_2O)]^{2-} \rightleftharpoons \{H_2O\text{—}Rhpy_4\text{—}Cl\text{—}RhCl_4OH_2\}^- \xrightarrow{fast} trans\text{-}[Rhpy_4Cl(OH_2)]^{2+} + Rh^I \xrightarrow[fast]{py} trans\text{-}[Rhpy_4Cl_2]^+ \quad (158)$$

With general agreement that a reduced species must be catalyzing substitutions at Rh^{III}, polarographic studies were used to investigate the nature of the reduced (and presumably catalytically active) species. Early work, using pyridine-supporting electrolyte, found the approximate reduction potentials, and provided evidence for a two-electron reduction.[836–838] Gillard and co-workers used DC polarography at a DME to examine many Rh^{III} complexes,[839,840] and proposed a two-electron reduction, noting that complexes with aza aromatic ligands are reduced at significantly more positive potentials than their amine analogs. They suggested Rh^I or Rh^{III}—H species as the primary reduction products. For py-containing complexes, a second reduction wave was observed, which was assigned to pyridine reduction; no second wave was observed for the ethylenediamine-containing ligands. For *cis*-α-$[Rh(trien)Cl_2]^+$, however, two waves were observed, ($E_{\frac{1}{2}} = -0.38$ and -0.75 V; both with $n \approx 2$), and monohydride and dihydride species were presumed to be the

product of these two reductions (equation 159). Reinvestigation[839] of the previously studied[841] reduction of $[Rh(H_2edta)Cl_2]^-$ (initially thought to involve a three-electron reduction) indicated a similar two-wave system ($n \approx 2$ for each wave), presumably also leading to monohydride and dihydrido Rh^{III} species, although the products were not separated, and NMR signals from the resulting hydrides could not be detected.

$$[Rh(trien)Cl_2]^+ \xrightarrow[+H_2O,\ -Cl^-,\ -OH^-]{2e^-,\ E_{\frac{1}{2}} = -0.38\,V} [Rh(trien)Cl(H)]^+ \xrightarrow[+H_2O,\ -Cl^-,\ -OH^-]{2e^-,\ E_{\frac{1}{2}} = -0.75\,V} [Rh(trien)(H)_2]^+ \quad (159)$$

The formation of a single Rh^{III} hydride was questioned in a detailed study of the polarography and coulometry of $[Rhpy_4Cl_2]^+$. In an aqueous pyridine–pyridinium chloride–sodium chloride electrolyte (pH 5.3), this ion displays two distinctive types of polarographic behavior.[842] The 'normal' wave ($E_{1/2} = -0.43$ V *vs.* SCE) is a diffusion-controlled, two-electron reduction at the DME to give an uncharacterized Rh^I product; in solutions with high pyridine concentrations, an 'enhanced' reduction also occurs at the DME surface, which often masked the 'normal' reduction, leading to H^+ consumption and the generation of hydrides. In large-scale reductions of $[Rhpy_4Cl_2]^+$, they observed the consumption of 1.4 mol of H^+ per mol of Rh^{III} species reduced, which is not consistent with a single Rh^{III} hydride product. Their proposed sequence (equations 160–162) does not, however, clearly illuminate what must be a complex reaction sequence.[842]

$$Rh^{III} + 2e^- \longrightarrow Rh^I \quad \text{(normal wave)} \quad (160)$$

$$Rh^I + pyH^+ \longrightarrow Rh^{III} + H^- + py \quad \text{(enhanced wave)} \quad (161)$$

$$xRh^I + yH^+ \longrightarrow \text{products, where } y > x \quad (162)$$

Controlled-potential reduction of aqueous solutions of *trans*-$[Rh(en)_2Cl_2]^+$ in oxygen-free environments leads to the two-electron reduction product *trans*-$[Rh(en)_2(OH)(H)]^+$.[675] In the process of reduction, 2 *F* per Rh atom are consumed, but an intermediate with an absorption band at 338 nm ($\varepsilon = 9000$) reached maximum concentration at *ca.* 0.9 *F* per Rh. This oxygen-sensitive, diamagnetic intermediate does not catalyze substitutions at Rh^{III} centers, which suggests its formulation as the Rh^{II} dimer $[(H_2O)(en)_2Rh—Rh(en)_2(H_2O)]^{4+}$.[843] Atomic absorption analysis of the one-electron reduced solution (reduced at a Hg electrode) revealed the presence of mercury, which led Anson and Gulens to question the Rh^{II} dimer formulation and to propose that mercury leads to a Hg^{2+}-bridged, Rh^I dimer (equation 163). This same species, with the electronic spectra reported by Gillard for the Rh^{II} dimer, could also be prepared by oxidizing *trans*-$[Rh(en)_2(H)(H_2O)]^{2+}$ at mercury electrodes, and by mixing Hg^{2+} solutions with solutions of *trans*-$[Rh(en)_2(H)(H_2O)]^{2+}$. The formation of this trinuclear species can be regarded as a Lewis acid–base complex between Hg^{2+} and the extremely basic $[Rh(en)_2]^+$.[844]

$$2[Rh(en)_2Cl_2]^+ + Hg + 2e^- \longrightarrow \{[Rh(en)_2]_2Hg\}^{4+} + 4Cl^- \quad (163)$$

The two-electron reduction product, *trans*-$[Rh(en)_2(OH)(H)]^+$ displays a sharp ^1H NMR signal at 30.6 τ. The pseudo acid–base equilibrium, represented in equation (164), was proposed to explain the observation that this peak broadens as the pH is raised, disappearing completely by pH 13.

$$[Rh(en)_2]^+ + H_3O^+ \rightleftharpoons [Rh(en)_2(H)(H_2O)]^{2+} \rightleftharpoons [Rh(en)_2(H)(OH)]^+ + H^+ \quad (164)$$

The formation of the hydridohydroxo ion can be considered to be the result of stereoretentive oxidative addition of H_2O across the $[Rh(en)_2]^+$. Acidic solutions of $[Rh(en)_2(OH)(H)]^+$ are stable, even in the presence of O_2, but in alkaline solution it reacts rapidly with oxygen, giving the hydroxoperoxo Rh^{III} monomer, *trans*-$[Rh(en)_2(OH)(OOH)]^+$ (equation 165). Interference from the secondary reaction (equation 166) complicates the overall stoichiometry of the reaction.[675] Concentration of this reaction mixture ($[Rh(en)_2(OH)_2]^+ + [Rh(en)_2(OH)(OOH)]^+$) in the presence of oxygen (pH 9–10) causes a color change to red and then to deep blue, with the formation of the superoxo-bridged Rh^{III} dimer, identified as $[(H_2O)(en)_2RhO_2Rh(en)_2(H_2O)]^{5+}$.[675] The transient red color is reminiscent of the electrochemical reduction of $[Rh(NH_3)_4(OH)(OOH)]^+$, which passes through a pink transient, after the consumption of 1 *F* per Rh, tentatively identified as the hydroxosuperoxo complex.[845]

$$[Rh(en)_2(OH)(H)]^+ + O_2 \longrightarrow [Rh(en)_2(OH)(OOH)]^+ \quad (165)$$

$$[Rh(en)_2(OH)(OOH)]^+ + [Rh(en)_2(OH)(H)]^+ \longrightarrow 2[Rh(en)_2(OH)_2]^+ \quad (166)$$

The catalytic properties of these reduced species have been actively studied by Gillard and co-workers.[601,846–850] Among other things, they have shown that H_2 also initiates Delépine's reaction of $[RhCl_6]^{3-}$,[846] that O_2 dramatically impedes the catalyst,[847] and that halide substitution at *trans*-$[Rhpy_4Cl_2]^+$ (equation 167) is also catalyzed by primary and secondary alcohols.[847] Consistent with the pseudo acid–base equilibrium (equation 164), the rate of catalyzed halide substitution is pH dependent, with little catalytic activity occurring in acidic solutions.[850] There is an induction period for the reaction (the more alcohol in the solution the shorter the period), suggesting that deoxygenation of the solution must occur before the reduced catalyst can be effective.

$$[Rhpy_4Cl_2]^+ + 2Br^- \longrightarrow [Rhpy_4Br_2]^+ + 2Cl^- \quad (167)$$

The lack of alcohol catalysis of halide substitutions in the $[Rh(en)_2X_2]^+$ system has been attributed to the relative ease of reduction of the two Rh complexes ($E_{1/2}$ for *trans*-$[Rhpy_4Cl_2]^+$ is -0.39 V, while it is -0.79 V (*vs.* SCE) for *trans*-$[Rh(en)_2Cl_2]^+$), accounting for their differing behavior toward mild reductants.[850] Stronger reducing agents, such as BH_4^- do catalyze halide exchange at $[Rh(en)_2Cl_2]^+$; $[Rh(en)_2(OH)(H)]^+$ (but not $[Rhpy_4]^+$) is also an effective catalyst for halide exchange in neutral, deoxygenated solutions of $[Rh(en)_2X_2]^+$.[850] Kinetic evidence inconsistent with the mechanism proposed by Basolo has led to an alternative mechanism involving catalysis by the poorly characterized Rh^I species, and a $[Rh^I—X—Rh^{III}]$-bridged intermediate. Unlike the Pt^{II}–Pt^{IV} system, where *trans* geometry is needed, BH_4^- catalyzes bromide substitution at *cis*-α- and *cis*-β-$[Rh(trien)Cl_2]^+$, and the reactions proceed with retention of geometric configuration.[851] Gillard and Heaton have summarized the available mechanistic arguments,[851] but the last shoe has yet to fall in this inadequately understood area.

48.6.2.6 Halonitrile complexes

The first examples of halonitrile complexes were reported by Johnson *et al.*,[852] who found that $RhCl_3 \cdot 3H_2O$ reacts readily when dissolved in an alkyl or aryl cyanide to form non-ionic complexes of the form $[RhCl_3(RCN)_3]$ (R = Me, Et, Ph or $MeOCH_2CH_2$). Electronic spectra all show a *d–d* band near 425 nm, and a second band near 370 nm (in nitromethane solution). Under the same conditions, the potentially bifunctional glutaronitrile ($NC(CH_2)_3CN$) reacts with $RhCl_3$ to give an ill-characterized orange solid, which is presumed to be polymeric with bridging nitrile groups.[852] Using 'less extreme conditions', Catsikis *et al.*, prepared *fac*-$[RhCl_3(MeCN)_3]$, characterized by elemental analysis, electronic spectra (Table 57), and IR and proton NMR spectroscopy.[855] Assignment of geometry has been debated, as Johnson used far-IR spectra to assign a *mer* geometry,[856] while Walton later suggested a *fac* structure.[857] Gillard and co-workers used NMR, electronic and Raman spectroscopy to assign the *mer* geometry to a variety of $[RhX_3(RCN)_3]$ complexes (R = CD_3, Et, Pr^n, Pr^i, Ph or $PhCH_2$).[853] They found evidence for a *fac* isomer, but only for $[RhCl_3(MeCN)_3]$.

Anionic halonitrile complexes have been prepared by taking advantage of the insolubility of the $(Et_4N)^+$ salts. If $RhCl_3 \cdot 3H_2O$ is heated with $[Et_4N]Cl$ in a H_2O/MeCN (1:1) solution, *trans*-$[Et_4N][RhCl_4(MeCN)_2]$ is isolated. If $[RhCl_6]^{3-}$ is used as a starting material, and the electrolyte is added after heating, salts of the form $M_2[RhCl_5(MeCN)]$ (M = Cs^+, NH_4^+ or Et_4N^+) can be isolated.[858] Some bromo analogs were similarly prepared.[854] Gillard prepared cationic complexes by the reaction of the neutral $[Rh(MeCN)_3X_3]$ (X = Cl, Br) with $AgNO_3$ (or $AgClO_4$) in acetonitrile

Table 57 Electronic Spectra of some Halonitrile Complexes of Rh^{III}

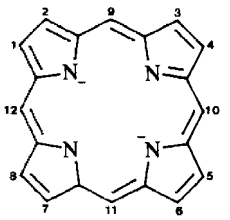
Compound	λ_{max} (nm) (ε)	*Ref.*
$[RhCl_3(MeCN)_3]$	430 (100), 371 (109)	852[a]
$[RhCl_3(EtCN)_3]$	429 (120), 370 (109)	852[a]
	422	853
$[RhCl_3\{MeO(CH_2)_2CN\}_3]$	425 (136), 376 (142)	852[a]
$[RhCl_3(Pr^nCN)_3]$	429	853
$[RhCl_3(Pr^iCN)_3]$	425	853
$[RhCl_3(PhCN)_3]$	426	853
$[RhCl_3(PhCH_2CN)_3]$	425	853
$(Et_4N)[RhCl_4(PhCN)_2]$	490 (65), 418 (194)	854
$(Et_4N)[RhBr_4(PhCN)_2]$	490 (167), 450 (620), 344 (6200), 304sh (9000), 269 (34 000)	854[b]
$[RhBr_3(MeCN)_2(H_2O)]$	465sh (317), 334 (2960), 266 (4370)	854[b]

[a] In nitromethane solution. [b] In acetonitrile solution.

solution.[853] Dissolution of this tetrakis(acetonitrile) cation in other nitrile solvents (RCN) leads to nitrile replacement, and is a general route to *trans*-$[Rh(RCN)_4X_2]^+$ cations.[853] The IR spectra of these complexes all showed the expected shift in the ν_{C-N} to higher energy, from 2257 cm^{-1} in pure MeCN to around 2300 cm^{-1} for the coordinated molecules.

48.6.2.7 Porphyrin and phthalocyanine complexes

The chemistry of Rh^{III} complexes with porphyrin and phthalocyanine ligands is quite distinctive, as these rigidly planar, tetradentate amine ligands form complexes *via* unique synthetic routes, and the chemistry of the resulting complexes differs substantially from that of complexes with less constrained ligands. A variety of porphyrin complexes of Rh^{III} have been characterized, and a list of the abbreviations used in this section is found in (**54**) and Table 58.



(54)

Fleischer was an early leader in this area, and found that when the dimeric Rh^I complex $[Rh(CO)_2Cl]_2$ was mixed with mesoporphyrin IX diethyl ester (MePDEE) in glacial acetic acid, a weakly paramagnetic complex, formulated as [Rh(MePDEE)], was generated.[859] The source of the paramagnetism was not explained, and the coordination geometry about the Rh was not discussed, but the IR of the complex showed no N—H or C—O stretches. The two-electron oxidation of a Rh^I complex represents an unusual synthetic route to a Rh^{III} complex, but it has since become a general route to Rh^{III} porphyrins, and was quickly extended[860,861] to include TPP, TPyP and MePDEE analogues. The synthetic path is thought[860] to pass through a $[Rh^I(porph)(CO)Cl]$ (presumably a dianion) intermediate, which is oxidized by O_2 in solution to give the final Rh^{III} species.

All of these porphyrin complexes are intensely colored, with the characteristic α, β and Soret bands near 550, 520 and 400 nm respectively. Fleischer postulated that they are five coordinate (four porphyrin nitrogens and one coordinated H_2O), with the sixth site available for substitution by other ligands.

The source of the weak paramagnetism ($\mu \approx 0.4$ BM)[859] was proposed to be due to the presence of a monomeric Rh^{II} complex, $[Rh^{II}(TPP)]$, formed upon incomplete oxidation of the $[Rh^I(TPP)]^-$ intermediate.[862] Surprisingly, the proposed Rh^{II} monomer did not bind O_2 despite the known reactions of $[Rh(NH_3)_4]^{2+}$ with O_2,[863] and the well-established reactions of Co^{II} and Fe^{II} porphyrin

Table 58 Numbering Scheme for Substituted Porphyrins

Abbreviation	*Name*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
		Meso positions (9–12) contain H							
Meso	Mesoporphyrin IX	Me	Et	Me	Et	Me	P^H	P^H	Me
Meso-DME	Mesoporphyrin dimethyl ester	Me	Et	Me	Et	Me	P^{Me}	P^{Me}	Me
HMP	Hematoporphyrin IX	Me	EOH	Me	EOH	Me	P^H	P^H	Me
HMP-DME	Hematoporphyrin dimethyl ester	Me	EOH	Me	EOH	Me	P^{Me}	P^{Me}	Me
Deut	Deuteroporphyrin IX	Me	H	Me	H	Me	P^H	P^H	Me
Deut-DME	Deuteroporphyrin dimethyl ester	Me	H	Me	H	Me	P^{Me}	P^{Me}	Me
OEP	Octaethylporphyrin	Et	Et	Et	Et	Et	Et	Et	Et
Etio	Etioporphyrin I	Me	Et	Me	Et	Me	Et	Me	Et
		Meso-substituted porphyrins (sites 1–8 = H)							
		sites 9–12							
TPP	tetraphenylporphyrin	Phenyl							
TPyP	tetrapyridinylporphyrin	Pyridine							
TPPS	tetra-*p*-sulfonatobenzeneporphyrin[a]	$C_6H_4SO_3^-$							

[a] 6^- anion; other porphyrins listed are 2^- anions; Me = Methyl, Et = Ethyl, EOH = C(OH)HMe, $P^H = CH_2CH_2COOH$, $P^{Me} = CH_2CH_2COOMe$.

complexes with O_2. Wayland and Newman argued against the existence of a monomeric Rh^{II} porphyrin complex,[864] and proposed that the only Rh^{II} species present was a dimeric $[Rh(porph)]_2$ with a Rh—Rh bond. The diamagnetic $[Rh(OEP)]_2$ dimer, prepared by photolysis of [Rh(OEP)(H)], was convincingly characterized, and while it reacts as if it were a source of the $[Rh^{II}(OEP)]$ moiety, no stable Rh^{II}–porphyrin monomers have yet been thoroughly characterized. The paramagnetism observed by Fleischer and James[859,860,862] was attributed to $[Rh(OEP)(O_2)]$, which forms when $[Rh(OEP)]_2$ is exposed to dioxygen. The complex was characterized by electronic, IR and EPR spectra, and formulated as a Rh^{III}–superoxo complex, with end-on bonding by the O_2^- ligand. The superoxo complex reacts with alkyl phosphines and phosphites,[864] and with piperidine[865] to give 1:1 adducts, and when warmed to 20 °C, its paramagnetism decreases, presumably due to the formation of the peroxo-bridged Rh^{III} dimer.

Wayland has explored the chemistry of the dimeric $[Rh(OEP)]_2$, and found that it reacts with NO to generate [Rh(OEP)NO], which can be subsequently oxidized by O_2 (in air) to give the nitrite (NO_2^-) complex.[865] The same [Rh(OEP)(NO)] can be prepared by the reaction of NO with [Rh(OEP)Cl], although this reaction passes through a metastable intermediate, identified as [Rh(OEP)(Cl)(NO)].[865] Subsequent reaction with NO leads to the stable [Rh(OEP)(NO)] product. The intermediate is characterized as a 'π-cation radical' complex, containing an OEP^- radical ligand, not a Rh^{IV}. Support for the radical anion assignment comes from electrochemical oxidation of a variety of porphyrin-containing species, which revealed that the ease of removing the first two electrons from a porphyrin system is not strongly dependent on the cation bonded to the porphyrin (Table 59), implying that the electron is removed from a ligand-localized orbital which does not interact strongly with the metal. The second electron is also thought to come from a ligand-localized orbital, leaving a diamagnetic, π dication complex.[865]

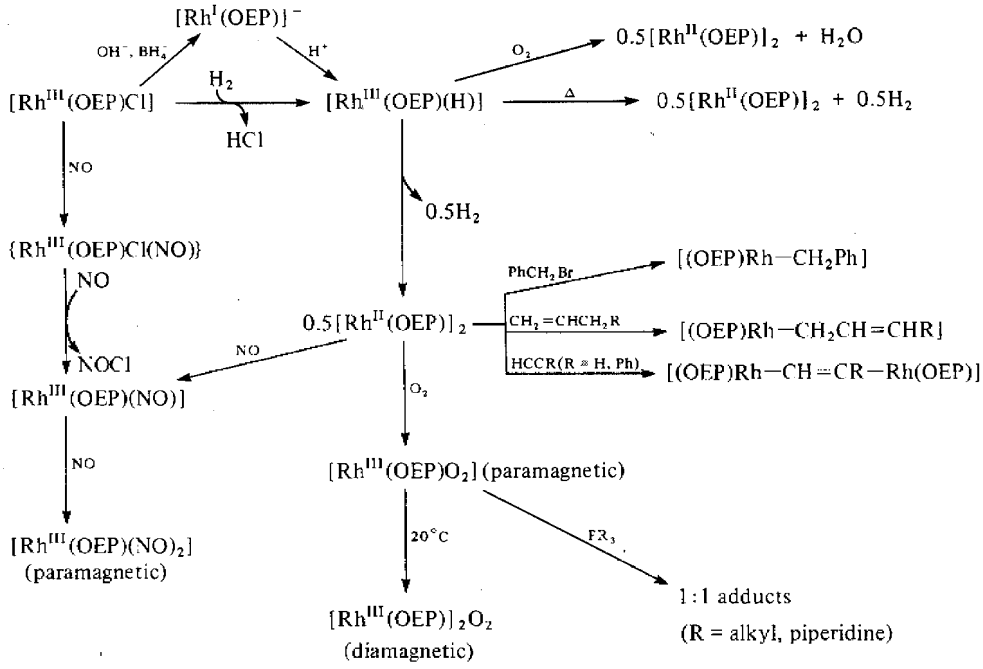
An interesting series of substitution/redox reactions involving both dimeric Rh^{II} and monomeric Rh^{III} complexes of OEP has been reported.[408,409] In methanolic solution, H_2 reacts with [Rh(OEP)Cl] to generate [Rh(OEP)H] and HCl; borohydride reduction of [Rh(OEP)Cl] leads to a species identified as $[Rh^{I}(OEP)]^-$, which forms the same hydrido species when acidified (ν_{Rh-H} at 2220 cm^{-1}, and when prepared with DCl, ν_{Rh-D} at 1595 cm^{-1}). Dioxygen reacts with [Rh(OEP)Cl] to form the dimeric $[Rh(OEP)]_2$ (an unusual use of O_2 to reduce Rh^{III}); the Rh^{II} dimer can also be formed by heating a degassed toluene or benzene solution of the hydrido complex. The reaction of the $[Rh(OEP)]_2$ dimer with a variety of organic substrates leads to a series of organo-Rh^{III} (OEP) complexes. The reactions described in the past two paragraphs are summarized in Scheme 32.

Single-crystal X-ray structures of several Rh^{III} porphyrins have been reported. The structure of octahedral $[Rh(Me_2HN)_2(Etio)]Cl \cdot 2H_2O$ showed that the Rh^{III} fits nicely into the plane of the porphyrin nitrogens, with an average Rh—N distance of 2.038 Å; the axial dimethylamine nitrogens are 2.090 Å from the metal.[866] A square-pyramidal complex [Rh(OEP)(Me)] showed similar distances around the metal, with the Rh in the plane of the porphyrin nitrogens, and the apical C atom 2.031 Å from the rhodium.[867] (Ogoshi notes that this Rh—C bond is significantly shorter than the 2.081 Å observed for the Rh—Me distance in another five-coordinate Rh^{III} complex $[Rh(PPh_3)_2(Me)(I)_2]$.[868] The geometries of the two complexes are quite different, however, as the Rh is 0.25 Å out of the plane established by the two P and the two I atoms, but is in the plane of the porphyrin nitrogens.[867] An early report by Fleischer[869] describes the crystal structure of a paramagnetic ($\mu = 1.95$ BM) species, identified as [Rh(TPP)(Ph)(Cl)], which is said to have the 'usual planarity of the pyrrole rings and phenyl rings'. Despite its paramagnetism, the method of synthesis ($[Rh(CO)_2Cl]_2$ is allowed to react with TPP in refluxing benzene) and the Rh—N and Rh—C distances (2.04 and 2.05 Å respectively) are reminiscent of Rh^{III} porphyrins, suggesting that this may be a radical-anion–Rh^{III} complex, not the Rh^{IV} species tentatively proposed by Fleischer.[869]

Table 59 Oxidation Potentials[a] for some Rh^{III} Porphyrins[865]

Complex	*First oxidation*	*Second oxidation*
H_2TPP	0.97	1.25
$[Rh^{III}(TPP)Cl]$	0.98	1.36
$[Rh^{III}(TPP)(NO)]$	0.94	1.36
H_2OEP	0.84	1.16
$[Rh^{III}(OEP)Cl]$	0.82	1.34
$[Rh^{III}(OEP)(NO)]$	0.77	1.27

[a] Potentials are ±0.01 V *vs.* SCE, measured in CH_2Cl_2.



Scheme 32

Quantitative studies on the reactivity of Rh^{III} porphyrins have centered on substitutions (and proton exchanges) at the fifth and sixth coordination sites in $[Rh(TPPS)(H_2O)]^{3-}$; Ferraudi and co-workers have also presented a detailed study on the photophysics and photochemical reactivity of Rh^{III}–phthalocyanine complexes. Bailey studied the acid–base equilibrium (equation 168) for a variety of metalloporphyrins, and found a pK_{OH} of 5.1 ± 0.1 for [Rh(HMP)], while [Rh(TPPS)] had a pK_{OH} of 6.8 ± 0.1[870] (a pK_{OH} of 7.5 had been reported earlier for the TPPS complex[871]). After analyzing the acid–base behavior of a variety of metalloporphyrins, Bailey found that the results could be most effectively interpreted in terms of a simple crystal field model, and argues that while the porphyrin ligands are certainly delocalized, this need not imply delocalized metal–ligand interactions. He reached the heartening conclusion that his 'observations strongly suggest that metalloporphyrin electronic structure . . . is much simpler than is generally appreciated'.[870]

$$[Rh(porph)(H_2O)_n]^+ \rightleftharpoons [Rh(porph)(H_2O)(OH)] + H^+ \qquad (168)$$

The thermodynamics and kinetics of NCS^-, CN^-,[871] Cl^-, Br^-, NCS^- and I^-[872] substitutions at $[Rh(TPPS)(H_2O)]$ have been reported; the reactions involved are shown in equation (169), and the parameters determined are summarized in Table 60. Spectrophotometric titrations showed two inflection points as OH^- is added to $[Rh(TPPS)(H_2O)_2]^{3-}$, and the consecutive pK_A values (7.01 and 9.80 at 20 °C) correspond to the pK_A values for *fac*- and *mer*-$[RhCl_3(H_2O)_3]$, suggesting that the $TPPS^{6-}$ anion and 3 Cl^- ligands are comparable electron donors toward the Rh center.[872] The trends in the equilibrium constants (Table 60) imply that Rh^{III} is a soft (class B) acid in these complexes; the NCS^- ion is presumed to be sulfur bonded, although no direct evidence is presented to support this assumption.

$$[Rh(TPPS)(L)_2]^{5-} \underset{H_2O}{\overset{H_2O}{\underset{L}{\overset{K_1,\ k\ L}{\rightleftharpoons}}}} [Rh(TPPS)(H_2O)L]^{4-} \underset{H_2O}{\overset{H_2O}{\underset{L}{\overset{K_2\ L}{\rightleftharpoons}}}} [Rh(TPPS)(H_2O)_2]^{3-} \underset{+H^+}{\overset{K_A^1,\ -H^+}{\rightleftharpoons}}$$

$$[Rh(TPPS)(H_2O)(OH)]^{4-} \underset{+H^+}{\overset{-H^+,\ K_A^2}{\rightleftharpoons}} [Rh(TPPS)(OH)_2]^{5-} \qquad (169)$$

The substitutions follow the two-term rate expression: rate $= (k_1[L] + k_{-1})[Rh^{3-}]$. As observed with Co and Cr porphyrins, the rate of ligand substitutions at the Rh^{III}–porphyrin moiety is much faster than for the comparable reactions of non-porphyrin complexes. For example, the rate of Cl^-

Table 60 Kinetic and Thermodynamic Parameters for Substitutions at $[Rh(TPPS)(H_2O)_2]^{+}$ [a]

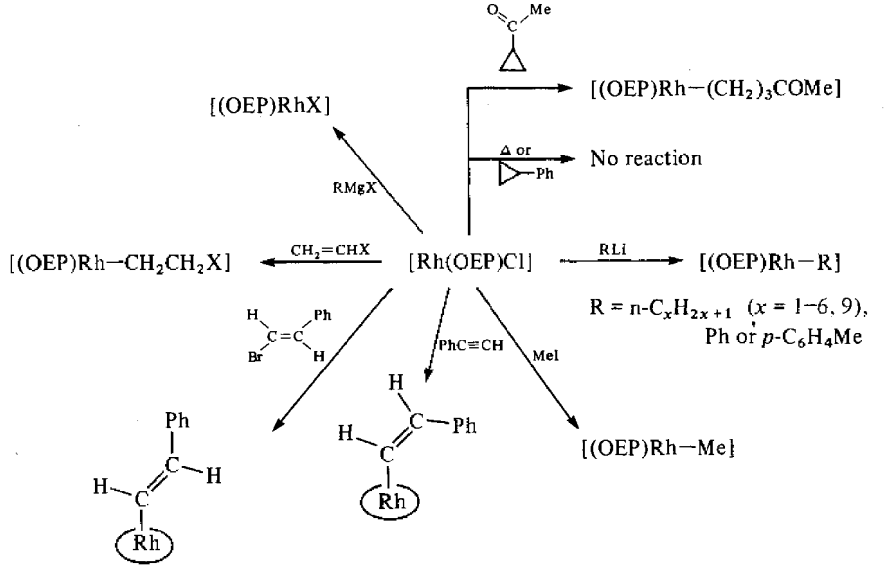
Anating anion	ΔH_f^* ($kJ\,mol^{-1}$)	ΔS_f^* ($J\,K^{-1}\,mol^{-1}$)	K_1	K_2	*Ref.*
Cl	56.1 ± 2.5	−106 ± 7.9	0.74 ± 0.11	< 0.03	872[b]
Br	57.7 ± 1.3	−54.6 ± 4.6	1.82 ± 0.10	< 0.03	872
I	53.6 ± 3.3	−97.9 ± 16.5	41.2 ± 1.8	< 0.03	872
NCS	69.0 ± 0.8	−43.1 ± 2.5	1.22(± 0.04) × 10^4	3.68 ± 0.42	872
	89.3 ± 9.1	−1.1 ± 14.3	39	—	871[c]
CN	59.6 ± 2.1	−77.8 ± 39.1	1880	—	874[d]

Proton exchanges	K_A^1	K_A^2	
OH	9.67(± 0.12) × 10^{-8}	1.59(± 0.24) × 10^{-10}	385
	3.55 × 10^{-8}	—	384
	6.3(± 1.3) × 10^{-8}	—	383

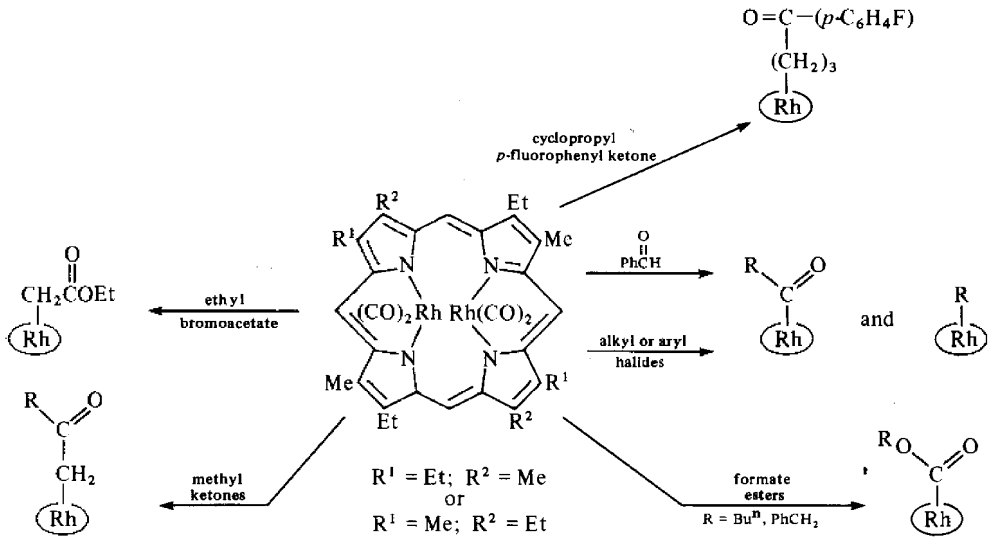
[a] Numbered reactions shown in equation (169). [b] In ref. 385, 0.10 M H^+, μ = 1.0 ($NaClO_4$). [c] pH 4.7 (phthalate buffer), μ = 0.5 (KSCN + KNO_3). [d] pH 10.50 (borate buffer), μ = 0.5 (NaCN + $NaClO_4$).

anation of $[Rh(TPPS)(H_2O)_2]^{3-}$ is 10^7 and 10^5 times faster than the rate of Cl^- attack on *trans*-$[RhCl_4(H_2O)_2]^-$, and *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$, respectively. Based on the very negative ΔS^* values observed, an associative interchange (I_a) mechanism for these substitutions was suggested.[872] (Pasternack and co-workers[873] had earlier suggested that a porphyrin could be expected to strongly stabilize a five-coordinate geometry, suggesting that dissociative interchanges would be expected for substitutions at metalloporphyrins.) Studies on the effect of pressure on the rates of NCS^- substitution at $[Rh(TPPS)(H_2O)_2]^{3-}$ support the dissociative model.[874] The ΔV^* of 8.8 $cm^3\,mol^{-1}$ is similar to that observed for the Cr^{III} analog (7.4 $cm^3\,mol^{-1}$), but significantly smaller than observed for Co^{III} (15.4 $cm^3\,mol^{-1}$); this parallels the trend to more negative ΔS^* values for the Cr and Rh analogs. vanEldik concludes that for $[Rh(TPPS)(H_2O)_2]^{3-}$, the 'experimentally observed values are in good agreement with those expected for an interchange mechanism in which the rate determining step is dissociatively activated'; noting the differences between the Co, Cr and Rh systems, he also states that 'the central metal atom seems to control the extent to which the porphyrin can modify the reactivity and mode of the substitution process'.[874]

Numerous Rh^I porphyrin complexes have been prepared (*vide supra*), and these have been used to obtain Rh^{III} porphyrins. Sodium ethoxide nucleophilically attacks the C atom of [Rh(TPP)Cl(CO)] (in methylene chloride/ethanol solutions), leading to orange-red crystals of a diamagnetic ethoxycarbonyl(TPP)Rh^{III} complex with a Rh—C σ bond. Reaction of [Rh(TPP)Cl(CO)] with the basic $LiNEt_2$ in diethylamine leads to the analogous $[Rh(TPP)C(O)NEt_2]$, while no reaction of [Rh(TPP)Cl(CO)] is observed with the analogous $NaSEt_2$.[875] Ogoshi and co-workers have studied the reactions of $[Rh^I(OEP)Cl]$ with a variety of reactive organic materials. As summarized in Scheme 33 this Rh^I porphyrin undergoes oxidative

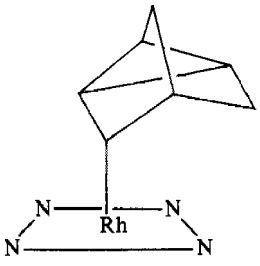


Scheme 33



Scheme 34

additions with an activated cyclopropane,[876] alkyl halides,[877] organolithiums, alkenes and alkynes, and Grignards;[878] all but the Grignards lead to complexes with a Rh^{III}—C σ bond. While Rh^{I} complexes generally catalyze the quadricyclane → norbornadiene valence isomerization, the reaction of [Rh^{I}(OEP)Cl] with quadricyclane leads to the cleavage of only one of the two cyclopropane rings, and the Rh^{III}(OEP) species represented in (**55**). Grigg and co-workers have studied a wide variety of oxidative additions at some dirhodium(I)porphyrin complexes.[879–882] As summarized in Scheme 34, the Rh^{III} products are generally monomeric, five-coordinate species with a Rh—C σ bond.

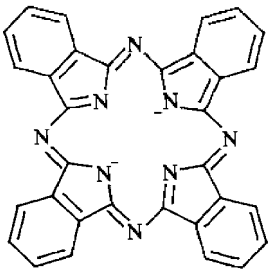


(**55**)

Sperm whale apomyoglobin, reconstituted with Rh^{III}, leads to stable Rh–myoglobin complexes which are inert to external anions (F^-, OCN^-, N_3^- and CN^-) and to reducing agents (dithionite, borohydride and dihydrogen).[883] The mesoporphyrin–Rh^{III} complex itself, however, is reactive, and readily binds CN^- ion. While the meso—Rh^{III}—Mb resembles the native protein in some ways (its tight binding of the apoprotein and prosthetic group, metal–imidazole bonding, and NMR-determined protein conformation), the inertness of the meso—Rh^{III}—Mb to external anions leads to the supposition that there are no exchangeable aqua ligands coordinated to the Rh^{III}, but that the rhodium binds to both the proximal and the distal imidazoles. This would make the Rh^{III} system a poor ferrimyoglobin model (in which only the proximal histidine is bound to the metal), and a better model of an internal hemichrome. Access to the sixth coordination site is blocked in the reconstituted meso—Me—Rh^{III}—Mb, however, as a methyl group occupies the sixth site; the ^{1}H NMR of the Me resonances are shifted 2 p.p.m. downfield upon incorporation into the myoglobin, due to the compression effect of the amino acid residues at the distal site. (This meso—Me—Rh^{III}—Mb is the first example of a reconstituted hemoprotein with an organometalloporphyrin.) Not surprisingly, the meso—Me—Rh^{III}—Mb is also inert toward substitution and reduction, but the effect of the coordinated methyl group is apparent in studies which compare the ability of meso—Rh^{III} and meso—Me—Rh^{III} to compete with Fe^{III} for coordination within the myoglobin. When meso—Rh^{III} is mixed with Fe^{III}—Mb (at a 4/1:Rh/Fe ratio, 35 °C, pH = 7.0, 24 h), 90% of the resulting prosthetic protohemin in the native myoglobin is replaced by the meso—Rh^{III}. Under similar conditions, only 15% of the meso—Me—Rh^{III} is incorporated, supporting the supposition

that coordination by the distal imidazole occurs in the meso—Rh^{III}—Mb, and that this binding is blocked by the coordinated methyl, decreasing the stability of meso—Me—Rh^{III}—Mb.[883]

Ferraudi and co-workers have presented detailed studies of the photochemical[884,885] and photophysical behavior[886,887] of Rh(phthalocyanine) complexes. Like the porphyrins, the phthalocyanine dianion (ph, **56**) is rigidly planar, with extensively delocalized intraligand bonding around four amine nitrogen donors. Photolysis (254 nm light) of Co^{III} phthalocyanines causes reduction of the metal and oxidation of an axially coordinated ligand, consistent with the population of a ligand-to-metal charge transfer excited state.[888] In contrast, ligand substitutions, without net redox chemistry, were observed when the isoelectronic [Rh(ph)X] (X = Cl, Br, I) complexes were photolyzed under similar conditions. The simplicity of the net reaction belies the complexity observed when the reaction is studied by conventional and laser flash techniques. As Ferraudi states[887] 'the photonic energy is degraded in a complex manner that involves photochemical, radiative and nonradiative paths'. The proposed mechanism for the photochemical path is represented in equations (170)–(177). In the first phase, electron transfer occurs, the anionic ligand is released, and a labile [Rh^{II}(ph)] and a solvent radical are formed (equations 170–172); a Rh^{III}–(radical anion) species is also implicated. Reoxidation of the Rh^{II} involves a complex set of reactions (equations 173–177). Equation (173) has a rate constant of about $10^{10}\,M^{-1}\,s^{-1}$, making the acetonitrile radical ($CH_2CN\cdot$) a poor candidate for the oxidation of the Rh^{II} complex (equation 174). The ESR and the absorbance spectra of the Rh^{III}–ligand radical complex have been recorded,[885] and the absorbance spectrum ($\lambda_{max} \approx 510$ nm) is similar to that observed upon one-electron oxidation of uncoordinated phthalocyanine.[888] This radical–ligand complex is thought to result from population of the $n\pi^*$ ligand-centered states involving the lone electron pairs of the bridging nitrogens of the ph ring.



(56)

$$[Rh^{III}(ph)(MeOH)X] + MeCN \longrightarrow [Rh^{III}(ph\cdot H)(MeOH)X] + CH_2CN\cdot \quad (170)$$

$$[Rh^{III}(ph\cdot H)(MeOH)] \rightleftharpoons [Rh^{III}(ph\cdot)(MeOH)X]^- + H^+ \quad (171)$$

$$[Rh^{III}(ph\cdot)(MeOH)X]^- \rightleftharpoons [Rh^{II}(ph)] + MeOH + X^- \quad (172)$$

$$CH_2CN\cdot + [Rh^{III}(ph)(MeOH)X] \xrightarrow{H^+} MeCN + [Rh^{III}(ph\cdot)(MeOH)X]^+ \quad (173)$$

$$CH_2CN\cdot + [Rh^{II}(ph)] \xrightarrow{H^+} MeCN + [Rh^{III}(ph)(solvent)_2]^+ \quad (174)$$

$$[Rh^{III}(ph\cdot)(MeOH)X]^+ + [Rh^{II}(ph)] \longrightarrow [Rh^{III}(ph)(MeOH)X] + [Rh^{III}(ph)(solvent)_2]^+ \quad (175)$$

$$CH_2CN\cdot + Me_2CHOH \longrightarrow MeCN + Me_2\dot{C}OH \quad (176)$$

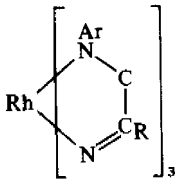
$$[Rh^{III}(ph\cdot)(MeOH)X]^+ + Me_2CHOH \longrightarrow [Rh^{III}(ph)(MeOH)X] + Me_2\dot{C}OH + H^+ \quad (177)$$

In O_2-free solutions, [Rh(ph)(MeOH)Cl] luminesces ($\lambda_{max} \approx 420$ nm, $\phi = 1.3 \times 10^{-3}$) when excited with light of 400 nm or less.[866] Excitation spectra show that the emitting state is well above the lowest π–π^* state, making this an apparent violation of Kasha's rule. Similar luminescence is oberved for the Co^{III}, Ru^{II}, Al^{III}, and weakly observed for Cu^{II} phthalocyanine complexes, and the luminescence is thought to originate from an upper-level, ligand-centered triplet. The action spectrum for photoinduced hydrogen abstraction is independent of X in [Rh(ph)(MeOH)(X)] (X = Cl, Br, I). The photosubstitutions are therefore proposed to originate from a ligand-centered $^3n\pi^*$ state, while emission comes from a ligand-centered upper-level $^3\pi$–π^* state, with another, lower-lying $^3\pi$–π^* state available. Ferraudi presents a detailed investigation of the time dependence

of the two $^3\pi$–π^* states (emission and absorption studies), and of the relationship between the photoemissive and photoreactive states.[888]

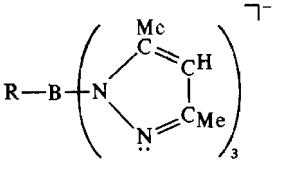
48.6.2.8 Miscellaneous nitrogen ligands

The electronic and IR spectra of $[Rh(NO_2)_6]^{3-}$ are consistent with the expected RhN_6 chromophore, and while ligand field bands were not observed, CT absorbances occur at 317 and 275 nm.[889] Arylazo oximes (N—N) form $[Rh(N—N)_3]$ complexes with Rh^{III} in which the arylazo oxime acts as a bidentate ligand (five-membered rings; **57**).[890] Reaction of $Rh(NO_3)_3 \cdot 3H_2O$ with the appropriate arylazo oxime in ethanol at pH 4 (with CO_3^{2-} used to adjust pH) leads to a precipitate of *fac*- and *mer*-$[Rh(N—N)_3]$. The geometric isomers can be separated on alumina, and ^1H NMR showed that approximately equivalent amounts of the *fac* and *mer* isomers formed (for R = Me or Pr and Ar = Ph). This represents an unexpected (and unexplained) enhancement of the population of the *fac* isomer, as statistically, a *fac*/*mer* ratio of 1/3 would be expected; only the *mer* form was detected for $[Co(N—N)_3]$.[891] These rhodium complexes all display intense absorption bands near 480 and 320 nm, which are presumed to be intraligand bands.[890]



(57) R = H, alkyl, aryl
Ar = aryl

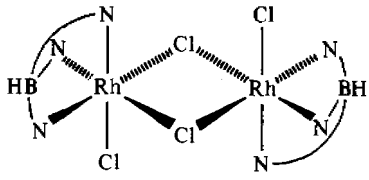
The tripyrazolylborate anion ($RB(pz)_3$, **58**) acts as a tridentate ligand, and frequently results in complexes which are analogous to cyclopentadienyl complexes. The first Rh^{III}–$RB(pz)_3$ complexes were prepared by the oxidative addition of I_2 to $[Rh_2\{RB(pz)_3\}(CO)_3]$, and resulted in octahedral, monomeric complexes $[Rh\{RB(pz)_3\}(CO)I_2]$ (R = H, and, in low yield, for R = pz).[892] For the tetrapyrazolyl species (R = pz) the NMR spectrum showed two, non-interconverting pyrazole environments in a 3/1 ratio, consistent with a tridentate configuration for the borate. The C—O stretch is very high (2090 cm^{-1}), consistent with the formal Rh^{III} designation.[892]



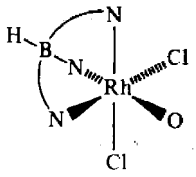
(58) R = H, pz

Powell and co-workers have extensively studied the Rh^{III} chemistry of the hydrotripyrazolylborate anion (R = H).[893] They found that the reaction of equimolar amounts of $Na[HB(pz)_3)]$ with $RhCl_3 \cdot 3H_2O$ in refluxing methanol leads to two types of complexes, depending on reaction conditions. Dilute solutions and short reflux times (*ca.* 1 h) yield chloro-bridged dimeric species (**59a**), while more concentrated solutions, refluxed for longer periods (*ca.* 4 h), generate the methanol-solvated monomer $[Rh\{HB(pz)_3\}Cl_2(MeOH)]$ (**59b**). These two species are convenient starting materials for a variety of reactions, and Powell reported over 60 derivatives.[893] The coordinated methanol can readily be replaced by other neutral monodentates (*e.g.* PR_3, AsR_3, py, NR_3, RNC or CO), and reaction with the appropriate Ag or Tl salts gives $[Rh\{HB(pz)_3\}YCl]$ (Y = acac, hfacac, Et_2NCS_2) and $[Rh\{HB(pz)_3\}Y_2L]$ (Y = Ac^-, no L; Y = $CF_3CO_2^-$, L = H_2O). Reduction of the monomer with H_2/Et_3N leads to the anionic hydride, $[Rh\{HB(pz)_3\}Cl_2(H)]^-$. Similar reactions were observed starting with the dimeric species.[893]

Schlemper and co-workers have reported the X-ray structures of the products of the reaction of $RhCl_3 \cdot 3H_2O$ with a series of similar amine oximes (A–O; **60**). The reaction product is intriguingly dependent on the length of the hydrocarbon chain linking the two amine oxime moieties, and

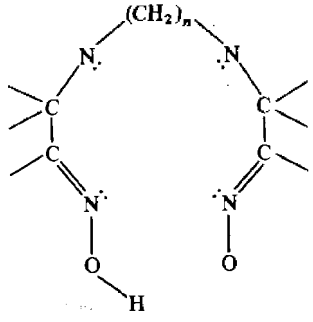


(59a)

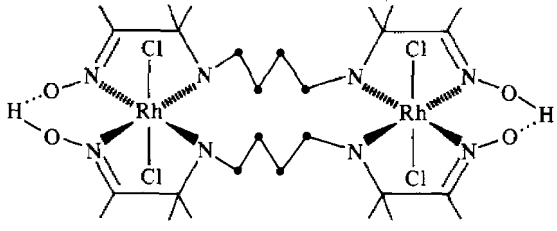


(59b)

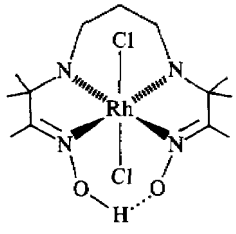
representations of the structures are shown in (**61**).[894,895] For the longest hydrocarbon chain ($n = 4$), a binuclear species results, with both (A–O) ligands bridging between the two Rh centers (**61a**). At each end of this molecule there is a very strong hydrogen bond between the two oximes (O—O distance is 2.387 Å).[894] With one less carbon ($n = 3$), the hydrocarbon chain is apparently not long enough to span the two Rh centers, as a monomeric *trans*-[Rh(A–O)Cl_2] complex results (**61b**).[895] Again, a strong hydrogen bond between the two oximes (O—O distance 2.474 Å) makes the (A–O) ligand virtually cyclic. For the even shorter hydrocarbon ($n = 2$), another dinuclear species is formed, but with a chloride and the two oxime moieties bridging the Rh centers (**61d**). There is no evidence of hydrogen bonding in this structure.[894] The last species studied has no hydrocarbon chain (in essence, $n = 0$), but the product has a structure similar to that observed when $n = 3$: a monomeric, *trans*-RhN_4Cl_2 chromophore, with a hydrogen bond between the *cis* oximes (O—O distance of 2.459 Å).[895]



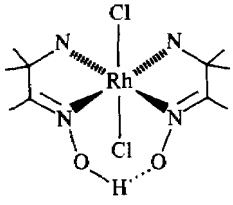
(60)



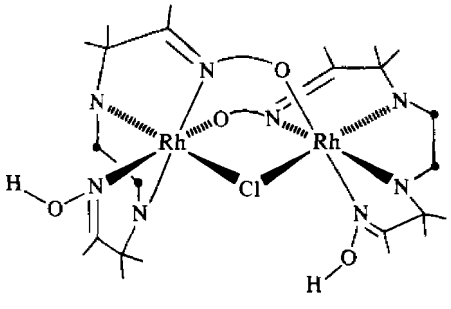
(61a) $n = 4$



(61b) $n = 3$

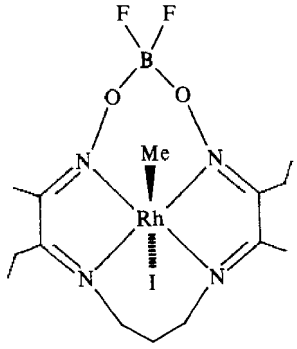


(61c) $n = 0$



(61d) $n = 2$

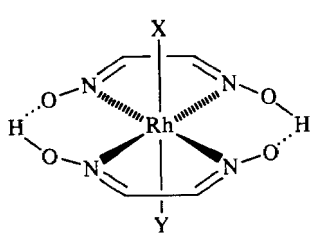
The single crystal X-ray structure of *trans*-methyliodo{difluoro[3,3′-(trimethylenedinitrolo)bis(2-pentanone oximato)]borate}rhodium(III) (**62**) shows that the Rh sits in the plane established by the four N atoms, with the I and the Me in the axial positions (2.813 Å and 2.090 Å, respectively). The two six-membered rings resemble a chair conformation, with the BF_2 bridge bent toward the axial methyl group, and the propylene bent toward the iodine atom.[896]



(62)

Complexes of the form $[Rh(RBig)_2Cl_2]Cl$ (RBig = N^1-(*p*-chlorophenyl), N^1-phenyl, N^1-(*o*-tolyl), N^5-isopropylbiguanide) have been prepared in which the biguanide is presumably acting as a N—N bidentate. Substitutions in acidic solution lead to $[Rh(RBig)_2X_2]X$ for X = Br, I, NO_2, CNS and N_3, and oxidation of the dichloro species with $NaClO_2$ is reported to lead to a Rh^{IV} complex $[Rh(RBig)_2Cl_2]Cl_2$.[897]

Dimethylglyoxime (HON=C(Me)CC(Me)=NOH, abbreviated here as HDMG) forms several unbridged Rh^{II} dimers (Section 48.5.2.1.iv) and has a rich chemistry with Co^{III} (the cobaloximes[898]); examples of Rh^{III} complexes are less common, but interest in its Rh^{III} chemistry is growing. As in other metal systems, HDMG, or its monoanionic conjugate base (DMG), acts as a bidentate ligand, bonding through the two nitrogen atoms. Dwyer and Nyholm[899] first reported the preparation of $[Rh(DMG)_2Cl_2]^-$ ion (isolated as the H^+ salt), but this formulation was questioned by Gillard *et al.*[601] who pointed to O—H stretches in the IR spectrum, and suggested that while the $[Rh(DMG)_2Cl_2]^-$ anion undoubtedly exists in solution, the solid state species is more accurately represented as $[Rh(DMG)(HDMG)Cl_2]$.[601] An early report[900] that refluxing HDMG with *trans*-$[Rhpy_4Cl_2]Cl$ leads to *trans*-$[Rh(DMG)_2(py)Cl]$ was also questioned by Gillard[601] who found $[Rhpy_3Cl_3]$ as the major product under the cited conditions. In ethanolic solution in the presence of trace amounts of BH_4^- they precipitated the $[Rh(DMG)_2Cl_2]^-$ anion, either as the pyH^+ or the $[Rhpy_4Cl_2]^+$ salts. The chloropyridine adduct was eventually prepared by adding H_3PO_2 to a hot suspension of $pyH^+[Rh(DMG)_2Cl_2]^-$ in pyridine.[601] Powell has reported the syntheses of many $[Rh(DMG)_2LX]$ complexes [L = PPh_3, $AsPh_3$, $SbPh_3$; X = Cl, Br, I (no $SbPh_3$)], prepared by heating aqueous ethanolic solutions of $RhCl_3 \cdot 3H_2O$, L and HDMG in the presence of the appropriate potassium halide.[901] A similar route was used to prepare $[Rh(DMG)_2(Cl)(ZMe_3)]$ (Z = P or As) and $[Rh(DMG)_2(X)(thiourea)]$ (X = Cl, Br).[902] Single crystal X-ray structures of $[Rh(DMG)_2(Cl)(PPh_3)]$,[903] $[Rh(DMG)_2(Cl)(SbPh_3)]$[904] and $[Rh(DMG)(HDMG)(Cl)(PPh_3)]Cl \cdot CH_2Cl_2$[905] show that these complexes all share a *trans* geometry with the rhodium in the plane established by the bidentate DMG ligands. This geometry is characteristic of bis(DMG) complexes (no *cis* Rh^{III} examples have been reported) as it allows hydrogen bonding between the oxime groups (**63**), so that the two DMG ligands may be considered to form one pseudo-macrocyclic dianion.



(63)

Aqueous substitutions of $[Rh(DMG)_2Cl_2]^-$ have led to $NH_4[Rh(DMG)_2Cl(X)]$ (X = Br, I, NCS), and $[Rh(DMG)_2(thiourea)Cl]$,[906] $[Rh(DMG)_2(NH_3)Cl]$,[907] $[Rh(DMG)_2(H)(PPh_3)]$,[908] and

$[Rh(DMG)_2(Cl)(PPh_3)]$.[909] Reduction of Nyholm's $[Rh(DMG)_2Cl_2]^-$ with BH_4^- in alkaline H_2O/MeOH (1:1) in the presence of MeI leads to methylrhodoxime, *trans*-$[Rh(DMG)_2(H_2O)(Me)]$ (λ_{max} (ε) at 400 (456), 329 (6300), 262 (7690), 225 (11 900) nm).[899,910] A recent kinetic study has shown that the methyl group strongly labilizes the *trans* site.[911] Anation of methylrhodoxime by N_3^-, SCN^-, I^-, py or thiourea is very rapid; about 100 times faster than anations at cobaloxime and six orders of magnitude faster than anations at $[Rh(TPPS)(H_2O)_2]^{3-}$, another complex with a *trans*-$(H_2O)Rh(Me)$ moiety. Activation parameters (for thiourea anation $\Delta H^* = 32.4 \pm 1.3\,kJ\,mol^{-1}$, $\Delta S^* = -61 \pm 4.4\,J\,K^{-1}\,mol^{-1}$) indicate that the lability is due to the low ΔH^* values. The pK_a of the coordinated water (9.78) does not suggest an unusually weak Rh—O bond, so that the low ΔH^* value must arise from a stabilization of the transition state. The anation rates are practically independent of the nature of the nucleophile, suggesting a dissociative process, but the very negative ΔS^* values suggest a mechanism which is more associative than for the cobaloxime.[911]

Espenson has found that the rhodoxime behaves very much like the cobaloxime in its association with iron(III) ion to form the bimetallic $[Rh(DMG)(DMGFe)(H_2O)Me]^{2+}$. Its formation constant (equation 178) is 68.8 ± 4.0 (for cobaloxime, $K_f = 15.3 \pm 0.8$[912]). This unusual cation can be considered to be derived from the structure shown in (**63**), in which X = Me, Y = H_2O, and one of the hydrogen-bonded hydrogens is replaced by an Fe^{3+}. The presence of the iron adduct is readily signalled by an intense absorption near 440 nm ($\varepsilon \approx 47\,000$), and a comparison of the kinetic and thermodynamic parameters shows a strong similarity to the previously studied Fe^{3+} adducts of cobaloxime.[913] Even in the presence of 'forcing concentrations' of Fe^{3+}, there was no evidence of incorporation of a second iron(III) ion.[912]

$$[Rh(DMG)_2(H_2O)Me] + Fe^{3+} \rightleftharpoons [Rh(DMG)(DMGFe)(H_2O)Me]^{2+} + H^+ \qquad (178)$$

Reduction of $[Rh(DMG)_2Cl_2]^-$ in basic aqueous ethanol (to an unspecified Rh^I complex) is autocatalyzed, with a rate expression of the form: rate = $k[Rh^{III}][Rh^I]$.[914] The rate of reduction is not affected by added chloride ion, but varies as the inverse fourth (!) power of $[OH^-]$. A mechanism, involving deprotonation of the DMG ligands, and Cl^--bridged Rh^{III}—Cl—Rh^I intermediates, has been proposed.[914]

48.6.3 Complexes of Heavier Group V Ligands

There is an extensive chemistry of tertiary phosphine rhodium(III) complexes. However, there are comparatively few complexes of monodentate tertiary arsines, although the complexes of ditertiary arsines are more numerous. There are virtually no tertiary stibine complexes. The two main preparative routes to the complexes described in this section are: (i) direct reaction of the ligands with rhodium trichloride, which usually yields trichloro complexes; and (ii) oxidative addition to rhodium(I) tertiary phosphine complexes, which gives rise to more diverse products of the type $[RhXYZ(PR_3)_n]$. Metathetical reactions on the complexes prepared by either method (i) or (ii) have been used to prepare most of the remaining compounds.

48.6.3.1 Anionic complexes

The anionic complexes containing phosphorus and arsenic ligands are shown in Table 61. It will be noted that there are no anionic complexes containing antimony ligands.

Table 61 Anionic Rhodium(III) Complexes Containing Tertiary Phosphine or Arsine Ligands

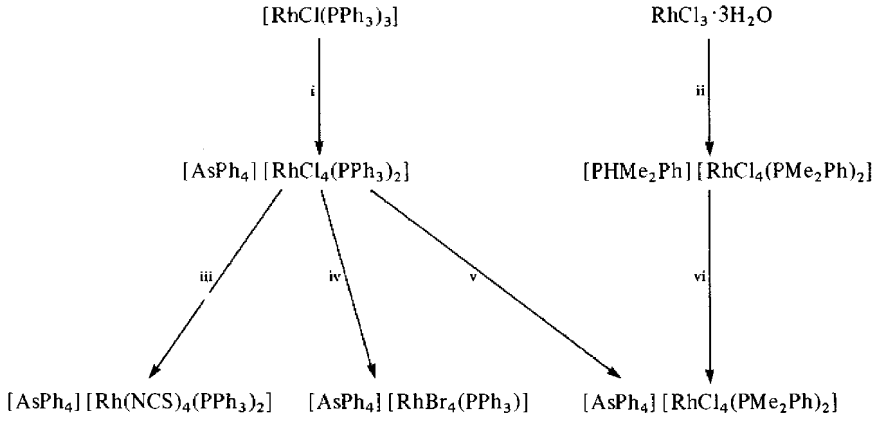
Complex	*Color*	*M.p.* (°C)	*Ref.*
$K[Rh(S_2CO)_2(PMe_2Ph)_2]$	Yellow	195[a]	915
$[AsPh_4][Rh(SCN)_4(PPh_3)_2]$	Lemon yellow	96–98	916
$[AsPh_4][RhCl_4(PMe_2Ph)_2]$	Red-brown	224–26	916
$[NMe_4][RhCl_4(PPh_3)_2]$	Orange-yellow	230–34	916
$[AsPh_4][RhCl_4(PPh_3)_2]$	Orange-yellow	206	916
$[AsPh_4][RhBr_4(PPh_3)_2]$	Yellow-brown	170[a]	916
$[RhCl_2(\mathbf{64})_2][RhCl_4(\mathbf{64})]$	Pale yellow	—	917
$[RhBr_2(\mathbf{64})_2][RhBr_4(\mathbf{64})]$	Yellow-orange	—	917
$[RhI_2(\mathbf{64})_2][RhI_4(\mathbf{64})]$	Brown	—	917

[a] With decomposition.

The most-studied anionic complex is $[AsPh_4][RhCl_4(PPh_3)_2]$. It results from the reaction between tetraphenylarsonium chloride and tris(triphenylphosphine)rhodium(I) complexes. However, if *trans*-$[RhCl(CO)(PPh_3)_2]$ is selected as the starting material then the major product is $[RhCl_3(CO)(PPh_3)_2]$. The less stable tetramethylammonium salt can also be prepared from *trans*-$[RhCl(CO)(PPh_3)_2]$ (equation 179).

$$\textit{trans}\text{-}[RhCl(CO)(PPh_3)_2] + (Me_4N)Cl + HCl \xrightarrow{Me_2CO} (Me_4N)[RhCl_4(PPh_3)_2] \quad (179)$$

The reactions of $[AsPh_4][RhCl_4(PPh_3)_2]$ are shown in Scheme 35; both the chloro and triphenylphosphine ligands of the anion can be substituted by ligands of similar character. For the thiocyanato complex $\nu_{C\equiv N}$ has been found to be 2105 cm^{-1}.[915] Under a nitrogen atmosphere, neat dimethylphenylphosphine slowly displaces the PPh_3 ligands from the complex. The anion $[RhCl_4(PMe_2Ph)_2]^-$ has also been prepared in a 2% yield from $RhCl_3 \cdot 3H_2O$ and PMe_2Ph.[918]



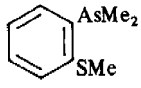
i, $[AsPh_4]Cl \cdot HCl$, Me_2CO;[916] ii, PMe_2Ph, (a) EtOH, (b) Me_2CO;[915] iii, LiNCS, Me_2CO;[916] iv, LiBr, Me_2CO;[916] v, PMe_2Ph, N_2, slow;[916] vi, $[AsPh_4]Cl$, EtOH[915]

Scheme 35 Preparation and reactions of anionic rhodium(III) complexes

It is generally considered that the chloro ligands in the above complexes are not *trans* to the tertiary phosphine ligands by virtue of ν_{Rh-Cl} in their far IR spectra being above 300 cm^{-1}. The PMe_2Ph complex has a ^{31}P NMR spectrum consistent with *trans* tertiary phosphine ligands.[918]

The PMe_2Ph ligands in the bis(dithiocarbonato) complex $K[Rh(S_2CO)_2(PMe_2Ph)_2]$ have been shown to be *trans* by X-ray crystallography.[919] The rhodate(III) salt was prepared by allowing $RhCl_3(PMe_2Ph)_3$ to react with potassium *O*-ethyldithiocarbonate in refluxing ethanol.[916]

If the thioarsine ligand (**64**) is allowed to react with aqueous rhodium trichloride then the tetrachlororhodate salt is formed. A similar reaction gives rise to the tetrabromo complex (equation 180). The tetraiodo complex can be prepared by addition of LiI to sodium hexachlororhodate(III) and the ligand (equation 181).[916]



(**64**)

$$RhX_3 \cdot 3H_2O + (\mathbf{64}) \xrightarrow{HX_{(aq)}/EtOH} [RhX_2(\mathbf{64})_2][RhX_4(\mathbf{64})] \quad (180)$$

$$Na_3[RhCl_6] + LiI + (\mathbf{64}) \xrightarrow{H_2O/EtOH} [RhI_2(\mathbf{64})_2][RhI_4(\mathbf{64})] \quad (181)$$

48.6.3.2 [RhX₃L] complexes

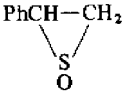
This is a rare stoichiometry which can be achieved by the coordination of two bidentate anionic ligands. The most authentic examples of this stoichiometry have been prepared by oxidative

addition to rhodium(I) complexes. Three bis(1,3-diaryltriazenido) complexes have been prepared by oxidative addition of the appropriate diaryltriazene to $RhCl(PPh_3)_3$ under mild conditions (equation 182).

$$[RhCl(PPh_3)_3] + ArN_3Ar \xrightarrow[20°C]{C_6H_6} [RhCl(ArN_3Ar)_2(PPh_3)_2] \quad (182)$$

$$Ar = Ph, p\text{-}C_6H_4Me, p\text{-}C_6H_4Cl^{231}$$

The reaction of $RhCl(PPh)_3$ with pentane-2,4-dione (equation 183) is more complex, some *trans*-$[RhCl(CO)(PPh_3)_2]$ is formed as a result of carbonyl abstraction in a side reaction.[920] An even more complex reaction results from the trapping by $RhX(PPh_3)_3$ (X = Cl, Br) of the SO moiety produced in the decomposition of stilbene episulfoxide (**65**; equations 184). The dimeric product is unstable in the presence of PPh_3 and is reduced to the starting material (equation 185).[921]



(65)

$$[RhCl(PPh_3)_3] + acacH \longrightarrow [RhCl(acac)_2(PPh_3)] \quad (183)$$

$$[RhX(PPh_3)_3] + (65) \xrightarrow{CH_2Cl_2} [RhX(SO)(PPh_3)]_2 + OPPh_3 + SPPh_3 + PhCH{=}CHPh \quad (184)$$

$$[RhX(SO)(PPh_3)]_2 + 8PPh_3 \longrightarrow 2OPPh_3 + 2SPPh_3 \quad (185)$$

An even more bizarre example of this stoichiometry is provided by the two dithiophosphorus complexes $[Rh(S_2PPh_2)_3PPh_3]$ and $[Rh\{S_2P(OEt)_2\}_3PPh_3]$. These have been prepared from uncharacterized rhodium(II) substrates by allowing the latter to react with PPh_3 and the sodium salt of the dithioacid. In these two complexes the dithioanion *trans* to PPh_3 is monodentate.

The same nominal stoichiometry is adopted by a few tetrafluoroborate salts of cations which contain similar bidentate thioanions; however, these cations are presumably five-coordinate having the formula $[RhX_2(PPh_3)]^+$ (X = S_2CNMe_2; XH = 2-mercaptobenzothiazole, 2-mercaptopyridine, toluene-3-thiol).[121]

48.6.3.3 [RhX_3L_2] complexes

Complexes adopting this stoichiometry are: (i) genuine five-coordinate complexes, or (ii) six-coordinate complexes containing either a bidentate anionic ligand, or (iii) an uncharacteristically bidentate neutral ligand. The final type of complex in this class is the six-coordinate binuclear complex such as $[RhCl_3(PBu_3)_2]_2$. Examples of the first three types of complex are: (i) $[RhHCl_2(PR_3)_2]$, (ii) $[RhH_2\{S(NPh)CHMe_2\}(PPh_3)_2]$, and (iii) $[RhCl_3\{Me_2As(o\text{-}C_6H_4OMe)\}_2]$.

(*i*) *Five-coordinate complexes*

The many hydrido and dihydrido complexes are a feature of this class. Their coordinative unsaturation undoubtedly arises from the high *trans* effect of their hydrido ligands. In this sense they can be regarded as the rhodium(III) analogs of the $[RhHL_2]$ complexes (Section 48.4.2.1). A lesser number of five-coordinate complexes containing bulky ligands are also known. This latter type can be regarded as the rhodium(III) analogs of the $[RhXL_2]$ complexes from which most can be obtained by suitable oxidative addition reactions.

The dihydrido complexes (Table 62) can be obtained by the oxidative addition of molecular hydrogen to rhodium(I) complexes (equation 186).[10,119,922–926] The tri(*t*-butyl)phosphine complexes can be prepared either from the chlororhodium(I) complex,[923] or rhodium trichloride.[927] The former method seems more reliable since the latter reports the complex as a matt green substance, a color uncharacteristic of tertiary phosphine rhodium(III) complexes. Indeed, Masters and Shaw report that the related tertiary phosphines PBu^t_2R (R = Et, Pr) give green rhodium(II) complexes in this reaction (see Section 48.5.2.1 above).[268,269]

The X-ray crystal structure of $[RhH_2Cl(PBu^t_3)_2]$ (**66**) has been determined.[923] The space group reported[928] for $[RhD_2(PPh_3)_3]$, P_{21}/c, differs from the C_2/c of the former complex.

Table 62 Physical Properties of $[RhH_2XL_2]$ Complexes

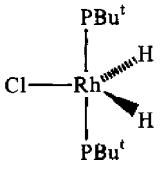
Complex	*Color*	*M.p.* (°C)	τ_{Rh-H} (p.p.m.)	ν_{Rh-H} (cm^{-1})	*Ref.*
$[RhH_2(CN)(PPh_3)_2]$	Yellow	—	—	2090, 1940[a]	119
$[RhH_2(SiHEt_2)(PPh_3)_2]$	Pale yellow	147–49	—	2085	922
$[RhH_2(SiMe_2Ph)(PPh_3)_2]$	Pale yellow	104–06	—	2070	922
$[RhH_2\{Si(OMe)_3\}(PPh_3)_2]$	Pale yellow	136–42	—	2055	922
$[RhH_2\{SiPh(OMe)_2\}(PPh_3)_2]$	Pale yellow	93–96	—	2070, 2030	922
$[RhH_2Cl(PBu^t{}_3)_2]$	Yellow	168–72[c]	23.6	2220	923
$[RhH_2Cl(PCy_3)_2]$	Yellow	—	32.7	2165, 2120[b]	924
$[RhH_2Cl(PPh_3)_2]$	Yellow	—	28.2, 21.5, 18.8	2078, 2013	10, 925
$[RhH_2Br(PPh_3)_2]$	Yellow	—	28.2, 21.5, 18.8	2177, 2057	10
$[RhH_2Cl\{P(p\text{-}C_6H_4Cl)_3\}_2]$	Red	—	—	2100, 2040	926
$[RhH_2Br\{P(p\text{-}C_6H_4Cl)_3\}_2]$	Red	—	—	2140, 2030	926
$[RhH_2I\{P(p\text{-}C_6H_4Cl)_3\}_2]$	Red	—	—	2115, 2000	926
$[RhH_2Cl(PBu^t{}_2Me)_2]$	Orange	160–76	32.3	2212, 2137	269
$[RhH_2Cl(AsPh_3)_2]$	Yellow	—	29.0, 22.1	2051	140
$[RhH_2Cl(SbPh_3)_2]$	Yellow	—	27.9, 19.9	—	140

[a] ν_{C-N} 2110 cm^{-1}. [b] ν_{Rh-D} 1560, 1528 cm^{-1}. [c] With decomposition.

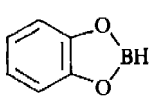
$$[RhX(PR_3)_3] + H_2 \longrightarrow [RhH_2X(PR_3)_2] + PR_3 \quad (186)$$

R = Ph, X = CN,[119] Cl, Br, I;[10] R = Bu^t, X = Cl[923]; R = Cy, X = Cl[924]; R = p-C_6H_4Cl, X = Cl, Br, I[925]

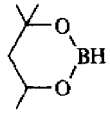
The dihydrido complex $[RhH_2Cl(PPh_3)_2]$ is a very important intermediate in the homogeneous catalytic hydrogenation of alkenes.[20] The monohydrido complexes (Table 63) can be made by the oxidative addition of HY species to rhodium(I) complexes (equation 187). Similar complexes can be obtained when bulky tertiary phosphines are allowed to react with alcoholic solutions of hydrated rhodium trichloride.[268,269]



(66)



(67)



(68)

Table 63 Physical Properties of $[RhHX_2L_2]$ Complexes

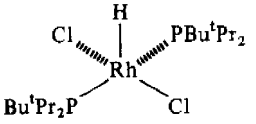
Complex	*Color*	*M.p.* (°C)	τ_{Rh-H} (p.p.m.)	ν_{Rh-H} (cm^{-1})	*Ref.*
$[RhHCl_2(PPh_3)_2]\cdot 0.5CH_2Cl_2$	Yellow	116–18[a]	26.1	2160	930, 931
$[RhHCl_2(PCy_3)_2]$	Orange	—	40.5	1943	932
$[RhHCl_2(PBu^tPr_2)_2]$	Red	122–25[a]	41.37	1945	269
$[RhHCl_2(PBu^t{}_2Me)_2]$	Red	170–90[a]	41.40	1938	269
$[RhHCl_2(PBu^t{}_2Et)_2]$	Red	157–62[a]	41.10	1940	269
$[RhHCl_2(PBu^t{}_2Pr)_2]$	Khaki	175–90[a]	—	1936	269
$[RhHBr_2(PBu^tPr_2)_2]$	Dark red	161–71[a]	41.10	1946	269
$[RhHBr_2(PBu^t{}_2Me)_2]$	Dark red	150–70[a]	41.10	1938	269
$[RhHBr_2(PCy_3)_2]$	Orange	—	—	—	924
[RhHCl(**67** − H)$(PPh_3)_2$]	—	131–32	—	2120	933
[RhHCl(**68** − H)$(PPh_3)_2$]	—	115–16	—	2080	933
[RhHBr(**67** − H)$(PPh_3)_2$]	—	134–35	—	2125	933
[RhHBr(**68** − H)$(PPh_3)_2$]	—	103–04	—	2080	933
$[RhHCl(HS)(PPh_3)_2]\cdot 0.5CH_2Cl_2$	Yellow	116–18[a]	—	2160	929
$[RhHCl(p\text{-}SC_6H_4Me)(PPh_3)_2]$	—	160	26.5	2119	929
$[RhHClBr(PCy_3)_2]$	Orange	—	—	—	924
$[RhHClI(PCy_3)_2]$	Red	—	—	—	924
$[RhHCl_2(AsPh_3)_2]$	Yellow	—	25.9	2069	140
$[RhHCl_2(SbPh_3)_2]$	Yellow	—	28.3	2014	140

[a] With decomposition.

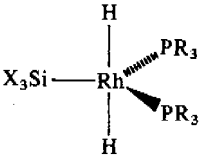
$$[RhX(PR_3)_3] + HY \longrightarrow [RhHXY(PR_3)_2] + PR_3 \quad (187)$$

R = Ph, X = Cl, Y = Cl[930,931], CN, *p*-MeC_6H_4S[929]; X = Cl, Br, Y = (**67**), (**68**)[933]; R = Cy, X = Cl, Y = Cl, Br, I[924]

Usually the monohydrido species have the square pyramidal structure (**69**),[268] although the populous and important hydridosilylrhodium(III) complexes have been shown to adopt the trigonal bipyramidal structure (**70**) in the solid state.[934]



(69)



(70)

The five-coordinate monohydrido complexes shown in Table 63 are less reactive and less important catalytically than their dihydrido analogs. One of the few reactions noted is the addition of pyridine to the tricyclohexylphosphine complexes to form six-coordinate products (equation 188).[924] Six-coordinate complexes can also be obtained if the preparation of $[RhH_2Cl(PPh_3)_2]$ is carried out in coordinating solvents.[10]

$$[RhHCl_2(PCy_3)_2] + py \longrightarrow [RhHCl_2(PCy_3)_2py] \quad (188)$$

By contrast the silyl complexes are important catalysts in a variety of hydrosilylation reactions.[20] They can be prepared by the similar oxidative addition of hydrosilanes to rhodium(I) complexes, either directly or in solution (equation 189).[935] However, in the presence of both additional base and triphenylphosphine a hydridorhodium(I) complex results (equation 190).[936] Alternatively in the presence of a large excess of hydrosilane the monohydrido complex is transformed into a dihydrido complex.[922]

$$[RhCl(ZPh_3)_3] + SiHR_3 \longrightarrow [RhHCl(SiR_3)(ZPh_3)_2] + ZPh_3 \quad (189)$$

Z = P, As, Sb; X = Cl, Br, I; R = Cl, OEt

$$[RhCl(PPh_3)_3] + Et_3SiH + Et_3N \xrightarrow[C_6H_6]{PPh_3} [RhH(PPh_3)_4] + Et_3SiCl{-}NEt_3 \quad (190)$$

The complexes produced, although five-coordinate, often contain hydrosilane of crystallization. This additional hydrosilane is not associated with rhodium.[934]

Despite the widespread use of such hydridosilyl complexes in hydrosilylation reactions, only a fraction of those employed have been isolated and characterized (Table 64).

Solutions of the complexes are unstable due to loss of the silyl ligands, which are also readily displaced by other ligands. In the solid state the $[RhHCl(SiX_3)(PPh_3)_2]$ complexes are more stable and only decompose upon heating *in vacuo* above 100 °C (equation 191).[939] The thermal stability of the complexes increases with increasing electronegativity of groups bound to silicon, but decreases with increasing size of tertiary phosphine ligands. Some of the reactions of the silyl complexes are shown in Figure 4.

$$2[RhHCl(SiR_3)(PPh_3)_2] \longrightarrow 2SiHR_3 + [RhCl(PPh_3)_2]_2 \quad (191)$$

The analogous hydridogermyl complexes may be prepared similarly using hydrogermanes.[940,941] However, a 14-fold excess of hydrogermane forms anionic complexes (equation 192). The germyl complexes have a similar structure to their five-coordinate silyl analogs, and, despite being less extensively dissociated in solution, undergo many of the same reactions. Thus, they are decomposed by either carbon monoxide or ethylene (equation 193).

$$[RhCl(PPh_3)_3] + 14GeHCl_3 \longrightarrow [Ph_3PH][Rh(GeCl_3)_6] + H_2 + HCl \quad (192)$$

$$[RhHCl(GeX_3)(PPh_3)_2] + L \longrightarrow \textit{trans}\text{-}[RhCl(PPh_3)_2L] + GeHX_3 \quad (193)$$

L = CO, C_2H_4

Table 64 Physical Properties of Five-coordinate Hydrido Silyl and Germyl Complexes

Complex	*Color*	*M.p.* (°C)	τ_{Rh-H} (p.p.m.)	ν_{Rh-H} (cm^{-1})	*Ref.*
$[RhHCl(SiMe_3)(PPh_3)_2]$[a]	Yellow	92–97	—	2055	937
$[RhHCl(SiEt_3)(PPh_3)_2]$	Yellow	103–07	—	2020	937
$[RhHCl(SiPh_3)(PPh_3)_2]$	Yellow	133–37	—	2140	937
$[RhHCl\{Si(OEt)_3\}(PPh_3)_2]$	Yellow	127–32	—	2060	937
$[RhHCl(SiCl_3)(PPh_3)_2]$[a]	Bright yellow	168–73	24.30	2040	937
$[RhHCl(SiClMe_2)(PPh_3)_2]$	Yellow	123–28	24.8	2060	937
$[RhHCl(SiClEt_2)(PPh_3)_2]$	Yellow	142–47	—	2110	937
$[RhHCl(SiCl_2Me)(PPh_3)_2]$[a]	Bright yellow	143–47	24.45	2050	937
$[RhHCl(SiCl_2Et)(PPh_3)_2]$	Bright yellow	158–63	23.2	2130	937
$[RhHCl\{Si(OEt)_3\}(PPh_2Pr^i)_2]$	Yellow	126–32	—	—	938
$[RhHCl(SiEt_3)(PPh_2Cy)_2]$	Yellow	—	—	—	938
$[RhHCl\{Si(OEt)_3\}(PPh_2Cy)_2]$	Yellow	145–50[b]	—	—	938
$[RhHCl\{Si(OEt)_3\}(PPhCy_2)_2]$	Yellow	132–36	—	—	938
$[RhHCl\{Si(OEt)_3\}(PPh_2(p\text{-}C_6H_4Me)\}_2]$	Yellow	122–28[b]	—	—	938
$[RhHBr(SiEt_3)(PPh_3)_2]$	Yellow	108–12	—	2070	937
$[RhHBr\{Si(OEt)_3\}(PPh_3)_2]$	Bright yellow	127–32	24.6, 23.6	2060	935, 939
$[RhHBr(SiCl_3)(PPh_3)_2]$	Orange-yellow	165–70	23.40	2120	937
$[RhHBr(SiClMe_2)(PPh_3)_2]$	Bright yellow	128–33	23.8	2050	937
$[RhHBr(SiClEt_2)(PPh_3)_2]$	Bright yellow	143–47	—	2130	937
$[RhHBr(SiCl_2Me)(PPh_3)_2]$	Bright yellow	147–52	—	2045	937
$[RhHBr(SiCl_2Et)(PPh_3)_2]$	Bright yellow	155–60	23.1	2130	937
$[RhHI\{Si(OEt)_3\}(PPh_3)_2]$	Orange	125–30	21.70	2060	937
$[RhHI(SiCl_3)(PPh_3)_2]$	Orange	163–67	—	2050	937
$[RhHCl\{Si(OEt)_3\}(AsPh_3)_2]$	Yellow	142–47	26.3	2065	937
$[RhHCl(SiCl_3)(AsPh_3)_2]$	Yellow	178–82	—	2080	937
$[RhHCl\{Si(OEt)_3\}(SbPh_3)_2]$	Gray	152–57	21.3	2080	937
$[RhHCl(SiCl_3)(SbPh_3)_2]$	Orange-yellow	183–88	—	2080	937
$[RhHCl(GeMe_3)(PPh_3)_2]$	Yellow	90–94[b]	—	2080, 2035	940, 941
$[RhHCl(GeEt_3)(PPh_3)_2]$	Yellow	117–19[b]	—	2107, 2062	940, 941
$[RhHCl(GeCl_3)(PPh_3)_2]$	Orange-yellow	148–52[b]	—	2123, 2098	940, 941
$[RhHCl(GeMe_3)(AsPh_3)_2]$	Green	90–95[b]	—	2057, 2025	940, 941
$[RhHCl(GeEt_3)(AsPh_3)_2]$	Green	118–21[b]	—	2114, 2042	940, 941

[a] Dichloromethane hemisolvate also known.[939] [b] With decomposition.

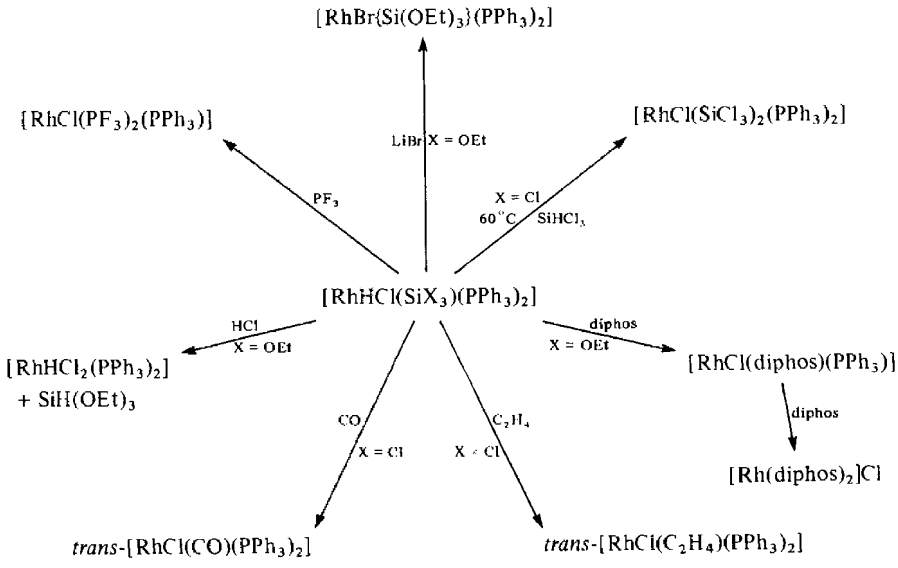


Figure 4 Reactions of $[RhHCl(SiX_3)(PPh_3)_2]$ complexes

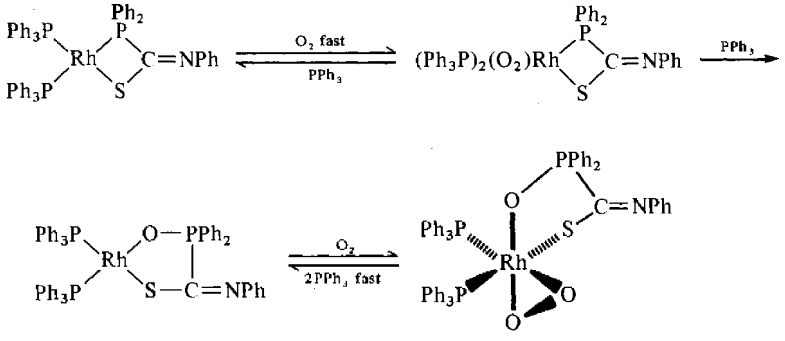
Many rhodium(I) tertiary phosphine complexes react readily with molecular oxygen, although it is not always easy to characterize the products of these reactions.[943,944] The complexes isolated are listed in Table 65.

One problem is that coordinated oxygen oxidizes the tertiary phosphine ligands to form free tertiary phosphine oxide. Often the course of this reaction is solvent dependent; in ethanol the phosphine oxide is more likely to be formed than in hydrocarbon solvents.[945] The oxidation of ligands also occurs in the solid state reaction.[942]

Table 65 Physical Properties of $[RhXO_2L_2]$ Complexes

Complex	*Color*	$\nu_{O-O}(cm^{-1})$	*Ref.*
$[RhCN(O_2)(PPh_3)_2]$	Light brown	900	930
$[RhCl(O_2)(PPh_3)_2]$	Green	870	119
cis-$[Rh(O_2)\{S(NPh)(CNMe_2)\}(PPh_3)_2]$	—	870	942
trans-$[Rh(O_2)\{S(NPh)CNMe_2)\}(PPh_3)_2]$	Ocher	870	942
trans-$[Rh(O_2)\{Me_2N(CS)N(CS)NMe_2\}(PPh_3)_2]$	Ocher	878	942
cis-$[Rh(O_2)(S_2CNMe_2)(PPh_3)_2]$	—	866	942
trans-$[Rh(O_2)(S_2CNMe_2)(PPh_3)_2]$	Green-yellow	—	942
cis-$[Rh(O_2)\{Ph_2P(O)(CS)NPh)\}(PPh_3)_2]$	—	869	942

One of the best studies on the oxidation involves the rhodium(I) complex $[(Ph_3P)_2RhS(PPh)C{=}NPh]$. These reactions are shown in Scheme 36. The *N,N*-dimethyldithiocarbamato complex merely undergoes oxidative addition.

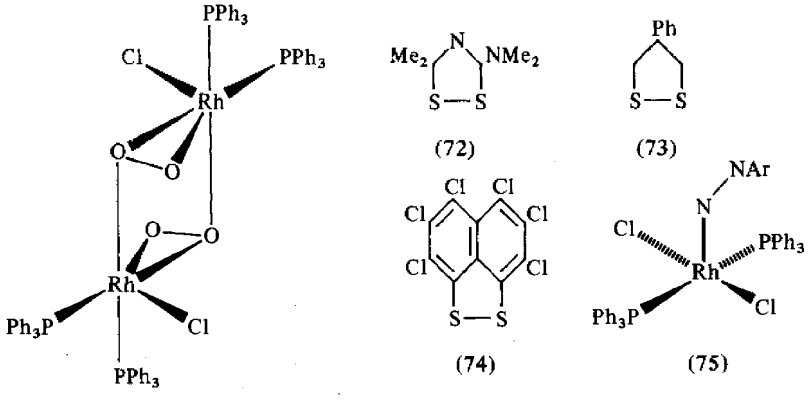


Scheme 36 Reactions of $[Rh\{S(PPh_2)CNMe\}(PPh_3)_2]$ with O_2 in the presence of PPh_3

The reaction of dioxygen with $[RhCl(PPh_3)_3]$ has long been known.[930,944,945] The cyano analog reacts similarly.[119] However, the product from the latter reaction may be six-coordinate with bridging dioxygen ligands since both the chloro complex and its dichloromethane solvate adopt structure (**71**).[946,947] The chlorobis(triphenylphosphine) complex is not the sole possible product; under slightly different conditions $[RhCl(O_2)(PPh_3)_3]$ is formed (see Section 48.6.3.5). Most of the dioxygen complexes exhibit bands between 871 and 900 cm^{-1} in their IR spectra, which have been assigned to ν_{O-O}.

There remain a number of other five-coordinate complexes whose physical properties are shown in Table 66. Of these complexes only the $AsCy_3$ complex has been prepared from a rhodium(III) source (equation 194). The remainder have been prepared from oxidative addition reactions of $[RhCl(PPh_3)_3]$. The arylazo complexes have structure (**75**),[948] whilst the sulfinato complexes are bound through sulfur.[950]

$$RhCl_3 \cdot 3H_2O + AsCy_3 \xrightarrow{MeO(CH_2)_2OH} [RhCl_3(AsCy_3)_2] \qquad (194)$$



(71)

(72)

(73)

(74)

(75)

Table 66 Physical Properties of Five-coordinate $[RhX_3L_2]$ Complexes

Complex	*Color*	*M.p.* (°C)	*Ref.*
$[Rh(NCS)_3(PPh_3)_2]$	—	159–60	121
$[RhCl_2(N_2Ph)(PPh_3)_2]$	Brown[a]	189–93	948
$[RhCl_2\{N_2(p\text{-}C_6H_4Me)\}(PPh_3)_2]$	Brown[b]	230–32	948
$[RhCl_2\{N_2(p\text{-}C_6H_4OMe)\}(PPh_3)_2]$	Brown[c]	218–21	948
$[RhCl_2\{N_2(p\text{-}C_6H_4Cl)\}(PPh_3)_2]$	Orange-brown[d]	204–07	948
$[RhCl_2\{N_2(p\text{-}C_6H_4NO_2)\}(PPh_3)_2]$	Brown[e]	142–44	948
$[RhBr_2(N_2Ph)(PPh_3)_2]$	Brown[f]	157–60	948
$[RhCl(C_6Cl_4O_2)(PPh_3)_2]$	Green	—	949
$[RhCl_2(SO_2Me)(PPh_3)_2]$	[g]	—	950
$[RhCl_2\{SO_2(p\text{-}CH_2C_6H_4)\}(PPh_3)_2]$	[h]	—	950
$[RhCl_2\{SO_2(p\text{-}CH_2C_6H_4NO_2)\}(PPh_3)_2]$	[i]	—	950
$[RhCl(\mathbf{72})(PPh_3)_2]$	Orange	—	951
$[RhCl(\mathbf{73})(PPh_3)_2]$	Purple	—	951
$[RhCl(\mathbf{74})(PPh_3)_2]$	Orange	—	951
$[RhBr(\mathbf{72})(PPh_3)_2]$	Brown	—	951
$[RhBr(\mathbf{73})(PPh_3)_2]$	Brown	—	951
$[RhBr(\mathbf{74})(PPh_3)_2]$	Brown	—	951
$[RhCl_3(AsCy_3)_2]$	—	—	952

$\nu_{N=NR}$ (cm^{-1}) [a] 1610, 1645; [b] 1615, 1557; [c] 1558; [d] 1605, 1660; [e] 1610, 1553; [f] 1620, 1565.
$\nu_{SO_2(asym)}$ (cm^{-1}), $\nu_{SO_2(sym)}$ (cm^{-1}) [g] 1255, 1090; [h] 1255, 1085; [i] 1260, 1060.

(*ii*) *Six-coordinate complexes*

The complexes which contain a bidentate anion are listed in Table 67. Two preparative routes exist to these complexes. One involves oxidative addition of two monoanions to a rhodium(I) complex containing a bidentate anion. These are usually complexes containing a disulfur anion (equation 195).[65] Dibenzoylmethane, in contrast to pentane-2,4-dione (see Section 48.6.3.2 above) adds in a similar fashion (equation 196).[920]

$$[Rh(S_2PR_2)(PPh_3)_2] + I_2 \xrightarrow{C_5H_{12}} [RhI_2(S_2PR_2)(PPh_3)_2] \quad (195)$$

$$R = Cy, OPh$$

$$[RhCl(PPh_3)_3] + (PhCO)_2CH_2 \longrightarrow [RhCl_2\{(PhCO)_2CH\}(PPh_3)_2] \quad (196)$$

Table 67 Physical Properties of Six-coordinate $[RhX_3L_2]$ Complexes

Complex	*Color*	*M.p.* (°C)	*Ref.*
$[RhH_2(BH_4)(PCy_3)_2]$	Yellow	—	924
$[RhH_2(BH_4)(PBu^t_2Me)_2]$	White	—	924
$[RhH_2(PhN_3Ph)(PPh_3)_2]$	Orange-red	144–47	231
$[RhH_2\{(p\text{-}MeC_6H_4)_2N_3\}(PPh_3)_2]$	Brown	106–11	231
$[RhH_2\{(p\text{-}ClC_6H_4)_2N_3\}(PPh_3)_2]$	Green	142–45	231
$[RhH_2\{(p\text{-}MeC_6H_4)N_3(p\text{-}C_6H_4OMe)\}(PPh_3)_2]$	Brown	107–14	231
$[RhHCl(CN)(PPh_3)_2(HCN)]$	Yellow	180–90	929
$[RhCl_2(NO_3)(PMePh_2)_2]$	—	—	953
$[RhBr_2(NO_3)(PMePh_2)_2]$	—	—	953
$[RhCl_2\{(PhCO)_2CH\}(PPh_3)_2]$	—	250–55	920
$[RhHCl(2\text{-}SC_2H_4PHPh)(PPh_3)_2]$	Yellow-brown	218–20	954
trans-$[RhCl_2(S_2CNMe_2)(PMe_2Ph)_2]$	Orange	207–08	915
cis,cis,cis-$[RhCl_2(S_2PMe_2)(PMe_2Ph)_2]$	Orange	184–86	915
cis,cis,cis-$[RhCl_2(S_2PPh_2)(PMe_2Ph)_2]$	Orange	208–10	915
mer-$[RhCl_2(S_2PMe_2)(PMe_2Ph)_2]$	Orange	140–42[a]	915
trans-$[RhCl_2(S_2PMe_2)(PMe_2Ph)_2]$	Orange	235–37[a]	915
trans-$[RhCl_2(S_2PPh_2)(PMe_2Ph)_2]$	Orange	228–29[a]	915
trans-$[RhCl_2(S_2COEt)(PMe_2Ph)_2]$	Orange	155–57	915
cis-$[Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2]$	Yellow	172–73[a]	915
trans-$[Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2]$	Yellow	150–53[a]	915
$[RhI_2(S_2PCy_2)(PPh_3)_2]$	Brown	—	65
$[RhI_2\{S_2P(OPh)_2\}(PPh_3)_2]$	Brown	—	65
$[RhCl_2(NO_3)(AsMePh_2)_2]$	—	—	953
$[RhBr_2(NO_3)(AsMePh_2)_2]$	—	—	953

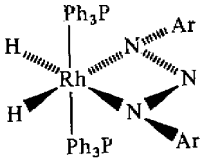
[a] With decomposition.

It is possible that the nitrato complexes $[RhX_2(NO_3)(PMePh_2)_2]$, prepared by the decidedly hazardous addition of concentrated nitric acid to ethanolic solutions of $[RhX_2H(PMePh_2)_2]$, are also six-coordinate but the IR spectrum of the nitrato ligand reputedly gave no clue to its denticity.[953]

Numerous complexes containing bidentate 1,3-diaryltriazenido ligands have been prepared by Robinson and his co-workers. These complexes have been prepared by allowing the 1,3-diaryltriazene to react with a rhodium(I) complex under mild conditions (equation 197)[231,955] or directly from $RhCl_3 \cdot 3H_2O$.[231] The structure (**76**) has been deduced from the ^{31}P and high field ^1H NMR spectra.[231]

$$[RhH(PPh_3)_4] + ArN_3Ar \longrightarrow [RhH_2(ArN_3Ar)(PPh_3)_2] \quad (197)$$

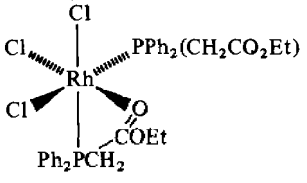
$$Ar = Ph, p\text{-}C_6H_4Me, p\text{-}C_6H_4Cl$$



(76)

Besides those complexes which contain bidentate anionic ligands there are also complexes which contain one bidentate neutral ligand. Very frequently this type of complex contains two identical neutral ligands one of which is monodentate and the second bidentate by virtue of complexing to rhodium through a second functional group on the ligand.

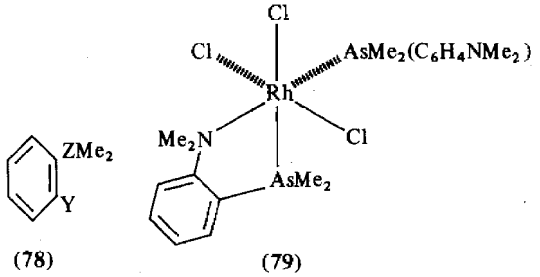
The tertiary phosphine $Ph_2P(CH_2COOEt)$ has been shown by Braunstein and his co-workers to form a rhodium(III) complex when allowed to react with rhodium trihalides. The products are the facial isomers (**77**). This is in accordance with their NMR spectra which show $^2J(P\text{–}P) = 23.5$ Hz.[956]



(77)

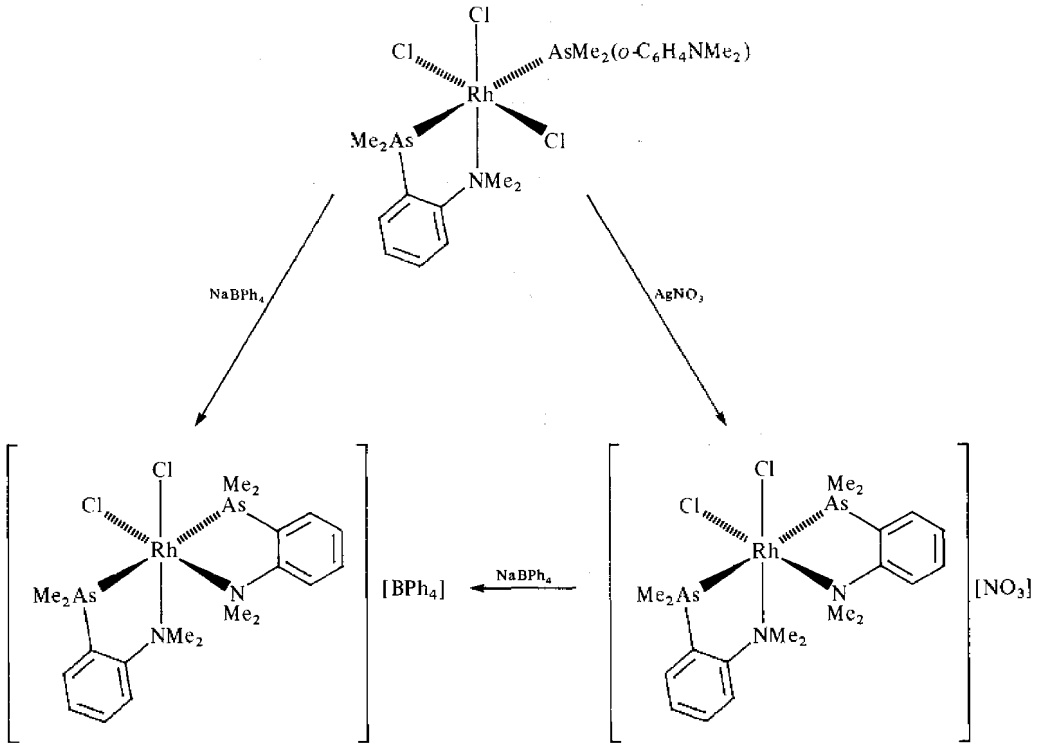
This behavior is in contrast to that of the bulky ligands $Bu^t_2P(CH_2)_nCOOEt$ ($n = 2, 3$), which form rhodium(II) complexes under these conditions,[275] and the cyanophosphine $PPh_2(CH_2CN)$, which forms *mer*-$[RhCl_3\{PPh_2(CH_2CN)\}_3]$.[956]

When hydrated rhodium trichloride is allowed to react with (**78**; Y = OMe, NMe_2; Z = As), complexes of empirical formula $[RhCl_3(\mathbf{78})_2]$ are obtained. The orange-red dimethylaminophosphine complex has been shown to have the meridional structure (**79**).[957–959] However, one chloro ligand is labile and can be replaced in the inner coordination sphere by the previously uncoordinated nitrogen atom of the second neutral ligand. This process is enhanced by allowing the complex to react with metal salts whose anions are of low coordinating power (Scheme 37).[957]



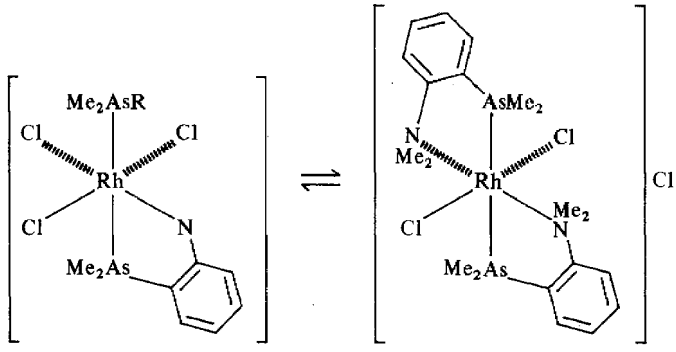
(78) (79)

The dark red *o*-anisyl complex can be prepared similarly. It has also been shown to have a meridional structure by X-ray crystallography.[960–962] It too reacts with silver nitrate to form an ionic complex in which all four potential donor atoms of the two neutral ligands coordinate to rhodium.[960]



Scheme 37 Reactions of *mer*-$[RhCl_3\{AsMe_2(o\text{-}C_6H_4NMe_2)\}_2]$[957]

The kinetics of the isomerization (equation 198) and analogous reactions have attracted much attention.[963–969] It is not surprising that the rate of the forward reaction is increased in polar solvents.[969]



(198)

The antimony ligands (**78**; Y = OMe, NMe_2; Z = Sb) also form $[RhX_3(\mathbf{78})_2]$ complexes when allowed to react with hydrated rhodium trihalides, except that rhodium tribromide and the anisyl ligand form the complex $[RhBr_3(\mathbf{78})_3]$. These reddish complexes presumably have similar structures to those of their well-characterized arsenic analogs. Whilst there is no evidence that loss of a halo ligand occurs in 1,2-dichloroethane, silver nitrate displaces one halo ligand. Presumably the *trans*-dihalo nitrate complex is formed.[970] This behavior is confined to antimony ligands of type (**78**). The three ligands $Ph_2Sb(o\text{-}MeOC_6H_4)$, $MeSb(o\text{-}MeOC_6H_4)_2$ and $Me_2Sb(o\text{-}MeOC_6H_4)$ all form $[RhCl_3L_3]$ complexes.[971]

(*iii*) *Dinuclear complexes*

These complexes are produced when rhodium trichloride is allowed to react with two, or less, equivalents of tertiary phosphine or arsine (equation 199). Their physical properties are listed in Table 68, and the complexes have been shown to adopt the non-centrosymmetric structure (**80**).[977] This is in agreement with the dipole moment[972] and ^{31}P NMR spectrum[978] of the tributylphosphine

Table 68 Physical Properties of $[RhX_3L_2]_2$ Complexes

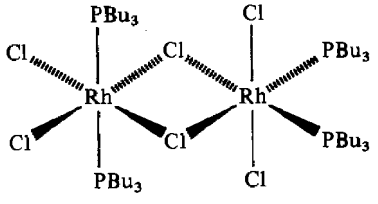
Complex	*Color*	*M.p.* (°C)	*Ref.*
$[RhCl_3(PMe_3)_2]_2$	Red-orange	250–54	114
$[RhCl_3(PEt_3)_2]_2$	Red-purple	248–61[a]	972
$[RhCl_3(PPr_3)_2]_2$	Orange-brown	180–92	972
$[RhCl_3(PBu_3)_2]_2$	Red-brown	172–80[a]	972
$[RhCl_3\{P(C_5H_{11})_3\}_2]_2$	Brown	146–50	972
$[RhCl_3(PCy_3)_2]_2$	Red	205–10	114
$[RhCl_3(PMePh_2)_2]_2$	Red	220–25	114
$[RhCl_3(PEtPh_2)_2]_2$	Yellow	271	973
$[RhBr_3(PBu_3)_2]_2$	Red-brown	168–71	972
$[RhCl_3(AsEt_3)_2]_2$	Orange-brown	240–56	972
$[RhCl_3\{As(CH_2Ph)_3\}_2]_2$	—	—	974
$[Rh_2Cl_6\{(Ph_2As)_2C_2H_4\}_3]$	Yellow	225	975
$[RhBr_3(AsEt_3)_2]_2$	Red-brown	248–55[a]	972
$[RhCl_3\{(Ph_2Sb)_2CH_2\}_3]_2$	Red	220[a]	976
$[RhBr_3\{(Ph_2Sb)_2CH_2\}_3]_2$	Red	244–46[a]	976
$[RhI_3\{(Ph_2Sb)_2CH_2\}_3]_2$	Dark brown	228–30[a]	976

[a] With decomposition.

complex. However, working up solutions of this complex causes it to disproportionate (equation 200).[979]

$$RhCl_3 \cdot 3H_2O + 4ZR_3 \longrightarrow [RhCl_3(ZR_3)_2]_2 \quad (199)$$

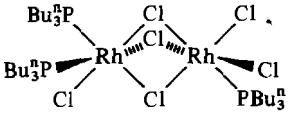
$Z = P$, $R_3 = Et_3$, Pr_3, Bu_3, $(C_5H_{11})_3$,[972] $EtPh_2$[973]; $Z = As$, $R_3 = Et$,[972] CH_2Ph[974]



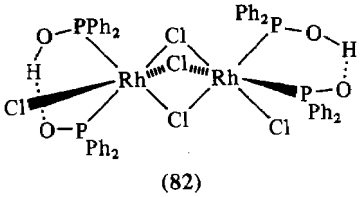
(80)

$$3[RhCl_3(PBu_3)_2]_2 \longrightarrow [Rh_2Cl_6(PBu_3)_3] + mer\text{-}[RhCl_3(PBu_3)_3] \quad (200)$$

The trihalobridged structure (**81**) has been confirmed by X-ray crystallography.[980] The disposition of each phosphorus atom *trans* to a different bridging chloro ligand is reminiscent of the structure of the $[Rh_2Cl_5\{Ph_2PO\}_2H_2]^-$ anion (**82**).[981]



(81)



(82)

The trihalobridged species can also be obtained by allowing rhodium trichloride to react with 0.92 equivalents of tertiary phosphine. The trihalobridged complexes revert to dihalobridged complexes in the presence of more ligand (equation 201).

$$[Rh_2Cl_6(PBu_3)_3] + PBu_3 \longrightarrow [RhCl_3(PBu_3)_2]_2 \quad (201)$$

An unstable tri(perfluorophenyl)phosphine complex can be obtained by oxidative addition of chlorine to the dimeric rhodium(I) complex. The ethyldiphenylphosphine complex prepared in this way is more stable (equation 202).

$$[RhCl(PR_3)_2]_2 + Cl_2 \longrightarrow [RhCl_3(PR_3)_2]_2 \quad (202)$$

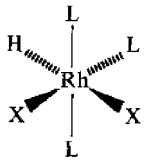
$R_3 = (C_6F_5)_3$,[73] $EtPh_2$[972]

Apart from the triethylarsine[972] and the tribenzylarsine[974] complexes the remaining tertiary arsine complex is formed by the ditertiary arsine 1,2-$(Ph_2As)_2C_2H_4$; clearly this cannot adopt structure (**80**). However, the ditertiary stibine complexes[976] may well adopt structure (**80**), since their stoichiometry implies that only half the antimony atoms are coordinated to rhodium.

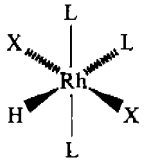
48.6.3.4 [RhH_2XL_3] and [$RhHX_2L_3$] complexes

The dihydrido complexes, despite their catalytic potential, are sparsely represented. It has been shown by X-ray photoelectron spectroscopy that the interaction of hydrogen with solid [$RhCl(PPh_3)_3$] yields the complex [$RhH_2Cl(PPh_3)_3$].[982] This complex has also been detected in solutions containing excess PPh_3 and its NMR spectrum measured.[983] It was noted in Section 48.6.3.3 (i) above that [$RhH_2Cl(PPh_3)_2$] reacts with coordinating solvents to give complexes of this stoichiometry.[10] The lability of the third triphenylphosphine ligand has also enabled the α-methylbenzylamine complex [$RhH_2Cl(PPh_3)_2(PhCHMeNH_2)$] to be prepared and used as a chiral hydrogenation catalyst.[983] The smaller $PEtPh_2$ ligand is less labile and [$RhH_2Cl(PEtPh_2)_3$] can be prepared by oxidative addition of H_2 to [$RhCl(PEtPh_2)_3$] in the presence of excess ligand.[973]

In the monohydrido complexes the neutral ligands adopt the *mer* configuration, thus giving rise to two isomeric forms. The first of these, designated α (**83**), has the hydrido ligand *trans* to an anionic ligand; the β isomer (**84**) has the hydrido ligand *trans* to a neutral ligand. The physical properties of the two series are listed in Tables 69 and 70, respectively.



(83)



(84)

It is not surprising that the α isomers are the more stable, given that the neutral ligands are invariably higher in the *trans* effect series than halogeno ligands. The isomerization from β to α isomers is accelerated by light or by heating, but it is inhibited by the presence of excess neutral ligand. It seems probable, therefore, that a dissociative mechanism is involved.[986]

The ligand *trans* to the hydrido ligand influences the properties of the latter. The rhodium–hydrogen bond is weaker in the β isomer than in the α isomer, ν_{Rh-H} being typically some 100 cm^{-1} lower in the latter (Tables 69 and 70). The ^1H NMR spectra of the isomers are quantitatively similar, consisting of a pair of double triplets in both cases. However, in the spectra of the α isomers all the J(H–P) values are in the range 9–22 Hz, whereas in the spectra of the β isomers the whole spectrum is displaced to lower fields and J(H–P) is about 200 Hz. This is indicative of the hydrido ligand being *trans* to the unique phosphorus ligand.[986]

The complexes have been prepared by several methods. When ethanolic KOH and rhodium

Table 69 Physical Properties of α-[$RhHX_2L_3$] Complexes

Complex	*Color*	*M.p.* (°C)	ν_{Rh-H} (cm^{-1})	*Ref.*
[$RhHCl_2(PPh_3)_3$]	Yellow	160[c]	2220	973
[$RhHCl_2(PMe_2Ph)_3$]	Yellow-orange	160–65	—	114
[$RhHCl_2(PEt_2Ph)_3$]	Yellow	140–45	—	114
[$RhHBr_2(PEt_2Ph)_3$]	Yellow	—	—	973
[$RhHCl_2(PMePh_2)_3$]	—	167–70	—	984
[$RhHBr_2(PMePh_2)_3$]	—	183–87	—	984
[$RhHCl_2(PEtPh_2)_3$]	Yellow	210[c]	2120	973
[$RhHBr_2(PEtPh_2)_3$]	Yellow	—	2110	973
[$RhHI_2(PEtPh_2)_3$]	—	—	2100	973
[$RhHCl_2(AsMePh_2)_3$]	Yellow	172–75	2077[a]	985
[$RhHBr_2(AsMePh_2)_3$]	Orange-yellow	175–78	2073[b]	985
[$RhHI_2(AsMePh_2)_3$]	Orange-brown	164	2058	985
[$RhHCl_2(AsPh_2Pr)_3$]	Yellow	145–48	2107	986
[$RhHBr_2(AsPh_2Pr)_3$]	Orange-yellow	141–45	2107	986
[$RhHI_2(AsPh_2Pr)_3$]	Brown	127–29	2090	986

[a] ν_{Rh-D} 1485 cm^{-1}. [b] ν_{Rh-D} 1483 cm^{-1}. [c] With decomposition.

Table 70 Physical Properties of β-[$RhHX_2L_3$] Complexes

Complex	*Color*	*M.p.* (°C)	ν_{Rh-H} (cm^{-1})	*Ref.*
$[RhHCl_2(PMe_3)_3]$	Yellow	210–19	—	114
$[RhHCl_2(PEt_3)_3]$	Yellow-orange	140–220	—	114
$[RhHCl_2(PPh_3)_3]$	Pale yellow	100[a]	—	973
$[RhHCl_2(PMe_2Ph)_3]$	Yellow	215–20	—	114
$[RhHCl_2(PMePh_2)_3]$	—	158–61	—	984
$[RhHCl_2(PEtPh_2)_3]$	Yellow	180–85	1982	973
$[RhHBr_2(PEtPh_2)_3]$	Yellow	—	1964	973
$[RhHI_2(PEtPh_2)_3]$	—	—	1960	973
$[RhHCl_2(AsMePh_2)_3]$	—	158–61	—	984
$[RhHCl_2(PBu^tPr_2)_2(CNMe)]$	Orange	124–31	—	269
$[RhHCl_2(PBu^tPr_2)_2(NCMe)]$	Orange	99–105	—	269
$[RhHCl_2(PBu^tPr_2)_2py]$	Orange	122–26	—	269
$[RhHCl_2(PBu^tPr_2)_2\{P(OMe)_3\}]$	Orange	85–100	—	269

[a] With decomposition.

trichloride are allowed to react with $PEtPh_2$ at room temperature α-$[RhHCl_2(PEtPh_2)_3]$ is formed.[987] Piperidine/ethanol mixtures have also been used as the solvent.[988] Prolonged refluxing of the solvent results in carbonyl complexes being isolated. Phosphinic acid has been used as the source of the hydrido ligand in other reactions.[986,989] Zinc dust has also been used as the reducing agent.[990] Alternatively, α-$[RhHCl_2(PMePh_2)_3]$ has been synthesized by the oxidative addition of HCl to the rhodium(I) complex (equation 203).[986] However, treatment of rhodium(III) complexes with phosphinic acid yields the β isomers (equation 204).[986]

$$[RhCl(PEtPh_2)_3] + HCl \longrightarrow \alpha\text{-}[RhHCl(PEtPh_2)_3] \quad (203)$$

$$mer\text{-}[RhX_3(ZMePh_2)_3] + H_3PO_2 \longrightarrow \beta\text{-}[RhHX_2(ZMePh_2)_3] \quad (204)$$

$$Z = P, X = Cl, Br; Z = As, X = Cl, Br, I$$

The tertiary arsine complexes were first prepared by Dwyer and Nyholm,[5] but, before the advent of NMR spectrometry, were erroneously considered to be rhodium(II) complexes.[989] Further investigations have shown that in preparations starting from rhodium trihalides using a higher tertiary arsine:rhodium ratio and lower reaction temperatures favor the formation of the β isomer (equations 205 and 206).[986]

$$RhX_3 \cdot 3H_2O + 2AsEtPh_2 \xrightarrow[78°C]{EtOH/H_2O} \alpha\text{-}[RhHX_2(AsEtPh_2)_3] \quad (205)$$

$$RhX_3 \cdot 3H_2O + 3AsEtPh_2 \xrightarrow{0°C} \beta\text{-}[RhHX_2(AsEtPh_2)_3] \quad (206)$$

Few studies have been made of the reactions of this class of complex. The action of bases upon the complexes brings about reductive elimination of hydrogen halide (equation 207).[973] However, if this reaction is carried out in dichloromethane it appears that the hydrido ligand reduces the solvent since, although the base hydrochloride is formed, a rhodium(III) complex results (equation 208).[953] The action of bromine[989] or SO_2[953] also produces hydrogen halide (equations 209 and 210). (The reaction with concentrated nitric acid has already been mentioned in Section 48.6.3.3.ii above.[953])

$$\alpha\text{-}[RhHCl_2(PEtPh_2)_3] \xrightarrow{PhNH_2} [RhCl(PEtPh_2)_3] \quad (207)$$

$$\alpha\text{-}[RhHCl(PEtPh_2)_3] + base \xrightarrow{CH_2Cl_2} [RhCl_3(PEtPh_2)_3] \quad (208)$$

$$[RhHBr(AsMePh_2)_3] + Br_2 \xrightarrow{CH_2Cl_2} [RhBr_3(AsMePh_2)_3] + HBr \quad (209)$$

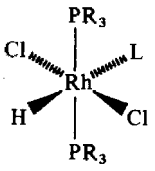
$$[RhHX_2(ZMePh_2)_3] + SO_2 \xrightarrow[78°C]{EtOH} [RhX(ZMePh_2)_3(SO_2)] + HX \quad (210)$$

$$X = Cl, Br; Z = P, As$$

It has been shown that strongly coordinating ligands will displace one tertiary phosphine ligand from β complexes (equation 211). The products have been assigned structure **(85)**.[992]

$$\beta\text{-}[RhHCl_2(PBu^tPr_2)_3] + L \longrightarrow \beta\text{-}[RhHCl_2(PBu^tPr_2)_2L] + PBu^tPr_2 \quad (211)$$

$$L = MeCN, MeNC, py, P(OMe)_3$$



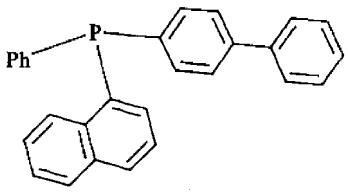
(85)

48.6.3.5 [RhX_3L_3] complexes

This is a populous class of complex: most known tertiary phosphines seem to have been utilized in preparing at least one complex of this type. Meridional isomers are normally the rule, but small tertiary phosphines are also capable of forming facial isomers.

As might be expected, the structures of both isomers are essentially octahedral. However, even in the *mer* complexes, where steric repulsions between tertiary phosphines are minimized, there are slight deviations from orthogonality. Further, in the *mer* complexes the length of the Rh—P bond *trans* to X is less than the length of the mutually *trans* Rh—P bonds. Both these features are apparent from the X-ray crystal structure of *mer*-[$RhCl_3(PEt_3)_3$].[991]

The crystal structure of *mer*-[$RhCl_3(PBu^n_3)_2\{(POMe)_3\}$] has also been determined, and is in accordance with that predicted from its ^{31}P NMR spectrum.[992] The facial and meridional complexes that have been characterized are listed in Tables 71 and 72 respectively.



(86)

Both far IR and ^{31}P NMR spectrometry have been widely used to determine the configuration of the complexes in solution. Generally *mer* complexes have three bands arising from rhodium—halogen stretching, whilst the *fac* isomers only exhibit two such bands in their IR spectra. Such features are also apparent in the solid state Raman spectra of the complexes.[998] Early assignments of IR[94,999] or Raman[998] bands in the 300 cm^{-1} region to ν_{Rh-Cl} are probably erroneous, since bands in this region are found in the spectra of the analogous tribromo or iridium complexes. Goggin and Knight assign these bands in the spectra of [$MX_3(PMe_3)_3$] complexes as PC_3 asymmetric deformation modes.[1000]

The ^{31}P NMR spectra have been recorded with increasing precision with the passing years.[918,993,1001,1002] The work of Shaw's group is regarded as being more accurate since random noise decoupling was employed to enable certain Rh–P couplings in the meridional complexes to be determined.[1002] The spectra of certain trimethylphosphine complexes have also been studied in some detail (see Table 73).[1003,1004]

Both ^1H NMR[1005] and EPR[1006] spectrometry have been used to show that [$RhCl_3(PEt_2Ph)_3$] adopts the meridional configuration. The X-ray photoelectron spectrum of *fac*-[$RhCl_3(PMe_2Ph)_3$]

Table 71 Physical Properties of *fac*-[$RhX_3(PR_3)_3$] Complexes

Complex	*Color*	*M.p.* (°C)	*Ref.*
[$RhCl_3(PHPh_2)_3$]	Yellow	150–70	112
[$RhCl_3(PMe_3)_3$]	Yellow-orange	160–70	114
[$RhCl_3(PEt_3)_3$]	Yellow	160–70	114
[$RhCl_3(PMe_2Ph)_3$]	Yellow	210–15	114
[$RhCl_3(PEt_2Ph)_3$]	Yellow	174–78	993
[$RhCl_3(PPhPr^i_2)_3$]	Yellow	163–78	993
[$RhCl_3(PBu_2Ph)_3$]	Yellow	153–56	993
[$RhCl_3\{P(CH_2OH)_3\}_3$]	Yellow	155–65[a]	994

[a] With decomposition.

Table 72 Physical Properties of *mer*-$[RhX_3(PR_3)_3]$ Complexes

Complex	*Color*	*M.p.* (°C)	*Ref.*
$[RhCl_3(PHPh_2)_3]$	Yellow-brown	150–70[a]	112
$[RhCl_3(PMe_3)_3]$	Orange	230–45	114
$[RhCl_3(PEt_3)_3]$	Orange-red	114–17	972
$[RhCl_3(PPr_3)_3]$	Orange	179–86[a]	972
$[RhBr_3(PPr_3)_3]$	Red	160–63	972
$[RhCl_3(PPr^i_3)_3]$	Dark orange	40–50	114
$[RhCl_3(PBu_3)_3]$	Orange-red	139–42	972
$[RhCl_3(PBu^t_3)_3]$	Orange	30–35	114
$[RhCl_3(PCy_3)_3]$	Red	200–10	114
$[RhCl_3(PPh_3)_3]$	Ocher	—	995
$[RhCl_3\{P(CH_2Ph)_3\}_3]$	Yellow	150–61	114
$[RhCl_3\{P(C_8H_{15})_3\}_3]$	Dark yellow	−20	114
$[RhCl_3(PMe_2Ph)_3]$	Orange	218–24	972
$[RhBr_3(PMe_2Ph)_3]$	Dark orange	195–201	918
$[RhI_3(PMe_2Ph)_3]$	Dark maroon	179–82	918
$[Rh(NCO)_3(PMe_2Ph)_3]$	Pale yellow	159–61	918
$[Rh(SCN)_3(PMe_2Ph)_3]$	Bright yellow	196–202	918
$[Rh(N_3)_3(PMe_2Ph)_3]$	Bright yellow	206–14	918
$[RhCl_2Br(PMe_2Ph)_3]$	Orange	206–24	918
$[RhCl_2I(PMe_2Ph)_3]$	Dark brown	176–79	918
$[RhCl_2(NCO)(PMe_2Ph)_3]$	Yellow	158–65	918
$[RhCl_2(NCS)(PMe_2Ph)_3]$	Orange	134–38	918
$[RhCl_2(SCN)(PMe_2Ph)_3]$	Yellow	85–89	918
$[RhCl_2(N_3)(PMe_2Ph)_3]$	Pale orange	150–55[a]	918
$[RhCl_2(NO_2)(PMe_2Ph)_3]$	Pale orange	138[a]	918
$[RhCl_3(PEt_2Ph)_3]$	Orange	183–96	972
$[RhCl_3(PPr_2Ph)_3]$	Yellow	168–73	993
$[RhCl_3(PBu_2Ph)_3]$	Yellow	153–56	993
$[RhCl_3(PMePh_2)_3]$	Orange	170–73	918
$[RhCl_3(PEtPh_2)_3]$	Orange	140–45	918
$[RhCl_3\{P(1\text{-}C_{10}H_7)Me_2\}_3]$	Orange	190–95	136
$[RhCl_3\{(-)\text{-}(PMePhPr)\}_3]$	[b]	212–16	996
$[RhCl_3\{P(CH_2OCOMe)_3\}_3]$	Orange	148–53	994
$[RhCl_3\{PMe(CH_2OCOMe)_2\}_3]$	Orange	127–29	994
$[RhCl_3\{PEt(CH_2OCOMe)_2\}_3]$	Orange	109–11	994
$[RhCl_3\{PPh(CH_2OCOMe)_2\}_3]$	Orange	165–71	994
$[RhCl_3(\mathbf{86})_3]$	—	—	997
$[RhCl_3(PEt_3)_2(PhN_2H_3)]$	Orange	151–55[a]	972
$[RhCl_3(PPr_3)_2py]$	Orange	142–46	972
$[RhCl_3(PBu_3)_2(PhN_2H_3)]$	Bright orange	142–46[a]	972

[a] With decomposition. [b] $[\alpha]_D^{25}$ −56°.

Table 73 NMR Spectral Data for $[RhX_3(PR_3)_3]$ Complexes

Complex	*δP(1,3)* (p.p.m.)	*δP(2)* (p.p.m.)	*J[Rh–P(2,3)]* (Hz)	*J[Rh–P(2)]* (Hz)	*J(P–P)* (Hz)	*Frequency* (MHz)	*Ref.*
$[RhCl_3(PMe_3)_3]$	+8.6	−7.6	82	103	22	24.3[a]	1001
$[RhCl_3(PEt_3)_3]$	−4.3	−20.0	84	109	—	24.3[a]	1001
	−4.3	−20.0	83.8	112	24.2	36.43[b]	1002
$[RhCl_3(PPr_3)_3]$	+1.1	−14.2	84	115	19	24.3[a]	1001
	+0.6	−14.9	83.8	111.9	24.2	36.43[b]	1002
$[RhCl_3(PBu_3)_3]$	+0.7	−14.7	84	114	21	24.3[a]	1001
	+0.3	−15.1	83.6	112.5	24.0	36.43[b]	1002
$[RhCl_3(PMe_2Ph)_3]$	+5.5	−4.4	86	112	20.4	24.3[a]	1001
	+5.0	−3.7	84.6	112.3	24.7	36.43[b]	1002
$[RhCl_3(PEt_2Ph)_3]$	−3.9	−17.5	84	108	13	24.3[a]	1001
	−3.9	−17.1	84.0	111.1	23.2	36.43[b]	1002
$[RhCl_3(PPhPr_2)_3]$	+0.8	−12.7	85	115	20	24.3[a]	1001
	+0.4	−12.7	84.2	110.9	23.1	36.43[b]	1002
$[RhCl_3(PBu_2Ph)_3]$	+0.7	−12.7	84	113	19	24.3[a]	1001
	+0.2	−12.8	84.1	111.0	22.9	36.43[b]	1002
$[RhCl_3(PMePh_2)_3]$	+6.8	+3.4	—	—	—	24.3[a]	1001
	+4.7	+2.8	86.0	114.5	24.5	36.43[b]	1002
$[RhCl_3(PEtPh_2)_3]$	−9.4	−20.0	85	116	14	24.3[a]	1001
	−10.1	−19.9	84.8	114	22.8	36.43[b]	1002
$[RhCl_3(PPh_2Pr)_3]$	−6.8	−16.0	85	117	14	24.3[a]	1001
$[RhCl_3(PBuPh_2)_3]$	−7.4	−15.9	85	120	18	24.3[a]	1001

[a] Relative to 85% H_3PO_4. [b] In CH_2Cl_2 containing *ca.* 10% C_6F_6.

has been obtained and compared with those of similar complexes of second and third transition series elements.[1007] This technique has also been used to show that solid $[RhCl(PPh_3)_3]$ undergoes oxidative addition of hydrogen or oxygen to form $[RhClY_2(PPh_3)_3]$ complexes (Y = H, O).[982]

Perusal of Tables 71 and 72 shows the wide range of complexes that can be obtained. The essential problem is in selecting the correct preparative conditions for the isolation of the required complex in pure form. Many alternative products can be formed from the apparently simple reaction between hydrated rhodium trichloride and tertiary phosphines, some of which are shown in Figure 5. Accordingly many preparative methods have been devised for complexes of this stoichiometry, unfortunately none seem of very wide applicability, and many are specific for only one complex. Those intending their preparation should consult the methods given in the references of Tables 71 and 72, and should be cautioned that slight changes in the preparative methods employed invariably lead to other complexes.

The facial isomers are obtained only from small tertiary phosphines, usually in poor yield. They are both less soluble and less stable than the meridional isomers.

Comparatively little effort has been expended in investigating the reactions of the complexes, as opposed to the application of physical methods in determining their structures. However, in the meridional complexes the halo ligand *trans* to the tertiary phosphine is more labile than the other two and its replacement by other anionic ligands allows the preparation of $[RhX_2X'(PR_3)_3]$ complexes from the trihalo complexes obtained from rhodium(III) halides (equation 212). Prolonged reaction with salts of other anions results in all three halo ligands being replaced (equation 213).[918]

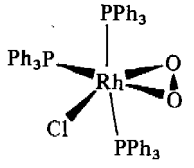
$$mer\text{-}[RhCl_3(PMe_2Ph)_3] + NaS_2Y \xrightarrow[25°C]{MeOH} mer\text{-}[RhCl_2(S_2Y)(PMe_2Ph)_3] + NaCl \quad (212)$$

$$Y = CNMe_2,\ PMe_2$$[915]

$$mer\text{-}[RhCl_3(ZMe_2Ph)_3] + M^IX \longrightarrow [RhX_3(ZMe_2Ph)_3] \quad (213)$$

$$X = Br,\ I,\ NCO,\ SCN,\ N_3$$

It has been shown that the dioxygen complex $[RhClO_2(PPh_3)_3]$, which X-ray crystallography[1008] reveals to have the structure (**87**), decomposes to dimeric $[RhClO_2(PPh_3)_2]_2$ and $OPPh_3$.[1009]



(87)

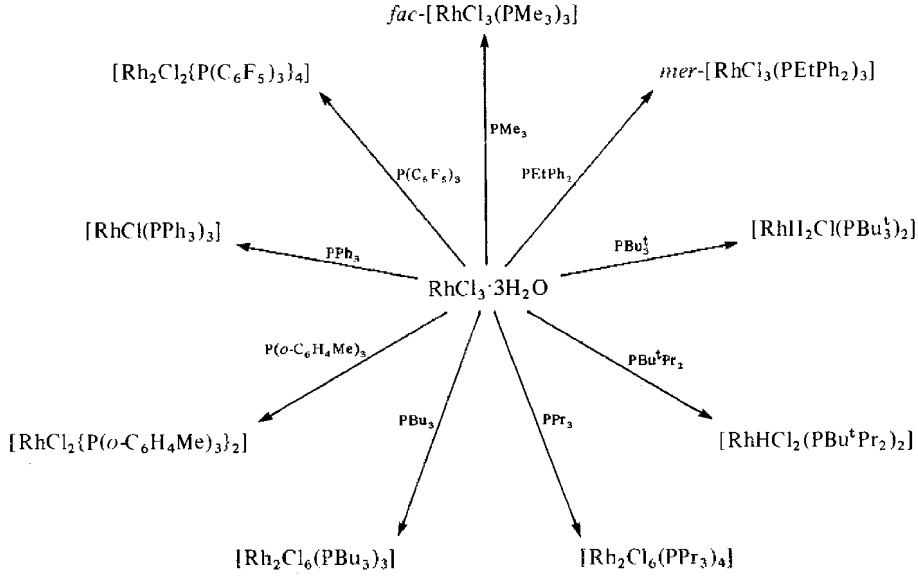


Figure 5 Reactions of $RhCl_3 \cdot 3H_2O$ with tertiary phosphines

The replacement of the tertiary phosphine ligands has seldom been attempted, and the $[RhX_3(PR_3)_2L]$ complexes have usually been prepared by addition of a neutral ligand to the coordinatively unsaturated $[RhX_3(PR_3)_2]$ complexes (see equations 188 and 211). Nevertheless, ditertiary phosphines replace the tertiary phosphine ligands in these complexes (equation 214).[229]

$$mer\text{-}[RhBr_3(PBu_3)_3] + Me_2PCH_2CH_2PMe_2 \xrightarrow[50°C]{C_6H_{14}} cis\text{-}[RhBr_2(Me_2PCH_2CH_2PMe_2)_2]Br + 3PBu_3 \quad (214)$$

The tertiary arsine complexes (Table 74) are much less numerous than those containing tertiary phosphines. They are usually prepared by the interaction of tertiary arsines with rhodium trihalides. The poorer reducing properties of tertiary arsines make it much less likely that rhodium(I) complexes will be formed in this reaction.

The halo ligands of these complexes can be replaced by other anionic ligands.[918] One of the mutually *trans* tertiary arsine ligands can be replaced by other monodentate ligands such as pyridine (equation 215). Two ligands can be replaced by bidentate nitrogen ligands (equation 216);[1014] these latter products are discussed below in Section 48.6.3.6.

$$mer\text{-}[RhX_3(AsMe_2Ph)_3] + py \longrightarrow mer\text{-}[RhX_3(AsMe_2Ph)_2py] \quad (215)$$

$$[RhX_3(AsMe_2Ph)_3] + bipy \longrightarrow [RhX_2(AsMe_2Ph)_2(bipy)]X + AsMe_2Ph \quad (216)$$

One interesting reaction undergone by the tri(styryl)arsine complexes is the bromination of the C=C bond by bromine in CCl_4 (equation 217).[1013] Similar behavior[970] is exhibited by the few tertiary stibine complexes (Table 75) that have been isolated. Few physical properties of these complexes have been investigated, but the ^{121}Sb Mössbauer parameters for both rhodium(III) complexes and the free ligands have been determined.[1016]

$$[RhBr_3\{AsMe_2(C_6H_4CH{=}CH_2)\}_3] + 3Br_2 \xrightarrow[25°C]{CCl_4} [RhBr_3\{AsMe_2(C_6H_4CHBrCH_2Br)\}_3] \quad (217)$$

Table 74 Physical Properties of $[RhX_3(AsR_3)_3]$ Complexes

Complex	*Color*	*M.p.* (°C)	*Ref.*
fac-Isomers			
$[RhCl_3(AsEt_3)_3]$	Yellow	166–73	972
$[RhCl_3(AsMe_2Ph)_3]$	Bright yellow	198–206[a]	972
mer-Isomers			
$[RhCl_3(AsEt_3)_3]$	Red	111–13	972
$[RhCl_3(AsBu_3)_3]$	Red	110–22[a]	972
$[RhCl_3(AsMe_2Ph)_3]$	Orange-red	190–94[a]	972
$[RhBr_3(AsMe_2Ph)_3]$	Red	192–200[a]	918
$[RhCl_2Br(AsMe_2Ph)_3]$	Orange	191–95	918
$[RhCl_2I(AsMe_2Ph)_3]$	Blood red	167–73	918
$[RhCl_3(AsMePh_2)_3]$	—	191–95	1010
$[RhBr_3(AsMePh_2)_3]$	—	216–19	1010
$[RhCl_3(AsPh_2Pr)_3]$	Orange	209–12	1011
$[RhBr_3(AsPh_2Pr)_3]$	Orange-red	188–90	1011
$[RhCl_3\{AsMe_2(1\text{-}C_{10}H_7)\}_3]$	Orange	209	1012
$[RhBr_3\{AsMe_2(1\text{-}C_{10}H_7)\}_3]$	Orange-red	214	1012
$[RhBr_3\{AsMe_2(o\text{-}C_6H_4CH{=}CH_2)\}_3]$	Orange	135–40	1013
$[RhBr_3\{AsMe_2(m\text{-}C_6H_4CH{=}CH_2)\}_3]$	—	—	1013
$[RhBr_3\{AsMe_2(p\text{-}C_6H_4CH{=}CH_2)\}_3]$	Orange	172[a]	1013
$[RhBr_3\{AsMe_2(o\text{-}C_6H_4CHBrCH_2Br)\}_3]$	Orange	103–05[a]	1013
$[RhBr_3\{AsMe_2(m\text{-}C_6H_4CHBrCH_2Br)\}_3]$	Orange	105–10[a]	1013
$[RhBr_3\{AsMe_2(p\text{-}C_6H_4CHBrCH_2Br)\}_3]$	Orange	110–25[a]	1013
$[RhCl_3(AsEtPh_2)_2py]$	Yellow	238–39	1014
$[RhBr_3(AsEtPh_2)_2py]$	Yellow	255–56	1014
$[RhCl_3(AsPrPh_2)_2py]$	Yellow	247–49	1014
$[RhBr_3(AsPrPh_2)_2py]$	Yellow	252–54	1014
$[RhCl_3(AsBuPh_2)_2py]$	Yellow	196–97	1014
$[RhBr_3(AsBuPh_2)_2py]$	Yellow	184–86	1014

[a] With decomposition.

Table 75 Physical Properties of $[RhX_3(SbR_3)_3]$ Complexes

Complex	*Color*	*Ref.*
$[RhCl_3(SbPh_3)_3]$	Orange	1015
$[RhCl_2Br(SbPh_3)_3]$	Orange-brown	1015
$[RhCl_2I(SbPh_3)_3]$	Brown	1015
$[RhCl_2(NCS)(SbPh_3)_3]$	Orange	1015
$[RhCl_2(SnCl_3)(SbPh_3)_3]$	Orange	1015
$[RhCl_3\{Sb(o\text{-}C_6H_4OMe)_3\}_3]$	Dull orange	971
$[RhBr_3\{Sb(o\text{-}C_6H_4OMe)_3\}_3]$[a]	Red-orange	970
$[RhCl_3\{Sb(o\text{-}C_6H_4OMe)Me_2\}_3]$	Yellow	971
$[RhCl_3\{Sb(o\text{-}C_6H_4OMe)Ph_2\}_3]$	Orange-red	971
$[RhCl_3\{Sb(o\text{-}C_6H_4OMe)_2Ph\}_3]$	Dull orange	971

[a] M.p. = 158°C.

48.6.3.6 $[RhX_2L_4]X$ complexes

The most numerous complexes of this general type are those containing two bidentate neutral ligands, which are discussed in Section 48.6.3.7 below. These can easily be obtained by the oxidative addition of two anionic ligands to the numerous $[Rh(LL)_2]X$ complexes. There are, however, a considerable number of complexes which contain monodentate neutral ligands. These include the catalytically important $[RhH_2(PR_3)_2(solv)_2]X$ complexes,[1017–1019] and a number of dioxygen complexes.[1020]

The cationic dihydrido complexes (Table 76) were first discovered by Schrock and Osborn during their search for alternative homogeneous hydrogenation catalysts to the ubiquitous $[RhCl(PPh_3)_3]$.[1017–1019] They found that if the cleavage of $[RhCl(diene)]_2$ complexes by PPh_3 was carried out in polar solvents in the presence of a non-coordinating anion, $[Rh(diene)(PPh_3)_2]X$ complexes were formed (equation 218). These complexes in turn underwent oxidative addition of dihydrogen to form rhodium(III) complexes. During the latter reaction the dienes were reduced to alkanes and their place in the coordination sphere occupied by solvent molecules (equation 219). The stability of the dihydrido complex obtained depends markedly upon the tertiary phosphine present. Many complexes readily lose H_2 and revert to rhodium(I) complexes.[1025] Since the dihydrido complexes catalyze the hydrogenation of alkenes by the dihydride route, and the rhodium(I) complexes by the alkene route, their stability and rates of formation are of considerable mechanistic importance.[1026] It has also been shown that their stability is affected by the alkene present.[1027]

$$[RhCl(diene)]_2 + 4PPh_3 \xrightarrow{X^-} [Rh(diene)(PPh_3)_2]X \quad (218)$$

$$[Rh(diene)(PPh_3)_2]X + 3H_2 \xrightarrow{\text{solvent}} [RhH_2(PPh_3)_2(solvent)_2]X + \text{alkane} \quad (219)$$

Unlike the ligands in other normally kinetically inert rhodium(III) complexes, these solvent ligands undergo rapid exchange in the dihydrido complexes with rates of $10^4 s^{-1}$ having been observed. The unusual rapidity of the exchange is due to the geometry of the cation in which the solvent molecules are *trans* to the hydrido ligands. However, the rate of exchange also depends upon the tertiary phosphine ligand present.[1024]

The solvent ligands can be displaced by bidentate ligands, such as bipy,[1019] to form the complex

Table 76 Physical Properties of $[RhH_2L_4]X$ Complexes

Complex	*Color*	τ_{Rh-H} (p.p.m.)	ν_{Rh-H} (cm^{-1})	*Ref.*
cis-$[RhH_2(PBu_3)_4][BPh_4]$[a]	White	21.4	2020	1023
$[RhH_2(PPh_3)_2(MeCN)_2][ClO_4]$	—	27.07	2150, 2100	1019
$[RhH_2(PPh_3)_2(EtOH)_2][ClO_4]$	—	32.31	2190, 2140	1019
$[RhH_2(PPh_3)_2(Me_2CO)_2][ClO_4]$	—	31.69	2190, 2135[c]	1019
$[RhH_2(PPh_3)_2(bipy)][ClO_4]$	White	25.7	2120, 2050	1028
$[RhH_2(PMePh_2)_2(bipy)][PF_6]$	Pale yellow	—	—	1019
$[RhH_2(PCyPh_2)_2(MeCN)_2][PF_6]$	—	27.91	2120, 2080	1019
$[RhH_2(PCyPh_2)_2(Me_2CO)_2][PF_6]$	White	—	2140, 2115	1019
$[RhH_2(PCy_3)_2(MeCN)_2][PF_6]$	—	28.9	—	1024
cis-$[RhH_2\{P(OMe)_3\}_4][BPh_4]$[b]	White	—	1976	1023

[a] M.p. = 79–81°C. [b] M.p. = 80–165°C. [c] ν_{Rh-D} = 1585, 1544 cm^{-1}.

$[RhH_2(PPh_3)_2(bipy)][ClO_4]$, which had previously been prepared by the borohydride reduction of $[RhRX(bipy)_2][ClO_4]$ complexes in the presence of PPh_3 (equations 220 and 221). Its IR spectrum indicates that the hydrido ligands are *cis*.[1028] Other complexes of this type have been prepared by the oxidative addition of dihydrogen to $[RhL_4]X$ complexes. The hydrido ligands are also *cis* in these complexes. The dihydrido cation $[RhH_2(PPr^i_3)_2(H_2O)_2]^+$ is less well characterized but it has been used in the photochemical production of hydrogen (equation 222).[1029]

$$[RhH_2(PR_3)_2(Me_2CO)_2]X + bipy \longrightarrow [RhH_2(PPh_3)_2(bipy)]X \quad (220)$$

$$R_3 = Ph_3, X = ClO_4; R_3 = Me_2Ph, X = PF_6$$

$$[RhRX(bipy)_2][ClO_4] + 2PPh_3 \xrightarrow[NaBH_4]{MeOH/PPh_3} [RhH_2(PPh_3)_2(bipy)][ClO_4] \quad (221)$$

$$R = Me, Et, Ph, X = I; R = PhCH_2, X = Cl, Br$$

$$[RhH_2(PPr^i_3)_2(H_2O)_2]^+ + H^+ \xrightarrow{h\nu} [RhH(PPr^i_3)_2(H_2O)_3]^{2+} + H_2 \quad (222)$$

There are two monohydrido complexes which have been prepared by the oxidative addition of hydrogen halides to $[Rh\{P(OMe)_3\}_5][BPh_4]$ (equation 223). Two other monohydrido complexes having hydrogen-bonded anions have been prepared by simultaneous substitution of and oxidative addition to dinuclear rhodium(I) complexes (equation 224). The anions give resonances at very low fields in the ^1H NMR spectra of the complexes.[1030] The physical properties of the monohydrido complexes are listed in Table 77.

$$[Rh\{P(OMe)_3\}_5][BPh_4] + HX \xrightarrow[MeOH]{NaBPh_4} [RhHX\{P(OMe)_3\}_4][BPh_4] + P(OMe)_3 \quad (223)$$

$$X = Br, I^{1023}$$

$$[RhClL_2]_2 + PPh_2(OMe) \xrightarrow[CH_2Cl_2]{HX} [RhHCl\{PPh_2(OMe)\}_4](X_2H) \quad (224)$$

$$X = Cl, CF_3CO_2$$

Yet other monohydrido complexes have been prepared by allowing α-$[RhHX_2(PEtPh_2)_3]$ to react with ethanolic perchloric acid and a bidentate ligand (equation 225).[980] Under similar conditions the β isomer forms dihalo complexes but these are better obtained from the trihalo complexes (equation 226).[1014] The coordinatively saturated complex $[Rh\{P(OMe)_3\}_5][BPh_4]$ also forms dihalo complexes upon longer reaction with hydrogen halides (equation 227; *cf*. equation 223 above). The *cis* isomer is also the major product when bromine is allowed to react with the rhodium(I) complex (equation 228). The two isomers can be separated by fractional crystallization, the minor isomer being the least soluble.[1023]

$$\alpha\text{-}[RhHX_2(ZEtPh_2)_3] + LL \xrightarrow[EtOH]{HClO_4} [RhHX(ZEtPh_2)_2(LL)][ClO_4] \quad (225)$$

Table 77 Physical Properties of $[RhHXL_4]X'$ Complexes

Complex	*Color*	*M.p.* (°C)	τ_{Rh-H} (p.p.m.)	ν_{Rh-H} (cm^{-1})	*Ref.*
$[RhHCl(PEtPh_2)_2(bipy)][ClO_4]$	Yellow	184–86	23.80	2070[a]	1014
$[RhHCl(PEtPh_2)_2(phen)][ClO_4]$	Yellow	179–82	23.33	2080	1014
$[RhHBr(PEtPh_2)_2(bipy)][ClO_4]$	Yellow	179–82	28.81	2073	1014
$[RhHBr(PEtPh_2)_2(phen)][ClO_4]$	Yellow	168–70	23.63	2071	1014
$[RhHCl\{PPh_2(OMe)\}_4][(CF_3CO_2)_2H]$	Pale yellow	110	—	2100	1030
$[RhHCl\{PPh_2(OMe)\}_4][PF_6]$	White	110	—	2100	1030
$[RhHCl\{PPh_2(OMe)\}_4][Cl_2H]$	—	100	—	2100	1030
trans-$[RhHBr\{P(OMe)_3\}_4][BPh_4]$	White	129–30	—	2072	1023
trans-$[RhHI\{P(OMe)_3\}_4][BPh_4]$	White	133–34	—	2051[a]	1023
$[RhHCl(AsMePh_2)_2(bipy)][ClO_4]$	—	212–15	—	2050	1014
$[RhHCl(AsMePh_2)_2(phen)][ClO_4]$	—	165–68	—	2060	1014
$[RhHBr(AsMePh_2)_2(bipy)][ClO_4]$	—	250–52	—	2053	1014
$[RhHCl(AsEtPh_2)_2(bipy)][ClO_4]$	—	170–74	—	2045	1014
$[RhHBr(AsEtPh_2)_2(bipy)][ClO_4]$	—	178–80	—	2056	1014
$[RhHCl(AsPh_2Pr)_2(bipy)][ClO_4]$	Yellow	202–05	—	—	1014
$[RhHCl(AsPh_2Pr)_2(phen)][ClO_4]$	Yellow	160–63	—	—	1014
$[RhHBr(AsPh_2Pr)_2(bipy)][ClO_4]$	Yellow	186–89	—	2053	1014
$[RhHBr(AsPh_2Pr)_2(phen)][ClO_4]$	Yellow	235–37	—		1014

[a] Nujol mull.

Table 78 Physical Properties of $[RhX_2L_4]X'$ Complexes

Complex	*M.p.* (°C)	*Ref.*
$[RhCl_2(PEtPh_2)_2(bipy)][ClO_4]$	172–75	1014
$[RhCl_2(PEtPh_2)_2(phen)][ClO_4]$	219–21	1014
$[RhCl_2(PMe_2Ph)_3py][PF_6]$	180–82	1031
$[RhCl_2(PMe_2Ph)_3(NCC_6F_5)][PF_6]$[a]	159–61	1031
$[RhCl_2(PMe_2Ph)_3(p\text{-}NCC_6F_4CN)_{0.5}][PF_6]$	172–74	1031
$[RhCl_2(PMe_2Ph)_3(OH_2)][PF_6]$	120–21	1031
$[RhCl_2(PMe_2Ph)_4][PF_6]$	150–51	1031
cis-$[Rh(Br_2\{P(OMe)_3\}_4][BPh_4]$[b]	147–50	1023
trans-$[RhBr_2\{P(OMe)_3\}_4][BPh_4]$[c]	151–53	1023
cis-$[RhI_2\{P(OMe)_3\}_4][BPh_4]$[b]	154–56	1023
$[RhCl_2(AsMePh_2)_2(bipy)][ClO_4]$	269–73	1014
$[RhCl_2(AsMePh_2)_2(phen)][ClO_4]$	169–72	1014
$[RhBr_2(AsMePh_2)_2(bipy)][ClO_4]$	263–65	1014
$[RhBr_2(AsMePh_2)_2(phen)][ClO_4]$	174–76	1014
$[RhCl_2(AsEtPh_2)_2(bipy)][ClO_4]$	223–26	1014
$[RhCl_2(AsEtPh_2)_2(phen)][ClO_4]$	136–38	1014
$[RhCl_2(AsEtPh_2)_2(bipy)][ClO_4]\cdot 2H_2O$	> 280	1014
$[RhCl_2(AsEtPh_2)_2(phen)][ClO_4]\cdot 2H_2O$	136–38	1014
$[RhBr_2(AsEtPh_2)_2(bipy)][ClO_4]$	231–33	1014
$[RhBr_2(AsEtPh_2)_2(phen)][ClO_4]$	218–21	1014
$[RhCl_2(AsEtPh_2)_2(bipy)][BPh_4]$	212–14	1014
$[RhCl_2(AsEtPh_2)_2(phen)][BPh_4]$	222–25	1014
$[RhCl_2(AsPh_2Pr)_2(bipy)][ClO_4]$	252–54	1014
$[RhCl_2(AsPh_2Pr)_2(phen)][ClO_4]$	238–40	1014
$[RhBr_2(AsPh_2Pr)_2(bipy)][ClO_4]$	200–05	1014
$[RhBr_2(AsPh_2Pr)_2(phen)][ClO_4]$	255–57	1014
$[RhBr_2(AsBuPh_2)_2(bipy)][ClO_4]$	255–57	1014
$[RhBr_2(AsBuPh_2)_2(phen)][ClO_4]$	212–14	1014

[a] Orange. [b] White. [c] Yellow.

$$\beta\text{-}[RhHX(ZR_3)_3] + LL \xrightarrow[EtOH]{HClO_4} [RhX_2(ZR_3)_2(LL)][ClO_4] \quad (226)$$

$$[Rh\{P(OMe)_3\}_5][BPh_4] + HX \longrightarrow cis\text{-}[RhX_2\{P(OMe)_3\}_4][BPh_4] + P(OMe)_3 \quad (227)$$

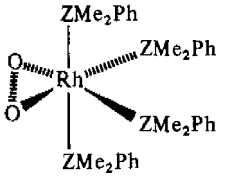
$$[Rh\{P(OMe)_3\}_5][BPh_4] + Br_2 \longrightarrow [RhBr_2\{P(OMe)_3\}_4][BPh_4] + P(OMe)_3 \quad (228)$$

The lability of the halo ligand *trans* to the tertiary phosphine in *mer*-$[RhX_3(PR_3)_3]$ complexes has been exploited in the preparation of substituted cationic complexes (equation 229).[1031]

$$[RhCl_3(PMe_2Ph)_3] + L + AgPF_6 \xrightarrow[Me_2CO]{MeOH\ or} [RhCl_2(PMe_2Ph)_3L][PF_6] \quad (229)$$

$$L = py,\ PMe_2Ph,\ H_2O,\ C_6F_5CN,\ 0.5\ p\text{-}NCC_6F_4CN$$

The dioxygen complexes $[RhO_2(ZMe_2Ph)_4]X$ (Z = P, X = BPh_4; Z = As, X = ClO_4) contain peroxo ligands. In the IR spectra of these complexes ν_{O-O} is about 854 cm^{-1}.[1031] They have been shown to have structure (**88**) by X-ray crystallography.[1032,1033]

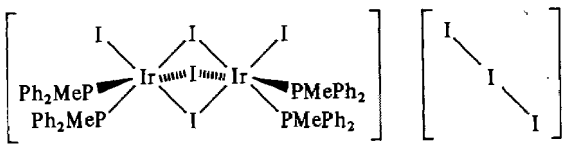


(88)

There are many complexes containing one bidentate and two monodentate neutral ligands. A preliminary crystal study has been made on one of them.[1034] It may finally be noted that the oxidative addition of sundry reagents to rhodium(I) complexes is not an infallible preparative method for complexes of this type. Nitronium tetrafluoroborate, for example, gives only a five-coordinate cation (equation 230).[1035]

$$[RhCl(PPh_3)_3] + [NO_2][BF_4] \xrightarrow{C_6H_6} [RhCl(NO_2)(PPh_3)_3][BF_4] \quad (230)$$

The addition of bromine or iodine to $[RhL_4]^+$ cations gives products whose solutions are poorly conducting. The corresponding iridium complex has been shown to be (**89**). The formation of polyhalogeno anions would explain why no corresponding complexes can be prepared by the oxidative addition of Cl_2.[1036]

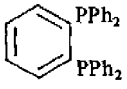


(**89**)

48.6.3.7 [RhX₂(LL)₂]X′ complexes

Complexes of this type can be prepared in three principal ways. The most obvious is by allowing hydrated rhodium trichloride to react with the bidentate ligand (equation 231).[229] Unfortunately this method gives rise to both *cis* and *trans* products. However, the reactions between rhodium(III) halides and 1,2-bis(diphenylphosphino)benzene (**90**) yield the *trans* product in the case of the chloride, whilst both the bromide and iodide form the *cis* product.[1037]

$$RhCl_3 \cdot 3H_2O + 2Me_2PCH_2CH_2PMe_2 \longrightarrow [RhCl_2(Me_2PCH_2CH_2PMe_2)_2]Cl \quad (231)$$



(**90**)

Pure samples of the 1,2-bis(dimethylphosphino)ethane complexes can be obtained by using the bidentate ligand to displace monodentate ligands from *mer*-rhodium(III) complexes.[228] Again the larger halo ligands give rise to *cis* products (equations 232 and 233).

$$mer\text{-}[RhCl_3(PBu_3)_3] + 2Me_2PCH_2CH_2PMe_2 \longrightarrow trans\text{-}[RhCl_2(Me_2PCH_2CH_2PMe_2)_2]Cl \quad (232)$$

$$mer\text{-}[RhBr_3(PBu_3)_3] + 2Me_2PCH_2CH_2PMe_2 \longrightarrow cis\text{-}[RhBr_2(Me_2PCH_2CH_2PMe_2)_2]Br \quad (233)$$

The third preparative method is to oxidize rhodium(I) complexes of the type $[Rh(LL)_2]X'$ (equation 234). Thus, oxidation gives the other geometric isomer to that provided by ligand displacement (equations 232 and 233).

$$[Rh(Me_2PCH_2CH_2PMe_2)_2]Cl \xrightarrow[CCl_4]{Cl_2} cis\text{-}[RhCl_2(Me_2PCH_2CH_2PMe_2)_2]Cl \quad (234)$$

However, although either chlorine or bromine can displace carbon monoxide from the five-coordinate rhodium(I) cation $[Rh(CO)\{(Me_2P)_2C_2H_4\}_2]^+$, chlorine forms the *cis* isomer, whilst bromine forms the *trans* isomer (equations 235 and 236). Similar complexes can be prepared by metathetical reactions involving the ionic halide (equation 237).[229]

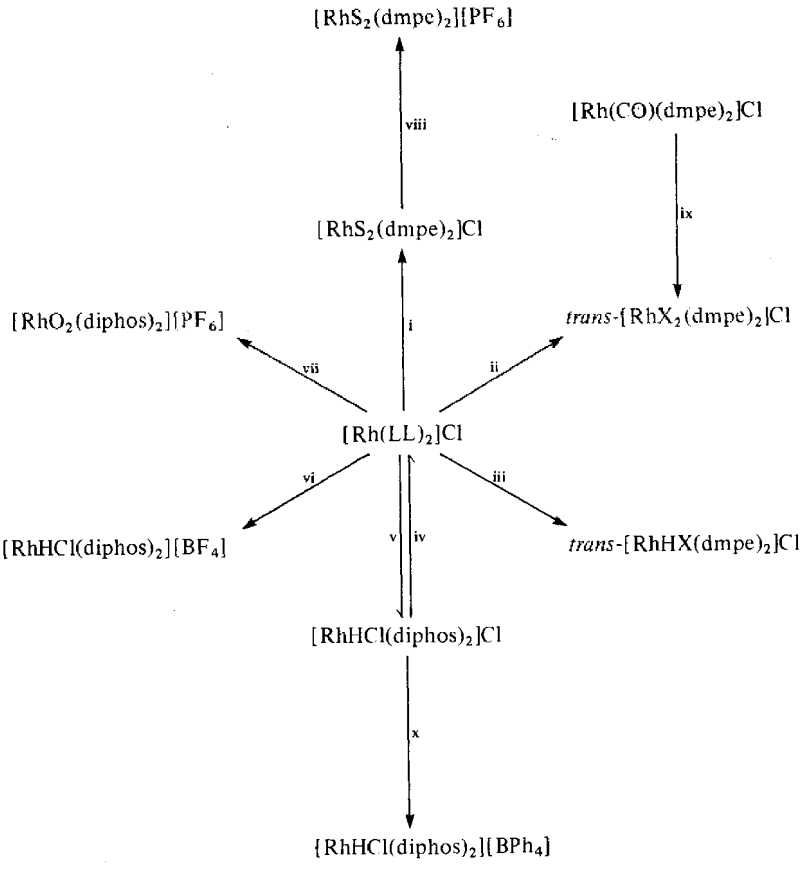
$$[Rh(CO)(Me_2PCH_2CH_2PMe_2)_2]Cl + Cl_2 \longrightarrow cis\text{-}[RhCl_2(Me_2PCH_2CH_2PMe_2)_2]Cl + CO \quad (235)$$

$$[Rh(CO)(Me_2PCH_2CH_2PMe_2)_2]Cl + Br_2 \longrightarrow trans\text{-}[RhBr_2(Me_2PCH_2CH_2PMe_2)_2]Br + CO \quad (236)$$

$$trans\text{-}[RhCl_2(Me_2PCH_2CH_2PMe_2)_2]Cl + LiBr \longrightarrow trans\text{-}[RhCl_2(Me_2PCH_2CH_2PMe_2)_2]Br \quad (237)$$

The range of products that can be obtained from oxidative addition reactions is illustrated by those of $[Rh(diphos)_2]Cl$ (Figure 6). Other small molecules besides the halogens add oxidatively to $[Rh(LL)_2]X$ complexes. Hydrogen adds reversibly to $[Rh\{(Me_2P)_2C_2H_4\}_2]Cl$, to form a dihydrido complex (equation 238). The dihydrido complexes have generally been prepared by oxidative addition reactions; their physical properties are listed in Table 79.

Hydrogen chloride, on the other hand, adds irreversibly to both four and five coordinate



i, LL = dmpe, S_8, CH_2Cl_2;[1042] ii, LL = dmpe, X_2 (X = Cl, Br);[228] iii, LL = dmpe, HX (X = Cl, Br);[228] iv, $HClO_4$;[214] v, LL = diphos, HCl;[214] vi, LL = diphos, $NaBF_4$, $HCl_{(g)}$, MeOH;[223] vii, LL = diphos, NH_4PF_6, O_2, MeOH;[1039] viii, NH_4PF_6;[1042] ix, X_2 (X = Cl, Br);[228] x, $NaBPh_4$, EtOH[214]

Figure 6 Oxidative addition and metathetical reactions of complexes containing ditertiary phosphines

$$[Rh(Me_2PCH_2CH_2PMe_2)_2]Cl + H_2 \rightleftharpoons [RhH_2(Me_2PCH_2CH_2PMe)_2]Cl \quad (238)$$

rhodium(I) complexes of this ligand (equation 239). Oxidative additions of hydrogen chloride to other rhodium(I) complexes can be reversed by addition of base to a solution of the resulting monohydrido complex (equation 240).[223]

$$[Rh(Me_2PCH_2CH_2PMe_2)_2]Cl + HCl \longrightarrow [RhHCl(Me_2PCH_2CH_2PMe_2)_2]Cl \quad (239)$$

$$[Rh(LL)_2][BF_4] + HCl \underset{Et_3N/CDCl_3}{\overset{MeOH}{\rightleftharpoons}} [RhHCl(LL)_2][BF_4] \quad (240)$$

LL = $CH_2(PPh_2)_2$, $CHMe(PPh_2)_2$, diphos, $Ph_2P(CH_2)_3PPh_2$

The other hydrogen halides add oxidatively to rhodium(I) complexes of ditertiary phosphines or arsines giving rise to numerous monohydrido complexes, whose physical properties are also listed in Table 79. However, it is possible to prepare certain monohydrido complexes from rhodium(III) halides. One interesting reaction, carried out under an atmosphere of CO, gives rise to dicarbonyldichlororhodate(I) salts (equation 241).[226]

$$RhCl_3 \cdot 3H_2O + 2LL \xrightarrow[C_6H_6/EtOH]{CO,\ 78°C} [RhHCl(LL)_2][RhCl_2(CO)_2] \quad (241)$$

LL = **(19)**, **(91)**, diars

Tetrafluoroborate,[223] tetraphenylborate and iodide[227] salts of a large range of rhodium(I) complex cations react oxidatively with dioxygen (equation 242). The physical properties of the dioxygen complexes are given in Table 80. The claim that a rhodium(I) species containing a ditertiary arsine

Table 79 Physical Properties of Hydridorhodium(III) Complexes Containing Bidentate Ligands

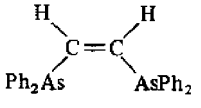
Complex	*Color*	*M.p.* (°C)	τ_{Rh-H} (p.p.m.)	ν_{Rh-H} (cm^{-1})	*Ref.*
cis-$[RhH_2\{(Me_2P)_2C_2H_4\}_2]Cl$	Buff-white	—	—	1900, 1870	228, 229
$[RhH_2\{(Ph_2P)(CH_2)_3(PPh_2)\}_2][BF_4]$	White	86	18.5	2052	1038
$[RhH_2(DIOP)_2][BF_4]$	White	153	20.0	2080, 2020	1038
cis-$[RhH_2(\mathbf{91})_2]Cl$	—	—	—	1982, 1969	239
cis-$[RhH_2(\mathbf{27})_2][PF_6]$	Yellow	160[d]	22.6	1982, 1981	241
trans-$[RhHCl\{(Me_2P)_2C_2H_4\}_2]Cl$	White	183–87	—	2050	228, 229
trans-$[RhHBr\{(Me_2P)_2C_2H_4\}_2]Cl$	Pale yellow	—	—	2030	228
trans-$[RhHCl\{(Ph_2P)_2CH_2\}_2][BPh_4]$	Cream	—	—	2080	223
trans-$[RhHCl\{(Ph_2P)_2CH_2\}_2][BF_4]$	Cream	—	—	2078	223
trans-$[RhHCl\{(Ph_2P)_2CHMe\}_2][BF_4]$	Cream	—	—	2105, 2099	223
trans-$[RhHCl\{(Ph_2P)_2C_2H_4\}_2][BF_4]$	Cream	—	—	2078	223
trans-$[RhHCl\{(Ph_2P)_2(CH_2)_3\}_2][BF_4]$	Cream	—	—	2110	223
trans-$[RhHCl\{(Ph_2P)_2(CH_2)_3\}_2]Cl$	Cream	—	—	2090	223
$[RhHCl(\mathbf{19})_2][PF_6]$	—	—	—	2000	226
$[RhHCl(\mathbf{19})_2]Cl$	—	—	25.9[a]	2078	226
$[RhHCl(\mathbf{19})_2][RhCl_2(CO)_2]$	—	—	26.0[b]	2079	226
$[RhHBr(\mathbf{19})_2][RhBr_2(CO)_2]$	—	—	24.9[c]	e	226
$[RhHCl(\mathbf{91})_2]Cl$	—	—	—	2052	226, 229
$[RhHBr(\mathbf{91})_2]Cl$	—	—	—	2045	226, 229
$[RhHCl(\mathbf{91})_2][RhCl_2(CO)_2]$	—	—	29.3[f]	—	226
$[RhHBr(\mathbf{91})_2][RhBr_2(CO)_2]$	—	—	27.9[g]	—	226
$[RhHCl(diars)_2][PF_6]$	Pale yellow	—	—	2000	226
cis-$[RhHCl(\mathbf{27})_2][PF_6]$[h]	Yellow-orange	230[d]	—	—	241
cis-$[RhHBr(\mathbf{27})_2][PF_6]$	Orange	239[d]	—	—	241
cis-$[RhHI(\mathbf{27})_2][PF_6]$	Orange	235[d]	—	—	241
trans-$[RhHCl(\mathbf{27})_2][PF_6]$[j]	Yellow	183[d]	28.17	2032	241
trans-$[RhHBr(\mathbf{27})_2][PF_6]$[k]	Yellow	182[d]	27.07	2024	241
trans-$[RhHI(\mathbf{27})_2][PF_6]$	Yellow-green	202[d]	25.07	2018	241

[a] J(RH) 16.1 Hz, J(P–H) 12.6 Hz. [b] J(Rh–H) 16.2 Hz, J(P–H) 12.5 Hz. [c] J(Rh–H) 18 Hz, J(P–H) 11.5 Hz. [d] With decomposition. [e] ν_{Rh-D} 1502 cm^{-1}. [f] J(Rh–H) 11.3 Hz. [g] J(Rh–H) 11.9 Hz. [h] 0.25 Me_2CO solvate. [j] 0.5 THF solvate. [k] 0.7 THF solvate.

dioxide ligand is formed in a reaction carried out under aerobic conditions is almost certainly erroneous.[1041]

$$[Rh(LL)_2]X + O_2 \longrightarrow [RhO_2(LL)_2]X \qquad (242)$$

$$LL = CH_2(PPh_2)_2,\ CHMe(PPh_2)_2,\ Ph_2P(CH_2)_3PPh_2$$



(91)

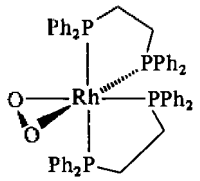
Table 80 Physical Properties of Dioxygen, Disulfur and Diselenium Rhodium(III) Complexes containing Bidentate Ligands

Complex	*Color*	*M.p.* (°C)	ν_{O-O} (cm^{-1})	*Ref.*
$[RhO_2\{(Ph_2P)_2CH_2\}_2][BF_4]$	Off-white	—	869, 875	223
$[RhO_2\{(Ph_2P)_2CHMe\}_2][BF_4]$	Off-white	—	870	223
$[RhO_2\{(PhMeP)_2C_2H_4\}_2][PF_6]$	Pale brown	150[a]	—	230
$[RhO_2(diphos)_2][BF_4]$	—	—	880	223
$[RhO_2(diphos)_2][PF_6]$	Brown	—	—	1039
$[RhO_2\{(Ph_2P)_2(CH_2)_3\}_2][BF_4]$	Off-white	—	885	223
$[RhO_2\{(Ph_2P)_2(CH_2)_3\}_2]Cl$	—	—	—	1039
$[RhO_2(\mathbf{91})_2][PF_6]$	Tan	130[a]	—	230
$[RhO_2\{Ph_2P(CH_2)_2SEt\}_2][BPh_4]$	Brown	—	—	242
$[RhO_2\{Ph_2P(CH_2)_2SPh\}_2][BPh_4]$	Brown	—	—	242
$[RhS_2\{(Me_2P)_2C_2H_4\}_2][PF_6]$	Orange-yellow	174–75	520[b]	1040
$[RhS_2\{(Me_2P)_2C_2H_4\}_2]Cl$	Light yellow-brown	154–55	520[b]	1040
$[RhS_2(diphos)_2]Cl$	Purple	*ca.* 200	550[b]	1040
$[RhS_2(\mathbf{91})_2][PF_6]_2$	Dark brown	250[a]	—	230
$[RhS_2(\mathbf{91})_2]Cl$	Light purple	217[a]	—	230
$[RhSe_2\{(Me_2P)_2C_2H_4\}_2]Cl$	Yellow-green	217–19[a]	—	1040

[a] With decomposition. [b] ν_{Rh-S_2}.

The $[RhO_2(diphos)_2][PF_6]$ complex can easily be prepared (equation 243), but it loses oxygen upon dissolution in anaerobic methanol. In the solid state the dioxygen complex is sufficiently stable for its structure to have been determined by X-ray crystallography. The structure (**92**) is best described as trigonal bipyramidal with monodentate dioxygen,[1039] which is in accordance with the NMR evidence.[242] The similarity to a corresponding complex containing monodentate ligands (**88**) is readily apparent. Dioxygen reacts with solid $[Rh\{(Me_2P)_2C_2H_4\}_2]Cl$ to give a material exhibiting a band attributed to ν_{O-O} in its IR spectrum at 845 cm^{-1}, but satisfactory analytical results were not obtained.[229]

$$[Rh(diphos)_2]Cl + O_2 \xrightarrow[MeOH]{NH_4PF_6} [RhO_2(diphos)_2](PF_6) \quad (243)$$



(92)

The analogous $[Rh\{Ph_2P(CH_2)_2SR\}_2][BPh_4]$ complexes also react with dioxygen (equation 244).[242] Disulfur analogs of the dioxygen complexes can be prepared by the oxidative addition of S_2 fragments from cyclooctasulfur (equation 245).

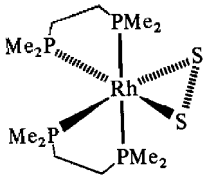
$$[Rh\{Ph_2P(CH_2)_2SR\}_2][BPh_4] + O_2 \longrightarrow [RhO_2\{Ph_2P(CH_2)_2SR\}_2][BPh_4] \quad (244)$$

R = Et, Ph

$$[Rh(LL)_2]Cl + S_8 \longrightarrow [RhS_2(LL)_2]Cl \xrightarrow{NH_4PF_6} [RhS_2(LL)_2][PF_6] \quad (245)$$

LL = $Me_2PCH_2CH_2PMe_2$,[1040,1042] diphos[1040]

Since the structure of $[IrSe_2(diphos)_2]^+$ is similar to (**93**), it may be assumed that the disulfurido-rhodium(III) cation has this structure. Indeed, such a structure has been proposed for the cation $[RhS_2\{(Me_2P)_2C_2H_4\}_2]^+$ on the basis of its IR spectrum, which has a band (attributed to $\nu_{Rh\cdot S\ S}$) at 525 cm^{-1} in both the chloride and hexafluorophosphate salts.[1042]



(93)

The dioxygen complexes undergo a number of interesting addition reactions with the lower oxides of non-metals that give rise to $[RhXX'(LL)_2]X''$ species containing coordinated oxoanions (equations 246 and 247).[230]

$$[RhO_2\{(MePhP)_2C_2H_4\}_2][PF_6] + SO_2 \longrightarrow [Rh(O_2SO_2)\{(MePhP)_2C_2H_4\}_2][PF_6] \quad (246)$$

$$[RhO_2\{(MePhP)_2C_2H_4\}_2][PF_6] + N_2O_4 \longrightarrow [Rh(ONO_2)_2\{(MePhP)_2C_2H_4\}_2][PF_6] \quad (247)$$

There remain a number of other complexes of this stoichiometry that have been prepared from rhodium(III) halides; their cations usually contain halo ligands.[235] The number of these complexes has been increased by allowing them to undergo metathetical reactions with sundry metal salts (equations 248 and 249).[214] There are also a number of complexes that have been prepared from the oxidative addition of other compounds to rhodium(I) complexes. Among these are the alkyl or aryl sulfinato complexes that can be prepared by the oxidative addition of suitable sulfonyl chlorides to $[Rh\{(MePhP)_2C_2H_4\}_2][PF_6]$ (equation 250). Whilst methane sulfonyl chloride gave the S-bonded adduct (ν_{S-O} (asym) 1214, 1194; ν_{S-O} (sym) 1035 cm^{-1}), the arene sulfonyl chlorides formed mixtures of *O*- and *S*-sulfinates, the IR spectra of which showed an additional band in the region 1040–1060 cm^{-1} attributable to the latter isomer. Although no isomerization occurred in solution, the proportion of the S isomer in the solids slowly increased over a period of years.[230]

$$RhCl_3 \cdot 3H_2O + 2(Bu^tCH_2)_2PC_2H_4P(CH_2Bu^t)_2 \xrightarrow[EtOH]{NH_4PF_6} [RhCl_2\{(Bu^tCH_2)_2PC_2H_4P(CH_2Bu^t)_2\}_2][PF_6] \quad (248)$$

$$[RhHCl(diphos)_2]Cl + NaBPh_4 \xrightarrow{EtOH} [RhHCl(diphos)_2][BPh_4] + NaCl \quad (249)$$

$$[Rh\{(MePhP)_2C_2H_4\}_2][PF_6] + RSOCl \longrightarrow [RhCl(RSO)\{(MePhP)_2C_2H_4\}_2][PF_6] \quad (250)$$

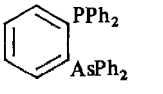
R = Me, *m*-$C_6H_4NO_2$, *p*-C_6H_4Me, 2-$C_{10}H_7$

Since, in the main, complexes of this type are themselves derivatives of other rhodium complexes there seem to have been few investigations of their chemical reactions apart from the metathetical reactions outlined above. Apart from spectral studies there has been little interest shown in their physical properties, although it may be noted that the emission observed from $[RhCl_2\{(Ph_2Z)_2C_2H_4\}_2]Cl$ (Z = P, As) complexes has been attributed to metal-localized phosphorescence.[1043] The ditertiary phosphine complexes are listed in Table 81.

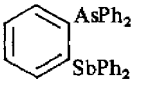
The complexes of this stoichiometry containing ditertiary arsines probably outnumber those of tertiary phosphines. They have been prepared by the same general methods as the tertiary phosphine complexes, although unusually $[RhCl_2(diars)_2]Cl$ has been prepared from $Na_3[RhCl_6]$. Despite the relative antiquity of this method,[1044] it has not been generally adopted (equation 251). The physical properties of the ditertiary arsine complexes are listed in Table 82. It may be noted that the IR spectra of the sulfinato complexes indicate that these are S-bonded like their phosphorus analogs.[230]

$$Na_3[RhCl_6] + diars \longrightarrow [RhCl_2(diars)_2]Cl \quad (251)$$

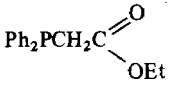
There are also several complexes containing ditertiary stibines of the type $Ph_2Sb(CH_2)_3SbPh_2$, and there would probably be more were the 1,2-bis(diphenylantimono)ethane ligand known.[1046] Ligands containing two different group V donor atoms also form complexes of this type. These include the ligands (**94**)[1045] and (**95**).[1037] There are also complexes formed by other ligands which contain but one group V donor atom. These include the hexafluorophosphate salt of (**96**),[1047] and the anionic complexes of (**64**), which have been mentioned in Section 48.6.3.1 above.[917]



(94)



(95)



(96)

However, not all bidentate ligands form complexes of this stoichiometry. Although sulfur dioxide displaces CO from a binuclear rhodium(I) complex, the product (**97**) retains a rhodium–rhodium bond.[1048] The complexes of (**98**) form primarily *fac* products when allowed to react with rhodium trichloride.[1049] The strength of the rhodium–sulfur bond is also shown in the failure of diphos or

Table 81 Physical Properties of $[RhX_2(LL)_2]X'$ Complexes Containing Ditertiary Phosphines

Complex	*Color*	*M.p.* (°C)	*Ref.*
cis-$[RhCl_2\{(Me_2P)_2C_2H_4\}_2]Cl$	Yellow	330	229
trans-$[RhCl_2\{(Me_2P)_2C_2H_4\}_2]Cl$	Yellow	188–90	229
trans-$[RhCl_2\{(Me_2P)_2C_2H_4\}_2]Br$	Yellow	185–87	229
trans-$[RhCl_2\{(Me_2P)_2C_2H_4\}_2][BPh_4]$	Pale yellow	180–83	229
cis-$[RhBr_2\{(Me_2P)_2C_2H_4\}_2]Br$	Yellow	334–35	229
trans-$[RhBr_2\{(Me_2P)_2C_2H_4\}_2]Cl$	Dark yellow	335[a]	229
$[RhCl_2\{(MePhP)_2C_2H_4\}_2][PF_6]$	Pale yellow	—	230
$[RhBr_2\{(MePhP)_2C_2H_4\}_2][PF_6]$	Bright yellow	301[a]	230
$[RhI_2\{(MePhP)_2C_2H_4\}_2][PF_6]$	Brown	—	230
$[RhSO_4\{(MePhP)_2C_2H_4\}_2][PF_6]$	Yellow	172[a]	230
$[Rh(OH)(NO_3)\{(MePhP)_2C_2H_4\}_2][PF_6]$	Off-white	203[a]	230
trans-$[RhCl(SO_2Me)\{(MePhP)_2C_2H_4\}_2][PF_6]$	Yellow	298[a]	230
trans-$[RhCl(m\text{-}O_2SC_6H_4NO_2)\{(MePhP)_2C_2H_4\}_2][PF_6]$	Yellow	232[a]	230
trans-$[RhCl(p\text{-}O_2SC_6H_4Me)\{(MePhP)_2C_2H_4\}_2][PF_6]$	Yellow	274[b]	230
trans-$[RhCl(2\text{-}O_2SC_{10}H_7)\{(MePhP)_2C_2H_4\}_2][PF_6]$	Yellow	225[a]	230
$[RhCl_2\{(Bu^tCH_2)_4P_2C_2H_4\}_2][PF_6]$	Yellow	211–13	235
$[RhCl_2(Ph_2PCH_2CO_2Et)_2][PF_6]$	—	—	1047

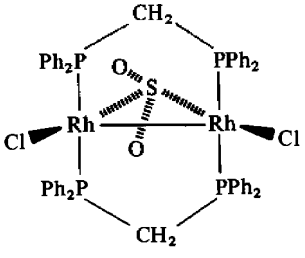
[a] With decomposition.

Table 82 Physical Properties of $[RhX_2(LL)_2]X'$ Complexes Containing Ditertiary Arsines

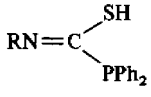
Complex	*Color*	*M.p.* (°C)	*Ref.*
$[RhCl_2(diars)_2][PF_6]$[a]	Yellow	> 330	230
$[RhBr_2(diars)_2][PF_6]$[b]	Yellow	> 330	230
$[RhI_2(diars)_2][PF_6]$[b]	Yellow	—	230
$[RhSO_4(diars)_2][PF_6]$	Pale yellow	> 330	230
$[RhCl(NO_3)(diars)_2][PF_6]$	Pale yellow	310[c]	230
$[RhCl(MeSO_2)(diars)_2][PF_6]$	Yellow	155[c]	230
$[RhCl(EtSO_2)(diars)_2][PF_6]$	Yellow	195[c]	230
$[RhCl(PhSO_2)(diars)_2][PF_6]$	Yellow	235[c]	230
$[RhCl(p\text{-}BrC_6H_4SO_2)(diars)_2][PF_6]$	Yellow	181[c]	230
$[RhCl(p\text{-}MeC_6H_4SO_2)(diars)_2][PF_6]$	Yellow	255[c]	230
$[RhCl(m\text{-}O_2NC_6H_4SO_2)(diars)_2][PF_6]$	Yellow	255[c]	230
$[RhCl(2\text{-}C_{10}H_7SO_2)(diars)_2][PF_6]$	Yellow	117[c]	230
$[RhCl(MeSO_2)(\mathbf{91})_2][PF_6]$	Yellow	201	230
$[RhCl(EtSO_2)(\mathbf{91})_2][PF_6]$	Yellow	195[c]	230
$[RhCl(PhSO_2)(\mathbf{91})_2][PF_6]$	Yellow	217	230
$[RhCl(p\text{-}BrC_6H_4SO_2)(\mathbf{91})_2][PF_6]$	Yellow	220[c]	230
$[RhCl(p\text{-}MeC_6H_4SO_2)(\mathbf{91})_2][PF_6]$	Yellow	194[c]	230
$[RhCl(m\text{-}O_2NC_6H_4SO_2)(\mathbf{91})_2][PF_6]$	Yellow	205[c]	230
$[RhCl(2\text{-}C_{10}H_7SO_2)(\mathbf{91})_2][PF_6]$	Yellow	210	230
$[RhBr_2(\mathbf{91})_2][PF_6]$[b]	Yellow-orange	309[c]	230
$[RhI_2(\mathbf{91})_2][PF_6]$	Yellow-brown	299[c]	230
$[RhSO_4(\mathbf{91})_2][PF_6]$	Yellow	290[c]	230
$[RhCl(NO_3)(\mathbf{91})_2][PF_6]$	Light yellow	—	230
$[Rh(NO_2)(NO_3)(\mathbf{91})_2][PF_6]$	Light orange	—	230
$[RhCl(p\text{-}O_2SC_6H_4Me)\{(Ph_2As)_2C_2H_4\}_2][PF_6]$	Yellow	185	230
$[RhCl(p\text{-}O_2SC_6H_4Br)\{(Ph_2As)_2C_2H_4\}_2][PF_6]$	Yellow	189[c]	230
trans-$[RhBr_2(\mathbf{91})_2][PF_6]$	Yellow-orange	273[c]	241
trans-$[RhI_2(\mathbf{91})_2][PF_6]$	Brown	288[c]	241
cis-$[Rh(SMe)_2(\mathbf{91})_2][PF_6]$	Red-orange	—	241
$[RhSO_4(\mathbf{91})_2][PF_6]$[b]	Dark red	238[c]	241
trans-$[RhCl(MeSO_2)(\mathbf{91})_2][PF_6]$	Dark red	245[c]	241

[a] Me_2CO hemisolvate. [b] Me_2CO solvate. [c] With decomposition.

$Ph_2PCH_2CH_2AsPh_2$ to displace all the dithiophosphinato ligand despite demethylation of the latter occurring during the reaction (equation 252).[1050]



(97)



(98)

$$[Rh\{S_2P(OMe)_2\}_3] + LL \longrightarrow [Rh\{S_2P(OMe)_2\}\{S_2P(O)(OMe)\}(LL)] \quad (252)$$

$$LL = \text{diphos, } Ph_2PCH_2CH_2AsPh_2$$

48.6.3.8 Complexes containing polydentate ligands

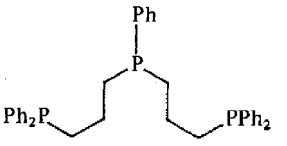
Polydentate ligands form both rhodium(I) and rhodium(III) complexes. Both oxidation states will be considered in this section since most of the rhodium(I) complexes readily undergo oxidative addition reactions.

Bis(3-diphenylphosphinopropyl)phenylphosphine (**99**) forms chloro, bromo and iodo rhodium(I) complexes (equations 253 and 254). The bromo complex can be obtained by addition of a large excess of LiBr to $[RhCl(cod)]_2$ prior to addition of the neutral ligand.[1051] The iodo complex has also been prepared from $[RhI(C_8H_{12})]_2$.[1051,1052] The halo complexes (**100**) have been shown to be square planar by X-ray crystallography.[1051]

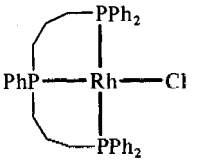
$$[RhCl(cod)]_2 + (\mathbf{99}) \longrightarrow [RhCl(\mathbf{99})] \quad (253)$$

$$[RhCl(cod)]_2 + (\mathbf{99}) \xrightarrow{LiX} [RhX(\mathbf{99})] \quad (254)$$

$$X = Br, I$$

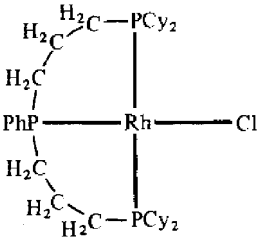


(99)



(100)

A similar square planar complex (**101**) has been formed by the ligand $PhP\{(CH_2)_3PCy_2\}_2$. The chloro complex has been prepared by synthesizing the ligand on a rhodium(I) template as shown in Scheme 38.[1053] The related tri(tertiary arsine) ligand $PhAs\{(CH_2)_3AsMe_2\}_2$ also forms a complex of similar structure to (**101**). The triarsine complex can be formed by displacement of neutral ligands from other chlororhodium(I) complexes (equation 255).[1054]



(101)

$$[RhCl(cod)]_2 + 2Cy_2P(CH_2)_3Cl \xrightarrow[25\,^\circ C]{C_7H_8} 2[RhCl(cod)\{Cy_2P(CH_2)_3Cl\}] \xrightarrow[Cy_2P(CH_2)_3PHPh]{Et_3N} (\mathbf{101}).$$

Scheme 38 Template synthesis of $[RhP\{(CH_2)_3PCy_2\}_2]$

$$\left.\begin{matrix}[RhCl(PPh_3)_3]\\ [RhCl(C_2H_4)_2]_2\\ [RhCl(cod)]_2\end{matrix}\right\} \xrightarrow{PhAs\{(CH_2)_3AsMe_2\}_2} [RhClAsPh\{(CH_2)_3AsMe_2\}_2] \quad (255)$$

The complexes readily undergo oxidative addition reactions but can easily add additional small neutral ligands to form five coordinate complexes (equation 256).[1055] The structure of the *S*-sulfur dioxide complex has been determined.[1056] The corresponding triarsine complex also forms a sulfur dioxide adduct. The chloro ligand can be replaced by non-coordinating anions (equation 257),[1051] or in the case of the triarsine complex by carbon monoxide.[1054] The ^{31}P NMR spectra of an extensive series of derivatives have been determined, but no preparative details have been given.[1057] The bis(diphenylphosphinosilyl)amide anion functions as a tridentate ligand and displaces the majority of the monodentate tertiary phosphines from rhodium(I) complexes (equations 258 and 259).[1058]

$$[RhCl(\mathbf{99})] + L \longrightarrow [RhCl(\mathbf{99})L] \quad (256)$$

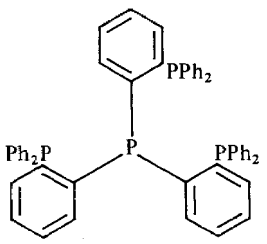
$$L = SO_2, BF_3$$

$$[RhCl(\mathbf{99})] + NH_4PF_6 \xrightarrow{MeCN} [Rh(MeCN)(\mathbf{99})][PF_6] \quad (257)$$

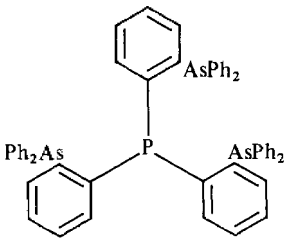
$$[RhCl(PPh_3)_3] + LiN(SiMe_2CH_2PPh_2)_2 \longrightarrow [Rh\{N(SiMe_2CH_2PPh_2)_2\}(PPh_3)] \quad (258)$$

$$[Rh(PMe_3)_4]Cl + LiN(SiMe_2CH_2PPh_2)_2 \longrightarrow [Rh\{N(SiMe_2CH_2PPh_2)_2\}(PMe_3)] \quad (259)$$

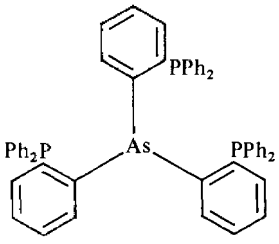
Chloro and iodo complexes of the quadridentate ligands (**102**), (**103**) and (**104**) have been prepared. No preparative details are available and the complexes are all too insoluble to confirm the speculation that they are trigonal bipyramidal.[1059]



(102)

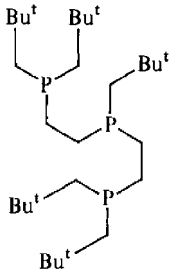


(103)



(104)

The rhodium(III) complexes can be prepared either by oxidative addition to the corresponding rhodium(I) complexes or by direct reaction of the ligands with rhodium(III) salts. Normally the reducing properties of tertiary polyphosphines ensure that rhodium(I) complexes are formed; hence the rhodium(III) complexes of these ligands have been prepared *via* oxidative addition reactions. However, the sterically hindered ligand (**105**) fails to reduce hydrated rhodium trichloride even when allowed to react with the latter in refluxing ethanol (equation 260).[235]



(105)

$$RhCl_3 \cdot 3H_2O + (\mathbf{105}) \longrightarrow [RhCl_3(\mathbf{105})] \quad (260)$$

The complexes of $[PhP\{(CH_2)_3PPh_2\}_2]$ (**99**) readily undergo oxidative addition reactions (equations 261–263). Dioxygen forms a rhodium(III) complex which reacts with sulfur dioxide to give a sulfato complex and with carbon monoxide to yield a carbonato complex (equations 264–266).[1051] Similarly, the thermally stable dioxygen complex $[RhCl(O_2)PhAs\{(CH_2)_3AsMe_2\}_2]$, which can be prepared by allowing dioxygen to react with the rhodium(I) complex, is a useful source of other rhodium(III) complexes of this ligand (equation 267). Like the similar diphenylphosphino complex above it reacts with sulfur dioxide to form a yellow sulfato complex and with carbon monoxide to form a yellow-orange carbonato complex. Upon formation of these two complexes the characteristic ν_{O-O} band at 852 cm^{-1} disappears from its IR spectrum and is replaced by bands at 1255, 1140 and 640 cm^{-1} (bidentate sulfato ligand) or bands at 1650 and 1620 cm^{-1} (bidentate carbonato ligand).[1054]

$$[RhCl(\mathbf{99})] + H_2 \longrightarrow [RhH_2Cl(\mathbf{99})] \quad (261)$$

$$[RhCl(\mathbf{99})] + HCl \longrightarrow [RhHCl_2(\mathbf{99})] \quad (262)$$

$$[RhCl(\mathbf{99})] + S_8 \longrightarrow [Rh(S_2)Cl(\mathbf{99})] \quad (263)$$

$$[RhCl(\mathbf{99})] + O_2 \longrightarrow [Rh(O_2)Cl(\mathbf{99})] \quad (264)$$

$$[Rh(O_2)Cl(\mathbf{99})] + SO_2 \longrightarrow [Rh(SO_4)Cl(\mathbf{99})] \quad (265)$$

$$[Rh(O_2)Cl(\mathbf{99})] + CO \longrightarrow [Rh(CO_3)Cl(\mathbf{99})] \quad (266)$$

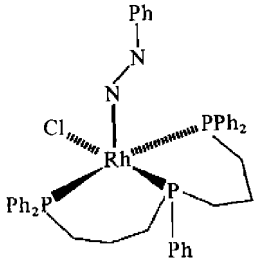
$$[RhClPhAs\{(CH_2)_3AsMe_2\}_2] + O_2 \longrightarrow [Rh(O_2)ClPhAs\{(CH_2)_3AsMe_2\}_2] \quad (267)$$

Tetrafluoroborate species also undergo two fragment oxidative addition reactions to the tritertiary phosphine complex (equation 268). The hydrido complex exhibits ν_{Rh-H} at 2199 cm^{-1}. On heating the square pyramidal[1060] diazonium complex (**106**) it is converted to the hydrido complex.[1052]

The preparation of the hydrido complex from tetrafluoroboric acid is difficult to reproduce. It has been reported that the preparation from $HBF_4 \cdot Et_2O$ is successful only if ethanol is present. Under these conditions $[RhHCl(L)(EtOH)][BF_4]$ is formed. In THF solution the THF solvate is formed.[1061]

$$[RhCl(\mathbf{99})] + [A][BF_4] \longrightarrow [RhCl(A)(\mathbf{99})][BF_4] \quad (268)$$

A = H, NO, N_2Ph

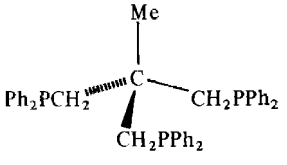


(106)

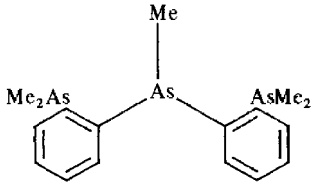
The halogens form trihalo complexes when allowed to react with [RhClL] (equation 269).[1051] The trichloro complex containing the tritertiary phosphine (**107**) can be prepared by the oxidative addition of chlorine to a rhodium(I) carbonyl complex (equation 270).[246]

$$[RhCl(\mathbf{99})] + X_2 \longrightarrow [RhX_3(\mathbf{99})] \quad (269)$$

X = Cl, Br, I



(107)



(108)

$$[RhCl(CO)(\mathbf{107})] + Cl_2 \xrightarrow{EtOH} [RhCl_3(\mathbf{107})] \quad (270)$$

The poorer reducing properties of tertiary arsines usually result in rhodium(III) complexes being formed when these polydentate ligands are allowed to react with rhodium(III) salts. Thus, the tri(tertiary arsine) ligand (**108**) forms mixtures of facial and meridional rhodium(III) complexes (equations 271 and 272). The facial isomer is the more soluble of the two bromo complexes and it can be obtained from the mother liquors after the *mer* complex has crystallized out. Only the *fac* isomer of the iodo complex is known. It can be prepared by addition of lithium iodide to the reaction mixture (equations 273 and 274). The formation of this isomer is, perhaps, surprising on steric grounds, but if the preparation of the meridional complex is essayed by allowing lithium iodide to react with the *mer*-trichloro complex only one chloro ligand is replaced (equation 275). In acid solution the *mer*-tri(nitrato) complex can be obtained from a metathetical reaction (equation 276).

$$RhCl_3 \cdot 3H_2O + (\mathbf{108}) \xrightarrow[EtOH]{12\,M\ HCl} \textit{fac}\text{-}[RhCl_3(\mathbf{108})] \quad (271)$$

$$RhCl_3 \cdot 3H_2O + (\mathbf{108}) \xrightarrow[EtOH]{6\,M\ HCl} \textit{mer}\text{-}[RhCl_3(\mathbf{108})] \quad (272)$$

$$RhBr_3 + (\mathbf{108}) \xrightarrow{HBr} \textit{fac}\text{- and } \textit{mer}\text{-}[RhBr_3(\mathbf{108})] \quad (273)$$

$$RhCl_3 \cdot 3H_2O + (\mathbf{108}) + LiI \longrightarrow \textit{fac}\text{-}[RhI_3(\mathbf{108})] \quad (274)$$

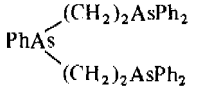
$$\textit{mer}\text{-}[RhCl_3(\mathbf{108})] + LiI \longrightarrow \textit{mer}\text{-}[RhCl_2I(\mathbf{108})] \quad (275)$$

$$\textit{mer}\text{-}[RhBr_3(\mathbf{108})] + AgNO_3 \xrightarrow{HNO_3} \textit{mer}\text{-}[Rh(NO_3)_3(\mathbf{108})] \quad (276)$$

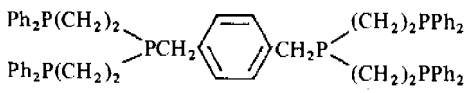
The proposed structures of the two trichloro complexes are based upon their IR spectra. Bands due to ν_{Rh-Cl} occur at 332, 302 and 296 cm^{-1} in the spectrum of the *fac* isomer. The *mer* isomer has bands at 339, 307 and 262 cm^{-1}.

A rhodium(III) perchlorate complex containing two molecules of the tritertiary arsine can also

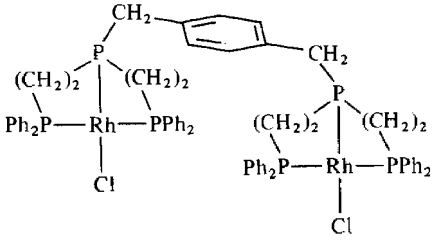
be prepared (equation 277).[1062] There is also a poorly characterized trichloro complex of the tridentate ligand (**109**).[1063] The hexa(tertiary phosphine) ligand (**110**) displaces neutral ligands, including some that are quite strongly bound, from rhodium(I) complexes, as in equation (278). The low value of 276 cm^{-1} for ν_{Rh-Cl} in the far-IR spectrum has led to the structure (**111**) being proposed for the product. The ligand (**110**) fails to reduce $RhCl_3 \cdot 3H_2O$ when allowed to react with it in ethanolic solution (equation 279). Further evidence for the ionic nature of the product (**112**) is provided by the reaction with NH_4PF_6 (eqution 280).[1064,1065]



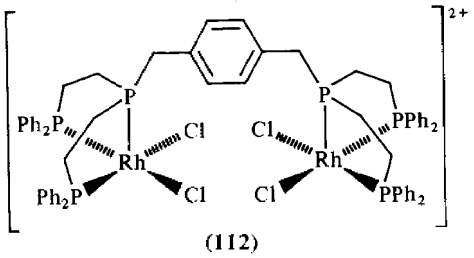
(109)



(110)



(111)



(112)

$$Rh(ClO_4)_3 + (\mathbf{108}) + HClO_4 \xrightarrow{EtOH} [Rh(\mathbf{108})_2][ClO_4]_3 \quad (277)$$

$$[RhCl(CO)(PPh_3)_2] + (\mathbf{110}) \longrightarrow [Rh_2Cl_2(\mathbf{110})] \longleftarrow [RhCl(PPh_3)_3] + (\mathbf{110}) \quad (278)$$

$$2RhCl_3 \cdot 3H_2O + (\mathbf{110}) \xrightarrow{EtOH} [Rh_2Cl_4(\mathbf{110})]Cl_2 \quad (279)$$

$$[Rh_2Cl_4(\mathbf{110})]Cl_2 + NH_4PF_6 \longrightarrow [Rh_2Cl_4(\mathbf{110})][PF_6]_2 \quad (280)$$

48.6.4 Mixed N—O and N—S Ligand Complexes

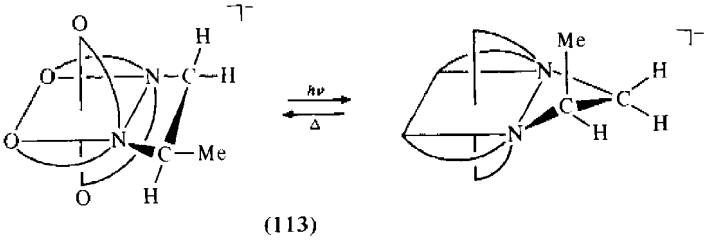
48.6.4.1 N—O ligand complexes

Surprisingly little work has been reported on tris(amino acid) complexes of Rh^{III}. Reaction of $RhCl_3 \cdot 3H_2O$ with sodium bicarbonate causes precipitation of Rh_2O_3, which forms [Rh(D-ala)$_3$] if heated immediately with D-alanine. Fractional crystallization allows separation of *mer*(−) and *mer*(+) isomers, as well as some impure *fac* isomer.[1066] Reaction of the Li salt of DL-methionine ($Li^+MeSCH_2CH_2CH(NH_2)COO^-$) with anhydrous $RhCl_3$ in refluxing ethanol leads to the precipitation of [Rh(DL-methionine)$_3$], in which the methionines act as anionic bidentates, bonded through the O and N atoms.[1067] The solid state reaction of $RhCl_3$ with glycine is reported to lead to [Rh(gly)$_3$], characterized thermogravimetrically and by IR, UV and ^1H NMR spectroscopy.[1068] Several $[Rh(en)_2(\text{amino acid})]^{2+}$ complexes have been prepared and resolved[644,647] (Section 48.6.2.2.ii).[644,647]

Early reports by MacNevin and co-workers[1069–1071] indicated that Rh^{III} did not form complexes with ethylenediaminetetraacetic acid (H_4edta), although MacNevin finally did report indirect evidence of a Rh^{III}–edta interaction.[1072] The first well-characterized complex was reported by Dwyer and Garvan, who overcame the inertness of Rh^{III} by heating the H_4edta with an aqueous solution of $RhCl_3 \cdot 3H_2O$ in an autoclave at 145–150 °C for four hours;[1073] this pressurized 'sealed-tube' technique remains the standard route to aminocarboxylate complexes of Rh^{III}. The resulting complex was shown to have a five-coordinate edta ligand with one uncoordinated carboxyl arm and a water coordinated at the sixth coordination site. The pK_a of the free carboxyl group is 2.32 ± 0.08, while the coordinated water has a pK_a of 9.15 ± 0.02. The complex was resolved by precipitation of the (−)-$[Co(en)_2(NO_2)_2]$(−)-[Rh(edta)(H_2O)] diastereomer, followed by recrystallization of the Rh species as the K^+ salt. Reaction of the monoaqua species with HCl or HBr leads to the tetradentate anions $[Rh(H_2edta)X_2]^-$ (X = Cl, Br) and these complexes were resolved,[1073] compared

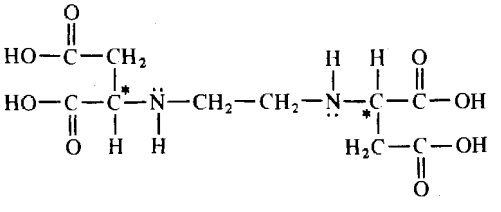
to Co analogs[1074] and characterized by IR spectroscopy.[1075] Other workers have prepared and characterized a variety of NH_4^+, K^+ and Na^+ salts.[1076–1078] NMR spectra were used to confirm that edta is pentadentate in strongly acidic solution, but that in a limited range (pH between 4 and 8), it is hexadentate, as $[Rh(edta)(H_2O)]$ reacts to form $[Rh(edta)]^-$.[1079] A coordinated water is necessary, as ^1H NMR showed that $[Rh(edta)Cl]^-$ remains unchanged between pH 1 and 9 (except for the deprotonation of the free carboxylate). Analysis of the NMR spectra also suggested that the sixth coordination site in these five-coordinate edta complexes is in the diamine plane.[1079] Solid salts of the six-coordiante $[Rh(edta)]^-$ anion have not been reported.

Dwyer and Garvan also prepared and resolved the Rh^{III} complex of 1-propylenediaminetetraacetic acid (pdta), and suggested it was a five-coordinate chelate, forming $[Rh(pdta)(H_2O)]^-$.[1080] Like the edta analog,[1073] resolved samples of the pdta complex rapidly racemize when exposed to light, but unlike the edta ion, the pdta complex spontaneously returns to the resolved form in the dark. This chromophoric behavior was not studied, but ascribed to the reversible formation of a diaqua species.[1080] Wing questioned this, showing that photolysis does not change the acetate portion of the ^1H NMR spectrum,[1081] clearly inconsistent with photoinduced aquation of an acetate arm of the pdta. He proposed that the mutarotation was due to the photoinduced formation of an unstable (axial methyl group) configuration as shown in (**113**); collapse to the stabler (equatorial methyl) configuration then occurs in the dark. The methyl group provides the driving force for this back-reaction, so the edta complex would not be expected to spontaneously re-resolve in the dark, consistent with observation.[1073,1080,1081]



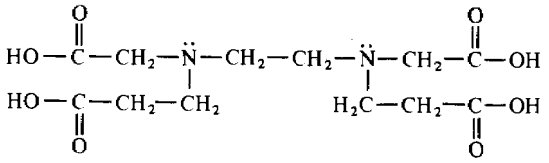
(113)

An isomer of edta with two chiral centers, ethylenediaminedisuccinic acid (edds; **114**) also forms a stable hexadentate complex with Rh^{III}.[1082] The ^1H NMR spectrum of $[Rh(S,S\text{-edds})]^-$ is virtually unchanged between pH 2 and 9, and the IR and NMR spectra are both consistent with a six-coordinate geometry. At pH ≈ 1, $[Rh(S,S\text{-edds})(H_2O)]$ forms, and at pH ≈ 10, the $[Rh(S,S\text{-edds})(OH)]^{2-}$ anion was identified in solution.[1082] The X-ray structure of Co–edta complexes shows that the glycinate rings which are in the plane of the two amine groups (the G rings) are strained, while the out-of-plane rings (R rings) are not strained. For the larger Rh^{III}, such a strain should be enhanced, leading Douglas and co-workers to study Rh^{III} complexes of a variety of aminopolycarboxylates with different chain lengths.[1083–1085] The 'sealed-tube technique' was used to react $RhCl_3 \cdot 3H_2O$ with ethylenediamine-*N*,*N*′-diacetic-*N*,*N*′-di-3-propionic acid (H_4eddda; **115a**) to form *trans*-O_5- and *trans*-(O_5O_6)-Na[Rh(eddda)] (**115b,c**). Isomer assignment was made on the basis of ^1H and ^{13}C NMR, and IR spectra.[1083] The Rh^{III} complex with 1,3-propanediaminetetraacetate (1,3-pdta) is also hexadentate, and, based on CD spectra (Table 83), comparisons to Co analogs and to the CD spectrum of $[Rh(S,S\text{-edds})]^-$, $(-)_D$-$[Rh(1,3\text{-pdta})] \cdot 2H_2O$ has been assigned the Λ configuration. The CD spectra are more intense, and broader than those of the Co^{III} and Cr^{III} analogs, as the low symmetry (C_2) components are not resolved, presumably due to the larger spin–orbit coupling of the Rh.

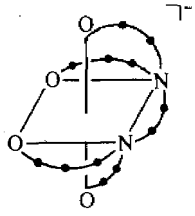


(114)

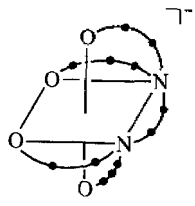
Nitrilotriacetate (NTA), *N*-methyliminodiacetate (MIDA) and iminodiacetate (IDA) (**116**) form a series of 1:1 and 1:2 (metal:ligand) complexes with Rh^{III} (and Co^{III}), which have been characterized by ^1H NMR and electronic spectra.[1087] On the basis of the NMR and a comparison to the Co analog,



(115a)

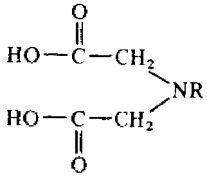


(115b) *trans*-(O_5)

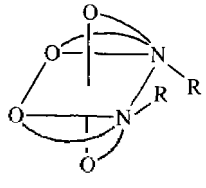


(115c) *trans*-(O_5O_6)

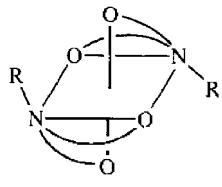
an ill-characterized 1:1 adduct of NTA is proposed, $[Rh(NTA)(H_2O)_2]$, in which the NTA is a tetradentate. For all but one of the 1:2 adducts, the ^1H NMR spectra show clean AB patterns, implying the *trans–fac* geometry (**117**). The more soluble isomer of $[Rh(IDA)_2]^-$ shows two AB patterns, consistent with *trans–mer* geometry. The $[Rh(NTA)_2]^-$ ion has two free carboxylate arms (one per NTA), and the NMR shows that averaging of environments between the coordinated and uncoordinated acetates is not observed.[1087]



(116) NTA, R = CH_2COOH
MIDA, R = Me
IDA, R = H

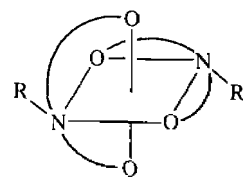


cis



trans-fac

(117)



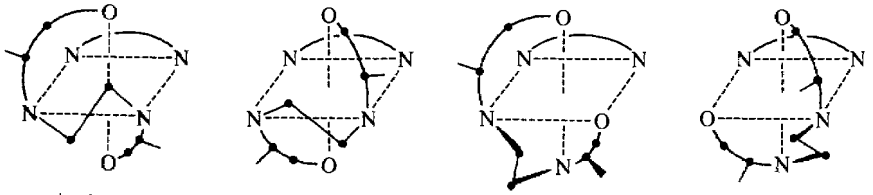
trans-mer

Table 83 Electronic and CD Spectra of some Aminepolycarboxylatorhodium(III) Complexes[a]

Complex	*Absorption* λ_{max} (nm) (ε)	*Circular dichroism* λ_{max} (nm) ($\Delta\varepsilon$)	*Ref.*
trans-(O_5)-[Rh(EDDDA)]$^-$ $(-)_D$	~378sh (405) 335 (745) ~295sh (480)	340 (−2.10) 286 (+0.36)	1084
trans-(O_5O_6)-[Rh(EDDDA)]$^-$ $(-)_D$	~380sh (390) 344 (565) 298sh (380)	393 (−1.80) 345 (+2.84) 280 (−0.55)	1084
trans-(O_5)-[Rh(*S,S*-EDDS)]$^-$ $(+)_D$	~375sh (215) 328 (565) ~285sh (245)	363 (−2.29) 317 (+2.74)	1084
[Rh(1,3-pdta)]$^-$ $(-)_D$	358sh (284) 338sh (274) 293 (243)	392 (−1.03) 333 (+2.05) 294 (−0.65) 263 (+0.09)	1085
mer-$[HRh(NTAH)_2]\cdot 2H_2O$	~400sh (~26.5), 334.5 (154), ~280sh		1087
mer-$[HRh(MIDA)_2]\cdot 2H_2O$	404 (25), 328 (149), 282 (24)		1087
mer-$[HRh(IDA)_2]\cdot 3H_2O$	~400sh (~28), 328 (132.5), 284 (104.5)		1087
fac-$[HRh(IDA)_2]\cdot 2H_2O$	362 (274), 295 (237)		1087
Δ-*cis*-α-[Rh(EDDP)(*S*-ala)]	350 (196) 283 (232)	360 (−5.15) 308 (+0.87) 270 (−0.98)	1088
Δ-*cis*-α-[Rh(EDDP)(*R*-ala)]	350 (188) 283 (214)	360 (−3.92) 308 (+0.89) 270 (−0.76)	1088
Δ-*cis*-α-[Rh(EDDP)(*R,S*-ala)]	350 (188) 283 (213)	360 (−4.66) 310 (+0.94) 270 (−0.94)	1088
Δ-*cis*-α-[Rh(EDDP)gly]	360 (321) 290 (255)	360 (−4.11) 308 (+0.71) 270 (−1.44)	1088
Λ-*cis*-β-[Rh(EDDP)(*S*-ala)]	348 (202) 283 (261)	346 (+1.25) 306 (−0.82)	1088

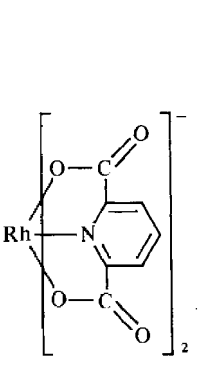
[a] Ligand abbreviations given in text.

M. E. Sheridan *et al.* have recently presented an interesting series of reports on the Rh^{III} complexes formed with the optically active tetradentate, ethylenediamine-*N,N'*-di-*S*-propionate, (*S,S*-eddp).[1088–1091] Four geometric isomers of $[Rh(S,S\text{-eddp})X_2]^{n+}$ are possible (**118**), but for Rh^{III}, only the Δ-*cis*-α and λ-*cis*-β isomers could be detected ($X_2 = 2Cl^-$, $n = -1$; ala^-, $n = 0$; en, $n = +1$). For $[Co(S,S\text{-eddp})(en)]^+$, three isomers were observed, with only the Δ-*cis*-β not formed.[1092] The electronic spectra for the two isomers of $[Rh(S,S\text{-eddp})(en)]^+$ are very similar, but the ^1H NMR is diagnostic of isomeric configuration; the α isomer shows one methyl doublet and one H quartet on the propionate arm, while the β form has dissimilar environments for the propionate arms, and shows two methyl doublets and two H quartets. Substitution of the en by two Cl^- ions occurs with retention of configuration in the Δ-*cis*-α case, and subsequent substitution of the chlorides by *S*-ala, *R*-ala and *S,R*-ala also occurs with retention of the Δ-*cis*-α configuration.[1089,1090] Reaction of λ-*cis*-β-$[Rh(S,S\text{-eddp})Cl_2]^-$ with *R*-ala, *S*-ala or OH^- leads to an unusual (but not unprecedented[1093–1096] in Co systems) isomerization to the Δ-*cis*-α configuration; even the Ag^+-induced chloride hydrolysis of the β isomer occurred with isomerization of the *S,S*-eddp backbone to the Δ-*cis*-α configuration.

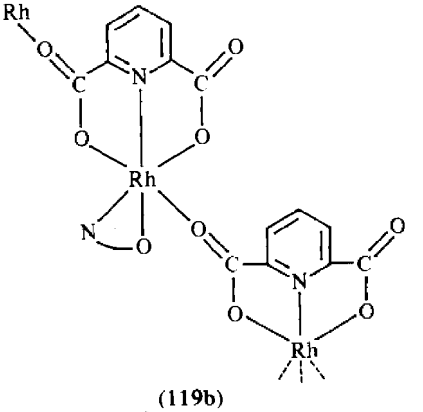


(118)

The dianion of dipicolinic acid (dipic) acts as a tridentate, forming $Na[Rh(dipic)_2]$ and a series of complexes of the form $[Rh(dipic)(N—O)]\cdot nH_2O$ (N—O = an N and O donating bidentate, including the conjugate bases of picolinic acid, nicotinic acid, isonicotinic acid, glycine and aminophenol).[1097] The bis complexes (**119a**) are diamagnetic monomers, characterized by UV/visible and IR spectra, magnetic susceptibility, and conductance measurements. The [Rh(dipic)(N—O)] complexes are presumed to be polymeric, with two oxygen atoms of a dipic carboxylate bonding to two different Rh centers, thus maintaining octahedral coordination of each Rh^{III} (**119b**). The complex $[Rh(L)_2Cl_2]Cl$ (L = isonicotinic acid hydrazide), in which L acts as an N—O bidentate, has been characterized by elemental analysis, conductance, magnetic susceptibility and electronic spectrum.[1098]



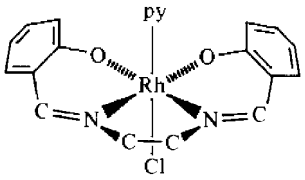
(119a)



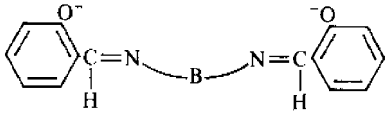
(119b)

When a mixture of $RhCl_3\cdot 3H_2O$ with Zn dust is added to a hot pyridine solution containing *N,N'*-ethylenebis(salicylideneiminate) (the Schiff base salen), yellow crystals of [Rh(salen)py(Cl)] (**120**) form.[1099] If the Schiff base is mixed with the $RhCl_3\cdot 3H_2O$ before adding the reducing agent, a pale yellow solid, formulated as [Rh(salen)py], precipitates. The lack of solubility and reactivity of this diamagnetic solid hindered identification, and both polymeric[1099] and dimeric Rh^{II},[413] analogous to $[Rh(DMG)_2(py)]_2$, have been suggested. This same material could be prepared by reacting a methanolic solution of $salenH_2$ in Zn(Hg) with $[Rhpy_4Cl_2]Cl$.[1200] Reaction of [Rh(salen)Cl(py)] with Na(Hg) or BH_4^- in the presence of organic halides leads to [Rh(salen)R(py)] (R = Me, Et, Pr^n,

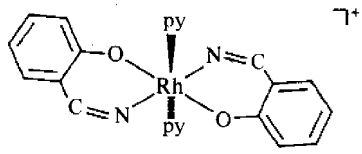
Pr^i, Bu^n, MeCO, $CH_2{=}CHCH_2$, aniline).[1099] The $[Rhpy_4Cl_2]^+$ ion reacts with a variety of Schiff bases in boiling pyridine solution (in the presence of Zn dust and PF_6^-), to generate a family of complexes of the form $[Rh(SB)py_2]PF_6$ (**121**).[1100] These all formed methyl adducts with Rh^{III}—Me bonds when reacted with methyl iodide.[413] A similar reaction path ($[Rh(py)_4Cl_2]Cl$ + Zn dust + Schiff base) was used to prepare $[Rh(N{-}O)_2py_2]^+$ (**122**). In the absence of Zn dust, $[Rh(py)_4Cl_2]^+$ is unreactive toward Schiff bases, even when refluxed in pyridine for many hours. The best yields are obtained when equivalent amounts of Zn and Rh are reacted.[1100]



(120)



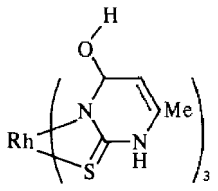
(121) B = 1,2-phenylene
4-methyl-1,2-phenylene
4,5-dimethyl-1,2-phenylene
ethylene (salen)
1,3-propylene
1,4-butylene



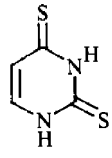
(122)

48.6.4.2 N—S bidentate complexes

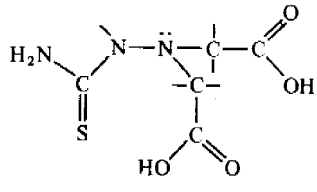
Cyclohexanone thiosemicarbazide ($C_5H_{10}C{=}N{-}N(H)C{=}SNH_2$ = HL) reacts with $RhCl_3{\cdot}3H_2O$ in refluxing ethanol to form the 3:1 electrolyte $[Rh(HL)_3]Cl_3$, in which the neutral semicarbazide is a sulfur- and nitrogen-bonded bidentate. The conjugate base also forms the non-electrolyte $[Rh(L)_3]$ in which the anionic thiosemicarbazide is again an N- and S-bonded bidentate. These complexes were characterized by conductivity measurements, magnetic susceptibility (both diamagnetic), IR and electronic spectra.[1101] Another N—S bidentate, 6-methyl-2-thiouracil, forms $[Rh(L)_3]Cl_3$ salts (**123a**),[1102] and IR analysis indicates that the thiouracil is bonded through the S and the N (at the 3 position), to form four-membered chelate rings, rather than the S and N-1 bonding observed for $[M(L)_2]^{2+}$ (M = Pt or Pd). A brown diamagnetic solid, which analyzes as $[Rh(tu)_2Cl]$ (tu = the monoanion of thiouracil, where Htu = $C_4H_4N_2S_2$; (**123b**), has been characterized by IR and electronic spectra. It is 'highly insoluble in common organic and inorganic solvents', and IR analysis suggests a polymeric structure, with bridging thiouracil and chloride ligands, with the thiouracil bonded through the N and S atoms, although a specific bonding geometry was not suggested.[1103] Reaction of $RhCl_3{\cdot}3H_2O$ with 4-amino-3,5-mercapto-1,2,4-triazole (H_2TZ) leads to two incompletely characterized complexes: a brick-red solid identified as $[Rh(HTZ)_2Cl(H_2O)]$ and an orange-red $[Rh_2(TZ)_3]$.[1104] Both the HTZ^- and TZ^{2-} ions are presumably acting as bidentates, and weak IR bands near 330 and 430 cm^{-1} are assigned as Rh—S and Rh—N stretches respectively, suggesting coordination through a S and a N atom.



(123a)



(123b)



(124)

Thiosemicarbazidodiacetic acid (H_2L) (**124**) reacts with $RhCl_3{\cdot}3H_2O$ in ethanol in the presence of Lewis bases (B), forming $[Rh(L)(B)Cl]{\cdot}nH_2O$ (B = OH^-, py, α-picolone, PPh_3, aniline); in the presence of bipy or phen (NN), the product is formulated as $[Rh(L)(NN)]Cl$.[1105] Examination of models and IR analysis suggest that the thiosemicarbazide diacetic acid acts as a dianionic tripodal tetradentate, bonding to the Rh through two O, an N and an S atom.

48.6.5 Oxygen Ligands

48.6.5.1 The hexaaqua ion

Early references to Rh perchlorate complexes were presumably the first reports of the $[Rh(H_2O)_6]^{3+}$ ion. When freshly precipitated $Rh(OH)_3$ is reacted with one-third of the indicated molar quantity of perchloric acid, the resulting species in solution was identified as '$Rh(OH)_2^+$',[1106] and recrystallization of $Rh(OH)_3$ from perchloric acid led to a solid identified as '$Rh(OH)_2ClO_4$'.[1107] More recent work[1108] show that reaction of $RhCl_3 \cdot 3H_2O$ with conc. $HClO_4$ leads (after recrystallization) to 'yellow, light, fluffy needles' of $[Rh(H_2O)_6](ClO_4)_3$ with a face-centered cubic lattice. Isotopic dilution studies revealed a hydration number of 5.9 (± 0.4).[1109] It is acidic in aqueous solution (at 64 °C,[111] $K_a = 4 \times 10^{-3}$ and at 25 °C, $pK_a = 3.3$[1110]), and attempts to predict its acidity on the basis of optical basicities shows that outer-sphere solvent molecules significantly affect the experimentally determined pK_a value.[1111] The crystals are hygroscopic, and Forrester noted that replacement of the coordinated waters 'may easily be made by other ligands'.[1108]

Harris and co-workers have extensively studied the kinetics of water substitutions in $[Rh(H_2O)_6]^{3+}$ (equation 281; X = H_2O,[1109] Cl^-,[1112] Br^-[1113]). A two-term rate law was found in all three cases, as was an inverse $[H^+]$ effect. Reaction of the substituting ligand with either $[Rh(H_2O)_6]^{3+}$, or its conjugate base $[Rh(H_2O)_5OH]^{2+}$, accounts for the two-term rate law, while the inverse $[H^+]$ effect occurs because the $[Rh(H_2O)OH]^{2+}$ is several orders of magnitude more reactive than the hexaaqua ion, making the base-catalyzed path the dominant route in all but the most acidic solutions. For Cl and Br anations, the monohalo-substituted species were not isolated, as rapid substitution of a second halide leads to the (presumably *trans*) $[Rh(H_2O)_4X_2]^+$ ions. The kinetic *trans* effect was also cited to explain the reactivity of the $[Rh(H_2O)_5OH]^{2+}$ ion; for the $[Rh(H_2O)_5X]^{2+}$ series, the order of the kinetic *trans* effect induced by X was shown to be $OH \gg Br > Cl$.[1113] Kinetic studies of the anation of $[Rh(H_2O)_6]^{3+}$ by NCS^- (equation 281; X = NCS^-) have been presented by Pilipenko and co-workers;[1114–1116] at 80 °C, $k_{for} = 0.104\ M^{-1}\ s^{-1}$, $k_{rev} = 36.8\ s^{-1}$, $\Delta H^* = 160\ kJ\ mol^{-1}$,[1114], $K = 2.74 \times 10^3$.[1115]

$$[Rh(H_2O)_6]^{3+} + X \rightleftharpoons [Rh(H_2O)_5X]^{n+} + H_2O \qquad (281)$$

48.6.5.2 The tris(oxalato) ion

First prepared by Werner,[1117] the $[Rh(ox)_3]^{3-}$ ion has an electronic spectrum[1118–1120] consistent with an octahedral RhO_6 chromophore. Interest in the chemistry of this ion was piqued by a suggestion, based on solid state broad-line NMR and dehydration data, that what had been called 'hydrated $K_3[Rh(ox)_3]$' was actually $K_6[Rh(ox)_3][Rh(ox)_2(oxH)(OH)] \cdot 8H_2O$,[1121] with one of the six oxalates acting as a monodentate, and an OH^- in the remaining coordination site. This was challenged by Gillard and coworkers,[1122] who noted that aqueous solutions of $[Rh(ox)_3]^{3-}$ are neutral, the NMR shows no rapidly exchanging protons and the Raman, electronic and CD spectra are virtually invariant between pH 2 and 11. Their differential thermal analysis also did not support the monodentate oxalate model.[1122] A single-crystal X-ray structure showed that in the solid state, $K_3[Rh(ox)_3]$ is a tris-chelated, distorted octahedral complex, but that the K^+ ions are unusually close to the Rh center.[1123] Each K^+ ion is coordinated by seven H_2O molecules, and sits directly above a triangular plane of oxygens of the Rh coordination sphere only 3.48 Å from the rhodium; the earlier suggestion[1121] of a monodentate oxalate ligand was readily explained in terms of this structure.[1123]

The $[Rh(ox)_3]^{3-}$ ion was initially resolved as the strychnine salt,[1117] and more recently by precipitation of $(-)[Co(en)_3](-)[Rh(ox)_3]$.[1124] The CD spectrum of $(+)$-$[Rh(ox)_3]^{3-}$ in a crystal of $NaMgAl(ox)_3 \cdot 9H_2O$ is consistent with a trigonal structure in solution, again inconsistent with the monodentate model.[1125] The slow racemization of $[Rh(ox)_3]^{3-}$ was first noticed by Werner,[1117] and Odell *et al.* have studied the acid-catalyzed racemization;[1126] at 44.6 °C in a 1.0 M $HClO_4$ solution, the rate of racemization is $5.03 \times 10^{-5}\ s^{-1}$ with a ΔE^* of 84 kJ mol^{-1}. Odell did not suggest a racemization mechanism, but noted that the 'rate of racemization increases at a rate greater than the stoichiometric acidity'.[1126]

Reaction of $[Rh(ox)_3]^{3-}$ in refluxing perchloric acid leads to *cis*-$[Rh(ox)_2(H_2O)_2]^-$; subsequent substitutions lead to *cis* and *trans* isomers of $[Rh(ox)_2X_2]^{n-}$ (X = H_2O, Cl^-) which have been characterized by electronic and IR spectroscopy.[1120] Exchange of labelled ox^{2-} ion with $[Rh(ox)_3]^{3-}$ proceeds *via* a three-term kinetic expression, with a neutral path ($k = 6 \times 10^{-6}\ s^{-1}$ at 133.2 °C) as

well as acid- ($k_{H^+} = 1.5 \times 10^{-2}\,M^{-1}s^{-1}$) and base-catalyzed paths ($k_{OH^-} = 1.3 \times 10^{2}\,M^{-1}s^{-1}$).[1127] Replacement of one oxalato ligand by two waters (equation 282) was shown to be acid catalyzed, and presumed to involve a rapid acid–base preequilibrium between the $[Rh(ox)_3]^{3-}$ and $[Rh(ox)_2(mono\text{-}ox)(H_2O)]^{3-}$. A related study[1128] found $\Delta H^* = 113\,kJ\,mol^{-1}$ for equation (282).

$$[Rh(ox)_3]^{3-} + 2H_2O \longrightarrow [Rh(ox)_2(H_2O)_2]^{-} + ox^{2-} \quad (282)$$

A series of reports by Milburn and coworkers[660–662,1129] has given a convincing model for the reactivity of $[Rh(ox)_3]^{3-}$. The acid-catalyzed exchange of oxygen atoms (between solvent water and the coordinated oxalato ligands) has been studied for a variety of complexes ($[M(ox)_3]^{3-}$ for M = Co, Cr and for $[Pt(ox)_2]^{2-}$) and in each of these cases all 12 (or eight for Pt) oxygen atoms exchange at indistinguishable rates. For $[Rh(ox)_3]^{3-}$, however, half of the oxygens exchange more rapidly than the other half.[660] The outer oxygens (the more rapidly exchanging, uncoordinated atoms) exchange at a rate similar to those of $[Pt(ox)_2]^{2-}$ and $H(ox)^-$.[661] The rates of inner-oxygen exchange and racemization (of $[Rh(ox)_3]^{3-}$) are also similar.

A comprehensive study[662] of the kinetics of racemization and aquation of $[Rh(ox)_3]^{3-}$ showed that both racemization and aquation proceed by two-term rate laws:

$$\text{Rate of racemization} = \{k_{r2}[H^+] + k_{r3}[H^+]^2\}\{[Rh(ox)_3]^{3-}\}$$

$$\text{Rate of aquation} = \{k_{a2}[H^+] + k_{r3}[H^+]^2\}\{[Rh(ox)_3]^{3-}\}$$

Activation parameters for these reactions, and for inner-oxygen exchange, are given in Table 84. The similarity in the rate of inner-oxygen exchange and the second-order racemization term (k_{r2}) suggests parallel mechanisms. The racemization is significantly faster than the aquation (at 56 °C, when 50% of the ions have racemized, only 3% have aquated), and the rate order for the four processes is: outer-oxygen exchange > inner-oxygen exchange ≈ racemization > aquation. This is rationalized in Scheme 39 in which outer-oxygen exchange (steps 1 and 2) does not require ring-opening before exchange, and thus should not be very sensitive to the nature of the metal; the similarity of exchange rates for Rh^{III}, Pt^{II} and H^+ oxalates supports this. Odell's observation[1126] that the rate of racemization increases at a rate greater than the stoichiometry is also rationalized by this scheme.[662]

The one-electron oxidation of $[Rh(ox)_3]^{3-}$ by Ce^{4+} in sulfuric acid solution (1 M) is two orders of magnitude slower than the analogous reaction of $[Cr(ox)_3]^{3-}$, but there are many similarities.[1129] The first step is presumed to be oxidation of coordinated oxalate to the ox^- radical anion, followed by the formation of (presumably *cis*) $[Rh(ox)_2(H_2O)_2]^-$, Ce^{III} and two equivalents of CO_2. A transition state with an oxalate acting as a bridge between Rh and Ce (with bidentate linkages to both metals) was proposed, but is not supported by the large (positive) entropy of activation for the reaction ($\Delta S^* = +146\,J\,K^{-1}\,mol^{-1}$; $\Delta H^* = 136\,kJ\,mol^{-1}$).[1129]

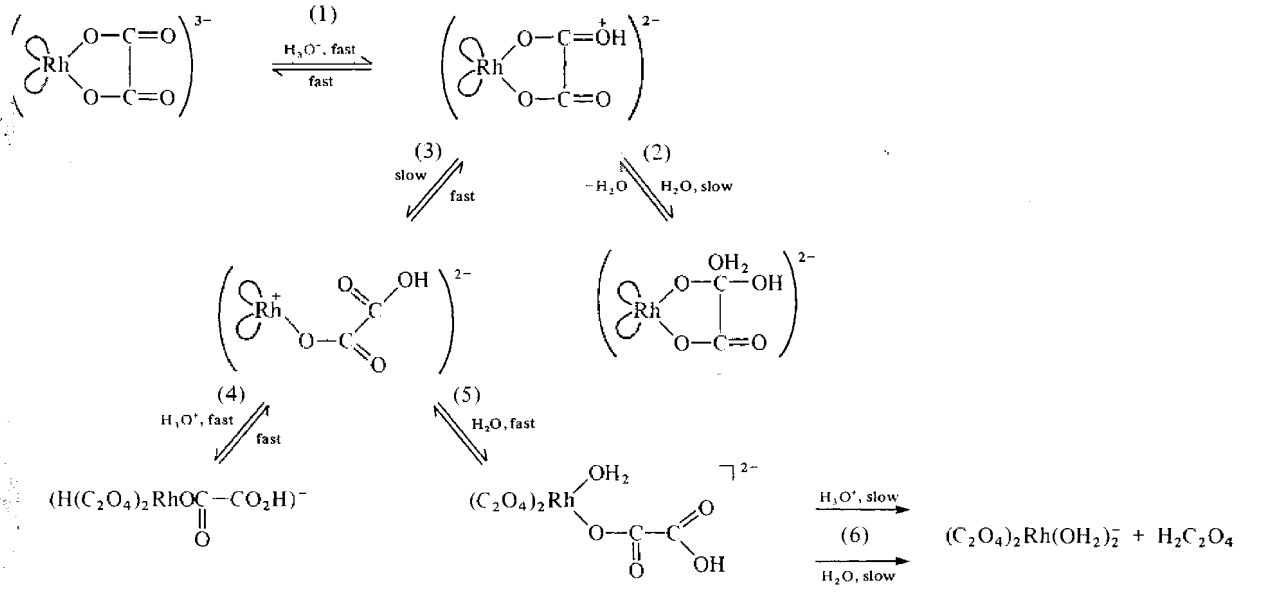
48.6.5.3 Acetylacetonato complexes

The neutral $[Rh(acac)_3]$ complex was first prepared by reacting $Rh(NO_3)_3$ with acetylacetone in an aqueous (pH 4) solution;[1130] the $[Rh(hfacac)_3]$ and $[Rh(tfacac)_3]$ (hfacac = hexafluoroacetylacetonate; tfacac = trifluoroacetylacetonate) analogs were later prepared in a similar manner.[1131] These complexes are extremely stable, as $[Rh(acac)_3]$ can be recovered unchanged from boiling dilute acid, cold concentrated sulfuric acid, and from 10% caustic soda solutions. The pseudo aromaticity of the chelate rings is demonstrated by the NMR of the ring proton (4.4τ), and by the nitration (using hydrated $Cu(NO_3)_2 \cdot 3H_2O$/acetic anhydride solutions) and monoformylation (using $POCl_3$ in dry DMF) of the chelated rings.[1131] The nitrated species is resistant to reduction,

Table 84 Activation Parameters for Reactions of $[Rh(ox)_3]^{3-}$

Reaction	*Term*[a]	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	*Ref.*
Racemization	k_{r2}	97.5 ± 6.3	−34.3 ± 17	662
	k_{r3}	112.1 ± 6.3	+24.3 ± 17	662
Inner-O exchange	—	97.9 ± 8.4	−26.4 ± 25	660
Aquation	k_{a2}	106.7 ± 8.4	−32.6 ± 25	662
	k_{a3}	108.4 ± 8.4	−12.1 ± 25	662

[a] Labeled terms given in text.



Scheme 39

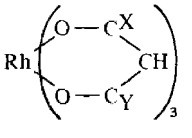
as an acidic tin(II) chloride solution leaves the nitro function unaltered, while reaction with Zn/HAc causes decomposition.[1131] IR studies of the adducts $[Rh(acac)_3]\cdot 2(urea)$ and $[Rh(acac)_3]\cdot 3(thiourea)$ indicate that the urea and thiourea are not directly bonded to the rhodium, and that hydrogen bonding is important in the structure of the urea, but not the thiourea, adduct.[1132]

If the reaction between hydrated $RhCl_3$ and hfacac is carried out in dry ethanol, two different species (brown-yellow and red sublimates) of the composition $\{RhCl(hfacac)_2(H_2O)_3\}$ can be separated. While their insolubility makes study difficult, they were assumed to be the two possible geometric isomers of the doubly chloro-bridged dimer $[(hfacac)_2Rh(\mu\text{-}Cl)_2Rh(hfacac)_2]$.[1133]

Electron impact ionization potentials of successively substituted acac complexes $[Rh(acac)_n(3\text{-}NO_2acac)_{3-n}]$ ($n = 1$, 2 or 3) has shown that the first ionization potential is linearly related to the number of nitro substituents, increasing as the number of NO_2- substituted acac ligands increases. The authors argue that such a monotonic relationship implies that ionization occurs from a metal-centered orbital, rather than from the highest filled orbital on any of the ligands.[1134] Ionization from a metal-centered orbital is unexpected, as the lowest energy electronic transitions for these complexes have been assigned to ligand-centered π–π^* transitions (unlike the metal-centered *d*–*d* transitions observed for the analogous Co^{III} and Cr^{III} complexes),[1135] and luminescence of $[Rh(acac)_3]$ occurs from the ligand dominated $\pi^* \rightarrow \pi$ transition.[1136] (Rogerson does note that ionization from ligand orbitals could be rationalized if a delocalized ring model is used.[1134])

Reaction of the dioxygen adduct of $[RhCl(PPh_3)_3]$ with Hacac in room temperature benzene leads to a hydroperoxo complex of Rh^{III}, identified as $[Rh(PPh_3)_2(OOH)Cl(acac)]$. In the presence of triphenylphosphine, triphenyl phosphite is released, with the formation of $[Rh(PPh_3)_2(OH)\text{-}Cl(acac)]$, with *trans* phosphines (geometries were determined by ^{31}P NMR).[1137]

Morris *et al.* have presented an interesting study of the ion dissociation reactions of the molecular ions of $[Rh(acac)_3]$ and fluorinated analogs (**125**) (despite the article's title, which identifies Rh as rhenium).[1138] The ion reactions are surprisingly sensitive to changes in ligand composition. For $[Rh(hfacac)_3]$ over 60% of the metal-containing ions are in the successively formed $Rh(hfacac)_3^+$, $Rh(hfacac)_2^+$ and $Rh(hfacac)^+$ ions. The $Rh(hfacac)^+$ ion is formally a Rh^{II} species, and unlike the Co analog,[1139] it is reduced further, generating numerous Rh^I ions (*e.g.* $Rh(CO)^+$, $RhCF_3^+$). In sharp contrast, $Rh(tfacac)_2^+$ is the base peak in the mass spectrum of the trifluoro analog $[Rh(tfacac)_3]$ and undergoes virtually no reduction to Rh^{II} or Rh^I species. For the unfluorinated $[Rh(acac)_3]$, an ion reaction pattern similar to that of $[Rh(hfacac)_3]$ is observed.



$[Rh(acac)_3]$ Y = X = Me
$[Rh(tfacac)_3]$ X = Me, Y = CF_3
$[Rh(hfacac)_3]$ X = Y = CF_3

(125)

Unlike fluorinated acac complexes of most other metals, there is no evidence of F^- migration to the metal in either of these fluorinated acac complexes of Rh^{III}, but methyl migration does occur in the decomposition of $[Rh(acac)_3]$. Morris comments that Rh is the only example of the metals so far investigated that shows such sensitivity to changes in the ligand composition. When compared to their ruthenium analogs, the authors conclude that bonds to rhodium appear to be more easily broken and formed, an important aspect of the well-known catalytic activity of rhodium.[1138]

Photolysis of $[Rh(tfacac)_3]$ (tfacac is the unsymmetrically substituted 1,1,1-trifluoromethyl-acac) reveals the existence of two photoinduced reaction paths; the relative efficiency of the two paths is dramatically solvent dependent.[1140] In cyclohexane, *mer* → *cis* isomerization is the only observed photoreaction, but if ethanol or 2-propanol is added to the solvent, the photoisomerization efficiency decreases, and photodecomposition occurs. The nature of the photodecomposition products is not specified, but the enhanced photoreactivity in the presence of tri(*n*-butyl)stannane, a hydrogen atom donor, and flash and continuous photolysis studies in mixed-solvent systems 'strongly implicate hydrogen atom abstraction from the solvent as a key step in the photodecomposition of *mer*-$[Rh(tfacac)_3]$ and suggests that the photoreactive states have considerable radical character'.[1140] Analysis of quantum efficiencies implies that at least two distinct photoproduced excited states must be involved.

48.6.5.4 Dioxygen complexes

Complexes containing the Rh—O_2 moiety are now well known, but there have been a few false starts and misunderstandings along the way. The first claim for an O_2 complex of rhodium was made by Wilkinson and co-workers,[1141] who reported that $[Rh(H)(CN)_4(H_2O)]^{2-}$ reacted with O_2 to give the peroxide-bridged dimer $[(H_2O)(CN)_4Rh—O_2—Rh(CN)_4(H_2O)]^{4-}$. This was later disputed, and the reaction product identified as the protonated, peroxo monomer of Rh^{III}, $[Rh(O_2H)(CN)_4(H_2O)]^{2-}$.[1142] The solid is diamagnetic, and displays O—O stretches at 839 and 825 cm^{-1}, characteristic of an unsymmetric monomer; no such bands appear in the Co–peroxo dimer.[1142]

Reaction of $[Rh(py)_4Cl_2]Cl \cdot 5H_2O$ with O_3 (in O_2) in alkaline ethanol leads to solutions which pass through yellow-orange to green to deep blue.[1143] Addition of perchloric acid and recrystallization from conc. HCl leads to deep blue crystals identified as the superoxo-bridged dimer $[Cl(py)_4Rh—O_2—Rh(py)_4Cl](ClO_4)_3$. Variations on this theme are possible, as analogs have been prepared in which the N-heterocycle is pyridine, 4-methylpyridine or picoline; if the reaction is run in base, chloride is replaced by OH^- (or H_2O, depending on the pH). The dimers are paramagnetic, and have low energy electronic transitions characteristic of O_2^-. They are strong one-electron oxidants in H_2O, and reaction with I^- and Fe^{2+} leads to the peroxo-bridged dimer; the superoxo species is not oxidized by MnO_4^-, Cl_2 or Ce^{4+}, consistent with its assignment as a superoxo species.[1143] The analogous $[Cl(bipy)_2Rh—O_2—Rh(bipy)_2Cl](ClO_4)_3$ has been prepared by the reaction of $[Rh(bipy)_2]ClO_4$ with O_2 and Cl_2 in MeCN solution.[1144] The superoxo assignment is supported by an ESR spectrum showing $S = \frac{1}{2}$ with g factors virtually identical to those of the analogous Co^{III} complexes.[1145]

Photolysis of *cis*-$[Rh(en)_2(NO_2)_2]^+$ in the presence of O_2 leads to a red species, identified as the monomeric superoxo cation $[Rh(en)_2(NO_2)(O_2)]^+$, isolated as the chloride or nitrate salt.[1146] Elemental analyses were not presented, but electronic spectra show a low-energy charge-transfer transition (485 nm) characteristic of the superoxo ligand, and the Raman spectrum shows an O—O stretch at 1052 cm^{-1}. The *cis* isomer is much more reactive than the *trans*, and in the presence of Rh^{III} aqua species, the red-brown monomer reacts to form the familiar blue or purple dimers, $[X(en)_2Rh—O_2—Rh(en)_2X]^{n+}$ (X = Cl^-, NO_2^-, or H_2O). The ESR spectra of a variety of these complexes are consistent with the superoxo assignment.[1147] A molecular-orbital-based bonding model suggests that the unpaired electron is in a π^* orbital located largely on the O_2, consistent with the $[Rh^{III}—O_2^-]$ designation, and with the tendency of the monomeric species to dimerize.[1147]

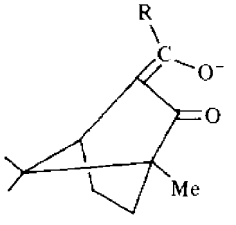
Reaction of $[Rh(CO)_2Cl]_2$ with tetraphenylporphyrin (TPP) in glacial acetic acid generates a material identified as '[Rh(TPP)]' and the authors state that they found 'no evidence . . . for the formation of oxygen complexes . . .'.[862] This was questioned by Wayland and Newman[864] who found that octaethylporphyrin (OEP) formed a monomeric Rh^{III} superoxo complex $[Rh(OEP)(O_2)]$. Its spectral and chemical properties strongly support the superoxo designation; reexamination of the TPP complex implied that the previously identified Rh^{II} complex [Rh(TPP)] is actually the Rh^{III} superoxo complex $[Rh(TPP)(O_2)]$.[864] Dioxygen (in air) reacts with the (presumably) Rh^{II} dimers

$[Rh(L)]_2$ (L = the tetradentates, salen, salpn or saloph — see Section 48.6.4.1) to form paramagnetic (μ_{eff} = 1.80 BM at room temperature) hyperoxo–Rh^{III} complexes.[414]

48.6.5.5 Miscellaneous oxygen ligands

Solid rhodium sesquioxide, Rh_2O_3, was first identified in 1927,[1148] and has the corundum structure[1149] (hexagonally close packed O^{2-} anions distorted by the presence of Rh^{3+} cations in $\frac{2}{3}$ of the octahedral interstices). Each Rh is surrounded by six oxygens, three at 2.03 Å and three at 2.07 Å. An orthorhombic phase forms above 750 °C.[1150]

There are two examples of chiral O—O chelates (camphor derivatives) which form neutral [Rh(O—O)$_3$] complexes. Reaction of $RhCl_3 \cdot 3H_2O$ with the β-keto aldehyde (+)-hydroxymethylenecamphorate (+hmc; **126a**) in refluxing benzene leads to the two *fac* diastereoisomers D-(−)-[Rh(+hmc)$_3$] and L-(+)-[Rh(+hmc)$_3$],[1151] separable on an alumina column, and characterized by NMR, ORD/CD and UV/visible spectra. Unlike the Co^{III} analog, no *mer* isomers were detected. When $RhCl_3 \cdot 3H_2O$ is suspended in a hot, alkaline solution of (+)-3-acetylcamphorate (+atc; **126b**) for 20 h, four diastereomers (both Δ and Λ forms of both the *mer* and *fac* isomers) of [Rh(+atc)$_3$] were separated *via* silica gel plate chromatography, and identified by NMR, ORD/CD and UV/visible spectroscopy.[1152]



(**126**) **a**: R = H, (+)-hydroxymethylenecamphorate (+hmc)
b: R = Me, (+)-3-acetylcamphorate (+atc)

Several complexes with DMSO ligands have been prepared,[1153–1155] and IR spectra and the ease of formation of $[Rh(DMSO)_2Cl_4]^-$ in Cl^- saturated aqueous solution led to the suggestion that $[Rh(DMSO)_6](BF_4)_3$ has four O-bonded and two S-bonded DMSO ligands.[1154] An X-ray structure of $[RhCl_3(DMSO)_3]$ (prepared by DMSO substitution at *trans*-$[Rh(DMSO)_2Cl_4]^-$) shows that two of the DMSO ligands are S-bonded, while the third is bonded through its oxygen atom.[1155] The chlorides in $[RhCl_3(DMSO)_3]$ lie along a meridional edge, with the two S-bonded DMSO ligands in mutually *cis* sites, in contrast to a calculation which indicated that mutual repulsion would prevent mutually *cis* S-bonded DMSO ligands.[1156]

A study of the thermodynamics and kinetics of the reaction between $[Rh(H_2O)_6]^{3+}$ and the NpO_2^+ ion (equation 283) found an equilibrium constant of 3.31 ± 0.06 at 25 °C ($\Delta H = -15.0 \pm 3.8$ kJ mol^{-1}; $\Delta S = -42 \pm 13$ J K^{-1} mol^{-1}).[1157] In the presence of excess Rh^{III} the reaction is pseudo first order in $[NpO_2^+]$ ($\Delta H^* = 114 \pm 4$ kJ mol^{-1}; $\Delta S^* = 36 \pm 4$ J K^{-1} mol^{-1}). The reaction is also first order in F^- ion, but the role of the fluoride ion is not understood. Fluoride ion does not catalyze water exchange at $[Rh(H_2O)_6]^{3+}$, and the rate of formation of $[ONpORh(H_2O)_5]^{4+}$ is twice as fast as the rate of H_2O exchange at the hexaaqua ion, so it is unlikely that a dissociative ligand exchange is rate-determining in the dissociation of $[ONpORh(H_2O)_5]^{4+}$.[1157] Mössbauer spectroscopy of the ^{237}Np nucleus in the product shows that the Np is in the 5+ oxidation state, is not magnetically split by the Rh atom and that the neptunyl ion maintains its axial symmetry, supporting the suggestion that an oxygen atom of NpO_2^+ simply replaces a water in the inner coordination sphere of the Rh^{III}.[1154] The presence of the actinide gives $[ONpORh(H_2O)_5]^{4+}$ a rich electronic spectrum, but formation of the Np—O—Rh linkage hardly changes the IR and electronic spectra observed in the separate NpO_2^+ and $[Rh(H_2O)_6]^{3+}$ moieties.

$$[Rh(H_2O)_6]^{3+} + O{-}Np{-}O^+ \rightleftharpoons [O{-}Np{-}O{-}Rh(H_2O)_5]^{4+} + H_2O \qquad (283)$$

In an effort to use $[Rh(H_2O)_6]^{3+}$ as a redox-stable, diamagnetic probe, its reactivity with a variety of polyphosphates has been explored.[1159,1160] Several complexes of the form $[Rh(H_2O)_4(PP)]^{n-}$ (PP = $2PO_4^{3-}$, $HP_2O_7^{3-}$, $HP_2O_8^{5-}$, ADP or ATP) have been prepared, and characterized by electronic spectroscopy.[1160] The potential tridentate $H_2P_3O_{10}$ (PPP) is reported to form $[Rh(H_2O)(PPP)]$.[1160]

48.6.6 Sulfur and Heavier Group VI Ligands

48.6.6.1 Monodentate sulfur ligands

Alkyl and aryl sulfides coordinate to Rh^{III}. Dwyer and Nyholm first reported that refluxing aqueous ethanolic solutions of $RhCl_3 \cdot 3H_2O$ and diethyl sulfide leads to the neutral $[RhCl_3(Et_2S)_3]$.[1161] The tribromo and triiodo analogs were also reported; all three complexes are prone to dissociation of the sulfide ligand, as they smell of diethyl sulfide, and cryoscopic measurements in benzene consistently gave less than the theoretical molecular weight values. A study of their dissociation pressures showed that the stability of the Rh—S bond is greatest for the trichloro, and weakest for the triiodo complex.[1162] They are diamagnetic monomers, electronic spectra (ethanol solutions) have been recorded, and X-ray powder patterns show that they are similar to the Ir analogs,[1163] and thus were assigned the *mer* geometry.[1162] Reaction of $[RhCl_3(R_2S)_3]$ (R = Me, Et, Pr) with bipyridyl has led to *fac*- and *mer*-$[Rh(bipy)(R_2S)Cl_3]$ (R = Pr), while reaction with pyridine has generated *fac* and *mer* isomers of $[Rhpy(R_2S)_2Cl_3]$ (R = Me, Et).[1164] Walton prepared complexes of the form $[RhX_3(C_4H_8OS)_3]$ (X = Cl or Br, and C_4H_8OS is the cyclic 1,4-thioxane) and characterized them by far-IR, IR, NMR and electronic spectroscopy.[1165] The far-IR spectra imply a *fac* geometry.

Initial loss of a labile sulfide group is thought to be the first step in the catalytic reactions of $[RhCl_3(Et_2S)_3]$. In a basic solvent (which promotes sulfide labilization) it catalyzes the homogeneous hydrogenation of various alkenic substrates.[1166] The kinetics of the hydrogenation of *trans*-cinnamic acid or maleic acid using $[RhCl_3L_3]$ (L = Et_2S or $(PhCH_2)_2S$) as catalysts have been interpreted to suggest a path involving initial loss of a sulfide, followed by reaction of the coordinatively unsaturated Rh^{III} complex with H_2 and reduction to Rh^I.[1166,1167] The intermediacy of a Rh^{III} hydride was also postulated.

Initial dissociation of a NCS^- ligand is also thought to lead to the electrochemically active $[Rh(SCN)_5]^{2-}$ ion. One irreversible reduction wave ($E_{1/2} = -0.36$ V *vs.* SCE) was observed in a polarographic study of Rh^{III} in aqueous NCS^- solution, but the system was complicated by poisoning of the DME due to catalytic decomposition of SCN^- and sulfate formation.[1168]

Refluxing $RhCl_3 \cdot 3H_2O$ with a variety of alkyl phenyl sulfides (PhSR for R = Me, Et, Pr^n, Bu^n) in methanol is a straightforward path to both isomeric forms of $[RhCl_3(PhSR)_3]$.[1169] The *mer* forms have been characterized in all four cases, and the *fac* form was cleanly characterized for R = Et and Pr^n; reaction of LiBr (in acetone) with *mer*-$[RhCl_3(PhSEt)_3]$ leads to *mer*-$[RhBr_3(PhSEt)_3]$. The trisulfide, $MeC(CH_2SEt)_3$ reacts with $RhCl_3 \cdot 3H_2O$ in refluxing ethanol to give *fac*-$[RhCl_3\{MeC(CH_2SEt)_3\}]$.[1169]

48.6.6.2 Sulfur chelates

(*i*) *Four-membered rings*

Stimulated by an interest in determining the position of sulfur in the spectrochemical series, Jørgensen prepared and studied the electronic spectra (Table 85) of $[Rh(dtp)_3]$ and $[Rh(dtc)_3]$ (dtp = $(EtO)_2PS_2^-$: dtc = $Et_2NCS_2^-$).[1177] The complexes were prepared by heating an aqueous solution of $RhCl_3 \cdot 3H_2O$ with the sodium salt of the ligand; the addition of a small amount of ethanol to the solution (see Section 48.6.2.5.iii) allows the reaction to proceed at room temperature and yields a cleaner product.

A series of metal dithiocarboxylates (RCS_2^-), including $[Rh(dtb)_3]$, $(NH_4)[Rh(dtb)_2Cl_2]$ and $[Rh(dtpa)_3]$, has been characterized by magnetic measurements, molecular weight determinations and electronic spectra.[1174] Because of the strong intraligand bands, characteristic of dithiocarboxylates, they display rich electronic spectra (Table 85), but the low energy transitions could be assigned to the transitions expected for a high-field, d^6 Rh^{III} center in an octahedral environment. The syntheses involve the straightforward reaction of Rh^{III} salts with the Na salt of the ligand, but of the numerous metals studied, Rh is unique in that the nature of the resulting (dtb) complex depends on the nature of the Rh^{III} starting material. If $RhCl_3 \cdot 3H_2O$ is used, $[Rh(dtb)_3]$ forms, but if $[RhCl_6]^{3-}$ reacts under virtually the same conditions, the product is $[Rh(dtb)_2Cl_2]^-$.[1174]

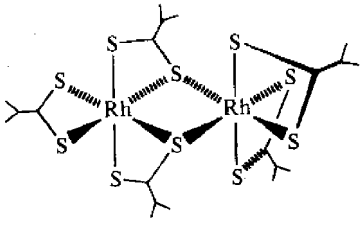
The N,N-disubstituted dithiocarbamate ligand ($R_2NCS_2^-$) stabilizes high oxidation states of the some first row transition metals, and BF_3 oxidation of $[Rh(Me_2NCS_2)_3]$ was reported to lead to the Rh^{IV} cation.[1178] This was questioned by Hendrickson *et al.*, who showed that the product is actually the dimeric cation $[Rh_2(Me_2NCS_2)_5]^+$.[1179] Characterization was by conductivities, IR and NMR spectroscopy and by a single crystal X-ray structure of $[Rh_2(Me_2NCS_2)_5]BF_4 \cdot 0.5CH_2Cl_2$. The

Table 85 Electronic Spectra of some Sulfur Complexes of Rhodium(III)[a]

Compound	λ_{max} (nm) (ε)	*Ref.*
$[RhSCN)_6]^{3-}$	515sh, 290	1170
$[Rh(SeCN)_6]^{3-}$	305, 262	1171
	304 (26400), 262 (20200)	1172
$[RhCl(C_4H_8OS)_3]$	424sh, 346, 274, 219	1165[b]
	422sh (< 100), 358sh (< 580), 285 (2910), 232 (1930)	1165[c]
$[RhBr_3(C_4H_8OS)]$	490, 373, 260, 221	1165[b]
trans-$[Rh(dth)_2Cl_2]^+$	431 (190), 354 (300), 266, 219	1165
trans-$[Rh(dth)_2Br_2]^+$	455, 366, 263, 227	1165
$[NEt_4][Rh(dth)Cl_4]$	460sh, 405 (692)	1173
$[Rh(dtb)_3]$	510sh (912), 472sh (1900), 391 (6600), 334 (16200), 306 (17400)	1174[d]
$[Rh(dtb)_2Cl_2]^-$	535 (1320), 510 (1410), 426 (3800), 360 (9120), 328 (43700)	1174[d]
$[Rh(dtpa)_3]$	420sh (3020), 382 (5370), 320sh (14500), 291sh (29500), 260 (63100)	1174
$[Rh(sacsac)_3]$	526 (19000), ~240 (~81000)	1175[e]
cis-$[Rh(TTP)Cl_2]Cl$	350 (2270), 320sh (1900), 252 (26950)	1176
cis-$[Rh(TTX)Cl_2]Cl$	350 (1935), 255 (20300)	1176
cis-$[Rh(TTP)Br_2]Br$	370 (2180), 245 (24150)	1176
cis-$[Rh(TTP)I_2]I$	405 (2460), 320 (8550)	1176
$[Rh(dtp)_3]$	470 (1090), 410 (780), 321 (12600), 273sh (18000), 258 (23200), 227sh (8000)	1177
$[Rh(dtc)_3]$	423, 282, 252, 226	1177

[a] Ligand abbreviations in text. [b] Diffuse reflectance spectrum. [c] In MeCN solution. [d] In $CHCl_3$ solution. [e] In CCl_4 solution.

cation consists of a $[Rh(Me_2NCS_2)_2]^+$ unit coordinated to an octahedral $[Rh(Me_2NCS_2)_3]$ unit through two mutually *cis* sulfur atoms (**127**). The two Rh atoms have opposite absolute configurations, and the long Rh—Rh distance (3.556 Å) indicates that there is no significant metal–metal bonding.[1179] The structure is similar to that of the Co^{III} analog,[1180] but is in sharp contrast to the $[Ru(Et_2NCS_2)_5]^+$ cation, which has two distinct types of bridging dithiocarbamates and a short Ru—Ru distance.[1181]



(127)

Reaction of 'commercial rhodium trichloride' with HS_2PF_2 (solvent unspecified) leads to a sublimate identified as $[Rh(S_2PF_2)_3]$.[1182] A diamagnetic, red-orange solid, it is monomeric in the gas phase. While one of the least reactive of the difluorodithiophosphate metal complexes, it is rapidly hydrolyzed in air. IR analysis implies that the ligands are chelated. Red crystals of $[Rh(S_2PPh_2)_3]$ can be isolated after refluxing rhodium trichloride and diphenyldithiophosphate in $CHCl_3/CCl_4$ solution.[1183]

(*ii*) *Five-membered rings*

Complexes of the form $[Rh(S—S)_2X_2]Y$ (X = Cl, Br; Y = Cl, ClO_4, $0.5S_2O_8$, PF_6 or BPh_4), involving two different S—S bidentate [S—S = 2,5-dithiahexane (dth), $MeSCH_2CH_2SMe$ or 1,2-di(phenylthio)ethane ($PhSCH_2CH_2SPh$)] have been characterized.[1165] The methyl-substituted complexes $[Rh(dth)_2X_2]^+$ are water soluble and insoluble in organic solvents, while the phenyl derivatives are soluble in MeCN and $MeNO_2$; electronic spectra imply both complexes have the *trans* geometry. An incompletely characterized, very insoluble complex of the composition $[Rh(dth)Cl_3]$ was also isolated, and is assumed to be a dichloro-bridged dimer. These dithiahexane complexes

have resisted spirited efforts (both chemical and electrochemical) to oxidize the rhodium center to the 4+ oxidation state. Both $[Rh(dth)_2]BF_4$ and $[Rh(dth)Cl_3]_n$ are unaffected by Cl_2 in chloroform or by Ce^{4+}; $[Rh(dth)Cl_4]^-$ could not be oxidized by Cl_2 or by cyclic voltametry.[1173]

The dynamics of inversion at coordinated sulfur have been studied by variable temperature ^1H NMR for a series of 2,5-dithiahexane complexes, including $[Rh(dth)X_4]^-$ (X = Cl, Br).[1184] At room temperature in DMSO-d^6, the $[Rh(dth)Cl_4]^-$ ion displays two NMR peaks due to the SMe groups in the *meso* and the (±) isomers; as the temperature increases, the peaks broaden and coalescence occurs at 100 °C. An interfering reaction occurs in DMSO (equation 284), resulting in dimeric $[Rh_2(dth)_2Cl_6]$. Detailed interpretation of the NMR of this material was not done (five possible geometric isomers), but a *trans* geometry was assumed. The ΔG^* of coalescence for $[Rh(dth)X_4]^-$ (X = Cl, Br) and $[Rh(dth)_2Cl_6]$ are identical, within experimental error (87.3, 85.5 and 85.3 kJ mol^{-1}, respectively).[1184]

$$[Rh(dth)Cl_4]^- \xrightarrow[-Cl^-]{+DMSO} [Rh(dth)(DMSO)Cl_3] \longrightarrow 0.5[Rh_2(dth)_2Cl_6] + DMSO \qquad (284)$$

The crystal structure of tris-(*S*-methylene-1,2-dithiolato)rhodium(III) ($[Rh(S_2C_3H_5]$) shows it to be octahedral with no intraligand S–S interactions in the chelated ligands.[1185]

(*iii*) *Six-membered rings*

The dithio derivative of acetylacetone (sacsac) forms a neutral, diamagnetic monomer with Rh^{III}. The synthesis of $[Rh(sacsac)_3]$ requires the substitution of sulfur for oxygen in (presumably) coordinated acac ligands (the sacsac ligand has not been isolated in the monomeric state), and is accomplished by bubbling H_2S through an ethanol/HCl solution of $RhCl_3 \cdot 3H_2O$ and acetylacetone at 0 °C.[1175] The resulting $[Rh(sacsac)_3] \cdot 0.5\,Me_2CO$, in the form of red needles, is stable up to 250 °C, and shows two ^1H NMR signals in a 1:6 ratio (ring proton at 6.95 and the six methyl protons at 2.36 δ). Unlike its Fe^{III}, Ru^{III} and Os^{III} analogs, which all undergo a reversible one-electron reduction near 0 V (*vs.* Ag/AgCl), $[Rh(sacsac)_3]$ undergoes an irreversible two-electron reduction at −1.05 V (*vs.* Ag/AgCl).[1186] A single crystal X-ray structure confirmed that the complex is monomeric, and that the large cavities in the lattice are suitable to hold the acetones of crystallization (the acetones were not found in the crystal structure, however).[1187] The complex is a distorted octahedron, with intraligand S—Rh—S angles near 97°, and non-planar chelate rings.

The unsymmetrically substituted dithioacac ligand, *O*-ethylthioacetothioacetate (*O*-Etsacsac), reacts with an ethanolic solution of $RhCl_3 \cdot 3H_2O$ to form $[Rh(O\text{-Etsacsac})_3]$. The orange-red complex is kinetically stable, and its IR and far-IR spectra suggest an octahedral complex with three bidentate ligands in a *fac* geometry.[1188] The authors argue that the position of the methine proton in the NMR spectrum of $[M(sacsac)_3]$ (or an *O*-Etsacsac analog) is not a valid measure of the degree of aromaticity in the chelate ring. A comparison of complexes for a variety of metals shows that the chemical shift of the methine proton is linearly related to the metal's *d* shell population, the molecular geometry, and the nature of the substituent, but is not a reliable measure of the pseudo aromaticity of the sacsac chelate ring.[1188]

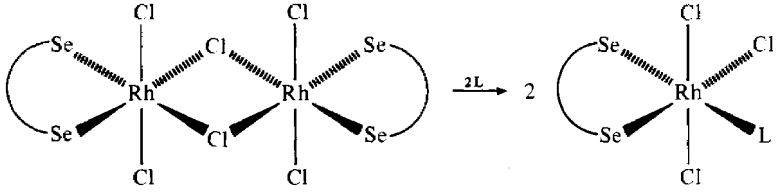
(*iv*) *Cyclic polysulfides*

The cyclic, tetradentate thioether (TTP = 1,4,8,11-tetrathiacyclotetradecane) reacts with $RhX_3 \cdot 3H_2O$ in boiling ethanol to generate $[Rh(TTP)X_2]X$ (X = Cl, Br).[1178] If LiI or $LiNO_2$ is added to the $RhCl_3 \cdot 3H_2O$ solution before the addition of the TTP, the corresponding diiodo or dinitro cations were formed. The complexes are 1:1 electrolytes in $MeNO_2$, and display IR and electronic spectra (Table 85) consistent with a *cis* geometry. The ligand field splitting of the sulfur ligands is comparable to the analogous macrocyclic amines. If the ethanol used in the preparation is not boiling, an insoluble material of the composition $[Rh(TTP)Cl]_xCl_{2x}$ forms, presumably a polymer or a chloro-bridged dimer.[1176]

48.6.6.3 Miscellaneous group VI ligands

The thiocyanate and selenocyanate ions (SCN^- and $SeCN^-$) react with $RhCl_3 \cdot 3H_2O$ to form $[RhX_6]^{3-}$ anions.[1170–1172] Both the SCN^- and the $SeCN^-$ are chalcogen-bonded, consistent with the soft character of the Rh^{III} in many complexes.

Two different selenium-containing bidentates have been coordinated to Rh^{III} centers. Reaction of 1,2-diselenocyanatoethane (Se_2E = $SeCNCH_2CH_2NCSe$) with $RhCl_3 \cdot 3H_2O$ in refluxing acetone/ethanol (1:1) solution generates a diamagnetic dimer $[Rh_2(Se_2E)_2Cl_6]$. It is non-conducting in DMSO, and reacts with *p*-toluidine (L) in refluxing MEK to give the diamagnetic monomer $[Rh(Se_2E)(Cl)_3(L)]$ (equation 285).[1189] IR spectra show the ν_{CN} of the $SeCN^-$ is hardly affected by coordination to the Rh^{III}, implying that Se_2E is acting as a bidentate selenium donor. Reaction of $RhCl_3 \cdot 3H_2O$ with the dipotassium salt of 1,1-dicyano-2,2-diselenoethene $(KSe)_2C{=}C(CN)_2$ in aqueous solution containing $(Ph_4P)Cl$ causes precipitation of red 'semi-solid masses', identified as the monomeric $[Ph_4P]_3[Rh\{Se_2C_2(CN)_2\}_3]$, with an octahedral Rh^{III} surrounded by three diselenolate dianionic bidentates.[1190] Conductance measurements indicate it is a 3:1 electrolyte in acetone, but attempts to recrystallize this salt caused decomposition and the formation of solid diselenides.



(285)

Collman and co-workers have presented synthetic routes to a variety of thiolato and selenido complexes of Rh^{III} with the heavy atoms covalently bonded in a linear array; one-dimensional, soluble polymers with a heavy-atom backbone surrounded by organic ligands—complexes which should have unusual electrical properties—are the ultimate goal.[1191] Oxidative addition of diphenyl diselenide to the very reactive square planar Rh^I complex [difluoro-3,3′-(trimethylenedinitrolo)bis(2-pentanone oximato)borate]Rh^I (abbreviated as $[RhL_4]$)[1192,1193] leads to *trans*-$[RhL_4(SePh)_2]$.[1194] A single-crystal X-ray structure shows the phenyl selenides are both bonded to the Rh^{III} through the Se atoms, and are *trans* to each other. Numerous complexes, including *trans*-$[RhL_4X_2]$ (where X = HS, $SGeEt_3$, $SeGeEt_3$ and the monothiol *trans*-$[RhL_4(H)(HS)]$, have also been characterized.[1191]

48.6.7 Hexahalo and Aquahalo Complexes

First reported in 1951, $K_3[RhCl_6]$ was prepared by mixing 'previously ignited NaCl' with finely ground Rh in a combustion furnace at 750 °C while Cl_2 was passed through the mixture.[1195] Work-up in aqueous HCl led to a solution which contained the $[RhCl_6]^{3-}$ ion. This octahedral ion undergoes consecutive aquations in acidic aqueous solution (*vide infra*), but it is unusually photoinert for a Rh^{III} complex. The quantum yield for aquation of the low-energy ligand field band (518 nm) is 0.02, an order of magnitude less than the higher ligand field strength amine complexes.[1196] Raman spectral studies of the analogous $[RhBr_6]^{3-}$ ion show that the ion has an octahedral ground state,[1197] and resonance Raman and far IR studies of $[RhBr_6]^{3-}$ in AgBr crystals are consistent with the expected (cubic) ground state.[1198]

The $[trenH_3]^{3+}$ cation has been used to precipitate the $[RhCl_3X_3]^{3-}$ (X = Cl, Br, I) and $[RhBr_6]^{3-}$ anions;[1199] the electronic spectra are given in Table 86. If a solution of $Na_3[RhCl_6]$ or $RhCl_3 \cdot 3H_2O$ is extracted with a benzene solution of a long chain quaternary ammonium chloride, silica gel separation of the organic layer leads to $(NX_4)_3[Rh_2Cl_9]$ (X = Et or a C_8 to C_{10} aliphatic chain).[1204] Characterized by far IR and UV/visible spectra, the X-ray powder patterns show that $[NEt_4]_3[Rh_2Cl_9]$ is isomorphous with its Cr^{III} analog,[1205] and thus consists of two pyramidally distorted $RhCl_6$ octahedra sharing a face of three Cl ligands.

Hydration of $[RhCl_6]^{3-}$ leads to a variety of aquachloro complexes of the form $[Rh(H_2O)_nCl_{6-n}]^{(n-3)+}$; the spectra and reactivity of these ions have been thoroughly studied, as aqueous solutions of $RhCl_3 \cdot 3H_2O$ vary from yellow to various shades of red and brown. Approximate formation constants have been determined[1200] and synthetic routes to specific isomers have been reported.[1201]

The ubiquitous '$RhCl_3 \cdot 3H_2O$' appears to contain a variety of aquachloro species, as do solutions prepared by aquation of $[RhCl_6]^{3-}$ or 'hydrous rhodium oxide'. Solutions of 'hydrated $RhCl_3$', treated with base, perchloric acid and then with various amounts of LiCl exhibited ^{103}Rh NMR signals which can be assigned to the 10 possible isomers of $[Rh(H_2O)_nCl_{6-n}]^{(n-3)+}$ (n = 0–6).[1206]

Table 86 Electronic Spectra of some Aquahalorhodium(III) Complexes[a]

Complex	λ_{max} (nm) (ε)	*Ref.*
$[Rh(H_2O)_6]^{3+}$	396 (62.0), 311 (67.4)	1200
	395 (57.9), 323 (32.5)	1112
$[Rh(H_2O)_5Cl]^{2+}$	426 (50.4), 335 (50.0)	1200
	420 (50.4), 335 (52.4)	460
cis-$[Rh(H_2O)_4Cl_2]^+$	450 (~68), 355 (~72)	1201
trans-$[Rh(H_2O)_4Cl_2]^+$	450 (64.9), 349 (49.5)	1200
	450 (~78), 350 (~60)	1201
mer-$[Rh(H_2O)_3Cl_3]$	471 (77.1), 370 (71.6)	1200
	471 (85.2), 370 (71.6)	1202
fac-$[Rh(H_2O)_3Cl_3]$	474 (68.3), 376 (93.5)	1200
	474 (78.4), 376 (99.6)	1202
cis-$[Rh(H_2O)_2Cl_4]^-$	492 (101), 392 (113)	1203
$[Rh(H_2O)_2Cl_4]^{-b}$	484 (99.6), 384 (78.2)	1203
	488 (72.0), 385 (54.1)	1200
$[Rh(H_2O)Cl_5]^{2-}$	507 (72.8), 402 (73.4)	1200
$[RhCl_6]^{3-}$	518 (111.5), 411 (93.8)	1200
$[RhBr_6]^{3-}$	562, 441, 340	1199
$[RhCl_3Br_3]^{3-}$	541, 457, 303	1199
$[RhCl_3I_3]^{3-}$	332	1199
$[Rh_2Cl_9]^{3-}$	540 (98.0), 435 (308.8)	1204
$[Rh(H_2O)_5Br]^{2+}$	550sh (37), 454 (81), 350sh (81)	460
	441 (70.6), 342 (70.6), 268 (582)	460
cis-$[Rh(H_2O)_4Br_2]^+$	478 (122), 208 (34 000)	1113
trans-$[Rh(H_2O)_4Br_2]^+$	483 (130), 256 (33 000)	1113
mer-$[Rh(H_2O)_3Br_3]$	505 (155), 256 (16 000), 213 (25 000)	1113
$[Rh(H_2O)_5I]^{2+}$	548 (98.4), 329 (567)	460

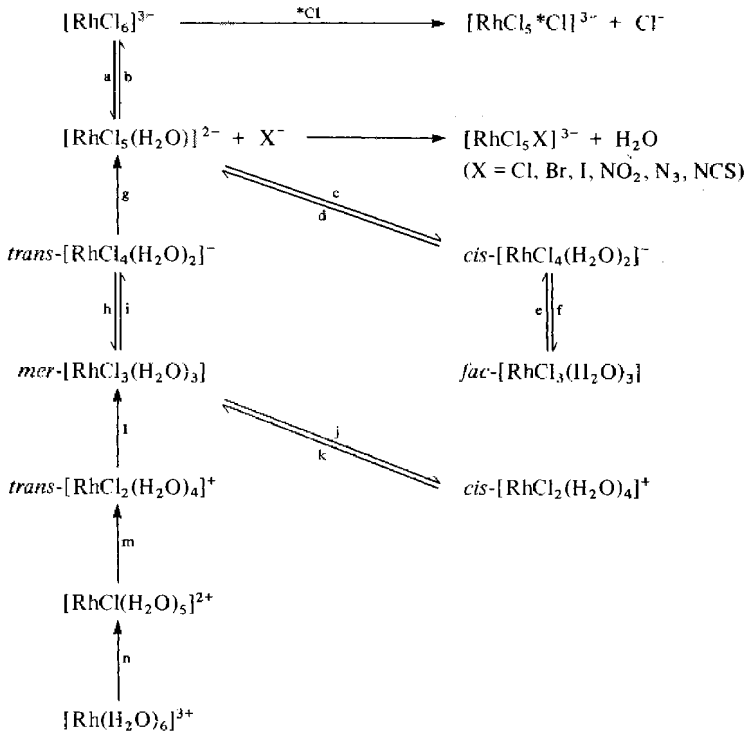
[a] Spectra recorded in acidic aqueous solution, except that of $[Rh_2Cl_9]^{3-}$, which was recorded in benzene. [b] Isomer assignment originally not given. Later assigned as *trans* isomer.[1203]

Commercially available samples (from three different suppliers) of '$RhCl_3 \cdot 3H_2O$' (in aqueous solution) initially displayed different ^{103}Rh NMR spectra, with varying amounts of *fac*- and *mer*-$[Rh(H_2O)_3Cl_3]$, *cis*-$[Rh(H_2O)_4Cl_2]^+$ and small amounts of *trans*-$[Rh(H_2O)_4Cl_2]^+$ (the cations presumably as chloride salts).[1200] Overnight at 80 °C, all three solutions give identical ^{103}Rh NMR spectra; solution composition was shown to be independent of the Rh^{III} concentration, implying that monomeric species dominate, and when heated in conc. HCl, all give $[RhCl_6]^3$ as the dominant species.[1206]

Similar aquahalo equilibria have been reported for aqueous hydrofluoric acid solutions of hexafluororhodate(III), and ^{19}F NMR and electronic spectroscopy have been used to identify species in the series, $[RhF_{6-n}(H_2O)_n]^{(n-3)+}$.[1207] In the presence of Cl^- ion, aquachloro complexes form, but there was no evidence of any mixed F–Cl species. (These are the only Rh^{III} complexes which claim to have a Rh—F bond.) All 10 isomers of the $[RhBr_nCl_{6-n}]^{3-}$ series have been identified (^{103}Rh NMR) in solutions prepared by dissolving commercially available hydrated rhodium trichloride in various HCl and HBr solutions.[1208] The ^{103}Rh resonances vary from 7985 p.p.m. for $[RhCl_6]^{3-}$, decreasing by about 150 p.p.m. for each bromide substituent, reaching 7077 p.p.m. for the hexabromo anion. Splitting for the expected *cis*/*trans* ($n = 2$ or 4) and *mer*/*fac* isomers ($n = 3$) was observed, although the claim that the observed 3/1 *mer*/*fac* ratio is the statistically expected ratio[1208] is not valid; statistical arguments would lead to a *mer*/*fac* ratio of 3/2.

The single crystal X-ray structure of $(NH_4)_2[RhCl_5(H_2O)]$ shows it to have the expected octahedral structure, but the Cl *trans* to the water has the shortest Rh—Cl distance, consistent with the known *trans* influence of the chloride ligand.[1209] The solid has significant intermolecular (Rh—O—H···Cl—Rh) hydrogen bonding. Aqueous solutions of $[Rh(H_2O)_nCl_{6-n}]^{(n-3)+}$ catalyze the hydration of acetylene under mild conditions.[1210] The catalytic activity is reported to increase as the number of coordinated chlorides increases, up to five chlorides, with the aquapentachloro complex being the most active, and the hexachloro ion inactive. The immense field of Rh-catalyzed catalytic hydration of unsaturated organics has been covered elsewhere[17] and generally involves π interactions between Rh and C systems, and thus will not be covered here.

Harris, Robb and co-workers have thoroughly studied the kinetics of ligand substitutions of the aquachlororhodium(III) complexes.[1201,1202,1211–1213] The reactions studied are summarized in Scheme 40, and the activation parameters for the labeled reactions are recorded in Table 87. The stereochemical course of these reactions is dominated by the *trans*-labilizing effect of chloride ligands. For



Scheme 40

Table 87 Activation Parameters for the Reactions Shown in Scheme 40[a]

Reaction	*Type*	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	*Ref.*
(a)	Aquation	105 (101 ± 21)	(+42 ± 71)	1211
(b)	Anation	71 (69 ± 7)	(−92 ± 21)	1211
(c)	Aquation	108 (105 ± 5)	(+25 ± 17)	1212
(d)	Anation	92 (90 ± 6)	(+13 ± 21)	1212
(e)	Aquation	129 ± 6.3	79 ± 21	1202
(f)	Anation	110 ± 1	38 ± 4	1202
(g)	Anation	132 ± 2	150 ± 8	1202
(h)	Aquation	b	b	1202
(i)	Anation	117 ± 2	54 ± 8	1202
(j)	Aquation	137 ± 3	79 ± 8	1202
(k)	Anation	112.5 ± 1	33 ± 4	1202
(l)	Anation	143 ± 3	54 ± 8	1202
(m)	Anation	(120 ± 5)	(38 ± 17)	1213
(n)	Anation	(137 ± 10)	(54 ± 29)	1112

[a] Values in parentheses determined from original data but analyzed with a different program.[1202] Unparenthesized values from original references. [b] At 50°C, $k = 2.1 \times 10^{-4}$ s^{-1} but a temperature variation study was not reported.

example, aquation of $[RhCl_5(H_2O)]^{2-}$ leads to only *cis*-$[RhCl_4(H_2O)_2]^-$, which undergoes subsequent aquation to yield only *fac*-$[RhCl_3(H_2O)_3]$. With no chlorides *trans* to each other, *fac*-$[RhCl_3(H_2O)_3]$ is extremely resistant to further chloride hydrolysis. Similarly, anations by chloride ion, starting with either $[Rh(H_2O)_6]^{3+}$ or *fac*-$[Rh(H_2O)_3Cl_3]$, occur more readily at a site *trans* to a coordinated chloride.[1202] Such regiospecific substitutions only occur in strongly acidic solutions, where all of the coordinated waters are fully protonated. Since OH^- has a *trans*-labilizing influence comparable to Cl^-,[1201] formation of hydroxo species dramatically alters this sequence; relevant acid dissociation constants are given in Table 88.

The mechanisms of these reactions are discussed by Palmer and Harris, and after allowing for the inevitable uncertainty caused by ion pairing, they conclude that 'the evidence tends to favor a clear dissociative (five-coordinate intermediate) mechanism'.[1202] Additional support for a dissociative mechanism in the substitutions of aquachlororhodium(III) complexes comes from Cl^- isotopic exchange studies of $[RhCl_6]^{3-}$ and $[RhCl_5(H_2O)]^{2-}$, which suggested that the reactions proceed *via*

Table 88 pK_a Values of some Aquachlororhodium(III) Complexes

Complex	pK_a	*Ref.*
$[Rh(H_2O)_6]^{3+}$	3.40	1112
$[Rh(H_2O)_5Cl]^{2+}$	4.86 ± 0.01	1201
cis-$[Rh(H_2O)_4Cl_2]^+$	5.69 ± 0.03	1202
trans-$[Rh(H_2O)_4Cl_2]^+$	6.0 ± 0.1	1202
fac-$[Rh(H_2O)_3Cl_3]$	7.31 ± 0.03	1202
mer-$[Rh(H_2O)_3Cl_3]$	6.96 ± 0.04	1202

initial aquation, followed by anation, rather than *via* the exchange path expected if an associative mechanism were operating.[1212] The rates of bromide and chloride anation of $[Rh(H_2O)_6]^{3+}$ are virtually identical, further suggesting a common (Rh—O bond cleavage) rate-determining step in both reactions.[1112,1113]

Robb and co-workers have studied the kinetics of the anation of $[Rh(H_2O)Cl_5]^{2-}$ by a variety of monoanions (equation 286; X = Cl, Br, I, NO_2, N_3 or NCS).[1213] The rates of anation are relatively independent of the nature of the anating ligand ($k \approx 2.9 (\pm 1) \times 10^{-2} s^{-1}$ at 35 °C), consistent with a dissociative mechanism. The rates of equilibration of the hexachloro, pentachloro and *cis*-tetrachloro anions were studied as a function of chloride concentration and the data were fitted to the kinetic expression: $k_{obs} = k_{aq} + k_{anat}[Cl^-]$. The effect of pressure (1–1500 bar) was also monitored;[1214] for an associative reaction, ΔV^* should be negative (as low as $-18 cm^3 mol^{-1}$) and substrate independent, while a dissociative reaction should show a positive value (up to $+18 cm^3 mol^{-1}$) and be sensitive to changes in the substrate. As shown in Table 89, the results are again consistent with a dissociative mechanism. In addition, the authors note that the ΔV^* values for the aquations and anations are similar to the known partial molar volumes of the leaving groups (Cl^- and H_2O), which implies that the leaving groups are fully solvated in the transition state.[1214] A dissociative process is clearly indicated.

$$[Rh(H_2O)Cl_5]^{2-} + X^- \rightleftharpoons [Rh(X)Cl_5]^{3-} + H_2O \qquad (286)$$

Not surprisingly, Hg^{II} ion enhances the rate of Cl^- aquation from a variety of these complexes. Chan and Harris have presented a detailed kinetic study of the Hg^{II}-induced aquation of *fac*-$[Rh(H_2O)_3Cl_3]$, and the subsequently formed *cis*-$[Rh(H_2O)_4Cl_2]^+$ and $[Rh(H_2O)_5Cl]^{2+}$ ions.[1215] For each of the reactions the data are consistent with a mechanism involving preequilibrium between the Rh—Cl substrate and the Hg^{2+} ion, followed by the rate determining cleavage of the Rh—ClHg bond. For equation (287) (and the analogous reactions of *fac*-$[Rh(H_2O)_3Cl_3]$ or *cis*-$[RhCl_2(H_2O)_4]^+$), the kinetic expression: $k_{obs} = kK[Hg^{2+}]/(1 + K[Hg^{2+}])$ is observed. A double reciprocal plot (k_{obs}^{-1} as a function of $[Hg^{2+}]^{-1}$) was used to determine values for K and k. For the *fac*-trichloro, *cis*-dichloro and monochloro complexes, the values for k (s^{-1}) are 1.07 $(\pm 0.04) \times 10^{-2}$, 4.3 $(\pm 0.3) \times 10^{-5}$ and 8.9 $(\pm 1.8) \times 10^{-6}$ respectively. This decrease in rate constant parallels the rate decrease for the analogous uncatalyzed reactions. The corresponding K values (137 ± 5, 10 ± 1 and 3.0 ± 0.6, respectively), are consistent with a coulombic interpretation, as K decreases as the positive charge on the Rh substrate increases. The association constants for these aquachloro complexes are surprisingly large when one considers that there is no identifiable Hg^{2+} complex formed when Hg^{2+} is added to $[Rh(NH_3)_5Cl]^{2+}$.[1216] The value of K is relatively independent of whether the Cl—Hg moiety is *trans* to a H_2O or a Cl^-, but the rate of the subsequent reaction (k) is markedly increased by the *trans* labilizing influence of a Cl^- ligand. This observation rationalizes the rapid reaction of Hg^{2+} with *mer*-$[Rh(H_2O)_3Cl_3]$, studied by Palmer and co-workers,[1217] who used the same reaction sequence and found the same kinetic scheme for this reaction, but found the association constant (K) for *mer*-$[Rh(H_2O)_3Cl_3]$ is 758 ± 63, significantly

Table 89 Volumes of Activation of some Aquachlororhodium(III) Ions[121]

Substrate	*Reaction*[a]	ΔV^* ($cm^3 mol^{-1}$)
$[RhCl_6]^{3-}$	Aquation (a)	$+21.5 \pm 0.6$
$[RhCl_5(H_2O)]^{2-}$	Aquation (c)	$+14.3 \pm 0.5$
$[RhCl_5(H_2O)]^{2-}$	Anation (b)	$+15.7 \pm 6.5$
cis-$[RhCl_4(H_2O)_2]^-$	Anation (d)	$+14.7 \pm 1.6$

[a] Labeled reactions shown in Scheme 40.

larger than the 137 found for the *fac* isomer.[1215] The Hg^{2+} and $HgCl^{+}$ ions have comparable effects on the reaction rates, but, not surprisingly, $HgCl_2$ does not enhance Cl^- hydrolysis of these complexes.[1217]

$$[Rh(H_2O)_5Cl]^{2+} + Hg^{2+} \overset{K}{\rightleftharpoons} \{Rh(H_2O)ClHg\}^{4+} \xrightarrow{k} [Rh(H_2O)_6]^{3+} + HgCl^{+} \qquad (287)$$

The addition of trace amounts of Rh^{III} halides to photographic emulsions can marginally decrease the sensitivity, but dramatically increase the gradation of the emulsion, and is generally known as 'the rhodium effect'. The mechanism of the rhodium effect is not understood, but the available evidence suggests that the Rh^{III} is chemisorbed on the surface of the Ag halide grains,[1218] and that the Rh^{III} exerts its effect in the formation of the latent image, not in the film development.[1219] Studies monitoring the effects of $[RhX_6]^{3-}$ (X = Cl, Br, CN, SCN), $[Rh(bipy)_2Cl_2]Cl$, $[Rh(NH_3)_5Cl]Cl_2$ and $[Rh(NH_3)_6]Cl_3$, demonstrated that at least one halide (or pseudohalide) must be coordinated to the Rh^{III} for the rhodium effect to occur, suggesting a halide or pseudohalide bridge between Rh^{III} and Ag^{I} centers is involved.[1220] (Of the complexes listed above, only the hexaammine had no measurable effect on either the sensitivity or gradation of the film.) Clearly, study of the chemistry behind this effect deserves further attention.

48.7 RHODIUM(IV) COMPLEXES

Beyond the 3+ oxidation state, rhodium forms a limited number of complexes in the 4+, 5+ and 6+ oxidation states. A recent review[1221] gives an excellent summary of the chemistry of the higher oxidation state chemistry of Rh (as well as Ru, Os, Ir, Pd and Pt). For the 4+ oxidation state, the hexafluoro, hexachloro and trioxo dianions are well characterized. The known neutral species include RhF_4 and some oxides. There are also scattered reports of Rh^{IV} complexes containing substituted biguanides and Schiff base chelates.

48.7.1 Anionic Complexes

The $[RhF_6]^{2-}$ anion has been prepared by several techniques, and a variety of cations have been used to precipitate it. Yellow crystals of $M_2[RhF_6]$ were prepared by the direct reaction of F_2 with $M_2[RhCl_5]$ (M = K, Rb, Cs).[1222] All three salts have room temperature magnetic moments characteristic of one unpaired electron ($\mu_{eff} = 1.98 \pm 0.03$ BM),[1222] consistent with a high field octahedral environment (t_{2g}^5). Mixtures of NaCl and $RhCl_3$ were fluorinated with BrF_3 to yield $Na_2[RhF_6]$ ($\mu_{eff} = 2.0$ BM at room temperature);[1223] X-ray powder patterns show that anhydrous $Cs_2[RhF_6]$ is isomorphous with Na_2PtF_6, and that the earlier reported $Na_3[RhF_7]$[1224] is actually a mixture of NaF and $Na_2[RhF_6]$.[1223] Other monovalent cations used to precipitate $[RhF_6]^{2-}$ have included Li^+[1225] and NO^+.[1226] Yellow or brown salts of divalent cations (Ca, Sr, Ba, Zn, Mg, Ni or Hg) have been prepared,[1227] and the unusual Ag^{2+} ion is stabilized in the black $Ag[RhF_6]$ salt.[1228] The peroxo salt, $[O_2][RhF_6]$ has been prepared,[1226] and in $NOF_{(g)}$ it reacts to give $(NO)_2[RhF_6]$. This latter salt can also be prepared by the reaction of rhodium sponge with a mixture of gaseous NOF and F_2; if a large excess of F_2 is used, the Rh^{V} salt, $(NO)[RhF_6]$ is formed.[1226] The peroxo and nitrosyl salts of $[RhF_6]^{2-}$ have been characterized by Raman spectroscopy.

The K and Rb salts of $[RhF_6]^{2-}$ belong to the $K_2[GeF_6]$ (trigonal) structural type, while the Cs salt exists in both trigonal and hexagonal forms.[1229] With the exception of the Sr and Ba salts, $[RhF_6]^{2-}$ is quite sensitive to hydrolysis; a qualitative listing of rates of hydrolysis of group VIIIB hexafluoro dianions is $PdF_6^{2-} > RhF_6^{2-} > RuF_6^{2-} > PtF_6^{2-} > IrF_6^{2-} > OsF_6^{2-}$, with only the palladium analog more reactive.[1230]

The vibrational spectrum of the potassium salt has been measured (Rh—F stretch at 589 cm^{-1}) and it is consistent with the expected octahedral geometry for $[RhF_6]^{2-}$.[1231] Both solid state absorption spectra[1232] and diffuse reflectance spectra[1233] of $[RhF_6]^{2-}$ salts show two weak, spin-forbidden $^2T_{2g} \rightarrow {}^4T_{1g}$ and $^2T_{2g} \rightarrow {}^4T_{2g}$ transitions at long wavelength (diffuse reflectance maxima at 862 and 625 nm). A variety of stronger, spin-allowed transitions occur at higher energy (521, 472, 362 and 305 nm). Several moderately strong bands below 2500 nm were assigned to transitions between spin–orbit components of the electronic ground state.[1223]

The only other anionic Rh^{IV} halide complex, $[RhCl_6]^{2-}$, has been prepared by the oxidation of an ice-cold aqueous suspension of $Cs_3[RhCl_6]$ by Cl_2 or Ce^{IV}.[1234,1235] The cesium salt is isomorphous with $(NH_4)_2[PtCl_6]$[1234] and $Cs_2[IrCl_6]$.[1236] The reflectance spectrum of $Cs_2[RhCl_6]$ has aroused interest, as

$Cs_2[RhCl_6]$ displays the lowest energy charge-transfer transition of the platinum metal hexachloride dianions.[1237] The Cs salt is paramagnetic (μ_{eff} = 1.7 BM at 298 K),[1238] and the variation in magnetic susceptibility as a function of temperature[1238] and when diluted in a diamagnetic, isomorphous lattice of $Cs_2[PtCl_6]$[1239] was interpreted to imply a significant amount of Rh—Cl bonding in the $[RhCl_6]^{2-}$ ion. The dilution study[1239] also confirmed earlier work[1235] which showed it is exceedingly difficult to prepare pure $Cs_2[RhCl_6]$, as at least one-third of the Rh atoms in each sample studied had been reduced to Rh^{III}.

The $[RhCl_6]^{2-}$ ion is very reactive in solution, and rapidly oxidizes coordinated chlorides to chlorine; this reaction has not been thoroughly studied, but 85–88% of the anticipated Cl_2 has been recovered, and the Rh-containing product is presumably an aquachlororhodium(III) anion.[1238] Attempts to prepare salts other than cesium have not been successful,[1237] presumably because of the rapid internal redox reaction which occurs in solution; the rapid precipitation of the insoluble Cs salt lessens this contamination.

A temperature-jump study of the outer-sphere reduction of $[RhCl_6]^{2-}$ (equation 288) showed that at 10°C the equilibrium constant is 9.08 (μ = 0.05 M) and the rate of both the forward and reverse reactions are approximately diffusion controlled (the lower limit of k_{for} is $2.5 \times 10^9\ M^{-1}\ s^{-1}$).[1240]

$$[RhCl_6]^{2-} + [Ru(phen)_3]^{2+} \rightleftharpoons [RhCl_6]^{3-} + [Ru(phen)_3]^{3+} \quad (288)$$

There are scattered reports of solid salts of Rh^{IV} oxyanions. Early descriptions of a number of uncharacterized 'rhodites' have not been confirmed in recent years; these rhodites, $Na_2O \cdot 8RhO_2$ and $K_2O \cdot 6RhO_2$, were prepared by heating $M_3[Rh(NO_2)_6]$ (M = Na, K) in air at 440 °C.[1241] Heating Rh metal in Na_2CO_3 in air leads to $Na_2[RhO_3]$ with a sodium stannite type lattice.[1242] The Li salt is also reported. The solid state structure of $Sr_4[RhO_6]$ is similar to the well-characterized $Sr_4[PtO_6]$, and has a hexagonal lattice, with each rhodium octahedrally coordinated by six oxygen atoms, and linked in one-dimension through Sr atoms.[1243] The synthesis of this latter compound was not reported, and it was stated that the compound analyzed to be 'oxygen deficient', again suggesting Rh^{III} contamination.

48.7.2 Neutral Complexes

The reaction of anhydrous $RhBr_3$ with BrF_3 was reported to lead to a bromine-contaminated sample (5.8% Br) of a purple-red solid identified as RhF_4.[1223,1224] It is paramagnetic (μ_{eff} = 1.1 BM at room temperature).[1244] There is a more recent report of the preparation of RhF_4 by the direct reaction of $F_{2(g)}$ (2–3 atm, 250 °C) with Rh sponge.[1245] This material was shown to be paramagnetic, very susceptible to hydrolysis in air, and isomorphous with IrF_4 and PtF_4. This latter RhF_4 was identified as 'brown', while the earlier reported material was identified as 'purple-red'.[1223] Attempts to reduce RhF_4 with SeF_4 lead to the formation of a pale pink solid identified as $(RhF_4)_2SeF_4$.[1246] The nature of these adducts has not been reported, but the color calls to mind the pale pink, unstable RhF_4–BrF_3 adduct reported by Sharpe.[1224]

Hydrated RhO_2 has been prepared by the electrochemical or Cl_2 oxidation of Rh^{III} salts.[1247] Little solution chemistry has been reported for this species, but the hydrate is green in alkali, and blue in acetic acid solution; variation in the oxygen analyses suggests that the hydrate may be a peroxide. Thermal treatment causes decomposition of the oxide, not dehydration.[1247] Anhydrous Rh^{IV} oxide has been prepared by heating hydrated Rh_2O_3 in oxygen,[1248] or by heating $Rh(OH)_3$ or $Rh(NO_3)_3 \cdot 6H_2O$ in air at 450 °C.[1249] When heated and squeezed (700 °C, 3000 atm, 24 h) anhydrous RhO_2 forms an undistorted rutile structure, in which the Rh^{4+} ion has an effective radius of 0.62 Å (the effective radius of Pt^{4+} is 0.63 Å).[1250] There is mass spectral evidence for RhO_2, and electron impact measurements suggest an ionization potential of 10.0 eV.[1251]

Some uncharacterized Rh^{IV} complexes, presumably with Rh—O bonds, have been reported. A red solution of Rh^{IV} perchlorate has been claimed,[1252] and chemical and electrochemical oxidation of $Rh_2O_3 \cdot H_2O$ (or $[Rh(H_2O)_6]^{3+}$) in a variety of mineral acids leads to a green solution, which presumably contains some Rh^{IV} species.[1253]

48.7.3 Miscellaneous Rh^{IV} Complexes

Cyclic voltametry of the Rh^{III} complexes [Rh(R)(salen)py] (R = Me, Pr^n, Pr^i; salen = dianion of bis(salicylidene)ethylenediamine) displays reversible one-electron oxidations of the metal center. The ease of formation of the organometallic cation $[Rh(R)(salen)py]^+$ depends on the nature of the

σ-bonded alkyl ligand.[1254] Several complexes of Rh^{IV} (and Ir^{IV}) with the bidentate N^1-*p*-chlorophenyl-N^5-isopropylbiguanide (L) have been reported. The magnetic moments of $[Rh(L)_3]Cl_4$, $[Rh(L)_2X_2]Cl_4$ (X = NH_3, py), and $[Rh(L)_2Y_2]Y_2$ (Y = Cl, NO_2) are consistent with one unpaired electron (μ_{eff} = 1.65–1.82 BM).[1255] The $[Rh(L')_2Cl_2]Cl_2$ (L' = N^1-phenyl or N^1-*o*-tolyl-N^5-isopropylbiguanide) have been prepared by the $NaClO_2$ oxidation of the corresponding $[Rh(L')_2Cl_2]Cl$ salt.[1256]

Oxidation of $[Rh(S_2CNMe_2)_3]$ with BF_3 was reported to lead to '$[Rh(S_2NCMe_2)_3BF_4]$', presumably a Rh^{IV} dithiocarbamate complex.[1257] This was questioned by later work in which cyclic voltammetry was used to show that $[Rh(S_2CNMe_2)_3]$ is irreversibly oxidized (in acetone/Et_4NClO_4) at a potential of 1.24 V *vs.* Ag/AgCl. In dichloromethane or benzene, reaction of $[Rh(S_2CNMe_2)_3]$ with BF_3 leads to the binuclear Rh^{III} complex $[Rh_2(S_2CNMe_2)_5]BF_4$, not a Rh^{IV} monomer (Section 48.6.6.2).[1179] Fleischer has reported[869] that the reaction of $[Rh(CO)_2Cl]_2$ with tetraphenylporphyrin in refluxing benzene leads to the paramagnetic [Rh(TPP)(Ph)(Cl)] molecule. This unusual species was formulated as an organometallic Rh^{IV} complex, but the similarity of its structure and reactivity to other Rh^{III}–porphyrin complexes casts doubt on this oxidation state assignment (Section 48.6.2.7).

Oxidation of the Rh^{II} dimer $[Rh_2(O_2CMe)_4]$ in air with an excess of the disodium salt of 1,1-dicyano-2,2-dithiolatoethylene [in the presence of $(PPh_4)Br$ or $[NBu^n_4]I$, (MX)] affords $[M]_2[Rh\{S_2C{=}C(CN)_2\}_3]$; the same salts could be obtained starting from hydrated rhodium trichloride. While no ESR signal was detected at room temperature, a broad, featureless line was observed at −170 °C, and the anion is paramagnetic (μ_{eff} = 1.1 BM at room temperature). Voltammetric studies showed two oxidation waves, the first of which is a reversible, one-electron oxidation, presumably yielding $[Rh\{S_2C{=}C(CN)_2\}_3]^-$, but no reduction waves between 0.0 and −1.8 V could be detected.[1258]

48.8 RHODIUM(V) COMPLEXES

The complexes of Rh^V are limited to RhF_5, RhF_6^-, and a series of less thoroughly characterized oxide ions.

48.8.1 Anionic Complexes

48.8.1.1 $[RhF_6]^-$

Bright yellow, moisture sensitive salts of $M[RhF_6]$ (M = Na, K, Rb, Cs) have been prepared by heating $RhCl_5$ and MCl in IrF_5.[1259] (The Cs^+ salt was elsewhere reported to be 'red-brown'.[1260]) The sodium salt appears to be the most stable, with a room temperature magnetic moment of 2.8 BM, consistent with a high field, t_{2g}^4 electronic configuration for this octahedral cation.[1260] Considerable deviation from Curie behavior was noted for the Na^+ salt, and attempts to prepare the Li^+ salt were unsuccessful. Alkali and alkaline earth salts of RhF_6^- have been prepared using ClF_3 as a vapor phase fluorinating agent.[1261] Non-metal cation salts of RhF_6^-, such as $[XeF_6]^+$, $[KrF_6]^+$,[1262] O_2^+ or NO^+,[1263] have been prepared; some vibrational data are available on the NO^+ salt.[1263]

48.8.1.2 Oxyanions of Rh^V

Various ionic oxides of Rh^V have been reported to result from the oxidation of Rh^{III} salts by hypochlorite, hypobromite or BiO_3^-.[1264–1266] The color of the hypochlorite oxidation product is very pH sensitive, ranging through yellow-orange (pH 11), green (pH 8), blue (pH 6) and purple (pH 2). The blue material is anionic, and tentatively identified as RhO_3^- (or $RhCl_6^-$), while the purple species (pH 2) is cationic, and tentatively identified as RhO_2^+ or RhO^{3+}. The 5+ oxidation state assignment is based on the used of equimolar amounts of Rh^{III} and two-electron oxidants, such as OCl^-.[1265] Perbromate oxidation of $RhCl_6^{3-}$ (excess perbromate) leads to a violet solution at pH 11. Presumably a Rh^{VI} species, this violet solution gradually turns blue (Rh^V). (Use of less OBr^- leads to the yellow-orange Rh^V species discussed above.) The blue Rh^V species is also unstable, and is reported to disproportionate (equation 289).[1265] The most carefully characterized oxyanion of Rh^V is RhO_4^{3-}. First reported by Berzelius[1267] upon chemical oxidation of Rh^{III} salts, it has also been reported to form upon anodic oxidation of Rh^{III}.[1268] In acidic solution the Rh^V oxide is reported to dispropor-

tionate (equation 290), and its oxidation half-reaction (equation 291) has a standard potential of 1.87 V *vs.* NHE.[1269]

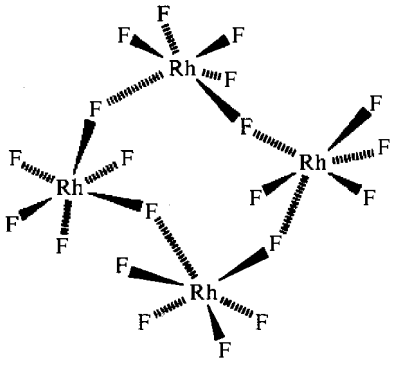
$$3Rh^{V} \longrightarrow 2Rh^{VI} + Rh^{III} \quad (289)$$

$$3[HRhO_4]^{2-} + 2H^+ \longrightarrow 2[RhO_4]^{2-} + Rh(OH)_3 + H_2O \quad (290)$$

$$[HRhO_4]^{2-} \longrightarrow H^+ + [RhO_4]^{2-} + e^- \quad (291)$$

48.8.2 RhF_5

The pentafluoride is a dark red, paramagnetic solid (μ_{eff} = 2.93 BM at 298 K) prepared by the reaction of solid RhF_3 and F_2 (6 atm) at 400 °C.[1260] A single-crystal X-ray structure shows that solid RhF_5 has a tetrameric structure analogous to RuF_5 and IrF_5 (**128**).[1270] Each rhodium is coordinated by six fluorine atoms in an approximately octahedral arrangement. The terminal Rh—F distance averages 1.808 Å, while the Rh—F distance is significantly longer (2.01 Å) for the bridging fluorines. This compound is isostructural with the pentafluorides of Ru, Os and Ir.[1271,1272]



(128)

Numerous transition metals form $[MF_5]_n$ species, and there is an interesting correlation between the structure of the pentafluoride and the nature of the metal. All pentafluorides of the metals in Figure 7 have octahedral metal centers with bridging fluorines. Those in group A are tetrameric, with a square structure, featuring linear M—F—M bridges. Group B metals display polymeric chains, with M—F—M angles near 150°, while group C metals have tetrameric structures with M—F—M angles near 135°. All have MF_6 units with close-packed fluorine atoms; group A display distorted c.c.p. lattices, with metals in 1/5 of the octahedral holes, while group C (which includes Rh) are h.c.p. For the left side of Figure 7, bonding can be rationalized with an ionic model, involving $(MF_4^+)(F^-)$ units, while on the right side, covalent bonding is more appropriate, with two-electron/three-center bonds needed to account for the M—F—M bridges.[1270]

The mass spectrum of RhF_5 is not typical of a metal pentafluoride, and is relatively rich in ions containing more than one Rh atom.[1273] For example, as the temperature increases, the concentration of $Rh_2F_9^+$ ion increases at the expense of monomeric RhF_5^+ and RhF_6^+ fragments.

48.9 RHODIUM(VI) COMPLEXES

The 6+ state is the highest formal oxidation state recorded for rhodium, and RhF_6 is the only carefully characterized example. Following the method used to prepare RuF_6,[1274] it can be prepared

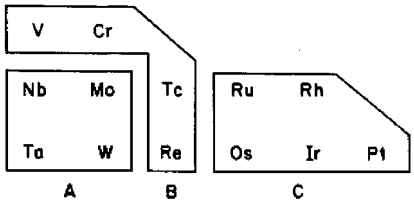


Figure 7 Metals which form $[MF]_n$ species having octahedral metal centers and bridging fluorines

by burning rhodium metal in an atmosphere of F_2/N_2 in a cooled quartz reactor.[1275] Earlier workers[1276] had attempted the direct oxidation of rhodium metal in hot (500–600 °C) F_2, but found the major product was RhF_3, with a red-brown sublimate which contained some impurities of RhF_4 and RhF_5. The highest Rh fluoride obtained using BrF_3 as the fluorinating reagent was RhF_4.[1277]

One of the least stable of the metal hexafluorides, RhF_6, is a black volatile solid ($P_{20\,°C} = 49.5$ Torr). The gas phase is deep red brown and monomeric.[1275] At room temperature it has a body-centered cubic lattice, and, like numerous other hexafluorides, it undergoes a phase change at reduced temperature. The low temperature phase has not been well defined, but is of lower symmetry, and is probably orthorhombic.[1278] For RhF_6 the phase change occurs at -23 °C, which is comparable to the transition temperatures (°C) for other metal hexafluorides:

Mo(−36)	Tc(−19)	Ru(−30)	Rh(−23)		
W(−20)	Re(−22)	Os(−21)	Ir(−11)	Pt(−11)	U(+25)

The electronic spectrum of RhF_6 has not been reported, but ligand field calculations have been used to predict its spectrum.[1279] The IR spectrum of RhF_6 has been reported,[1280] and it is consistent with the expected O_h symmetry. Like IrF_6, the rhodium hexafluoride does not show the Jahn–Teller splittings of the E_g mode observed for the analogous Tc, Re and Os hexafluorides.

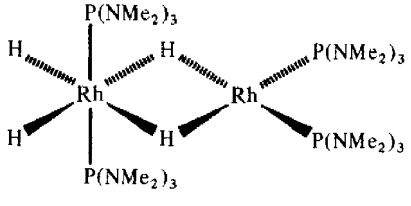
Not surprisingly, RhF_6 is a strong oxidizing agent, and, as is its ruthenium analog, is capable of oxidizing Xe.[1281] Virtually everyone who works with RhF_6 comments on its instability, however, which may account for the lack of studies dealing with its use as an oxidant.

There are several reports of Rh^{VI} oxides, but none of the compounds have been thoroughly characterized. There is a brief report of the existence of gas phase RhO_3, with an ionization potential of 11.4 eV.[1282] Differential thermal analysis indicates that RhO_2 (in the rutile form) decomposes to RhO_3 (and presumably to $Rh_{(s)}$) at 850 °C. The trioxide then decomposes to Rh metal and oxygen at 1050 °C.[1250] The most commonly reported Rh^{VI} oxide is the rhodate ion RhO_4^{2-}. The potassium salt was first reported (in 1860) as the blue crystalline product of Cl_2 oxidation of RhO_2 in concentrated KOH solutions.[1283] Brilliant blue solutions, presumed to contain the rhodate ion, have since been reported upon oxidation of alkaline solutions of Rh^{III} salts by hypochlorite,[1284] hypobromite[1285] and persulfates.[1286] Anodic oxidation of RhO_2 in dilute $HClO_4$ has also been reported to yield rhodate solutions. Little is known of the spectra or reactivity of this ion, but the Ba^{2+} salt is reported to be paramagnetic, with a susceptibility characteristic of one unpaired electron,[1286] suggesting that the presumably tetrahedral rhodate ion may exist in the unusual low spin, e_g^3 configuration.

48.10 MISCELLANEOUS RHODIUM COMPLEXES

48.10.1 Complexes of Mixed Oxidation State

There seem to be very few complexes in which there are two rhodium ions in different oxidation states. The best-authenticated examples are the $[RhH_2(PR_3)_2]_2$ complexes [R = NMe_2, $P(OPr^i)_3$]. The dimethylamino complex has been shown to have the structure (**129**) and contains both rhodium(I) and rhodium(III).[1287] The other example is provided by the $[Rh(O_2CMe)_2]^+$ ion in $[Rh(O_2CMe)_2]_2ClO_4$. This ion retains the classic lantern structure of the rhodium(II) carboxylato complexes, but the salt contains both rhodium(II) and rhodium(III).[1288]



(129)

48.10.2 Nitrosyl Complexes

Nitrosyl complexes are included in this section since, as Feltham and Enemark have noted, the predominantly covalent interactions between nitric oxide and transition metals make assignment of

charge to the nitrosyl ligand irrelevant.[1289] The ternary nitrosyl complexes $[Rh(NO)_2X]_n$ can be prepared from the carbonyl halides,[1290–1292] or from rhodium(I) cyclooctadiene complexes (equation 292).[1293] The structures of these polymeric materials are uncertain. Griffiths has speculated that they are tetrameric cubanes rather than halo-bridged dimers.[1291]

$$[RhClL_2]_2 + NO \longrightarrow [RhCl(NO)_2]_x \quad (292)$$

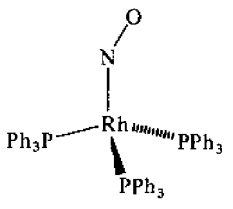
$$L = CO^{1290–1292}, cod^{1293}$$

The reaction between rhodium trichloride and nitric oxide forms another ternary nitrosyl whose formulation is unknown.[1294] However, nitric oxide ligates rhodium(II) acetate (equation 293).[1295] The ternary complexes have been used to prepare other complexes, but these derivatives are commonly prepared from more accessible starting materials.

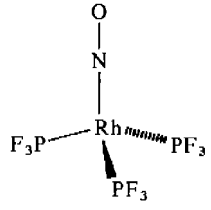
$$[Rh(O_2CMe)_2]_2 + NO \longrightarrow [Rh(O_2CMe)_2(NO)]_2 \quad (293)$$

48.10.2.1 [Rh(NO)L$_3$] complexes

X-Ray crystallography shows [Rh(NO) $(PPh_3)_3$] to adopt the structure (**130**).[1296] The bent NO group (mean Rh—N—O = 156.7°) is uncharacteristic of the nitrosyl ligand in $\{MNO\}^{10}$ complexes, which normally contain linear nitrosyl groups.[1289] Three independent molecules exist within the unit cell. In each of these three molecules the Rh—N—O plane makes a different angle with the vertical mirror plane containing a Rh—P bond. The electron diffraction study of gaseous $[Rh(NO)(PF_3)_3]$ shows it to have a nominally C_{3v} structure (**131**).[1297] The C_{3v} symmetry exhibited in the gas phase is retained in CCl_4 solution. ^{19}F NMR spectrometry shows ϕF to be 3.8 p.p.m. and coupling constants of $^1J(P–F) + 2^3J(P–F) = 1416$ Hz and $^2J(Rh–F) = 18.0$ Hz have been determined. The approximate value for $^2J(P–P)$ was 85 Hz.[1298] Nevertheless, it has been claimed that the results from X-ray photoelectron spectroscopy are more consistent with their formulation as Rh^INO^- complexes.



(130)



(131)

Nitrosyltris(triphenylphosphine)rhodium(I) was first prepared, in admixture with $[Rh(NO)Cl_2(PPh_3)_2]$, by allowing excess triphenylphosphine to react with $[Rh(NO)_2Cl]$ in tetrahydrofuran.[1299] Since that time four other preparative methods, shown in Scheme 41, have been devised.[199,201,202,1300–1303] Of these methods that using *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide is the most convenient.[199,201,202] The dark crimson-red crystals of the complex start to decompose at 115 °C in air, but at 225 °C in a helium atmosphere.[180]

Tertiary phosphine analogs have been prepared from $[Rh(NO)_2Cl]_x$.[1301] Nitrosyltris(phosphorus trifluoride)rhodium has been prepared from both rhodium(−I) and rhodium(I) complexes (equations 294–296).[1297] Their physical properties are listed in Table 90. The triphenylphosphine complex is quite reactive (Scheme 42). Both electronic[1312] and ^{31}P NMR spectrometry show the equilibrium constant for the reaction (297) to be of the order of 10^{-4} mol dm^{-3} in dichloromethane, benzene[1312,1313] or THF,[1313] so the reactivity of the complex cannot arise from the facile loss of a triphenylphosphine ligand. The invariance of the line width of the doublet at −48.8 p.p.m. ($^1J(Rh–P) = 175$ Hz) with solvent suggests that the species is unsolvated.[1313] This lack of dissociation makes the preparation of the bis(triphenylphosphine) complex to appear erroneous.[1314]

$$[RhCl(NO)_2]_x + PR_3 \longrightarrow [Rh(NO)(PR_3)_3] \quad (294)$$

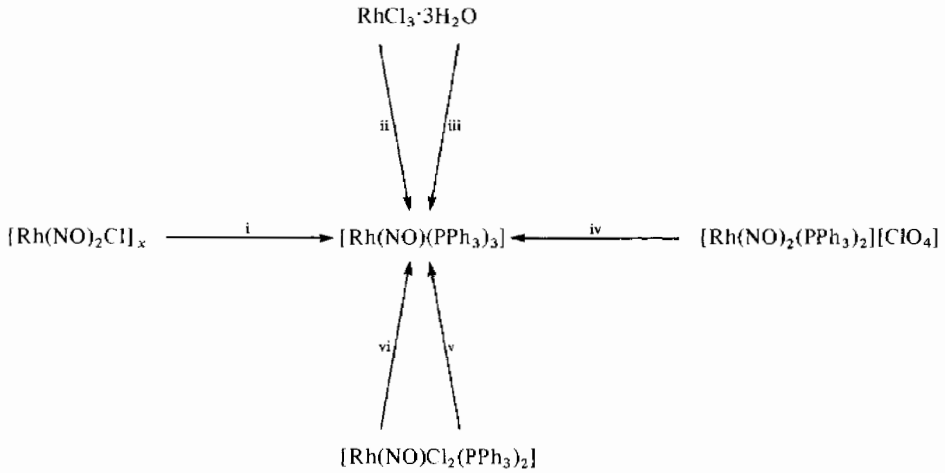
$$R_3 = Ph_3, (p\text{-}C_6H_4Me)_3, (p\text{-}C_6H_4F)_3, MePh_2$$

$$K[Rh(PF_3)_4] + NO \longrightarrow [Rh(NO)(PF_3)_3] \quad (295)$$

Table 90 Physical Properties of $[Rh(NO)L_3]$ Complexes

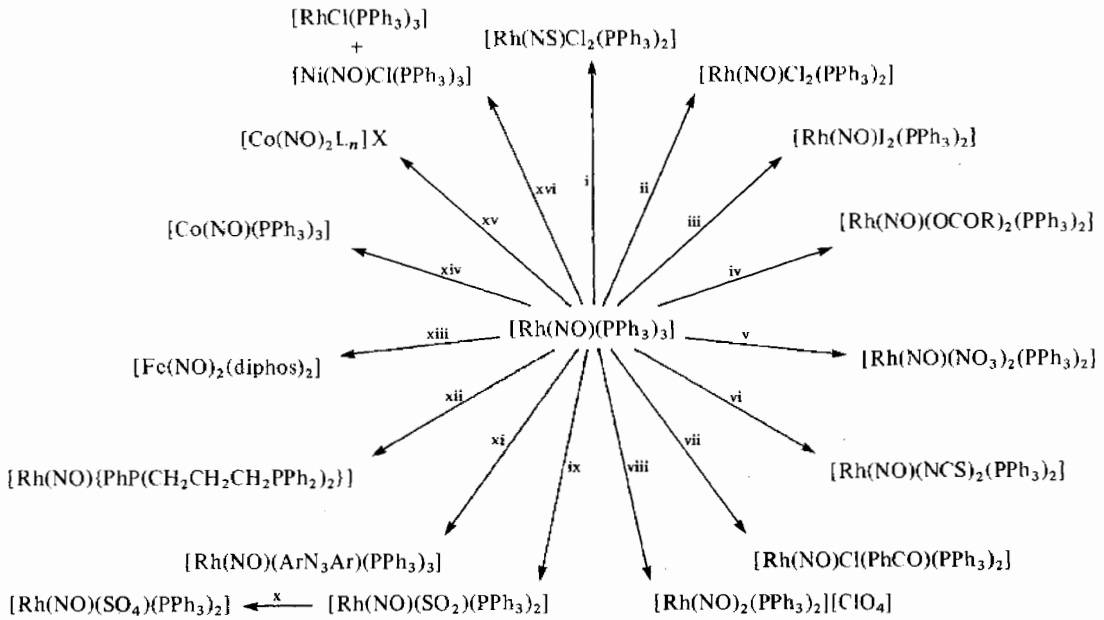
Complex	*Color*	*M.p.* (°C)	ν_{N-O} (cm^{-1})	*Ref.*
$[Rh(NO)(PPh_3)_3]$	Crimson	205–06[a]	1610	202
$[Rh(NO)\{P(p\text{-}C_6H_4Me)_3\}_3]$	Red	209–09[a]	1600	1301
$[Rh(NO)\{P(p\text{-}C_6H_4F)_3\}_3]$	Red	—	1630	1301
$[Rh(NO)\{P(p\text{-}C_6H_4Cl)_3\}_3]$	—	100–06	1598	1301
$[Rh(NO)(PMePh_2)_3]$	Red-orange	—	1570	1301
$[Rh(NO)(PF_3)_3]$	—	—	1820	1297
[Rh(NO)(**99**)]	—	—	1699	1052
$[Rh(NO)(PPh_3)_2(SO_2)]$	—	—	1600	1310

[a] Under N_2.



i, PPh_3, Na/Hg, THF;[1299,1301] ii, PPh_3, $NaBH_4$, p-$MeC_6H_4SO_2N(NO)Me$;[199,201,202] iii, PPh_3, NO, Zn, THF;[1302] iv, PPh_3, EtOH;[1304] v, Na/Hg, THF;[1301] vi, PPh_3, N_2H_4[1303]

Scheme 41 Preparations of $[Rh(NO)(PPh_3)_3]$



i, $(NSCl)_3$, $CHCl_3/CCl_4$;[1305] ii, CH_2Cl; $CHCl_3$;[1306] CCl_4;[1294,1306] PhCl; $CH_2{=}CHCH_2Cl$;[1306] iii, I_2; $+HgI_2$, $-Hg$;[1300] iv, O_2, RCO_2H;[201] v, 4 M HNO_3;[1309] vi, HNCS, Cl_2;[1304] vii, PhCOCl, C_6H_6;[1301] viii, $AgClO_4$, C_6H_6;[131] ix, SO_2, C_6H_6/C_7H_{16};[1310] x, O_2, C_6H_6;[1310,1311] xi, $(p\text{-}MeC_6H_4)_2N_3$;[231] xii, (**99**), C_6H_6, 80°C;[1317] xiii, $[FeCl_2(diphos)]$, THF;[151] xiv, $[CoCl(PPh_3)_3]$, C_6H_6;[151] xv, L = PPh_3, $[CoCl_2(PPh_3)_2]$, THF; L = diphos, $[Co(diphos)_2][ClO_4]_2$, C_6H_6;[151] xvi, $[NiCl_2(PPh_3)_2]$, C_6H_6[151]

Scheme 42 Reactions of $[Rh(NO)(PPh_3)_3]$

$$[RhCl(PF_3)_2]_2 + PF_3 + NO \longrightarrow [Rh(NO)(PF_3)_3] \quad (296)$$

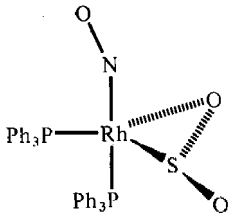
$$[Rh(NO)(PPh_3)_3] \rightleftharpoons [Rh(NO)(PPh_3)_2] + PPh_3 \quad (297)$$

The nitrosyl group is retained in the majority of the reactions. Usually two anionic ligands are added to form analogs of the important complex $[Rh(NO)Cl_2(PPh_3)_2]$ (see Section 48.10.2.2). The complex has also been used to catalyze homogeneous catalytic hydrogenation.[1315] Other reactions include the nitrosylation of iron, cobalt or nickel complexes, and conversion to the cation $[Rh(NO)_2(PPh_3)_2]^+$ by allowing the complex to react with $AgClO_4$.[151]

One reaction in which the oxidation state of the metal remains unchanged is that with sulfur dioxide (equation 298).[1310]

X-ray crystallography has shown that the SO_2 ligand binds through both sulfur and oxygen.[1310,1316] The sulfur dioxide complex (**132**) is easily oxidized by dioxygen in benzene solution to form the sulfato complex $[Rh(NO)(SO_4)(PPh_3)_2]$.[1310,1316] The product distribution when $^{18}O_2$ is the reactant implies that an intermediate sulfur bound sulfato complex is formed.[1316]

$$[Rh(NO)(PPh_3)_3] + SO_2 \xrightarrow{C_6H_6/C_7H_{16}} [Rh(NO)(PPh_3)_2(SO_2)] \quad (298)$$



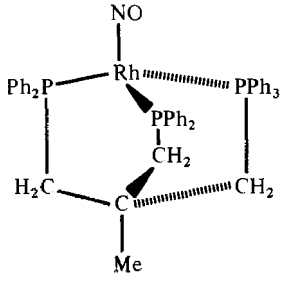
(132)

Analogs of $[Rh(NO)(PPh_3)_3]$ containing tri(*p*-tolyl)-,[201,1316] tri(*p*-fluorophenyl)-[1301] or tri(*p*-chlorophenyl)-phosphine[201] have been prepared using *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide (equation 299),[201] or from $[Rh(NO)_2Cl]_x$.[1301] Only one of their reactions has been investigated (equation 300). The tritertiary phosphine (**107**) displaces all three PPh_3 ligands when allowed to react with $[Rh(NO)(PPh_3)_3]$ to form the complex (**133**).[1301] The ^{31}P NMR spectra of (**133**) and related complexes have been obtained.[1317]

$$RhCl_3 \cdot 3H_2O + 10PR_3 + p\text{-}MeC_6H_4SO_2N(NO)Me \xrightarrow[78°C]{EtOH} [Rh(NO)(PR_3)_3] \quad (299)$$

$$R = p\text{-}C_6H_4Me,\ p\text{-}C_6H_4F,\ p\text{-}C_6H_4Cl$$

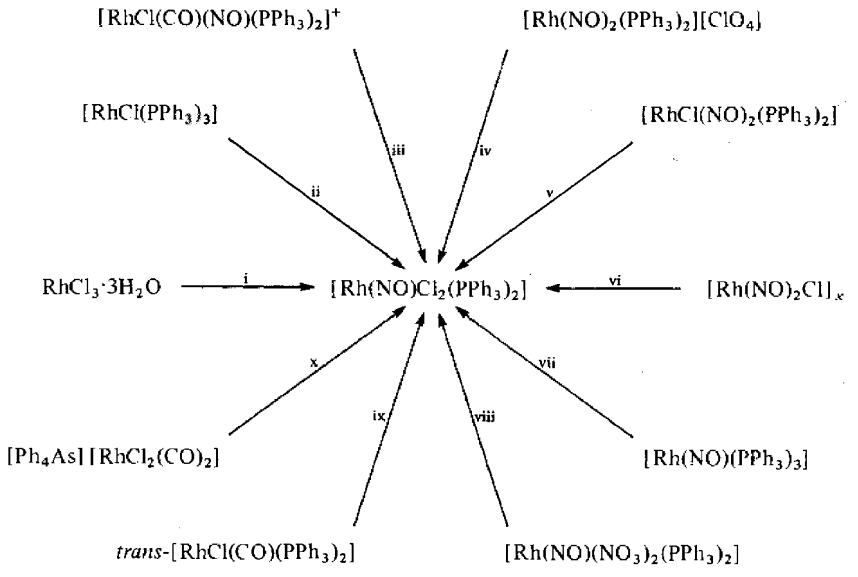
$$[Rh(NO)\{P(p\text{-}C_6H_4Me)_3\}_3] + PhCOCl \longrightarrow [Rh(NO)Cl_2\{P(p\text{-}C_6H_4Me)_3\}_2] \quad (300)$$



(133)

48.10.2.2 [Rh(NO)X₂L₂] complexes

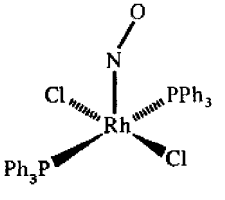
The most important complex of this type is $[Rh(NO)Cl_2(PPh_3)_2]$, which was first prepared in 1962. The tri(cyclohexyl)phosphine and triphenylarsine analogs were also prepared at this date. The dichloro complexes were precipitated when excess neutral ligand was allowed to react with $[Rh(NO)_2Cl]_x$. The preparative routes available for $[Rh(NO)Cl_2(PPh_3)_2]$ are summarized in Scheme 43. Again *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide is the most convenient source of the nitrosyl ligand.[202,1323]



i, *p*-$MeC_6H_4SO_2N(NO)Me$;[202,1323] N_2, PPh_3, EtOH;[1294] ii, NOCl, CH_2Cl_2;[1319] iii, Cl^-;[1321] iv, HCl;[1304] v, NOCl;[1303] vi, PPh_3, THF;[1299] vii, CH_2Cl_2; $CHCl_3$;[1306] CCl_4;[1294,1306] PhCl; $CH_2{=}CHCH_2Cl$;[1306] HCl, C_6H_6;[1301] viii, HCl;[1309,1330] ix, H_3O^+, KNO_2; NO, $CHCl_3$, H_3O^+;[1320] x, *p*-$MeC_6H_4SO_2N(NO)Me$[201]

Scheme 43 Preparations of $[Rh(NO)Cl_2(PPh_3)_2]$

The dichlororhodium complex adopts the square pyramidal structure (**134**; L = PPh_3). The nitrosyl group is bent but the nitrogen and oxygen atoms lie on the P—Rh—P plane.[1324] The nitrosyl group in $[Rh(NO)Br_2\{P(OPh)_3\}_2]$ is also bent.[1325] Vibrational frequencies of the nitrosyl group in $[Rh(NO)X_2L_2]$ complexes are given in Table 91.



(134)

According to the ^{31}P NMR spectrum $[Rh(NO)Cl_2(PPh_3)_2]$ is not dissociated in solution.[1313]

Many analogs of $[Rh(NO)Cl_2(PPh_3)_2]$ are known since other group V ligands may replace PPh_3, and other monodentate anions the chloro ligands. However, the latter are not derivatives of $[Rh(NO)Cl_2(PPh_3)_2]$ since they have all been obtained from other sources.

If nitrosyl bromide is allowed to react with hydrated rhodium trichloride and PPh_3 in ethanol, the mixed chlorobromo complex is obtained (equation 301).[1303] When $[RhCl(PPh_3)_3]$ is the substrate the dibromo complex is formed (equation 302). This complex can also be obtained from rhodium tribromide, *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide and PPh_3. Replacement of PPh_3 by other tertiary phosphines permits analogous dibromo complexes to be prepared (*cf.* equation 299). Another source of the triphenylphosphine complex is $[Rh(NO)_2Br]_n$. The diiodo complex can be obtained from a similar reaction mixture containing LiI (equation 304).[1293]

$$RhCl_3{\cdot}3H_2O + NOBr + PPh_3 \xrightarrow{EtOH} [Rh(NO)ClBr(PPh_3)_2] \quad (301)$$

$$[RhCl(PPh_3)_3] + NOBr \xrightarrow{CH_2Cl_2} [Rh(NO)Br_2(PPh_3)_2] \quad (302)$$

$$RhBr_3 + PR_3 + p\text{-}MeC_6H_4SO_2N(NO)Me \longrightarrow [Rh(NO)Br_2(PR_3)_2] \quad (303)$$

R_3 = Et_3, Pr^i_3, Bu_3, Ph_3, $(p\text{-}C_6H_4Cl)_3$, $MePh_2$

Table 91 Physical Properties of $[Rh(NO)X_2L_2]$ Complexes

Complex	*Color*	*M.p.* (°C)	ν_{N-O} (cm^{-1})	*Ref.*
$[Rh(NO)(CNS)_2(PPh_3)_2]$	—	—	1690	1304
$[Rh(NO)(NO_3)_2(PPh_3)_2]$	Yellow	200–01[a]	1645	1304, 1309
$[Rh(NO)(O_2CMe)_2(PPh_3)_2]$	—	—	1614	127
$[Rh(NO)(O_2CEt)_2(PPh_3)_2]$	—	—	1639	127
$[Rh(NO)(p\text{-}O_2CC_6H_4Me)_2(PPh_3)_2]$	—	—	1624	127
$[Rh(NO)(p\text{-}O_2CC_6H_4NO_2)_2(PPh_3)_2]$	—	—	1632	127
$[Rh(NO)(p\text{-}O_2CC_6H_4Cl)_2(PPh_3)_2]$	—	—	1627	127
$[Rh(NO)(O_2CCF_3)_2(PPh_3)_2]$	Green	—	1665	1308
$[Rh(NO)(O_2CC_2F_5)_2(PPh_3)_2]$	Green	—	1665	1308
$[Rh(NO)(O_2CC_6F_5)_2(PPh_3)_2]$	Green	—	1665	1308
$[Rh(NO)Cl_2(PEt_3)_2]$	Brown	—	—	1323
$[Rh(NO)Cl_2(PPr^i{}_3)_2]$	Dark brown	—	—	1323
$[Rh(NO)Cl_2(PBu_3)_2]$	Light brown	—	—	1323
$[Rh(NO)Cl_2(PPh_3)_2]$	Light brown	—	1630	202
$[Rh(NO)Cl_2\{P(p\text{-}C_6H_4Me)_3\}_2]$	Pink	—	—	1323
$[Rh(NO)Cl_2\{P(p\text{-}C_6H_4OMe)_3\}_2]$	Brown	—	—	1323
$[Rh(NO)Cl_2\{P(p\text{-}C_6H_4Cl)_3\}_2]$	Fawn	—	—	1323
$[Rh(NO)ClBr(PPh_3)_2]$	—	230–32	1610–1660	1303
$[Rh(NO)Cl(PhCO)(PPh_3)_2]$	Green	—	1608	1301
$[Rh(NO)Br_2(PEt_3)_2]$	Brown	—	—	1323
$[Rh(NO)Br_2(PPr^i{}_3)_2]$	Maroon	—	—	1323
$[Rh(NO)Br_2(PBu_3)_2]$	Brown	—	—	1323
$[Rh(NO)Br_2(PMePh_2)_2]$	Brown	—	—	1323
$[Rh(NO)Br_2(PPh_3)_2]$	Orange-brown	211–15	1632	1293
$[Rh(NO)I_2(PPh_3)_2]$	Violet-brown	234–38	—	1293
$[Rh(NO)Cl_2(AsPh_3)_2]$	Brown	230	1632	1293
$[Rh(NO)Br_2(AsPh_3)_2]$	Red-brown	259–60	1629	1293
$[Rh(NO)I_2(AsPh_3)_2]$	Violet-brown	249–50	1626	1293

[a] With decomposition.

$$RhCl_3 \cdot 3H_2O + PR_3 + p\text{-}MeC_6H_4SO_2N(NO)Me \xrightarrow{MI} [Rh(NO)I_2(PR_3)_2] \quad (304)$$

$$M = Li, R = Ph, MeC_6H_4, p\text{-}C_6H_4Cl; M = K, R = Et, Bu$$

The bis(thiocyanato) complex has been obtained by addition of KCNS to $[Rh(NO)_2(PPh_3)_2][ClO_4]$.[1304]

The green chloro(nitro) complex $[Rh(NO)Cl(NO_2)(PPh_3)_2]$ has often been observed as an intermediate in the preparation of $[Rh(NO)Cl_2(PPh_3)_2]$, but it has only been isolated when $[RhCl(PPh_3)_3]$ or *trans*-$[RhCl(CO)(PPh_3)_2]$ have been used as the starting materials (equations 305–308).[244,1318,1325]

$$[RhCl(PPh_3)_2L] + N_2O_3 \xrightarrow{CH_2Cl_2} [Rh(NO)Cl(NO_2)(PPh_3)_2] \quad (305)$$

$$[RhCl(PPh_3)_3] + 4NO \xrightarrow{PhCl} [Rh(NO)Cl(NO_2)(PPh_3)_2] + PPh_3 + N_2O \quad (306)$$

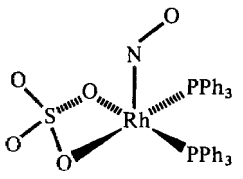
$$[RhCl(CO)(PPh_3)_2] + NO \xrightarrow{C_6H_6} [Rh(NO)Cl(NO_2)(PPh_3)_2] + CO \quad (307)$$

$$[RhCl(CO)(PPh_3)_2] + NOCl \longrightarrow [Rh(NO)Cl(NO_2)(PPh_3)_2] + CO \quad (308)$$

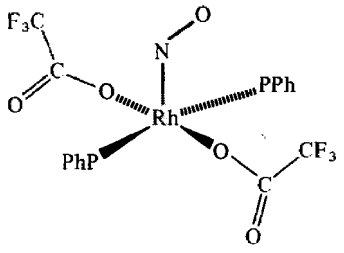
The IR spectrum of this complex usually shows two nitrosyl absorption bands, which have been ascribed to the presence of isomers. The bands which occur at 1508, 1309 and 816 cm^{-1} arise from the nitro ligand and imply that it is N-bonded.[1325] Whilst the dichloro complex (**134**) has *trans* chloro ligands,[244] the preparation of $[Rh(NO)Cl(NO_2)(diphos)]$, in which the anionic ligands must be *cis*, allows the possibility of geometrical isomerism in $[Rh(NO)Cl(NO_2)(PPh_3)_2]$. *Cis* anionic ligands have been found in the sulfato complex $[Rh(NO)(SO_4)(PPh_3)_2]$ (**135**),[1326] and in the triphenyl phosphite complex $[Rh(NO)Br_2\{P(OPh)_3\}_2]$.[1327] However, the trifluoroacetato complex (**136**) has *trans* basal ligands.[1328]

If a green solution of $[Rh(NO)Cl(NO_2)(PPh_3)_2]$ in benzene is allowed to stand, a brown complex is precipitated.[244] This may be the dinitrosyl complex which can be obtained from *trans*-$[RhCl(CO)(PPh_3)_2]$ and nitric oxide when the reaction is carried out in carbon tetrachloride[234] or toluene[1329] solution.

No corresponding dinitro complex is known, but two routes have been discovered to the dinitrato complex $[Rh(NO)(NO_3)_2(PPh_3)_2]$ (equations 309 and 310).[1330,1331]



(135)



(136)

$$[RhH(PPh_3)_3] \text{ or } [RhH(CO)(PPh_3)_3] \xrightarrow{HNO_3} [Rh(NO)(NO_3)_2(PPh_3)_2] \quad (309)$$

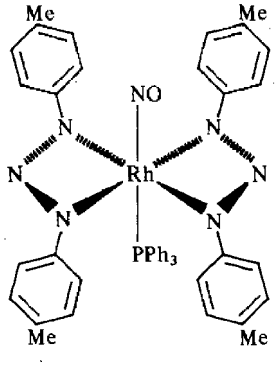
$$[Rh(NO)Cl_2L_2(CO)] + AgNO_3 \xrightarrow{CHCl_3} [Rh(NO)(NO_3)_2L_2] \quad (310)$$

The most numerous complexes of this stoichiometry are the bis(carboxylato) complexes. They can be obtained from the reaction between $[Rh(NO)Cl(NO_2)(PPh_3)_2]$ and carboxylic acids in aerated solution (equation 311).[127,1308] The IR spectra of the carboxylato ligands (Table 92) are consistent with their monodentate bonding shown in the structure (**136**).[1328]

$$[Rh(NO)(PPh_3)_3] + RCO_2H \xrightarrow[Me_2CO]{O_2} [Rh(NO)(OCOR)_2(PPh_3)_2] \quad (311)$$

R = Me, Et, *p*-C_6H_4Me, *p*-$C_6H_4NO_2$, *p*-C_6H_4Cl,[127] CF_3, C_2F_5, C_6F_5[1308]

Unlike all the other complexes described in this subsection the bis{di(*p*-tolyl)triazenido} complex (**137**) contains six-coordinate rhodium. It can be prepared from the reaction between the triazene and $[Rh(NO)Cl(NO_2)(PPh_3)_2]$ (equation 312). The single methyl resonance at τ 7.80 in its proton NMR spectrum is the reason for assigning it the symmetric structure.[231]



(137)

$$[Rh(NO)(PPh_3)_3] + (p\text{-}MeC_6H_4)_2N_3 \longrightarrow [Rh(NO)\{(p\text{-}MeC_6H_4)_2N_3\}_2(PPh_3)] \quad (312)$$

Table 92 IR Spectra of $[Rh(NO)(O_2CR)_2(PPh_3)_2]$ Complexes[a]

Complex	ν_{COO} *(asym)* (cm^{-1})	ν_{COO} *(sym)* (cm^{-1})	$\Delta\nu$(cm^{-1})
$[Rh(NO)(O_2CMe)_2(PPh_3)_2]$	1600	1362	238
$[Rh(NO)(O_2CEt)_2(PPh_3)_2]$	1667	1376	231
$[Rh(NO)(p\text{-}O_2CC_6H_4Me)_2(PPh_3)_2]$	1618	1348	270
$[Rh(NO)(p\text{-}O_2CC_6H_4Cl)_2(PPh_3)_2]$	1614	1344	270
$[Rh(NO(p\text{-}O_2CC_6H_4NO_2)_2(PPh_3)_2]$	1601	1332	269

[a] Data from ref. 127.

Many of the methods that have been used to prepare the $[Rh(NO)X_2(PR_3)_2]$ complexes can be adapted to yield similar tertiary arsine complexes. For example, *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide still functions as a source of the nitrosyl ligand in the presence of tertiary arsines (equations 313 and 314).

$$RhBr_3 + p\text{-}MeC_6H_4SO_2N(NO)Me + AsPh_3 \longrightarrow [Rh(NO)Br_2(AsPh_3)_2] \quad (313)$$

$$RhCl_3 \cdot 3H_2O + p\text{-}MeC_6H_4SO_2N(NO)Me + AsPh_3 \xrightarrow{LiI} [Rh(NO)I_2(AsPh_3)_2] \quad (314)$$

Additionally all three dihalo complexes can be prepared from $[Rh(NO)X_2]_n$ species (equation 315).[1293] The dichloro complex is also produced when $AsPh_3$ is allowed to react with $[Rh(NO)_2Cl]$ (equation 316).[1299]

$$[Rh(NO)X_2]_x + AsPh_3 \longrightarrow [Rh(NO)X_2(AsPh_3)_2] \quad (315)$$

$$[Rh(NO)_2Cl]_x + AsPh_3 \longrightarrow [Rh(NO)Cl_2(AsPh_3)_2] \quad (316)$$

The action of nitrosyl chloride[1303] or dinitrogen trioxide[1318] on $RhCl_3 \cdot 3H_2O$ in the presence of $AsPh_3$ also yields the dichloro complex. There have been reports of the preparation of $[Rh(NO)XL_2]$ complexes.[1329,1332–1334] However, these complexes have only been prepared in the Soviet Union, and it has been claimed that their preparation cannot be repeated.[1335]

48.10.2.3 Cationic complexes

A number of cationic complexes have been prepared. The physical properties of these complexes are shown in Table 93. The first examples were prepared by allowing ammonia or other nitrogenous bases to react with $[RhX(NO)_2]_n$ complexes (equation 317).[1292]

$$[Rh(NO)_2X]_x + L \longrightarrow [Rh(NO)_2L_2]X \quad (317)$$

$$X = Cl, Br; L = NH_3, py, morpholine, 0.5\,bipy$$

They are more usually prepared by the action of nitrosyl compounds on rhodium(I) complexes containing labile ligands.[1336–1339] It has also proved possible in one instance to prepare this type of complex by anion metathesis (equations 318 to 320).[1340]

$$[Rh(cod)_2][BF_4] + NOBF_4 \xrightarrow{MeCN} [Rh(NO)(MeCN)_4][BF_4]_2 \quad (318)$$

$$[RhCl(PPh_3)_3] + PPh_3 + NOBF_4 \xrightarrow[C_6H_6]{N_2} [Rh(NO)Cl(PPh_3)_3][BF_4] \quad (319)$$

$$[Rh(bipy)L_2] + NOPF_6 \xrightarrow{MeCN} [Rh(NO)(MeCN)_3(bipy)][PF_6]_2 \quad (320)$$

$$L = CO, cod$$

Table 93 Physical Properties of Cationic Nitrosyl Complexes

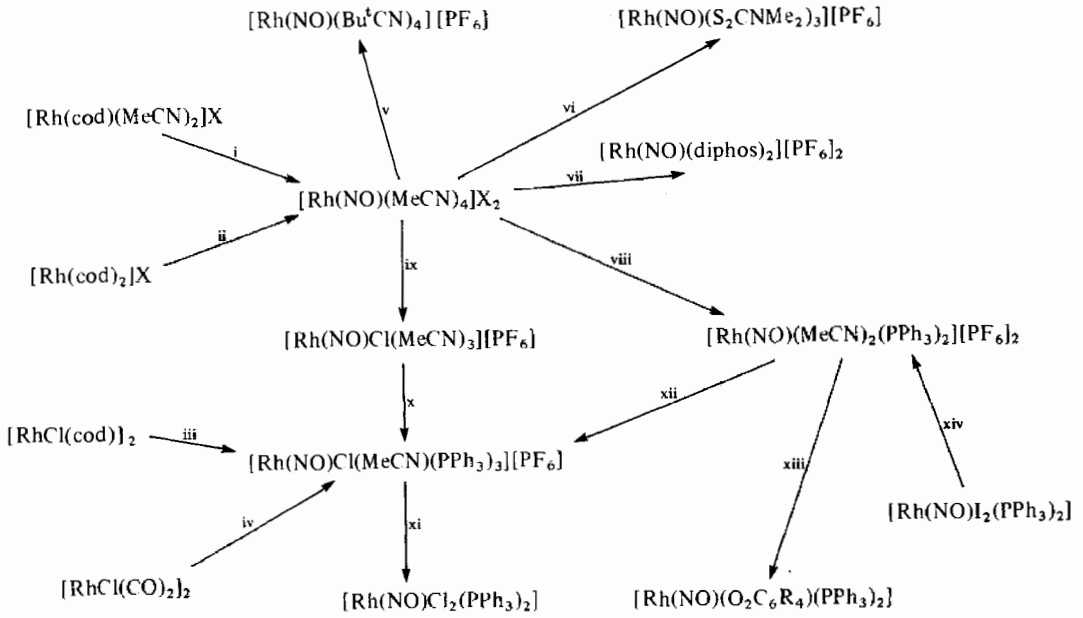
Complex	*Color*	ν_{N-O} (cm^{-1})	*Ref.*
$[Rh(NO)(MeCN)_4][BF_4]_2$	Emerald green	1754	1337
$[Rh(NO)(MeCN)_4][PF_6]_2$	Emerald green	1758	1336
$[Rh(NO)(Bu^tCN)_4][PF_6]_2$	Green	1765	1336
$[Rh(NO)(diphos)_2][BF_4]_2$	Olive green	1730	1337
$[Rh(NO)(diphos)_2][PF_6]_2$	Green	—	1336
$[Rh(NO)(MeCN)_2(PPh_3)_2][BF_4]_2$	Green	1734	1337
$[Rh(NO)(MeCN)_2(PPh_3)_2][PF_6]_2$	Olive green	—	1336
$[Rh(NO)(MeCN)_2(AsPh_3)_2][BF_4]_2$	Olive green	1720	1337
$[Rh(NO)Cl(MeCN)_3][PF_6]$	Green-brown	1700	1336
$[Rh(NO)Cl(PPh_3)_3][BF_4]$	Red-violet	1720	1338
$[Rh(NO)Cl(MeCN)(PPh_3)_2][PF_6]$	Yellow-green	1698	1336
$[Rh(NO)(S_2CNEt_2)(PPh_3)_2][PF_6]$	—	—	1336
$[Rh(NO)(S_2CNMe_2)_3][BF_4]$	Brown	1545	1337
$[Rh(NO)(S_2CNMe_2)_3][PF_6]$	Brown	—	1336

There are two interesting reactions of $[Rh(NO)(CO)(PPh_3)_2][BF_4]_2$ that give rise to complexes of this type. The first can be classed as an esterification whilst the second is a disproportionation (equations 321 and 322).[1341]

$$[Rh(CO)(NO)(PPh_3)_2][BF_4]_2 \xrightarrow[C_6H_6]{ROH,\ -H^+} [Rh(NO)(O_2CR)(ROH)][BF_4] \quad (321)$$

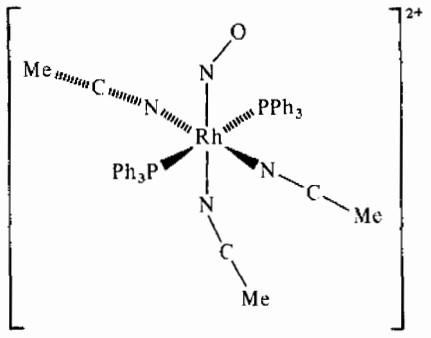
$$[Rh(CO)(NO)(PPh_3)_2][BF_4]_2 \xrightarrow{PriOH} [Rh(CO)_2(PPh_3)_2][BF_4]_3 + [Rh(NO)_2(PPh_3)_2][BF_4] \quad (322)$$

The complexes containing organonitrile ligands themselves undergo a variety of reactions (Scheme 44). Whilst the structures of the five-coordinate cations remain a matter for speculation, the six-coordinate cation $[Rh(NO)(MeCN)_3(PPh_3)_2]^{2+}$ has been shown to have the structure (**138**) by X-ray crystallography.[1343]

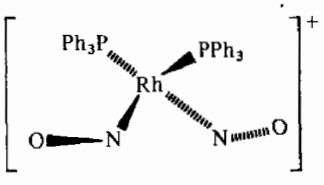


i, NOX (X = BF_4, PF_6);[1337] ii, $NOPF_6$, MeCN;[1336,1337] iii, $NOPF_6$, MeCN;[1336] iv, $NOPF_6$, MeCN;[1336] v, Bu^{t}CN;[1337] vi, $Na_2S_2CNEt_2$;[1336] vii, diphos;[1336] viii, PPh_3;[1336] ix, Cl^-;[1336] x, PPh_3;[1336] xi, Cl^-;[1336] xii, Cl^-;[1336] xiii, 1,2-$(HO)_2C_6R_4$ (R_4 = H_4, Br_4, H_3-4-NO_2, H_3-4-CHO, H_3-4-CO_2Me);[1342] xiv, $AgPF_6$, MeCN[1340]

Scheme 44 Preparations and reactions of cationic rhodium nitrosyl complexes



(138)



(139)

The crystal structure of the dinitrosyl cation (**139**) has been determined.[1344] This cation can be prepared from other rhodium nitrosyl complexes (equations 323 and 324).[151,1304]

$$[Rh(NO)(PPh_3)_3] + AgClO_4 \xrightarrow{C_6H_6} [Rh(NO)_2(PPh_3)_2][ClO_4] \quad (323)$$

$$[Rh(NO)_2(NO_2)(PPh_3)_2] + HClO_4 \longrightarrow [Rh(NO)_2(PPh_3)_2][ClO_4] \quad (324)$$

The hexafluorophosphate analog can be prepared from $[Rh(nbd)(PPh_3)_2][PF_6]$ (equation 325). Bis-1,2-(diphenylphosphino)ethane displaces all ligands from the cation, but the reaction is obviously more complex since N_2O and $OPPh_3$ are also produced (equation 326).[234]

$$[Rh(nbd)(PPh_3)_2][PF_6] + NO \longrightarrow [Rh(NO)_2(PPh_3)_2][PF_6] \quad (325)$$

$$[Rh(NO)_2(PPh_3)_2][PF_6] + \text{diphos} \longrightarrow [Rh(\text{diphos})_2][PF_6] + N_2O + OPPh_3 + PPh_3 \quad (326)$$

48.10.2.4 Thionitrosyl complexes

There are a few thionitrosyl complexes of rhodium, many of which contain thionitrosyl bridges. They have been prepared by allowing $[NSCl]_3$ to react with sundry rhodium nitrosyl complexes (equations 327 and 328).

$$[Rh(NO)(PPh_3)_3] + [NSCl]_3 \xrightarrow[CHCl_3]{CCl_4} [Rh(NS)Cl_2(PPh_3)]_2 \quad (327)$$

$$[Rh(NO)Cl_2(ZPh_3)_2] + [NSCl]_3 \xrightarrow[CHCl_3]{CCl_4} [Rh(NS)Cl_2(ZPh_3)]_2 \quad (328)$$

$$Z = As,^{1305}\ P^{1346}$$

The dihalo complexes are believed to contain thionitrosyl bridges since the band in their IR spectra at *ca.* 840 cm^{-1} disappears when the complexes are cleaved by excess neutral ligand (equation 329). In the latter complexes ν_{N-S} occurs at 1116–1120 cm^{-1}.[1305,1345,1346]

$$[Rh(NS)Cl_2(ZPh_3)]_2 + ZPh_3 \xrightarrow{CH_2Cl_2} 2[Rh(NS)Cl_2(ZPh_3)_2] \quad (329)$$

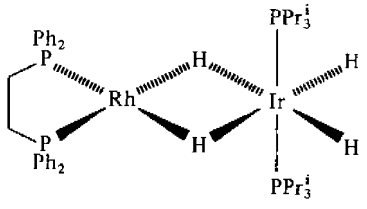
$$Z = As,^{1305}\ P^{1346}$$

48.10.3 Bimetallic Complexes

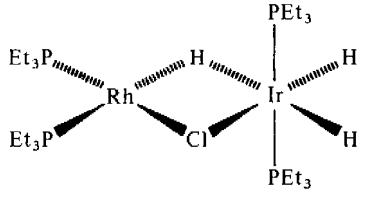
The complexes included in this section are those in which rhodium and at least one other metallic element are present. Normally the second metal is not bound to rhodium although complexes in which a metal–metal bond is supplemented by a bridging ligand are also included.

It has been noted above that the weakly solvated cation $[Rh(diphos)(MeOH)_2]^+$ can be obtained by hydrogenation of $[Rh(diphos)(C_7H_8)][BF_4]$. If the former compound is allowed to react with an equimolar quantity of $[IrH_5(PPr^i_3)_2]$ the di-μ-hydrido complex (**140**) is formed (equation 330). The presence of base merely increases the yield. Only the heavy atoms have been located by X-ray crystallography.[1347]

$$[Rh(diphos)(MeOH)_2]^+ + [IrH_5(PPr^i_3)_2] \xrightarrow[NEtPr^i_2]{MeOH} [(diphos)RhH_2IrH_2(PPr^i_3)_2] \quad (330)$$



(140)



(141)

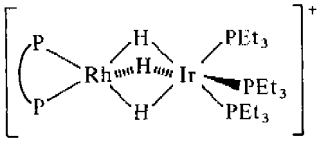
Two related orange brown μ-hydrido-μ-chloro complexes (**141**) can also be obtained from $[IrH_5(PEt_3)_2]$. Further structural details are available. The ^{31}P NMR spectrum of (**141**) ($PPh_3 = PEt_3$) has a doublet of doublets at 80 p.p.m. and a set of four triplets at 58.8 p.p.m. The latter group arises from the phosphorus atom bound to rhodium which is *cis* to the hydrido bridge.[1348]

$$[RhCl(PR_3)_2]_2 + [IrH_5(PEt_3)_2] \xrightarrow{C_7H_8} [(R_3P)_2Rh(H)ClIr(PEt_3)_2] \quad (331)$$

$$R_3P = Et_3P,\ 0.5\ \text{diphos}$$

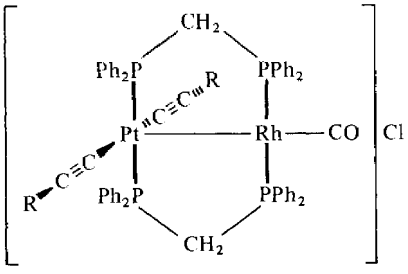
Generation of the $[Rh(diphos)(MeOH)_2]^+$ cation in the presence of *mer*-$[IrH_3(PEt_3)_2]$ gives a dark green cation (**142**) that contains three hydrido bridges (equation 332). Again only the heavy atoms have been located by X-ray crystallography. The ^1H NMR spectrum shows a multiplet at τ 22.0 due to the hydrido ligands. As might be expected the ^{31}P NMR spectrum is complicated, having multiplet peaks arising from the diphos ligand. The IR spectrum of the hydrido ligands shows peaks at 1800 and 1686 cm^{-1}, whilst the corresponding trideuterio complex has peaks at 1300 and 1100 cm^{-1}.[1349]

$$[Rh(diphos)(MeOH)_2]^+ + \textit{mer}\text{-}[IrH_3(PEt_3)_3] \xrightarrow[MeOH]{NaBPh_4} [(diphos)RhH_3Ir(PEt_3)_3][BPh_4] \quad (332)$$

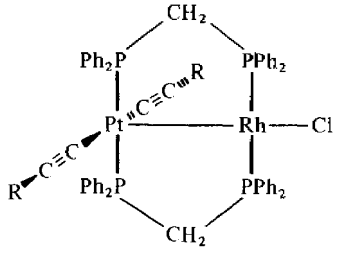


(142)

It is also possible to prepare bimetallic rhodium(I) complexes containing 'A-frame' ditertiary phosphine ligands. However, the majority of these complexes contain carbonyl ligands and have been dealt with in the companion volume.[17] Nevertheless (**143**) upon heating in toluene decarbonylates and forms the bimetallic complex (**144**).[1350]

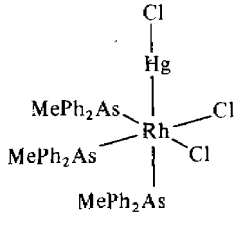


(143)



(144)

Probably the most numerous bimetallic complexes of rhodium are those containing mercury. The complex β-$[RhHCl_2(AsMePh_2)_3]$ reacts with mercury(II) halides,[1351] phenylmercury(II) halides,[1352] or mercury(I) halides[1351,1352] to produce *fac*-rhodium–mercury complexes (**145**) (equation 333). The physical properties of the products are shown in Table 94.



(145)

$$\beta\text{-}[RhHCl_2(AsMePh_2)_3] + HgX_2 \longrightarrow \textit{mer}\text{-}[RhCl_2(HgX)(AsMePh_2)_3] \quad (333)$$

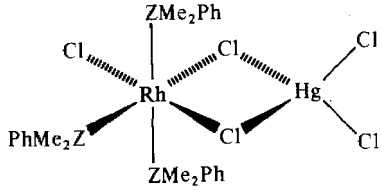
$$X = F, Cl, Br, I, MeCO_2$$

Meridional rhodium(III) complexes also undergo reaction with mercury(II) halides. Unlike the corresponding reaction with rhodium(I) complexes where a rhodium–mercury bond was formed,[186] in these instances the tetrahedral $[HgCl_4]^{2-}$ ion acts as a bidentate ligand (**146**; equation 334). Three bands in the far-IR spectrum of the chloro complex at 345, 310 and 242 cm^{-1} have been assigned to $\nu_{Rh\ Cl\ Hg}$, $\nu_{Hg\ Cl}$ and ν_{Rh-Cl} respectively. However, the reaction between the corresponding tertiary phosphine complex *mer*-$[RhCl_3(PMe_2Ph)_3]$ and $HgCl_2$ also forms a polynuclear mercury complex (equation 335).[1353]

Table 94 Physical Properties of Rhodium–Mercury Compounds

Complex	*Color*	*M.p.* (°C)	*Ref.*
$[RhCl_2(HgF)(AsMePh_2)_3]$	Pale green	195	1351
$[RhCl_2(HgCl)(AsMePh_2)_3]$	Yellow	205	1352
$[RhCl_2(HgBr)(AsMePh_2)_3]$	Orange-yellow	165	1352
$[RhCl_2(HgI)(AsMePh_2)_3]$	Orange	155	1352
$[RhCl_2(HgO_2CMe)(AsMePh_2)_3]$	Yellow	172	1352
$[RhBr_2(HgF)(AsMePh_2)_3]$	Yellow	154	1352
$[RhBr_2(HgCl)(AsMePh_2)_3]$	Yellow	202	1352
$[RhBr_2(HgBr)(AsMePh_2)_3]$	Yellow-orange	187	1352
$[RhBr_2(HgI)(AsMePh_2)_3]$	Orange	148	1352
$[RhBr_2(HgO_2CMe)(AsMePh_2)_3]$	Pale yellow	190	1352
$[RhHgCl_5(PMe_2Ph)_3]$	Orange	127–30	1353
$[RhHgCl_5(AsMe_2Ph)_3]$	Red	156–65[a]	1353

[a] With decomposition.



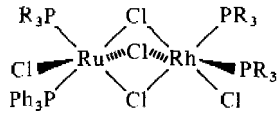
(146)

$$mer\text{-}[RhCl_3(AsMe_2Ph)_3] + HgCl_2 \xrightarrow{MeOH} [RhCl_3(AsMe_2Ph)_3(HgCl_2)] \quad (334)$$

$$mer\text{-}[RhCl_3(PMe_2Ph)_3] + HgCl_2 \xrightarrow[CHCl_3]{MeOH} [Hg_4Cl_8(PMe_2Ph)_2] + [RhCl_3(PMe_2Ph)_3(HgCl_2)] \quad (335)$$

Similar bimetallic complexes to (**146**), except that they contain a bidentate, square planar, anionic ligand of the type $[MCl_3L]^-$ (M = Pt, L = PEt_3, PBu_3, PBu^tPr_2; M = Pd, L = PBu_3) are believed to be formed as intermediates in ligand exchange reactions.[1354]

Trihalo-bridged complexes (**147**) are formed in the reactions between $[RuCl_2(PPh_3)_3]$ and *mer*-$[RhCl_3L_3]$ complexes (equation 336).[1355,1356]

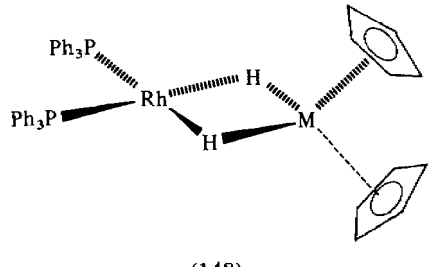


(147)

$$mer\text{-}[RhCl_3(PR_3)_3] + [RuCl_2(PPh_3)_3] \longrightarrow [(R_3P)_2ClRhCl_3RuCl(PPh_3)(PR_3)] \quad (336)$$

$$R_3 = Bu_3, Ph_3, Me_2Ph, Et_2Ph, Bu_2Ph$$

The dihydridobis(cyclopentadienyl) complexes of both molybdenum and tungsten react with $[RhH_2(PPh_3)_2(Me_2CO)_2][PF_6]$ to form deep brown complexes. Their proton NMR spectra indicate that the hydrido ligands are bound to both metals (**148**) since large coupling constants are observed (J(Rh–H) = 29 Hz, J(W–H) = 107 Hz). When the tungsten compound is heated in acetone/D_2O mixtures, deuterium is incorporated in the cyclopentadienyl ligands.[1357]



(148)

$$[RhH_2(PPh_3)_2(Me_2CO)_2][PF_6] + [MH_2(Cp)_2] \longrightarrow [(Ph_3P)_2RhH_2M(Cp)_2] \quad (337)$$

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Iridium

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49.1 INTRODUCTION

The coordination chemistry of iridium is concerned primarily with the I, III and IV oxidation states; complexes with iridium in the −I, 0, V and VI oxidation states are also known. Of these latter states, Ir^{-I} and Ir^0 are found in carbonylate anions, oligonuclear and substituted carbonyls, hydrides and ammines. Iridium(V) and (VI) complexes are predominantly hexahalide compounds.

Diamagnetic iridium(I) complexes (d^8) form with π-acid ligands such as tertiary phosphines and arsines, carbonyls, nitrosyls and alkenes, as well as with hydride and halide ions. Several Ir^I complexes undergo oxidative addition reactions to yield six-coordinate octahedral Ir^{III} species. Kinetically inert iridium(III) complexes (d^6) are almost invariably low spin (t_{2g}^6) and six coordinate, though a few five- and seven-coordinate complexes have been reported. By and large, iridium(III) complexes occur with 'soft' ligands, including CO, ER_3 (E = P, As, Sb), R_2S, NO_2^-, NH_3, SCN^-, SO_4^{2-}, SO_3^{2-} and X^- (X = Cl, Br, I). Additionally, there are numerous iridium(III) hydride complexes, usually containing carbonyl, phosphine, arsine and/or stibene ligands. Neutral as well as anionic and cationic iridium(III) complexes exist. A number of six-coordinate paramagnetic

Table 1 Oxidation States and Associated Coordination Numbers and Geometries of Iridium Complexes

Oxidation state	*Coordination number*	*Geometry*	*Examples*
$-I$, d^{10}	Four	Tetrahedral	$Na[Ir(CO)_3(PPh_3)]$
	Four	Tetrahedral	$[Ir(NO)(PPh_3)_3]$
	Four	—	$K[Ir(PF_3)_4]$
O, d^9	Four	Cluster	$[Ir_4(CO)_{12}]$
	Four	—	$[Ir(CO)(PPh_3)_3]$
	Four	—	$[Ir(NO)(CO)(PPh_3)_2]^+$
I, d^8	Four	Square planar	$[Ir(Cl)(CO)(PEt_3)_2]$
	Five	Trigonal bipyramidal	$[Ir(H)(CO)(PPh_3)_3]$
II, d^7	Four	—	$[Ir(Cl)_2(CO)_2]$
	Five	—	$[Ir(I)_3(CO)_2]$
III, d^6	Five	Trigonal bipyramidal	$[Ir(H)_3(PR_3)_2]$
	Five	—	$[Ir(H)_3(AsPh_3)_2]$
	Six	Octahedral	$[Ir(H)_3(PPh_3)_3]$
	Six	—	$[Ir(H_2O)(NH_3)_5]^{3+}$
	Six	—	$[IrCl_6]^{3-}$
IV, d^5	Six	Octahedral	$[Ir(C_2O_4)_3]^{2-}$
	Six	—	$[IrCl_6]^{2-}$
	Six	—	$M[Ir(OH)_6]$, M = Zn, K_2
V, d^4	Six	Octahedral	$Cs[IrF_6]$
	Seven	—	$[Ir(H)_5(PPhEt_2)_2$
VI, d^3	Six	Octahedral	$[IrF_6]$

iridium(IV) complexes (d^5) are known, in contrast to rhodium(IV). Stable Ir^{IV} complexes are formed with halogen, oxygen and nitrogen donors; these complexes are easily reduced to Ir^{III} with P, As and S donor ligands. Table 1 summarizes the coordination chemistry of iridium in terms of oxidation state and associated coordination numbers and coordination geometries.

This chapter will not deal with iridium complexes in which the coordination chemistry of the iridium–carbon bond is implicated inasmuch as Leigh and Richards[1] have very recently (1982) provided an excellent detailed review on such compounds; organoiridium[2] and iridium carbonyl[3] complexes were also previously reviewed. Iridium complex chemistry has been reviewed (1980) along with rhodium,[4] and in annual reviews.[5] Additionally, iridium complexes have been treated in 'Comprehensive Inorganic Chemistry'.[6]

49.2 IRIDIUM(−I)

49.2.1 Nitrogen Ligands

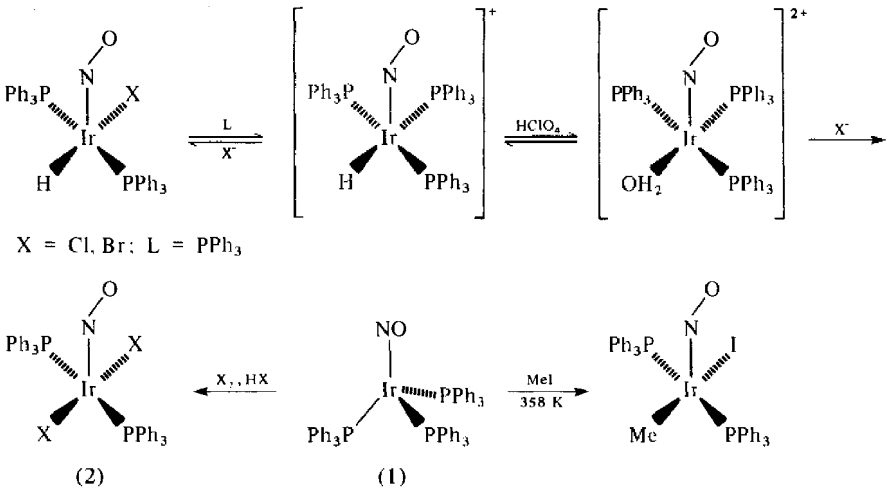
49.2.1.1 Nitrosyl ligands

Several iridium(−I) nitrosyl complexes are known. Those with the general formula $[Ir(NO)_2X(PPh_3)_2]$ (X = Cl, Br, I) are produced upon reduction of $[Ir(NO)_2(PPh_3)_2]$ with the appropriate lithium halide. IR spectral data for these complexes indicate bridging NO groups, as shown by the low N—O frequencies [ν(N—O) $\approx$ 1540–1490 cm^{-1}].[7] Reaction of $[Ir(NO)_2X(PPh_3)_2]$ with NO results in the oxidation of NO according to reaction (1).[8]

$$[Ir(X)(NO)_2(PPh_3)_2] + 2NO \longrightarrow [Ir(X)(NO_2)(NO)(PPh_3)_2] + N_2O \quad (1)$$

The d^{10} complex $[Ir(NO)(PPh_3)_3]$ (**1**) has been prepared in a variety of ways, including (i) reaction of $[Ir(NO)_2(PPh_3)_2](ClO_4)$ with excess PPh_3;[7] (ii) reaction between $[Ir(NO)(CO)(PPh_3)_2]$ and excess PPh_3;[9] and (iii) the reduction of $[IrCl_3]\cdot 3H_2O$ or $[Ir(Cl)(N_2)(PPh_3)_2]$ with sodium amalgam (or zinc metal) in the presence of PPh_3 and NO.[10] An X-ray crystal structure determination of $[Ir(NO)(PPh_3)_3]$ has shown a tetrahedral geometry about Ir. The Ir—N—O interaction was considered in terms of $[Ir(PPh_3)_3]^-$ and $[NO]^+$ moieties, wherein the NO group serves as a three-electron donor in a σ–π synergistic interaction with Ir.[11] The crystal structure of $[Ir(NO)(PPh_3)_3]\cdot C_3H_6$ has also been determined; presumably, this represents the first reported occurrence of unsubstituted cyclopropane in a crystal structure determined with X-rays.[12] An ESCA study of $[Ir(NO)(PPh_3)_3]$ led to an O(1*s*)—N(1*s*) ionization potential difference of 131.9 eV, indicative of the presence of a linear nitrosyl ligand.[13] Moreover, $[Ir(NO)(PPh_3)_3]$ undergoes oxidative additions with MeI, halogens and stoichiometric amounts of hydrogen halides to yield five-coordinate complexes (**2**) with

tetragonal pyramidal structures in which the NO ligand is bent (see Scheme 1). However, reaction of $[Ir(NO)(PPh_3)_3]$ (**1**) with an excess of HBr and HCl produces $[Ir(NH_2OH)(X)_3PPh_3)_2]$, in which the nitrosyl ligand is converted to a bound hydroxylamine. Also, $[Ir(NO)(PPh_3)_3]$ undergoes protonation with non-complexing acids to yield hydride species.[9] The $[Ir(NO)(CO)(PPh_3)_2]$ complex can be prepared *via* the treatment of $[Ir(H)(CO)(PPh_3)_3]$ with NO.[7] The iridium(−I) dinitrosyl complex $[Ir(NO)_2(PR_3)_2]^+$ has also been reported.[14]



Scheme 1

The tetraazadiene complex $[Ir(NO)(N\text{-}p\text{-tolyl})_4(PPh_3)]$ exhibits a conformational effect, and thereby a temperature dependent ^1H NMR spectrum. Also, this complex readily forms a CO adduct.[15]

49.2.2 Phophorus Ligands

49.2.2.1 Phosphine ligands

The salt $Na[Ir(CO)_3(PPh_3)]$ reduces $[Ni(Cl)_2(PPh_3)_2]$ to yield $[Ir(CO)_3(PPh_3)]_2$ with $[Ni(CO)_2(PPh_3)_2]$. Reaction of the iridium(−I) complex with *trans*-$[Pt(Cl)_2(py)_2]$ (py = pyridine) affords $[M_2(CO)_2(PPh_3)(py)]_n$ where $M_2 = Pt_2$, PtIr or Ir_2.[16]

49.3 IRIDIUM(0)

49.3.1 Nitrogen Ligands

49.3.1.1 Aliphatic amine ligands

Iridium(0) is present in carbonyl and substituted carbonyl complexes, and perhaps in $[Ir(NH_3)_5]$, if indeed this species exists. Although the ammine complex $[Ir(NH_3)_5]$ has been reported,[17] the diamagnetism of this complex suggests an irridium(I) hydride species.

49.3.1.2 Nitrosyl ligands

The iridium(0) nitrosyl complexes $[Ir(NO)(CO)(PPh_3)_2]^+$ and $[Ir(NO_3)_2(NO)_2(CO)(PPh_3)_2]$[18,19] have been synthesized *via* reaction of $[Ir(CO)_3(PPh_3)_2]^+$ with NO and N_2O_4, respectively. The reaction between $[Ir(NO)(PPh_3)_3]$ and RCO_2H reportedly yields $[Ir(O_2CR)(NO)(PPh_3)_2]$, where R is CF_3 or C_2F_5.[20]

The preparation of $[Ir(NO)(PPh_3)]_2O\cdot C_6H_6$ (**3**) involves reaction of *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ and excess $NaNO_2$ under a nitrogen atmosphere. The complex (**3**) is diamagnetic and stable in air, but rapidly decomposes in solution on exposure to air.[21] The dinuclear oxygen-bridged complex $[Ir(NO)(PPh_3)]_2O$ appears to be a good candidate for a strong, considerably bent Ir—Ir bond.

SCF–X_α–SW calculations on this complex have led to the conclusion that the NO ligands are crucial in stabilizing and in determining the exact nature of the substantially bent Ir—Ir bond (2.555 Å). Contour maps suggest the complex to be closer to Ir^I—NO^0 than to Ir^0—NO^+, with square planar coordination about each Ir atom.[22] The X-ray crystal structure of complex (**3**)[23] shows a bent Ir—Ir bond with the NO group π bonded to Ir, with an Ir—N—O angle of 177° and an Ir—N bond length of 1.76 Å suggesting that the Ir—N bond has some double bond character. Complex (**3**) does not undergo oxidative addition reactions with H_2, Cl_2, Br_2, I_2 or HgX_2. However, upon reaction with I_2, $HgCl_2$ or $HgBr_2$, oxidation of the Ir—Ir bond occurs without disruption of the oxygen bridge (reactions 2 and 3). Also, complex (**3**) reacts with tetracyanoethylene to form a 1:1 adduct, wherein the alkene inserts into the Ir—Ir bond with one carbon atom bonded to each Ir atom. With excess PPh_3, complex (**3**) affords $[Ir(NO)(PPh_3)_3]$ and Ph_3PO.[21]

$$(3) + HgX_2 \longrightarrow [Ir(X)(NO)(PPh_3)]_2O^+ + HgX \quad (2)$$

$$(3) + I_2 \longrightarrow [Ir(I)(NO)(PPh_3)]_2O \quad (3)$$

49.3.2 Phosphorus Ligands

49.3.2.1 Phosphine ligands

Several series of dinuclear iridium(0) complexes with tertiary phosphine ligands are known. These include (a) $[Ir(CO)_7(PR_3)]$, where $PR_3 = PPr^n_3$, PPr^i_3, PBu^n_3, PPh_3 and $P(tolyl)_3$; (b) $[Ir_2(CO)_6(PR_3)_2]$, where $PR_3 = PPr^i_3$, PPh_3, $P(OPh)_3$ and $P(tolyl)_3$; (c) $[Ir_2(CO)_5(PR_3)_3]$, where $PR_3 = PPh_3$ or $PPh_2(tolyl)$; and (d) $[Ir_2(CO)_4(PR_3)_4]$, where $PR_3 = PPh_3$ or $P(OPh)_3$.[24,25] The complex $[Ir_2(CO)_6(PPh_3)_2]$ (**4**) reacts with $P(OPh)_3$ to yield $[Ir_2(CO)_4\{P(OPh)_3\}_4]$, from which $[Ir_2(CO)_6\{P(OPh)_3\}_2]$ is obtained on decomposition. Other reactions of these complexes are depicted in reactions (4)–(6).[25] The reduction of $[Ir(Cl)(CO)(PPh_3)_2]$ under 20 atm CO pressure in the presence of $HNEt_2$ affords $[Ir_2(CO)_6(PPh_3)_2]$.[26]

$$(4) + PPh_3 \xrightarrow[303\,K]{C_6H_6} [Ir_2(CO)_5(PPh_3)_3] + CO \quad (4)$$

$$(4) + 2[PPh_2(p\text{-tolyl})] \xrightarrow[reflux]{C_6H_6} [Ir_2(CO)_5(PPh_3)\{PPh_2(p\text{-tolyl})\}_2] + PPh_2 + CO \quad (5)$$

$$(4) + SO_2 \xrightarrow{C_6H_6} [Ir_2(CO)_4(PPh_3)_2(\mu\text{-}SO_2)_2] + CO \quad (6)$$

49.4 IRIDIUM(I)

The coordination chemistry of iridium(I) involves π-acid ligands. Both four- and five-coordinate species form. Iridium(I) complexes are invariably prepared *via* some form of reduction, either from analogous iridium(III) complexes or from halide complexes in the presence of the complexing ligand, or *via* substitution.

49.4.1 Group IV Ligands

49.4.1.1 Cyanide, isocyanide and fulminate ligands

The yellow iridium(I) complex $[Ir(CN)(CO)(PPh_3)_2]$ has been prepared in two ways; (i) by the action of CN^- on the $[Ir(MeCN)(CO)(PPh_3)_2]^+$ salt; or (ii) by treating $[Ir(Cl)(CO)(PPh_3)_2]$ in a chloroform solution of PPh_3 with an anionic resin in the CN^- form. The IR spectrum of the cyano analogue of Vaska's complex exhibits a $\nu(CN)$ band at 2120 cm^{-1}.[27]

Transition metal complexes containing isocyanide ligands have been reviewed by Malatesta and Bonati.[28] $[\{Ir(Cl)(CO)_3\}_n]$ reacts with alkyl and aryl isocyanides (CNR) to give the iridium(I) isocyanide complexes $[Ir(CNR)_4]^+$, where $R = C_6H_{11}$, p-MeC_6H_4 or p-$MeOC_6H_4$. IR spectra support a square planar structure for $[Ir(CNR)_4]^+$. These complexes undergo *trans* oxidative addition with halogens (X_2) to produce $[Ir(X)_2(CNR)_4]^+$, with MeI to yield $[Ir(I)(Me)(CNR)_4]^+$ ($R = C_6H_{11}$), and with O_2 to give $[Ir(CNR)_4(O_2)]^+$ ($R = C_6H_{11}$). The results indicate that the alkyl isocyanide complexes are more reactive toward oxidative addition than aryl isocyanide complexes.[29] Electronic absorption and MCD spectroscopies have been employed to characterize $[Ir(CNEt)_4]^+$, which exhibits intense visible absorption assigned to MLCT (metal-to-ligand change transfer)

transitions from the occupied metal *d* orbitals to the lowest energy π^* CNEt orbital. The MLCT spectra have been interpreted in terms of a model which involves a single π^* CNEt acceptor orbital and includes metal spin–orbit coupling in the MLCT excited states.[30] IR and electronic absorption spectra of $[Ir(CNR)_4]^+$ (R = Bu^t) are indicative of normal monomeric Ir^I/L_4 complex behaviour. However, $[Ir(CNMe)_4]Cl$ exhibits a very different absorption spectrum, interpreted in terms of an oligomeric species $[Ir(CNMe)_4]_n^{n+}$.[31] Additionally photolysis of this $[Ir(CNMe)_4]_n^{n+}$ species reportedly affords $[Ir(CNMe)_4]^+$.[31] $[Ir(CNR)_4]^+$ and $[Ir(Cl)(CNR)_3(CO)]$ (R = C_7H_7) have also been prepared and characterized.[32] The complexes $[Ir(CNR)_4]^+$ (R = alkyl or aryl) readily undergo oxidative addition to obtain *trans*-$[Ir(X)(Y)(CNR)_4]^+$, where X = Me, Pr, I, Y = I; X = MeCO, σ-C_3H_5, HgCl, $SnCl_3$, $SnPh_3$, Y = Cl; X = Y = Br; X = CN, Y = Br.[33] The reactivity and structures of some tetrakis(aryl isocyanide)iridium(I) complexes have been investigated by Tanaka *et al.*[34]

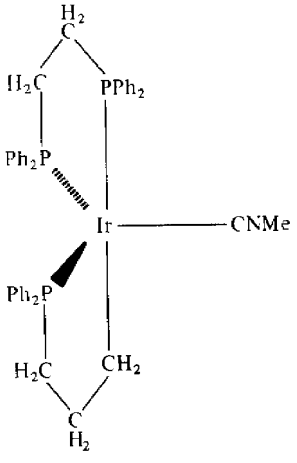
The addition of HX to $[Ir(CNR)_3(PPh_3)_2]^+$ (R = alkyl or aryl) reportedly proceeds by displacing X^- from the addendum YX to produce an ionic intermediate from which L is subsequently displaced by X^- as depicted in Scheme 2.[35]

$$[Ir(L)_5]^+ + YX \longrightarrow [Ir(Y)(L)_5]^{2+} + X^- \longrightarrow [Ir(X)Y(L)_4]^+ + (L)$$

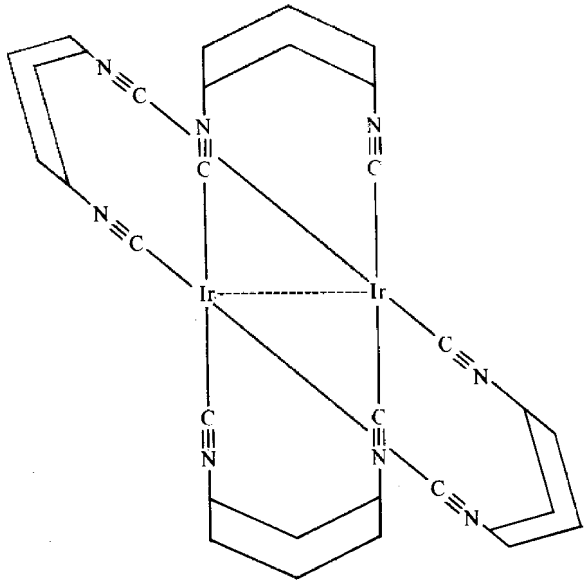
Scheme 2

X-Ray crystal and molecular structures for the stable five-coordinate iridium(I) isocyanide complex $[Ir(CNMe)(dppe)_2]^+$ (**5**) reveal this complex to possess a trigonal bipyramidal geometry. The isocyanide ligand occupies an equatorial position and each dppe chelate bridges one axial and one equatorial site.[36] In contrast to $[Ir(CNR)_3(PPh_3)_2]^+$,[35] the $[Ir(CNR)(P—P)_2]^+$ complexes (where P—P = dppe, dppen and R = Me, *p*-MeC_6H_4) undergo oxidative addition of proton acids (including MeOH), halogens and $HgCl_2$ without loss of a ligand to yield $[Ir(CNR)(P—P)_2Y]^{2+}$ (Y = H, Cl, I, HgCl). However, $[Ir(CNR)(P—P)_2]^+$ does not react with alkyl, allyl or acyl halides. The addition of proton acids yields *cis* products which, on heating, isomerize. Reaction of $[Ir(CNR)(P—P)_2]^+$ with H_2 or O_2 affords *cis*-$[Ir(H)_2(P—P)_2]^+$ and $[Ir(O_2)(P—P)_2]^+$, respectively.[37]

t-Butyl isocyanide (CNBu^t) is known to react with the A-frame complex $[Ir_2(Cl)(CO)(P—P)_2]X$ (P—P = dppm, dpam; X = BPh_4^-, BF_4^-, PF_6^-) affording $[Ir_2(Cl)(CNBu^t)(CO)_3(P—P)_2]X$, $[Ir_2(Cl)(CNBu^t)_2(CO)_2(P—P)_2]X$ (P—P = dppm, X = BPh_4^-; P—P = dpam, X = BF_4^-) and $[Ir_2(CNBu^t)_4(CO)(P—P)_2](BPh_4)_2$. These complexes were characterized by IR, ^{13}C and ^{31}P NMR spectroscopic techniques.[38] Bidentate diisocyanocyclohexane ligands have been prepared. *meso*-1,3-Diisocyanocyclohexane reacts with $[Ir(Cl)(cod)]_2$ to produce $[Ir_2(meso\text{-}1,3\text{-}C_8H_{10}N_2)_4](Cl)_2$ (**6**) for which a windmill structure has been proposed.[39]



(5)



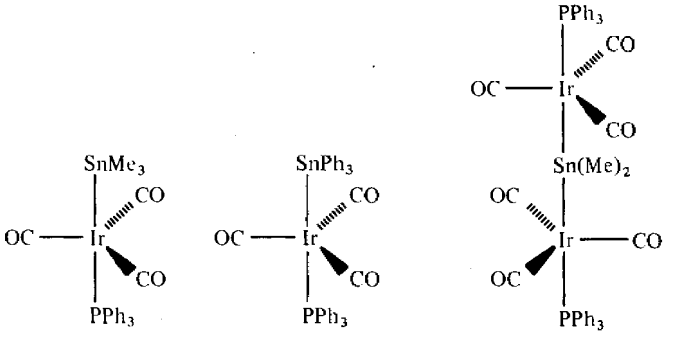
(6)

49.4.1.2 Sn-containing ligands

The reduction of Vaska's complex, $[Ir(Cl)(CO)(PPh_3)_2]$, with sodium amalgam in THF yields a non-isolable anionic species (**7**; reaction 7). Upon addition of $SnMe_3Cl$, $SnPh_3Cl$ or $SnMe_2Cl_2$, high yields of (**8**)–(**10**), respectively, are obtained.[40] Reaction of (**9**) with Br_2, I_2 or mercury(II) halides results in the cleavage of the Sn—Ir bond. The Ph_3Ge—Ir analogue of (**9**) has also been prepared.[41]

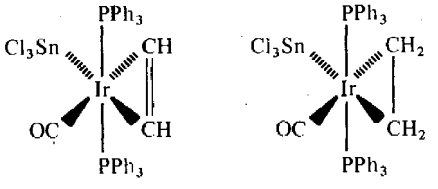
$$trans\text{-}[Ir(Cl)(CO)(PPh_3)_2] \xrightarrow[THF,\ CO]{Na/Hg} Na[Ir(CO)_3(PPh_3)] \quad (7)$$

(7)



(8) (9) (10)

The addition of anhydrous $SnCl_2$ and C_2H_2 or C_2H_4 to *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ yields $[Ir(SnCl_3)(C_2H_2)(CO)(PPh_3)_2]$ and $[Ir(SnCl_3)(C_2H_4)(CO)(PPh_3)_2]$ with structures (**11**) and (**12**), respectively. A five-coordinate structure was assigned to the intermediate product $[Ir(Cl)(SnCl_2)(CO)(PPh_3)_2]$ based on IR spectral data. This five-coordinate complex reacts with H_2, hydrocyanic acid and HX to yield stable products. Addition of HCl yields $[Ir(H)(Cl)(SnCl_3)(PPh_3)_2]$.[42]



(11) (12)

The structure of the complex resulting from the reaction between $[Ir(Cl)(CO)(PPh_3)_2]$ and $SnCl_4$ has been discussed.[43] Recently, the existence of the Sn—Ir bond in the product was questioned.[44] Based on ^{119}Sn NMR data, the iridium(I) complexes from the reaction between $[Ir(Cl)(CO)(PR_3)_2]$ ($PR_3 = P(p\text{-}XC_6H_4)_3$; X = H, F, Cl, OMe) and $SnCl_2$ are isomers of composition $[Ir(Cl)(SnCl_2)(CO)(PR_3)_2]$; they contain bridging halogen ligands and Sn is not coordinated to Ir. When reacted with HCl or H_2, the expected iridium(III) complexes $[Ir(H)(Cl)(SnCl_3)(CO)(PR_3)_2]$ or $[Ir(H)_2(SnCl_3)(CO)(PR_3)]$ are obtained. These iridium(III) complexes do contain an Sn—Ir bond.[44]

Reduction of $[Ir(X)(CO)(PPh_3)_2]$ under the reaction conditions of reaction (7) to yield $[Ir(CO)_3(PPh_3)]^-$, followed by the addition of MX (M = $SnCl_2$, $SnMe_2$; X = Cl), has yielded the dinuclear iridium(I) complex $[\{Ir(CO)_3(PPh_3)\}_2M]$.[45]

49.4.2 Nitrogen Ligands

49.4.2.1 Ammonia and amine ligands

The reduction of $[Ir(Br)(NH_3)_5]$ with potassium in liquid ammonia purportedly yields the yellow iridium(0) complex $[Ir(NH_3)_5]$.[17] However, the diamagnetism of the product is suggestive of an iridium(I) hydride species, $[Ir(H)(NH_3)_5]$.

49.4.2.2 Nitrosyl ligands

Transition metal nitrosyl complexes have been reviewed by Johnson and McCleverty.[46] The nitrosyl analogue of Vaska's complex $[Ir(Cl)(NO)(PPh_3)_2]^+$, is known,[47] as is $[Ir(NO)(CO)(PPh_3)_2]$.[7] The latter complex is prepared by the action of nitric oxide on $[Ir(H)(CO)(PPh_3)_3]$. $[Ir(Cl)(NO)(PPh_3)_2]^+$ has been obtained[9] from the reaction of $[Ir(H)(Cl)(NO)(PPh_3)_2]$ with $HClO_4$, and undergoes several addition reactions to form five-coordinate nitrosyl complex cations as summarized in reactions (8) through (13).[47] The carbonylation of complexes of the type $[M(NO)(PPh_3)_3]$ reportedly proceeds to mixed nitrosyl–carbonyl species (*e.g.* $[M(NO)(CO)(PPh_3)_3]$). The kinetics of CO absorption by $[Ir(NO)(PPh_3)_3]$ in chlorobenzene to yield $[Ir(NO)(CO)(PPh_3)_2]$ and PPh_3 have been studied.[48] At constant pressure, kinetics first order in $[Ir(NO)(PPh_3)_3]$ were observed. Rate constants and activation parameters for CO absorption are consistent with the mechanism in reactions (14) and (15).

$$[Ir(Cl)(NO)(PPh_3)_2]^+ + CO \longrightarrow [Ir(Cl)(NO)(CO)(PPh_3)_2]^+ \quad (8)$$

$$[Ir(Cl)(NO)(PPh_3)_2]^+ + PPh_3 \longrightarrow [Ir(Cl)(NO)(PPh_3)_3]^+ \quad (9)$$

$$[Ir(Cl)(NO)(PPh_3)_2]^+ + dppe \longrightarrow [Ir(Cl)(NO)(dppe)(PPh_3)_2]^+ \quad (10)$$

$$[Ir(Cl)(NO)(PPh_3)_2]^+ + Cl_2 \longrightarrow [Ir(Cl)_3(NO)(PPh_3)_2]^+ \quad (11)$$

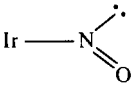
$$[Ir(Cl)(NO)(PPh_3)_2]^+ + Cl^- \longrightarrow [Ir(Cl)_2(NO)(PPh_3)_2] \quad (12)$$

$$[Ir(Cl)(NO)(PPh_3)_2]^+ + H_2O \longrightarrow [Ir(OH_2)(Cl)(NO)(PPh_3)_2]^+ \quad (13)$$

$$[Ir(NO)(PPh_3)_3] \underset{}{\overset{+\text{solvent}}{\rightleftharpoons}} [Ir(NO)(PPh_3)_2(\text{solvent})] + PPh_3 \quad (14)$$

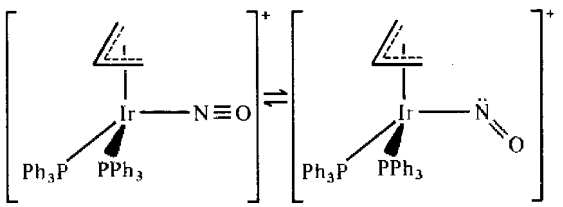
$$[Ir(NO)(PPh_3)_2(\text{solvent})] + CO \longrightarrow [Ir(NO)(CO)(PPh_3)_2] + \text{solvent} \quad (15)$$

Several five-coordination iridium(I) nitrosyl complexes have been reported, including $[Ir(X)_2(NO)(PR_3)_2]$ (X = Cl, Br, I; PR_3 = phosphine) and $[Ir(Cl)(NO)(PPh_3)_2]^+$. The crystal structure of the latter reveals an Ir—N—O angle of 124°. The coordination about Ir is tetragonal pyramidal with the NO ligand at the apex, and Cl, CO and *trans* P atoms in the basal plane. The Ir—N distance is quite long (1.97 Å), suggestive of coordinated NO^- with sp^2 hybridization on the N atom (see **13**).[49] The X-ray crystal structure of $[Ir(I)(NO)(CO)(PPh_3)_2](BF_4)\cdot C_6H_6$ has revealed it to be rather similar to $[Ir(Cl)(NO)(CO)(PPh_3)_2]^+$, with a distorted tetragonal pyramidal geometry about Ir. The Ir—N bond length is 1.89 Å, while the Ir—N—O angle is 125°.[50] The $[Ir(NO)(phen)(PPh_3)_2](PF_6)_2$ complex contains an iridium(I) atom in a trigonal bipyramidal environment with the phen and NO ligands in equatorial positions. The NO ligand is present at NO^+.[4]



(13)

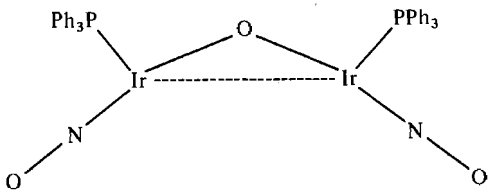
The complex $[Ir(NO)(PPh_3)_2(\eta^3\text{-}C_3H_5)](PF_6)$ (**14**) can be prepared from the reaction of $[Ir(Cl)(NO)(PPh_3)_2](PF_6)$ and $Sn(C_3H_5)_4$ at 273 K in THF. Repetition of the synthesis employing $[Ir(Cl)(NO)(PPh_3)_2](BF_4)$ afforded $[Ir(NO)(PPh_3)_2(\eta^3\text{-}C_3H_5)](BF_4)\cdot 0.5H_2O$ (**15**). Though evidence for the linear $\rightleftharpoons$ bent equilibrium (**14** $\rightleftharpoons$ **15**) of metal nitrosyl complexes remains scarce, it has been postulated that $[Ir(NO)(PPh_3)_2(\eta^3\text{-}C_3H_5)]^+$ exhibits a facile, well-defined equilibrium. IR and ^1H NMR spectroscopic studies suggest the presence of several dynamic processes in solution. An X-ray crystal structure of complex (**15**) confirmed a bent nitrosyl ligand. Additionally, $[Ir(NO)(PPh_3)_2(\eta^3\text{-}C_3H_5)]^+$ reacts with CO to yield acrolein oxime and $[Ir(CO)_3(PPh_3)_2]^+$, most probably *via* an intramolecular coupling process.[51]



(14) (15)

The dinitrosyl cation $[Ir(NO)_2(PPh_3)_2]^+$ (**16**) was synthesized and characterized by X-ray crystallography. A ^{31}P NMR study of complex (**16**) has suggested that phosphine exchange occurs primarily *via* an associative pathway.[52] The X-ray crystal and molecular structures of (**16**) have been determined.[53] Reaction of complex (**16**) with PPh_3 yields $[Ir(NO)(PPh_3)_3]$ and NO^+, though reaction with less bulky phosphines PR'_3 affords $[Ir(PR'_3)_4]^+$.[52] Carbon monoxide reacts with complex (**16**) to give $[Ir(CO)_3(PPh_3)_2]^+$, CO_2 and N_2O; with tertiary phoshines, (PR_3), R_3PO and N_2O are afforded. The carbon monoxide reaction was unexpected, the NO ligand being usually resistant to CO substitution. The proposed mechanism involves the prior formation of a five-coordinate adduct, $[Ir(NO)_2(CO)(PPh_3)_2]^+$, which subsequently and rapidly undergoes oxygen transfer from a coordinated NO ligand to the combined CO, followed by an intramolecular attack of the other NO ligand on the Ir—N system thus produced.[54]

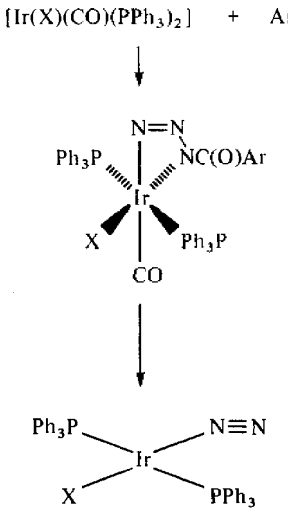
The X-ray crystal structure of $[Ir(Cl)(NO)(PPh_3)]_2O$ (**17**) reveals two identical square planar iridium(I) entities, linked by a common oxygen bridge.[55] $[Ir(X)(NO)(PPh_3)]_2O$ (X = Cl, Br) reacts with excess PPh_3 in CH_2Cl_2 to yield $[Ir(X)_2(NO)(PPh_3)_2]$ and $[Ir(NO)(PPh_3)_3]$.[21]



(17)

49.4.2.3 Dinitrogen, azide, diazo, triazene, tetrazene and selenocyanate ligands

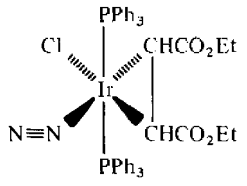
Dinitrogen complexes of the type $[Ir(X)(N_2)(PPh_3)_2]$ (**18**) (X = Cl, Br, I) have been synthesized *via* the mechanism illustrated in Scheme 3. This mechanism is supported by IR spectral and kinetic evidence.[56] Furthermore, complex (**18**) forms the six-coordinate species (**19**) upon reaction with certain alkenes in which the N_2 ligand remains intact. However, reaction of (**18**) with PPh_3, CO or aryl cyanates leads to N_2 displacement.[56] In addition to the dinitrogen analogue of Vaska's complex, $[Ir(Cl)(N_2)(PPh_3)_2]$, impure samples of $[Ir(Cl)(N_2)(PR_3)_2]$, where PR_3 is $PEtPh_2$, PBu^nPh_2, PMe_2Ph or PEt_2Ph, have been obtained.[57] Oxidative addition of HBF_4, CF_3SO_3H or $BuSO_3H$ to *trans*-$[Ir(Cl)(N_2)(PPh_3)_2]$ affords the reactive iridium(III) complexes $[Ir(H)(Cl)(L)(N_2)(PPh_3)_2]$ (L = FBF_3, OSO_2CF_3, OSO_2Bu). The tetrafluoroborate complex $[Ir(H)(Cl)(FBF_3)(N_2)(PPh_3)_2]$ reacts with valinate, diethyldithiocarbamate and PPh_3 to give (**20**), (**21**) and (**22**), respectively.[58]



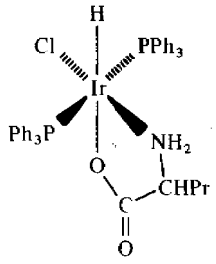
(18)

Scheme 3

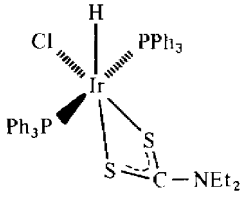
The treatment of $[Ir(Cl)(CO)(PPh_3)_2]$ with an acid azide $RC(O)N_3$ at 273 K has afforded complex (**24**), presumably through the 1,3-dipolar intermediate (**23**) which subsequently eliminates *N*-acyl isocyanate (Scheme 4). Complex (**24**) reacts with diethyl maleate (DEM) to give complex (**25**; see Scheme 4).[59]



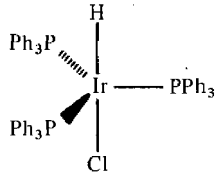
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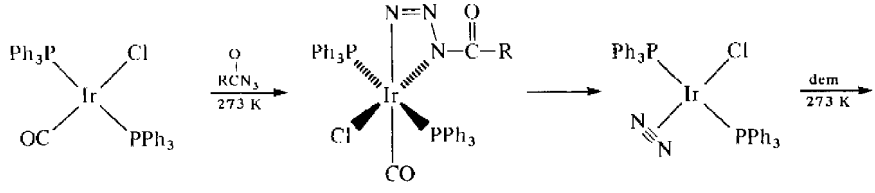
(20)



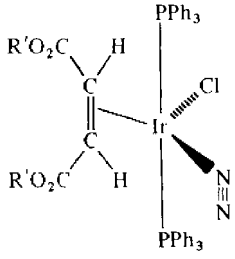
(21)



(22)



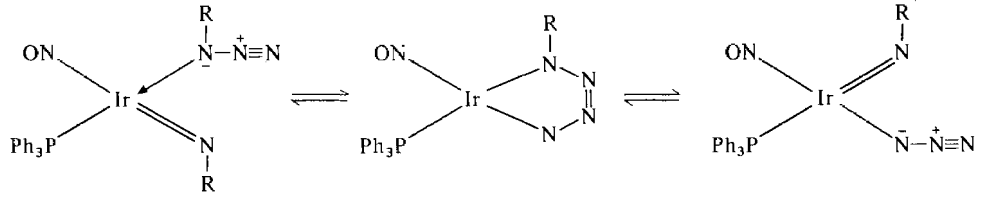
(23) (24)



(25)

Scheme 4

A complex with the formula $[Ir(NO)(N_4R_2)(PPh_3)]$ (**26**) (R = $SO_2C_6H_4Me$) has been synthesized from $[Ir(NO)(PPh_3)_3]$ and *p*-toluenesulfonyl azide in benzene. The tetrazene complex (**26**) is believed to involve in solution an equilibrium between closed-ring (**26**b) and opened-ring forms (**26**a) and (**26**c). Structure (**26**b) is favoured in the solid state. Complex (**26**) reacts with gaseous HCl to yield $[Ir(Cl)_2(NO)(PPh_3)]$ and the corresponding amide (RNH_2) and azide (RN_3).[19]

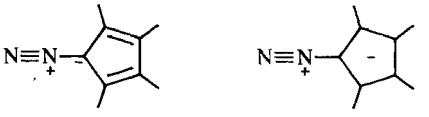


(26a) (26b) (26c)

The neutral arenediazo iridium(I) complex $[Ir(Cl)(N_2C_5Cl_4)(PPh_3)_2]$ (**27**) ($N_2C_5Cl_4$ = 2,3,4,5-tetrachlorodiazocyclopentadiene) has been prepared *via* reaction (16). An X-ray crystal structure determination of complex (**27**) reveals a singly bent arenediazo ligand.[60] Further, complex (**27**) is somewhat similar to the cationic complex $[Ir(Cl)(N_2Ph)(PPh_3)_2]^+$,[61] in that both complexes form

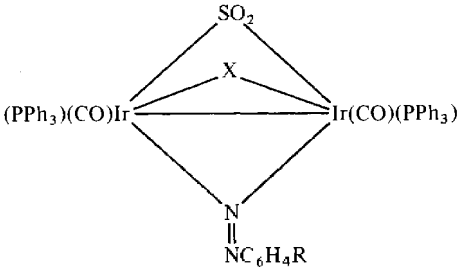
five-coordinate adducts with phosphines and isocyanides. However, reactions with NO^+, CO or N_2Ph^+ are quite different for the two iridium complexes. Complex (**27**) reacts with NO^+, CO, N_2Ph^+, PMe_3, PMe_2Ph, $PMePh_2$ or Bu^tNC (= L) to give the five-coordinate species $[Ir(Cl)(N_2C_5Cl_4)(PPh_3)_2(L)]^+$. Both complex (**27**) and $[Ir(Cl)(N_2Ph)(PPh_3)_2]^+$ have the singly bent diazo linkage perpendicular to the P—P vector.[60,61] The related complexes $[Ir(Cl)(N_2C_5X_4)(PR_3)_2]$ (X = Cl, Br; R = Ph, *p*-FC_6H_4, *p*-MeC_6H_4) have been prepared, wherein iridium is in a square planar environment with mutually *trans* PR_3 ligands and a singly bent $N_2C_5X_4$ ligand. Complex (**27**) reacts with HCl to yield the six-coordinate iridium(III) complex $[Ir(H)(Cl)_2(N_2C_5Cl_4)(PPh_3)_2]$.[62] A square planar environment for Ir has also been observed for $[Ir(Cl)(N_2C_5Cl_4)(PPh_3)_2]\cdot C_7H_8$, having mutually *trans* PPh_3 ligands. The neutral diazo ligand possesses a singly bent geometry in this complex; it appears that there is significant contribution from both canonical structures (**28**a) and (**28**b), though a greater contribution was expected from (**28**b).[63]

$$[Ir(Cl)(CO)(PPh_3)_2] \xrightarrow[CHCl_3/EtOH,\ 273\ K]{ArC(O)N_3,\ N_2C_5Cl_4} [Ir(Cl)(N_2C_5Cl_4)(PPh_3)_2] + CO \qquad (16)$$



(28a) (28b)

$[Ir(CO)_2(PPh_3)(\mu\text{-}SO_2)]_2$ is known to react with *p*-substituted arenediazonium salts, yielding $\{[Ir(CO)_2(PPh_3)]_2(\mu\text{-}N_2C_6H_4R)(\mu\text{-}SO_2)\}^+$ (**29**; R = *p*-tolyl, *p*-methoxy, *p*-fluoro), in which a molecule of SO_2 is replaced by an arenediazonate molecule. The protonated derivatives of (**29**), $\{[Ir(CO)_2(PPh_3)]_2(\mu\text{-}N{=}NHC_6H_4R)(\mu\text{-}SO_2)\}^{2+}$, were obtained by treating (**29**) with HBF_4. Reaction of (**29**) with alkali metal halides, MX, affords the diamagnetic complexes $\{Ir(CO)(PPh_3)]_2(\mu\text{-}X)(\mu\text{-}N_2C_6H_4R)(\mu\text{-}SO_2)\}$ (**30**), which contain halogen atoms (X) bridging the two Ir atoms as shown.[64]



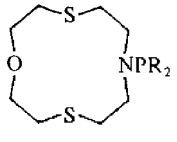
(30)

McGlinchley and Stone[65] have reported the preparation and characterization (^{19}F NMR and IR spectra) of $[Ir(Cl)(CO)(NCF_2CHFCF_3)(PPh_3)_2]$, synthesized from $[Ir(Cl)(CO)(PPh_3)_2]$ and 2H-hexafluoropropyl azide in benzene. Reaction between $[Ir(Cl)(N_2)(PPh_3)_2]$ and $CF_3CHFCF_2N_3$ has afforded the four-coordinate complex $[Ir(Cl)(NCF_2CHFCF_3)(PPh_3)_2]$ and molecular nitrogen.[65]

The crystal and molecular structures of $[Ir(CO)(dtt)(PPh_3)_2]$ (dtt = *p*-$MeC_6H_4NN{=}NC_6H_4Me$-*p*) have been determined by counter data. In this square planar iridium(I) complex, the diaryltriazenido ligand (dtt) is unidentate and *trans* to the CO ligand.[66]

The five-coordinate iridium(I) selenocyanate complex *trans*-$[Ir(CO)(NCSe)(Me_2CO)(PPh_3)_2]$ was prepared *via* metathesis with the corresponding chloro complex $[Ir(Cl)(CO)(PPh_3)_2]$. The complex contains an N-bonded selenocyanate ligand.[67] *trans*-$[Ir(NCS)(CO)(PPh_3)_2]$ has been prepared and contains an N-bonded thiocyanato ligand.[67] The large π-withdrawing character of the *trans* carbonyl ligand in the thiocyanato and selenocyanato complexes probably favours N-bonding.

The aminophosphine ligands (**31a,b**) ($\subset NPR_2$) are prepared from 1-aza-4,10-dithia-7-oxacyclododecane and chlorodiphenylphosphine or chlorodimethylphosphine. Complex (**31**) reacts with $[Ir(Cl)(CO)(cod)]_2$ to produce *trans*-$[Ir(Cl)(CO)(\subset NPR_2)_2]$.[68]

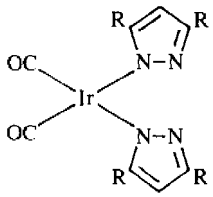


(31a) R = Ph
(31b) R = Me

49.4.2.4 Polypyrazolylborate ligands

Trofimenko[69] has reviewed the preparation of polypyrazolylborate ligands and the syntheses of metal complexes containing such ligands. An update has also appeared.[70]

$[Ir(Cl)(CO)_2]_2$ reacts with bispyrazolylborate anions to yield $[Ir(CO)_2\{H_2B(pz)_2\}]$ and $[Ir(CO)_2\{H_2B(3,5\text{-}Me_2pz)\}]$ (**32**) (pz = 1-pyrazolyl; 3,5-Me_2pz = 3,5-dimethylpyrazolyl).[71] Displacement of a CO ligand by the π-accepting PPh_3 ligand affords $[Ir(CO)\{H_2B(pz)_2\}(PPh_3)]$. These complexes were characterized by ^{1}H NMR, IR and mass spectroscopy.



(32) R = H, Me

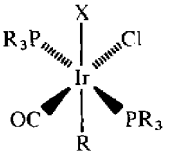
49.4.3 Phosphorus and Arsenic Ligands

The chemistry of iridium(I) Vaska-type complexes $[Ir(A)(CO)(PPh_3)_2]$ (A = various anions) has been reviewed,[1,72] and therefore is not exhaustively dealt with here. These complexes are prepared by refluxing an iridium halide in a CO-releasing solvent (alcohol or DMF), or by treating the iridium halide with CO, followed by PPh_3. The analogous complexes $[Ir(A)(CO)(ER_3)_2]$, in which the phosphine ligands are replaced by other group Vb donor ligands are also well known. X-Ray crystal structure, dipole moment and 'virtual coupling' studies have shown that the majority of complexes of the type $[Ir(A)(CO)(L)_2]$ (L = PR_3 or ER_3) possess the *trans* configuration.[73] For complexes with bulky monodentate phosphine ligands (*e.g.* $PR_3 = PMeBu^t_2$), the *trans* configuration is maintained, though there is restricted rotation about the Ir—P bonds as a result of the steric requirements of these ligands.[74] However, the *cis* configuration was found for *cis*-$[Ir(Cl)(CO)(Ph_2AsCH{=}CHAsPh_2)]$,[75] $[Ir(CO)\{N(R)C(Me)CHC(Me)CO\}(PPh_3)]$ (R = *p*-naphthyl, *p*-tolyl),[76] $[Ir\{NHC(CF_3){=}C(CMe{=}CH_2)C(CF_3){=}NH\}(CO)(ER_3)]$ ($ER_3 = PPh_3$, $AsPh_3$),[77] $[Ir(OCRCOCR')(CO)(PPh_3)]$ (R = CF_3, Ph, Me; R' = Me),[76] and $[Ir(Cl)_2(PMePh_2)_2(R)]$ (R = Me, Et, Pr^n).[78]

Bradley and coworkers[79] have examined the electronic absorption spectra at 298 K of a series of d^8 planar complexes with the general formulae $[Ir(A)(CO)(PPh_3)_2]$ (A = OH, F, OCO_2H, ONO_2, Cl, $OReO_3$, $OClO_3$, N_3, NCO, Br, NCS, NO_2, I, NCSe, CN), $[Ir(Cl)(CO)(ER_3)_2]$ (ER_3 = P(*o*-$MeC_6H_4)_3$, PCy_3, $PEtPh_2$, PPh_2Bu, $AsPh_3$, P{*p*-$MeOC_6H_4)_3$}, and $[Ir(CO)(NCBH_3)(PCy_3)_2]$ (Cy = cyclohexyl). The visible spectra reveal three bands; the order of the derivatives noted above corresponds to decreasing energies of the longest-wavelength visible absorption bands and hence to the observed spectrochemical series orders. The two low-lying bands were assigned to the $^1A_1 \rightarrow A_1$, $B_2(^3B_1)$, and $^1A_1 \rightarrow B_1$ transitions, respectively. Similar absorption spectra were obtained from the planar complexes $[Ir(dppe)_2]^+$ and $[Ir(dppen)_2]^+$.[80]

The iridium(I) Vaska-type complexes *trans*-$[Ir(X)(CO)(PPh_3)_2]$ readily undergo oxidative addition with a wide variety of reagents to yield iridium(III) products.[81] Kinetic data for oxidative addition to *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ are usually interpreted in terms of two limiting mechanisms: (i) a concerted process involving a relatively non-polar transition state, resulting in *cis* addition; and (ii) an S_N2 attack by iridium at an electrophilic centre in the substrate molecule involving a polar transition state and usually yielding a *trans* product.[72] With gaseous HX' (X' = Cl, Br, F, HS, *etc.*), solid $[Ir(X)(CO)(PPh_3)_2]$ yields $[Ir(H)(X)(X')(CO)(PPh_3)_2]$; the addition is presumably stereospecifically *cis* (H *trans* to X), based on observations that Ir—H stretching frequencies are sensitive to X and on the absence of H/CO vibrational coupling.[82] *Cis* addition of H_2[83] and O_2[84] to *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ has also been observed. The resulting stereochemistry of the iridium(III) complexes formed as a result of oxidative addition of X_2, HX, RX and acetyl halides to *trans*-$[Ir(Cl)(CO)(PMe_2Ph)_2]$ has been elucidated by NMR and far-IR spectroscopy.[85] Oxidative addition of acyl chlorides, allyl chlorides, methyl bromide and hydrogen halides to *trans*-$[Ir(X)(CO)(PEt_2Ph)_2]$ (X = Cl, Br, I) has been reported.[86] Complexes of the type *trans*-$[Ir(Cl)(CO)(PR_3)_2]$ [$PR_3 = PMe_2$(*o*-$MeOC_6H_4$), PMe_2(*p*-$MeOC_6H_4$)] undergo oxidative addition with MeI, MeCOCl, PhCOCl, or $CH_2{=}CHCH_2Cl$ (RX) to yield octahedral derivatives of the type depicted in (**33**). The reaction rates are faster than that where $PR_3 = PMe_2Ph$; this has been

interpreted in terms of a direct electronic interaction between the methoxy oxygen of PR_3 and the Ir atom.[87] A related paper[88] describes mechanistic studies on the oxidative addition of optically-active α-bromo esters {(*RS*,*SR*)-PhCHFCHBrCO$_2$Et} to *trans*-[Ir(Cl)(CO)(PMe$_3$)$_2$]. NMR spectral data (^{1}H, ^{13}C, ^{19}F) were interpreted in terms of the reactions involving loss of stereochemistry at carbon and proceeding *via* a free radical mechanism, as shown by retarded rates being observed in the presence of electron scavengers. Proton NMR spectroscopy has been employed to monitor the stereochemical changes at carbon during the oxidative addition of alkyl halides to *trans*-[Ir(Cl)(CO)(PR$_3$)$_2$]. Complete loss of stereochemistry at carbon is observed. Two mechanistic pathways were postulated, one having characteristics consistent with a radical chain pathway as exhibited by several saturated alkyl halides, aryl and vinyl halides, and α-halo esters. By contrast, methyl, benzyl and allyl halides, and α-halo ethers react in a different manner, as shown by their insensitivity toward inhibitors.[89]



(33)

Acyl chlorides, RCOCl, react with [Ir(Cl)(PMePh$_2$)$_3$], or with a solution containing [Ir(Cl)(cod)]$_2$ and PMePh$_2$, to yield the six-coordinate alkyl iridium(III) complexes with mutually *cis* PMePh$_2$ groups, *cis*-[Ir(Cl)(CO)(PMePh$_2$)$_2$(R)] (R = Me, Et, Pr^n). In solution, complexes for which R = Et and Pr^n rapidly equilibrate with the five-coordinate acyl iridium(III) complex [Ir(Cl)$_2$(COR)-(PMePh$_2$)$_2$], which also has mutually *cis* PMePh$_2$ ligands.[78] *trans*-[Ir(Cl)(CO)(PR$_3$)$_2$] and [Ir-(Cl)(CO)(PR$_3$)$_2$] (PR$_3$ = PMe$_2$Ph, PEt$_2$Ph) react with each other, presumably *via* a double-chloro-bridged intermediate, and undergo rapid oxidative addition–reductive elimination. A mixture of *trans*-[Ir(Cl)(CO)(PMe$_2$Ph)$_2$] and [Ir(Cl)$_3$(CO)(PEt$_2$Ph)$_2$] was converted almost completely to *trans*-[Ir(Cl)(CO)(PEt$_2$Ph)$_2$] and [Ir(Cl)$_3$(CO)(PMe$_2$Ph)$_2$] after 15 min at 295 K in C$_6$H$_6$/C$_6$D$_6$.[90] The iridium(I) complex [Ir(CO)(C$_2$Ph)(PPh$_3$)$_2$] (**34**) has been prepared from the reaction of [Ir-(CO)$_3$(PPh$_3$)$_2$]$^+$ and phenylacetylene in acetone, presumably *via* the intermediate species '[Ir(CO)$_2$(HC$_2$Ph)(PPh$_3$)$_2$]$^{+}$'. Complex (**34**) adds SO$_2$, HgCl$_2$, H$_2$, O$_2$, CF$_3$CO$_2$H, MeCO$_2$H, C$_2$(CO$_2$Me)$_2$, MeI and C$_2$(CN)$_4$ *via* attack at the metal centre; in contrast, addition of HX and X$_2$ (X = Cl, Br, I) proceeds by attack at both the metal centre and the alkyne linkage. Thus, addition of Br$_2$ yields [Ir(H)(Br)(CH=CBrPh)(CO)(PPh$_3$)$_2$] and [Ir(H)(Br)(CBr=CHPh)(CO)(PPh$_3$)$_2$].[91]

Titration calorimetry has been employed to determine enthalpies of oxidative addition of RI (= I$_2$, HI, MeI, EtI, Pr^{n}I, Pr^{i}I, PhCH$_2$I, PhC(O)I, MeC(O)I, (*o*-O$_2$C$_6$Cl$_4$), SO$_2$ and C$_2$(CN)$_4$) to complexes of the type *trans*-[Ir(X)(CO)(ER$_3$)$_2$] (X = Cl, ER$_3$ = PMe$_3$;[92,93] ER$_3$ = PPh$_3$, X = F, Cl, Br, I, NCS, N$_3$; X = Cl, ER$_3$ = P(OPh)$_3$, PMe$_2$Ph, PMePh$_2$, PEt$_2$Ph, PPh$_2$Bu^t, PCy$_3$, AsPh$_3$).[94] The enthalpy changes along with other thermochemical data were used to give a relative scale of Ir —R bond energies. The enthalpy of adduct formation between [Ir(Cl)(CO)(PPh$_3$)$_2$] and SO$_2$ was also determined by GLC techniques, permitting tentative characterization of the donor in terms of the E and C model.[95]

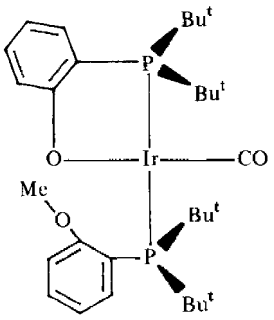
The irreversible electrochemical oxidation of [Ir(X)(CO)(PR$_3$)$_2$] (X = Cl, Br, I; PR$_3$ = PPh$_3$, PPh$_2$Et, PPhEt$_2$, PEt$_3$) on rotating Pt electrodes in Bu$_4$NClO$_4$/CH$_2$Cl$_2$ reportedly proceeds at diffusion-controlled rates. In the redox addition process, atom transferability predominates over complex redox properties. Evidence indicates that the insoluble product of the one-electron oxidation of [Ir(X)(CO)(PR$_3$)$_2$] is a dimeric iridium(II) complex with an iridium–iridium bond.[96]

The reaction of [Ir(Cl)(CO)(PPh$_3$)$_2$] with the hydroperoxide Bu^{t}O$_2$H has yielded [Ir(Cl)(CO)-(PPh$_3$)$_2$(Bu^{t}O$_2$H)$_2$] and a blue Ir/PPh$_3$/Cl substance, along with CO$_2$ and OPPh$_3$. It was proposed that the reaction might occur *via* coordination at a vacant site, with the possibility of oxygen transfer to oxidizable ligands.[97]

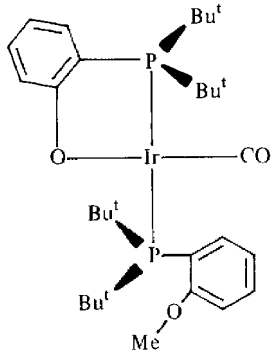
The displacement of MeCN in [Ir(CO)(PPh$_3$)$_2$(MeCN)]$^+$ by the coordinating anions A$^-$ (= CN$^-$, C≡CPh$^-$, SH$^-$, O$_2$CCF$_3^-$, O$_2$CH$^-$, NCS$^-$, NCO$^-$, OH$^-$, F$^-$ and *p*-toluenesulfinate) yields [Ir(A)(CO)(PPh$_3$)$_2$], except where A$^-$ = CN$^-$, and the five-coordinate [Ir(CN)(CO)(PPh$_3$)$_3$] was obtained.[98] Oxidative addition of HCl to [Ir(Cl)(cod)(PEtPh$_2$)] gives [Ir(H)(Cl)$_2$(cod)(PEtPh$_2$)] *via* the intermediate species [Ir(Cl)$_2$(cod)(PEtPh$_2$)]$^-$. Generally, the oxidation of the substrate precedes the nucleophilic attack of the anionic species; in this case, however, it was suggested that the oxidizing step is preceded by the nucleophilic attack affording the intermediate species.[99] [Ir-(Cl)(cod)(PCy$_3$)] has been prepared *via* addition of PCy$_3$ to [Ir(H)(Cl)$_2$(cod)]$_2$. In contrast, the

addition of PCy_3 to $[Ir(Cl)(cot)_2]_2$ (cot = cyclooctene) at 293 K in toluene affords $[Ir(H)_2(Cl)\{(P(C_6H_9)Cy_2\}(PCy_3)]$, in which one cyclohexyl group has been dehydrogenated to cyclohexane, the double bond being coordinated to Ir. Under refluxing conditions, the four-coordinate complex $[Ir(Cl)\{P(C_6H_9)Cy_2\}(PCy_3)]$ was formed. The syntheses of $[Ir(Cl)(CO)(PCy_3)_2]$ and $[Ir(H)_2(Cl)(PCy_3)_2]$ have also been reported.[100] The basic and bulky PCy_3 ligand is a potentially good ancillary ligand for a coordinatively unsaturated complex likely to react with small gas molecules. Complexes of the type $[Ir(cod)\{P(p\text{-}RC_6H_4)_3\}_2]A$ (R = Cl, F, H, Me, OMe; A = ClO_4^-, BPh_4^-) have been prepared from $[Ir(Cl)(cod)]_2$ and stoichiometric amounts of the appropriate phosphine, and undergo oxidative and displacement reactions. Thus, $[Ir(cod)\{P(p\text{-}RC_6H_4)_3\}_2]^+$ undergoes oxidative addition with Cl_2, I_2 and MeI, and displacement of cod when reacted with CO or H_2.[101]

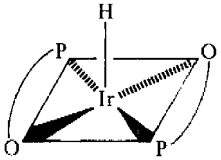
Transition metal complexes containing bulky tertiary phosphine ligands are expected to exhibit unusual physical and chemical properties. Complexes of the type *trans*-$[Ir(X)(CO)(PBu^t_2R)_2]$ (**35**; X = Cl, Br; R = Me, Et, Pr^n) have been prepared by passing CO through a solution of $[IrCl_6]^{2-}$ (or $[IrBr_6]^{2-}$) followed by phosphine addition.[102] A modified method has been employed to prepare the O-metallated iridium(I) complex $[Ir(CO)\{PBu^t_2(C_6H_4O)\}\{PBu^t_2(C_6H_4O)Me\text{-}2)\}]$ (**36**).[103] Complexes of the type (**35**) exist as rotational conformers which interconvert at room temperature.[74] For complex (**36**), two rotational conformers are possible (**36a,b**) and thought to interconvert at room temperature.[103] Complex (**36**) can be demethylated to yield $[Ir(CO)\{PBu^t_2(C_6H_4O)\}\{PBu^t_2(C_6H_4OH\text{-}2)\}]$, which on treatment with air yields CO_2 and the paramagnetic iridium(II) complex *trans*-$[Ir\{PBu^t_2(C_6H_4O)\}_2]$ (**37**). Complex (**37**) has been characterized by X-ray structural analysis and magnetic measurements. Presumably, the formation of (**37**) proceeds by initial O_2 uptake to form an 'end-on' species. Hydrogenation of complex (**37**) yields the iridium(III) complex $[Ir(H)\{PBu^t_2(C_6H_4O)\}_2]$ (**38**), which reacts with CO to yield complex (**39**), $[Ir(H)\{PBu^t_2(C_6H_4O)\}_2]$. Complex (**37**) in benzene, when allowed to stand for 24 h, affords the C-metallated iridium(III) complex $[Ir\{PBu^t_2(C_6H_4O)\}\{PBu^t(C_6H_4O)(CMe_2CH_2)\}]$ (**40**).[103]



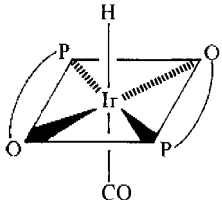
(36a)



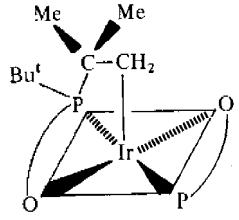
(36b)



(38)



(39)

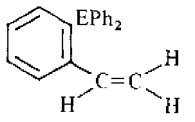


(40)

The bulky phosphine ligand $PBu^t_2(C{\equiv}CPh)$ reacts with $[IrCl_6]^{2-}$ in ethanol to give *trans*-$[Ir(Cl)(CO)\{PBu^t_2(C{\equiv}CPh)\}_2]$. This iridium(I) complex further reacts with HCl to yield $[Ir(H)(Cl)_2(CO)\{PBu^t_2(C{\equiv}CPh)\}_2]$, with sodium propan-2-olate in propan-2-ol to yield $[Ir(CO)\{PBu^t_2[CH{=}C(O)Ph]\}\{PBu^t_2(C{\equiv}CPh)\}]$, and with sodium methoxide to give $[Ir(CO)\{PBu^t_2[CH{=}C(O)Ph]\}\{PBu^t_2[CH{=}C(OMe)Ph]\}]$.[104]

(*o*-Vinylphenyl)diphenylphosphine [*o*-$CH_2{=}CHC_6H_4PPh_2$, spp] and its arsenic analogue [*o*-CH_2

$=CHC_6H_4AsPh_2$, spas} (**41**) form five-coordinate complexes of iridium(I) with the general formula $[Ir(Cl)(L)_2]$ (L = spp, spas). The cationic derivatives $[Ir(L)_2A]^+$ (A = CO, PF_3, $PMePh_2$, py) have been obtained from $[Ir(Cl)(L)_2]$ and $AgBF_4$, NH_4PF_6 or $NaBPh_4$ in the presence of ligand A. All of these complexes are reportedly trigonal bipyramidal with the spp (or spas) ligands in axial sites. The vinyl groups are in equatorial sites and probably lie in the equatorial plane. Proton and ^{31}P NMR data reveal the existence of two isomers (i) a 'symmetric' isomer having equivalent vinyl groups; and (ii) an 'unsymmetric' isomer having inequivalent vinyl groups. The isomerism reportedly arises from the different possible orientations of the vinyl groups with respect to each other.[105]



(**41**) spp, E = P; spas, E = As

The metal-containing phosphine $[PPh_2Fe(CO)_2(\eta\text{-}C_5H_4R)]$ (R = H, Me) reacts with $[Ir(C_8H_{12})(solvent)_x]^+$ to yield a variety of cationic mixed metal cluster species, including $[Ir\{FePPh_2(CO)_2(Cp)\}_2]^+$, $[Ir\{FePPh_2(CO)_2(Cp)\}_2(solvent)_x]^+$, $[Ir(CO)_3\{FePPh_2(CO)_2(Cp)\}_2]^+$, $[Ir(CO)\{FePPh_2(CO)_2(Cp)_2Cl\}]$, $[Ir(X)(CO)\{FePPh_2(CO)_2(Cp)\}_2]^+$ (X = CN, Br, I), $[Ir(Cl)(CO)\{FePPh_2(CO)_2(\eta\text{-}C_5H_4Me)\}_2]$ and $[Ir(I)\{FePPh_2(CO)_2(Cp)\}_2]$. The behaviour of the mixed metal cluster complexes toward CO and H_2 have also been reported.[106]

Several iridium(I) complexes containing the secondary phosphine ligands HPR_2 have been prepared. These include $[Ir(HPR_2)_4]^+$, where HPR_2 is $HPEt_2$, HPEtPh, $HPPh_2$, $HPPh(C_6H_{11})$ or $HP(C_6H_{11})_2$, and were prepared from $[Ir(Cl)(C_8H_{14})]_2$ and HPR_2.[107] Reactions of $[Ir(HPR_2)_4]^+$ with CO, H_2 and HCl are summarized in reactions (17)–(19). IR spectral data of the dihydrido iridium(III) complex (reaction 18) were interpreted in terms of a *cis* arrangement of the H ligands; this has been corroborated by ^1H NMR. In contrast, IR and NMR studies of $[Ir(H)(Cl)(HPR_2)_4]^+$ (reaction 19) suggest a *trans* structure.[107] *trans*-$[Ir(Cl)(CO)(HPBu^t_2)_2]$ is formed from hydrated iridium(III) chloride and PBu^t_3 in DMF. This would appear to be the first example of a P—C bond cleavage of a tertiary phosphine resulting in the formation of a secondary phosphine complex.[108]

$$[Ir(CO)(HPR_2)_4]^+ \longleftarrow [Ir(HPR_2)_4]^+ + CO \longrightarrow [Ir(CO)_2(HPR_2)_3]^+ \quad (17)$$

$R_2 = Ph_2, PhC_6H_{11}$ $\qquad$ $R_2 = (C_6H_{11})_2$

$$[Ir(HPR_2)_4]^+ + H_2 \longrightarrow [Ir(H)_2(HPR_2)_4]^+ \quad (18)$$

$$[Ir(HPR_2)_4]^+ + HCl \longrightarrow [Ir(H)(Cl)(HPR_2)_4]^+ \quad (19)$$

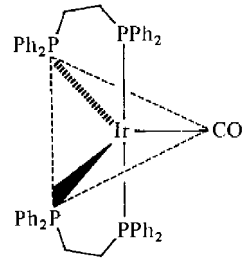
The cationic complexes $[Ir(CO)_2(SbPh_3)_3]^+$ and $[Ir(CO)_2(PR_3)_2]^+$ (R = Ph, C_6H_{11}) have been synthesized from iridium carbonyl halide derivatives with halogen acceptors in the presence of CO.[109]

Several iridium(I) diphosphine complexes have been synthesized with the ligands $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PC_6H_4PPh_2$ (dpbe), $Ph_2PCH_2CH_2AsPh_2$ (arphos), $Ph_2PCH{=}CHPPh_2$ (dppen), $Ph_2AsCH_2CH_2AsPh_2$ (dpae) and $Ph_2P(CH_2)_nPPh_2$ ($n = 3$, 4). Room temperature electronic absorption and MCD spectra of $[Ir(dppe)_2]^+$ and $[Ir(dppen)_2]^+$ reveal intense UV and visible absorptions that have been attributed to MLCT transitions.[110] Excitation polarization of these two luminescent complexes in propan-1-ol at 108 K permitted detailed spectral assignments based on the spin–orbit coupling model for d^8 metal ions complexed with π-acceptor ligands.[111] The absorption and excitation band energies of $[Ir(P{—}P)_2]^+$ and $[Ir(cod)(P{—}P)]^+$ (P—P = dppe, dppen, dpbe, arphos) are relatively insensitive to all ligands except cod. The red shift observed in complexes containing the cod ligand was attributed to destabilization of all the *d* orbitals due to closer approach of the diphosphine ligand to the Ir centre. The emission spectra and lifetimes of $[Ir(P{—}P)_2]^+$ and $[Ir(cod)(P{—}P)]^+$ have been interpreted in terms of a two-level spin–orbit split-triplet manifold.[112]

The crystal and molecular structures of the five-coordinate complex $[Ir(dppe)_2(CNMe)](ClO_4)$ have revealed a somewhat distorted trigonal bipyramidal geometry about Ir, with each dppe ligand bridging an axial and an equatorial coordination site.[113] The key structural parameters in this complex are the Ir–isocyanide ligand bond length and the angle in the trigonal plane *trans* to the unique ligand. A discussion of the effects of π-acceptor orbitals on substituents in the equatorial position (CNMe) was consistent with the finding that this iridium(I) complex exhibits the largest

P—Ir—P bond angle (120.36°) when compared to complexes containing NO^+ and CO as the unique ligand. The fluxionality of this complex appears to involve a stereochemically non-rigid TBP structure. However, the geometry of $[Ir(dppe)_2(CNMe)]^+$ is similar to that found for several other dppe complexes of iridium, including $[Ir(CO)(dppe)_2]^+$, $[Ir(dppe)_2(O_2)]^+$ and $[Ir(dppe)_2(S_2)]^+$.[114-116]

$[Ir(dppe)_2(O_2)]^+$ reversibly binds CO in solution.[83] The crystal structure of the CO adduct $[Ir(CO)(dppe)_2]^+$ (**42**) reveals a distorted trigonal bipyramid with CO occupying an equatorial position.[114]

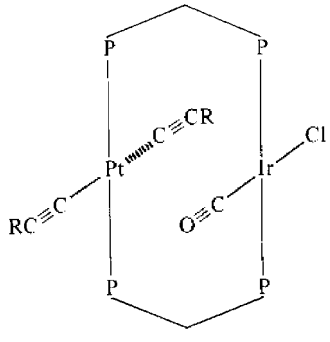


(42)

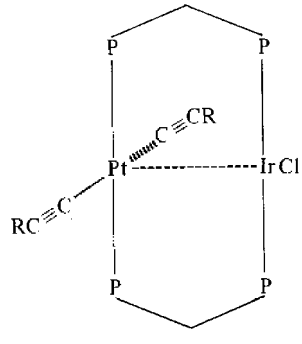
The four- and five-coordinate iridium(I) cations $[Ir(dppe)_2]^+$ and $[Ir(CO)(dppe)_2]^+$ react with $B_{10}H_{14}$, $B_{10}H_{13}$(Cl-6) and $(B_{10}H_{13})^-$ to yield a variety of ionic compounds, some of which are given in reactions (20) and (21).[117] Reaction of *t*-butyl isocyanide with the A-frame complex $[Ir_2(Cl)(CO)_3(P—P)_2](X)$ (P—P = dppm, dpam) affords $[Ir_2(CO)_3(P—P)_2(Bu^tNC)](X)$, $[Ir_2(Cl)(CO)_2(P—P)_2(Bu^tNC)_2](X)$ (P—P = dppm, X = BPh_4; P—P = dpam, X = BF_4) and $[Ir_2(CO)(P—P)_2(Bu^tNC)_4](BPh_4)_2$, as characterized by IR and ^{13}C and ^{31}P NMR spectroscopies.[118] Other neutral and cationic binuclear carbonyl complexes of iridium(I) containing dppm have been reported.[119] The dppm ligand is excellent for stabilizing homo-bimetallic complexes with metal—metal bonds, A-frames, and eight-membered rings. The treatment of *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ with $[Pt(C{\equiv}C\text{-}p\text{-}tolyl)_2(\eta'\text{-dppm})_2]$ in refluxing benzene has yielded $[Pr(C{\equiv}C\text{-}p\text{-}tolyl)_2(\mu\text{-dppm})_2Ir(Cl)(CO)]$ (**43**) in >80% yields. Also, $[Ir(Cl)_2(C_8H_{14})_4]$ reacts with $[Pt(C{\equiv}CPh)_2(\eta'\text{-dppm})_2]$ in benzene at 293 K to give $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Ir(Cl)]$ (**44**).[120] Dialkynediphosphines of the type $L = Bu^t_2PC{\equiv}C(CH_2)_nC{\equiv}CPBu^t_2$ (n = 4, 5) are known to react with $Na_2[IrCl_6]$ and CO in hot ethanol to yield $[Ir(H)(Cl)_2(CO)(L)]$ (n = 5) which, when treated with NEt_3, gives *trans*-$[Ir(Cl)(CO)(L)]$.[121] Alkynic groups promote the formation of large rings as a result of favourable conformational and entropy effects. The crystal and molecular structures of $[Ir(Cl)(CO)\{Bu^t_2PC{\equiv}C(CH_2)_5C{\equiv}CPBu^t_2\}]$ reveal a distorted planar coordination geometry about Ir with P atoms mutually *trans*.[122]

$$[Ir(dppe)_2]^+ + B_{10}H_{13}X \xrightarrow[X = H,\ 6\text{-}Cl]{} [Ir^{III}(H)(Cl)(dppe)_2][B_{10}H_{12}X] \quad (20)$$

$$[Ir(CO)(dppe)_2]^+ + (NEt_3H)[B_{10}H_{13}] \longrightarrow [Ir^{I}(CO)(dppe)_2][B_{10}H_{13}] + [Ir(H)_2(dppe)_2][B_9H_{14}] \quad (21)$$



(43)

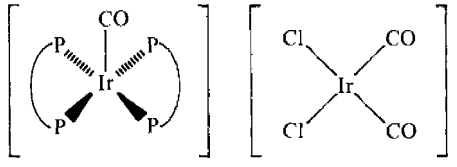


(44)

The double bond present in $Ph_2PCH{=}CHPPh_2$ (dppen) sometimes imparts different character to $[Ir(dppen)_2]X$ and $[Ir(dppen)_2Y]X$ complexes (X = Cl, Br, I, ClO_4, BPh_4; Y = CO, H_2, O_2, HCl, HI) than that present in the corresponding $Ph_2PCH_2CH_2PPh_2$ (dppe) complexes. The different behaviour was attributed[123] to the presence of the double bond. The tendency of the dppen ligand to favour electron delocalization leads to a lowering of its basicity and to a π-bonding ability greater

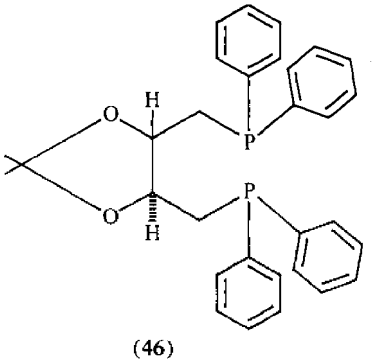
than that of dppe. Thus, the dppen ligand makes less demand for $d\pi$ electrons of Ir, and the back-donation involves mainly the carbonyl group in $[Ir(CO)(dppen)_2]^+$.

Studies by Shaw *et al.*[124] have shown that the ligands $Bu^t_2P(CH_2)_nPBu^t_2$ ($n \geqslant 9$) bridge rhodium(I) and palladium(II) atoms, but chelate iridium(I) and platinum(II) atoms in a *trans* manner. The diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–4) form *trans* carbonyl complexes of iridium(I) with the stoichiometry $[\{Ir(Cl)(CO)(diphosphine)\}_m]$, in which the diphosphine ($m = 1, 3, 4$) bridges the metal atoms. Thus, the complex $[Ir(CO)\{Ph_2P(CH_2)_2PPh_2\}_2][Ir(Cl)_2(CO)]$ forms with the structure (**45**).[119b] The intramolecular barriers to rearrangement of the trigonal bipyramidal complexes $[Ir(CO)\{Ph_2P(CH_2)_nPPh_2\}_2]^+$ decrease with decreasing ring size. This phenomenon has been suggested as a criterion for quantitative assessment of metal-to-ligand bonding.[125]



(45)

The isolation of a series of iridium(I) complexes with the optically-active diop ligand (**46**) [diop = 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane] has been reported. Equivalent portions of diop and $[Ir(Cl)(cod)]_2$ in ethanol yield $[Ir(Cl)(diop)(cod)]\cdot EtOH$.[126] The X-ray crystal structure of this complex shows a distorted trigonal bipyramid in which diop serves as an apical–equatorial bidentate ligand. The structure is maintained in solution, as evidenced by ^{31}P NMR data in $CDCl_3$ at 223 K.[127] In acetone solution, reaction between $[Ir(Cl)(cod)]_2$ and two or more equivalents of diop affords $[Ir(diop)_2](BPh_4)$, which reacts with CO to yield $[Ir_2(CO)_2(diop)_3](BPh_4)_2$.[126]

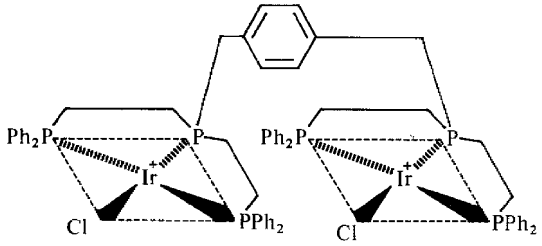


(46)

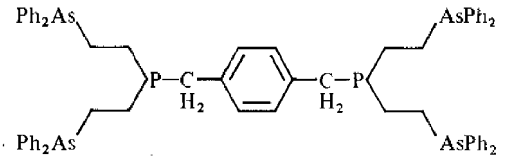
As well as serving as bidentate ligands, dppm, $Bu^t_2PC{\equiv}C(CH_2)_5C{\equiv}CPBu^t_2$ and $Ph_2P(CH_2)_3PPh_2$ are also capable of bridging two iridium atoms. These ligands are incorporated in $[Ir_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]^+$, $[Ir_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_3(\mu\text{-}dppm)_2]^+$, $[Ir(Cl)(CO)\{Ph_2P(CH_2)_3PPh_2\}]_2$ and $[Ir(Br)(CO)\{Bu^t_2PC{\equiv}C(CH_2)_5C{\equiv}CPBu^t_2\}]_2$.[121,128]

The sexidentate ligand P,P,P′,P′-tetrakis-(2-diphenylphosphinoethyl)-α,α′-diphospha-*p*-xylene (TDDX) forms, upon reaction with $[Ir(Cl)(CO)(PPh_3)_2]$, the binuclear diamagnetic non-ionic complex $[Ir_2(Cl)_2(TDDX)]$ (**47**). The TDDX complex is formed *via* complete displacement of CO and PPh_3 from Vaska's complex.[129] The ^1H NMR spectrum of complex (**47**) resembles that of [Ir(triphos)(CO)](Cl),[130] in which the triphos coordinates three coordination sites in the square plane of the Ir ion. Thus, complex (**47**) is likely to be square planar with TDDX as a sexidentate donor binding three coordination positions on each Ir ion of the binuclear complex, as shown.[129] The similar P,P,P′,P′-tetrakis-(2-diphenylarsinoethyl)-α,α′-diphospha-*p*-xylene ligand (TDADX) (**48**) reacts with Vaska's complex in benzene to give [Ir(TDADX)](Cl). In this complex, the potentially sexidentate TDADX ligand appears to bind in a tetradentate manner through the As atoms. Reactions of [Ir(TDADX)](Cl) with H_2, CO and NO are summarized in reactions (22)–(24), respectively.[131]

The internally metallated iridium(I) complex (**51**) results from treatment of $[Ir(Cl)(PPh_3)_3]$ with 1-Li-2R-1,2-$B_{10}C_2H_{10}$ (R = Me, Ph) in ether. The reaction presumably proceeds by initial formation of a carborane iridium(I) complex (**49**), which is transformed to (**51**) *via* the intermediate species (**50**)



(47)



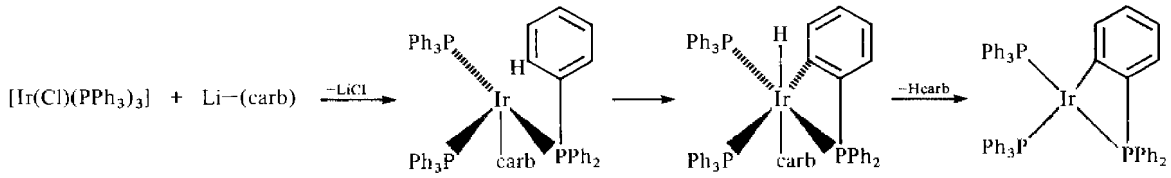
(48)

$$[Ir(TDADX)Cl + H_2 \xrightarrow{CHCl_3} [Ir(H)_2(TDADX)]Cl \quad (22)$$

$$[Ir(TDADX)]Cl + CO \xrightarrow{CHCl_3} [Ir(CO)(TDADX)]Cl \quad (23)$$

$$[Ir(TDADX)]Cl + NO \longrightarrow [Ir(NO)(TDADX)]^{2+} \quad (24)$$

by rapid intramolecular oxidative addition and reductive elimination (see Scheme 5).[132,133] A similar reaction sequence was postulated for $[Ir(PPh_3)_3(Me)]$.[134] Complex (**51**) reacts with CO, H_2 and MeOH in solution according to reactions (25)–(27), respectively, depending on reaction conditions. Proton NMR and IR spectroscopy have been employed to derive the product stereochemistries.[135]



(49) (50) (51)

Scheme 5

$$(51) + CO \longrightarrow [Ir(CO)\{P(C_6H_4)Ph_2\}(PPh_3)] + PPh_3 \quad (25a)$$

$$(51) + CO \longrightarrow [Ir(CO)\{P(C_6H_4)Ph_2\}(PPh_3)_2] \quad (25b)$$

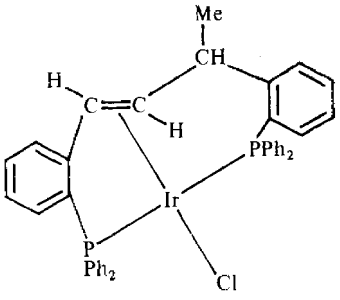
$$(51) + 2CO \longrightarrow [Ir(CO)_2\{P(C_6H_4)Ph_2\}(PPh_3)] \quad (25c)$$

$$(51) + H_2 \longrightarrow fac\text{-}[Ir(H)_3(PPh_3)_3] \quad (26)$$

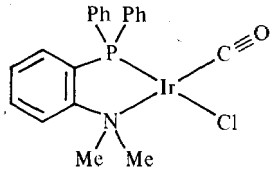
$$(51) + MeOH \longrightarrow [Ir(H)_2\{P(C_6H_4)Ph_2\}(PPh_3)_2] \quad (27)$$

o-$Ph_2PC_6H_4CH{=}^{t}CHCH(Me)C_6H_4PPh_2$-*o* (1-bdpb) reacts with $[Ir(Cl)(cod)]_2$ to yield [Ir(Cl)-(1-bdpb)] (**52**), which exists as a mixture of isomers having differing conformations of the chelate ligand. Possible conformational interconversions have been reported.[136] Complex (**52**) undergoes irreversible oxidative addition at Ir with Cl_2 and HCl, and reversible oxidative addition with H_2.[136] The similar ligands *o*-$Ph_2PC_6H_4(CH_2)_2C_6H_4PPh_2$-*o* (bdpbz) and *o*-$Ph_2AsC_6H_4(CH_2)_2C_6H_4$ PPh_2-*o* (bdabz) are found in [Ir(Cl)(bdpbz)(CO)] and [Ir(Cl)(bdabz)(CO)], respectively. The group Vb donor ligands span *trans* coordination sites. The bdpbz complex isomerizes in solution at room temperature by transferring a benzylic hydrogen atom to Ir and forming a chelate–Ir–carbon σ-bonded complex; the bdabz complex behaves in a similar fashion under more rigorous conditions.[137]

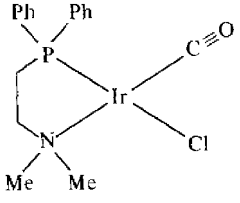
The crystal structure of the square planar complex $[Ir(Cl)(CO)(Ph_2PC_6H_4NMe_2)]$ (**53**) has been determined. IR and ^{31}P NMR spectra for complexes (**53**), (**54**) and (**55**) have suggested that all three complexes possess the same stereochemistry.[138] It was also observed that these complexes are more effective than Vaska's complex for the isomerization of 1-hex-1-ene under hydrogenation conditions.[138]



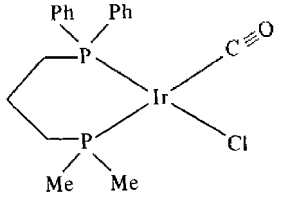
(52)



(53)



(54)

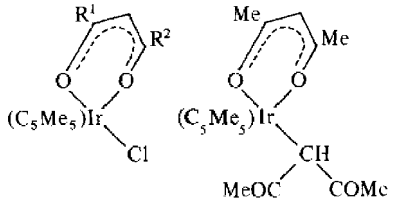


(55)

49.4.4 Oxygen Ligands

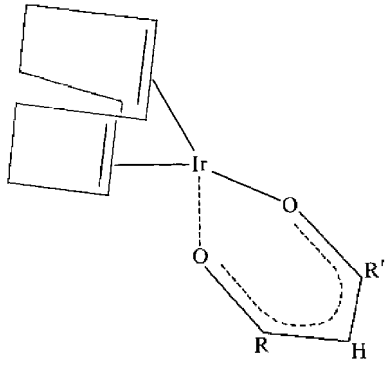
49.4.4.1 β-Diketonate, catecholate and semiquinone ligands

The syntheses and properties of $[Ir(acac)(\eta^5\text{-}C_5Me_5)]$ and $[Ir(hfac)(\eta^5\text{-}C_5Me_5)]$ **(56)** (acac = acetylacetonate, hfac = hexafluoroacetylacetonate) have been reported.[139] These iridium(I) complexes are afforded upon reaction of $[Ir(Cl)_2(\eta^5\text{-}C_5Me_5)]_2$ and the sodium salt of the appropriate acetylacetonate. Under more rigorous conditions, the bis-acac complex $[Ir(acac)_2(\eta^5\text{-}C_5Me_5)]$ **(57)** results, in which the two acac ligands are OO′- and C-bonded to iridium.



(56) (57)

Complexes of the type in **(58)** have been prepared and their properties investigated by IR and ^1H NMR spectroscopy.[140] Proton NMR spectra reveal a regular variation of the chemical shifts of the alkene protons of the cod ligand with the electronic properties of the β-diketonates. Analogous results are obtained from Ir—cod IR frequencies. Treatment of $[Ir(Cl)(C_7H_8)_3]_x$ (C_7H_8 = norbornadiene) with acetylacetone yields a species $[Ir(acac)(C_7H_8)_3]$ **(59)** having two of the norbornadiene units half-linked together with *exo–trans–exo* stereochemistry in a five-membered metallacycle. The crystal structure of complex **(59)** shows the acac ligand to be essentially planar.[141]



(58)

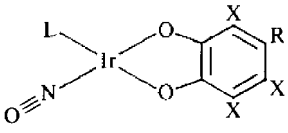
R = R′ = CF_3
R = R′ = Me
R = CF_3, R′ = Me
R = R′ = CMe_3
R = Me, R′ = Ph
R = R′ = Ph
R = Me, R′ = Ph
R = CF_3, R′ = C_4H_3S

IR, Raman and ^{13}C NMR spectroscopic studies have been performed on various $[Ir(acac)(L)_2]$ complexes (L = ethylene, propene, vinyl chloride, vinyl acetate, methyl acrylate, styrene) for the elucidation of the bonding between Ir and the alkene ligand.[142] Also, the square planar iridium(I) acetylacetonate complexes $[Ir(LL)(L')_2]$, where LL is a β-diketonate and L′ is CO or ethylene, have been studied by UVPES.[143] The enthalpies of reaction of the crystalline $[Ir(acac)(L)_2]$ complexes with gaseous CO (reaction 28) have been determined by differential scanning calorimetry. The enthalpies for the gaseous reaction have been derived from these results and Ir—L bond strengths estimated.[143]

$$[Ir(acac)(L)_2](s) + 2CO(g) \longrightarrow [Ir(acac)(CO)_2](s) + 2L(g) \quad (28)$$

IR studies on the photochemistry of the complexes $[Ir(L)(CO)_2]$ (L = acac, hfac, tfac; tfac = trifluoroacetylacetonate) in inert (CH_4·Ar) and reactive (CO, N_2) gas matrices at 12 K have shown that $[Ir(L)(CO)]$, $[Ir(CO)(N_2)]$ and $[Ir(CO)_2(L')]$ (L′ = unidentate form of L) are produced.[144]

The syntheses and characterization of nitrosyl catecholato complexes of the type in (**60**) have been reported.[145] The addition reaction of PPh_3 to various $[Ir(NO)(cat)(PPh_3)]$ (catecholato) complexes to give $[Ir(NO)(cat)(PPh_3)_2]$ has been examined in order to determine if a reversible association of a neutral molecule to a potentially catalytic d^8 four-coordinate complex can be considered as a model of one of the steps involved in the overall catalytic process. The $[Ir(NO)(1,2\text{-}O_2C_6Br_4)(PPh_3)]$ complex has been prepared and characterized. The Ir—O bond length *trans* to the NO ligand is unusually short; this probably results from the bonding effect of having a strong π-acceptor *trans* to a strong π-donor.[147] Studies of the catalytic activity of $[Ir(NO)(1,2\text{-}O_2C_6Br_4)(PPh_3)]$ and $[Ir(NO)(1,2\text{-}O_2C_6H_4)(PPh_3)]$ in the homogeneous hydrogenation of cyclic alkenes, dienes and trienes indicate that the activity is related to the electron density on the central iridium atom.[148]



X = R = Cl, Br, H
X = H;
R = NO_2, CHO, CO_2Me, CH_2OH, Me

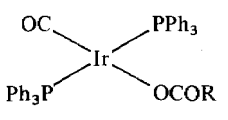
(60)

49.4.4.2 Bicarbonate and carboxylate ligands

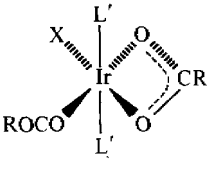
The hydroxy complex *trans*-$[Ir(OH)(CO)(PPh_3)_2]$ reacts with CO_2 in ethanol to produce the monodentate bicarbonato complex $[Ir(OCO_2H)(CO)(PPh_3)_2]$. The rate of reaction is first order in complex and independent of CO_2 and H_2O concentrations.[149,150] The bicarbonato complex reacts with O_2, affording $[Ir(OCO_2H)(CO)(O_2)(PPh_3)_2]$.[149]

$[Ir(CO)(PPh_3)_2(MeCN)]^+$ reacts with the peroxycarboxylic acids RCO_3H in the presence of NEt_3 to yield $[Ir(O_2CR)(CO)(PPh_3)_2]$ (**61**) (R = *m*-ClC_6H_4, Ph, Me). The alkyl peroxy complex (**61**) (R = *m*-ClC_6H_4) reacts with MeI according to reaction (29). Reaction of NaO_2COR' (R′ = *m*-ClC_6H_4) with $[Ir(CO)(PPh_3)_2(MeCN)]^+$ gives an inseparable mixture of $[Ir(O_2CR')(CO)(PPh_3)_2]$, $[Ir(O_2CR')(CO)(O_2)(PPh_3)_2]$, $[Ir(O_3CR')(CO)(PPh_3)_2]$ and $[Ir(O_3CR')(CO)(O_2)(PPh_3)_2]$. However, reaction of NaO_2Bu^t with $[Ir(CO)(PPh_3)_2(MeCN)]^+$ or $[Ir(F)(CO)(PPh_3)_2]$ gave only $[Ir(OH)(CO)(PPh_3)_2]$.[151] $[Ir(X)(L)(L')]$ (L = CO, N_2; L′ = phosphine or arsine) complexes are known to react with RCO_3H to yield $[Ir(X)(O_2CR)_2(L')_2]$ (**62**) (X = Cl, R = *m*-ClC_6H_4, L′ = PPh_3, PPh_2Me, $AsPh_3$; X = Cl, R = Ph, L′ = PPh_3, $AsPh_3$; X = Cl, R = Me, L′ = PPh_3; X = Br, R = *m*-ClC_6H_4, L′ = PPh_3) and CO_2. The complex (**62**) possesses unidentate and bidentate carboxylate ligands, as illustrated.[152]

$$(61) + MeI \longrightarrow [Ir(I)(OCOC_6H_4Cl\text{-}m)(CO)(PPh_3)_2(Me)] \quad (29)$$



(61)

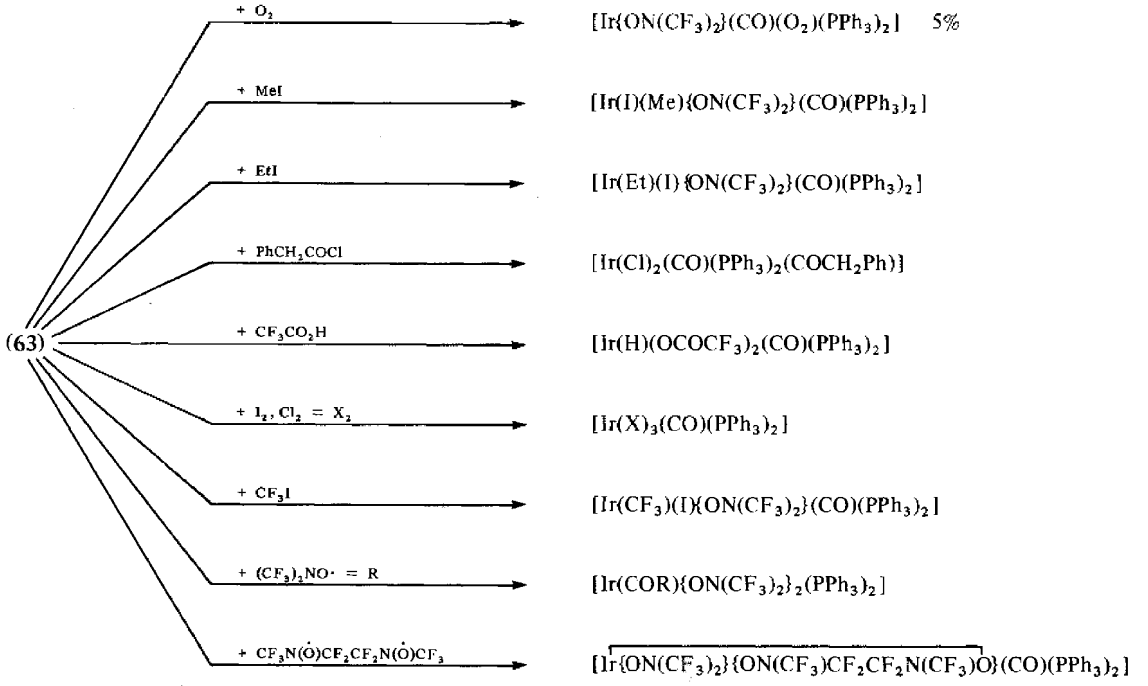


(62)

Perfluorocarboxylic acids R_FCO_2H ($R_F = CF_3$, C_2F_5) are reported[153] to react with $[Ir(NO)(PPh_3)_3]$ in boiling acetone to give $[Ir(NO)(OCOR_F)(PPh_3)_2](OCOR_F)$. The formation of this salt presumably involves successive protonations at the metal centre followed by elimination of

dihydrogen and coordination of the perfluorocarboxylate anion. A similar mechanism has been postulated for the reaction of $[Ir(NO)(PPh_3)_3]$ with HCl.[154]

Metathetical chlorine exchange employing $Na[ON(CF_3)_2]$ and $[Ir(CO)(PPh_3)_2(MeCN)]^+$ has yielded the iridium(I) complex *trans*-$[Ir\{ON(CF_3)_2\}(CO)(PPh_3)_2]^+$ (**63**). This complex undergoes a wide variety of oxidative addition reactions, as revealed in Scheme 6.[155] Complex (**63**) also reacts with the $CF_3\dot{N}(\dot{O})CF_2CF_2N(\dot{O})CF_3$ diradical to yield the seven-membered iridium(III) metallacycle $[Ir\{ON(CF_3)(CF_2CF_2N(CF_3)O\}\{ON(CF_3)_2\}(CO)(PPh_3)_2]$, as given in the last reaction in Scheme 6.[156]



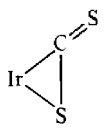
Scheme 6

49.4.5 Sulfur Ligands

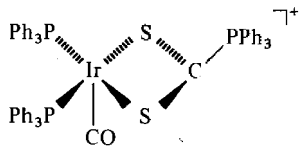
49.4.5.1 S_2, CS_2, thiocarbamate and related ligands

An investigation of the side-on-bonded disulfur and diselenium complexes $[Ir(P—P)_2(Y_2)]^+$ (P—P = dppe, dmpe; Y = S, Se) has been reported.[157] An X-ray structure of $[Ir(dppe)_2(Se_2)]^+$ revealed it to have a structure very much similar to that of its dioxygen and disulfur analogues. The Se_2 group is side-on bonded to Ir at the equatorial positions of a distorted octahedron. The S_2 or Se_2 groups readily undergo reactions in which they are reduced. Thus, mercury or tertiary phosphines strip S or Se from the complex to form HgS (HgSe) or R_3PS (R_3PSe). $[Ir(dppe)_2(S_2)]^+$ is oxidized by periodate to $[Ir(dppe)_2(S_2O)]^+$ and $[Ir(dppe)_2(SO)_2]^+$.[158] Also, $[Ir(dppe)_2(S_2)]^+$ is methylated at the S_2 group by $MeSO_3F$ to yield $[Ir(dppe)_2(S_2Me)]^+$.[159] The iridium(I) disulfide complexes $[Ir\{S(CH_2CH_2SPh)_2\}(cod)]^+$ and $[Ir(Cl)(cod)(MeSCH_2CH_2SMe)]$ have been prepared from $[Ir(Cl)(cod)]_2$, PPh_3 and the sulfide.[160]

When $[Ir(Cl)(CO)(PPh_3)_2]$ is treated with CS_2, a dark violet solution results and the addition of $NaBPh_4$ leads to the formation of dark violet crystals, which analyze as $[Ir(CO)(CS_2)(PPh_3)_2](BPh_4)$. It was formulated as an octahedral species with a π-bonded CS_2 ligand, as in (**64**). However, when attempts were made to alkylate $[Ir(CO)(CS_2)(PPh_3)_2]^+$ to form the dithioester complex, which should have reacted with acids in an alternative route to the thiocarbonyl complex, the reactions proved unsuccessful. The complex turned out to be $[Ir(CO)(S_2CPPh_3)(PPh_3)_2]^+$ (**65**). $[Ir(CO)(S_2CPPh_3)(PPh_3)_2](BPh_4)$ (**65**) exhibits a distorted trigonal bipyramidal arrangement of donor atoms about the central Ir atom. The (S_2CPPh_3) ligand behaves as a non-planar bidentate zwitterionic species $Ph_3P^+CS_2^-$, in which the S atoms occupy an axial and an equatorial position. The CO ligand occupies the other axial position, while the two PPh_3 groups occupy equatorial sites.



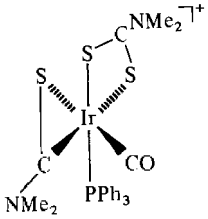
(64)



(65)

Very few examples of σ-bonded CS_2 complexes are known in which the CS_2 ligand is bonded to iridium solely through an S atom. $[Ir(Cl)(PPh_3)_3]$ reacts with CS_2 to yield $[Ir(PPh_3)_3(\sigma\text{-}CS_2)(\pi\text{-}CS_2)](BPh_4)$, which slowly decomposes at room temperature or reduced pressures resulting in the isolation of $[Ir(PPh_3)_3(\pi\text{-}CS_2)]^+$.[163] The iridium(I) complex $[Ir(PPh_3)_2(CS)(\sigma\text{-}CS_2)(\pi\text{-}CS_2)]^+$ was initially formed upon reaction of *trans*-$[Ir(Cl)(CS)(PPh_3)_2]$ with CS_2, but the σ-bonded CS_2 ligand was slowly lost to leave the π-CS_2 complex $[Ir(CS)(PPh_3)_2(\pi\text{-}CS_2)]^+$.[164]

The iridium(I) species $[Ir(CO)(\eta^2\text{-}CSNMe_2)(PPh_3)(S_2CNMe_2)](X)$ (**66**; X = Cl, PF_6) is formed upon reaction of $[Ir(Cl)(CO)(PPh_3)_2]$ with $(MeNCS)_2$.[165] Vaska-type complexes presumably react with Me_2NCSCl in a similar manner to yield *trans*-$[Ir(Cl)(CO)(\eta^2\text{-}CSNMe)_2(PPh_3)_2]^+$.

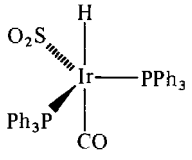


(66)

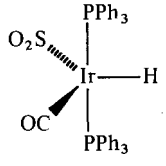
49.4.5.2 SO_2 and phosphine sulfide ligands

Levison and Robinson[166] have established that SO_2 reacts with $[Ir(H)(CO)(PPh_3)_2]$ to give $[Ir(H)(CO)(PPh_3)_2(SO_2)]$. A tautomeric equilibrium (reaction 30) involving a rapid hydride migration between Ir and the coordinated SO_2 ligand was postulated. A more recent investigation[167] of the reaction of SO_2 with $[Ir(H)(CO)(PPh_3)_3]$ indicates the product to be $[Ir(H)(CO)(PPh_3)_2(SO_2)]$ on the basis of ^1H and ^{31}P NMR evidence. At low temperatures, a six-coordinate hydrido(sulfur dioxide) intermediate, $[Ir(H)(CO)(PPh_3)_3(SO_2)]$, was proposed. The favoured structure for $[Ir(H)(CO)(PPh_3)_2(SO_2)]$ is (**67**), although spectroscopic data also appear consistent with structure (**68**). No evidence (from NMR studies) was obtained in support of equilibrium (30) or for any fluxional process involving the coordination sphere of the five-coordinate d^8 complex.[167] The crystal and molecular structures of $[Ir(Cl)(CO)(PPh_3)_2(SO_2)]$ (**69**) reveal a tetragonal pyramidal coordination geometry around Ir, with CO, Cl and *trans* P atoms in the base and the S of SO_2 at the apex. The O of the CO ligand, Cl and the two P atoms are coplanar, while the Ir—SO_2 moiety is non-planar. The Ir—S vector makes an angle of 31.6° with the normal to the SO_2 plane. The Ir—S interaction (2.49 Å) is weak.[168]

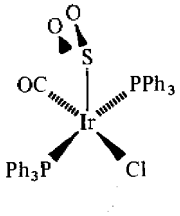
$$[(PPh_3)_2(CO)Ir(H)(SO_2)] \rightleftharpoons [(PPh_3)_2(CO)Ir—SO_2H] \qquad (30)$$



(67)



(68)

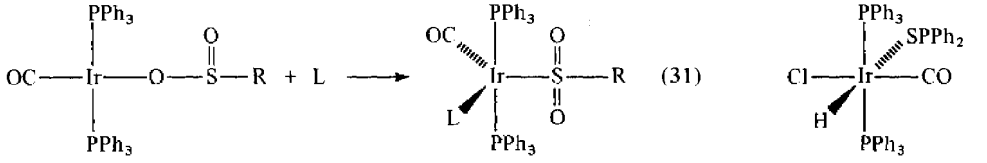


(69)

The four-coordinate iridium(I) complex $[Ir(O_2S\text{-}p\text{-tolyl})(CO)(PPh_3)_2]$ (**70**) (O_2S-*p*-tolyl = *p*-toluenesulfinate) has been prepared from $[Ir(CO)(PPh_3)_2(MeCN)]^+$ and sodium *p*-toluenesulfinate.[169] This complex contains an O-bonded sulfinate ligand, as indicated by IR spectral evidence.[98] On addition of methyl iodide to (**70**), an iridium(III) complex with O-bonded sulfinate is formed.

However, uptake of CO or O_2 by (**70**) affords isomerization to S-bonded sulfinate and complex (**71**; reaction 31).[98,169]

The secondary phosphine sulfide Ph_2HPS reacts with $[Ir(Cl)(CO)(PPh_3)_2]$ under mild conditions, giving $[Ir(H)(CO)(PPh_3)_2(SPPh_2)]$ (**72**). ^{31}P NMR data have suggested that the $SPPh_2$ ligand is S-bonded to Ir. Complex (**72**) reactors with MeI or EtI to yield $[Ir(H)(Cl)(I)(CO)(PPh_3)_2]$, most probably by initial S-alkylation of the coordinated Ph_2PS group.[170]



(70) (71) (72)

Reaction of $[\{Ir(Cl)(CO)_3\}_n]$ or $[Ir(Cl)(cod)]_2$ with $(C_6H_{11})_2PSSNH_4$ or $(PhO)_2PSSNH_4$ results in the formation of $[Ir(CO)_2(S—S)]$ (**73**) and $[Ir(cod)(S—S)]$ (**74**) (S—S = $(C_6H_{11})_2PSS$, $(PhO)_2PSS$), respectively. Complex (**74**) reacts with PPh_3 and CO according to reactions (32) and (33), respectively. The dicarbonyl complexes produced in reaction (33) react with PPh_3 and PEt_3 (= L) according to reactions (34) and (35), respectively. The *P,P'*-dithiophosphate ligand of complex (**75**) remains bidentate and iridium is four coordinate. A structure for complex (**76**) was not reported; however, IR spectral data indicate *O,O'*-dithiophosphate ligand behaves as a unidentate ligand. The different behaviour of the dicarbonyl complexes toward L could be rationalized in terms of electronic effects for which the $\{SSP(OPh)_2\}$ ligand is expected to be a stronger π-acceptor than $\{SSP(C_6H_{11})_2\}$ and therefore a stronger Ir—S bond is envisaged. This contrasts with the observed cleavage of the Ir—S bond in reaction (34). Complex (**73**) reacts with 1,2-bis(diphenylphosphine)ethane (dppe) to produce $[Ir(CO)(dppe)_2](S—S)$, in which the $(S—S)^-$ is a counterion. Also, complex (**73**) undergoes oxidative *trans* addition with X_2 (= Cl_2, Br_2, I_2) and MeI to yield $[Ir(X)_2(CO)_2(S—S)]$ and $[Ir(CO)_2(S—S)(MeI)]$, respectively.[171]

$$[Ir(cod)(S—S)] + PPh_3 \longrightarrow [Ir(PPh_3)_2(S—S)] \quad (32)$$

$$[Ir(cod)(S—S)] + CO \longrightarrow [Ir(CO)_2(S—S)] \quad (33)$$

$$[Ir(CO)_2\{SSP(C_6H_{11})_2\}] + L \longrightarrow [Ir(CO)(L)\{SSP(C_6H_{11})_2\}] \quad (34)$$

(**75**)

$$[Ir(CO)_2\{SSP(OPh)_2\}] + L \longrightarrow Ir(CO)_2(L)_2\{SSP(OPh)_2\}] \quad (35)$$

(**76**)

49.4.6 Halogens as Ligands

The iridium(I) halide complexes [IrCl], [IrBr] and [IrI] are believed to exist. Heat treatment (to 1043 K) of $[IrCl_3]$ causes sublimation of [IrCl], which decomposes above 1071 K and is insoluble in both alkaline and acidic media.[172] [IrBr] may be obtained by heating the iridium(III) bromide to 758 K in an HBr atmosphere. The monobromide complex is stable at lower temperatures, and is slightly soluble in water, in acidic and in alkaline media.[173] [IrI] forms upon heating either $[IrI_2]$ or $[IrI_3]$ to 628 K in an HI atmosphere.[173]

49.4.7 Hydrogen and Hydrides as Ligands

The electrochemical reduction of α-$[Ir(H)(Cl)_2(ER_3)_3]$ (ER_3 = PPh_3, $AsPh_3$) in $MeCN/C_6H_6$ solution has afforded $[Ir(H)(PPh_3)_4]$ and $[Ir(H)(AsPh_3)_4]$, respectively. The iridium(I) hydride complexes are stable as solids, but rapidly decompose in solution. Cryoscopic studies have suggested that in solution these complexes dissociate according to reaction (36). IR spectra and elemental analyses support the formulation as $[Ir(H)(ER_3)_4]$.[174] Related iridium(I) hydride complexes may be synthesized *via* replacement of either H_2[175] or HX[176] by a phosphine ligand (reactions 37 and 38), or by phosphine ligand exchange (reaction 39).[177] Alternatively, complexes of this type can be prepared according to reactions (40)(–(43).[14,164,178,179]

$$[Ir(H)(ER_3)_4] \rightleftharpoons [Ir(H)(ER_3)_3] + (ER_3) \quad (36)$$

$$[Ir(H)_2(SiR_3)(CO)(PPh_3)_2] + PR_3 \xrightarrow[298\,K]{C_6H_6} [Ir(H)(CO)(PPh_3)_3] + R_3SiH \quad (37)$$

$$[Ir(H)_2(Cl)(CO)(PPh_3)_2] + PPh_3 + KOH \xrightarrow{EtOH} [Ir(H)(CO)(PPh_3)_3] + KCl + H_2O \quad (38)$$

$$[Ir(H)_3(PPh_3)_3] + P(OPh)_3 \longrightarrow [Ir(H)\{P(OPh)_3\}_4] \quad (39)$$

$$[IrCl_2] + Cu + PF_3 + H_2 \longrightarrow [Ir(H)(PF_3)_4] \quad (40)$$

$$[Ir(Cl)(C_8H_{12})]_2 + PrMgBr + PPh_3 \longrightarrow [Ir(H)(PPh_3)_4] \quad (41)$$

$$[Ir(Cl)(CO)(PPh_3)_2] \xrightarrow{NaBH_4} [Ir(H)(CO)_2(PPh_3)_2] \quad (42)$$

$$[Ir(Cl)(CS)(PPh_3)_2] + NaBH_4 + PPh_3 \longrightarrow [Ir(H)(CS)(PPh_3)_3] \quad (43)$$

$[Ir(H)(CO)_2(PPh_3)_2]$ (from reaction 42) adopts a single structure in the solid state, but appears to exist as an equilibrium mixture of five-coordinate isomers in solution. The isomeric equilibrium is both solvent and temperature dependent.[180] $[Ir(H)\{P(OPh)_3\}_4]$ (from reaction 39) undergoes a reversible ligand–metal hydrogen-transfer with hydrogen elimination and metal–carbon bond formation. In this reaction, an aryl C—H bond in a donor ligand coordinated to Ir reacts with the Ir atom to form a metal–carbon bond; the hydrogen is transferred from the carbon atom to the Ir atom, forming a hydride ligand. This may subsequently be eliminated as H_2.[181] Deuteration studies on rhodium analogues have shown that this intramolecular reaction involves an *ortho* C—H bond of the aromatic phosphorus donor ligand.[182]

49.4.8 Multidentate Macrocyclic Ligands

Few iridium(I) porphyrin complexes are known, owing to the difficulty in incorporating the iridium and the high resistance to reduction of the iridium(III) complex to an iridium(I) complex.

$$[Ir(Cl)(CO)_3]_2 + OEPH_2 \longrightarrow \mu\text{-OEP}[Ir(CO)_3]_2 + [Ir(Cl)(CO)(OEP] \quad (44)$$

(77)

$$[Ir(Cl)(CO)_3]_2 + N\text{-MeOEPH} \longrightarrow N\text{-MeOEP}[Ir(Cl)(CO)_3]_2 \quad (45)$$

(78)

Complexes (**77**) and (**78**) (see reactions 44 and 45) have been synthesized *via* reaction of octaethylporphyrin ($OEPH_2$) or *N*-methyloctaethylporphyrin (*N*-MeOEPH) with $[Ir(Cl)(CO)_3]_2$. The IR and visible spectra of (**77**) are quite similar to those of μ-OEP$[Rh^I(CO)_2]$, indicative of similar structures for the two complexes. No evidence for centrosymmetry in (**77**) was obtained, probably due to the reduction in molecular symmetry by coordination of three CO ligands to each Ir atom.[183]

Complex (**78**) is more readily formed than (**77**), probably the result of the distortion of the porphyrin ring due to N-alkylation of the pyrrolic N—H bond. The spectroscopic properties of (**78**) appear similar to those of *N*-MeOEP$[Rh(Cl)(CO)_2]_2$,[184] and thus similar structures for the Ir^I and Rh^I porphyrin complexes have been proposed, in which the two Ir atoms of the iridium dimer are bonded to the two adjacent nitrogen atoms of the porphyrinato core.[183]

49.5 IRIDIUM(II)

Only a few complexes containing iridium(II) are known, most of which are of a special type as they are either dimeric and diamagnetic or contain non-innocent ligands. More likely, many reported iridium(II) complexes are hydrides of iridium(III) or iridium(III) complexes containing a σ Ir—C bond rather than a supposed π Ir—C bond. Furthermore, iridium(II) complexes, with a d^7 electronic configuration, are expected to be paramagnetic.

49.5.1 Nitrogen Ligands

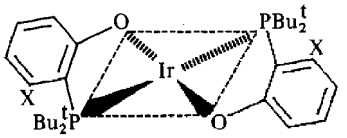
49.5.1.1 Nitrosyl ligands

The iridium(II) complex $[Ir(Br)_3(NO)(PPh_3)_2]$ has been reported by Malatesta and coworkers.[7] A + II oxidation state assignment depends on the formalism used regarding the nitrosyl ligand. The complex is considered iridium(II) if the NO ligand is assigned as $(NO)^+$.

49.5.2 Phosphorus and Arsenic Ligands

49.5.2.1 Phosphine ligands

The syntheses and structures of *trans*-[Ir(Bu$^t_2$PC$_6$H$_4$O)$_2$] and *trans*-[Ir{Bu$^t_2$PC$_6$H$_3$(OMe)O}$_2$] (**79**) have been reported by Mason and Thomas.[185] The iridium(II) state is presumably stabilized by the O,P bidentate ligands. X-Ray analysis of these complexes reveal C_i symmetry and planarity.

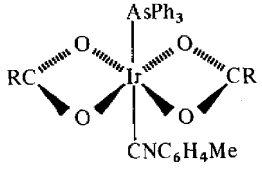


X = OMe

(79)

49.5.2.2 Arsenic ligands

Reaction between [Ir(H)$_3$(AsPh$_3$)$_2$(CNC$_6$H$_4$Me-*p*)] and RCO$_2$H (R = Me, Ar) results in the formation of the iridium(II) complexes [Ir(O$_2$CR)$_2$(AsPh$_3$)(CNC$_6$H$_4$Me-*p*)] (**80**), where R = Me, *p*-ClC$_6$H$_4$, *p*-MeOC$_6$H$_4$, 2,4,6-Me$_3$C$_6$H$_3$ and RCO$_2$ = pentane-2,4-dionate. The complexes are paramagnetic, and, based on EPR spectra, have the structure depicted in (**80**). A tetragonally distorted octahedral geometry was proposed, for which the distortion increases with the ability of the planar ligands to delocalize the electronic charge of the iridium. Thus, complex (**80**) for which R = Me is least distorted. The EPR spectra indicate that the arsine and isocyanide ligands are mutually *trans*.[186]



(80)

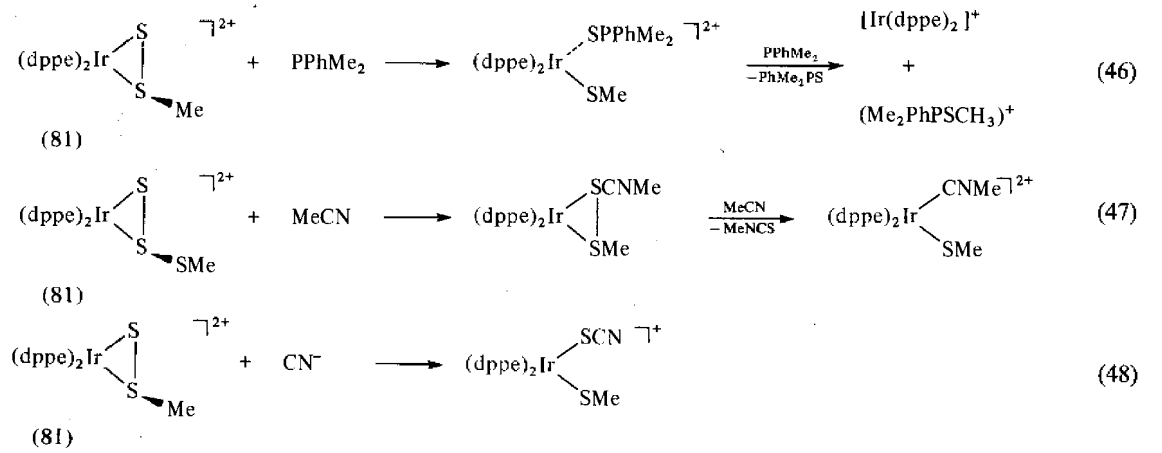
49.5.3 Sulfur Ligands

49.5.3.1 Mononuclear complexes

Salts of [Ir(dppe)$_2$(η^2-S$_2$Me$_3$)]$^{2+}$ (**81**) were initially[159] prepared in 1979 *via* the alkylation of [Ir(dppe)$_2$(S$_2$)]$^+$. The geometry about the perthio ligand in complex (**81**) was thought to resemble that found crystallographically in [Os(CO)$_2$(PPh$_3$)$_2$(η^2-S$_2$Me)](ClO$_4$);[187] that is the η^2-S$_2$Me ligand should be structurally and electronically related to other derivatives of the S$_2$ ligand such as in [Ir(dppe)$_2$(S$_2$O)]$^+$.[158b] Hoots and Rauchfuss[188] have recently reported on the stereochemistry and reactivity of [Ir(dppe)$_2$(Z$_2$R)]$^{2+}$ (**82**; Z = S, Se; R = H, Me). In solution, [Ir(dppe)$_2$(Z$_2$Me)]$^{2+}$ exists as a mixture of two diastereomers in a 20:1 (Z = S) and 6:1 (Z = Se) ratio, depending on the disposition of the methyl group relative to the dppe chelate rings. Figure 1 depicts the perspective views of the four stereoisomers of complex (**82**). The (Λ, *S*), (Δ, *R*) pair of enantiomers was thought to predominate, based on steric considerations. Complex (**81**) reacts with the nucleophiles PPhMe$_2$, MeCN and CN$^-$ according to the reactions (46)–(48), respectively.[188]

49.5.3.2 Dinuclear complexes

The dimeric iridium(III) hydride [{Ir$_2$(H)$_2$(CO)$_4$(PPh$_3$)$_2$}(SO$_2$)] (**83**) results from the reaction of [Ir$_2$(CO)$_4$(PPh$_3$)$_2$(μ-SO$_2$)] with H$_2$.[25,189] The SO$_2$ molecule may be considered formally as a diradical, sharing two electrons with Ir to form two covalent bonds; alternatively, SO$_2$ can be thought of as a two-electron acceptor from Ir to form the SO_2^{2-} anion which bridges as a bidentate ligand. Either way, S is sp^3 hybridized. Other complexes containing Ir—S—Ir bridge systems include [Ir$_2$(I)$_2$(CO)$_2$(SCMe$_3$)$_2$(L)$_2$] (**84**),[190] [Ir(CO)(PR$_3$)(μ-SBu^t)]$_2$ (**85**), [Ir(H)(CO)(PR$_3$)(μ-SBu^t)]$_2$ (**86**),[191] [Ir$_2$(Br)$_2$(CO)$_2$(PPh$_3$)$_2$(TTN)] (TTN = tetrathionaphthalene) (**87**),[192] and [Ir$_2$(CO)$_4$(SR)$_2$] (SR = SPh, SBu^t) (**88**).[193] Complex (**85**; R = Me, Ph, NMe, OMe) reacts irreversibly with H$_2$ to



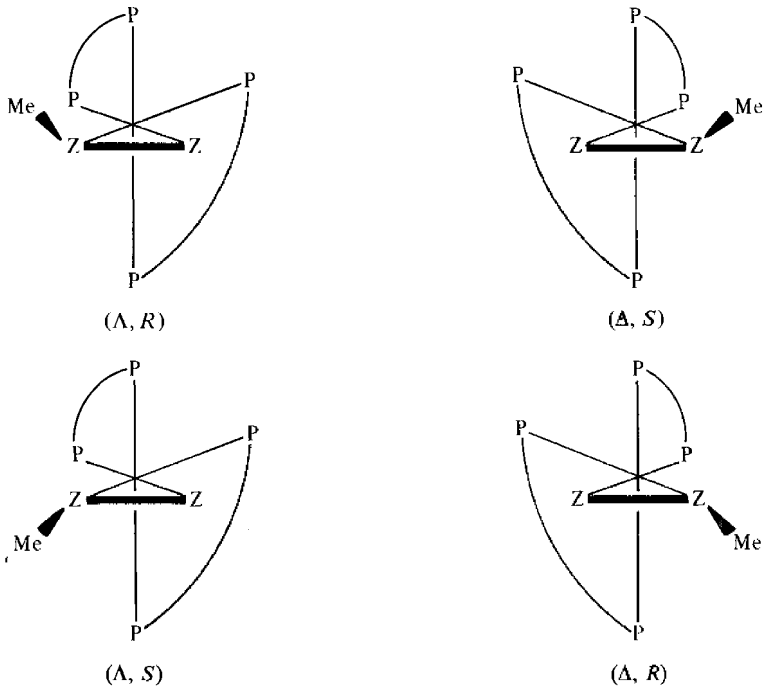
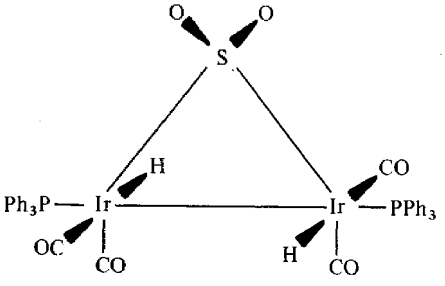
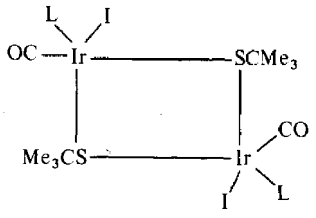


Figure 1 Perspective views of the four stereoisomers of $[Ir(Z_2R)(dppe)_2]^{2+}$ (**82**)

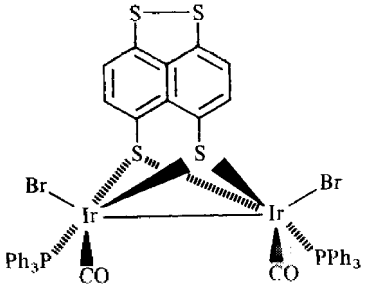
produce complex (**86**). Elemental analyses, NMR and IR spectra, H_2 uptake measurements and molecular weight data reveal that the one-electron oxidative addition of H_2 results in the cleavage of the H—H bond, yielding complex (**86**), wherein each hydrogen atom is bound to a different Ir atom. The formally d^7 Ir^{II} atoms in complex (**86**) are linked together with a single bond, in agreement with the diamagnetic behaviour of complex (**86**).[191a] The reactivity of (**86**) towards protonation (H^+) has been investigated, and reveals the formation of a dimeric monocationic species containing a two-electron three-centre bent Ir—H—Ir bond of the type $\{[Ir(H)(CO)(PR_3)(\mu\text{-}SBu^t)]_2(H)\}^+$ (R = Me, Ph, OMe). A bridging position for the added proton has been postulated on the basis of high-field ^1H NMR and Ir—H stretching frequencies of the product complex and of its deuterated analogue $\{[Ir(D)(CO)(PR_3)(\mu\text{-}SBu^t)]_2(H)\}^+$.[191b] The oxidative addition of I_2 to $[Ir_2(CO)_2(L)_2(SCMe_3)_2]$ (L = CO, PMe_3, $P(OMe)_3$, $PPhMe_2$) affords $[Ir_2(I)_2(CO)_2(L)_2(SCMe_3)_2]$ (**84**).[190] Complex (**87**) is interesting: it is the first tetrathiolene complex in which TTN adopts a six-electron-donating bis-bidentate di(μ-S) bridging configuration, rather than the usual four-electron-donating bis-didentate (μ-TTN) bridging configuration. The $[Ir_2(CO)_4(SR)_2]$ complexes (**88**) possess a butterfly structure with intermolecular associations in the crystal. When treated with PR_3 (= PMe_3, $P(OMe)_3$, PPh_3, $P(NMe_2)_3$), the SBu^t derivative yields $[Ir_2(CO)_4(PR_3)_2(SBu^t)_2]$ and $[Ir_2(CO)_2(PR_3)_2(SBu^t)_2]$. The latter complex reacts with dihydrogen to give $[Ir_2(H)_2(CO)_2(PR_3)_2(SBu^t)_2]$ activation of H_2 at one of the Ir atoms followed by intramolecular H transfer; protonation of this hydride species yields complex (**88**).[193]



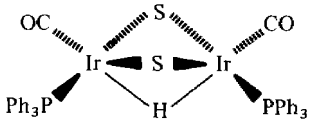
(83)



(84)



(87)



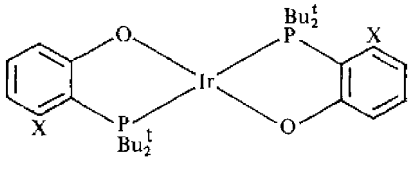
(88)

49.5.4 Halogens as Ligands

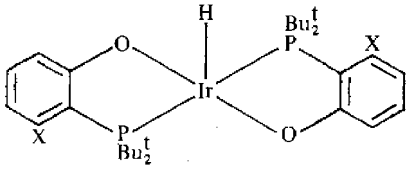
The existence of iridium(II) halide complexes remains somewhat doubtful, although the preparation of both $[IrBr_2]$ and $[IrI_2]$ has been described.[173] Heating $[IrBr_3]$ at 713 K in a stream of HBr reportedly yields the reddish-brown species $[IrBr_2]$, while $[IrI_2]$ was similarly obtained from the iridium(II) iodide in HI at 603 K. EPR studies on the product of electron irradiation of $[IrCl_6]^{3-}$ in an NaCl matrix reveal a paramagnetic species formulated $[IrCl_6]^{4-}$.[194]

49.5.5 Mixed Donor Atom Ligands

The stable iridium(II) complex $[Ir\overline{\{PBu^t_2(C_6H_4O)\}}\{PBu^t_2(C_6H_4OH)\}(CO)]$ has been synthesized by refluxing 2-methoxyphenyldi-*t*-butylphosphine with $[IrCl_6]^{3-}$ in propan-2-ol under a CO atmosphere. Upon exposure to air, CO_2 evolution occurs, producing the paramagnetic iridium(II) complex (**89**) and the iridium(III) complex (**90**), for which X = H, OMe.[195] A dioxygen adduct of (**89**) (X = OMe) has been isolated.



(89)



(90)

The cyclometallated iridium(II) complex $[Ir\overline{\{PBu^t_2(C_6H_4O)\}_2}]$ (**91**) is afforded when $[Ir\overline{\{PBu^t_2(C_6H_4O)\}}\{PBu^t_2(C_6H_4OH)\}(CO)]$ is exposed to air. Additional air exposure results in hydrogen abstraction from one of the Bu^t groups, yielding a square pyramidal complex containing one cyclometallated and one bicyclometallated ligand. The complex (**91**) forms $[Ir(H)\overline{\{PBu^t_2(C_6H_4O)\}_2}]$ when treated with H_2.[103]

49.5.6 Multidentate Macrocyclic Ligands

49.5.6.1 Schiff base ligands

The reaction between $[Ir^{III}(H)_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ and the quadridentate Schiff bases *NN'*-ethylenebis(salicylideneimine) (Hsalen) and *NN'*-ethylenebis(acetylacetoneimine) (acacen) yield the iridium(II) complexes $[Ir(AsPh_3)(salen)(CNC_6H_4Me\text{-}p)]$ and $[Ir(AsPh_3)(acacen)(CNC_6H_4Me\text{-}p)]$, respectively.[196]

49.6 IRIDIUM(III)

Iridium(III) complexes (d^6) are diamagnetic and low-spin (t_{2g}^6). The coordination number of most known iridium(III) complexes is six, though a few five- and seven-coordinate complexes have been reported. Iridium(III) forms complexes with 'soft' ligands. The $[Ir(H_2O)_6]^{3+}$ ion is unknown; no solid iridium(III) complexes with coordinated H_2O groups are known with the exception of a few aquachloro complexes.[197]

49.6.1 Mercury-containing Compounds as Ligands

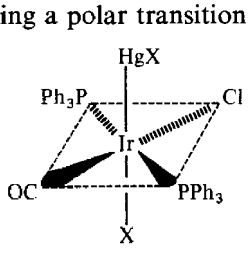
Complexes of the type $[Ir(Cl)(HgY)(Y)(CO)(PPh_3)_2]$ (Y = Cl, Br, I, OAc, CN, SCN) and $[Ir(Br)_2(HgBr)(CO)(PPh_3)_2]$ can be formed by the reaction of *trans*-$[Ir(X)(CO)(PPh_3)_2]$ with HgY_2. Oxidation of these Ir—Hg complexes occurs with halogens (I_2, Br_2) and with gaseous HCl, as shown in reactions (49)–(51).[198] Rapid substitution of the halide ions influences the nature of the halide in the reaction products; the halides preferentially coordinate to Ir in the order Cl > Br > I.[199] The hydride complex produced in reaction (51) can also be obtained by oxidizing $[Ir(Cl)_2(HgCl)(CO)(PPh_3)_2]$ with H_2. The physical and chemical properties of these Ir—Hg complexes clearly indicate that they contain a normal covalent Ir—Hg bond. Reaction of $[Ir(Cl)_2(HgCl)(CO)(PPh_3)_2]$ with PPh_3 in benzene results in the elimination of $(PPh_3)_2HgCl_2$ to yield $[Ir(Cl)(CO)(PPh_3)_2]$.[198]

$$[Ir(Cl)(HgI)(I)(CO)(PPh_3)_2] + I_2 \longrightarrow [Ir(Cl)(I)_2(CO)(PPh_3)_2] + HgI_2 \quad (49)$$

$$[Ir(Br)(Cl)(HgBr)(CO)(PPh_3)_2] + Br_2 \longrightarrow [Ir(Br)_2(Cl)(CO)(PPh_3)_2] + HgBr_2 \quad (50)$$

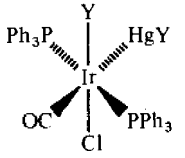
$$[Ir(Cl)_2(HgCl)(CO)(PPh_3)_2] + HCl(g) \longrightarrow [Ir(H)(Cl)_2(CO)(PPh_3)_2] + HgCl_2 \quad (51)$$

Crystal structure investigations of $[Ir(Cl)_2(HgCl)(CO)((PPh_3)_2]$ and $[Ir(Br)(Cl)(HgBr)(CO)(PPh_3)_2]$ have suggested that the oxidative addition of $HgCl_2$ or $HgBr_2$ to *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ is predominantly *trans*, and the two complexes are isomorphous. The X (= Cl, Br) ligands are mutually *cis*, while the PPh_3 ligands are mutually *trans*, as in (**92**). An S_N2 attack by iridium at an electrophilic centre in HgX_2 involving a polar transition state has been proposed.[200]



(92)

Oxidative addition reactions of $HgCl_2$ to $[Ir(Cl)(NCF_2CHFCF_3)(PPh_3)_2]$, and of diphenylethynylmercury or di-*n*-heptynylmercury to $[Ir(Cl)(CO)(PPh_3)_2]$ yield $[Ir(Cl)_2(HgCl)(NCF_2CHFCF_3)(PPh_3)_2]$ (**93a**)[65] and $[Ir(Cl)(HgC{\equiv}Y)(CO)(PPh_3)_2(C{\equiv}CY)]$ (Y = Ph, C_5H_{11}; **93b**),[201] respectively. The structures of (**93**), as illustrated, were characterized by IR spectroscopy.



(**93a**) Y = Cl

(**93b**) Y = C_5H_{11}, C_6H_5

Electrolysis of $[Ir(Cl)(CO)(PPh_3)_2]$ on anodically polarized mercury electrodes in CH_2Cl_2 leads to the formation of a product mixture of $[\{Ir(Cl)(CO)(PPh_3)_2\}_3Hg]^{2+}$ (**94**) and $[\{Ir(Cl)(CO)(PPh_3)_2\}_4Hg]^{2+}$ (**95**) as perchlorate salts when tetrabutylammonium perchlorate is employed as the supporting electrolyte. In the presence of tetraethylammonium nitrate, the product $[\{Ir(Cl)(CO)(PPh_3)_2\}Hg(NO_3)_2]$ (**96**) is obtained. Complexes (**94**)–(**96**) are converted to $[Ir(Cl)(HgX_2)(CO)(PPh_3)_2]$ (X = Cl, Br, I) on reaction with X^-.[202]

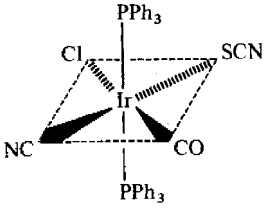
49.6.2 Group IV Ligands

49.6.2.1 Cyanide, isocyanide and fulminate ligands

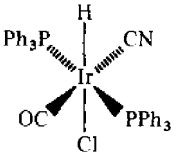
$[Ir(CN)_3]$ is reportedly obtained by heating $(NH_4)_3[Ir(CN)_6]$ at 603 K, decomposes at 633 K and exhibits ν(CN) at 2202 and 2155 cm^{-1}. On addition of ammonia, $[Ir(CN)_3]$ is converted to $[Ir(CN)_3(NH_3)_2]\cdot 1.5H_2O$.[203] The hexacyano complex $K_3[Ir(CN)_6]$ is obtained on treating $(NH_4)_3[IrCl_6]$ with KCN, followed by crystallization from water.[204] Additionally, a series of complexes of the type $M_3^{III}[Ir(CN)_6]\cdot xH_2O$, where M is Mn to Zn, are known.[205]

$[Ir(CN)_5(H_2O)]^{2-}$ is formed upon UV irradiation of $[Ir(CN)_6]^{3-}$ in aqueous solution. The aquapentacyano anion undergoes thermal anation by Cl^-, Br^-, I^-, OH^- and NCMe (=X), for which the $[Ir(CN)_5X]^{3-}$ anions were isolable in the solid form as $[Co(NH_3)_6]^{3+}$ salts.[206] The lowest energy electronic absorption band in the UV spectra of $[Ir(CN)_5X]^{3-}$ has been assigned to the $^1A_1 \rightarrow {}^3E^a$ and $^1A_1 \rightarrow {}^1E^a$ transitions. The position of these bands established the order of increasing field strength of X as $I^- < Br^- < Cl^- < H_2O < OH^- < NCMe$.

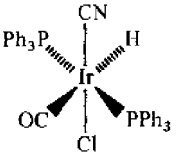
Reaction between $[Ir(Cl)(CO)(PPh_3)_2]$ and $S(CN)_2$ gave $[Ir(Cl)(CN)(NCS)(CO)(PPh_3)_2]$ (**97**) *via* an *S*-thiocyanato intermediate. An X-ray crystal structure of (**97**) shows that the complex is essentially octahedral, and the N—C—S linkage is essentially linear. Of the nine *S*-thiocyanato isomers possible, the crystal structure and IR spectral results appear consistent with those in (**97**).[207] $[Ir(H)(Cl)(CN)(CO)(PPh_3)_2]$ (**98**) and $[Ir(Cl)(CN)(HgCN)(CO)(PPh_3)_2]$ have been prepared from the reaction of Vaska's complex with HCN and $Hg(CN)_2$, respectively.[208,209] Assuming a *cis* addition of HCN, two possible structures of complex (**98**) are possible: (**98a**) and (**98b**). Proton NMR and IR data are best interpreted in terms of structure (**98b**).[208]



(97)



(98a)



(98b)

Those iridium(III) isocyanide complexes obtained from oxidative addition to an iridium(I) isocyanide complex have been treated in Section 49.4.1.1.

The iridium(III) complex $[Ir(H)_3(AsPh_3)_2(p\text{-}MeC_6H_4NC)]$ (**99**) is known to react with HX (or pseudohalides) to yield substitution products $[Ir(H)_2(X)(AsPh_3)(p\text{-}MeC_6H_4NC)]$ (X = Cl, Br, I, N_3).[210] With carboxylic acids or pentane-2,4-dione, complex (**99**) yields the chelated complexes $[Ir(L_2)(AsPh_3)(p\text{-}MeC_6H_4NC)]$ (L_2 = carboxylate or pentane-2,4-dionate) in which Ir^{III} is reportedly reduced to Ir^{II}.[186] Reactions (52)–(60) reveal the utility of complex (**99**) in synthesizing complexes with iridium in various oxidation states.[196]

$$(\mathbf{99}) + HO_2CCH(OH)Me \longrightarrow [Ir^{IV}\{O_2CCH(O)Me\}_2(AsPh_3)(p\text{-}MeC_6H_4NC)] \quad (52)$$

$$(\mathbf{99}) + o\text{-}OHC_6H_4CO_2H \longrightarrow [Ir^{IV}(o\text{-}OC_6H_4CO_2)_2(AsPh_3)(p\text{-}MeC_6H_4NC)] \quad (53)$$

$$(\mathbf{99}) + HO_2CCH(NH_2)CH_2Ph \longrightarrow [Ir^{IV}\{O_2CCH(NH)CH_2Ph\}_2(AsPh_3)(p\text{-}MeC_6H_4NC)] \quad (54)$$

$$(\mathbf{99}) + HOC_6H_4OH\text{-}o \longrightarrow [Ir^{IV}(o\text{-}OC_6H_4O)_2(AsPh_3)(p\text{-}MeC_6H_4NC)] \quad (55)$$

$$(\mathbf{99}) + o\text{-}NH_2C_6H_4OH \longrightarrow [Ir^{IV}(o\text{-}NHC_6H_4O)_2(AsPh_3)(p\text{-}MeC_6H_4NC)] \quad (56)$$

$$(\mathbf{99}) + o\text{-}NH_2C_6H_4CO_2H \longrightarrow [Ir^{IV}\{o\text{-}NHC_6H_4CO_2\}_2(AsPh_3)(p\text{-}MeC_6H_4NC)] \quad (57)$$

$$(\mathbf{99}) + p\text{-}MeOC_6H_4CO_2H \longrightarrow [Ir^{III}(H)_2(Cl)(AsPh_3)(p\text{-}MeC_6H_4NC)] \quad (58)$$

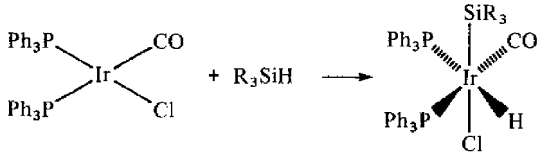
$$(99) + \text{tfac} \longrightarrow [Ir^{III}(H)_2(\text{tfac})(AsPh_3)(p\text{-}MeC_6H_4NC)] \quad (59)$$

$$(99) + \text{acac} \longrightarrow [Ir^{II}(\text{acac})(AsPh_3)(p\text{-}MeC_6H_4NC)] \quad (60)$$

Beck and coworkers[211] have reviewed transition metal complexes of the fulminate ion, CNO^-, which bonds to the metal *via* the carbon atom. Fulminate complexes are, in general, similar to those with CN^- ligands. An extensive series of stable, non-explosive fulminates has been examined, including $[Ir(CNO)_6](AsPh_4)_3$. $[Ir(CNO)_6]^{3-}$ was prepared from hydrated iridium(III) chloride and $Hg(CNO)_2$, and characterized by IR spectroscopy.[211d]

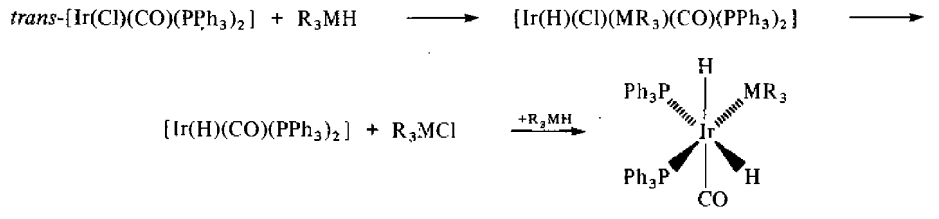
49.6.2.2 Si-, Ge- and Sn-containing ligands

Most iridium(III) complexes containing Group IVb donor ligands are six coordinate and are more stable than their rhodium(III) analogues. The complexes are prepared *via* oxidative addition to an iridium(I) complex. Thus, the facile reaction between Vaska's complex and silanes with electronegative substituents [R_3SiH] gives an iridium(III) complex with an Ir—Si bond. Reaction (61) occurs for $R_3SiH = (EtO)_3SiH$, Cl_3SiH, $EtCl_2SiH$ and $PhCl_2SiH$.[212] Proton NMR and IR



(61)

spectroscopy have been employed to elucidate the structure of the adducts formed between [Ir(X)-(CO)$(PEt_3)_2$] (X = Cl, I) and MN_3Q (M = Si, Q = H, Cl, Br, I,.Me; M = Ge, Q = H, Cl, Br, I). The addition yields *trans*-[Ir(H)(MH_2Q)(X)(CO)$(PEt_3)_2$]. When M = Si, the major product contains H *trans* to Si; and when M = Ge, the major product contains H *trans* to X.[213] Additionally, organosilanes and organogermanes (R_3MH) add to *trans*-[Ir(Cl)(CO)$(PPh_3)_2$] to yield dihydrido complexes, wherein the expected Ir—MR_3 products are intermediates (see Scheme 7).[214,215,216]

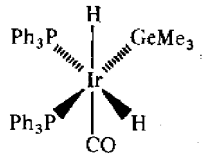


Scheme 7

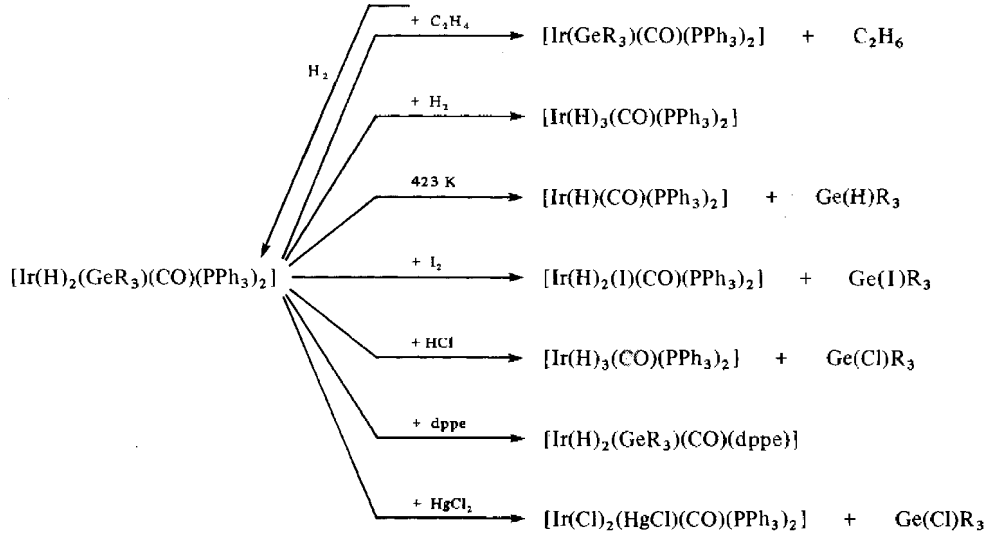
The kinetics of the oxidative addition of silicon hydrides to $[Ir(dppe)_2]^+$ (reaction 62) have been investigated.[217] No conclusive results were obtained on whether reaction (62) proceeds *via* a concerted three-centre transition state or *via* a transition state analogous to that proposed for the Menschutkin reaction. The iridium(I) species *trans*-[Ir(X)(CO)$(PEt_3)_2$] reacts with $Y(SiH_3)_2$ (Y = O, S, Se) in benzene to yield [Ir(H)(I)(SiH_2YSiH_3)(CO)$(PEt_3)_2$] or [{Ir(H)(I)(SiH_2)(CO)$(PEt_3)_2\}_2$Y]. Reaction between *trans*-[Ir(X)(CO)$(PEt_3)_2$] and $P(SiH_3)_3$ affords [Ir(H)(I){$SiH_2P(SiH_3)_2$}-(CO)$(PEt_3)_2$], [{Ir(H)(I)$(SiH_2)_2$(CO)$(PEt_3)_2\}_2$$PSiH_3$] or [{Ir(H)(I)$(SiH_2)(CO)(PEt_3)_2\}_3$P], depending on the proportions of reactants employed. With $N(SiH_3)_3$, *trans*-[Ir(X)(CO)$(PEt_3)_2$] gives [Ir(H)(I){$SiH_2N(SiH_3)_2$}(CO)$(PEt_3)_2$] and [{Ir(H)(I)(SiH_2)(CO)$(PEt_3)_2\}_2$$NSiH_3$]. The reaction products have all been characterized by ^1H and ^{31}P NMR spectroscopy. The oxidative addition reactions are similar to those between *trans*-[Ir(X)(CO)$(PEt_3)_2$] and silyl halides,[213] and similar stereochemistries have also been proposed.[218]

$$[Ir(dppe)_2]^+ + [Si(H)(Me)_n(EtO)_{3-n}] \longrightarrow [Ir(H)(dppe)_2\{SiMe_n(EtO)_{3-n}\}]^+ \quad (62)$$

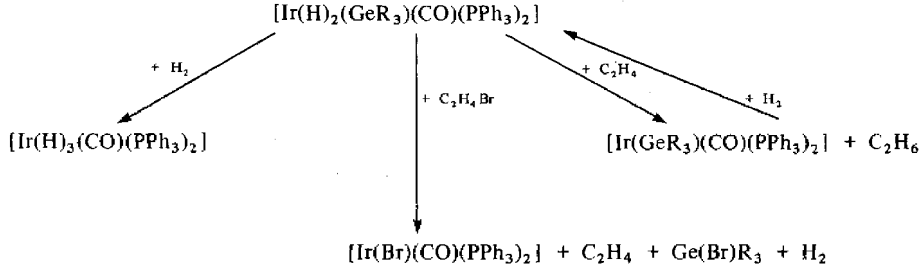
Six-coordinate dihydrido complexes of the type [$Ir(H)_2(GeR_3)$(CO)$(PPh_3)_2$] (R = Cl, Me, Et) can be produced *via* Scheme 7. However, for R = Ph, the five-coordinate complex [Ir(H)-(Cl)$(GePh_3)$(CO)(PPh_3)] is formed. For the complex where R = Me, crystal structural, ^1H NMR and IR spectral data are consistent with structure (**100**).[216] These iridium(III) complexes containing Ge donor ligands undergo several reactions, as summarized in Scheme 8.[216] Furthermore, ethylene is hydrogenated by [$Ir(H)_2(GeR_3)$(CO)$(PPh_3)_2$] to yield the iridium(I) complex [$Ir(GeR_3)$-(CO)$(PPh_3)_2$], as per Scheme 9.



(100)

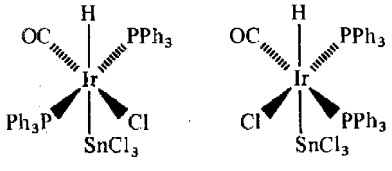


Scheme 8

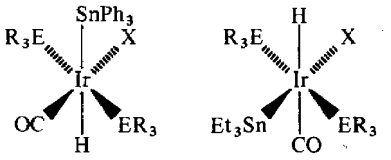


Scheme 9

$K_2[IrBr_6]$ reportedly reacts with $SnBr_2$ in aqueous HBr solution, from which $(Me_4N)[Ir(Br)_4(SnBr_3)_2]$ was obtained upon addition of Me_4NBr.[4] The syntheses of $[Ir(H)(Cl)(X)(PPh_3)_3]$, $[Ir(H)(Cl)(X)(CO)(PPh_3)_2]$, $[Ir(D)(Cl)(X)(CO)(PPh_3)_2]$, $[Ir(H)_2(X)(CO)(PPh_3)_2]$ and $[Ir(D)_2(X)(CO)(PPh_3)_2]$ (X = $SnCl_3$) *via* oxidative addition of $SnCl_2$ to iridium(I) complexes have been described. $SnCl_2$ serves as a weak σ-donor ligand (*i.e.* $SnCl_3^-$), and exhibits a large *trans* effect due to its ability to form $d\pi$-$d\pi$ bonds to the central Ir atom. IR and ^1H NMR spectral data have been interpreted in terms of structure (**101**) for $[Ir(H)(Cl)(SnCl_3)(CO)(PPh_3)_2]$, although structure (**102**) cannot be excluded.[219] The complexes $[Ir(X)(SnR_3)(CO)(PR'_3)_2]$ (X = Cl, Br, I; R = Me, Et, Ph; PR'_3 = PPh_3, PPh_2Me, $PPhEt_2$) have been prepared and characterized by ^1H NMR and IR spectroscopy. The Ph_3Sn—Ir complexes have been assigned the stereochemistry in (**103**), while the Et_3Sn—Ir complexes are consistent with structure (**104**). Two isomers of the Me_3Sn—Ir complexes were isolable, and assigned to structures analogous to (**103**) and (**104**).[220]

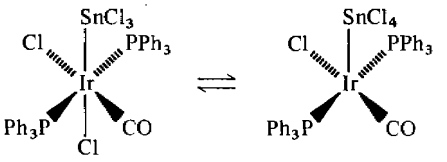


(101) (102)



(103) (104)

Intramolecular oxidation–reduction isomerism involving changes in formal oxidation state at the metal centre are rather uncommon in transition metal chemistry. However, from IR and ^{1}H NMR spectral studies on $[Ir(Cl)(SnCl_4)(CO)(PPh_3)_2]$ and $[Ir(Cl)(SnCl_3Me)(CO)(PPh_3)_2]$, it was concluded that each complex consists of two rapidly interconverting isomers. Further, the available data for the $SnCl_4$—Ir complex are consistent with the isomerism arising from rapidly equilibrating oxidative addition and donor–adduct isomers (**105a**) ⇌ (**105b**).[220]



(105a) (105b)

49.6.3 Nitrogen Ligands

49.6.3.1 Ammonia and amine ligands

The iridium(III) pentaamine complexes $[Ir(X)(NH_3)_5]^{2+}$ undergo octahedral substitution reactions in aqueous solution, similar to Co^{III} and Rh^{III} analogues.[221] $[Ir(X)(NH_3)_5]^{2+}$ (X = NO_3, Cl, Br, I) undergoes aquation (reaction 63) with the reactivity increasing in the order X = Cl < Br < I < NO_3; a linear free energy relationship was observed.[222] The aquation rates of $[Ir(X)(NH_3)_5]^{2+}$ are smaller than those of the cooresponding Rh^{III} complexes, consistent with considerations of crystal field theory. Additionally, $[Ir(Br)(NH_3)_5]^{2+}$ undergoes acid hydrolysis at 298 K with a rate constant $k \approx 2 \times 10^{-10}\,s^{-1}$; $E_a = 113\,kJ\,mol^{-1}$ and $\Delta S^{\ddagger} = -59\,J\,mol^{-1}\,K^{-1}$.[222] The rate constant k_{ex} for the base-catalysed hydrogen exchange of $[Ir(NH_3)_6]^{3+}$ at 298 K in D_2O (reaction 64) has been determined ($k_{ex} = 1.5 \times 10^{-8}\,M^{-1}\,s^{-1}$).[223] The chloride anation of $[Ir(H_2)(NH_3)_5]^{3+}$ is three times faster than the water exchange rate, and has been attributed to an associative interchange mechanism.[224]

$$[Ir(X)(NH_3)_5]^{2+} + H_2O \rightleftharpoons [Ir(H_2O)(NH_3)_5]^{3+} + X^- \quad (63)$$

$$Ir—NH + OD^- \xrightarrow[k_{ex}]{} Ir—ND + OH^- \quad (64)$$

Iridium(III) ammine complexes have been shown to be photoactive.[225,226] Ligand field (LF) excitation (350 nm) of $[Ir(N_3)(NH_3)_5]^{2+}$ leads to efficient decomposition of N_3^- with the formation of $[Ir(NH_2Cl)(NH_3)_5]^{3+}$ and N_2 in aqueous HCl.[226] The principal photoreactions observed on LF excitation (254 or 313 nm) of $[Ir(NH_3)_6]^{3+}$, $[Ir(H_2O)(NH_3)_5]^{3+}$ and $[Ir(Cl)(NH_3)_5]^{2+}$ in aqueous solution at 298 K are summarized in reactions (65) and (66); $[Ir(H_2O)(NH_3)_5]^{3+}$ is virtually unreactive under the conditions employed.[227] The photochemical properties of $[Ir(X)(NH_3)_5]^{2+}$ (X = Cl, Br, I), *trans*-$[Ir(I)_2(NH_3)_4]^+$, *trans*-$[Ir(I)(H_2O)(NH_3)_4]^{2+}$ and $[Ir(L)(NH_3)_5]^{3+}$ (L = H_2O, NH_3, MeCN, PhCN) have been investigated in aqueous solution. LF photolysis leads to ligand photoaquation only, while irradiation of ligand-to-metal charge transfer (LMCT) absorption bands suggest the presence of a redox component as well as aquation. Quantum yields and product distribution are wavelength independent for LF excitation. Also, LF excitation is followed by efficient internal conversion/intersystem crossing to produce a common 'triplet' LF state.[228] Essentially, rhodium(III) and iridium(III) amine complexes behave in a parallel manner.

$$[Ir(NH_3)_6]^{3+} + H_3O^+ \xrightarrow{h\nu} [Ir(NH_3)_5(H_2O)]^{3+} + NH_4^+ \quad (65)$$

$$[Ir(Cl)(NH_3)_5]^{2+} + H_2O \xrightarrow{h\nu} [Ir(H_2O)(NH_3)_5]^{3+} + Cl^- \quad (66)$$

The synthesis and characterization of *cis*- and *trans*-$[Ir(X)_2(en)_2]^+$ (X = Cl, Br, I) and *trans*-$[Ir(X)(Y)(en)_2]^{n+}$ (X = Cl, Y = Br, I, H_2O, OH, NCS, NO_2, ONO; X = Y = NO_3, N_3; en = ethylenediamine) were reported by Bauer and Basolo,[229] following Kida's[230] paper on the synthesis of *cis*- and *trans*-$[Ir(Cl)_2(en)_2]^+$. *trans*-$[Ir(Cl)_2(en)_2]^+$ can be prepared by a catalytic method employing H_3PO_2, while the *cis* isomer is obtained in a high ionic strength medium. Structural assignments were made on the basis of IR spectra and resolution of the *cis* isomer.

Ligand substitution at *trans*-$[Ir(X)_2(en)_2]^+$ occurs without stereochemical change, and with substitution rates independent of the concentration and nature of the incoming ligand and the ionic strength. The substitution mechanism involves an aqua intermediate, as illustrated in Scheme 10.[231] Aquation kinetics of complexes such as *trans*-$[Ir(X)_2(en)_2]^+$ were not directly accessible, the equilibrium in Scheme 10 lying to the left. Table 2 shows various ligand substitution rates and activation parameters for *trans*-$[Ir(X)(en)_2(L)]^+$. The base hydrolysis of *cis*- and *trans*-$[Ir(Cl)_2(en)_2]^+$ also proceeds with stereoretention.

$$[Ir(X)_2(en)_2]^+ \underset{RDS}{\overset{H_2O,\ slow}{\rightleftharpoons}} [Ir(X)H_2O(en)_2]^{2+} \overset{+Y,\ fast}{\rightleftharpoons} [Ir(X)(Y)(en)_2]^{2+}$$

Scheme 10

Table 2 Rates of Ligand Substitution Reactions of *trans*-$[Ir(X)(en)_2(L)]^{+a}$

L	*Leaving group*	$k \times 10^6$ (s^{-1})[b]	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
Cl	Cl	5.9	122.1	−25.1
Br	Cl	9.0	113.3	−37.6
I	Cl	159	105.8	−16.7
NO_2	Cl	107	—	—
Br	Br	14.5	113.7	−37.6
I	Br	104	113.3	−20.9
I	I	58	120	−12.5

[a] Taken, in part, from ref. 231.
[b] At 378 K.

The geometric structure of *cis*-$[Ir(Cl)_2(en)_2]^+$ has been proved by resolution into its optical isomers.[232] Proton NMR studies have shown that the ammination of *cis*-$[Ir(Cl)_2(en)_2]^+$ proceeds with retention of configuration to yield *cis*-$[Ir(en)_2(NH_3)_2]^{3+}$. The absolute configurations of optically-active *cis*-$[Ir(Cl)_2(en)_2]^+$ and *cis*-$[Ir(en)_2(NH_3)_2]^{3+}$ have been inferred by comparing their electronic absorption and CD spectra with those of Co^{III} and Rh^{III} analogues; the Λ configuration has been proposed.[233]

The complexes *trans*-$[Ir(X)_2(en)_2]^+$ (X = Cl, Br, I) in aqueous solution undergo rapid photosubstitution to yield *trans*-$[Ir(X)(en)_2(H_2O)]^{2+}$. LF excitation (350 nm) of *trans*-$[Ir(Cl)_2(en)_2]^+$ affords photoaquation of Cl^- with a quantum yield of *ca.* 0.1 mol einstein^{-1}.[234] Irradiation into the LF bands of *cis*- and *trans*-$[Ir(X)(Y)(en)_2]^+$ (X = Y = Cl, Br, I; X = OH, Y = Cl) in aqueous solution leads to halide photolabilization. For X = Y = Cl, the quantum yields are pH independent. In acidic solution, the *trans* dihalo complexes give *trans*-$[Ir(X)(en)_2(H_2O)]^{2+}$ with complete retention of configuration. But the *cis* analogues undergo simultaneous photoisomerization to yield a mixture of *cis*- and *trans*-$[Ir(X)(en)_2(H_2O)]^{2+}$ with the extent of photoisomerization following the order X = Cl < Br < I.[235] The principal photoreactions observed for these complexes are consistent with theories[236] that propose ligand labilization from the lowest LF excited states being confined to the weak field axis. With an excess of Br^- and I^-, *trans*-$[Ir(Cl)_2(en)_2]^+$ reacts photochemically to yield *trans*-$[Ir(Br)_2(en)_2]^+$ and *trans*-$[Ir(I)_2(en)_2]^+$, respectively.[237]

The photoaquations of X in *trans*-$[Ir(X)_2(en)_2]^+$ provide a useful route for the rapid and clean preparation of various *trans*-$[Ir(X)(Y)(en)_2]^{n+}$ and *trans*-$[Ir(X')_2(en)_2]^+$ complexes (reactions 67–70).[229,237] The products obtained were those expected on the basis of the *trans*-effect behaviour in such systems.

$$trans\text{-}[Ir(Cl)_2(en)_2]^+ \xrightarrow{h\nu,\ I^-} trans\text{-}[Ir(Cl)(I)(en)_2]^+ \longrightarrow trans\text{-}[Ir(I)_2(en)_2]^+ \quad (67)$$

$$trans\text{-}[Ir(I)_2(en)_2]^+ \xrightarrow{h\nu,\ Cl^-} trans\text{-}[Ir(Cl)(I)(en)_2]^+ \quad (68)$$

$$trans\text{-}[Ir(Cl)_2(en)_2]^+ \xrightarrow{h\nu,\ OH^-} trans\text{-}[Ir(OH)_2(en)_2]^+ \quad (69)$$

$$trans\text{-}[Ir(X)_2(en)_2]^+ \xrightarrow{h\nu,\ H_2O} trans\text{-}[Ir(X)(H_2O)(en)_2]^{2+} \xrightarrow{+Ag^+}$$

$$trans\text{-}[Ir(X)(H_2O)(en)_2]^{2+} + AgX(s) \xrightarrow{+Y^-} trans\text{-}[Ir(X)(Y)(en)_2]^+ \quad (70)$$

The kinetics of chloride exchange in *trans*-$[Ir(Cl)_2(trien)]^+$[238] (trien = triethylenetetramine) show behaviour similar to that of *cis*- and *trans*-$[Ir(Cl)_2(en)_2]^+$.[239] Also, the rate constant dependency on chloride concentration is similar for all three complexes. This dependency has been interpreted[238] either in terms of an ion pair or a dissociative mechanism, with the latter being more favourable.

The bis-pyridino complexes *trans*- and *cis*-$[Ir(Cl)_4(py)_2]^-$ and *trans*-$[Ir(Cl)_3(H_2O)(py)_2]$ have been prepared and characterized. The thermal aquation of *cis*-$[Ir(Cl)_4(py)_2]^-$ yields 5% *trans* product, and a trigonal bipyramidal intermediate species is postulated.[240]

trans-$[Ir(Cl)_2(py)_4]^+$[241,242] undergoes photoaquation of Cl^- at 350 and 254 nm irradiation. A significant amount of amine release also occurs during photolysis of this complex.[243] The photochemistry of several pyridine complexes has been reviewed by Balzani and Carassiti,[225] including $[Ir(Cl)_5(py)]^{2-}$,[244] *cis*- and *trans*-$[Ir(Cl)_4)py)_2]^-$,[245,246] *trans*-$[Ir(X)_3(py)_3]$ (X = Cl,[247] Br[248]), and *cis*- and *trans*-$[Ir(Cl)_2(py)_4]^+$.[249]

49.6.3.2 N-heterocyclic ligands

A proton NMR spectroscopic investigation of a complex originally thought to be $[Ir(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridyl) has assigned the complex as *cis*-$[Ir(Cl)_2(bipy)_2]^+$.[250] In agreement, Gillard and Heaton[251] have found that earlier reports of the syntheses of $[Ir(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) and $[Ir(bipy)_3]^{3+}$ were erroneous.

The preparation of *cis*-$[Ir(Cl)_2(4,4'\text{-}Ph_2bipy)_2]^+$, *cis*-$[Ir(Cl)_2(4,7\text{-}Cl_2phen)_2]^+$ and *cis*-$[Ir(Cl)_2(bipy)_2]^+$ (4,4′-Ph_2bipy = 4,4′-diphenyl-2,2′-bipyridyl; 4,7-Cl_2phen = 4,7-dichloro-1,10-phenanthroline) has been reported. The similarities between the UV spectra of the free ligands and the complexes led to an assignment of ligand-localized transitions in this region. Absorption bands in the visible region were assigned to charge-transfer transitions. All three complexes exhibit luminescence at 19.5–21.1 kK at 77 K, ascribed to a charge-transfer ($d\pi^*$) → A_1 transition.[252] Emission quantum yields, lifetimes and spectra, along with photosolvation yields, are reported for *cis*-$[Ir(Cl)_2(bipy)_2]^+$ and its deuterated analogue *cis*-$[Ir(Cl)_2(bipy\text{-}d_8)_2]^+$ in H_2O, DMF, MeOH and MeCN. Both charge-transfer and ligand-field excited states contribute to the decay properties in fluid media. Photosolvation rates are solvent dependent and thus consistent with either a dissociative or a dissociative interchange mechanism.[253]

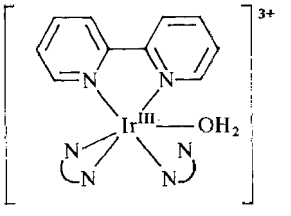
The luminescence decay curves of *cis*-$[Ir(Cl)_2(phen)(5,6\text{-}Me_2phen)]^+$[254] and *cis*-$[Ir(Cl)_2(phen)(4,7\text{-}Me_2phen)]^+$[255] (5,6-$Me_2$phen = 5,6-dimethyl-1,10-phenanthroline; 4,7-Me_2phen = 4,7-dimethyl-1,10-phenanthroline) have been recorded as a function of excitation and/or emission wavelength. From emission wavelength studies, the total emission spectrum of the 5,6-Me_2phen complex is decomposed into two component spectra, one arising from $d\pi^*$ and the other from $\pi\pi^*$ orbital parentages. Excitation wavelength studies have led to the proposal that upper states of $d\pi^*$ parentage feed the $d\pi^*$ emission while states of $\pi\pi^*$ parentage feed the $\pi\pi^*$ emission. The data obtained from emission wavelength studies of the 4,7-Me_2phen complex best fit a model in which the luminescence occurs as a result of three sets of thermally non-equilibrated levels (lifetimes $\tau = 6.0$, 8.7 and 22 μs), arising from mixed $d\pi^*$–$\pi\pi^*$, $d\pi^*$, and d–d orbital parentages, respectively.

A synthesis of $[Ir(bipy)_3]^{3+}$ has been reported by Flynn and Demas.[256] ^{13}C and proton NMR spectra have confirmed the tris-complex assignment. $[Ir(bipy)_3]^{3+}$ exhibits a phosphorescence at 22.3 kK with a mean lifetime of ~ 80 μs in MeOH/EtOH glass at 77 K; luminescence was assigned as predominantly π–π^* ligand phosphorescence.

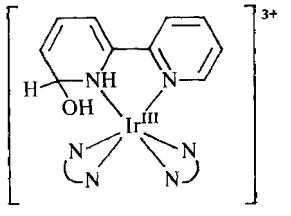
Gillard[257] has summarized many of the so-called 'anomalies' existing for transition metal polypyridyl complexes in aqueous solution, and postulated covalent hydrate formation to explain these 'anomalies'. Nord and coworkers[258] have questioned the validity, and indeed the premise upon which covalent hydration in polypyridyl complexes is based.

The nature of the complex(es) containing three 2,2′-bipyridyls per iridium atom has been the subject of a controversial debate[259–263] since the report by Flynn and Demas[256] of the successful preparation of the $[Ir(bipy)_3]^{3+}$ cation. This species was formulated as having all three bipyridyl ligands ligated to iridium(III) *via* the nitrogen atoms, as demonstrated by ^{13}C NMR spectroscopy (D_3 symmetry, five well-resolved ^{13}C resonances). Later, Watts *et al.*[259] identified another complex also containing three bipyridyl ligands per iridium atom but having distinct absorption and emission spectral properties, as well as different photophysical characteristics from $[Ir(bipy)_3]^{3+}$. The complex exhibits an emission in both acidic and basic media at lower energies than that for $[Ir(bipy)_3]^{3+}$, and

visible absorption bands in these media do not correspond with the tris complex. The complex was described as being comprised of iridium, two bidentate bipy ligands, one water molecule, and one monodentate bipy′, $[Ir(bipy)_2(H_2O)(bipy')]^{3+}$ (**106a**); this complex can be converted to the hydroxo form and isolated by treatment with base. The luminescence spectrum of complex (**106a**) arises primarily from interligand π–π^* transitions of the bipy ligands, with some mixing from charge-transfer from iridium(III) to bipy.[264] The luminescence lifetimes of complex (**106a**) and its hydroxo analogue, $[Ir(bipy)_2(OH)(bipy')]^{2+}$, along with their related emission quantum yields in H_2O and D_2O, have been reported as well.[259] Together with the above information, the IR spectrum of (**106a**) is consistent with a formulation of the complex as the covalently hydrated species (**106b**); however, because there is no facile equilibrium between $[Ir(bipy)_3]^{3+}$ and the covalent hydrate $[Ir(bipy)_2(bipy \cdot H_2O)]^{3+}$ (**106b**), as revealed by the identical emission spectra in both 0.1 M base and 0.1 M acid for $[Ir(bipy)_3]^{3+}$, the nature of the complex isolated by Watts *et al.*[259] cannot be (**106b**). Gillard and coworkers[262] have argued 'because there is no facile equilibrium, it is not to say that no equilibrium exists', and explained the 'puzzling' properties of the complex in terms of the species (**106b**).

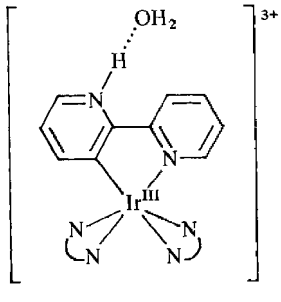


(106a)

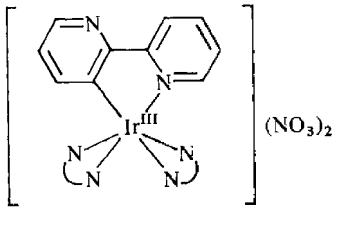


(106b)

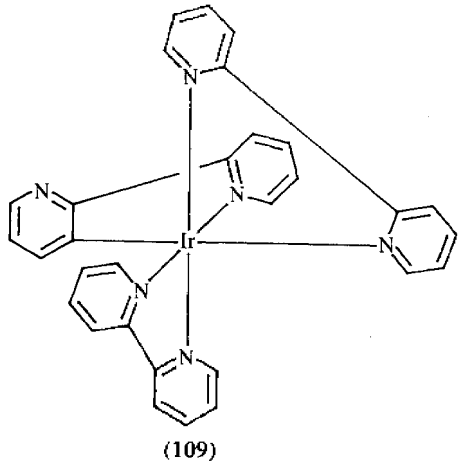
Another source of controversy about the formulation of this iridium(III) complex rests on its ^1H and ^{13}C NMR spectra.[263] The data from these spectra preclude the existence of structure (**106b**) and were taken as consistent with structure (**106a**).[259] A single crystal X-ray structural study[265] on the ClO_4^- salt of this complex has demonstrated unequivocally that the species contains neither a monodentate nor a covalently hydrated bipyridyl ligand, at least in the solid state. All three bipyridyl ligands are chelated to iridium(III), but one bipy ligand is chelated *via* the nitrogen of one ring and the C-3 carbon of the other ring, reminiscent of *o*-metallated complexes. It has been proposed[267] that the data[259–262] can be understood in terms of, and are all consistent with, structure (**107**). Clearly, for complexes where monodentate or covalently hydrated species have been postulated, renewed consideration must be given in the light of (**107**) or equivalent species. Watts[268] has reconsidered the ^1H and ^{13}C NMR data, as has Seddon.[269] Furthermore, recent studies by Serpone *et al.*[270] reveal that the nitrate salt of this cation contains two NO_3^- units per iridium(III), consistent with structure (**108**). A very recent crystal structure determination of the red complex [Ir(bipy-N,N')$_2$(bipy-C^3, N')]$^{2+}$ (**109**) has revealed that each Ir atom is coordinated, in a distorted octahedron, to five nitrogen atoms and one carbon atom of the bipy ligands. In both N-bonded bipy rings and the C-bonded ring, the C(2)—N and C(6)—N distances are short, suggestive of rings 5, 7 and 13 being bonded to Ir *via* carbon (three $Ir(bipy)_3^{3+}$ units per asymmetric unit). Proton NMR and UV spectra of complex (**109**) were in accordance with the crystal structure analysis depicted in (**109**).[271] Also, Spellane *et al.*[272] have recently cited some ^1H and ^{13}C NMR data for [Ir(Hbipy-C^3, N')(bipy-N,N')$_2$]$^{3+}$ in DMSO-d_6 which indicate the presence of a C-bonded ring to Ir. Experiments employing a lanthanide shift reagent confirmed the presence of a site of Lewis basicity on the carbon-bonded pyridine ring.[272]



(107)



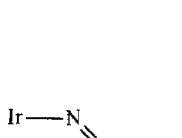
(108)



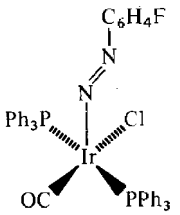
(109)

49.6.3.3 Diazenato and diazo ligands

Transition metal complexes of aryldiazenato ($ArN{=}N^-$) and aryldiazene ($ArN{=}NH$) ligands serve as valuable models of the catalytic activation of N_2 and for its preliminary reduction to N_2H_2. Aryldiazenato and aryldiazene derivatives of *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ have been investigated by several groups.[273] $[Ir(X)(CO)(PPh_3)_2]$ (X = Cl, Br) reacts with arenediazonium tetrafluoroborates in the presence of LiCl to give $[Ir(Cl)(X)(CO)(N{=}NAr)(PPh_3)_2]$. In the absence of LiCl, the cationic complex $[\{Ir(X)(CO)(N{=}Ar)(PPh_3)_2\}_n]^+$ is obtained. A crystal structural analysis of $[Ir(Cl)_2(CO)(N{=}NC_6H_4NO_2\text{-}o)(PPh_3)_2]$ confirmed the presence of a 'doubly-bent' aryldiazenato ligand (**110**).[274] The N-ligand appears to exert a strong *trans* influence. The five-coordinate cation $[Ir(Cl)(CO)(N{=}NC_6H_4F)(PPh_3)_2]^+$ (**111**) also contains a doubly-bent ArN_2^- ligand. Further addition of neutral or negative ligands affords six-coordinate iridium(III) complexes.[275]

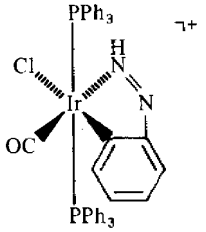


(110)

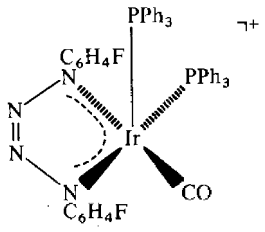


(111)

The reaction between $[Ir(Cl)(CO)(PPh_3)_2]$ and diazonium ions in the presence of ethanol or propan-2-ol affords the *o*-metallated diazene (**112**)[276] and the iridium(III) tetrazene complex (**113**).[277] A mechanism for the synthesis of (**113**) has been presented.[278]

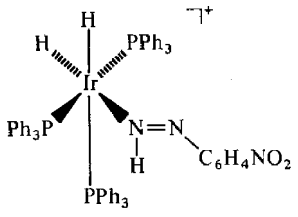


(112)

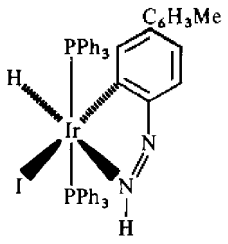


(113)

$[Ir(Cl)_2(NH{=}NAr)(PPh_3)_3]^+$ and $[Ir(Cl)_3(NH{=}NAr)(PPh_3)_2]$ have been synthesized from $[Ir(H)(Cl)_2(PPh_3)_3]$.[279] Insertion of diazonium ions into *mer*-$[Ir(H)_3(PPh_3)_3]$ yields $[Ir(H)_2(NH{=}NAr)(PPh_3)_3]^+$; a preliminary X-ray investigation has suggested the structure (**114**).[280] The crystal and molecular structures of $[Ir(H)(I)(NH{=}NC_6H_3Me\text{-}p)(PPh_3)_2]$ (**115**) have been elucidated.[281] More recently, it was shown that reaction between $[Ir(H)_3(PPh_3)_2]$ and *p*-substituted arenediazonium salts gives $[Ir(H)_2(NH{=}NC_6H_4R)(PPh_3)_2]^+$ at low temperatures (263 K) and the *o*-metalated complexes $[\overline{Ir(H)(NH{=}NC_6H_3R)}(PPh_3)_2]^+$ (**116**; R = F, OMe) at higher temperatures (313–323 K). The *o*-metallated complexes (**116**) react with CO, PPh_3, NaI and HCl according to reactions (71–74), respectively.[282]



(114)



(115)

$$(116) + CO \longrightarrow [\overline{Ir(H)(CO)(NH{=}NC_6H_3R)}(PPh_3)_2]^+ \quad (71)$$

$$(116) + PPh_3 \longrightarrow [\overline{Ir(H)(NH{=}NC_6H_3R)}(PPh_3)_3]^+ \quad (72)$$

$$(116) + NaI \longrightarrow [\overline{Ir(H)(I)(NH{=}NC_6H_3R)}(PPh_3)_2] \quad (73)$$

$$(116) + HCl \longrightarrow [\overline{Ir(H)(Cl)_2(NH{=}NC_6H_3R)}(PPh_3)_2] \quad (74)$$

49.6.3.4 Azide ligands

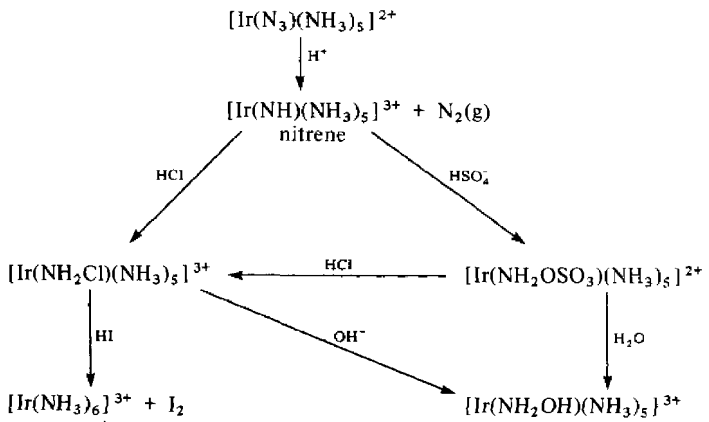
The synthesis of the iridium(III) azide complex $(Bu^n_4N)_3[Ir(N_3)_6]$ occurs *via* reaction (75). The visible and near-UV absorption and reflection spectra of this complex have been recorded; the assignment of bands in this and rhodium(III) azide complexes has led to the location of the N_3^- ligand in the spectrochemical and nephelauxetic series.[283]

$$Na_3[IrCl_6]\cdot 12H_2O + NaN_3 \xrightarrow[Bu^n_4N^+]{H_2O/EtOH} (Bu^n_4N)_3[Ir(N_3)_6] \quad (75)$$

trans-$[Ir(N_3)(en)_2]^+$ readily reacts with acid to liberate N_2 gas.[229] Subsequent investigation of this system suggested that the reaction occurs *via* a low-energy metal–nitrene (M—NH) pathway.[284] $[Ir(N_3)(NH_3)_5]^{2+}$ also liberates gaseous N_2 upon reaction with acid,[285] presumably by way of reaction (76). Kinetic studies were consistent with a nitrene intermediate pathway. Scheme 11 shows some reactions of $[Ir(N_3)(NH_3)_5]^{2+}$, all of which are in agreement with a nitrene path; furthermore, the coordinated nitrene serves as a powerful electrophile. Basolo[284] has given a brief review of the preparation and reactivity of transition metal nitrene complexes. Photolysis of $[Ir(N_3)(NH_3)_5]^{2+}$ in aqueous HCl proceeds by reaction (77). A mechanism consistent with steady state and flash photolysis results is given in Scheme 12.[284]

$$[Ir(N_3)(NH_3)_5]^{2+} + 2H^+ + X^- \longrightarrow [Ir(NH_3)_5(NH_2X)]^{3+} + N_2(g) \quad (76)$$

$$[Ir(N_3)(NH_3)_5]^{2+} + 2H^+ + Cl^- \xrightarrow{h\nu} [Ir(NH_3)_5(NH_2Cl)]^{3+} + N_2(g) \quad (77)$$



Scheme 11

$[Ir(N_3)(NH_3)_5]^{2+} \xrightarrow{h\nu} {}^*[Ir(N_3)(NH_3)_5]^{2+}$

${}^*[Ir(N_3)(NH_3)_5]^{2+} \longrightarrow [Ir(N_3)(NH_3)_5]^{2+} + \text{heat}$

${}^*[Ir(N_3)(NH_3)_5]^{2+} \longrightarrow [Ir(N)(NH_3)_5]^{2+} + N_2$

$[Ir(N)(NH_3)_5]^{2+} + H^+ \longrightarrow [Ir(NH)(NH_3)_5]^{3+}$

$[Ir(NH)(NH_3)_5]^{3+} + Cl^- \longrightarrow [Ir(NHCl)(NH_3)_5]^{2+}$

$[Ir(NH)(NH_3)_5]^{2+} + ClO_4^- \longrightarrow [Ir(NHOClO_3)(NH_3)_5]^{2+} \longrightarrow [Ir(NH_2OH)(NH_3)_5]^{3+}$

$[Ir(NHCl)(NH_3)_5]^{2+} + H^+ \longrightarrow [Ir(NH_2Cl)(NH_3)_5]^{3+}$

Scheme 12

Zink[286] has applied a molecular orbital approach to photochemical assignments of excited states of iridium(III) azide complexes. The observed products of 250–400 nm irradiation of $[Ir(N_3)(NH_3)_5]^{2+}$ are $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ and N_2, the same products expected on the basis of populating the LL (ligand-localized $\pi_{non} \rightarrow \pi^*$) excited state. It was suggested, therefore, that the photoreaction originates in the LL excited state. The formation of a coordinated nitrene intermediate has been ascribed to a combination of LMCT and LL states rather than to the LL state alone.

49.6.3.5 Polypyrazolylborate ligands

From a structural point of view, the complex chemistry of the tripyrazolylborate anion frequently resembles that of cyclopentadienyl or pentamethylcyclopentadienyl complexes. The iridium(III) tripyrazolylborate complexes $[Ir(Cl)_2\{HB(3,5\text{-}Me_2pz)_3\}]_2$, $[Ir(Cl)_2\{HB(3,5\text{-}Me_2pz)_3\}(AsPhMe_2)]$, $[Ir(CF_3CO_2)_2\{HB(3,5\text{-}Me_2pz)_3\}(H_2O)]$ and $[Ir(acac)(Cl)\{HB(3,5\text{-}Me_2pz)_3\}]$ have been prepared and characterized by ^1H NMR spectroscopy. None of these complexes exhibited a ν(B—H) mode in the region of *ca.* 2500 cm^{-1}, as do their rhodium analogues.[287]

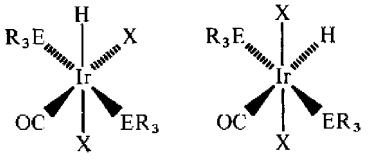
49.6.4 Phosphorus, Arsenic and Antimony Ligands

49.6.4.1 Unidentate ligands

Iridium(III) phosphine complexes obtained *via* the oxidative addition to Vaska-type iridium(I) complexes have been discussed (Section 49.4.3).

The stereochemistries of $[Ir(X)_n(ER_3)_3(Me)_{3-n}]$ (X = Cl, Br, I; ER_3 = PMe_2Ph, $AsMe_2Ph$; n = 0, 1, 2) have been assigned from the methyl resonance patterns of their ^1H NMR spectra.[288] Structural assignments of *trans*-$[Ir(X)_4(PMe_3)_2]$, *mer*- and *fac*-$[Ir(X)_3(PMe_3)_3]$ and *trans*-$[Ir(X)_2(PMe_3)_4]$ (X = Cl, Br) have been made on the basis of IR and Raman (< 800 cm^{-1}) spectral data; additionally, the significance of the Ir—P and Ir—Cl stretching frequencies has been discussed.[289]

Tri-*t*-butylphosphine reacts with hydrated iridium(III) chlorides to yield $[Ir(H)_2(Cl)(PBu^t_3)_2]$.[290] The two isomeric series, α and β, of hydrido carbonyls of the type $[Ir(H)(X)(CO)(ER_3)_2]$ (X = Cl, Br; ER_3 = $AsMePh_2$, $AsEtPh_2$) have been prepared. The structures of the α and β configurations are shown in (**117a**) and (**117b**), respectively.[291] Other complexes containing unidentate As donor ligands have been prepared *via* oxidative addition and characterized, including $[Ir(H)_3(AsPh_3)_2(CO)]$[292] and $[Ir(H)(X)(CO)(ER_3)_2]$ (ER_3 = $AsPh_3$, $AsMe_2Ph$).[293] Reaction between $[Ir(H)_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ (**118**) and HX (or pseudohalides) leads to the substitution products $[Ir(H)_2(AsPh_3)_2(CNC_6H_4Me\text{-}p)(X)]$ (X = Cl, Br, I, N_3).[210] With carboxylic acids and pentane-2,4-dione, complex (**118**) yields the chelated complexes $[Ir(L)_2(AsPh_3)(CNC_6H_4Me\text{-}p)]$ (L = carboxylate or pentane-2,4-dionate), in which Ir^{III} is reportedly reduced to Ir^{II}.[186] Reactions (78)–(86) reveal the utility of complex (**118**) in synthesizing complexes with iridium in various oxidation states.[196]



(117a) (117b)

(**118**) + acac ⟶ $[Ir^{II}(acac)_2(AsPh_3)(CNC_6H_4Me\text{-}p)]$ (78)

(**118**) + tfac ⟶ $[Ir^{III}(H)_2(tfac)(AsPh_3)(CNC_6H_4Me\text{-}p)]$ (79)

(**118**) + $HO_2CC_6H_4OMe\text{-}p$ ⟶ $[Ir(H)_2(Cl)(AsPh_3)(CNC_6H_4Me\text{-}p)]$ (80)

(**118**) + $HO_2CCH(OH)Me$ ⟶ $[Ir^{IV}\{O_2CCH(O)Me\}_2(AsPh_3)(CNC_6H_4Me\text{-}p)]$ (81)

(**118**) + $HO_2CC_6H_4OH\text{-}o$ ⟶ $[Ir^{IV}(O_2CC_6H_4O\text{-}o)_2(AsPh_3)(CNC_6H_4Me\text{-}p)]$ (82)

(**118**) + $HO_2CCH(NH_2)CH_2Ph$ ⟶ $[Ir^{IV}\{O_2CCH(NH)CH_2Ph\}_2(AsPh_3)(CNC_6H_4Me\text{-}p)]$ (83)

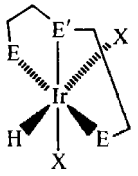
$$(\mathbf{118}) + HOC_6H_4OH\text{-}o \longrightarrow [Ir^{IV}(OC_6H_4O\text{-}o)_2(AsPh_3)(CNC_6H_4Me\text{-}p)] \quad (84)$$

$$(\mathbf{118}) + HOC_6H_4NH_2\text{-}o \longrightarrow [Ir^{IV}(OC_6H_4NH\text{-}o)_2(AsPh_3)(CNC_6H_4Me\text{-}p)] \quad (85)$$

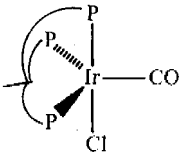
$$(\mathbf{118}) + HO_2CC_6H_4NH_2\text{-}o \longrightarrow [Ir^{IV}(O_2CC_6H_4NH\text{-}o)(AsPh_3)(CNC_6H_4Me\text{-}p)] \quad (86)$$

49.6.4.2 Polydentate ligands

Reaction of $[Ir(H)(X)_2(PPh_3)_2]$ (X = Cl, Br) and the potentially tridentate ligands $(o\text{-}Ph_2EC_6H_4)_2E'Ph$ (TP: E = E′ = P; PDAS: E = As, E′ = P; ASDP: E = P, E′ = As; TAS: E = E′ = As] has afforded complexes of the type $[Ir(H)(X)_2(L)]$ (**119**), where L = TP, PDAS, ASDP or TAS. The syntheses and characterizaton of complexes (**119**) by ^1H and ^{31}P NMR spectroscopy have revealed the meridional isomer, as shown, to be preferred.[294] The tripodal ligand 1,1,1-tris-(diphenylphosphinomethyl)ethane ($MeC(CH_2PPh_2)_3$ = TDPME) reacts with $[Ir(Cl)(CO)(PPh_3)_2]$ in benzene to yield [Ir(Cl)(CO)(TDPME)], for which a trigonal bipyramidal structure (**120**) was tentatively assigned. The reaction of complex (**120**) with CO has been postulated as proceeding by way of Scheme 13 to give complex (**121**).[295]

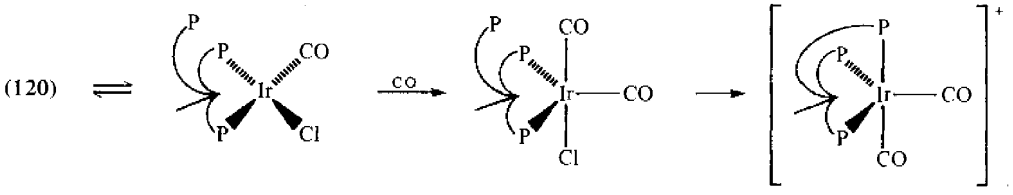


(119)



(120)

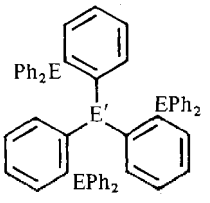
TP: E = E′ = P
PDAS: E = As; E′ = P
ASDP: E = P; E′ = As
TAS: E = E′ = As



(121)

Scheme 13

Reaction of $[Ir(H)(Br)_2(PPh_3)_3]$ with the tetradentate ligand tris(*o*-diphenylphosphinophenyl)-phosphine, QP (**122**), gives $[Ir(H)(Br)(PPh_3)(QP)](BPh_4)$, which was assigned a seven-coordinate structure.[296] With the similar tetradentate ligands ASTP, PTAS and QAS (**122**), $[Ir(H)(X)_2(PPh_3)_2]$ (X = Cl, Br) reacts to produce $[Ir(PPh_3)(ASTP)]^+$, $[Ir(PPh_3)(PTAS)]^+$ and $[Ir(PPh_3)(QAS)]^+$, respectively.[297] Under the conditions employed $[Ir(X)(PPh_3)_3]$ (X = Cl, Br) reacted with QP according to reaction (87), and [Ir(Cl)(PPh$_3$)(cod)] reacted with QP to give [Ir(Cl)(QP)] and $[Ir(PPh_3)(QP)]^+$. [Ir(Cl)(QP)] reacts with HCl and Cl_2 according to reactions (88) and (89), respectively.[297]



(122)

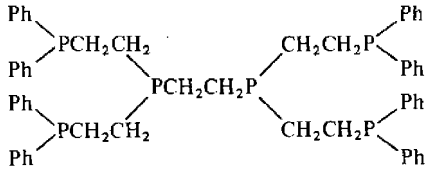
QP: E = E′ = P
ASTP: E = P; E′ = As
PTAS: E = As; E′ = P
QAS: E = E′ = As

$$[Ir(X)(PPh_3)_3] + QP \longrightarrow [Ir(PPh_3)(QP)]^+ + [Ir(X)(QP)] \quad (87)$$

$$[Ir(Cl)(QP)] + HCl \longrightarrow [Ir(H)(Cl)(QP)]^+ \quad (88)$$

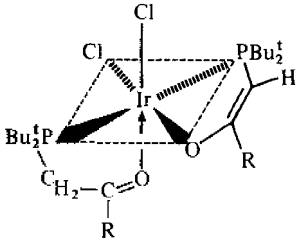
$$[Ir(Cl)(QP)] + Cl_2 \longrightarrow [Ir(Cl)_2(QP)]^+ \quad (89)$$

The trinuclear derivative $[Ir_3(Cl)_9\{P_2(-Pf)_4\}_2]$ results from the reaction between hydrated iridium(III) chloride and the hexatertiary phosphine $(Ph_2PCH_2CH_2)_2PCH_2CH_2P(CH_2CH_2PPh_2)_2$ $(=P_2(-Pf)_2)$ (**123**). Far-IR spectra for the trinuclear complex were interpreted in terms of three Cl atoms of each $IrCl_3$ moiety occupying meridional positions in an octahedron, and the $P_2(-Pf)_4$ ligand bridging the three $IrCl_3$ groups. Also, bridging Cl atoms could be present.[298]

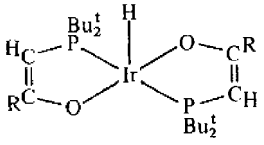


(123)

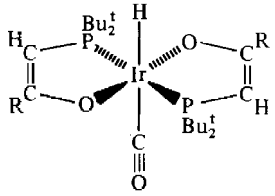
The bulky β-ketophosphine ligands $PBu^t_2(CH_2COPh)$ (Q) and $PBu^t_2(CH_2COBu^t)$ (Q′) are known to behave as either (i) unidentate ligands through the P atom; (ii) bidentate ligands through the P atom and the keto group; or (iii) bidentate enolate ions. Iridium trichloride reacts with Q and Q′, affording the six-coordinate complexes (**124**). Complex (**124**) reacts with $NaNO_2$ to give the five-coordinate square-pyramidal hydride complexes (**125**), which take up CO to yield (**126**).[299] Carbonylation of $Na[IrCl_6]$ followed by the addition of Q yields (**127**) with an uncoordinated keto group. On treatment of complex (**127**) with NaOEt, a mixture of (**126a**) and (**128**) was reportedly formed. Proton and ^{31}P NMR spectroscopic data were employed to elucidate the structures.[299]



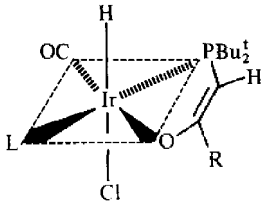
(124a) R = Ph
(124b) R = Bu^t



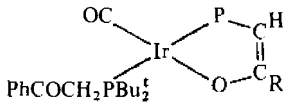
(125a) R = Ph
(125b) R = Bu^t



(126a) R = Ph
(126b) R = Bu^t



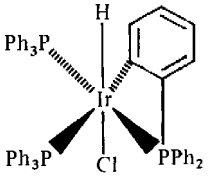
(127) L = $PBu^t_2(CH_2COPh)$



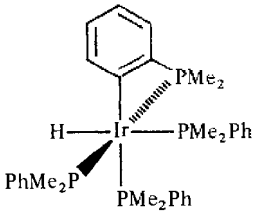
(128) R = Ph

The cyclometallated chlorohydrido iridium(III) complex (**129**) is obtained upon treatment of $[Ir(Cl)(PPh_3)_3]$ with organometallic derivatives of either the unsubstituted 1,2- and 1,7-carborane (-2-H-1,2-$B_{10}C_2H_{10}$) or the C(7)-methyl- and -phenyl-substituted carborane (-7-R-1,7-$B_{10}C_2H_{10}$) (R = H, Me, Ph). Proton NMR spectral data revealed evidence that the H ligand is *trans* to Cl and mutually *cis* to three non-equivalent P nuclei.[133] In MeCN, $[Ir(PMe_2Ph)_4]^+$ reacts with H_2 to yield *cis*-$[Ir(H)_2(PMe_2Ph)_4]^+$; however, on refluxing for 6 h in the absence of H_2, the complex *fac*-$[Ir(H)(PMe_2C_6H_4)(PMe_2Ph)_3]^+$ (**130**) results.[300] *o*-Metallation in $[Ir(H)(X)_2\{P(OPh)_3\}_3]$ (X = Cl, Br) apparently proceeds *via* a reductive elimination of HX to produce $[Ir(X)\{P(OPh)_3\}_3]$ followed by an internal oxidative addition process. For the iodo analogue, $[Ir(H)(I)_2\{P(OPh)_3\}_3]$, a mixture

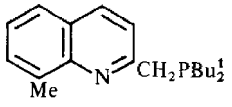
of H_2 and HI is eliminated, which might suggest that a pathway which does not involve prior generation of an iridium(I) species is plausible.[301] Duff and Shaw[302] have reported on the *o*-metallation of six-coordinate iridium(III) dimethylnaphthylphosphine complexes, for which a 1,2-hydrometallation of coordinated ligand followed by H_2 elimination was postulated to account for *o*-metallation in a coordinatively saturated complex. The 8-methylquinoline derivative mqp (**131**) reacts with $[Ir(Cl)(cot)_2]_2$ and [$^2H_5$]-pyridine in hexane to produce $[Ir(H)(Cl)(mqp\text{-}H^3)(NC_5D_5)_2]$ (**132**), one of three possible isomers being illustrated.[303] Analogous complexes have been obtained employing R_2PCH_2Ph (R = Bu^t, C_6H_{11}).[304] An oxidative addition–reductive elimination sequence was favoured for the *o*-metallation of the coordinatively unsaturated methyl iridium(III) complexes $[Ir(Cl)(X)(PPh_3)_2(Me)]$ (X = Cl, Br) to yield $[Ir(Cl)(X)\{PPh_2(C_6H_4)\}(PPh_3)]$.[305]



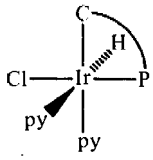
(129)



(130)

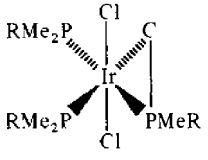


(131)

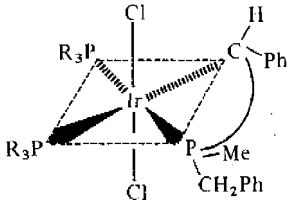


(132)

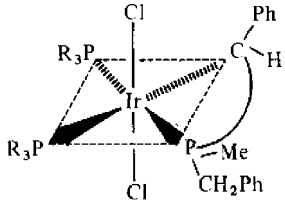
The treatment of *mer*-$[Ir(Cl)_3(PMe_2R)_3]$ (R = Ph, Me) with strong bases (*e.g.* $LiNPr^i_2$, LiBu^n or $Li(CH_2)_5Li$) affords the three-membered ring metallacycles $[Ir(Cl)_2(CH_2PMeR)(PMe_2R)_2]$ (**133**). The crystal structural data of complex (**133**) (R = Ph) prompted Al-Jibori *et al.*[306] to suggest that the base removes a proton from a methyl group of coordinated PMe_2Ph to yield a carbanion, which subsequently attacks the metal with removal of the labile Cl ligand *trans* to PMe_2Ph. The geometrical isomers (**134a**) and (**134b**), together with their corresponding enantiomers, were thought to be produced upon reaction of *mer*-$[Ir(Cl)\{PMe(CH_2Ph)_2\}_3]$ and $LiNPr^i_2$.[306] On exposure to excess dry HCl, complex (**133**) is rapidly and quantitatively converted to *mer*-$[Ir(Cl)_3(PMe_2R)_3]$. When treated with Cl_2, complex (**133**) (R = Ph) undergoes ring opening to give *mer*-$[Ir(Cl)_3(PMe_2Ph)_2(PMePhCH_2Cl)]$ (**135**). Complex (**135**) converts to the corresponding *fac* isomer (**136**) on exposure to visible radiation.[306]



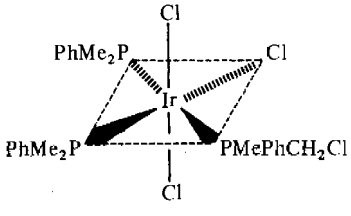
(133)



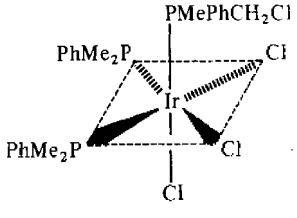
(134a)



(134b)



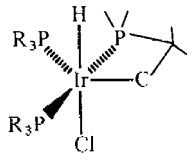
(135)



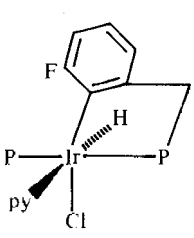
(136)

Four- and five-membered ring metallacycles (*e.g.* **137**) have been synthesized *via* reaction of tertiary aliphatic phosphines (*e.g.* $PBu^t_2Pr^n$, $PBu^t_2Bu^n$, PBu^t_3, PPr^i_3) with $[Ir(Cl)(cot)_2]_2$ in the presence of γ-picoline or MeCN. The steric effects of the phosphines and the coligand were observed to determine the composition and the stereochemistry of the products.[307] The reaction of the alkenic phosphine P(allyl)R_2 (R = Bu^t, C_6H_{11}) with $[Ir(Cl)(cot)_2]_2$ in the presence of γ-picoline produces the metallated complexes $[Ir(H)(Cl)(CH{=}CHCH_2PR_2)(R_2PCHCH{=}CH_2)(NC_6H_7)]$. For the complex in which R = Bu^t and γ-picoline was absent, the five-coordinate complex $[Ir(H)(Cl)(CH{=}CHCH_2PR_2)(R_2PCHCH{=}CH_2)]$ was obtained. The product stereochemistries

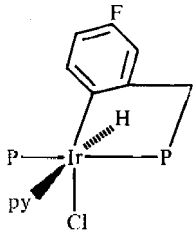
were inferrred from ^1H and ^{31}P NMR and IR spectral data.[308] Reaction between $[Ir(Cl)(cot)_2]_2$ and *m*-$FC_6H_4CH_2P(C_6H_{11})_2$ affords two isomers in an 8:1 molar ratio; NMR (^{31}P and ^{19}F) spectroscopic data have been interpreted in terms of structures (**138a**) and (**138b**), and a nucleophilic mechanism.[304]



(137)



(138a)



(138b)

The tertiary phosphine $PBu^t_2\{C_6H_3(OMe)_2\text{-}2,6\}$ is known to react with iridium(III) chloride in propan-2-ol to yield the five-coordinate hydride complex $[Ir(H)\{OC_6H_3(OMe\text{-}3)(PBu^t_2\text{-}2)\}_2]$ (**139**), which converts, in air, to the paramagnetic iridium(II) species $[Ir\{OC_6H_3(OMe\text{-}3)(PBu^t_2\text{-}2)\}_2]$, which reversibly adds O_2 and reacts with NO. The dioxygen adduct $[Ir(O_2)\{OC_6H_3(OMe\text{-}3)(PBu^t_2\text{-}2)\}_2]$ slowly converts to the coordinatively unsaturated C-cyclometallated iridium(III) complex $[Ir\{CH_2CMe_2PBu^tC_6H_3(OMe\text{-}6)O\}\{OC_6H_3(OMe\text{-}3)PBu^t_2\text{-}2)\}]$. Complex (**139**) also reversibly adds pyridine and CO.[309]

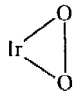
49.6.5 Oxygen Ligands

49.6.5.1 Hydroxy ligands

$[Ir(OH)_3]$ precipitates as a result of the reaction between $K_3[IrCl_6]$ and KOH under a CO_2 atmosphere. The product is usually colloidal, and ranges in colour from yellow-green to blue-black. Iridium(III) hydroxo species (including $[Ir(OH)_6]^{3-}$ and $[Ir(OH)_5(H_2O)]^{2-}$ are thought to be present in alkaline solutions of Ir_2O_3.[310]

49.6.5.2 Dioxygen ligands

Molecular oxygen adducts of transition metal complexes are of interest and importance to catalytic processes and commercial oxidation processes, as well as being intermediates in oxidation reactions. Vaska[311] has reviewed the nature of dioxygen bound to transition metal complexes. All known iridium dioxygen complexes possess the 'peroxo' structure (**140**). Experimental data reveal that the formation of covalent Ir—(O_2) bonds on dioxygen addition to IrL_x is accompanied by extensive redistribution of electrons, and the electron transfer is from the iridium to dioxygen. SCF–X_α–SW calculations on $[Ir(O_2)(Ph_3)_4]^+$ and $[Ir(Ph_3)_4]^{3+}$ indicate 'peroxo'–metal bonding.[312]



(140)

Relative rates of O_2 uptake by *trans*-$[Ir(X)(CO)(PPh_2R)_2]$ (X = F, Cl, Br, I; R = Ph, Et, Me) in CH_2Cl_2 follow the order R = Me > Et > Ph and X = I > Br > Cl > F.[313] If dioxygen addition is considered as an acid–base reaction (metal complex = Lewis base), then factors which increase the electron density at the metal centre should (in the absence of unfavourable steric effects) enhance the addition of O_2 (reaction 90). The results suggest that as the basicity of the phosphine ligand increases and the electronegatively of X decreases, the rate of O_2 addition also increases.[313] The X-ray crystal structure of $[Ir(Cl)(CO)(O_2)(PPh_2Et)_2]$ reveals a side-on coordination with the O_2 centre, CO and Cl moieties defining the equatorial plane, or a distorted octahedral iridium(III) system with O_2^{2-}.[314]

$$ML_x + O_2 \rightleftharpoons O_2 \cdot ML_x \quad (90)$$

The structures of $[Ir(X)(CO)(O_2)(PPh_3)_2]$ (X = Cl, I[315–317]) have similar inner coordination spheres, the only significant difference being the considerably longer O—O internuclear distance in the iodo complex (1.51 Å for X = I *vs.* 1.30 Å for X = Cl). Based on internuclear distance criteria, the chloro complex could be viewed as a 'superoxo' complex with iridium in the II oxidation state, and the iodo complex as a 'peroxo' complex with iridium in the III oxidation state. However, both complexes are diamagnetic, and other similarities between the two complexes leads to an iridium(III) 'peroxo' assignment. CNDO-type molecular orbital calculations on these complexes have shown that the iridium ion has a formal charge of +3, and that the O_2 molecule coordinates to the metal ion through oxidative addition.[318]

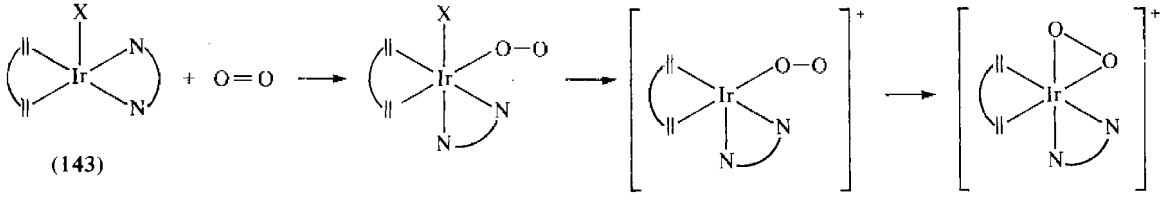
Dioxygen addition to $[Ir(A)(CO)(PPh_3)_2]$ (A = F, OH, NCO, NCS, O_2CH, O_2CCF_3, SH, C, CPh and *p*-toluenesulfinate) gives the iridium(III) complexes $[Ir(A)(CO)(O_2)(PPh_3)_2]$.[319] The readily reversible O_2 uptake by $[Ir(SCN)(CO)(PPh_3)_2]$ probably accounts for a previous report[317] that $[Ir(SCN)(CO)(O_2)(PPh_3)_2]$ does not form.

X-Ray crystal structure determinations of $[Ir(dppe)_2(O_2)]^+$,[320,321] and $[Ir(O_2)(PPhMe_2)_4]^+$[322] have implied that the O—O bond length is essentially independent of the metal and the basicity of the phosphine ligand. Analogous rhodium complexes exhibit similar structures.[322] A comparison[320] of the crystallographic data for $[Ir(dppe)_2(O_2)]^+$ and $[Ir(X)(CO)(O_2)(PPh_3)_2]$ led to the following conclusions: (i) a short O—O bond length (1.30–1.42 Å) corresponds to reversible O_2 uptake, while a long O—O bond (1.50–1.625 Å) corresponds to irreversible O_2 uptake; and (ii) increasing the donor strength of the phosphine ligand favours longer O—O bond lengths. Conclusion (ii) was determined to be invalid based on a comparison of $[Ir(dppe)_2(O_2)]^+$[320,321] and $[Ir(O_2)(PPhMe_2)_4]^+$ (see above).[322] Conclusion (i) is invalidated inasmuch as the O—O bond length (1.46 Å) in $[Ir(Cl)(CO)(O_2)(PPh_2Et)_2]$ would seem to indicate irreversible O_2 uptake, though reversible O_2 uptake was observed.[323] Furthermore, a redetermination[321] of the structure of $[Ir(dppe)_2(O_2)]^+$ indicates that the unusually long O—O bond distance reported previously is actually an artifact caused by crystal decomposition during irradiation.[320]

The preparation of $[Ir(X)(CO)(ER_3)_2(O_2)]$ (ER_3 = $AsMePh_2$, $AsEtPh_2$; X = Cl, Br),[291] and crystal structures of $[Ir(O_2)(PMe_2Ph)_4]^+$, $[Ir(PMe_2Ph)_4]^+$[324] and the PF_6^- and ClO_4^- salts of $[Ir(dppm)_2(O_2)]^+$[325] have been reported. In the latter complex, identical O—O bond lengths (within experimental error) are observed, as well as similar geometries around iridium. Only different packings were observed for the PF_6^- and ClO_4^- salts of this complex.

The conclusions to be drawn from dioxygen uptake reactions and crystal structure investigations of the resultant dioxygen complexes include: (i) the O—O bond length is constant, regardless of the metal or the other ligands present in the inner coordination sphere; (ii) the short and long O—O bond lengths observed are most likely artifacts caused by disorder and crystal decomposition; (iii) there is no correlation between O—O bond length and reversibility of O_2 uptake; and (iv) O_2 uptake can be viewed as an oxidation process, even if it is reversible.

Kinetic measurements have indicated that O_2 reacts more rapidly with the five-coordinate complex [Ir(I)(phen)(cod)] (**141**) than with the four-coordinate complex $[Ir(phen)(cod)]^+$ (**142**) to yield $[Ir(O_2)(phen)(cod)]^+$. The analysis was consistent with complex (**141**) being more susceptible to oxygenation than complex (**142**).[326] The reaction of complex (**142**; Cl^- salt) with O_2 in methanol was investigated kinetically in the presence and absence of SCN^- and I^-. On addition of NaX (X = SCN, I), the five-coordinate complex [Ir(X)(phen)(cod)] (**143**) forms. An 'end-on' oxidative addition of O_2 to complex (**142**) has been proposed (see Scheme 14).[327]



(143)

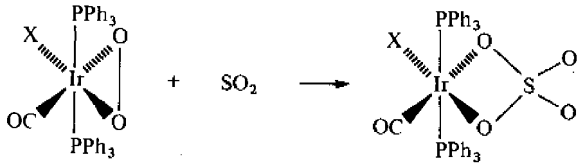
Scheme 14

An investigation of the thermal deoxygenation of solid $[Ir(Cl)(CO)(O_2)(PPh_3)_2]$ in nitrogen has revealed two rate-controlling steps, depending on the temperature. The steps are associated with the nucleation and growth of product, and a phase boundary mechanism.[328]

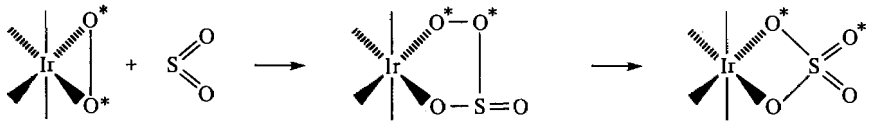
Complexes of the type $[Ir(CO)(PPh_3)_2(Ar)]$ undergo reaction with dioxygen to yield [Ir-

$(CO)(O_2(PPh_3)_2(Ar)]$ wherein Ar = Ph, *m*-MeC_6H_4 and *p*-MeC_6H_4. However, complexes with *o*-substituted Ar ligands do not react with O_2, reportedly due to steric shielding of the metal centre.[329]

The stoichiometric reaction of SO_2 with coordinated O_2 to form coordinated sulfate appears to be general for dioxygen complexes. ^{18}O isotope substitution and IR spectroscopy have been employed to study the reaction betwen $[Ir(X)(CO)(O_2)(PPh_3)_2]$ (X = Cl, Br, I) and SO_2 (reaction 91). IR spectral results are consistent with a bidentate sulfate ligand. The mechanism proposed for sulfate formation involves a peroxosulfate intermediate, that is insertion of SO_2 into one of the Ir—O bonds and bond formation between S and the leaving O, with subsequent rearrangement of the peroxo–sulfite intermediate thus generated (see Scheme 15).[330,331]



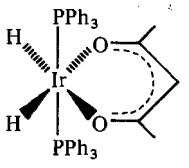
(91)



Scheme 15

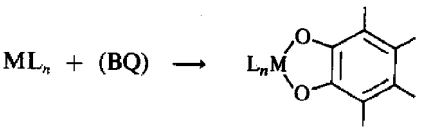
49.6.5.3 β-Diketonate, catecholate and semiquinone ligands

The syntheses and stereochemical assignments of $[Ir(H)_2(L)(PPh_3)_2]$ (**144**) (L = acac, tfac, hfac) and $[Ir(H)(Cl)(acac)(PPh_3)_2]$ have been reported.[332,333] The dihydride complex (**144**) is prepared *via* reaction of $[Ir(H)_3(PPh_3)_2]$ with the appropriate β-diketone. IR spectral data for this complex are consistent with the β-diketonate ligands coordinated to Ir as bidentate ligands, and, combined with ^1H NMR data, are consistent with structure (**144**). Both complexes have *trans* PPh_3 ligands. Reaction of the iridium(I) complex $[Ir(acac)(C_2H_4)_2]$ with alkenic phosphines in the presence of γ-picoline and acetonitrile produces the six-coordinate metallated iridium(III) complex $[Ir(H)(L)(CH_2CH{=}CH)(R_2P)]$ (R_2P = Bu^t_2P, $(C_6H_{11})_2P$; L = γ-picoline, MeCN). The ligand L is displaced by CO, CNR and $P(OMe)_3$.[334] Reaction between allene and the iridium(I) complex $[Ir(acac)(\eta\text{-}C_8H_{14})_2]$ at 195 K, followed by treatment with pyridine in heptane at 243 K, yields the iridium(III) complex $[Ir(acac)(C_3H_4)_3(py)]$ (**145**) with evolution of allene. The crystal structure of complex (**145**) reveals a distorted octahedral coordination geometry in which the acac ligand and an allene dimer serve as chelating ligands with a pseudo-*fac* configuration relative to each other. The coordination about Ir is completed by one of the double bonds of the allene molecule and by pyridine.[335]

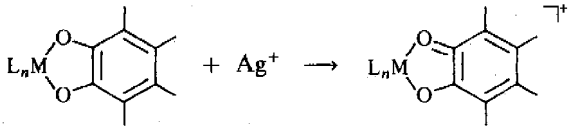


(144)

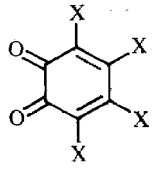
Transition metal complexes containing catecholate and semiquinone ligands have been reviewed by Pierpont and Buchanan.[336] The syntheses of catecholate adducts of platinum group metals by oxidative addition of benzoquinone (BQ) have been reported (reaction 92).[337] The coordinated catechol can then be oxidized to the semiquinone with silver ion (reaction 93). In reactions (92) and (93), L_nM = $[Ir(Cl)(CO)(PPh_3)_2]$ and the benzoquinones (BQ) are shown in (**146**). The oxidative addition of phenanthrenequinone to $[Ir(Cl)(CO)(PPh_3)_2]$ has also been cited.[338]



(92)



(93)



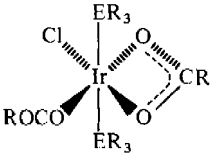
(146) X = Cl, Br

On coordination to metals, the quinone–CO stretching frequency shifts at least 200–300 cm^{-1}, which infers a formal reduction to catechol with oxidation of the metal. The possibility of an intermediate radical anion coordination mode for *o*-benzoquinones has been demonstrated[339] by the reversible chemical and electrochemical oxidation of reduced quinone complexes. ESR spectra of $[Ir(Cl)(1,2\text{-}O_2C_6Cl_4)(CO)(PR_3)_2]$ ($PR_3 = PPh_3$, $PMePh_2$) indicate that the unpaired electron is localized in the semiquinone ligand. The quinone coordination mode is strongly affected by the oxidizing ability of the quinone and the nature of the complex itself.

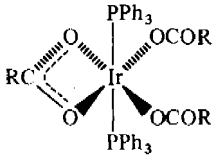
49.6.5.4 Carboxylate, chelating carboxylate CO_3^{2-}, CO_4^{2-}, RCO_2^- and oxalate ligands

Iridium(I) complexes of the type *trans*-$[Ir(X)(CO)(PR_3)_2]$ ($PR_3 = PEt_3$, PPh_3, $PPhMe_2$; X = Cl, Br, I) undergo rapid oxidative addition with carboxylic acids RCO_2H (R = H, Me, CF_3, Ph, 1-naphthyl) to yield the iridium(III) complexes $[Ir(H)(X)(O_2CR)(CO)(PR_3)_2]$ corresponding to both formal *cis* and *trans* addition of RCO_2H to the Ir^I complex. In solution, the carboxylato complexes undergo rapid anion exchange such that at equilibrium two additional hydride complexes, $[Ir(H)(X)_2(CO)(PR_3)_2]$ and $[Ir(H)(O_2CR)(CO)(PR_3)_2]$, are present. For all the complexes, the phosphine ligands are mutually *trans*, the H and CO ligands are mutually *cis*, and O_2CR is unidentate.[340] The ease of protonation of the Ir^I complexes by RCO_2H to yield the Ir^{III} complexes has been observed[341] to be dependent on the nature of PR_3, yielding an order of ligand basicity $PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$.

$[Ir(X)(ER_3)_2(L)]$ (L = N_2, CO) is known to react with peroxycarboxylic acids, RCO_3H, affording the carboxylato complexes $[Ir(X)(O_2CR)_2(ER_3)_2]$ (**147**; X = Cl, R = 3-ClC_6H_4, $ER_3 = PPh_3$, PPh_2Me, $AsPh_3$; X = Cl, R = Ph, $ER_3 = PPh_3$, $AsPh_3$; X = Cl, R = Me, $ER_3 = PPh_3$; X = Br, R = 3-ClC_6H_4, $ER_3 = PPh_3$) and CO_2. These complexes possess one unidentate carboxylate ligand and one bidentate ligand yielding a coordination number of six. The stereochemistry is revealed in (**147**). In contrast, reaction between $[Ir(I)(CO)(PPh_3)_2]$ and RCO_3H has yielded $[Ir(O_2CR)_3(PPh_3)_2]$ (**148**; R = Ph, 3-ClC_6H_4), and a mixture of $[Ir(O_2CPh)_3(CO)(PPh_3)_2]$ and $[Ir(I)_3(CO)(PPh_3)_2]$ with RCO_3H = dibenzyl peroxide. A tentative stereochemical assignment for complex (**148**) has been shown.[152]



(147)



(148)

The formation and decarboxylation kinetics of $[Ir(OCO_2)(NH_3)_5]^+$ have been studied as a function of pressure, based on activation volumes for CO_2 uptake ($\Delta V^{\ddagger} = -4.0\,cm^3\,mol^{-1}$) and decarboxylation ($\Delta V^{\ddagger} = +2.5\,cm^3\,mol^{-1}$), and partial molar volume measurements. The suggested mechanism for the formation and decarboxylation is given in Scheme 16. Bond formation during CO_2 uptake and bond breaking during decarboxylation were believed to be *ca.* 50% completed in the transition state (**149**) of these processes.[342]

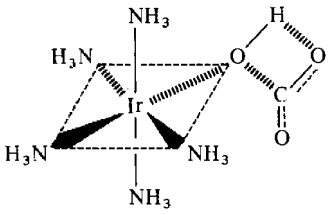
The peroxocarbonato iridium complexes $[Ir(OCO_3)(CO)(PPh_3)_2(R)]$ (R = Me, Ph) have been synthesized from $[Ir(CO)(O_2)(PPh_3)_2(R)]$ and liquid CO_2, probably *via* external attack by CO_2 on

$$[Ir(OH_2)(NH_3)_5]^{3+} \overset{K_A}{\rightleftharpoons} [Ir(OH)(NH_3)_5]^{2+} + H^+$$

$$[Ir(OH)(NH_3)_5]^{2+} + CO_2 \overset{k_1}{\underset{k_2}{\rightleftharpoons}} [Ir(OCO_2H)(NH_3)_5]^{2+}$$

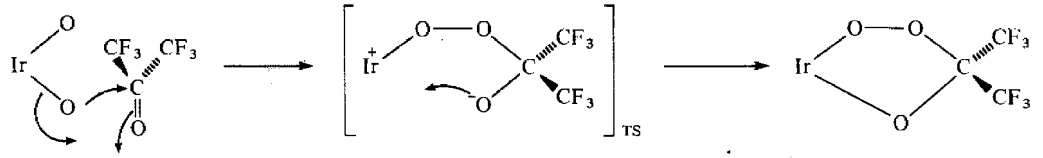
$$[Ir(OCO_2H)(NH_3)_5]^{2+} \overset{K_B}{\rightleftharpoons} [Ir(OCO_2)(NH_3)_5]^{+} + H^+$$

Scheme 16



(149)

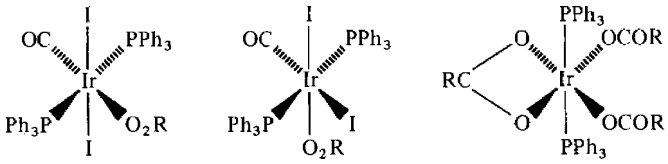
coordinated O_2.[343] The reaction mechanism was thought to be similar to that proposed for the reaction of hexafluoroacetone with $[Ir(Cl)(CO)(O_2)(PPh_3)_2]$.[344] The mechanism of the addition of hexafluoroacetone ($CF_3C(O)CF_3$) to $[Ir(X)(CO)(O_2)(PPh_3)_2]$ presumably involves direct nucleophilic attack of $CF_3C(O)(CF_3$ on the coordinated O_2 ligand to give the iridium(III) ozonide product (**151**) *via* an ionic transition state (**150**; see Scheme 17).[344]



(150) (151)

Scheme 17

The bis(alkylperoxy) iridium(III) complexes $[Ir(X)(O_2Bu^t)_2(CO)(ER_3)_2]$ (**152**; X = Cl, ER_3 = PPh_3, $AsPh_3$, PPh_2Me; X = Br, ER_3 = PPh_3, $AsPh_3$) and $[Ir(X)(O_2CPhMe_2)_2(CO)(ER_3)_2]$ (**153**; X = Cl, ER_3 = PPh_3, $AsPh_3$; X = Br, ER_3 = PPh_3) have been prepared *via* reaction of Bu^tO_2H or $PhMeCO_2H$ with the appropriate *trans*-$[Ir(X)(CO)(ER_3)_2]$ (X = Cl, Br) complex. The analogous reaction with *trans*-$[Ir(I)(CO)(PPh_3)_2]$ affords $[Ir(I)_2(O_2CR)(CO)(PPh_3)_2]$ (**154**) (R = Bu^t, $PhMe_2$). The diiodide complex reveals IR and ^1H NMR spectra interpreted in terms of the two PPh_3 ligands being mutually *trans*, and possessing either structure (**154a**) or (**154b**).[345] Spectroscopic data on complexes (**152**) and (**153**) suggest the structure in (**155**).[152] Treatment of (**152**) or (**153**) with organic acids $R'CO_2H$ results in the substitution of only one of the alkylperoxy ligands, with formation of $[Ir(X)(OCOR')(O_2R)(CO)(PPh_3)_2]$ (X = Cl, R = Bu^t, R′ = CF_3, CCl_3, $CHCl_2$, CO_2H, *cis*-CH=CHCO$_2$H, Ph, H; X = Cl, R = CMe_2Ph, R′ = CF_3; X = Br, R = Bu^t, R′ = CF_3, H).[346] The related complexes $[Ir(X)(Y)(O_2Bu^t)(CO)(PPh_3)_2]$ (X = Y = Cl, Br; X = Cl, Y = Br, NO_3) have been prepared *via* reaction of $[Ir(X)(O_2Bu^t)_2(CO)(PPh_3)_2]$ (X = Cl, Br) with HCl, HBr or HNO_3 at 273 K.[346]

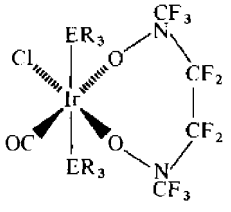


(154a) (154b) (155)

Several iridium(III) oxalato (ox) complexes have been reported, including $K_3[Ir(ox)_3]_n \cdot H_2O$, $KH_2[Ir(ox)_3] \cdot 4H_2O$, $K_3[Ir(Cl)_3(NO_2)(ox)] \cdot 2H_2O$, $M_3[Ir(Cl)_4(ox)]$ (M = Na, Rb, Cs, NH_4), $M_3[Ir(Cl)_2(ox)_2] \cdot nH_2O$, $M_3[Ir(Cl)_2(NO_2)_2(ox)] \cdot nH_2O$ (M = Li, Na, K, Rb, Cs, NH_4) and $H_3[Ir(ox)_3] \cdot n$-

H_2O.[310] The synthesis of $K_3[Ir(ox)_3]$ has been reported by several groups.[347] More recently, Flynn and Demas[348] have reported a simple high-yield preparation of this complex with a novel solvent extraction step. Various methods, including IR, Raman and ^1H NMR spectroscopy, thermogravimetry and pH invariance results, have been employed to determine the role played by water in the structures of crystalline transition metal oxalato complexes. For $K_3[Ir(ox)_3]\cdot 4.5H_2O$, a tris-chelated structure with one water molecule hydrogen bonded in a unique fashion has been postulated.[347c] The rates of racemization of $[Ir(ox)_3]^{3-}$ have been measured,[349] as well as the circular dichroism.[350] While $K_3[Ir(Cl)_2(ox)_2]$ exists as *cis* and *trans* isomers (*cis*-$[Ir(Cl)_2(ox)_2]\cdot 3H_2O$ and *trans*-$[Ir(Cl)_2(ox)_2]\cdot 4H_2O$) $K_3[Ir(ox)_3]\cdot 4.5H_2O$ has been resolved into optical enantiomers which do not racemize in hot water.[351]

Addition of the bis(trifluoromethyl)nitroxy radical $[(CF_3)_2NO\cdot]$ to $[Ir(Cl)(CO)(ER_3)_2]$ yields the complexes $[Ir(Cl)(CO)(ER_3)_2\{ON(CF_3)_2\}]$ ($ER_3 = PPh_3$, PPh_2Me, $AsPh_3$).[155] Several iridium(III) complexes containing the $ON(CF_3)_2$ ligand have been prepared *via* oxidative addition to $[Ir(CO)(PPh_3)_2\{ON(CF_3)_2\}]$.[155] The stable diradical $CF_3N(\dot{O})CF_2N(\dot{O})CF_3$ reacts with *trans*-$[Ir(Cl)(CO)(ER_3)_2]$ ($ER_3 = PPh_3$, PPh_2Me, $AsPh_3$) and *trans*-$[Ir(CO)(PPh_3)_2\{ON(CF_3)_2\}]$ to form the seven-membered metallacyclic iridium(III) complexes $[\overline{Ir\{ON(CF_3)CF_2CF_2N(CF_3)O\}}(Cl)(CO)(ER_3)_2]$ (**156**) and $[\overline{Ir\{ON(CF_3)CF_2CF_2N(CF_3)O\}}\{ON(CF_3)_2\}(CO)(PPh_3)_2]$. IR spectra have been interpreted in terms of structure (**156**) for the former complex; the iradacycle is presumably fluxional.[156]



(156)

49.6.5.5 Nitrito–nitro and nitrate ligands

Several iridium(III) complexes containing the nitrito (NO_2) ligand have been prepared *via* reaction of N_2O_4 (or NO_2^-) with an iridium(I) complex, as per reactions (94)–(99).[352] The nitrito ion $[Ir(ONO)(NH_3)_5]^{2+}$ rearranges to the nitro form $[Ir(NO_2)(NH_3)_5]^{2+}$ in aqueous base according to equation (100), for which $k_s = 3.0 \times 10^{-5}\,s^{-1}$ and $k_{OH} = 2.7 \times 10^{-5}\,dm^3\,mol^{-1}\,s^{-1}$. A base-catalyzed pathway was proposed[353] for the Co^{III}, Rh^{III} and Ir^{III} complexes, as depicted in Scheme 18. The temperature and pressure dependencies of the rates of linkage isomerization of $[Ir(ONO)(NH_3)_5]^{2+}$ in aqueous solution indicate $\Delta V^{\ddagger} = -5.9 \pm 0.6\,cm^3\,mol^{-1}$, $\Delta H^{\ddagger} = 95.3 \pm 1.3\,kJ\,mol^{-1}$ and $\Delta S^{\ddagger} = -11 \pm 4\,J\,K^{-1}\,mol^{-1}$.[354] The similarity between these results and those previously obtained for Rh^{III} and Co^{III} analogues[355] are indicative of an intramolecular mechanism.

$$\left.\begin{matrix}[Ir(Cl)(CO)(PPh_3)_2] \\ [Ir(Cl)(NO)(CO)(PPh_3)_2]^+\end{matrix}\right\} + N_2O_4 \longrightarrow [Ir(Cl)(NO_2)(NO_3)(CO)(PPh_3)_2] \quad (94)$$

$$[Ir(Cl)(CO)(PPh_3)_2] + 3NO_2 \longrightarrow [Ir(Cl)(NO_2)(NO_3)(CO)(PPh_3)_2] \quad (95)$$

$$[Ir(H)(CO)(PPh_3)_2 + N_2O_4 \longrightarrow [Ir(H)(NO_2)(NO_3)(CO)(PPh_3)_2] \quad (96)$$

$$[Ir(Cl)(NO)(CO)(PPh_3)_2]^+ + N_2O_4 \longrightarrow [Ir(Cl)(NO_2)(NO_3)(CO)(PPh_3)_2] \quad (97)$$

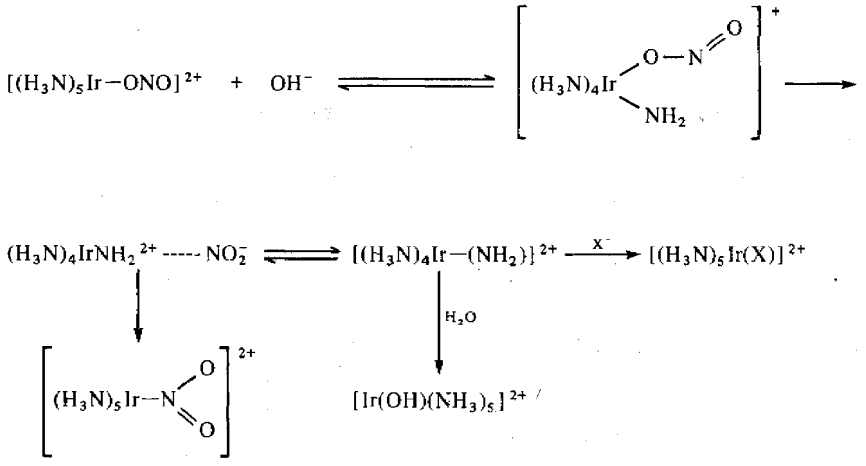
$$[Ir(CO)_3(PPh_3)_2]^+ + N_2O_4 \longrightarrow [Ir(NO_2)(NO_3)_2(CO)(PPh_3)_2] \quad (98)$$

$$[Ir(dppe)_2]^+ + N_2O_4 \longrightarrow [Ir(NO_2)_2(dppe)_2]^+ \quad (99)$$

$$k_{obs} = k_s + k_{OH}[OH^-] \quad (100)$$

$[Ir(NO_3)_3]$ is as yet unknown, though the $[Ir(NO_3)_6]^{3-}$ complex anion is documented. The latter complex is afforded upon dissolution of $[IrCl_3]$ in concentrated HNO_3 at 373 K.[356]

Treatment of $[Ir(H)(CO)(PPh_3)_3]$ in benzene with warm, concentrated HNO_3 yields a yellow crystalline solid formulated as $[Ir(NO_3)_3(PPh_3)_2]$.[357,358] The white crystalline complex $[Ir(Cl)(NO_3)_2$-



Scheme 18

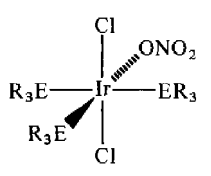
$(CO)(PPh_3)_2]$ results from oxidative addition of NO_3^- to $[Ir(X)(CO)(PPh_3)_2]$. Several reaction pathways have been cited, including (i) reaction of $[Ir(Cl)(CO)(PPh_3)_2]$ with concentrated HNO_3 in THF at 313 K;[359] (ii) reaction between $[Ir(X)(CO)(PPh_3)_2]$ (X = Cl, Br, N_3, NCO, NCS) and $(NH_4)_2[Ce(NO_3)_6]$, $[Cu(NO_3)_2]$ or $[Fe(NO_3)_3]$ in the presence of NO_3^- at ambient temperatures;[360] or (iii) reaction of the dioxygen adduct of $[Ir(Cl)(CO)(PPh_3)_2]$ with NO_2/N_2O_4.[361] The related complex $[Ir(Cl)(NO_3)_2(CO)(AsPh_3)_2]$ was prepared *via* pathway (iii).[361]

The green iridium(III) complex $[Ir(NO_3)_2(NO)(PPh_3)_2]$ is formed by the action of ethanolic HNO_3 on $[Ir(NO)(PPh_3)_3]$ or $[Ir(NO)(CO)(PPh_3)_2]$. A bent Ir—N—O moiety has been proposed on the basis of the low $\nu(NO)$ in the IR spectrum.[358]

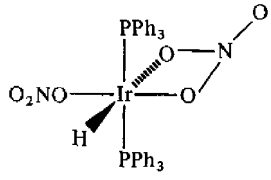
Reaction of *mer*-$[Ir(Cl)_3(ER_3)_3]$ (ER_3 = PMe_2Ph, PEt_2Ph, $AsMe_2Ph$) and $AgNO_3$ in acetone/water solutions forms $[Ir(Cl)_2(NO_3)(ER_3)_3]$, with the structure in (**157a**). In a similar fashion, $[Ir(I)_2(NO_3)(PMe_2Ph)_3]$ has been synthesized from *mer*-$[Ir(I)_3(PMe_2Ph)_3]$.[362]

Complexes of the type $[Ir(Cl)(NO_3)(X)(PPh_3)_2]$ (X = Cl, Br, I, N_3, NCO, NCS) are prepared *via* electrophilic attack by O_2 on the bent NO ligand in $[Ir(Cl)(X)(NO)(CO)(PPh_3)_2]$ in benzene solution at ambient temperature. The rates of oxygenation decrease with X as I > Br > Cl > NCS > NCO > N_3,[363] which approximates the decreasing electron release by X.

When $[Ir(NO_3)_2(NCO)(CO)(PPh_3)_2]$ is allowed to react in $EtOH/CH_2Cl_2$ solutions exposed to air, yellow crystals of $[Ir(H)(NO_3)_2(PPh_3)_2]$ (**157b**) result. An X-ray crystal structural analysis of complex (**157b**) reveals the PPh_3 ligands as mutually *trans*, with one unidentate and one bidentate nitrate ligand (see structure **157b**). Complex (**157b**) reacts with CO to yield $[Ir(H)(NO_3)_2(CO)(PPh_3)_2]$, in which both NO_3^- ligands are unidentate.[364] The related iridium(III) cation $[Ir(NO_3)_2(CO)(PMePh_2)_3]^+$ (isolated as the BF_4^- or ClO_4^- salt) has been synthesized by the reaction of NO_2/N_2O_4 with $[Ir(CO)(O_2)(PMePh_2)_3]^+$.[365] Other iridium(III) nitrato complexes which have been prepared are outlined in reactions (101)–(106).[366]



(157a)



(157b)

$$[Ir(Cl)(CO)(PPh_3)_2] + N_2O_4 \longrightarrow [Ir(Cl)(NO_2)(NO_3)(CO)(PPh_3)_2] \quad (101)$$

$$[Ir(Cl)(NO)(CO)(PPh_3)_2]^+ + N_2O_4 \longrightarrow [Ir(Cl)(NO_2)(NO_3)(CO)(PPh_3)_2] \quad (102)$$

$$[Ir(Cl)(CO)(PPh_3)_2] + 3NO_2 \longrightarrow [Ir(Cl)(NO_2)(NO_3)(CO)(PPh_3)_2] \quad (103)$$

$$[Ir(H)(CO)(PPh_3)_3] + N_2O_4 \longrightarrow [Ir(H)(NO_2)(NO_3)(CO)(PPh_3)_2] \quad (104)$$

$$[Ir(Cl)(NO)(CO)(PPh_3)_2]^+ + N_2O_4 \longrightarrow [Ir(Cl)(NO_2)(NO_3)(CO)(PPh_3)_2] \quad (105)$$

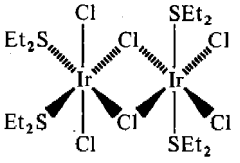
$$[Ir(CO)_3(PPh_3)_2]^+ + N_2O_4 \longrightarrow [Ir(NO_2)(NO_3)_2(CO)(PPh_3)_2] \quad (106)$$

49.6.6 Sulfur Ligands

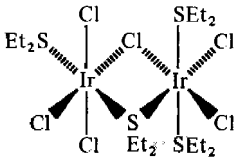
49.6.6.1 Sulfide ligands

Reaction between H_2S and *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ in CH_2Cl_2 leads to the formation of one of the first iridium(III) complexes containing an SH ligand, namely $[Ir(H)(Cl)(SH)(CO)(PPh_3)_2]$. This complex possesses a pseudooctahedral coordination geometry with *trans* PPh_3 ligands and *trans* H—Ir—Cl and HS—Ir—CO arrangements. The oxidative addition of H_2S to Vaska's complex is *cis* addition.[367]

$[Ir(Cl)_2(SEt_2)_4][Ir(Cl)_4(SEt_2)_2]$ and *fac*-$[Ir(Cl)_3(SEt_2)_3]$ can be prepared from an iridium(III) halide and a monosulfide. The anion $[Ir(Cl)_4(SEt_2)_2]^-$ can be oxidized to *trans*-$[Ir(Cl)_4(SEt_2)_2]$.[368] Irradiation of *fac*-$[Ir(Cl)_3(SEt_2)_3]$ gives $[Ir_2(Cl)_6(SEt_2)_4]$, which exists in two isomeric forms.[160] Also, the complexes $[Ir(Cl)_3(SEt_2)_{3-n}(py)_n]$ ($n = 1, 2$), $[Ir(Cl)_3(SMe_2)_2]$ and $[Ir_2(Cl)_5(SR_2)_4]$ (R = Me, Et) have been reported[160] though not well characterized. Photolysis (*d–d* excitation) of *mer*-$[Ir(Cl)_3(SEt_2)_3]$ in benzene or toluene solution yields a mixture of $[Ir_2(Cl)_4(\mu\text{-}Cl)_2(SEt_2)_4]$ (**158**) and $[Ir_2(Cl)_5(\mu\text{-}Cl)(\mu\text{-}SEt_2)(SEt_2)_3]$ (**159**).[369] The unusual bridging SEt_2 group in (**159**) was identified by the absence of rapid inversion at the tetrahedrally coordinated S atom in the ^1H NMR spectrum. The crystal structures of complexes (**158**)[370] and (**159**)[371] have been determined.

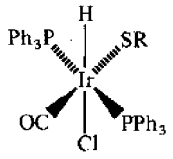


(158)



(159)

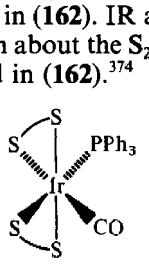
Hydrogen sulfide, 4-methylbenzenethiol and 4-methylbenzene-1,2-dithiol add to *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ to yield the iridium(III) complex $[Ir(H)(Cl)(CO)(PPh_3)_2(SR)]$, wherein SR is SH, SC_6H_4Me or SC_6H_3MeSH, respectively. Spectroscopic data are consistent with the structure (**160**) with CO and SR groups *trans* to each other.[372]



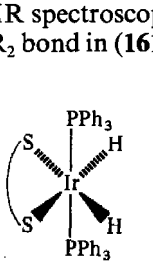
(160)

49.6.6.2 Dithiocarbamate and CS_2-based ligands

The X-ray crystal and molecular structures of the iridium(III) dithiocarbamate complex $[Ir(S_2CNC_4H_8)_3](C_6H_5)_{0.5}$ shows a trigonally-distorted octahedral metal–ligand coordination sphere. A comparison with analogous Fe^{III} and Cr^{III} complexes indicates that the iridium complex is closest to octahedral in its environment.[373] The dithiocarbamato and *O*-dithiocarbamato derivatives $[Ir(H)_2(S—S)(PPh_3)_2]$ (S—S = $R_2NCS_2^-$, $ROCS_2^-$; R = Me, Et) were prepared by treating the appropriate chloro or carboxylato complex with sodium salts of the S—S ligands. $[Ir(S_2CNMe_2)_2(CO)(PPh_3)_2]^+$ formed upon reaction of Vaska's complex with tetramethylthiuram disulfide; the assigned stereochemistry is that illustrated in (**161**).The stereochemistry assigned to $[Ir(H)_2(S—S)(PPh_3)_2]$ is depicted in (**162**). IR and NMR spectroscopy have confirmed the presence of a substantial barrier to rotation about the $S_2C—NR_2$ bond in (**161**), but nothing comparable was observed for the $S_2C—OR$ bond in (**162**).[374]

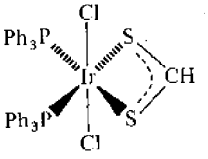


(161)

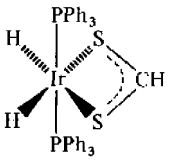


(162)

The iridium(III) hydrides *trans*-$[Ir(H)(Cl)_2(PPh_3)_3]$ and *mer*-$[Ir(H)_3(PPh_3)_3]$ react with CS_2 to yield the dithioformato complexes $[Ir(Cl)_2(S_2CH)(PPh_3)_2]$ (**163**) and $[Ir(H)_2(S_2CH)(PPh_3)_2]$ (**164**), respectively. Both complexes exhibit IR absorption at *ca.* 1215–1235 and 900–930 cm^{-1}, attributable to $\nu(S_2CH)$. Proton NMR spectra established the stereochemistry of these complexes, as shown in (**163**) and (**164**).[375,376] The equivalent coupling of the dithioformate proton to two ^1H nuclei (as in **164**) clearly favours the symmetrical structure for the dithioformate ligands, as opposed to any asymmetric alternatives.



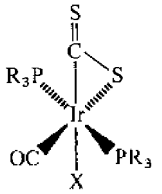
(163)



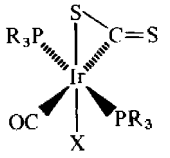
(164)

Insertion of CS_2 into $[Ir(H)(CO)(PPh_3)_3]$ has been monitored by NMR spectroscopy. A definitive assignment of the product, either $[Ir(S_2CH)(CO)(PPh_3)_2]$ or $[Ir(CS_2H)(CO)(PPh_3)_2]$, could not be made owing to the lack of documentation on the SH proton chemical shift. However, the observed signal at $\delta = 5.0$ p.p.m. may be indicative of $[Ir(CS_2H)(CO)(PPh_3)_2]$.[377]

Carbon disulfide reacts with $[Ir(H)(CO)_2(PPh_3)_2]$ to yield an iridium(III) species containing two CS_2 molecules bonded to each Ir atom. The proposed formulations for this species included $[Ir(SSCH)(CO)(PPh_3)_2(\pi\text{-}CS_2)]$ and $[Ir(CSSH)(CO)(PPh_3)_2(\pi\text{-}CS_2)]$. Here again, no definitive structural assignment was put forward as no NMR signal was observed nor an analysis reported.[377] However, the dithioformato ligand is most likely unidentate in either case. It has been proposed[378] that the complex obtained by the addition of CS_2 to $[Ir(I)(CO)(PPh_3)_2]$ has the orientation isomers of configuration (**165**) and (**166**). However, Deeming and Shaw[379] have suggested that $[Ir(Cl)(CO)(PMe_2Ph)_2(CS_2)]$ exists as only one of these isomers in solution, as well as in the solid state.



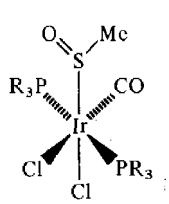
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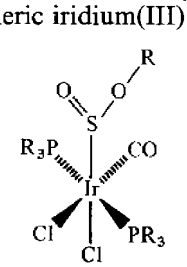


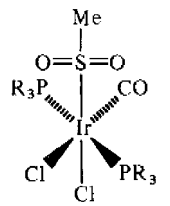
(166)

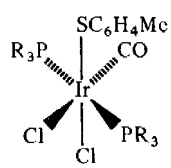
49.6.6.3 Other S-containing ligands

The first sulfenato and alkylsulfenato complexes of iridium(III) were prepared by George and Watkins.[380] The sulfenato complexes $[Ir(Cl)_2(MeSO)(CO)(PR_3)_2]$ (**167**; $PR_3 = PPh_3$, PPh_2Me) were prepared from $[Ir(Cl)(CO)(PR_3)_2]$ and MeS(O)Cl; the alkylsulfenato complexes $[Ir(Cl)_2(ROSO)(CO)(PR_3)_2]$ (**168**; $PR_3 = PPh_3$, R = Me, Et; $PR_3 = PMe_2Ph$, R = Me) were obtained *via* reaction of $[Ir(Cl)(CO)(PR_3)_2]$ and the appropriate ROS(O)Cl. These complexes do not rearrange to yield sulfinato complexes. The preparation of the sulfinato complex $[Ir(Cl)_2(MeSO_2)(CO)(PPh_2Me)_2]$ (**169**) and the thio complex $[Ir(Cl)_2(SC_6H_4Me\text{-}p)(CO)(PR_3)_2]$ (**170**; $PR_3 = PPh_3$, PPh_2Me) have also been reported.[380] Their stereochemistries were assigned on the basis of ^1H NMR and IR spectral data. Oxidative-elimination products of the type $[Ir(X)(SC_6H_4Y)\{SC_6H_3(NO_2)_2\}(CO)(PPh_3)]_2$ (**171**) were prepared from *trans*-$[Ir(X)(CO)(PPh_3)_2]$ (X = Cl, Br, I) and a series of 2,4-dinitrophenyl 4-Y-phenyl disulfides (Y = NO_2, Br, F, H, Me, MeO; reaction 107). The S—S bond in the unsymmetrical disulfide ArS—SAr′ is cleaved by Vaska's complex, and the resulting fragments then coordinate to Ir to form a dimeric iridium(III) complex, as depicted in Scheme 19.[381]

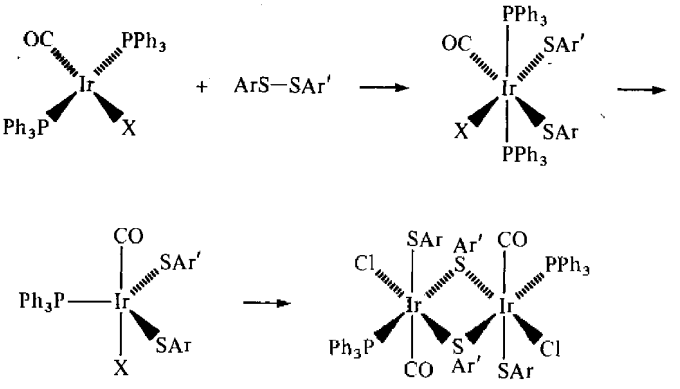








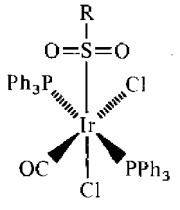
$$2[Ir(X)(CO)(PPh_3)_2] + 2ArS{-}SAr' \longrightarrow [Ir(X)(CO)(PPh_3)(SAr)(SAr')]_2 + 2PPh_3 \quad (107)$$



(171)

Scheme 19

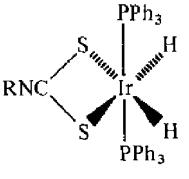
The oxidative addition of sulfonyl chlorides [RSO_2Cl] to Vaska's complex gives the iridium(III) sulfinate complex $[Ir(Cl)_2(RSO_2)(CO)(PPh_3)_2]$ (**172**; R = Me, Et, Pr^n, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$) in which the SO_2 group is bound to Ir through the S atom. A tentative structure (**172**) was suggested based on ^1H NMR spectral interpretation.[382] From the addition of RSO_2 to $[Ir(Cl)(CO)(PMe_2Ph)_2]$, $[Ir(Cl)_2(RSO_2)(CO)(PMe_2Ph)_2]$ is obtained, with stereochemical arrangements analogous to (**172**).[379]



(172)

The organoperthio group RSS^- is capable of complexing with *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ to form $[Ir(Cl)_2(SSC_6F_5)(CO)(PPh_3)_2]$.[387] The reaction is analogous to the addition of RSH,[383] RSSR[381] and RSCl[380] to square planar iridium(I) complexes.

The monomeric iridium(III) complexes $[Ir(S{-}S)_2(\eta\text{-}C_5Me_5)]$ (S—S = S_2CNMe_2, S_2PMe_2) have been prepared *via* reaction of $[Ir(Cl)_2(\eta\text{-}C_5Me_5)]_2$ and excess dithioacid anion $S{-}S^-$. Analytical and IR, ^1H, ^{13}C and ^{31}P NMR spectroscopic results were interpreted in terms of the occurrence of uni- and bi-dentate dithioacid exchange, probably *via* a dissociatively controlled intramolecular mechanism.[384] Another report[385] on the preparation of $[Ir(S_2CNMe_2)_2(\eta\text{-}C_5Me_5)]$ suggests that the complex contains one uni- and one bi-dentate dithio ligand. The preparation of $[Ir\{S_2C_2(CN)_2\}(\eta\text{-}C_5Me_5)]$ was also reported.[385] Complexes of the type $[Ir(H)_2(Rdtc)(ER_3)_2]$ (**173**) [ER_3 = PPh_3, $AsPh_3$; Rdtc = piperidine dithiocarbamate (Pipdtc), piperazine dithiocarbamate (Pzdtc), *N*-methylpiperazine dithiocarbamate (Me—Pzdtc), morpholine dithiocarbamate (Timdtc)] have been prepared and characterized by IR and ^1H NMR spectroscopy. The stereochemistry proposed for these complexes is shown in (**173**).[386]



(173)

49.6.7 Selenium Ligands

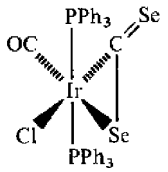
The electrochemical behaviour of the iridium(III) complexes $[Ir(dppe)_2(L_2)]^+$ (L_2 = Se_2, S_2, O_2) has been investigated,[388] revealing the dissociation of L_2^- consequent to the addition of one electron to the antibonding orbital of the π component of the Dewar–Chat–Duncanson model for ML_2 bonding. The mechanism for the electrolytic reduction is given in Scheme 20. The progression of the

first reduction wave (A) to more negative potential for $L_2 = Se_2 \rightarrow S_2 \rightarrow O_2$ was taken to be indicative of the π-back-bonding interaction enhancing in the same direction; thus, a stepwise destabilization of the lowest unoccupied molecular orbital follows the same order. Two iridium complexes containing Se donor ligands have been prepared *via* oxidative addition of carbon diselenide and areneselenols to *trans*-[Ir(Cl)(CO)(PPh_3)$_2$].[389] As such, addition of CSe_2 to Vaska's complex produced [Ir(Cl)(CO)(CSe_2)(PPh_3)$_2$] (**174**), while addition of *p*-MeC_6H_4SeH resulted in [Ir(H)(Cl)(CO)(PPh_3)$_2$(SeC_6H_4Me-*p*)] (**175**). The IR spectrum of complex (**174**) exhibits a low ν(Ir—Cl) value, suggesting that the Cl ligand is *not trans* to CO. However, the IR data are consistent with the configuration in (**174**), and are analogous to those reported for [Ir(Cl)(CO)(CS_2)(PPh_2Me)$_2$].[379] The ^{1}H NMR spectrum of complex (**175**) is consistent with a structure in which the two PPh_3 ligands are *cis* to the hydride ligand and *trans* to each other. The suggested configuration of [Ir(H)(Cl)(CO)(SeC_6H_4Me-*p*)(PPh_3)$_2$] is that given in (**175**), based on ^{1}H NMR and IR spectral interpretation.[389]

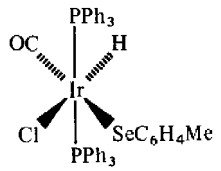
$$[Ir(X)_2(dppe)_2]^+ \xrightarrow[1e^-]{(A)} [Ir(X)_2(dppe)_2]^0 \xrightarrow{k_d} [Ir(dppe)_2]^+ + X_2^- \xrightarrow{1e^-}$$

$$[Ir(dppe)_2]^0 \xrightarrow{k_H} [Ir(H)(dppe)_2]$$

Scheme 20

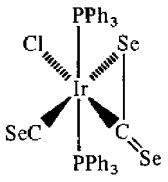


(174)

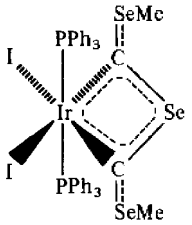


(175)

[Ir(Cl)(CSe)(PPh_3)$_2$] readily undergoes oxidative addition with Cl_2, O_2 and $AgClO_4$ in MeCN to yield [Ir(Cl)$_3$(CSe)(PPh_3)$_2$], [Ir(Cl)(CSe)(O_2)(PPh_3)$_2$] and [Ir(CSe)(PPh_3)$_2$(MeCN)](ClO_4), respectively. However, reaction of [Ir(Cl)(CSe)(PPh_3)$_2$] with BH_4^- and PPh_3 affords the Ir—Se complex [Ir(H)$_2$(SeMe)(PPh_3)$_3$]. Also, reaction between [Ir(Cl)(CSe)(PPh_3)$_2$] and CSe_2 gives the complex shown in (**176**), which on reaction with MeI leads to complex (**177**).[390]

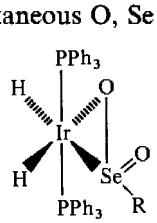


(176)



(177)

The seleninato iridium(III) complexes [Ir(H)$_2$(XPhSeO$_2$)(PPh_3)$_2$] (X = H, *p*-Cl, *m*-Cl, *m*-Br, *m*-NO_2) have been synthesized from [Ir(H)$_3$(PPh_3)$_2$] and the appropriate sodium benzeneseleninate salt. The monomeric diamagnetic complexes have the hydride ligands in a *cis* arrangement and the $RSeO_2$ ligand coordinated through simultaneous O, Se bonding, as in structure (**178**).[391]



(178)

49.6.8 Halogens as Ligands

Iridium(III) fluoride is prepared by reducing [IrF_6] with metallic iridium at 323 K. [IrF_3] is black, possesses a hexagonal close-packed structure and is relatively inert toward water.[310]

The red octahedral complex $[IrCl_3]$ results from direct chlorination of metallic iridium at 773 K;[310] two forms of $[IrCl_3]$ are known, both water insoluble.[392] The dark green hydrate, $[IrCl_3]\cdot 3H_2O$, is obtained upon heating the oxychloride $[Ir(Cl)_2(OH)]\cdot 3H_2O$ in HCl.[343]

Ferguson and Rankin[394] have recently reviewed the various preparative routes and structural chemistry of iridium(III) chloro and bromo complexes. In general, iridium(III) chloro complexes of the type $M_3[IrCl_6]\cdot 12H_2O$ (M = Li, Na), $M_3[IrCl_6]\cdot H_2O$ (M = K, Rb, Cs, NH_4), $M_3[IrCl_6]$ (M = Na, K, NH_4) and $M_2[Ir(Cl)_5(H_2O)]$ (M = K, Rb, Cs, NH_4) are prepared *via* the reduction of $M_2[IrCl_6]$ by reagents such as Fe^{2+},[395] ethanedioate (oxalate),[396–398] or hydrogen sulfide.[399,400] Factors affecting product composition include chloride ion concentration, choice of M, method of recrystallization and solution age. The crystal structures of iridium(III) chloro complexes depend on M as well as the presence or absence of water of crystallization. Single-crystal X-ray structures of $K_3[IrCl_6]$, $K_3[IrCl_6]\cdot H_2O$ and $(NH_4)_3[IrCl_6]\cdot H_2O$ reveal them to be isostructural with their rhodium analogues, though each complex belongs to a different space group.[394b]

The aquation of $[IrCl_6]^{3-}$ yields $[Ir(Cl)_5(H_2)]^{2-}$, $[Ir(Cl)_4(H_2O)_2]^-$ and $[Ir(Cl)_3(H_2O)_3]$.[401] The activation entropy associated with this reaction was suggestive of a dissociative mechanism. In the presence of added salts, the calculated activation entropies were attributed to the orienting effect of the cation (*e.g.* Li^+) on the water adjacent to the $[IrCl_6]^{3-}$ anion.[402] Irradiation of $K_3[IrCl_6]$ doped into NaCl reportedly yields $[IrCl_6]^{4-}$, based on ESR data.[403]

The reddish-brown $[IrBr_3]$ is also known, and thought to be formed upon treatment of '$[IrBr_2]$' with bromine.[393] More likely, however, is that $[IrBr_3]$ is grey-brown in colour and obtained *via* direct bromination of metallic iridium at 843 K under 8 atm pressure.[404] Additionally, the hydrated complexes $[IrBr_3]\cdot H_2O$, $[IrBr_3]\cdot 3HBr\cdot 3H_2O$ and $[IrBr_3]\cdot H\beta r\cdot H_2O$ are thought to exist.[310]

Iridium(III) bromo complexes of the type $M_3[IrBr_6]$, $M_3[IrBr_6]\cdot 12H_2O$, $M_3[IrBr_6]\cdot H_2O$ and $[Co(NH_3)_6][IrBr_6]$ have been cited. They are, in general, prepared *via* reduction of $[IrBr_6]^{2-}$,[310] treatment of $[Ir(OH)_3]$ with HBr,[405] or treatment of the iridium(III) chloro analogue with HBr.[394,406,407] The hydrated complexes $K_3[IrBr_6]\cdot 4H_2O$[405] and $K_3[IrBr_6]\cdot 3H_2O$[408] are thought[394a] to actually be $(H_3O)K_8[IrBr_6]_3\cdot 9H_2O$.

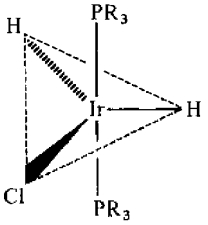
A single-crystal X-ray structure determination of $Rb_3[IrBr_6]\cdot H_2O$ has shown it to be isostructural with $(NH_4)_3[IrCl_6]\cdot H_2O$.[394b] X-Ray powder photographs, along with comparative analyses, suggest that the complexes $[Co(NH_3)_6][IrX_6]$ (X = Cl, Br) crystallize in the cubic space group P_a3.[394b] Preliminary single-crystal X-ray studies[394b] on $(NH_4)_3[IrBr_6]\cdot H_2O$, $Cs_3[IrBr_6]\cdot H_2O$ and $(H_3O)K_8[IrBr_6]_3\cdot 9H_2O$, as well as $Rb_3[IrBr_6]\cdot H_2O$, have revealed the $[IrX_6]^{3-}$ anions to be distorted as a consequence of the non-spherical packing of the cations and, in some cases, of the water molecules surrounding the anions.

The reaction between Ir_2O_3 and HI presumably gives $[IrI_3]$, while $[IrI_6]^{3-}$ can be synthesized from $[IrI_3]\cdot 3H_2O$ and KI.[310,401] Additionally, the hydrated complex $[IrI_3]\cdot 3H_2O$ has been reported.[310]

The dinuclear complexes $M_3[Ir_2(Cl)_9]$ (M = Rb, Cs) and $M_3[Ir_2(Br)_9]$ (M = Rb, Cs, Me_4N) have recently been prepared. Heating $M_2[Ir(Cl)_5(H_2O)]$ under vacuum to 623 K, followed by cooling and treating with water, led to the isolation of impure samples of $M_3[Ir_2(Cl)_9]$. The $M_3[Ir_2(Br)_9]$ complexes result from treatment of $M_3[IrCl_6]\cdot H_2O$ or $M_2[Ir(Cl)_5(H_2O)]$ with HBr.[394b]

49.6.9 Hydrogen and Hydrides as Ligands

The five-coordinate iridium(III) dihydrates $[Ir(H)_2(Cl)(PR_3)_2]$ (PR_3 = PBu^t_3, PBu^t_2Ph) have been synthesized from $IrCl_3\cdot xH_2O$ and PR_3, and have the structure depicted in (**179**). Reactions of complex (**179**) with NaI, CO and H_2 are summarized in reactions (108)–(110).[290b] Hydride complexes of the type $[Ir(H)_n(Cl)_{3-n}(PRBu^t_2)_2]$ (n = 1, R = Me; n = 2, R = Bu^t) react with $NaBH_4$ to yield the non-fluxional complexes $[Ir(H)_2(BH_4)(PRBu^t_2)_2]$.[290b] In toluene, $[Ir(Cl)(N_2)(PPh_3)_2]$ and HCl react to yield $[Ir(H)(Cl)_2(PPh_3)_2]$; in ethanol, however, CO is abstracted from the solvent affording $[Ir(H)(Cl)_2(CO)(PPh_3)_2]\cdot EtOH$.[409] Reaction between $[Ir(Cl)(cod)]_2$ and HCN produced the unusual five-coordinate species $[Ir(H)(Cl)(CN)(cod)]$.[410]



(179)

$$[Ir(H)_2(Cl)(PBu^t_2Ph)_2] + NaI \longrightarrow [Ir(H)_2(I)(PBu^t_2Ph)_2] \quad (108)$$

$$[Ir(H)_2(Cl)(PBu^t_2Ph)_2] + CO \longrightarrow [Ir(H)_2(Cl)(CO)(PBu^t_2Ph)_2] \quad (109)$$

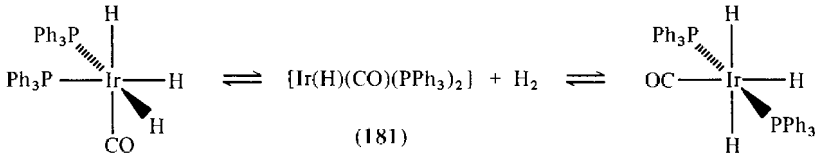
$$[Ir(H)_2(Cl)(PR_3)_2] + H_2 \xrightarrow{Na(propan\text{-}2\text{-}olate)} [Ir(H)_5(PR_3)_2] \quad (110)$$

Oxidative addition of H_2 to iridium(I) complexes yields a variety of six-coordinate iridium(III) dihydrides. Dihydrogen reacts with $[Ir(Cl)(CO)(PPh_3)_2]$ in benzene at 298 K to produce $[Ir(H)_2(Cl)(CO)(PPh_3)_2]$;[411] the reaction is reversible and a kinetic investigation has been reported.[412] $[Ir(Cl)(PPh_3)_3]$ reacts with H_2 at 298 K and atmospheric pressure to give $[Ir(H)_2(Cl)(PPh_3)_3]$.[413] The four-coordinate iridium(I) complex $[Ir(dppe)_2]^+$ reversibly reacts with H_2, affording $[Ir(H)_2(dppe)_2]^+$.[414]

The addition of hydrogen halides (*e.g.* HCl) to iridium(I) complexes also affords iridium(III) hydrides. The stereochemistry of these additions to $[Ir(Cl)(CO)(PPh_3)_2]$[414b] and related complexes has been studied in some detail.[415–417] In the solid state or in non-polar solvents *cis* adducts are formed, while the use of polar solvents gives mixtures of *cis* and *trans* adducts. Reaction between $[Ir(Cl)(PPh_3)_3]$ and HCl gives $[Ir(H)(Cl)_2(PPh_3)_3]$; the corresponding arsine and stibene complexes are similarly obtained.[413] $[Ir(dppe)_2]^+$ undergoes oxidative addition with HCl to yield $[Ir(H)(Cl)(dppe)_2]^+$.[414] Oxidative addition of HCN to $[Ir(Cl)(CO)(PPh_3)_2]$ gives $[Ir(H)(Cl)(CN)(CO)(PPh_3)_2]$.[418] Additionally, pentafluorobenzenethiol oxidatively adds to $[Ir(Ph)(CO)(PPh_3)_2]$ to produce $[Ir(H)(Ph)_2(CO)(PPh_3)_2]$, and to $[Ir(Cl)(CO)(PPh_3)_2]$ under mild conditions to give the same product.[419]

Five-coordinate iridium(I) complexes may react with hydrogen halides (HX) to eliminate a ligand and form Ir—H and Ir—X bonds. Both $[Ir(CO)(PMe_2Ph)_4]^+$ and $[Ir(CO)_2(PMe_2Ph)_3]^+$ react with HCl to yield $[Ir(H)(Cl)(CO)(PMe_2Ph)_3]^+$.[420] Dimethylphenylarsine is displaced from $[Ir(CO)(AsMe_2Ph)_2(PMe_2Ph)_2]^+$ by HCl, yielding $[Ir(H)(Cl)(AsMe_2Ph)(CO)(PMe_2Ph)_2]^+$.[420] Thiophenol reacts with $[Ir(Cl)(CO)(PPh_3)_2]$, from which $[Ir(H)(Cl)(Ph)(PPh_3)_2]$ is obtained.[419] Substituted thiophenols react similarly with Vaska's complex.[410,419,421] Salts of $[Ir(H)_2(CO)_2(ER_3)_2]^+$ (ER_3 = tertiary phosphine or arsine) have been prepared *via* reversible hydrogen displacement of CO from $[Ir(CO)_3(ER_3)_2]$.[422]

The preparation and interconversion of two isomeric iridium(III) trihydrides, *fac*- and *mer*-$[Ir(H)_3(CO)(PPh_3)_2]$ (**180**), have been studied. Under a hydrogen atmosphere, both isomers undergo spontaneous interconversion to a dynamic equilibrium. The kinetic data obtained from the interconversion and H_2 displacement from both isomers by PPh_3 suggest that the interconversion process occurs *via* a reversible reductive elimination–oxidation sequence. Both processes are believed to involve the intermediate species $[Ir(H)(CO)(PPh_3)_2]$ (**181**). It has further been postulated that the interconversion process proceeds by slow unimolecular loss of H_2 (reductive elimination), followed by a rapid readdition of H_2 to the coordinatively unsaturated intermediate species (**181**), as depicted in Scheme 21.[423]



(180) (181) (180)

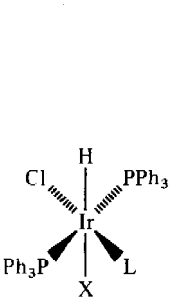
Scheme 21

The addition of $Na_3[IrCl_6]$ to a hot ethanolic solution of PPh_3 followed by $NaBH_4$ addition gives *mer*-$[Ir(H)_3(PPh_3)_3]$ on cooling; *fac*-$[Ir(H)_3(PPh_3)_3]$ is obtained by evaporating the filtrate obtained under reduced pressure.[424] The structure of *mer*-$[Ir(H)_3(PPh_3)_3]\cdot 0.5C_6H_6$ shows a very distorted octahedral coordination geometry about Ir with three adjacent sites occupied by P atoms.[425] Both *fac*- and *mer*-$[Ir(H)_3(PPh_3)_3]$ react with carboxylic acids in boiling 2-methoxyethanol to give $[Ir(H)_2(O_2CR)(PPh_3)_3]$ (R = Me, *p*-tolyl, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$).[426]

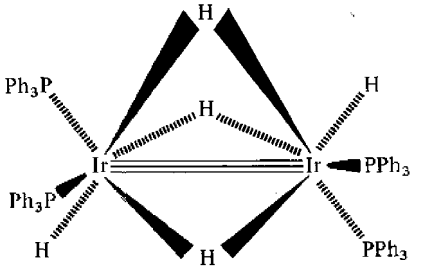
The oxidative addition of HBF_4, CF_3SO_3H and $BuSO_3H$ to *trans*-$[Ir(Cl)(L)(PPh_3)_2]$ (L = CO, N_2) has afforded the highly reactive iridium(III) complexes $[Ir(H)(Cl)(X)(L)(PPh_3)_2]$ (X = BF_4, CF_3SO_3, $BuSO_3$) (**182**), in which X can easily be substituted by σ and π donors. The stereochemistry of the hydride complex (**182**) is shown.[58]

The dimeric hydrido complex $[Ir(H)(X)_2(CO)(PR_3)]_2$ (X = Cl, Br; PR_3 = PEt_3, PPh_3) has been synthesized by carbonylation of iridium halides followed by phosphine addition; the complex

contains halide bridges.[427] Hydride bridges are present in $[Ir_2(\mu\text{-}H)_3(H)_2(PPh_3)_4](PF_6)$ (**183**) for which X-ray structural, IR and ^1H NMR spectral data have been interpreted in terms of the presence of an iridium–iridium triple bond (2.518 Å).[428]

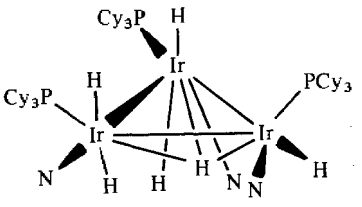


(182)

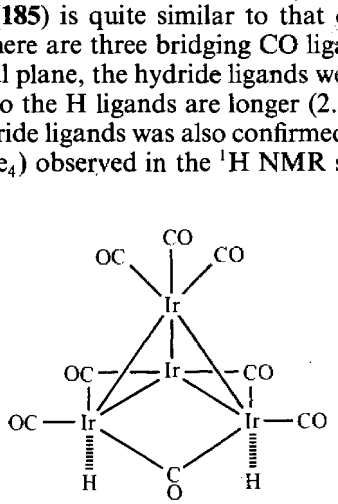


(183)

The trimeric complex $[\{Ir(H)_2(PCy_3)_3(C_5H_5N)\}_3(\mu\text{-}H)]^{2+}$ (**184**; N = Pyridine) has been characterized by X-ray crystallography, IR and ^1H NMR spectroscopy, and found to contain a tricoordinate hydrogen ligand within a triangle of iridium atoms.[429] The tetranuclear complex anion $[Ir_4(H)(CO)_{11}]^-$ has been isolated as the tetraalkylammonium salt by treating $[Ir_4(CO)_{12}]$ with K_2CO_3 and CO in methanol.[430] The dihydride species $[Ir_4(H)_2(CO)_{11}]$ was produced upon treatment of the anion with acetic acid.[430] In concentrated H_2SO_4, slow dissolution of $[Ir_4(CO)_{12}]$ gives rise to a non-isolable solution thought to contain $[Ir_4(H)_2(CO)_{12}]^{2+}$.[431] The dihydrido anion $[Ir_4(H)_2(CO)_{10}]^{2-}$ (**185**) was synthesized in two stages: $[Ir_4(CO)_{12}]$ reacts with RO^- in ROH (R = Me, Et) to yield $[Ir_4(CO_2R)(CO)_{11}]^-$, which, when added to alkaline hydroxide, gives the dianion.[432] The X-ray crystal structure of complex (**185**) is quite similar to that of $[Rh_4(CO)_{12}]$, wherein the iridium atoms form a tetrahedron and there are three bridging CO ligands. Inasmuch as two terminal CO ligands are missing from the basal plane, the hydride ligands were suggested to occupy these positions. The two Ir—Ir bonds *trans* to the H ligands are longer (2.802 Å) than the remaining Ir—Ir bonds (2.71 Å). The presence of hydride ligands was also confirmed by the hydride NMR resonance ($\delta = -16.15$ p.p.m. relative to $SiMe_4$) observed in the ^1H NMR spectrum of the dianion (**185**) in CD_3CN.[432]

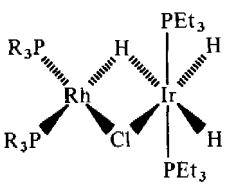


(184)

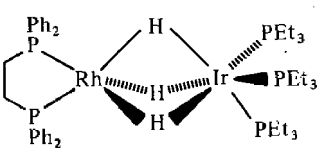


(185)

The hydrido-bridged dinuclear complex $[(PR_3)_2Rh^I(\mu_2\text{-}H)(\mu_2\text{-}Cl)Ir^{III}(H)_2(PEt_3)_2]$ (**186a**; $PR_3 = PEt_3$, or $2PR_3$ = dppe) was produced upon treatment of $[Ir(H)_5(PEt_3)_2]$ with $[Rh(\mu\text{-}Cl)_2(PR_3)_2]_2$. An X-ray crystal structure determination reveals a distorted octahedral geometry about Ir and a distorted square planar geometry around Rh.[433] The similar complex $[(dppe)Rh^I(\mu_2\text{-}H)_2Ir^{III}(H)_2(PPr^i_3)_2]$ has been prepared and characterized by X-ray crystal structure and NMR analyses. Its structure is similar to that of complex (**186a**).[434] Another hydrido-bridged dinuclear complex, $[(dppe)Rh(\mu_2\text{-}H)_3Ir(PEt_3)_3]^+$, has the structure shown in (**186b**).[435]

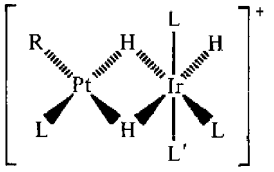


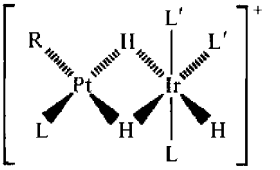
(186a)



(186b)

Reaction between $[Ir(H)_2(OCMe_2)_2(PPh_3)_2]^+$ and $[M(H)_2(Cp)_2]$ (M = Mo, W) has yielded $[(PPh_3)_2(H)Ir(\mu\text{-}H)_2(\eta\text{-}\sigma\text{:}1\text{-}5\text{-}\eta\text{-}C_5H_4)M(Cp)]^+$. Intermediate formation of $[(PPh_3)_2(H)_2Ir(\mu\text{-}H)_2M(Cp)_2]^+$ was reportedly observed, and kinetic parameters were obtained for the C—H insertion reaction. Reversible hydride bridge cleavage for M = W occurs with pyridine and acetonitrile.[436] The hydrido-bridged bimetallic complexes (**187**)–(**190**) have been synthesized from *trans*-$[Pt(L)_2(MeOH)(R)]^+$ and $[Ir(H)_5(L')_2]$. Complex (**187**) reacts with CO at room temperature to yield $[Ir(H)_2(CO)(PEt_3)_3]^+$. Reaction of complex (**187**) with ethylene gives (**190b**); complex (**190**) reacts with H_2 at moderate temperatures and pressures to produce $[(PEt_3)_2Pt(\mu\text{-}H)_2Ir(H)_2(PEt_3)_2]^+$.[437]





(187a) R = H, L = L′ = PEt_3 (187b) R = H, L = L′ = PEt_3

(188a) R = Ph, L = L′ = PEt_3 (188b) R = Ph, L = L′ = PEt_3

(189a) R = H, L = PEt_3, L′ = PPr_3 (190b) R = Et, L = L′ = PEt_3

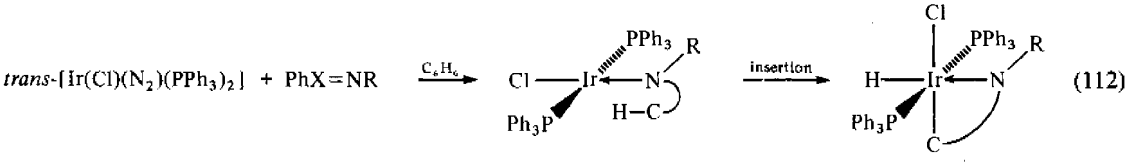
(190a) R = Et, L = L′ = PEt_3

49.6.10 Mixed Donor Atom Ligands

49.6.10.1 Bidentate N–C ligands

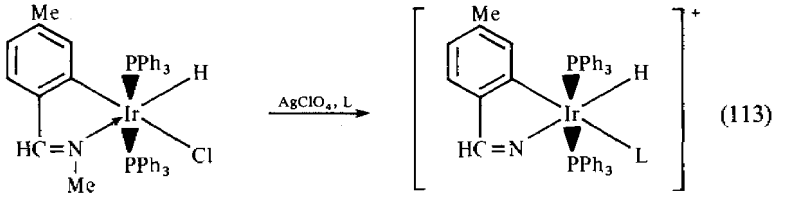
Organometallic intramolecular coordination complexes consist of those which have at least one M—C bond and at least one group forming an intramolecular coordination bond. Iridium(III) complexes containing an N donor intramolecular coordination bond are well known, and conform to the five-membered ring structure theory first proposed by Matsuda *et al.*:[438] organometallic intramolecular coordination complexes tend to form five-membered ring structures. Transition metal organometallic intramolecular coordination complexes containing an N donor ligand have been reviewed by Omae.[439]

Reactions of *trans*-$[Ir(Cl)(N_2)(PPh_3)_2]$ with benzylideneamines have afforded the *o*-metallated complexes (**191**) for X = CH, N (see reaction 112).[440] Whereas square planar palladium(II) benzylideneamine complexes are formed *via* a substitution reaction of the metal with the hydrogen at the *ortho* position, octahedral iridium(III) analogues are more probably formed by an insertion reaction arising from the affinity of the Ir atom to the H atoms (reaction 112). The insertion mechanism involves $\sigma(N)$ coordination of the imine ligand, which brings an *ortho* or alkenic CH group close to the Ir atom, followed by oxidative addition of the *ortho* or alkenic CH group to the Ir atom. Treatment of complex (**191**) with $AgClO_4$ and then with $C_6H_{11}NC$ or CO (= L) gives rise to the formation of complex (**192**) with the metallacyclic ring remaining intact (see reaction 113).[441]



(112)

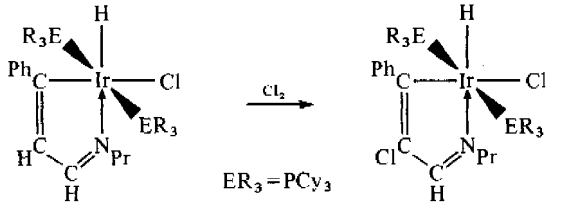
(191)



(113)

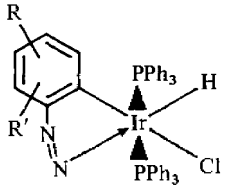
(191) (192)

Five-membered cyclometallated complexes similar to (**191**) are produced from the reaction between alkenic imines and iridium complexes. The reaction of alkenic imines with $[Ir(Cl)(C_8H_{14})_2]_2$ in the presence of cyclohexylphosphine yields complex (**193**),[442] which, when treated with Cl_2, undergoes substitution without Ir—C bond rupture to give (**194**; reaction 114).[441] Azobenzene or its derivatives react with $[Ir(Cl)(C_8H_{14})_2]_2$ in the presence of PR_3 (R=Ph, cyclohexyl) according to reaction (112) to yield the cyclometallated complex (**195**).[441,442]



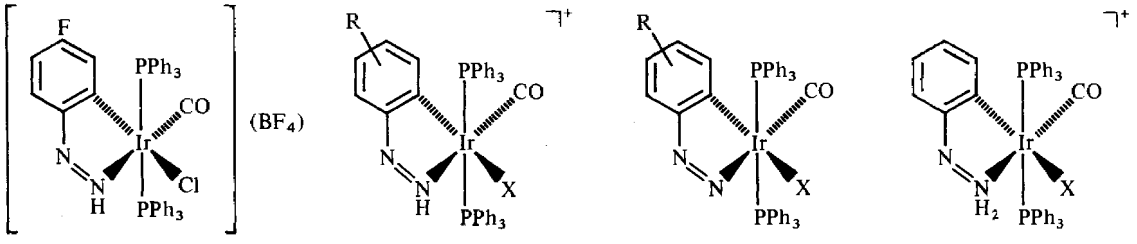
(114)

(193) (194)



(195) R = Ph, Me, tolyl, xylyl; R′ = H, Me

Two products are formed *via* the reaction of *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$ with *p*-fluorobenzenediazonium tetrafluoroborate.[443,444] One is a red, air-stable, diamagnetic tetrazene complex,[445,446] while the other is the yellow, air-stable diamagnetic complex (**196**). The X-ray crystal structure of the acetone solvate of complex (**196**) has been determined. Various substituted arene diazonium ions react with $[Ir(Cl)(CO)(PPh_3)_2]$ and its analogues in the presence of lithium chloride, benzene/ethanol, or benzene/propan-2-ol to yield *o*-metallated aryldiazene complexes (**197**) (where X = Cl, Br, F, I, $OClO_3$; R = H, F, Br, Cl, Me, CF_3, NH_2, NO_2, OMe; and Y = BF_4^-, ClO_4^-).[447–448] The complex (**197**) may undergo deprotonation, affording an aryldiazenato complex (**198**), as well as hydrogenation in the presence of a palladium catalyst to produce an *o*-metallated arylhydrazine complex (**199**). The X-ray crystal structure of (**196**) and (**197**), dichloro(4-methoxyphenyldiimide)-C^2,N^1-bis(triphenylphosphine)iridium–chloroform (1:1), has been determined. The iridium atom displays a distorted octahedral coordination and is bonded to the terminal nitrogen atom.[449]



(196) (197) (198) (199)

An insertion product is obtained upon reaction of $[Ir(H)_3(PPh_3)_3]$ with *p*-anisolediazonium tetrafluoroborate, and undergoes *o*-metallation to yield $[Ir(H)(NHNC_6H_3OMe)(PPh_3)_3]^+ (BF_4)^-$ (**200**).[450] The neutral complex $[Ir(H)(X)(NHNC_6H_3OMe)(PPh_3)_2]$ (**201**) results from the action of halides X^- on complex (**200**). The reaction of complex (**201**) with halogens, X_2, affords $[Ir(X)_2(NHNC_6H_3OMe)(PPh_3)_2]$.

The syntheses of phenyldiimide complexes have been reported by Toniolo and coworkers.[451] One example is the *o*-metallation reaction of the aryldiazenato iridium(III) complex (**202**) with phenylacetylene (reaction 115) to yield complex (**203**).

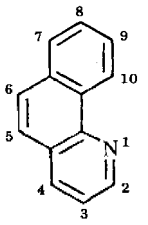
$$[Ir(Cl)(CO)(N_2C_6H_4R\text{-}p)(PPh_3)_2](BF_4) + HC{\equiv}CH \xrightarrow{\text{EtOH or } C_6H_6/\text{acetone}} \quad (115)$$

(**202**)

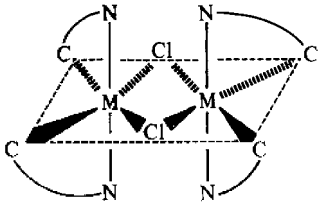
$$[Ir(Cl)(CO)(NH{=}NC_6H_4R\text{-}p)(PPh_3)_2(C{\equiv}CPh)]^+(BF_4)^-$$

(**203**)

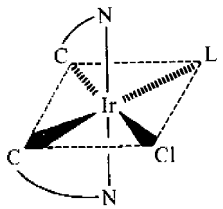
The reaction of $Na_3[IrCl_6]$ in 2-methoxyethanol with benzo[*h*]quinoline (bhqH; **204**) yields $[Ir(Cl)(bhq)_2]_2$ (**205**), in which the bhq ligand is coordinated at N-1 and C-10 atoms. Proton NMR and IR spectra support a structure similar to that of the rhodium(III) analogue (**205**). Complex (**205**) reacts with L (= PBu^n_3, SEt_2) to give $[Ir(Cl)(bhq)_2(L)]$ (**206**).[452]



(204)



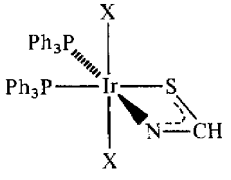
(205) M = Rh, Ir



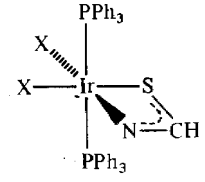
(206)

49.6.10.2 Bidentate N–S ligands

Alkyl and aryl isothiocyantes, RCNS, parallel CS_2 in their capability to insert into M—H bonds and yield products having the *N*-alkyl- or *N*-aryl-formamide chelate ligand RN===CH===S. The iridium(III) complexes $[Ir(X)_2(RN{=}{=}{=}CH{=}{=}{=}S)(PPh_3)_2]$ (**207**; X = Cl, Br; R = Me, Et, Ph) can be prepared from *trans*-$[Ir(H)(X)_2(PPh_3)_2]$ and the appropriate alkyl or aryl isothiocyanate. Two isomeric forms of (**207**) were deemed plausible, with (**207a**) the preferred stereochemistry for the alkyl products and (**207b**) for the aryl products.[453]



(207a)



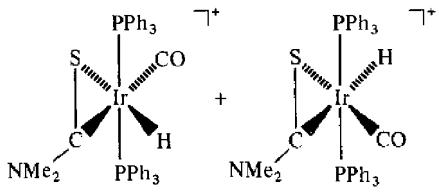
(207b)

49.6.10.3 Bidentate S–C ligands

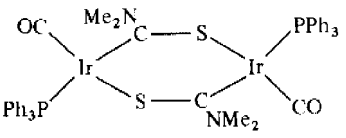
The X-ray crystal structure of $[Ir(CO)(PPh_3)(\eta^2\text{-}SCNMe_2)_2]^+$ (as the BF_4^- salt) reveals that both $IrSCNMe_2$ units are virtually planar and coordinated *via* C and S, with bond distances comparable to other η^2-$SCNMe_2$ complexes. The coordination geometry about Ir is a distorted octahedron.[454] IR spectra on the products of reactions (116) and (117) have also been interpreted in terms of η^2 coordination of the $SCNMe_2$ ligand, *via* C and S.[454] Interestingly, the product of reaction (117), *trans*-$[Ir(Cl)(CO)(PPh_3)_2(\eta^2\text{-}SCNMe)_2)]^+$, has been reported[455] to be formed in the absence of additional Cl^-; whereas, in the presence of Cl^-, $[Ir(Cl)_2(CO)(PPh_3)_2(\eta^1\text{-}SCNEt)]$ was formed.[377] Thus, it would appear that $SCNMe_2$ is capable of η^2 coordination *via* displacement of Cl^- from Ir^{III}, whereas SCNMe is not. The reaction of $[Ir(H)(CO)(PPh_3)_3]$ with $Me_2NC(S)Cl$ results in immediate precipitation of an intermediate complex, $[Ir(H)(CO)(PPh_3)_2(\eta^2\text{-}SCNMe_2)]^+$, that exists in two isomeric forms (**208a**) and (**208b**). Reaction of complex (**208**) with Et_3N in C_6H_6 affords complex (**209**), $[Ir(CO)(PPh_3)(\mu\text{-}SCNMe_2)]_2$, as in reaction (118).[454] In the complex analogous to (**208**), $[Ir(H)(Cl)(CO)(PPh_3)_2(\eta^1\text{-}SCNMe)]$, η^1 coordination of SCNMe is present and Cl^- is not displaced from the coordination sphere.[455]

$$[Ir(Cl)_2(PPh_3)_2] + Me_2NC(S)Cl \xrightarrow{C_6H_6} cis\text{-}[Ir(Cl)_2(\eta^2\text{-}SCNMe_2)(PPh_3)_2] \quad (116)$$

$$[Ir(Cl)(CO)(PPh_3)_2] + Me_2NC(S)Cl \xrightarrow{C_6H_6} trans\text{-}[Ir(Cl)(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+ \quad (117)$$



(208a) (208b)



(209)

(118)

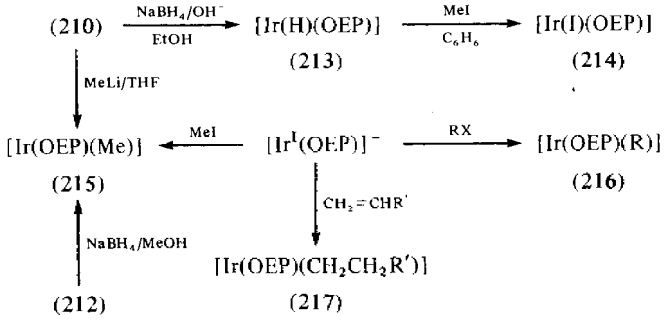
49.6.11 Multidentate Macrocyclic Ligands

The iridium(III) octaethylporphyrin (OEP) complexes (**210**)–(**212**) have been prepared and characterized spectroscopically by Ogoshi *et al.*[183] (reactions 119–121). Scheme 22 depicts various reactions of complexes (**210**) and (**212**) to yield hydrido- (**213**) and organo-iridium(III) (**214**)–(**217**) porphyrin complexes. The preparation and influence of axial ligands on the central iridium atom of several iridium(III) octaethylporphyrin complexes has been reported. The complexes investigated include [Ir(X)(CO)(OEP)] (**218**; X = Cl, Br, ClO_4, CN, BF_4, Me) and [Ir(L)(OEP)(Me)] (**219**; L = no ligand, *N*-methylimidazole (mim), pyridine, NH_3, CN). For the carbonyl complexes (**218**), the CO stretching frequencies and absorption peak wavenumbers varied in the order Me^-, $Br^- \approx Cl^-$, $ClO_4^- \approx BF_4^-$, that is in the order of decreasing electron-donating tendency of the axial ligand X. Proton NMR studies were employed to determine the *cis* and *trans* influence of the porphyrin ligand. A linear correlation between the chemical shift of the *meso* protons (*cis* influence) and the reversible redox potential (Ir^I/Ir^{III}) in the range +0.4 to +1.3 V has been observed. These results were explained[456] in terms of the change of electron density caused by chelation of the axial ligands depending on their electron-donating tendency; the order to this tendency varies for complexes (**218**) and (**219**) as: CO < no ligand < py < NH_3 < mim < CN^- < $ClO_4^- \approx BF_4^-$ < $Cl^- \approx Br^-$ < Me^-.

$$[Ir(Cl)(CO)_3]_2 + OEPH_2 \longrightarrow \underset{(\mathbf{210})}{[Ir(Cl)(CO)(OEP)]} + \mu\text{-}OEP[Ir(CO)_3]_2 \quad (119)$$

$$[Ir(Cl)(cod)]_2 + OEPH_2 \longrightarrow \underset{(\mathbf{211})}{[Ir(cod)(OEP)]} + \underset{(\mathbf{210})}{[Ir(Cl)(CO)(OEP)]} \quad (120)$$

$$[Ir(Cl)(cod)]_2 + N\text{—}Me\cdot OEPH \longrightarrow \underset{(\mathbf{212})}{[Ir(Cl)_2(N\text{—}Me\cdot OEP)]} \quad (121)$$



Scheme 22

The reaction of *meso*-porphyrin IX diethyl ester with $[Ir(Cl)(CO)_3]_2$ or $[Ir(Cl)(CO)(cot)_2]$ yields the iridium(III) porphyrin derivative [Ir(CO)(HePDEE)] (HePDEE = hematoporphyrin diethyl ester).[457] This complex, along with the dimethyl ester derivative, has been characterized by electronic, IR, electron spin resonance and mass spectroscopic techniques as well as magnetic susceptibility measurements. The iridium complexes differ from their rhodium analogues in that they retain a CO ligand in the coordination shell.

49.7 IRIDIUM(IV)

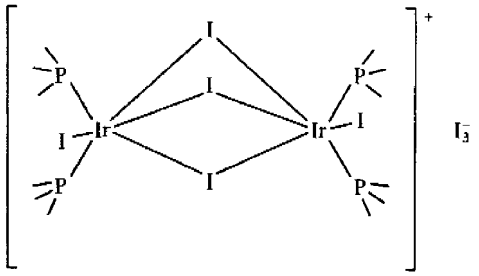
49.7.1 Phosphorus and Arsenic Ligands

The paramagnetic iridium(IV) complexes *trans*-$[Ir(Cl)_4(ER_3)_2]$ (ER_3 = tertiary phosphine or arsine) have been prepared *via* chlorine oxidation of $(ER_3H)[Ir(Cl)_4(ER_3)_2]$.[458] These iridium(IV) complexes are considered attractive as potential oxidizing agents inasmuch as they are soluble in a variety of organic solvents and thus as oxidizing agents of organic molecules and organometallic complexes.[459] Chlorine oxidation of $[Ir(Cl)_4(PMe_3)_2]^-$ in $CHCl_3$ yields *trans*-$[Ir(Cl)_4(PMe_3)_2]$, for which IR spectra were interpreted in terms of *trans* Cl ligands.[460] The electronic and MCD spectra of the D_{4h} iridium(IV) complexes *trans*-$[Ir(Cl)_4(ER_3)_2]$ (Er_3 = PMe_2Ph, PEt_2Ph, $AsPr^n_3$) have re-

vealed LMCT bands occurring at exceptionally low energies. These transition energies aid in the approximation of the bonding orbitals of ER_3 with respect to the metal; and from these energies, correlations were made between the energy of the ligand σ orbital and the Ir—ER_3 bond stability. The LMCT transition parallels the reducing power of ER_3.[461] The *trans*-$[Ir(Cl)_4(PMe_2Ph)_2]$ complex is reduced to *trans*-$[Ir(Cl)_4(PMe_2Ph)_2]^-$ at 0.90 V (*vs.* Ag–AgCl) in MeCN. The utility of this complex as an oxidizing agent with $[M(Cp)_2]$ (M = Ni, Fe), $[Pt(C_2H_4)(PPh_3)_2]$ and *trans*-$[Pd(Cl)_2(AsMe_3)_2]$ has been investigated.[462] For example, with $[Pt(C_2H_4)(PPh_3)_2]$, the iridium(III)–platinum(II) complex $[(Cl)_2(PMe_2Ph)_2Ir(\mu\text{-}Cl)_2Pt(PPh_3)_2]^+$ is formed.[459]

The iridium(IV) complexes $[Ir(R'CO_2)_2(ER_3)(RNC)]$ (ER_3 = $AsPh_3$; RNC = *p*-MeC_6H_4NC; R′ = $MeCH(O)CO_2$, *o*-$OC_6H_4CO_2$, $PhCH_2CH(NH)CO_2$, *o*-$NHC_6H_4CO_2$), $[Ir(o\text{-}C_6H_4O)_2(ER_3)(RNC)]$ and $[Ir(o\text{-}NHC_6H_4O)_2(ER_3)(RNC)]$ have been prepared from the iridium(III) complex $[Ir(H)_3(AsPh_3)_2(p\text{-}MeC_6H_4NC)]$.[196]

On treating $[Ir(ER_3)_4]^+$ (ER_3 = $P(OMe)Ph_2$, $PMePh_2$) with excess I_2 in CH_2Cl_2 or acetone, a complex of stoichiometry $[Ir(I)_4(ER_3)_2]$ is obtained. An X-ray structure determination of the complex of $[Ir(I)_4(PMePh_2)_2]$ established this compound as a salt of formula $[Ir_2(I)_5(PMePh_2)_4]^+(I)_3^-$, as depicted in (**220**).[463] The coordination about Ir is a distorted octahedron, and the complex has a triple I bridge with three I atoms shared by both Ir atoms. There is no Ir—Ir bond (> 3.5 Å).[463]



(220)

49.7.2 Oxygen Ligands

49.7.2.1 Hydroxy ligands

The complex $K_2[Ir(OH)_6]$ can be synthesized by treating $Na_2[IrCl_6]$ with KOH, and has been characterized by absorption spectroscopy, thermogravimetric analysis and voltage–current curves.[464] $Cd[Ir(OH)_6]$ possesses a tetragonal structure and serves as a magnetically dilute insulator, while $Zn[Ir(OH)_6]$ has a cubic structure and exhibits an anomalous magnetic behaviour.[465]

49.7.2.2 Oxalate ligands

The oxidation of $[Ir(ox)_3]^{3-}$ by cerium(IV) in aqueous acidic sulfate or perchlorate media has given $[Ir(ox)_3]^{2-}$. That the product is indeed $[Ir(ox)_3]^{2-}$ and not $[Ir^{III}(ox)_2(C_2O_4^-\cdot)]^{2-}$ finds support from the slow reaction observed in the presence of excess cerium(IV); free or coordinated oxalate radical anion would be expected to react rapidly with Ce^{IV}. In solution, $[Ir(ox)_3]^{2-}$ undergoes slow pseudo-first-order reaction to yield the highly reactive intermediate $[Ir^{III}(ox)_2(C_2O_4^-\cdot)]^{2-}$.

49.7.2.3 Nitrato ligands

The iridium(IV) nitrato complexes $M_2[Ir(NO_3)_6]$ (M = K, Rb, Cs), isomorphous with $K_2[Pt(NO_3)_6]$ and possessing magnetic moments consistent with a d^5 electronic configuration, are attained from the reaction of $M_2[IrBr_6]$ with N_2O_5. ESR spectra at 77 K reveal extensive π bonding between Ir and the NO_3 ligands.[467] The ESR spectrum of $K_2[Ir(NO_3)_6]$ in $K_2[Pr(NO_3)_6]$ was found to be isotropic at 77 K, indicating that any ^2T_g ground state Jahn–Teller term must be dynamic. Considerable $Md \rightarrow L_\pi^*$ delocalization was shown by the hyperfine constants. The presence of symmetrically bidentate NO_3 groups in $K_2[Ir(NO_3)_6]$ was supported by IR, Raman and ESR spectroscopic analyses.[468] The solution properties, IR spectra, magnetic properties and X-ray powder diffraction data for $M_2[Ir(NO_3)_6]$ have been reported more recently.[469]

49.7.3 Sulfur Ligands

Chlorine oxidation of the iridium(III) anions $[Ir(Cl)_5(SPh_2)]^{2-}$, $[Ir(Cl)_4(SPh_2)]^-$, *cis*- and *trans*-$[Ir(Cl)_4(SMe_2)_2]^-$ and $[Ir(Cl)_4(L)]^-$ (L = $RS(CH_2)_nSR$, RSCH=CHSR, 1,2-$C_6H_4(SR)_2$; R = Me, Ph; $n = 2$, 3) has led to the formation of the corresponding iridium(IV) complexes. The Ir^{IV} complexes $[Ir(Cl)_4(L)]$ have a *cis*-octahedral geometry. All complexes have been characterized on the basis of IR, Raman and electronic absorption spectra, as well as ^1H NMR spectra.[470]

49.7.4 Halogens as Ligands

The IV oxidation state is the most stable for iridium halogeno complexes. The preparation of $[IrF_4]$ has been reported,[471] though the actual product is probably $[IrF_5]$. A subsequent paper[472] reported the formation of $[IrF_4]$ from $[IrF_5]$ and iridium metal; on heating $[IrF_4]$ disproportionates to $[IrF_3]$ and $[IrF_5]$. Additionally, the formation of $[IrF_4]$ in high yields (95–100%) was reportedly obtained upon hydrogen reduction of $[IrF_6]$ or $[IrF_5]$. Polyisotopic mass spectra, visible and IR spectra, as well as chemical analyses and X-ray powder patterns support the proposed composition.[473] $(NO)_2[IrF_6]$ has been synthesized by the action of NOF and F_2 on metallic iridium, and analyzed by resonance Raman spectroscopy.[474]

Hexachloroiridates(IV) may be prepared by (i) chlorinating a mixture of iridium powder and an alkali metal chloride; (ii) in solution, by the addition of an alkali metal chloride to a suspension of hydrous IrO_2 in aqueous HCl;[475] or (iii) by the oxidation of $[IrCl_6]^{3-}$ by O_2 in acidic media.[476–478] Oxidation by O_2 probably occurs *via* reaction (122), with $E^0 = +0.21$ V.[14] Fine[479] has suggested that the reverse of reaction (122) occurs in alkaline media. The black crystalline sodium salt $Na_2[IrCl_6]$ is water soluble, and is the usual starting material for the synthesis of other iridium(IV) coordination complexes. The resonance Raman spectrum of $(NBu_4)_2[IrCl_6]$ reveals anomalous polarization of all bands; this has been ascribed to Jahn–Teller distortions present in the excited electronic state.[475] The single-crystal electronic spectra of various $[IrCl_6]^{2-}$ salts have also been reported.[480]

$$4[IrCl_6]^{3-} + O_2 + H^+ \longrightarrow 4[IrCl_6]^{2-} + 2H_2O \quad (122)$$

Reduction of $[IrCl_6]^{2-}$ by a variety of agents has been cited. The reduction of $[IrX_6]^{2-}$ (Cl, Br) by 2-thiouracil and 2-thiopyrimidine follows second-order rate laws, first-order with respect to both the concentration of the oxidant and the reductant. A pH–rate profile as well as activation parameters have been presented, and a free radical mechanism proposed.[481] Reduction in aqueous alcoholic solution by aquated electrons, hydrogen and alkyl radicals was investigated by pulse radiolysis, and found to result in the production of $[IrCl_6]^{3-}$.[482] A kinetic examination of reaction (123) in aqueous solution shows that this outer-sphere electron transfer reaction proceeds by parallel paths first and second order in substrate (SCN^-).[483] The kinetics of the oxidation of hydrazine by $[Ir(Cl)_4(H_2O)_2]$, $[Ir(Cl)_5(H_2O)]^-$, $[IrCl_6]^{2-}$, as well as $[IrBr_6]^{2-}$, in aqueous acidic perchlorate solution have been investigated.[484]

$$6[IrCl_6]^{2-} + SCN^- + 4H_2O \longrightarrow 6[IrCl_6]^{3-} + SO_4^{2-} + CN^- + 8H^+ \quad (123)$$

The *j–j* model has been employed to assign ligand-to-metal charge-transfer bands in the absorption and MCD spectra of $(NBu_4)_2\{trans\text{-}[Ir(Cl)_4(Br)_2]\}$ and $(NEt_4)_2\{trans\text{-}[Ir(Br)_4(Cl)_2]\}$.[485] Irradiation of CT or *d–d* absorption bands of $[IrCl_6]^{2-}$ results in substitution and redox processes.[486] Irradiation at 254 nm (CT bands) produces $[Ir(Cl)_5(H_2O)]^-$ and $[Ir(Cl)_5(H_2O)]^{2-}$; by contrast, *d–d* band irradiation yields only $[Ir(Cl)_5(H_2O)]^-$, except in the presence of added Cl^- when $[IrCl_6]^{3-}$ is formed.

Salts of $[IrBr_6]^{2-}$ are obtained by repeated treatments of the corresponding chloro complexes with HBr. The reaction between $[IrBr_6]^{2-}$ and Cr^{II} proceeds, at least in part, through an inner-sphere redox mechanism in two stages. Initially, Ir^{IV} and Cr^{II} react *via* parallel inner- and outer-sphere paths to give $[(Br)_5Ir^{III}BrCr^{III}(H_2O)_5]$, and $[IrBr_6]^{3-}$ and $[Cr(H_2O)_6]^{3+}$, respectively. Subsequently, the binuclear species dissociates *via* a parallel bond-rupture process to yield $[Ir(Br)_5(H_2O)]^{2-}$ and $[Cr(Br)(H_2O)_5]^{2+}$.[487] The reaction between $[IrCl_6]^{2-}$ and Cr^{II} also proceeds through parallel inner- and outer-sphere reactions.[488] A kinetic investigation of reaction (124) in aqueous solution reveals a similar mechanism to that exhibited in reaction (123).[483]

$$2[IrBr_6]^{2-} + 2I^- \longrightarrow 2[IrBr_6]^{3-} + I_2 \quad (124)$$

49.8 IRIDIUM(V) AND IRIDIUM(VI)

49.8.1 Iridium(V)

Very few iridium(V) (d^4) complexes are known; for those known, hydride or halogen ligands are usually present.

The iridium(V) fluoro complex $[IrF_5]$ has been prepared *via* reduction of $[IrF_6]$ with silicon or dihydrogen.[473] In the gas phase, $[IrF_5]$ possesses D_{3h} symmetry,[489] while in the solid state, a fluoride-bridged polymeric structure with bridges mutually *cis* is indicated on the basis of IR[473] and ^{19}F NMR studies.[490] $M[IrF_6]$ (M = alkali metal) has been obtained from the reaction of $[IrBr_3]$, KBr and BrF_3.[491] $(NO)[IrF_6]$, $[SeF_4][IrF_5]$ and $[SeF_4][IrF_5]_2$ have also been reported.[492]

The pentahydride complexes $[Ir(H)_5(PR_3)_2]$ ($PR_3 = PMe_3$,[493] PEt_2Ph[494]) have been prepared and characterized by IR and NMR spectroscopy. $[Ir(H)_5(PMe_3)_2]$ exhibits one of the most intense Ir—H absorptions at 1920 cm^{-1}. The ^{31}P NMR spectrum of this complex established the presence of five magnetically equivalent hydride ligands.[493] The IR and ^1H NMR spectra of $[Ir(H)_5(PEt_2Ph)_2]$ have also been reported.[494]

49.8.2 Iridium(VI)

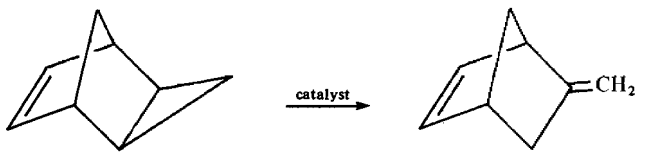
Direct fluorination of metallic iridium at 543 K has produced the rather unstable, yellow d^3 complex $[IrF_6]$, which is isomorphous with its osmium(VI) analogue. $[IrF_6]$ tends toward dissociation, yielding fluorine and lower iridium fluorides. The octahedral $[IrF_6]$ species decomposes in water; this is accompanied by ozone liberation. The magnetic moment of $[IrF_6]$ is $\mu_{eff} = 3.3$ BM at 300 K.[492b]

49.9 CATALYTIC ACTIVITY OF IRIDIUM COORDINATION COMPLEXES

Iridium coordination complexes are known to serve as homogeneous catalysts in a wide variety of reactions, including hydrogenation of C—C multiple bonds, isomerization of alkenes, dienes and alkynes, and oxidation of various organic substrates. In general, the iridium complex catalysts are less active than their rhodium analogues, presumably due to the increased activation energy required for substance coordination as well as the rearrangement within the coordination sphere.

Iridium(I) complexes are well suited for hydrogenation catalysis owing to their ready capability to undergo addition. Vaska-type complexes, $[Ir(X)(CO)(PPh_3)_2]$, iridium(I) and iridium(III) hydride complexes have been shown to catalyze such reactions efficiently; the substrates catalytically hydrogenated by these complexes are collected in Table 3. The isomerization of alkenes and dienes, as well as the oxidation of several organic substrates, are catalyzed by iridium complexes in homogeneous solution; these are summarized in Tables 4 and 5, respectively. Several other types of reactions are catalyzed by iridium complexes in homogeneous solution as well; among them are ring-opening, disproportionation, deuterium exchange, cyclotrimerization, SO_2 elimination, C—H bond activation, decarbonylation (and carbonylation) and hydrogen transfer processes.

In the presence of catalytic amounts of $[Ir(Cl)(CO)(PPh_3)_2]$, *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**221**) rearranges selectively and quantitatively to 5-methylenebicyclo[2.2.1]hept-2-ene (**222**) upon heating at 403 K in benzene (reaction 125).[495] Under similar conditions, *exo,exo*-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane (**223**) rearranges to *exo*-6-methylenetricyclo[3.2.1.$0^{2,4}$]octene (**224**) (reaction 126).[495]



(125)

(221) (222)



(126)

(223) (224)

Table 3 Hydrogenation Catalysts

Catalyst	*Substrate*	*Refs.*
$[IrCl_4]$	Ketones	514
$[Ir(Cl)(CO)(PPh_3)_2]$	Alkenes	500, 515
$[Ir(X)(CO)(PPh_3)_2]$	Alkenes, alkynes	516
$[Ir(X)(CO)(PPh_3)_2]$	Maleic acid	517
$[Ir(X)(CO)(PR_3)_2]$	Alkenes	518–521
$[Ir(Cl)(CO)(PR_3)_2]$	Acid esters	522
$[Ir(Cl)(CO)(PPh_3)_2]$	Unsaturated substrates	523
$[Ir(Cl)(PPh_3)_3]$	Unsaturated substrates	523
$[Ir(H)(CO)(PPh_3)_3]$	Unsaturated substrates	523
$[Ir(H)_3(PPh_3)_3]$	Unsaturated substrates	523
$[Ir(H)_3(PPh_3)_2]$	α-Alkenes, hex-1-ene	524
$[Ir(H)(PPh_3)_2(solvent)]$	α-Alkenes, hex-1-ene	524
$[Ir(H)(CO)(PPh_3)_3]$	Ethylene, acetylene	525, 526
$[Ir(H)(CO)(PPh_3)_3]$	Butadiene	527
$[Ir(H)(CO)(PPh_3)_3]$	Dimethyl maleate	528
$[Ir(H)_2(PPh_3)_2(solvent)_2]$	Cycloocta-1,5-diene, hexa-1,3-diene, norbornadiene, butyraldehyde, alkynes	529,530
$[Ir(H)(Cl)_2(DMSO)_3]$	4-*t*-Butylcyclohexanone	531
$[Ir(H)(Cl)_2(DMSO)_3]$	Diphenylacetylene	532
$[Ir(H)_2(SnCl_3)(PR_3)_2]$	Hept-1-ene	533
$[Ir(Cl)(cod)(PR_3)_2]$	Hex-1-ene	534
$[Ir(OAc)(cod)_2]$	Hex-1-ene	534
$[Ir(OAc)(cod)(PPh_3)]$	Hex-1-ene	534
$[Ir(cod)(PR_3)_2]^+$	cod	535
$[Ir(cod)(PR_3)_2]^+$	Cyclohexenes	536
$[Ir(cod)(py)(PR_3)]^+$	Cyclohexenes	536
$[Ir_2(\mu\text{-}S)(CO)_2(\mu\text{-}dppm)_2]$	Alkenes, alkynes	537

Table 4 Isomerization Catalysts

Catalyst	*Substrate*	*Refs.*
$[Ir(Cl)(CO)(PPh_3)_2]$	Alkenes	518–521, 523
$[Ir(Cl)(CO)(PPh_3)_2]$	Pent-1-ene	538
$[Ir(Cl)(CO)(AsPh_3)_2]$	Cyclohexadiene	539
$[Ir(H)(CO)(PPh_3)_3]$	3-Chlorobut-1-ene, pent-1-ene	520, 521, 523, 538
$[Ir(Cl)_2(C_5Me_5)]_2$	Cyclooctadienes	540
$[Ir(H)(Cl)_2(PEt_2Ph)_3]$	Pent-1-ene	538
$[Ir(Cl)(CO)(O_2)(PPh_3)_2]$	Pent-1-ene	538

Table 5 Oxidation Catalysts

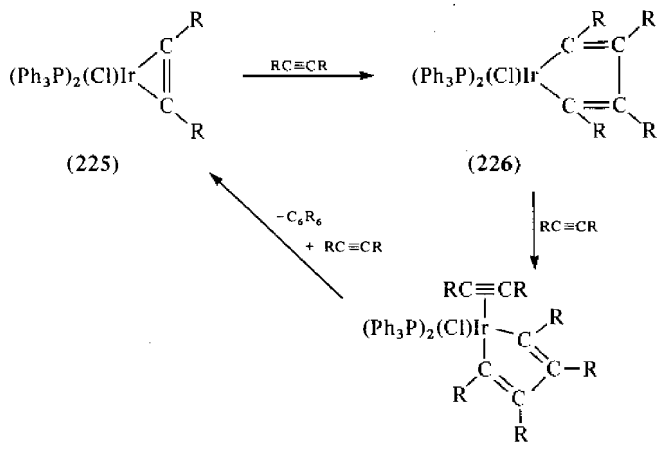
Catalyst	*Substrate*	*Refs.*
$[Ir(Cl)(CO)(PPh_3)_2]$	Ketones	541
$[Ir(Cl)(CO)(PPh_3)_2]$	Styrene	542
$[Ir(X)(CO)(PPh_3)_2]$	PPh_3	542
$[Ir(X)(CO)(PPh_3)_2]$	Alkenes	543
$[Ir(X)(CO)(PPh_3)_2]$	Ketones	541
$[Ir(Cl)(CO)(PPh_3)_2]$	NO, CO	544, 545
$[Ir(Cl)(CO)_2(PPh_3)_2]$	NO, CO	544, 545
$[Ir(Cl)(PPh_3)_3]$	NO, CO	544, 545
$[Ir(CO)_3(PPh_3)_2]^+$	NO, CO	544, 545
$[Ir(Cl)(N_2)(PPh_3)_2]$	NO, CO	544, 545
$[Ir(CO)(PPh_3)_2(solvent)]^+$	NO, CO	544, 545
$[Ir(Br)(NO)_2(PPh_3)_2]$	NO, CO	544, 545
$[Ir(NO)_2(PPh_3)_2]^+$	NO, CO	544, 545
$[Ir(C)(XO)(O_2)(PPh_3)_2]$	α-Methylstyrene, cyclohexene	546
$[Ir(Cl)(cod)]_2$	Cyclooctene	547

The disproportionation of cyclohexa-1,4-diene to benzene and cyclohexane is catalyzed by $[Ir(X)(CO)(PPh_3)_2]$ (X = Cl, I), $[Ir(Cl)(CO)(AsPh_3)_2]$ and $[Ir(H)_2(Cl)(CO)(PPh_3)_2]$.[496] The iridium(I) complex $[Ir(cod)(MeCN)_2]^+$ reportedly catalyzes both the disproportionation of cyclohexa-1,3-diene to benzene and cyclohexene, as well as the isomerization of cyclohexa-1,4-diene to the conjugated isomer.[497] $[Ir(Cl)_2(C_5Me_5)]_2$ catalyzes the disproportionation of acetaldehyde to acetic

acid and ethanol in water in the absence of base.[498] The disproportionation of $PhMeH_2$ is also catalyzed by Vaska's complex.[499]

Barefield *et al.*[493] report that $[Ir(H)_5(ER_3)_2]$ (ER_3 = $PPhEt_2$, PEt_3, PMe_3) catalyzes the exchange between D_2 and benzene, probably *via* oxidative addition of the C—H bond to a coordinately unsaturated intermediate species. Also, Vaska's complex catalyzes the exchange between D_2 and C_2H_4, concomitantly with hydrogenation.[500]

$[Ir(Cl)(N_2)(PPh_3)_2]$ reacts with dialkyl acetylenedicarboxylates to form complex (**225**) *via* N_2 displacement. The complex (**225**) may react with an alkyne at 383 K to yield the iradacyclopentadiene complex (**226**) and then hexasubstituted benzenes (Scheme 23).[501]



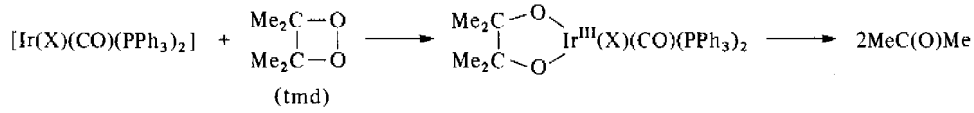
Scheme 23

The elimination of sulfur dioxide from arenesulfonyl chlorides is catalyzed by Vaska's complex,[502] while this same iridium complex apparently catalyzes the aromatization of various 1,4-dihydro derivatives of aromatic hydrocarbons.[503]

The diphosphine complexes $[Ir(dppe)_2]^+$ and $[Ir(dppe)(cod)]^+$ reportedly catalyze the decarbonylation of aldehydes.[504,505] Methanol carbonylation is catalyzed by $[Ir(Cl)_4]\cdot H_2O$ to yield acetic acid. The active species is thought to be an acetyl iridium(III) species, wherein the rate-determining step involves electrophilic attack of this species on methanol. The effects of added iodide ion on reaction rates have also been investigated.[506]

Hydrogen transfer reactions are catalyzed by several iridium complexes, including the dimethyl sulfoxide (DMSO) complexes *cis*- and *trans*-$[Ir(Cl)_4(DMSO)_2]^-$, $[Ir(Cl)_3(DMSO)_3]$ and $[Ir(H)(Cl)_2(DMSO)_3]$,[507] as well as the cyclooctadiene (cod) complexes $[Ir(Cl)(cod)]_2$[508] and $[Ir(3,4,7,8\text{-}Me_4phen)(cod)]^+$,[509] and *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$.[510] Vaska's complex catalyzes the conversion of *p*-methoxybenzoyl chloride to the corresponding aldehyde.[510] The dimethyl sulfoxide iridium(III) complexes catalyze hydrogen transfer from propan-2-ol to unhindered cyclohexanones to yield cyclohexanols,[507] while the cod complexes serve as catalysts in the transfer of hydrogen from propan-2-ol to alkenes, ketones[508] and α,β-unsaturated ketones.[509]

Additionally, $[Ir(X)(CO)(PPh_3)_2]$ (X = Cl, Br) catalyzes the cleavage of tetramethyl-1,2-dioxetane (tmd), presumably *via* reactions depicted in Scheme 24.



Scheme 24

The redistribution of siloxanes has been observed[512] to be catalyzed by Vaska's complex. The water-gas shift reaction is homogeneously catalyzed by iridium complexes, including $[Ir(L)_2(cod)]^+$ where $(L)_2$ is $(PMePh_2)_2$, $(PPh_3)_2$, dppe, phen, 4,7-Ph_2phen, 4,7-Me_2phen, 3,4,7,8-Me_4phen or phenS (phenS = 4,7-diphenyl-1,10-phenanthrolinesulfonate). The catalytic activity increases for those catalysts with bidentate (L_2) ligands and is sensitive to temperature.[513]

49.10 AD INTEGRATUM

The activity in the chemistry of iridium remains unabated. Since the writing of this chapter, several hundred papers have been published that are germane. These have been integrated below in terms of ligands bound to Ir.

49.10.1 Nitrosyl Ligands

The iridium(I) nitrosyl complex $[Ir(NO)(PPh_3)_3]$ reacts with perfluorocarboxylic acids RCO_2H in the presence and absence of O_2 to yield $[Ir(NO)(O_2CR)_2(PPh_3)_2]$. A crystal structure determination of the trifluoroacetate derivative $[Ir(NO)(O_2CCF_3)_2(PPh_3)_2]$ reveals an essentially trigonal bipyramidal coordination about Ir, with an equatorial linear NO ligand, unidentate carboxylate ligands and axial PPh_3 ligands.[548] NMR spectroscopy and gas uptake/evolution measurements have elucidated the role of O_2 in the conversion of $[Ir(NO)(PPh_3)_3]$ to $[Ir(NO)(O_2CCF_3)_2(PPh_3)_2]$.[549] The reaction of $[Ir(NO)(dppn)(PPh_3)_2](PF_6)_2$ or $[Ir(X)(NO)(dppn)(PPh_3)_2](PF_6)$ (dppn = bis(2′-pyridyl)pyridazine; X = Cl, Br, I) with $[Pd(Cl)_2(PhCN)_2]$ or with $[Pt(I)_2(cod = cyclooctadiene)$ gives mixed metal binuclear species, *e.g.* $[Ir(NO)(dppn)(PPh_3)_2(PdCl_2)](PF_6)_2$. IR and ^{31}P NMR spectroscopic results and conductivity measurements suggest a structure possessing a bridging NO, *i.e.* [Ir—N(O)—Pd].[550]

49.10.2 Nitrogen

The compounds $[Ir(cod)L_2](BF_4)$ have been prepared for which L is benzonitrile (bzn), phenylacetonitrile ($PhCH_2CN$), 4-methoxybenzonitrile (4-MeObzn) and 2-chlorobenzonitrile (2-Clbzn).[551] IR spectra are consistent with the coordination of the benzonitrile ligand *via* the free electron pair of the nitrogen atom. Also, the complexes $[Ir(cod)L_2]A$, where L = 2-methylpyridine, 2-ethylpyridine, 5-nitro-6-methylquinoline, quinoline, 4,7-dichloroquinoline and [Ir(cod)(L—L)]A, where L is succinonitrile, 8-aminoquinoline, ethylenediamine, 1,2-diphenylethylenediamine, and *N,N,N′,N′*ptetramethylethylenediamine, have also been synthesized.[551] Nitriles, $Na(RCN)_4$, add to azide ligands of $[Ir(N_3)(CO)(PPh_3)_2]$ to give the 5-R-tetraazolato complexes $[Ir(CO)(N_4CR)(PPh_3)_2]$ (R = Me, CF_3).[552] Amino-, phosphino- and thionitriles also add, *via*, 1,3-cycloaddition, to azide ligands of $[Ir(N_3)(CO)(PPh_3)_2]$ to give corresponding 5-*R*-tetraazolato complexes.[553]

The dinuclear iridium(I) complex $[Ir(CO)(PPh_3)(\mu\text{-pz})]_2$ (pzH = pyrazolyl, $C_3N_2H_4$) is afforded *via* reaction between $[Ir(Cl(CO)(PPh_3)_2]$ and Napz.[554] The analogous complex $[Ir(cod)(\mu\text{-pz})]_2$ is obtained by reaction of $[IrCl(cod)]_2$ with pzH, followed by CO and PPh_3 treatment. The product reacts with I_2 or Br_2 to form $[IrX(CO)(PPh_3)(\mu\text{-pz})]_2$ (X = I, Br), and with Cl_2 to give $[Ir(Cl)(CO)(PPh_3)(4\text{-Clpz})]_2$.[555] The synthesis and characterization of a number of iridium(I) complexes containing the bidentate, chelating pyrazolylgallate ligand Me_2Gapz has been reported.[556] Crystal structural studies of $[Ir(cod)(Me_2Gapz)]$, $[Ir(CO)_2(\mu\text{-pz})]_2$ and $[Ir(CO)_2(\mu\text{-3,5-Me}_2pz)]$ have confirmed the expected boat conformations for the six-membered M—(N—N)$_2$—Ir rings (M = Ir, Ga).

Oxidative addition of MeI to the iridium(I) complex $[Ir(\mu^2\text{-}C_8H_{14})\{N(SiMe_2CH_2PR_2)_2\}]$ (R = Ph, Pr^i) yields monomeric, five-coordinate complexes of the type $[Ir(I)(Me)\{N(SiMe_2CH_2PR_2)_2\}]$. Spectroscopic and crystallographic measurements reveal the complexes to have a square pyramidal geometry with the methyl ligand in an apical position. In the presence of H_2, these complexes rapidly form the iridium(III) amine hydrides $[Ir(I)(H)(Me)\{NH(SiMe_2CH_2PR_2)_2\}]$ with a stereochemistry corresponding to an overall *trans* addition of H_2.[557] It appears that H_2 activation by these iridium complexes occurs *via* an oxidative addition/reductive transfer pathway rather then a direct heterolytic cleavage of H_2.

$[Ir(Cl)_3(PPh_3)_3]$ reacts with NaN_3 in alcoholic solution giving *cis*-$[Ir(H)_2(N_3)(PPh_3)_3]$; on exposure to light, the product releases H_2 and $[Ir(N_3)(PPh_3)_3]$ in a reversible manner. The crystal structure of the dihydride shows one H ligand is *trans* to N_3 and the other H ligand is *trans* to a PPh_3 ligand.[558]

Base hydrolysis of *cis*-$[Ir(Cl)_2(en)_2](Cl)$ gives *cis*-$[Ir(OH)(en)_2(H_2O)](S_2O_6)$ in 80% yields. By contrast, a 3:2 mixture of *cis*- and *trans*-$[Ir(OH)(en)_2(H_2O)](ClO_4)_2$ is obtained from the base hydrolysis of *trans*-$[Ir(Cl)_2(en)_2](Cl)$, as indicated by chemical analyses, electronic spectra and potentiometric titrations. The concentration acidity constants are: $K_{a1} = 10^{-6.290\pm0.007}$ and

$K_{a2} = 10^{-8.097\pm0.009}$ mol l^{-1} for the *cis* isomer, and $K_{a1} = 10^{-4.798\pm0.004}$ and $K_{a2} = 10^{-7.856\pm0.010}$ mol l^{-1} for the *trans* isomer.[559] The properties of the iridium(III) species $[Ir(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$ were characterized by EPR spectroscopy, magnetic susceptibility measurements and X-ray diffractometry. The crystal structure suggests layers of magnetically inequivalent $Cu_2Cl_8^{4-}$ dimers with antiferromagnetic intradimer coupling. The dimers appear well separated by large $[Ir(en)_3]^{3+}$ dimagnetic complexes.[560]

Complexes of the type $[Ir(H)_2L'(PPh_3)_2]A$ (L′ = 8-methylquinoline, caffeine) each posses a C—H---Ir bridge, structurally characterized for the methylquinoline case where A = SbF_6. On the basis of the C—H + M → C—M—H reaction trajectory, the authors propose that for a given metal species capable of breaking C—H bonds,[561] conformational and steric effects will play an important role in determining whether cyclometallation or attack on an external substrate (*e.g.* alkane) will occur. Moreover, it would seem that sterically uncongested metal systems will favour the occurrence of alkane activation, rather than cyclometallation.[561] The triply *o*-metallated complex *fac*-$[Ir(ppy)_3]$ (ppy = 2-phenylpyridine) has been characterized in its ground and luminescent excited states.[562] The dichloro-bridged dimers $[Ir(Cl)L_2]_2$ (L = 2-phenylpyridine (ppy), benzo[*h*]quinoline (bzq)] were investigated by ^{13}C and ^1H NMR and by absorption and luminescence spectroscopy. The NMR results confirm previous formulation of the complex as dichloro-bridged *o*-metallated dimers in halocarbon solvents, but indicate they are cleaved to monomeric species of the type $[Ir(Cl)L_2(S)]$ (S = solvent, *e.g.* DMF) in ligating solvents S. Comparison of the results suggests that the *o*-metallated ligands are considerably higher than bipy or phen in the spectrochemical series.[563] The observations are consistent with the synergistic function of the *o*-metallated ligands as both strong σ donors and π acceptors.

cis-$[Ir(bipy)_2(OSO_2CF_3)_2](CF_3SO_3)$ has been isolated and employed in the synthesis of new hydrido complexes of iridium(III): *cis*-$[Ir(H)(bipy)_2(PPh_3)](PF_6)_2$ and *cis*-$[Ir(H)_2(bipy)_2](PF_6)$. Additionally, an improved high-yield synthesis of $[Ir(bipy)_3](PF_6)_3$ has been reported.[564] The two *bis* bipyridyl complexes have interesting spectral and electrochemical properties. Ohashi and Nakamura[565] have obtained the emission decay curves of *cis*-$[Ir(Cl)_2(bipy)_2](Cl)$, *cis*-$[Ir(Cl)_2(phen)_2](Cl)$, *cis*-$[Ir(Cl)_2(4,7\text{-}Me_2phen)_2](Cl)$ and *cis*-$[Ir(Cl)_2(5,6\text{-}Me_2phen)_2](Cl)$. The spectra exhibit a dependency on the solvent character of the DMF/H_2O mixed solvents at 77 K and at 298 K. It appears there are at least two kinds of emitting states for these species in DMF/H_2O solvents. The iridium(III) bipyridyl complex $[Ir(C^3,N'\text{-bipy})(bipy)_2]^{2+}$ is an attractive photosensitizer in aqueous bromide solutions. Based on product analysis, steady-state emission and pulsed laser experiments, the photosensitization proceeds along a mechanism that involves two exciplexes and the transients $Br_2^- \cdot$ and HO_2.[566]

The complexes of *p*-dimethylaminoanil and of 3-acetyl-4-hydroxycoumarin glyoxal with some third row transition metal ions (Ir^{3+}, Pr^{4+}, UO_2^{2+}) have been produced, and $[Ir(C_{19}H_{15}O_4N_2)_2](Cl)$ has been characterized by IR spectroscopy and magnetic measurements.[567]

The thermally stable, Schiff base complexes $[M(PPD)(Cl_x] \cdot yH_2O$ (M = Ir, Pt; $x = 4$; PPD = *p*-$Me_2C_6H_4CH{=}N(CH_2)_3NH_2$) have been prepared; characterization by IR spectroscopy shows the dimethylamino and free amino groups to be the coordinating sites. Further characterization by magnetic moment measurements and NMR and electronic spectral data indicates the iridium(IV) complex to be octahedral.[568]

49.10.3 Phosphorus Ligands

The complexes *trans*-$[Ir(Cl)L\{P(CHMe_2)_3\}_2]$ (L = CO, py, MeCN) were prepared from $[Ir(Cl)(cod)_2]_2$ *via* the intermediate $[Ir(Cl)\{P(CHMe_2)_3\}_2]$ complex. *trans*-$[Ir(Cl)(CO)\{P(CHMe_2)_3\}_2]$ reacts with LiC_2Ph to give *trans*-$[Ir(C_5Ph)(CO)\{P(CHMe_2)_3\}_2]$, which, on treatment with HX, yields $[Ir(H)(X)C_2Ph(CO)\{P(CHMe_2)_3\}_2]$ (X = Cl, CF_3CO_2). *trans*-$[Ir(Cl)(N_2)\{P(CHMe_2)_3\}_2]$ is obtained from the carbonyl complex and 2-furfuryl azide.[569] Some new mono- and di-nuclear iridium(I) complexes containing the *bis*(tertiary phosphine) ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 2$, dppe; $n = 3$, dppp) have been prepared, and the formation of iridium(III) hydrides by H_2 oxidative addition has been studied by Fisher and Eisenberg.[570] The dinuclear complexes $[Ir(X)(CO)(dppp)]_2$ (X = Br, I) possess *trans* phosphine donors, with the dppp ligands bridging the iridium(I) centre. All the dppp complexes are mononuclear, with dppp serving as a chelating ligand. The complexes $[M(CN)_2(dppmP)_2]$ (M = Pt, Pd), when treated with $[Ir(Cl)(CO)_2(NH_2C_6H_4Me\text{-}p)]$ or *trans*-$[Ir(Cl)(CO)(PPh_3)_2]$, give the heterometallics $[Ir(Cl)(CO)(\mu\text{-dppm})_2M(CN)_2]$.[571] The treatment of $[Ir(CNB^t)_2(\mu\text{-dppm})]_2(Cl)_2$ with dppm gives labile systems at 293 K. At 213 K, ^{31}P–^1H NMR spectroscopy reveals complete conversion to the *tris*-monodentate dppm complexes

$[Ir(CNBu^t)_2(dppmP)_3](Cl)$. Reaction of $[Ir(Cl)(cod)_2]_2$ with four equivalents of dppm, six equivalents of Bu^tCN, and two equivalents of $[Au(Cl)(PPh_3)]$ yields the fluxional molecule $[Ir(CNBu^t)_3(\mu\text{-dppm})_2Au](Cl)_2$; however, reaction between $[Ir(CO)(dppmPP')_2](Cl)$ and $[Ag(Cl)(CNBu^t)]$ affords $[Ir(CNBu^t)(CO)(\mu\text{-dppm})_2Ag(Cl)]$.[572]

Some novel five-coordinate iridium(I) complexes of the type $[Ir(CO)(chel\text{-}P_3)(R)]$ (chel-P_3 = $PhP(CH_2CH_2CH_2PPh_2)_2$, R = CH_2CMe_3, CH_2SiMe_3; chel-P_3 = $MeP(CH_2CH_2CH_2PPh_2)_2$, R = CH_2SiMe_3; chel-P_3 = $PhP(CH_2CH_2PPh_2)_2$, R = CH_2SiMe_3, 4-MeC_6H_4) have been synthesized from $[Ir(CO)(PPh_3)_2(R)]$ and the respective triphosphine. ^{31}P NMR studies show these complexes to be stereochemically rigid at normal temperatures.[573] Reaction between $[Ir(\eta^4\text{-cod})(\eta^3\text{-}2\text{-}XC_3H_4)]$ (X = Me, H) and di-*t*-butylphosphine gives $[Ir(\eta^4\text{-cod})(\eta^3\text{-}C_3H_5)\{PH(Bu^t)_2\}]$. X-Ray crystallographic investigations suggest that where X = Me the complex possesses the square pyramidal geometry with the phosphine ligand in an axial position.[574]

In the complex $[Ir(\eta^2\text{-}o\text{-}BrC_6H_4PPh_2)(cod)](SbF_6)$, $o\text{-}BrC_6H_4PPh_2$ chelates to Ir *via* P and the Br bound to the aromatic ring. The complex reacts with Cl^- to give $[Ir(Cl)(\eta'\text{-}BrC_6H_4PPh_2)(cod)]$, with MeCN to produce $[Ir(\eta'\text{-}BrC_6H_4PPh_2)(cod)(MeCN)](SbF_6)$, and with H_2 to yield $[Ir(H)_2(\eta^2\text{-}o\text{-}BrC_6H_4PPh_2)(cod)(SbF_6)$.[575] Reaction between Vaska's complex and the phosphine–thiol chelate (diphenylphosphino)ethanethiol (PSH) gives $[Ir(H)(CO)(PS)(PSH)](Cl)$.[576] Two equivalents of *o*-(diphenylphosphino)benzoylpinacolone (HacacP) react with $[Ir(Cl)(CO)_2(p\text{-}NH_2C_6H_4Me)]$ giving $[Ir(Cl)(CO)(HacacP)_2]$, which undergoes smooth metallation with copper(II) carboxylates to give $[Ir(Cl)(CO)\{Cu(acacO)_2\}]$. The *trans*-$[Ir(Cl)(CO)\{Zn(acacP)_2\}]$ complex can be synthesized by treating $ZnEt_2$ with two equivalents of HacacP followed by $[Ir(Cl)(CO)_2(p\text{-}H_2NC_6H_4Me)]$. EPR data for the Ir—Cu complex indicate the formation of an enolate bridge between Ir and Cu.[577]

The solid state structure of $[Ir(Cl)(PF_3)_2]_2$ consists of infinite zigzag chains of Ir atoms with short inter- and intra-molecular Ir---Ir contacts. By contrast, related complexes containing PF_2NMe_2, *e.g.* $[Ir(Cl)(PF_2NMe_2)_3]$ and $[Ir(Cl)(PFNMe_2)_2]_2$, do not appear to have extended metal–metal interactions.[578] ^{31}P spin–lattice relaxation times T_1, and ^{31}P–^1H nuclear Overhauser enhancement values for $CDCl_3$ solutions of the compounds $P(C_6H_4\text{-}p\text{-}X)_3$, $[Ir(Cl)(CO)\{P(C_6H_4\text{-}p\text{-}X)_3\}_2]$ (X = H, Me, F, Cl, OMe) and $[Au(Cl)\{P(C_6H_4\text{-}p\text{-}X)_3\}]$ (X = H, OMe) have been determined.[579] For the uncoordinated tertiary phosphines T_1 = 26–28 s, except for X = OMe, where T_1 = 14 s. For the iridium(I) complexes, T_1 = 4.4–8.7 s, whereas for the gold(I) compounds, T_1 = 15.7 s (H) and 11.3 s (OMe). Differing relaxation mechanisms within each class of compound seem to be indicated by the data.[579]

Vaska's complex reacts with F-*t*-butyl hypochlorite to yield a complex tentatively postulated as $[Ir(Cl)(CO)\{(CF_3)_3CO\}_2(L)_2]$, where L presumably is a complex ligand containing $(CF_3)_3CO$ and Cl groups.[580] Stang and coworkers[581] have determined the k_H/k_{D3} (= secondary kinetic deuterium isotope effect) values for the reaction of $[Ir(Cl)(CO)(PPh_3)_2]$ with MeI (k_H/k_{D3} = 0.93) and MeO-SO_2CF_3 (k_H/k_{D3} = 1.13) at 308 K in toluene. The values are consistent with a Menschutkin-type S_N2 displacement process. Reaction of Vaska's complex with $Li[W(CO)_5(PPh_2)]$ yields the dinuclear complex $[IrW(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2]$. Also, reaction between Vaska's complex and $Li[W(CO)_4(PPh_2H)(PPh_2)]$ gives $[IrW(H)(CO)_5(\mu\text{-}PPh_2)_2(PPh_3)_2]$, characterized by X-ray diffractometry. The hexacarbonyl complex above adds H_2 and CO at the Ir centre, while the pentacarbonyl complex reacts with LiPh and LiMe to yield the acyl–halide derivatives $[Li(THF)_x][IrW(H)(CO)_4(\mu\text{-}PPh_2)_2(PPh_3)C(O)R]$ (R = Ph, Me) with the acyl ligand terminally bound to W and the hydride to Ir.[582] PH_3 adds oxidatively in toluene to *trans*-$[Ir(X)(XO)(PEt_3)_2]$ (X = Br, Cl) to give $[Ir(X)(H)(CO)(PEt_3)_2(PH_2)]$. The $[Ir(X)(H)(CO)(PEt_3)_2(AsH_2)]$ complexes have also been isolated. The complexes were characterized by ^1H and ^{31}P NMR spectroscopy. $[Ir(H)(CO)(PEt_3)_2(PH_2)(PH_3)]^+$ is produced upon reaction of *trans*-$[Ir(X)(CO)(PEt_3)_2]$ and PH_3 in CH_2Cl_2 at 180 K, followed by internal oxidative addition at greater than 230 K.[583]

Dimethyl- and diethyl-phosphine oxide, methylphosphonite, and ethylmethylphosphonite all add oxidatively to $[Ir(Cl)(Me_2PhP)_3]$ to produce hydrido(dialkylphosphinito) or alkyl(alkylphosphinito) iridium(III) complexes, $[Ir(Cl)(H)(PPhMe_2)_3\{P(O)RR'\}]^+$. The nature of these species was ascertained by ^1H and ^{31}P NMR.[584] $[Re(H)_3(\eta^4\text{-}C_5H_6)(PPh_3)_2]$ reacts with $[Ir(Br)(CO)(dppe)]$ in C_6D_6 to give $[Re(H)_2(Cp)(PPh_3)_2]$ and $[Ir(Br)(H)_2(CO)(dppe)]$. The isomer of the iridium complex formed exclusively is the thermodynamically favoured isomer having H *trans* to P and Br. The driving force for the dehydrogenation of the Re complex by the Ir complex is attributed to the stronger M—H bond for iridium and the greater thermodynamic stability of the dehydrogenated product $[Re(H)_2(Cp)(PPh_3)_2]$.[585]

Homobimetallic iridium(I) complexes containing the binucleating PNNP ligand undergo oxidative addition and reductive elimination reactions with acetyl chloride and methyl iodide. Thus,

$[Ir_2(\mu\text{-}PPh_2)(CO)(PNNP)]$ reacts in two successive irreversible oxidative addition steps with either acetyl chloride or methyl iodide to give the diacyl $[Ir_2(\mu\text{-}PPh_2)(CO)_2(PNNP)(MeCO)_2(Cl)_2]$ and dimethyl $[Ir_2(\mu\text{-}PPh_2)(CO)_2(PNNP)(Me)_2(I)_2]$ complexes, respectively, in which iridium is Ir^{III}.[586]

The hydrido-bridged dinuclear complexes $[Ir(Cl)(L)_3(\mu\text{-}H)(\mu\text{-}Cl)Rh(dppe)]^+$ can be prepared by reacting $[Rh(acetone)_2(dppe)]^+$ with *mer,trans*-$[Ir(Cl)_2(H)(L)_3]$ (L = PMe_2Ph, PEt_2Ph, PEt_3, dppe). The X-ray crystal structure of the dinuclear complex shows a distorted octahedral coordination around Ir. In a similar manner, one can produce the isoelectronic complex $[Ir(H)(PEt_3)_3(\mu\text{-}Cl)(\mu\text{-}H)Rh(dppe)](BF_4)$ from *mer,cis*-$[Ir(Cl)(H)_2(PEt_3)_3]$.[587] $[Ir(H)_5(PEt_3)_2]$ reacts with complexes containing the 'RhClL$_2$' moiety (L = PEt_3 or L_2 = dppe) to give $[Ir(H)_2(PEt_3)_2(\mu\text{-}Cl)(\mu\text{-}H)Rh(L)_2]$. The crystal structure of $[Ir(H)_2(PEt_3)_2(\mu\text{-}Cl)(\mu\text{-}H)Rh(PEt_3)_2]$ indicates a distorted octahedral geometry about Ir, with the bridging chlorine atom asymmetrically bonded to both Ir and Rh.[588]

Reaction of Vaska's complex with the functionalized silanes $PPh_2CH_2CH_2SiR'R''H$ (R′ = R″ = Me, Ph; R′ = Me, R″ = Ph; R′ = Me, Ph, R″ = H) yields the iridium(III) adducts $[Ir(Cl)(^nH)(CO)(PPh_2CH_2CH_2SiR'R'')(PPh_3)]$ (n = 1, 2). The complexes are chiral at Ir; however, while the complexes with R′ = R″ = Me and R′ = R″ = Ph are enantiomeric, those with R′ = Me, R″ = Ph, R′ = Me, R″ = H, and R′ = Ph, R″ = H are diastereomeric.[589] The five-coordinate iridium(III) complex $[Ir(Cl)(PPh_2CH_2CH_2SiMe_2)_2]$, prepared *via* reaction of $[Ir(Cl)(cod)]_2$ and excess $PPh_2CH_2CH_2SiMe_2H$ in THF solution, has been characterized by IR and ^1H NMR spectroscopy and by X-ray diffractometry. The complex reacts with NaX (X = Br, I) in acetone to give $[Ir(X)(PPh_2CH_2CH_2SiMe_2)_2]$.[590] Auburn *et al.*[591] have described the synthesis of a chelate-silyl iridium(I) complex from iridium(III) *via* reductive elimination. Thus, photolysis of $[Ir(H)_2(CO)(PPh_2CH_2CH_2SiMe_2)(PPh_3)]$ evacuated in THF gives < 30% yield of $[Ir(CO)(PPh_2(CH_2CH_2SiMe_2)(PPh_3)]$. In a CO atmosphere, the same reaction gives > 80% yield of the same product. Crystal structural studies of the iridium(I) complex show a five-coordinate Ir atom with Si in an axial position *trans* to PPh_3, and two CO ligands in the equatorial plane.[591]

Rhodes and coworkers[592] have reported on the unexpected results of reaction between Cu^I and the *mer* and *fac* isomers of $[Ir(H)_3(P)_3]$, where P is PMe_2Ph. ^1H NMR spectroscopy has identified $[\{mer\text{-}Ir(H)_3(P)_3\}_2Cu](PF_6)$ as the product of reaction between $[Cu(MeCN)_4](PF_6)$ and two equivalents of *mer*-$[Ir(H)_3(P)_3]$ in THF. In the addition of $[Cu(MeCN)_4(PF_6)$ to $[\{fac\text{-}Ir(H)_3(P)_5\}_2Cu](PF_6)$, there is no conversion of the *fac* to the *mer* isomer in MeCN at 298 K over several hours. The Ag^I adduct of *fac*-$[Ir(H)_3(P)_3]$ has also been synthesized.[592] The stoichiometric protonation of *fac*-$[Ir(H)_3(P)_3]$ in $CDCl_3$ using $HBF_4 \cdot Et_2O$ shows complete conversion to $[Ir(H)_4(P)_3]^+$. The latter possess a pentagonal bipyramidal structure at 193 K. Protonation of *mer*-$[Ir(H)_3(P)_3]$ yields an identical product. Although spectroscopically undetectable, H_2 elimination from $[Ir(H)_4(P)_3]^+$ would seem to give rise to $[Ir(H)_2(L)(P)_3]^+$ (L = N_2, CO, MeCN). In essence, what has occurred is reductive elimination (Ir^V to Ir^{III}).[593] An investigation of the Cu^+/*fac*-$[Ir(H)_3(PMe_2Ph)_3]$ system at Ir:Cu stoichiometries of less than 2:1 has led to evidence of an unexpected yet isolable aggregate. At an Ir:Cu ratio of 2:3, the product is consistent with the formulation $[Ir_2Cu_3(H)_6(MeCN)_3(PMe_2Ph)_6](PF_6)_3$.[594]

The X-ray crystal structure of $[Ir(Cl)_2(C_3H_5)(CO)(PMePh_2)_2]$[595] and $[Ir_4(CO)_8(PMe_2Ph)_4]$[596] have been determined.

49.10.4 Arsenic and Antimony Ligands

Pentacoordinate iridium(I) complexes of the general formula $[Ir(Cl)L_2(TFB)]$ or $[Ir(Cl)(L{-}L)(TFB)]$ (TFB = tetrafluorobenzobicyclo[2.2.2]octatriene; L = PPh_3, $AsPh_3$, $SbPh_3$; L—L = dppe, bipy, phen) have been synthesized from $[Ir(Cl)(TFB)_2]$ and the appropriate ligand.[597] Bis(diphenylphosphinomethyl)phenyl arsine, dpma, reacts with $[Ir(Cl)(CO)(p\text{-toluidine})]$ to give $[Ir_2(Cl)_2(CO)_2(\mu\text{-dpma})_2]$. The latter dimeric complex subsequently reacts with bis(benzonitrile)palladium(II) chloride in CH_2Cl_2 to obtain $[Ir_2Pd(Cl)_3(CO)_2(\mu\text{-dpma})_2](BPh_4)$. The dpma ligand is sufficiently flexible for it to accommodate a range of metal–metal interactions within the polynuclear units.[598]

49.10.5 Oxygen Ligands

Homo- and hetero-dinuclear bis(di-μ-amide or -oxo)iridium(I) complexes of formula $[MM'(\mu\text{-}L)(cod)_2]$ (L = 1,8-$(NH_2)_2$naphthalene, 1,8-$(O)_2$naphthalene, 2,3-$(O)_2$naphthalene) have been synthesized and characterized by IR spectroscopy.[599] Two different routes to the preparation of the first

iridium(I) carbon-bonded diketonate complex, [Ir(acac-C^3)(cod)(phen)], have been reported.[600] The crystal structure of this complex reveals pentacoordinate iridium in a distorted pyramidal stereochemistry. The synthesis and characterization of binuclear complexes containing the flexible bridging bis(2,4-pentanedionato) ligand have been cited.[601] Thus, $[Ir(cod)]_2\{xyl(acac)_2\}]$ is afforded upon reaction of $[Ir(\mu\text{-Cl})(cod)]_2$ with *p*-silylenebis[3-(2,4-pentanedione)], xyl(Hacac)$_2$. The methylene complexes $[Ir(I)(CO)(=CH_2)(PPh_3)_2]$ and $[Os(Cl)(NO)(=CH_2)(PPh_3)_2]$ form 1:1 adducts with SO_2, and an X-ray crystal structure determination of the osmium complex shows the sulfene fragment in $[Os(Cl)(NO)\{CH_2S(O)O\}(PPh_3)_2]$ to be C,O-bound forming a non-planar, four-membered ring with the S atom having pyramidal geometry.[602]

49.10.6 Boron Ligands

Reaction between $K[B_4H_9]$ and *trans*-$[Ir(Cl)(CO)(PMe_2Ph)_2]$ in the presence of an additional equivalent of KH gives $[Ir(\eta^4\text{-}B_4H_9)(CO)(PMe_2Ph)_2]$. In the crystalline state, this iridapentaborane consists of an open five-atom cluster in which the $[Ir(CO)(PMe_2Ph)_2]$ fragment occupies an apical vertex site and is bound to the four boron atoms of the $(\eta^4\text{-}B_4H_9)$ ligand.[603] $Li[CB_8H_{13}]$ reacts with $[Ir(Cl)(PPh_3)_3]$ in diethyl ether to produce several products, including *closo*-[1-PPh_3)-2,2,2-$H(PPh_3)_2$-2,10-$IrCB_8H_8$]. An X-ray diffraction study of this *closo* complex shows the ten-vertex cage to have bicapped Archimedean square antiprismatic geometry, with Ir in an equatorial position. The apical sites are occupied by the carbon, and a boron covalently bonded to the P of a PPh_3 ligand.[604] NMR spectroscopy characterized the *arachno*-6,9-dimetalladecarborane complex $[(PMe_3)_2Pt\text{-}B_8H_{10}Ir(H)(PMe_3)_2(CO)]$, obtained on deprotonation of an *arachno*-4-iridanoborane with KH followed by reaction with *cis*-$[Pt(Cl)_2(PMe_3)_2]$. Mild thermolysis or UV photolysis of the *arachno*-4-iridanoborane produces the corresponding *nido*-2-iridanoborane. This is the first *nido* nine-vertex metalloborane to be structurally characterized. The *arachno* → *nido* transformation, occurring *via* dihydrogen loss, follows first-order kinetics.[605]

49.10.7 Sulfur and Selenium Ligands

Claver and coworkers[606] have prepared the cationic iridium(I) complexes $[Ir(cod)(\mu\text{-L})]_2(ClO_4)_2$ and $[Ir(cod)\{\mu\text{-(L—L)}\}]_2$, where L is SMe_2, SEt_2, tetrahydrothiophene (tht), or trimethylene sulfide (tms), and (L–L) is 1,4-dithiacyclohexane (dt), $(SBu^t)_2(CH_2)_2$ (tmdto), or $(SMe)_2$. These same authors have also isolated the mononuclear complexes $[Ir(cod)(L)_2](ClO_4)$ (L = tht, tms) and [Ir(cod)(L—L)](ClO_4) (L—L = dth).[607] These react with H_2 to give the corresponding iridium(III) dihydride complexes, with $[Ir(cod)(L)_2]^+$ (L = tht, tms) react with one or two moles of PPh_3 to yield the pentacoordinate derivatives $[Ir(cod)(L)_2(PPh_3)]^+$ or $[Ir(cod)(L)(PPh_3)_2]^+$.

The thiolato-bridged dinuclear iridium(I) complexes $[Ir(CO)(L)(\mu\text{-}SBu^t)]_2$ react with dihalomethane to produce $[Ir(X)(CO)(\mu\text{-}SBu^t)]_2(\mu\text{-}CH_2)$ (X = I, L = CO, $P(OMe)_3$, PPh_3, PPh_2Me, PMe_2; X = Br, L = PPh_3). A crystal structure determination of $[Ir(I)(CO)(\mu\text{-}SBu^t)\{P(OMe)_3\}]_2(\mu\text{-}CH_2)$ reveals Ir to be octahedrally coordinated to one CO, one $P(OMe)_3$, one I, two bridging S atoms of the thiolato ligands, and the bridging C atom of the CH_2 group. The phosphite ligands are mutually *trans*, as are the carbonyl ligands.[608] $[Ir(dppe)_2(S_2O)]^+$ reacts with $MeOSO_2F$ to yield $[Ir(dppe)_2(\eta^2\text{-}S_2OMe)]^{2+}$, which has been characterized by X-ray crystallography, and which can be converted to $[Ir(dppe)(MeCN)(\eta^1\text{-SOMe})]^{2+}$ upon reaction with two equivalents of MeCN.[609] Teo and Snyder-Robinson[610] have elucidated the crystal structure of $[Ir(X)(CO)(PPh_3)_2(TCTTN)]\cdot C_6H_6\cdot MeCN$ (X = Cl, H; TCTTN = tetrachlorotetrathionaphthalene, $C_{10}Cl_4S_4$). The Ir atom is octahedrally coordinated to two *trans* PPh_3 ligands, two S atoms from TCTTN, one CO ligand and one X ligand. Crystallographic studies have characterized $[Ir(Cl)(H)(CO)(PPh_3)_2(SH)]$, obtained *via* reaction of Vaska's complex with H_2S in CH_2Cl_2 solutions.[611]

The stepwise oxidation of $[Ir(dppe)_2(\eta^2\text{-}S_2)](PF_6)$ with *m*-chloroperbenzoic acid gives $[Ir(dppe)_2(\eta^2\text{-}S_2O)](PF_6)$ and $[Ir(dppe)_2(\eta^2\text{-}S_2O_2](PF_6)$. Oxidation of $[Ir(dppe)_2(\eta^2\text{-}Se_2)](PF_6)$ with peracetic acid affords $[Ir(dppe)_2(\eta^2\text{-}Se_2O)](PF_6)$. Though the preparation of η^2- or η^2-OSO complexes *via* selective sulfur-abstraction reactions is not possible, the unsymmetrical dichalcogenide complex $[Ir(dppe)_2(\eta^2\text{-SSe})]^+$ can be prepared from $[Ir(dppe)_2](Cl)$ and $[Ti(Cp)_2S_xSe_{5-x}$ $(x \approx 3)$.[612] Complete reduction of the selenocarbonyl ligand of $[Ir(Cl)(CSe)(PPh_3)_2]$ by $NaBH_4$ in the presence of PPh_3 produces $[Ir(H)_2(PPh_3)_3(SeMe)]$. Additionally, CSe_2 reacts with $[Ir(Cl)(CSe)(PPh_3)_2]$ to form the iridium(III) adduct $[Ir(Cl)(\eta^2\text{-}CSe_2)(CSe)(PPh_3)_2]$.[613]

49.10.8 Halide Ligands

$[Ir(Cl)_6(H)_2]$ can be prepared *via* the electrochemical dissolution of powdered iridium in HCl. The rate of dissolution was studied as a function of current density, HCl solution concentration, temperature, and as a function of the number of bipolar electrodes.[614] The first Cl-containing compound of iridium(V) has been isolated from reaction between $[Ir(Cl)_6]^{2-}$ and BrF_3 in liquid HF giving $[Ir(Cl)_{6-n}(F)_n]^-$ ($n = 1$–6). The deep red $Cs[Ir(Cl)(F)_5]$ has been characterized by IR and Raman spectroscopy.[615]

49.10.9 Hydride Ligands

Oxidative addition of H_2 to the iridium(I) chelates $[Ir(X)(CO)(dppe)]^{n+}$ ($n = 0$, X = Cl, Br, I, CN, H; $n = 1$, X = PPh_3, dppe) proceeds with > 99% stereoselectivity to yield a *cis*-dihydride product with one H *trans* to P(dppe) and the other H *trans* to CO. The addition reaction is controlled by electronic factors of the CO and X ligands. Where X is Cl, Br or I, the stereoselectivity has a kinetic origin with subsequent conversion of the initially formed isomer to the more stable *cis*-dihydride isomer. The basis for the electronic factor is attributable either to (i) enhanced overlap in the π-back-bonding interaction between metal *d* and $\sigma^*(H_2)$ orbitals; or (ii) preferred bonding of one set of *trans* ligands as the reaction proceeds.[616] $[Ir(H)(CO)_2(PPh_3)_2]$ reacts with the coordinatively unsaturated dihydride cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to yield $[Os_3(H)_3(CO)_{11}\{Ir(PPh_3)\}]$. The X-ray crystal structure of the product reveals that the Ir atom caps the Os_3 triangle to form a distorted tetrahedral metal framework.[617] Reaction between an acetone solution of $[IrAu_3(NO_3)(PPh_3)_5](BF_4)$ and 1 atm H_2 yields the hydride cluster complex $[IrAu_4(H)_2(PPh_3)_6](BF_4)$. The two hydride ligands in this complex could not be located by X-ray analysis; they are believed to be bridging-Ir–axial-Au bonds. ^1H NMR spectral data support this assignment, though a terminal Ir—H bonding description also appears plausible.[618]

Trimethylphosphine reacts with $[Ir(C_5Me_5)]_2(\mu\text{-}H)_3A$ (A = PF_6, BF_4) to give the monohydride-bridged dimer $[Ir(H)(C_5Me_5)(PMe_3)]_2(\mu\text{-}H)A$. The product for which A = BF_4 reacts with a third equivalent of PMe_3 at elevated temperatures to produce the monomeric species $[Ir(H)_2(C_5Me_5)(PMe_3)]$ and $[Ir(H)(C_5Me_5)(PMe_3)_2](BF_4)$. Deprotonation of $[Ir(H)_2(C_5Me_5)(PMe_3)]$ with LiBu^t/pmdeta leads to $[Ir(H)(C_5Me_5)(PMe_3)][Li(pmdeta)_x]$, which reacts with alkylating agents to yield complexes of the type $[Ir(H)(C_5Me_5)(PMe_3)(R)]$ (R = alkyl).[619] $LiBH_4$ reacts with $[Ir(C_5Me_5)]_2(\mu\text{-}H)_3(PF_6)$ to give the borohydride-bound dimer $[\{Ir(C_5Me_5)\}_2(H)_3](BH_4)$, while $LiEt_3BH$ reacts with $[Ir_2(C_5Me_5)]$ to yield the mononuclear salt $[Ir(H)_3(C_5Me_5)][Li(THF)_x]$. The anion of the latter product can be hydrolyzed to the iridium(V) complex $[Ir(H)_4(C_5Me_5)]$. Hydrolysis of $[\{Ir(C_5Me_5)\}_2(H)_3](BH_4)$ leads to the iridium(IV) dimer $[Ir(H)_3(C_5Me_5)]$.[620]

Crabtree and coworkers[621] have synthesized $[Ir(H)_2(MeCN)_2(PPh_3)_2]^+$ from $[Ir(H)_5(PPh_3)_2]$ and HBF_4 in MeCN, and $[Ir(H)_2(PPh_3)_2(S)_2]^+$ (S = H_2O, Me_2CO, MeOH). The crystal structural analysis of $[Ir(H)_2(Me_2CO)_2(PPh_3)_2]^+$ shows an unusually long Ir—O distance (2.220–2.235 Å). The crystal structure of $[Ir(H)_3(PMe_2Ph)_2]_2$ reveals molecules as $(\mu\text{-}H)_2$-bridged dimers possessing strict crystallographic inversion symmetry. The Ir atom is approximately octahedrally coordinated by four H (two bridging) and two phosphine ligands. In solution, the dimers exhibit fluxional behaviour.[622] Vibrational and NMR spectroscopic data have recently been reported for $[Ir(CN)_5(H)]^{3-}$.[623]

$[\{Ir(C_5Me_5)\}_2(Cl)_4]$ reacts with $SiEt_3$ to form $[Ir(Cl)(H)_2(C_5Me_5)(SiEt_3)]$, which, under more drastic conditions, reacts further to give $[Ir(H)_2(C_5Me_5)(SiEt_3)_2]$. The $[Ir(Cl)(H)_2(C_5Me_5)(SiEt_3)]$ complex is also obtainable *via* reaction of $SiEt_3H$ with $[\{Ir(C_5Me_5)\}_2(Cl)_2(H)_2]$. This is an example of the highly unusual oxidative addition of iridium(III) to iridium(V).[624]

49.10.10 Catalytic Activity of Iridium Coordination Complexes

Complexes of the type $[Ir(bzn)(cod)(L)](ClO_4)$ (bzn = benzonitrile; L = tricyclohexylphosphine, neomenthyldiphenylphosphine) catalyze the homogeneous hydrogenation of tetrasubstituted prochiral amido alkenes $R^1R^2C{=}CR^4N'$. Under very mild conditions, the catalysis occurs for $N' = NHCOR^3$, $R^3 = CO_2Me$; $R^1 = R^2 = Me$, $R^4 = Me$, Ph; $R^1 = Me$, $R^2 = Ph$, $R^4 = Me$, Ph; $R^1 = Ph$, $R^2 = Me$, $R^4 = Ph$.[625] $[Ir(cod)(PCy_3)(py)](PF_6)$ serves as a catalyst in the hydroxyl-directed hydrogenation of cyclic and acyclic alkenic alcohols, wherein the reaction shows diastereoselectivity dependent on catalyst substrate stoichiometry.[626] Park *et al.*[627] have noted that the iridium(I)

complex $[Ir(CO)L(PPh_3)_2]^+$ and the iridium(III) complex $[Ir(H)_2(CO)L(PPh_3)_2]^+$ (L = *cis*-MeCH=CHCN, *trans*-MeCH=CHCN, CH_2=$CHCH_2CN$) play an important role in the catalytic hydrogenation and isomerization of the corresponding L. The homogeneous catalysis of cyclohexene hydrogenation by iridium and rhodium complexes has been accomplished by Khan and coworkers.[628]

Kinetic studies of the oxidation of nickel(II) dimethylglyoximate by periodate, catalyzed by iridium(IV), has been published recently.[629] Additionally, the kinetics and mechanism of iridium(III)- and ruthenium(III)-catalyzed oxidation of isopropyl alcohol by iodosoacetate have been elucidated.[630]

The integrated system made up of $[Ir(Cl)(cod)]_2$ and $P(C_6H_4OMe\text{-}2)_3$ catalyzes selective transfer hydrogenation of the CO group in $CH_2CHCH_2CH_2COMe$.[631] The resulting yield of unsaturated alcohol, CH_2=$CHCH_2CHMeOH$, is maximum at high P:Ir ratios. This may be understood in terms of an intramolecular interaction between the substrate and the OMe groups of the phosphine. The same system reacts with PhCH=CHCOMe to give the unsaturated alcohol, along with the saturated ketone and alcohol. While hexan-2-one can be reduced to the alcohol, the sterically crowded Me_2C=$CHCH_2CH_2COMe$ gave only unsaturated alcohol on reduction.[632] The selective reduction of α,β-unsaturated carbonyl compounds with alcohols is known to be catalyzed by iridium(I) complexes containing 2,2′-bipyridyl, 1,10-phenanthroline and substituted derivatives.[633] Homogeneous catalytic dehydrogenation of cyclooctane into cyclooctene is effected with $[Ir(H)_5(PPr^i_3)_2]$ and $[Ir(H)_5\{P(C_6H_4\text{-}F\text{-}p)_3\}_2]$ at 423 K in the presence of an alkene that can serve as the hydrogen acceptor.[634] Hydrogen transfer reactions from cyclopentanol to substituted cyclohexanones are catalyzed by iridium complexes containing nitrogen donor chelating ligands.

The species $[Ir(cod)(PPh_3)(pz)]$ or $[Ir(cod)(pz)]_2$ in the presence of PPh_3 (pz = pyrazolato) dissolves in acetone to yield catalytic solutions which partially hydroformylate and hydrogenate alkynes and alkenes.[635] Results were reported for the hydroformylation of hept-2-yne. The hydrosilylation of styrene by $[Si(Cl)_2(H)Me]$ is catalyzed by complexes of the type $[ML_nL'_m]$ (M = Ir, Co, Ni, Ru, Rh, Os, Pd, Pt; L = halide, NO_2^-, SCN^-; L′ = DMSO, Et_2SO, Et_2S, NH_3). The catalytic activity and regioselectivity of these catalysts have been examined after immobilization on AV17X8 or KU 2X8 anion exchangers.[636]

$[Ir(Cl)_3]$ catalyzes the isomerization of methyl formate at 473–508 K/33–250 bar CO in the presence of an MeI promoter. The major product is acetic acid, with methyl acetate as a by-product.[637] The synthesis of PhNCO *via* carbonylation of $PhNO_2$ at 398 K under 80 atm CO pressure can be catalyzed by $[Ir(CO)_2(PPh_3)_2]^+$.[638]

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44.1

Iron(II) and Lower States

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44.1.1 GENERAL SURVEY

44.1.1.1 Introduction

Iron is the most abundant transition metal in the earth's crust, occurring to the extent of some 5% in igneous rocks.[1] It is thought metallic iron is a major component of the earth's core.[2] Iron has a rich coordination chemistry and many of its complexes find use in practical applications.

44.1.1.2 Iron Complexes in Analysis

The widespread occurrence of iron ores, coupled with the relative ease of extraction of the metal, has led to its extensive use as a constructional material with the result that the analysis of steels by both classic 'wet' and instrumental methods has been pursued with vigour over many years.[3] Iron complexes are themselves widely used as the basis of convenient analytical methods for the detection and estimation of iron down to parts per million. Familiar tests for iron(III) in aqueous solution include the formation of 'Prussian blue' as a result of reaction with $[Fe(CN)_6]^{4-}$, and the formation of the intensely red-coloured $[Fe(H_2O)_5SCN]^{2+}$ on reaction with thiocyanate ion.[4] Iron(II) forms particularly stable red tris chelates with α,α'-diimines such as 1,10-phenanthroline or 2,2′-bipyridine that have been used extensively in spectrophotometric determinations of iron and in the estimation of various anions.[5] In gravimetric estimations, iron(III) can be precipitated as the insoluble 8-hydroxyquinoline or α-nitroso-β-naphthol complex which is then ignited to Fe_2O_3.[6] In many situations the levels of free $[Fe(H_2O)_6]^{3+}$ may be controlled through complex formation by addition of edta.

44.1.1.3 Biological Systems

The versatility of the chemistry of iron is reflected by the variety of roles it plays in biological systems where it is frequently found at the active centres involved in processes such as oxygen and

electron transport in nitrogenase, many oxidases and in metalloenzymes such as hydrogenases and reductases. While sustained research over the last two decades has provided much detailed information about the coordination environment of iron in several important natural systems (*e.g.* haemoglobin, ferredoxins and cytochromes), there are still many cases in which the exact location of the iron is not known.

44.1.1.4 Organometallic Chemistry

There have been rapid developments in the organometallic chemistry of iron and during recent years a huge amount of work has been published in this area, as can be judged from there being some 2000 references concerned with iron compounds in the companion work 'Comprehensive Organometallic Chemistry'.[7] As a result of the effort that has gone into the biological and organometallic areas, the basic coordination chemistry of iron has been rather overshadowed and there have been relatively few reviews or books published on the subject in recent years.

44.1.1.5 Iron Mössbauer Spectroscopy

There are few direct spectroscopic probes for iron; for instance, in most complexes charge transfer bands obscure the *d–d* transitions and magnetic measurements cannot provide information on low-spin iron(II) complexes. Therefore when the Mössbauer technique became generally available in the late 1960s, it was widely used for the study of iron complexes. The effect[8] arises from the resonant absorption of γ-rays by the ^{57}Fe nucleus, which has a natural abundance[9] of $\sim 2\%$. When the γ-ray source and sample nuclei are in different environments, the shift in the energy of resonant absorption is expressed as a velocity relative to some arbitrary zero such as stainless steel or $Na_2[Fe(CN)_5NO]\cdot 2H_2O$. Whilst the value of the shift is temperature dependent, it is also affected by the electronic environment.

The chemical or isomer shift (δ) arises from the interaction of electrons with the ^{57}Fe nucleus. This interaction is strong for electrons with zero angular momentum, that is *s* electrons, and δ is a linear function of *s* electron density at the nucleus. The contribution of the outer *s* orbitals make δ sensitive to the chemical environment. In high-spin complexes δ depends markedly on oxidation state, and Mössbauer spectroscopy may be used to indicate the oxidation state of high-spin iron complexes. At room temperature δ varies from $+1.0$ to $+1.6\,mm\,s^{-1}$ for high-spin iron(II) complexes, and from $+0.45$ to $+0.75\,mm\,s^{-1}$ for high-spin iron(III) complexes (Figure 1). The chemical shifts of high-spin complexes also depend on the nature of the bound ligands. For example, the effect of ligand electronegativity on δ is in the same order as the nephelauxetic series.[10] Such large effects are not seen in low-spin complexes. Both iron(II) and iron(III) low-spin complexes have δ values between 0.0 and $+0.3\,mm\,s^{-1}$ (relative to $Na_2[Fe(CN)_5NO]\cdot 2H_2O$) illustrating the importance of back donation.[11] Indeed, π bonding effects appear to be the main cause of chemical shift variation in low-spin complexes. Bancroft and coworkers derived 'partial isomer shifts' (PIS) for a number of ligands, which allow the chemical shift to be calculated for a range of low-spin iron(II) complexes.[12] As expected the values of PIS are in the same order as the spectrochemical series.

The Mössbauer effect has its origin in the nuclear $I = \frac{1}{2}$ to $I = \frac{3}{2}$ spin transition. This transition is split by the electric quadrupole interaction to give a two line spectrum. Figure 2 illustrates the relevant transitions together with the six line spectrum which results from the simultaneous interaction of a magnetic field. The electric field gradient at the iron nucleus can arise from both asymmetric occupation of the *d* orbitals and asymmetry of the ligand field. There are therefore a number of factors affecting the quadrupole splitting energy ΔE_Q.

In high-spin d^5 complexes where the coordinated ligands are identical, the symmetric population of the *d* levels normally results in very small values for ΔE_Q. In contrast, high-spin d^6 centres with one spin-paired $3d$ orbital have sufficient field gradient at the nucleus for a two line Mössbauer spectrum to be observed. Low-spin d^6 complexes have a symmetrical configuration and, for example, $[Fe(CN)_6]^{4-}$ displays a single line spectrum, whilst the incomplete t_{2g} set in low-spin d^5 iron(III) creates a field gradient which induces splitting similar to that observed in high-spin iron(II) complexes. In complexes where the ligand environment is not symmetrical, a field gradient is created and electric quadrupole splitting is observed. There are many low-spin iron(II) complexes which show two line spectra and a range of compounds of the type $[FeA_4B_2]$, $[FeA_5B]$ and $[FeB_4A_2]$ have been investigated.[16] Theoretically the relation in equation (1) would be expected and this has been

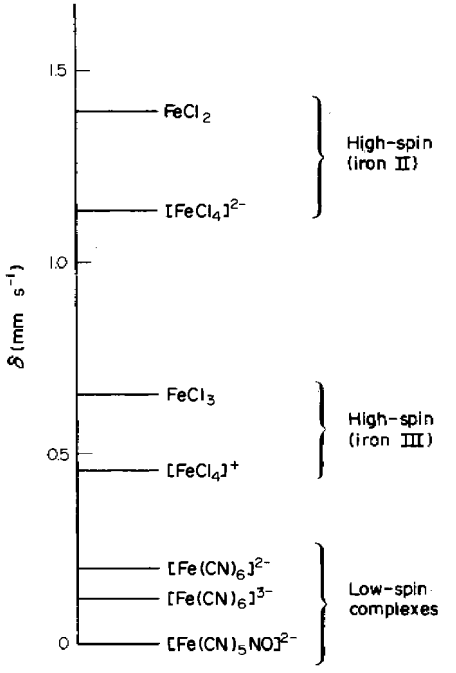


Figure 1 Variation of chemical shift (δ) at 25 °C with oxidation state for low-spin cyanide and high-spin chlorides. Data from refs. 13–15

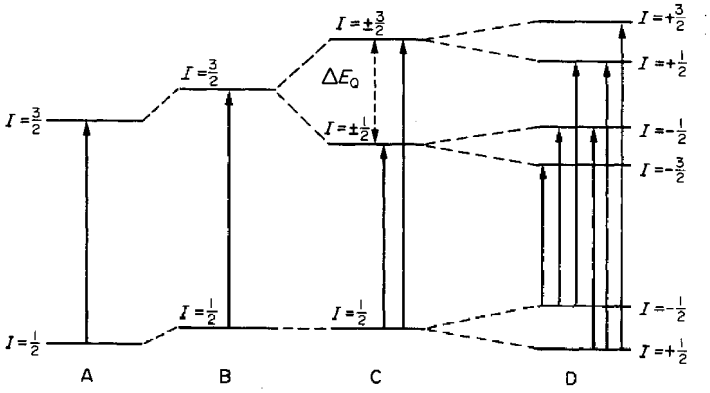


Figure 2 Schematic description of some ^{57}Fe Mössbauer spectra showing original nuclear energy levels (A) slightly perturbed through interaction with S electron density (B) giving rise to a chemical shift (δ) resulting from quadrupole interactions (C) and magnetic splitting of the ground and excited states (D). Arrows indicate transitions responsible for one, two and six line Mössbauer spectra

observed within the limits of experimental error. Thus observed ΔE_Q values may support structural assignments, as well as helping to define oxidation state and spin state. Much of the chemically important information to be derived from Mössbauer spectroscopy is obtained from the chemical shift and the quadrupole splitting energy. Additional information can be obtained by measuring the spectrum of the sample in a magnetic field which further removes nuclear spin degeneracy[17] and often results in a six line spectrum.

$$\Delta E_Q\ (trans) = 2\Delta E_Q\ (cis) \quad (1)$$

44.1.1.6 Oxidation States and Coordination Numbers

Iron compounds are known in which the oxidation state of the metal ranges from $-$II (d^{10}) to

VI (d^2), and the examples in Table 1 illustrate the kinds of complexes formed and their stereochemistries. Several of these oxidation states are not well characterized; the −I and V states are rare, while I is not common. The most frequently encountered oxidation states in complexes of a conventional coordination type (particularly in aqueous media) are II (d^6) and III (d^5): the ferrous and ferric states respectively. The preferred nomenclature, and that used here, indicates these oxidation states as iron(II) and iron(III).

Table 1 Selected Examples of Iron Complexes Illustrating the Range of Oxidation States and Coordination Geometries

Oxidation state	*Coordination number*	*Complex*	*Coordination geometry*	*Comments*	*Ref.*
-II (d^{10})	4	$[Fe(CO)_4]^{2-}$	Tetrahedral	Uncommon oxidation state, but familiar as Collman's reagent $Na_2[Fe(CO)_4]$ and other carbonyl anions	1
0 (d^8)	5	$[Fe(CO)_3(PPh_3)_2]$	Trigonal bipyramidal	Uncommon oxidation state in classical complexes but extensively found in organometallic compounds	2
I (d^7)	5	$[Fe(dppe)_2H]^a$	Square pyramidal	Very few paramagnetic iron(I) complexes have been reported	3
II (d^6)	4	$[FeBr_2(PPh_3)_2]$	Tetrahedral	Common oxidation state in aqueous solution.	4
	5	$[FeBr(Me_6tren)]^+$	Trigonal bipyramidal	Stabilized by high-field ligands, otherwise easily oxidized to iron(III). Octahedral geometry is most	5
	5	$[Fe(ClO_4)(OAsMe_3)_4]^+$	Square pyramidal	common.	6
	6	$[Fe(phen)_3]^{2+}$	Octahedral		7
	7	$[Fe(HPAP)(H_2O)_2]^{2+d}$	Pentagonal bipyramidal		8
	8	$[Fe(1,8\text{-naph})_4]^{2+b}$	Dodecahedral		9
III (d^5)	3	$[Fe\{N(SiMe_3)_2\}_3]$	Trigonal	Most iron(III) complexes are octahedral but	10
	4	$[FeCl_4]^-$	Tetrahedral	tetrahedral and square pyramidal geometries are also	11
	5	$[FeCl(dtc)_2]^c$	Square pyramidal	important. In aqueous media, Fe^{3+} readily hydrolyzes and bridged dimeric species are common.	12
	5	$[Fe(N_3)_5]^{2-}$	Trigonal bipyrimidal	Low-spin complexes are only obtained with the strongest field ligands	13
	6	$[Fe(phen)_3]^{2+}$	Octahedral		14
	7	$[Fe(edta)(H_2O)]^-$	Pentagonal bipyramidal		15
	8	$[Fe(NO_3)_4]^-$	Dodecahedral		16
IV (d^4)	4	$[Fe(l\text{-norbornyl})_4]$	Tetrahedral	Iron(IV) is not common; known in mixed oxides.	17
	6	$[Fe(diars)_2Cl_2]^{2+}$	Octahedral	Most easily prepared complexes are those with dithiocarbamate ligands	18
V (d^3)	4	FeO_4^{3-}	Tetrahedral	Only known in the solid oxides M_3FeO_4 and not well characterized	19
VI (d^2)	4	FeO_4^{2-}	Tetrahedral	Blue FeO_4^{2-} is very strongly oxidizing, finds uses in organic chemistry	20

[a] dppe = 1,2-bis(diphenyphosphino)ethane.
[b] 1,8-naph = 1,8-naphthyridine.
[c] dtc = dithiocarbamate.
[d] HPAP = macrocycle from 2,9-di(1-methylhydrazino)-1,10-phenanthroline and 2,6-diacetylpyridine.

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44.1.1.6.1 Low oxidation states

As expected, the lower oxidation states of iron are stabilized by π acceptor ligands such as phosphines and carbon monoxide, and there is a large volume of 'organometallic' chemistry involving what are formally iron(0) centres.[7] There are very few examples of iron in the oxidation states $-$II (d^8) and $-$I (d^9). While the $-$II oxidation state is rare, the pale yellow compound $Na_2[Fe(CO)_4]$ (best prepared by reducing $[Fe(CO)_5]$ with sodium amalgam in THF) and other derivatives of $[Fe(CO)_4]^{2-}$ are familiar because they are being increasingly used in the synthesis of aldehydes and ketones.[18,19] The $[Fe(CO)_4]^{2-}$ anion is isoelectronic and isostructural[20] with tetrahedral $[Ni(CO)_4]$. Many iron(0) compounds are known, most of which are best regarded as organometallic compounds.[7] However, species such as $[Fe(CO_3)L_2]$ (L = PPh_3, $AsPh_3$ *etc.*) are considered in this chapter. Reduction of conventional iron coordination complexes can yield species containing iron(0). For instance, alkali metal reduction[21] of red $[Fe(bipy)_3]^{2+}$ affords black $[Fe(bipy)_3]$, but care is necessary when assigning oxidation states in such complexes without complete spectroscopic characterization, since reduction of the ligand (rather than at the metal) may take place where extensively delocalized ligand systems are involved such as with the macrocyclic porphyrins[22] and phthalocyanines.[23]

While not common, a number of iron(I) complexes have been isolated and characterized, although as might be expected, disproportionation to the more stable iron(0) and iron(II) will take place in many situations. Several iron(I) complexes with phosphine ligands such as the trigonal bipyramidal $[FeCl(dppe)_2]$ have been reported. Alkali metal reduction of iron(II) phthalocyanine ([FePc]) gives $[FePc]^-$ that contains iron(I). More highly reduced species may also contain iron in the same oxidation state with additional electrons being localized on the ligand.[23] Several nitric oxide complexes are considered to contain iron(I) centres, including the coloured species $[Fe(H_2O)_5NO]$ of the nitrate 'brown ring test'. Assignment of oxidation state in these complexes is often not straightforward, and accordingly it has not been firmly established in many instances. Therefore, in this chapter nitric oxide complexes have been grouped together rather than divided according to oxidation state. A number of more or less transient iron(I) complexes have also been generated using electrochemical or radiolysis techniques and characterized *in situ* by spectroscopic methods.

44.1.1.6.2 Iron(II)

An extremely large number and wide range of iron(II) and iron(III) complexes are known. These d^6 and d^5 configurations represent the most important oxidation states of iron. Most iron(II) complexes have an octahedral geometry, although there are examples of four-, five- and even eight-coordination. Salts of tetrahedral $[FeCl_4]^{2-}$ are readily obtained with large cations;[24] other tetrahedral complexes include $[Fe(OPPh_3)_4]^{2+}$, $[Fe\{OP(NMe_2)_3\}_4]^{2+}$ and the iron(II) centre in the rubredoxins with four sulfur donors. Some tetrahedral rubredoxin model compounds have also been characterized.[25] Square planar iron(II) complexes are formed with tetradentate nitrogen donor macrocycles of which the most familiar are phthalocyanine and the porphyrins, to which in recent years have been added a large number of additional 'synthetic' macrocycles.[26] The magnetic properties of some of these complexes indicate the relatively unusual intermediate spin ($S = 1$) ground state. There is a strong tendency for all of these compounds to acquire two axial ligands (usually nitrogen donors) and become six-coordinate and low-spin. Carbon monoxide and dioxygen adducts are also formed with these complexes[27] and it is now understood how, *via* kinetic or steric effects, to inhibit oxidation to μ-oxo iron(III) species so mimicking the behaviour of haemoglobins and related oxygen carriers.

Numerous five-coordinate high-spin iron(II) complexes, with tetradentate nitrogen donor macrocyclic ligands, have been reported in which the fifth coordination site is occupied by a halide ion. Other five-coordinate complexes include $[Fe(terpy)X_2]$ (refs. 28–30) and examples with tripod ligands, such as $[Fe\{N(CH_2CH_2PPh_2)_3\}X]^+$. High-spin and low-spin complexes with tripod ligands are known,[31] as well as those displaying spin cross-over.

The iron(II) $^5D_2$ ground state is split by octahedral fields into $^5T_{2g}$ and ^5E_g states. High-spin octahedral iron(II) complexes have magnetic moments typically about 5.2 BM and show broad $^5T_{2g}$ to ^5E_g transitions[32] occurring in the visible/near-IR region of the spectrum. Thus salts of the familiar $[Fe(H_2O)_6]^{2+}$ ion are pale green in solution, with an absorption peak at 10 400 cm^{-1} and a shoulder at $\sim$8300 cm^{-1} that may result from a Jahn–Teller effect.[32] Most simple iron(II) salts are susceptible

to air oxidation, a process catalyzed by copper(II) and palladium(II) that has been extensively studied.[33] With very strong-field ligands, like cyanide ion and α,α′-diimines, spin pairing can take place with the result that complexes such as $[Fe(phen)_2(CN)_2]$ are essentially diamagnetic, although some temperature independent paramagnetism, amounting to rather less than 1 BM, is commonly reported.[34,35] These low-spin complexes are usually intensely coloured (typically red or purple) due to strong metal–ligand charge transfer[36] bands that obscure *d–d* transitions. An important feature of low-spin octahedral iron(II) complexes, which is in accord with crystal field stabilization energy considerations,[37] is their stability and kinetic inertness. As a result of this, though not as extensive as that of the isoelectronic, highly inert cobalt(III) centre, a considerable amount of work on their preparation and the kinetics and mechanisms of their reactions has been accumulated. While $[Fe(phen)_2(CN)_2]$ is low-spin, most complexes of the type $[Fe(phen)_2X_2]$ are high-spin. However, by appropriate choice of the anion X^-, it is possible to obtain complexes having strongly temperature-dependent magnetic moments that cross over from being low-spin to high-spin as the temperature is increased. A number of other iron(II) complexes display similar behaviour.[38] Moreover, complexes such as $[Fe(phen)_2(ox)]$ have two unpaired electrons,[39] an unusual situation for a d^6 centre that results from deviation from strict octahedral symmetry.

Although very high coordination numbers are rare for iron(II), eight-coordination is well characterized in the red-orange high-spin complex with 1,8-naphthyridine, $[Fe(naph)_4]^{2+}$, which in the perchlorate salt has a distorted dodecahedral geometry.[40,41] Seven-coordination is more common than eight-coordination, and is known in several macrocyclic complexes.[42]

44.1.1.6.3 Iron(III)

As with iron(II), most iron(III) complexes are octahedral; however, four- (tetrahedral) and five-coordination are also well known (see Table 1). There are also examples of higher coordination number that include the relatively uncommon seven-coordination found in some iron(III) nitrogen macrocycle complexes[43] and in $[Fe(edta)(H_2O)]^-$ (ref. 44). Eight-coordination is exemplified[45] by $[Fe(NO_3)_4]^-$. Iron(III) has a strong affinity for oxygen ligands and a marked tendency to form oxo-bridged complexes. With μ-oxo bridges, as for instance in $[\{Fe(salen)\}_2O]$ (ref. 46) and $[(FeCl_3)_2O]^{2-}$ (ref. 47) that contain two five- and two four-coordinate centres respectively, there is strong antiferromagnetic coupling that results in low and temperature dependent magnetic moments. Monomeric five-coordinate complexes such as $[Fe(S_2CNR_2)_2X]$ have[48] three unpaired electrons. A large number of iron(III) complexes with sulfur donors are known.

In most octahedral monomeric complexes, iron(III) is high-spin, for instance $[Fe(acac)_3]$, and these complexes have magnetic moments close to the expected spin-free value. Complexes containing very high field ligands, as in $[Fe(CN)_6]^{3-}$ and $[Fe(phen)_3]^{3+}$, are low-spin and they display higher than predicted room temperature magnetic moments due to large orbital contributions. As expected in this situation, the observed magnetic moment decreases as the temperature is lowered. Like low-spin iron(II) complexes, low-spin iron(III) centres are significantly more kinetically inert than their high-spin analogues.

As previously noted, spin cross-over behaviour is well established in iron(II) complexes and there are also examples involving iron(III) species. For example, a variety of iron(III) dithiocarbamate complexes of the type $[Fe(S_2CNR_2)_3]$ having a trigonally distorted octahedral geometry display high-spin/low-spin cross-over behviour.[49,50] Little is known about the spin forbidden *d–d* transitions of iron(III) complexes due to near-UV charge transfer bands that 'tail' into the visible part of the spectrum. Even simple iron(III) salts in aqueous media are yellow.

44.1.1.6.4 Iron(II)–iron(III) redox behaviour

The $[Fe(H_2O)_6]^{2+}$ cation is oxidized by molecular oxygen to $[Fe(H_2O)_6]^{3+}$. The usually quoted potential for the $Fe^{3+/2+}$ couple is +0.77 V, but the latest discussion[51] gives +0.738 V. The standard electrode potential is strongly influenced by the nature of the ligands involved, and a wide range of E^0 values is covered depending on the complex concerned. Indeed, it is this ability of iron to span a wide range of redox potential that is exploited in a number of biological systems. Figure 3 illustrates the standard electrode potentials of some typical complexes. In general the high field α,α′-diimine ligands stabilize iron(II) relative to the aqua cations when a low-spin complex is formed,

and the importance of back-bonding in these complexes is emphasized by the significant stabilizing effect of *electron withdrawing* substituents in the ligand.

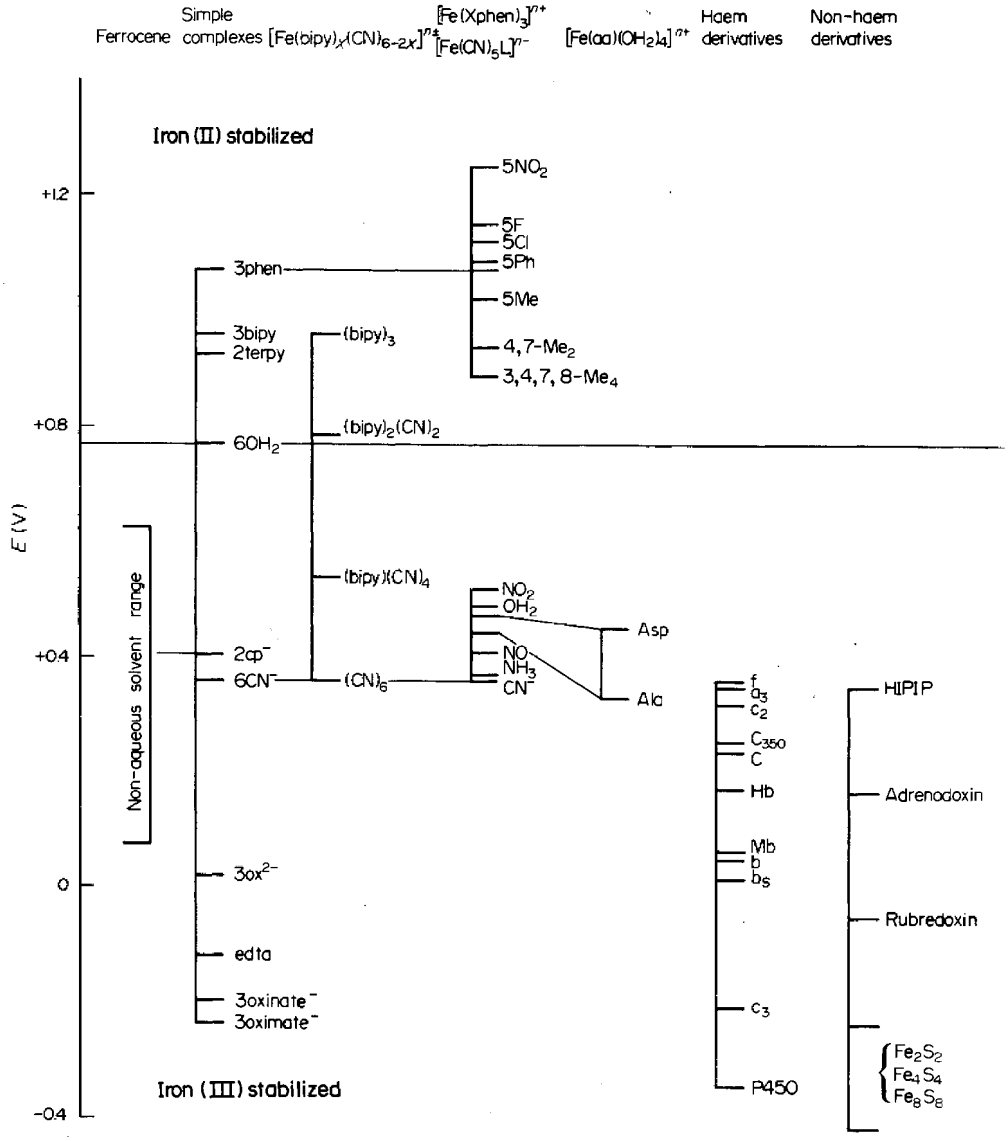


Figure 3 Standard oxidation potential for iron complexes in aqueous solution

The anionic cyano iron(III) complexes $[Fe(CN)_6]^{3-}$ and $[Fe(bipy)(CN)_4]^-$ are more stable than the iron(II) forms relative to the aqua cations. This is at variance with the expectation of the iron(II)–cyanide bond having greater strength than the iron(III)–cyanide bond. It appears that in these instances the electrode potentials are influenced by the large negative entropies of hydration of the anionic iron(II) complexes, and it is this that destabilizes them with respect to the higher oxidation state.[52,53] That is, the higher bond strength (enthalpy) of the iron(II) complex is outweighed by a hydration (entropy) term which no doubt involves structure-forming hydrogen bonding between the cyanide nitrogen atoms and the solvent water. In keeping with this proposal, the iron(III) oxidation state becomes progressively more stable along the series $[Fe(bipy)_2(CN)_2]^{0/+}$, $[Fe(bipy)(CN)_4]^{2-/-}$ and $[Fe(CN)_6]^{4-/3-}$ as the number of cyanide ligands increases.

In the solid state, iron complexes can display interesting internal redox behaviour as a result of applying high pressure.[54] Reduction of iron(III) to iron(II) on the application of pressure is well documented and is usually monitored by Mössbauer or optical spectroscopy. For instance, conversion to iron(II) in $[Fe(acac)_3]$ proceeds continuously with pressure over the range above 30 kbar,

but does not go to completion. After the pressure is released and mechanical strain removed by grinding the sample, iron(III) is reformed. In examples of this kind it appears it is the ligand that is being oxidized. Application of high pressure to solid complexes that are high-spin, but close to the cross-over point, can cause them to go low-spin (*e.g.* $[Fe(phen)_2(SCN)_2]$) but there are examples where application of pressure causes a low-spin complex to become high-spin. Thus at pressures approaching 200 kbar low-spin $[Fe(CN)_6]^{4-}$ becomes high-spin, and $[Fe(phen)_3]^{2+}$ similarly displays a Mössbauer spectrum characteristic of high-spin iron(II). Clearly, in order to interpret these results the overall total volume for the different forms has to be considered, as well as the spin-transition energetics.

44.1.1.6.5 Mixed iron(II)–iron(III) complexes

Both delocalized and localized Fe^{II}/Fe^{III} mixed valence complexes are known, the most comprehensively investigated being Prussian blue which has the limiting formula $Fe_4^{III}[Fe^{II}(CN)_6]_3 \cdot 14H_2O$. The single crystal structure has been reported,[55] and the degree of valence delocalization has been extensively probed.[56] Recently, thin films of insoluble Prussian blue have been intensively studied because of their electrochromic behaviour; electrochemical oxidation gives continuous mixed valence composition (up to complete oxidation) while reduction to Prussian white takes place cleanly at a critical potential.[57] A number of other delocalized systems have been studied involving aromatic bridging ligands. In contrast, the mixed valence compound $Fe_2F_5 \cdot 2H_2O$ is a nonmolecular solid with a three-dimensional network structure with distinct Fe^{II} and Fe^{III} coordination sites, in which the water is bound to the Fe^{II} centres.[58]

44.1.1.6.6 Higher oxidation states

The IV, V and VI oxidation states of iron are all known in oxyanions. However, relatively few well-characterized complexes with iron in an oxidation state higher than three are known. A review[59] concerned with these oxidation states was published in 1974. Complexes containing iron(IV) are not large in number. This appears to be the highest oxidation state of iron in the catalases,[60] and a considerable body of information has been collected on the strongly oxidizing iron(IV) porphyrins.[61,62]

The green/black low-spin d^4 $[Fe(diars)_2X_2]^{2+}$ (X = Cl, Br) obtained by oxidation of $[Fe(diars)_2X_2]^+$ with concentrated nitric acid[63] appears to have a *trans* configuration and is not very stable. More recent examples of well-characterized (X-ray) iron(IV) species involve dithiocarbamate ligands.[64,65] For example, low-spin $[Fe(S_2CNEt_2)_3]^+$ is obtained by merely treating the corresponding iron(III) complex with an excess of iodine.[66,67] The interpretation of the Mössbauer spectra of these complexes is based on that applied to d^5 and d^6 systems.[68] An organometallic compound of the type $[FeR_4]$ has been reported[69] with R being the particularly favourable 1-norbornyl group, and this could be thought of as being an iron(IV) derivative. This 'oxidation state' is, however, rare in organometallic compounds.

The +5 oxidation state is not well defined and seems only to exist in M_3FeO_4 (M = alkali metal), but even these compounds have not been obtained pure.[70] The +6 oxidation state is more familiar. Deep red/purple salts, containing discrete tetrahedral FeO_4^{2-} units, are obtained by anodic oxidation, or the hypochlorite oxidation of freshly precipitated iron(III) hydroxide.[71] Water soluble potassium ferrate(VI) (K_2FeO_4) is fairly stable in basic solution, but gives iron(III) and oxygen in neutral or acid solution. It is more strongly oxidizing than permanganate and has some application in organic oxidations. Other than these oxyanions there appear to be no stable coordination complexes of iron(V) or iron(VI).

44.1.2 NITRIC OXIDE COMPLEXES

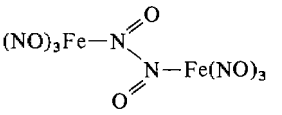
44.1.2.1 Introduction

The nitric oxide molecule shows many similarities to carbon monoxide in its ability to form complexes with transition metals. Nitric oxide has an extra electron, occupying a π^* antibonding orbital, which is relatively easily lost. In the case of terminally bound NO, simple MO theory predicts that whilst $M—NO^+$ will be linear, $M—NO^-$ may be a 'bent' bond. The potential thus

exists to establish the formal oxidation state of the metal centre in nitric oxide complexes by examining their IR spectra. Although well-authenticated examples of bent M—NO bonds exist,[72] they are rare and there have been numerous discussions of the bonding in transition metal nitrosyl complexes.[73–81] Iron nitrosyl complexes have not been classified by oxidation state but are discussed here separately.

44.1.2.2 Simple and Binary Nitrosyls

Reports in the older literature suggested the existence of $[Fe(NO)_4]$. However, this is likely to be a dimeric compound[82] containing a bridging hyponitrite ligand (**1**). One electron reduction of the complex $[Fe(NO)_2Cl]_2$, chemically[83] or electrochemically,[84] leads to a species which acts as a catalyst for the cyclodimerization of dienes. This has been described as '$Fe(NO)_2$', which probably exists in THF solution as $[Fe(NO)_2(THF)_n]$. Aqueous solutions of ferrous salts absorb nitric oxide to give the familiar colour of the 'brown ring test', which is due[85] to the complex ion $[Fe(H_2O)_5NO]^{2+}$.



(1)

44.1.2.3 Nitrosyl Carbonyls

(i) $[Fe(CO)_2(NO)_2]$

Several preparations of dicarbonyl dinitrosyl iron have been reported including treatment of $[Fe_3(CO)_{12}]$ or $[Fe_2(CO)_9]$ with nitric oxide,[86,87] acidification of a mixture of $[HFe(CO)_4]^-$ and nitrite ion,[88] reaction of iron pentacarbonyl with nitrosyl chloride[89] and acidification of a mixture of $[Fe(CO)_3NO]^-$ and nitrite ion[90] as in equations (2) and (3).

$$[Fe(CO)_5] + NaNO_2 + 2NaOH \xrightarrow{H_2O} Na[Fe(CO)_3NO] + CO + Na_2CO_3 + H_2O \quad (2)$$

$$Na[Fe(CO)_3NO] + NaNO_2 + 2MeCO_2H \longrightarrow [Fe(CO)_2(NO)_2] + CO + 2MeCO_2Na + H_2O \quad (3)$$

Red crystalline $[Fe(CO)_2(NO)_2]$ has a distorted tetrahedral geometry. It is somewhat air sensitive, melts at 18 °C and is readily transferred in the vapour phase in a vacuum system. The IR spectrum in cyclohexane solution contains strong carbonyl bands at 2083 and 2034 cm^{-1} and strong nitrosyl bands at 1810 and 1756 cm^{-1}. A full IR assignment has been reported.[91] $[Fe(CO)_2(NO)_2]$ reacts with a wide variety of ligands with preferential CO displacement; both monomeric and dinuclear complexes result. A kinetic study of CO displacement reactions of $[Fe(CO)_2(NO)_2]$ by phosphines, phosphites and triphenylarsine supports[92] a bimolecular displacement mechanism where the entering ligand attacks the 'soft' iron atom to give a five-coordinate transition state. The substitution can be catalyzed by various hard bases.[93] This is thought to occur *via* attack on a carbonyl carbon atom which destabilizes the M—CO bond so making carbonyl a better leaving group.

(ii) The $[Fe(CO)_3NO]^-$ anion

The $[Fe(CO)_3NO]^-$ anion is formed by the reaction of $[Fe(CO)_5]$ with nitrite ion in methanol, and isolated as $[Hg\{Fe(CO)_3NO\}_2]$ by reaction with aqueous mercurous cyanide[90,94] but many other salts are also known.[95–97] The anion can be conveniently prepared in high yield[98] as the bright yellow salt $[(Ph_3P)_2N][Fe(CO)_3NO]$ by the reaction of $[(Ph_3P)_2N](NO_2)$ with $[Fe(CO)_5]$ in THF (ν_{CO}, 1982 m, 1876 s; ν_{NO}, 1650 m cm^{-1}). IR studies suggest that in the mercury derivative the three metals are bonded in a linear fashion, each iron atom having trigonal bipyramidal geometry.[99] Carbon monoxide is readily displaced by π acceptor ligands[100–102] in benzene at room temperature to give $[Hg\{Fe(CO)_2(NO)L\}_2]$ (L = R_3P, R_3As, R_3Sb, $(RO)_3P$) in which the geometry of the iron and mercury atoms remains unchanged.[101] In the case of reaction with pyridine (or other N bases and isocyanides) however,[100] disproportionation yields a mixture of $[Fe(py)_6][Fe(CO)_3NO]$ and

$[Fe(py)_2(NO)_2]$. Interestingly, $[Hg\{Fe(CO)_3NO\}_2]$ reacts slowly with tris(dimethylamino)phospine (Tdp) in refluxing benzene[94] to give first partial then complete substitution of CO (equation 4). Mercury iron nitrosyl complexes are the basis for two routes[103,104] to iron–tin, iron–germanium and iron–lead bonds. These are illustrated in equations (5) and (6).

$$[Hg\{Fe(CO)_3NO\}_2] + (Me_2N)_3P \xrightarrow[\text{benzene}]{\text{reflux}} \begin{cases} \xrightarrow{6\,h} [Fe(Tdp)_2(CO)_2NO][Fe(CO)_3NO] \\ \xrightarrow{20\,h} [Fe(Tdp)_2(NO)_2] \end{cases} \quad (4)$$

$$[Hg\{Fe(CO)_2(NO)(PPh_3)\}_2] + 2SnCl_4 \xrightarrow[25\,^\circ C]{\text{benzene}} [Cl_3SnFe(CO)_2(NO)(PPh_3)] + HgCl_2 \quad (5)$$

$$[Hg\{Fe(CO)_2(NO)(P(OPh)_3)\}_2] \xrightarrow[THF]{Na/Hg} Na[Fe(CO)_2(NO)(P(OPh)_3)] \xrightarrow{Ph_3GeBr} \xrightarrow{Ph_3GeBr} [Ph_3GeFe(CO)_2(NO)(P(OPh)_3)] + NaBr \quad (6)$$

The $[Fe(CO)_3NO]^-$ anion reacts with LAuX (L = $(MeO)_3P$, Me_3P, Ph_3P, $(p\text{-}ClC_6H_4)_3P$) to give complexes $[LAuFe(CO)_3NO]$ containing gold–iron bonds[105] which undergo CO substitution reactions in a fashion similar to $[Hg\{Fe(CO)_3NO\}_2]$ as in equation (7), where L = $(PhO)_3P$, Ph_3P. Conductimetric titration has been employed to study[106] the reduction of $[Fe(CO)_3NO]^-$ through to $[Fe(CO)_3NO]^{5-}$ although the oxidation state of the metal at any particular stage is uncertain.

$$[Ph_3PAuFe(CO)_3(NO)] + L \xrightarrow[25\,^\circ C/dark]{\text{benzene}} [Ph_3PAuFe(CO)_2(NO)L] \quad (7)$$

44.1.2.4 The Nitroprusside Ion

Sodium nitroprusside ($Na_2[Fe(CN)_5NO]\cdot 2H_2O$), possibly the best known of all nitrosyl complexes,[107] is made either by the action of nitric acid (equation 8) or sodium nitrite (equations 9 and 10) on the hexacyanoferrate(II) anion. The equilibria (9) and (10) are driven to the right by the addition of barium chloride to the reaction mixture and by removing HCN in a stream of CO_2 passing through the hot solution. The overall process[108] is shown in equation (11).

$$[Fe(CN)_6]^{4-} + 4H^+ + NO_3^- \longrightarrow [Fe(CN)_5NO]^{2-} + CO_2 + NH_4^+ \quad (8)$$

$$[Fe(CN)_6]^{4-} + NO_2^- \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + CN^- \quad (9)$$

$$[Fe(CN)_5NO_2]^{4-} + H_2O \rightleftharpoons [Fe(CN)_5NO]^{2-} + 2OH^- \quad (10)$$

$$2[Fe(CN)_6]^{4-} + 2NO_2^- + 3Ba^{2+} + 3CO_2 + H_2O \longrightarrow 2[Fe(CN)_5NO]^{2-} + 2HCN + 3BaCO_3 \quad (11)$$

Red crystals of sodium nitroprusside are readily soluble in water and ethanol; aqueous solutions undergo a complex decomposition process in light.[109] Low-spin (diamagnetic) $[Fe(CN)_5NO]^{2-}$, as the sodium, iron(II), copper(II) and zinc(II) salts, shows considerable conversion to the high-spin state at 20–110 °C under high pressure.[110] The nitroprusside anion has an N—O bond length of 1.13 Å, an Fe—NO angle of 180 ° and an NO stretching frequency of 1947 cm^{-1} indicating an NO^+ complex of iron(II) with extensive π bonding. However, the Mössbauer spectrum and shortness of the Fe—N bond (1.63 Å) argue[111] for a less positively charged NO ligand and indeed the X-ray photoelectron spectrum[112] indicates a positive charge on NO of approximately +0.35. One-electron reduction of $[Fe(CN)_5NO]^{2-}$ by sodium in liquid ammonia,[113] or a variety of radicals formed in aqueous solution in radiolysis experiments,[114] results in the formation of $[Fe(CN)_5NO]^{3-}$, which undergoes a first order decay with loss of cyanide to give $[Fe(CN)_4NO]^{2-}$. Both the tetragonal pyramidal structure[115] of $[Fe(CN)_4NO]^{2-}$ and the likelihood that it is a *cis*-cyanide which is lost in both this transformation and reactions involving nucleophilic attack on nitroprusside are predicted from INDO molecular obital calculations[116] based on recent structure determinations. Multielectron

electrochemical reduction in nonaqueous solvents results[117] in the formation of $[Fe(CN)_5NH_2OH]^-$.

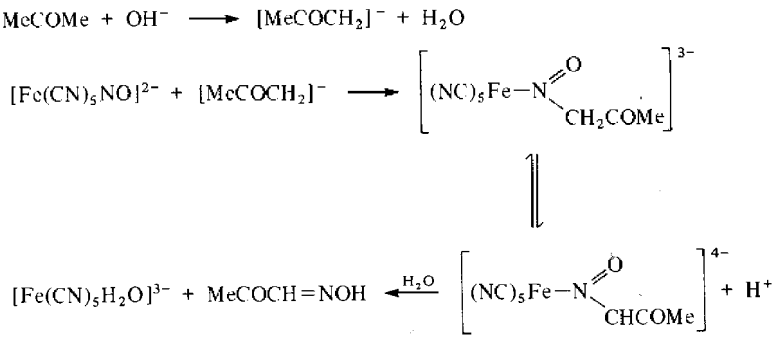
The nitroprusside ion is attacked by hydroxide to yield the corresponding nitro compound $[Fe(CN)_5NO_2]^{4-}$. The rate of formation of $[Fe(CN)_5NO_2]^{4-}$ is first order in OH^- and nitroprusside concentrations[118] and electrochemical studies suggest[119] the formation of the transient intermediate $[Fe(CN)_5(N(=O)OH)]^{3-}$ (equations 12 and 13).

$$[Fe(CN)_5NO]^{2-} + OH^- \xrightarrow{slow} [Fe(CN)_5NO_2H]^{3-} \quad (12)$$

$$[Fe(CN)_5NO_2H]^{3-} + OH^- \xrightarrow{fast} [Fe(CN)_5NO_2]^{4-} + H_2O \quad (13)$$

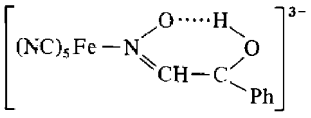
The yellow solid $Na_4[Fe(CN)_5NO_2]$ is prepared[120] by the reaction of concentrated aqueous NaOH with a methanolic solution of sodium nitroprusside at 2 °C. The kinetics of the hydrolysis equilibrium (14) have been investigated.[118] $[Fe(CN)_5H_2O]^{3-}$ is also the usual product in the reaction of nitroprusside ion with ketones, and molecules containing active methylene groups, in alkaline solution.[109] The reaction with acetone has been studied in some detail[121] and the overall reaction in Scheme 1 proposed. Salts of the type (**2**) shown in Scheme 1 can be isolated. The red ion $[Fe(CN)_5N(O)CHCOPh]^{4-}$ formed in the reaction of nitroprusside with acetophenone can be protonated[122] to yield a blue, isolable complex thought to have structure (**3**).

$$[Fe(CN)_5NO_2]^{4-} + H_2O \rightleftharpoons [Fe(CN)_5H_2O]^{3-} + NO_2^- \quad (14)$$



(2)

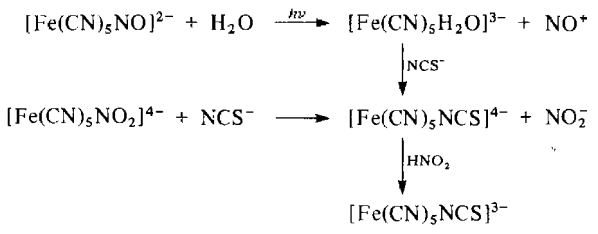
Scheme 1



(3)

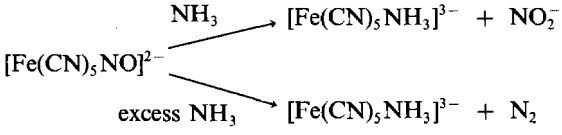
Colour reactions of the nitroprusside ion such as these have been known for many years.[123] Most of these reactions involve nucleophilic attack on the coordinated NO group resulting in either displacement of NO or the formation of an unusual ligand bound to the iron. In the Gmelin test for SH^- a purple-violet colour is formed. This has been reported[124] as being due to the ion $[Fe(CN)_5NOS]^{4-}$; however this is probably an oversimplification[125] and no definite structural assignment has been made. Na_2Se and Na_2Te react with nitroprusside to give[126] respectively blue-green and black colours. Alkaline solutions of mercaptans react with nitroprusside to form purple-red colours[127] and thus this reaction has been used to identify cysteine in mildly basic solution.[128] Thiourea and its derivatives react with nitroprusside[129] to give red coloured adducts which, in the case of thiourea, slowly becomes blue. The structures of these adducts are uncertain but the final blue colour[130] may be due to $[Fe(CN)_5(NCS)]^{3-}$, which can be produced by the photolysis of nitroprusside ion in the presence of aqueous thiocyanate, or by acidification of alkaline solutions of $[Fe(CN)_5NO_2]^{4-}$ containing thiocyanate. The reaction path shown in Scheme 2 has been proposed.[131]

Whilst crystals of $[Fe(CN)_5(NCS)][Bu_4N]_3$ are orange, the colours of the salt vary[107] from orange in acetone, to purple in ethanol and blue or purple in aqueous solutions. The analagous selenium compound $[Fe(CN)_5(NCSe)][Bu_4N]_3$ is formed[132] in the reaction of $Na_3[Fe(CN)_5NH_3]$ with *n*-butyl ammonium chloride and KNCSe in acetone.



Scheme 2

Nitroprusside ion reacts with ammonia[133] at pH 11.0–12.5 to give $[Fe(CN)_5NH_3]^{3-}$ and nitrite as in equation (15); with higher concentrations of ammonia nitrogen is evolved, presumably following attack on the NO ligand by ammonia. Similar behaviour is observed with primary aliphatic amines.[134] In liquid ammonia nitroprusside is attacked by NaNHPh to give $Na_4[Fe(CN)_5\{(N{=}O)NPh\}]$, whereas only $Na_3[Fe(CN)_5NH_3]$ is isolated[135] following the reaction with NaNRR′.

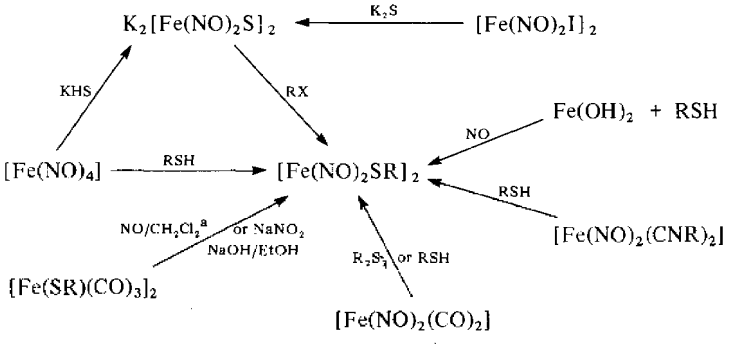


(15)

Sodium nitroprusside is a rapidly acting peripheral vasodilator which has been known[136,137] for some time to lower blood pressure swiftly in emergencies. Whilst useful for controlling blood pressure during surgery, only low doses have been recommended because sodium nitroprusside apparently forms free cyanide *in vivo*. The concentrations of CN^- measured in the past may, however, have been an artefact[138] due to photodecomposition during lengthy colorimetric analysis. The reactions of sodium nitroprusside with amines have been investigated[139] as part of a study to identify its mode of biological action.

44.1.2.5 Complexes Containing Nitric Oxide and Sulfur Donors

The most familiar complexes in this class are Roussin's red and black salts[140] obtained as a mixture from the reaction of iron(III) sulfide with nitric oxide and an alkali metal sulfide.[141] The dimeric and diamagnetic red salt, $K_2[Fe(NO)_2S]_2$ gives rise to a series of stable esters $[Fe(NO)_2SR]_2$ (R = Me, Et, Ph *etc.*) which are also diamagnetic, dark red and soluble in organic solvents. Some preparative routes[142] to the red salt and its esters are shown in Scheme 3.

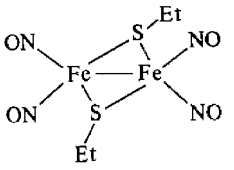


[a] A. R. Butler, C. Glidewell and J. McGinnis, *Inorg. Chim. Acta*, 1982, **64**, L77.

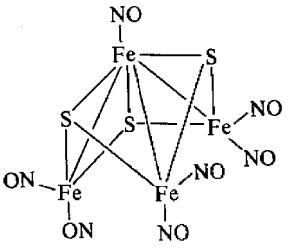
Scheme 3

The structure of the red ethyl ester[143] (**4**) has two iron and two sulfur atoms in a planar configuration, the iron atoms being approximately tetrahedrally coordinated by two bridging sulfur and two nitrosyl ligands. The angle at sulfur is 73.7°, the Fe—Fe distance 2.72 Å and the N—Fe—N bond angle 117°. The X-ray structure[143] reveals the presence of only the C_{2h} isomer whereas NMR measurements in d^8-toluene show both C_{2h} and C_{2v} forms.[144] The activation energies for the interconversion of the two forms (typically $\Delta G^{\neq} = 75.3\,kJ\,mol^{-1}$) have been derived for a variety of alkyl substituents.

The black salts $M[Fe_4S_3(NO)_7]$ (M = Na, K, Cs, $AsPh_4$) are classically prepared[141] from $NaNO_2$, KHS and iron(II) sulfate. They may also be prepared in good yield[144] by nitrosylation of $[Fe_2S_2(CO)_6]$, $[Fe_2S_2(CO)_6]^{2-}$ or $[Fe_3S_2(CO)_9]$ by reaction with sodium nitrite in a refluxing solution of sodium hydroxide in aqueous ethanol. The structure (**5**) consists of a trigonal pyramid of iron atoms with triply-bridged sulfur atoms and iron–iron bonds between the apical Fe—NO group and three basal $Fe(NO)_2$ groups. The three $Fe(NO)_2$ groups are also joined by the triply bridging sulfur atoms. An early structural study[145] found the Fe—N bond length shorter in the apical group. More recent work[146] on the $AsPh_4^+$ salt, prepared by Na/Hg reduction of $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$ in THF, has however shown that all Fe—N and N—O bond lengths in the black monoanion are essentially the same. This observation prompted a reexamination of the bonding in both the red and black salts in comparison with the closely related $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$ clusters. The black salt can be formally constructed[146] from the dimensionally similar groupings present[147,148] in the red salt and in $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$. The bonding models developed for these two molecules suggest that the bonding in the monoanion of the black salt can be analagously described under C_{3v} symmetry.

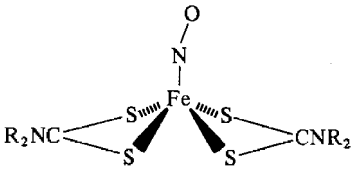


(4)



(5)

The preparation of the five-coordinate iron nitrosyl dithiocarbamate complexes $[Fe(NO)(S_2CNR_2)_2]$ was first reported[149] by Cambi and Cagnasso. These compounds may be prepared[150] by reacting a solution of a divalent iron salt and NaS_2CNR_2 with NO in methanol. Crystal structures of $[Fe(NO)(S_2CNR_2)_2]$ (R = Et, (**6**), at room temperature[151] and subsequently for R = Me at −80 °C) show[152] a square pyramidal geometry with an approximately linear apical iron nitrosyl group (Fe—N—O = 174° and 170° respectively) in contrast to the bent (M—N—O = 135°) metal nitrosyl group in the isomorphous complex[153] $[Co(NO)(S_2CNMe_2)_2]$. Both iron complexes are paramagnetic. ESR and Mössbauer spectra of $[Fe(NO)(S_2CNR_2)_2]$ have been interpreted[154–156] in terms of a formal iron(I) species in which the unpaired electron resides in the iron d_{z^2} orbital. This conclusion is supported[157] by a study of 14 iron nitrosyl dithiocarbamate complexes with differing organic substituents. The pK_a of the corresponding dialkylammonium ion was shown to be an effective measure of the mesomeric effect of the $-NR_2$ groups of the dithiocarbamate ligand which in turn affects ν_{NO} and the Fe—N bond length.



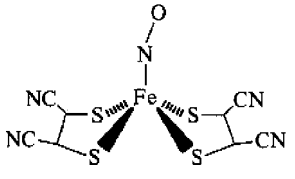
(6)

Green-black five-coordinate $[FeNO(S_2CNR_2)_2]$ is reportedly[158] converted into the dark brown six-coordinate molecule $[Fe(NO)_2(S_2CNR_2)_2]$ by action of NO in chloroform. Subsequent investigation,[159] however, has failed to confirm this although some evidence for the existence of the molecule as an intermediate was gained from $^{14}N/^{15}N$ exchange studies.

Direct oxidation of $[Fe(NO)(S_2CNMe_2)_2]$ at room temperature[160] leads to *cis*-$[Fe(NO)(S_2CNMe_2)_2X]$ (X = Br, I, NO_2) whilst at −78 °C *trans*-$[Fe(NO)(S_2CNMe_2)_2(NO_2)]$ is formed.[159] In this case, the *trans* isomer is the kinetic product which isomerizes at 5 °C to the thermodynamically favourable *cis* isomer. *Trans* products are apparently favoured by ligands such as MeCN and $-NCS^-$ which are relatively weak σ donors and poor π acceptors. Ligands which have either strong σ donor (and strong π acceptor) properties such as MeNC and NO_2^-, or which are able directly to donate from large π orbitals into vacant *cis* π^* orbitals (such as halides) favour a *cis* configuration.[159] In the *cis* nitro compound, NO and NO_2^- undergo[161] a novel intramolecular exchange reaction. The *cis* octahedral geometry of the halogeno derivative $[Fe(NO)(S_2CNEt_2)_2I]$ has been confirmed[162] by

magnetically perturbed Mössbauer spectroscopy at 4.2 K. Whilst the bis-nitrosyl bis-dithiocarbamate complex has not been substantiated, an analagous complex *cis*-$[Fe(NO)_2(Sacsac)_2]$ (Sacsac = dithioacetylacetonate) has been reported[163] (ν_{NO} = 1765, 1790 cm^{-1}).

Other examples of the stabilization of an iron nitrosyl complex by chelating sulfur ligands are the bis-dithiolene complexes[164] $[Fe(NO)(S_2C_2R_2)_2]^Z$ ($Z = 0, -1, -2, -3$; $S_2C_2R_2$ = disubstituted *cis*-ethylene-1,2-dithiolates, tetrachlorobenzene-1,2-dithiolate, toluene-3,4-dithiolate). These complexes have square pyramidal geometry, analagous to the iron nitrosyl bis-dithiocarbamate complexes discussed above, as exemplified in a crystal structure[165] of $[Fe(NO)\{S_2C_2(CN)_2\}_2]$ (**7**). The Fe—N—O bond angle (measured at room temperature) is reported to be 168°. These complexes undergo a series of one-electron transfer reactions[164] which have been investigated voltammetrically. The half-wave potential for each redox step is dependent on the dithiolene ligand, becoming more positive as the ligand becomes more electron withdrawing; the order $S_2C_2(CN)_2 > S_2C_2(CF_3)_2 > S_2C_6Cl_4 > S_2C_6H_3Me > S_2C_2Ph_2$ has been observed.[164] The effect is also seen in substituted diaryldithiolenes,[166] half-wave potentials becoming more positive as substituents on the aryl group become more electron withdrawing. The complexes $[Fe(NO)(S_2C_2R_2)_2]$ undergo ligand exchange reactions, $[Fe(NO)\{S_2C_2(CN)_2\}(S_2C_2Ph_2)]^-$ for example resulting[167] from mixing the two corresponding bis-dithiolene monoanionic complexes.



(7)

In the formation of $[Fe(NO)(S_2C_2Ph_2)_2]$ by the reaction between $[Fe(S_2C_2Ph_2)_2]_n$ and NO in cold chloroform, a purple complex[168] $[Fe_2(NO)_2(S_2C_2Ph_2)_3]\cdot CHCl_3$ can also be obtained. The monoanion can be isolated as a green solid by reaction of the neutral complex with $NaBH_4$. The Mössbauer spectrum of the neutral complex[169] shows that the two iron atoms are not equivalent, possibly due to interaction with the chloroform molecule. Interesting structure-related effects are also observed[170] in the complexes $[Fe(NO)(S_2CO_2Me_2)(P,P)]$ (P,P = diphos, $2PPh_3$). ESR spectra indicate that the unpaired electron may reside in different metal orbitals depending on the steric influence of the phospine ligands on the basic square pyramidal geometry of the complexes.

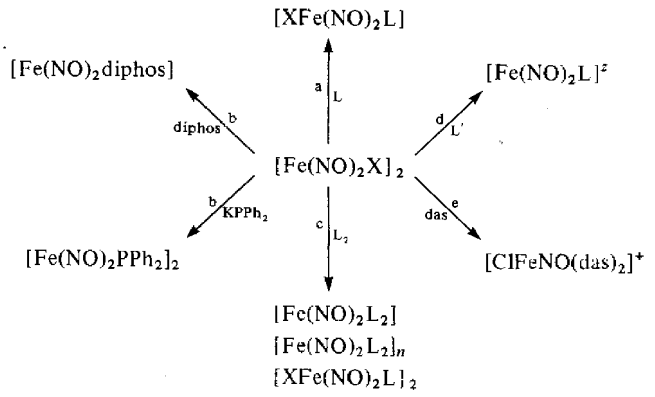
44.1.2.6 Nitrosyl Halides

$[Fe(NO)_3X]$ and $[Fe(NO)_2X]_2$ (X = Cl, Br, I) are known, although the former is highly unstable. $[Fe(NO)_3Cl]$ is prepared[171] by the action of NO on $FeCl_2$ at 70 °C in the presence of iron powder; the bromide and iodide analogs are prepared[172] from their respective tetracarbonyl halides as in equation (16). The more stable diamagnetic halides $[Fe(NO)_2X]_2$ are nonpolar and dissolve in organic solvents. The iodide, which has been studied in the most detail, may be prepared by direct reaction of NO with FeI_2 at elevated temperature, from $[Fe(NO)_2(CO)_2]$ by carbon monoxide displacement[172] with iodine or by the room temperature reaction[173] of NO with FeI_2 in acetone in the presence of iron powder. The dimeric nature of $[Fe(NO)_2X]_2$ has been confirmed by a crystal structure determination of the iodide (**8**).[174] The iron atoms are essentially tetrahedrally coordinated with iodine bridges. Although the bond is long (3.05 Å) there is a considerable iron–iron interaction. Both types of halide react with a variety of ligands to form monomeric complexes $[Fe(NO)_2LX]$.

$$[Fe(CO)_2X]_2 + Fe + 6NO \longrightarrow 2Fe(NO)_3X + 4CO \qquad (16)$$



(8)



[a] L = PPh_3, $AsPh_3$, $SbPh_3$, $C_5H_{11}N$; W. Hieber and R. Kramolowsky, *Z. Naturforsch., Teil B*, 1961, **16**, 555. W. Hieber and R. Kramolowsky, *Z. Anorg. Allg. Chem.*, 1963, **321**, 94. W. Beck and K. Lottes, *Chem. Ber.*, 1965, **98**, 2657.

[b] W. Hieber and G. Neumair, *Z. Anorg. Allg. Chem.*, 1966, **342**, 93.

[c] L_2 = $(Ph_2P)_2$, $(Ph_2As)_2$; W. Hieber and R. Kummer, *Z. Anorg. Allg. Chem.*, 1966, **344**, 292.

[d] L' = acac, amino acid, diamine, thioamide, *o*-(SH)$(NH_2)C_6H_5$; W. Hieber and H. Fuhrling, *Z. Anorg. Allg. Chem.*, 1971, **381**, 235; W. Hieber and H. Fuhrling, *Z. Anorg. Allg. Chem.*, 1970, **377**, 29; W. Hieber and K. Kaiser, *Z. Anorg. Allg. Chem.*, 1968, **358**, 271.

[e] The bromo and iodo derivatives $[XFeNO(das)_2]^+$ were not prepared from the nitrosyl halide dimer. W. Silverthorn and R. D. Feltham, *Inorg. Chem.*, 1967, **6**, 1662.

Scheme 4

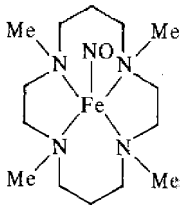
Some reactions of $[Fe(NO)_2X]_2$ are illustrated in Scheme 4. The complexes $[Fe(NO)_2X_2]$ and $[FeNOX_3]$ are also known. $[Fe(NO)_2X_2][N(PPh_3)_2]$ is prepared[175] by the reaction of alkyl halides with $[Fe(CO)_3NO][N(PPh_3)_2]$ (X = Cl, Br or I). Reaction of the carbonyl nitrosyl with halogens affords[175] $[FeX_3(NO)][N(PPh_3)_2]$ (X = Cl, Br) or $[FeX_2(NO)_2][N(PPh_3)_2]$ (X = I).

44.1.2.7 NO Adducts of Complexes Containing Polydentate Ligands

There are few examples of simple nitrosyl complexes containing σ N donor ligands. The Fe—NO moiety requires to be stabilized by appreciable d–π interaction and this is at odds with the classically 'hard' nature of N donor bases. In cases where iron nitrosyls are stabilized in coordination with a nitrogen (or oxygen) donor ligand, there is usually a degree of π acceptor character associated as, for example, with delocalized planar systems.[176] Nitric oxide reacts with solid β-iron phthalocyanine[177] to yield a 1:1 adduct (from which NO is readily displaced by pyridine). A similar route has been used to prepare nitrosylmyoglobin[179] and nitrosylhaemoglobin[178] for single crystal ESR studies which have been interpreted on the basis of a bent metal–nitrosyl bond. Iron nitrosyl complexes of tetraphenylporphyrin (TPP) have been investigated as possible models for the haem protein systems. The five-coordinate[180] complex [Fe(NO)TPP] has an Fe—NO bond angle of 151°, whereas[181] in [Fe(NO)(TPP)(1-MeIm)] (MeIm = 1-methylimidazole) it is 142°. The analogous complex [Fe(NO)(TPP)(4-MePip)] (4-MePip = 4-methylpiperidine) was found to crystallize in two distinct forms, with and without chloroform solvate,[182] in which the Fe—NO angles are 138.5° and 143.7° respectively. A structural correlation has been noted[182] between the stretching frequency of the coordinated nitrosyl and the length of the *trans* Fe—N bond.

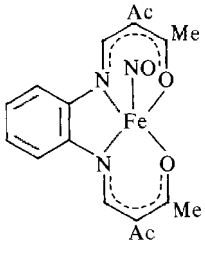
Nitrosyl (*meso*-2,3,7,8,12,13,17,18-octaethyl-5-nitroporphyrinato)iron(II) has been shown[183] to dimerize at high concentration at 9 K. This observation implies an explanation of the ESR spectrum of the NO-haem-salicylate system, which is in turn a model of the observation that the interaction of oxyhaemoglobin with salicylate causes enhanced oxygen uptake in the presence of a substrate such as ascorbate. An interesting example of an iron nitrosyl complex with an N donor ligand without a delocalized π system is provided[184] by the complex $[Fe(TMC)(NO)]^{2+}$ (**9**) (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). The complex is stabilized with considerable distortion from tetragonal pyramidal towards trigonal bipyramidal geometry.

Nitric oxide reacts with an ethanolic solution of [Fe(salen)] [salen = *N*,*N*′-ethylenebis(salicylideniminato)] at room temperature to give the black complex [Fe(salen)NO]. This compound exhibits[185] an $S = \frac{3}{2}$ to $S = \frac{1}{2}$ spin cross-over at 175 K. The corresponding complex of the 5-chloro-salen ligand [Fe(5-Cl-salen)NO], however, shows no sharp spin cross-over transition but a steady decrease in magnetic moment from 3.8 to 0.5 BM over the temperature range 4–100 K, indicative[186]

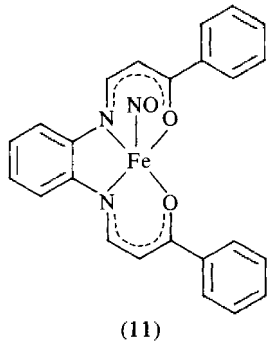


(9)

of an antiferromagnetic interaction and this implies a different lattice arrangement than in [Fe(salen)NO], possibly involving dimer formation. [Fe(TMC)NO] also exhibits an $S = \frac{3}{2}$ to $S = \frac{1}{2}$ spin transition although without a sharp transition temperature. Interestingly the $S = \frac{3}{2}$ to $S = \frac{1}{2}$ interconversion rate is considerably slower in [Fe(salen)NO]. The spin state equilibria have also been described for [Fe(salphen)NO] {salphen = *N,N'-o*-phenylenebis(salicylideniminato)} and here as in [Fe(salen)NO] hysteresis accompanies the spin cross-over at around 175 K. Indeed the existence of $S = \frac{3}{2}$ to $S = \frac{1}{2}$ spin equilibria are a feature of iron nitrosyl complexes of quadridentate Schiff bases and analogous compounds. For example the complex [Fe(J-ph)NO] (**10**) shows a sharp transition[187] in μ_{eff} from 2.0 BM at 90 K to 3.2 BM at 70 K whilst [Fe(bza-ph)NO] (**11**) shows[187] a gradual transition in μ_{eff} from 2.1 BM at 90 K to 2.6 BM at 300 K. Recently iron nitrosyl complexes of the bidentate ligand Q (Q = 8-quinolinolate) have been isolated.[188] [Fe(5-chloro-Q)$_2$(NO)(DMF)] and [Fe(2-methyl-Q)(NO)$_2$] have magnetic moments of 4.21 BM and 1.97 BM respectively, whilst μ_{eff} for [Fe(Q)$_2$NO]$_2$ varies[188] from 4.4 at 285 K to 4.0 BM at 83 K.



(10)



(11)

44.1.3 IRON(0) AND LOWER OXIDATION STATES

44.1.3.1 Introduction

The zero and lower oxidation states are relatively unimportant in the classical coordination chemistry of iron. With increased electron density on the iron, *d–d* and *d–π* interactions are particularly important, and systems with π acceptor orbitals are the dominant ligand species. Amongst the most common ligands encountered are carbon monoxide, phosphines, phosphites and unsaturated hydrocarbons. There are, however, a few relatively well-characterized iron(0) complexes derived from the reduction of higher oxidation state complexes containing N donor ligands possessing delocalized π systems.

44.1.3.2 Nitrogen Ligands

Herzog and co-workers[189] reduced $[Fe(bipy)_3]^{2+}$ to the zerovalent complex with Li_2bipy. Reduction of $FeCl_3$ in the presence of 2,2′-bipyridine also results in the formation of $[Fe(bipy)_3]$ as in equation (17). The black crystalline complex $[Fe(bipy)_3]$ dissolves in THF, dioxane or benzene to give red-violet solutions, while in protic solvents such as water, dilute acid or alcohols the complex is oxidized to $[Fe(bipy)_3]^{2+}$ with liberation of hydrogen. $[Fe(bipy)_3]$ decomposes at 145 °C *in vacuo* to iron and 2,2′-bipyridine. The compound appears to be paramagnetic[190] although its magnetic susceptibility has not been reported since the measurement is distorted by traces of metallic iron. Conductance and ESR measurements ($g_{av} = 2.075$) are in agreement[190] with a d^8 configuration with

neutral ligands. If an excess of reducing agent is used[191,192] a species is generated which apparently contains iron(−1) as in equation (18). However, ESR evidence suggests that the unpaired electrons in Na[Fe(bipy)$_3$] occupy molecular orbitals composed mainly of ligand orbitals. A similar reduction route can be used to prepare [Fe(terpy)$_2$] and related iron(0) complexes.[193] [Fe(bipy)$_3$] and coordinatively unsaturated [Fe(bipy)$_2$] can also be prepared[194] by the thermal decomposition of the alkyl complex [Et$_2$Fe(bipy)$_2$]; the tris derivative is formed when the decomposition takes place in the presence of free 2,2′-bipyridine.

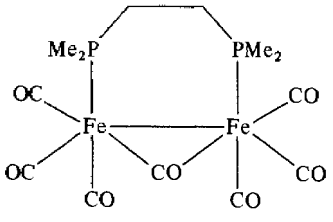
$$2FeCl_2 + 6bipy + 3Li_2bipy \xrightarrow{THF} 2[Fe(bipy)_3] + 4LiCl + 3bipy \quad (17)$$

$$3Nabipy + [Fe(bipy)_3]Cl_2 \longrightarrow Na[Fe(bipy)_3] + 3bipy + 3NaCl \quad (18)$$

The reduction of the classic iron(II) tris α,α′-diimine chelates has also been investigated electrochemically.[195,196] Whilst the first two reduction steps to the one and zero oxidation states are well understood, the nature of further reduced species is unclear. Such studies, however, do appear to demonstrate a limit to which increased electron density at the iron can be supported before charge becomes resident on the ligands. In the case of [Fe(bipy)$_3$] the increased electron density at iron must be stabilized by *d*-π back-donation. The structure of [Fe$_2$(CO)$_7$(bipy)] demonstrates[197] that 2,2′-bipyridine is a poorer π acceptor than two carbon monoxide ligands. Substitution of two carbon monoxide ligands in [Fe$_2$(CO)$_9$] by bipy leads to this complex which has one not three bridging CO groups. This is explained[197] in that bridging CO is a poorer π acid than terminal CO. The structure generated has a reduced number of bridging CO (increased number of terminal CO) ligands to make up for the poorer π acidity of bipyridine. Whilst the π acceptor properties of 2,2′-bipyridine represent a limit to the formation of less than zerovalent complexes with neutral ligands, the structure and spectra of [(η^6-toluene)Fe(bipy)] clearly demonstrate[198] that 2,2′-bipyridine does have considerable ability to accept π electron density from iron(0). The strength of the interaction is apparent from the Fe—N distance of 1.9 Å and the inertness of the toluene ligand which is only displaced by a very strong π acid such as dppe.

44.1.3.3 Phosphorus Ligands

Commonly, many iron(0) compounds containing phosphorus donor ligands are thought of as 'organometallic' rather than coordination complexes. Nonetheless, a brief discussion of some of their more important structural features is appropriate. Iron carbonyls react thermally[199,200] or photochemically[201] with PPh_3 to yield a mixture of [Fe(CO)$_4$PPh$_3$] and [Fe(CO)$_3$(PPh$_3$)$_2$]. Especially bulky phosphines such as P(Bu^t)$_3$ or P(EMe$_3$)$_3$ (E = Ge, Si, Sn) produce[202] only [Fe(CO)$_4$PR$_3$]. [Fe(CO)$_3$(PR$_3$)$_2$] are stable pale yellow complexes which can also be obtained from a variety of organometallic compounds containing the Fe(CO)$_3$ moiety. IR and Mössbauer spectra of [Fe(CO)$_3$(PR$_3$)$_2$] are consistent with a trigonal bipyramidal structure and these complexes are only known as the *trans* isomers. [Fe(CO)$_5$] reacts with bidentate phosphines to give mononuclear products containing mono and bidentate phosphine ligands, and binuclear complexes containing bridging phosphine ligands. The complex [Fe(CO)$_3$dmpe] (dmpe = 1,2-dimethylphospinoethane) has a geometry intermediate between square pyramidal and trigonal bipyramidal because of the small ligand 'bite'. The iron atoms in the dinuclear bridged complex (**12**) are coordinated in a trigonal bipyramidal geometry with the phosphorus ligands occupying *cis* axial positions.

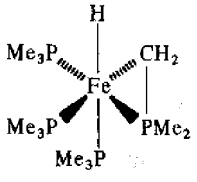


(12)

The carbonyl ligands in [Fe(CO)$_3$(PR$_3$)$_2$] compounds are rather inert towards substitution, but these compounds do find use as starting materials for a number of complexes *via* an oxidative route (*vide infra*). Although [Fe(CO)$_3$(PPh$_3$)$_2$] is only sparingly soluble in most common organic solvents,

it is rather more soluble in concentrated sulfuric acid giving a yellow solution shown by NMR spectroscopy to contain a protonated species. Careful halogenation of $[Fe(CO)_3(PR_3)_2]$ affords[201] $[Fe(CO)_3(PR_3)X_2]$. The controlled one-electron oxidation of $[Fe(CO)_3(L)_2]$ complexes generates deep green iron(I) complexes, some of which can be isolated and are useful in the preparation of novel iron(II) complexes. These reactions are discussed in Section 44.1.4.3. *trans*-$[Fe(CO)_3L_2]$ complexes react with mercury(II) halides to form adducts (L = PPh_3 adduct is 1:1, L = $P(OPh)_3$ adduct is 1:2). Carbon monoxide is displaced photochemically from $[Fe(CO)_3(PEt_3)_2]$ by sulfur dioxide to give $[Fe(CO)_2(PEt_3)_2(SO_2)]$, which undergoes oxidative[204] elimination with HI to yield $[Fe(CO)_2(PEt_3)_2I_2]$. The analogous complex $[Fe(CO)_2(Ph_3)_2I_2]$ has been shown[205] to contain *cis* iodides, *cis* carbonyls and *trans* phosphines. The analogous phosphite complexes $[Fe(CO)_2\{P(OR)_3\}_2X_2]$, however, are thought[206] to have *cis* carbonyl, *cis* phosphite and *cis* halides for X = I but *trans* halides for X = Br.

Higher degrees of carbonyl substitution by phosphorus donor ligands in iron(0) complexes may be obtained by reduction of the corresponding halide in the presence of free ligand, or by direct synthesis using iron atoms. Thus reduction of $\{Fe(dmpe)_2Cl_2]$ by sodium naphthalenide in THF yields[207] red-brown air sensitive $[Fe(dmpe)_2]$. Sodium amalgam reduction of $[Fe\{P(OMe)_3\}_3Cl_2]$ in the presence of $P(OMe)_3$ gives[208] the very air sensitive yellow complex $[Fe\{P(OMe)_3\}_5]$. This complex reacts with carbon monoxide in ether to yield the remaining two members of the series $[Fe(CO)_x\{P(OMe)_3\}_{5-x}]$, namely $[Fe(CO)\{P(OMe)_3\}_4]$ and $[Fe(CO)_2\{P(OMe)_3\}_3]$. Reduction of $[FeCl_2(PMe_3)_3]$ with sodium amalgam in THF in the presence of excess PMe_3 under argon gives $[Fe(PMe_3)_4]$ (**13**) in which a hydride transfer has taken place to yield[209,210] an octahedral iron(II) species.



(13)

Iron pentacarbonyl reacts with PF_3 at elevated temperature and pressure giving the series of complexes $[Fe(CO)_{5-x}(PF_3)_x]$. $[Fe(PF_3)_5]$ may also be made by the direct reaction[211] of iron atoms with PF_3 at low temperature. This route enables the novel binuclear complex $[(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3]$, not available by other means, to be obtained. The metal atom technique[212] has been extended to the synthesis of a number of d^8 iron complexes[213–215] with phosphorus donor ligands. In the low temperature reaction[216] of iron atoms with cycloocta-1,5-diene (1,5-cod), the very temperature-sensitive and highly reactive compound $[Fe(1,5\text{-cod})_2]$ is formed. This compound reacts with PMe_3 to yield $[Fe(1,5\text{-cod})(PMe_3)_3]$ but with $P(OMe)_3$ to yield $[Fe(1,3\text{-cod})\{P(OMe)_3\}_3]$. $[Fe(1,5\text{-cod})_2]$ reacts with dppe in ether/methylcyclohexane at −20 °C to yield, presumably, $[Fe(dppe)_2]$, which decomposes above 0 °C but reacts[216] with nitrogen to give the five-coordinate dinitrogen complex $[Fe(dppe)_2N_2]$.

44.1.4 IRON(I)

44.1.4.1 Introduction

Although isoelectronic with cobalt(II), d^7 iron(I) complexes show a marked instability, particularly with respect to disproportionation to iron(0) and iron(II) complexes. Accordingly few iron(I) compounds have been isolated and characterized. It is therefore not appropriate to group iron(I) complexes by the ligand classification used for other complexes. The scheme which has been adopted is to discuss reports of iron(I) complexes under the headings of: carbon monoxide and arsine ligands, phosphorus-containing ligands, cyanide ligands, complexes of macrocyclic ligands and organometallic complexes.

44.1.4.2 Carbon Monoxide and Arsine Ligands

There are several examples of iron(I) complexes in which the +1 oxidation state is stabilized by coordination of carbon monoxide or arsine ligands. In an early paper[217] Hieber and Lagally

described the formation of $[Fe(CO)_2I]$ by heating $[Fe(CO)_2I_2]$ in a stream of CO_2 as in equation (19). Careful oxidation of $[Fe(CO)_3pdma]$ with iodine in benzene/nitrobenzene (equation 20) under nitrogen has been reported[216] to give brown yellow $[Fe(CO)_3pdma]^+I^-$ (pdma = *o*-phenylenebis-dimethylarsine).

$$[Fe(CO)_2I_2] \longrightarrow [Fe(CO)_2I] + \tfrac{1}{2}I_2 \quad (19)$$

$$[Fe(CO)_3pdma] + \tfrac{1}{2}I_2 \longrightarrow [Fe(CO)_3pdma]^+ I^- \quad (20)$$

Amongst dimeric organometallic compounds which formally contain iron(I) is the well-known[219] diamagnetic dimeric carbonyl complex $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$. Recently a series of paramagnetic monomeric iron carbonyl hydrides has been generated[220] by UV irradiation of dilute solutions of $[Fe(CO)_5]$ in pentane under hydrogen at low temperatures. The iron(I) species $[HFe(CO)_4]$ was characterized by ESR spectroscopy ($g = 2.0120$). One-electron electrochemical oxidation of $[Fe(CO)_5]$ in trifluoroacetic acid is reported[221] to yield transient $[Fe(CO)_5]^+$ (half-life = 50–500 ms). The naked ion Fe^+ has been observed in ion cyclotron resonance studies of its interaction with alkanes.[222] Fe^+ was generated in the gas phase by electron impact on $[Fe(CO)_5]$.

44.1.4.3 Phosphorus Ligands

In much of the reported chemistry of iron(I) the low oxidation state is stabilized by coordination to phosphorus-containing ligands. Thus, Sacco and co-workers prepared[223] the paramagnetic iron(I) hydride $[FeH(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane) by the sodium reduction of $[FeHCl(dppe)_2]$ in benzene under nitrogen as in equation (21) and also by its reaction with $[Co(N_2)(PEt_2Ph)_3]Na$ in THF. Deep red crystalline $[FeH(dppe)_2]$ is soluble in benzene and toluene but insoluble in pentane. The compound is paramagnetic both in the solid state and in solution and obeys the Curie–Weiss law between 97 K and 297 K ($\theta = 14.5°$). It is isomorphous[224] with $[CoH(dppe)_2]$ and shows a strong ESR signal at room temperature in toluene solution centred[225] at $g = 2.085$. Under a nitrogen atmosphere $[FeH(dppe)_2]$ reacts with trityl salts (Ph_3CX; X = BF_4, ClO_4) in benzene to yield $[FeH(N_2)(dppe)_2]X$ as in equation (22) and with stoichiometric amounts of HCl or $HClO_4$ in ethanol to yield respectively $[FeHCl(dppe)_2]$ and $[FeH(N_2)(dppe)_2]^+ClO_4^-$. The reaction with acids appears to proceed *via* the oxidative addition of a proton to give an unstable iron(III) dihydride $[FeH_2(dppe)_2]^+$. With a large excess of hydrochloric acid at 80 °C $[FeCl_2(dppe)_2]$ is formed. The reduction of $[FeCl_2(dppe)_2]$ with stoichiometric amounts of sodium in the presence of free phosphine as in equation (23) yields the analogous iron(I) halide $[FeCl(dppe)_2]$.

$$[FeHCl(dppe)_2] + Na \longrightarrow [FeH(dppe)_2] + NaCl \quad (21)$$

$$[FeH(dppe)_2] + Ph_3CX + N_2 \longrightarrow [FeH(N_2)(dppe)_2]X \quad (22)$$

$$[FeCl_2(dppe)_2] + Na \longrightarrow [FeCl(dppe)_2] + NaCl \quad (23)$$

The red crystals of this complex have a bulk magnetic moment of 2.11 BM ($\theta = 8$ K) and in toluene solution a strong ESR signal with a partially resolved hyperfine structure[226] is centred at $g = 2.075$. The complexes $[FeX(dppe)_2]$ (X = Br, I) have also been prepared. Reaction of $[Fe(dppe)_2]$ with $AlEt_3$, $AlEt_2Cl$ or $Al(Bu^i)_2H$ affords $[Fe(dppe)_2]^+X^-$ ($X^- = AlH_2R_2^-$ or $AlCl_2R_2^-$). These four-coordinate iron(I) complexes react with ligands L to give the five-coordinate cations $[FeL(dppe)_2]^+$ (L = C_2H_4, CO, N_2, MeCN).[227] The ESR spectra of a range of iron(I) bis-dppe complexes have been measured; the reported g values (Table 2) are sensitive to both coordination number and the nature of the additional ligand. On the basis of their ESR spectra the complexes $[FeH(dppe)_2]$ and $[FeCl(dppe)_2]$ have been assigned respectively square pyramidal and trigonal bipyramidal coordination geometries.[227]

In deaerated methanolic solution, iron(II) hydrido complexes of the type $[FeH(L)(dppe)_2]^+$ (L = MeCN, $MeCH_2CN$, $CH_2{=}CHCN$, PhCN and *p*-MeC_6H_4CN) are reduced to $[FeH(L)(dppe)_2]$ by solvated electrons produced by γ-radiolysis of the solvent.[228] In pulsed radiolysis studies $[FeH(L)dppe_2]$ decays to five-coordinate $[FeH(dppe)_2]$ (half-life $\leqslant$ 1 s). In continuous radiolysis however, $[FeH(dppe)_2]$ is not the final product and here as in its reaction with acids it is suspected that oxidative addition of a proton yields an unstable iron(III) dihydride which decom-

Table 2 ESR g values for dppe Complexes of Iron(I)[a]

Complex	g_0
$[FeH(dppe)_2]$	2.0856
$[FeCl(dppe)_2]$	2.0768
$[FeBr(dppe)_2]$	2.0900
$[FeI(dppe)_2]$	2.1068
$[Fe(C_2H_4)(dppe)_2]^+$	2.085
$[Fe(CO)(dppe)_2]^+$	2.0515
$[Fe(MeCN)(dppe)_2]^+$	2.0981
$[Fe(dppe)_2]^+$	2.21

[a]dppe = 1,2-bis(diphenylphosphino)-ethane; data from M. Gargano, P. Giannoccaro, M. Rossi, G. Vassapollo and A. Sacco, *J. Chem. Soc., Dalton Trans.*, 1975, 9.

poses to hydrogen and $[Fe(dppe)_2]^+$. Further oxidation yields $[FeH(dppe)_2]^{2+}$ which is itself reduced by the iron(I) species $[FeH(dppe)_2]$ to $[FeH(dppe)_2]^+$. This coordinatively unsaturated species then binds the neutral ligand present in solution and so regenerates the starting complex.[228] Pulsed radiolysis studies of the complexes $[FeH(L)(dppe)_2]^+$ (L = $P(OMe)_3$, CO) in deaerated methanol solution showed the existence of a novel five-coordinate iron(I) intermediate $[FeH(L)(dppe)_2]$ in which one dppe is monodentate. Ring closure by dppe with elimination of L results in the familiar[229] iron(I) complex $[FeH(dppe)_2]$. These processes are outlined in Scheme 5. Interestingly, pulse radiolysis techniques have also been used to generate transient iron(I) species in aqueous solution.[230]

$$[FeH(L)(dppe)_2]^+ \xrightarrow[e^-]{\text{pulsed } \gamma \text{ radiolysis}} [FeH(L)(dppe)_2] \longrightarrow [FeH(dppe)_2] + L \xrightarrow[MeOH_2^+]{\text{continuous } \gamma \text{ radiolysis}}$$

$$[FeH_2(dppe)_2]^+ \longrightarrow [FeH(dppe)_2]^+ + H_2 \xrightarrow{MeOH_2^+} [FeH(dppe)_2]^{2+} \xrightarrow{[FeH(dppe)_2]} [FeH(dppe)_2]^+$$

Scheme 5

Cyclic voltammetric studies of $[Fe(CO)_3L_2]$ {L = PPh_3, $PMePh_2$, $P(NMe_2)_3$, $P(OPh)_3$; L_2 = dppe, dppm (dppm = bis(diphenylphosphino)methane)} in dichloromethane showed reversible one-electron oxidation to $[Fe(CO)_3L_2]^+$, which was identified spectroscopically.[231,232] Oxidation of $[Fe(CO)_3(AsPh_3)_2]$ is apparently not reversible but the corresponding iron(I) cation was identified by ESR and IR spectroscopy. The complexes $[Fe(CO)_3L_2]^+$ are generated chemically as deep green solutions[231] by the oxidation of $[Fe(CO)_3L_2]$ with $[N(C_6H_4Br\text{-}p)_3]^+PF_6^-$ in dichloromethane (formed by the reaction between $N(C_6H_4Br\text{-}p)_3$ and $AgPF_6$ followed by filtration to remove metallic silver) (equation 24). The salt $[Fe(CO)_3(PPh_3)_2]^+PF_6^-$ was isolated as the hemidichloromethane solvate, which is soluble in polar solvents. Reaction with halogens (X_2, X = Cl, Br, I; 1:1 ratio Fe:X) in dichloromethane (equation 25), is rapid to give $[FeX(CO)_3(PPh_3)_2]^+$. With halide ions $[Fe(CO)_3(PPh_3)_2]^+$ (1:1 molar ratio) forms the paramagnetic intermediate $[FeX(CO)_3(PPh_3)_2]$ which disproportionates to give $[Fe(CO)_3(PPh_3)_2]$ and $[FeX_2(CO)_{4-n}(PPh_3)_n]$, (X = I, n = 1; X = Br, n = 1, 2; X = Cl, n = 2). The iron(I) species $[FeX(CO)_3(PPh_3)_2]$ is an intermediate in the oxidative elimination reactions of $[Fe(CO)_3(PPh_3)_2]$ with halogen. It is not clear whether this species contains an Fe—X bond or a halogen–acyl group.[231]

$$[Fe(CO)_3L_2] + N(C_6H_4Br\text{-}p)_3^+ \longrightarrow [Fe(CO)_3L_2]^+ \quad (24)$$

$$[Fe(CO_3)L_2]^+ + X_2 \longrightarrow [FeX(CO)_3L]^+ + X^- \quad (25)$$

The electrochemical reduction of a series of cationic iron(II) hydrido complexes *trans*-$[FeH(L)(dppe)_2]^+$ (L = N_2, C_5H_5N, PhCN, CH_2CHCN, MeCN, $P(OMe)_3$, $P(OEt)_3$, CO) has been shown to proceed *via* transient d^7 iron(I) species which lose one of the neutral ligands. Further reduction of the resulting five-coordinate intermediates yields stable d^8 iron(0) anionic hydrides.[233]

The oxidative substitution and radical coupling reactions of $[Fe(CO)_3(PPh_3)_2]^+$ have led to a number of unusual iron(0) and iron(II) complexes, *e.g.* equation (25), which cannot be obtained[234] from its diamagnetic precursor $[Fe(CO)_3(PPh_3)_2]$. The iron(I) species is relatively unstable, probably due to poor charge delocalization by the phosphine ligands. The presence of an imidazolidinylidene

Table 3 Properties of Carbene–Iron(I) Complexes[a]

Complex[b]	*M.P.* (°C)	*Colour*	*ν(CO) in MeCl* (cm^{-1})	*ν(CN₂)* (cm^{-1})	g_{av} *CH_2Cl_2 solution*	*a(³¹P)* (mT)	*Stable solution* (°C)	μ_{eff} (BM)
$[Fe(CO)_3(L)_2][BF_4]$	109	Very dark green	2058m, 1978vs, 1964sh	1522ms	2.043	−s	20	
$[Fe(CO)_3(L)(PPh_3)][BF_4]$		Dark green	2067m, 2001s, 1985s	1526ms	2.047	2.26d	10	
$[Fe(CO)_3(L)(PEt_3)][BF_4]$		Very dark green	2061m, 1991s, 1976s	1525ms	2.046	2.39d	20	
$[Fe(CO)_3L(\frac{1}{2}\text{-dppe})][BF_4]$	130 decomp.	Dark green	2065m, 2004s, 1980s	1528ms	2.045	2.38d	10	2.65 per binuclear unit
$[Fe(CO)_2(L)_2(PPh_3)][BF_4]$		Very dark green	1973s, 1904s	1513 ms	2.045	1.85d	20	
$[Fe(CO)_2(L)(PPh_3)_2][BF_4]$		Green	1980s, 1918s	1517ms	2.047	2.03t	20	1.68
$[Fe(CO)_2(L)(PEt_3)_2][BF_4]$		Dark blue-green	1969s, 1900s	1515ms	2.046	2.22t	20	
$[Fe(CO)_2(L)\{P(OPh)_3\}_2][BF_4]$		Grass green	2022s, 1960s		2.048	3.15t	20	
$[Fe(L)_2(NO)_2][BF_4]$		Brown	1781s, 1710s, {ν(NO)}	1530s	2.034	−s	20	

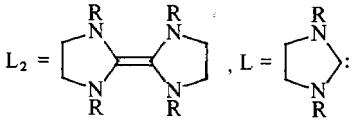
[a] From M. F. Lappert, J. J. MacQuitty and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1981, 1583

[b] L = $\overbrace{CN(Me)CH_2CH_2NMe}$

ligand allows more efficient charge delocalization.[235] Several carbenecarbonyl–iron(I) complexes have been isolated by oxidation of $[Fe(CO)_3(L)(L')]$ (L = :CN(Me)CH_2CH_2NMe; L′ = PPh_3, PEt_3, ½dppe, $P(OPh)_3$) using a variety of agents (I_2, $AgBF_4$, $AlCl_3$, MeI, Ph_3CCl, TCNE, AgCN, $AgPF_6$, $AgSbF_6$) in THF or dichloromethane under argon. Nine crystalline complexes have been reported, and these are listed in Table 3 together with some of their properties. The iron(I) salts are susceptible to neutral ligand exchange reactions, in particular CO displacement as for example in equation (26). When a THF solution of an allyl iron halide $[Fe(\eta\text{-}C_3H_5)(CO)_2L'(X)]$ (X = Br or I; L′ = CO, phosphine or the carbene ligand L above) is stirred with the electron rich alkene L_2, the neutral iron(I) complexes $[Fe(\eta\text{-}C_3H_5)(CO)_2L']$ are formed (equation 27). These green complexes have been characterized spectroscopically in THF solution and data are given in Table 4.

$$[Fe(CO)_3(L)_2][BF_4] \xrightarrow[THF\ 25^\circ C]{PPh_3} [Fe(CO)_2(L)_2(PPh_3)][BF_4] \quad (26)$$

$$4[Fe(\eta\text{-}C_3H_5)(CO)_2L'(X)] + L_2 \xrightarrow[20^\circ C]{THF} 4[Fe(\eta\text{-}C_3H_5)(CO)_2L] + 4(L{-}X)X \quad (27)$$



L′ = CO, PR_3, L

Table 4 IR and ESR Spectroscopic Data for THF Solutions of the Complexes $[Fe(\eta\text{-}C_3H_5)(CO)_2L']$

L′	g_{av}	$a\ (^{31}P)$ (mT)	$\nu(CO)$ (cm^{-1})
CO	2.045		2049, 1065
PMe_2Ph	0.048	0.72	1957, 1892
PPh_3	2.050	1.69	1956, 1893
PEt_3	2.046	1.15	1947, 1889
L	2.051		1968, 1907

M. F. Lappert, J. J. MacQuitty and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1981, 1583.

44.1.4.4 Cyanide Complexes

Treadwell and Huber reported[236] the electrolytic reduction of aqueous $K_4[Fe(CN)_6]$ in the presence of excess KCN yielding a colourless solution which reduces one mole of $[Fe(CN)_6]^{3-}$. This was interpreted as indicating the formation of an iron(I) cyano complex, although the possible formation of a hydrido species such as $[Fe(CN)_5H]^{3-}$ has not been ruled out by subsequent chemical studies.[237] The complex ions $[Fe(CN)_6H]^{4-}$ and $[Fe(CN)_5]^{4-}$ have been observed in pulse radiolysis studies of aqueous hexacyanoferrate(II) solutions.[238] γ-Irradiation of single crystals of alkali halides doped with hexacyanoferrate(II) ions have yielded ESR spectra characteristic of a number of iron(I) species.[239,240] These include $[Fe(CN)_5]^{4-}$, $[Fe(CN)_5(H_2O)]^{4-}$, $[Fe(CN)_5Cl]^{5-}$, $[Fe(CN)_4Cl_2]^{5-}$, $[Fe(CN)_5Br]^{5-}$ and $[Fe(CN)_4Br_2]^{5-}$. The spectra of the pentacyano species contain some evidence for a 'bent' cyanide ligand.[239]

44.1.4.5 Macrocyclic Ligands

There have been a number of reports of iron(I) complexes generated by the reduction of iron phthalocyanine compounds. The assignment of metal oxidation state is complicated by the ability of the phthalocyanine ring to undergo reduction. Progressive reduction of iron(II) phthalocyanine with sodium in THF first yields a purple solution which shows a strong ESR spectrum centred at $g = 2.01$, and on further reduction the solution turns blue and the ESR signal collapses. A final reduction stage yields a green solution whose ESR signal[241] is a single isotropic line at $g = 2.003$. Subsequently further electrochemical investigation of this sequence identified a fourth (earlier) stage

in the sequential reduction though this stage could not be reproduced using Na/THF.[242] These authors postulate the sequence shown in Scheme 6.

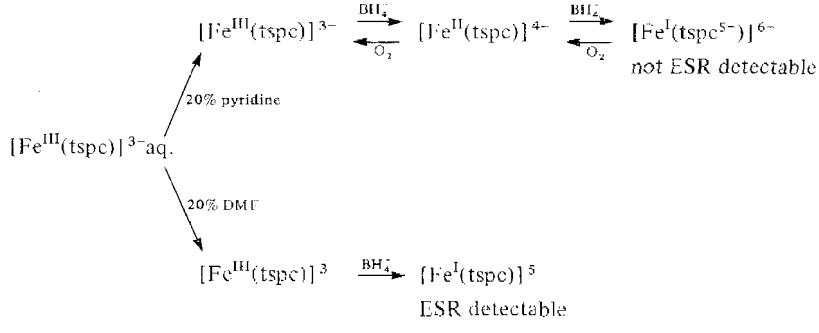
$$\underset{\text{green}}{[Fe^{II}pc]} \xrightarrow{e^-} \underset{\text{pink}}{[Fe^{II}pc]^-} \xrightarrow{e^-} \underset{\text{purple}}{[Fe^{I}pc]^{2-}} \xrightarrow{e^-} \underset{\text{blue-violet}}{[Fe^{I}pc]^{3-}} \xrightarrow{e^-} \underset{\text{green-blue}}{[Fe^{I}pc]^{4-}}$$

Scheme 6

The redox couple $[Fe^{II}pc]/[Fe^{I}pc]$ is sensitive to solvent since the extent of π back-donation to phthalocyanine is influenced by the electron donating ability of axial solvent ligands. Thus the iron(II) complex is more easily reduced in solvent systems where π back-donation is minimized. The ease of reduction of $[Fe^{II}pc]$ lies in the sequence pyridine > DMSO > DMF as solvents.[242] By contrast the Fe^{II}/Fe^{I} redox potentials of iron(II) porphyrin complexes show little solvent dependence because their capability for π back-donation is relatively small.[242]

The iron(I) anion [Fe(TPP)]$^-$ (TPP = tetraphenylporphine dianion) is produced[243] by the reduction of μ-oxo-bis(tetraphenylporphineiron(III)) with Na/Hg in THF. The product appears to exist in different spin states in THF solution (200–300 K) and frozen THF matrix at 77 K. A recent study, however,[244] is unequivocal about the d^7 Fe^{I} nature of the complex in the presence of pyridine.

Carbon monoxide reacts with [Fe(TPP)]$^-$ to form a five-coordinate complex [Fe(TPP)CO], which can be reduced electrochemically to the corresponding iron(I) species from which, however,[245] CO spontaneously dissociates. The Fe—CO interaction is stabilized by the presence of hydrocarbon chains bound by amide linkages to the *ortho* position of the TPP phenyl rings. Carbon monoxide adducts of iron(I) complexes of a number of these 'superstructured' porphyrins have been reported.[245] The chemistry of these highly reduced species is of relevance to understanding[246] the reactions of cytochrome P-450 and the peroxidases.



Scheme 7

Deep blue [iron(III)(tspc)] (tspc = 3,10,17,24-tetrasulfonatophthalocyanine) is reduced in aqueous solutions to give two iron(I) tspc species[247,248] as shown in Scheme 7. Stoichiometric sodium reduction[249] of $[Fe^{II}(salen)]$ in THF affords high-spin d^7 [Fe(salen)]$^-$. At room temperature this complex has a magnetic moment of 3.7 BM and the Curie-Weiss law is obeyed down to 90 K ($\theta = -46\,^\circ$). The sodium salt is freely soluble in THF forming air and moisture sensitive deep green solutions. The [Fe(salen)]$^-$ anion is a strong nucleophile reacting, as in equation (28) for instance, with benzyl chloride at $-60\,^\circ$C to give the corresponding iron(III) benzyl derivative[249] which is high-spin.

$$[Fe(salen)]^- + PhCH_2Cl \longrightarrow [PhCH_2Fe(salen)] + Cl^- \qquad (28)$$

Controlled potential electrolysis of the iron(II) complex $[Fe(L)(MeCN)_2]^{2+}$ (L = Me_6[14]1,3,8,10-tetraeneN_4, see Section 44.1.5.12.3) in acetonitrile at the first reduction plateau gives[250] the purple iron(I) cation $[Fe(L)]^+$, isolable in high yield as the $CF_3SO_3^-$ salt. The ESR spectrum in frozen acetonitrile is characteristic of low-spin d^7 iron(I) having a rhombic distortion from octahedral geometry. The effective magnetic moment measured by an NMR technique is 2.3 BM. A second quasi-reversible reduction step yields the analogous iron(0) complex; however, repeated scanning of this redox system results in hydride abstraction from the supporting electrolyte $Bu^n_4NBF_4$ to form a second iron(I) complex [FeH(L)(MeCN)]. The purple-black product also shows the appropriate ESR spectrum for low-spin d^7 iron(I) (μ_{eff} = 2.1 BM). An Fe—H stretching vibration is observed as a sharp IR absorbtion at 1890 cm^{-1}. The iron(I) alkyl and aryl derivatives [FeR(L)] result[250] from the sequential reaction of the iron(II) complex $[Fe(L)Cl]^+$ with two equivalents of the appropriate lithium alkyl or aryl as in equations (29) and (30). ESR and magnetic data are again consistent with

d^7 iron(I) and the unpaired electron occupies a molecular orbital which is predominantly metal ion in character.

$$[Fe(L)Cl]^+ + LiR \longrightarrow [Fe(L)Cl] + Li^+ + \tfrac{1}{2}R{-}R \quad (29)$$

$$[Fe(L)Cl] + LiR \longrightarrow [Fe(L)R] + LiCl \quad (30)$$

44.1.4.6 Organometallic Complexes

The oxidation state of +1 in iron chemistry is interesting for its rarity and so it is appropriate to include a description of some compounds which would not classically be regarded as coordination complexes. The iron(I) complexes $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6Me_6)]$, $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6Et_6)]$ and $[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6Me_6)]$ are obtained by Na/Hg reduction of the corresponding cationic compounds[251] in DME at 20 °C. The parent compound $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]$ is highly unstable with respect to dimerization through the arene ring which is preceded by intramolecular electron transfer to an arene carbon atom.

A catalytically active species containing iron(I) has been postulated[252,253] in the cross coupling of 1-bromopropene with a variety of alkylmagnesium bromides in the presence of a reagent derived from the reduction of tris(dibenzoylmethido)iron(III). At intense ESR signal centred at $g = 2.08$ is observed on treating $[Fe(DBM)_3]$ with excess ethylmagnesium bromide in THF at −40 °C. A similar spectrum is observed on treating $FeCl_3$ and $[Fe(acac)_3]$ in this way. The existence of an iron(I) intermediate has been postulated in certain systems studied for the fixation of molecular nitrogen. Thus, an ESR signal at $g = 2.01$ observed[254] on mixing $FeCl_3$ and LiPh in ether was assigned to d^7 iron(I).

44.1.4.7 Nitric Oxide Complexes

One of the earliest assignments of an oxidation state of +1 for an iron complex was that of Wilkinson and co-workers[85] based on the magnetic susceptibility, IR and absorbtion spectra of $[Fe(H_2O)_5NO]^{2+}$. The potential for nitric oxide to act as either a two or three electron donor in its coordination to transition metal ions, however, has led to much controversy. For this reason iron nitrosyl complexes are discussed separately in Section 44.1.2.

44.1.5 IRON(II)

44.1.5.1 Introduction

For many years the coordination chemistry of iron(II) was overshadowed by the Werner complexes of its isoelectronic neighbour cobalt(III). Compared with cobalt(III) a substantially higher ligand field is needed to produce low-spin iron(II) complexes; once formed, however, they are usually thermodynamically very stable and kinetically inert. Complexes of this type are easily prepared, and a number have been known for a long time. Classic examples include mixed oxidation state cyanides (Prussian blues) and tris-(α,α′-diimine) complexes ('ferroins'). More recent examples include complexes containing phosphorus and sulfur donors. With weaker field ligands oxidation to iron(III) species is a common preparative problem, and no doubt this has been one of the reasons for the slow early development of what has become such a rich area. In complexes having intermediate ligand field strengths thermally induced spin transitions become possible and these have been extensively investigated. With strong field tetradentate macrocyclic ligands the relatively unusual $S = 1$ spin state is often observed. A major objective has been to devise complexes that mimic the behaviour of the natural iron(II) oxygen carrying proteins, and a range of synthetic porphyrin complexes are now available that do this. Another important biologically relevant area is that of the iron/sulfide clusters that provide convincing models for several electron transfer systems.

A notable feature of the literature concerned with iron chemistry is that while a number of excellent reviews are available that deal with specific topics, there are none that deal with the whole coordination chemistry of iron(II). The present review first deals with cyanide complexes followed by complexes containing simple monodentate nitrogen donors. The huge amount of work published

on diimine and related complexes is covered in several subsections before considering complexes with phosphorus, oxygen and sulfur donors. Then halide complexes are discussed before finally considering the N donor macrocyclic systems.

44.1.5.2 Cyanide Complexes

44.1.5.2.1 The hexacyano complex

The exceptionally high affinity[255] of iron(II) for cyanide ion is reflected in the heat of formation[256,257] of the $[Fe(CN)_6]^{4-}$ anion (equation 31). The stability of this, the ferrocyanide ion, is illustrated by the nature and history[258] of its iron(III) salt, Prussian blue, possibly the first isolated coordination complex, which is discussed in Section 44.1.5.2.4.

$$[Fe(H_2O)_6]^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-} + 6H_2O \qquad \Delta H_f^0 = -358.9\,kJ\,mol^{-1} \qquad (31)$$

The addition of aqueous cyanide to a solution containing an excess of an iron(II) salt results[259] in the precipitation of an impure iron cyanide. On the other hand, the addition of excess cyanide to iron(II) solutions rapidly gives the hexacyanoferrate(II) ion. The rate of uptake of the sixth cyanide ion is significantly slower than for the previous five due to low-spin $[Fe(CN)_5H_2O]^{3-}$ being kinetically inert. This second order stage of the reaction has[260] an activation energy of 104 kJ mol^{-1} and an equilibrium constant of $\sim 10^8$. In fact, these data relate to the formation of $[Fe(CN)_6]^{4-}$ from both $[Fe(CN)_5H_2O]^{3-}$, itself very stable, and $[Fe_2(CN)_{10}]^{6-}$, both of which are present in the reacting solution. The inner sphere reduction of $[Fe(CN)_6]^{3-}$ with a variety of mild reducing agents readily forms $[Fe(CN)_6]^{4-}$. Such reactions may be mechanistically complex, as for example in the reduction with sulfite ion which involves[261] an intermediate formed from $[Fe(CN)_6]^{3-}$ and SO_3^- radical anion as shown in Scheme 8. The octahedral geometry of the ferrocyanide ion has been established[262] in $K_4[Fe(CN)_6]\cdot 3H_2O$. When ammonium hexacyanoferrate(II) is heated to 320 °C *in vacuo*, a pale green substance of empirical formula 'Fe(CN)$_2$' results about which little is known.

$$[Fe(CN)_6]^{3-} + SO_3^{2-} \longrightarrow [Fe(CN)_6]^{4-} + SO_3^-$$

$$[Fe(CN)_6]^{3-} + SO_3^- \longrightarrow [Fe(CN)_5(CN\cdot SO_3)]^{4-}$$

$$[Fe(CN)_5(CN\cdot SO_3)]^{4-} + H_2O \longrightarrow [Fe(CN)_6]^{4-} + SO_4^{2-} + 2H^+$$

Scheme 8

With the exception of the barium salt, which is only sparingly soluble, the ferrocyanides of the alkali and alkaline earth metals are easily soluble in water though not in alcohols. All these soluble salts separate from aqueous solution as well-defined pale yellow crystals. Large numbers of sparingly soluble salts of general formula $K_2M^{II}[Fe(CN)_6]$ and $KM^{III}[Fe(CN)_6]$ are obtained by precipitation, as are the salts of most transition metal ions. These have polymeric structures involving M—N≡C—Fe coordination. In some cases linkage isomerization has been demonstrated, for example $KFeCr(CN)_6$ is less stable than $KCrFe(CN)_6$ which has been shown[263] to contain Cr—N≡C—Fe linkages. Many of the insoluble transition metal salts of $[Fe(CN)_6]^{4-}$ are useful ion exchange materials and the copper(II) salt has a classic use as a semipermeable membrane in the measurement of osmotic pressure. The alkali metal salts may also be made *via* the acid $[H_4Fe(CN)_6]$, which is obtained in aqueous solution by ion exchange. This strong tetrabasic acid can be precipitated as an ether addition compound by adding ether to a strongly acid solution of $[Fe(CN)_6]^{4-}$. Subsequent removal of the ether is readily accomplished to afford $[H_4Fe(CN)_6]$ as a white powder which slowly becomes blue in moist air and is soluble in water and ethanol. The protons have been shown[264,265] to be bound to the nitrogen atoms of the CN groups. The acid dissolves without decomposition in liquid hydrogen fluoride[266] to give $[Fe(CNH)_6]^{2+}$. An X-ray crystal structure[267] of $[Fe(NCD)_6]^{2+}$ as the $[FeCl_4]^-$ salt reveals tetrahedral $[FeCl_4]^-$ and octahedral $[Fe(NCD)_6]^{2+}$ moieties joined together by Fe^{II}—NCD···Cl—Fe^{III} deuterium bonds. The rigidity of the linear N—C—D group results in some tetragonal distortion of the FeN_6 octahedron. The acid $[H_4Fe(CN)_6]$ decomposes[268] on heating in various atmospheres to form Prussian blue type compounds. Both the acid and the potassium salt react[269] with BF_3 to give adducts whose IR and Mössbauer spectra are consistent with the Lewis acid bound to the nitrogen atoms of the cyanide as in equations (32) and (33).

$$[Fe(CN)_2(CNH)_4] + 2BF_3 \longrightarrow [Fe(CNH)_4(CN\cdot BF_3)_2] \quad (32)$$

$$K_4[Fe(CN)_6] + 6BF_3 \longrightarrow K_4[Fe(CN\cdot BF_3)_6] \quad (33)$$

The kinetic inertness of $[Fe(CN)_6]^{4-}$ is typified by the extremely slow thermal displacement of CN^- by α,α'-diimines. Such reactions are however catalyzed[270] by a variety of metal ions such as Hg^{2+} and the stability constants for some of the intermediate heteropolynuclear complexes have been determined.[271]

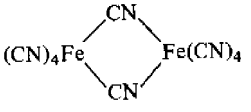
44.1.5.2.2 Pentacyano complexes

On a small scale, photolysis of $[Fe(CN)_6]^{4-}$ in aqueous solutions[272,273] affords some $[Fe(CN)_5H_2O]^{3-}$. When the reaction is carried out in the presence of nitrosobenzene the loss of cyanide is accelerated resulting in the formation of the violet PhNO complex. The rate of this process is also enhanced by the presence of certain metal ions, for example Hg^{2+} or Pb^{2+}. Larger scale preparations usually involve[274] reductive removal of NO from the nitroprusside ion in the absence of potential donor ligands other than water. Thus the reaction of $[Fe(CN)_5NO]^{2-}$ with hydroxylamine in the presence of sodium carbonate yields a yellow deliquescent powder formulated as $Na_3[Fe(CN)_5H_2O]$. The violet PhNO complex $[Fe(CN)_5PhNO]^{3-}$, which has $\lambda_{max} = 528$ nm in aqueous solution, is formed when this salt reacts with nitrosobenzene. In common with many other $[Fe(CN)_5L]^{3-}$ ions, reaction[275] with an excess of cyanide yields $[Fe(CN)_6]^{4-}$.

Solutions resulting from the preparation of $[Fe(CN)_5H_2O]^{3-}$ by reducing nitroprusside ion contain dimeric species, as indeed may solutions resulting[276] from the photolysis of $[Fe(CN)_6]^{4-}$. Two dimers have been identified, as $[Fe_2(CN)_{10}]^{6-}$ and $[Fe_2(CN)_{11}]^{7-}$. The structure proposed for $[Fe_2(CN)_{10}]^{6-}$ requires[277] two non-linear cyano bridges. A single equivalent oxidation of $[Fe_2(CN)_{10}]^{6-}$ yields a green complex $[Fe_2(CN)_{10}]^{5-}$ ($\lambda_{max} = 1200$ nm; $\varepsilon = 10^4$) and a second equivalent oxidation gives a purple ion $[Fe_2(CN)_{10}]^{4-}$ ($\lambda_{max} = 560$ nm; $\varepsilon = 1600$). The UV and visible spectra[278,279] of $[Fe_2(CN)_{10}]^{6-}$ and $[Fe_2(CN)_{10}]^{4-}$ are similar to those of the single bridged dinuclear complexes $[Fe_2(CN)_{11}]^{7-}$ and $[Fe(CN)_{11}]^{5-}$. The structure of the dimeric species derived from $[Fe(CN)_5H_2O]^{3-}$ has not been fully resolved despite recent work. Structures (**14**) and (**15**) have been proposed containing one or two cyanide bridges respectively.

$[(NC)_5Fe-CN-Fe(CN)_4H_2O]^{6-}$

(14)



(15)

Competition ratios for the reaction of the dimer with several nucleophiles have been determined[280] and the similarity between the ratios for the dimer and for $[Fe(CN)_5H_2O]^{3-}$ suggests the presence of an aqua ligand in the former. $[Fe(CN)_5H_2O]^{3-}$ is also generated by dissociation of $[Fe(CN)_5NH_3]^{3-}$ or $[Fe(CN)_5SO_3]^{5-}$ in aqueous solution; it then equilibrates with the dimeric species. In the case of the ammine complex[277] the dimerization step is rate determining in acidic solution (rate constant: 1.1 $dm^3\,mol^{-1}\,s^{-1}$ at 298 K) whilst in alkaline solution it is the reaction of $[Fe(CN)_5H_2O]^{3-}$ with another $[Fe(CN)_5NH_3]^{3-}$ which is the slowest step. $[Fe(CN)_5H_2O]^{3-}$ also reacts[278] with a variety of $[M(CN)_6]^{n-}$ complexes to give bridged dimeric species $[FeM(CN)_{11}]^{m-}$ (*e.g.* M = Fe, $m = 7$, M = Co, $m = 6$). The formation of binuclear species also takes place through bound organonitriles, for example $[Fe(CN)_5H_2O]^{3-}$ reacts[283] with $[Co(NH_3)_5L]^{3+}$ (L = 3- or 4-cyanopyridine) to form $[(NC)_5Fe(\mu\text{-}L)Co(NH_3)_5]$ which then undergoes intramolecular electron transfer to give iron(III). The ease with which oligomeric species are formed in this system has probably contributed to the difficulty in fully characterizing the products. In the absence of oxygen $[Fe(CN)_5H_2O]^{3-}$ decomposes[284] on heating to give $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$.

44.1.5.2.3 Reactions of $[Fe(CN)_5L]^{3-}$

Useful starting materials for the synthesis of $[Fe(CN)_5L]^{3-}$ are the aquapentacyanoferrate(II) ion $[Fe(CN)_5H_2O]^{3-}$ and the amminepentacyanoferrate(II) ion $[Fe(CN)_5NH_3]^{3-}$. These react with a variety of ligands with displacement of H_2O or NH_3 by L to give $[Fe(CN)_5L]^{3-}$ (*e.g.* CO displaces

NH_3 to give $[Fe(CN)_5CO]^{3-}$). $[Fe(CN)_5NH_3]^{3-}$ is best prepared[285] from the nitroprusside ion by standing in a solution of concentrated ammonia buffered with sodium acetate as in equation (34).

$$[Fe(CN)_5NO]^{2-} + 2NH_3 + OH^- \longrightarrow [Fe(CN)_5NH_3]^{3-} + N_2 + H_2O \quad (34)$$

$$[Fe(CN)_5NO]^{2-} + 2RNH_2 + OH^- \longrightarrow [Fe(CN)_5RNH_2]^{3-} + N_2 + ROH + H_2 \quad (35)$$

Nitroprusside may also be reduced with Na/Hg to give $[Fe(CN)_5NH_3]^{3-}$. Complexes containing primary amines can also be made[286] from the nitroprusside ion in the presence of sodium acetate with the formation of nitrogen and the corresponding alcohol as in equation (35). The ammonia ligand in $[Fe(CN)_5NH_3]^{3-}$ is rapidly hydrolyzed ($t_{\frac{1}{2}} \sim 40$ s, 25 °C). If the reaction is carried out in the presence of a small amount of ascorbic acid, to prevent aerial oxidation to iron(III), this represents a convenient route to $[Fe(CN)_5H_2O]^{3-}$. The kinetics of ligand dissociation from pentacyanoferrates(II), $[Fe(CN)_5L]^{n-}$, have been extensively investigated. These reactions proceed through a limiting dissociative mechanism. Variation of the rate constant with different incoming ligands has been reported in relatively few cases. The dependence of reactivity on the nature of the leaving ligand, however, has been examined in detail. Whilst charge effects are small, solvation effects are important. The strength of the iron–ligand bond is paramount in determining dissociation rates and attempts have been made to assess the σ and π bonding contributions from metal–ligand charge-transfer bands and ligand pK_a values. Table 5 contains data for the formation of $[Fe(CN)_5L]^{n-}$ complexes from $[Fe(CN)_5H_2O]^{3-}$ and Table 6 contains kinetic parameters for dissociation of L from $[Fe(CN)_5L]^{n-}$ complexes.

Photolysis of six-coordinate $[Fe(CN)_5en]^{3-}$ results in the loss of one cyanide to give[287] the chelated complex $[Fe(CN)_4en]^{2-}$ in high quantum yield. With ligands such as the cyanopyridines that have two donor sites $[Fe(CN)_5L]^{n-}$ complexes have been observed to exhibit coordination isomerization. Several such compounds have been studied[288,289] and interestingly some of the isomerizations involve an intramolecular mechanism.

Table 5 Kinetic Data for Formation of $[Fe(CN)_5L]^{n-}$ from $[Fe(CN)_5(OH_2)]^{3-}$ and L

L	k_f(25 °C) ($M^{-1}s^{-1}$)	$\Delta H^{\neq}$ ($kJ\,mol^{-1}$)	$\Delta S^{\neq}$ ($J\,K^{-1}mol^{-1}$)	*Ref.*
Ethane-1,2-diamine	230			1
Ethane-1,2-diamineH$^+$	410			1
Hydrazine	400			1
Hydrazinium$^+$	250			1
AA^{2-} [a]	9			2
AA^{1-} [a]	18–30	56–74	−14 to +21	2
AA[a]	240–370			2
3-Acetylpyridine	473[b]	64	79	3
4-Acetylpyridine	471[b]	67	33	3
Quinoxaline	425	64	25	4
Thiourea	194	60	1	5
Thioacetamide	271	65	21	5
Dithiooxamide	460	65	22	5
Benzotriazole	330	60	6	6, 7
Carbon monoxide	310	63	15	8

[a] AA = amino acids in dianionic (Glu^{2-}, Tyr^{2-}), monoanionic and zwitterionic forms
[b] At 297.2 K

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7. H. E. Toma, E. Giesbrecht and R. L. E. Rojas, *Quim. Nova*, 1983, **6**, 72.
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44.1.5.2.4 Prussian blue

Reaction of an excess of iron(II) salt with $[Fe(CN)_6]^{3-}$ or an excess of an iron(III) salt with $[Fe(CN)_6]^{4-}$ produces voluminous deep blue precipitates formerly known as Turnbull's blue and

Table 6 Kinetic Data for Dissociation of L from $[Fe(CN)_5L]^{n-}$

L	10^3k (25°C) (s^{-1})	$\Delta H^{\neq}$ ($kJ\,mol^{-1}$)	$\Delta S^{\neq}$ ($J\,K^{-1}mol^{-1}$)	$\Delta V^{\neq}$ ($cm^3\,mol^{-1}$)	*Ref.*
Ammonia	17.5	94	33		1
Nicotinate	0.48	116	82		2
Isonicotinate	0.29	114	70		2
Methyl isonicotinate	0.67				3
Ethyl isonicotinate	0.57				3
Nicotinic acid	1.42	96	21		2
Isonicotinic acid	0.71	97	17		2
Nicotinamide	0.90	106	53		2
Pyridylpyridinium	1.78	110	76		2
Hydrazine	1.6	107	57		4
Hydrazininum	50	108	94		4
1,2-Dimethylethane-1,2-diamine	4.4	94	27		5
Amino acids	2.7–26	92–99	28–51		6
Piperidine	8.8	94	25		7
	6.2	88	5		8
Pyridine	1.1	104	46		
3-Acetylpyridine	0.86	106	59		1
4-Acetylpyridine	1.61	113	75		9
3-Cyanopyridine	2.2	93	16	20.6	9
4-Cyanopyridine	1.0	105	50	20.6	10
2-Methylpyrazine	0.77	114	44	19.4	10
Pyrazine	0.42	110	59		10
Pyrazine *N*-oxide	9.0	111	70		1
Pyrimidine	1.3	91	8		2
Quinoxaline	620	82	17		11
Dimethyl sulfoxide	0.075	110	46		11
Thiourea	12.60	88	21		12
Thioacetamide	27.1	106	64		13
Dithiooxamide	46	108	70		13
N-1-benzotriazole	3.7	93	19		13
N-2-benzotriazole	9.0	89	11		14
Carbon monoxide	10^{-5}				14

1. H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 1039.
2. P. J. Morando and M. E. Blesa, *J. Chem. Soc., Dalton Trans.*, 1982, 2147.
3. N. D. Lis de Katz and N. E. Katz, *Monatsh. Chem.*, 1982, **113**, 745.
4. J. A. Olabe and L. A. Gentil, *Transition Met. Chem. (Weinheim, Ger.)*, 1983, **8**, 65.
5. D. B. Soria, M. del V. Hidalgo and N. E. Katz, *J. Chem. Soc., Dalton Trans.*, 1982, 1555.
6. H. E. Toma, A. A. Batista and H. B. Gray, *J. Am. Chem. Soc.*, 1982, **104**, 7509.
7. J. A. Salas, M. Katz and N. E. Katz, *J. Solution Chem.*, 1983, **12**, 115.
8. G. C. Pedrosa, J. A. Salas, M. Katz and N. E. Katz, *J. Coord. Chem.*, 1983, **12**, 145.
9. N. Y. M. Iha and H. E. Toma, *An. Accad. Bras. Cienc.*, 1982, **54**, 491.
10. M. J. Blandamer, A. Burgess, J. W. Morecom and R. Sherry, *Transition Met. Chem. (Weinheim, Ger.)*, 1983, **8**, 354.
11. A. L. Coelho, H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1983, **22**, 2703.
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Prussian blue (PB) respectively. They are identical mixed oxidation state polymeric complexes having the idealized composition $Fe_4[Fe(CN)_6]_3$, *i.e.* iron(III) ferrocyanide. If precipitation is rapid in the presence of potassium ions, these are incorporated with the formation of a so-called 'soluble PB' that is readily peptized. Prussian blue is an historically important salt which is amongst the first identified coordination compounds. Its early isolation is due in part to the especially strong affinity of iron(II) for cyanide and to the stability of the resulting complexes. Small almost black crystals of PB, free from alkali metal ions, separate slowly when $FeCl_3$ reacts[290] with $[H_4Fe(CN)_6]$ in 10 M HCl (approximately ten weeks). X-Ray and neutron (powder) diffraction studies[291] confirm that the structure (analogous to other polynuclear cyanides) consists of a cubic $Fe^{III}NCFe^{II}$ framework where a quarter of the iron(III) sites are vacant. The average compositon[292] of the pseudo-octahedral coordination sphere of iron(III) is $FeN_{4.5}O_{1.5}$. In the ideal stoichiometry of $Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$, six of the water molecules occupy coordination sites around the iron(III) atoms whilst eight occupy uncoordinated interstitial sites. Recent studies employing DTA and NMR techniques appear[293] to show a third type of water molecule in the Prussian blue structure. These authors[293] conclude that of the eight uncoordinated water molecules four are 'lattice' water molecules in the second coordination sphere and four are 'zeolitic' water molecules in the third coordination sphere of the paramagnetic iron(II) centres. Mössbauer and magnetic measurements

on a series of Prussian blue analogues, $M_j^A[M^B(CN)_6]_k \cdot mH_2O$, show[294] that the ions bound to the carbon end of the cyanides (M^B) are low-spin and all ions in M^A sites are high-spin. As in Prussian blue itself the analogues are characterized by well-defined octahedral cyanide sites, extensive water of hydration and variations in the M^A sites.

Individual iron atoms in Prussian blue appear to have well-defined electronic configurations with lifetimes of around 10^{-7} seconds. An interpretation[295] of the electronic spectrum suggests that the blue colour arises from electron transfer between the $[Fe(CN)_6]^{4-}$ and iron(III) ions and that the relevant electrons reside on the ferrocyanide moiety in the ground state. Vacuum pyrolysis of Prussian blue can result in valence reversal to give[296] iron(II) ferricyanide, which has also been identified[297] in aqueous solution, the complex previously thought to have been 'Turnbull's blue'.

The redox chemistry of the Prussian blue family (Table 7) has attracted considerable attention. The generation of thin films of Prussian blue[298] has led to studies of its mediation in electron transfer reactions[299] and of the electrochemical processes[300,301] involved in its deposition and redox reactions. This work has been spurred by its electrochromic properties which have been used in prototype electronic display devices based, for example,[302] on Prussian blue modified SnO_2 electrodes. A recent review[303] deals with the electrochemistry of electrodes modified by depositing thin films of PB and related compounds on them. Interestingly, true Prussian blue is somewhat difficult to process and modern 'iron blue' pigments such as Milori blue are derived from the oxidation of 'Berlin white' $\{Fe(NH_4)_2[Fe(CN)_6]\}$ to give iron(III) ammonium ferrocyanides.

Table 7 The Prussian Blue Family

Trivial name	*Idealized formula*	*Ref.*
Soluble Prussian blue	$KFe^{III}[Fe^{II}(CN)_6]$	1
Insoluble Prussian blue	$Fe^{III}_4[Fe^{II}(CN)_6]_3$	1
Prussian brown / Berlin green	$Fe^{III}[Fe^{III}(CN)_6]$	2, 3, 4
Prussian green	$KFe_3^{III}[Fe^{II}(CN)_6][Fe^{III}(CN)_6]_2$	2, 3
Prussian white / Everitts salt	$K_2Fe^{II}[Fe^{II}(CN)_6]$	2

1. D. Davidson, *J. Chem. Educ.*, 1937, **14**, 277.
2. J. F. De Wet and R. Rolle, *Z. Anorg. Allg. Chem.*, 1965, **336**, 96.
3. P. Ellis, M. Eckhoff and V. D. Neff, *J. Phys. Chem.*, 1981, **85**, 1225.
4. N. V. Sidgwick, 'The Chemical Elements and Their Compounds', Oxford University Press, London, 1958, 1339.

44.1.5.2.5 Isocyanide complexes

Organic isocyanides react directly with iron(II) salts to form complexes containing no more than four isocyanide ligands. Thus FeX_2 reacts in alcoholic solution to give[304] the stable diamagnetic complexes $[FeX_2(CNR)_4]$ (X = Cl, Br, I, SCN; R = alkyl, aryl). Both *cis*[305] and *trans* isomers[306] exist and these can easily be separated by chromatography on alumina. In some cases the *cis*/*trans* ratio is determined by the temperature of the reactant solution.[307] The addition of isocyanides to $Fe(ClO_4)_2$ in the absence of solvent yields diamagnetic $[Fe(CNR)_4](ClO_4)_2$, which apparently contains four-coordinate iron(II). A wide range of iron(II) isocyanide complexes is obtained by the alkylation of the corresponding low-spin cyanides. As early as 1888 Freund[308] synthesized $[Fe(CN)_2(CNEt)_4]$ by the alkylation of silver ferrocyanide with ethyl iodide (equation 36).

$$Ag_4[Fe(CN)_6] + 4EtI \longrightarrow [Fe(CN)_2(CNEt)_4] + 4AgI \quad (36)$$

This and related reactions were studied by Hartley[309,310] who obtained[311] some $[Fe(CNMe)_6]$ by methylation of $Ag_3[Fe(CN)_6]$ with MeI. Originally these complexes were incorrectly formulated and were not recognized as coordination compounds until 1933. An early X-ray structure determination was reported[312] in 1945 for $[Fe(CNMe)_6]Cl_2$. Transalkylation of iron(II) isocyanide complexes can be accomplished[313] by reacting the CNR complex with alkyl halide R'X that has a higher boiling point than RX which is continuously distilled from the reaction mixture. The reaction is general for aliphatic iron(II) isocyanide complexes and yields up to 80% are possible although usually several products are formed which require chromatographic separation. Although $[Fe(CNMe)_6]^{2+}$ results from the reaction[314] of ferrocyanide with dimethyl sulfate as in equation (37), the product of the reaction between diazomethane and ferrocyanic acid[315] is $[Fe(CN)_2(CNMe)_4]$ as shown in equation

(38). On heating (150 °C, 10 h) $[Fe(CNMe)_6]Cl_2$ is converted[316] to a mixture of *cis*- and *trans*-$[FeCl_2(CNMe)_4]$. Somewhat surprisingly, $[H_4Fe(CN)_6]$ reacts with aliphatic alcohols to form $[Fe(CN)_2(CNR)_4]$ and other complexes. Intermediate species formed during this reaction can polymerize with the evolution of hydrogen cyanide. Addition of HCN displaces isocyanide, however, and so constitutes a catalytic cycle for the synthesis[313] of RNC from HCN and ROH.

$$[Fe(CN)_6]^{4-} + 3Me_2SO_4 \longrightarrow [Fe(CNMe)_6]^{2+} + 3SO_4^{2-} \quad (37)$$

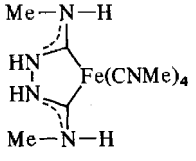
$$[H_4Fe(CN)_6] + 4CH_2N_2 \longrightarrow [Fe(CN)_2(CNMe)_4] + 4N_2 \quad (38)$$

Controlled alkylation of $[Fe(CN)_2(CNMe)_4]$ with one equivalent of MeI (90 °C, 4 h) affords $[Fe(CN)(CNMe)_5]I$ in 70% yield.[317] Iron(II) complexes containing more than four isocyanide ligands can also be obtained by the reaction of free ligand with an iron compound in another oxidation state. Thus $[Fe(CNMe)_6][FeCl_4]_2$ results[318] from the room temperature reaction between $FeCl_3$ and CNMe. The cation $[Fe(H)(CNBu^t)_5]^+$ is obtained by protonation of $[Fe(CNBu^t)_5]$ which is formed[319] by sodium amalgam reduction of $FeBr_2$ in the presence of an excess of the isocyanide (equation 39). The structure of $[Fe(CNBu^t)_5]$ differs from the ideal trigonal bipyramidal configuration, and the equatorial ligands are non-linear[320] having a CNC angle of 135° as in $[FeCl_2(CNMe)_4]$ for which an angle of ~166° was reported.[306] In contrast, the reported[312] CNC angle in $[Fe(CNMe)_6]^{2+}$ is 173°.

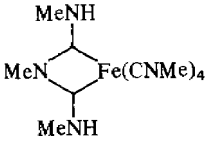
$$FeBr_2 \xrightarrow[CNR]{Na/Hg} [Fe(CNR)_5] \xrightarrow{HBF_4} [Fe(H)(CNR)_5]BF_4 \quad (39)$$

Hydrazine reacts with $[Fe(CNMe)_6]^{2+}$ to form the chelate (**16**) in which addition to two adjacent isocyanide ligands has taken place.[321] Methylamine reacts[322] in a related way to give (**17**), while reaction with ammonia results in the formation[323] of a monodentate carbene complex (**18**). Methylation of $[Fe(CN)_2(phen)_2]$ with Me_2SO_4 yields $[Fe(CNMe_2)(phen)_2]$,[26] which reacts with hydrazine to give[323] the tris chelate (**19**) in a similar fashion to the formation of (**16**).

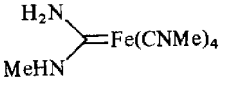
Amongst the aromatic isocyanide iron(II) complexes, those containing benzyl isocyanide are the best studied. Coordination influences the reactivity of the ligand resulting[324] in rapid nitration which, in common with sulfonation and bromination, takes place at the *para* position.[313,325] This effect may result from anchimeric assistance as shown in structure (**20**). This argument is supported by the effect being destroyed in the presence of a strong Lewis acid which prevents the participation of the nitrogen lone pair. Aliphatic aldehydes in 96% sulfuric acid alkylate the aromatic ring to give substituted benzyl alcohols, which subsequently react to form polymeric materials.[325]



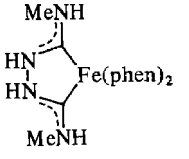
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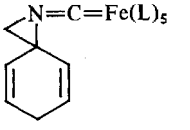
(17)



(18)



(19)



(20)

44.1.5.3 Alkyl Cyanides

Metallic iron reacts with nitrosyl tetrafluoroborate in acetonitrile to yield[327] off-white $[Fe(NCMe)_6](BF_4)_2$ (μ_{eff} = 5.2 BM). The $[Fe(NCMe)_6]^{2+}$ cation is readily formed when iron is oxidized by a number of strong oxidizing agents in rigorously anhydrous and oxygen free acetonitrile. Early workers investigated the use of chlorine, bromine and iodine[328] as oxidizing agents, whilst more recent work[329] has employed high oxidation fluorides such as WF_6, MoF_6 or PF_5. Oxidation of $[Fe(NCMe)_6]^{2+}$ with chlorine in acetonitrile yields $[Fe(NCMe)_6][FeCl_4]_2$. This salt and its bromine analog are reduced[328] by refluxing over iron wire to give complexes with the stoichiometry $[FeX_2(NCMe)_2]$. Some properties of these complexes are given in Table 8. The hexakis acetonitrile iron(II) cation reacts with $P(OMe)_3$ [but not under similar conditions with PF_3 or $P(OPh)_3$] in acetonitrile solutions[329] with stepwise replacement of MeCN by $P(OMe)_3$. The final species obtained at room temperature is $[Fe(NCMe)\{P(OMe)_3\}_5][PF_6]_2$; four intermediate cations can be positively identified by NMR spectroscopy and a fifth tentatively assigned. Formation of $[Fe(NCMe)_5P(OMe)_3]^{2+}$ is very rapid[330] and cross-over from high- to low-spin iron(II) probably

occurs with the next step, *i.e.* formation of $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$, which is thought to have a *cis* configuration. This red species creates the initial colour seen on mixing $P(OMe)_3$ with an acetonitrile solution of $[Fe(NCMe)_6]^{2+}$. Subsequent substitutions are far slower and give rise to colour ranges from red to orange and finally yellow on standing for several days. As expected the crystal structure of $[Fe(NCMe)_6][FeCl_4]_2$ reveals octahedral $[Fe(NCMe)_6]^{2+}$ cations and tetrahedral $[FeCl_4]^-$ anions.[331,332]

Table 8 Properties of selected MeCN Complexes[a]

Compound	*Colour*	μ_{obs} (BM)	*IR* (cm^{-1})
$[FeCl_2(NCMe)_2]$	Off-white	—	2275, 2285
$[FeBr_2(NCMe)_4]$	Brown	—	—, —
$[Fe(NCMe)_6][FeCl_4]_2$	Yellow	5.92	2270, 2290
$[Fe(NCMe)_6][FeBr_4]_2$	Red	5.89	2285, 2305
$[Fe(NCMe)_6][FeI_4]_2$	Dark green	5.48	2270, 2290

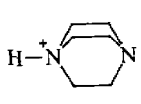
[a] B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, 1964, 2408.

44.1.5.4 Simple Amines

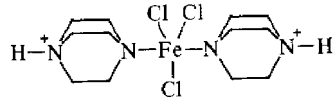
44.1.5.4.1 Saturated and primary aromatic amines

Although not commonly encountered because of their facile oxidation to brown compounds of uncertain composition, iron(II) hexaammine salts can be prepared[333] under carefully controlled conditions. Thus, addition of ammonia to freshly prepared $FeBr_2$ under an atmosphere of hydrogen gives a green precipitate which is converted with excess ammonia to light blue-grey crystals of $[Fe(NH_3)_6]Br_2$. Principal IR absorbances are 1595m, 1159vs, 625vs cm^{-1} (NH_3) and 315s cm^{-1} (Fe—N).[334] In common with other +2 transition metal ions, iron(II) forms stable complexes with a wide range of simple amines, and these are generally high-spin and sensitive towards oxidation. Iron(II) chloride reacts directly[335] with excess anhydrous primary amines (NH_2R, R = Me, Et, Pr^n and Bu^n) to form the complexes $[Fe(NH_2R)_2Cl_2]$. Interestingly, $FeCl_3$ is reduced[335] by primary amines to form the same white air sensitive microcrystalline solids, which are thought to have tetrahedral geometry.

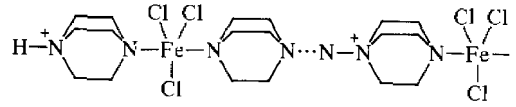
Complexes of stoichiometry $[Fe(SO_4)(L)_2]$ are formed[336] by the direct reaction of iron(II) sulfate and aniline or *para*-toluidine. The unusual monodentate, monoprotonated ditertiary amine ligand dabcoH$^+$ (**21**) reacts[337] with FeX_2 in anhydrous ethanol to yield complexes $[FeX_3(dabcoH^+)_2]X$ which have trigonal bipyramidal geometry (**22**), unusual[338] for high-spin complexes of monodentate ligands (X = Cl, μ_{eff} = 5.21 BM; X = Br, μ_{eff} = 5.13 BM). Hydrogen bonding and electrostatic forces play an important part in directing the stereochemistry of these compounds. Other workers[339] using the same method have obtained $[FeCl_3(dabco)(dabcoH^-)]$ (**23**), which upon heating (184 °C) loses dabco to form tetrahedral $[FeCl_3(dabcoH^+)]$. Under the appropriate conditions[340] this complex may be formed from the reaction between $FeCl_2$ and dabcoH$^+$ in the presence of Cl^-. Under carefully controlled conditions the less stable $[FeX_3(dabcoMe^+)(H_2O)]$ and $[FeX_3(dabcoMe^+)(NH_3)]$ (X = Cl, Br) can also be obtained.[341] In contrast, with FeI_2 the four-coordinate pseudotetrahedral $[FeI_3(dabcoH^+)]$ is the only species detected.[340] With the analagous monotertiary amine[342] quinuclidine (**24**) in which electrostatic hydrogen bonding effects are essentially absent, only pseudotetrahedral $[FeCl_2(quin)_2]$ is formed.



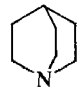
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(22)



(23)

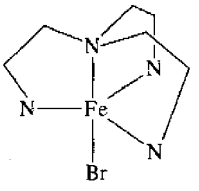


(24)

Unlike the reactions of pyridine and other tertiary amines with $[Fe(CO)_5]$ that give products such as $[Fepy_6][Fe_4(CO)_{13}]$, primary and secondary amines under anhydrous conditions form adducts prior to reaction giving $[Fe(CO)_4(amine)]$. In some instances two amine molecules are invovled in adduct formation and one of these is thought to attack a CO ligand whilst the other is hydrogen bonded to the complex.[343,344]

Iron(II) forms[345] stable complexes with a range of polyethyleneamine and related polydentate amines. There has been considerable research effort[346] devoted to the measurement of the thermodynamics of formation of these complexes in aqueous solution. Thus, for example, ethylenediamine[347] forms mono, bis and tris complexes in aqueous media with successive enthalpies of reaction being 21.1, 43.5 and 66.3 kJ mol^{-1} respectively. Similar thermochemical measurements have been made on a number of other polydentate amines, for example diethylenetriamine,[348] 2,2′,2″-triaminotriethylamine,[349] triethylenetetramine,[350] tetraethylenepentamine[351] and *N,N,N′,N′*-tetra(2-aminoethyl)ethylenediamine.[352]

Many aliphatic polydentate amines form stable iron(II) octahedral complexes and in some instances these are obtained directly from Fe^{III} precursors. Thus anhydrous ethylenediamine or propylenediamine react with $FeCl_3$ to give octahedral $[Fe(en)_3]Cl_2$ and $[Fe(pen)_3]Cl_2$ respectively.[353] In contrast bis(2-dimethylaminoethyl)methylamine reacts[354] with $FeCl_2$ in hot butanol to yield amethyst, air sensitive crystals of high-spin ($\mu_{eff} = 5.2$ BM) five-coordinate $[Fe(dien)Cl_2]$. A number of similar iron(II) complexes have been isolated with tri- or tetra-dentate amines.[355,356] For example, the trigonal bipyramidal coordination geometry (**25**) of $[Fe(Me_6tren)Br]Br$ (Me_6tren = tris(2-dimethylaminoethyl)amine) has been confirmed[357] by an X-ray crystal structure determination.



(25)

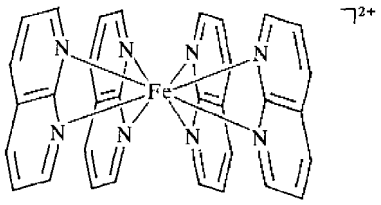
Interestingly an attempt[358] to measure the heat of formation of the nonmethylated propyl derivative (3,3′,3″-triaminotripropylamine) in aqueous solution failed because of hydroxide precipitation in advance of any complex formation. Stability constants for a range of metal(II) ions with Me_6tren and Me_5dien in aqueous solution have been interpreted[355] as showing that six-coordinate octahedral geometry is the preferred configuration for iron(II); presumably five-coordination results from steric factors. When possible, the donor atoms of these polydentate ligands are compressed into octahedral symmetry. Thus tetren (tetraethylenepentamine) reacts with $FeSO_4$ under acid conditions to form a solution which when alkalized to pH 8.5 takes up carbon monoxide to form[359] six-coordinate $[Fe(tetren)CO]^{2+}$. A large number of high-spin six-coordinate iron(II) complexes of di-and tri-dentate polyamines have been synthesized[360] having picrate counterions.

44.1.5.4.2 1,8-Naphthyridine

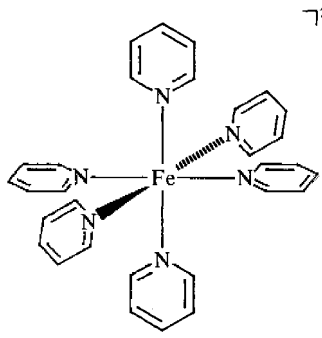
When a solution of 1,8-naphthyridine (napy) in ethyl acetate is added to $[Fe(H_2O)_6](ClO_4)_2$ in refluxing 2,2-dimethoxypropane/ethanol, a red–orange product may be isolated[361] which has the stoichiometry $[Fe(napy)_4](ClO_4)_2$ (**26**). The complex has been shown[362] to possess an eight-coordinate iron(II) centre with distorted dodecahedral geometry. Eight-coordination is rare in transition metal complexes having a more than half filled *d* shell and in this case gives rise to unusual Mössbauer effects,[363,364], for example an extremely high quadrupole splitting of 4.49 mm s^{-1} (at 77 K). The four-membered chelate ring having a 'bite' of 2.2 Å is maintained in iron(II) complexes of substituted naphthyridines (2,7-dimethyl-1,8-naphthyridine = dmnapy; 2-methyl-1,8-naphthyridine = mnapy). However, the markedly lower quadrupole splittings observed in $[Fe(mnapy)_4](ClO_4)_2$ and $[Fe(dmnapy)_3](ClO_4)_2$ are interpreted[365] as being derived from an octahedral coordination geometry.

44.1.5.5 Monodentate Aromatic Amines

Although pyridine has relatively weak coordinating properties,[366] a very large number of iron complexes containing one or more pyridine ligands are known.[367] In dilute aqueous solution it appears that only two molecules of pyridine are bound to Fe^{2+}_{aq} with formation constants[368] of $\log_{10}K_1 = 0.6$ and $\log_{10}\beta_2 = 0.9$. Increasing the pyridine concentration decreases the dielectric constant of the medium so favouring the formation of inner-sphere complexes with anions. Thus in concentrated solutions $[FeX_2py_4]$ complexes are obtained (see below). Steric effects are not an important factor here since the $[Fepy_6]^{2+}$ cation can be formed in the absence of other potential ligands. The reaction of $[Fe(CO)_5]$ and $[Fe_3(CO)_{12}]$ with pyridine was first investigated by Hieber and coworkers in 1930, and the products formulated as $[Fe_2(CO)_4py_3]$ and $[Fe(CO)_3py]$ respectively.[369,370] Subsequent work showed that only one complex salt is formed in these reactions, $[Fepy_6]^{2+}[Fe_4(CO)_{13}]^{2-}$ having a magnetic moment in keeping with a high-spin iron(II) centre (5.47 BM).[371,372] The X-ray crystal structure of this salt shows[373] that in the $[Fepy_6]^{2+}$ cation (**27**) the pyridine ligands occupy three mutually perpendicular planes with each pair of *trans* pyridine rings being coplanar. The $[Fepy_6]^{2+}$ cation is also obtained from reaction of $[C_4F_7Fe(py)_2(CO)_2I]$ with pyridine.[374]

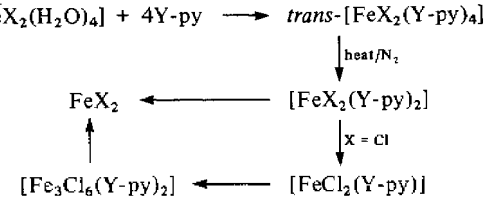


(26)



(27)

Yellow *trans*-$[FeCl_2py_4]$ is precipitated[375] when a saturated aqueous solution of $FeCl_2$ is added to an excess of pyridine in the absence of air. This complex is isotypic[376] with the analogous cobalt and nickel complexes known to have *trans* configurations. Being significantly more stable towards oxidation than simple iron(II) salts, and since $[FeCl_2py_4]$ has moderate solubility in common organic solvents, it is a convenient source of iron(II) for the preparation of other complexes. When heated under nitrogen solid *trans*-$[FeCl_2py_4]$ loses pyridine, successively forming three polymeric pyridine complexes.[377] Related complexes *e.g.* $[FeCl_2(4\text{-Mepy})_4]$, $[Fe(NCS)_2py_4]$) form only a single well-defined intermediate phase containing two pyridine ligands as shown in Scheme 9.



Scheme 9

The enthalpy for loss of two molecules of pyridine from $[FeCl_2py_4]$ has been estimated[378] to be $113.0 \pm 1.7\,kJ\,mol^{-1}$ and $128.0 \pm 1.3\,kJ\,mol^{-1}$ for loss of the remaining two pyridine molecules to form $FeCl_2$. *trans*-$[FeX_2(Y\text{-}py)_4]$ complexes containing a wide range of anions and substituted pyridines have been prepared[379] and their IR spectra reported.[380–384] The main features are strong sharp bands characteristic of coordinated pyridine. The complexes *trans*-$[FeI_2py_4]\cdot 2py$ and *trans*-$[Fe(NCO)_2py_4]\cdot 2py$ display bands due to coordinated and free pyridine and are therefore formulated as written.[383] All of these complexes have absorptions in the near IR assignable to *d–d* transitions, and splitting of the ^5E_g level is in accord with a tetragonally distorted octahedral structure.[384] Magnetic properties and Mössbauer spectra of these complexes have been interpreted on this basis.[384,385] Only the splitting of the e_g orbitals can be obtained from the electronic spectra,

but from measurement of ΔE_Q in the Mössbauer spectra the splitting of the t_{2g} orbitals has been estimated[386] for $[FeX_2L_4]$ where X = Cl, Br, I, NCS; L = py, 4-Mepy, isoquinoline. Table 9 lists properties of a number of $[FeX_2L_4]$ complexes. The complex $[Fe(NCS)_2py_4]$ can be obtained in yellow[387] and black[388] forms that have been claimed[389] to be *trans* and *cis* isomers. However, their magnetic moments are similar[390] and Mössbauer spectroscopy indicates they are not different isomers.[391,392] X-Ray crystallography[393] confirms that the yellow complex has the *trans* configuration with N-bound thiocyanate ligands. It appears the black form contains small amounts of Fe^{III} impurity, which is readily formed since the Fe^{3+}/Fe^{2+} and $(SCN)_2/SCN^-$ redox potentials are similar. In keeping with this explanation solutions of yellow *trans*-$[Fe(NCS)_2py_4]$ do not darken, even over long periods under oxygen-free conditions[391,392] and dark violet solutions formed by exposure to air are reconverted to the yellow form by sulfur dioxide.[392]

Table 9 Solid State Magnetic and Spectroscopic Properties of some *trans*-$[FeX_2py_4]$ Complexes

Complex	*Absorption max.*[1] (cm^{-1})	*Magnetic moments*[2] (BM)	*Mössbauer parameters*[2] ΔE_Q ($mm\,s^{-1}$)	δ ($mm\,s^{-1}$)
$[FeCl_2py_4]$	10 300, ~8550sh	5.34	3.14	1.13
$[FeBr_2py_4]$	10 650, 7750	5.28	2.52	1.16
$[FeI_2py_4]$	11 200[2]	5.90	0.65	1.25
$[FeI_2py_4]\cdot 2py$	11 000[2]	5.64	0.83	1.17
$[Fe(NCS)_2py_4]$	11 250, ~9900sh	5.47	1.52	1.21
$[Fe(NCSe)_2py_4]$	11 200, ~9900sh			
$[Fe(NCO)_2py_4]$	12 200, 9000[2]	5.13	2.52	1.24
$[Fe(NCO)_2py_4]\cdot 2py$	12 200, 9000[2]	5.20	2.59	1.24

[1] D. M. L. Goodgame, M. Goodgame, M. A. Hitchman and M. J. Weeks, *Inorg. Chem.*, 1966, **5**, 635.
[2] J. F. Duncan, R. M. Golding and K. F. Mok, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1114.

As with pyridine, β-picoline, γ-picoline and isoquinoline, complexes of the type $[FeX_2(amine)_4]$ (X = Cl, Br, I) are obtained by adding a slight excess of the free amine to an aqueous solution of the iron(II) halide.[385,394] In contrast the less basic ligands 4-cyanopyridine and 3,5-dichloropyridine, which are solids and therefore have to be added as an alcoholic solution, afford[385] complexes of the type $[FeX_2(ligand)_2]$ (X = Cl, Br). With X = NCO, $[Fe(NCO)_2(4\text{-}CNpy)_4]$ and $[Fe(NCO)_2(4\text{-}CNpy)_2]$ have been isolated as have the corresponding 3-cyanopyridine complexes. It appears that the bis complexes have polymeric tetragonal structures.[395] Sterically crowded quinoline forms tetrahedral complexes, $[FeX_2(quinoline)_2]$ (X = Cl, Br, I, NCS) whose Mössbauer, electronic and IR spectra have been extensively investigated.[396,397] A high-spin hydrated δ-amino-2-methylquinoline sulfate iron(II) complex has been isolated that is thought to be octahedral and monomeric with a monodentate sulfate ligand.[398]

Another sterically demanding ligand, 2-methylimidazole (2-Meimid), forms brown tetrahedral complexes $[Fe(2\text{-}Meimid)_4]X_2$ ($X = ClO_4^-$, BF_4^-) that are not well characterized, while with halides neutral complexes are obtained.[399] The complexes $[FeX_2(Me_2imid)_2]$ (X = Cl, Br) are formed[400] with the equally bulky 1,2-dimethylimidazole (Me_2imid). However, when the anion is thiocyanate the tetragonal complex $[Fe(NCS)_2(Me_2imid)_4]$ is obtained.[400] In contrast to the behaviour of the more sterically hindered pyridine, imidazole itself[401,402] and its *N*-alkyl derivatives[403–405] readily form yellow/orange salts of the type $[Fe(imid)_6]^{2+}$ that are easily isolated with anions such as NO_3^-, Br^-, I^- and ClO_4^-. The physical properties of these solid high-spin air sensitive complexes are well documented (Table 10), and in methanol solution proton NMR isotropic shifts of $[Fe(imid)_6](ClO_4)_2$ indicate the cation has O_h symmetry.[406]

Several simple iron(II) complexes containing pyrazoles (pz) have been prepared, usually from ethanol solutions dehydrated with a small addition of triethyl orthoformate. Thus light yellow $[Fe(pz)_6]X_2$ ($X = BF_4^-$, ClO_4^-) are high-spin complexes[401] with room temperature magnetic moments of 5.4 BM. With the tautomeric ligand 3(5)-methylpyrazole, (**28**) (Mepz), tetragonal complexes of the type $[Fe(Mepz)_4X_2]$ (X = Cl, Br, I) are formed[406] with magnetic moments ~5.6 BM. The complex formulated as $Fe(Mepz)_7(ClO_4)_2$ that has a room temperature magnetic moment of 5.43 BM undoubtedly contains the $[Fe(Mepz)_6]^{2+}$ cation.[407] Table 10 lists magnetic and Mössbauer parameters for several monodentate aromatic nitrogen donor complexes.

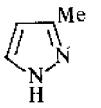
Several iron(II) triazole complexes are known and the unsubstituted ligand forms bridged species *via* the 2- and 4-nitrogen atoms. Addition of 1,2,4-triazole (**29**) (trz) to a slightly acidified solution of $FeCl_2$ and NH_4SCN in the presence of SO_2 [to prevent formation of iron(III)] affords pale green crystals of $[Fe(NCS)_2(trz)_2]$. This polymeric complex has an interesting layer structure[408] containing somewhat distorted N_6 octahedra, with the layers separated by hydrogen-bonded NCS^- groups.

Table 10 Selected Iron(II) Complexes Containing Monodentate Aromatic Nitrogen Donors

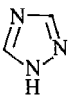
Complex	*Colour*	μ_{eff} (BM)	*Mössbauer parameters* δ	ΔE_Q	*Ref.*
$[Fe(imid)_6](ClO_4)_2$	Yellow	5.59	1.30[a]	1.19	1
$[Fe(Meimid)_6](ClO_4)_2$	Yellow	5.72		1.22	2
$[Fe(pz)_6](ClO_4)_2$	Yellow	5.55	1.30[a]	3.14	1
$[FeCl_2(py)_4]$	Yellow	5.34	1.13[b]	3.18	3
$[FeCl_2(isoquinoline)_4]$	Yellow	5.30	0.85[c]	3.19	6
$[Fe(2\text{-}Meimid)_4](ClO_4)_2$	Brown				4
$[FeCl_2(Me_2imid)_2]$	Yellow		1.15[a]	3.19	5
$[FeBr_2(Me_2imid)_2]$	Yellow		1.11[a]	3.32	5
$[FeCl_2(quinoline)_2]$	Yellow	5.20	0.87[a]	2.72	7

Chemical shifts relative to: [a] sodium nitroprusside; [b] not reported; [c] ^{57}Co—Pd source; [d] natural iron

1. J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 1285; C. D. Burbridge and D. M. L. Goodgame, *Inorg. Chim. Acta*, 1970, **4**, 231.
2. J. Reedijk, *Inorg. Chim. Acta*, 1969, **3**, 517.
3. J. F. Duncan, R. M. Golding and K. F. Mok, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1114.
4. J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 507.
5. J. Reedijk, *J. Inorg. Nucl. Chem.*, 1973, **35**, 239.
6. C. Burbridge, D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc. (A)*, 1967, 349.
7. C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc. (A)*, 1968, 1074.

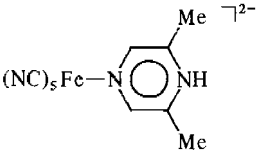


(28)



(29)

Magnetic properties are anisotropic with antiferromagnetic intralayer exchange.[409] In contrast, with the sterically hindered 4-substituted derivatives (particularly *t*-butyl) the ligand is forced to be monodentate or bidentate *via* the 1,2-nitrogen atoms, and an asymmetrical dinuclear complex, $[Fe(NCS)_2(Butrz)_4]\cdot H_2O$, is formed[410a] that is readily oxidized to iron(III). Protonation of the 2,6-dimethylpyrazine complex $[Fe(CN)_5(dmpz)]^{3-}$ brings about dramatic spectral changes associated with the metal to ligand charge transfer. This shifts from 440 nm to 600 nm, and the pK_a of the coordinated ligand (**30**) is 2.80 compared with 1.9 for the free ligand.[410b]



(30)

44.1.5.6 Diimines and Related Ligands

44.1.5.6.1 Introduction

Good σ donor properties and appropriate π back-bonding abilities, supplemented by the chelate effect, result in most α,α'-diimines being high-field bidentate ligands which, when steric effects do not interfere as in, for example, 2,9-dimethylphenanthroline,[411,412] are comparable in strength with cyanide ion. Consequently most complexes of the type $[Fe(\alpha,\alpha'\text{-diimine})_3]^{2+}$ are low-spin and essentially diamagnetic, displaying but a small temperature independent paramagnetism of ~ 1 BM. Metal-to-ligand charge transfer results in characteristic[413,414] intense absorption in the visible region of the spectrum ($\varepsilon \sim 10^4$), and their magnetic circular dichroism spectra have been studied[415] down to 4.2 K. Since the tris complexes are readily formed in dilute solution (with extremely large stability constants — see Table 11) they have been used extensively for the spectrophotometric determination of iron.[416] Another analytical application is the use of large $[Fe(\alpha,\alpha'\text{-diimine})_3]^{2+}$ cations to precipitate anions in gravimetric procedures. These complexes have also found application as reversible high potential (~ 1.1 volt) redox indicators since in solution the iron(III) complexes are virtually colourless in comparison with intensely coloured iron(II) species.[417]

The redox potentials of a very wide range of substituted $[Fe(LL)_3]^{3+/2+}$ complexes in aqueous

Table 11 Absorption Maxima, Extinction Coefficients and Stability Constants of Substitued $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ Complexes in Aqueous Solution

Ligand	λ^a_{max} (nm)	ε^a	$log_{10}\beta_3{}^b$
Phen	510	1.11×10^4	21.2
2-Mephen			10.8
5-Mephen	512	1.22×10^4	21.9
3,8-Me_2phen	496	1.15×10^4	
4,7-Me_2phen	512	1.40×10^4	23.1
5,6-Me_2phen	520	1.26×10^4	23.0
3,8-Ph_2phen	525	7.02×10^3	
4,7-Ph_2phen	533	2.24×10^4	21.8*
5-Phphen	522	1.27×10^4	21.1
5-NH_2phen	524	1.21×10^4	
5-Clphen	512	1.17×10^4	19.7
5-Brphen	515	1.25×10^4	
5-Fphen	509	1.20×10^4	
5-NO_2phen	510	1.15×10^4	17.8
4,7-$(HO)_2$phen	520	1.48×10^4	
4,7-$(MeO)_2$phen	500	1.13×10^4	
4,7-$(PhO)_2$phen	500	1.47×10^4	
5,6-$(MeO)_2$phen	518	1.20×10^4	
3-SO_3Hphen	517	1.08×10^4	
5-SO_3phen	512	1.22×10^4	
bipy	522	8.70×10^3	17.4
4,4′-Me_2bipy	528	9.30×10^3	
4,4′-Ph_2bipy	552	2.11×10^4	
4,4′-$(CO_2H)_2$bipy	540	1.48×10^4	
4,4′-$(NH_2)_2$bipy	569	1.36×10^4	
4,4′-Cl_2bipy	532	8.30×10^3	

*In 10% ethanol

[a] A. A. Schilt, 'Analytical Applications of 1,10-Phenathroline and Related Compounds', Pergamon, Oxford, 1969.

[b] W. A. E. McBryde, 'A Critical Review of Equilibrium Data for Proton and Metal Complexes of 1,10-Phenanthroline, 2,2′-Bipyridine and Related Compounds', Pergamon, Oxford, 1978.

media have been reported[418] but there is little data available on the effect of the solvent.[419] Preparatively the iron(III) complexes are easily obtained from the corresponding iron(II) cations using cerium(IV) in acid solution. The optically active iron(III) complexes can be prepared from the corresponding optically active iron(II) complexes. They racemize slowly in the solid state, but only take a few minutes in solution.[420]

As expected from crystal field considerations[421] the low-spin iron(II) complexes are substitution inert, and thermodynamically very stable with respect to Fe^{2+} and the free ligand; overall formation constants (β_3) can be as large as 10^{23}. The consecutive formation constants for iron(II) 2,2′-bipyridine and 1,10-phenanthroline complexes derived by Irving and Mellor[422] are not in the usual order $K_1 > K_2 > K_3$, but rather $K_1 > K_2 \ll K_3$ (Table 12) and this was attributed to spin pairing on addition of the third ligand since $[Fe(H_2O)_2(LL)_2]^{2+}$ and $[Fe(H_2O)_4(LL)]^{2+}$ will be high-spin by analogy with the corresponding chloro complexes. While this behaviour is consistent with enhanced stability of the low-spin tris complexes, Brisbin and McBryde[423] have cast considerable doubt on the numerical significance of the reported K_2 values. There is no doubt, however, that in these systems $K_1 \ll K_2K_3$. With 2-methyl-1,10-phenanthroline steric hindrance is responsible for the tris complex being high-spin and the more usual order $K_1 > K_2 > K_3$ is observed.[424]

Table 12 Successive Formation Constants for Iron(II) 2,2′-Bipyridine and 1,10-Phenanthroline Complexes[a]

Complex	K_1	K_2	K_3	$log_{10}\beta_3$
2,2′-Bipyridine	1.6×10^4	5.0×10^3	3.5×10^9	17.5
1,10-Phenanthroline	7.2×10^5	1.8×10^5	1.1×10^{10}	21.1

[a] At 25.0 °C, H. Irving and D. H. Mellor, *J. Chem. Soc.*, 1962, 5222; 1962, 5237. See also criticism of K_2 values: D. A. Brisbin and W. A. E. McBryde, *Can. J. Chem.*, 1963, **41**, 1135.

$$[Fe(H_2O)_6]^{2+} + LL \overset{K_1}{\rightleftharpoons} [Fe(H_2O)_4(LL)]^{2+} + 2H_2O \quad (40)$$

$$[Fe(H_2O)_4(LL)]^{2+} + LL \overset{K_2}{\rightleftharpoons} [Fe(H_2O)_2(LL)_2]^{2+} + 2H_2O \quad (41)$$

$$[Fe(H_2O)_2(LL)_2]^{2+} + LL \overset{K_3}{\rightleftharpoons} [Fe(LL)_3]^{2+} + 2H_2O \quad (42)$$

Over recent years there have been a number of publications concerned with formation constants of $[Fe(\alpha,\alpha'\text{-diimine})_3]^{2+}$ complexes at various temperatures. Consequently additional $\Delta H°$ and $\Delta S°$ values are now available (Table 13),[425-428] and some data concerning mixed solvents have also been reported.[424,429-431] Most of the substitution reactions of the tris ligand, low-spin, intensely coloured complexes proceed at rates conveniently monitored by conventional spectrophotometric techniques, and a considerable body of literature dealing with these kinetic and mechanistic aspects has been published. The most important α,α'-diimine ligands are 2,2′-bipyridine and 1,10-phenanthroline, and their iron(II) complexes are dealt with first before considering complexes of other α,α'-diimines.

Table 13 Thermodynamic Parameters for Formation of Selected $[Fe(\alpha,\alpha'\text{-diimine})_3]^{2+}$ Complexes from Fe^{2+} and Ligand

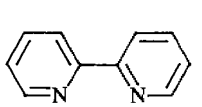
Ligand	$-\Delta G°$ (kJ mol^{-1})	$-\Delta H°$ (kJ mol^{-1})	$-\Delta S°$ (J K^{-1} mol^{-1})	*Ref.*
phen	118.1	130.7 ± 1.1	41.7 ± 3.4	1
5-NO_2phen	92.2	136.9 ± 3.8	127.2 ± 11.8	1
5,6-Me_2phen	125.2	128.5 ± 2.8	10.9 ± 14.6	2
bipy	93.3	128.7 ± 2.0	98.7 ± 5.8	1

1. R. D. Alexander, D. H. Buisson, A. W. L. Dudeney and R. J. Irving, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 1081.
2. S. C. Lahiri and S. Aditya, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2487.

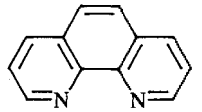
44.1.5.6.2 2,2′-Bipyridine and 1,10-phenanthroline

(*i*) *Tris complexes*

The intensely red cation $[Fe(bipy)_3]^{2+}$ was first described by Blau[432] in 1888 who obtained 2,2′-bipyridine (**31**) by pyrolyzing copper(II) picolinate. Ten years later Blau reported[433] the synthesis of 1,10-phenanthroline (**32**) and showed that it forms a similar tris complex with iron(II). He also noted some of the redox properties of these complexes. It was not until 1931 that they were introduced as reversible high potential redox indicators.[434] In 1912 Werner demonstrated the octahedral geometry of $[Fe(bipy)_3]^{2+}$ by the successful resolution of its optical isomers.[435] More recent studies showed that complexes related to $[Fe(phen)_3]^{2+}$ have biological activity.[436] Solutions containing $[Fe(bipy)_3]^{2+}$ or $[Fe(phen)_3]^{2+}$ are obtained by addition of a slight excess of the ligand in ethanol, methanol or acetone to an aqueous solution of an iron(II) salt. The red solutions so obtained are indefinitely stable at pH ~7; addition of a concentrated solution containing a large anion such as ClO_4^-, Br^- or I^- precipitates the cations, and the complex salts can be recrystallized from organic solvents. However, when the anion (X) is a moderately good ligand, complexes of the type $[Fe(NN)_2X_2]$ can result on recrystallization (see below). The small ligand bite in $[Fe(phen)_3]^{2+}$ results in a slight compression along the pseudo-three-fold axis as well some twist distortion from O_h geometry.[437,438] In $[Fe(phen)_3]I_2 \cdot 2H_2O$ each complex is surrounded by four others with one of the ligands protruding into the 'pockets' of the neighbouring complexes.[438]



(31)



(32)

Optically active $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ are readily obtained (*via* the antimony *d*-tartrate[439]). Racemization in the solid-state is very slow and available kinetic results have been discussed in a recent review.[440] The volume of activation for racemization of crystalline $[Fe(phen)_3](ClO_4)_2$ has been estimated[441,442] to be -0.9 ± 0.1 cm^3 mol^{-1} at room temperature. The volume of activation for racemization in solution is positive and large (14.2 ± 0.3 cm^3 mol^{-1} in

0.01 M HCl[443]) and similar to that for dissociative acid aquation,[444] possibly implying a common mechanism. However, the rate of racemization is some nine times faster than dissociation, arguing against a common mechanism (see below). Mechanisms involving excitation of the low-spin iron(II) centre to the high-spin $^5T_2$ state, and twist processes have been considered for the racemization process, which is enhanced by the presence of organic cosolvent.[445,446] Very recently it has been reported[446a] that the iron(II) complex of sulfonated 4,7-diphenyl-1,10-phenanthroline, $[Fe\{(SO_3Ph)_2phen\}_3]^{4-}$, dissociates and racemizes at the same rate in water (15–35 °C) but the addition of a cosolvent affects these processes differently. In all but extremely dilute solutions of mineral acid, protonation of free ligand causes $[Fe(phen)_3]^{2+}$, $[Fe(bipy)_3]^{2+}$ and related complexes to dissociate in an attempt to restore equilibrium conditions as in equation (43). As a result the intensely coloured solutions fade, obeying simple first order kinetics and become colourless over a period of minutes to hours depending on temperature and the complex concerned. Being easily monitored[447] these reactions have been the subject of numerous kinetic studies. Dissociation can also be induced by the presence of a large amount of metal ion such as Hg^{2+} that forms a relatively stable colourless complex with the α,α′-diimine ligand.[444,448] Dissociation also takes place when a high concentration of a ligand is added that complexes with the iron and successfully competes with the α,α′-diimine. The latter approach is particularly effective with polycarboxylates under mildly oxidizing conditions (*e.g.* with air), when iron(III) polycarboxylates result.[449] First order rate constants for the acid aquation of $[Fe(phen)_3]^{2+}$ and tris complexes of substituted 1,10-phenanthrolines not having ionizable groups only vary slightly (decreasing) with acid concentration. In keeping with a dissociative mechanism, activation energies are as high as 125 kJ mol^{-1} and entropies of activation are large and positive (Table 14).[450] Variations in aquation rate for complexes such as $[Fe(NH_2phen)_3]^{2+}$ with acid concentration are attributed to protonation equilibria involving the substituent.[451]

Table 14 Rate Constants and Activation Parameters for Aqueous Solutions of Complexes of the Type $[Fe(Xphen)_3]^{2+}$ in 1 M Sulfuric Acid

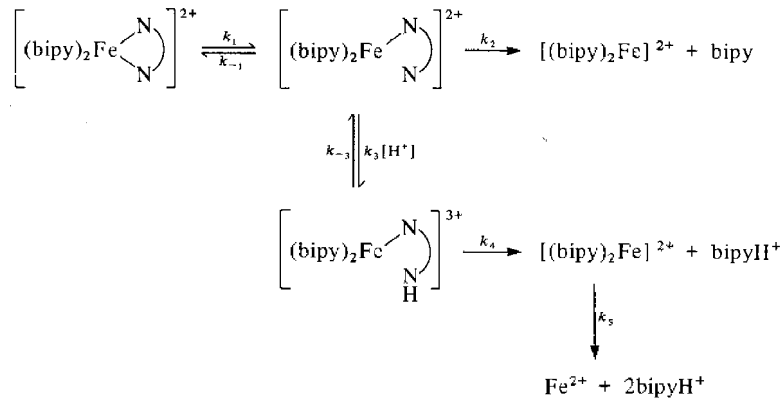
X	$k_{25°C}$ (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V^{\neq}$ (cm^3 mol^{-1})
H	7.3×10^{-5}	122.5	+87.8	+15.4 ± 0.4
5-NO_2	4.9×10^{-4}	117.0	+74.8	+17.9 ± 0.3
4,7-Me_2	2.2×10^{-5}	116.2	+54.3	+11.6 ± 0.6

Standard deviations associated with $\Delta H^{\neq}$ are ± 0.8 kJ mol^{-1} and with $\Delta S^{\neq}$ ± 3 J K^{-1} mol^{-1} in each case. J.-M. Lucie, D. R. Stranks and J. Burgess, *J. Chem. Soc., Dalton Trans.*, 1975, 245; J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1963, 5762.

$$[Fe(LL)_3]^{2+} + 3H^+ \longrightarrow Fe^{2+}_{aq} + 3LLH^+ \quad (43)$$

The behaviour of $[Fe(bipy)_3]^{2+}$ towards acid aquation is not the same as $[Fe(phen)_3]^{2+}$. In the presence of sufficient mineral acid $[Fe(bipy)_3]^{2+}$ dissociates, the rate of aquation increasing with acid concentration until a rate limit is reached[452] at ~2 N. This is interpreted[453,454] in terms of a mechanism involving species containing monodentate protonated 2,2′-bipyridine as illustrated in Scheme 10, rather than the original suggestion[455] of a protonated intermediate with six iron–nitrogen bonds (although related species have been claimed[456]). The 1,10-phenanthroline ligand appears too rigid to easily form monodentate protonated species so the acid dependent path ($k_3[H^+]$ in Scheme 10) is not available for $[Fe(phen)_3]^{2+}$. It has been deduced that the only low-spin species in Scheme 10 is $[Fe(bipy)_3]^{2+}$ itself.[457] This scheme does not, however, account for all of the reported observations. In concentrated hydrochloric acid $[Fe(bipy)_3]^{2+}$ dissociates[458] but in other concentrated acids the situation is more complex.[459] In fact it is difficult to obtain the iron(II) complexes in concentrated solutions of nitric or sulfuric acids due to oxidation to iron(III), and the overall pattern of behaviour may be related to the activity of water in the concentrated acids.[460] In this connection it is interesting to note that rates of dissociation are significantly less in D_2O/HCl than in H_2O/HCl solutions.[461] A considerable amount of work, notably by Burgess,[462] has made use of these dissociation reactions as a probe for structure in mixed solvent systems.

Both $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ and their substituted derivatives undego relatively rapid reactions with strong nucleophiles such as OH^-, CN^- and N_3^- to give nucleophile dependent products. With cyanide ion the low-spin first formed product[463] is $[Fe(CN)_2(LL)_2]$, which after long reaction periods is converted[464] to $[Fe(CN)_4(LL)]^{2-}$ as in equation (44). These cyanide complexes show strong solvatochromatic charge-transfer bands.[465–467] For instance the absorption maximum of $[Fe(CN)_2(bipy)_2]$ in the visible region in water is 515 nm while in pyridine it is 629 nm; there are also



Scheme 10

$$[Fe(LL)_3]^{2+} \xrightarrow{CN^-} [Fe(CN)_2(LL)_2] \xrightarrow{CN^-} [Fe(CN)_4(LL)]^{2-} \quad (44)$$

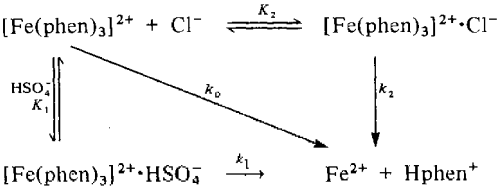
correspondingly large changes in extinction coefficient. Reaction of $[Fe(LL)_3]^{2+}$ complexes with hydroxide ion leads to complete displacement of the ligand from the iron and formation of iron(III) hydroxide[468] as in equation (45). It appears that formation of highly insoluble iron(III) hydroxide provides the thermodynamic driving force for the overall reaction. Addition of edta to chelate the iron(III) prevents precipitation of $Fe(OH)_3$ while not inhibiting the reaction. In the absence of oxygen there is no reaction. The effect of micelles on the aquation and base hydrolysis of $[Fe(phen)_3]^{2+}$ has been reported.[469] Reactions with both cyanide and hydroxide ions under pseudo first order conditions follow the second order rate law shown in equation (46). At very high nucleophile concentrations higher orders in nucleophile have been reported[470] (*e.g.* $k_3[X^-]^2$ and $k_4[X^-]^3$), and it seems likely these result from specific ion effects. The k_1 term is assigned to ligand independent rate determining dissociation of the complex, and the k_2 term to associative reaction with the nucleophile.[471–473] The latter second order path is usually dominant and surprisingly is associated with a positive volume of activation.[474] Since there are no ionizable hydrogens present, a conjugate base mechanism is not possible, so the observed kinetic behaviour might result from direct nucleophilic attack on the metal centre, or perhaps through a mechanism involving ion-pairs (see below). Support for the second order reactions involving attack on the iron centre comes from the reaction of optically active $[Fe(phen)_3]^{2+}$ with CN^- which gives[475] some *inverted* $[Fe(CN)_2(phen)_2]$. Both retention and inversion paths are involved and although interpretation of the kinetic data is not straightforward, it is concluded that the optical inversions are true chemical inversions.[476,476a] Curiously, however, the reaction of optically active $[Fe(bipy)_3]^{2+}$ with CN^- involves some *retention* of activity[477] with a greater dependence on $[CN^-]$ than is the case for inversion of $[Fe(phen)_3]^{2+}$. An alternative, and interesting, mechanism involving an initial reaction of the nucleophile with the coordinated α,α′-diimine ligand was postulated[478] by Gillard in 1975. By analogy with reaction of some quaternary nitrogen heterocyclic compounds[479,480] it was suggested the second order path corresponds to nucleophilic attack on the coordinated (*i.e.* quaternary) ligand at a position close to the metal which is followed by rapid transfer of the nucleophile to the metal.

$$[Fe(LL)_3]^{2-} + OH^-/O_2 \longrightarrow Fe(OH)_3 + 3LL \quad (45)$$

$$k_{obs} = k_1 + k_2[X^-] \quad (46)$$

It was further suggested that in some situations water might add across the C=N bond (covalent hydration) with subsequent deprotonation in alkali leading to formation of a pseudo base that rapidly undergoes intramolecular shift of the OH from ligand to metal. These suggestions stimulated much work both by Gillard's group and others, most of which has been reviewed,[481] but there remains disagreement concerning the importance of covalent hydration and pseudo base formation in reactions of iron(II) α,α′-diimine complexes and also complexes of other metals.[482,483] It appears that the best evidence for nucleophilic attack on the ligand in iron(II) 2,2′-bipyridine and 1,10-phenanthroline complexes involves 5-nitro-1,10-phenanthroline. However, this results from Meisenheimer complex formation with attack taking place on the 6-position, which is remote from the iron centre rather than adjacent to it.[484,485]

The participation of reaction paths involving ion pairs has been proposed to explain the second order behaviour of $[Fe(LL)_3]^{2+}$ complexes with OH^- and CN^-. Margerum first suggested[486] the $[Fe(phen)_3]^{2+}\cdot nOH^-$ ion pairs are likely to dissociate at rates different from $[Fe(phen)_3]^{2+}$ itself, and pointed out that other anions such as Cl^-, F^-, NO_3^-, ClO_4^- *etc.* might be expected to form ion pairs as readily as OH^-, though none of these ions significantly enhance the rate of dissociation in aqueous media.[445,487] This could be due to a number of factors including hydration/steric effects and unfavourable competition with dipolar interactions. Ion pairing of $[Fe(LL)_3]^{2+}$ cations with a range of common anions in nonaqueous media is well established and in some instances hydrophobic effects are operative.[488] They have been used over a number of years as a means of concentrating these complex cations (*via* solvent extraction into an immiscible liquid) in spectrophotometric determinations.[489–494] There are reports of enhanced rates of acid solvolysis of $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ by common anions in dimethyl sulfoxide[495] and methanol.[496] In the latter solvent the effectiveness in accelerating the rate is $Cl^- \gg Br^- \sim MeC_6H_4SO_3^- > HSO_4^- \sim NO_3^- > ClO_4^-$. In $DMSO$, acid solvolysis of $[Fe(phen)_3]^{2+}$ is dramatically increased by Cl^- (added in the form of LiCl or $Et_3\overset{+}{N}CH_2PhCl^-$) and this effect is inhibited by HSO_4^-. These observations were quantitatively accounted for by the competitive ion-pair formation mechanism shown in Scheme 11 involving a reactive ion pair with Cl^- and a more inert $[Fe(phen)_3]^{2+}\cdot HSO_4^-$ ion pair.[497]



Scheme 11

Similar ion-pair competition has been reported for the reaction of CN^- with $[Fe(phen)_3]^{2+}$ in water where addition of I^- inhibits the reaction by formation of a relatively inert iodide ion pair.[498] In this instance there is independent evidence for ion-pair formation with iodide.[499] There is, however, criticism of ion-pair mechanisms although the observed kinetic behaviour is not in accord with the proposed[500] alternative mechanism involving a preequilibrium to form a bis chelate. A recent lengthy paper[501] dealing with reaction of several $[Fe(LL)_3]^{2+}$ complexes with CN^- highlights the importance of other effects in some instances. $[Fe(LL)_3]^{2+}$ (LL = phen, bipy), in the presence of long chain alkyl sulfonates, are readily extracted into chloroform,[502] and dissociation and racemization rates are enhanced *via* specific interactions.[503]

(*ii*) *Bis complexes*

Complexes of the type $[FeX_2(LL)_2]$ (LL = phen, bipy) where X is a unidentate anionic ligand have been studied extensively[504] because they display a range of spin states depending on the nature of X. $[Fe(CN)_2(LL)_2]$ complexes are low-spin ($^1A_1$) and kinetically inert. Weak field ligands (X^-) result in high-spin complexes ($^5T_2$), while with some ligands, notably NCS^- and $NCSe^-$, the $^5T_2$ to $^1A_1$ spin transition can be observed in the form of abrupt changes in magnetic and spectral properties over a fairly narrow temperature range.[505] Low-spin *cis*-$[Fe(CN)_2(phen)_2]$ is obtained from the reaction of $[Fe(phen)_3]^{2+}$ with CN^- in aqueous solution. There has been controversy over its stereochemistry with some IR data suggesting *cis* and *trans* isomers exist, but Mössbauer experiments[506] indicate the existence of a single isomer ($\Delta E_Q = 0.58\ mm\ s^{-1}$, $\delta = +0.27$ relative to stainless steel). The *cis* complex is only very slightly soluble in water, but readily extractable with chloroform or nitrobenzene and as noted previously it exhibits remarkable solvatochromic properties (Table 15). In aqueous solution it is orange and in chloroform or nitrobenzene it is violet. The reaction of $[Fe(phen)_3]^{2+}$ with CN^- has been recommended for the selective and sensitive determination of cyanide.[507] If excess $[Fe(phen)_3]^{2+}$ is present only $[Fe(CN)_2(phen)_2]$ is formed, with excess CN^- reaction to give $[Fe(CN)_4(phen)]^{2-}$ is so extremely slow at room temperature that it does not interfere.

The cyanide ligands in $[Fe(CN)_2(LL)_2]$ (LL = phen, bipy) are sensitive towards protonation: successive protonation of both cyanide ligands causes the colour of the complex to change from violet through orange-red to yellow.[508,509] Protonation in liquid hydrogen fluoride has also been examined in detail,[510] and a *cis* configuration confirmed for the diprotonated cation. Both

Table 15 Wavelengths (nm) of Maximum Absorption of $[Fe(LL)_2(CN)_2]$ Complexes in Various Solvents

Solvent	*$[Fe(bipy)_2(CN)_2]$*	*$[Fe(phen)_2(CN)_2]$*	*$[Fe(4,7\text{-}Me_2phen)_2(CN)_2]$*
Water	515[a]	516	505
MeOH	555[b]	545	534
EtOH	568[c]	557	548
Pr^nOH	572	566	555
Bu^nOH	574	570	557
MeCN	604	596	588
DMF	619	614	605
Me_2CO	626	625	607
C_5H_5N	629[d]	619	618

Extinction coefficient: [a] 5.5×10^3, [b] 6.4×10^3, [c] 6.9×10^3, [d] 8.6×10^3.
A. A. Schilt, *J. Am. Chem. Soc.*, 1960, **82**, 3000; J. Burgess, *Spectrochim. Acta, Part A*, 1970, **26**, 1369.

$[Fe(CN)_2(phen)_2]$ and the corresponding bipy complex can be oxidized to give iron(III) complexes.[511] They are useful as indicators for titration of weak bases in nonaqueous solvents, and also for redox titrations. The reaction of $[Fe(CN)_2(bipy)_2]$ with hydroxide ion follows a first-order rate law with rates *independent* of $[OH^-]$ to give, presumably, hydrated iron(III) oxide *via* air oxidation.[512] Other low-spin complexes of the $[FeX_2(LL)_2]$ (LL = phen, bipy) type[504] are with $X^- = NO_2^-$ and CNO^-, while most others are high-spin. In this respect the halide complexes are typical with magnetic moments of ~ 5.3 BM at room temperature. They are obtained from reaction of the anhydrous iron(II) salt with the diimine in a low polarity solvent,[513] or from the corresponding tris complex by extraction or refluxing with hot organic solvent, or pyrolysis in the absence of oxygen. Thermal decomposition of the tris complex as in equation (47) achieved by refluxing or extracting with a hot solvent such as chloroform, benzene, or methylcyclohexane, can be satisfactory although long reaction times are necessary in some instances.[513,514] This procedure does not make use of water or methanol, because in these solvents most of the high-spin bis ligand species are not stable. They usually dissociate forming the tris complex according to equation (48), although there are instances where, depending on the nature of X^-, recrystallization from methanol or ethanol affords the bis complex.

$$[Fe(LL)_3]X_2 \longrightarrow [Fe(LL)_2X_2] + LL \quad (47)$$

$$3[FeX_2(phen)_2] \longrightarrow 2[Fe(phen)_3]^{2+} + Fe^{2+} + 6X^- \quad (48)$$

Japanese workers[515] have reexamined the pyrolysis of $[Fe(bipy)_3]Cl_2 \cdot 5H_2O$, a means of making $[FeX_2(LL)_2]$ complexes originally investigated by German[516] and later by American groups.[517,518] Using Mössbauer spectroscopy they found[515] $[FeCl_2(bipy)_2]$ is obtained in the temperature range 140–200 °C with dissociation of the bipy ligand taking place at ~ 140 °C before dehydration is complete. However volatilization of the dissociated ligand from the solid proceeds only slowly below 200 °C. The room temperature Mössbauer parameters of $[FeCl_2(bipy)_2]$ ($\delta = 1.01$ mm s^{-1}, $\Delta E_Q = 2.98$ mm s^{-1}) obtained in this way are the same as previously reported[519–521] for $[FeCl_2(bipy)_2]$ made in acid aqueous solution from the ligand and Fe^{2+}.

While most $[FeX_2(LL)_2]$ (LL = phen, bipy) complexes are high-spin ($^5T_2$) and a few low-spin ($^1A_1$), some, such as $[Fe(ox)(phen)_2]$ (ox = oxalate) and $[FeF_2(phen)_2]$, are claimed[512,522] to be of intermediate spin. Of particular interest are those complexes (notably when $X^- = NCS^-, NCSe^-$) in which the high-spin to low-spin transition can be observed in the form of an abrupt change in magnetic and spectral properties over a fairly narrow temperature range.[504,505] These complexes can be obtained from the red precipitates formed when aqueous solutions of Fe^{2+} and the anion are treated with the calculated amount of ligand. These red hydrated compounds on dehydration afford, for example,[523] purple *cis*-$[Fe(NCS)_2(phen)_2]$. The red compound containing phen dissolves in solvents such as dimethyl sulfoxide and nitromethane, but not in diethyl ether or dioxane. In acetonitrile rapid isomerization takes place[524] to give the insoluble purple *cis*-$[Fe(NCS)_2(phen)_2]$. This behaviour is consistent with the red compound being $[Fe(phen)_3]_2[Fe(NCS)_4](NCS)_2 \cdot nH_2O$ and this formulation is supported by Mössbauer and IR spectra as well as other measurements.[524] Equations (49) and (50) represent the process taking place. At room temperature the magnetic

$$3Fe^{2+} + 6SCN^- + 6phen \longrightarrow [Fe(phen)_3]_2[Fe(NCS)_4](NCS)_2 \quad (49)$$

$$[Fe(phen)_3]_2[Fe(NCS)_4](NCS)_2 \longrightarrow 3\ cis\text{-}[Fe(NCS)_2(phen)_2] \quad (50)$$

moments of $[Fe(NCS)_2(phen)_2]$, $[Fe(NCSe)_2(phen)_2]$ and $[Fe(NCS)_2(bipy)_2]$ are in the range characteristic of high-spin complexes (4.9 to 5.2 BM) but at lower temperatures abruptly decrease (*e.g.* in $[FeX_2(phen)_2]$ at 174 K for $X^- = NCS^-$; at 232 K for $X^- = NCSe^-$). The observed magnetic moments tend to approach values more typical of low-spin complexes at 77 K. The existence of several polymorphs complicates the situation, but spectroscopic studies, and in particular Mössbauer data (Table 16) conclusively show that the transition involves a change from the $^5T_2$ to $^1A_1$ spin state. However, a simple model based on a 'pure' Boltzmann distribution over a fixed set of energy levels is an inadequate interpretation of the experimental results. It seems likely that solid state effects such as domain size have an important role in this behaviour. Thus samples of $[Fe(phen)_2(NCS)_2]$, prepared by precipitation in methanol and by acetone extraction of $[Fe(phen)_3](NCS)_2$, show a number of differences resulting from different crystal size and quality. The spin transition in the sample obtained from methanol is gradual while that of the extracted sample is abrupt. Their thermal behaviour (DTA) and temperature dependent X-ray diffraction patterns also show significant differences.[525]

Table 16 Mössbauer Data for Complexes of the Type $[Fe(LL)_2X_2]$ (LL = phen, bipy) Displaying Anomalous Temperature Dependent Magnetic Moments

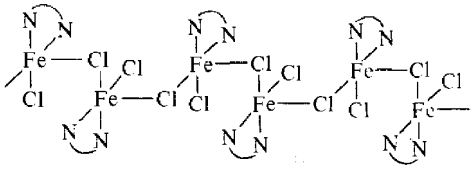
Complex	*Liquid nitrogen temperature* δ (mm s^{-1})	ΔE_Q (mm s^{-1})	*Room temperature* δ (mm s^{-1})	ΔE_Q (mm s^{-1})	*Ref.*
$[Fe(phen)_2(NCS)_2]$	0.37	0.34	0.98	2.67	1
$[Fe(phen)_2(NCS)_2]$[a]	0.46	0.36	1.01	2.71	2
$[Fe(phen)_2(NCS)_2]$[b]	0.42	0.33	0.94	2.64	2
$[Fe(phen)_2(NCSe)_2]$	0.35	0.18	1.03	2.52	1
$[Fe(Clphen)_2(NCS)_2]$	—	0.30	—	2.73	3
$[Fe(Mephen)_2(NCS)_2]$	—	0.41	—	2.55	3
$[Fe(NO_2phen)_2(NCS)_2]$	—	0.34	—	2.67	3
$[Fe(Me_2phen)_2(NCS)_2]$	0.34	0.46	0.97	2.59	4
$[Fe(bipy)_2(NCS)_2]$	0.36	0.50	1.06	2.18	5

[a] From methanol.
[b] Acetone extracted $[Fe(phen)_3](NCS)_2$.
1. E. König and K. Madeja, *Inorg. Chem.*, 1967, **6**, 48.
2. P. Ganguli, P. Gutlich, E. W. Muller and W. Irler, *J. Chem. Soc., Dalton Trans.*, 1981, 441.
3. A. J. Cunningham, J. E. Fergusson, H. K. J. Powell, E. Sinn and H. Wong, *J. Chem. Soc., Dalton Trans.*, 1972, 2155.
4. E. Konig, G. Ritter and B. Kanellakopulos, *J. Phys. Chem., Solid State Phys.*, 1974, **7**, 2681.
5. E. Konig, K. Madeja and K. J. Watson, *J. Am. Chem. Soc.*, 1968, **90**, 1146.

(*iii*) *Mono complexes*

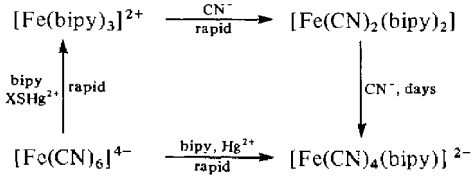
In solution yellow iron(II) species containing one α,α'-diimine ligand can be obtained[526] from an excess of Fe^{2+} in an acidified solution of the ligand (which controls the amount of available free ligand *via* protonation). Formation constants for many such complexes of substituted 1,10-phenanthrolines have been reported and tabulated.[425] The rate of formation of $[Fe(phen)(H_2O)_4]^{2+}$ is rapid and has a very unfavourable entropy of activation ($E_a = 53.6$ kJ mol^{-1}, $\Delta S^{\neq} = -66.9$ J K^{-1} mol^{-1}.[527] Kinetics of the corresponding reactions with 2,2′-bipyridine have also been reported.[528] Reaction of $[FeF_2py_4]$ with 1,10-phenthroline in pyridine affords violet $[FeF_2(phen)]$ (4.4 BM) which is no doubt polymeric.[513] Other dihalo complexes can be obtained by pyrolysis of the corresponding tris complexes. From $[Fe(bipy)_3]Cl_2 \cdot 5H_2O$ two $[FeCl_2(bipy)]$ isomers have been characterized by Mössbauer spectroscopy.[515] The orange isomer originally thought to be monomeric and possibly tetrahedral ($\delta = 0.93$ mm s^{-1}; $\Delta E_Q = 3.58$ mm s^{-1} at 293 K) is obtained from the first formed $[FeCl_2(bipy)_2]$, on further heating it is converted to a rose-red polymeric form. This is similar to that prepared from $FeCl_2$ and the ligand in hydrochloric acid,[519] for which the Mössbauer data are consistent with the presence of polymeric, chloride-bridged, octahedral high-spin iron(II), as are IR spectra and magnetic moments. It has been suggested the corresponding 5,5′-dimethyl-2,2′-bipyridine complex is probably a dimer containing five-coordinate iron(II).[517] Very recently, however, the orange isomer of $[Fe(bipy)Cl_2]$ has been obtained from ethanol solutions of $FeCl_2 \cdot 4H_2O$ and a deficiency of bipy, and on the basis of low temperature magnetic data structure (**33**) comprising a chain of five-coordinate iron(II) centres with single chloro bridges was proposed.[520]

The $[Fe(CN)_4(LL)]^{2+}$ (LL = bipy, phen) complexes have not been extensively studied. They are low-spin, and the proton NMR spectra of the complexes with LL = bipy and 5,5′-Me_2bipy are consistent with the expected two-fold symmetry of the diimine. With LL = phen an unexpected



(33)

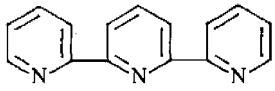
inequivalence has been observed that was postulated to be due to addition of water to an imine double bond.[529] Like $[Fe(CN)_2(LL)_2]$, the anionic mono diimine complexes exhibit solvatochromatic effects. $[Fe(CN)_4(LL)]^{2-}$ complexes can be obtained by prolonged (days) reaction of $[Fe(LL)_3]^{2+}$ with cyanide ion, but a better route is from $[Fe(CN)_6]^{4-}$, which reacts with bipy in the presence of a deficiency of Hg^{2+} to form predominantly $[Fe(CN)_4(bipy)]^{2-}$. With an excess of Hg^{2+} only $[Fe(bipy)_3]^{2+}$ is formed (Scheme 12).[530] The pyrolysis of $[Fe(CN)_4(LL)]^{2-}$ complexes, including the diprotonated species, has been studied extensively by Hungarian workers.[531–533]



Scheme 12

44.1.5.6.3 2,2′:6′,2″-Terpyridine

The terdentate ligand 2,2′:6′,2″-terpyridine, terpy (**34**), forms mono and bis complexes with iron(II). On the basis of a comparison of X-ray powder data it was suggested[534] that $[Fe(terpy)X_2]$ (X = Br, I) has a five-coordinate structure similar to that of $[Zn(terpy)Cl_2]$. In spite of early reports[535,536] claiming that the chloro complex is isomorphous with the zinc analogue, its X-ray powder pattern is different and it has been reformulated[537] as $[Fe(terpy)_2][FeCl_4]$, which is in accord with an observed[538] magnetic moment of 4.60 BM, well below the spin-only value.



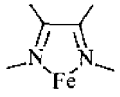
(34)

Fe^{2+}_{aq} in the presence of an excess of terpy forms[539,540] the very stable low-spin complex $[Fe(terpy)_2]^{2+}$, for which $\log \beta_2 = 20.4$, $\Delta H = -113\,kJ\,mol^{-1}$ and $\Delta S = -13\,J\,K^{-1}\,mol^{-1}$. The rate of ligand exchange is slow and has been examined using tritium-labelled terpy.[541] In acid solution, ligand dissociation takes place[542] and the observed kinetic behaviour as a function of acid concentration is complex.[543] Reaction of $[Fe(terpy)_2]^{2+}$ with CN^- follows second order kinetics to give $[Fe(terpy)(CN)_3]^-$ whose maximum absorption in the visible region (metal–ligand ct) varies markedly with the nature of the solvent.[543] Oxidation of $[Fe(terpy)_2]^{2+}$ yields the iron(III) complex (~1.1 V), while controlled reduction affords the +1 and 0 formal oxidation states.[544,545]

44.1.5.6.4 Other diimines and related ligands

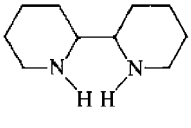
The basic iron(II) α-diimine five-membered unsaturated chelate ring (**35**) is a key unit in iron chemistry. In this review the classic ligands important in the early development of the area have been allocated separate sections: 2,2′-bipyridine and 1,10-phenanthroline (44.1.5.6.2), and 2,2′:6′,2″-terpyridine (44.1.5.6.3). The closely related dioximes are discussed in Section 44.1.5.7, while the many macrocyclic systems containing such linkages are covered in later sections. Once it was appreciated that only the basic structure (**35**) rather than a fully aromatic ligand is necessary to obtain stable, highly coloured (metal-to-ligand charge transfer[546a]) complexes, many ligands containing this moiety were synthesized and their iron(II) complexes prepared. Some of the most readily

accessible complexes are obtained *via in situ* Schiff base formation, and several useful reviews concerned with them are available.[546b–546e] These species are discussed first, before dealing with complexes of fully aromatic ligands. Most of these complexes are red or purple, and many with six nitrogen donors are low-spin and not of particular interest unless they display unusual ligand reactivity or because they have been the subject of kinetic studies. Several of these complexes can be obtained *via* oxidation/dehydrogenation of the corresponding saturated complex and this illustrates the thermodynamic stability of (**35**) in low-spin complexes. There has also been considerable interest in those complexes that exhibit spin transitions as a result of steric or electronic effects causing a weakening of the ligand field strength.

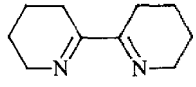


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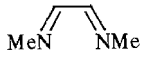
Blau reported[547] in 1898 that the *saturated* α,α′-dipiperidine (**36a**) forms a purple iron(II) complex. This surprising finding was later shown by Krumholz[548] to be due to air oxidation of the ligand in the presence of Fe^{2+} to give the tris chelate of (**36b**). He also demonstrated the template reaction of methylamine with glyoxal or biacetyl in the presence of Fe^{2+} that affords red tris complexes of the diimines (**37a**) and (**37b**). Although the free ligands are unstable, these complexes are very stable with respect to dissociation in acid but rather less so towards alkali. Their visible spectra are similar to those of $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$. For $[Fe(\mathbf{37b})_3]^{2+}$, $\lambda_{max} = 568$ ($\varepsilon = 1.07 \times 10^4$) and as with related complexes, on the high frequency side of this electronic band there are shoulders. These have been assigned to metal-to-ligand charge transfer,[547] while a later Raman study indicated they are largely due to vibronic transitions.[550] The range of complexes obtainable *via* this template synthesis is illustrated by the selected examples in equation (51). The isomer shifts of the tris complexes in their Mössbauer spectra[551] do not differ greatly ($\delta \sim -0.06\,mm\,s^{-1}$ at 298 K relative to $^{57}Co/Cu$) and the quadrupole splitting values fall within the range 0.5 to $0.6\,mm\,s^{-1}$ except for complexes with phenyl groups. These have $\Delta E_Q \sim 0.9\,mm\,s^{-1}$, that may result from steric effects or increased π acceptor ability. The former is favoured. The tris chelate derived from glyoxal and methylamine, $[Fe(\mathbf{37a})_3]^{2+}$, has been resolved and its racemization kinetics studied.[552] Racemization involves both intramolecular twist and bond breaking paths (~70% *via* twist at 69.4 °C). The activation enthalpy for bond breaking, as with $[Fe(bipy)_3]^{2+}$, is lower than that for twist racemization. In contrast with the more rigid $[Fe(phen)_3]^{2+}$, the activation enthalpy for dissociative bond breaking is larger than that for racemization.



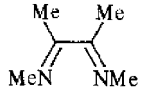
(36a)



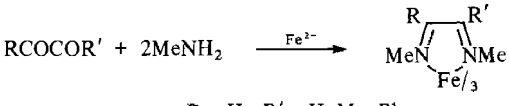
(36b)



(37a)



(37b)

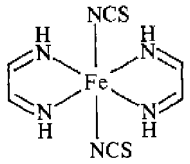


(51)

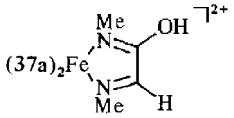
R = H; R′ = H, Me, Ph
R = Me; R′ = Me, Et, Ph
RR′ = $(CH_2)_6$

Calculations[553] on complex (**38**) confirm metal-to-ligand back-donation is important and indicate that HOMOs in complexes of this type have considerable ligand character. The latter result is relevant to the behaviour of related complexes upon oxidation. Oxidation of tris{(glyoxal)bis(methylimine)}iron(II), $[Fe(\mathbf{37a})_3]^{2+}$, by cerium(IV) is not like the reaction involving phen or bipy that simply gives the corresponding iron(III) complexes. Here oxidation of the coordinated ligand takes place to give two or more products including complex (**39**). It appears[554] that this reaction does not proceed *via* direct attack on the ligand but rather at the metal centre giving an intermediate iron(III) complex, which decomposes to give several products. Electrochemical and spectrophotometric monitoring of the reaction in 4.07 M H_2SO_4 led to evidence[555] supporting a mechanism in which intramolecular electron transfer in the first formed iron(III) complex is

assisted through nucleophilic attack by water on the ligand. This proton abstraction takes place at Me or CH, explaining the observed ligand oxidized products. However, these radicals may react with water at the same time reducing a molecule of $[Fe(\mathbf{37a})_3]^{3+}$. The basic correctness of this complicated mechanistic scheme was confirmed by electrochemical studies[556] that yielded values of the rate constants for some of the faster processes. As acidity is increased the thermodynamic stability of the iron(III) complex increases with respect to iron(II), and in strong sulfuric acid (> 10 M) $[Fe(\mathbf{37a})_3]^{3+}$ does not undergo ligand oxidation. Under these conditions activation parameters[557a] for the Ce^{IV} oxidation are $\Delta H^{\neq} = 43.9 \pm 4.2\,kJ\,mol^{-1}$ and $\Delta S^{\neq} = -33.5 \pm 8.4\,J\,K^{-1}\,mol^{-1}$.



(38)

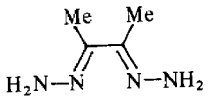


(39)

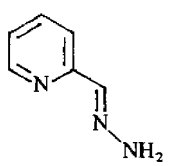
In acetonitrile electrochemical reduction gives iron(I) and iron(0) species.[557b] In this solvent ligand oxidation reactions are almost absent, but they are not completely avoided due to the presence of small amounts of water.[558] This problem was overcome by using a totally anhydrous low temperature (25 °C) molten salt comprising aluminum chloride and ethylpyridinium bromide (2:1 mole ratio). In this medium, reversible one-electron electrochemical oxidations take place[559] with $[Fe(\mathbf{37a})_3]^{2+}$, $[Fe(\mathbf{37b})_3]^{2+}$ and a number of related complexes.[560] Here the iron(III) form is thermodynamically more stable than is iron(II), whereas in aqueous solutions the reverse is true.

Addition of $[Fe(\mathbf{37a})_3]^{2+}$ to the Fe^{3+}_{aq}-catalyzed decomposition of hydrogen peroxide inhibits oxygen evolution by competing with Fe^{3+}_{aq} for $HO_2^{\cdot}$ radicals.[561] Thus the iron(II) complex is a trap for $HO_2^{\cdot}$, itself becoming oxidized in regenerating H_2O_2. In acid solutions $[Fe(\mathbf{37b})_3]^{2+}$ undergoes autooxidation through a free radical process. The reaction is first order in complex and half order in oxygen, suggesting protonation is involved in a preequilibrium step. The main product results form the oxidation of C-methyl to a hydroperoxide, and oxidation only takes place when a C-methyl or C-methylene group is present.

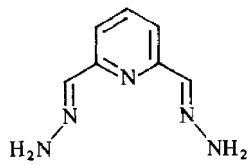
Dihydrazones of α-diketones can form low-spin tris complexes with iron(II). Thus the complex with biacetyldihydrazone (**40a**) is well characterized and related tris complexes derived from benzil and glyoxal are also low-spin,[563,564] while bis complexes of the type $[FeX_2(NN)_2]$ are paramagnetic[565] with magnetic moments of ~ 3 BM. These unusual values might be indicative of the complexes being incorrectly formulated. The bidentate and tridentate hydrazones (**40b**) and (**40c**) derived from pyridine aldehydes form low-spin tris and bis complexes respectively.[566] However, considerably more work has been carried out on the related Schiff bases (**41**) obtained from pyridine aldehydes[567] or ketones[568] and a primary amine (that can be aliphatic or aromatic). In both cases the resulting Schiff bases acts as a bidentate ligand and the low-spin tris iron(II) complexes are deep purple. They are prepared by adding a solution of an iron(II) salt to a mixture of a pyridine-2-carbaldehyde (or ketone) and the amine. This facile template synthesis can be used to prepare the free ligand *via* subsequent demetallation with edta. This is conveniently carried out in aqueous methanol, but if aqueous acetone is used, addition of acetone to the C=N bond takes place,[569] as shown in equation (52). When the complexes are formed in the presence of halide, green bis complexes $[FeX_2(NN)_2]$ result that are high-spin.[570] Extraction of these compounds with refluxing chloroform or cyclohexane yields mono complexes $[Fe(NN)X_2]$ that undoubtedly contain halide bridges.



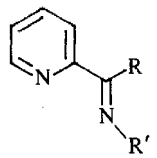
(40a)



(40b)

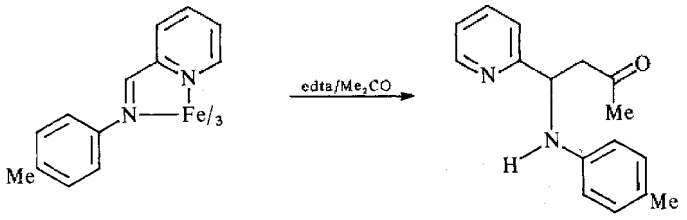


(40c)



(41)

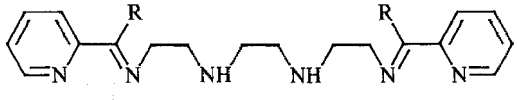
Acid dissociation of several iron(II) tris complexes of (**41**) has been well studied. For R = H, R′ = alkyl or phenyl the variation of rate with acid concentration is small,[567,571] like that for $[Fe(phen)_3]^{2+}$. This is surprising since these ligands might be expected to be flexible, and so form a monoprotonated intermediate in the way $[Fe(bipy)_3]^{2+}$ does. Perhaps this is due to the partially



(52)

dissociated intermediate having a very short life. Substitution in the phenyl ring does affect the dissociation rate in a way that can be correlated with Hammett constants. In contrast to the behaviour of most of these complexes, those with ligands derived from nitroanilines or pentafluoroaniline dissociate at rates that depend on acid concentration. Moreover, the results[571] are consistent with a rate law containing an [acid]^2 term that has been interpreted in terms of a rapid protonation preequilibrium, or hydrogen bonding with H_3O^+. With R = Ph isomeric complexes are obtained that dissociate at different rates,[568] and similar effects have been observed[572] with R = H, R′ = Me, Pr; and R = R′ = Me.[573] These and related complexes react with hydroxide ion[574] and cyanide ion in second order reactions. Iron(III) hydroxide is the product of the former and dicyano complexes of the latter. Like $[Fe(CN)_2(phen)_2]$ the analogous Schiff base complexes are low-spin, and display strong charge-transfer spectra that are very solvent dependent.[575a] Reaction of $[Fe(\mathbf{41})_3]^{2+}$ (R = Ph, R′ = 3,4-dimethylphenyl) with hydroxide ion has $\Delta V^{\neq} \sim 11\,cm^3\,mol^{-1}$, and this increases markedly as the solvent is made increasingly methanol rich highlighting the role of solvation.[575b] Complexes of the $[Fe(\mathbf{41})_3]^{2+}$ type react with hydrogen peroxide[574] at a rate independent of $[H_2O_2]$ that is limited by ligand dissociation. With peroxodisulfate in some instances two parallel reactions take place, one being independent, and the other dependent on the oxidant concentration. Thus, for R = R′ = Ph a single term rate law applies, whereas when R = H, R′ = Ph there is a two term rate law.[576] Oxidation of $[Fe(\mathbf{41})]^{2+}$ (R = R′ = Me) with the more powerful cerium(IV) is more complicated, and the reaction depends on acidity. Oxidation of the metal is followed by intramolecular reduction back to iron(II) with concomitant radical formation at the ligand that is assisted by water and retarded by acid.[577] Under appropriate conditions the major product is $[Fe(\mathbf{41})_3]^{2+}$ with R = CHO, R′ = Me.

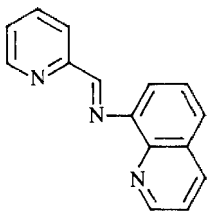
A large number of polydentate Schiff base ligands have been reported, and of particular interest are the iron(II) complexes of ligands such as (**42**) (R = H, Ph) because they are low-spin, even though they contain only two diimine units.[578] The rate of acid aquation of $[Fe(\mathbf{42})]^{2+}$ is slow, but this depends on acid concentration. Reaction with hydroxide ion is second order, as is that with cyanide ion. The product of the last reaction is not $[Fe(CN)_6]^{4-}$, but $[Fe(CN)_4(\mathbf{42})]^{2-}$ that has only one diimine bound to the metal. Related ligands have been prepared and much of the early work has been reviewed.[546b–546e]



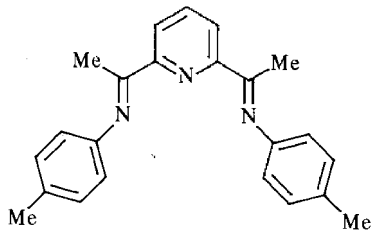
(42)

The tridentate ligands (**43a**) and (**43b**) form low-spin bis ligand complexes. The kinetics of several reactions of these, and related complexes have been studied.[579a] The *cis*/*trans* isomers (**43c**) and (**43d**) of pyridine-2-carbaldehyde 2-pyridylhydrazone can be isolated and both form iron(II) complexes.[579b] A tris complex is obtained with (**43d**). In water this is yellow, and when an acid solution is boiled it is converted to the bis complex $[Fe(\mathbf{43c})_2]^{2+}$. This complex is exceptionally stable (log $\beta_2 = 16.7$) and it is acidic so that in alkaline solution it forms a neutral complex.[579c] The hexadentate ligand (**43e**) forms a well-characterized purple low-spin complex,[579d] but substitution of methyl groups in the pyridine rings adjacent to the nitrogen atoms results in a complex displaying spin cross-over.[579e] The dynamics of this spin change have been monitored using laser temperature-jump methods.[597f]

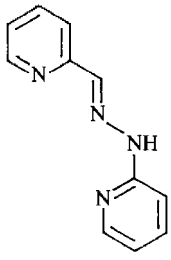
Iron(II) complexes containing saturated amines can undergo oxidative dehydrogenation to give thermodynamically more stable imine complexes. Mention has been made earlier in this section about the behaviour of α,α′-dipiperidine in this respect.[548] One of the most well-studied systems involves yellow diamagnetic 1,2-diamine complexes of the type $[Fe(CN)_4(diamine)]^{2-}$. Upon oxidation in alkaline solution these give red diimine complexes as in equation (53). The reaction goes *via* an iron(III) intermediate that can be isolated under acidic conditions. In the presence of base this gives complexes containing mono- and di-imine linkages.[580] The electrochemical and ferricyanide



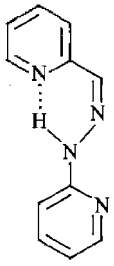
(43a)



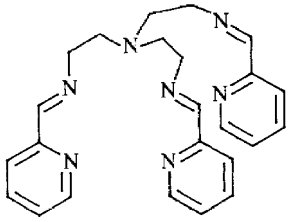
(43b)



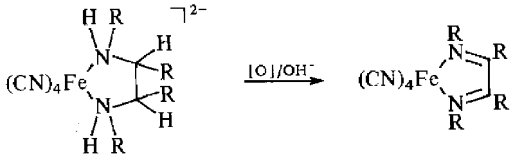
(43c)



(43d)

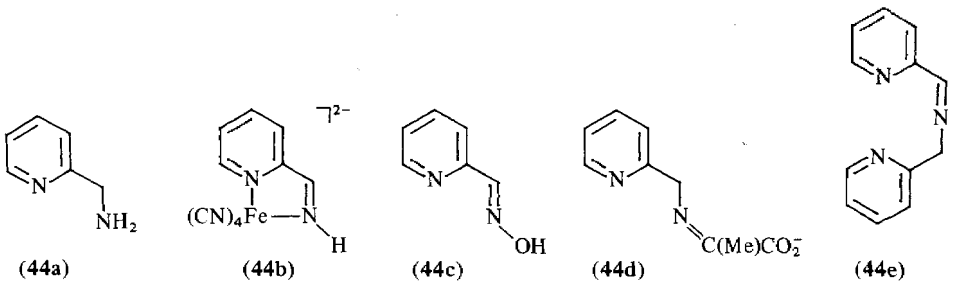


(43e)

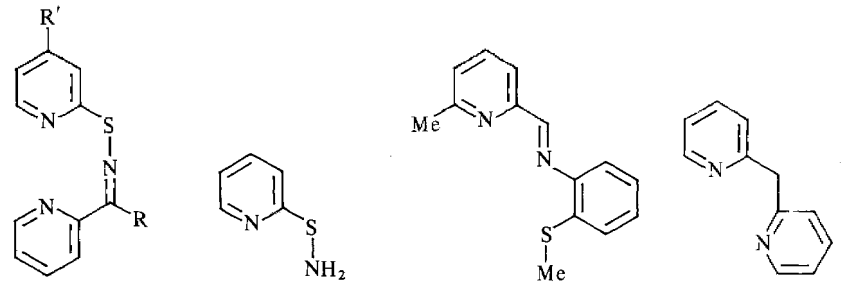


(53)

oxidation of the ethylenediamine complex $[Fe(CN)_4(en)]^{2-}$ has been studied in detail.[581] Reaction of the first formed low-spin iron(III) complex with OH^- leads to NH_2 deprotonation that is followed by internal electron transfer giving iron(II) with a NH radical, that forms the Fe^{II}=NH linkage on further oxidation. Tetracyano complexes containing optically active diamines have been prepared,[582] and their CD spectra recorded. Treatment with basic hydrogen peroxide gives the expected red diimine complexes. A large amount of work has been done on iron(II) complexes containing 2-aminomethylpyridine (α-picolylamine) (**44a**) and its derivatives. The tetracyano complex $[Fe(CN)_5(\mathbf{44a})]^{2}$ is smoothly oxidized to the imine complex (**44b**) that is quite stable in mildly acid solution.[583] In alkaline solution further oxidation gives the corresponding oxime (**44c**) complex together with uncharacterized decomposition products. Reaction of (**44a**) and sodium pyruvate with Fe^{2+}_{aq} does not give the expected complex containing (**44d**) because isomerization to the conjugated imine takes place that is followed by transamination with another molecule of (**44a**) to give the complex containing the tridentate ligand (**44e**) and α-alanine.[584] The related sulfur ligand (**44f**) forms a low-spin bis chelate,[585a] whereas the tris complex with (**44g**) has a magnetic moment of 2.8 BM. The mixed donor ligand (**44h**) forms a low-spin bis complex, and high-spin complexes of the type $[FeX_2(\mathbf{44h})]$ that may be five-coordinate.[585b] 2,2′-Dipyridylmethane (**44i**) appears[586] to form only high-spin iron(II) complexes but these are of the type $[FeCl_2(\mathbf{44i})_2]$ that has μ_{eff} = 5.3 BM. 2-Aminomethylpyridine (**44a**) itself forms $[Fe(\mathbf{44a})_3]^{2+}$, which exists in different colours and spin forms. As a methanol solvate, the high-spin chloride salt adopts the *mer* configuration whereas it is a *fac* isomer as the dihydrate (due to hydrogen bonding?) that is low-spin.[587a] The difference in Fe—N bond lengths in these complexes is large (~0.19 Å). The alcohol solvates of the bromide and chloride salts display sharp spin transitions to low-spin forms in the region 130–110 K, but removal of solvent molecules causes the transitions to become very gradual.[587b] The iodide salt contains two isomers in the lattice: the *mer* isomer has Fe—N = 2.20 Å and the *fac* form (with Fe—N = 2.06 Å) exists as a mixture of interconverting high- and low-spin species at room temperature.[587c] At room temperature the ethanol solvate of the chloride salt is yellow, but at liquid nitrogen temperature it is red. X-Ray structure work carried out at 298, 150 and 90 K shows the average Fe—N bond distances in the high- and low-spin forms are 2.195 Å and 2.013 Å respectively. The N—Fe—N bite angle increases by about 6° on going from high- to low-spin, and there are small changes in N—C distance consistent with increased d–π interaction.[587d] As suggested by Mössbauer work,[587e] the disorder of the alcohol molecules also varies with the spin transition, and their ordering may act as a trigger for the spin transition.

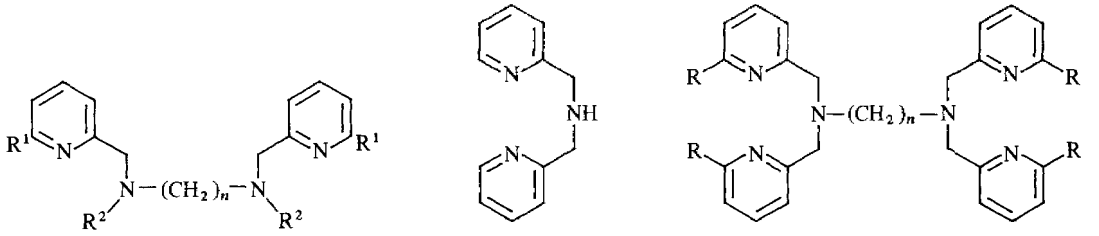


(44a) (44b) (44c) (44d) (44e)

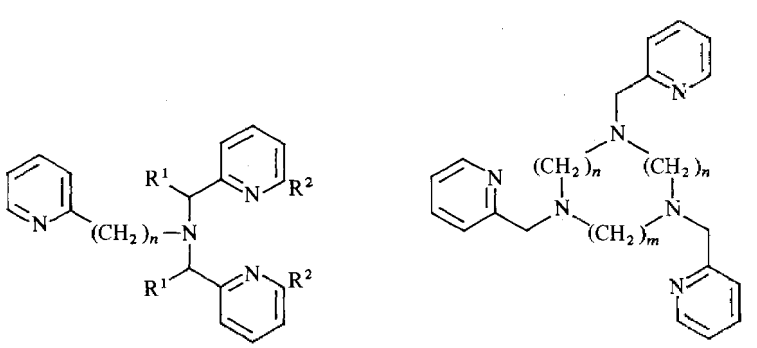


(44f) (44g) (44h) (44i)

Danish workers have synthesized several polydentate ligands derived from (**44a**) that illustrate the sensitivity of the spin transition to small ligand modifications and indicate that the chelate effect may be as important as conjugation in the ligand. Thus, with (**44j**; $n = 2, 3$ and $R^1 = R^2 = H$) low-spin complexes of the type $[Fe(NCS)_2(\mathbf{44j})]$ are obtained, but if R^1 or R^2 is methyl, high-spin complexes result.[588a] The bis complex of the tridentate ligand (**44k**) is red and low-spin,[588b] as is the complex of the hexadentate ligand (**44l**) when $n = 3$ and R = H, but high-spin for $n = 2$, R = Me, while complexes of closely related ligands display magnetic moments that are strongly temperature dependent.[588c] Complexes containing the tetradentate ligand (**44m**) similarly display a variety of spin behaviour.[588d] With $n = 1$, $R^1 = H$, $R^2 = Me$ $[Fe(NCS)_2(\mathbf{44m})]$ is high-spin whereas spin transition is observed when $n = 1$, $R^1 = H$, Me, $R^2 = H$. Triaza macrocycles (**44n**) with pendent pyridylmethyl groups making them hexadentate have been reported.[588e] When $n = m = 2$ the pseudooctahedral $[Fe(\mathbf{44n})]^{2+}$ is low-spin, but the complex with the somewhat expanded ligand having $n = m = 3$ the complex is high-spin.

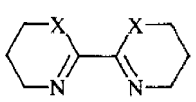


(44j) (44k) (44l)

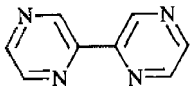


(44m) (44n)

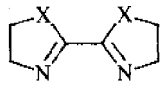
Ligands of the type (**45a**; X = NH, S, O) form a bridge between simple cyclic diimines and the fully aromatic ligands containing two heteroatoms. The tris complex with X = S is low-spin and the kinetics of its ligand dissociation reactions involving acid, hydroxide, peroxydisulfate, and heavy metals such as Ag^+, Hg^{2+} have been studied. Interestingly there is no catalysis by the heavy metals.[589a] The mixed ligand complex $[Fe(NCS)_2(\mathbf{45a})_2]$ (X = S) is high-spin at room temperature, but when the temperature is lowered it undergoes spin cross-over.[589b] The tris complex with X = NH displays a spin transition at the relatively high temperature of ~310 K, and its Mössbauer spectrum at 293 K has a poorly resolved quadrupole-split doublet centred at 0.29 mm s^{-1} (relative to natural iron) attributable to the major low-spin component. At 77 K only the resonance due to this form is present.[589c] The rapid (stopped-flow) reaction of $[Fe(\mathbf{45a})_3]^{2+}$ X = O (λ_{max} = 500, $\varepsilon = 1.6 \times 10^3$) with OH^- has been reported to involve attack by OH^- on the coordinated ligand followed by ligand decomposition and finally precipitation of $Fe(OH)_3$. The first stage is a preequilibrium for which thermodynamic data have been presented.[589d] The related tris complex of 2,2′-bipyrazine (**45b**) behaves similarly, and reaction rates for this and related complexes have been compared with charge densities based on INDO molecular orbital calculations.[589e] In contrast the tris complex with (**45c**; X = NH) is high-spin[589f] down to ~115 K, and when X = O the complex remains high-spin over the complete temperature range investigated.[489c] In acetonitrile $[Fe(\mathbf{45c})_3]^{2+}$ reacts with oxygen to form water and an iron(III) complex in which one of the ligands is deprotonated. The mechanism of this reaction is not fully resolved, but it is thought an intermediate containing coordinated oxygen may be involved.[589g]



(45a)

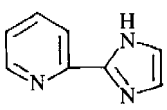


(45b)

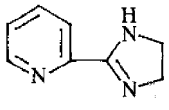


(45c)

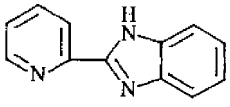
Octahedral tris ligand complexes containing the pyridylimidazole ligand (**45d**) or related ligands (**45e**) and (**45f**) display spin cross-over behaviour that in most instances is sensitive to both the nature of the anion and the number of molecules of water of crystallization. Several groups have examined[590a–590c] the deep red hydrated $[Fe(\mathbf{45d})_3](ClO_4)_2$ that is high-spin at around room temperature, but whose magnetic moment gradually decreases as the temperature is lowered until at about 100 K it rapidly falls to ~1 BM. As in other spin cross-over systems this behaviour cannot be described adequately by a simple Boltzmann distribution with a fixed energy difference.[590b]



(45d)



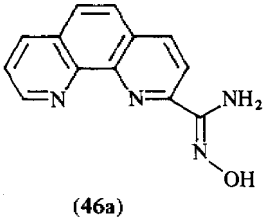
(45e)

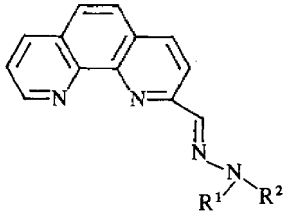


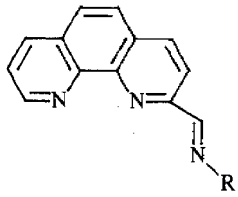
(45f)

Mössbauer spectra recorded[590c] down to 4.2 K readily distinguish between the low-spin and high-spin forms. $[Fe(\mathbf{45e})_3](ClO_4)_2$ exists in dark blue and dark purple forms.[590b] The former is low-spin and the latter high-spin at room temperature (5.25 BM at 295 K). The magnetic moment of the high-spin complex decreases rapidly at around 120 K. The complex $[Fe(\mathbf{45f})_3]^{2+}$ was first investigated for possible use in the spectrophotometric determination of iron, and although its extinction coefficient is not particularly large, it has the advantage of being extractable into isoamyl alcohol.[590d] This complex is expected to have a relatively stable high-spin form as a result of steric effects, and in fact with some of its salts it is not possible to characterize the low-spin ground state magnetically.[590e–590g] Mössbauer spectra show the coexistence of high- and low-spin forms that have a *mer* configuration, indicating that there is a substantial difference between the coordinated pyridine and benzimidazole nitrogen atoms. Rather surprisingly the bis diimine complex $[Fe(NCS)_2(\mathbf{45f})_2]$ is fully high-spin down to 4.2 K (ref. 590g). The dynamics of the spin equilibria in solution for $[Fe(\mathbf{45d})_3]^{2+}$ and $[Fe(\mathbf{45f})_3]^{2+}$ have been investigated using laser Raman temperature-jump[590h] and photochemical perturbation with a Q-switched laser. Recently volumes of activation have been determined for both forward and reverse processes. Both complexes show a marked solvent dependence for $\Delta V^{\neq}$ (high → low), but $\Delta V^{\neq}$ (low → high) is not very sensitive to the nature of the solvent. The former are negative, as are corresponding values of $\Delta S^{\neq}$, in agreement with there being substantial Fe—N bond contraction in the activation step.[590i,590j]

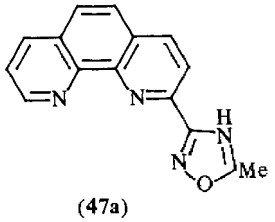
Just as bidentate ligands have been formed by attachment of an imine containing group, or other suitable donor, to the 2-position of a monodentate pyridine, so tridentate ligands have been obtained from 1,10-phenanthroline. Thus, the 2-amidoxime (**46a**) has a fairly strong ligand field and $[Fe(\mathbf{46a})_2]^{2+}$ is low-spin,[591a] but the spin cross-over point is approached in the bis ligand complexes of the hydrazones (**46b**). Magnetic properties of these complexes depend on the nature of R^1 and R^2, and are most pronounced when $R^1 = R^2 = Ph$. This complex has a sharp spin change near room temperature,[519b] and this is associated with X-ray powder diffraction pattern changes.[591c] Similar steric effects operate in the bis complex of the 2-carbaldehyde imines (**46c**). With R = Bu^t the complex is high-spin and there is a gradual spin cross-over as the temperature is lowered, but with almost all other R groups the complex is low-spin at room temperature.[591d]

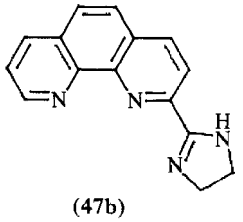

(46a)

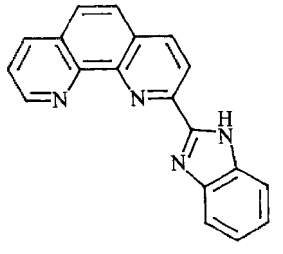

(46b)

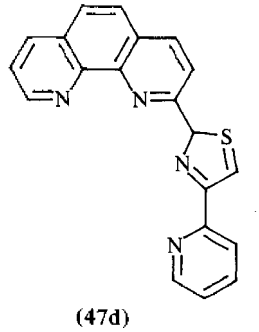

(46c)

Several 1,10-phenanthroline derivatives with a five-membered heterocyclic group in the 2-position have been prepared, and most of their bis iron(II) complexes display temperature dependent behaviour. Salts of $[Fe(\mathbf{47a})_2]^{2+}$ are high-spin and they undergo a spin change at low temperature, but this is so gradual it seems likely that solid-state effects are involved.[592a] However, no changes in the powder X-ray diffraction pattern are evident. The bis ligand complex of the imidazoline derivative (**47b**) is predominantly low-spin at room temperature (~1.8 BM) but the magnetic moment gradually increases as the temperature is raised.[592b] Both salts of the benzimidazole analogue complex $[Fe(\mathbf{47c})_2]^{2+}$ and its neutral deprotonated form, are low-spin at room temperature, and their magnetic moments only increase slightly at higher temperatures. A number of complexes of related ligands with 2-thiazole groups have been prepared and these usually display temperature dependent magnetic moments. At first sight however, it is rather surprising that $[Fe(\mathbf{47d})_2]^{2+}$ is high-spin over the entire experimental temperature range (83–363 K). This behaviour is attributed to the steric effect of the uncoordinated pyridyl group.[592c]


(47a)

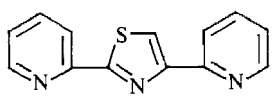

(47b)


(47c)

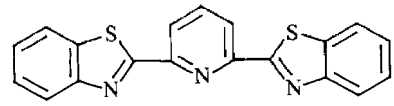

(47d)

Most heterocyclic tridentate ligands related to terpyridine (Section 44.1.5.6.3) have a smaller ligand field, and so salts of the bright red $[Fe(\mathbf{48a})]^{2+}$ are high-spin (~5.5 BM) at room temperature. Their magnetic moments decrease only gradually to ~3.3 BM at 80 K. At ~100 K the colour changes to intense purple, and the reason for the high limiting magnetic moment might be due to only half of the molecules becoming low-spin.[593a] Introduction of a methyl group adjacent to one of the pyridine nitrogen atoms results in the bis complex becoming fully high-spin.[593b] The dibenzothiazole (**48b**) forms reddish purple $[Fe(\mathbf{48b})_2]^{2+}$ that is high-spin at room temperature (4.49 BM at 313 K). The magnetic moment decreases as the temperature is lowered but some paramagnetism remains at 83 K (2.23 BM). When a solution of $FeBr_3$ is added to one of (**48b**) in alcohol the black crystalline salt $[Fe(\mathbf{48b})_2][FeBr_4]Br$ is obtained,[593c] in which it was deduced the magnetic moment of the iron(II) cation only varies slightly with temperature.

The tripyridyl-*s*-triazine ligand (**49**) is also tridentate and forms a very stable low-spin bis complex with iron(II) for which $\log \beta_2 = 11.05$ at 23 °C (ref. 594a). It proved possible to separate the stepwise

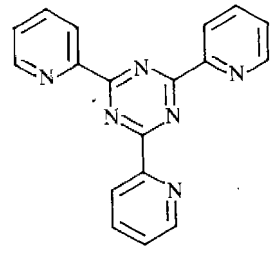


(48a)



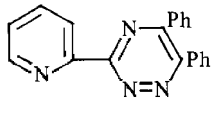
(48b)

formation constants, and the value of K_2 (log $K_2 = 6.26$) is significantly larger than K_1 (log $K_1 = 4.81$), in keeping with the mono complex (presumably $[Fe(\mathbf{49})(H_2O)_3]^{2+}$) being high-spin. The kinetics of formation and dissociation of $[Fe(\mathbf{49})_2]^{2+}$ have been studied[594b] and surprisingly it appears that addition of the first ligand to $[Fe(H_2O)_6]^{26}$ is rate determining, while as expected, formation of the mono complex is rate determining in the dissociation. As expected for dissociation of a basic tridentate ligand, and as found[543] for $[Fe(terpy)_2]^{2+}$, the acid dissociation kinetics are complex—particularly so because of the uncoordinated basic nitrogen sites. Reaction of $[Fe(\mathbf{49})_2]^{2+}$ with hydroxide ion is first order in both complex and hydroxide, and it has been suggested[594c,594d] this is due to a rapid preequilibrium with CN^- or OH^- which is followed by ligand dissociation. The derived activation parameters support this proposal. Electrochemical reduction of $[Fe(\mathbf{49})_2]^{2+}$ affords neutral $[Fe(\mathbf{49})_2]$, that has been suggested[595] contains anionic ligands.

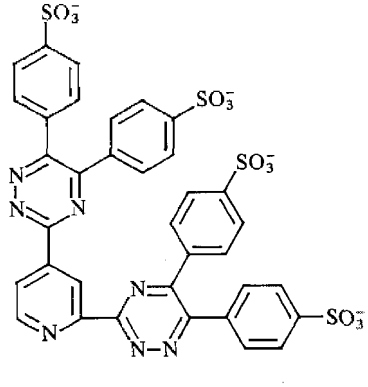


(49)

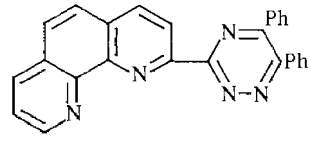
The unsymmetrical 1,2,4-triazine ring is present in several ligands recommended for use in the spectrophotometric determination of iron. Sulfonation of **(50a)** affords[596] a water soluble reagent that is bidentate forming a tris diimine complex with $\beta_3 \sim 4.9 \times 10^{15}$, for which an extinction coefficient as high as 2.86×10^4 ($\lambda_{max} = 652$ nm) has been reported.[597] The course of its reaction with hydroxide ion proceeds[598a] *via* an intermediate (formed by some ligand reaction) that in turn undergoes dissociation. Reaction with cyanide ion follows a simple pattern in water,[598b] but this is not the case in aqueous DMSO. Here spectral evidence suggests cyanide ion attacks one ligand, while parallel ligand displacements take place.[598c] The related sulfonated ligand **(50b)** is claimed[599a] to be the most sensitive chromogen for iron(II) with $\varepsilon = 3.22 \times 10^4$ ($\lambda_{max} = 565$ nm). The presence of the sulfonic acid groups has little effect on the absorption maximum or extinction coefficient of the iron(II) tris ligand complex.[599b] Reaction of $[Fe(\mathbf{50b})_3]^{10-}$ with cyanide ion is complex, there being several intermediate species. The tridentate derivative of 1,10-phenanthroline with a 2-(1,2,4-triazine) ring (**51**) forms a deep purple low-spin complex $[Fe(\mathbf{51})_2]^{2+}$.[600]



(50a)



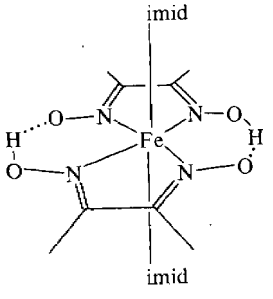
(50b)



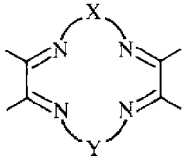
(51)

44.1.5.7 Dioximes

In the absence of a reducing agent and strong axial ligands, $[Fe(DMG)_2]$ (DMG = dimethylglyoxime) is unstable. Hydrazine can fulfil both of these roles, and red $[Fe(DMG)_2(N_2H_4)_2]$ (λ_{max} 525 nm, $\varepsilon \sim 10^4$) is an air stable low-spin complex.[601] The structure of the analogous $[Fe(DMG)_2(imid)_2]$ (**52**) has been determined[602] by X-ray diffraction; the two DMG ligands are planar and the six nitrogen atoms bound to the low-spin iron(II) centre exhibit the expected tetragonal distortion from octahedral symmetry. Bis-methylimidazole complexes of iron(II) dimethylglyoxime systems have been synthesized[603] with varying degrees of ring closure that extend to macrocycles and in such complexes one axial imidazole ligand may be substituted by either carbon monoxide or benzyl isocyanide. For the complexes [Fe(**53**)(Meimid)(CO)]$^{n+}$ the order of CO lability is: DMGH < DOHpn < DOHen < TIM < TAAB, 14aneN$_4$ < porphyrin, phthalocyanine < 15aneN$_4$.



(52)

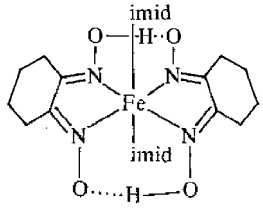


(53)

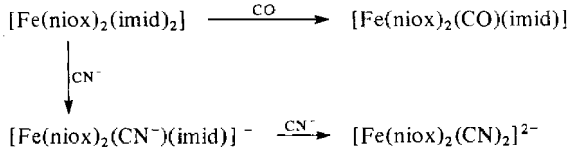
DMGH: X = Y = O·HO
DOHpn: X = $(CH_2)_3$
Y = O·HO
DOHen: X = $(CH_2)_2$
Y = O·HO
TIM: X = Y = $(CH_2)_3$

Increasing net positive charge on the iron results in increased lability of the π acceptor carbon monoxide ligand. The cationic complexes of TIM, TAAB and 14aneN$_4$ show very similar CO dissociation rates despite large variations in ring size and ligand unsaturation. The larger rings achieve the environment needed to stabilize low-spin iron(II) by puckering to avoid conformational strain. There is an underlying trend with ring size however as shown by the sharp increase in CO dissocation rate for the 15aneN$_4$ complex.

The structure of the 1,2-cyclohexanedione dioxime (niox) complex, $[Fe(niox)_2(imid)_2]$ (**54**), which is more soluble than the analogous DMG complex, has also been determined,[604] but because of disorder in the cyclohexyl rings some of the important structural parameters were ill defined. However, the Mössbauer spectra of $[Fe(niox)_2L_2]$ (L = py, imid, NH_3, $BuNH_2$) and related complexes have been studied in detail and are consistent with considerable tetragonal distortion.[605,606] $[Fe(niox)_2(imid)_2]$ reacts with CN^- to give $[Fe(niox)_2(CN)_2]^{2-}$, and by using only one equivalent of CN^- $[Fe(niox)_2(CN)(imid)]^-$ can be obtained.[605] Reaction with CO affords $[Fe(niox)_2(imid)(CO)]$ as in Scheme 13.

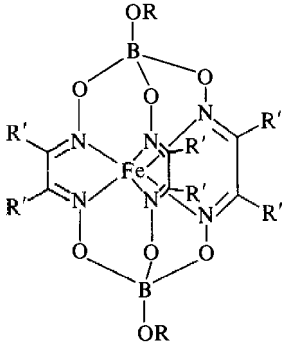


(54)



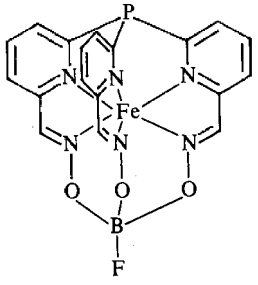
Scheme 13

Iron(II) complexes of monooximes derived from pyrazole-4,5-dione have been reported.[607] These are high-spin with the iron coordinated to oxygen donors. The preparation has been reported[608] of oligomeric iron(II) tetraoxime complexes having molecular weights between 2600 and 3100. These oximes have aliphatic backbones which are very flexible and as a result the FeN_4 units appear to be independent of one another with protons α or β to the oxime groups undergoing no shift upon complexation. Other related oxime complexes are discussed in a review.[609] However, of more interest are the encapsulated complexes obtained by capping oxime oxygen atoms of the, formally intermediate, tris oxime complexes with suitable groups. Thus reaction[610] of $FeCl_2$ with dimethylglyoxime (R′ = Me) or 1,2-diphenylethane-1,2-dione dioxime (R′ = Ph) and boric acid in refluxing alcohol (ROH, R = H, Me, Et, Pr^i, Bu^n) affords red low-spin complexes (**55**). No doubt these complexes, like their Co^{III} analogues, approach a trigonal prismatic configuration.[611,612] Russian workers[613] obtained the corresponding 1,2-cyclohexanedione dioxime complex capped with BF by using BF_3 in acetonitrile in place of boric acid in alcohol. Alcoholysis of this complex affords the BOR derivatives. Experimental methods for the substitution of a wide variety of groups have subsequently been developed.[614]



(55)

A correlation has been established between the iron(II)/iron(III) redox couple of such complexes and the substituent on the apical boron atoms; no corresponding trend in ^{11}B NMR shifts has been observed, however. The related dark red low-spin, non-octahedral complex (**56**) is obtained[615] by encapsulation of the preformed hexadentate ligand with BF_3. X-Ray crystallography reveals[616] that the coordination geometry deviates by approximately 21.5° from the ideal trigonal prismatic configuration in this complex which has a formally 'chiral' iron centre. The analogous complex $[Fe(py_3TPN)]^{2+}$ is closer to an idealized octahedral geometry[617] having an 'angle of twist' of 17°. An analysis[618] of a number of crystal structures suggests that geometry may be rationalized on the basis that ligand rigidity favours trigonal prismatic coordination. Amongst the most 'octahedral' of such complexes is $[Fe(py_3tren)]^{2+}$ which shows a high ⇌ low spin transition both in the solid state and in solution.[618] A variable temperature X-ray structure analysis shows that steric interactions between methyl groups and neighbouring pyridine rings is responsible for variations in magnetic behaviour as the number of methyl groups varies. Additionally, it was noted that the Fe—N bond distance contracted by approximately 0.12 Å in the solid state transition from high-spin (μ_{eff} = 5.0 BM, 300 K) to intermediate-spin (μ_{eff} = 2.3 BM, 205 K).



(56)

44.1.5.8 Phosphorus and Arsenic Donors

44.1.5.8.1 Monodentate ligands

A considerable number of stable organometallic iron(0) compounds containing phosphorus donors are known, but comparatively few with arsenic donors have been reported. In contrast many simple iron(II) phosphine complexes tend to be unstable, and undergo dissociation in solution. It appears that phosphites (notably trimethyl phosphite) tend to form more stable simple iron(II) complexes than do the corresponding phosphines. However, with polydentate phosphines more stable complexes result, and five-coordination is relatively common. Complexes in several spin states, including some displaying spin-equilibrium behaviour, are known. Diamagnetic octahedral complexes of the type $[FeX_2(PP)_2]$ are well characterized, and interesting bis carbonyl complexes containing monodentate or polydentate phosphorus donors are obtained upon reaction with carbon monoxide under surprisingly mild conditions. Few iron(II) complexes containing arsenic donors have been well characterized.

Colourless needles, assumed to be $[FeCl_2(PEt_3)_2]$, have been isolated[619] from $FeCl_2$ and the phosphine in benzene. In ethanol, apparently, there is no reaction[620] which illustrates the relatively poor affinity of iron(II) for trialkylphosphines. Refluxing anhydrous FeX_2 with a tertiary phenylphospine PR_3 ($R_3 = Ph_3$, Ph_2Et, $PhEt_2$) in benzene affords[619] the high-spin complexes $[FeX_2(PR_3)_2]$ for which magnetic moments over the range 4.8–5.3 BM have been reported; this and the electronic spectrum of $[FeBr_2(PPh_3)_2]$ are consistent with a tetrahedral configuration.[621] Iron(II) halides react with the secondary phosphines HPR_2 (R_2 = MePh, EtPh, Et_2) in anhydrous ethanol to form complexes of the type $[FeX(HPR_2)_4]^+$ that have been isolated as their BF_4^- and PF_6^- salts.[622] These red/violet complexes are paramagnetic (~3 BM) with triplet ground states. In solution, some phosphine dissociation takes place to form tetrahedral complexes. With carbon monoxide at room temperature bis carbonyl complexes are formed as in equation (54); they are yellow and appear to have *trans*-carbonyl ligands in solution. '$Fe(PF_6)_2$' and $Fe(BF_4)_2 \cdot 6H_2O$ react with an excess of secondary phosphine (HPR_2, R_2 as above) in 2-propanol to give yellow or yellow/brown $[Fe(HPR_2)_5]X_2$ (X = PF_6, BF_4). These complexes are paramagnetic with μ_{eff} in the range 1.3–2.5 BM, but the presence of paramagnetic impurities makes it difficult to establish the actual ground state. Reaction of $[Fe(HPR_2)_5](PF_6)_2$ with carbon monoxide takes place in two stages:[622] addition of the first CO is rapid with subsequent phosphine substitution being relatively slow to give diamagnetic *trans*-$[Fe(HPR_2)_4(CO)_2]$ as in equation (55).

$$[FeX(HPR_2)_4]^+ + 2CO \longrightarrow [FeX(CO)_2(HPR_2)_3]^+ + HPR_2 \quad (54)$$

$$[Fe(HPR_2)_5]^{2+} \xrightarrow{CO} [Fe(HPR_2)_5CO]^{2+} \xrightarrow{CO} \textit{trans}\text{-}[Fe(HPR_2)_4(CO)_2]^{2+} + HPR_2 \quad (55)$$

While the secondary phosphine PCy_2H forms the colourless tetrahedral complex $[FeCl_2(PCy_2H)_2]$ (5.12 BM) with $FeCl_2$, the complex $[FeCl_2(PEt_2H)_2]$ is red with a magnetic moment of 3.61 BM, which is claimed to be consistent with a square planar structure.[623] With $FeCl_2$ or $FeBr_2$ and the primary phosphine $PPhH_2$, the orange/red square planar complex $[Fe(PPhH_2)_4]X_2$ can be formed,[624] but $PCyH_2$ is said to be anomalous in forming $[FeBr_2(PCyH_2)_3]$ (3.48 BM), while with $FeCl_2$ square planar $[FeCl_2(PCyH_2)_2]$ results.[625] The phosphides $[Fe(PCy_2)_2]$ and $Li[Fe(PCy_2)_3]$ are formed from the reaction[626] of $FeBr_2$ with$LiPCy_2$.

Carbon monoxide reacts with mixed alkyl/aryl phosphine iron(II) complexes (but not those of PPh_3) to give well-defined high-spin complexes of the type $[FeCl_2(PR_3)_2(CO)_2]$.[619] The IR spectra of $[FeX_2(PEt_3)_2(CO)_2]$ (X = NCS, Cl, Br, I) have been recorded.[627] Carbonylation of a mixture of $FeCl_2$ and diphos in benzene affords[628] $[FeCl_2(diphos)(CO)_2]$, which on the basis of its IR spectrum has *cis* CO ligands. However, when THF is the solvent a different isomer results that has *trans* CO ligands, and refluxing the *cis* isomer in acetone causes it to isomerize to the *trans* form.[628] A wide range of low-spin iron(II) complexes of the type $[FeX_2(CO)_2P_2]$ have been reported and characterized in which P = phosphine or phosphite.[629] Readily available $P(OMe)_3$ is a good ligand due to the low steric requirements associated with strong σ donor and π acceptor properties. In many respects, $P(OMe)_3$ mimics the behaviour of isocyanides, and many low-spin iron(II) complexes containing CO and $P(OMe)_3$ have been reported.[630] Reaction of $FeCl_2$ with $P(OMe)_3$ in benzene or methanol produces an uncharacterized, readily oxidized mixture which may contain $[Fe\{P(OMe)_3\}_6]^{2+}$, $[FeCl_2\{P(OMe)_3\}_4]$ and other products. However, $FeCl_2$ and $P(OMe)_3$ with $SnCl_2$ react in stoichiometric amounts to give *cis*-$[Fe(SnCl_3)Cl\{P(OMe)_3\}_4]$, which reacts with $NaBPh_4$ in methanol to give $[Fe(SnCl_3)\{P(OMe)_3\}_5]$ as a yellow precipitate.[630] In the presence of $NaBH_4$, reaction of $FeCl_2$ with an excess of $P(OMe)_3$ affords a high yield of sightly soluble off-white

material said to be $[Fe\{P(OMe)_3\}_6]$, but complete analytical results supporting this formulation were not reported.[630] In contrast, sodium amalgam reduction of $[FeCl_2\{P(OMe)_3\}_3]$ in the presence of free $P(OMe)_3$ affords[208] yellow crystals of $[Fe\{P(OMe)_3\}_5]$ (see Section 44.1.3.3) that reacts with NH_4PF_6 according to equation (56). On the NMR timescale the hydride so formed is kinetically inert with respect to exchange reactions, but reaction with CF_3CO_2H gives hydrogen and ostensibly $[Fe\{P(OMe)_3\}_5]^{2+}$ that was characterized[632] by NMR. It also reacts[210] with MeI to give $[FeMe\{P(OMe)_3\}_5]^+$.

$$[Fe\{P(OMe)_3\}_5] + NH_4PF_6 \longrightarrow [FeH\{P(OMe)_3\}_5]PF_6 + NH_3 \quad (56)$$

$$FeCl_2 + NaBH_3(CN) + P(OR)_3 \xrightarrow{MeOH} \textit{trans}\text{-}[Fe(BH_3CN)_2\{P(OR)_3\}_4] \quad (57)$$

Reaction of hydrated $FeCl_2$ with excess $Na(BH_3CN)$ and $P(OR)_3$ (R = Me, Et) in methanol gives[631] low-spin *trans*-$[Fe(BH_3CN)_2\{P(OR)_3\}_4]$ as in equation (57). However, a mixture of *cis* and *trans* isomers resulted when the iron was obtained by electrolytic dissolution in acetonitrile, and it appears both solvent effects and the nature of the phosphite are important in determining the isomer ratio. Diethylphenyl phosphonite ($P(OEt)_2Ph$) reacts[632] with $FeCl_2$ in ethanol to give well-characterized, light yellow, diamagnetic *cis*-$[FeH_2\{P(OEt)_2Ph\}_4]$ as in equation (58). The product has Fe—H distances of 1.51 Å, with a geometry intermediate between octahedral and tetrahedral. It is indefinitely stable under argon or nitrogen, but the crystals turn brown after a few days exposure to air. The related, though less well-characterized, trimethyl phosphite dihydride complex $[FeH_2\{P(OMe)_3\}_3]$, as well as a tetrahydride, have also been described.[210]

$$FeCl_2 + P(OEt)_2Ph \xrightarrow{BH_4^-/EtOH} \textit{cis}\text{-}[FeH_2\{P(OEt)_2Ph\}_4] \quad (58)$$

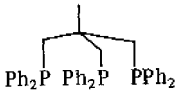
44.1.5.8.2 Polydentate ligands

Many iron complexes having interesting structures and reactions are formed with polydentate arsenic and phosphorus ligands.[633] However, in the present context the coordination chemistry of the arsines is considerably less extensive than that of the phosphines, and there are many examples when it is not possible to prepare the corresponding arsine analogue of a well-characterized phosphine complex. The most well-known ditertiary arsine is *o*-phenylenebis(dimethylarsine), (diars) and the complexes $[FeX_2(CO)_2(diars)]$ (X = Br, I) and $[FeI_2(diars)]$ are readily obtained by halogen oxidation of appropriate iron(0) species.[218] Nitric acid oxidation[63] of $[FeCl_2diars]$ affords the iron(IV) complex $[FeCl_2(diars)]^{2+}$. Iron powder reacts with *o*-phenylenebis(diethylphosphine) ($C_6H_4(PEt_2)_2$) under an atmosphere of hydrogen at 200 °C to give[634] small amounts of the dihydride *trans*-$[FeH_2\{C_6H_4(PEt_2)_2\}]$. The monohydride complex[635–637] *trans*-$[FeHCl(depe)_2]$ (depe = 1,2-bis(diethylphosphino)ethane) reacts with $NaBPh_4$ in acetone under nitrogen to give the relatively stable cationic dinitrogen complex *trans*-$[FeH(N_2)(depe)_2]^+$, as in equation (59), which was isolated as the BPh_4^- salt.[638] The same reaction carried out in the presence of a wide range of ligands (L), including phosphites, affords[639] the complexes *trans*-$[FeHL(depe)_2]^+$. Mössbauer spectra obtained at 4.2 K in a high applied magnetic field permit discussion of the bonding in these complexes. It is concluded[640] that the instability of N_2 complexes is associated mostly with the weak σ donor properties of N_2. Even though the related complex *trans*-$[Fe(\eta^2\text{-}H_2)(H)(diphos)_2]^+$ is stable to loss of hydrogen up to 50 °C, it must be stored under hydrogen or argon since it slowly reacts[641] with molecular nitrogen to give *trans*-$[FeH(N_2)(diphos)_2]^+$. The reactant η^2-H_2 complex undergoes intramolecular exchange of terminal hydride with the hydrogens of the η^2-H_2 ligand,[642] for which the activation parameters are $\Delta H^{\neq} = 58.2 \pm 2.9\,kJ\,mol^{-1}$ and $\Delta S^{\neq} = -4.2 \pm 12.6\,J\,K^{-1}\,mol^{-1}$. The X-ray structure of *trans*-$[Fe(\eta^2\text{-}H_2)(H)(diphos)_2]BF_4$ has been determined.[642] Reaction of this complex with good donor ligands gives complexes of the type *trans*-$[FeH(L)(diphos)_2]^+$, like those of depe previously discussed. The bidentate phosphines $R_2PCH_2CH_2PR_2$ (R = Me, Et) readily form octahedral low-spin *trans* dichloro complexes, *trans*-$[FeCl_2(R_2PCH_2CH_2PR_2)_2]$. They have been the subject of high precision X-ray structure determinations[643] that show Fe—P distances (~2.2 Å) are dramatically shorter than in related high-spin complexes. For example, the polytertiary phosphine $(Ph_2PCH_2CH_2)_2PPh_2$ acts as a bidentate ligand in the distorted octahedral $[FeCl_2\{(Ph_2PCH_2CH_2)_2PPh_2\}_2]$ that is high-spin with Fe—P distances[643] in the range 2.66–2.71 Å.

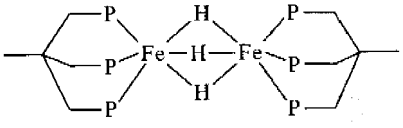
The tripod ligand (**57**) reacts with iron(II) salts in the presence of $NaBH_4$ to give the structurally novel diamagnetic binuclear iron(II) complex (**58**), which contains two octahedra sharing a face

$$\textit{trans}\text{-}[FeHCl(depe)_2] + NaBPh_4/N_2 \longrightarrow \textit{trans}\text{-}[FeH(N_2)(depe)_2]BPh_4 + NaCl \quad (59)$$

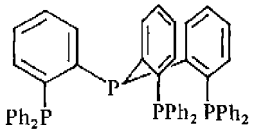
having three hydride ligands at the edges.[644] Thus, the iron centres are bridged by three hydrides. As expected, treatment with hot acid gives hydrogen and liberation of the tripod ligand. No complex was isolated when the corresponding arsenic ligand was used. Similarly the arsenic analogue of the tetrateritary phosphine (**59**) does not appear[645] to complex with iron(II). Reaction of (**59**) itself with anhydrous $FeCl_2$ in ethanol gives an intense purple solution containing five-coordinate $[FeCl(\mathbf{59})]^+$, and similar complexes are formed with other halides that have magnetic moments of ~3.1 BM. With NCS^- and CN^-, however, six-coordinate diamagnetic complexes of the type $[FeX_2(\mathbf{59})]$ are obtained.[645]



(57)

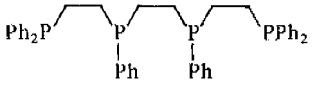


(58)

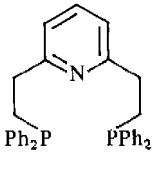


(59)

In contrast, the more flexible tripod ligand $P(CH_2CH_2CH_2PMe_2)_3$ reacts rapidly with anhydrous iron(II) halides to give deeply coloured solutions which afford violet crystals of $[FeX_2P(CH_2CH_2CH_2PMe_2)_3]$ that are diamagnetic and non-electrolytes.[646] X-Ray structure determination confirms these complexes have *cis* halides with a slightly distorted octahedral geometry, rather than the five-coordinate trigonal bipyramidal structures[646] of the cationic complexes formed with (**59**) and $P(CH_2CH_2PPh_2)_3$. The reason for the change in geometry from five- to six-coordination for the halide complexes on going from the more rigid ligands to $P(CH_2CH_2CH_2PMe_2)_3$ is no doubt associated with the flexibility of the C_3 chains that provides a larger chelate bite angle {(**59**) has only 84 ± 2°} and enhanced Fe—P overlap. Like ligand (**59**), $P(CH_2CH_2PPh_2)_3$ forms[647] a diamagnetic six-coordinate dithiocyanate complex $[Fe(NCS)_2P(CH_2CH_2PPh_2)_3]$. In contrast to the triplet ground state of the five-coordinate halide complexes of the tripod ligand (**59**), the corresponding complexes of the linear tetradentate ligand (**60**), $[FeX(\mathbf{60})]^+$ (X = Cl, Br, I; isolated as their BPh_4^- salts) have room temperature magnetic moments between those expected for $S = 0$ and $S = 1$. Spin equilibria between a singlet ground-state and low-lying triplet state could be responsible for the non-Curie–Weiss temperature behaviour.[647] An X-ray structure determination of the five-coordinate bromo complex shows it to have distorted trigonal bipyramidal geometry.[648] As with ligand (**59**), the dithiocyanato complex $[Fe(NCS)_2(\mathbf{60})]$ is diamagnetic and presumably octahedral.[647] The mixed donor ligand 2,6-bis(2-diphenylphosphinoethyl)pyridine (**61**) forms a series of 1:1 five-coordinate complexes with iron(II) halides.[649] The yellow chloride and bromide complexes $[Fe(\mathbf{61})XY]$, (X = Y = Cl, Br) are high-spin (~5.35 BM) and obey the Curie–Weiss law over the entire temperature range studied (93–293 K). However, the corresponding brown diiodo complex (X = Y = I) and the red mixed iodo–thiocyanate (X = I, Y = NCS) show anomalous behaviour with their magnetic moments abruptly falling at low temperatures, but even at the lowest temperature employed (93 K) neither complex completely reached the low-spin state.[649]



(60)



(61)

44.1.5.9 Oxygen Donors

With simple oxygen donor ligands, iron(II) complexes are high-spin and usually easily oxidized by air to iron(III) species. The number of complexes studied containing oxygen donors is much less than those having nitrogen donors. However, some mixed donor complexes involving oxygen are particularly important, and the most notable of these are the iron(II) nitrogen macrocycles which bind dioxygen. These are considered in the section concerned with porphyrins (44.1.5.12.5).

44.1.5.9.1 Water

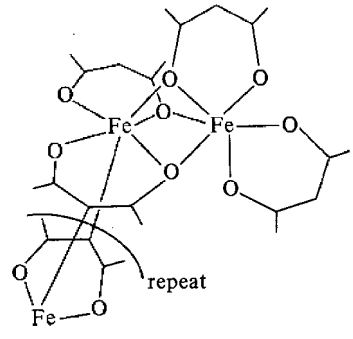
Dissolution of iron in dilute mineral acid affords $[Fe(H_2O)_6]^{2+}$. Although thermodynamically unstable towards air oxidation, the process is slow unless a strong oxidizing agent is used. In alkaline solution however, iron(II) is strongly reducing and is readily oxidized by atmospheric oxygen, and there is evidence that it will even reduce N_2 to ammonia.[650] Iron(II) oxide species are also active in the photoassisted reaction of water with nitrogen to give ammonia.[651] White $Fe(OH)_2$ is much more soluble that its Fe^{III} counterpart and in the presence of air darkens rapidly through oxidation. Solutions of the $[Fe(H_2O)_6]^{2+}$ are only slightly acidic (equation 60), so that iron(II) carbonate precipitates on addition of Na_2CO_3 and no carbon dioxide is evolved. Aqueous solutions of $[Fe(H_2O)_6]^{2+}$ are pale blue-green and this octahedral cation is present in many hydrated iron(II) salts such as the sulfate and the perchlorate. In the double salt $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ (Mohr's salt or Tutton's salt), which is rather more resistant to oxidation than the simple sulfate, the octahedron has principally a tetragonal distortion whilst in $FeSiF_6 \cdot 6H_2O$ the hexaaqua complex has a trigonal distortion.[652] In natural waters, iron is mostly present as insoluble iron(III) hydroxide. However, decomposition of inorganic matter, particularly in subsurface waters, can reduce iron(III) to iron(II) (lowering pH), whose hydroxide is relatively soluble, and this phenomenon can cause difficulties in water purification. The common method for removing iron from domestic water supplies involves aeration, which increases the pH by removing CO_2 and provides enough oxygen for the oxidation of iron(II) to iron(III) as shown in equation (61). The kinetics of this oxidation have been studied by several groups and a number of different rate equations proposed.[653–657] The reaction is catalyzed by copper(II) compounds[658–661] and it is particularly rapid in the presence of aquapalladium(II) ions.[33] The oxidation of $[Fe(H_2O)_6^{2+}]$ by molecular oxygen in perchloric acid solution yields a green intermediate complex having an absorption band at 337 nm. This green complex consists of one iron(II) and three iron(III) octahedra linked by oxo bridges.[662]

$$[Fe(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^+ + H_3O^+ \qquad K_1 = 10^{-9.5} \tag{60}$$

$$2Fe^{2+} + 5H_2O + \tfrac{1}{2}O_2 \longrightarrow Fe(OH)_{3(s)} + 4H^+ \tag{61}$$

44.1.5.9.2 Acetylacetonate

In the presence of piperidine, *trans*-$[FeCl_2(H_2O)_4]$ reacts with acetylacetone in degassed water under nitrogen, to form[663] hydrated bis(2,4-pentanedionato)iron(II). This classic neutral coordination complex is, however, coordinatively unsaturated and has an unusual tetrameric structure. X-Ray crystallography[664] reveals that the structure (**62**) consists of a pair of asymmetric Fe_2 units linked by rather long Fe—C bonds (2.785 Å). The $acac^-$ ligand which contains the bonding carbon atom also has an oxygen atom which bridges two iron atoms within the asymmetric unit. It is therefore somewhat unusual in having four coordination bonds to three separate metal atoms. The zero field Mössbauer spectrum of the tetramer consists[665] of two overlapped quadrupole doublets representing the two metal environments. The hyperfine splitting observed between 16.0 and 1.67 K, low temperature susceptibility[666] data (approaching the spin only value at 4.2 K), and the tetrameric structure indicate the unusual phenomenon of slow paramagnetic relaxation.



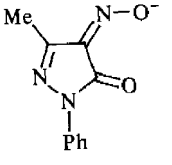
(62) $[Fe_4acac_8]$

Magnetic data for other iron(II) β-diketonates, *e.g.* 1-(3-pyridyl)-1,3-butanedione and 4,4-trifluoro-1-(3-pyridyl)-1,3-butanedione, indicate[667] the complexes to be polymeric. These com-

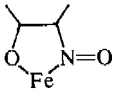
pounds are all highly air-sensitive, although the hexafluoroacetylacetone complex $[Fe(F_6acac)_2(H_2O)_2]$ is somewhat more stable.[668] $[Fe(acac)_2]$ itself reacts with a variety of bases to form hexacoordinate adducts.[669,670] Where the base is a heterocyclic diamine such as 4,4′-bipyridine, some polymeric products are observed and the 1:1 adducts are highly stable.[671] The polymeric species can be oxidized with iodine to give[672] a mixture of iron(II) and iron(III) centres and the ratio of the oxidation states is characterizable by Mössbauer spectroscopy. The choice of diamine, and in particular its degree of electron delocalization, has a marked influence on the conductivity of the polymeric materials. This allows a strategy for the accurate control of the conductivity of a low dimensional coating material.

44.1.5.9.3 Pyridine N*-oxide*

$[Fe(H_2O)_6](ClO_4)_2$ reacts with pyridine *N*-oxide in methanol to form[673] dark red crystals of $[Fe(pyO)_6](ClO_4)_2$, whose IR spectrum has been analyzed in some detail.[674,675] Analogous complexes are formed with a variety[676] of substituted pyridine *N*-oxides, for example 2-, 3- and 4-cyanopyridine *N*-oxides form[677] octahedral hexakis complexes. A number of complexes containing bidentate oxygen donors have been reported; the oxime of pyrazoledione, for example, forms[678] a bis iron(II) complex. Thus, iron(II) ammonium sulfate reacts with (**63**) to form the turquoise complex $[Fe(\mathbf{63})_2 \cdot H_2O]$, whose magnetic moment decreases with temperature; it has a large negative Weiss constant and is almost certainly polymeric. The complex reacts with pyridine to form $[Fe(\mathbf{63})_2(py)_2]$, whose magnetic behaviour is the opposite of the starting material suggesting it is a monomeric pseudooctahedral complex.[678] Iron(II) oxime complexes with the basic coordination illustrated in structure (**64**) occur in the green biological pigment ferroverdin.[679] The reaction between $[Fe(H_2O)_6]^{3+}$ and catechol provides a series of complexes whose iron(II)/iron(III) redox reactions have been investigated[680] by Mössbauer spectroscopy as a model system for the microbial transport of iron by enterobactins. In contrast, hydrated iron(II) perchlorate reacts with a number of phosphate esters to yield stable high-spin five-coordinate complexes. Thus the perchlorate hydrate, dehydrated by treatment with triethyl orthoformate, reacts with dimethyl-methylphosphonate (DMMP) to form an oil which when extracted with ether yields buff $[Fe(DMMP)_5](ClO_4)_2$ ($\mu_{eff} = 5.14$ BM).[681] In an analagous preparation trimethyl phosphate (TMP) yields first the monohydrate $[Fe(TMP)_5H_2O](ClO_4)_2$, which is readily dehydrated[682] to the five-coordinate complex, which is stable in air ($\mu_{eff} = 5.12$ BM). In anhydrous acetone the iron(II) salt also reacts with trimethylphosphine oxide or trimethylarsine oxide to yield[683,684] high-spin five-coordinate complexes $[FeL_4(ClO_4)](ClO_4)$ (L = Me_3AsO, $\mu_{eff} = 4.94$ BM). In the case of the more sterically bulky ligand diphenylmethylarsine oxide, a compound with the stoichiometry $FeL_4(ClO_4)_2$ was formed, but the IR spectrum[685] did not show the presence of coordinated perchlorate ion. Indeed, the electronic spectrum and magnetic data point to an essentially tetrahedral structure.[686] A four-coordinate tetrahedral structure is also observed[687] for the complex $[Fe(HMPA)_4](ClO_4)_2$ (HMPA = hexamethylphosphoramide) ($\mu_{eff} = 5.19$ BM). The neutral four-coordinate complex $[Fe(TPO)_2Cl_2]$ is formed when $FeCl_2$ is refluxed in an acetone solution of triphenylphosphine oxide under nitrogen.[688]



(63)



(64)

44.1.5.9.4 Miscellaneous oxygen donors

When an iron(II) salt is added to an aqueous solution of iron(III) citrate, the greenish yellow colour intensifies and a mixed valence complex containing one iron(II) and three iron(III) centres together with one citrate ion has been described.[689] In aqueous solution iron(II) reacts with oxalic acid to form a precipitate having a stoichiometry of $FeC_2O_4 \cdot 2H_2O$, for which two crystalline habits have been identified.[690] In methanol, a monomethanolate complex with stoichiometry $[FeC_2O_4(MeOH)H_2O]$ is formed, the hexacoordinate iron(II) has a symmetric tetragonal distortion in the

hydrate but the position of the iron atom is not symmetric in the latter complex.[691] The perchlorate salt of hexaaqua iron(II) reacts[692] with DMSO in acetone to give the pale green complex $[Fe(DMSO)_6](ClO_4)_2$, which explodes on heating. Iron(II) halides react with a variety of ethers (THF, 1,2-dimethoxyethane, 1,4-dioxane) to yield adducts which have been studied by electronic and IR spectroscopy, and magnetic methods.[693] Decomposition of $FeSO_4 \cdot 6H_2O$ on heating involves stepwise loss of water, and when heated in air, anhydrous $FeSO_4$ gives $Fe(OH)SO_4$ that decomposes to give $Fe_2O(SO_4)_2$.

44.1.5.9.5 Mixed donor ligands containing oxygen

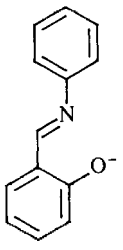
This class of complex comprises mostly mixed O and N donors. Bidentate donors such as the Schiff base derived[695] from salicylaldehyde and aniline (**65**) form unusually stable complexes with iron(II). In the case of 1,10-phenanthroline *N*-oxide[696] however, the iron(II) complex $[Fe(phenNO)_3](ClO_4)_2$ is high-spin ($\mu_{eff} = 5.47$ BM) in contrast to $[Fe(phen)_3]^{2+}$ (Section 44.1.5.6). Amino acids are N,O donors and form a series of iron(II) complexes.[697] They are high-spin, hexacoordinate and are thought to have extended carboxylate-bridged structures. Interestingly, the sulfur-containing amino acid methionine is also a bidentate N,O donor to iron(II). Here again, a carboxylate-bridged polymer structure has been proposed.[698] A low-spin iron(II) complex is formed with the violurate ion (**66**) and X-ray structural analysis[699] shows $[FeV_3](NH_4)$ to have *fac* geometry similar to ferroverdin (**67**), a tris-nitrosophenyl iron(II) complex.[700] Ferroverdin was the first naturally occurring nitrosophenyl complex observed. Early reports on the extremely air sensitive Schiff base complex of iron(II) (**65** and **68**) have in some cases been shown[701] to have involved oxidation products. Their Mössbauer and electronic spectra show (for closely related systems) a linear relation between isomer shift and quadrupole splitting. The temperature dependence of the splitting implies[701] a large axial distortion in these six-coordinate complexes. Temperature dependence has also been observed[702] for at least one quinone adduct of [Fe(salen)], $[Fe(salen)_2(C_6H_4O_2)]$ (salen = **68**, R = $(CH)_2$). However, the Curie–Weiss behaviour and magnetic susceptibility of this complex ($\mu_{eff} = 5.76$ BM, 297 K) suggest that it is in fact d^5 high-spin iron(III). Of greater interest however, is the nitrosyl adduct of [Fe(salen)]. This complex has been observed[703] to have a relatively rare $S = \frac{3}{2}$ to $S = \frac{1}{2}$ spin cross-over near 175 K. An X-ray crystal structure[704] has established a square pyramidal geometry relatively undistorted towards trigonal bipyramidal, unlike the macrocyclic complex $[Fe(Me_4 14aneN_4)NO]$.[705] The latter complex has an essentially linear NO group, whilst in the salen complex it is bent. These features persist through the spin transition.[706] There are a series of ligands known as 'strati-Schiff bases' which form complexes of iron(II).[707] These ligands are being explored as potential models for enzyme systems in which metal coordination sites are 'stacked'.

Tridentate mixed O,N donors include (**69**) and (**70**)[708] and the sulfur-containing system TAN. A crystal structure[709] of $[Fe(TAN)_2]$ (**71**) shows the two ligands to be nearly planar with the two planes essentially perpendicular to one another and the ligands in *mer* coordination. The tetradentate O_2N_2 ligand H_2acacen forms a dimeric high-spin iron(II) complex [Fe(acacen)$_2$] ($\mu_{eff} = 4.84$ BM, 294 K). An X-ray structure has confirmed[710] that the pentacoordination of iron(II) is maintained on reaction with EtONa when a tetranuclear Fe_2Na_2 complex is formed in which the iron atoms are doubly bridged by EtONa (**72**). A five-coordinate complex is also obtained with the terdentate ligand[711] Me_4daeo, $[Fe(Me_4daeo)Cl_2]$ (**73**), $\mu_{eff} = 5.26$ BM, 295 K, and the quinquedentate ligand[712] bis(salicylidinimine-3-propyl)amine (SALRDPT, **74**). This and related complexes have been discussed as model systems for oxygen transport and activation.[713]

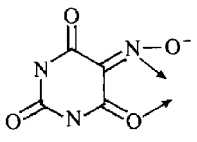
The pentadentate N_3O_2 ligand 2,6-diacetylpyridenebissemicarbazone forms a seven-coordinate iron(II) complex having axial chloride and water ligands. The ligand is formed *in situ* as an alcohol solution of diacetylpyridine and $FeCl_2$ is treated with semicarbazide hydrochloride. X-Ray structural analysis[714] shows the ligand to be planar. The unusual planar hexadentate N_4O_2 ligand (**75**) forms[715] binuclear iron(II) complexes $[Fe_2(\mathbf{75})L_4]^{2+}$ (L = py, im, Meim). These high-spin complexes (L = Meim, $\mu_{eff} = 4.71$ BM, 298 K) show a marked antiferromagnetic exchange interaction. Analysis shows that there is little difference in the magnitude of this interaction between the six-coordinate and comparable five-coordinate complexes.

44.1.5.10 Sulfur Donors

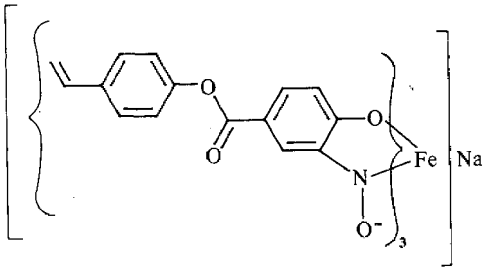
Iron–sulfur chemistry has developed over recent years to become a very rich area. A feature of many complexes is their redox behaviour, with more than one oxidation state being important. This



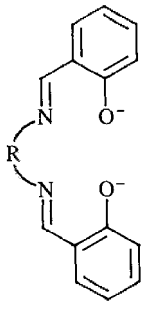
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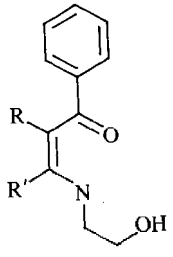
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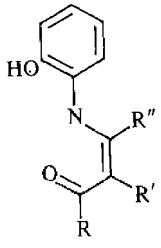
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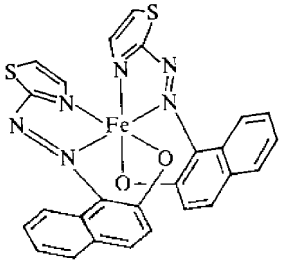
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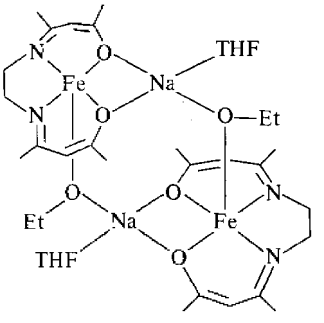
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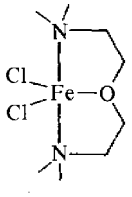
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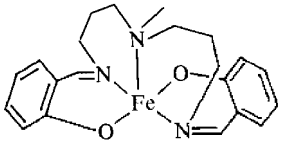
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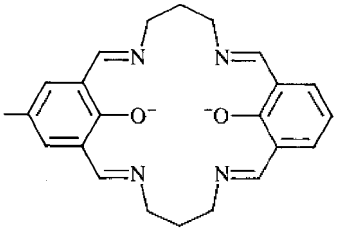
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(73)



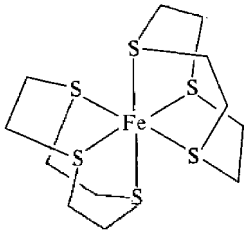
(74)



(75)

section is mainly concerned with iron(II) complexes but inevitably some iron(III) complexes are discussed (notably in mixed oxidation state clusters). Similarly, some iron(II) sulfur donor complexes are included in Section 44.2.5, which deals with higher oxidation states, and accordingly readers should consult both sections. Those sulfur complexes containing nitric oxide are contained in Section 44.1.2.5.

With the recent availability of 1,4,7-trithiacyclononane ([9]aneS$_3$) *via* an elegant template synthesis[716] there has been inerest in comparing its complexing ability with that of the surprisingly high-field ligand [9]aneN$_3$ that forms an octahedral low-spin iron(II) complex.[717] Purple $[Fe([9]aneS_3)_2]^{2+}$ is also low-spin and its stability is such that it is obtained when Fe^{II} and Fe^{III} salts are reacted with the free ligand. Its electronic spectrum exhibits two *d–d* transitions typical of Fe^{II} in an octahedral ligand field, that are not obscured by intense charge-transfer bands. X-Ray structure determination[718] confirmed an octahedral geometry shown in (**76**).



(76)

44.1.5.10.1 Binary sulfides

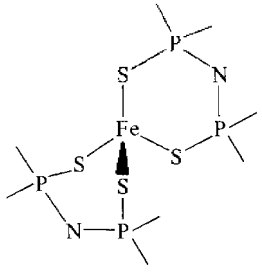
Iron(II) sulfide is ordinarily dark grey to brown, but when very pure it has been reported to form almost colourless crystals.[719] It is quite insoluble in water, and its reaction with oxygen is exothermic to give Fe_2O_3 or Fe_3O_4 depending on conditions. Rarely is the iron to sulfur ratio unity and formulae ranging from Fe_6S_7 to $Fe_{11}S_{12}$ have been assigned to these iron deficient non-stoichiometric phases. There are a number of iron(II) sulfide minerals which contain an approximately octahedral environment of sulfur atoms. Troilite, stoichiometric FeS, is hexagonal with the NiAs superstructure[720] having Fe—S bond lengths[721] ranging from 2.38 to 2.72 Å with an average of ~2.5 Å. Pyrrhotite $Fe_{1-x}S$ exists in hexagonal and monoclinic forms, with the Fe—S bond lengths[722] in the latter ranging from 2.37 Å to 2.67 Å. The cubic disulfide pyrite FeS_2 contains a regular FeS_6 octahedron with Fe—S bond lengths of 2.26 Å;[723] marcasite, a tetragonal polymorph of FeS_2 has an octahedral geometry distorted by elongation along the *c* axis. In both pyrite and marcasite the anions are disulfide (S_2^{2-}) and not sulfide (S^{2-}). Troilite (FeS) and pyrrhotite ($Fe_{1-x}S$) are high-spin, but pyrite (FeS_2) is low-spin and each have been studied by Mössbauer spectroscopy.[724] Application of high pressure converts the high-spin forms to low-spin, and the transition is reversed when the applied pressure is removed.[725,726]

Molecular orbital/energy band calculations have been performed for a range of iron(II) sulfides[727,728] and there is interest in the band-like valence-electron states in FeS_2[729] and also in their bulk and surface properties typified by studies using Auger spectroscopy[730] and X-ray absorption.[731–733] The extensive work in this area published during the period 1960–1969 is contained in an excellent review by Ward.[734] Unfortunately, discussion about the fascinating tricyclic iron(III) polysulfide anion $[Fe_2S_{12}]^{2-}$[735] and its reactions with, for example, activated alkynes[736] are outside of the scope of this section.

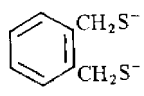
44.1.5.10.2 Iron sulfur clusters

Tetrahedral iron sulfide species that can have two or more charge states are involved in many electron transfer proteins.[737] The core structures that have been identified in proteins include the single iron centres of rubredoxin, and the two iron/two sulfide and four iron/four sulfide centres of various ferredoxins. A wide range of model complexes have been prepared and characterized, and the results of this work, as well as that on the natural system, have been extensively reviewed.[737,744]

Trimethylarsine sulfide forms[745] two types of tetrahedral iron(II) complexes $[Fe(SAsMe_3)_4](ClO_4)_2$ and $[FeX_2(SAsMe_3)_2]$ (X = Cl, Br), but one of the first structurally well-characterized tetrahedral iron(II) sulfur complexes was $[Fe(SPMe_2NPMe_2S)_2]$ (**77**) that has a magnetic moment of 5.25 BM in the solid state and 4.99 BM in dichloromethane solution.[746] The measured[747] Fe—S bond lengths range from 2.339 to 2.380 Å and the S—Fe—S bond angles from 100.5° to 114.9°. Simpler synthetic analogues of the single iron centre of bacterial rubredoxins have been prepared using PhS^-, *i.e.* $[Fe(SPh)_4]^{2-}$, but the best characterized species involve the *o*-xylyldithiolate ligand (**78**). Discrete tetrahedral complexes of both iron(II) and iron(III) have been isolated.[748] Thus reaction of $[FeCl_4]^{2-}$ with excess *o*-xyl$(SH)_2$ affords orange $[Fe(S_2\text{-}o\text{-xyl})_2]^{2-}$, whereas use of a 2:1 ligand to metal ratio gives the dimer $[Fe_2(S_2\text{-}o\text{-xyl})_3]^{2-}$, which on treatment with excess thiol is converted to the monomer. Controlled aerial oxidation of $[Fe(S\text{-}o\text{-xyl})_2]^{2-}$ affords the iron(III) complex $[Fe(S_2\text{-}o\text{-xyl})_2]^-$, which is readily isolated as the Et_4N^+ salt. The structures of both complexes have been determined by X-ray methods.[748] The mean Fe^{II}—S bond length is 2.356 Å, which is some 0.09 Å longer than that of the Fe^{III} monomer.



(77)



(78)

The oxidation state of the iron centres within a sulfide cluster can be the same or formally inequivalent. However, in all oxidation states antiferromagnetic spin coupling can take place directly or *via* bridging sulfur atoms. The $[Fe_2S_2]$ core is present in spinach ferredoxin, and a number of model complexes of the type $[Fe_2S_2(SR)_4]^{2-}$ containing iron(III) have been prepared and fully characterized. In particular salts of $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$ and $[Fe_2S_2(S\text{-}p\text{-tol})_2]^{2-}$ (prepared from $FeCl_3$, NaSH and ArSH in the presence of NaOMe) have been the subject of high resolution X-ray structure determinations.[749,750] In this oxidized form the iron(III) centres are in an approximately tetrahedral environment of sulfur ligands, but at low temperatures the complexes are diamagnetic and display no ESR signals due to antiferromagnetic coupling. At room temperature, population of the $S = 1$ level can give rise to some paramagnetism. One-electron reduction of $[Fe_2S_2(SR)_4]^{2-}$ produces inequivalent iron centres on the Mössbauer timescale. The isomer shifts correspond to the presence of Fe^{II} and Fe^{III} centres that are both high-spin and antiferromagnetically coupled. Work on the corresponding reduced natural spinach ferredoxin continues,[751] and its chemistry parallels that of these model complexes. In contrast however, under conditions used to prepare $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$, 1,2-ethanedithiol forms a black iron(III) dimer, $[Fe_2(edt)_4]^{2-}$, that contains no sulfide.[752] Moreover, the iron environment is not tetrahedral, but consists of five sulfur atoms with a distorted trigonal bipyramidal geometry.[753] Although iron sulfur complexes are usually kinetically labile with respect to exchange, $[Fe_2(edt)_4]^{2-}$ fails either to undergo thiolate ligand substitution reactions or to incorporate sulfide ion. Unlike the sulfide-containing dimers that undergo two one-electron reductions, $[Fe_2(edt)_4]^{2-}$ exhibits a single two-electron reduction.[752] This difference may reflect the relatively long Fe—Fe distance in $[Fe_2(edt)_4]^{2-}$.

A considerable number of ferredoxins are known that contain one or more $[Fe_4S_4]$ clusters. At low temperatures these are diagmagnetic in the oxidized form but weak ESR signals can often be detected and the reduced forms display strong ESR signals. The structural features of the cubane-like $[Fe_4S_4]$ core have been well defined in several proteins, and a series of thermodynamically stable model complexes of the type $[Fe_4S_4(SR)_4]^{2-}$ have been prepared and thoroughly investigated.[739,740] In the natural systems SR is a cysteine ligand. Three overall charge levels are accessible as indicated in equation (62).

$$\underset{\text{'}3Fe^{II}1Fe^{III}\text{'}}{[Fe_4S_4(SR)_4]^{3-}} \rightleftharpoons \underset{\text{'}2Fe^{II}2Fe^{III}\text{'}}{[Fe_4S_4(SR)_4]^{2-}} \rightleftharpoons \underset{\text{'}1Fe^{II}3Fe^{III}\text{'}}{[Fe_4S_4(SR)_4]^{-}} \qquad (62)$$

It appears that no single protein in aqueous media will undergo reversible redox reactions between all three oxidation levels. The '$3Fe^{II}1Fe^{III}$'/'$2Fe^{II}2Fe^{III}$' couple is found in many bacterial proteins, while the '$2Fe^{II}2Fe^{III}$'/'$1Fe^{II}3Fe^{III}$' couple is only found in the so-called high-potential iron protein from photosynthetic bacteria. In marked contrast to the dimeric '$Fe^{II}Fe^{III}$' complexes that display two pairs of doublets in their Mössbauer spectra that are typical of isolated iron(II) and iron(III) centres in tetrahedral environments, the Mössbauer spectra of $[Fe_4S_4(SR)_4]^{2-}$ complexes show them to be largely valence delocalized.[754] Only limited spin delocalization, which is more readily detected, is present in the paramagnetic complexes $[Fe_4S_4(SR)_4]^{3-}$ and $[Fe_4S_4(SR)_4]^{-}$. Simple molecular orbital descriptions of these complexes have been presented.[755] Preparatively they are easily obtained from $FeCl_3$, NaSR, NaSH and MeONa in methanol. Usually the reaction is carried out in two stages;[756] $FeCl_3$ is reacted with NaSR to give an insoluble (if R = aryl) polymeric dark green sulfide, which is then treated with NaHS/MeONa to give the corresponding disulfide and the desired mixed oxidation state cluster $Na_2[Fe_4S_4(SR)_4]$. The overall reaction is illustrated in equation (63). A wide variety of thiols have been used in these reactions including β-mercaptopropionic acid ($R = CH_2CH_2CO_2H$), which affords[757] the water soluble $[Fe_4S_4\{S(CH_2)_2CO_2\}_4]^{6-}$, which has a half-wave potential[758] (0.58 V *vs.* SCE) similar to that of natural ferredoxin.

$$4FeCl_3 + 6NaSR + 4NaSH + 4NaOMe \longrightarrow Na_2[Fe_4S_4(SR)_4] + RSSR + 4MeOH + 12NaCl \qquad (63)$$

Thiolate exchange reactions of the dimeric iron(III) and the iron(II)/iron(III) cubane tetramers, $[Fe_2S_2(SR)_4]^{2-}$ and $[Fe_4S_4(SR)_4]^{2-}$, have been studied[750,759] in some detail and provide routes to several related complexes. Exchange takes place with other thiols (R'SH) as in equation (64).

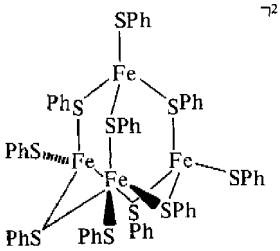
$$[Fe_nS_n(SR)_4]^{2-} + mR'SH \longrightarrow [Fe_nS_n(SR)_{4-m}(SR')_m]^{2-} + mRSH \quad n = 2, 4;\ m = 0\text{–}4 \qquad (64)$$

Phenols also react to give the corresponding complexes, *e.g.* $[Fe_4S_4(OPh)_4]^{2-}$, salts of which have been isolated.[760] With benzoyl chlorides the fully substituted clusters $[Fe_4S_4Cl_4]^{2-}$ ($n = 2, 4$) are obtained, which have been structurally characterized.[761,762] The tetramer $[Fe_4S_4Cl_4]^{2-}$ and related iron(II)-containing cubane complexes are discussed in more detail later in this section.

Since the initial work on $[Fe_4S_4(SR)_4]^{2-}$ clusters, spectrophotometric and NMR studies have provided further insight into routes to their formation, and highlighted the importance of solvent effects in these reactions. The route from $FeCl_3/RS^-$ and HS^- may be summarized[763] as in equation (63). With methanol or acetonitrile as solvent, in the absence of HS^-, and with the ratio $PhS^-:Fe = 3.5:1$ reaction (65) takes place to give the insoluble adamantane-like[764] iron(II) cluster $[Fe_4(SPh)_{10}]^{2-}$ (79) in high yield. This is oxidized by elemental sulfur in a surprisingly smooth reaction, in view of the degree of reorganization involved, to give the '$2Fe^{II}2Fe^{III}$' cubane complex $[Fe_4S_4(SPh)_4]^{2-}$ according to equation (66).

$$4FeCl_3 + 14PhS^- \longrightarrow [Fe_4(SPh)_{10}]^{2-} + 2PhSSPh + 12Cl^- \quad (65)$$

$$[Fe_4(SPh)_{10}]^{2-} + \tfrac{1}{2}S_8 \longrightarrow [Fe_4S_4(SPh)_4]^{2-} + PhSSPh \quad (66)$$



(79)

However, in acetonitrile with the ratio $PhS^-:Fe \leqslant 5:1$, the mononuclear tetrahedral iron complex $[Fe(SPh)_4]^{2-}$ is formed first, which reacts with sulfur to form the iron(III) dimer $[Fe_2S_2(SPh)_4]^{2-}$ according to equations (67) and (68). No further reaction takes place, but addition of methanol facilitates the reductive elimination of PhSSPh from the dimer to give the '$2Fe^{II}2Fe^{III}$' cubane complex as in equation (69). Although this series of reactions has been written for PhS^-, it appears similar reactions take place with alkyl as well as aryl thiolates.

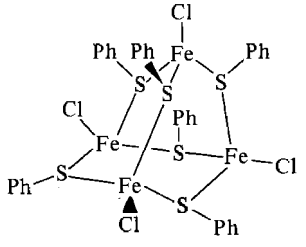
$$2FeCl_3 + 10PhS^- \longrightarrow 2[Fe(SPh)_4]^{2-} + PhSSPh + 6Cl^- \quad (67)$$

$$2[Fe(SPh)_4]^{2-} + \tfrac{1}{4}S_8 \longrightarrow [Fe_2S_2(SPh)_4]^{2-} + PhSSPh + 2PhS^- \quad (68)$$

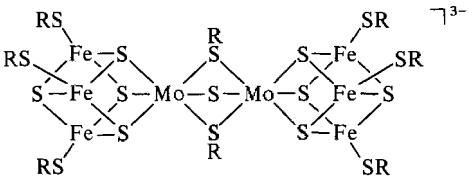
$$2[Fe_2S_2(SPh)_4]^{2-} \longrightarrow [Fe_4S_4(SPh)_4]^{2-} + PhSSPh + 2PhS^- \quad (69)$$

The convenient route to $[Fe_4S_4(SR)_4]^{2-}$, using $FeCl_3$, RS^- and sulfur, depends on thiolate reducing half of the iron(III) to iron(II), and all of the sulfur to sulfide. As a result more thiolate is required than with procedures starting with sulfide ion. This requirement can be reduced by using an iron(II) salt[765] rather than iron(III). The overall reaction is then as in equation (70).

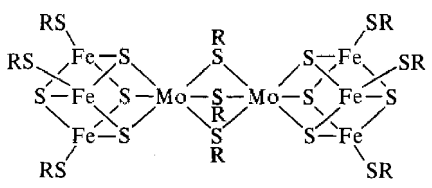
$$4FeCl_2 + 4S + 10RS^- \longrightarrow [Fe_4S_4(SR)_4]^{2-} + 8Cl^- + 3RSSR \quad (70)$$



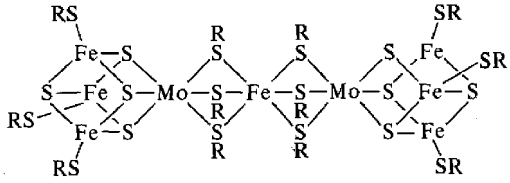
(80)



(81)



(82)



(83)

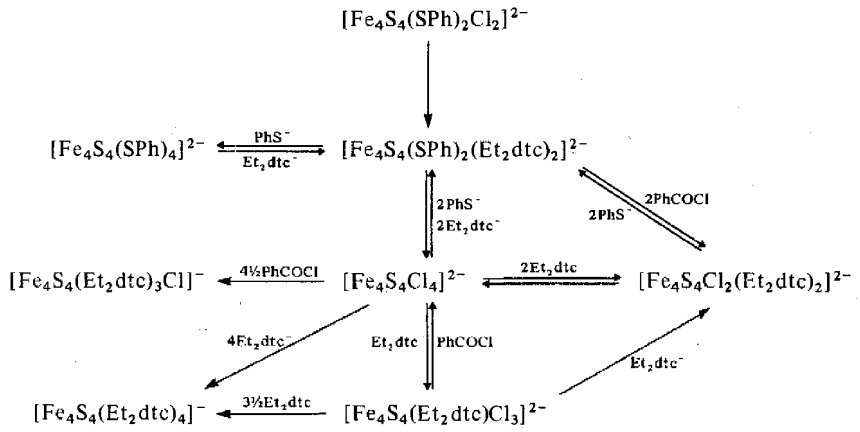
A further oxidative addition reaction of $[Fe(SPh)_4]^{2-}$ is that with organic trisulfides to give $[Fe_2S_2(SPh)_4]^{2-}$ in high yield.[766] $[Fe(SPh)_4]^{2-}$ also reacts with additional $FeCl_2$ or $FeBr_2$ (1:2.4 molar ratio) to give the paramagnetic clusters $[Fe_4(SPh)_6X_4]^{2-}$ (**80**), which have been isolated as their PPh_4^+ salts. The X-ray structure of $[Fe_4(SPh)_6Cl_4](PPh_4)_2$ shows[766] a nearly regular tetrahedron of iron atoms within a slightly irregular octahedron of bridging sulfur atoms in an adamantane type of cage. The mean Fe—Fe and Fe—S bond distances are 3.94 Å and 2.36 Å respectively. A series of novel bridged cluster complexes result from the reaction of MoS_4^{2-} with RS^- and $FeCl_3$ in methanolic solution containing quaternary ammonium cations. Depending on reaction conditions, yields of three such complexes as their R_4N^+ salts can be optimized:[767–770] $[Mo_2Fe_6S_9(SR)_8]^{3-}$ (**81**), $[Mo_2Fe_6S_8(SR)_9]^{3-}$ (**82**) and $[Mo_2Fe_7S_8(SR)_{12}]^{3-/4-}$ (**83**). The first complexes of this type were reported in 1978 by two research groups simultaneously; these were $[Mo_2Fe_6S_9(SEt)_8]^{3-}$[767] and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$.[771,772] The iron atoms in the $[Mo_2Fe_6S_8(SR)_9]^{3-}$ anions are similar to those in the $[Fe_4S_4(SR)_4]^{2-}$ clusters and their Mössbauer spectra are consistent with extensive delocalization over the metal centres. Tungsten analogues have been prepared, and the properties of these complexes are similar to those containing molybdenum.[773,774] Amongst the most extensively investigated complexes in this series are (**82**) and (**83**), and analogues containing bridging methoxide ligands have also been isolated.[773] Equations (71) and (72) give the overall stoichiometries for formation of structures (**82**) and (**83**) respectively. The first identifiable complex formed in these reactions is the sulfur-bridged dimer $[(RS)_2Fe(S)_2MoS_2]^2$, which is well characterized.[775,776] A growing number of related trimers containing Fe_2Mo or $FeMo_2$ centres with bridging sulfides have been reported. Much of the work on these and their tungsten counterparts has been reviewed by Coucouvanis.[777]

$$2MoS_4^{2-} + 6FeCl_3 + 17RS^- \longrightarrow [Mo_2Fe_6S_8(SR)_9]^{3-} + 4RSSR + 18Cl^- \quad (71)$$

$$2MoS_4^{2-} + 7FeCl_3 + 20RS^- \longrightarrow [Mo_2Fe_6S_8(SR)_{12}]^{3-} + 4RSSR + 21Cl^- \quad (72)$$

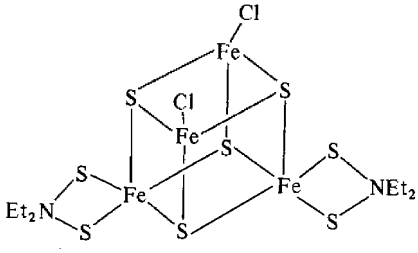
A number of iron sulfide/nitrosyl complexes are known; these include $[Fe_2S_2(NO)_4]^{2-}$, $[Fe_2(SR)_2(NO)_4]$ and the black tetramer $[Fe_4S_3(NO)_7]^-$ (Roussin's salts), as well as neutral $[Fe_4S_4(NO)_4]$. All these are diamagnetic and are discussed in Section 44.1.2.5, which is concerned with iron nitrosyl complexes. A variety of other iron/sulfide clusters are known and their range is illustrated by the following examples. Amongst the first Fe_4S_4 complexes to be structurally well characterized was $[Cp_4Fe_4S_4]$ obtained from reaction of $[Cp_2Fe_2(CO)_4]$ with elemental sulfur.[778] A related complex is $[Cp_2Fe_2S_2(SEt)_2]$, obtained from reaction of $[Cp_2Fe_2(CO)_4]$ with ethyl polysulfide in refluxing methylcyclohexane.[779] This dark green diamagnetic complex contains an unusual planar FeSSFe bridge,[780] and its electrochemical behaviour suggests the diamagnetism results from a unique electron pair coupling.[781] The planarity of the FeSSFe bridge is retained on one-electron oxidation to $[Cp_2Fe_2S_2(SEt)_2]^+$ and following further one-electron oxidation (nonreversible) $[Fe_2Cp_2(NCCH_3)_2(SEt)_2]^{2+}$ was isolated.[781] As previously noted, benzoyl chloride reacts with $[Fe_2S_4(SR)_4]^{2-}$ to give $[Fe_4S_4Cl_4]^{2-}$, which has bridging sulfides and terminal chloride ligands. Salts of this black anion are air sensitive, and its cubane core structure is similar to that of the thiolate precursor. There is a departure from ideal cubic symmetry with the Fe_4 portion being essentially tetrahedral.[762] Treatment of $[Fe_4S_4Cl_4]^{2-}$ with sodium iodide affords the iodo complex $[Fe_4S_4I_4]^{2-}$. The bromo analogue is obtained in the same way, but not the fluoro complex.[761] Electrochemical reduction of the dimer $[Fe_2S_2Cl_2]^{2-}$ gives[761] the corresponding tetramer as in equation (73). A similar scheme accounts for the behaviour of the analogous thiolate complexes. Their reduced dimers are sufficiently stable for the 3 −/4 − process involving dimers to be observed together with that for the 3 −/4 − and 2 −/3 − tetramers.[782] A range of mixed halide/diethyldithiocarbamate (Et_2dtc) cubane clusters have been prepared[783,784] from $[Fe_4S_4Cl_4]^{2-}$, PhS^- and Et_2dtc^- *via* the series of reactions shown in Scheme 14.

$$2[Fe_2S_2Cl_4]^{2-} \underset{[FeCp_2]^+}{\overset{e^-}{\rightleftharpoons}} [Fe_4S_4Cl_4]^{2-} + 4Cl^- \quad (73)$$



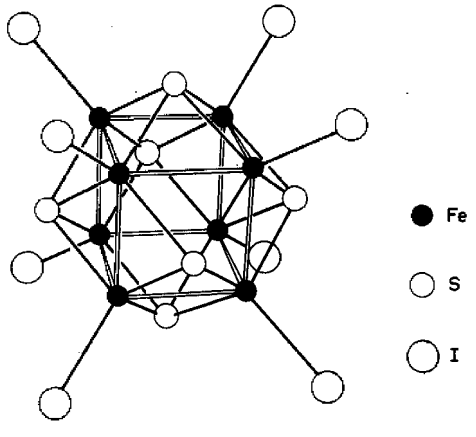
Scheme 14

Structures of the complexes $[Fe_4S_4(Et_2dtc)_nX_{4-n}]^{2-}$ ($X = Cl^-$, PhS^-; $n = 1$, 2) have been determined[784] and each have the familiar iron/sulfur core. There are relatively long distances between the five-coordinate iron atoms bound to Et_2dtc ligands, as for example in $[Fe_4S_4Cl_2(Et_2dtc)_2]^{2-}$ (**84**).

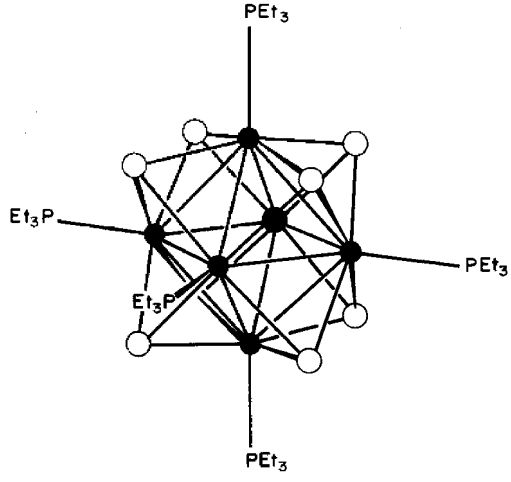


(84)

A number of large and structurally interesting iron sulfide/halide clusters have been isolated and characterized. Refluxing a mixture of iron, sulfur and Et_4NI in THF for 24 hours[785] gives a moderate yield of $(Et_4N)_2[Fe_6S_6I_6]$ in the form of small black platelets, as in equation (74). The formal oxidation state of the iron is +2.67, that is '$4Fe^{III}2Fe^{II}$'. This reacts further with iron and I_2/I^- in dichloromethane over a protracted period to give $(Et_4N)_3[Fe_8S_6I_8]$ according to equation (75). The eight iron atoms in this complex (**85**) form an almost perfect cube with terminal iodide ligands and μ_4-bonded sulfides on each face.[786] A Fe_6 cluster with triply bridging sulfide ligands is obtained by reaction of $Fe(BF_4)_2$ and PEt_3 (1:3 molar ratio) with H_2S in an acetone/ethanol mixture. After several days in air the green solution becomes black, and addition of $NaBPh_4$ deposits crystals of $[Fe_6S_8(PEt_3)_6](BPh_4)_2$. This iron(III) cationic complex (**86**) contains an octahedral arrangement of iron atoms with terminal phosphine ligands.[787]



(85)



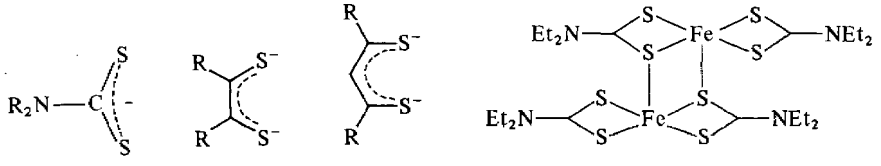
(86)

$$6Fe + 6S + 2I_2 + 2I^- \longrightarrow [Fe_6S_6I_6]^{2-} \quad (74)$$

$$[Fe_6S_6I_6]^{2-} + 2Fe + I^- + \tfrac{1}{2}I_2 \longrightarrow [Fe_8S_6I_8]^{3-} \quad (75)$$

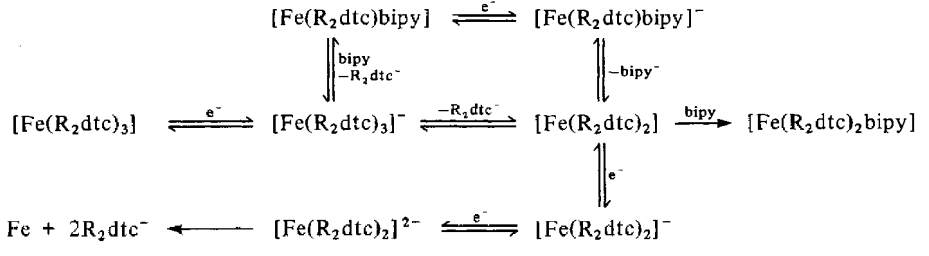
44.1.5.10.3 Dithio ligands

This section is concerned with 1,1-, 1,2- and 1,3-dithio chelates typified by dithiocarbamates (**87**), the dithiolenes (**88**) and dithoacetylacetonates (**89**) together with the $[FeX_4]^{2-}$ dithiolinium salts. All of these iron complexes are of interest because of both their novel electronic structures and redox processes involving high and low oxidation states. Relatively few monothiocarbamate transition metal complexes have been prepared and the limited chemistry of polymeric $[Fe(SOCNMe_2)_2]$ is discussed in a recent review.[788] In contrast, many transition metal dithiocarbamates are known and their chemistry has recently been reviewed.[789] Very large quadrupole splittings ($\sim 4.2\ mm\ s^{-1}$) in the Mössbauer spectra of $[Fe(R_2dtc)_2]$ complexes indicate a dimeric structure in the solid state and magnetic susceptibility measurements show antiferromagnetic coupling (Néel temperature = 110 K).[790,791] The X-ray structure of $[Fe(Et_2dtc)_2]$ (**90**) confirms it is dimeric and shows the two dithiocarbamate ligands; each bridges one axial and one equatorial position of the trigonal bipyramidal geometry around the iron atoms.[792] Generally, in solution these iron(II) complexes are extremely air sensitive being rapidly oxidized[791–793] to the iron(III) complex $[Fe(R_2dtc)_3]$. In the presence of excess R_2dtc^- the tris complex $[Fe(R_2dtc)_3]^-$ is formed.[794] This is also air sensitive and its stability depends on the cation. Oxidation of the iron(III) complex in benzene by air[795] or iodine[796,797] affords the corresponding iron(IV) complex. Electrochemical reduction of the iron(III) complex $[Fe(R_2dtc)_3]$ in acetone and acetonitrile using platinum electrodes gives[798] the high-spin tris iron(II) complex *via* a process indicated by cyclic voltammetry to be reversible. Measurements obtained during controlled potential electrolysis, however, indicate that there is some loss of ligand on reduction. With mercury electrodes additional reduction reactions have been observed.[799,800]



(87) (88) (89) (90)

$[Fe(R_2dtc)_3]^-$ is formed first, followed by loss of R_2dtc^- and sequential reduction to give $[Fe(R_2dtc)_2]^-$ and $[Fe(R_2dtc)_2]^{2-}$ as shown in Scheme 15. In the presence of bipy, reduction of $[Fe(R_2dtc)_3]$ gives[800] the well-characterized iron(II) mixed ligand complex $[Fe(R_2dtc)_2(bipy)]$, and this process can generate $bipy^-$ radical anion. The iron(I) complex $[Fe(CO)_3(PPh_3)_2]^+$ undergoes[801] oxidative substitution with R_2dtc^- (and $^-S_2CPPh_2$) to give the cationic dicarbonyl complexes *cis,trans*-$[Fe(CO)_2(PPh_3)_2(S_2CNR_2)]^-$. The same complex is obtained with $Me_2NC(S)SS(S)NMe_2$. Golden yellow $[Fe(Me_2dtc)_2(CO)_2]$ is obtained from the reaction of $[FeBr_2(CO)_4]$ with Me_2dtc^- in acetone.[802] The UV photoelectron spectra of several $[Fe(R_2dtc)_2(CO)_2]$ complexes have been examined.[803] In the vapour phase CO is lost to give $[Fe(R_2dtc)_2]$. The analogous cyclopentamethylene dtc dicarbonyl complex is the product from addition of the corresponding disulfide to $[Fe(CO)_5]$ in THF. In crystals of this complex analyzed by X-ray crystallography,[804] only one of the possible structural isomers was present, resulting from the relative orientation of the chair-form piperidine rings.



Scheme 15

Whilst little information is available concerning iron(II) xanthates, the preparations of $[Fe(S_2COEt)_2]$ and $[Fe(S_2COEt)_3]^-$ have been described[805] and addition of potassium xanthate to a solution of $FeCl_2$ and 1,10-phenanthroline (2:1:1 ratio) yields $[Fe(S_2COEt)_2(phen)]$. If 1,10-phenanthroline is replaced by 2,2′-bipyridine, two crystalline modifications of $[Fe(S_2COEt)_2(bipy)]$ are formed.[805] Pyridine reacts with iron(III) xanthates to form[806] high-spin iron(II) complexes as in equation (76).

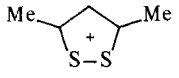
$$2[Fe(S_2COR)_3] + 4py \longrightarrow 2[Fe(S_2COR)_2py_2] + ROC(S)SSC(S)OR \quad (76)$$

The thioxanthate complex $[Fe(S_2CSEt)_3]^-$ is obtained from reaction of *trans*-$[FeCl_2(H_2O)_4]$ with potassium ethylthioxanthate in methanol or THF. Initially, a violet/red-brown solution is obtained although this can become bluish-green at high ligand-to-metal ratios. However, addition of R_4N^+ yielded only one product, namely the tetraalkylammonium salt of $[Fe(S_2CSEt)_3]^-$. An X-ray crystal structure analysis[807] shows the FeS_6 core to be distorted from a regular octahedron towards a trigonal prism with an average Fe—S distance of 2.52 Å. The blue colour of dilute solutions of $Et_4N[Fe(S_2CSEt)_3]$ in acetonitrile fades over a period of a few days at 10 °C to give some brown material and black crystals of an unusual iron(III) trithiocarbamate $(Et_4N)_2[Fe(SEt)(S_2CSEt)(CS_3)]_2$. This complex has a relatively short Fe—Fe distance. The iron atoms are bridged[808] by two ethylthio and two ethylthioxanthate ligands. The very reactive high-spin complex $[Fe(S_2PF_2)_2]$ is formed[809] in the absence of air and water from iron metal or $FeCl_2$ with anhydrous HS_2PF_2.

Oxidation states higher than +2 are favoured by the presence of dithiolene ligands and these complexes are discussed in Sections 44.2.5.2 and 44.3. In the present section, discussion is restricted to the reaction of $[Fe(Et_2dtc)_2]$ with $S_2C_2(CF_3)_2$. In THF solution in the absence of air this reaction yields the complex $[Fe(Et_2dtc)_2\{S_2C(CF_3)_2\}]$ as in equation (77). The geometry of this complex is slightly distorted[810] from an octahedron towards a trigonal prism. As is frequently the case with complexes of this type, the assignment of oxidation state to the metal ion is somewhat ambiguous. Nonetheless, there is a high degree of Fe^{II} character associated with the structural data. Magnetic data for both the solid complex and in solution are consistent with a singlet/triplet spin equilibrium. In solution two stereochemical rearrangements are observed[811] on the NMR timescale: inversion ($\Delta H^{\neq} \sim 37.7\,kJ\,mol^{-1}$) and C—N bond rotation ($\Delta H^{\neq} \sim 66.9\,kJ\,mol^{-1}$). In electrochemical experiments in acetonitrile solution, two reduction and one oxidation steps have been observed.[812]

$$[Fe(Et_2dtc)_2] + S_2C_2(CF_3)_2 \longrightarrow [Fe(Et_2dtc)_2\{S_2C_2(CF_3)_2\}] \quad (77)$$

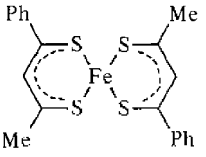
The complex $[Fe(SPMe_2NPMe_2S)_2]$ containing an unusual 1,3-dithio ligand has a tetrahedral structure, and is discussed in Section 44.1.5.10.2. Early reports[813,814] of attempts to prepare complexes of dithioacetylacetone describe a reaction mixture of Fe^{3+}, acetylacetone, HCl and H_2S in ethanol, which somewhat surprisingly yielded a deep purple 3,5-dimethyl-1,2-dithiolinium salt (**91**) of the $[FeCl_2]^{2-}$ anion. Simple $[FeX_4]^{2-}$ salts are pale cream and dithiolinium cations have no appreciable absorption in the visible region. Thus many workers[815] suspected the presence of Fe—S bonds. The discrete $[FeCl_4]^{2-}$ ion has, however, been demonstrated in an X-ray structure determination.[816] The intense colour of this and related salts is due to a broad absorption (around $20\,000\,cm^{-1}$) arising from charge transfer between the sulfur-containing cation and the reducing tetrachloroferrate anion. The structure of $(\mathbf{91})_2[FeCl_4]$ contains several potential S · · · Cl interactions. Each cation participates in three relatively short S—Cl contacts which represent a ready route for charge transfer. A variety of substituted 1,2-dithiolinium tetrachloroferrate(II) salts have been characterized, and their charge-transfer behaviour rationalized in terms of a combination of steric and electronic effects. Chemical reduction of $(\mathbf{91})_2[FeCl_4]$ (*e.g.* with $NaBH_4$ or $Na_2S_2O_4$) gives[817] a moderate yield of the low-spin neutral iron(III) dithio-β-diketone complex $[Fe(C_5H_7S_2)_3]$.



(91)

Red-brown crystals of this complex dissolve in chloroform and are reduced further, on shaking the solution with aqueous $Na_2S_2O_4$, to give the bis-dithio-β-diketone iron(II) complex $[Fe(C_5H_7S_2)_2]$, which is very sensitive to reoxidation. A similar complex is postulated by Japanese workers,[818] resulting from the reduction of 3-methyl-5-phenyl-1,2-dithiolium perchlorate in the presence of Fe^{2+}. The exact structure is unknown but is thought to be as shown in (**92**). $[FeCl_4]^{2-}$ forms[819] a

related charge-transfer complex with the dication of *N,N'*-dimethyl-4,4'-bipyridine (paraquat). EPR spectroscopy shows the presence of some completely reduced radical cation pq^+ although the Mössbauer spectrum indicates that the majority of iron is present as iron(II) in the complex. The X-ray powder diffraction pattern is very similar to that for an equivalent cobalt salt whose X-ray crystal structure shows[820] the paraquat cation to be planar.



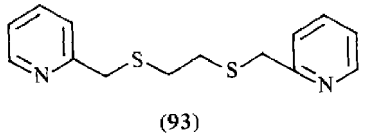
(92)

44.1.5.10.4 Mixed sulfur nitrogen donors

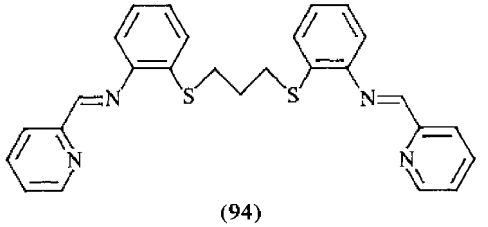
A variety of iron(II) complexes with sulfur and nitrogen donors are known. Many have unusual coordination geometries and interesting magnetic behaviour. The iron(II) complexes of (**93**) with stoichiometry [Fe(**93**)Y_2] (Y = Cl, Br, I, NCS) are high-spin and their magnetic moments, in the range 5.3–5.4 BM, are consistent with octahedral coordination. The halide complexes are orange or yellow, whilst the thiocyanate is dark green. The complexes dissociate in nitromethane and reaction (78) has been proposed[821] for which the equilibrium constant increases in the order Cl ~ NCS < Br < I.

$$[Fe(\mathbf{93})Y_2] + CN_3NO_2 \longrightarrow [Fe(\mathbf{93})Y(CH_3NO_2)]^+Y^- \qquad (78)$$

In contrast, the more delocalized hexadentate ligand (**94**), which provides an S_2N_4 donor set, forms[822] a low-spin iron(II) complex. Here, the higher degree of conjugation demands that the geometry of each NNS sequence must at least approximate to being planar with the result that only two enantiomeric forms are possible. The stability of this iron(II) complex is illustrated by its formation from iron(III) salts. If excess $FeCl_3$ is used, the product is blue [Fe(**94**)][$FeCl_4$]$_2$, whereas excess $FeCl_2$ affords [Fe(**94**)][$FeCl_4$].



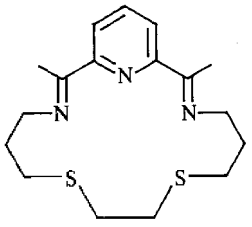
(93)



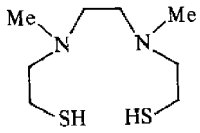
(94)

The Schiff base condensation of 2,6-diacetylpyridine with 4,7-dithiadecane-1,10-diamine yields the macrocyclic ligand (**95**), which has an S_2N_3 donor set. The six-coordinate complexes [Fe(**95**)Y]$^+$ can be high- or low-spin depending on the nature of Y, for example magnetic moments for Y = Cl, Br, I and NCS are 5.2, 5.3, 0.3 and 0.6 respectively. Three distinct structural modifications of the stoichiometry Fe(**95**)$(NCS)_2$ have been characterized in the solid state. In acetonitrile solution, however, there appears to be a common structure. Two of the solid state structures are high-spin and the other low-spin; no doubt these involve different conformations of the macrocyclic ligand. X-Ray crystal structure analysis of the low-spin complex shows[823] the macrocycle wrapped around the iron(II) centre as a pentadentate ligand with a nitrogen bound NCS^- group completing a distorted octahedral geometry. The neutral bis complexes of the linear aliphatic ligands (**96**) and (**97**) are both high-spin and have slightly distorted trigonal bipyramidal structures involving dimercapto-bridged dimers. The extent of distortion from the trigonal bipyramidal dimer structure (**98**) is greater for the ligand (**96**) (which is the less flexible of the two) than for (**97**). The two iron atoms are sufficiently close (3.2 Å) for significant antiferromagnetic exchange to occur by direct overlap of iron[824] orbitals. Because of the closeness of the participating nuclei and the orbital dependence of the effect, it is possible to evaluate[825] electron pair exchange parameters for the temperature dependence of the magnetic susceptibility of the complexes [Fe(**96**)]$_2$ and [Fe(**97**)]$_2$.

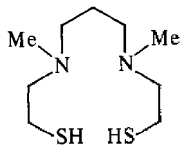
Neutralization of an alcoholic solution of *o*-aminobenzenethiol (**99**) with a slight deficiency of



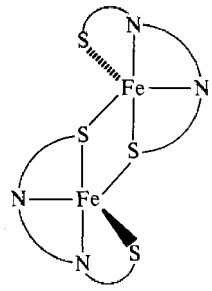
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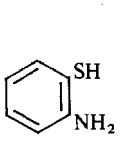


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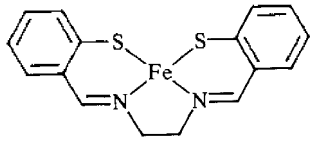


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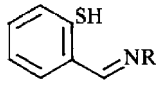
NaOH in the presence of $FeSO_4$ affords a pale yellow precipitate of $[Fe(SC_6H_4NH_2)_2]$. It is insoluble in most common solvents but slightly soluble in DMF. This iron(II) complex is not well characterized; it is antiferromagnetic with a well-defined Néel point of 138 K and a magnetic moment of 3.95 BM (rather low due to exchange). The reflectance spectrum of the complex indicates six-coordination and it may be assumed that its structure is polymeric and involves sulfur bridges. Ethylenediamine reacts with bis(thiosalicylideniminato)iron(II) to give[827] (**100**), which has a magnetic moment of 1.9 BM. The well-known oxygen analogue of this complex, [Fe(salen)], has in contrast a spin-only value of 4.77 BM.[282] The low temperature Mössbauer spectrum of (**100**) is compatible with the intermediate $S = 1$ spin state, while the temperature dependence of its magnetic moment between 4.2 K and 300 K is consistent with coupling in a polymeric structure. The complex reacts with oxygen in pyridine at room temperature, affording the corresponding iron(III) μ-oxo dimer. The room temperature UV spectrum of (**100**) in pyridine is similar to that in dichloromethane, but at $-23\,^{\circ}C$ a dramatic change from blue-black to red ($\lambda = 508$ nm) takes place. This has been ascribed[829] to pyridine coordination. When carbon monoxide is passed into such a solution it also becomes red and the complex [Fe(**100**)(CO)(py)] is formed. This has been characterized by X-ray crystal structure determination,[830] which shows the pyridine and carbon monoxide ligands to be *trans* to each other. A variety of complexes have been prepared[829] with ligands formally similar to (**100**) but with the CH_2CH_2 moiety exchanged for different groups. Some of these also have the unusual $S = 1$ spin state.[831] In contrast the neutral bis-ligand complexes of the bidentate (**101**) are high-spin (magnetic moments approximately 5.1 BM)[829] and the assignment of an $S = 2$ spin state is supported by Mössbauer data.[831]



(99)

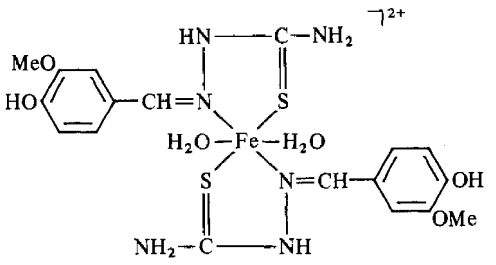


(100)



(101)

The quadrupole splitting in the Mössbauer spectrum of the thiosemicarbazide complex $[Fe(NH_2NHCSNH_2)_2]SO_4$ is particularly large[832] (4.65 mm s^{-1}) and an X-ray crystal structure showed[833] an unusual chain-like polymer formed by SO_4^{2-} bridges between *cis*- and *trans*-$[Fe(NH_2NHCSNH_2)_2]^{2+}$ units. These are thus two different iron environments and the Mössbauer spectrum observed is less complex than expected. The origin of the large quadrupole splitting remains unclear. A vanillin thiosemicarbazone iron(II) complex (**102**) has been reported[834] and its fungicidal properties investigated. Cysteine reacts with Fe^{2+} under acidic or neutral conditions to give a light brown complex of 1:1 stoichiometry. This complex probably involves bonding through the carboxylate oxygen atoms. If, however, the reaction is carried out in alkaline solution, a 1:2 (FeL_2) complex is formed. Under the same conditions and in the presence of carbon monoxide, a red dicarbonyl $[FeL_2(CO)_2]$ results. The IR and Raman spectra of these complexes have been recorded.[835] The $[FeL_2]$ complex has a polymeric structure[836] with antiferromagnetic coupling[837] which probably occurs *via* thiolate bridging groups. The Mössbauer spectra of these complexes have also been reported;[838] however, their structures are not known with any certainty.



(102)

44.1.5.11 Halides

44.1.5.11.1 Fluorides

Iron difluoride is an off-white sparingly soluble material, which may be prepared by the reaction of metallic iron with HF,[839,840] dehydration of the tetrahydrate,[841] displacement[842] of chlorine in $FeCl_2$ by HF, reduction of $FeF_3 \cdot xH_2O$[843] or reaction of Fe_2O_3 with carbon and HF.[841] It has been shown[844] to be monomeric in the gas phase between 692 °C and 876 °C. The solid has the rutile structure in which FeF_6 octahedra are tetragonally distorted with iron–fluorine bond distances[845] of 1.99 Å (× 2) and 2.12 Å (× 4). Structural transformations have been observed at very high pressures.[846] Above 100 K, FeF_2 has a magnetic moment of 5.56 BM.

Iron difluoride tetrahydrate is a white solid which browns in air. It may be prepared by dissolving metallic iron in warm hydrofluoric acid and precipitating with ethanol. The structure[847] is described as an array of discrete $[FeF_2(H_2O)_4]$ octahedra in which H_2O and F^- are randomly distributed over 12 possible sites, each site being occupied by an average of $\frac{1}{3}O$ and $\frac{1}{6}F^-$. A saturated aqueous solution of the hydrate forms[848] a yellow precipitate of composition $Fe_2F_5 \cdot 7H_2O$ on standing in air for several days. This complex is dehydrated at 100 °C in nitrogen to give $Fe_2F_5 \cdot 2H_2O$ and completely dehydrated at 180 °C to give the grey mixed oxidation state salt Fe_2F_5. The structure of the hydrate contains distinct Fe^{II} and Fe^{III} centres.[849]

44.1.5.11.2 Chlorides

Iron dichloride is a hygroscopic white solid readily soluble in water and ethanol. It may be prepared by reaction of metallic iron with HCl at red heat,[850] under mild conditions in THF[851] or methanol,[852] or with a mixture of the acid and chlorine at 700 °C. The trichloride decomposes[854] at 300 °C *in vacuo* or may be reduced for example with H_2[842] or H_2S[855] to yield $FeCl_2$. Thermal decomposition of $FeCl_3$ aids purification of $FeCl_2$ by vacuum sublimation. Anhydrous $FeCl_2$ may also be prepared by dehydration of $[FeCl_2(H_2O)_4]$ and the reaction of metallic iron with CCl_4.[857]

Whilst the vapour of $FeCl_2$ is monomeric ($\nu = 492\,cm^{-1}$) at lower temperatures,[850] an increasing proportion of dimer ($\nu = 430 cm^{-1}$)[858,859] is present as the temperature is raised. Crystalline $FeCl_2$ has the $CdCl_2$ structure[860] under normal conditions. The packing geometry of the $FeCl_6$ octahedra appears to be dependent on the mode of crystallization. At high pressures structural changes occur; a magnetically observable change to a CdI_2 structure is seen[861] at low temperatures at 2 kbar pressure and the structure undergoes a similar modification[862] at 5.7 kbar at room temperature. The anhydrous dichloride has a magnetic moment of $\mu_{eff} = 5.87$ BM at 300 K. $FeCl_2$ reacts readily with a wide variety of ligands to form $[FeCl_2L_n]$ complexes, many of which are discussed elsewhere in this chapter.

Also of interest is the tetrahedral anion $[FeCl_4]^{2-}$ found in a number of complexes. Tetrachloroferrates may be prepared by the reaction of alkali metal chlorides with $FeCl_2$ in the melt[863] or, for example, the reaction of triphenylmethylarsonium chloride or tetraethylammonium chloride with $FeCl_2$ in deoxygenated ethanol.[864] The tetrachloroferrate(II) anion is less common than its iron(III) counterpart and there have been few structural determinations. The geometry of $[FeCl_4]^{2-}$ is frequently complicated by interaction with other species, as for example in the case of the complex $\{[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_3SbCl\}_2[FeCl_4] \cdot CH_2Cl_2$ in which hydrogen bonding between $[FeCl_4]^{2-}$ and chloroform is thought[865] to cause a significant distortion from perfect tetrahedral symmetry. In $[NMe_4]_2[FeCl_4]$, which is isostructural with the analogous cobalt, nickel and zinc salts which have

no close interactions, the anion is nearer to ideal tetrahedral symmetry.[866] Interestingly the bond lengths (Fe—Cl = 2.29 Å) in the iron(II) anion are 0.11 Å longer than those found in the iron(III) anion $[FeCl_4]^-$. This is in contrast to the octahedral case where, for equivalent spin states, bond lengths differ[866] by about 0.04 Å between the iron(II) and iron(III) oxidation states. This difference has important implications in the study of iron–sulfur proteins where oxidation state changes in tetrahedral iron anions are frequently observed. The interesting charge transfer observed between $[FeCl_4]^{2-}$ and dithiolium cations is discussed in Section 44.1.5.10.3. A number of other complex binary iron chlorides exist, often poorly characterized. The $[FeCl_6]^{4-}$ anion is found as the mineral rinneite[867] in potash deposits. The tetrahydrate $[FeCl_2(H_2O)_4]$ may be prepared[868] by dissolving metallic iron in aqueous HCl and crystallizing the product at room temperature. The distorted octahedral structure[869] has *trans* chloride ligands and there is extensive hydrogen bonding in the crystal lattice (Fe—Cl = 2.38 Å; Fe—O = 2.09, 2.5 Å). Crystallization at 75° yields the dihydrate,[870] which can also be prepared by careful dehydration of the tetrahydrate. The structure of $FeCl_2 \cdot 2H_2O$ consists of chains of $[FeCl_4(H_2O)_2]^{2-}$ octahedra with *trans* aqua ligands which are linked by two bridging chlorine atoms[870] (Fe—O = 2.075 Å; Fe—Cl = 2.488, 2.542 Å).

44.1.5.11.3 Bromides

Iron dibromide is a pale yellow-to-brown hygroscopic solid that is soluble in water, ethanol, ether and acetonitrile. It is prepared[871] by the reaction between metallic iron and bromine in a flow tube at 200 °C. $FeBr_2$ is purified from $FeBr_3$ by sublimation in nitrogen or under vacuum. Other preparative routes include the reaction of metallic iron with HBr in methanol,[852] hydrobromination of Fe_2O_3[872] in a flow tube at 200 °C–350 °C and dehydration[873] of $[FeBr_2(H_2O)_4]$. $FeBr_2$ crystallizes in a layer lattice of the CdI_2 type[873] and has a magnetic moment of 5.71 BM at 295 K. Like the chloride, $FeBr_2$ readily forms adducts with a wide range of donor molecules including amines, pyridines, phosphines, arsines and oxygen donor ligands. A series of hydrates may be crystallized from aqueous solution at different temperatures,[874] a 9-hydrate below −29.3 °C, a 6-hydrate[875] at room temperature, a tetrahydrate above 49 °C and a dihydrate above 83 °C.

44.1.5.11.4 Iodides

FeI_2 is a red-black crystalline solid which is hygroscopic, very soluble in water and also soluble in ethanol and ether. It may easily be prepared[876–878] from elemental iron and iodine because of the non-existence of the triiodide. Anhydrous FeI_2 has the CdI_2 structure[879] and a magnetic moment of 5.75 BM at 295 K. As with the dibromide, a series of hydrates are obtainable from aqueous solutions of FeI_2; for example, the green tetrahydrate results from evaporation at room temperature. FeI_2 also forms a wide range of adducts with suitable donor ligands. Recent work has identified significant advantages[877] in the use of high purity FeI_2 in discharge lamps.

44.1.5.12 N Donor Macrocycles

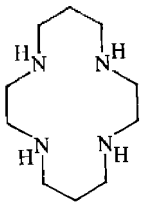
44.1.5.12.1 Introduction

There is a particularly extensive and rich coordination chemistry associated with iron(II) N donor macrocycles. The coordination chemistry of the biologically important iron porphyrin complexes has been of interest since the classic studies of Fischer, and over recent years there has been a resurgence of work on these and also on a wide range of related synthetic macrocyclic complexes. This section concentrates on their coordination chemistry, and where appropriate highlights enhanced ligand reactivity specifically induced by the iron(II) centre. First saturated ligands are discussed and then the unsaturated systems, with the particularly well-studied porphyrins and phthalocyanines being dealt with in separate subsections.

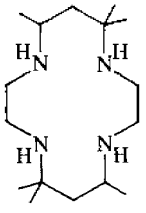
44.1.5.12.2 Saturated macrocycles

This section is concerned with complexes formed by macrocycles which are effectively polydentate ethylene or propylene amines. The prototype ligand is 'cyclam' or [14]aneN$_4$[880,881] (**103**) (1,4,8,11-

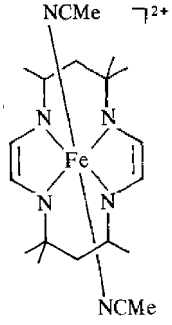
tetraazacyclotetradecane). Thus, when $FeCl_2 \cdot 4H_2O$ is added to a warm solution of Me_6[14]aneN$_4$ (**104**) in DMF, a tan precipitate of [Fe(Me_6[14]aneN$_4$)Cl$_2$] forms[882] on cooling to room temperature. A similar complex with axial acetonitrile ligands results[883] from the reaction of Me_6[14]aneN$_4$ with iron(II) acetate or perchlorate in anhydrous acetonitrile. This complex is low-spin, highly air sensitive and, in acetonitrile solution, is progressively oxidized to yield the diimine complex [Fe(Me_6[14]1,3,8,10-tetraeneN$_4$)]$^{2+}$ (**105**).



(103)



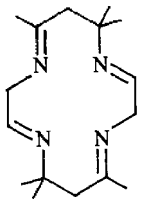
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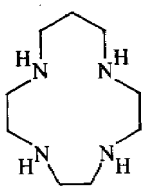
(105)

Reactions of [Fe(hfpd)(H_2O)$_2$] (hfpd = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) with (**104**) and related macrocycles in rigorously anaerobic conditions afford[884] complexes of the type [Fe(L)(hfpd)] (L = **104**). Mössbauer spectroscopy indicates six-coordinate high-spin iron(II), but the nature of the bonding of the axial ligands is not fully resolved. TMC (tetramethylcyclam), the tetra-*N*-methyl derivative of (**103**), reacts[885] readily with [Fe(NCMe)$_6$](BF$_4$)$_2$ in acetonitrile to give the five-coordinate high-spin iron(II) complex [Fe(TMC)(NCMe)](BF$_4$)$_2$. Substitution of the co-ordinated acetonitrile yields [Fe(TMC)X]$^+$ (X = Br, Cl, NCS$^-$, N$_3^-$), which are also five-coordinate. All these complexes react in the solid state with moist ambient air to give dark red-brown compounds which are reported[885] to be six-coordinate $S = 1$ iron(II) species, having a water molecule in the sixth coordination position. Complex (**105**) shows three well-defined reversible electrochemical reduction steps,[883] corresponding to Fe^{I}, Fe^{0} and Fe^{-I} oxidation states, whereas in acetonitrile [Fe(Me_6[14]aneN$_4$)(MeCN)$_2$]$^{2+}$ reduces irreversibly. The saturated nitrogen atoms in such ligands are relatively 'hard' but complexes with strong field axial ligands tend to be low-spin. Thus when the axial acetonitrile ligands in purple, low-spin [Fe(Me_6[14]aneN$_4$)(MeCN)$_2$](BF$_4$)$_2$ are removed *in vacuo*[886,887] a powder-blue high-spin species [Fe(Me_6[14]aneN$_4$)(BF$_4$)](BF$_4$) containing coordinated BF_4^- is formed. A series of complexes [Fe(Me_6[14]aneN$_4$)X$_2$] have been synthesized.[887] In the order of the spectrochemical series, low-spin complexes were observed for X = CN$^-$, NO$_2^-$ (and MeCN as BF_4^- and PF_6^- salts), high-spin complexes for X = MeCO$_2^-$ ($\mu_{eff} = 5.7$ BM) Cl$^-$ (5.95), Br$^-$ (5.47), I$^-$ (5.37) and BF_4^- (5.7, five-coordinate). The X = NCS$^-$ complex exists in a mixture of spin states having a room temperature magnetic moment of 1.5 BM and a weak ESR signal at $g = 2.285$. The stabilization of iron(II) in complexes having predominantly saturated nitrogen donor ligands is unusual, and may be ascribed to the conformation of the macrocycle, which maintains the planarity of the donor set, and hence a relatively high ligand field strength. Significantly increasing ligand field strength, however, results in the formation of five-coordinate high-spin complexes, probably because the metal ion is then too large to fit inside the plane of the high-field ligand. Thus, with relatively weak-field axial ligands such as halide, the tetraimine (**106**) forms[888] a five-coordinate complex [Fe(Me_6[14]1,4,8,11-tetraeneN$_4$)(Cl)](ClO$_4$). Mössbauer studies have shown[889] that the π-accepting power of the tetradentate macrocyclic amines increases with the degree of unsaturation and that π bonding to iron(II) is especially important for ligands containing the α-diimine moiety. Iron(II) complexes of a range of saturated macrocyclic amines of varying ring size, *i.e.* [13]aneN$_4$ (**107**), [15]aneN$_4$ (**108**) and [16]aneN$_4$ (**109**), have been synthesized[890] in addition to those of the non-methylated ligand cyclam [14]aneN$_4$ (**103**). The ligand field strength of the macrocycle varies markedly with ring size, being greater in smaller rings. This difference is demonstrated[890] by the spin states of tetragonal iron(II) complexes with rings of differing size (Table 17).

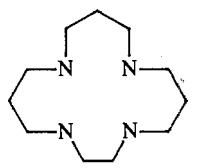
Interestingly, the presence of methyl substituents on the saturated tetraaza macrocycles also affects the properties of their iron(II) complexes. Whilst [Fe(Me_6[14]aneN$_4$)(NCS)$_2$] shows a $^1A_{1_g} \rightleftharpoons {}^5T_{2_g}$ spin transition, [Fe([14]aneN$_4$)(NCS)$_2$] is low-spin. Furthermore, [Fe([14]aneN$_4$)(MeCN)$_2$](PF$_6$)$_2$ does not lose MeCN to form a five-coordinate species which is in contrast to the analogous complex [Fe(Me_6[14]aneN$_4$)(MeCN)$_2$](BF$_4$)$_2$. A further example of the



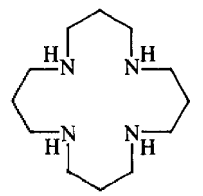
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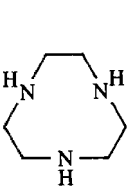
Table 17 Physical Properties[1] of $[FeX_2([y]aneN_4)]$ Complexes with y = 13, 14, 15 and 16

	X =	*MeCN*[2]	*NCS*$^-$	*NO*$_2^-$	*CN*$^-$
[13]ane	Colour		White[3]		Orange
	μ_{eff}(BM)	Not isolable	5.42		0.76
	δ (mm s^{-1})		1.12		0.40
	ΔE_Q (mm s^{-1})		1.92		0.79
[14]ane	Colour	Purple	Blue	Red	Orange
	μ_{eff}(BM)	0.43	0.72	0.57	0.77
	δ (mm s^{-1})	0.57	0.62	0.49	0.44
	ΔE_Q (mm s^{-1})	0.66	0.35	0.67	0.94
[15]ane	Colour	White	White	Magenta[4]	Lavender
	μ_{eff}(BM)	5.52	5.32	3.36	0.69
	δ (mm s^{-1})	1.14	1.20	0.33	0.48
	ΔE_Q (mm s^{-1})	1.29	1.22	< 0.40	1.44
[16]ane	Colour	White	White	Orange[5]	Not isolable
	μ_{eff} (BM)	5.55	5.52	5.53	
	δ (mm s^{-1})	1.17	1.25	1.05	
	ΔE_Q (mm s^{-1})	1.38	1.97	1.91	

Magnetic moments measured at 25 °C, Mössbauer parameters relative to stainless steel.
1. D. D. Watkins, D. P. Riley, J. A. Stone and D. A. Busch, *Inorg. Chem.*, 1976, **15**, 387.
2. As PF_6^- salt.
3. High-spin state indicates NCS^- are coordinated *cis*.
4. Stoichiometry $[Fe[15]aneN_4(NO_2)]^+$, severe distortion from octahedral symmetry results in a triplet ground state.
5. Compound has stoichiometry $[Fe([16]aneN_4)(NO_2)]NO_2$.

effect of ring size is given[891] by the reversible uptake of carbon monoxide by low-spin $[Fe([14]aneN_4)(MeCN)_2]^{2+}$ and high-spin $[Fe([15]aneN_4)(MeCN)_2]^{2+}$. The latter complex becomes low-spin on substitution of one MeCN by CO, which was the first example of a non-haem complex changing spin state on binding CO. The relatively weaker ligand field of $[15]aneN_4$ and the proximity of the CO complex to the spin cross-over contributes to a 2000-fold increase[891] in the lability of CO in $[Fe([15]aneN_4)(CH_3CN)(CO)]^{2+}$ over the analogous $[14]aneN_4$ complex.

The macrocyclic triamine $[9]aneN_3$ (**110**) can only coordinate 'facially', in contrast with common open chain polyamines and macrocycles of larger ring size. Reaction[892] of the free ligand with $FeCl_2$ leads to the precipitation of blue $[Fe([9]aneN_3)_2]Cl_2$, which may easily be converted to the bromide. Surprisingly, this complex is diamagnetic and stable in aqueous solution although air sensitive. The formal redox potential at 3 °C in 0.1 M KCl is +0.13 V. Thus the iron(III) complex is but a weak oxidant.



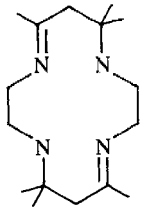
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44.1.5.12.3 Partially unsaturated macrocycles

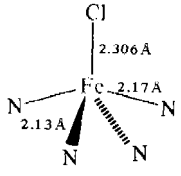
Interest in complexes of new synthetic macrocyclic ligands (and especially amines) was sparked by the discovery of the so-called Curtis ligands (**111**) first observed[893] as the product from the

reaction of tris(ethylenediamine)nickel(II) with acetone. The ligand (**111**) (Me_6[14]dieneN$_4$) forms[894] stable, high-spin complexes of the type [Fe(Me_6[14]dieneN$_4$)X](ClO$_4$) with X = Cl, Br, I. An X-ray crystal structure determination[895] shows five-coordinate iron(II) in [Fe(Me_6[14]dieneN$_4$)Cl]I. The macrocycle however is not planar but adopts a puckered configuration. Steric constraints prevent the high-spin iron(II) from fitting inside a plane containing the four nitrogen atoms and the iron sits slightly proud of the ring as illustrated in structure (**112**) with one axial chloride. The ligand is too rigid to allow coordination of a second *cis* halide.

The *d–d* electronic spectrum of this complex in solution is the same as the solid-state spectrum and this, together with the fact that the iron(II) centre remains high-spin, indicates that the unusual five-coordinate structure persists in solution. A related series of complexes have been prepared,[896] which show that the spin state and coordination number of the iron are dependent on the non-macrocyclic ligand (Table 18). The acetonitrile complex [Fe(Me_6[14]dieneN$_4$)(MeCN)$_2$]$^{2+}$ exists as two distinct isomers (which have different IR, visible and NMR spectra) that are interconvertible and derive from the *meso* and racemic forms of the asymmetric nitrogen atoms in the macrocyclic ligand. Interestingly, in the case of [Fe(Me_6[14]dieneN$_4$)(phen)](ClO$_4$)$_2$ the phen ligand is constrained to coordinate in a *cis* fashion if it is to be bidentate. This complex shows a thermal $^1A_{1g} \rightleftharpoons {}^5T_{2g}$ spin equilibrium. The UV/visible spectrum contains mainly strong charge transfer bands, and as the marked dependence of magnetic moment on temperature suggests, spectral characteristics also change with temperature. Thus at room temperature the complex is purple-black, whilst at 150 °C it undergoes a reversible change to a pink-red colour.



(111)



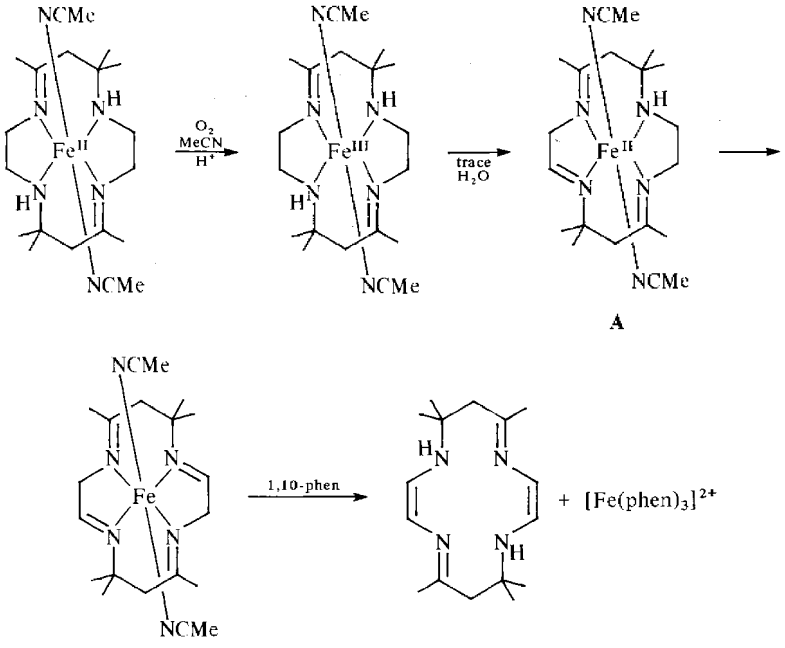
(112)

Table 18 Some Properties of Fe^{II} Complexes of the Macrocycle L (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene(111))

Complex	*Colour*	μ_{eff} *(r.t.)* (BM)	Λ_m *(in MeNO$_2$)* *(cm^2 ohm^{-1} mol^{-1})*	*Electronic spectra (molar extinction coefficient)* (kK)	*Solvent*
[FeL(MeCN)$_2$](ClO$_4$)$_2$	Pink[4]	0.4	199	19.6 (85), 29.1 (2400)	MeCN
[FeL(NCS)$_2$]	Brown	0.5	8	19.0w, 23.25, 25.0s	solid
[FeL(MeCN)$_2$]I$_2$	Dark red	0.62	244	19.6 (81), 29.4 (5200)	MeCN
[FeL(MeCN)(imidazole)](BPh$_4$)$_2$	Red-brown	0.42	170	20.0 (70), 24.9s, 31.7s	MeCN
[FeL(phen)](ClO$_4$)$_2$	Purple-black[2]	3.70[5]	189		
[FeL(Cl)](ClO$_4$)	Off white	5.50	95	4.2 (7), 12.2 (5)	$MeNO_2$
[FeL(Br)](ClO$_4$)	Off white	5.11	106	~5 (~5), 12.2 (4.9)	$MeNO_2$
FeL(I)](ClO$_4$)	Pale yellow-green	5.15	93	~4.5 (~4), 12.2 (4)	$MeNO_2$
{FeL}$_2$OH](ClO$_4$)$_3$·H$_2$O	White	Ref. 3		5.12w, 12.2w	Solid
FeL(I)$_2$]	Brown	5.25	90	12.2 (13)	MeOH

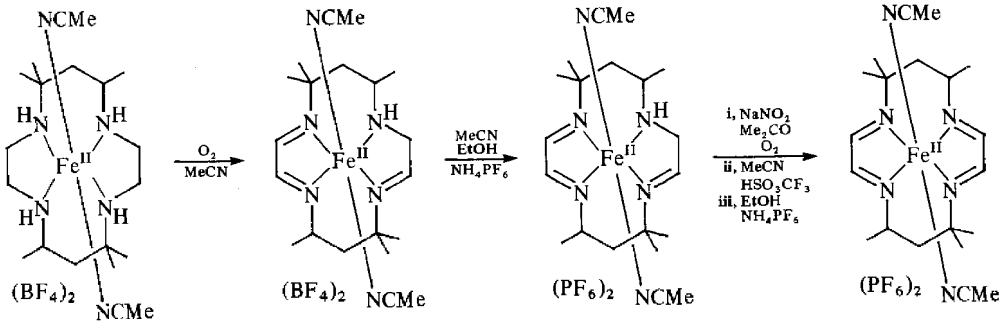
1. V. L. Goedken, P. H. Merrell and D. H. Busch, *J. Am. Chem. Soc.*, 1972, **94**, 3397.
2. Undergoes a reversible colour change to pink-red at 150 °C.
3. A value of 4.85 BM reported but the authors suspected some contamination.
4. Two forms with different solubilities were reported.
5. A strongly temperature dependent χ_m is observed.

These complexes are very sensitive and many decompose rapidly on exposure to air. Controlled reaction of low-spin six-coordinate complexes with oxygen, however, can lead to oxidative dehydrogenation of the ligand forming iron(II) complexes of tetraaza macrocycles,[897] which in some cases are isolable as the free ligand (Scheme 16). The high-spin five-coordinate halide complexes [Fe(Me_6[14]dieneN$_4$)X]$^+$ react with controlled amounts of oxygen to yield[830] intense blue precipitates in which oxidative dehydrogenation of the ligand is apparently accompanied by the tautomerization of the β-diimine to the α-diimine. This tautomerization also occurs to some extent during the oxidation of low-spin six-coordinate complexes with strong field axial ligands such as CN^-, NCS^- or imidazole.



Scheme 16

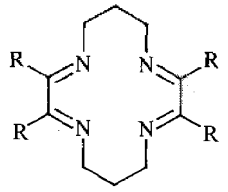
Oxidative dehydrogenation of the fully saturated 14-membered tetraaza macrocycle iron(II) complex affords different products. Thus when $[Fe(Me_6[14]aneN_4)(MeCN)_2](BF_4)_2$ is oxidized in acetonitrile solution, the resulting complex contains[898] a macrocyclic tetraazatriimine ligand with one α-diimine group. If the BF_4^- salt is exchanged with NH_4PF_6, the resulting red-violet complex is further oxidized in basic acetone with the solution becoming deep blue. Extraction of the resulting mixture with chloroform, followed by acidification in acetonitrile and crystallization from ethanol saturated with NH_4PF_6, yields the violet complex of the corresponding tetraazatetraimine having two α-diimine groups as shown in Scheme 17. The axial acetonitrile ligands in the triimine complex **A** in Scheme 16 are readily exchanged[898] to give highly air sensitive products which are dehydrogenated by molecular oxygen to the corresponding tetraimine complexes (L = imidazole, SCN^-, NO_2^-, CN^-, CNH, CNMe and Cl^-).



Scheme 17

The analogous complexes $[Fe(TIM)L_2](PF_6)_2$ (TIM = **113**, R = Me; L = MeCN, imidazole) may be synthesized[899] from iron dichloride/tin dichloride and the reaction product of 2,3-butanedione and 1,3-diaminopropane in methanol followed by addition of acetonitrile. The X-ray crystal structure of $[Fe(TIM)(MeCN)_2](PF_6)_2$ has been determined[900] and the iron shown to be coplanar with the ligand. Both acetonitrile ligands in the burgundy-red low-spin complex may be exchanged for imidazole, or a single acetonitrile exchange for CO. Substituents on the macrocyclic ligand influence the redox potential[901] such that the iron(III) oxidation state is stabilized with increasing σ donor strength of the ring. The iron(II) oxidation state is stabilized with increasing π acceptor ability.

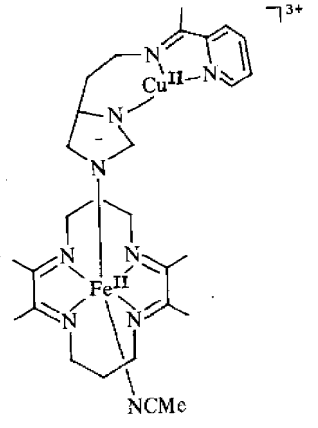
An $[Fe(TIM)L_2]^{2+}$ complex forms the starting point for the synthesis[902] of novel bimetallic



(113)

complex (**114**) in which an imidazole group bridges Cu^{II} and Fe^{II} atoms. It is thought such a system might mimic the interaction between the haem a_3 centre and the Cu(β) protein compounds of cytochrome oxidase. The kinetics of axial acetonitrile substitution by *N*-methylimidazole have been investigated[903,904] for the complexes $[Fe(TIM)L_2](PF_6)_2$ (R = Me, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Ph; L = MeCN). The reactions proceed *via* a dissociative mechanism but whether the loss of the first or second acetonitrile is the rate determining step is the subject of discussion.

Activation parameters for this process are given in Table 19 together with data for the same reaction of complexes with two related macrocycles. For these complexes there is a linear free energy relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}$ but data for the equivalent complexes with ligands (**106**) and (**121**) (Table 19) are not within this correlation. However, there appears to be a relationship[905] between $\Delta H^{\ddagger}$ (or k_1) and the donor ability of the macrocyclic ligand as measured by the half-wave redox potentials of the complexes.



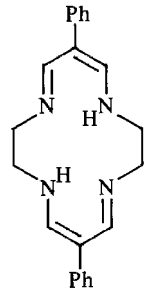
(114)

Table 19 Activation Parameters for Loss of Acetonitrile from *trans*-$[FeL(MeCN)_2]^{2+}$ in Acetone

L	$E_{1/2}$ *vs. SCE* (V)	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	*Ref.*
(**113**), R = *p*-MePh	1.22	91.2 ± 1.3	73.2	2
(**113**), R = Ph	1.25	90.8 ± 8.8	66.9	1
(**121**)	1.18	82.4 ± 4.2	91.2	3
(**113**), R = *p*-MeOPh	1.12	81.6 ± 15.9	49.0	2
(**106**)	0.89	74.5 ± 6.7	58.2	3
(**113**), R = Me	0.97	67.8 ± 10.5	22.2	1

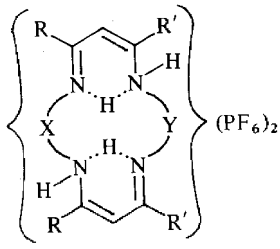
1. D. E. Hamilton, T. J. Lewis and N. K. Kildahl, *Inorg. Chem.*, 1979, **18**, 3364.
2. N. K. Kildahl, T. J. Lewis and G. Antonopoulos, *Inorg. Chem.*, 1981, **20**, 3952.
3. N. K. Kildahl, K. J. Balkus and M. J. Flynn, *Inorg. Chem.*, 1983, **22**, 589.

Iron(II) complexes of the dianion of the macrocycle Ph_2[14]tetraeneN_4 (**115**) have been prepared[906] by the convenient reaction of anhydrous iron(II) acetate with the free ligand in DMF. The iron(II) complex of the analogous Ph_2[16]tetraeneN_4 ligand is prepared in the same way but the preparation of the complex of the macrocycle of intermediate ring size Ph_2[15]tetraeneN_4 requires the presence of two equivalents of pyridine to assist in incorporation of the metal. Interestingly, these complexes are well-defined examples of intermediate spin state ($S = 1$) and have reduction potentials (in DMF at 25 °C) in the range −3.2 to −3.7 V. Oxidation of these complexes with Br_2 in chloroform affords the equivalent iron(III) complexes and reaction with diphenyl sulfide (with a catalytic amount of PhSH) gives the iron(III) benzene thiolate complexes in good yield.

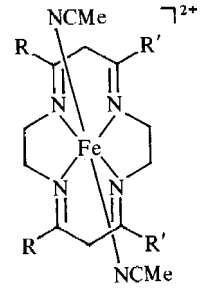


(115)

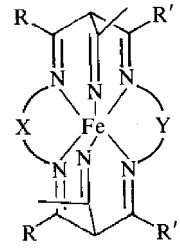
The macrocyclic ligands (**116**) may be synthesized by a modified Jaeger method (Ni^{II} template synthesis). These ligands react differently according to their ring size to form[907] complexes of iron(II). When the 14-membered ligands react with $[Fe(NCMe)_6]^{2+}$, a complex containing axial *trans* acetonitrile groups and a bis-β-diimine macrocyclic ligand (**117**) is formed. In the corresponding experiment with the 15- and 16-membered ligands however, acetonitrile molecules undergo an electrophilic reaction with the apical carbon atoms of the six-membered β-diimine moieties in the complex. The resulting compound is an iron(II) complex of a partially cyclized bis-β-triimine hexadentate ligand (**118**). The X-ray crystal structure[908] of (**118**) (R = Me, R′ = H, X = Y = $(CH_2)_3$) shows the six imine nitrogen donors to form a slightly distorted octahedron. The double bonds are localized (C—N average = 1.26 Å) and the macrocycle is folded to accommodate *cis* coordination of the iminoethyl groups.



(116)



(117)

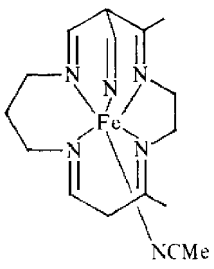


(118)

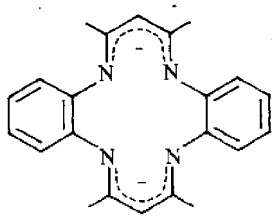
Both complexes (**117**) and (**118**) may be deprotonated (*e.g.* complex (**117**) by reaction with triethylamine in acetonitrile, complex (**118**) by reaction with Bu^tOK in Et_2O) to yield[909] novel square planar complexes of the corresponding dianionic tetraaza macrocyclic ligands. These unusual complexes exist in an intermediate $S = 1$ ground state. Subsequent reprotonation of the square planar complex of the 14-membered ring system [Fe(Me_2[14]tetraeneato(2−)N_4)] in acetonitrile regenerates complex (**117**). However, similar treatment of [Fe(Me_2[15]tetraeneato(2−)N_4)] yields a *trans* acetonitrile pentaimine iron(II) complex (**119**), whilst in the case of [Fe(Me_2[16]tetraeneato(2−)N_4)] the *trans* hexaimine analog of complex (**118**) is formed. Similar reactions in the presence of pyridine generate the expected *trans* pyridine tetraaza macrocyclic iron(II) complexes. Novel iron(III) complexes are generated[910] by the oxidation of the square planar tetraaza macrocyclic dianion iron(II) species.

The X-ray crystal structure[911] of the square planar complex of the dianion (**120**) shows that the ligand has a saddle shape, resulting from interaction between the methyl groups and the benzene rings. The structure of the free neutral ligand is remarkably similar to its structure in the complex. The average Fe—N bond distance is 1.92 Å (noticeably shorter than in equivalent $S = 0$ or $S = 1$ iron(II) porphyrin complexes) and the ligand conformation helps to place the iron atom 0.114 Å above the plane of the donor set. Iron(II) complexes of this ligand readily form[912] monocarbonyl complexes, with or without a second axial ligand. The geometry of the ligand allows for geometric isomers to be formed for complexes [Fe(L)(CO)(L′)] (L = **120**, L′ = amine *etc.*) depending upon which side of the ligand CO is coordinated to iron. For both L′ = NH_2NH_2 and the five-coordinate complex [Fe(L)CO], the CO ligand is located on the side of the macrocycle toward which the planar benzene rings are inclined. (This orientation is also observed[913] in the case of the iron(III) complex [Fe(L)Cl], L = **120**). In the case where L = py however, an X-ray crystal structure confirms[912] that

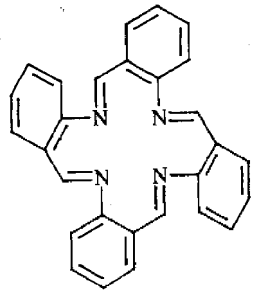
the CO is coordinated on the opposite side of the ligand. It is thought that this isomer may be more stable because steric interactions between the α-hydrogen atoms of pyridine and the macrocyclic ring are thus minimized. Iron(II) complexes of the tetraaza macrocycle (**121**) are reportedly formed[914] in low yield from the tetramerization of *o*-aminobenzaldehyde.



(119)

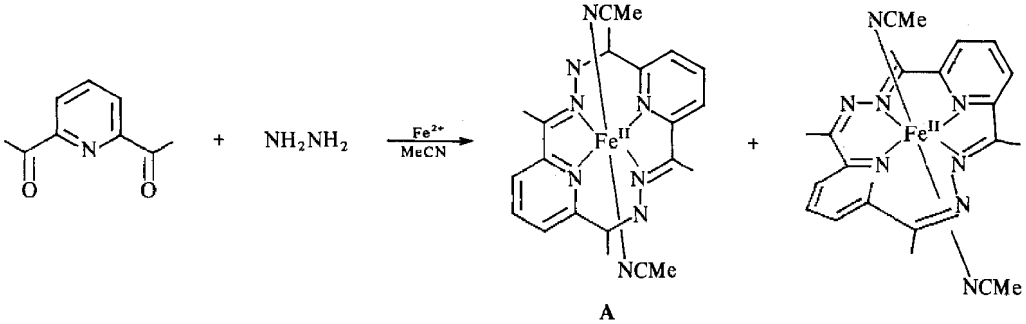


(120)



(121)

'Template condensation' has been used to obtain other fully conjugated macrocycles as their iron(II) complexes shown in Scheme 18. The reaction takes place readily over 20 minutes with the dropwise addition of hydrazine to a solution of 2,6-diacetylpyridine and $Fe(ClO_4)_2 \cdot 6H_2O$ in acetonitrile. The product separates as an intense blue-green precipitate.[915] Other six-coordinate low-spin complexes of these ligands are obtained with a variety of other axial ligands (NO_2^-, CO, Cl^-, Br^-, NCS^-, N_3^-). An X-ray crystal structure of complex **A** (Scheme 18) shows[915] that the macrocycle ligand is planar. The iron–nitrogen distances are somewhat compressed (1.899 Å and 1.892 Å) and the bond lengths of the macrocycle ring show a conjugated rather than an aromatic structure. The electronic spectrum argues for considerable delocalization, beyond that which would be expected based solely on the α-diimine linkages present in the molecule. The planarity of the macrocycle can, however, be disturbed[915] by the coordination of a bidentate ligand such as phen or bipy. In this case the 'puckering' of the ring causes the electronic spectrum to revert toward that characteristic of a tris-α,α′-diimine complex. The macrocycle (**120**) results from the template condensation of *o*-phenylenediamine with pentane-2,4-dione on nickel(II) after Jaeger. The hydrochloride salt of (**120**) (obtained free of Ni after treatment with HCl) forms[916] mono carbon monoxide complexes [Fe(L)(base)CO] (L = **120**, base = MeCN, py, 4-picoline, hydrazine) on reaction with anhydrous iron(II) salts under an atmosphere of carbon monoxide. An X-ray crystal structure of $[Fe(L)(NH_2NH_2)CO]$ shows[916] that, here too, the macrocycle is slightly saddle shaped (non-planar) as a result of steric interactions (*vide supra*[911]). The carbon monoxide is linear and shows a CO stretching frequency for a series of such complexes (1930–1940 cm^{-1}) slightly lower than that of carbon monoxyhaemoglobin (1951 cm^{-1}).

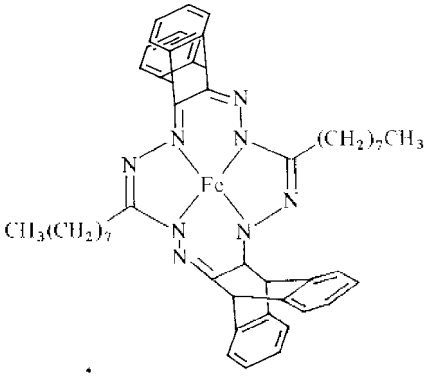


A

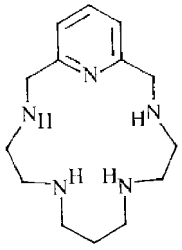
Scheme 18

The ability to exchange small ligand molecules in tetraaza macrocyclic complexes of iron(II) is relevant to the well-known reversible binding of molecular oxygen to haemoglobin.[917] The first such reversible binding of O_2 to an iron(II) complex was observed in 1973. Previously molecular oxygen was bound to iron(II) complexes irreversibly, usually with oxidation to iron(III) which was thought to proceed *via* the formation of an O_2-bridged dinuclear intermediate. The complex (**122**) was designed[918] to have a steric cage which would allow entry to O_2 but effectively prevent sufficiently close approach on the part of another iron(II) centre to form the bridged intermediate. The dark

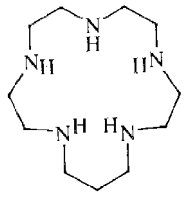
blue-black complex (**122**) reacts with one molecular equivalent of oxygen in THF/dimethoxyethane containing 4% pyridine to form a cherry red solution. When the complex was dissolved in toluene/1% pyridine and oxygen take-up was monitored by optical spectroscopy, it was found[918] to be reversible over a number of freeze–thaw cycles. An X-ray crystal structure[919] of complex (**122**) shows the iron coordination geometry to be essentially square planar with two relatively short Fe—N bond lengths (1.846 and 1.826 Å). The short bonds are probably due in part to the constricting nature of the macrocycle, which is itself slightly puckered. The deep 'pocket', which effectively prevents the formation of the dinuclear species, is evident. This has subsequently been shown to be a useful feature (though not a necessary one) for reversible oxygen uptake as is demonstrated by this behaviour in, for example, tetraphenylporphyriniron(II) (see Section 44.1.5.12.5). Iron(II) complexes of the ligands (**123**) and (**124**) have been prepared. The pyridine ring in (**123**) greatly stabilizes the reversible formation of a pink-violet oxygen adduct formulated[920] as $[(\{FeL\}^{2+})_2O_2]$ (L = **123**) in aqueous solution. By contrast the complex of the fully saturated ring (**124**) yields a very short lived oxygen iron(II) adduct and autooxidation is very rapid.



(122)



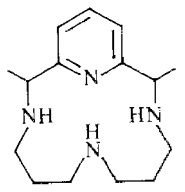
(123)



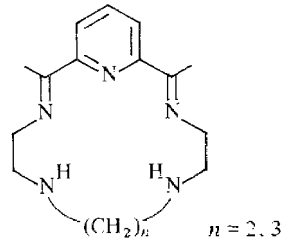
(124)

There are a series of macrocyclic ligands incorporating the pyridine moiety. The 14-membered macrocycle (**125**) forms[921] a series of high-spin five-coordinate iron(II) complexes $[Fe(L)X]^+$ (L = **125**; X = Cl, Br, I). The corresponding complexes where the monodentate ligands are azide or bidentate acetate are also high-spin but six-coordinate whilst the dithiocyanate complex is low-spin and six-coordinate (Table 20). The coordination numbers were identified on the basis of Mössbauer spectroscopy. Large ΔE_Q values in five-coordinate complexes of iron(II) are thought to arise from a combination of the nonspherical electron distribution about the iron nucleus and the dissymmetry of the ligand field. The assignment of a $^5B_2$ rather than a ^5E ground state (derived from the tetragonal distortion of an octahedral field) to iron in these complexes is supported by a magnetically perturbed Mössbauer study[922] on the five-coordinate high-spin complex $[Fe(Me_6[14]dieneN_4)Cl]ClO_4$. The ΔE_Q value for the acetate complex is similar to that found for high-spin six-coordinate iron(II) and it is assumed that the bidentate acetate ion causes some folding of the macrocycle. ΔE_Q values for the azide and thiocyanate complexes are consistent with high-spin six-coordinate and low-spin six-coordinate iron(II) complexes respectively.

Examples of seven-coordination in pyridine-containing macrocycles have also been osberved. Thus the iron(II) complexes $[Fe(L)X_2]\cdot xH_2O$ (L = **126**; X = halide or pseudohalide) are formed[923] when the corresponding seven-coordinate iron(III) complexes are reduced with aqueous sodium dithionite in the presence of excess NaX or by the direct template synthesis with 2,6-diacetylpyridine and the corresponding tetramine in the presence of iron(II). The triimine moiety gives rise to a strong



(125)



(126)

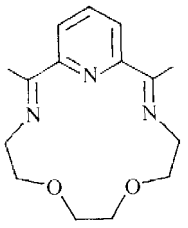
Table 20 Some Properties[1] of Iron(II) Complexes of the Macrocyclic Ligand (**125**)

Complex	*Coordination number*	*Colour*	μ_{eff} *(25 °C)* (BM)	*Spin state* S	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	ν *(N—H)* (cm^{-1})	ν *(C=N)* (cm^{-1})
[Fe(**125**)Cl]Cl	5	Yellow	5.2	2	1.11	3.72	3215, 3155	1597, 1575
[Fe(**125**)Br]Br	5	Yellow	5.11	2	1.12	2.84	3215, 3185	1597, 1575
[Fe(**125**)I]I	5	Yellow	5.05	2	1.08	3.84	3185, 3155	1597, 1575
[Fe(**125**)Cl]PF_6	5	Yellow	4.95	2	1.075	3.85	3290, 3270	1590, 1560
[Fe(**125**)Br]PF_6	5	Yellow	5.11	2	1.063	3.91	3279, 3270	1590, 1555
[Fe(**125**)I]PF_6	5	Yellow	5.20	2	1.051	3.77	3265	1590, 1555
[Fe(**125**)$(N_3)_2$]	6	Orange	5.50	2	1.24	1.68	3236	1597, 1580
[Fe(**125**)(OAc)]PF_6	6	Green	5.11	2	1.19	2.40	3279, 3175	1600 br
[Fe(**125**)$(NCS)_2$]	6	Red/black	0.8	0	0.71	0.67	3195	1597, 1575

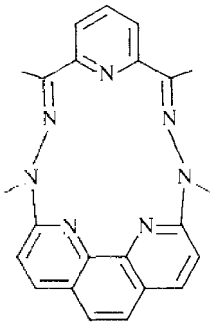
1. D. P. Riley, P. H. Merrell, J. A. Stone and D. H. Busch, *Inorg. Chem.*, 1975, **14**, 490; Mössbauer data relative to sodium nitroprusside.

visible absorption derived from metal-to-ligand charge transfer; the complexes are deep blue or blue-green. An X-ray crystal structure[924] of the iron(II) dithiocyanate complexes of the 15- and 16-membered macrocycles (**126**) confirms seven-coordination with a distorted pentagonal bipyramidal geometry. The thiocyanate ligands occupy the axial positions and the macrocycle is somewhat puckered. Replacement of the anionic thiocyanate ligands with neutral water molecules makes almost no difference[925] to the structure.

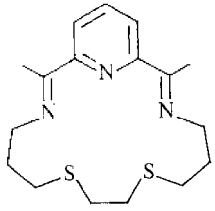
The substitution of 3,6-dioxaoctane-1,8-diamine for 3,6-diazaoctane-1,8-diamine in a template synthesis with 2,6-diacetylpyridine on iron(II) yields the mixed donor macrocycle (**127**). This molecule also forms[926] a seven-coordinate iron(II) complex $[Fe(L)(NCS)_2]$ (L = **127**). This blue high-spin complex (room temperature magnetic moment = 5.44 BM) exhibits an electronic spectrum and electrochemical behaviour which indicate that the complex of the mixed donor oxygen-containing macrocycle stablizes the +2 oxidation state to a greater extent than the same complex of the corresponding macrocyclic pentamine. The seven-coordinate high-spin iron(II) complex $[Fe(L)(H_2O)_2]$ (L = **128**) of the related macrocycle (**128**) is formed by the condensation of 2,9-di-(1-methylhydrazino)-1,10-phenanthroline with 2,6-diacetylpyridine in the presence of fresh $FeCl_2 \cdot 4H_2O$. The X-ray crystal structure[927] of this complex clearly shows that the iron(II) atom is coplanar with the macrocyclic donor set.



(127)



(128)

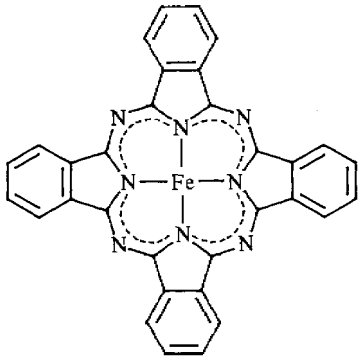


(129)

The Schiff base condensation of 2,6-diacetylpyridine with 4,7-dithiadecane-1,10-diamine yields the similar N_3S_2 macrocycle (**129**). This ligand is able to form complexes with iron(II) but its mode of coordination adapts to the monodentate coligand. Thus X-ray crystal structures[928] show that in $[Fe(L)(NCS)]^+$ and $[Fe(L)(MeOH)Cl]^+$ (L = **129**) the iron atom has a distorted octahedral geometry. In the first complex the macrocycle is quinquedentate and wraps around the iron atom. In the second complex the macrocycle is quadridentate with one sulfur atom weakly coordinated and one free. A compound with the formulation $[Fe(L)(NCS)_2]$ (L = **129**) has been observed[928] and evidently exists in three different forms (from IR, Mössbauer and magnetic data). Although X-ray structural data are not available on these isomers it is likely that they also reflect different ligand conformations of the N_3S_2 macrocycle.

44.1.5.12.4 Phthalocyanine

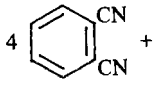
Iron(II) phthalocyanine (**130**) was originally discovered[929,930] by chance during the manufacture of phthalimide at the Grangemouth works of Scottish Dyes Ltd (subsequently part of ICI plc). Commercially, phthalocyanines are an important class of blue/green pigments and they are also used in some dyestuffs, having very good colour intensity with excellent light fastness as well as thermal stability and chemical inertness.[931–934] The iron(II) complex can be obtained by the heterogeneous reaction of iron salts with the parent macrocycle(metal-free)phthalocyanine[935,936] (PcH_2) in a high boiling basic solvent as in equation (79), or from the metal exchange reaction of Fe^{2+} with Li_2Pc in acetone[937] (equation 80). However, the best laboratory procedure makes use of the reductive cyclization of phthalonitrile with very finely divided iron generated from $[Fe(CO)_5]$ as in equation (81) in a high boiling solvent such as 1-chloronaphthalene.[938] Good yields of pure product are obtained over about an hour, and extensive washing with organic solvent removes remaining reactants and by-products. The same procedure enables the perfluoro derivative to be obtained from tetrafluorophthalonitrile (equation 82). Unlike the unsubstituted compound, the perfluoro derivative is soluble in several organic solvents, including acetone, to give intensely deep blue solutions.[839]



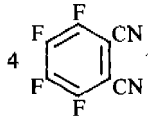
(130)

$$PcH_2 + Fe^{2+} \longrightarrow [FePc] + 2H^+ \quad (79)$$

$$PcLi_2 + Fe^{2+} \longrightarrow [FePc] + 2Li^+ \quad (80)$$



$$+ [Fe(CO)_5] \rightarrow [FePc] + 5CO \quad (81)$$

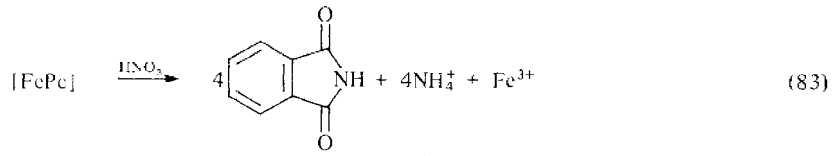


$$+ [Fe(CO)_5] \rightarrow [Fe(PcF_{16})] + 5CO \quad (82)$$

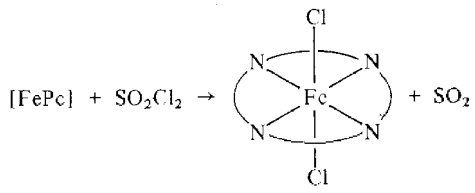
Solid phthalocyanine complexes of the first row transition metals exist in at least two well-characterized forms (α and β) that differ in the relative orientation of the macrocycle planes.[940,941] In the iron(II) complex, the resulting different intermolecular interactions give rise to differences in their Mössbauer spectra.[942] The most stable β-form is obtained as long purple needles by slow high-vacuum sublimation and the physical properties of this material have been studied in detail by many workers. Several groups have examined the magnetic properties of [FePc] and although all the measurements confirm the $S = 1$ intermediate spin state, there is some disagreement about the electronic configuration. One of the more exact Mössbauer determinations on a powdered sample over the temperature range 4.2–100 K was interpreted in terms of a ^3E_g ground state,[943,944] while other low temperature magnetic measurements are consistent with the $^3B_{2g}$ ground state.[945] However, the directly determined electron density distribution mapped from a set of accurate X-ray reflections collected at 100 K indicates ^3E_g as being the major contributor to the ground state.[946,947] This study also shows a deficiency of iron electron density along the axis perpendicular to the molecular plane, with an excess density along the diagonals of the Fe—N(pyrrole) directions. Magnetic circular dichroism spectra of [FePc] in dichlorobenzene could support a $^3A_{2g}$ ground state[948] and bands at 714 nm and 800 nm were assigned to metal–ligand charge transfer, although such spectra could be associated with protonated species.[949,950] Nevertheless, it may be possible that the ground state is not the same in the solid as in poorly coordinating solvents.

Iron(II) phthalocyanine is insoluble in most non-coordinating organic solvents but it does dissolve in very strong acids such as sulfuric and chlorosulfonic acids due to protonation of the basic bridging aza nitrogen atoms.[951,952] Although not soluble in hot hydrochloric acid, a reaction occurs which produces a dark material originally called[953] 'chloroferric phthalocyanine' and formulated [ClFePc]. Since this material is formed in the absence of air,[954] and even from gaseous hydrogen chloride,[955] it appears likely that it is a hydrochloride of iron(II) phthalocyanine ($FePcH^+Cl^-$) in which a bridging aza nitrogen atom is protonated. There is, however, evidence[956] indicating that when the reaction with hydrochloric acid is carried out in air some iron(III) species are formed, and it is possible that mixtures of protonated iron(II) complexes together with μ-oxo iron(III) dimers can be formed (see below). In warm concentrated nitric acid the first formed, purple, cationic radical species degrade to phthalimide and ammonium ion (equation 83).

Reaction of [FePc] with thionyl chloride produces [$FePcCl_2$], as in equation (84), which is considered to contain iron(III) and the oxidized macrocycle Pc^-, with chloride ions in the axial positions.[956,957] The overall oxidation level is confirmed by oxidative titration and the observed magnetic moment (3.1 BM) indicates a low-spin $S = \frac{1}{2}$ state. Considerable care is needed to exclude



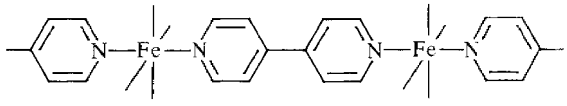
(83)



(84)

traces of water during the preparation of [FePcCl$_2$] to avoid formation of the hydrochloride. However, once formed [FePcCl$_2$] appears stable towards water.[956] Although α-[FePc] does not react with nitric oxide, the β form after a long period at room temperature forms [FePcNO], which is quite stable.[177,958] [FePcNO] reacts with pyridine forming [FePcpy$_2$] and when heated at 250 °C [FePc] is reformed. The IR spectrum (ν_{NO} 1737 cm^{-1}) suggests it should be regarded as an Fe^{III}–NO$^-$ complex.

Addition of ligands in the axial positions of [FePc] takes place readily in solution to form six-coordinate low-spin complexes. Thus, [FePc] dissolves in pyridine to form a deep green complex [FePcpy$_2$] that is easily isolated and has moderate solubility in solvents such as chloroform and toluene.[959,960] Interesting one-dimensional polymeric bridged complexes (**131**) result when bidentate aromatic amines such as pyrazine or 4,4′-bipyridine are used.[961,962] In solution [FePcpy$_2$] reacts with CO to form [FePcpy(CO)],[963] as shown in equation (85), and diamagnetic red-violet crystals of [FePc(DMF)(CO)] are formed from phthalonitrile and [Fe(CO)$_5$] at moderate temperatures[964] in DMF, as in equation (86).



(131)

$$[FePcpy_2] + CO \longrightarrow [FePcpy(CO)] + py \quad (85)$$

$$[Fe(CO)_5] + 4o\text{-}C_6H_4(CN)_2 \xrightarrow{DMF} [FePc(DMF)(CO)] \quad (86)$$

[FePc(DMF)(CO)] is only stable in air for a few minutes, but it is stable under an atmosphere of carbon monoxide. In a vacuum at ~ 80 °C it decomposes to a mixture of α- and β-[FePc]. In DMSO, [FePc(DMSO)$_2$] reacts[965] with a large excess of carbon monoxide to form [FePc(DMSO)(CO)] at a rate given by $k_{obs} = k_f[CO] + k_r$ with an equilibrium constant of $\sim 1 \times 10^4$ dm^3 mol^{-1} at 20 °C. Related monocarbonyl complexes with *N*,*N*-diethylacetamide, pyridine, piperidine, hexamethylphosphoramide and Ph$_3$PO *trans* ligands have been reported.[966] Exposure of [FePc] in a hydrocarbon solvent to carbon monoxide at high pressure affords [FePc(CO)$_2$]. Other mixed ligand complexes of the type [FePcLL′] containing a range of ligands have also been isolated or characterized in solution (Table 21).[967–969] The structure of [FePc(4-Mepy)$_2$] has been determined[970] by X-ray methods and an Fe—N(4-Mepy) distance of 2.00 Å reported. A similar bond length of 1.94 Å was derived for the axial Fe—N in [FePc(BuNH$_2$)$_2$] from the induced shift of NMR proton resonances.[971] These structural determinations are in agreement with Mössbauer spectra of [FePcL$_2$] complexes.[972–974] Relatively large quadrupole splitting (Table 22) is in accord with a tetragonal structure with the in-plane ligand field being greater than the axial field. Moreover, with π acceptor ligands the π interaction is generally only weak. In the essentially diamagnetic [FePc(DMSO)$_2$] (0.74 BM) the iron is coordinated to the *sulfur* atoms of the axial DMSO ligands.[975] The in-plane Fe—N bond distances are similar to those in [FePc(4-Mepy)$_2$] and [FePc] itself, while the Fe—S distance of 2.31 Å suggests there is very little π back-donation.

The thermodynamics and mechanisms of axial ligand exchange in [FePcLL′] complexes shown in equations (87) and (88) have been extensively studied using visible spectroscopy. For L′ = substituted pyridines (L = DMSO) the binding strength order is 4-NH$_2$py > 4-Mepy > pyridine > 4-MeCOpy > 4-CNpy, which follows the Lewis basicity of the ligands and highlights the importance of σ bonding.[976] With nitrogen ligands of different types the order is imidazole > piperidine > pyridine indicating that π bonding must be important with the relatively poorly basic imidazole. But

Table 21 Selected Complexes of the Type [FePcLL′] Characterized in the Solid State or in Solution

L	*L′*	*Ref.*
imid	imid	1
4(5)-Me imid	4(5)-Me imid	1
1-Me imid	1-Meimid	1
Bu^nNH_2	Bu^nNH_2	2
pip	pip	3
4-Mepy	4-Mepy	4
DMSO	DMSO	5
Bu^tNC	Bu^tNC	6
Hex^cNC	Hex^cNC	6
PhNC	PhNC	6
$2,6\text{-}Me_2C_6H_3NC$	$2,6\text{-}Me_2C_6H_3NC$	6
$PhCH_2NC$	$PhCH_2NC$	6
$PhCH_2NC$	$PhCH_2NC$	7
$PhCH_2NC$	py	7
$PhCH_2NC$	pip	7
$PhCH_2NC$	1-Meimid	7
PhNO	Bu^nNH_2	8
$P(OPh)_3$	Bu^nNH_2	8
$p\text{-}MeC_6H_4NO$	1-Meimid	8
$C_6H_{11}NC$	1-Meimid	8
$P(OEt)_3$	$P(OEt)_3$	8
PBu_3	PBu_3	9
CO	DMF	10
CO	py	11
CO	pip	11
CO	Ph_3PO	11
CO	CO	11

1. H. Giesemann, *J. Prakt. Chem.*, 1956, **4**, 169.
2. J. E. Maskasky, J. R. Mooney and M. E. Kenney, *J. Am. Chem. Soc.*, 1972, **94**, 2132.
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11. F. Calderazzo, S. Frediani, B. R. James, G. Pampaloni, K. J. Reimer, J. R. Sams, A. M. Sera and D. Vitali, *Inorg. Chem.*, 1982, **21**, 2302.

with carbon monoxide, bonding is considerably weaker[963] than in iron(II) porphyrin complexes where π bonding is generally considered important. As expected, steric effects in [FePcLL′] complexes are important. Thus 2-methylpyridine and 2-methylimidazole only form very weakly bound complexes. This may indicate that displacement of the iron from the macrocycle core is more difficult with phthalocyanine than porphyrins. The rates of ligand exchange reactions in [FePcLL′] are moderately fast and must be studied by rapid mixing techniques such as stopped flow.[977–979] These reactions (equations 89 and 90) are dissociative in nature involving the coordinatively unsaturated [FePcL]. As evidenced by the ratio of the rate constants k_{-1}/k_2 the intermediate does discriminate between ligands, again suggesting the geometry to be square pyramidal with the iron centre in the macrocycle plane. Thus no spin change is required, which would be the case if the metal moved out of the plane. Depending on the relative values of the rate constants involved, this mechanism can result in reaction rates that are independent of the concentration of the incoming ligand [L″], (k_2[L″] > k_{-1}[L′]) or first order in [L″] (k_{-1}[L′] > k_2[L″]) and examples of both kinds of behaviour have been reported.[977–981] The rates of these reactions are significantly slower than the corresponding reactions of porphyrin complexes, which may be due to a higher charge on the iron atom, or the phthalocyanine being more rigid than the porphyrin ring system.

Reaction of [FePc] with sodium metal or dilithium benzophenone in THF affords reduced solvated species of the type M_n[FePc]·mTHF (n = 1–4). Magnetic and ESR measurements

Table 22 Mössbauer Parameters* for Iron(II) Phthalocyanine and Selected Derivatives at Room and Liquid Nitrogen Temperatures

Complex	*Temp* (°C)	ΔE_Q (mm s^{-1})	δ (mm s^{-1})	*Ref.*
[FePc]**	25	2.58	0.63	1
	22	2.67	0.68	2
	20	2.64	0.66	3
	−162	2.60	0.74	1
	−185	2.64	0.64	3
	−196	2.71	0.77	2
[FePcpy$_2$]	22	2.05	0.53	2
	−196	1.89	0.62	2
[FePcim$_2$]	22	1.79	0.54	2
	−196	1.71	0.63	2
Li[FePc]	26	3.24	0.61	1
	−153	3.25	0.69	1
Li$_2$[FePc]	25	1.86	0.52	1
	−160	1.87	0.61	
Li$_3$[FePc]	25	1.77	0.58	1
	−163	1.78	0.66	1
Li$_4$[FePc]	25	1.65	0.61	1
	−160	1.66	0.71	1

* Relative to $Na_2[Fe(CN)_5NO]\cdot 2H_2O$

** For results at high temperatures see: J. Blomquist and L. C. Moberg, *Phys. Scr.*, 1974, **9**, 350; and for results at 4.2 K in applied magnetic fields see ref. 3 and B. W. Dale, R. J. P. Williams, P. R. Edwards and C. E. Johnson, *J. Chem. Phys.*, 1968, **49**, 3445; T. H. Moss and A. B. Robinson, *Inorg. Chem.*, 1968, **7**, 1692.

1. E. Fluck and R. Taube, *Develop. Appl. Spec.*, 1970, **8**, 244.
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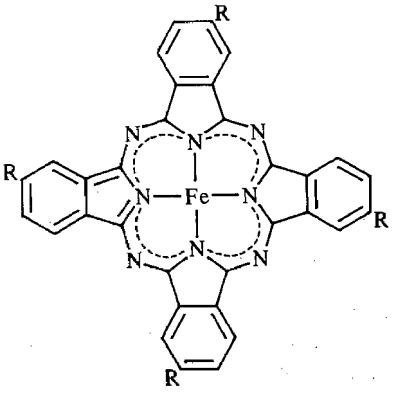
$$[FePcL_2] + L' \overset{K_1}{\rightleftharpoons} [FePcLL'] + L \quad (87)$$

$$[FePcLL'] + L' \overset{K_2}{\rightleftharpoons} [FePcL'_2] + L \quad (88)$$

$$[FePcLL'] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [FePcL] + L' \quad (89)$$

$$[FePcL] + L'' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [FePcLL''] \quad (90)$$

suggest[982,241] the first formed product contains iron(I) and the more highly reduced compounds iron(0) with additional electrons being located on the macrocycle ligand. However, electronic spectra were subsequently interpreted[983] in terms of only iron(I) centres being present. The reduced compounds undergo oxidative addition reactions with organic halides to produce interesting organometallic iron species[982,241] and this work has recently been reviewed.[984] A recent electrochemical/ESR study of [FePc] indicates the first reduction product (purple) is a five-coordinate iron(I) species. The voltage between the first and second reduced species is significantly solvent dependent (~0.2 V in pyridine and ~0.6 V in dma), and again it is concluded the second product is an iron(I) complex of the reduced ligand Pc^{3-}, but not all of the earlier observations are completely explained.[244]



(132)

Among the water soluble derivatives of [FePc] the tetrasulfonated complex (**132**; R = SO_3^-) is the most studied although many aspects of its chemistry are not completely resolved. Direct sulfonation of [FePc] is not clean,[985] and it is better to start with 4-sulfophthalic acid in a cyclization procedure. Weber and Busch[986] formulated their product obtained in this way as the iron(II) complex $Na[FePc(SO_3H)_3(SO_3^-)]\cdot 3H_2O$, but other workers favour a mixture of iron(III) complexes,[987] $Na_3[FePc(SO_3^-)_4]\cdot 7H_2O$ and $Na_4[FePc(SO_3^-)_4(OH)]\cdot 2H_2O$. In solution a magnetic moment of 1.8 BM was reported and that of the solid 3.0 BM.[996] In solution, as with other phthalocyanines,[988] dimerization takes place, but here perhaps involving μ-oxo Fe^{III} dimers. When Fe^{2+} is added to a neutral solution of the tetrasulfonated metal-free ligand $\{H_2Pc(SO_3H)_4\}$ a green solution is formed[989] that has a visible spectrum characteristic of a first row transition metal complex (λ_{max} 671 nm), with a strong absorption at 425 nm similar to well-characterized $[FePcL_2]$ complexes. At pH = 6.5 this reacts with oxygen according to the 1:2 (O_2 to Fe) stoichiometry shown in equations (91) and (92). New bands at 637 nm and 344 nm due to the oxygenated complex disappear when the solution is purged with nitrogen at 70 °C. These results[989] favour the participation of an iron(II) rather than an iron(III) complex and it is of interest that it is possible to obtain reconstituted haemoglobins with tetrasulfonated iron phthalocyanine in the place of haem,[990] and furthermore that these complexes reversibly combine with oxygen. Continuous UV irradiation of sulfonated iron phthalocyanine in solution causes low quantum yield degradation of the macrocycle with liberation of Fe^{3+}, but in the presence of 2-propanol iron(I) species result.[991]

$$[FePc(SO_3^-)_4(H_2O)_2]^{4-} + O_2 \rightleftharpoons [FePc(SO_3^-)_4(H_2O)(O_2)]^{4-} + H_2O \quad (91)$$

$$[FePc(SO_3^-)_4(H_2O)(O_2)]^{4-} + [FePc(SO_3^-)_4(H_2O)_2]^{4-} \rightleftharpoons$$

$$[(SO_3^-)_4PcFe(H_2O)(O_2)(H_2O)FePc(SO_3^-)_4]^{8-} + H_2O \quad (92)$$

The nature of products resulting from the reaction of oxygen with [FePc] itself has only recently been clarified. In 1965 Weber and Busch reported that the solid sulfonated complex reacts reversibly with oxygen.[986] The rigorously dried complex in the absence of oxygen displayed a magnetic moment of 4.80 BM, but only 3.08 BM in air. In contrast to the reversible oxygen carrying behaviour in solution discussed above,[989] Weber and Busch found the complex was oxidized in aqueous solution.[986] Reexamination of this system also led to the conclusion that irreversible oxidation takes place.[992] While very dilute solutions ($\sim 10^{-5}$ M) of [FePc] in DMSO slowly fade at a rate proportional to the concentration of oxygen,[977,978] more concentrated solutions form a precipitate[993] on standing which was subsequently identified as a Fe^{III} μ-oxo dimer.[994] In sulfuric acid, a kinetic study showed[995] the initial reaction of [FePc] with oxygen is reversible and the species formed decomposes irreversibly with formation of Fe^{3+} and oxidation of the macrocycle. Two crystalline forms of the μ-oxo dimer have been claimed on the basis of X-ray powder patterns and magnetic properties,[996] but the results of Mössbauer experiments indicated[997] that one of these is in fact a mixture of two species —perhaps a small amount of the μ-oxo dimer with an unidentified low-spin iron(II) complex. The quadrupole splitting for $[(FePc)_2O]$ is the smallest so far reported for a μ-oxo-bridged iron dimeric species. ESR data have also been interpreted[998] in terms of only one species. However, other evidence has very recently been presented[999] for the presence of two compounds. Preparatively, solid $[(FePc)_2O]$ is best obtained by the interaction of oxygen with [FePc] suspended in DMF or other solvents. The soluble substituted complex $[FePcR_4]$ (R = dodecylsulfonamide) forms $[(FePcR_4)_2O]$, which when irradiated with visible light is photoreduced to the iron(II) complex.[1000] Reaction with bases such as imidazole similarly causes reduction, and bis-base iron complexes are formed.[1000] $[(FePc)_2O]$ itself oxidizes PPh_3 to $OPPh_3$ in the presence of pyridine under mild conditions[1001] as in equation (93), and [FePc] is a catalyst for PPh_3 oxidation at room temperature if high pressures of oxygen are used.[1002]

$$[(FePc)_2O] + PPh_3 \xrightarrow{py} 2[FePcpy_2] + OPPh_3 \quad (93)$$

Reaction of $[(FePc)_2O]$ or [FePc] with NaN_3 in 1-chloronaphthalene affords[1003] the highly insoluble, but stable, nitrido-bridged complex $[(FePc)_2N]$, which is more resistant to reduction than $[(FePc)_2O]$. Oxidation of $[(FePc)_2N]$ by strong oxidizing agents causes one-electron oxidation, and a PF_6^- salt can be crystallized in the presence of pyridine: $[(pyFePc)_2N]^+PF_6^-$. The electrochemistry of both $[(FePc)_2O]$ and $[Fe(Pc)_2N]$ in pyridine has been examined in considerable detail.[1004] A range of six-coordinate iron(III) phthalocyanine complexes of the type $[FePcL_2]^-$ ($L = OH^-$, OPh^-, NCO^-, NCS^-, N_3^-, CN^-) have been reported[1005–1007] that are low-spin with magnetic moments 2.05–2.49 BM. With halide and oxygen donor ligands five-coordinate complexes are formed [FePcX]

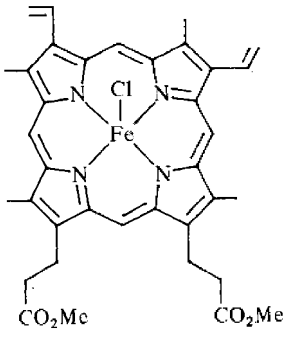
(X = Cl, Br, I, RCO_2, RSO_3) that have magnetic moments 3.9–4.53 BM indicative of $S = \frac{3}{2}$ or mixed spin states ($S = \frac{3}{2}, \frac{5}{2}$). Work on iron(III) phthalocyanine complexes has been hampered by their intractable nature and the use of derivatives soluble in organic solvents is likely to facilitate characterization. Recent examples of such ligands include a phthalocyanine having a long chain ester substituent (**132**) with R = $O_2C(CH_2)_9Me$. On the basis of magnetic (4.4 BM in CH_2Cl_2 and 5.0 BM in $CHCl_3$) and ESR results, the iron complex is assigned the +3 oxidation state. The mono-imidazole complex is also high-spin, but the bis-imidazole species is low spin. The formation constants for this process have $K_1 \gg K_2$.[1008,1009] The iron(III) complex of (**132**) (R = $O_2C(CH_2)_9Me$) and related phthalocyanines appears[1010] to coexist in high- and low-spin forms. Much needed X-ray structural data on iron(III) phthalocyanine complexes is now becoming available, for instance the structure of $[FePc(CN)_2]^-$ has been reported.[1011] Others are the products of [FePc] oxidation by iodine in hot chloronaphthalene: [FePcI] and a dimer $[FePcCl]_2I_2$. The former is a one dimensional molecular conductor that is best formulated as $[FePc]^{1/3+}$ $\frac{1}{3}(I_3^-)$ in which there are I_3^- chains. The dimer has a structure in which the chlorine atoms have been abstracted from the solvent. In this five-coordinate iron(III) complex, the iron atom is 0.3 Å above the plane of the inner nitrogens and the phenylene rings are slightly bent away from the iron atoms.[1012]

44.1.5.12.5 Porphyrins

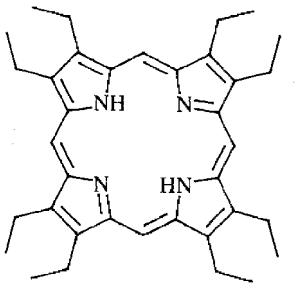
The iron porphyrins and related compounds constitute an extremely important class of coordination complex due to their chemical behaviour and involvement in a number of vital biological systems. Over recent years a vast amount of work on them has been published. Chapter 21.1 deals with the general coordination chemistry of metal porphyrins, hydroporphyrins, azaporphyrins, phthalocyanines, corroles, and corrins. Low oxidation state iron porphyrin complexes are discussed in Section 44.1.4.5 and those containing nitric oxide in Section 44.1.4.7, while a later section in this chapter (44.2.9.2) is mainly concerned with iron(III) and higher oxidation state porphyrin complexes. Inevitably however, a considerable amount of information on iron(II) complexes is contained in that section as well as in Chapter 21.1. Therefore in order to prevent excessive duplication, the present section is restricted to highlighting some of the more important aspects of the coordination chemistry of the iron(II) porphyrins while the related unusually stable phthalocyanine complexes are discussed in the previous section.

Much of the older work (including some useful practical procedures) concerned with natural iron porphyrins is contained in Falk's classic book 'Porphyrins and Metalloporphyrins', which was published in 1964.[1013] Subsequently an enlarged multiauthor edition appeared[1014] that covered the literature to the end of 1974. Since then a number of reviews concerned with iron porphyrins have been published.[1015–1022] The most important recent books are the seven volumes entitled 'The Porphyrins' edited by Dolphin,[1015] and 'Iron Porphyrins' edited by Lever and Gray,[1016] while Berezin's book[1017] is a useful guide to some of the less familiar Russian literature.

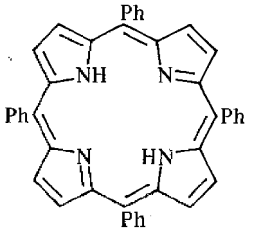
The most widely studied natural complexes are those of protoporphyrin IX whose chloro iron(III) complex is readily available. This is often used as its dimethyl ester which is also commercially available and is known as hemin ester (**133**) and which is soluble in organic solvents. However, this and related compounds suffer irreversible photodegradation in the presence of oxygen, while water soluble derivatives are susceptible to acid-catalyzed hydration of the reactive vinyl substituents (the so-called mesoporphyrin has ethyl groups instead of vinyl groups). Moreover, until comparatively recently the exact nature of the species present in aqueous solutions was often poorly defined. Therefore the use of more stable and better characterized synthetic porphyrins in nonaqueous media has usually been preferred. The iron complexes of octaethylporphyrin (**134**) (OEP), 5,10,15,20-tetraphenylporphyrin (**135**) (TPP) and its derivatives are among the most widely studied, with TPP complexes being the most popular. A further problem with many metalloporphyrins is that they dimerize or aggregate in solution. The extent and type of aggregation depend on several parameters, but in general TPP complexes do not show these effects as markedly as natural porphyrins.[1023] Purple H_2TPP and its derivatives are prepared[1024] by the often vigorous reaction of pyrrole with benzaldehyde or another aromatic aldehyde. Although simple to perform, these reactions afford only moderate yields of product that may be freed from chlorin by chromatography on alumina. It is usual to insert iron(III) into the preformed macrocycle using acetic acid or DMF as solvent. Reduction of [XFeTPP] (typical X = Cl) by chromium(II),[1025] borohydride[1026] *etc.* gives the iron(II) complex. This can also be obtained[1027] from the free ligand *via* reaction with freshly prepared iron(II) propionate in propionic acid. Solid [FeTPP] is best purified by vacuum sublimation, which gives lustrous dark blue crystals; in noncoordinating solvent it is air sensitive.[1028] The solid-state



(133)



(134)



(135)

structure[1029] of [FeTPP] crystallized from benzene/ethanol has Fe—N bond lengths (1.97 Å) characteristic of an intermediate $S = 1$ spin state that is consistent with a room temperature magnetic moment of ~4.4 BM and low temperature Mössbauer data obtained in large magnetic fields. The structure has a slightly ruffled core with the phenyl rings rotated ~10° from being perpendicular to the porphyrin core. Other iron(II) four-coordinate porphyrins also have $S = 1$. The magnetic behaviour of readily purified [FeTPP] has been thoroughly investigated and this work has recently been reviewed.[1030] The structure of iron(II) octaethylporphyrin has been reported[1031] and compared with that of the corresponding chlorin. Both, like [FeTPP], have intermediate $S = 1$ spin states. Overall, however, there is surprisingly little published magnetic data for iron(II) porphyrins compared with that available for the iron(III) complexes.

Like related complexes, [FeTPP] reacts with many nitrogen bases to give low-spin bis-base species. The stability of these complexes is such that even refluxing iron(III) [ClFeTPP] in piperidine affords[1032] [Fe(TPP)(pip)$_2$] *via* a poorly understood process which may involve an axial radical ligand.[1033,1034] In the presence of pyridine addition of OH^- also induces reduction.[1035] This may involve addition of OH^- to coordinated pyridine.[1036] The structure of [Fe(TPP)(pip)$_2$] has been determined[1037] by X-ray methods and the rather long Fe—N(pip) bond distance of 2.127 Å attributed to steric interaction involving the piperidine NH. With bases having even stronger steric effects, such as 2-methylimidazole, mono-base high-spin five-coordinate complexes result[1038] that in this instance have a significantly shorter Fe—N(base) distance of 2.014 Å. In this complex the iron centre is displaced from the porphyrin core by about 0.5 Å, and there is also substantial doming of the porphyrin core itself.[1039] The molecular packing of [Fe(TPP)(2-Meimid)] has been examined in considerable detail[1040] The iron is similarly displaced from the macrocycle in [(ON)Fe(TPP)] (about 0.2 Å), which has a bent NO and is best described as a low-spin iron(II) complex.[1041,1042] Nitric oxide complexes of this type are capable of binding[1043] an axial nitrogen or sulfur ligand so becoming six-coordinate. The Mössbauer spectra of several five-coordinate protoporphyrin IX iron(II) complexes in frozen aqueous solutions display[1044] large quadrupole splittings (4.0 to 4.4 mm s^{-1}). The largest value is with acetone, but this complex is incompletely formed. The splitting order for the more stable complexes is F^- > catechol < phenol. In dichloroethylene the formation constant for the reaction[1045] of F^- with [Fe(TPP)] is ~600 M^{-1}. In organic solvents such as chloroform and benzene, iron(II) porphyrins are free of axial ligands and there have been several studies concerned with the thermodynamics of binding axial nitrogen bases, both in non-coordinating and donor solvents that are ligand replacement reactions (equations 94 and 95). The results of some early work[1046] concerned with measuring stability constants for these reactions may be in error due to incomplete reduction of iron(III) by hydrazine monohydrate. The successive equilibrium constants[1047] for binding pyridine to [Fe(TPP)] in benzene are $K_1 \sim 1.5 \times 10^3\ M^{-1}$ and $K_2 \sim 1.9 \times 10^4\ M^{-1}$ respectively. The larger value for K_2 is in keeping with the monopyridine complex being high-spin and the extra stability of the final product being associated with a transition to the low-spin state. In this instance the monopyridine intermediate is five-coordinate and may have a structure similar to that of [Fe(TPP)(2-Meimid)] with the iron centre displaced from the porphyrin plane. The redox self exchange rates for [Fe(por)B$_2$] complexes are rapid and rate constants for this process $\{Fe^{III}/Fe^{II}\}$ do not vary in a regular fashion with steric hindrance on the periphery of the macrocycle,[1052] although it is thought[1048,1049] electron transfer takes place *via* the edge of the macro-

$$[Fe(por)] + B \longrightarrow [Fe(por)B] \quad (94)$$

$$[Fe(por)B] + B \longrightarrow [Fe(por)B_2] \quad (95)$$

cycle in natural systems such as cytochromes.[1050,1051] The rates of thermal ligand substitution reaction are within the stopped flow range[1053] but photodissociation is extremely rapid and it appears only one ligand is released on excitation of the six-coordinate complex,[1054] in the primary process. The overall recombination kinetics can be complex due to spontaneous dissociation of the first formed five-coordinate complex.

Cyanide ion binds strongly[1056] to iron(II) porphyrins to give complexes typified by $[Fe(por)(CN)_2]^{2-}$ that are low-spin. In DMSO the intermediate complex $[Fe(por)(CN)(DMSO)]^-$ appears relatively stable. The self exchange rate for $[Fe(TPP)(CN)_2]^{2-/-}$ in DMSO is $5.8 \times 10^7 M^{-1}s^{-1}$ (27 °C) while cyanide exchange is relatively slow. The bis(isocyanide) complex $[Fe(TPP)(Bu^tNC)_2]$ has Fe—C bond distances of 1.90 Å and the Fe—C—N angle is significantly less than 180°, which may result from packing effects.[1058] Sulfur donors may also act as axial ligands; the X-ray structure analysis of the thioether complex $[Fe(TPP)(THT)_2]$ shows an Fe—S distance of 2.338 Å, very similar to that in related iron(III) systems.[1059,1060] With weak field axial oxygen donor ligands iron(II) porphyrins are usually high-spin, kinetically labile and susceptible to air oxidation (see below). In THF it appears [FeTPP] is mainly in the form of the five-coordinate species [Fe(TPP)(THF)].[1047] However, it is possible to crystallize $[Fe(TPP)(THF)_2]$ and, as might be expected, it contains[1061] substantially longer Fe—O bonds (2.31 Å) than do related low-spin complexes. Both bis-phosphite and bis-phosphine iron(II) porphyrins are low-spin, and Mössbauer data for a series of these complexes have been interpreted[1062] in terms of changes of the axial ligands causing substantial changes in the iron–porphyrin bonding. Thus the macrocycle ligand tends to act as an electron sink.[1063,1064] Aliphatic hydroxylamines react with [Fe(TPP)Cl] in the presence of pyridine to give[1065] the corresponding iron(II) pyridine nitroso complex. This reaction is shown in equation (96) for isopropylhydroxylamine, and treatment of the product with additional pyridine liberates acetone oxime with formation of $[Fe(TPP)(py)_2]$ as in equation (97).

$$[Fe(TPP)Cl] + Me_2CHNOH/py \longrightarrow [Fe(TPP)(py)(Me_2CHNO)] \quad (96)$$

$$[Fe(TPP)(py)(Me_2CHNO)] + py \longrightarrow [Fe(TPP)(py)_2] + Me_2CNOH \quad (97)$$

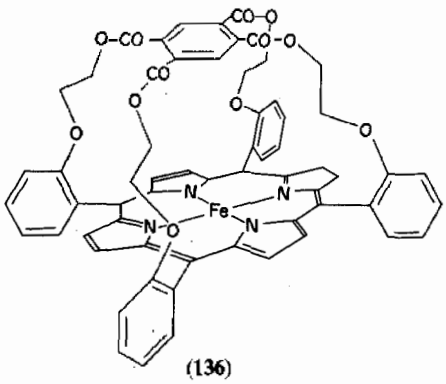
Carbon monoxide reacts[1066] with [Fe(TPP)] in toluene to give apparently low-spin [Fe(TPP)CO] and $[Fe(TPP)(CO)_2]$ with successive equilibrium constants of 6.6×10^4 and 140 respectively at 20 °C. Similar values have been reported for reaction of carbon monoxide with natural porphyrins.[1028,1067,1068] Simple bis-nitrogen base iron(II) porphyrins in noncoordinating solvents react with carbon monoxide as in equation (98) to give monocarbonyl complexes. The thermodynamics and kinetics for por = TPP have been studied[1069] in detail as well as for more complex sterically hindered porphyrins (see below). Considerable attention has been given to the reversible oxygenation of iron(II) porphyrins due to the importance of haemoglobin and related natural systems.[1070] (For an excellent review of the non-haem oxygen carrier hemerythrin, see ref. 1071). The unliganded iron(II)–porphyrin complexes, in the absence of a reducing agent, react with oxygen to form iron(III) μ-oxo dimers. The dimer $[(FeTPP)_2O]$ is now well characterized[1072] and intermediate adducts of the type $[Fe(TPP)O_2]$ have been observed[1073] using matrix isolation techniques. In the presence of excess nitrogen base there is no reaction with oxygen, but the simple bis complexes $[Fe(por)L_2]$ in dichloromethane at low temperatures (−79 °C) undergo oxygenation according to equation (99) that is reversed when the solution is purged with nitrogen. Solvent effects are important in this process. Thus in contrast to the behaviour in dichloromethane, oxygenation of $[Fe(TPP)py_2]$ is not complete in toluene under 1 atm oxygen pressure.[1069]

$$[Fe(por)L_2] + CO \longrightarrow [Fe(por)(CO)L] + L \quad (98)$$

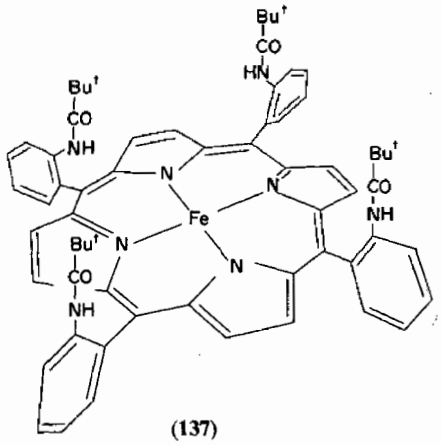
$$[Fe(por)L_2] + O_2 \longrightarrow [Fe(por)(O_2)L] + L \quad (99)$$

The rate determining step in these reactions with oxygen or carbon monoxide is dissociative loss of nitrogenous base from $[Fe(por)L_2]$ to generate a five-coordinate intermediate that rapidly reacts with either oxygen or carbon monoxide to generate the product. The five-coordinate intermediate shows no marked kinetic preference for nitrogen base or oxygen, reflecting the high reactivity of this species. However, in the presence of oxygen and carbon monoxide the five-coordinate intermediate has a kinetic preference for oxygen, although this first formed species subsequently converts to the thermodynamically favoured carbonyl product.[1069] The displacement of oxygen from $[Fe(TPP)(L)(O_2)]$ is also dissociative[1074] with the kinetic *trans* effect of L being pyridine > piperidine ≫ 1-methylimidazole. However, as solutions of the oxygenated complexes are

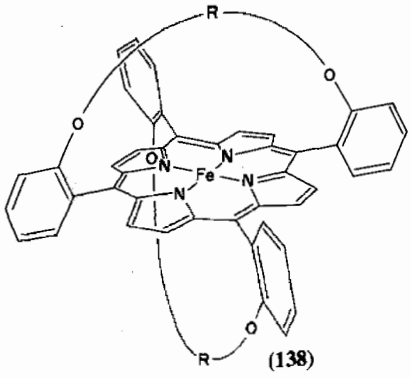
warmed to room temperature, oxidation rather than oxygenation becomes increasingly important. Embedding the porphyrin in a polymer matrix[1075,1076] or attachment to a surface[1077] inhibits μ-oxo dimer formation by physical separation of the iron centres and can yield systems capable of reversibly binding oxygen. Steric protection of the oxygen binding site itself can also inhibit the reactions that result in formation of iron(III) μ-oxo dimers. Examples of such complexes are the 'capped' porphyrins (**136**),[1078–1080] 'picket fence' porphyrins (**137**),[1081] 'basket handle' porphyrins (**138**)[1082] and the 'cyclophane hemes' (**139**)[1083] that have been extensively studied in connection with the biological iron(II) oxygen carriers myoglobin and haemoglobin.



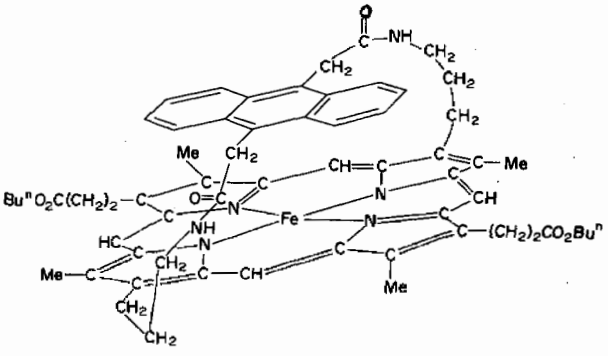
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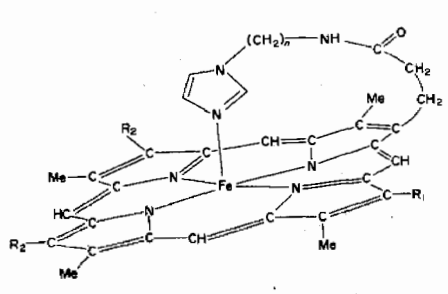


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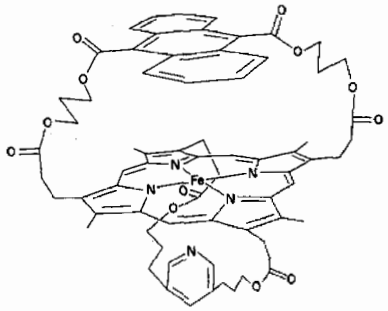


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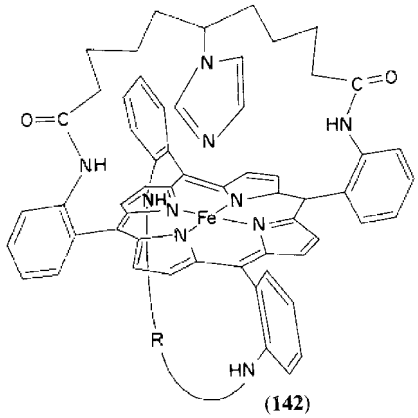
Reversible oxygenation of these complexes in solution usually requires the presence of an added axial ligand such as pyridine or 1-methylimidazole which coordinates to the unprotected face of the porphyrin, and so stops μ-oxo-dimer formation taking place from this side. Thiolate can also fulfil this role[1084–1087] as it does in cytochrome P-450. This fifth ligand site can be conveniently occupied by a nitrogen donor covalently bound to the macrocycle so effectively making the ligand quinquedentate. Complexes of this type include the 'tail base' or 'chelate heme' (**140**),[1088,1089] while those that involve two links to the base forming a more rigid system are typified by the 'double strapped' (**141**)[1090] and 'hanging base' (**142**) complexes.[1091–1093] Rigidity of the strapping groups can favour four- or five-coordination so eliminating the undesired oxidation reactions, but if too rigid, motion of the iron(II) centre can be inhibited resulting in decreased affinity for molecular oxygen.[1094]



(140)



(141)



(142)

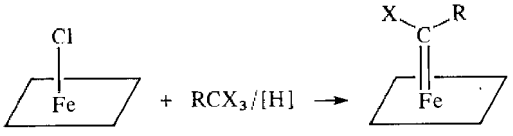
The oxygen-binding properties of model complexes are similar to those of myoglobin and haemoglobin, although their affinity for carbon monoxide is much less than it is for most model complexes. It appears[1095,1096] this is due to steric constaints in the natural oxygen carriers that demand a bent or tilted geometry of the diatomic ligand. This is satisfactory for the inherently bent Fe—O—O group, whereas the linear Fe—C≡O group is significantly destabilized. This 'distal-side' steric hindrance involves imidazole and isopropyl groups in the globin chain. Similar effects have been observed with some sterically demanding model complexes.[1097] The rates of reaction of carbon monoxide with a range of five-coordinate iron(II) porphyrin species have[1098] reduced equilibrium constants for systems with severe steric effects. This is caused by slower reaction with CO rather than a change in the rate of dissociation from the six-coordinate complex.

However, a variety of quite subtle electronic and steric effects may be operative in these processes, including free movement of the iron (and if appropriate doming or ruffling of the macrocycle) when forming the five-coordinate intermediate, polarity and specific interactions such as hydrogen bonding at or near the binding site, as well as the electronic behaviour of the porphyrin and the influence of solvation. The importance of polarity is demonstrated by an amide strapped complex that has an affinity for oxygen an order of magnitude greater than that of the ether analogue,[1099] presumably due to enhanced stabilization of the charged $\{Fe^{III}(O_2)^-\}$ contribution to the oxygenated species. However, care in interpretation in such situations is needed because quite small steric changes can also be important. The nature of the *trans* axial base may also influence the O_2 affinity of iron(II) porphyrins. Early reports[1074,1100] suggested pyridine produces a weaker iron/O_2 interaction than does imidazole. This could be due to the decreased π basicity of pyridine compared with that of imidazole.[1101] With various 'capped' porphyrins the reverse is true[1102] and it has been concluded[1103] that, generally, substitution of pyridine for imidazole does not have large effects on carbon monoxide affinities. However, the relative differences induced by changing the base differ[1104] for binding CO and O_2. Clearly care is needed when trying to separate the importance of small electronic and steric changes in these systems. Often in these studies different solvents have been used. It has been shown[1105] for both an unprotected and a bis-pocket porphyrin[1106] whose 1,2-dimethylimidazole adduct has moderate affinity for reversible oxygenation, that solvent polarity enhances oxygen affinity but decreases carbon monoxide affinity. Here ΔG for oxygenation correlates well with empirical solvent parameters such as π^*. Earlier, it was noted[1107] that π donor/acceptor interactions involving the macrocycle do not influence carbon monoxide binding rates. As expected, the very large binding constants for nitric oxide to a series of iron(II) 'capped' porphyrins to form [Fe(por)(B)(NO)] (with bent Fe—N—O) correlate well with oxygenation data implying similar steric effects.[1108] In the absence of an axial base [Fe(por)(NO)] reacts with excess nitric oxide to give a product formulated[1109] as $[Fe(por)(NO^-)(NO_2^+)]$ as shown in equation (100).

$$[Fe(por)(NO)] + 3NO \longrightarrow [Fe(por)(NO)(NO_2)] + N_2O \qquad (100)$$

Several iron porphyrin carbenes are known[1110] that are obtained by the general reaction of the chloro iron(III) complex with RCX_3 (X = Cl, Br) in the presence of iron powder or sodium dithionite as in equation (101). The air sensitivity of the product depends on the nature[1111,1112] of R. Formally these complexes could be described as iron(II) species. They are diamagnetic, and can bond an additional axial ligand. The structure of the dichlorocarbene complex $[Fe(TPP)(CCl_2)(H_2O)]$ has been determined by X-ray methods,[1113] which showed a short Fe—C distance of 1.83 Å. This complex is reactive and, for instance, with primary amines a coordinated

isocyanide results. A novel bridged, or 'double carbene' [{Fe(TPP)}$_2$C] has been obtained from the use of CBr_4 in the reductive procedure shown in equation (101). Alkyl radicals react with iron(II) porphyrins to form [Fe(por)(R)]. Methyl radicals are captured rapidly, but chloromethyl radicals react slowly and it has been suggested[1114] this is a possible cause for the toxicity of chloromethyl compounds. Reaction of chloro iron(III) complexes with Grignard reagents also affords alkyl derivatives. Chemical oxidation of the phenyl complex [Fe(por)(Ph)] causes migration of the aryl group onto a pyrrolic nitrogen to form an iron(III) N-substituted complex. Reduction induces the reverse reaction, while the metal free N-substituted porphyrin is obtained on demetallation.[1115,1116] These transformations may be viewed as initial oxidation of the metal centre to Fe^{IV}, with the reverse reduction involving oxidative addition of NPh to an iron(I) centre. These and other reactions of an organometallic nature are the subject of a recent review.[1117]



(101)

Acknowledgement

Thanks are due to all of those who provided reprints or preprints, and to J. Burgess and the late S. M. Nelson for information and helpful discussions.

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$RuCl_3(AsPh_3)_2(OAsPh_3)$, 416
$As_3Ru_2C_{63}H_{63}Cl_6$
$[Ru_2Cl_6\{As(C_6H_4Me\text{-}4)_3\}_3]$, 415
$As_4CoC_{12}H_{28}$
$[Co(Me_2AsCH{=}CHAsMe_2)_2]^+$, 769
$As_4CoC_{12}H_{28}Br_2$
$[CoBr_2(Me_2AsCH{=}CHAsMe_2)_3]^+$, 773
$As_4CoC_{12}H_{28}Cl$
$[CoCl(Me_2AsCH{=}CHAsMe_2)_2]^+$, 769
$As_4CoC_{12}H_{32}$
$[Co(Me_2AsCH_2CH_2AsMe_2)_2]^+$, 769
$As_4CoC_{18}H_{34}Br_2$
$[CoBr_2\{1,2\text{-}(Me_2AsCH_2CH_2CH_2AsMe)_2C_6H_4\}]^+$, 774
$As_4CoC_{18}H_{34}O_2$
$[Co(O_2)\{1,2\text{-}(Me_2AsCH_2CH_2CH_2AsMe)_2C_6H_4\}]^+$, 774
$As_4CoC_{18}H_{35}Br$
$CoHBr\{1,2\text{-}(Me_2AsCH_2CH_2CH_2AsMe)_2C_6H_4\}]^+$, 774
$As_4CoC_{18}H_{36}$
$[CoH_2\{1,2\text{-}(Me_2AsCH_2CH_2CH_2AsMe)_2C_6H_4\}]^+$, 774
$As_4CoC_{20}H_{32}$
$[Co(diars)_2]^{2+}$, 772
$As_4CoC_{20}H_{32}BrNO$
$[CoBr(NO)(diars)_2]^+$, 773
$As_4CoC_{20}H_{32}Cl_2$
$[CoCl_2(diars)_2]^+$, 773
$As_4CoC_{20}H_{32}I_2$
$[CoI_2(diars)_2]^+$, 773
$As_4CoC_{20}H_{32}NO$
$[Co(NO)(diars)_2]^+$, 773
$As_4CoC_{20}H_{32}O_2$
$[Co(O_2)(diars)_2]^+$, 773, 784
$As_4CoC_{20}H_{32}O_8Cl_2$
$Co(OCl_3)_2(diars)_2$, 772
$As_4CoC_{20}H_{33}Cl$
$[CoHCl(diars)_2]^+$, 773
$As_4CoC_{20}H_{34}$
$[CoH_2(diars)_2]^+$, 773, 784
$As_4CoC_{20}H_{35}O$
$[CoH(H_2O)(diars)_2]^{2+}$, 773
$As_4CoC_{20}H_{36}O_2$
$[Co(H_2O)_2(diars)_2]^{3+}$, 772, 784
$As_4CoC_{21}H_{33}O_3$
$[Co(CO_3)(diars)_2]^+$, 773
$As_4CoC_{22}H_{32}N_2S_2$
$Co(NCS)_2(diars)_2$, 769
$As_4CoC_{22}H_{38}O_2$
$[CoMe_2(diars)_2]^+$, 773
$As_4CoC_{24}H_{38}Cl_2$
$[CoCl_2\{(Me_2As(CH_2)_3AsPhCH_2\}_2]]^+$, 773, 784
$As_4CoC_{24}H_{38}O_2$
$[Co(O_2)\{(Me_2As(CH_2)_3AsPhCH_2\}_2]]^+$, 773, 784
$As_4CoC_{24}H_{42}O_2$
$[Co\{(Me_2As(CH_2)_3AsPhCH_2\}_2](H_2O)_2]^{3+}$, 784
$As_4CoC_{40}H_{64}BrNO$
$[Co(NO)Br(diars)_2]^+$, 666
$As_4CoC_{40}H_{64}ClNO$
$[Co(NO)Cl(diars)_2]^+$, 658
$[Co(NO)Cl(diars)_2]^{2+}$, 658
$As_4CoC_{40}H_{64}NO$
$[Co(NO)(diars)_2]^{2+}$, 658, 661, 664
$As_4CoC_{41}H_{64}N_2OS$
$[Co(NO)(NCS)(diars)_2]^+$, 661, 664
$As_4CoC_{53}H_{44}NS$
$[Co(NCS)(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 769
$As_4CoC_{72}H_{61}$
$[CoH(AsPh_3)_4]^-$, 769
$As_4FeC_{12}H_{36}ClO_8$
$[Fe(OAsMe_3)_4(ClO_4)]^+$, 1183, 1237
$As_4FeC_{12}H_{36}S_4$
$[Fe(SAsMe_3)_4]^{2+}$, 1240
$As_4FeC_{15}H_{36}Cl_2$
$[Fe\{As(CH_2CH_2CH_2AsMe_2)_3\}Cl_2]^+$, 226
$As_4FeC_{20}H_{32}Cl_2$
$[Fe(diars)_2Cl_2]^{2+}$, 1183, 1187
$As_4IrC_{64}H_{64}NOP_2$
$[Ir(NO)\{1,4\text{-}\{(Ph_2AsCH_2CH_2)_2PCH_2\}_2C_6H_4\}]^+$, 1114
$As_4IrC_{64}H_{64}P_2$
$[Ir\{1,4\text{-}\{(Ph_2AsCH_2CH_2)_2PCH_2\}_2C_6H_4\}]^+$, 1113
$As_4IrC_{64}H_{66}P_2$
$[IrH_2\{1,4\text{-}\{(Ph_2AsCH_2CH_2)_2PCH_2\}_2C_6H_4\}]^+$, 1114
$As_4IrC_{65}H_{64}OP_2$
$[Ir(CO)\{1,4\text{-}\{(Ph_2AsCH_2CH_2)_2PCH_2\}_2C_6H_4\}]^+$, 1114
$As_4IrC_{72}H_{57}P$
$[Ir(PPh_3)\{As(C_6H_4AsPh_2\text{-}2)_3\}]^-$, 1135
$As_4IrC_{72}H_{61}P_4$
$IrH(AsPh_3)_4$, 1119
$As_4MnC_{72}H_{60}ClO_8$
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$As_4OsC_{20}H_{32}ClNO$
$[Os(NO)(diars)_2Cl]^{2+}$, 547
$As_4OsC_{20}H_{32}ClN_2$
$[Os(N_2)(diars)_2Cl]^+$, 555, 565
$As_4OsC_{20}H_{32}ClN_3$
$Os(N_3)(diars)_2Cl$, 565
$As_4OsC_{20}H_{32}Cl_2$
$[Os(diars)_2Cl_2]^{2+}$, 579
$As_4OsC_{22}H_{32}N_2S_2$
$Os(diars)_2(SCN)_2$, 566
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$[Os(bipy)(diars)_2]^{2+}$, 540
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$As_4OsC_{54}H_{42}Cl_2$
$Os\{As(C_6H_4AsPh_2\text{-}2)_3\}Cl_2$, 579
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$Rh_2Cl_3(\mu\text{-}H)(\mu\text{-}CO)(dpam)_2$, 941
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$[ReCl_2(diars)_2]^+$, 162
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$ReH_3(Ph_2AsCH_2CH_2AsPh_2)_2$, 150
$As_4Re_2C_{72}H_{68}$
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$As_4Re_3C_{68}H_{66}Cl_9P_2$
$Re_3Cl_9\{(Ph_2AsCH_2CH_2)_2PPh\}_2$, 162
$As_4RhC_{20}H_{32}ClNO_3$
$[RhCl(NO_3)(diars)_2]^+$, 1040
$As_4RhC_{20}H_{32}Cl_2$
$[RhCl_2(diars)_2]^+$, 1039, 1040
$As_4RhC_{20}H_{32}O_4S$
$[Rh(SO_4)(diars)_2]^+$, 1040
$As_4RhC_{20}H_{33}Cl$
$[RhHCl(diars)_2]^+$, 1037
$As_4RhC_{21}H_{35}ClO_2S$
$[RhCl(O_2SMe)(diars)_2]^+$, 1040
$As_4RhC_{26}H_{36}ClNO_4S$
$[RhCl(4\text{-}O_2SC_6H_4NO_2)(diars)_2]^+$, 1040
$As_4RhC_{26}H_{37}ClO_2S$
$[RhCl(O_2SPh)(diars)_2]^+$, 1040
$As_4RhC_{27}H_{39}ClO_2S$
$[RhCl(4\text{-}O_2SC_6H_4Me)(diars)_2]^+$, 1040
$As_4RhC_{52}H_{44}S_2$
$[RhS_2(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 1037
$As_4RhC_{52}H_{45}Cl$
$[RhHCl(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 1037
$As_4RhC_{52}H_{46}$
$[RhH_2(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 1037
$As_4RhC_{53}H_{47}ClO_2S$
$[RhCl(O_2SMe)(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 1040
$As_4RhC_{58}H_{49}ClO_2S$
$[RhCl(O_2SPh)(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 1040
$As_4RhC_{59}H_{55}ClO_2S$
$[RhCl(4\text{-}O_2SC_6H_4Me)(Ph_2AsCH_2CH_2AsPh_2)_2]^+$, 1040
$As_4Rh_2C_{24}H_{60}Cl_6$
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$As_4Rh_2C_{51}H_{44}Cl_2O$
$Rh_2Cl_2(\mu\text{-}CO)(dpam)_2$, 941
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$As_4Rh_2C_{68}H_{64}Cl_2$
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$[RuCl(NH_3)(diars)_2]^+$, 391
$As_4RuC_{20}H_{32}ClNO$
$[RuCl(NO)(diars)_2]^{2-}$, 394
$As_4RuC_{20}H_{32}ClNO_2$
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$As_4RuC_{20}H_{32}Cl_2$
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$[RuCl_2(diars)_2]^+$, 418
$As_4RuC_{20}H_{32}INO$
$[RuI(NO)(diars)_2]^{2+}$, 394
$As_4RuC_{20}H_{32}N_6$
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$As_4RuC_{24}H_{44}P_2S_4$
$Ru(S_2PMe_2)_2(diars)_2$, 405
$As_4RuC_{32}H_{44}Cl_2$
$RuCl_2(AsMe_2Ph)_4$, 379
$As_4RuC_{50}H_{44}Cl_3NO$
$RuCl_3(NO)(dpam)_2$, 393
$As_4RuC_{52}H_{44}Cl_2$
$RuCl_2(Ph_2AsCH{=}CHAsPh_2)_2$, 379
$As_4RuC_{52}H_{44}Cl_2O_2$
$RuCl_2(CO)_2(dpam)_2$, 383
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$RuHCl(Ph_2AsCH_2CH_2AsPh_2)_2$, 453
$As_4RuC_{54}H_{42}Br_2$
$RuBr_2\{As(C_6H_4AsPh_2\text{-}2)_3\}$, 380
$As_4RuC_{54}H_{44}N_2$
$Ru(CN)_2(Ph_2AsCH{=}CHAsPh_2)_2$, 282
$As_4RuC_{64}H_{64}ClP_2$
$[RuCl\{1,4\text{-}\{(Ph_2AsCH_2CH_2)_2PCH_2\}_2C_6H_4\}]^+$, 377
$As_4Ru_2C_{52}H_{48}Cl_5$
$Ru_2Cl_5(Ph_2AsCH_2CH_2AsPh_2)_2$, 415
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$\{RuI_2(NO)(AsMePh_2)_2\}_2$, 374
$As_4Ru_2C_{54}H_{48}Cl_4O_2$
$\{RuCl_2(CO)(Ph_2AsCH_2CH_2AsPh_2)\}_2$, 413
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$[\{RuCl_2(AsPh_3)_2\}_2(\mu\text{-}O_2)]^{2+}$, 401
$As_4Ru_2C_{72}H_{60}Cl_5$
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$[Mn(Me_3AsO)_5]^{2+}$, 40
$As_6CoC_{18}H_{42}$
$[Co(Me_2AsCH{=}CHAsMe_2)_3]^{3+}$, 773
$As_6CoC_{30}H_{48}$
$[Co(diars)_3]^{3+}$, 773
$As_6CoC_{34}H_{46}$
$[Co\{MeAs(C_6H_4AsMe_2\text{-}2)_2\}_2]^{2+}$, 772
$As_6CoC_{42}H_{54}$
$[Co\{1,8\text{-}(Me_2As)_2C_{10}H_6\}_3]^{2+}$, 772
$As_6Co_2C_{82}H_{81}$
$\{Co\{MeC(CH_2AsPh_2)_3\}\}_2(\mu\text{-}H)_3$, 769, 773
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$Ir_2Cl_2(CO)_2\{PhAs(CH_2AsPh_2)_2\}_2$, 1164
$As_6Ir_2PdC_{80}H_{72}Cl_3O_2$
$[Ir_2PdCl_3(CO)_2\{PhAs(CH_2AsPh_2)_2\}_2]^+$, 1164
$As_6OsC_{75}H_{66}N_2S_2$
$Os(SCN)_2(dpam)_3$, 579
$As_6RhC_{34}H_{46}$
$[Rh\{MeAs(C_6H_4AsMe_2\text{-}2)_2\}_2]^{3+}$, 1044
$As_6Rh_2C_{78}H_{72}Cl_6$
$Rh_2Cl_6(Ph_2AsCH_2CH_2AsPh_2)_3$, 1025
$As_6RuC_{75}H_{66}Cl_2P_6$
$RuCl_2(Ph_2AsCH_2AsPh_2)_3$, 380
$As_6Ru_2C_{108}H_{90}Cl_4O_2$
$[\{RuCl_2(AsPh_3)_3\}_2(\mu\text{-}O_2)]^{2-}$, 416
$As_8Co_2C_{40}H_{68}O_2$
$[\{Co(H_2O)(diars)_2\}_2]^{4+}$, 772
$As_{12}Co_3C_{164}H_{156}I_6$
$Co_3\{MeC(CH_2AsPh_2)_3\}_4I_6$, 769
$AuFeC_{21}H_{15}NO_4P$
$AuFe(CO)_3(NO)(PPh_3)$, 1189
$AuFeC_{38}H_{30}NO_3P_2$
$AuFe(CO)_2(NO)(PPh_3)_2$, 1189
$AuIrC_{65}H_{71}N_3P_4$
$[Ir(CNBu^t)_3(\mu\text{-}dppm)_2Au]^{2+}$, 1163
$AuRhC_{18}H_{15}F_{12}P_5$
$Rh(PF_3)_4AuPPh_3$, 904
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$Co(BH_4)(terpy)$, 686, 691
$BCoC_{36}H_{34}P_2$
$Co(BH_4)(PPh_3)_2$, 702
$BCoC_{36}H_{71}P_2$
$CoH(BH_4)\{P(C_6H_{11})_3\}_2$, 702, 704
$BCoC_{54}H_{49}N_2P_3$
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$BCoC_{54}H_{49}P_3$
$Co(BH_4)(PPh_3)_3$, 702
$BCoC_{55}H_{49}NP_3$
$CoH(BH_3CN)(PPh_3)_3$, 702
$BFeC_{16}H_{34}F_4N_4$
[Fe(hexamethyl-1,4,8,11-tetraazacyclotetradecane)-$(BF_4)]^+$, 1251

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$[Fe\{FB(ON{=}CC_5H_3N)_3P\}]^{2+}$, 1232
$BIrAsC_{23}H_{33}Cl_2N_6$
$IrCl_2\{HB(NN{=}CMeCH{=}CMe)_3\}(AsPhMe_2)$, 1134
$BIrC_8H_8N_4O_2$
$Ir(CO)_2\{H_2B(NN{=}CHCH{=}CH)_2\}$, 1108
$BIrC_{12}H_{16}N_4O_2$
$Ir(CO)_2\{H_2B(NN{=}CMeCH{=}CMe)_2\}$, 1108
$BIrC_{18}H_{47}P_2$
$IrH_2(BH_4)(PBu^t{}_2Me)_2$, 1149
$BIrC_{19}H_{27}F_6N_6O_5$
$Ir(O_2CCF_3)_2\{HB(NN{=}CMeCH{=}CMe)_3\}(H_2O)$, 1134
$BIrC_{20}H_{29}ClN_6O_2$
$Ir(acac)Cl\{HB(NN{=}CMeCH{=}CMe)_3\}$, 1134
$BIrC_{36}H_{31}ClF_4N_2P_2$
$IrHCl(FBF_3)(N_2)(PPh_3)_2$, 1105
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$Ir(CO)(NCBH_3)\{P(C_6H_{11})_3\}_2$, 1108
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$BOsC_{36}H_{73}P_2$
$Os(BH_4)H_3\{P(C_6H_{11})_3\}_2$, 616
$BReBr_7N$
$[Re(NBBr_3)Br_4]^-$, 194
$BReC_{27}H_{25}Cl_2N_6P$
$ReCl_2(PPh_3)\{HB(NN{=}CHCH{=}CH)_3\}$, 154
$BRhC_9H_{11}Cl_2N_6$
$[Rh\{HB(NN{=}CHCH{=}CH)_3\}Cl_2H]^-$, 1012
$BRhC_{10}H_{10}I_2N_6O$
$Rh\{HB(NN{=}CHCH{=}CH)_3\}(CO)I_2$, 1012
$BRhC_{10}H_{14}Cl_2N_6O$
$Rh\{HB(NN{=}CHCH{=}CH)_3\}Cl_2(MeOH)$, 1012
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$RhMeI(F_2BON{=}CEtCMe{=}N(CH_2)_3N{=}CEtCMe{=}NO)$, 1014
$BRhC_{21}H_{26}P$
$RhH(BH_4)\{P(C_6H_4Me\text{-}2)_3\}$, 932
$BRhC_{30}H_{38}O_6P_2$
$[Rh(BPh_4)\{P(OMe)_3\}_2]$, 930
$BRhC_{36}H_{72}P_2$
$RhH_2(BH_4)\{P(C_6H_{11})_3\}_2$, 1022
$BRhC_{42}H_{36}ClO_2P_2$
$RhHCl(2\text{-}OC_6H_4OBH)(PPh_3)_2$, 1018
$BRuCH_{18}N_6$
$[Ru(BH_3CN)(NH_3)_5]^+$, 282
$[Ru(BH_3CN)(NH_3)_5]^{2+}$, 282
$BRuC_9H_{32}P_3$
$RuH(\eta^2\text{-}BH_4)(PMe_3)_3$, 454
$BRuC_{18}H_{18}N_8$
$[Ru\{B(NN{=}CHCH{=}CH)_4\}(C_6H_6)]^+$, 356
$BRuC_{26}H_{31}P_2$
$RuH(\eta^2\text{-}BH_4)(PMePh_2)_2$, 454
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$RuH(\eta^2\text{-}BH_4)\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 454
$BRuC_{37}H_{71}OP_2$
$RuH(BH_4)(CO)\{P(C_6H_{11})_3\}_2$, 457
$BRuC_{39}H_{30}NO_2P_2$
$RuH(BH_3CN)(CO)_2(5\text{-}Ph\text{-}dibenzophosphole)_2$, 457
$BRuC_{54}H_{50}P_3$
$RuH(BH_4)(PPh_3)_3$, 454
$BRuC_{55}H_{50}OP_3$
$RuH(BH_4)(CO)(PPh_3)_3$, 457
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$Fe(CNH)_4(CNBF_3)_2$, 1205
$B_2FeC_{14}H_{42}N_2O_{12}P_4$
$Fe(BH_2CN)_2\{P(OMe)_3\}_4$, 1234
$B_2Ir_2C_{30}H_{44}Cl_4N_{12}$
$\{IrCl_2\{HB(NN{=}CMeCH{=}CMe)_3\}\}_2$, 1134
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$\{RhCl\{HB(NN{=}CHCH{=}CH)_3\}\}_2(\mu\text{-}Cl)_2$, 1012
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$B_6FeC_6F_{18}N_6$
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$B_8IrC_{55}H_{54}P_3$
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$PtB_8H_{10}IrH(CO)(PMe_3)_4$, 1165
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$OsB_{10}H_8(PMe_2Ph)_2(OEt)_2$, 616
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$Os_2Cl_2(PPh_3)_2(PMe_2Ph)_2B_{10}H_8(OEt)_2$, 616
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$RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$, 451
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$Co(HDMG)_2(AsMe_2)$, 774
$CoAsC_{15}H_{23}ClN_4O_5$
$CoCl\{As(OH)MePH\}(HDMG)_2$, 774
$CoAsC_{18}H_{16}N_2$
$CoH(N_2)(AsPh_3)$, 769
$CoAsC_{20}H_{15}NO_3$
$Co(NO)(CO)_2(AsPh_3)$, 660
$CoAsC_{27}H_{49}N_4O_4P$
$Co(HDMG)_2(PBu_3)(AsMePh)$, 775
$CoAsFeMoWC_2H_6S$
$CoFeMoWS(AsMe_2)$, 832
$CoAsH_{16}N_5O_4$
$[Co(OAsO_3H)(NH_3)_5]^+$, 775
$CoAsH_{18}N_5O_4$
$[Co(OAsO_3H_3)(NH_3)_5]^{3+}$, 775
$CoAs_2C_{26}H_{22}I_2$
$CoI_2(Ph_2AsCH{=}CHAsPh_2)$, 769
$CoAs_2C_{26}H_{24}Cl_2$
$CoCl_2(Ph_2AsCH_2CH_2AsPh_2)$, 769
$CoAs_2C_{36}H_{30}I_2$
$CoI_2(AsPh_3)_2$, 769
$CoAs_2C_{40}H_{30}N_4$
$[Co(CN)_4(AsPh_3)_2]^-$, 773
$CoAs_3C_{17}H_{23}Cl_3$
$CoCl_3\{MeAs(C_6H_4AsMe_2\text{-}2)_2\}$, 774
$CoAs_3C_{43}H_{39}O_2$
$[Co\{MeC(CH_2AsPh_2)_3\}(CO)_2]^+$, 769, 773
$CoAs_3C_{54}H_{48}$
$CoH_3(AsPh_3)_3$, 769
$CoAs_4C_{12}H_{28}$
$[Co(Me_2AsCH{=}CHAsMe_2)_2]^+$, 769
$CoAs_4C_{12}H_{28}Br_2$
$[CoBr_2(Me_2AsCH{=}CHAsMe_2)_2]^+$, 773
$CoAs_4C_{12}H_{32}$
$[Co(Me_2AsCH_2CH_2AsMe_2)_2]^+$, 769
$CoAs_4C_{18}H_{34}Br_2$
$[CoBr_2\{1,2\text{-}(Me_2AsCH_2CH_2CH_2AsMe)_2C_6H_4\}]^+$, 774
$CoAs_4C_{18}H_{34}O_2$
$[Co(O_2)\{1,2\text{-}(Me_2AsCH_2CH_2CH_2AsMe)_2C_6H_4\}]^+$, 774
$CoAs_4C_{18}H_{35}Br$
$CoHBr\{1,2\text{-}(Me_2AsCH_2CH_2CH_2AsMe)_2C_6H_4\}]^+$, 774
$CoAs_4C_{18}H_{36}$
$[CoH_2\{1,2\text{-}(Me_2AsCH_2CH_2CH_2AsMe)_2C_6H_4\}]^+$, 774
$CoAs_4C_{20}H_{32}$
$[Co(diars)_2]^{2+}$, 772
$CoAs_4C_{20}H_{32}BrNO$
$[CoBr(NO)(diars)_2]^+$, 773
$CoAs_4C_{20}H_{32}Cl_2$

$[CoCl_2(diars)_2]^+$, 773
$CoAs_4C_{20}H_{32}Cl_2O_8$
$Co(OClO_3)_2(diars)_2$, 772
$CoAs_4C_{20}H_{32}I_2$
$[CoI_2(diars)_2]^+$, 773
$CoAs_4C_{20}H_{32}NO$
$[Co(NO)(diars)_2]^+$, 773
$CoAs_4C_{20}H_{32}O_2$
$[Co(O_2)(diars)_2]^+$, 773, 784
$CoAs_4C_{20}H_{33}Cl$
$[CoHCl(diars)_2]^-$, 773
$CoAs_4C_{20}H_{34}$
$[CoH_2(diars)_2]^-$, 773, 784
$CoAs_4C_{20}H_{35}O$
$[CoH(H_2O)(diars)_2]^{2+}$, 773
$CoAs_4C_{20}H_{36}O_2$
$[Co(H_2O)_2(diars)_2]^{3+}$, 772, 784
$CoAs_4C_{21}H_{33}O_3$
$[Co(CO_3)(diars)_2]^+$, 773
$CoAs_4C_{22}H_{32}N_2S_2$
$Co(NCS)_2(diars)_2$, 769
$CoAs_4C_{22}H_{38}O_2$
$[CoMe_2(diars)_2]^-$, 773
$CoAs_4C_{24}H_{38}Cl_2$
$[CoCl_2\{\{Me_2As(CH_2)_3AsPhCH_2\}_2\}]^+$, 773, 784
$CoAs_4C_{24}H_{38}O_2$
$[Co(O_2)\{\{Me_2As(CH_2)_3AsPhCH_2\}_2\}]^+$, 773, 784
$CoAs_4C_{24}H_{42}O_2$
$[Co\{\{Me_2As(CH_2)_3AsPhCH_2\}_2\}(H_2O)_2]^{3+}$, 784
$CoAs_4C_{40}H_{64}BrNO$
$[Co(NO)Br(diars)_2]^+$, 666
$CoAs_4C_{40}H_{64}ClNO$
$[Co(NO)Cl(diars)_2]^+$, 658
$CoAs_4C_{40}H_{64}NO$
$[Co(NO)(diars)_2]^{2+}$, 658, 661, 664
$CoAs_4C_{41}H_{64}N_2OS$
$[Co(NO)(NCS)(diars)_2]^+$, 661, 664
$CoAs_4C_{53}H_{44}NS$
$[Co(NCS)(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 769
$CoAs_4C_{55}H_{42}O$
$Co\{As(C_6H_4AsPh_2\text{-}2)_3\}(CO)]^+$, 769
$CoAs_4C_{72}H_{61}$
$[CoH(AsPh_3)_4]^-$, 769
$CoAs_6C_{18}H_{42}$
$[Co(Me_2AsCH{=}CHAsMe_2)_3]^{3+}$, 773
$CoAs_6C_{30}H_{48}$
$[Co(diars)_3]^{3+}$, 773
$CoAs_6C_{34}H_{46}$
$[Co\{MeAs(C_6H_4AsMe_2\text{-}2)_2\}_2]^{2+}$, 772
$CoAs_6C_{42}H_{54}$
$[Co\{1,8\text{-}(Me_2As)_2C_{10}H_6\}_3]^{2+}$, 772
$CoBC_{15}H_{15}N_3$
$Co(BH_4)(terpy)$, 686, 691
$CoBC_{36}H_{34}P_2$
$Co(BH_4)(PPh_3)_2$, 702
$CoBC_{36}H_{71}P_2$
$CoH(BH_4)\{P(C_6H_{11})_3\}_2$, 702, 704
$CoBC_{54}H_{49}N_2P_3$
$Co(N_2)(BH_4)(PPh_3)_3$, 709, 710
$CoBC_{54}H_{49}P_3$
$Co(BH_4)(PPh_3)_3$, 702
$CoBC_{55}H_{49}NP_3$
$CoH(BH_3CN)(PPh_3)_3$, 702
$CoCH_3N_4O_9$
$[Co(CO_3)(NO_2)_3(NH_3)]^-$, 668
$CoCH_{12}N_4O_3$
$[Co(CO_3)(NH_3)_4]^+$, 638, 813, 815
$CoCH_{12}N_5O_3S$
$Co(CN)(SO_3)(NH_3)_4$, 650
$CoCH_{15}F_3N_5O_3S$
$[Co(OSO_2CF_3)(NH_3)_5]^{2+}$, 638
$CoCH_{15}N_5O_3$
$[Co(CO_3)(NH_3)_5]^+$, 638, 816, 960
$[Co(CO_3)(NH_3)_5]^{2+}$, 814
$[Co(OCO_2)(NH_3)_5]^-$, 790, 814
$CoCH_{15}N_6$
$[Co(CN)(NH_3)_5]^{2+}$, 650, 654
$CoCH_{15}N_6O$
$[Co(NCO)(NH_3)_5]^{2+}$, 677, 679
$CoCH_{15}N_6S$
$[Co(NCS)(NH_3)_5]^{2+}$, 679, 681
$[Co(SCN)(NH_3)_5]^{2+}$, 680, 681, 698
$CoCH_{15}N_6Se$
$[Co(NCSe)(NH_3)_5]^{2+}$, 680
$CoCH_{16}N_4O_6P_2$
$[Co\{\{OP(O)(OH)\}_2CH_2\}(NH_3)_4]^+$, 763, 766
$CoCH_{16}N_5O_2$
$[Co(O_2CH)(NH_3)_5]^{2+}$, 791, 792, 793
$CoCH_{16}N_5O_3$
$[Co(OCO_2H)(NH_3)_5]^-$, 814
$[Co(OCO_2H)(NH_3)_5]^{2-}$, 814
$CoCH_{16}N_7$
$[Co(NH_3)_5(NCNH)]^{2+}$, 677
$CoCH_{17}N_6O_2$
$[Co(NH_3)_5(HNCO_2H)]^{2+}$, 682
$[Co(NH_3)_5(O_2CNH_2)]^{2+}$, 679
$CoCH_{17}N_7$
$[Co(NH_3)_5(NCNH_2)]^{3+}$, 675, 677
$CoCH_{18}N_5O_3S$
$[Co(OSO_2Me)(NH_3)_5]^{2+}$, 817
$CoCH_{18}N_6O_2$
$[Co(NH_3)_5(H_2NCO_2H)]^{3+}$, 679, 682
$CoCH_{19}N_7O$
$[Co(NH_3)_5(H_2NCONH_2)]^{3+}$, 677, 682
$CoCH_{19}N_9$
$[Co(NH_3)_5\{NCN(NH_2)_2\}]^{3+}$, 675
$CoC_2H_2O_4$
$Co(O_2CH)_2$, 791
$CoC_2H_8N_6O_8$
$[Co(NO_2)_4(en)]^-$, 668, 671
$CoC_2H_8O_{10}$
$[Co(CO_3)_2(H_2O)_4]^{2-}$, 811
$CoC_2H_{12}N_4O_4$
$[Co(C_2O_4)(NH_3)_4]^+$, 800
$CoC_2H_{12}N_6S_2$
$[Co(NCS)_2(NH_3)_4]^+$, 679
$CoC_2H_{15}N_5O_4$
$[Co(OC_2O_3)(NH_3)_5]^+$, 802
$CoC_2H_{16}N_5O_4$
$[Co(OC_2O_3H)(NH_3)_5]^{2+}$, 800
$CoC_2H_{17}IN_6$
$[Co(NH_3)_5(NCCH_2I)]^{3+}$, 678
$CoC_2H_{18}N_5O_2$
$[Co(OAc)(NH_3)_5]^{2+}$, 790, 793
$CoC_2H_{18}N_5O_5P$
$[Co\{OP(O)_2OAc\}(NH_3)_5]^+$, 760
$CoC_2H_{18}N_6$
$[Co(NH_3)_5(NCMe)]^{3+}$, 675, 676, 678
$CoC_2H_{18}N_9$
$[Co(NH_3)_5(\overline{N{=}NN{=}N}CMe)]^{2+}$, 698
$CoC_2H_{19}N_9$
$[Co(NH_3)_5(\overline{NHN{=}NN{=}C}Me)]^{3+}$, 698
$[Co(NH_3)_5\{\overline{N{=}NNHC(Me){=}N}\}]^{3+}$, 697
$[Co(NH_3)_5(\overline{N{=}NNHN{=}C}Me)]^{3+}$, 697
$CoC_2H_{21}N_5OS$
$[Co(NH_3)_5(DMSO)]^{3+}$, 690, 697, 790
$CoC_2H_{23}N_6O_3P$
$[Co\{OP(O_2H)CHMeNH_3\}(NH_3)_5]^{2+}$, 766
CoC_2N_2
$\{Co(CN)_2\}_n$, 648
$CoC_2N_2O_3$
$[Co(CN)(CO)_2(NO)\}^-$, 646
$CoC_2N_4O_2$
$[Co(CN)_2(NO)_2]^-$, 646, 658
CoC_2N_6
$[Co(CN)_2(N_2)_2]^+$, 650

$CoC_3H_6N_3S_6$
$Co(S_2CNH_2)_3$, 864
$CoC_3H_6N_6S_6$
$[Co(S_2C{=}NNH_2)_3]^{3-}$, 864
$CoC_3H_9N_6$
$Co(CN)_3(NH_3)_3$, 650
$CoC_3H_9N_6S_6$
$Co(S_2CNHNH_2)_3$, 864
$CoC_3H_9N_9S_3$
$Co(HN{=}NCSNH_2)_3$, 858
$CoC_3H_{12}N_2O_5$
$[Co(CO_3)(H_2O)_2(en)]^+$, 815
$CoC_3H_{12}N_4O_6S_2$
$Co(SO_3)_2\{N(CH_2NH_2)_3\}$, 822
$CoC_3H_{14}N_4O_4S$
$[Co(OSO_2)(H_2O)\{N(CH_2NH_2)_3\}]^+$, 822
$CoC_3H_{15}N_9S_3$
$[Co(H_2NNHCSNH_2)_3]^{3+}$, 857
$CoC_3H_{17}N_7$
$[Co(NH_3)_5(NCCH_2CN)]^{3+}$, 675
$CoC_3H_{17}N_8O_2$
$[Co(\overline{NCH{=}NC(NO_2){=}CH})(NH_3)_5]^{2+}$, 694
$CoC_3H_{18}N_6$
$[Co(NH_3)_5(NCCH{=}CH_2)]^{3+}$, 675, 676
$CoC_3H_{18}N_8O_2$
$[Co(NH_3)_5(\overline{HNCH{=}NCH{=}CNO_2})]^{3+}$, 699
$CoC_3H_{19}N_7$
$[Co(\overline{HNCH{=}NCH{=}CH})(NH_3)_5]^{3+}$, 696
$[Co(NH_3)_5(\overline{HNCH{=}NCH{=}CH})]^{3+}$, 697, 699
$CoC_3H_{21}N_7$
$[Co(NH_3)_5(NCNMe_2)]^{3+}$, 677
$CoC_3H_{22}N_6O$
$[Co(DMF)(NH_3)_5]^{3+}$, 790
$[Co(NH_3)_5(DMF)]^{3+}$, 682
$CoC_3H_{23}N_7O$
$[Co(NH_2CONMe_2)(NH_3)_5]^{3+}$, 698
$[Co(NH_3)_5(H_2NCONMe_2)]^{3+}$, 677
$CoC_3H_{24}N_5O_4P$
$[Co\{OP(OMe)_3\}(NH_3)_5]^{3+}$, 752, 755
CoC_3NO_4
$Co(NO)(CO)_3$, 662, 663
$CoC_3N_2O_3$
$[Co(NO)(CN)(CO)_2]^-$, 658
$CoC_3N_3O_2$
$[Co(CN)_2(CO)(NO)]^{2-}$, 646, 658
CoC_3N_4O
$[Co(NO)(CN)_3]^{3-}$, 646, 658, 662
$CoC_3N_{21}N_7$
$[Co(NH_3)_5(NCNMe_2)]^{3+}$, 675
$CoC_3O_3P_3$
$Co(CO)_3P_3$, 699
$CoC_3O_3S_6$
$[Co(S_2CO)_3]^{3-}$, 864
CoC_3O_9
$[Co(CO_3)_3]^{3-}$, 638, 813, 816, 866
CoC_3S_9
$[Co(S_2CS)_3]^{3-}$, 869
CoC_4HO_4
$CoH(CO)_4$, 704
$CoC_4H_2N_4O_4S$
$[Co(CN)_4(SO_3)(H_2O)]^{3-}$, 652, 823
$[Co(CN)_4(SO_3)(H_2O)]^{4-}$, 653
$CoC_4H_4S_4$
$[Co(S_2C_2H_2)_2]^-$, 876
$CoC_4H_8N_2O_6$
$[Co(CO_3)_2(en)]^-$, 815
$CoC_4H_8N_3O_6$
$Co(C_2O_4)(NO_2)(en)$, 674
$CoC_4H_8N_4O_8$
$[Co(NO_2)_2(Gly\text{-}O)_2]^+$, 668
$CoC_4H_{12}N_4O_3$
$[Co(CO_3)\{N(CH_2NH_2)_3\}]^+$, 816
$CoC_4H_{12}OP_2S_3$
$Co(S_2PMe_2)(SOPMe_2)$, 870
$CoC_4H_{12}O_8S_4$
$[Co(O_2SMe)_4]^{2-}$, 835
$CoC_4H_{12}P_2S_4$
$Co(S_2PMe_2)_2$, 870
$CoC_4H_{13}Cl_3N_3$
$CoCl_3(dien)$, 765
$CoC_4H_{13}N_6O_6$
$Co(NO_2)_3(dien)$, 668, 670
$CoC_4H_{14}N_{11}O_2$
$Co(NO)\{H_2NC(=NH)NC(=NH)NH_2\}_2(H_2O)$, 658
$CoC_4H_{15}N_6S$
$[Co(SCN)\{N(CH_2NH_2)_3\}(NH_3)]^{2+}$, 680, 681
$CoC_4H_{16}ClN_4O_3S_3$
$Co\{S(S)SO_3\}Cl(en)_2$, 817
$CoC_4H_{16}ClN_5O$
$[Co(NO)Cl(en)_2]^+$, 658, 661
$CoC_4H_{16}ClN_5O_5$
$[Co(NO)(OClO_3)(en)_2]^-$, 658, 661
$CoC_4H_{16}Cl_2N_4$
$[CoCl_2(en)_2]^+$, 638
$CoC_4H_{16}N_4O_3S$
$[Co(SO_3)(en)_2]^+$, 820
$CoC_4H_{16}N_4O_3S_2$
$[Co(S_2O_3)(en)_2]^+$, 817
$CoC_4H_{16}N_4O_4P$
$Co(O_2PO_2)(cn)_2$, 752
$[Co(O_2PO_2)(en)_2]^+$, 750, 753
$CoC_4H_{16}N_4O_4S$
$[Co(O_2SO_2)(en)_2]^+$, 817
$CoC_4H_{16}N_4O_6S_2$
$[Co(SO_3)_2(en)_2]^-$, 822, 823
$CoC_4H_{16}N_4O_6S_4$
$[Co(S_2O_3)_2(en)_2]^-$, 817
$CoC_4H_{16}N_6O_2$
$[Co(NO_2)_2(en)_2]^+$, 667, 670
$CoC_4H_{16}N_6O_4$
$[Co(NO_2)_2(dien)(NH_3)]^+$, 670
$[Co(NO_2)(ONO)(en)_2]^-$, 668, 672, 673
$[Co(NO_2)_2(en)_2]^+$, 638, 666, 668, 673, 788
$[Co(ONO)_2(en)_2]^+$, 668, 672, 673
$CoC_4H_{16}O_{10}S_4$
$Co(O_2SMe)_4(H_2O)_2$, 835
$CoC_4H_{17}N_4O_7P_2$
$Co\{O_2P_2O_4(OH)\}(en)_2$, 760
$CoC_4H_{18}IN_4O_4$
$[Co(OIO_2)(en)_2(H_2O)]^{2+}$, 826
$CoC_4H_{18}N_4O_3S$
$[Co(SO_3)(OH_2)(en)_2]^+$, 823
$CoC_4H_{18}N_4O_4S$
$[Co(SO_3)(H_2O)(en)_2]^+$, 823
$CoC_4H_{18}N_4O_4S_2$
$[Co(S_2O_3)(H_2O)(en)_2]^+$, 817, 857
$CoC_4H_{18}N_4O_4S_3$
$[Co\{S(S)SO_3\}(OH_2)(en)_2]^+$, 817
$CoC_4H_{18}N_4O_5S$
$[Co(OSO_3)(H_2O)(en)_2]^+$, 817
$CoC_4H_{19}N_4O_2$
$[Co(OH)(H_2O)(en)_2]^{2+}$, 786, 800, 822, 825
$CoC_4H_{19}N_6O_2$
$[Co(ONO)(NH_3)(en)_2]^+$, 668
$[Co(ONO)(NH_3)(en)_2]^{2+}$, 672
$CoC_4H_{19}N_7$
$[Co(NH_3)_5(\overline{N{=}CHCH{=}NCH{=}CH})]^{3+}$, 688
$CoC_4H_{20}N_4O_2$
$[Co(H_2O)_2(en)_2]^{3+}$, 679, 786, 800, 825
$CoC_4H_{20}N_4O_6P_2$
$[Co\{\{OP(O)(OH)\}_2CH_2\}(en)_2]^+$, 766
$CoC_4H_{20}N_4O_6Te$
$[Co(en)_2\{O_2Te(OH)_4\}]^+$, 817
$CoC_4H_{20}N_7$
$[Co(NH_3)_5(\overline{NCH{=}NCH{=}CMe})]^{2+}$, 697
CoC_4N_4

$[Co(CN)_4]^{2-}$, 648
$[Co(CN)_4]^{3-}$, 647, 655
$CoC_4N_4O_3S$
$[Co(CN)_4(SO_3)]^{3-}$, 653, 823
$[Co(CN)_4(SO_3)]^{5-}$, 650
$CoC_4N_4O_6S_2$
$[Co(CN)_4(SO_3)_2]^{5-}$, 638, 650, 653, 773
CoC_4N_6
$[Co(CN)_4(N_2)]^{-}$, 650
CoC_4O_6
$Co(CO)_4(O_2)$, 781
CoC_5HN_5
$[CoH(CN)_5]^{3-}$, 647, 649, 655
CoC_5HN_5O
$[Co(CN)_5(OH)]^{3-}$, 652, 830
$CoC_5H_2N_5O$
$[Co(CN)_5(H_2O)]^{2-}$, 650, 653, 784
$CoC_5H_3N_6$
$[Co(CN)_5(NH_3)]^{2-}$, 650
$CoC_5H_5Cl_2N$
$[CoCl_3(py)]^{-}$, 685
$CoC_5H_5Cl_2N_5$
$CoCl_2$(adenine), 694
$CoC_5H_7N_2O_2S_2$
$Co\{MeC(S)CHC(S)Me\}(NO)_2$, 660, 880
$CoC_5H_{11}N_6$
$Co(CN)_3(NH_3)(en)$, 650
$CoC_5H_{16}N_6O_2$
$[Co(ONO)(CN)(en)_2]^{+}$, 672
$CoC_5H_{16}N_6O_2S$
$[Co(NCS)(NO_2)(en)_2]^{+}$, 670
$[Co(NCS)(ONO)(en)_2]^{+}$, 668, 670, 672, 673
$CoC_5H_{18}N_5OS$
$[Co(OSCH_2CH_2NH_2)\{N(CH_2NH_2)_3\}]^{2+}$, 845
$CoC_5H_{18}N_5OSe$
$[Co(OSeCH_2CH_2NH_2)\{N(CH_2NH_2)_3\}]^{2+}$, 882
$CoC_5H_{19}N_4O_3$
$[Co(CO_2H)(H_2O)(en)_2]^{2+}$, 802
$[Co(O_2CH)(H_2O)(en)_2]^{2+}$, 791
$CoC_5H_{19}N_6S$
$[Co(SCN)(NH_3)(en)_2]^{2+}$, 680, 681
$CoC_5H_{22}N_6O_2$
$[Co(NH_3)_5(NCCH_2CO_2Et)]^{3+}$, 676
$CoC_5N_3O_2$
$[Co(CN)_3(CO)_2]^{2-}$, 647, 655
CoC_5N_5
$[Co(CN)_5]^{3-}$, 647, 648, 652, 681, 830
$[Co(CN)_5]^{4-}$, 647
CoC_5N_5I
$[Co(CN)_5I]^{3-}$, 638
$CoC_5N_5O_2$
$[Co(CN)_5(O_2)]^{2-}$, 777
$[Co(CN)_5(O_2)]^{3-}$, 650, 654, 780
$CoC_5N_5O_3S$
$[Co(CN)_5(SO_3)]^{4-}$, 650
$CoC_5N_5O_3S_2$
$[Co(CN)_5(S_2O_3)]^{4-}$, 650
CoC_5N_6O
$[Co(CN)_5(NO)]^{3-}$, 657, 658
$CoC_5N_6O_2$
$[Co(CN)_5(NO_2)^{3-}$, 652
CoC_5N_8
$[Co(CN)_5(N_3)]^{3-}$, 654
$CoC_6HN_3O_2S_4$
$[Co\{S_2C{=}C(CN)_2\}(S_2C{=}CHNO_2)$, 869
$CoC_6H_6N_4$
$\{Co(\overline{NCH{=}NCH{=}CH})_2\}_n$, 694
$CoC_6H_6O_6S_3$
$[Co(SCH_2CO_2)_3]^{3+}$, 838
$CoC_6H_8Cl_2N_4$
$CoCl_2(\overline{HNCH{=}NCH{=}CH})_2$, 694
$CoC_6H_8Cl_2N_4S_2$
$CoCl_2\{\overline{SC(NH_2){=}NCH{=}CH}\}_2$, 694
$CoC_6H_8N_2O_8$
$[Co(C_2O_4)_2en]^{-}$, 638, 802
$CoC_6H_{10}N_2O_4S_2$
$[Co\{SCH_2CH(NH_2)CO_2\}_2]^{-}$, 847
$CoC_6H_{12}N_3OS_4$
$Co(NO)(S_2CNMe_2)_2$, 658, 660, 664
$CoC_6H_{12}N_6S_3$
$Co(HN{=}NCSMe)_3$, 858
$CoC_6H_{12}S_3$
$[Co(1,4,7\text{-trithiacyclononane})]^{2-}$, 849
$CoC_6H_{12}S_6$
$[Co(SCH_2CH_2S)_3]^{3-}$, 838
$CoC_6H_{14}N_2O_6S_2$
$[Co\{SCH_2CH(NH_2)CO_2\}_2(H_2O)_2]^{-}$, 837
$CoC_6H_{16}Cl_2N_2S_2$
$[CoCl_2\{(H_2NCH_2CH_2SCH_2)_2\}]^{+}$, 852
$CoC_6H_{16}F_6N_4O_6S_2$
$[Co(OSO_2CF_3)_2(en)_2]^{+}$, 638
$CoC_6H_{16}N_4O_3S$
$[Co(SOC_2O_2)(en)_2]^{-}$, 846
$CoC_6H_{16}N_4O_4$
$[Co(C_2O_4)(en)_2]^{+}$, 801, 802, 803
$CoC_6H_{16}N_5O_6$
$Co(NO_2)(OC_2O_3)(en)_2$, 790
$CoC_6H_{16}N_6$
$[Co(CN)_2(en)_2]^{+}$, 650, 654
$CoC_6H_{18}N_2O_8P_2$
$[Co(NO)_2\{P(OMe)_3\}_2]^{+}$, 750
$Co(NO_3)_2(OPMe_3)_2$, 768
$CoC_6H_{18}N_3O_3S_3$
$Co\{S(O)CH_2CH_2NH_2\}_3$, 838
$CoC_6H_{18}N_3S_3$
$Co(SCH_2CH_2NH_2)_3$, 838
$[Co(SCH_2CH_2NH_2)_3]^{3-}$, 838
$CoC_6H_{18}N_4O_2S$
$[Co(SCH_2CO_2)(en)_2]^{+}$, 840, 846, 856
$CoC_6H_{18}N_4O_3S$
$[Co\{OSCH_2CO_2)(en)_2]^{+}$, 846
$CoC_6H_{18}N_4O_5$
$[Co(OC_2O_3)(OH_2)(en)_2]^{+}$, 800
$CoC_6H_{18}N_6O_2$
$[Co(NO_2)_2\{(H_2NCH_2CH_2NHCH_2)_2\}]^{2+}$, 670
$CoC_6H_{18}N_6O_4$
$[Co(NO_2)_2\{H_2NCH_2CH_2NHCH_2)_2\}]^{+}$, 668
$CoC_6H_{18}N_6S_3$
$[Co(H_2NNHCSMe)_3]^{3+}$, 858
$CoC_6H_{18}O_6P_3S_6$
$Co\{S_2P(OMe)_2\}_3$, 871
$CoC_6H_{19}N_4O_5$
$[Co(OC_2O_3H)(H_2O)(en)_2]^{2+}$, 800
$CoC_6H_{19}N_6O_6P$
$[Co\{OP(O)_2OC_6H_4NO_2\text{-}4\}(NH_3)_5]^{+}$, 755
$CoC_6H_{20}N_6O_4$
$[Co(NO_2)_2\{H_2N(CH_2)_3NH_2\}_2]^{2+}$, 670
$CoC_6H_{20}N_6O_5P$
$[Co\{OP(OH)OC_6H_4NO_2\text{-}4\}(NH_3)_5]^{2+}$, 766
$CoC_6H_{21}N_5S$
$[Co(MeSCH_2CH_2NH_2)\{N(CH_2NH_2)_3\}]^{3+}$, 851
$CoC_6H_{21}N_5Se$
$[Co(MeSeCH_2CH_2NH_2)\{N(CH_2NH_2)_3\}]^{2+}$, 882
$CoC_6H_{21}N_6O_2$
$[Co(ONO)(en)(dien)]^{2+}$, 672
$CoC_6H_{22}N_5OS$
$[Co(OSCH_2CH_2NH_2)(en)_2]^{+}$, 840
$[Co(OSCH_2CH_2NH_2)(en)_2]^{2+}$, 845, 846
$CoC_6H_{22}N_5OSe$
$[Co(OSeCH_2CH_2NH_2)(en)_2]^{2+}$, 881
$CoC_6H_{22}N_5O_2S$
$[Co(O_2SCH_2CH_2NH_2)(en)_2]^{+}$, 840, 845
$CoC_6H_{22}N_5O_2Se$
$[Co(O_2SeCH_2CH_2NH_2)(en)_2]^{2+}$, 881
$CoC_6H_{22}N_5S$
$[Co(SCH_2CH_2NH_2)(en)_2]^{2+}$, 840, 846, 850, 856

$CoC_6H_{22}N_5Se$
$[Co(SeCH_2CH_2NH_2)(en)_2]^{2+}$, 881
$CoC_6H_{23}N_4O_2$
$[Co(OH)(OH_2)\{H_2N(CH_2)_3NH_2\}]^{2+}$, 765
$CoC_6H_{23}N_6O_2$
$[Co(ONO)(NH_3)\{H_2N(CH_2)_3NH_2\}_2]^{2+}$, 672
$CoC_6H_{24}N_6$
$[Co(en)_3]^{3+}$, 808, 809, 827
CoC_6N_6
$[Co(CN)_6]^{3-}$, 646, 650, 652, 654
$[Co(CN)_6]^{4-}$, 652
CoC_6N_6O
$[Co(CN)_5(NCO)]^{3-}$, 650, 680
CoC_6N_6S
$[Co(CN)_5(NCS)]^{3-}$, 650, 681
$[Co(CN)_5(SCN)]^{3-}$, 650, 680, 681
$CoC_6N_6S_6$
$[Co(S_2C{=}NCN)_3]^{3-}$, 869
CoC_6N_6Se
$[Co(CN)_5(NCSe)]^{3-}$, 650, 680
$[Co(CN)_5(SeCN)]^{3-}$, 680, 681
CoC_6O_{12}
$[Co(C_2O_4)_3]^{3-}$, 692, 802
$CoC_7HF_4N_5$
$[Co(CN)_5(CF_2CF_2H)]^{3-}$, 654
$CoC_7H_4NO_4$
$[Co\{2,6\text{-}(CO_2)_2py\}]_n$, 685
$CoC_7H_{10}N_2O_7$
$[Co\{O_2CCH_2NH(CH_2)_2NHCH_2CO_2\}(CO_3)]^{-}$, 803
$CoC_7H_{10}O_3S_6$
$Co(S_2COEt)_2(S_2CO)$, 867
$CoC_7H_{12}N_4O_5$
$Co(CO_3)(H_2O)_2(\overline{HNCH{=}NCH{=}CH})_2$, 694, 811
$CoC_7H_{13}F_9N_3O_9S_3$
$Co(OSO_2CF_3)_3(dien)$, 638
$CoC_7H_{13}N_6$
$Co(CN)_3(dien)$, 650
$CoC_7H_{15}N_5O_4$
$[Co(2\text{-}O\text{-}5\text{-}ONC_6H_3CO_2(NH_3)_4]^{+}$, 803
$[Co(2\text{-}O\text{-}5\text{-}ONC_6H_3CO_2)(NH_3)_4]^{2+}$, 803
$CoC_7H_{15}N_5O_5$
$[Co(2\text{-}O\text{-}5\text{-}O_2NC_6H_3CO_2)(NH_3)_4]^{+}$, 803
$[Co(2\text{-}O\text{-}5\text{-}O_2NC_6H_3CO_2)(NH_3)_4]^{2+}$, 803
$CoC_7H_{15}PS_2$
$Co(S_2CPEt_3)$, 860
$CoC_7H_{16}N_4O_3$
$[Co(CO)_3(en)_2]^{+}$, 813
$CoC_7H_{18}Cl_2N_2S_2$
$[CoCl_2\{(H_2NCH_2CH_2SCH_2)_2CH_2\}]^{+}$, 852
$CoC_7H_{20}ClN_6$
$[CoCl(\overline{HNCH{=}NCH{=}CH})(en)_2]^{2+}$, 694, 696
$CoC_7H_{20}N_5O_2S$
$[Co\{O_2CCH(NH_2)CH_2SNHCH_2CH_2NH_2\}(en)]^{2+}$, 856
$CoC_7H_{20}N_6$
$[Co(NH_3)_5(NCPh)]^{3+}$, 678
$CoC_7H_{21}N_4O_2S$
$[Co(MeSCH_2CO_2)(en)_2]^{2+}$, 846
$CoC_7H_{21}N_5O_2S$
$[Co\{SCH_2CH(NH_2)CO_2\}(en)_2]^{+}$, 839, 850
$CoC_7H_{21}N_5O_3S$
$[Co\{OSCH_2CH(NH_2)CO_2\}(en)_2]^{+}$, 845
$CoC_7H_{21}N_5O_4S$
$[Co\{O_2SCH_2CH(NH_2)CO_2\}(en)_2]^{+}$, 822
$CoC_7H_{21}N_6OS$
$[Co(NH_3)_5\{SC(O)NHPh\}]^{2+}$, 860
$CoC_7H_{22}N_5O_2S$
$[Co\{HSCH_2CH(NH_2)CO_2\}(en)_2]^{2+}$, 840
$CoC_7H_{22}N_5O_3S$
$[Co\{OSCH_2CH(NH_2)CO_2H\}(en)_2]^{2+}$, 845
$CoC_7H_{25}N_5OS$
$[Co(OSMeCH_2CH_2NH_2)(en)_2]^{3+}$, 846
$CoC_7H_{25}N_5S_2$
$[Co(MeSSCH_2CH_2NH_2)(en)_2]^{3+}$, 856
$CoC_8F_{12}S_4$
$[Co\{S_2C_2(CF_3)_2\}_2]^{-}$, 876
$CoC_8H_5N_3$
$[Co(CN)_3Cp]^{-}$, 650
$CoC_8H_5N_3O_2S_4$
$[Co\{S_2C{=}C(CN)_2\}\{S_2C{=}C(CN)CO_2Et\}$, 869
$CoC_8H_8Cl_2N_4$
$CoCl_2(\overline{N{=}CHCH{=}NCH{=}CH})_2$, 686
$CoC_8H_{10}N_2O_6$
$[Co\{O_2CCH(CH_2O)NCH_2CH_2NCH(CH_2O)CO_2\}]^{-}$, 809
$CoC_8H_{14}N_4O_4$
$Co(HDMG)_2$, 774
$CoC_8H_{14}N_4O_6$
$[Co(Gly\text{-}Gly)_2]^{-}$, 684, 685
$CoC_8H_{14}N_5O_5$
$Co(NO)(HDMG)_2$, 658, 662, 666
$CoC_8H_{14}N_5O_8$
$Co(NO_3)(HDMG)_2$, 662
$CoC_8H_{14}O_5P$
$Co(\eta^3\text{-}C_3H_5)\{P(OMe)_3\}(CO)_2$, 708
$CoC_8H_{16}N_4O_6$
$[Co(Gly\text{-}GlyH)_2]^{+}$, 682
$CoC_8H_{16}N_6O_4$
$[Co(NO_2)_2(en)_2]^{+}$, 666
$CoC_8H_{18}ClN_6S_2$
$CoCl(H_2NCSNHN{=}CMe_2)_2$, 857
$CoC_8H_{18}N_2P_2$
$Co(CN)_2(PMe_3)_2$, 725
$CoC_8H_{18}N_2P_2S_2$
$Co(NCS)_2(PMe_3)_2$, 725
$CoC_8H_{19}N_6O_5$
$Co(NH_3)_2(Gly_4)$, 684
$CoC_8H_{19}N_7$
$[Co(NH_3)_5\{1,2\text{-}(NC)_2C_6H_4\}]^{3+}$, 676
$CoC_8H_{20}Cl_2N_2S_2$
$[CoCl_2\{(H_2NCH_2CH_2CH_2SCH_2)_2\}]^{+}$, 852
$CoC_8H_{20}Cl_2N_4S$
$CoCl_2\{S(CH_2CH_2NMe_2)_2\}$, 849
$CoC_8H_{20}Cl_2O_4S_2$
$CoCl_2\{S(CH_2CH_2OH)_2\}_2$, 849
$CoC_8H_{20}Cl_2O_8S_4$
$Co(ClO_4)_2(MeSCH_2CH_2SMe)_2$, 849
$CoC_8H_{20}N_5S_3$
$[Co(N_3)\{(H_2NCH_2CH_2SCH_2CH_2)_2S\}]^{2+}$, 852
$CoC_8H_{20}N_6S_2$
$[Co(NCS)_2\{H_2N(CH_2)_3NH_2\}_2]^{+}$, 679
$CoC_8H_{20}O_2P_2Se_2$
$Co\{Se(O)PEt_2\}_2$, 871
$CoC_8H_{20}O_4P_2S_4$
$Co\{S_2P(OEt)_2\}_2$, 870
$CoC_8H_{20}P_2S_4$
$Co(S_2PEt_2)_2$, 870
$CoC_8H_{20}S_4$
$[Co(SEt_4)]^{2-}$, 834
$CoC_8H_{22}N_4O_2S$
$[Co(SCMe_2CO_2)(en)_2]^{+}$, 856
$CoC_8H_{22}N_6$
$[Co(en)_2(NCMe)_2]^{3+}$, 675
$CoC_8H_{22}N_7O_5$
$Co(NH_3)_3(Gly_4)$, 684
$CoC_8H_{23}N_5O_3S$
$[Co(OSO_2)\{HN(CH_2CH_2NHCH_2CH_2NH_2)_2\}]^{+}$, 822
$CoC_8H_{24}ClN_4O_2$
$[CoCl(MeNHCH_2CH_2NHMe)_2(O_2)]^{+}$, 778
$CoC_8H_{24}NOP_2$
$CoMe_2(NO)(PMe_3)_2$, 716
$CoC_8H_{24}N_4S_2$
$[Co\{S(CH_2CH_2NH_2)_2\}_2]^{3+}$, 852
$CoC_8H_{24}N_5O_2S$
$[Co\{MeSCH_2CH(NH_2)CO_2\}(en)_2]^{2+}$, 850
$[Co\{SCH_2CH(NH_2)CO_2Me\}(en)_2]^{2+}$, 850
$CoC_8H_{26}N_4O_2$

$[Co\{(H_2NCH_2CH_2NMeCH_2)_2\}(H_2O)_2]^{2+}$, 786
$CoC_8H_{26}N_6$
$[Co(dien)_2]^{3+}$, 852
$CoC_8N_4S_4$
$[Co\{S_2C_2(CN)_2\}_2]^-$, 876, 879
$[Co\{S_2C_2(CN)_2\}_2]^{2-}$, 638, 879
$[Co\{S_2C_2(CN)_2\}_2]^{3-}$, 879
$CoC_8N_5OS_4$
$[Co\{S_2C_2(CN)_2\}_2(NO)]^{2-}$, 879
$CoC_9H_{12}O_{12}S_9$
$[Co(S_2COC_2H_4SO_3)_3]^{3-}$, 866
$CoC_9H_{14}N_5O_7S$
$[Co(CN)(HDMG)_2(SO_3)]^{2-}$, 650
$CoC_9H_{15}N_3O_6S_3$
$[Co\{SCH_2CH(NH_2)CO_2\}_3]^{3-}$, 837, 838
$CoC_9H_{15}N_3O_9S_3$
$[Co\{S(O)CH_2CH(NH_2)CO_2\}_3]^{3-}$, 838
$CoC_9H_{15}N_3O_{12}S_3$
$[Co\{O_2SCH_2CH(NH_2)CO_2\}_3]^{3-}$, 839
$CoC_9H_{15}O_3S_6$
$Co(S_2COEt)_3$, 638, 867
$CoC_9H_{15}S_6$
$Co(SCH{=}CHSMe)_3$, 838
$CoC_9H_{15}S_9$
$Co(S_2CSEt)_3$, 866, 867
$CoC_9H_{16}N_5O_5$
$Co(CN)(HDMG)_2(H_2O)$, 654
$Co(NC)(HDMG)_2(H_2O)$, 653
$CoC_9H_{18}N_3O_6S_3$
$Co\{SCH_2CH(NH_2)CO_2H\}_3$, 837
$CoC_9H_{18}N_3S_6$
$Co(S_2CNMe_2)_3$, 865
$CoC_9H_{21}N_6S_6$
$Co(S_2CNHNMe_2)_3$, 864
$CoC_9H_{22}N_4O_2S$
$[Co\{SCMe_2CH(NH_2)CO_2\}(dien)]^+$, 847
$CoC_9H_{23}N_4O_2$
$Co(en)_2(acac)$, 790
$CoC_9H_{23}N_6S_2$
$[Co(N_3)\{(H_2NCH_2CH_2SCH_2CH_2)_2NMe\}]^{2+}$, 852
$CoC_9H_{26}N_5O_2S$
$[Co\{HSCMe_2CH(NH_2)CO_2\}(en)_2]^{2+}$, 840
$CoC_9H_{27}BrP_3$
$CoBr(PMe_3)_3$, 722
$CoC_9H_{27}Br_2P_3$
$CoBr_2(PMe_3)_3$, 725
$CoC_9H_{27}ClO_9P_3$
$CoCl\{P(OMe)_3\}_3$, 747
$CoC_9H_{27}ClP_3$
$CoCl(PMe_3)_3$, 723
$CoC_9H_{27}IP_3$
$CoI(PMe_3)_3$, 726
$CoC_9H_{27}I_2P_3$
$CoI_2(PMe_3)_3$, 726
$CoC_9H_{27}N_2P_3$
$[Co(N_2)(PMe_3)_3]$, 710, 711
$Co(N_2)(PMe_3)_3$, 711
$CoC_9H_{27}O_9P_3$
$Co\{P(OMe)_3\}_3$, 749
$CoC_9H_{27}P_3$
$Co(PMe_3)_3$, 718
$CoC_9H_{30}N_6$
$[Co(pn)_3]^{3+}$, 809
$CoC_{10}H_2F_{12}S_4$
$Co\{F_3CC(S)CHC(S)CF_3\}_2$, 880
$CoC_{10}H_8Cl_2N_2S_2$
$CoCl_2(pySSpy)$, 686
$CoC_{10}H_8N_4O_4$
$[Co(NO_2)_2(bipy)]^+$, 674
$CoC_{10}H_8N_8$
$[Co(purine)_2]^{2+}$, 685
$CoC_{10}H_{10}Cl_2N_2$
$CoCl_2(py)_2$, 683, 686
$CoC_{10}H_{10}N_4O_6$
$Co(H_2O)_2(N{=}CHCH{=}NCH{=}CCO_2)_2$, 686
$CoC_{10}H_{12}ClN_2O_5$
$[CoCl\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}]^-$, 809
$[CoCl\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}]^{2-}$, 811
$CoC_{10}H_{12}N_2O_8$
$[Co\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}]^-$, 638, 808, 809, 810, 811
$CoC_{10}H_{12}N_3O_{10}$
$[Co(NO_2)\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}]^{2-}$, 809
$CoC_{10}H_{13}BrN_2O_8$
$[CoBr\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)CH_2CO_2H\}]^-$, 808
$CoC_{10}H_{13}ClN_2O_8$
$[CoCl\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)CH_2CO_2H\}]^-$, 811
$CoC_{10}H_{13}N_3O_{10}$
$[Co(NO_2)\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)CH_2CO_2H\}]^-$, 809
$CoC_{10}H_{14}NOS_4$
$Co\{MeC(S)CHC(S)Me\}_2(NO)$, 880
$CoC_{10}H_{14}N_2O_9$
$[Co(H_2O)\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}]^-$, 809, 810
$CoC_{10}H_{14}N_4O_4$
$Co(OAc)_2(HN{=}CH{-}NH{=}CH{-}CH)_2$, 694
$CoC_{10}H_{14}N_6O_4$
$[Co(CN)_2(HDMG)_2]^-$, 650
$CoC_{10}H_{14}O_4$
$Co(acac)_2$, 638
$CoC_{10}H_{14}S_4$
$Co\{MeC(S)CHC(S)Me\}_2$, 880
$CoC_{10}H_{15}N_2O_9$
$Co(H_2O)\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)CH_2CO_2H\}$, 810, 811
$CoC_{10}H_{15}N_3O_8$
$[Co(NH_3)\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}]^-$, 809
$CoC_{10}H_{16}N_6O_6S$
$Co(NO_3)_2\{MeNC(SMe){=}NCH{=}CH\}_2$, 694
$CoC_{10}H_{18}BrN_4O_4S$
$Co(DMG)_2Br(Me_2S)$, 638
$CoC_{10}H_{18}N_2O_4S_2$
$[Co\{(MeSCH_2CH(CO_2)NHCH_2\}_2)]^+$, 847
$CoC_{10}H_{18}N_{10}O_4$
$[Co(H_2O)_4(adenine)_2]^{2+}$, 685, 694
$CoC_{10}H_{20}BrN_4O_4S$
$CoBr(Me_2S)(HDMG)_2$, 849
$CoC_{10}H_{20}Cl_2S_4$
$[CoCl_2(1,4,8,11\text{-tetrathiacyclotetradecane})]^+$, 852
$CoC_{10}H_{20}N_2O_9$
$[Co(H_2O)\{(O_2CCH_2)_2NCH(CH_2)_4CHN(CH_2CO_2)_2\}]^-$, 810
$CoC_{10}H_{20}N_5O_6P$
$[Co\{OP(O)_2OC_6H_4NO_2\text{-}4\}(en)_2]^+$, 753
$CoC_{10}H_{20}P$
$CoMe_2(PMe_3)Cp$, 727
$CoC_{10}H_{21}N_2O_9$
$Co(H_2O)\{(O_2CCH_2)_2NCH(CH_2)_4CHN(CH_2CO_2)CH_2CO_2H\}$, 810
$CoC_{10}H_{21}O_3P_2$
$Co(CO)_2(COMe)(PMe_3)_2$, 727
$CoC_{10}H_{22}ClN_6S_2$
$CoCl\{MeSC(=NH)NHN{=}CMe_2\}_2$, 857
$CoC_{10}H_{23}N_8O_{11}P_2$
$Co(ADP)(NH_3)_3(H_2O)$, 766
$CoC_{10}H_{24}N_9O_{10}P_2$
$Co(ADP)(NH_3)_4$, 764
$CoC_{10}H_{25}N_4O_4S_2$
$[Co(O_2CCH_2SSCMe_2CO_2H)(en)_2]^{2+}$, 856
$CoC_{10}H_{25}N_9O_{13}P_3$
$Co(ATP)(NH_3)_4$, 763, 764, 765
$[Co(ATP)(NH_3)_4]$, 765
$CoC_{10}H_{26}N_4O_3$

$[Co([14]aneN_4)(H_2O)(O_2)]^{2+}$, 780

$CoC_{10}H_{26}N_4S_2$
$[Co(SCH_2CH_2NMeCH_2CH_2NMeCH_2CH_2S)(en)]^+$, 847

$CoC_{10}H_{27}N_4O_2$
$[Co(OH)(OH_2)(1,4,8,11\text{-tetraazacyclotetradecane}]^{2+}$, 763

$CoC_{10}H_{27}N_4O_2S_2$
$[Co(O_2CCH_2SBu^t)(en)_2]^{2+}$, 856

$CoC_{10}H_{27}N_5O_7$
$[Co\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}(NH_3)_5]^-$, 811

$CoC_{10}H_{27}N_6O_2$
$[Co(ONO)(NH_3)(1,4,8,11\text{-tetraazacyclotetradecane})]^{2+}$, 672

$CoC_{10}H_{28}N_4O_2$
$[Co(1,4,8,11\text{-tetraazacyclotetradecane})(H_2O)_2]^{2-}$, 788

$CoC_{10}H_{29}N_5OS$
$[Co(H_2NCH_2CH_2SCH_2CH_2COMe)(en)_2]^{3+}$, 851

$CoC_{10}N_{10}O_2$
$[\{Co(CN)_5\}_2(O_2)]^{6-}$, 786

$CoC_{11}H_{12}N_3O_5$
$Co(CO_3)(H_2O)_2(bipyNH)$, 811

$CoC_{11}H_{14}N_2O_5$
$[Co(CO_3)(H_2O)_2(py)_2]^-$, 815

$CoC_{11}H_{14}N_2O_8$
$[Co\{\{(O_2CCH_2)_2NCH_2\}_2CH_2\}]^-$, 808, 809

$CoC_{11}H_{20}N_4O_3$
$[Co(2\text{-}OC_6H_4CO_2)(en)_2]^+$, 803
$[Co(CO_3)\{N{=}CHCH_2CH_2NHCH_2CH_2N{=}CHCH_2CH_2NHCH_2CH_2\}]^+$, 814

$CoC_{11}H_{23}P_2$
$CoCp(PMe_3)_2$, 728

$CoC_{11}H_{30}N_4O_2$
$[Co(1,4,8,12\text{-tetraazacyclopentadecane})(H_2O)_2]^{2+}$, 788

$CoC_{11}H_{31}BrP_3$
$CoBr(C_2H_4)(PMe_3)_3$, 722

$CoC_{11}H_{31}P_3$
$[Co(C_2H_4)(PMe_3)_3]^-$, 718

$CoC_{11}H_{32}P_3$
$CoEt(PMe_3)_3$, 724
$CoH(C_2H_4)(PMe_3)_3$, 702, 724

$CoC_{11}H_{33}BrP_3$
$CoBrMe_2(PMe_3)_3$, 727

$CoC_{11}H_{33}ClP_3$
$CoClMe_2(PMe_3)_3$, 726

$CoC_{11}H_{33}IP_3$
$CoIMe_2(PMe_3)_3$, 726

$CoC_{11}H_{33}P_3$
$CoMe_2(PMe_3)_3$, 726

$CoC_{12}H_8N_2O_6$
$[Co(CO_3)_2(bipy)]^-$, 689

$CoC_{12}H_8S_4$
$[Co(S_2C{=}CCH{=}CHCH{=}CH)_2]^{2-}$, 869

$CoC_{12}H_{10}N_2O_6$
$[Co(CO_3)_2(py)]_2^-$, 688
$[Co(CO_3)_2(py)_2]^-$, 815

$CoC_{12}H_{14}N_2O_4$
$[Co(acac)_2(CN)_2]^-$, 638, 650

$CoC_{12}H_{14}O_6Se_2$
$Co(O_2SePh)_2(H_2O)_2$, 881

$CoC_{12}H_{16}N_2O_8$
$[Co\{O_2CCH_2CH_2N(CH_2CO_2)CH_2CH_2N(CH_2CO_2)\text{-}CH_2CH_2CO_2\}]^-$, 809
$[Co\{(O_2CCH_2)_2N(CH_2)_4N(CH_2CO_2)_2\}]^-$, 808

$CoC_{12}H_{16}N_4S_2$
$[Co(2\text{-Spy})_2(en)]^+$, 840

$CoC_{12}H_{16}N_6O_4$
$Co\{O_2CCH(NH_2)CH_2C{=}CHNHCH{=}N\}_2$, 776

$CoC_{12}H_{16}N_8$
$[Co(HNCH{=}NCH{=}CH)_4]^{2+}$, 695

$CoC_{12}H_{18}N_4O_4$
$Co(O_2CEt)_2(HNCH{=}NCH{=}CH)_2$, 693

$CoC_{12}H_{18}N_6$
$[Co(NCMe)_6]^{2+}$, 638

$CoC_{12}H_{21}N_3O_4$
$Co\{\{MeCOCHC(Me){=}NCH_2\}_2\}(NH_3)(O_2)$, 780

$CoC_{12}H_{23}N_4O_7$
$Co\{O_2CC(O)(CH_2CO_2H)CH_2CO_2\}\text{-}\{(H_2NCH_2CH_2NHCH_2)_2\}$, 803

$CoC_{12}H_{24}N_3O_6S_3$
$Co\{SCH_2CH(NH_2)CO_2Me\}_3$, 838

$CoC_{12}H_{24}N_5O_6P$
$[Co\{O_2PO(OC_6H_4NO_2\text{-}4)\}\{H_2N(CH_2)_3NH_2\}_2]^+$, 753

$CoC_{12}H_{24}S_6$
$[Co(1,4,7,10,13,16\text{-hexathiacyclooctadecane})]^{2+}$, 849

$CoC_{12}H_{25}P_2$
$Co(C_5H_4Me)(PMe_3)_2$, 728

$CoC_{12}H_{30}N_2O_8P_2$
$[Co(NO)_2\{P(OEt)_3\}_2]^+$, 717

$CoC_{12}H_{32}O_9P_3$
$Co\{P(OMe)_3\}_3(\eta^3\text{-}C_3H_5)$, 708

$CoC_{12}H_{36}ClP_4$
$CoCl(PMe_3)_4$, 723
$[CoCl(PMe_3)_4]^+$, 724

$CoC_{12}H_{36}NO_{13}P_4$
$[Co(NO)\{P(OMe)_3\}_4]^{2+}$, 716

$CoC_{12}H_{36}N_2P_3$
$[Co(H_2NCH_2CH_2PMe_2)_3]^{3+}$, 737

$CoC_{12}H_{36}O_3P_2$
$CoMe_3(PMe_3)_2\{P(OMe)_3\}$, 726

$CoC_{12}H_{36}O_{12}P_4$
$Co\{P(OMe)_3\}_4$, 747
$[Co\{P(OMe)_3\}_4]^-$, 704, 718, 747
$[Co\{P(OMe)_3\}_4]^+$, 749

$CoC_{12}H_{36}P_3$
$CoMe_3(PMe_3)_3$, 726

$CoC_{12}H_{36}P_4$
$Co(PMe_3)_4$, 711, 718
$[Co(PMe_3)_4]^-$, 718, 723

$CoC_{12}H_{37}O_{12}P_4$
$CoH\{P(OMe)_3\}_4$, 702, 704, 747

$CoC_{12}H_{37}P_4$
$CoH(PMe_3)_4$, 702
$[CoH(PMe_3)_4]^+$, 702, 725

$CoC_{12}N_6S_6$
$[Co\{S_2C{=}C(CN)_2\}_3]^{3-}$, 869
$[Co\{S_2C_2(CN)_2\}_3]^{3-}$, 876

$CoC_{13}H_{19}ClN_5O_4$
$Co(HDMG)_2Cl(py)$, 638

$CoC_{13}H_{19}N_5O_4$
$[Co(HDMG)_2(py)]^-$, 774

$CoC_{13}H_{25}N_2S_7$
$Co(S_2CNEt_2)_2(S_2CSEt)$, 866

$CoC_{13}H_{34}NP_3$
$[Co(MeCN)(C_2H_4)(PMe_3)_3]^+$, 722

$CoC_{13}H_{37}P_4$
$CoMe_2(Me_2PCHPMe_2)(PMe_3)_2$, 727

$CoC_{13}H_{37}P_5$
$[Co(PMe_3)(Me_2PCH_2PMe_2)_2]^+$, 736

$CoC_{13}H_{39}O_{12}P_4$
$CoMe\{P(OMe)_3\}_4$, 749

$CoC_{13}H_{39}P_4$
$CoMe(PMe_3)_4$, 724

$CoC_{14}H_8N_2O_8$
$[Co(C_2O_4)_2(bipy)]^-$, 689

$CoC_{14}H_8O_8$
$[Co\{2,6\text{-}py(CO_2)_2\}_2]^-$, 690

$CoC_{14}H_{12}S_4$
$[Co(3,4\text{-}S_2C_6H_3Me)_2]^-$, 876

$CoC_{14}H_{16}N_6O_3$
$Co(2\text{-}O_2NC_6H_4NO)(MeN{=}CH{=}NCH{=}CH)_2$, 694

$CoC_{14}H_{18}N_2O_8$
$[Co\{(O_2CCH_2)_2NCH(CH_2)_4CHN(CH_2CO_2)_2\}]^-$, 808

$CoC_{14}H_{18}N_4O_4S_2$
$[Co(S_2O_3)(OH_2)(en)_2]^+$, 817

$CoC_{14}H_{19}N_4O_2$

$[Co(NO_2)\{HN(CH_2CH_2N{=}CHCH{=}CHCH{=}CH)_2\}]^{2+}$, 670

$CoC_{14}H_{19}N_4O_3$
$[Co(OOH)(en)_2(H_2O)]^{2+}$, 786

$CoC_{14}H_{19}N_6O_4S$
$Co(SCN)(HDMG)_2(py)$, 680

$CoC_{14}H_{22}N_5O_4$
$CoMe(HDMG)_2(py)$, 774

$CoC_{14}H_{22}N_5O_4S$
$Co(HDMG)_2(py)(SMe)$, 835

$CoC_{14}H_{28}N_3OS_4$
$Co(NO)(S_2CNPr^i_2)_2$, 660

$CoC_{14}H_{30}N_2P_2S_2$
$Co(NCS)_2(PEt_3)_2$, 725

$CoC_{14}H_{36}N_2O_{12}P_4S_2$
$[Co(NCS)_2\{P(OMe)_3\}_4]^+$, 750

$CoC_{15}H_{11}Cl_2N_3$
$CoCl_2(terpy)$, 686

$CoC_{15}H_{12}N_3S_3$
$Co(2\text{-}Spy)_3$, 838, 839

$CoC_{15}H_{12}N_3S_6$
$Co(S_2CNCH{=}CHCH{=}CH)_3$, 865

$CoC_{15}H_{15}Br_2N_3$
$CoBr_2(py)_3$, 685

$CoC_{15}H_{15}Cl_2N_3$
$CoCl_2(py)_3$, 685

$CoC_{15}H_{15}Cl_3N_3$
$CoCl_3(py)_3$, 687, 688

$CoC_{15}H_{17}F_2N_3O$
$[CoF_2(H_2O)(py)_3]^+$, 688

$CoC_{15}H_{21}N_3O_3$
$[Co(H_2O)_3(py)_3]^{3+}$, 688

$CoC_{15}H_{21}S_6$
$Co\{MeC(S)CHC(S)Me\}_3$, 880

$CoC_{15}H_{22}Cl_2S_4$
$[CoCl_2\{1,2\text{-}C_6H_4(CH_2SCH_2CH_2SCH_2)_2CH_2\}]^+$, 852

$CoC_{15}H_{24}N_5O_4S$
$Co(HDMG)_2(py)(SEt)$, 835

$CoC_{15}H_{27}N_3O_6S_3$
$[Co\{SCMe_2CH(NH_2)CO_2\}_2]^-$, 847

$CoC_{15}H_{28}O_3P$
$CoH(CO)_3(PBu_3)$, 708

$CoC_{15}H_{30}N_2OP_2$
$[Co(CN)_2(CO)(PEt_3)_2]^-$, 647

$CoC_{15}H_{30}N_3S_3Se_3$
$Co(SeSCNEt_2)_3$, 864

$CoC_{15}H_{30}N_3S_6$
$Co(S_2CNEt_2)_3$, 865, 866

$CoC_{15}H_{30}N_3Se_6$
$Co(Se_2CNEt_2)_3$, 864

$CoC_{15}H_{45}O_{15}P_5$
$[Co\{P(OMe)_3\}_5]^+$, 747

$CoC_{16}H_{12}FN_2O_2$
$Co(3\text{-}Fsalen)$, 775

$CoC_{16}H_{12}N_3O_4$
$Co(CO_3)(OH)(terpy)$, 686

$CoC_{16}H_{13}Cl_2N_2P$
$CoCl_2(PPhpy_2)$, 686

$CoC_{16}H_{14}N_2O_2$
$Co(salen)$, 775

$CoC_{16}H_{14}N_3O_3$
$Co(NO)(salen)$, 658, 660, 664

$CoC_{16}H_{15}ClN_3O_3$
$Co(CO_3)Cl(py)_3$, 688

$CoC_{16}H_{24}N_9O_3$
$[Co(NO_3)\{HNC(Me){=}NCH{=}CH\}_4]^+$, 694

$CoC_{16}H_{28}N_6$
$[Co(en)_2(Me_2bipy)]^{2+}$, 686

$CoC_{16}H_{30}N_3O_6S_3$
$[Co\{MeSCMe_2CH(NH_2)CO_2\}_2]^+$, 847

$CoC_{16}H_{33}O_9P_3$
$Co(\eta^3\text{-benzyl})\{P(OMe)_3\}_3$, 708

$CoC_{16}H_{44}BrP_4$
$[CoBr(PHEt_2)_4]^+$, 725

$CoC_{16}H_{44}Br_2P_4$
$CoBr_2(PHEt_2)_4$, 725

$CoC_{17}H_{11}N_5O_2$
$Co(NCO)_2(terpy)$, 686

$CoC_{17}H_{36}P_3$
$CoPh(C_2H_4)(PMe_3)_3$, 724

$CoC_{17}H_{40}O_9P_3$
$Co(\eta^3\text{-cyclooctenyl})\{P(OMe)_3\}_3$, 708

$CoC_{18}H_{12}N_3O_3$
$Co(NO)(8\text{-quinolinolate})_2$, 658, 666

$CoC_{18}H_{15}BrN_2O_2P$
$Co(NO)_2Br(PPh_3)$, 717

$CoC_{18}H_{15}IN_2O_2P$
$Co(NO)_2I(PPh_3)$, 660

$CoC_{18}H_{15}N_3O_4P$
$Co(NO)_2(NO_2)(PPh_3)$, 662

$CoC_{18}H_{22}I_2N_6S_2$
$CoI_2(H_2NCSNHN{=}CPhMe)_2$, 857

$CoC_{18}H_{22}N_2O_2P_2$
$Co(CN)_2(O_2)(PMe_2Ph)_2$, 725

$CoC_{18}H_{24}N_{12}$
$[Co(HNCH{=}NCH{=}CH)_6]^{2+}$, 694, 695

$CoC_{18}H_{27}N_6O_4S$
$Co(SCN)(Bu^tpy)(HDMG)_2$, 681

$CoC_{18}H_{27}O_5P$
$[Co(acac)_2(PMe_2Ph)(H_2O)]^+$, 728

$CoC_{18}H_{39}BrNS_3$
$[CoBr\{N(CH_2CH_2SBu^t)_3\}]^+$, 849

$CoC_{18}H_{48}P_3$
$Co(H)_3(PEt_3)_3$, 702

$CoC_{18}H_{48}P_6$
$[Co(Me_2PCH_2CH_2PMe_2)_3]^{3+}$, 737

$CoC_{18}H_{54}O_{12}P_6$
$[Co\{P(OMe)_3\}_6]^{3+}$, 750

$CoC_{19}H_{24}N_5O_4S$
$Co(HDMG)_2(py)(SPh)$, 835

$CoC_{20}H_8N_6S_4$
$[Co\{S_2C_2(CN)_2\}_2(phen)]^-$, 877

$CoC_{20}H_{14}N_3O_4$
$Co(NO_2)\{1,2\text{-}(2\text{-}OC_6H_4CH{=}N)_2C_6H_4\}$, 674

$CoC_{20}H_{15}NO_3P$
$Co(NO)(CO)_2(PPh_3)$, 660

$CoC_{20}H_{16}ClN_5O$
$[Co(NO)Cl(bipy)_2]^+$, 658, 662

$CoC_{20}H_{16}Cl_2N_4$
$[CoCl_2(bipy)_2]^+$, 688

$CoC_{20}H_{16}N_4$
$Co(bipy)_2$, 688, 691
$[Co(bipy)_2]^+$, 691

$CoC_{20}H_{16}N_5O_3$
$[Co(NO_3)(bipy)_2]^+$, 686

$CoC_{20}H_{20}Cl_2N_4$
$CoCl_2(py)_4$, 685
$[CoCl_2(py)_4]^+$, 638, 687, 688

$CoC_{20}H_{20}F_4N_4$
$[CoF_2(py)_4]^+$, 688

$CoC_{20}H_{20}N_4O_2$
$[Co(H_2O)_2(bipy)_2]^{3+}$, 688

$CoC_{20}H_{20}P_4$
$(CoCpP)_4$, 699

$CoC_{20}H_{23}N_3O_2$
$Co\{HN(CH_2CH_2CH_2N{=}CHC_6H_4O\text{-}2)_2\}$, 775

$CoC_{20}H_{23}N_3O_4$
$Co\{HN(CH_2CH_2CH_2N{=}CHC_6H_4O\text{-}2)_2\}(O_2)$, 780

$CoC_{20}H_{24}F_{12}N_8Si_2$
$\{Co(SiF_6)_2\{H_2C{=}CHNCH{=}NCH{=}CH)_4\}_n$, 694

$CoC_{20}H_{24}N_4O_2$
$[Co(H_2O)_2(py)_4]^{3+}$, 688

$CoC_{20}H_{26}BrN_6S_2$
$CoBr(PhNHCSNHN{=}CMe_2)_2$, 857

$CoC_{21}H_{15}S_6$
$Co(S_2CPh)_3$, 864

$CoC_{21}H_{16}N_4O_3$
$[Co(CO_3)(bipy)_2]^+$, 686, 688, 689
$CoC_{21}H_{19}N_3O_4$
Co(salen)(py)(O_2), 780
$CoC_{21}H_{20}N_4O_3$
$[Co(CO_3)(py)_4]^+$, 686, 688, 814
$CoC_{21}H_{25}N_3O_4$
$Co\{MeN(CH_2CH_2CH_2N{=}CHC_6H_4O\text{-}2)_2\}(O_2)$, 778, 780
$CoC_{21}H_{44}N_4O_4P$
$CoMe(HDMG)_2(PBu_3)$, 775
$CoC_{22}H_{15}F_3O_5PS$
$Co(O_2SCF_3)(CO)_3(PPh_3)$, 835
$CoC_{22}H_{16}N_4O_4$
$[Co(C_2O_4)(bipy)_2]^+$, 689, 802
$CoC_{22}H_{16}N_6$
$[Co(CN)_2(bipy)_2]^+$, 689
$CoC_{22}H_{16}N_6S_2$
$Co(NCS)_2(bipy)_2$, 686
$CoC_{22}H_{19}PS_4$
$Co(SCH{=}CHS)_2(PPh_3)$, 838
$CoC_{22}H_{20}N_6S_2$
$Co(NCS)_2(py)_4$, 686
$CoC_{22}H_{22}N_4$
$[CoMe_2(bipy)_2]^+$, 686, 692
$CoC_{22}H_{26}N_2O_2S_2$
$[Co\{\{2\text{-}OC_6H_4CH{=}N(CH_2)_3SCH_2\}_2\}]^+$, 854
$CoC_{22}H_{29}N_4PS_2$
$Co(NCS)_2(Ph_2PCH_2CH_2NHCH_2CH_2NEt_2)$, 746
$CoC_{22}H_{45}N_3S_{11}$
$Co(SEt)_2(S_2CSEt)(S_2CNEt_2)_3$, 867
$CoC_{23}H_{20}N_4O_3$
$[Co(CO)_3(py)_4]^+$, 687
$CoC_{24}H_{16}Cl_2N_4$
$[CoCl_2(phen)_2]^+$, 686, 688
$CoC_{24}H_{20}O_2P_2S_2$
$\{Co(SOPPh_2)_2\}_n$, 871
$CoC_{24}H_{20}O_8S_4$
$[Co(O_2SPh)_4]^{2-}$, 835
$CoC_{24}H_{20}P_2S_4$
$Co(S_2PPh_2)_2$, 870
$CoC_{24}H_{20}P_2Se_4$
$Co(Se_2PPh_2)_2$, 871
$CoC_{24}H_{20}S_4$
$[Co(SPh)_4]^{2-}$, 834
$CoC_{24}H_{22}ClN_4O$
$[CoCl(H_2O)\{2\text{-}(CHNPh)py\}_2]^+$, 686
$CoC_{24}H_{24}N_6S_2$
$Co(NCS)_2(PhNN{=}CMeCH{=}CMe)_2$, 694
$CoC_{24}H_{28}N_4$
$[Co(4\text{-}Mepy)_4]^{2+}$, 686
$CoC_{24}H_{32}N_4O_2$
$[Co(3\text{-}Mepy)_4(H_2O)_2]^{2+}$, 686
$CoC_{24}H_{40}Cl_2N_2P_2$
$[CoCl_2(H_2NCH_2CH_2PBuPh)_2]^+$, 737
$CoC_{24}H_{40}P_2$
$Co(C_6H_2Me_3\text{-}2,4,6)_2(PMe_3)_2$, 725
$CoC_{24}H_{60}ClO_{12}P_4$
$[CoCl\{P(OEt)_3\}_4]^+$, 749
$CoC_{24}H_{60}O_{12}P_4$
$Co\{P(OEt)_3\}_4$, 749
$[Co\{P(OEt)_3\}_4]^-$, 747, 749
$[Co\{P(OEt)_3\}_4]^+$, 749
$CoC_{24}H_{60}P_4$
$Co(PEt_3)_4$, 722
$CoC_{24}H_{61}O_{12}P_4$
$CoH\{P(OEt)_3\}_4$, 702
$CoC_{24}H_{72}N_{12}O_9P_3$
$[Co\{\{OP(NMe_2)_2\}_2O\}_3]^{2+}$, 768
$CoC_{25}H_{16}N_4O_3$
$[Co(CO_3)(phen)_2]^+$, 638, 686, 688, 693
$CoC_{25}H_{20}N_2P$
$Co(CN)_2(PPh_3)Cp$, 650
$CoC_{25}H_{26}P$
$CoMe_2(PPh_3)Cp$, 708, 727, 728
$CoC_{25}H_{34}O_2P_3$
$Co(O_2CH)(PMe_2Ph)_3$, 791
$CoC_{26}H_{16}N_4O_4$
$[Co(O_2C_2O_2)(phen)_2]^+$, 802
$CoC_{26}H_{22}N_2O_2P_2$
$Co(NO)_2(Ph_2PCH{=}CHPPh_2)$, 737
$CoC_{26}H_{22}O_2P_2$
$[Co(Ph_2PCH{=}CHPPh_2)(O_2)]^+$, 784
$CoC_{26}H_{24}Cl_2NOP_2$
$Co(NO)Cl_2(dppe)$, 712
$CoC_{26}H_{24}Cl_2O_2P_2$
$CoCl_2\{Ph_2P(O)CH_2CH_2P(O)Ph_2\}$, 768
$CoC_{26}H_{24}IN_2O_3P_2$
$Co(NO)_2I\{Ph_2PCH_2CH_2P(O)Ph_2\}$, 660
$CoC_{26}H_{24}N_2O_2P_2$
$[Co(NO)_2(dppe)]^+$, 660, 712, 717
$CoC_{26}H_{24}N_6$
$[Co(en)(phen)_2]^{3+}$, 689
$CoC_{26}H_{26}Cl_2NOP_2$
$CoCl_2(NO)(PPh_2Me)_2$, 664, 716
$CoC_{26}H_{28}P$
$CoMe_2(PPh_3)(C_5H_4Me)$, 728
$CoC_{26}H_{33}N_2P_3$
$Co(CN)_2(PMe_2Ph)_3$, 725, 785
$CoC_{26}H_{36}Cl_2NOP_2$
$Co(NO)Cl_2(PPh_2Me)_2$, 660
$CoC_{26}H_{36}O_4P_2$
$[Co(acac)_2(PMe_2Ph)_2]^+$, 728
$CoC_{27}H_{27}N_3S_3$
$[Co(2\text{-}pyCH_2SMe)_3]^{2+}$, 849
$CoC_{27}H_{27}N_4O$
$Co(NO)(2,6\text{-}Me_2C_6H_3NC)_3$, 660
$CoC_{27}H_{31}N_4O_4P$
$CoMe(HDMG)(DMG)(PPh_3)$, 728
$CoC_{27}H_{63}NO_{10}P_3$
$Co(NO)\{P(OPr^i)_3\}_3$, 712
$CoC_{27}H_{66}O_9P_3$
$Co(H)_3\{P(OPr^i)_3\}_3$, 702, 707
$CoC_{28}H_{20}N_4O_5$
$[Co\{O_2CCH(O)CH_2CO_2H\}(phen)_2]^+$, 803
$CoC_{28}H_{20}N_4O_6$
$[Co\{O_2CCH(O)CH(OH)CO_2H\}(phen)_2]^+$, 803
$CoC_{28}H_{20}S_4$
$[Co(S_2C_2Ph_2)_2]^-$, 876
$CoC_{28}H_{24}N_2P_2$
$Co(CN)_2(dppe)$, 736
$[Co(CN)_2(dppe)]^+$, 736
$CoC_{28}H_{24}N_2P_2S_2$
$Co(NCS)_2(diphos)$, 736
$CoC_{29}H_{24}NO_2P_2$
$Co(CN)(CO)_2(dppe)$, 648
$CoC_{29}H_{33}O_4P_4S_4$
$Co(dppe)\{S_2P(OMe)_2\}\{S_2P(O)(OMe)\}$, 871
$CoC_{30}H_{22}N_6$
$[Co(terpy)_2]^{2+}$, 686, 688, 691, 692
$[Co(terpy)_2]^{3+}$, 689
$CoC_{30}H_{22}S_4$
$Co\{PhC(S)CHC(S)Ph\}_2$, 880
$CoC_{30}H_{24}N_6$
$Co(bipy)_3$, 638
$[Co(bipy)_3]^+$, 686, 688, 691
$[Co(bipy)_3]^{2+}$, 686, 688, 691, 692
$[Co(bipy)_3]^{3+}$, 688, 691, 692
$CoC_{30}H_{36}N_3S_6$
$Co(S_2CNHCHEtPh)_3$, 865
$CoC_{30}H_{36}O_4P_4S_4$
$[Co(dppe)\{S_2P(OMe)_2\}_2]^+$, 871
$CoC_{30}H_{42}F_2N_{12}$
$[\{Co(NN{=}CMeCH{=}CMe)_3\}_2(\mu\text{-}F)_2]^{2+}$, 694
$CoC_{30}H_{45}NO_7P_3$
$Co(NO)\{P(OEt)_2Ph\}_3$, 712

$CoC_{32}H_{33}N_4O_4P$
$CoPh(HDMG)(DMG)(PPh_3)$, 728
$CoC_{32}H_{45}N_2P_3$
$Co(CN)_2(PEt_2Ph)_3$, 649
$CoC_{34}H_{30}N_4O_4S_2$
$Co(O_2SC_6H_4Me\text{-}4)_2(bipy)_2$, 835
$CoC_{34}H_{36}P_3$
$Co(H)_3\{PhP(CH_2CH_2PPh_2)_2\}$, 707
$CoC_{36}H_{24}N_6$
$[Co(phen)_3]^+$, 688
$[Co(phen)_3]^{2+}$, 686, 688, 692
$[Co(phen)_3]^{3+}$, 686, 688, 692
$CoC_{36}H_{30}Br_2P_2$
$CoBr_2(PPh_3)_2$, 725
$CoC_{36}H_{30}Cl_2NOP_2$
$CoCl_2(NO)(PPh_3)_2$, 724
$CoC_{36}H_{30}Cl_2NO_6P_2S$
$Co(NS)Cl_2\{P(OPh)_3\}_2$, 858
$CoC_{36}H_{30}Cl_2NO_7P_2S$
$Co(NSO)Cl_2\{P(OPh)_3\}_2$, 858
$CoC_{36}H_{30}Cl_2O_2P_2$
$CoCl_2(OPPh_3)_2$, 768
$CoC_{36}H_{30}Cl_2P_2$
$CoCl_2(PPh_3)_2$, 722
$CoC_{36}H_{30}NO_3P_2S$
$Co(NO)(SO_2)(PPh_3)_2$, 660
$CoC_{36}H_{30}N_2O_2P_2$
$[Co(NO)_2(PPh_3)_2]^+$, 660, 712, 717
$CoC_{36}H_{36}NO_3P_2S$
$Co(NO)(SO_2)(PPh_3)_2$, 716
$CoC_{36}H_{38}P_2$
$Co(H)_2(PPh_3)_2$, 704
$CoC_{36}H_{44}O_2P_4$
$[Co\{O(CH_2CH_2PPhCH_2CH_2PPhCH_2CH_2)_2O\}]^{2+}$, 746
$CoC_{36}H_{84}O_{12}P_4$
$Co\{P(OPr^i)_3\}_4$, 747
$CoC_{37}H_{30}NO_2P_2$
$Co(NO)(CO)(PPh_3)_2$, 660
$CoC_{37}H_{31}N_3O_4$
$Co\{\{PhCOCHC(Ph)=NCH_2\}_2\}(py)(O_2)$, 779, 784
$CoC_{37}H_{33}P_2$
$CoMe(PPh_3)_2$, 723
$CoC_{38}H_{52}N_3O_5$
$Co\{HN(CH_2CH_2CH_2N{=}CHC_6H_4O\text{-}2)_2\}\text{-}\{OOCBu^tCH{=}CBu^tCOC(Bu^t){=}CH\}$, 780
$CoC_{39}H_{30}N_3S_6$
$Co(S_2CNPh_2)_3$, 865
$CoC_{39}H_{33}N_6S_6$
$Co(S_2CNHNPh_2)_3$, 864
$CoC_{39}H_{66}N_3S_6$
$[Co\{S_2CN(C_6H_{11})_2\}_3]^-$, 866
$[Co\{S_2CN(C_6H_{11})_2\}_3]^+$, 866
$CoC_{40}H_{61}O_8P_4$
$CoH\{P(OEt)_2Ph\}_4$, 706, 707
$[CoH\{P(OEt)_2Ph\}_4]^+$, 706
$CoC_{40}H_{63}O_9P_4$
$[CoH(H_2O)\{P(OEt)_2Ph\}_4]^+$, 706
$CoC_{41}H_{39}P_5S$
$[Co(P_2S)(triphos)]^+$, 738
$CoC_{41}H_{39}P_6$
$Co(P_3)(triphos)$, 699, 738
$CoC_{41}H_{42}P_3$
$[Co(H)_3(triphos)]^+$, 702
$CoC_{42}H_{39}OP_3S_2$
$Co(S_2CO)(triphos)$, 646, 868
$CoC_{42}H_{39}O_2P_3$
$[Co(triphos)(CO)_2]^+$, 744
$CoC_{42}H_{39}P_3S_2$
$Co(CS_2)(triphos)$, 646, 744
$CoC_{42}H_{39}P_3S_3$
$Co(S_2CS)(triphos)$, 868
$CoC_{42}H_{40}OP_3$
$CoH(CO)(triphos)$, 744
$CoC_{42}H_{42}BrP_4$
$[CoBr\{P(CH_2CH_2PPh_2)_3\}]^+$, 745
$CoC_{42}H_{42}ClNP_3$
$[CoCl\{N(CH_2CH_2PPh_2)_3\}]^+$, 745
$CoC_{42}H_{42}INP_3$
$[CoI\{N(CH_2CH_2PPh_2)_3\}]^-$, 745
$CoC_{42}H_{42}NP_3$
$[Co\{N(CH_2CH_2PPh_2)_3\}]^+$, 744
$CoC_{42}H_{42}NP_6$
$Co\{N(CH_2CH_2PPh_2)_3\}P_3$, 700
$Co(P_3)\{N(CH_2CH_2PPh_2)_3\}$, 738
$CoC_{42}H_{42}N_2OP_3$
$Co(NO)\{N(CH_2CH_2PPh_2)_3\}$, 660, 712
$[Co(NO)\{N(CH_2CH_2PPh_2)_3\}]^+$, 658, 663, 712, 716
$CoC_{42}H_{43}NP_3$
$CoH\{N(CH_2CH_2PPh_2)_3\}$, 702
$CoC_{42}H_{43}P_4$
$CoH\{P(CH_2CH_2PPh_2)_3\}$, 702, 706
$CoC_{42}H_{43}P_4S$
$[Co(SH)\{P(CH_2CH_2PPh_2)_3\}]^+$, 829
$CoC_{42}NP_3S$
$[Co(SH)\{N(CH_2CH_2PPh_2)_3\}]^+$, 829
$CoC_{43}H_{42}NOP_3$
$[Co(CO)\{N(CH_2CH_2PPh_2)_3\}]^+$, 738
$[Co(CO)[N(CH_2CH_2PPh_2)_3]]^+$, 744
$CoC_{43}H_{42}O_2P_3$
$[Co(OAc)(triphos)]^-$, 745
$CoC_{43}H_{42}P_3S_3$
$[Co(S_2CSMe)(triphos)]^+$, 869
$[Co(S_2CSMe)(triphos)]^{2+}$, 867
$CoC_{43}H_{45}NP_3S$
$[Co(SMe)\{N(CH_2CH_2PPh_2)_3\}]^{2+}$, 834
$CoC_{44}H_{28}N_4$
Co(tetraphenylporphyrin), 781
$CoC_{44}H_{28}N_5O$
$Co(NO)$(tetraphenylporphyrin), 660
$CoC_{44}H_{54}N_{10}O_6$
$Co\{(Me_3CCONH)_4$porphyrin$\}(MeNCH{=}NCH{=}CH)\text{-}(O_2)$, 777
$CoC_{45}H_{48}O_4P_4$
$[Co(triphos)(CO)\{P(OMe)_3\}]^+$, 744
$CoC_{45}H_{105}O_{15}P_5$
$[Co\{P(OPr^i)_3\}_5]^+$, 747
$CoC_{48}H_{54}P_4S_2$
$[Co(S_2CPEt_3)(triphos)]^{2+}$, 867
$CoC_{48}H_{55}P_4S_2$
$[Co(S_2CHPEt_3)(triphos)]^+$, 868
$[Co(S_2CHPEt_3)(triphos)]^{2+}$, 868
$CoC_{49}H_{33}N_6O_2$
Co(tetraphenylporphyrin)$(py)(NO_2)$, 674
$CoC_{49}H_{48}OP_4$
$Co\{PhP(CH_2CH_2CH_2PPh_2)_2\}(CO)(PPh_2H)]^+$, 744
$CoC_{52}H_{44}Cl_2P_4$
$[CoCl_2(Ph_2CH{=}CHPPh_2)_2]^+$, 737
$CoC_{52}H_{44}O_2P_4$
$[Co(O_2)(Ph_2PCH{=}CHPPh_2)_2]^+$, 737
$CoC_{52}H_{44}P_4$
$[Co(Ph_2PCH{=}CHPPh_2)_2]^+$, 735, 736, 737
$CoC_{52}H_{48}BrP_4$
$CoBr(dppe)_2$, 736
$[CoBr(dppe)_2]^+$, 736
$CoC_{52}H_{48}ClP_4$
$[CoCl(dppe)_2]^+$, 736
$CoC_{52}H_{48}Cl_2P_4$
$CoCl_2(diphos)_2$, 736
$[CoCl_2(diphos)_2]^-$, 737
$CoC_{52}H_{48}NOP_4$
$[Co(NO)(dppe)_2]^{2-}$, 712
$CoC_{52}H_{48}P_4$
$Co(dppe)_2$, 728
$[Co(dppe)_2]^+$, 735, 737
$[Co(dppe)_2]^{2+}$, 736
$CoC_{52}H_{49}ClP_4$

$[CoHCl(dppe)_2]^-$, 703, 706

$CoC_{52}H_{49}P_4$
$CoH(dppe)_2$, 702, 706, 728

$CoC_{52}H_{50}P_4$
$[Co(H)_2(dppe)_2]^+$, 703

$CoC_{52}H_{52}P_4$
$Co(PPh_2Me)_4$, 718

$CoC_{53}H_{44}NP_4$
$Co(CN)(Ph_2PCH{=}CHPPh_2)_2$, 736, 737

$CoC_{53}H_{48}OP_4$
$[Co\{PhP(CH_2CH_2PPh_2)_2\}(CO)(PPh_3)]^+$, 744

$CoC_{54}H_{42}ClP_4$
$[CoCl\{P(C_6H_4PPh_2\text{-}2)_3\}]^+$, 745

$CoC_{54}H_{43}P_4$
$CoH\{P(C_6H_4PPh_2\text{-}2)_3\}$, 745

$CoC_{54}H_{44}N_2P_4$
$Co(CN)_2(Ph_2PCH{=}CHPPh_2)_2$, 736

$CoC_{54}H_{45}ClP_3$
$CoCl(PPh_3)_3$, 722, 737

$CoC_{54}H_{45}NOP_3$
$Co(NO)(PPh_3)_3$, 662, 712, 716, 717, 1067

$CoC_{54}H_{46}N_2P_3$
$CoH(N_2)(PPh_3)_3$, 638, 657, 707, 708, 709, 710, 711

$CoC_{54}H_{46}P_3$
$CoH(PPh_3)_3$, 726

$CoC_{54}H_{47}P_3$
$Co(H)_2(PPh_3)_3$, 702, 706

$CoC_{54}H_{48}N_2P_4$
$Co(CN)_2(dppe)_2$, 648, 649, 736, 737
$[Co(CN)_2(dppe)_2]^+$, 649

$CoC_{54}H_{48}P_3$
$Co(H)_3(PPh_3)_3$, 638, 702, 706, 707, 726

$CoC_{55}H_{45}OP_3$
$Co(CO)(PPh_3)_3$, 791

$CoC_{55}H_{46}OP_3$
$CoH(PPh_3)_3(CO)$, 711

$CoC_{55}H_{46}O_2P_3$
$Co(O_2CH)(PPh_3)_3$, 791

$CoC_{55}H_{46}O_{10}P_3$
$CoH\{P(OPh)_3\}_3(CO)$, 702

$CoC_{55}H_{48}P_3$
$CoMe(PPh_3)_3$, 723

$CoC_{55}H_{49}NP_3$
$CoH(BH_3CN)(PPh_3)_3$, 704

$CoC_{56}H_{49}NO_9P_3$
$CoH\{P(OPh)_3\}_3(MeCN)$, 708

$CoC_{68}H_{55}BrP_3$
$CoBr(PhC{\equiv}CPh)(PPh_3)_2$, 722

$CoC_{68}H_{55}P_3$
$[Co(PhC{\equiv}CPh)(PPh_3)_3]^+$, 722

$CoC_{72}H_{60}O_{12}P_4$
$Co\{P(OPh)_3\}_4$, 747

$CoC_{72}H_{61}N_2P_4$
$CoH(N_2)(PPh_3)_4$, 702

$CoC_{72}H_{61}O_{12}P_4$
$CoH\{P(OPh)_3\}_4$, 638, 702, 706, 707

$CoC_{79}H_{72}NP_6$
$Co(CN)(dppe)_3$, 648

$CoC_{84}H_{84}N_2P_6S$
$[Co[N(CH_2CH_2PPh_2)_3]\}_2(\mu\text{-}S)$, 828

$CoCrC_2H_{27}N_6O_5$
$[Co(NH_3)_5(NCCH_2)Cr(H_2O)_5]^{5+}$, 678

$CoCrC_{47}H_{39}O_5P_3S_2$
$Co(triphos)(\mu\text{-}CS_2)Cr(CO)_5$, 646, 744

$CoCrC_{47}H_{39}O_5P_3S_3$
$Co(triphos)(\mu\text{-}CS_3)Cr(CO)_5$, 869

$CoCrH_{15}N_5O_4$
$[Co(NH_3)_5OCrO_3]^+$, 825

$CoCr_2C_{51}H_{39}O_{10}P_6$
$Co(triphos)(\mu\text{-}P_3)\{Cr(CO)_5\}_2$, 738

$CoCuC_{12}H_{41}N_{10}$
$[Co(NH_3)_5(\mu\text{-}\overline{NCH{=}NCH{=}CH})Cu(Me_5dien)]^{4-}$, 694, 697

$CoCu_2C_{18}H_{46}N_9S$
$[\{Co(en)_2(H_2NCH_2CH_2S)\}\{Cu(NCMe_2)_2\}_2]^{6+}$, 848

$CoF_4P_2S_4$
$Co(S_2PF_2)_2$, 870

$CoF_6N_6S_6$
$[Co(NSF)_6]^{2+}$, 858

CoF_9NOP_3
$Co(NO)(PF_3)_3$, 712, 717

$CoF_{12}P_4$
$[Co(PF_3)_4]^-$, 718

$CoFeC_8H_{18}N_{12}$
$[Co(NH_3)_5(\overline{NCH{=}NCH{=}CH})Fe(CN)_5]^-$, 699

$CoFeC_9H_{19}N_{10}$
$[Co(NH_3)_5(\overline{N{=}CHCH{=}NCH{=}CH})Fe(CN)_5]^-$, 690

$CoFeC_{11}N_{11}$
$[Co(CN)_5(\mu\text{-}CN)Fe(CN)_5]^{3-}$, 650

$CoFeC_{20}H_{32}N_8OP_2$
$[Fe(CN)_5(\mu\text{-}CN)CO(CN)_2(PEt_3)_2(OH_2)]^{3-}$, 647

$CoFeMoC_{13}H_5O_8S$
$CoFeMoS(CO)_8Cp$, 832

$CoFeMoC_{22}H_{20}O_7S$
$CoFeMoS(CO)_7Cp(PMePrPh)$, 832

$CoHF_{12}P_4$
$CoH(PF_3)_4$, 702, 704, 706, 718

$CoHN_3S_5$
$Co(SNSNH)(SSSN)$, 858

$CoHO_7P_2$
$Co(O_2P_2O_5H)$, 762

$CoH_2N_4S_4$
$Co(SNSNH)_2$, 858

CoH_3NO_3S
$[Co(SO_3)(NH_3)]^+$, 820

$CoH_3N_3O_2$
$[Co(NO)_2(NH_3)]^{2+}$, 666

$CoH_6N_6O_8$
$[Co(NO_2)_4(NH_3)_2]^-$, 668, 670

$CoH_6N_7O_{10}$
$[Co(NO_2)_5(NH_3)_2]^{2-}$, 668

$CoH_9N_6O_6$
$Co(NO_2)_3(NH_3)_3$, 668

$CoH_{12}N_4O_6S_2$
$[Co(SO_3)_2(NH_3)_4]^-$, 822

$CoH_{12}N_4O_7P_2$
$Co(O_2P_2O_5)(NH_3)_4$, 763

$CoH_{12}N_4O_8P_2$
$[Co(OPO_3)_2(NH_3)_4]$, 762

$CoH_{12}N_4O_{10}P_3$
$[Co(OP_3O_9)(NH_3)_4]^{2-}$, 763
$[Co(O_2P_3O_8)(NH_3)_4]^{2-}$, 763

$CoH_{12}N_5O_2$
$[Co(NO_2)(NH_3)_4]^{2+}$, 670

$CoH_{12}N_6O_4$
$[Co(NO_2)_2(NH_3)_4]^+$, 668
$[Co(ONO)(NO_2)(NH_3)_4]^+$, 672
$[Co(ONO)_2(NH_3)_4]^+$, 668, 672

$CoH_{13}N_4O_7P_2$
$Co\{O_2P_2O_4(OH)\}(NH_3)_4$, 760

$CoH_{14}N_4O_{10}P_3$
$Co(O_2P_3O_8H_2)(NH_3)_4$, 763, 764

$CoH_{14}N_5O_3$
$[Co(OH_2)(ONO)(NH_3)_4]^{2+}$, 668, 672

$CoH_{14}N_5O_6P$
$[Co\{O_2P(O)NHP(O)(OH)O\}(NH_3)_4]^+$, 766

$CoH_{14}N_5O_6P_2$
$Co\{O_2P(O)NHP(O)(OH)O\}(NH_3)_4$, 763

$CoH_{15}ClN_5O_2$
$[Co\{OClO)(NH_3)_5]^{2+}$, 826

$CoH_{15}ClN_5O_4$
$[Co(OClO_3)(NH_3)_5]^{2-}$, 826

$CoH_{15}FN_5O_3P$
$[Co\{OP(O)_2F\}(NH_3)_5]^+$, 760

$CoH_{15}N_3O_3$
$[Co(NH_3)_3(H_2O)_3]^{3+}$, 638

$CoH_{15}N_4O_4S$
$[Co(SO_3)(OH_2)(NH_3)_4]^+$, 823
$CoH_{15}N_5O_3S$
$[Co(SO_3)(NH_3)_5]^+$, 820, 822, 823, 857
$CoH_{15}N_5O_3S_2$
$[Co(S_2O_3)(NH_3)_5]^+$, 817
$CoH_{15}N_5O_4S$
$[Co(OSO_3)(NH_3)_5]^+$, 817
$CoH_{15}N_5O_8P_2$
$[Co(OP_2O_7)(NH_3)_5]^-$, 763
$CoH_{15}N_5O_{10}P_3$
$[Co(OP_3O_9)(NH_3)_5]^{2-}$, 763
$CoH_{15}N_6O$
$[Co(NO)(NH_3)_5]^{2+}$, 657, 658, 661, 664
$CoH_{15}N_6O_2$
$[Co(NO_2)(NH_3)_5]^{2+}$, 666, 668, 671, 673, 822
$[Co(ONO)(NH_3)_5]^{2+}$, 666, 668, 670, 671, 672, 673, 698
$CoH_{15}N_8$
$[Co(N_3)(NH_3)_5]^{2+}$, 826, 963
$CoH_{16}FN_5O_3P$
$[Co\{OP(O_2H)F\}(NH_3)_5]^{2+}$, 760
$CoH_{16}N_4O_2$
$[Co(H_2O)_2(NH_3)_4]^{3+}$, 800
$CoH_{16}N_5O$
$[Co(OH)(NH_3)_5]^{2+}$, 760, 790, 822, 825, 860
$CoH_{16}N_5O_7P_2$
$Co\{OP(O)_2OPO_3H\}(NH_3)_5$, 760
$Co(OP_2O_6H)(NH_3)_5$, 760
$CoH_{17}N_5O$
$[Co(H_2O)(NH_3)_5]^{3+}$, 679, 690, 775, 790, 791, 800, 825, 826, 958
$CoH_{17}N_5O_4P$
$[Co(NH_2PO_3H)(H_2O)(NH_3)_4]^{2+}$, 766
$CoH_{17}N_6O_3S$
$[Co(NH_2SO_3)(NH_3)_5]^{2+}$, 698, 858
$[Co(OSO_2NH_2)(NH_3)_5]^{2+}$, 858
$CoH_{18}N_5O_4P$
$[Co\{OP(OH)_3\}(NH_3)_5]^{3+}$, 752
$CoH_{18}N_6$
$[Co(NH_3)_6]^{3+}$, 866
$CoH_{19}N_7O_2S$
$[Co(H_2NSO_2NH_2)(NH_3)_5]^{3+}$, 858
$CoH_{30}N_{10}O_2$
$[\{Co(NH_3)_5\}_2(\mu\text{-}O_2)]^{4+}$, 789
$[\{Co(NH_3)_5\}_2(O_2)]^{5+}$, 781
$CoHgCH_{15}N_6S$
$[Co(NH_3)_5(\mu\text{-}NCS)Hg]^{4+}$, 681
$CoIN_2O_2$
$\{Co(NO)_2I\}_n$, 660, 663
$CoKC_{16}H_{14}N_2O_2$
Co(salen)K, 637
$CoKC_{27}H_{34}N_2O_5$
$\{Co(Pr_2salen)(CO_2)K(THF)\}_n$, 638
$CoMnC_{49}H_{44}O_2P_3S_2$
Co(tripos)(μ-CS_2)Mn(CO)$_2$Cp, 646
$CoMoC_{10}H_2N_{10}O_4$
$[Co(CN)_5OOMoO(OH_2)(CN)_5]^{5+}$, 780
$CoMoH_{15}N_5O_4$
$[Co(NH_3)_5OMoO_3]^+$, 825
$CoMo_6H_6O_{24}$
$[Co\{Mo_6O_{18}(OH)_6\}]^{3-}$, 827
CoN_2S_6
$Co(SSSN)_2$, 858
$CoN_3O_2S_3$
$Co(NO)_2(S_3N)$, 658, 660, 858
CoN_3O_3
Co(NO)(ONNO), 658
CoN_3O_4
$\{Co(NO)_2(ONO)\}_n$, 660
CoN_4S_4
$Co(N_4S_4)$, 858
CoN_6O_{12}
$[Co(NO_2)_6]^{3-}$, 638, 667
$CoNb_6CH_3NO_{22}$
$[Co(Nb_6O_{19})(CO_3)(NH_3)]^{7-}$, 826
$CoReH_{15}N_5O_4$
$[Co(OReO_3)(NH_3)_5]^{2+}$, 198, 826
$CoRuC_3H_{31}N_{11}O_4S$
$[Co(NH_3)_5(\mu\text{-}HNCH{=}NCH{=}CH)Ru(NH_3)_4(SO_4)]^{2+}$, 696
$CoRuC_{10}H_{19}N_{11}$
$[Co(en)_2(NH_3)(\mu\text{-}NC)Ru(CN)_5]^-$, 283
$CoRuC_{10}H_{41}N_{11}O$
$[Co(NH_3)_4(H_2O)\{NCC(CH_2CH_2)_3CCN\}Ru(NH_3)_5]^{5+}$, 679
$CoRuC_{16}H_{11}ClO_4P$
$RuCoHCl(\mu\text{-}PPh_2)(CO)_4$, 373
$CoRuC_{18}H_{16}N_{12}O_4$
$Co\{L\text{-}O_2CCH(NH_2)CH_2C{=}CHNHCH{=}N\}_2(\mu\text{-}NC)Ru(CN)_5]^{3-}$, 283
$CoRuC_{19}H_{10}O_7P$
$RuCo(\mu\text{-}PPh_2)(CO)_7$, 373
$CoRuC_{36}H_{25}O_6P_2$
$RuCo(\mu\text{-}PPh_2)(CO)_6(PPh_3)$, 373
$CoRuC_{53}H_{40}O_5P_3$
$CoRu(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, 373
$CoSiC_7H_9O_4$
$Co(SiMe_3)(CO)_4$, 657
$CoSiC_{60}H_{62}O_3P_3$
$CoH_2\{Si(OEt)_3\}(PPh_3)_3$, 655
$CoW_{12}O_{40}$
$[CoW_{12}O_{40}]^{5-}$, 827
$Co_2AgC_{12}H_{36}N_4O_4S_2$
$[\{Co(en)_2(O_2CCH_2S)\}_2Ag]^{3+}$, 848
$Co_2AsC_{82}H_{81}$
$\{Co\{MeC(CH_2AsPh_2)_3\}\}_2(\mu\text{-}H)_3$, 773
$Co_2As_3C_{24}H_{23}F_6O_3$
$Co_2\{C_2(CF_3)_2\}(CO)_3\{MeAs(C_6H_4AsMe_2\text{-}2)_2\}$, 769
$Co_2As_6C_{82}H_{81}$
$\{Co\{MeC(CH_2AsPh_2)_3\}\}_2(\mu\text{-}H)_3$, 769
$Co_2As_8C_{40}H_{68}O_2$
$[\{Co(H_2O)(diars)_2\}_2]^{4+}$, 772
$Co_2CH_{20}N_6O_5$
$[\{Co(NH_3)_3\}_2\{\mu\text{-}(HO)_2CO_3\}]^{2+}$, 814
$Co_2CN_4OS_4$
$Co_2(CO)(N_4S_4)$, 858
$Co_2C_2H_{18}N_6S_7$
$Co_2(C_2S_7)(NH_3)_6$, 869
$Co_2C_2H_{27}N_9O_4$
$[Co(NH_3)_4(C_2O_4)Co(NH_3)_5]^{4+}$, 800
$Co_2C_2H_{29}N_9O_2$
$[\{Co(NH_3)_4\}_2(\mu\text{-}NH_2)(\mu\text{-}OAc)]^{4+}$, 794
$Co_2C_2H_{29}N_9O_5$
$[Co(NH_3)_5(C_2O_4)Co(NH_3)_4(H_2O)]^{4+}$, 800
$Co_2C_3H_9Br_4F_{12}N_3P_6$
$Co_2Br_4\{MeN(PF_2)_2\}_3$, 735
$Co_2C_5H_9F_{12}N_3O_2P_6$
$Co_2(CO)_2\{MeN(PF_2)_2\}_3$, 735
$Co_2C_5H_{15}F_{20}N_5P_{10}$
$Co_2\{MeN(PF_2)_2\}_5$, 735
$Co_2C_6H_{10}O_6S_3$
$[\{Co(SCH_2CH_2CO_2)(OH)\}_2]^{2-}$, 838
$Co_2C_6H_{15}N_{11}$
$Co(CN)_5(\mu\text{-}CN)Co(NH_3)_5$, 650, 654
$Co(CN)_5(\mu\text{-}NC)Co(NH_3)_5$, 650
$Co_2C_6H_{15}N_{11}S$
$Co(CN)_5(\mu\text{-}NCS)Co(NH_3)_5$, 650
$Co(CN)_5(\mu\text{-}SCN)Co(NH_3)_5$, 650, 654
$Co_2C_6H_{25}N_8O_3$
$[\{Co\{N(CH_2NH_2)_3\}\}_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+}$, 786
$Co_2C_6H_{30}N_{10}O_2$
$[\{Co\{N(CH_2NH_2)_3\}(NH_3)\}_2(O_2)]^{4+}$, 785
$Co_2C_6O_6P_2$
$Co_2(CO)_6P_2$, 699
$Co_2C_8H_{33}N_8O_3$
$[\{Co(en)_2\}_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+}$, 786, 788

$Co_2C_8H_{34}N_9O_2$
$[\{Co(en)_2\}_2(\mu\text{-}NH_2)(\mu\text{-}O_2)]^{3+}$, 781, 788
$[\{Co(en)_2\}_2(\mu\text{-}NH_2)(\mu\text{-}O_2)]^{4+}$, 817

$Co_2C_8H_{34}N_9O_4$
$[\{Co(en)_2\}_2(\mu\text{-}NH_2)(\mu\text{-}SO_4)]^{3+}$, 789

$Co_2C_8H_{34}N_{10}O_2$
$[\{Co\{N(CH_2NH_2)_3\}(H_2NMe)\}_2(O_2)]^{4+}$, 785

$Co_2C_8H_{34}N_{11}O_2$
$[\{Co(en)_2\}_2(\mu\text{-}NH_2)(\mu\text{-}NO_2)]^{4+}$, 789

$Co_2C_8H_{35}N_9O$
$[\{Co(en)_2\}_2(\mu\text{-}NH_2)(\mu\text{-}OH)]^{4+}$, 788

$Co_2C_8H_{35}N_9O_2$
$[\{Co(en)_2\}_2(\mu\text{-}NH_2)(\mu\text{-}OOH)]^{4+}$, 786

$Co_2C_8H_{36}N_8O_8Te$
$[\{Co(en)_2\}_2\{O_2Te(OH)_4O_2\}]^{2+}$, 817

$Co_2C_8H_{38}N_{10}O_2$
$[\{Co(en)_2(NH_3)\}_2(O_2)]^{4+}$, 785
$[\{Co(dien)(NH_3)_2\}_2(\mu\text{-}O_2)]^{4+}$, 785

$Co_2C_8N_8$
$[Co_2(CN)_8]^{8-}$, 646

$Co_2C_8O_8$
$Co_2(CO)_8$, 709

$Co_2C_9H_{36}N_{12}O_2$
$[\{Co\{N(CH_2NH_2)_3\}\}_2(\mu\text{-}O_2)\{\mu\text{-}N(CH_2NH_2)_3\}]^{4+}$, 786

$Co_2C_{10}H_{10}N_2O_2$
$(CoCp)_2(\mu_2\text{-}NO)_2$, 661

$Co_2C_{10}H_{14}N_8O_4$
$\{Co(NO)_2(\overline{NN{=}CMeCH{=}CMe})\}_2$, 660

$Co_2C_{10}H_{29}N_7O_9$
$[Co(NH_3)_5\{Co\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}(H_2O)\}]^{2+}$, 811

$Co_2C_{10}N_2O_2$
$\{CoCp(\mu\text{-}NO)\}_2$, 666

$Co_2C_{10}N_{10}$
$[Co_2(CN)_{10}]^{6-}$, 648, 649

$Co_2C_{10}N_{10}O_2$
$[\{Co(CN)_5\}_2(\mu\text{-}O_2)]^{5-}$, 650, 781, 784
$[\{Co(CN)_5\}_2(\mu\text{-}O_2)]^{6-}$, 650, 830
$[\{Co(CN)_5\}_2(\mu\text{-}O_2)]^{8-}$, 654

$Co_2C_{10}N_{10}S_2$
$[Co(CN)_4(\mu\text{-}NCS)(\mu\text{-}SCN)Co(CN)_4]^{4-}$, 650
$[\{Co(CN)_5\}_2(\mu\text{-}S_2)]^{6-}$, 830

$Co_2C_{10}N_{10}S_2O_2$
$[\{Co(CN)_5\}_2(\mu\text{-}SSO_2)^{6-}$, 830

$Co_2C_{10}N_{10}Se_2$
$[\{Co(CN)_5\}_2(\mu\text{-}Se_2)]^{6-}$, 830

$Co_2C_{11}H_{10}NO_2$
$(CoCp)_2(\mu_2\text{-}NO)(\mu_2\text{-}CO)$, 661

$Co_2C_{12}H_{28}Cl_2O_6$
$\{CoCl\{(MeOCH_2CH_2)_2O\}\}_2$, 828

$Co_2C_{12}H_{30}S_6$
$[\{Co(SEt)_2\}_2(\mu\text{-}SEt)_2]^{2-}$, 834

$Co_2C_{12}H_{37}N_8O_3$
$[\{Co\{(H_2NCH_2CH_2NHCH_2)_2\}\}_2(\mu\text{-}OH)(\mu\text{-}O_2)]^{3+}$, 786

$Co_2C_{14}H_{30}N_2O_{12}P_4$
$Co_2(CO)_4\{MeN\{P(OMe)_2\}_2\}_2$, 735

$Co_2C_{16}F_{24}S_8$
$\{Co\{S_2C_2(CF_3)_2\}_2\}_2$, 876
$[\{Co\{S_2C_2(CF_3)_2\}_2\}_2]^{-}$, 876
$[\{Co\{S_2C_2(CF_3)_2\}_2\}_2]^{2-}$, 876

$Co_2C_{16}H_6N_{10}O_4$
$[\{Co(CN)_5\}_2(MeO_2CC{=}CCO_2Me)]^{6-}$, 654

$Co_2C_{16}H_{30}S_{14}$
$\{Co(S_2CSEt)_2\}_2(\mu\text{-}SEt)_2$, 867

$Co_2C_{16}H_{36}N_4S_4$
$\{Co(SCH_2CH_2NMeCH_2CH_2NMeCH_2CH_2S)\}_2$, 662

$Co_2C_{16}H_{36}N_5OS_4$
$[\{Co(SCH_2CH_2NMeCH_2CH_2NMeCH_2CH_2S)\}_2(\mu_2\text{-}NO)]^{-}$, 661
$\{Co(SCH_2CH_2NMeCH_2CH_2NMeCH_2CH_2S)\}_2(\mu_2\text{-}NO)$, 662

$Co_2C_{16}H_{48}N_2O_2P_4$
$\{CoMe(PMe_3)_2\}_2(\mu\text{-}ONMe)_2$, 716

$Co_2C_{16}N_8S_4$
$[\{Co\{S_2C_2(CN)_2\}_2\}_2]^{2-}$, 879

$Co_2C_{19}H_{55}P_7$
$Co_2(PMe_3)_3(Me_2PCH_2PMe_2)_2$, 722

$Co_2C_{20}H_{20}Cl_2N_6O_6$
$\{Co(NO_3)(py)_2\}_2(\mu\text{-}Cl)_2$, 686

$Co_2C_{20}H_{52}N_8O_4$
$[\{Co(H_2O)(1,4,8,11\text{-tetraazacyclotetradecane})\}_2(O_2)]^{4+}$, 786

$Co_2C_{22}H_{48}N_{10}O_2S_2$
$[\{Co(SCN)(1,4,8,11\text{-tetraazacyclotetradecane})\}_2(O_2)]^{2+}$, 786

$Co_2C_{23}H_{15}O_5P_3$
$Co_2(CO)_5(PPh_3)(\mu\text{-}P_2)$, 699

$Co_2C_{24}Cl_{16}S_8$
$[\{Co(1,2\text{-}S_2C_6Cl_4)_2\}_2]^{2-}$, 876

$Co_2C_{24}H_{20}N_4O_4P_2$
$\{Co(NO)_2(PPh_2)\}_2$, 712

$Co_2C_{24}H_{72}O_{24}P_8$
$Co_2\{P(OMe)_3\}_8$, 747

$Co_2C_{28}H_{60}N_4P_4S_4$
$\{Co(NCS)(PEt_3)_2\}_2(NCS)_2$, 725

$Co_2C_{40}H_{46}N_6O_6$
$\{Co\{HN(CH_2CH_2CH_2N{=}CHC_6H_4O\text{-}2)_2\}\}_2(O_2)$, 778

$Co_2C_{44}H_{55}N_4O_2P_5$
$Co_2(CN)_4(PMe_2Ph)_5(O_2)$, 785

$Co_2C_{54}H_{48}Cl_2N_2P_4$
$CoCl_3(CN)Co(CN)\{dppc\}_2$, 649

$Co_2C_{56}H_{40}S_8$
$\{Co(S_2C_2Ph_2)_2\}_2$, 876

$Co_2C_{60}H_{90}N_2P_6$
$\{Co(PEt_2Ph)_3\}_2(\mu\text{-}N_2)$, 710, 711

$Co_2C_{65}H_{110}N_5S_{10}$
$[Co_2\{S_2CN(C_6H_{11})_2\}_5]^{+}$, 866

$Co_2C_{82}H_{78}P_6S_2$
$[Co_2(triphos)_2(\mu\text{-}S)_2]^{+}$, 834

$Co_2C_{82}H_{78}P_9$
$\{Co(triphos)\}_2(\mu\text{-}P_3)$, 738
$[\{Co(triphos)\}_2(\mu\text{-}P_3)]^{+}$, 701
$[\{Co(triphos)\}_2(\mu\text{-}P_3)]^{2+}$, 700
$[\{Co(triphos)\}_2(\mu\text{-}P_3)]^{3+}$, 701

$Co_2C_{82}H_{80}O_2P_6$
$[Co_2(\mu\text{-}OH)_2(triphos)_2]^{2+}$, 834

$Co_2C_{82}H_{81}P_6$
$[Co_2(H)_3(triphos)_2]^{+}$, 704

$Co_2C_{83}H_{78}P_6S_2$
$[\{Co(triphos)\}_2(\mu\text{-}CS_2)]^{2+}$, 646

$Co_2C_{84}H_{84}P_6S_2$
$[Co_2(triphos)_2(\mu\text{-}SMe)_2]^{2+}$, 834

$Co_2Cl_2N_4O_4$
$\{Co(NO)_2Cl\}_2$, 658, 660, 663, 717

$Co_2H_{18}N_{10}O_{12}Se$
$\{Co(NH_3)_3(NO_2)_2\}_2(O_2SeO_2)$, 880

$Co_2H_{24}N_8O_2$
$[\{Co(NH_3)_4\}_2(O_2)]^{4+}$, 775

$Co_2H_{26}N_9O_2$
$[\{Co(NH_3)_4\}_2(\mu\text{-}NH_2)(\mu\text{-}O_2)]^{3+}$, 786
$[\{Co(NH_3)_4\}_2(\mu\text{-}NH_2)(\mu\text{-}O_2)]^{4+}$, 781, 817

$Co_2H_{30}N_{10}O_2$
$[\{Co(NH_3)_5\}_2(\mu\text{-}O_2)]^{4+}$, 785
$[\{Co(NH_3)_5\}_2(O_2)]^{5+}$, 781

$Co_2H_{30}N_{12}O_2$
$\{Co(NH_3)_5\}_2(N_2O_2)$, 660, 661, 662
$[Co_2(N_2O_2)(NH_3)_{10}]^{4+}$, 658

$Co_2HgC_{24}H_{72}O_{24}P_8$
$Hg\{Co\{P(OMe)_3\}_4\}_2$, 718

$Co_2Hg_2C_{84}H_{84}N_2P_6$
$\{Co\{N(CH_2CH_2PPh_2)_3\}\}_2(\mu\text{-}Hg)_2$, 738

$Co_2Mo_{10}H_4O_{38}$
$[Co_2\{Mo_{10}O_{34}(OH)_4\}]^{6-}$, 827

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$Co_2RuC_{12}H_{36}N_6S_6$

$[Ru\{Co(SCH_2CH_2NH_2)_3\}_2]^{3-}$, 433
$Co_3As_2C_{46}H_{84}N_4O_6P_2$
$Co\{Co\{As(O)MePh\}(HDMG)(PBu_3)\}_2$, 775
$Co_3As_{12}C_{164}H_{156}I_6$
$Co_3\{MeC(CH_2AsPh_2)_3\}_4I_6$, 769
$Co_3C_9O_9P$
$Co_3(CO)_9P$, 699
$Co_3C_9O_9S$
$Co_3S(CO)_9$, 830
$Co_3C_9O_9Se$
$Co_3Se(CO)_9$, 830
$Co_3C_{12}H_{36}N_6S_6$
$[\{Co(SCH_2CH_2NH_2)_3\}_2(\mu_6\text{-}Co)]^{3+}$, 839
$Co_3C_{14}H_{25}O_4S_5$
$Co_3(SEt)_5(CO)_4$, 833
$Co_3C_{18}H_{30}ClF_9O_{16}S$
$Co_3Cl(SO_4)(O_2CCF_3)_3(DME)_3$, 828
$Co_3C_{24}H_{24}S_7$
$[Co_3(\mu_3\text{-}S)\{1,2\text{-}(SCH_2)_2C_6H_4\}_3]^{2-}$, 833
$Co_3C_{34}H_{70}O_6P_6$
$Co\{(OPEt_2)_3CoCp\}_2$, 767
$Co_3C_{48}H_{120}N_4P_{12}$
$[\{Co\{N(CH_2CH_2PMe_2)_3\}\}_3\{N(CH_2CH_2PMe_2)_3\}]^{6+}$, 745
$Co_3H_{25}C_2N_{12}O_5$
$[Co_3(CN)_2(OH)(NO_2)(NH_3)_8]^{3+}$, 654
$Co_4C_3H_{14}I_3NO_{24}$
$[Co_4I_3O_{18}(OH_2)_4\{O_2CCH(NH_2)Me\}]^{4-}$, 827
$Co_4C_{10}O_{10}S_2$
$Co_4(S)_2(CO)_{10}$, 830
$Co_4C_{16}H_{64}N_{16}O_{10}Te_2$
$[\{Co(en)_2\}_4\{O_4TeO_2TeO_4\}]^{4+}$, 817
$Co_4C_{20}H_{50}S_{10}$
$[Co_4(\mu\text{-}SEt)_6(SEt)_4]^{2-}$, 834
$Co_4C_{42}H_{35}ClS_7$
$[Co_4(\mu\text{-}SPh)_6(Cl)_2(SPh)]^{2-}$, 834
$Co_4C_{44}H_{124}P_{12}$
$[\{Co(C_2H_4)(PMe_3)_3\}_4]^{2-}$, 718
$Co_4C_{60}H_{50}S_{10}$
$[Co_4(\mu\text{-}SPh)_6(SPh)_4]^{2-}$, 832, 834
$Co_4H_{12}I_3O_{24}$
$[Co_4I_3O_{12}(OH)_{12}]^{3-}$, 827
$Co_5C_{20}H_{25}O_{10}S_5$
$Co_5(SEt)_5(CO)_{10}$, 834
$Co_6C_6O_6S_8$
$Co_6(\mu_3\text{-}S)_8(CO)_6$, 830, 833
$Co_6C_{13}O_{12}S$
$Co_6(C)(S)_2(CO)_{12}$, 830
$Co_6C_{14}O_{14}S_4$
$Co_6(S)_4(CO)_{14}$, 830
$Co_6C_{16}O_{16}P$
$[Co_6(CO)_{14}(\mu\text{-}CO)_2P]^{-}$, 699
$Co_6C_{19}H_{20}O_{11}S_5$
$Co_6S(SEt)_4(CO)_{11}$, 834
$Co_8C_{36}H_{30}S_{12}$
$[Co_8(\mu_4\text{-}S)_6(SPh)_6]^{5-}$, 833
$Co_6C_{36}H_{90}P_6S_8$
$[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^{+}$, 833
$Co_8C_{48}H_{40}S_{14}$
$[Co_8(\mu_4\text{-}S)_6(SPh)_8]^{4-}$, 832
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Co_9S_8, 833
$CrCoC_2H_{27}N_6O_5$
$[Co(NH_3)_5(NCCH_2)Cr(H_2O)_5]^{5+}$, 678
$CrCoC_{47}H_{39}O_5P_3S_2$
Co(triphos)(μ-CS_2)Cr(CO)$_5$, 646, 744
$CrCoC_{47}H_{39}O_5P_3S_3$
Co(triphos)(μ-CS_3)Cr(CO)$_5$, 869
$CrCoC_{51}H_{39}O_{10}P_6$
Co(triphos)(μ-P_3)$\{Cr(CO)_5\}_2$, 738
$CrCoH_{15}N_5O_4$
$[Co(NH_3)_5OCrO_3]^{+}$, 825
$CrFeC_6N_6$
$[CrFe(CN)_6]^{-}$, 1204
$CrH_{17}N_5O$
$[Cr(NH_3)_5(H_2O)]^{3-}$, 958
$CrReC_{40}H_{60}Cl_4N_2O_2P_4$
$CrCl_3(THF)_2\{(N_2)ReCl(PMe_2Ph)_4\}$, 133
$CrRuH_{21}NO_{10}$
$Ru(OH_2)_5(\mu\text{-}NH)Cr(OH_2)_5]^{5+}$, 362
$CrRuH_{25}N_5O_6$
$[Ru(NH_3)_4(OH_2)(\mu\text{-}NH)Cr(OH_2)_5]^{5+}$, 299
$CuC_8H_{12}N_4$
$[Cu(NCMe)_4]^{+}$, 174, 193
$CuCoC_{12}H_{41}N_{10}$
$[Co(NH_3)_5(\mu\text{-}\overline{NCH{=}NCH{=}CH})Cu(Me_5dien)]^{4+}$, 694, 697
$CuIrC_{16}H_{25}P_2$
$[IrH_3(PMe_2Ph)_2Cu]^{-}$, 1164
$Cu_2CoC_{18}H_{46}N_9S$
$[\{Co(en)_2(H_2NCH_2CH_2S)\}\{Cu(NCMe_2)_2\}_2]^{6-}$, 848
$Cu_3Ir_2C_{54}H_{81}N_3P_6$
$[Ir_2Cu_3H_6(MeCN)_3(PMe_2Ph)_6]^{3+}$, 1164

$ErMn_2H_4$
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$FeAsC_{18}H_{15}Cl_3$
$Fe(AsPh_3)Cl_3$, 226
$FeAsCoMoWC_2H_6S$
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$FeBr_2(CO)_2$(diars), 1234
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$Fe(CO)_3(AsPh_3)_2$, 1199
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$Fe\{AsMe(CH_2CH_2CH_2AsMe_2)_2\}(NCS)_2$, 226
$FeAs_4C_{12}H_{36}ClO_8$
$[Fe(ClO_4)(OAsMe_3)_4]^{-}$, 1183, 1237
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$[Fe\{As(CH_2CH_2CH_2AsMe_2)_3\}Cl_2]^{+}$, 226
$FeAs_4C_{20}H_{32}Cl_2$
$[Fe(diars)_2Cl_2]^{+}$, 266
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$FeAuC_{21}H_{15}NO_4P$
$AuFe(CO)_3(NO)(PPh_3)$, 1189
$FeAuC_{38}H_{30}NO_3P_2$
$AuFe(CO)_2(NO)(PPh_3)_2$, 1189
$FeBC_{16}H_{34}F_4N_4$
[Fe(hexamethyl-1,4,8,11-tetraazacyclotetradecane)-(BF_4)]$^{+}$, 1251
$FeBC_{18}H_9FN_6O_3P$
$[Fe\{FB(ON{=}CC_5H_3N)_3P\}]^{2+}$, 1232
$FeB_2C_6H_4F_3N_6$
$Fe(CNH)_4(CNBF_3)_2$, 1205
$FeB_2C_{14}H_{42}N_2O_{12}P_4$
$Fe(BH_2CN)_2\{P(OMe)_3\}_4$, 1234
$FeB_6C_6F_{18}N_6$
$[Fe(CNBF_3)_6]^{4-}$, 1205
$FeBrCl_3$
$[FeCl_3Br]^{-}$, 248
$FeBr_2Cl_2$
$[FeCl_2Br_2]^{-}$, 248
$FeBr_3Cl$
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$[FeBr_4]^-$, 218, 248
$FeCH_{10}NO_5S$
$[Fe(H_2O)_5(SCN)]^{2+}$, 1180
$FeC_2H_4ClN_2S_4$
$FeCl(S_2CNH_2)_2$, 1183
$FeC_2H_6I_2O_2P_2$
$Fe(CO)_2(PH_3)_2I_2$, 1197
$FeC_2H_{10}Cl_2N_2$
$Fe(NH_2Me)_2Cl_2$, 1210
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FeC_3NO_4
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$[Fe(CN)_4Cl_2]^{5-}$, 1201
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$FeC_4H_6Cl_2N_2$
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$FeCl_3(THF)$, 227
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$[Fe(NCO)_4]^-$, 222
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$[Fe(CN)_4(NO)]^{2-}$, 1189, 1190
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$[Fe(CO)_4]^{2-}$, 1183, 1184
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$[Fe(CN)_5Cl]^{5-}$, 1201
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$[Fe(CN)_5H]^{3-}$, 1201
$FeC_5H_2N_5O$
$[Fe(CN)_5(H_2O)]^{3-}$, 1190, 1204, 1205, 1206
$[Fe(CN)_5(H_2O)]^{4-}$, 1201
$FeC_5H_3N_6$
$[Fe(CN)_5(NH_3)]^{3-}$, 1190, 1191, 1205, 1206
$FeC_5H_3N_6O$
$[Fe(CN)_5(NH_2OH)]^-$, 1190
FeC_5N_5
$Fe(CN)_5]^{4-}$, 1201
$FeC_5N_5O_3S$
$[Fe(CN)_5(SO_3)]^{5-}$, 1205
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$[Fe(CN)_5(NOS)]^{4-}$, 1190
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$[Fe(CN)_5(NO_2)]^{4-}$, 1190
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$[Fe(CO)_5]^+$, 1198
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$FeC_6H_4N_6$
$Fe(CN)_2(CNH)_4$, 1205
$FeC_6H_5O_3$
$Fe(\eta\text{-}C_3H_5)(CO)_3$, 1201
$FeC_6H_6N_6$
$[Fe(CNH)_6]^{2+}$, 1204
$FeC_6H_6N_8S_2$
$Fe(NCS)_2(HNN{=}CHN{=}CH)_2$, 1213
$FeC_6H_8N_6$
$[Fe(CN)_4(en)]^{2-}$, 1206, 1225
$FeC_6H_{10}O_2S_4$
$Fe(S_2COEt)_2$, 1246
$FeC_6H_{10}S_6$
$[Fe(SEt)(S_2CSEt)(CS_3)]^{2-}$, 1246
$FeC_6H_{12}IN_3OS_4$
$Fe(NO)(S_2CNMe_2)_2Br$, 1192
$FeC_6H_{12}N_2O_2S_2$
$Fe(SOCNMe_2)_2$, 1245
$FeC_6H_{12}N_3OS_4$
$Fe(NO)(S_2CNMe_2)_2$, 1192
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$Fe\{ONMeC(S)H\}_3$, 234
$FeC_6H_{12}N_4O_3S_4$
$Fe(NO)(S_2CNMe_2)_2(NO_2)$, 1192
$FeC_6H_{13}Cl_3N_2$
$FeCl_3\{N(CH_2CH_2)_3NH\}$, 1210
$FeC_6H_{13}I_2N_2$
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$FeC_6H_{24}N_6$
$[Fe(en)_3]^{2+}$, 1211
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$[Fe(CN)_5(CO)]^{3-}$, 1206
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$[Fe(CN)_6]^{2-}$, 1182
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$[Fe(CN)_5(NCS)]^{3-}$, 1190
FeC_6N_6Se
$[Fe(CN)_5(NCS)]^{3-}$, 1190
$FeC_6N_6S_6$
$[Fe(NCS)_6]^{3-}$, 222
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$[Fe(S_2C_2O_2)_3]^{3-}$, 246
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$[Fe(C_2O_4)_3]^{3-}$, 229
$FeC_7H_8N_7$
$[Fe(CN)_5(en)]^{3-}$, 1206
$FeC_7H_{17}Cl_3N_2O$
$FeCl_3\{N(CH_2CH_2)_3NMe\}(H_2O)$, 1210
$FeC_7H_{18}Cl_3N_3$
$FeCl_3\{N(CH_2CH_2)_3NMe\}(NH_3)$, 1210
$FeC_8H_{12}Cl_2N_4$
$FeCl_2(CNMe)_4$, 1209
$FeC_8H_{12}N_2O_2S_4$
$Fe(CO)_2(S_2CNMe_2)_2$, 1245
$FeC_8H_{14}N_4O_4$
$Fe(HDMG)_2$, 1231
$FeC_8H_{20}Cl_2N_2O$
$FeCl_2\{O(CH_2CH_2NMe_2)_2\}$, 1238
$FeC_8H_{20}O_4S_8$
$[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$, 239
$FeC_8H_{20}S_4$
$[Fe(SEt)_4]^{2-}$, 237
$FeC_8H_{22}Cl_2P_2$
$FeCl_2(PEt_2H)_2$, 1233
$FeC_8H_{22}N_8O_4$
$Fe(HDMG)_2(N_2H_4)_2$, 1231
$FeC_8H_{24}Cl_2O_4S_4$
$[Fe(DMSO)_4Cl_2]^+$, 227
$FeC_8H_{24}N_2P_4S_4$
$Fe\{(SMe_2P)_2N\}_2$, 1240, 1246
$FeC_8N_5OS_4$
$Fe(NO)\{S_2C_2(CN)_2\}_2$, 1193
$FeC_9H_4N_6O_2$
$[Fe(CN)_5(NCOCHCOMe)]^{4-}$, 1190
$FeC_9H_{15}O_3S_6$
$Fe(S_2COEt)_3$, 244

$[Fe(S_2COEt)_3]^-$, 1246
$FeC_9H_{15}S_9$
$[Fe(S_2CSEt)_3]^-$, 1246
$FeC_9H_{16}O_3P_2$
$Fe(CO)_3(Me_2PCH_2CH_2PMe_2)$, 1196
$FeC_9H_{18}N_3O_3S_3$
$Fe\{SC(O)NMe_2\}_3$, 247
$FeC_9H_{18}N_3S_6$
$Fe(S_2CNMe_2)_3$, 244
$FeC_9H_{23}N_5O$
$[Fe\{HN(CH_2CH_2NHCH_2CH_2NH_2)_2\}CO]^{2+}$, 1211
$FeC_9H_{27}Cl_2O_9P_3$
$FeCl_2\{P(OMe)_3\}_3$, 1197, 1234
$FeC_9H_{27}Cl_2P_3$
$FeCl_2(PMe_3)_3$, 1197
$FeC_9H_{29}O_9P_3$
$FeH_2\{P(OMe)_3\}_3$, 1234
$FeC_9H_{30}N_6$
$[Fe\{H_2N(CH_2)_3NH_2\}_3]^{2+}$, 1211
$FeC_{10}H_6F_{12}O_6$
$Fe(hfacac)_2(H_2O)_2$, 1237
$FeC_{10}H_6N_6$
$[Fe(CN)_4(2\text{-}pyCH{=}NH)]^{2-}$, 1226
$FeC_{10}H_8Cl_2N_2$
$FeCl_2(bipy)$, 1221
$FeC_{10}H_8N_2O_2$
Fe(2-Me-quinolinolate)$(NO)_2$, 1195
$FeC_{10}H_{12}N_2O_8$
$[Fe\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}]^{2-}$, 692
$FeC_{10}H_{12}N_8$
$Fe(CN)_2(CNMe)_4$, 1209
$FeC_{10}H_{14}ClO_4$
$Fe(acac)_2Cl$, 230
$FeC_{10}H_{14}N_2O_2S_4$
$Fe(NO)_2(MeCSCHCSMe)_2$, 1193
$FeC_{10}H_{14}N_2O_9$
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$FeC_{10}H_{14}O_4$
$Fe(acac)_2$, 1236, 1237
$FeC_{10}H_{14}S_4$
$Fe(MeCSCHCSMe)_2$, 1246
$FeC_{10}H_{15}N_2O_2$
$Fe(\eta\text{-}C_3H_5)(CO)_2(\overline{CNMeCH_2CH_2NMe})$, 1201
$FeC_{10}H_{15}N_2O_9$
$Fe\{(O_2CCH_2)_2NCH_2CH_2(CH_2CO_2H)(CH_2CO_2)\}\cdot(H_2O)$, 253
$FeC_{10}H_{16}Cl_2N_4$
$FeCl_2(\overline{N{=}CMeNMeCH{=}CH})_2$, 1213, 1214
$FeC_{10}H_{16}N_2O_2P_2$
$Fe(NO)_2(diphos)$, 1194
$FeC_{10}H_{18}N_6$
$Fe\{C(NH_2)NHMe\}(CNMe)_4$, 1209
$FeC_{10}H_{20}IN_3OS_4$
$Fe(NO)(S_2CNEt_2)_2I$, 1192
$FeC_{10}H_{20}N_2S_4$
$Fe(S_2CNEt_2)_2$, 1245
$FeC_{10}H_{20}N_3OS_4$
$Fe(NO)(S_2CNEt_2)_2$, 1192
$FeC_{10}H_{24}Br_2N_4$
$[Fe\{1N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH(CH_2)_3\}Br_2]^+$, 256
$FeC_{10}H_{27}O_{11}P_3$
$Fe(CO)_2\{P(OMe)_3\}_3$, 1197
$FeC_{11}H_2O_2P$
$Fe(\eta\text{-}C_3H_5)(CO)_2PEt_3$, 1201
$FeC_{11}H_5N_6O$
$[Fe(CN)_5(ONPh)]^{3-}$, 1205
$FeC_{11}H_5N_7O$
$[Fe(CN)_5\{N(O)NPh\}]^{4-}$, 1191
$FeC_{11}H_8N_7$
$[Fe(CN)_5(\overline{N{=}CMeCH{=}NCH{=}CMe})]^{3-}$, 1214
$[Fe(CN)_5(2\text{-}pyCH_2NH_2)]^{2-}$, 1226
$FeC_{11}H_{11}$
$FeCp(\eta^6\text{-}C_6H_6)$, 1203
$FeC_{11}H_{15}N_6$
$[Fe(CN)(CNMe)_5]^+$, 1209
$FeC_{12}H_8Cl_3N_4$
$Fe(4\text{-}NCpy)_2Cl_3$, 222, 248
$FeC_{12}H_8F_2N_2$
$FeF_2(phen)$, 1221
$FeC_{12}H_{12}N_2S_2$
$Fe(SC_6H_4NH_2\text{-}2)_2$, 1248
$FeC_{12}H_{16}Cl_2O_2P_2$
$FeCl_2(diphos)(CO)_2$, 1233
$FeC_{12}H_{16}N_2O_4$
$[Fe(phen)(H_2O)_4]^{2-}$, 1221
$FeC_{12}H_{18}N_6$
$Fe(CNMe)_6$, 1208
$[Fe(CNMe)_6]^{2-}$, 1208–1210
$[Fe(NCMe)_6]^{2+}$, 1209, 1210
$FeC_{12}H_{22}N_8$
$Fe(CNMe)_4(MeNHCNHNHCNHMe)$, 1209
$FeC_{12}H_{24}N_6$
$[Fe(MeN{=}CHCH{=}NMe)_3]^{2+}$, 1223, 1224
$FeC_{12}H_{24}N_6S_2$
Fe(1,4,8,11-tetraazacyclotetradecane)$(NCS)_2$, 1251
$FeC_{12}H_{24}S_6$
$[Fe(\overline{SCH_2CH_2SCH_2CH_2SCH_2CH_2})_2]^{2+}$, 1239
$FeC_{12}H_{25}Cl_3N_4$
$FeCl_3\{N(CH_2CH_2)_3N\}\{N(CH_2CH_2)_3NH\}$, 1210
$FeC_{12}H_{26}Cl_2P_2$
$FeCl_2\{PH_2(C_6H_{11})\}_2$, 1233
$FeC_{12}H_{26}Cl_3N_4$
$[FeCl_3\{N(CH_2CH_2)_3NH\}_2]$, $^+$, 1210
$FeC_{12}H_{30}BrN_4$
$[FeBr\{N(CH_2CH_2NMe_2)_3\}]^+$, 1183, 1211
$FeC_{12}H_{30}Cl_2P_2$
$FeCl_2(PEt_3)_2$, 1233
$FeC_{12}H_{30}N_6$
$[Fe(1,4,7\text{-}triazacyclononane)_2]^{2+}$, 1252
$FeC_{12}H_{32}Cl_2P_4$
$Fe(Me_2PCH_2CH_2PMe_2)_2Cl_2$, 1197, 1234
$FeC_{12}H_{32}P_4$
$Fe(Me_2PCH_2CH_2PMe_2)_2$, 1197
$FeC_{12}H_{36}Cl_2O_{12}P_4$
$FeCl_2\{P(OMe)_3\}_4$, 1233
$FeC_{12}H_{36}N_8O_2P_2$
$Fe\{P(NMe_2)_3\}_2(NO)_2$, 1189
$FeC_{12}H_{36}O_6S_6$
$[Fe(DMSO)_6]^{2+}$, 1238
$FeC_{12}H_{36}P_4$
$Fe(PMe_3)_4$, 1197
$FeC_{12}N_6S_6$
$[Fe(S_2C_2(CN)_2)_3]^{3-}$, 245
$FeC_{12}N_9O_{12}$
$[Fe(violurate)_3)^-$, 1238
$FeC_{13}H_6N_6O_2$
$[Fe(CN)_5\{N(O)CHCOPh\}]^{4-}$, 1190
$FeC_{13}H_9N_3S$
$[Fe\{2\text{-}pyC{=}\overline{NC(py\text{-}2)CHS}\}]^{2+}$, 1229
$FeC_{13}H_{16}O_2P$
$Fe(\eta\text{-}C_3H_5)(CO)_2PMe_2Ph$, 1201
$FeC_{13}H_{20}N_4O_3$
$[Fe(CO)_3(\overline{CNMeCH_2CH_2NMe})_2]^+$, 1201
$FeC_{13}H_{23}N_7$
$Fe(CNMe)_4(MeNHCNMeCNHMe)$, 1209
$FeC_{13}H_{24}N_5O_3P$
$[Fe(NCMe)_5\{P(OMe)_3\}]^{2+}$, 1209
$FeC_{14}H_8N_6$
$[Fe(CN)_4(bipy)]^-$, 1186
$[Fe(CN)_4(bipy)]^{2-}$, 1217, 1221
$FeC_{14}H_8N_6O_2$
$Fe(NCO)_2(4\text{-}pyCN)_2$, 1213
$FeC_{14}H_{16}Cl_2N_2S_2$
$Fe\{(2\text{-}pyCH_2SCH_2)_2\}Cl_2$, 1247
$FeC_{14}H_{18}N_6O_4$

$[Fe\{ON{=}C(CH_2)_4C{=}NOH\}_2(CN)_2]^{2-}$, 1231

$FeC_{14}H_{20}F_6N_2S_6$
$Fe(S_2CNEt_2)_2\{S_2C_2(CF_3)_2\}$, 1246

$FeC_{14}H_{20}N_6$
$Fe(CN)_2(CNEt)_4$, 1208

$FeC_{14}H_{22}N_8O_4$
$Fe(HDMG)_2(HNCH{=}NCH{=}CH)_2$, 1231

$FeC_{14}H_{26}Cl_2N_2$
$FeCl_2\{N(CH_2CH_2)_3CH\}_2$, 1210

$FeC_{14}H_{26}P_2$
$FeH_2\{1,2\text{-}(Et_2P)_2C_6H_4\}$, 1234

$FeC_{14}H_{29}N_5O$
[Fe(1,4,8,12-tetraazacyclopentadecane)(MeCN)-(CO)]$^{2+}$, 1252

$FeC_{14}H_{30}Cl_2O_2P_2$
$FeCl_2(PEt_3)_2(CO)_2$, 1233

$FeC_{14}H_{30}N_4O_6P_2$
$[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$, 1210

$FeC_{14}H_{30}N_6$
[Fe(1,4,8,11-tetraazacyclotetradecane)(MeCN)$_2$]$^{2+}$, 1251, 1252

$FeC_{14}H_{30}O_4P_2S$
$Fe(CO)_2(PEt_3)_2(SO_2)$, 1197

$FeC_{14}H_{32}ClN_4$
[Fe(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)Cl]$^+$, 1251

$FeC_{14}H_{36}N_5O$
Fe(NO)(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), 1194

$FeC_{14}H_{36}N_7O_3P_2$
$[Fe\{P(NMe_2)_3\}_2(CO)_2(NO)]^+$, 1189

$FeC_{15}H_{15}Cl_3N_3$
$Fe(py)_3Cl_3$, 222

$FeC_{15}H_{21}O_3S_3$
$Fe\{MeC(S)CHC(O)Me\}_3$, 246

$FeC_{15}H_{21}O_6$
$Fe(acac)_3$, 229, 1185, 1186

$FeC_{15}H_{21}S_6$
$Fe\{MeC(S)CHC(S)Me\}_3$, 246, 1246

$FeC_{15}H_{22}O_6$
$Fe(acac)_3$, 1203

$FeC_{15}H_{24}N_3O_3S_6$
$Fe\{S_2CN(CH_2)_2O(CH_2)_2\}_3$, 244

$FeC_{15}H_{24}N_3S_6$
$Fe\{S_2CN(CH_2)_3CH_2\}_3$, 244, 266

$FeC_{15}H_{26}ClN_4$
$[Fe\{2,6\text{-}py(CHMeNHCH_2CH_2CH_2)_2NH\}Cl]^+$, 1258

$FeC_{15}H_{26}N_{10}$
$Fe\{2,6\text{-}py(CHMeNHCH_2CH_2CH_2)_2NH\}(N_3)_2$, 1258

$FeC_{15}H_{30}N_3O_3S_3$
$Fe\{SC(O)NEt_2\}_3$, 247

$FeC_{15}H_{30}N_3S_6$
$Fe(S_2CNEt_2)_3$, 244
$[Fe(S_2CNEt_2)_3]^+$, 266, 1187

$FeC_{15}H_{30}O_3P_2$
$Fe(CO)_3(PEt_3)_2$, 1197

$FeC_{15}H_{32}N_6$
[Fe(1,4,8,12-tetraazacyclopentadecane)(MeCN)$_2$]$^{2+}$, 1252

$FeC_{15}H_{36}Cl_2P_4$
$FeCl_2\{P(CH_2CH_2CH_2PMe_2)_3\}$, 1235

$FeC_{15}H_{36}O_{13}P_4$
$Fe(CO)\{P(OMe)_3\}_4$, 1197

$FeC_{15}H_{45}O_{15}P_5$
$[Fe\{(MeO)_2P(O)Me\}_5]^{2+}$, 1237
$Fe\{P(OMe)_3\}_5$, 1197, 1234
$[Fe\{P(OMe)_3\}_5]^{2+}$, 1234

$FeC_{15}H_{46}O_{15}P_5$
$[FeH\{P(OMe)_3\}_5]^+$, 1234

$FeC_{15}H_{47}O_{21}P_5$
$[Fe\{(MeO)_3PO\}_5(H_2O)]^{2+}$, 1237

$FeC_{16}H_8N_6$
$[Fe(CN)_4(phen)]^{2-}$, 1219, 1221

$FeC_{16}H_8N_6S_2$
$Fe(NCS)_2(HN{=}CHCH{=}NH)_2$, 1223

$FeC_{16}H_{13}ClN_3O_3$
Fe(5-Cl-salen)(NO), 1194

$FeC_{16}H_{14}ClN_2O_2$
Fe(salen)Cl, 250

$FeC_{16}H_{14}IN_2O_2$
Fe(salen)I, 251

$FeC_{16}H_{14}N_2O_2$
Fe(salen), 251
$[Fe(salen)]^-$, 251, 1202

$FeC_{16}H_{14}N_2O_4$
Fe(salen)O_2, 251

$FeC_{16}H_{14}N_2S_2$
$Fe\{(2\text{-}SC_6H_4CH{=}NCH_2)_2\}$, 1248

$FeC_{16}H_{14}N_3O_3$
Fe(salen)(NO), 1194, 1238

$FeC_{16}H_{16}ClN_2O_2$
Fe(salen-H)Cl, 252

$FeC_{16}H_{16}S_4$
$[Fe\{1,2\text{-}(SCH_2)_2C_6H_4\}_2]^-$, 235
$[Fe\{1,2\text{-}(SCH_2)_2C_6H_4\}_2]^{2-}$, 1240
$[Fe\{1,2\text{-}(SCH_2)_2C_6H_4\}_2]^-$, 1240

$FeC_{16}H_{16}S_6$
$[Fe_2S_2\{1,2\text{-}(SCH_2)_2C_6H_4\}_2]^{2-}$, 236

$FeC_{16}H_{18}N_2O_2S_4$
$Fe(S_2COEt)_2(bipy)$, 1246

$FeC_{16}H_{22}N_4O_2$
$[Fe\{N{=}CMeCOCH{=}N(CH_2)_2N{=}CHCOC(Me){=}N(CH_2)_2\}(MeCN)_2]^{2+}$, 257

$FeC_{16}H_{22}N_6O_5$
$Fe\{ON{=}C(CH_2)_4C{=}NOH\}_2(CO)(HNCH{=}NCH{=}CH)$, 1231

$FeC_{16}H_{22}N_7O_4$
$[Fe\{ON{=}C(CH_2)_4C{=}NOH\}_2(CN)(HNCH{=}NCH{=}CH)]^-$, 1231

$FeC_{16}H_{24}Cl_2N_8$
$Fe(HNN{=}CMeCH{=}CH)_4Cl_2$, 1213

$FeC_{16}H_{24}N_8$
$[Fe(N{=}CMeNHCH{=}CH)_4]^{2+}$, 1213, 1214

$FeC_{16}H_{25}N_4S_3$
$[Fe\{2,6\text{-}py(CMe{=}NCH_2CH_2CH_2SCH_2)_2\}(NCS)]^+$, 1260

$FeC_{16}H_{25}N_6$
$Fe\{N{=}CMeCH_2CH{=}N(CH_2)_3N{=}CHCH(CH{=}N)CMe{=}NCH_2CH_2\}(MeCN)$, 1256

$FeC_{16}H_{26}N_4$
$[Fe\{N{=}CMeCH_2CH{=}N(CH_2)_2N{=}CHCH_2C(Me){=}N(CH_2)_2\}(MeCN)_2]^{2+}$, 257

$FeC_{16}H_{26}N_6$
$[Fe(N{=}CMeCH_2CH{=}NCH_2CH_2N{=}CHCH_2CMe{=}NCH_2CH_2)(MeCN)_2]^{2+}$, 1256

$FeC_{16}H_{27}O_4P$
$Fe(CO)_4(PBu^t{}_3)$, 1196

$FeC_{16}H_{28}ClN_4$
$[Fe(N{=}CHCH_2N{=}CMeCH_2CMe_2N{=}CHCH_2N{=}CMeCH_2CMe_2)Cl]^+$, 1251

$FeC_{16}H_{28}N_4$
$[Fe(N{=}CHCH{=}NCHMeCH_2CMe_2N{=}CHCH{=}NCHMeCH_2CMe_2)]^+$, 1202

$FeC_{16}H_{29}ClN_3OS_2$
$[Fe\{2,6\text{-}py(CMe{=}NCH_2CH_2CH_2SCH_2)_2\}\text{-}(MeOH)Cl]^+$, 1260

$FeC_{16}H_{30}N_2O_2P_2S_2$
$Fe(NCS)_2(PEt_3)_2(CO)_2$, 1233

$FeC_{16}H_{30}N_4$
$[Fe(N{=}CMeCH_2CMe_2N{=}CHCH_2N{=}CMeCH_2CMe_2NH(CH_2)_2)]^{2+}$, 257

$FeC_{16}H_{32}ClN_4$
$[Fe(N{=}CMeCH_2CMe_2NHCH_2CH_2N{=}CMeCH_2CMe_2NHCH_2CH_2)Cl]^+$, 1253

$FeC_{16}H_{32}N_4$

[Fe{N=CMeCH$_2$CMe$_2$NH(CH$_2$)$_2$N=CMeCH$_2$CMe$_2$NH(CH$_2$)$_2$}]$^{3+}$, 257

$FeC_{16}H_{34}Cl_2N_4$
Fe(hexamethyl-1,4,8,11-tetraazacyclotetradecane)Cl$_2$, 1251

$FeC_{16}H_{35}N_2$
[Fe(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)(NCMe)]$^{2+}$, 1251

$FeC_{16}H_{36}O_6$
[Fe(THF)$_4$(H$_2$O)$_2$]$^{3+}$, 227

$FeC_{16}H_{48}O_{15}P_5$
[FeMe{P(OMe)$_3$}$_5$]$^+$, 1234

$FeC_{17}H_8N_2O_7$
Fe$_2$(CO)$_7$(bipy), 1196

$FeC_{17}H_{15}N_2$
Fe(bipy)(η^6-toluene), 1196

$FeC_{17}H_{20}N_6S_2$
Fe(NCS)$_2$(2-pyCH$_2$NHCH$_2$)$_2$CH$_2$}, 1227

$FeC_{17}H_{21}N_5O_2S_2$
Fe{2,6-py(CMe=NCH$_2$CH$_2$OCH$_2$)$_2$}(NCS)$_2$, 1260

$FeC_{17}H_{21}N_5S_4$
Fe{2,6-py(CMe=NCH$_2$CH$_2$SCH$_2$)$_2$}(NCS)$_2$, 1247

$FeC_{17}H_{21}N_7S_2$
[Fe{N=CMe-2,6-pyC(Me)=N(CH$_2$)$_2$N(CH$_2$)$_2$N(CH$_2$)$_2$}(NCS)$_2$]$^+$, 259

$FeC_{17}H_{23}$
FeCp(η^6-C$_6$Me$_6$), 1203

$FeC_{17}H_{23}N_7S_2$
Fe{2,6-py(CMe=NCH$_2$CH$_2$NHCH$_2$)$_2$}(NCS)$_2$, 1260

$FeC_{17}H_{25}ClN_4S_2$
[Fe{2,6-py(CMe=NCH$_2$CH$_2$CH$_2$SCH$_2$)$_2$}Cl]$^+$, 1247

$FeC_{17}H_{26}N_6S_2$
Fe{2,6-py(CHMeNHCH$_2$CH$_2$CH$_2$)$_2$NH}(NCS)$_2$, 1258

$FeC_{17}H_{29}N_4O_2$
[Fe{2,6-py(CHMeNHCH$_2$CH$_2$CH$_2$)$_2$NH}(OAc)]$^+$, 1258

$FeC_{17}H_{39}O_9P_3$
Fe(1,3-cod){P(OMe)$_3$}$_3$, 1197

$FeC_{17}H_{39}P_3$
Fe(cod)(PMe$_3$)$_3$, 1197

$FeC_{17}H_{48}NO_{15}P_5$
[Fe(NCMe){P(OMe)$_3$}$_5$]$^{2+}$, 1209

$FeC_{18}H_{10}N_3OS_4$
Fe(NO){S$_2$C$_2$(CN)$_2$}{S$_2$C$_2$Ph$_2$}, 1193

$FeC_{18}H_{11}N_8$
[Fe(terpy)(CN)$_3$]$^-$, 1222

$FeC_{18}H_{12}O_6$
[Fe(1,2-O$_2$C$_6$H$_4$)$_3$]$^{3-}$, 230

$FeC_{18}H_{14}Cl_2N_2$
FeCl$_2$(quinoline)$_2$, 1213, 1214

$FeC_{18}H_{15}Cl_3P$
Fe(PPh$_3$)Cl$_3$, 226

$FeC_{18}H_{15}N_6S_3$
Fe(py)$_3$(NCS)$_3$, 222

$FeC_{18}H_{16}N_3O_3$
Fe{1,2-(MeCOCAcC=N)$_2$C$_6$H$_4$}(NO), 1195

$FeC_{18}H_{18}N_2O_2S_4$
Fe(S$_2$COEt)$_2$(phen), 1246

$FeC_{18}H_{23}N_7S_2$
[Fe(N=CMe-2,6-pyC(Me)=N(CH$_2$)$_2$N(CH$_2$)$_3$N(CH$_2$)$_2$)(NCS)$_2$]$^+$, 259

$FeC_{18}H_{24}N_6$
[Fe(2-pyCH$_2$NH$_2$)$_3$]$^{2+}$, 1226

$FeC_{18}H_{24}N_6O_6$
[Fe(OCH$_2$CH$_2$N=CC=NCH$_2$CH$_2$NH)$_3$]$^{2+}$, 1228

$FeC_{18}H_{24}N_6S_6$
Fe(NCS)$_2$(S(CH$_2$)$_3$N=CC=N(CH$_2$)$_3$S}, 1228

$FeC_{18}H_{24}N_{12}$
[Fe(HNCH=NCH=CH)$_6$]$^{2+}$, 1213, 1214
[Fe(HNN=CHCH=CH)$_6$]$^{2+}$, 1213, 1214

$FeC_{18}H_{25}N_7S_2$
Fe{2,6-py(CMe=NCH$_2$CH$_2$NHCH$_2$)$_2$CH$_2$}(NCS)$_2$, 1260

$FeC_{18}H_{26}N_6$
[Fe{N=CMeCH(CMe=N)CH=N(CH$_2$)$_3$N=CHCH(CMe=N)CMe=N(CH$_2$)$_3$}], 1256

$FeC_{18}H_{26}N_6O_6S_2$
[Fe(3-MeO-4-HOC$_6$H$_3$CH=NNHCSNH$_2$)$_2$(H$_2$O)$_2$]$^{2+}$, 1248

$FeC_{18}H_{30}N_3S_6$
Fe{S$_2$CN(CH$_2$)$_4$CH$_2$}$_3$, 244

$FeC_{18}H_{30}N_6$
[Fe{N=CMeCMe=N(CH$_2$)$_3$N=CMeCMe=N(CH$_2$)$_3$}(MeCN)$_2$]$^{2+}$, 1254, 1255

$FeC_{18}H_{30}N_6S_6$
[Fe(2,2′-bi-2-thiazolinyl)$_3$]$^{2+}$, 224

$FeC_{18}H_{30}N_{12}$
[Fe(HNCH$_2$CH$_2$N=CC=NCH$_2$CH$_2$NH)$_3$]$^{2+}$, 1228
[Fe(HNCH$_2$CH$_2$N=CC=NCH$_2$CH$_2$NH)$_3$]$^{3+}$, 224

$FeC_{18}H_{32}N_5$
FeH(N=CHCH=NCHMeCH$_2$CMe$_2$N=CHCH=NCHMeCH$_2$CMe$_2$)(MeCN), 1202

$FeC_{18}H_{34}N_6$
Fe(hexamethyl-1,4,8,11-tetraazacyclotetradecane)-(CN)$_2$, 1251

$FeC_{18}H_{34}N_6S_2$
Fe(hexamethyl-1,4,8,11-tetraazacyclotetradecane)-(NCS)$_2$, 1251

$FeC_{18}H_{36}N_6$
[Fe(MeN=CMeCMe=NMe)$_3$]$^{2+}$, 1223, 1224

$FeC_{18}H_{36}N_8O_4$
Fe{ON=C(CH$_2$)$_4$C=NOH}$_2$(HNCH=NCH=CH)$_2$, 1231

$FeC_{18}H_{39}Br_2P_3$
FeBr$_2$(PH$_2$(C$_6$H$_{11}$)}$_3$, 1233

$FeC_{18}H_{54}O_{18}P_6$
Fe{P(OMe)$_3$}$_6$, 1234
[Fe{P(OMe)$_3$}$_6$]$^{2+}$, 1233

$FeC_{19}H_{11}N_3S_2$
[Fe{2,6-py(C=NC$_6$H$_4$S)$_2$}]$^{2+}$, 1229

$FeC_{19}H_{25}N_5S_4$
Fe{2,6-py(CMe=NCH$_2$CH$_2$CH$_2$SCH$_2$)$_2$}(NCS)$_2$, 1260

$FeC_{20}H_{12}N_4S$
[Fe{2-phenC=NC(py)=CHS}]$^{2+}$, 1229

$FeC_{20}H_{14}N_3O_3$
Fe{1,2-(2-OC$_6$H$_4$CH=N)$_2$C$_6$H$_4$}(NO), 1195

$FeC_{20}H_{16}Cl_2N_4$
FeCl$_2$(bipy)$_2$, 1220

$FeC_{20}H_{16}Cl_3N_4$
FeCl$_3$(bipy)$_2$, 1221

$FeC_{20}H_{16}N_4$
Fe(bipy)$_2$, 1196

$FeC_{20}H_{18}N_6O_5$
Fe(ON=CCONPhN=CMe)$_2$(H$_2$O), 1237

$FeC_{20}H_{18}N_6S_2$
Fe(NCS)$_2$(2-pyCH$_2$)$_3$N}, 1227

$FeC_{20}H_{20}Cl_2N_4$
FeCl$_2$(py)$_4$, 1212, 1214

$FeC_{20}H_{20}F_2N_4$
FeF$_2$(py)$_4$, 1221

$FeC_{20}H_{20}I_2N_4$
FeI$_2$(py)$_4$, 1212

$FeC_{20}H_{32}N_6$
[Fe(N=CHCH=NCHMeCH$_2$CMe$_2$N=CHCH=NCHMeCH$_2$CMe$_2$)(MeCN)$_2$]$^{2+}$, 1251, 1254

$FeC_{20}H_{34}N_6$
[Fe(N=CHCH=NCHMeCH$_2$CMe$_2$N=CHCH$_2$NHCHMeCH$_2$CMe$_2$)(MeCN)$_2$]$^{2+}$, 1254
Fe{N=CMeCH$_2$CMe$_2$N=CHCH$_2$N=CMeCH$_2$CMe$_2$N=CHCH$_2$}(MeCN)$_2$, 256

$FeC_{20}H_{38}N_6$
[Fe(N=CMeCH$_2$CMe$_2$NHCH$_2$CH$_2$N=CMeCH$_2$CMe$_2$NHCH$_2$CH$_2$)(MeCN)$_2$]$^{2+}$, 1253
Fe{N=CMeCH$_2$CMe$_2$NH(CH$_2$)$_2$N=CMeCH$_2$CMe$_2$NH(CH$_2$)$_2$}(MeCN)$_2$, 256

$FeC_{20}H_{40}N_4O_4$

Fe(hexamethyl-1,4,8,11-tetraazacyclotetradecane)-$(OAc_2)_2$, 1251

$FeC_{20}H_{40}N_6$

[Fe(hexamethyl-1,4,8,11-tetraazacyclotetradecane)-$(MeCN)_2]^{2+}$, 1251, 1254

$FeC_{20}H_{49}ClP_4$

$FeHCl(depe)_2$, 1234

$FeC_{20}H_{49}N_2P_4$

$[FeH(N_2)(depe)_2]^+$, 1234

$FeC_{21}H_{17}Cl_2N_4O_4$

Fe(5-Cl-8-quinolinolate)$_2$(NO)(DMF), 1195

$FeC_{21}H_{18}N_3O_3S_3$

$Fe\{ONHC(S)Ph\}_3$, 234

$FeC_{21}H_{18}N_3O_6$

$Fe\{ONHCOPh\}_3$, 234

$FeC_{21}H_{19}N_3O_2$

Fe(salen)(py), 251

$FeC_{21}H_{25}N_3O_2$

$Fe\{(2\text{-}OC_6H_4CH{=}NCH_2CH_2CH_2)_2NMe\}$, 1238

$FeC_{21}H_{35}F_6N_4O_2$

Fe(hexamethyl-1,4,8,11-tetraazacyclotetradecane)-(hfacac), 1251

$FeC_{22}H_{15}O_4P$

$Fe(CO)_4(PPh_3)$, 1196

$FeC_{22}H_{16}N_6$

$Fe(bipy)_2(CN)_2$, 1186, 1217, 1220, 1222

$[Fe(bipy)_2(CN)_2]^+$, 223

$FeC_{22}H_{16}N_6S_2$

$Fe(NCS)_2(bipy)_2$, 1221

$FeC_{22}H_{19}N_3OS_2$

$Fe\{(2\text{-}SC_6H_4CH{=}NCH_2)_2\}(CO)(py)$, 1248

$FeC_{22}H_{20}Cl_2N_4$

$FeCl_2\{(2\text{-}py)_2CH_2\}_2$, 1226

$FeC_{22}H_{20}N_6O_2$

$Fe(NCO)_2(py)_4$, 1212

$FeC_{22}H_{20}N_6S_2$

$Fe(NCS)_2(py)_4$, 1212, 1213

$FeC_{22}H_{20}N_6Se_2$

$Fe(NCSe)_2(py)_4$, 1213

$FeC_{22}H_{22}ClN_4$

$Fe(\overline{NC_6H_4NCMeCHCMeNC_6H_4NCMeCHC}Me)Cl$, 1256

$FeC_{22}H_{22}N_4$

$Fe(\overline{NC_6H_4NCMeCHCMeNC_6H_4NCMeCHC}Me)$, 1256

$FeC_{22}H_{26}N_4O_4$

$[Fe\{2\text{-}OC_6H_4\overline{C{=}NNHC(Me){=}CH}\}_2(MeOH)_2]^+$, 231

$FeC_{22}H_{28}N_8$

$Fe\{\overline{N{=}CMe\text{-}2,6\text{-}pyCHMeNHN{=}CMe\text{-}2,6\text{-}py\text{-}CHMeNH}\}(MeCN)_2$, 1257

$FeC_{22}H_{30}N_6O_4$

$[Fe\{5\text{-}O_2NC_6H_4CH{=}N(CH_2)_2NMe_2\}_2]^+$, 252

$FeC_{22}H_{32}N_4$

$[Fe\{PhCH{=}N(CH_2)_2NMe_2\}_2]^+$, 253

$FeC_{22}H_{32}N_{10}S_2$

$Fe(NCS)_2(\overline{N{=}CMeNMeCH{=}CH})_4$, 1213

$FeC_{22}H_{33}$

$Fe(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)$, 1203

$FeC_{23}H_{20}O_2P$

$Fe(\eta\text{-}C_3H_5)(CO)_2(PPh_3)$, 1201

$FeC_{23}H_{21}N_2O_2$

$Fe(CH_2Ph)$(salen), 251, 1202

$FeC_{23}H_{22}N_7O_2$

$Fe\{2,6\text{-}py(CMe{=}NNMe)_2phen\text{-}2,9\}(H_2O)_2$, 1260

$FeC_{23}H_{22}N_4O$

$Fe(\overline{NC_6H_4NCMeCHCMeNC_6H_4NCMeCHC}Me)(CO)$, 1256

$FeC_{23}H_{26}N_6O$

$Fe(\overline{NC_6H_4NCMeCHCMeNC_6H_4NCMeCHC}Me)(CO)\text{-}(NH_2NH_2)$, 1256

$FeC_{24}H_8Cl_{12}O_4$

$[Fe(OC_6H_2Cl_3\text{-}2,4,6)_4]^-$, 230

$FeC_{24}H_{16}Cl_2N_4$

$[Fe(phen)_2Cl_2]^+$, 223

$FeC_{24}H_{16}F_2N_4$

$FeF_2(phen)_2$, 1220

$FeC_{24}H_{16}N_3O_3$

$Fe\{1,2\text{-}(PhCOCHC{=}N)_2C_6H_4\}(NO)$, 1195

$FeC_{24}H_{18}N_{12}$

$[Fe(2,2\text{-bipyrazine})_3]^{2+}$, 1228

$FeC_{24}H_{20}S_4$

$[Fe(SPh)_4]^{2-}$, 1240, 1242

$FeC_{24}H_{21}N_9$

$(Fe(2\text{-}py\overline{C{=}NCH{=}CHNH})_3]^{2+}$, 1228

$FeC_{24}H_{21}S_7$

$Fe(4\text{-}S_2CC_6H_4Me)_2(4\text{-}S_3CC_6H_4Me)$, 246

$FeC_{24}H_{24}N_3O_3S_3$

$Fe(ONMeC(S)Ph)_3$, 234

$FeC_{24}H_{24}N_3S_6$

$Fe(S_2CNMePh)_3$, 244

$FeC_{24}H_{26}N_6$

$[Fe\{(2\text{-}pyCH_2)_2NH\}_2]^{2+}$, 1227

$FeC_{24}H_{27}N_9$

$[Fe(2\text{-}py\overline{C{=}NCH_2CH_2NH})_3]^{2+}$, 1228

$FeC_{24}H_{28}Cl_2N_4$

$FeCl_2(4\text{-Mepy})_4$, 1212

$FeC_{24}H_{28}P_4$

$[Fe(PH_2Ph)_4]^{2+}$, 1233

$FeC_{24}H_{30}N_6$

$[Fe\{2\text{-}pyCH_2\overline{NCH_2CH_2N(CH_2py\text{-}2)CH_2CH_2N(CH_2py\text{-}2)CH_2CH_2}\}]^{2+}$, 1227

$FeC_{24}H_{30}O_{12}S_6$

$[Fe(S_2C{=}C(CO_2Et)_2)_3]^-$, 266

$FeC_{24}H_{36}N_4O_2$

$[Fe(5\text{-}MeOC_6H_4CH{=}N(CH_2)_2NMe_2)_2]^+$, 252

$FeC_{24}H_{36}N_6O_6$

$[Fe\{\overline{O(CH_2)_3N{=}CC{=}N(CH_2)_3O}\}_3]^{2+}$, 1228

$FeC_{24}H_{36}N_6S_6$

$[Fe\{\overline{S(CH_2)_3N{=}CC{=}N(CH_2)_3S}\}_3]^{2+}$, 1228

$FeC_{24}H_{36}N_{12}$

$[Fe(\overline{HNN{=}CMeCH{=}CH})_6]^{2+}$, 1213

$FeC_{24}H_{42}N_{12}$

$[Fe\{\overline{HN(CH_2)_3N{=}CC{=}N(CH_2)_3NH}\}_3]^{3+}$, 224

$[Fe\{\overline{HN(CH_2)_3N{=}CC{=}N(CH_2)_3NH}\}_3]^{2+}$, 1228

$FeC_{24}H_{44}P_2$

$Fe\{P(C_6H_{11})_2\}_2$, 1233

$FeC_{24}H_{46}Cl_2P_2$

$FeCl_2\{PH(C_6H_{11})_2\}_2$, 1233

$FeC_{24}H_{72}N_{12}O_4P_4$

$[Fe(HMPA)_4]^{2+}$, 1184, 1237

$FeC_{25}H_{21}N_6$

$[Fe(\overline{N{=}CHC_6H_4N{=}CHC_6H_4N{=}CHC_6H_4N{=}CHC_6H_4})(MeCN)_2]^{2+}$, 1255

$FeC_{25}H_{45}N_5$

$Fe(CNBu^t)_5$, 1209

$FeC_{25}H_{46}N_5$

$[FeH(CNBu^t)_5]^+$, 1209

$FeC_{26}H_{14}Cl_2N_6S_2$

$Fe(NCS)_2(Clphen)_2$, 1221

$FeC_{26}H_{14}N_8O_4S_2$

$Fe(NCS)_2(O_2Nphen)_2$, 1221

$FeC_{26}H_{16}N_4O_4$

$Fe(C_2O_4)(phen)_2$, 224, 1185, 1220

$FeC_{26}H_{16}N_6$

$Fe(CN)_2(phen)_2$, 1185, 1218, 1219, 1220

$[Fe(CN)_2(phen)_2]^+$, 223

$FeC_{26}H_{16}N_6O_2S_2$

$Fe\{1\text{-}(\overline{SCH{=}CHN{=}CN{=}N})\text{-}2\text{-}OC_{10}H_6\}_2$, 1238

$FeC_{26}H_{16}N_6S_2$

$Fe(NCS)_2(phen)_2$, 1220, 1221

$Fe(SCN)_2(phen)_2$, 1187

$FeC_{26}H_{16}N_6Se_2$

$Fe(NCSe)_2(phen)_2$, 1220

$FeC_{26}H_{16}N_{10}O_2$

$Fe(NCO)_2(4\text{-pyCN})_4$, 1213

$FeC_{26}H_{18}N_6$

$Fe(CN)_2(phen)_2$, 1220

$FeC_{26}H_{18}N_8S_2$
Fe(NCS)$_2$(2-pyC=NC$_6$H$_4$NH)$_2$, 1228
$FeC_{26}H_{20}N_8O_2$
[Fe{2-phenC(NH$_2$)=NOH}$_2$]$^{2+}$, 1229
$FeC_{26}H_{28}Cl_2N_6$
[Fe{(2-pyCH$_2$)$_2$NCH$_2$CH$_2$N(CH$_2$py-2)$_2$}Cl$_2$]$^+$, 226
$FeC_{26}H_{31}N_6O_3$
[Fe{(2-pyCH$_2$)$_2$NCH$_2$CH$_2$N(CH$_2$py-2)$_2$}-(H$_2$O)(OH)]$^{2+}$, 226
$FeC_{26}H_{48}N_{14}S_2$
Fe(NCS)$_2$(HNN=CHNBu^t=CH)$_4$, 1214
$FeC_{27}H_{24}N_4S_2$
[Fe{(2-pyCH=NC$_6$H$_4$SCH$_2$)$_2$CH$_2$}]$^{3+}$, 1247
$FeC_{27}H_{54}N_3S_6$
Fe(S$_2$CNBu$_2$)$_3$, 244
$FeC_{28}H_{20}FN_4$
[Fe(N=CHC$_6$H$_4$N=CHC$_6$H$_4$N=CHC$_6$H$_4$N=CHC$_6$H$_4$)F]$^{4+}$, 257
$FeC_{28}H_{20}NOS_4$
Fe(NO)(S$_2$C$_2$Ph$_2$)$_2$, 1193
$FeC_{28}H_{20}N_6S_2$
Fe(NCS)$_2$(Mephen)$_2$, 1221
$FeC_{28}H_{22}N_6$
[Fe(CNMe)$_2$(phen)$_2$]$^{2+}$, 1209
$FeC_{28}H_{26}N_8$
Fe(phen)$_2$(MeNHCNHNHCNHMe), 1209
$FeC_{28}H_{27}N_4S$
Fe{N=CHC(Ph)=CHN(CH$_2$)$_2$N=CHC(Ph)=CHN(CH$_2$)$_2$}(SPh), 256
$FeC_{28}H_{27}N_5O$
Fe(NC$_6$H$_4$NCMeCHCMeNC$_6$H$_4$NCMeCHCMe)(CO)-(py), 1256
$FeC_{28}H_{40}N_6$
[Fe(N=CMeCH$_2$CMe$_2$NHCH$_2$CH$_2$N=CMeCH$_2$CMe$_2$NHCH$_2$CH$_2$)(phen)]$^{2+}$, 1253
$FeC_{28}H_{44}$
Fe(1-norbornyl)$_4$, 267, 1183
$FeC_{29}H_{24}O_3P_2$
Fe(CO)$_3$(dppe), 1199
$FeC_{29}H_{29}N_4S$
Fe{N=CHC(Ph)=CHN(CH$_2$)$_2$N=CHC(Ph)=CHN(CH$_2$)$_3$}(SPh), 256
$FeC_{30}C_{18}F_9O_3S_3$
Fe(PhC(S)CHC(O)CF$_3$)$_3$, 247
$FeC_{30}H_{21}N_3O_{15}$
[Fe{2,3-O$_2$C$_6$H$_3$CONHCHCO$_2$CH$_2$CH(NHCO-C$_6$H$_3$O$_2$-2,3)CO$_2$CH$_2$CH(NHCOC$_6$H$_3$O$_2$-2,3)CO$_2$CH$_2$}]$^{3-}$, 230
$FeC_{30}H_{22}N_6$
Fe(terpy)$_2$, 1196
[Fe(terpy)$_2$]$^{2+}$, 225, 1222
[Fe(terpy)$_2$]$^{3+}$, 223, 225
$FeC_{30}H_{22}N_8O_2$
[Fe{2-phenC=NOC(Me)=NH}$_2$]$^{2\bullet}$, 1229
$FeC_{30}H_{24}Cl_2N_6$
[Fe(bipy)$_3$]Cl$_2$, 1220
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Fe(CN)$_2$(4,7-Me$_2$phen)$_2$, 1220
$FeC_{30}H_{24}N_6S_2$
Fe(NCS)$_2$(Me$_2$phen)$_2$, 1221
$FeC_{30}H_{24}N_8$
[Fe(2-phenC=NCH$_2$CH$_2$NH)$_2$]$^{2+}$, 1229
$FeC_{30}H_{26}N_8O_4$
Fe(ON=CCONPhN=CMe)$_2$(py)$_2$, 1237
$FeC_{30}H_{30}N_6$
[Fe(2,7-dimethyl-1,8-naphthyridine)$_3$]$^{2+}$, 1212
[Fe(py)$_6$]$^{2+}$, 1211, 1212
$FeC_{30}H_{30}N_6O_6$
[Fe(py *N*-oxide)$_6$]$^{2+}$, 1237
$FeC_{30}H_{31}N_4S$
Fe{N=CHC(Ph)=CHN(CH$_2$)$_3$N=CHC(Ph)=CHN(CH$_2$)$_3$}(SPh), 256
$FeC_{30}H_{34}N_3O_6$
Fe$_2$(2-OC$_6$H$_4$CH=N(CH$_2$)$_3$O)(2-OC$_6$H$_4$CH=N(CH$_2$)$_3$OH)$_2$, 250
$FeC_{30}H_{35}N_4O_2P$
[Fe(CO)$_2$(CNMeCH$_2$CH$_2$NMe)$_2$(PPh$_3$)]$^+$, 1201
$FeC_{30}H_{48}N_6$
[Fe{(CH$_2$)$_4$N=CC=N(CH$_2$)$_4$}$_3$]$^{2+}$, 1223
$FeC_{31}H_{33}N_4S$
Fe{N=CHC(Ph)=CHN(CH$_2$)$_3$N=CHC(Ph)=CHN(CH$_2$)$_3$}(SCH$_2$Ph), 256
$FeC_{32}F_{16}N_8$
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$FeC_{32}H_{12}N_8O_{12}S_4$
Fe{3,10,17,24-(O$_3$S)$_4$phthalocyanine}, 1202
[Fe{(O$_3$S)$_4$phthalocyanine}]$^{4-}$, 1265
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$FeC_{32}H_{16}ClN_8$
Fe(phthalocyanine)Cl, 1265
$FeC_{32}H_{16}Cl_2N_8$
Fe(phthalocyanine)Cl$_2$, 1261
$FeC_{32}H_{16}IN_8$
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$FeC_{32}H_{16}N_8O$
{Fe(phthalocyanine)}$_2$O, 1265
$FeC_{32}H_{16}N_8O_{14}S_4$
[Fe{(O$_3$S)$_4$phthalocyanine}(H$_2$O)$_2$]$^{4-}$, 1265
$FeC_{32}H_{16}N_8O_{15}S_4$
[Fe{(O$_3$S)$_4$phthalocyanine}(H$_2$O)(O$_2$)]$^{4-}$, 1265
$FeC_{32}H_{16}N_9O$
Fe(NO)(phthalocyanine), 1262
$FeC_{32}H_{24}N_8$
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$FeC_{32}H_{28}Cl_2N_4O_4$
{Fe(salen)Cl}$_2$, 257
$FeC_{32}H_{28}N_4OS_4$
Fe(2-SC$_6$H$_4$CH=NCH$_2$CH$_2$N=CHC$_6$H$_4$S-2)$_2$O, 253
$FeC_{32}H_{28}N_4O_5$
Fe(salen)$_2$O, 253
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FeCl$_2${2,6-py(CH$_2$CH$_2$PPh$_2$)$_2$}, 1235
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[Fe(2-pyC=NNHpy-2)$_3$]$^{2+}$, 1225
$FeC_{34}H_{16}N_{10}$
[Fe(phthalocyanine)(CN)$_2$]$^-$, 1266
$FeC_{34}H_{16}N_8O_2$
Fe(phthalocyanine)(CO)$_2$, 1262
$FeC_{34}H_{32}N_6$
[Fe(2-phenC=NBu^t)$_2$]$^{2+}$, 1229
$FeC_{35}H_{22}N_8O_2S$
Fe(phthalocyanine)(DMSO)(CO), 1262
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[Fe(5-O$_2$Nphen)$_3$]$^{2+}$, 1216, 1217
$FeC_{36}H_{23}N_9O_2$
Fe(phthalocyanine)(DMF)(CO), 1262
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$FeC_{36}H_{24}N_{12}$
[Fe{2,4,6-py)$_3$-*s*-triazine}$_2$]$^{2+}$, 1230
$FeC_{36}H_{27}N_9$
[Fe(H$_2$Nphen)$_3$]$^{2-}$, 1217

$[Fe(2\text{-}pyC{=}NC_6H_4NH)_3]^{2+}$, 1228
$FeC_{36}H_{28}Cl_2N_4$
$FeCl_2$(isoquinoline)$_4$, 1214
$FeC_{36}H_{28}N_8O_2S_2$
Fe(phthalocyanine)(DMSO)$_2$, 1262
$FeC_{36}H_{30}Br_2P_2$
$FeBr_2(PPh_3)_2$, 1183, 1233
$FeC_{36}H_{30}Cl_2O_2P_2$
$Fe(OPPh_3)_2Cl_2$, 1237
$FeC_{36}H_{32}N_8$
$[Fe(2\text{-methyl-}1,8\text{-naphthyridine})_4]^{2+}$, 1211
$FeC_{36}H_{44}ClN_4O_4$
[Fe(octaethylporphyrin)(ClO_4)], 261
$FeC_{36}H_{46}N_6O_3$
Fe(NO)(*meso*-2,3,7,8,12,13,17,18-octaethyl-5-nitroporphyrinato), 1194
$FeC_{36}H_{66}P_3$
$[Fe\{P(C_6H_{11})_2\}_3]^-$, 1233
$FeC_{38}H_{21}N_9O$
Fe(phthalocyanine)(py)(CO), 1262
$FeC_{38}H_{22}N_6S_4$
$[Fe\{2,6\text{-}py(C{=}NC_6H_4S)_2\}_2]^{2+}$, 1229
$FeC_{38}H_{23}N_9$
Fe(phthalocyanine)(4-pyMe), 1262
$FeC_{38}H_{24}N_8$
$[Fe(2\text{-}phenC{=}NC_6H_4NH)_2]^{2+}$, 1229
$FeC_{38}H_{24}N_8S_2$
$[Fe(phen)_3](NCS)_2$, 1221
$FeC_{38}H_{24}N_{12}$
Fe(phthalocyanine)($HNCH{=}NCH{=}CH)_2$, 1264
$FeC_{38}H_{30}I_2O_8P_2$
$Fe(CO)_2\{P(OPh)_3\}_2I_2$, 1197
$FeC_{38}H_{32}N_4O_6$
Fe(salen)$_2$(quinone), 1238
$FeC_{38}H_{38}N_6$
$[Fe\{N{=}CPhCPh{=}N(CH_2)_3N{=}OPhCPh{=}N(CH_2)_3\}$-$(MeCN)_2]^{2+}$, 1255
$FeC_{39}H_{30}ClO_3P_2$
$FeCl(CO)_3(PPh_3)_2$, 1199
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$[Fe(CO)_3(PPh_3)_2]^1$, 1199
$FeC_{39}H_{30}O_3P_3$
$[Fe(CO)_3(PPh_3)_2]^+$, 1183, 1199
$FeC_{39}H_{30}O_9P_2$
$Fe(CO)_3\{P(OPh)_3\}_2$, 1199
$FeC_{40}H_{38}N_{10}$
Fe(phthalocyanine)($BuNH_2)_2$, 1262
$FeC_{40}H_{52}O_4$
$[Fe(OC_6HMe_4\text{-}2,3,5,6)_4]^-$, 230
$FeC_{40}H_{56}N_4O_2$
[Fe(octaethylporphyrin)($EtOH)_2$]$^+$, 261
$FeC_{40}H_{62}O_8P_4$
$FeH_2\{P(OEt)_2Ph\}_4$, 1234
$FeC_{42}H_{26}N_{10}$
Fe(phthalocyanine)(py)$_2$, 1262, 1264
$FeC_{42}H_{36}N_6$
$[Fe(5,6\text{-}Me_2phen)_3]^{2+}$, 1216
$[Fe(4,7\text{-}Me_2phen)_3]^{2+}$, 1217
$FeC_{42}H_{42}ClP_4$
$[FeCl\{(Ph_2PCH_2CH_2PPhCH_2)_2\}]^+$, 1235
$FeC_{44}H_{28}ClN_4$
Fe(tetraphenylporphyrin)Cl, 261, 1267, 1268
$[Fe(tetraphenylporphyrin)Cl]^+$, 265
$FeC_{44}H_{28}ClN_4O_4$
[Fe(tetraphenylporphyrin)(ClO_4), 261
$FeC_{44}H_{28}F_2N_4$
$[Fe(tetraphenylporphyrin)F_2]^-$, 260
$FeC_{44}H_{28}N_4$
Fe(tetraphenylporphyrin), 1266–1268
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$FeC_{44}H_{28}N_4O_2$
Fe(tetraphenylporphyrin)O_2, 1268
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Fe(tetraphenylporphyrin)(NO), 1194, 1267
$FeC_{44}H_{33}N_4O_2$
$[Fe(tetraphenylporphyrin)(H_2O)_2]^-$, 261
$FeC_{44}H_{42}N_2P_4S_2$
$Fe(NCS)_2\{(Ph_2PCH_2CH_2PPhCH_2)_2\}$, 1235
$FeC_{45}H_{28}N_4O$
Fe(tetraphenylporphyrin)(CO), 1202, 1268
$FeC_{45}H_{30}Cl_2N_4O$
Fe(tetraphenylporphyrin)(CCl_2)(H_2O), 1270
$FeC_{45}H_{30}N_3O_{12}$
$[Fe(4\text{-}O\text{-}3\text{-}ONC_6H_3CO_2C_6H_4CH{=}CH_2\text{-}4)_3]^-$, 1238
$FeC_{45}H_{33}O_3S_3$
$Fe(PhC(S)CHC(O)Ph)_3$, 247
$FeC_{45}H_{33}O_6$
$Fe(PhCOCHCOPh)_3$, 1203
$FeC_{46}H_{28}N_4O_2$
Fe(tetraphenylporphyrin)$(CO)_2$, 1268
$FeC_{46}H_{28}N_6$
$[Fe(tetraphenylporphyrin)(CN)_2]^-$, 260
$[Fe(tetraphenylporphyrin)(CN)_2]^{2-}$, 1268
$FeC_{46}H_{42}N_2P_4S_2$
$Fe(NCS)_2\{P(CH_2CH_2PPh_2)_3\}$, 1235
$FeC_{47}H_{34}N_7O$
Fe(NO)(tetraphenylporphyrin)($MeNCH{=}$ $NCH{=}CH$), 1194
$FeC_{48}H_{34}N_6$
Fe(tetraphenylporphyrin)($N{=}CMeNHCH{=}CH$), 1267
$FeC_{48}H_{36}N_4O$
Fe(tetraphenylporphyrin)(THF), 1268
$FeC_{48}H_{40}N_4O_2$
$[Fe(tetraphenylporphyrin)(EtOH)_2]^+$, 260
$FeC_{48}H_{54}N_8$
$Fe\{N{=}C(C_8H_{17})NN{=}(C_{16}H_{10}){=}NN{=}C(C_8H_{17})NN{=}$ $(C_{16}H_{10}){=}N\}$, 1258
$FeC_{49}H_{41}N_6O$
Fe(NO)(tetraphenylporphyrin)-$\{HN(CH_2)_2CHMe(CH_2)_2\}$, 1194
$FeC_{50}H_{34}N_8$
$[Fe(2\text{-}phenC{=}NNPh_2)_2]^{2+}$, 1229
$FeC_{50}H_{36}N_8$
[Fe(tetraphenylporphyrin)(imidazole)$_2$]$^+$, 260
$FeC_{52}H_{40}N_6O$
Fe(tetraphenylporphyrin)(py)($ONCHMe_2$), 1268
$FeC_{52}H_{44}N_4O_2$
Fe(tetraphenylporphyrin)(THF)$_2$, 1268
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Fe(tetraphenylporphyrin)$\{S(CH_2)_4\}_2$, 1268
$[Fe(tetraphenylporphyrin)\{S(CH_2)_3CH_2\}_2]^+$, 260
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$FeC_{52}H_{48}Cl_2P_4$
$FeCl_2(dppe)_2$, 1198
$FeC_{52}H_{48}N_2O_2P_4$
$Fe(NO)_2(dppe)_2$, 1067
$FeC_{52}H_{48}N_2P_4$
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$FeC_{52}H_{48}N_8$
Fe(tetraphenylporphyrin)-$(HNCH_2CH_2NHCH_2CH_2)_2$, 1267
$FeC_{52}H_{48}P_4$
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$FeC_{52}H_{49}ClP_4$
$FeHCl(dppe)_2$, 1198
$FeC_{52}H_{49}N_2P_4$
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$FeC_{52}H_{49}P_4$
$FeH(dppe)_2$, 1183, 1198, 1199
$[FeH(dppe)_2]^+$, 1199
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$[FeH_2(dppe)_2]^-$, 1198
$FeC_{52}H_{51}P_4$
$[Fe(\eta_2\text{-}H_2)(H)(dppe)_2]^+$, 1234
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$[Fe(CO)(dppe)_2]^+$, 1199
$FeC_{53}H_{49}OP_4$
$[FeH(CO)(dppe)_2]^+$, 1199
$FeC_{54}H_{34}N_{10}$
$[Fe\{2\text{-}phenC{=}NN{=}CPhC(Ph){=}N\}_2]^{2+}$, 1230
$FeC_{54}H_{38}N_6$
Fe(tetraphenylporphyrin)$(py)_2$, 1268
$[Fe(tetraphenylporphyrin)(py)_2]^+$, 260
$FeC_{54}H_{42}ClP_4$
$[FeCl\{P(C_6H_4PPh_2\text{-}2)_3\}]^+$, 1235
$FeC_{54}H_{46}N_6$
Fe(tetraphenylporphyrin)$(Bu^tNC)_2$, 1268
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$[Fe(MeCN)(dppe)_2]^+$, 1199
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$[Fe(C_2H_4)(dppe)_2]^+$, 1199
$FeC_{55}H_{57}O_3P_5$
$[FeH\{P(OMe)_3\}(dppe)_2]^+$, 1199
$FeC_{56}H_{42}N_2P_4$
$Fe(CN)_2\{P(C_6H_4PPh_2\text{-}2)_3\}$, 1235
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$FeC_{60}H_{52}N_8O_5$
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$FeC_{68}H_{66}Cl_2P_6$
$FeCl_2\{PhP(CH_2CH_2PPh_2)_2\}_2$, 1234
$FeC_{72}H_{42}N_6O_{18}S_6$
$[Fe\{(O_3SC_6H_4)_2\ phen\}_3]^{4-}$, 1217
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$[Co(NH_3)_5\{NCH{=}NCH{=}CH\}Fe(CN)_5]^-$, 699
$FeCoC_9H_{19}N_{10}$
$[Co(NH_3)_5(N{=}CHCH{=}NCH{=}CH)Fe(CN)_5]^-$, 690
$FeCoC_{11}N_{11}$
$[Co(CN)_5(\mu\text{-}CN)Fe(CN)_5]^{3-}$, 650
$FeCoC_{20}H_{32}N_8OP_2$
$[Fe(CN)_5(\mu\text{-}CN)CO(CN)_2(PEt_3)_2(OH_2)]^{3-}$, 647
$FeCoMoC_{13}H_5O_8S$
$CoFeMoS(CO)_8Cp$, 832
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$FeH_8Cl_2O_4$
$[Fe(H_2O)_4Cl_2]^-$, 227, 247
$FeH_{10}ClO_5$
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$FeLiC_{45}H_{96}O_5$
$FeLi(OCHBu^t_2)_4(HOCHBu^t_2)$, 227
$FeMo_2S_8$
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$[Fe(NO_3)_4]^-$, 229, 1183, 1185
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$FeRhC_9H_{19}N_4O_5$
$[Rh(HDMG)(HDMG\text{-}Fe)(H_2O)Me]^{2+}$, 1015
$FeRuC_8H_{18}Cl_5O_2P_2$
$RuCl(FeCl_4)(CO)_2(PMe_3)_2$, 382
$FeRuC_9H_{19}N_{12}$
$[Fe(CN)_5(\mu\text{-}N{=}CHCH{=}NCH{=}CH)Ru(NH_3)_5]^-$, 317
$FeRuC_{11}H_{24}N_6$
$[Ru(NH_3)_5(FeCN)]^{2+}$, 317
$FeRuC_{13}H_{26}N_6$
$[Ru(NH_3)_5(FeCH{=}CHCN)]^{2+}$, 317
$FeRu_2C_{12}H_{38}N_{12}$
$[\{Ru(NH_3)_5\}_2\{Fe(CN)_2\}]^{4+}$, 320
$FeRu_2C_{44}H_{30}Cl_2O_8P_2$
$\{Ru(CO)_2(PPh_3)\}_2(\mu\text{-}Cl)_2\{\mu\text{-}Fe(CO)_4\}$, 413
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$Fe\{N(SiMe_3)_2\}_3$, 222, 1183
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$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$, 1233
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$Fe(SnCl_3)\{P(OMe)_3\}_5$, 1233
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$[Fe_2(N{=}CMe\text{-}2,6\text{-}pyC(Me){=}N(CH_2)_2N(CH_2)_2N(CH_2)_2)_2(ClO_4)_2O]^{2+}$, 259

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$IrBC_{12}H_{16}N_4O_2$
$Ir(CO)_2\{H_2B(\overline{NN{=}CMeCH{=}CMe})_2\}$, 1108
$IrBC_{18}H_{47}P_2$
$IrH_2(BH_4)(PBu^t{}_2Me)_2$, 1149
$IrBC_{19}H_{27}F_6N_6O_5$
$Ir(O_2CCF_3)_2\{HB(\overline{NN{=}CMeCH{=}CMe})_3\}(H_2O)$, 1134
$IrBC_{20}H_{29}ClN_6O_2$, 1134
$Ir(acac)Cl\{HB(\overline{NN{=}CMeCH{=}CMe})_3\}$, 1134
$IrBC_{36}H_{31}ClF_4N_2P_2$
$IrHCl(FBF_3)(N_2)(PPh_3)_2$, 1105
$IrBC_{38}H_{69}NOP_2$
$Ir(CO)(NCBH_3)\{P(C_6H_{11})_3\}_2$, 1108
$IrB_2C_{20}H_{37}$
$[\{Ir(C_5Me_5)\}_2H_3](BH_4)$, 1166
$IrB_4C_{27}H_{35}OP_2$
$Ir(\eta^4\text{-}B_4H_9)(CO)(PPh_2Me)_2$, 1165
$IrB_8C_{55}H_{54}P_3$
2,10-$IrCB_8H_8$-1-PPh_3-2,2,2-$H(PPh_3)_2$, 1165
$IrB_8PtC_{13}H_{47}OP_4$
$PtB_8H_{10}IrH(CO)(PMe_3)_4$, 1165
$IrBr_2Cl_4$
$[IrCl_4Br_2]^{2-}$, 1157
$IrBr_4Cl_2$
$[IrBr_4Cl_2]^{2-}$, 1157
$IrBr_6$
$[IrBr_6]^{2-}$, 1157
$[IrBr_6]^{3-}$, 1149, 1157
$IrCH_{15}N_5O_3$
$[Ir(NH_3)_5(CO_3)]^+$, 960
$[Ir(OCO_2)(NH_3)_5]^+$, 1141
$IrC_2Cl_2NO_6$
$IrCl_2(NO_2)(C_2O_4)]^{3-}$, 1142
$IrC_2Cl_3NO_6$
$[IrCl_3(NO_2)(C_2O_4)]^{3-}$, 1142
$IrC_2Cl_4O_4$
$[IrCl_4(C_2O_4)]^{3-}$, 1142
$IrC_3H_6N_5$
$Ir(CN)_3(NH_3)_2$, 1125
IrC_3N_3
$Ir(CN)_3$, 1125
$IrC_4Cl_2O_8$
$[IrCl_2(C_2O_4)_2]^{3-}$, 1142
$IrC_4H_{12}Cl_3S_2$
$IrCl_3(SMe_2)_2$, 1145
$IrC_4H_{12}Cl_4O_2S_2$
$[IrCl_4(DMSO)_2]^-$, 1160
$IrC_4H_{12}Cl_4S_2$
$[IrCl_4(SMe_2)_2]^-$, 1157
$IrC_4H_{16}ClIN_4$
$[IrClI(en)_2]^+$, 1129
$IrC_4H_{16}Cl_2N_4$
$[IrCl_2(en)_2]^+$, 1129, 1161
$IrC_4H_{16}N_{10}$
$[Ir(N_3)_2(en)_2]^+$, 1133
$IrC_4H_{18}ClN_4O$
$[IrCl(en)_2(H_2O)]^{2+}$, 1129
$IrC_4H_{18}N_4O_2$
$[Ir(OH)_2(en)_2]^+$, 1129
$IrC_4H_{19}N_4O_2$
$[Ir(OH)(en)_2(H_2O)]^+$, 1161
$IrC_4H_{22}N_6$
$[Ir(en)_2(NH_3)_2]^+$, 1129

IrC_5ClN_5
$[Ir(CN)_5Cl]^{3-}$, 1125
IrC_5HN_5
$[Ir(CN)_5(H)]^{3-}$, 1166
$IrC_5H_2N_5O$
$[Ir(CN)_5(H_2O)]^{2-}$, 1125
$IrC_5H_5Cl_5N$
$[IrCl_5(py)]^{2-}$, 1130
$IrC_6H_{17}Cl_2O_5S_3$
$IrHCl_2(DSMO)_3$, 1160
$IrC_6H_{18}ClF_6N_3P_3$
$IrCl(PF_2NMe_2)_3$, 1163
$IrC_6H_{18}Cl_2N_4$
$[IrCl_2\{(H_2NCH_2CH_2NHCH_2)_2\}]^+$, 1130
$IrC_6H_{18}Cl_3O_3S_3$
$IrCl_3(DMSO)_3$, 1160
$IrC_6H_{18}Cl_4P_2$
$IrCl_4(PMe_3)_2$, 1134, 1155
$IrC_6H_{19}Cl_2O_3S_3$
$IrHCl_2(DMSO)_3$, 1159
$IrC_6H_{23}P_2$
$IrH_5(PMe_3)_2$, 1158, 1160
$IrC_6H_{24}N_6$
$[Ir(en)_3]^+$, 1162
IrC_6N_6
$[Ir(CN)_6]^{3-}$, 1125
$IrC_6N_6O_6$
$[Ir(CNO)_6]^{3-}$, 1126
IrC_6O_{12}
$[Ir(C_2O_4)_3]^{2-}$, 1156
$[Ir(C_2O_4)_3]^{3-}$, 1142, 1156
$IrC_7H_7N_2O_2$
$Ir(CO)_2(\mu\text{-}\overline{NN{=}CMeCH{=}CMe})$, 1161
$IrC_7H_7O_4$
$Ir(acac)(CO)_2$, 1116
$IrC_7H_{18}ClOP_2$
$IrCl(CO)(PMe_3)_2$, 1109
$IrC_8H_{12}N_4$
$[Ir(CNMe)_4]^+$, 1102
$IrC_8H_{20}Cl_4S_2$
$IrCl_4(SEt_2)_2$, 1145
$[IrCl_4(SEt_2)_2]^-$, 1145
$IrC_9H_{13}ClN$
$IrHCl(CN)(cod)$, 1149
$IrC_9H_{15}O_2$
$Ir(acac)(C_2H_4)_2$, 1140
$IrC_9H_{27}Cl_3P_3$
$IrCl_3(PMe_3)_3$, 1134
$IrC_{10}H_{10}Cl_4N_2$
$[IrCl_4(py)_2]^-$, 1130
$IrC_{10}H_{12}Cl_3N_2O$
$IrCl_3(H_2O)(py)_2$, 1130
$IrC_{10}H_{18}$
$[IrH_3(C_5Me_5)]^-$, 1166
$IrC_{10}H_{19}$
$IrH_4(C_5Me_5)$, 1166
$IrC_{12}H_{10}Cl_4S$
$[IrCl_4(SPh_2)]^-$, 1157
$IrC_{12}H_{10}Cl_5S$
$[IrCl_5(SPh_2)]^{2-}$, 1157
$IrC_{12}H_{18}N_2$
$[Ir(cod)(MeCN)_2]^-$, 1159
$IrC_{12}H_{19}Cl_4N_3$
$Ir(4\text{-}Me_2NC_6H_4CH{=}NCH_2CH_2CH_2NH_2)Cl_4$, 1162
$IrC_{12}H_{20}N_4$
$[Ir(CNEt)_4]^+$, 1101
$IrC_{12}H_{22}ClS_2$
$IrCl(cod)(MeSCH_2CH_2SMe)$, 1117
$IrC_{12}H_{30}Cl_3S_3$
$IrCl_3(SEt_2)_3$, 1145
$IrC_{12}H_{35}P_2$
$IrH_5(PEt_3)_2$, 1151
$IrC_{12}H_{36}Cl_2P_4$
$IrCl_2(PMe_3)_4$, 1134
$IrC_{13}H_{19}O_2$
$Ir(acac)(cod)$, 1115
$IrC_{13}H_{25}P$
$[IrH(C_5Me_5)(PMe_3)]^+$, 1166
$IrC_{13}H_{26}P$
$IrH_2(C_5Me_5)(PMe_3)$, 1166
$IrC_{13}H_{33}ClOP_3$
$IrHCl(CO)(PEt_3)_2(PH_2)$, 1163
$IrC_{13}H_{36}OP_4$
$[IrH(CO)(PEt_3)_2(PH_2)(PH_3)]^+$, 1163
$IrC_{14}H_{10}O_4PS_2$
$Ir(CO)_2\{SSP(OPh)_2\}$, 1119
$IrC_{14}H_{15}N_2S_2$
$Ir\{S_2C_2(CN)_2\}(\eta\text{-}C_5Me_5)$, 1147
$IrC_{14}H_{22}O_2PS_2$
$Ir(CO)_2\{SSP(C_6H_{11})_2\}$, 1119
$IrC_{15}H_{15}Cl_3N_3$
$IrCl_3(py)_3$, 1130
$IrC_{15}H_{16}F_6O_2$
$Ir(hfacac)(\eta^5\text{-}C_5Me_5)$, 1115
$IrC_{15}H_{22}O_2$
$Ir(acac)(\eta^5\text{-}C_5Me_5)$, 1115
$IrC_{15}H_{24}N_3S_6$
$Ir(S_2CNC_4H_8)_3$, 1145
$IrC_{16}H_{22}Cl_4P_2$
$IrCl_4(PMe_2Ph)_2$, 1156
$[IrCl_4(PMe_2Ph)_2]^-$, 1156
$IrC_{16}H_{27}N_2S_4$
$Ir(S_2CNMe_2)_2(\eta\text{-}C_5Me_5)$, 1147
$IrC_{16}H_{34}P_2$
$[IrH(C_5Me_5)(PMe_3)_2]^+$, 1166
$IrC_{16}H_{40}Cl_2S_4$
$[IrCl_2(SEt_2)_4]^+$, 1145
$IrC_{17}H_{20}ClNOP$
$IrCl(CO)(Ph_2PCH_2CH_2NMe_2)$, 1115
$IrC_{17}H_{22}ClOP_2$
$IrCl(CO)(PMe_2Ph)_2$, 1108
$IrC_{17}H_{22}Cl_3OP_2$
$IrCl_3(CO)(PMe_2Ph)_2$, 1109
$IrC_{17}H_{38}ClOP_2$
$IrCl(CO)(HPBu^t_2)_2$, 1111
$IrC_{18}H_{22}ClOP_2$
$IrCl(CO)(Ph_2PCH_2CH_2CH_2PMe_2)$, 1115
$IrC_{18}H_{22}ClOP_2S_2$
$IrCl(CO)(PMe_2Ph)_2(CS_2)$, 1146
$IrC_{18}H_{27}O_3$
$Ir(OAc)(cod)_2$, 1159
$IrC_{18}H_{28}Cl_2P$
$IrHCl_2(cod)(PEtPh_2)$, 1109
$IrC_{18}H_{42}ClOP_2$
$IrCl(CO)(PPr^i_3)_2$, 1162
$IrC_{18}H_{47}ClN_2P_2$
$IrCl(N_2)(PPr^i_3)_2$, 1162
$IrC_{18}H_{47}P_2$
$IrH_5(PPr^i_3)_2$, 1167
$IrC_{19}H_{24}NO_2$
$Ir(acac)(C_3H_4)_3(py)$, 1140
$IrC_{19}H_{36}P$
$Ir(\eta^4\text{-}cod)(\eta^3\text{-}C_3H_5)(PHBu^t_2)$, 1163
$IrC_{19}H_{47}OP_3$
$[IrH_2(CO)(PEt_3)_3]^+$, 1152
$IrC_{20}H_{16}Cl_2N_4$
$[IrCl_2(bipy)_2]^+$, 1130, 1162
$IrC_{20}H_{18}N_4$
$[IrH_2(bipy)_2]^+$, 1162
$IrC_{20}H_{20}Cl_2N_4$
$[IrCl_2(py)_4]^+$, 1130
$IrC_{20}H_{20}IN_2$
$IrI(phen)(cod)$, 1139
$IrC_{20}H_{20}N_2$
$[Ir(phen)(cod)]^+$, 1139
$IrC_{20}H_{20}N_2O_2$

$[Ir(O_2(phen)(cod)]^+$, 1139

$IrC_{20}H_{29}O_4$
$Ir(acac)_2(\eta^5\text{-}C_5Me_5)$, 1115

$IrC_{20}H_{35}P_2$
$IrH_5(PEt_2Ph)_2$, 1158

$IrC_{20}H_{36}N_4$
$[Ir(CNBu^t)_4]^+$, 1102

$IrC_{21}H_{15}O_3P$
$[Ir(CO)_3(PPh_3)]^-$, 1100, 1103

$IrC_{21}H_{20}ClNOP$
$IrCl(CO)(2\text{-}Ph_2PC_6H_4NMe_2)$, 1114

$IrC_{21}H_{30}ClOP_2$
$IrCl(CO)(PEt_2Ph)_2$, 1108

$IrC_{21}H_{30}Cl_3OP_2$
$IrCl_3(CO)(PEt_2Ph)_2$, 1109

$IrC_{22}H_{16}F_6N_4O_6S_2$
$[Ir(bipy)_2(OSO_2CF_3)_2]^+$, 1162

$IrC_{22}H_{46}ClP_2$
$IrHCl(CH{=}CHCH_2PBu^t_2)(Bu^t_2PCH_2CH{=}CH)$, 1137

$IrC_{23}H_{26}ClNP_2S_2$
$IrHCl(PPh_3)_2(S_2CNEt_2)$, 1106

$IrC_{24}H_{15}Br_4NO_3P$
$Ir(NO)(1,2\text{-}O_2C_6Br_4)(PPh_3)$, 1116

$IrC_{24}H_{16}Cl_2N_4$
$[IrCl_2(phen)_2]^+$, 1162

$IrC_{24}H_{19}NO_3P$
$Ir(NO)(1,2\text{-}O_2C_6H_4)(PPh_3)$, 1116

$IrC_{24}H_{28}N_2$
$[Ir(3,4,7,8\text{-}Me_4phen)(cod)]^+$, 1160

$IrC_{24}H_{30}S_3$
$Ir\{S(CH_2CH_2SPh)_2\}(cod)]^+$, 1117

$IrC_{24}H_{32}Cl_2P_3$
$IrCl_2(CH_2PMePh)(PMe_2Ph)_2$, 1137

$IrC_{24}H_{32}Cl_4P_3$
$IrCl_3(PMe_2Ph)_2(PMePhCH_2Cl)$, 1137

$IrC_{24}H_{33}Cl_2NO_3P_3$
$IrCl_2(NO_3)(PMe_2Ph)_3$, 1144

$IrC_{24}H_{33}Cl_3P_3$
$IrCl_3(PMe_2Ph)_3$, 1137

$IrC_{24}H_{36}P_3$
$IrH_3(PMe_2Ph)_3$, 1164

$IrC_{24}H_{37}P_3$
$[IrH_4(PMe_2Ph)_3]^+$, 1164

$IrC_{24}H_{56}ClP_2$
$IrH_2Cl(PBu^t_3)_2$, 1134

$IrC_{25}H_{21}ClN_3O$
$IrCl(CNC_7H_7)_3(CO)$, 1102

$IrC_{25}H_{23}N_4OP$
$Ir(CO)\{H_2B(NN{=}CHCH{=}CH)_2\}(PPh_3)$, 1108

$IrC_{25}H_{27}N_2OPS_2$
$[Ir(CO)(PPh_3)(\eta^2\text{-}SCNMe_2)_2]^+$, 1154

$IrC_{25}H_{27}N_2OPS_3$
$[Ir(CO)(\eta^2\text{-}CSNMe_2)(PPh_3)(S_2CNMe_2)]^+$, 1118

$IrC_{25}H_{27}N_2O_2$
$Ir(acac)(cod)(phen)$, 1165

$IrC_{25}H_{34}ClOP_3$
$[IrHCl(CO)(PMe_2Ph)_3]^+$, 1150

$IrC_{26}H_{20}Cl_2N_4$
$[IrCl_2(phen)(5,6\text{-}Me_2phen)]^+$, 1130

$IrC_{26}H_{26}BrClP$
$IrCl(\eta^1\text{-}2\text{-}BrC_6H_4PPh_2)(cod)$, 1163

$IrC_{26}H_{26}BrP$
$[Ir(\eta^2\text{-}2\text{-}BrC_6H_4PPh_2)(cod)]^+$, 1163

$IrC_{26}H_{28}BrP$
$[IrH_2(\eta^2\text{-}2\text{-}BrC_6H_4PPh_2)(cod)]^+$, 1163

$IrC_{26}H_{31}O_2$
$Ir(acac)(nbd)_3$, 1115

$IrC_{26}H_{45}ClP$
$IrCl(cod)\{P(C_6H_{11})_3\}$, 1109

$IrC_{26}H_{46}ClOP_2$
$IrCl(CO)\{(Bu^t_2PC{\equiv}CCH_2CH_2)_2CH_2\}$, 1112

$IrC_{27}H_{22}F_6N_2OP$
$Ir\{NHC(CF_3){=}C(CMe{=}CH_2)C(CF_3){=}NH\}(CO)(PPh_3)$, 1108

$IrC_{27}H_{26}BrOP_2$
$IrBrH_2(CO)(dppe)$, 1163

$IrC_{27}H_{29}Cl_2P_2$
$IrCl_2(PMePh_2)_2(Me)$, 1108

$IrC_{28}H_{24}Cl_2N_4$
$[IrCl_2(4,7\text{-}Me_2phen)_2]^+$, 1162

$IrC_{28}H_{26}BrOP_2$
$IrBr(CO)\{(Ph_2PCH_2)CH_2\}$, 1162

$IrC_{28}H_{29}ClOP_2$
$IrCl(CO)(PMePh_2)_2(Me)$, 1109

$IrC_{28}H_{29}Cl_2O_3P_2S$
$IrCl_2(MeSO_2)(CO)(PPh_2Me)_2$, 1146

$IrC_{28}H_{30}O_2P$
$Ir(OAc)(cod)(PPh_3)$, 1159

$IrC_{28}H_{44}N_4$
$[Ir(CNC_6H_{11})_4]^+$, 1101

$IrC_{28}H_{44}N_4O_2$
$[Ir(CNC_6H_{11})_4(O_2)]^+$, 1101

$IrC_{28}H_{44}O_2P_2$
$Ir\{PBu^t_2(C_6H_4O\text{-}2)\}_2$, 1110, 1121, 1123

$IrC_{28}H_{45}O_2P_2$
$IrH\{PBu^t_2(C_6H_4O\text{-}2)\}_2$, 1110, 1123

$IrC_{28}H_{48}ClP_2$
$IrH_2Cl(PBu^t_2Ph)_2$, 1150

$IrC_{28}H_{53}ClNP_2$
$IrHCl(CH{=}CHCH_2PBu^t_2)(Bu^t_2PCH_2CH{=}CH_2)$(4-Mepy), 1137

$IrC_{29}H_{30}ClO_3P_2$
$IrCl(CO)(O_2)(PPh_2Et)_2$, 1138

$IrC_{29}H_{30}NOP_2S$
$[Ir(dppe)(MeCN)(\eta^1\text{-}SOMe)]^{2+}$, 1165

$IrC_{29}H_{30}N_2P$
$Ir(cod)(PPh_3)(NN{=}CHCH{=}CH)$, 1167

$IrC_{29}H_{30}OP_2S_2$
$IrH(CO)(SCH_2CH_2PPh_2)(HSCH_2CH_2PPh_2)$, 1163

$IrC_{29}H_{31}Cl_2OP_2$
$IrCl_2(COEt)(PMePh_2)_2$, 1109

$IrC_{29}H_{45}O_3P_2$
$Ir(CO)\{PBu^t_2(C_6H_4O\text{-}2)\}\{PBu^t_2(C_6H_4OH\text{-}2)$, 1110, 1123
$IrH(CO)\{PBu^t_2(C_6H_4O\text{-}2)\}_2$, 1110

$IrC_{29}H_{47}IN_4$
$[IrI(Me)(CNC_6H_{11})_4]^+$, 1101

$IrC_{29}H_{48}ClOP_2$
$IrH_2Cl(CO)(PBu^t_2Ph)_2$, 1150

$IrC_{30}H_{24}N_6$
$[Ir(bipy)_3]^{3+}$, 1130, 1162

$IrC_{30}H_{25}N_6O$
$[Ir(bipy)_3(OH)]^{2+}$, 1131

$IrC_{30}H_{26}N_6O$
$[Ir(bipy)_3(H_2O)]^{3+}$, 1131

$IrC_{30}H_{28}Cl_2OP_2$
$IrCl_2(C_3H_5)(CO)(PMePh_2)_2$, 1164

$IrC_{30}H_{46}Cl_2P_3$
$IrHCl_2(PEt_2Ph)_3$, 1159

$IrC_{30}H_{47}OP_2$
$Ir(C_5Ph)(CO)(PPr^i_3)_2$, 1162

$IrC_{30}H_{47}O_3P_2$
$Ir(CO)\{PBu^t_2(C_6H_4O\text{-}2)\}\{PBu^t_2(C_6H_4OMe\text{-}2)\}$, 1110

$IrC_{30}H_{47}O_4P_2$
$Ir\{CH_2CMe_2PBu^tC_6H_3(OMe\text{-}6)O\}\{OC_6H_3(OMe\text{-}3)(PBu^t_2\text{-}2)\}$, 1138

$IrC_{30}H_{48}O_4P_2$
$Ir\{OC_6H_3(OMe\text{-}3)(PBu^t_2\text{-}2)\}_2$, 1121, 1138

$IrC_{30}H_{48}O_6P_2$
$Ir(O_2)\{OC_6H_3(OMe\text{-}3)(PBu^t_2\text{-}2)\}_2$, 1138

$IrC_{30}H_{49}O_4P_2$
$IrH\{OC_6H_3(OMe\text{-}3)(PBu^t_2\text{-}2)\}_2$, 1138

$IrC_{31}H_{50}NP$
$[Ir(cod)\{P(C_6H_{11})_3\}(py)]^+$, 1166

$IrC_{32}H_{29}N_5O_5PS_2$

Ir(NO){$N_4(SO_2C_6H_4Me)_2$}(PPh_3), 1106

$IrC_{32}H_{44}O_2P_4$
$[Ir(O_2)(PhPMe_2)_4]^+$, 1139

$IrC_{32}H_{44}P_4$
$[IrH(PMe_2C_6H_4)(PMe_2Ph)_3]^+$, 1136

$IrC_{32}H_{46}P_4$
$[IrH_2(PMe_2Ph)_4]^+$, 1136

$IrC_{32}H_{49}Cl_2O_2P_2$
$IrCl_2(Bu^t_2PCH_2COPh)\{Bu^t_2PCH{=}C(O)Ph\}$, 1136

$IrC_{32}H_{49}O_2P_2$
$IrH\{Bu^t_2PCH{=}C(O)Ph\}_2$, 1136

$IrC_{33}H_{27}N_3$
$[Ir(2\text{-}Phpy)_3]^{3+}$, 1162

$IrC_{33}H_{46}ClOP_2$
$IrCl(CO)\{PBu^t_2(C{=}CPh)\}_2$, 1110

$IrC_{33}H_{47}Cl_2OP_2$
$IrHCl_2(CO)\{PBu^t_2(C{=}CPh)\}_2$, 1110

$IrC_{33}H_{47}O_2P_2$
$Ir(CO)\{PBu^t_2(CH{=}COPh)\}\{PBu^t_2(C{=}CPh)\}$, 1110

$IrC_{33}H_{49}O_3P_2$
$Ir(CO)\{Bu^t_2PCH{=}C(O)Ph\}(Bu^t_2PCH_2COPh)$, 1136
$IrH(CO)\{Bu^t_2PCH{=}C(O)Ph\}_2$, 1136

$IrC_{33}H_{50}ClO_3P_2$
$IrHCl(CO)\{Bu^t_2PCH{=}C(O)Ph\}(Bu^t_2PCH_2COPh)$, 1136

$IrC_{34}H_{36}P_2$
$[Ir(dppe)(cod)]^+$, 1160

$IrC_{34}H_{50}O_3P_2$
$Ir(CO)\{PBu^t_2(CH{=}COPh)\}\{PBu^t_2(CH{=}COMe^2h)\}$, 1110

$IrC_{36}H_{29}Cl_2P_2$
$IrCl_2\{PPh_2(C_6H_4)\}(PPh_3)$, 1137

$IrC_{36}H_{29}F_6P_2$
$IrH_5\{P(C_6H_4F\text{-}4)_3\}_2$, 1167

$IrC_{36}H_{30}BrN_2O_2P_2$
$IrBr(NO)_2(PPh_3)_2$, 1159

$IrC_{36}H_{30}Br_3NOP_2$
$IrBr_3(NO)(PPh_3)_2$, 1120

$IrC_{36}H_{30}ClNOP_2$
$[IrCl(NO)(PPh_3)_2]^+$, 1104

$IrC_{36}H_{30}ClN_2O_2P_2$
$Ir(NO)_2Cl(PPh_3)_2$, 1099

$IrC_{36}H_{30}ClN_2P_2$
$IrCl(N_2)(PPh_3)_2$, 1105, 1106, 1159, 1160

$IrC_{36}H_{30}Cl_2NOP$
$IrCl_2(NO)(PPh_3)$, 1106

$IrC_{36}H_{30}Cl_2NOP_2$
$IrCl_2(NO)(PPh_3)_2$, 1104

$IrC_{36}H_{30}Cl_2NO_3P_2$
$IrCl_2(NO_3)(PPh_3)_2$, 1144

$IrC_{36}H_{30}Cl_3NOP_2$
$[IrCl_3(NO)(PPh_3)_2]^+$, 1104

$IrC_{36}H_{30}N_2O_2P_2$
$[Ir(NO)_2(PPh_3)_2]^+$, 1105, 1159

$IrC_{36}H_{30}N_2O_6P_2$
$Ir(NO_3)_3(PPh_3)_2$, 1143

$IrC_{36}H_{30}N_3O_7P_2$
$Ir(NO_3)_2(NO)(PPh_3)_2$, 1144

$IrC_{36}H_{31}ClNOP_2$
$IrH(NO)Cl(PPh_3)_2$, 1100

$IrC_{36}H_{31}Cl_2P_2$
$IrHCl_2(PPh_3)_2$, 1135, 1149

$IrC_{36}H_{31}NO_2P_2$
$[Ir(OH)(NO)(PPh_3)_2]^+$, 1104

$IrC_{36}H_{31}N_2O_6P_2$
$IrH(NO_3)_2(PPh_3)_2$, 1144

$IrC_{36}H_{33}Cl_3NOP_2$
$Ir(NH_2OH)Cl_3(PPh_3)_2$, 1100

$IrC_{36}H_{44}N_4$
IrI(octaethylporphyrin), 1155

$IrC_{36}H_{44}N_4$
$[Ir(octaethylporphyrin)]^-$, 1155

$IrC_{36}H_{45}N_4$
IrH(octaethylporphyrin), 1155

$IrC_{36}H_{66}ClP_2$
$IrH_2Cl\{P(C_6H_9)(C_6H_{11})_2\}\{P(C_6H_{11})_3\}$, 1110

$IrC_{36}H_{68}ClP_2$
$IrH_2Cl\{P(C_6H_{11})_3\}_2$, 1110

$IrC_{37}H_{29}OP_2$
$Ir(CO)(C_6H_4PPh_2)(PPh_3)$, 1114

$IrC_{37}H_{30}ClNO_2P_2$
$[IrCl(NO)(CO)(PPh_3)_2]^-$, 1104

$IrC_{37}H_{30}ClN_2O_6P_2$
$IrCl(NO_2)(NO_3)(CO)(PPh_3)_2$, 1143, 1144

$IrC_{37}H_{30}ClN_2O_7P_2$
$IrCl(NO_3)_2(CO)(PPh_3)_2$, 1143

$IrC_{37}H_{30}ClOP_2$
$IrCl(CO)(PPh_3)_2$, 1105, 1108, 1109, 1138, 1158–1160, 1163

$IrC_{37}H_{30}ClO_2P_2Se$
$IrCl(CSe)(O_2)(PPh_3)_2$, 1148

$IrC_{37}H_{30}ClO_3P_2$
$IrCl(CO)(O_2)(PPh_3)_2$, 1139, 1140, 1159

$IrC_{37}H_{30}ClO_3P_2S$
$IrCl(CO)(PPh_3)_2(SO_2)$, 1118

$IrC_{37}H_{30}ClO_5P_2S$
$IrCl(CO)(O_2SO_2)(PPh_3)_2$, 1140

$IrC_{37}H_{30}ClP_2Se$
$IrCl(CSe)(PPh_3)_2$, 1148, 1165

$IrC_{37}H_{30}ClP_2Se_2$
$IrCl(CSe_2)(PPh_3)_2$, 1148

$IrC_{37}H_{30}Cl_3OP_2$
$IrCl_3(CO)(PPh_3)_2$, 1117

$IrC_{37}H_{30}Cl_3P_2Se$
$IrCl_3(CSe)(PPh_3)_2$, 1148

$IrC_{37}H_{30}IO_2P_2$
$[IrI(NO)(CO)(PPh_3)_2]^+$, 1104

$IrC_{37}H_{30}I_3OP_2$
$IrI_3(CO)(PPh_3)_2$, 1141

$IrC_{37}H_{30}NO_2P_2$
$Ir(NO)(CO)(PPh_3)_2$, 1100, 1104
$[Ir(NO)(CO)(PPh_3)_2]^+$, 1100

$IrC_{37}H_{30}N_3OP_2$
$Ir(N_3)(CO)(PPh_3)_2$, 1161

$IrC_{37}H_{30}N_3O_9P_2$
$Ir(NO_2)(NO_3)_2(CO)(PPh_3)_2$, 1143, 1144

$IrC_{37}H_{30}N_4O_9P_2$
$Ir(NO_3)_2(NO)_2(CO)(PPh_3)_2$, 1100

$IrC_{37}H_{31}ClIOP_2$
$IrHCl(CO)(PPh_3)_2$, 1119

$IrC_{37}H_{31}Cl_2OP_2$
$IrHCl_2(CO)(PPh_3)_2$, 1149

$IrC_{37}H_{31}Cl_2P_2S_2$
$IrCl_2(S_2CH)(PPh_3)_2$, 1146

$IrC_{37}H_{31}N_2O_6P_2$
$IrH(NO_2)(NO_3)(CO)(PPh_3)_2$, 1143, 1144

$IrC_{37}H_{31}N_2O_7P_2$
$IrH(NO_3)_2(CO)(PPh_3)_2$, 1144

$IrC_{37}H_{31}O_2P_2$
$Ir(OH)(CO)(PPh_3)_2$, 1116

$IrC_{37}H_{31}O_3P_2S$
$IrH(CO)(PPh_3)_2(SO_2)$, 1118

$IrC_{37}H_{32}ClOP_2$
$IrH_2Cl(CO)(PPh_3)_2$, 1150, 1159

$IrC_{37}H_{32}ClOP_2S$
$IrHCl(SH)(CO)(PPh_3)_2$, 1145, 1165

$IrC_{37}H_{33}Cl_2P_2$
$IrCl_2(PPh_3)_2(Me)$, 1137

$IrC_{37}H_{33}INOP_2$
$IrMe(NO)I(PPh_3)_2$, 1100

$IrC_{37}H_{33}OP_2$
$IrH_3(CO)(PPh_3)_2$, 1150

$IrC_{37}H_{33}P_2S_2$
$IrH_2(S_2CH)(PPh_3)_2$, 1146

$IrC_{37}H_{44}ClN_4O$
IrCl(CO)(octaethylporphyrin), 1120, 1155

$IrC_{37}H_{46}Cl_2N_4$
$IrCl_2$(μ-methyloctaethylporphryin), 1155
$IrC_{37}H_{47}N_4$
Ir(octaethylporphyrin)(Me), 1155
$IrC_{37}H_{56}ClF_2NP_2$
$IrCl\{(C_6H_{11})_2PC_6H_3F\}\{(C_6H_{11})_2PC_6H_4F\}$(py), 1138
$IrC_{37}H_{66}ClOP_2$
$IrCl(CO)\{P(C_6H_{11})_3\}_2$, 1110
$IrC_{38}H_{29}O_2P_2$
$Ir(CO)_2(C_6H_4PPh_2)(PPh_3)$, 1114
$IrC_{38}H_{30}ClO_2P_2$
$IrCl(CO)_2(PPh_3)_2$, 1159
$IrC_{38}H_{30}ClOP_2Se_2$
$IrCl(CO)(CSe_2)(PPh_3)_2$, 1148
$IrC_{38}H_{30}ClP_2Se_2$
$IrCl(\eta_2\text{-}CSe_2)(CSe)(PPh_3)$, 1148, 1165
$IrC_{38}H_{30}F_3NO_3P_2$
$Ir(O_2CCF_3)(NO)(PPh_3)_2$, 1100, 1116
$IrC_{38}H_{30}IOP_2$
IrI(SCS)(CO)$(PPh_3)_2$, 1146
$IrC_{38}H_{30}NOP_2$
Ir(CN)(CO)$(PPh_3)_2$, 1101
$IrC_{38}H_{30}NOP_2S$
Ir(NCS)(CO)$(PPh_3)_2$, 1107
Ir(SCN)(CO)$(PPh_3)_2$, 1139
$IrC_{38}H_{30}O_2P_2$
$[Ir(CO)_2(PPh_3)_2]^+$, 1111, 1167
$IrC_{38}H_{30}P_2S_3$
$[Ir(CS)(PPh_3)_2(\pi\text{-}CS_2)]^+$, 1118
$IrC_{38}H_{31}ClNOP_2$
IrHCl(CN)(CO)$(PPh_3)_2$, 1125, 1150
$IrC_{38}H_{31}OP_2S_2$
$Ir(CS_2H)(CO)(PPh_3)_2$, 1146
$Ir(S_2CH)(CO)(PPh_3)_2$, 1146
$IrC_{38}H_{31}O_2P_2$
$IrH(CO)_2(PPh_3)_2$, 1120
$IrC_{38}H_{31}O_4P_2$
$Ir(OCO_2H)(CO)(PPh_3)_2$, 1116
$IrC_{38}H_{31}O_6P_2$
$Ir(OCO_2H)(CO)(O_2)(PPh_3)_2$, 1116
$IrC_{38}H_{32}N_4P$
$[IrH(bipy)_2(PPh_3)]^{2+}$, 1162
$IrC_{38}H_{33}Cl_2O_2P_2S$
$IrCl_2(MeSO)(CO)(PPh_3)_2$, 1146
$IrC_{38}H_{33}Cl_2O_3P_2S$
$IrCl_2(MeSO_2)(CO)(PPh_3)_2$, 1146, 1147
$IrC_{39}H_{30}ClF_6NO_2P_2$
$IrCl(CO)(PPh_3)_2\{ON(CF_3)_2\}$, 1143
$IrC_{39}H_{30}ClN_2OP_2S$
IrCl(CN)(NCS)(CO)$(PPh_3)_2$, 1125
$IrC_{39}H_{30}F_6NO_2P_2$
$[Ir\{ON(CF_3)_2\}(CO)(PPh_3)_2]^+$, 1117
$IrC_{39}H_{30}F_6NO_4P_2$
$Ir\{ON(CF_3)_2\}(CO)(O_2)(PPh_3)_2$, 1117
$IrC_{39}H_{30}O_3P_2$
$[Ir(CO)_3(PPh_3)_2]^+$, 1105, 1159
$IrC_{39}H_{30}P_2S_5$
$[Ir(PPh_3)_2(CS)(\sigma\text{-}CS_2)(\pi\text{-}CS_2)]^+$, 1118
$IrC_{39}H_{31}ClF_6NP_2$
$IrCl(NCF_2CHFCF_3)(PPh_3)_2$, 1107
$IrC_{39}H_{31}OP_2S_4$
$Ir(CSSH)(CO)(PPh_3)_2(\pi\text{-}CS_2)$, 1146
$Ir(SSCH)(CO)(PPh_3)_2(\pi\text{-}CS_2)$, 1146
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$IrCl(2\text{-}Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2\text{-}2)(CO)$, 1114
$IrC_{39}H_{33}NOP_2$
$[Ir(CO)(PPh_3)_2(MeCN)]^+$, 1109
$IrC_{39}H_{33}NP_2Se$
$[Ir(CSe)(PPh_3)_2(MeCN)]^+$, 1148
$IrC_{39}H_{33}O_3P_2$
Ir(OAc)(CO)$(PPh_3)_2$, 1116
$IrC_{39}H_{33}O_5P_2$
$Ir(OCO_3)(CO)(PPh_3)_2(Me)$, 1141
$IrC_{39}H_{34}ClNOP_2S$
$IrHCl(CO)(\eta^1\text{-}SCNMe)(PPh_3)_2$, 1154
$IrC_{39}H_{35}NOP_2$
$[Ir(NO)(PPh_3)_2(\eta^3\text{-}C_3H_5]^+$, 1104
$IrC_{39}H_{36}Cl_2NSP_2$
$IrCl_2(\eta^2\text{-}SCNMe_2)(PPh_3)_2$, 1154
$IrC_{39}H_{39}ClP_3$
$IrCl(PMePh_2)_3$, 1109
$IrC_{39}H_{44}ClO_2P_2$
IrCl(diop)(cod), 1113
$IrC_{40}H_{30}F_6NO_5P_2$
$Ir(NO)(O_2CCF_3)_2(PPh_3)_2$, 1161
$IrC_{40}H_{31}ClF_6NOP_2$
$IrCl(CO)(NCF_2CHFCF_3)(PPh_3)_2$, 1107
$IrC_{40}H_{33}F_6INO_2P_2$
$IrI(Me)\{ON(CF_3)_2\}(CO)(PPh_3)_2$, 1117
$IrC_{40}H_{34}ClP_2$
$IrCl(2\text{-}CH_2{=}CHC_6H_4PPh_2)_2$, 1111, 1114
$IrC_{40}H_{36}ClNOP_2S$
$[IrCl(CO)(\eta^2\text{-}CSNMe_2)(PPh_3)_2]^+$, 1118
$[IrCl(CO)(\eta^2\text{-}SCNMe_2)(PPh_3)_2]^+$, 1154
$IrC_{40}H_{36}I_2P_2Se_3$
$IrI_2(MeSeCSeCSeMe)(PPh_3)_2$, 1148
$IrC_{40}H_{37}NOP_2S$
$[IrH(CO)(\eta^2\text{-}SCNMe_2)(PPh_3)_2]^+$, 1154
$IrC_{40}H_{38}N_2P_2$
$[IrH_2(MeCN)_2(PPh_3)_2]^+$, 1166
$IrC_{40}H_{39}N_2O_7P_3$
$[Ir(NO_3)_2(CO)(PMePh_2)_3]$, 1144
$IrC_{41}H_{30}ClF_{10}N_2O_3P_2$
$Ir\{ON(CF_3)CF_2CF_2N(CF_3)O\}Cl(CO)(PPh_3)_2$, 1143
$IrC_{41}H_{30}Cl_5N_2P_2$
$IrCl\{N_2CC(Cl){=}CClC(Cl){=}CCl\}(PPh_3)_2$, 1106
$IrC_{41}H_{31}Cl_6N_2P_2$
$IrHCl_2\{N_2CC(Cl){=}CClC(Cl){=}CCl\}(PPh_3)_2$, 1107
$IrC_{41}H_{31}F_6O_5P_2$
$IrH(O_2CCF_3)_2(CO)(PPh_3)_2$, 1117
$IrC_{41}H_{36}NO_2P_2Se$
Ir(CO)(NCSe)$(Me_2CO)(PPh_3)_2$, 1107
$IrC_{41}H_{38}ClO_2P_2$
IrHCl(acac)$(PPh_3)_2$, 1140
$IrC_{41}H_{39}O_2P_2$
IrH_2(acac)$(PPh_3)_2$, 1140
$IrC_{41}H_{41}ClNO_2P_2$
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$IrC_{42}H_{35}ClN_2P_2$
$[IrCl(N_2Ph)(PPh_3)_2]^+$, 1106
$IrC_{42}H_{35}FN_2P_2$
$[IrH(HN{=}NC_6H_3F)(PPh_3)_2]^+$, 1132
$IrC_{42}H_{36}ClP_2S$
IrHCl(SPh)$(PPh_3)_2$, 1150
$IrC_{42}H_{37}FN_2P_2$
$[IrH_2(HN{=}NC_6H_4F)(PPh_3)_2]^+$, 1132
$IrC_{42}H_{39}ClOP_3$
IrCl(CO)(triphos), 1135
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$IrCl_2(O_2CBu^t)(CO)(PPh_3)_2$, 1142
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$IrI_2(O_2CBu^t)(CO)(PPh_3)_2$, 1142
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[Ir(triphos)(CO)], 1113
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$[IrH_2(PPh_3)_2(Me_2CO)_2]^+$, 1166
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$IrCl_2(SSC_6F_5)(CO)(PPh_3)_2$, 1147
$IrC_{43}H_{30}Cl_5O_3$
$IrCl(1,2\text{-}O_2C_6Cl_4)(CO)(PPh_3)_2$, 1141
$IrC_{43}H_{30}F_{16}N_3O_4P_2$
$Ir\{ON(CF_3)CF_2CF_2N(CF_3)O\}\{ON(CF_3)_2\}(CO)$-$(PPh_3)_2$, 1143
$Ir\{ON(CF_3)_2\}\{ON(CF_3)CF_2CF_2N(CF_3)O\}(CO)$-$(PPh_3)_2$, 1117
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$IrCl(HN{=}NC_6H_3F\text{-}4)(CO)(PPh_3)_2$, 1153
$[IrCl(CO)(N{=}NC_6H_4F)(PPh_3)_2]^+$, 1132
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$IrCl_2(CO)(N{=}NC_6H_4NO_2\text{-}2)(PPh_3)_2$, 1132
$IrC_{43}H_{35}ClN_2OP_2$
$[IrCl(CO)(HN{=}NC_6H_4)(PPh_3)_2]^+$, 1132
$IrC_{43}H_{35}O_3P_2$
$Ir(CO)(O_2)(PPh_3)_2(Ph)$, 1140
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$IrCl_2(HN{=}NC_6H_3OMe\text{-}4)(PPh_3)_2$, 1153
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$IrH_2(PhSeO_2)(PPh_3)_2$, 1148
$IrC_{43}H_{38}ClN_2OP_2$
$IrHCl(NHNC_6H_2OMe)(PPh_3)_2$, 1153
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$IrHI(HN{=}NC_6H_3Me\text{-}4)(PPh_3)_2$, 1132
$IrC_{43}H_{39}O_2P_3$
$[Ir(CO)_2(triphos)]^+$, 1135
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$[Ir(S_2CNMe_2)_2(CO)(PPh_3)_2]^+$, 1145
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$Ir(O_2CC_6H_4Cl\text{-}3)(CO)(PPh_3)_2$, 1116
$IrC_{44}H_{37}Cl_2OP_2S$
$IrCl_2(SC_6H_4Me\text{-}4)(CO)(PPh_3)_2$, 1146
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$Ir(O_2SC_6H_4Me\text{-}4)(CO)(PPh_3)_2$, 1118
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$IrHCl(CO)(PPh_3)_2(SeC_6H_4Me\text{-}4)$, 1148
$IrC_{44}H_{39}ClNOP_3$
$[IrCl(NO)(dppe)(PPh_3)]^+$, 1104
$IrC_{44}H_{42}ClN_2O_4P_2$
$IrCl(N_2)(PPh_3)_2(EtO_2CCHCHCO_2Et)$, 1106
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$\{Ir(CO)(\mu\text{-}SCNMe_2)(PPh_3)\}_2$, 1154
$IrC_{44}H_{42}P_2$
$[Ir(cod)(PPh_3)_2]^+$, 1110
$IrC_{44}H_{56}N_4$
Ir(cod)(octaethylporphyrin), 1155
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$Ir(CO)(C_2Ph)(PPh_3)_2$, 1109
$IrC_{45}H_{37}ClO_3P_2$
$Ir(O_2CC_6H_4Cl\text{-}3)(CO)(PPh_3)_2(Me)$, 1116
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$IrCl_2(CO)(PPh_3)_2(COCH_2Ph)$, 1117
$IrC_{45}H_{42}ClNP_2$
$IrHCl(MeN{=}CHC_6H_4Me\text{-}4)(PPh_3)_2$, 1152
$IrC_{45}H_{50}ClO_5P_2$
$IrCl(CO)(PPh_3)_2(Bu^tOOH)_2$, 1109
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$Ir(NO)(NC_6H_4Me\text{-}4)_4(PPh_3)$, 1100
$IrC_{47}H_{30}Cl_5OP_2S_4$
$IrCl(CO)(PPh_3)$(tetrachlorotetrathionaphthalene), 1165
$IrC_{48}H_{36}O_6P_3$
$IrWH(CO)_4(\mu\text{-}PPh_2)_2(PPh_3)(OAc)$, 1163
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$[Ir(NO)(phen)(PPh_3)_2]^{2+}$, 1104
$IrC_{48}H_{44}P_4$
$[Ir(HPPh_2)_4]^-$, 1111
$IrC_{48}H_{80}Cl_2NP_2$
$IrHCl(PhC{=}CClCH{=}NPr)\{P(C_6H_{11})_3\}_2$, 1153
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$IrHCl(PhC{=}CHCH{=}NPr\{P(C_6H_{11})_3\}_2$, 1153
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$IrH(SC_6F_5)_2(CO)(PPh_3)_2$, 1150
$IrC_{49}H_{38}F_2N_4OP_2$
$[Ir(CO)(FC_6H_4NN{=}NNC_6H_4F)(PPh_3)_2]^+$, 1132
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$IrH(CO)(PPh_3)_2(SPPh_2)$, 1119
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$[Ir(dppm)_2(O_2)]^+$, 1139
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$Ir(CO)(4\text{-}MeC_6H_4NN{=}NC_6H_4Me\text{-}4)(PPh_3)_2$, 1107
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$[Ir(Ph_2PCH{=}CHPPh_2)_2]^+$, 1111, 1112
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$[Ir(NO_2)_2(dppe)_2]^+$, 1143
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$[Ir(dppe)_2(\eta^2\text{-}S_2O)]^-$, 1117, 1121, 1165
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$[Ir(dppe)_2(\eta^2\text{-}Se_2O)]^+$, 1165
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$[Ir(dppe)_2(\eta^2\text{-}SSe)]^+$, 1165
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$[IrHCl(dppe)_2]^+$, 1150
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$[Ir(CO)(Ph_2PCH{=}CHPPh_2)_2]^+$, 1113
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$IrCl\{P(OPh)_3\}_3$, 1136
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$IrC_{54}H_{46}Cl_2P_3$
$IrHCl_2(PPh_3)_3$, 1150
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$IrH(NO)(PPh_3)_3$, 1100
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$IrC_{55}H_{46}P_3S$
$IrH(CS)(PPh_3)_3$, 1120
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$IrH_2(PPh_3)_3(SeMe)$, 1148, 1165
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$[Ir(dppe)_2(CNMe)(SMe)]^{2+}$, 1122
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$IrH_2(OAc)(PPh_3)_3$, 1150
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$[Ir(PPh_3)_3(\sigma\text{-}CS_2)(\pi\text{-}CS_2)]^+$, 1118
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$[IrH_2(HN{=}NC_6H_4NO_2)(PPh_3)_3]^+$, 1132
$IrC_{61}H_{53}N_2OP_3$
$[IrH(NHNC_6H_3OMe)(PPh_3)_3]^+$, 1153
$IrC_{62}H_{64}O_4P_4$
$[Ir(diop)_2]^+$, 1113
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$[Ir(O_2)(PPh_3)_4]^+$, 1138
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$[Ir(PPh_3)_4]^{3+}$, 1138
$IrC_{72}H_{61}O_{12}P_4$
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$[IrClF_5]^{2-}$, 1166
$IrCl_6$
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$[IrBr(CO)\{FePPh_2(CO)_2Cp\}_2]^+$, 1111
$IrFe_2C_{39}H_{30}ClO_5P_2$
$[Ir(CO)\{FePPh_2(CO)_2Cp\}_2Cl$, 1111
$IrFe_2C_{41}H_{30}O_7P_2$
$[Ir(CO)_3\{FePPh_2(CO)_2Cp\}_2]^+$, 1111
$IrGeC_{37}H_{31}ClOP$
$IrHCl(GePh_3)(CO)(PPh_3)$, 1126
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$[IrI(H_2O)(NH_3)_4]^{2+}$, 1128
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$[IrBr(NH_3)_5]^{2+}$, 1128
$IrH_{15}ClN_5$
$[IrCl(NH_3)_5]^{2+}$, 1128
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$[Ir(NH_2Cl)(NH_3)_5]^{3+}$, 1128, 1133
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$[IrH_2(NH_3)_5]^{3+}$, 1128
$IrH_{17}N_5O$
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$IrH_{18}N_6$
$[Ir(NH_3)_6]^{3+}$, 1128
$IrH_{18}N_6O$
$[Ir(NH_2OH)(NH_3)_5]^{3+}$, 1133
$IrHgC_{37}H_{30}Br_2ClOP_2$
$IrBrCl(HgBr)(CO)(PPh_3)_2$, 1124
$IrHgC_{37}H_{30}ClN_2OP_2$
$\{IrCl(CO)(PPh_3)_2\}Hg(NO_3)_2$, 1125
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$IrCl(CN)(HgCN)(CO)(PPh_3)_2$, 1125
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$IrCl_2(HgCl)(NCF_2CHFCF_3)(PPh_3)_2$, 1124
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$[\{IrCl(CO)(PPh_3)_2\}_3Hg]^{2+}$, 1125
$IrHg_4C_{148}H_{120}Cl_4O_4P_8$
$[\{IrCl(CO)(PPh_3)_2\}_4Hg]^{2+}$, 1125
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[Ir(NO){(2′-py)$_2$pyridazine}(PPh$_3$)$_2$(PdCl$_2$)]$^{2+}$, 1161
IrPtC$_{24}$H$_{64}$P$_4$
[PtH(PEt$_3$)(μ-H)$_2$IrH(PEt$_3$)$_3$]$^+$, 1152
[Pt(PEt$_3$)$_2$(μ-H)$_2$IrH$_2$(PEt$_3$)$_2$]$^+$, 1152
IrPtC$_{52}$H$_{52}$Cl$_4$P$_4$
[IrCl$_2$(PMe$_2$Ph)$_2$(μ-Cl$_2$)Pt(PPh$_3$)$_2$]$^+$, 1156
IrPtC$_{53}$H$_{44}$ClN$_2$OP$_4$
IrCl(CO)(μ-dppm)$_2$Pt(CN)$_2$, 1162
IrPtC$_{66}$H$_{54}$ClP$_4$
Pt(C≡CPh)$_2$(μ-dppm)$_2$IrCl, 1112
IrPtC$_{69}$H$_{58}$ClOP$_4$
Pt(C≡CC$_6$H$_4$Me-4)$_2$(μ-dppm)$_2$IrCl(CO), 1112
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IrH$_2$(PEt$_3$)$_2$(μ-Cl)(μ-H)Rh(PEt$_3$)$_2$, 1074, 1151, 1164
IrRhC$_{44}$H$_{70}$P$_4$
Rh(dppe)(μ-H)$_2$IrH$_2$(PPr$^i_3$)$_2$, 1074
Rh(dppe)(μ$_2$-H)$_2$IrH$_2$(PPr$^i_3$)$_2$, 1151
IrRhC$_{44}$H$_{71}$ClP$_5$
[IrH(PEt$_3$)$_3$(μ-Cl)(μ-H)Rh(dppe)]$^+$, 1164
IrRhC$_{44}$H$_{72}$P$_5$
[Rh(dppe)(μ-H)$_3$Ir(PEt$_3$)$_3$]$^+$, 1075, 1151
IrSb$_3$C$_{56}$H$_{45}$O$_2$
[Ir(CO)$_2$(SbPh$_3$)$_3$]$^+$, 1111
IrSiC$_{16}$H$_{32}$Cl
IrH$_2$Cl(C$_5$Me$_5$)(SiEt$_3$), 1166
IrSiC$_{35}$H$_{35}$OP$_2$
Ir(CO)(PPh$_2$CH$_2$CH$_2$SiMe$_2$)(PPh$_3$), 1164
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IrH$_2$(C$_5$Me$_5$)(SiEt$_3$)$_2$, 1166
IrSi$_2$C$_{31}$H$_{37}$INP$_2$
IrI(Me){N(SiMe$_2$CHPPh$_2$)$_2$}, 1161
IrSi$_2$C$_{32}$H$_{40}$ClP$_2$
IrCl(PPh$_2$CH$_2$CH$_2$SiMe$_2$)$_2$, 1164
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IrHI{SiH$_2$N(SiH$_3$)$_2$}(CO)(PEt$_3$)$_2$, 1126
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IrHI{SiH$_2$P(SiH$_3$)$_2$}(CO)(PEt$_3$)$_2$, 1126
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Ir(CO)$_3$(SnMe$_3$)(PPh$_3$), 1103
IrSnC$_{36}$H$_{31}$Cl$_4$P$_2$
IrHCl(SnCl$_3$)(PPh$_3$)$_2$, 1103
IrSnC$_{36}$H$_{32}$Cl$_4$OP$_2$
IrH$_2$(SnCl$_3$)(CO)(PPh$_3$)$_2$, 1103
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IrCl(SnCl$_2$)(CO)(PPh$_3$)$_2$, 1103
IrSnC$_{37}$H$_{30}$Cl$_5$OP$_2$
IrCl(SnCl$_4$)(CO)(PPh$_3$)$_2$, 1128
IrSnC$_{37}$H$_{31}$Cl$_4$OP$_2$
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IrH$_2$(SnCl$_3$)(CO)(PPh$_3$)$_2$, 1127
IrSnC$_{38}$H$_{33}$Cl$_4$OP$_2$
IrCl(SnCl$_3$Me)(CO)(PPh$_3$)$_2$, 1128
IrSnC$_{39}$H$_{30}$O$_3$P
Ir(CO)$_3$(SnPh$_3$)(PPh$_3$), 1103
IrSnC$_{39}$H$_{32}$Cl$_3$OP$_2$
Ir(SnCl$_3$)(C$_2$H$_2$)(CO)(PPh$_3$)$_2$, 1103
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Ir(SnCl$_3$)(C$_2$H$_4$)(CO)(PPh$_3$)$_2$, 1103
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IrWH(CO)$_5$(μ-PPh$_2$)$_2$(PPh$_3$)$_2$, 1163
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Ir$_2$Cl$_2$(CO)$_2$(PhAs(CH$_2$AsPh$_2$)$_2$)$_2$, 1164
Ir$_2$As$_6$PdC$_{80}$H$_{72}$Cl$_3$O$_2$
[Ir$_2$PdCl$_3$(CO)$_2$(PhAs(CH$_2$AsPh$_2$)$_2$)$_2$]$^-$, 1164
Ir$_2$B$_2$C$_{30}$H$_{44}$Cl$_4$N$_{12}$
{IrCl$_2$(HB(NN=CMeCH=CMe)$_3$)}$_2$, 1134
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Ir$_2$C$_8$H$_{24}$Cl$_2$F$_4$N$_4$P$_4$
{IrCl(PFNMe$_2$)}$_2$, 1163
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{Ir(CO)$_2$(μ-NN=CHCH=CH)}$_2$, 1161
Ir$_2$C$_{16}$H$_{10}$S$_2$
Ir$_2$(CO)$_4$(SPh)$_2$, 1121
Ir$_2$C$_{16}$H$_{24}$Cl$_2$
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Ir$_2$C$_{16}$H$_{28}$P$_2$
{IrH$_3$(PMe$_2$Ph)}$_2$, 1166
Ir$_2$C$_{16}$H$_{40}$Cl$_6$S$_4$
Ir$_2$Cl$_4$(μ-Cl)$_2$(SEt$_2$)$_4$, 1145
Ir$_2$Cl$_5$(μ-Cl)(μ-SEt$_2$)(SEt$_2$)$_3$, 1145
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Ir$_2$C$_{17}$H$_{38}$I$_2$O$_8$P$_2$S$_2$
{IrI(CO)(μ-SBu^t){P(OMe)$_3$}}$_2$(μ-CH$_2$), 1165
Ir$_2$C$_{20}$H$_{30}$Cl$_4$
{IrCl$_2$(C$_5$Me$_5$)}$_2$, 1159
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Ir$_2$C$_{20}$H$_{36}$
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Ir$_2$C$_{22}$H$_{30}$N$_4$
{Ir(cod)(μ-NN=CHCH=CH)}$_2$, 1161, 1167
Ir$_2$C$_{25}$H$_{15}$O$_7$P
Ir$_2$(CO)$_7$(PPh$_3$), 1101
Ir$_2$C$_{25}$H$_{20}$NO$_2$P
{Ir$_2$(CO)$_2$(PPh$_3$)(py)}$_n$, 1100
Ir$_2$C$_{26}$H$_{51}$P$_2$
[{IrH(C$_5$Me$_5$)(PMe$_3$)}$_2$(μ-H)]$^+$, 1166
Ir$_2$C$_{32}$H$_{40}$N$_8$
[Ir$_2${*meso*-NCCHCH$_2$CHCN(CH$_2$)$_3$}$_4$]$^{2+}$, 1102
Ir$_2$C$_{32}$H$_{40}$O$_4$
{Ir(cod)}$_2${1,4-{(MeCO)$_2$C}C$_6$H$_4$}, 1165
Ir$_2$C$_{32}$H$_{44}$I$_5$P$_4$
[Ir$_2$I$_5$(PMe$_2$Ph)$_4$]$^+$, 1156
Ir$_2$C$_{36}$H$_{30}$Cl$_2$N$_2$O$_3$P$_2$
{IrCl(NO)(PPh$_3$)}$_2$O, 1105
Ir$_2$C$_{36}$H$_{30}$I$_2$N$_2$O$_3$P$_2$
{IrI(NO)(PPh$_3$)}$_2$O, 1101
Ir$_2$C$_{36}$H$_{30}$N$_2$O$_3$P$_2$
{Ir(NO)(PPh$_3$)}$_2$O, 1100
Ir$_2$C$_{38}$H$_{44}$N$_4$O$_6$
{Ir(CO$_3$)}$_2$(μ-octaethylporphyrin), 1155
Ir$_2$C$_{40}$H$_{30}$O$_6$P$_2$S
Ir$_2$(CO)$_4$(PPh$_3$)$_2$(μ-SO$_2$), 1121
Ir$_2$C$_{40}$H$_{30}$O$_8$P$_2$S$_2$
Ir$_2$(CO)$_4$(PPh$_3$)$_2$(μ-SO$_2$)$_2$, 1101
Ir$_2$C$_{40}$H$_{32}$O$_6$P$_2$S
Ir$_2$H$_2$(CO)$_4$(PPh$_3$)$_2$(SO$_2$), 1121
Ir$_2$C$_{42}$H$_{30}$O$_6$P$_2$
Ir$_2$(CO)$_6$(PPh$_3$)$_2$, 1101
Ir$_2$C$_{42}$H$_{30}$O$_{12}$P$_2$
Ir$_2$(CO)$_6${P(OPh)$_3$}$_2$, 1101
Ir$_2$C$_{42}$H$_{44}$N$_4$O$_6$
{Ir(CO)$_3$}$_2$(μ-octaethylporphyrin), 1120
Ir$_2$C$_{43}$H$_{46}$Cl$_2$N$_4$O$_6$
{IrCl(CO)$_3$}$_2$(*N*-methyloctaethylporphyrin), 1120
Ir$_2$C$_{44}$H$_{34}$Cl$_4$N$_4$O$_2$P$_2$
{IrCl(CO)(PPh$_3$){μ-NN=CHC(Cl)=CH}}$_2$, 1161
Ir$_2$C$_{44}$H$_{36}$I$_2$N$_4$O$_2$P$_2$
{IrI(CO)(PPh$_3$)(μ-NN=CHCH=CH)}$_2$, 1161
Ir$_2$C$_{44}$H$_{36}$N$_4$O$_2$P$_2$
{Ir(CO)(PPh$_3$)(μ-NN=CHCH=CH)}$_2$, 1161
Ir$_2$C$_{46}$H$_{48}$O$_2$P$_2$S$_2$
{Ir(CO)(PPh$_3$)(μ-SBu^t)}$_2$, 1121, 1122
Ir$_2$C$_{46}$H$_{50}$O$_2$P$_2$S$_2$
{IrH(CO)(PPh$_3$)(μ-SBu^t)}$_2$, 1121, 1122
Ir$_2$C$_{46}$H$_{51}$O$_2$P$_2$S$_2$

$[\{IrH(CO)(PPh_3)(\mu\text{-}SBu^t)\}_2H]^+$, 1122

$Ir_2C_{47}H_{37}N_2O_6P_2S$
$[\{Ir(CO)_2(PPh_3)\}_2(\mu\text{-}N_2C_6H_4Me\text{-}4)(\mu\text{-}SO_2)]^+$, 1107

$Ir_2C_{47}H_{38}N_2O_6P_2S$
$[\{Ir(CO)_2(PPh_3)\}_2(\mu\text{-}N{=}NHC_6H_4Me\text{-}4)(\mu\text{-}SO_2)]^{2+}$, 1107

$Ir_2C_{48}H_{34}Br_2O_2P_2S_4$
$Ir_2Br_2(CO)_2(PPh_3)_2$(tetrathionaphthalene), 1121

$Ir_2C_{48}H_{48}O_4P_2S_2$
$Ir_2(CO)_4(PPh_3)_2(SBu^t)_2$, 1122

$Ir_2C_{52}H_{44}O_2P_4S$
$Ir_2(\mu\text{-}S)(CO)_2(\mu\text{-}dppm)_2$, 1159

$Ir_2C_{53}H_{44}ClO_3P_4$
$[Ir_2Cl(CO)_3(dppm)_2]^+$, 1112

$Ir_2C_{53}H_{44}Cl_2O_3P_4$
$Ir_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]^+$, 1113

$Ir_2C_{54}H_{44}ClO_4P_4$
$[Ir_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_3(\mu\text{-}dppm)_2]^+$, 1113

$Ir_2C_{56}H_{52}Cl_2O_2P_4$
$\{IrCl(CO)\{Ph_2P(CH_2)_2CH_2\}\}_2$, 1113

$Ir_2C_{58}H_{53}ClNO_3P_4$
$[Ir_2Cl(CNBu^t)(CO)_3(dppm)_2]^+$, 1102

$Ir_2C_{59}H_{45}O_5P_3$
$Ir_2(CO)_5(PPh_3)_3$, 1101

$Ir_2C_{62}H_{62}ClN_2O_2P_4$
$[Ir_2Cl(CNBu^t)_2(CO)_2(dppm)_2]^+$, 1102

$Ir_2C_{64}H_{64}Cl_2P_6$
$Ir_2Cl_2\{1,4\text{-}(Ph_2PCH_2CH_2)_2PCH_2\}_2C_6H_4\}$, 1113

$Ir_2C_{71}H_{80}N_4OP_4$
$[Ir_2(CNBu^t)_4(CO)(dppm)_2]^{2+}$, 1102

$Ir_2C_{72}H_{65}P_4$
$[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]^+$, 1151

$Ir_2C_{76}H_{60}O_4P_4$
$Ir_2(CO)_4(PPh_3)_4$, 1101

$Ir_2C_{76}H_{60}O_{16}P_4$
$Ir_2(CO)_4\{P(OPh)_3\}_4$, 1101

$Ir_2C_{95}H_{96}O_8P_6$
$[Ir_2(CO)_2(diop)_3]^{2+}$, 1113

$Ir_2Cl_2F_{12}P_4$
$\{IrCl(PF_3)_2\}_2$, 1163

Ir_2Cl_9
$[Ir_2Cl_9]^{3-}$, 1149

$Ir_2Cu_3C_{54}H_{81}N_3P_6$
$[Ir_2Cu_3H_6(MeCN)_3(PMe_2Ph)_6]^{3+}$, 1164

$Ir_2Si_3C_{26}H_{69}I_2NO_2P_4$
$\{IrHI(SiH_2)(CO)(PEt_3)_2\}_2(NSiH_3)$, 1126

$Ir_2Si_5C_{26}H_{73}I_2O_2P_5$
$\{IrHI(SiH_2)_2(CO)(PEt_3)_2\}_2(PSiH_3)$, 1126

$Ir_2SnC_{42}H_{30}Cl_2O_6P_2$
$\{Ir(CO)_3(PPh_3)\}_2(SnCl_2)$, 1103

$Ir_2SnC_{44}H_{36}O_6P_2$
$\{Ir(CO)_3(PPh_3)\}_2(SnMe_2)$, 1103

$Ir_3C_{116}H_{120}Cl_9P_{12}$
$Ir_3Cl_9\{(Ph_2PCH_2CH_2)_2PCH_2CH_2P(CH_2CH_2PPh_2)_2\}_2$, 1136

$Ir_3C_{177}H_{319}N_3P_9$
$[\{IrH_2\{P(C_6H_{11})_3\}_3(py)\}_3(\mu\text{-}H)]^{2+}$, 1151

$Ir_3Si_3C_{39}H_{99}I_3O_3P_7$
$\{IrHI(SiH_2)(CO)(PEt_3)_2\}_3P$, 1126

$Ir_4C_{10}H_2O_{10}$
$[Ir_4H_2(CO)_{10}]^{2-}$, 1151

$Ir_4C_{11}HO_{11}$
$[Ir_4H(CO)_{11}]^-$, 1151

$Ir_4C_{11}H_2O_{11}$
$Ir_4H_2(CO)_{11}$, 1151

$Ir_4C_{12}H_2O_{12}$
$[Ir_4H_2(CO)_{12}]^{2+}$, 1151

$Ir_4C_{40}H_{44}O_8P_4$
$Ir_4(CO)_8(PMe_2Ph)_4$, 1164

$KCoC_{16}H_{14}N_2O_2$
Co(salen)K, 637

$KCoC_{27}H_{34}N_2O_5$
$\{Co(Pr_2salen)(CO_2)K(THF)\}_n$, 638

$La_4Re_2O_{10}$
$La_4Re_2O_{10}$, 177

$La_6Re_4O_{18}$
$La_6Re_4O_{18}$, 177

$LiFeC_{45}H_{96}O_5$
$FeLi(OCHBu^t_2)_4(HOCHBu^t_2)$, 227

$Li_2RuC_{47}H_{60}O_2P_4$
$RuHMe(PPh_3)_2(LiMeOEt_2)_2$, 454

$Ln_4Re_2O_{11}$
$Ln_4Re_2O_{11}$, 192

$Ln_6Re_4O_{18}$
$Ln_6Re_4O_{18}$, 192

$MnAlC_{12}H_{36}Br_2P_4$
$Mn(AlH_4)(Me_2PCH_2CH_2PMe_2)_2$, 32

$MnAlC_{12}H_{36}P_4$
$Mn(AlH_4)(Me_2PCH_2CH_2PMe_2)_2$, 9

$MnAl_2C_{24}H_{56}O_8$
$Mn\{Al(OPr^i)_4\}_2$, 37

$MnAl_2H_8$
$Mn(AlH_4)_2$, 61

$MnAsC_8H_{12}Br_2N$
$MnBr_2(2\text{-}H_2NC_6H_4AsMe_2)$, 34

$MnAsC_{13}H_{13}ClO_8$
$[Mn(ClO_4)(Ph_2MeAsO_4)]^+$, 40

$MnAsC_{16}H_{24}N_2$
$[Mn(2\text{-}H_2NC_6H_4AsMe_2)_2]^{2+}$, 34

$MnAsC_{27}H_{25}N_4$
$Mn\{2\text{-}(Me_2As)C_6H_4N{=}CPhC(Ph){=}NNHpyridyl\text{-}2\}$, 34

$MnAs_2C_{12}H_{16}Br_2O_2$
$MnBr_2(CO)_2$(diars), 31

$MnAs_2C_{19}H_{22}BrO_3$
$[MnBr(CO)_3(AsMe_2Ph)_2]^+$, 31

$MnAs_2C_{36}H_{30}Cl_3O_2$
$MnCl_3(Ph_3AsO)_2$, 90

$MnAs_2F_{24}N_4S_4$
$Mn(AsF_6)_2(NSF_3)_4$, 22, 60

$MnAs_4C_{72}H_{60}ClO_8$
$[Mn(ClO_4)(Ph_3AsO)_4]^+$, 47

$MnAs_5C_{15}H_{45}O_5$
$[Mn(Me_3AsO)_5]^{2+}$, 40

$MnBO_3$
$[MnBO_3]^-$, 42

MnB_2O_4
MnB_2O_4, 42

MnB_2O_5
MnB_2O_5, 42

MnB_4O_7
MnB_4O_7, 42

MnB_6O_{10}
MnB_6O_{10}, 42

$MnBr_2Cl_2$
$[MnBr_2Cl_2]^{2-}$, 59

$MnBr_2I_2$
$[MnBr_2I_2]^{2-}$, 59

$MnBr_4$
$[MnBr_4]^{2-}$, 11, 58

$MnBr_6$
$[MnBr_6]^{4-}$, 59

$MnCH_4Cl_2N_2S$
$MnCl_2(H_2NCSNH_2)$, 54

$MnCN_3O_4$
$Mn(CO)(NO)_3$, 7

$MnCN_4O_3$
$[Mn(CN)(NO)_3]^-$, 8

$MnCO_7P$
$[Mn(CO_3)(PO_4)]^{3-}$, 41

$MnC_2H_3N_4O_3$
$Mn(CNMe)(NO)_3$, 8

$MnC_2H_5N_3O_5S$

$Mn(SO_4)(H_2O)$(triazole), 21
MnC_2NO_4
$[Mn(CO)_2(NO)_2]^-$, 7
$MnC_2N_2O_8$
$[Mn(C_2O_4)(NO_2)_2]^{2-}$, 50
$MnC_2N_4O_2$
$[Mn(CN)_2(NO)_2]^{3-}$, 7
MnC_2O_6
$[Mn(CO_3)_2]^{2-}$, 41
$MnC_2O_7S_2$
$[Mn(C_2O_4)(S_2O_3)]^{2}$, 50
$MnC_3H_2O_4$
$Mn\{(O_2C)_2CH_2\}$, 50
MnC_3N_3
$Mn(CN)_3$, 83, 102
$[Mn(CN)_3]^-$, 11, 12
$MnC_4H_2O_6$
$[Mn\{O_2CCH(O)CH(O)CO_2\}]^{2}$, 51
$MnC_4H_4O_5$
Mn(malate), 51
$MnC_4H_5NO_4$
$Mn\{HN(CH_2CO_2)_2\}$, 66
$MnC_4H_6O_6$
Mn(glycollate)$_2$, 51
$MnC_4H_8N_2O_4$
$Mn(H_2NCH_2CO_2)_2$, 63
$MnC_4H_8S_4$
$[Mn(SCH_2CH_2S)_2]^{2}$, 53, 90
$MnC_4H_{10}Cl_2N_6O_4$
$MnCl_2(H_2NCONHCONH_2)_2$, 62
$MnC_4H_{10}N_2O_8S$
$MnSO_4(H_2NCH_2CO_2H)_2$, 62
$MnC_4H_{10}N_4O_{10}$
$Mn(NO_3)_2(H_2NCH_2CO_2H)_2$, 62
MnC_4H_{12}
$[MnMe_4]^{2-}$, 13
$MnC_4H_{14}N_4$
$Mn(C_2H)_2(NH_3)_4$, 14
$MnC_4H_{16}N_4O_4P_2$
$Mn\{O_2P(CH_2NH_2)_2\}_2$, 64
MnC_4NO_5
$Mn(CO)_4(NO)$, 7
$MnC_4N_2O_4$
$[Mn(CN)(CO)_3(NO)]^-$, 8
$MnC_4N_4O_4$
$[Mn(NCO)_4]^{2-}$, 22
$MnC_4N_4S_4$
$[Mn(NCS)_4]^{2-}$, 22
$MnC_4N_4Se_4$
$[Mn(NCSe)_4]^{2-}$, 22
MnC_4N_5O
$[Mn(CN)_4(NO)]^{4-}$, 8
$MnC_4O_4S_4$
$[Mn(S_2C_2O_2)_2]^{2-}$, 51
MnC_4O_8
$[Mn(C_2O_4)_2]^{2-}$, 50
MnC_5HN_5O
$[Mn(CN)_5(OH)]^{4-}$, 11
$[Mn(CN)_5(OH)]^{5-}$, 8
$MnC_5H_3N_2O_4$
$Mn(CNMe)(CO)_3(NO)$, 8
$MnC_5H_4Cl_2NO$
$MnCl_2$(2-pyridone), 61
$MnC_5H_5Cl_2N$
$MnCl_2$(py), 18
$MnC_5H_{17}NO_6$
$[Mn(HN(CH_2)_3CHCO_2H)(H_2O)_4]^{2+}$, 61
MnC_5N_5
$[Mn(CN)_5]^{3-}$, 12
$MnC_5N_5S_5$
$[Mn(NCS)_5]^{3-}$, 22
MnC_5N_6O
$[Mn(CN)_5(NO)]^{2-}$, 12, 83
$[Mn(CN)_5(NO)]^{3-}$, 12
$MnC_5N_6O_2$
$[Mn(CN)_5(NO_2)]^{3-}$, 12, 83
$MnC_6H_4N_6$
$Mn(CNH)_4(CN)_2$, 12
$MnC_6H_4O_{14}$
$[Mn(C_2O_4)_3(H_2O)_2]^-$, 89
$MnC_6H_6N_8S_2$
$Mn(NCS)_2$(triazole)$_2$, 21
$MnC_6H_8Cl_2N_4$
$MnCl_2$(pyrazole)$_2$, 20
$MnC_6H_8O_6$
Mn(L-lactate)$_2$, 51
$MnC_6H_9N_6O_6$
$[Mn(ON{=}CMeNO)_3]$, 63
$MnC_6H_{12}N_2O_2S_2$
$Mn(NCS)_2(EtOH)_2$, 22
$MnC_6H_{13}O_8$
$Mn(OAc)_3(H_2O)_2$, 88
$MnC_6H_{18}BrN_2O_8P_2$
$MnBr(NO)_2\{P(OMe)_3\}_2$, 9
$MnC_6H_{18}I_3P_2$
$MnI_3(PMe_3)_2$, 85
$MnC_6H_{24}N_6$
$[Mn(en)_3]^{2+}$, 23
$MnC_6H_{24}N_{12}O_6$
$[Mn(H_2NCONH_2)_6]^{3+}$, 90
$MnC_6N_3O_3$
$[Mn(CN)_3(CO)_3]^{2}$, 7, 8
$MnC_6N_4O_2$
$[Mn(CN)_4(CO)_2]^{3-}$, 7, 8
MnC_6N_6
$[Mn(CN)_6]^{2-}$, 5, 102
$[Mn(CN)_6]^{3-}$, 5, 83
$[Mn(CN)_6]^{4-}$, 5, 7, 11
$[Mn(CN)_6]^{5-}$, 8
$MnC_6N_6S_6$
$[Mn(NCS)_6]^{4-}$, 11, 22
$MnC_6N_6Se_6$
$[Mn(NCSe)_6]^{4-}$, 22
$MnC_6N_9O_6$
$[Mn_2(N_3)_3(CO)_6]^+$, 23
MnC_6O_{12}
$[Mn(C_2O_4)_3]^{3-}$, 89
MnC_8H_4
$[Mn(C_2H)_4]^{2-}$, 14
$MnC_8H_{10}Cl_2N_6O_2$
$MnCl_2$(cytosine)$_2$, 62
$MnC_8H_{11}I_2P$
$MnI_2(PMe_2Ph)$, 32, 59
$MnC_8H_{14}Cl_2N_2O_2$
$MnCl_2$(8-quinolinol)$_2$, 64
$MnC_8H_{16}Cl_2O_2$
$MnCl_2(THF)_2$, 38
$MnC_8H_{16}Cl_4O_8P_2$
$Mn(PO_2Cl_2)_2(EtOAc)_2$, 39
$MnC_8H_{18}O_2$
$Mn(OBu^t)_2$, 37
$MnC_8N_4S_4$
$[Mn\{S_2C_2(CN)_2\}_2]^{2-}$, 54
$MnC_8N_5OS_4$
$[Mn\{S_2C_2(CN)_2\}_2(NO)]^{2-}$, 54
$MnC_8O_4S_4$
$[Mn\{SC{=}C(S)COCO\}_2]^{2-}$, 53
$MnC_9H_{15}O_3S_6$
$[Mn(S_2COEt)_3]^-$, 55
$MnC_9H_{21}Cl_2N_3O_3$
$MnCl_2(H_2NCOEt)_3$, 39
$MnC_9H_{24}Br_2N_6O_3$
$MnBr_2(MeNHCONHMe)_3$, 39
$MnC_{10}H_8Cl_2N_2O_2$
Mn(bipy dioxide)Cl$_2$, 51
$MnC_{10}H_8Cl_4N_2$

$MnCl_4(bipy)$, 103, 108

$MnC_{10}H_8N_5O_9$
$Mn(NO_3)_3(bipy)$, 84

$MnC_{10}H_{10}Cl_2N_2$
$MnCl_2(py)_2$, 18

$MnC_{10}H_{10}Cl_2N_2O_8$
$Mn(ClO_4)_2(py)_2$, 19

$MnC_{10}H_{14}ClO_4$
$Mn(acac)_2Cl$, 89

$MnC_{10}H_{14}N_2O_9$
$[Mn(edta)(H_2O)]^-$, 96
$[Mn\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}(H_2O)]^-$, 69

$MnC_{10}H_{14}N_3O_4$
$Mn(acac)_2N_3$, 89

$MnC_{10}H_{14}O_4$
$Mn(acac)_2$, 49

$MnC_{10}H_{15}N_6O$
$[Mn(CNMe)_5(NO)]^{2-}$, 12

$MnC_{10}H_{16}Cl_2N_4$
$MnCl_2(1,2\text{-di-Me-imidazole})_2$, 20

$MnC_{10}H_{16}O_6$
$[Mn(acac)_2(H_2O)_2]^+$, 90

$MnC_{10}H_{18}N_5O_9$
$Mn(NO_3)_3(bipy)$, 87

$MnC_{10}H_{18}O_4$
$Mn(O_2CBu^t)_2$, 43

$MnC_{10}H_{18}O_6$
$Mn(acac)_2(H_2O)_2$, 11, 49

$MnC_{10}H_{20}N_2S_4$
$Mn(S_2CNEt_2)_2$, 54

$MnC_{10}H_{24}N_4$
$[MnCl_2\{HN\overline{CH_2CH_2NH(CH_2)_3NHCH_2CH_2}\text{-}\overline{NH(CH_2)_3}\}]^+$, 100

$MnC_{10}H_{28}P_2$
$MnMe_4(Me_2PCH_2CH_2PMe_2)$, 34, 103

$MnC_{10}H_{30}P_2$
$MnMe_4(PMe_3)_2$, 103

$MnC_{11}H_{14}NO_4S$
$Mn(acac)_2(NCS)$, 89

$MnC_{12}F_{18}O_9$
$[Mn\{(CF_3)_2COCO_2\}_3]^{3-}$, 89

$MnC_{12}H_8Br_2N_4S_2$
$Mn(NCS)_2(3\text{-Br-py})_2$, 19

$MnC_{12}H_{14}NO_4$
$Mn\{2\text{-}OC_6H_4CH{=}N(CH_2)_3O\}(OAc)$, 93

$MnC_{12}H_{14}O_8$
$Mn\{O_2CC(Me){=}C(Me)CO_2H\}_2$, 50

$MnC_{12}H_{18}Cl_2N_6$
$MnCl_2(2\text{-Me-imidazole})_3$, 19

$MnC_{12}H_{22}O_{14}$
$Mn(D\text{-gluconate})_2$, 51

$MnC_{12}H_{27}Br_2P$
$MnBr_2(PBu_3)$, 32

$MnC_{12}H_{27}I_2P$
$MnI_2(PBu_3)$, 32

$MnC_{12}H_{30}O_6$
$[Mn(DME)_3]^{2+}$, 47

$MnC_{12}H_{32}Br_2P_4$
$MnBr_2(Me_2PCH_2PMe_2)_2$, 32

$MnC_{12}H_{34}N_2O_{17}$
$[Mn(NO_3)(H_2O)_5](NO_3)(18\text{-crown-}6)$, 80

$MnC_{12}H_{35}P_4$
$MnH_3(Me_2PCH_2CH_2PMe_2)_2$, 93

$MnC_{12}H_{36}ClO_{16}$
$[Mn(H_2O)_6](ClO_4)(18\text{-crown-}6)$, 80

$MnC_{12}H_{36}N_2Si_4$
$Mn\{N(SiMe_3)_2\}_2$, 17

$MnC_{12}N_6S_6$
$[Mn\{S_2C_2(CN)_2\}_3]^{2-}$, 107

$MnC_{13}H_{27}NO_8$
$[Mn(18\text{-crown-}6)(MeNO_2)]^{2+}$, 80

$MnC_{14}H_8N_6S_4$
$[Mn(NCS)_4(bipy)]^{2-}$, 22

$MnC_{14}H_8O_6$
$Mn(2\text{-}HOC_6H_4CO_2)_2$, 51

$MnC_{14}H_{10}O_4$
$Mn(tropolonate)_2$, 48

$MnC_{14}H_{12}Br_2N_2O$
$MnBr_2(H_2O)\{2\text{-(2-pyridyl)quinoline}\}$, 24

$MnC_{14}H_{18}N_2O_8$
$[Mn(O_2CCH_2)_2N\overline{CH(CH_2)_4CH}N(CH_2CO_2)_2]^-$, 96

$MnC_{14}H_{24}P_2$
$Mn\{2\text{-}C_6H_4(CH_2)_2\}(Me_2PCH_2CH_2PMe_2)$, 14

$MnC_{14}H_{37}P_4$
$MnH(H_2C{=}CH_2)(Me_2PCH_2CH_2PMe_2)_2$, 93

$MnC_{14}H_{38}P_4$
$MnMe_2(Me_2PCH_2CH_2PMe_2)_2$, 34, 103

$MnC_{15}H_{11}Cl_2N_3O_3$
$MnCl_2(\text{terpy trioxide})$, 52

$MnC_{15}H_{12}Cl_2N_4$
$MnCl_2\{(2\text{-pyridyl})_3N\}$, 27

$MnC_{15}H_{15}Br_3N_3$
$[MnBr_3(py)_3]^-$, 19

$MnC_{15}H_{15}Cl_3N_3$
$MnCl_3(py)_3$, 84

$MnC_{15}H_{21}O_6$
$Mn(acac)_3$, 5, 89

$MnC_{15}H_{22}ClN_4$
$MnCl\{\overline{HN(CH_2)_3N{=}CMe\text{-}2,6\text{-}pyC(Me){=}N(CH_2)_2CH_2}\}$, 77

$MnC_{15}H_{23}Cl_2N_5$
$MnCl_2\{\overline{HN(CH_2)_2N{=}CMe\text{-}2,6\text{-}pyC(Me){=}N(CH_2)_2NH(CH_2)_2}\}$, 78
$[MnCl_2\{\overline{HN(CH_2)_2N{=}CMe\text{-}2,6\text{-}pyC(Me){=}N(CH_2)_2NH(CH_2)_2}\}]^+$, 101

$MnC_{15}H_{23}Cl_2N_5O_8$
$Mn(ClO_4)_2\{\overline{HN(CH_2)_2N{=}CMe\text{-}2,6\text{-}pyC(Me){=}N(CH_2)_2NH(CH_2)_2}\}$, 78

$MnC_{15}H_{24}N_3S_6$
$Mn(S_2C\overline{NCH_2CH_2OCH_2CH_2})_3$, 91

$MnC_{15}H_{24}O_6$
$[Mn(acacH)_3]^{2+}$, 48

$MnC_{15}H_{30}N_3S_6$
$Mn(S_2CNEt_2)_3$, 91

$MnC_{16}H_{10}O_2S_4$
$[Mn(SPh)_2\{SC{=}C(S)\overline{COCO}\}]^{2-}$, 53

$MnC_{16}H_{12}N_6O_6$
$Mn(NO_3)_2(1,8\text{-naphthyridine})_2$, 25

$MnC_{16}H_{14}N_2O_2$
$Mn(salen)$, 5, 11, 66

$MnC_{16}H_{16}N_2O_2$
$Mn(2\text{-}OC_6H_4CH{=}NMe)_2$, 64

$MnC_{16}H_{18}N_2O_2S_4$
$Mn(S_2COEt)_2(bipy)$, 55

$MnC_{16}H_{24}Br_2N_8$
$MnBr_2(5\text{-methylpyrazole})_4$, 19

$MnC_{16}H_{32}Br_6O_8$
$Mn(12\text{-crown-}4)_2(Br_3)_2$, 80

$MnC_{16}H_{36}Cl_2N_4$
$[MnCl_2\{\overline{HNCH_2CH_2NHCMe_2CH_2CHMeNHCH_2CH_2}\text{-}\overline{NHCMe_2CH_2CHMe}\}]^{2+}$, 100

$MnC_{16}H_{44}N_2OSi_4$
$Mn\{N(SiMe_3)_2\}_2(THF)$, 17

$MnC_{16}H_{44}Si_4$
$[Mn(CH_2SiMe_3)_4]^{2-}$, 13

$MnC_{17}H_{17}N_2O_3$
$Mn\{(2\text{-}OC_6H_4CH{=}NCH_2)_2CH_2\}(OH)$, 95

$MnC_{17}H_{21}N_5O_2S_2$
$Mn(NCS)_2\{\overline{O(CH_2)_2N{=}CMe\text{-}2,6\text{-}pyC(Me){=}N(CH_2)_2O(CH_2)_2}\}$, 80

$MnC_{17}H_{22}N_6S_2$
$Mn(NCS)_2\{\overline{HN(CH_2)_3N{=}CMe\text{-}2,6\text{-}pyC(Me){=}N(CH_2)_3}\}$, 77

$MnC_{17}H_{27}ClN_5[MnCl\{\overline{HN(CH_2)_3N{=}CMe\text{-}2,6\text{-}pyC(Me){=}N(CH_2)_3NH(CH_2)_2}\}]^+$, 78

$MnC_{18}Cl_{12}S_6$

$[Mn(S_2C_6Cl_4)_3]^{2-}$, 107
$MnC_{18}H_{12}N_2O_2$
Mn(8-quinolinolate)$_2$, 64
$MnC_{18}H_{12}N_3O_6$
Mn(2-pyCO$_2$)$_3$, 93
$MnC_{18}H_{14}N_2O_6$
$[Mn(2\text{-}OC_6H_4CH{=}NCH_2CO_2)_2]^-$, 94
$MnC_{18}H_{17}N_2O_4$
Mn(salen)(OAc), 5, 67, 95
$MnC_{18}H_{18}ClN_3P$
$[Mn\{(2\text{-pyridyl}CH_2)_3P\}Cl]^+$, 34
$MnC_{18}H_{18}N_2O_2S_4$
Mn(S$_2$COEt)$_2$(phen), 55
$MnC_{18}H_{22}N_4O_2$
Mn(salen)(en), 66
$MnC_{18}H_{24}N_2$
Mn(2-CH$_2$C$_6$H$_4$NMe$_2$)$_2$, 14
Mn(Me$_2$NCH$_2$C$_6$H$_4$)$_2$, 14
$MnC_{18}H_{30}N_3S_6$
$[Mn\{S_2CN(CH_2)_4CH_2\}_3]^+$, 107
$MnC_{18}H_{54}N_3Si_6$
Mn{N(SiMe$_3$)$_2$}$_3$, 84
$MnC_{19}H_{27}N_7S_2$
Mn(NCS)$_2${HN(CH$_2$)$_3$N=CMe-2,6-pyC(Me)=N(CH$_2$)$_3$NH(CH$_2$)$_2$}, 78
$MnC_{20}H_{20}Cl_4N_4$
$[MnCl_4(py)_4]^2$, 19
$MnC_{20}H_{20}O_2P_2$
Mn(OPPh$_2$)$_2$, 45
$MnC_{20}H_{27}N_6O$
$[Mn(NO)\{\{2\text{-pyC(Me)}{=}N(CH_2)_3\}_2NH\}]^{2+}$, 21
$MnC_{20}H_{36}N_{12}P_2O_2$
Mn{C(CN)$_3$}(HMPA)$_2$, 14
$MnC_{20}H_{40}P_4$
Mn{2-(CH$_2$)$_2$C$_6$H$_4$}(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$, 33
$MnC_{20}H_{42}N_4O_4$
Mn(OAc)$_2$(HNCH$_2$CH$_2$NHCMe$_2$CH$_2$CHMeNHCH$_2$-CH$_2$NHCMe$_2$CH$_2$CHMe), 77
$MnC_{21}H_{21}N_2O_4$
Mn(acac)(salen), 90
$MnC_{22}H_{16}N_6O_2$
Mn(CNO)$_2$(bipy)$_2$, 14
Mn(NCO)$_2$(bipy)$_2$, 24
$MnC_{22}H_{16}N_6O_4S_2$
Mn(bipy dioxide)$_2$(NCS)$_2$, 51
$MnC_{22}H_{16}N_6S_2$
Mn(NCS)$_2$(bipy)$_2$, 24
$MnC_{22}H_{20}N_6S_2$
Mn(NCS)$_2$(py)$_4$, 18
$MnC_{22}H_{22}N_2O_4$
Mn(acac)$_2$(phen), 49
$MnC_{22}H_{22}ClN_4$
MnCl{2-NC$_6$H$_4$N=CMeCH=CMeN-2-C$_6$H$_4$N=CMeCH=CMe}, 101
$MnC_{22}H_{30}O_4$
Mn(CH$_2$Ph)$_2$(OCH$_2$CH$_2$OCH$_2$CH$_2$)$_2$, 13
$MnC_{24}H_{12}F_9O_6$
$[Mn(furylCOCHCOCF_3)_3]$, 49
$MnC_{24}H_{18}Cl_2N_2O_2$
MnCl$_2$(2-pyCOPh)$_2$, 60
$MnC_{24}H_{20}P_2$
Mn(PPh$_2$)$_2$, 34
$MnC_{24}H_{20}S_4$
$[Mn(SPh)_4]^{2-}$, 53
$MnC_{24}H_{24}N_3O_3S_3$
Mn{ONMeC(S)Ph}$_3$, 96
$MnC_{24}H_{29}N_3P_2$
Mn(PPh$_2$)$_2$(NH$_3$)$_3$, 34
$MnC_{24}H_{48}O_6$
$[Mn(THF)_6]^{2+}$, 38
$MnC_{24}H_{48}O_6S_{12}$
$[Mn(OSCH_2CH_2SCH_2CH_2)_6]^{2+}$, 40
$MnC_{26}H_{16}N_6O_2$
Mn(CNO)$_2$(phen)$_2$, 14
$MnC_{26}H_{20}N_2O_2$
Mn(2-OC$_6$H$_4$CH=NPh)$_2$, 64
$MnC_{26}H_{28}N_6S_2$
Mn(NCS)$_2$(5-Me-py)$_4$, 19
$MnC_{26}H_{44}P_2$
Mn(CH$_2$CMe$_2$Ph)$_2$(PMe$_3$)$_2$, 13
$MnC_{27}H_{18}N_3O_3$
Mn(8-quinolinolate)$_3$, 64, 93
$MnC_{28}H_{37}N_5$
Mn{2-C$_6$H$_4$(N=CMeCH=CMeN)$_2$C$_6$H$_4$-2}(NEt$_3$), 77
$MnC_{28}H_{44}$
Mn(norbornyl)$_4$, 103
$MnC_{30}H_{22}N_6O_6$
$[Mn(terpy\ trioxide)_2]^{2+}$, 51, 52, 106
$MnC_{30}H_{24}N_6$
$[Mn(bipy)_3]^{2+}$, 23, 25
Mn(bipy)$_3$, 25
$[Mn(bipy)_3]^-$, 25
$[Mn(bipy)_3]^{4-}$, 25
$MnC_{30}H_{24}N_6O_6$
$[Mn(bipy\ dioxide)_3]^{2+}$, 106
$[Mn(bipy\ dioxide)_3]^{3-}$, 90
$MnC_{30}H_{30}N_6$
$[Mn(py)_6]^{2+}$, 5
$MnC_{30}H_{43}P$
MnPh$_2${P(C$_6$H$_{11}$)$_3$}, 13, 33
$MnC_{32}H_{16}ClN_8$
MnCl(phthalocyanine), 99
$MnC_{32}H_{16}N_8$
Mn(phthalocyanine), 5, 75, 99
$MnC_{32}H_{16}N_8O$
MnO(phthalocyanine), 5
$MnC_{32}H_{16}N_8O_2$
Mn(phthalocyanine)O$_2$, 76
$MnC_{32}H_{24}N_8$
$[Mn(1,8\text{-naphthyridine})_4]^{2+}$, 25
$MnC_{32}H_{26}N_6O_2$
$[Mn\{(2\text{-pyridyl})_3COH\}_2]$, 66
$[Mn\{(2\text{-pyridyl})_3COH\}_2]^{2+}$, 27
$MnC_{32}H_{34}N_7$
$[Mn\{\{(2\text{-pyridyl}CH_2)_2NCH_2\}_2\}]^{2+}$, 30
$MnC_{35}H_{19}N_{10}$
Mn(phthalocyanine)(HNCH=NCH=CH), 76
$MnC_{36}H_{24}N_6$
$[Mn(phen)_3]^{2+}$, 23
$MnC_{36}H_{30}Cl_3O_2P_2$
MnCl$_3$(Ph$_3$PO)$_2$, 90
$MnC_{36}H_{30}P_3$
$[Mn(PPh_2)_3]^-$, 34
$MnC_{36}H_{44}N_4O_2$
Mn(octaethylporphyrin)O$_2$, 73
$MnC_{37}H_{30}ClNO_2P_2S$
MnCl(NCS)(Ph$_3$PO)$_2$, 41
$MnC_{38}H_{38}O_4$
Mn(PhCOCHCOPh)$_2$(THF)$_2$, 49
$MnC_{38}H_{50}N_2O_4$
Mn(3,5-Bu$^t_2$-1,2-O$_2$C$_6$H$_2$)$_2$(py)$_2$, 106
$MnC_{42}H_{26}N_{10}$
Mn(phthalocyanine)(py)$_2$, 75
$MnC_{42}H_{60}O_6$
$[Mn(3,5\text{-}Bu^t_2\text{-}1,2\text{-}O_2C_6H_2)_3]^{2-}$, 106
$MnC_{44}H_{28}ClN_4$
MnCl(tetraphenylporphyrin), 72, 97, 98
$MnC_{44}H_{28}N_4$
Mn(tetraphenylporphyrin), 72
$[Mn(tetraphenylporphyrin)]^+$, 99
$MnC_{44}H_{28}N_4O_2$
Mn(tetraphenylporphyrin)O$_2$, 73
$MnC_{44}H_{28}N_5$
MnN(tetraphenylporphyrin), 110
$MnC_{44}H_{28}N_7$
Mn(N$_3$)(tetraphenylporphyrin), 98

$MnC_{44}H_{28}N_{10}$
$Mn(N_3)_2$(tetraphenylporphyrin), 108
$MnC_{46}H_{34}N_4O_2$
$Mn(OMe)_2$(tetraphenylporphyrin), 108
$MnC_{46}H_{36}N_4O_2$
$[Mn(tetraphenylporphyrin)(MeOH)_2]^+$, 97
$MnC_{47}H_{31}N_6$
Mn(tetraphenylporphyrin)(imidazolate), 97
$MnC_{48}H_{32}Cl_2N_8$
$MnCl_2(phen)_4$, 25
$MnC_{48}H_{34}N_6$
Mn(tetraphenylporphyrin)(MeNCH=NCH=CH)$_2$, 72
$MnC_{48}H_{40}N_2P_4S_4$
$Mn\{N(PPh_2S)_2\}_2$, 54
$MnC_{48}H_{40}P_4$
$[Mn(PPh_2)_4]^{2-}$, 34
$MnC_{48}H_{46}N_2P_4$
$[Mn(PPh_2)_4(NH_3)_2]^{2-}$, 34
$MnC_{49}H_{33}ClN_5$
MnCl(tetraphenylporphyrin)(py), 97
$MnC_{49}H_{33}N_5$
Mn(tetraphenylporphyrin)(py), 73
$MnC_{50}H_{34}N_8$
$[Mn(tetraphenylporphyrin)(imidazolate)_2]^-$, 97
$MnC_{52}H_{36}N_3O_3$
$Mn(2\text{-}OC_6H_4CH{=}NCH_2Ph)_3$, 93
$MnC_{52}H_{48}Cl_2P_4$
$[MnCl_2(diphos)_2]^+$, 85
$[MnCl_2(diphos)_2]^{2+}$, 104
$MnC_{54}H_{48}N_3P_3$
$[Mn(2\text{-pyridyl}CH_2PPh_2)_3]^{2-}$, 34
$MnC_{56}H_{48}Cl_2P_4$
$MnCl_2(diphos)_2$, 32
$[MnCl_2(diphos)_2]^+$, 32
$[MnCl_2(diphos)_2]^{2+}$, 32
$MnC_{68}H_{44}N_{12}O_4$
Mn{*meso*-α,α,α,α-tetrakis(2-nicotinamidophenyl)porphyrin}, 98
$MnC_{72}H_{60}IO_4P_4$
$[MnI(Ph_3PO)_4]^+$, 40
$MnC_{74}H_{42}N_{18}O$
$\{Mn(phthalocyanine)(py)\}_2O$, 5, 76
$MnClO_3$
MnO_3Cl, 110
$MnClO_6S$
MnO_3SO_3Cl, 110
$MnCl_2$
$MnCl_2$, 56
$MnCl_2I_2$
$[MnCl_2I_2]^{2-}$, 59
$MnCl_2O_2$
MnO_2Cl_2, 110
$MnCl_2O_8$
$Mn(ClO_4)_2$, 47
$MnCl_3$
$MnCl_3$, 91
$[MnCl_3]^-$, 57
$MnCl_3O$
$MnOCl_3$, 110
$MnCl_4$
$MnCl_4$, 108
$[MnCl_4]^{2-}$, 5, 11, 55, 58
$MnCl_4O_4P_2$
$Mn(Cl_2PO_2)_2$, 45
$MnCl_5$
$[MnCl_5]^{2-}$, 91, 92
$MnCl_6$
$[MnCl_6]^{2-}$, 108
$[MnCl_6]^{3-}$, 91
$[MnCl_6]^{4-}$, 58
$MnCoC_{49}H_{44}O_2P_3S_2$
Co(triphos)(μ-CS_2)Mn(CO)$_2$Cp, 646
$MnFO_3$
MnO_3F, 110
$MnFO_3P$
$Mn(PO_3F)$, 45
MnF_2
MnF_2, 56
MnF_3
MnF_3, 91
MnF_4
MnF_4, 107
$[MnF_4]^-$, 91
MnF_5
$[MnF_5]^-$, 107
$[MnF_5]^{2-}$, 91
MnF_6
$[MnF_6]^{2-}$, 5, 107
$[MnF_6]^{3-}$, 91
$[MnF_6]^{4-}$, 56
$MnGaC_{11}H_{23}N_5O_3$
Mn(3,5-dimethylpyrazole)-$(NO)_2(Me_2NCH_2CH_2OGaMe_2)$, 9
$MnHClO$
Mn(OH)Cl, 35
MnHI
MnHI, 60
$MnHO_2$
MnO(OH), 86
$MnHO_3P$
$MnHPO_3$, 45
$MnHO_4P$
$MnHPO_4$, 45
$MnHO_8Se_3$
$MnH(SeO_3)(Se_2O_5)$, 88
MnH_2
MnH_2, 60
MnH_2O_2
$Mn(OH)_2$, 35
MnH_3
MnH_3, 93
$MnH_3O_6P_2$
$MnH_3P_2O_6$, 87
$MnH_4F_4O_2$
$[MnF_4(H_2O)_2]^-$, 92
MnH_4N_2
$Mn(NH_2)_2$, 16
MnH_4O_4
$[Mn(OH)_4]^{2-}$, 35
$MnH_4O_8P_2$
$Mn(H_2PO_4)_2$, 45
MnH_6O_6
$[Mn(OH)_6]^{2-}$, 104
$[Mn(OH)_6]^{3-}$, 86
$[Mn(OH)_6]^{4-}$, 35
$MnH_6O_{21}P_6$
$[Mn(H_2P_2O_7)_3]^{3-}$, 87
$MnH_8Cl_2N_4$
$MnCl_2(N_2H_4)_2$, 17
MnH_8N_4
$[Mn(NH_2)_4]^{2-}$, 16
$MnH_{11}O_6$
$[Mn(OH)(H_2O)_5]^+$, 35
$MnH_{12}Cl_2N_4$
$MnCl_2(NH_3)_4$, 15
$MnH_{12}O_6$
$[Mn(H_2O)_6]^{2+}$, 11, 35, 60
$[Mn(H_2O)_6]^{3+}$, 85
$MnH_{18}N_6$
$[Mn(NH_3)_6]^{2+}$, 15
$MnHgC_4N_4S_4$
$HgMn(SCN)_4$, 22
MnI_2
MnI_2, 59
MnI_2O_6
$Mn(IO_3)_2$, 46, 47

MnI_3
$[MnI_3]^-$, 59
MnI_3O_{18}
$[Mn(IO_6)_3]^{11-}$, 105
MnI_4
$[MnI_4]^{2-}$, 11, 59
MnI_5O_{15}
$[Mn(IO_3)_5]^{2-}$, 88
MnI_6O_{18}
$[Mn(IO_3)_6]^{2-}$, 105
$MnK_2O_8S_2$
$K_2Mn(SO_4)_2$, 46
MnN_2O_4
$Mn(NO_2)_2$, 44
MnN_2O_6
$Mn(NO_3)_2$, 44, 87
MnN_4O_8
$[Mn(NO_2)_4]^{2-}$, 44
MnN_4O_{12}
$[Mn(NO_3)_4]^-$, 87
$[Mn(NO_3)_4]^{2-}$, 44
MnN_5O_{10}
$[Mn(NO_2)_5]^{3-}$, 44
MnN_6
$Mn(N_3)_2$, 23
MnN_{12}
$[Mn(N_3)_4]^2$, 23
$MnNa_2O_8Se_2$
$Na_2Mn(SeO_4)_2$, 46
MnO_2
MnO_2, 102, 104
MnO_3S
$MnSO_3$, 46
MnO_3Se
$MnSeO_3$, 46
MnO_3Si
$MnSiO_3$, 41
MnO_3Te
$MnTcO_3$, 46
MnO_4
$[MnO_4]^-$, 109, 525
$[MnO_4]^{2-}$, 109
$[MnO_4]^{3-}$, 109
$[MnO_4]^{4-}$, 104
MnO_4P
$MnPO_4$, 87
MnO_4S
$MnSO_4$, 46
MnO_4Se
$MnSeO_4$, 46
MnO_5
$[MnO_5]^{3-}$, 109
MnO_5Se_2
$MnSe_2O_5$, 46
MnO_6S_2
$[Mn(SO_3)_2]^{2-}$, 46
MnO_6Sc_2
$Mn(ScO_3)_2$, 46, 102, 105
$[Mn(SeO_3)_2]^-$, 88
MnO_7
$[Mn(O_2)_3O]^{4-}$, 105
MnO_7P_2
$[MnP_2O_7]^-$, 87
MnO_8
$[Mn(O_2)_4]^{4-}$, 105
MnO_8P_2
$[Mn(PO_4)_2]^{2-}$, 105
$[Mn(PO_4)_2]^{3-}$, 87
MnO_8S_2
$[Mn(SO_4)_2]^-$, 87
$[Mn(SO_4)_2]^+$, 86
MnO_9P_3
$Mn(PO_3)_3$, 87
$MnO_{18}Te_3$
$[Mn(TeO_6)_3]^{14-}$, 105
$MnRuC_{54}H_{40}O_6P_2$
$RuMn(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$, 373
$MnRuC_{55}H_{44}ClO_5P_4$
$RuMnCl(\mu\text{-dppm})_2(\mu\text{-}CO)_2(CO)_3$, 373
MnS
MnS, 53
$MnW_{11}H_2O_{44}P$
$[PMnW_{11}O_{39}(OH_2)]^{5-}$, 47
$MnW_{17}H_2O_{62}P_2$
$[P_2MnW_{17}O_{61}(OH_2)]^{8-}$, 47
Mn_2AsHO_5
$Mn_2(OH)AsO_4$, 45
$Mn_2BH_4I_4$
$Mn_2(BH_4)I_4$, 61
$Mn_2C_4N_8O_4$
$[Mn_2(CN)_4(NO)_4]^{4-}$, 7
$Mn_2C_6H_{18}Cl_4O_3$
$Mn_2Cl_4(EtOH)_3$, 37
$Mn_2C_6O_{12}$
$[Mn_2(C_2O_4)_3]^{2-}$, 50
$Mn_2C_8H_{16}S_8$
$[Mn_2(SCH_2CH_2S)_4]^{2-}$, 90
$Mn_2C_8O_{18}$
$[Mn_2O_2(C_2O_4)_4]^{4-}$, 105
$Mn_2C_{10}H_{12}N_2O_8$
$Mn_2\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}$, 70
$Mn_2C_{10}N_{10}O$
$[Mn_2O(CN)_{10}]^{6-}$, 83
$Mn_2C_{18}H_{27}N_9O_6$
$[Mn_2Cl(\text{isonicotinyl hydrazide})_3(H_2O)_3]^{3+}$, 64
$Mn_2C_{19}H_{25}N_{19}S_4$
$Mn_2(NCS)_4(\text{4-metriazole})_5$, 21
$Mn_2C_{20}H_{26}N_4O_{16}$
$Mn_3\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)\text{-}(CH_2CO_2H)\}_2$, 70
$Mn_2C_{24}H_{26}N_{16}$
$Mn_2(\text{imidozolate})_6(\text{imidazole})_2$, 21
$Mn_2C_{24}H_{72}N_4Si_8$
$Mn_2\{N(SiMe_3)_2\}_4$, 17
$Mn_2C_{26}H_{42}N_2O_8$
$Mn_2(acac)_4(H_2NCH_2CH{=}CH_2)_2$, 49
$Mn_2C_{30}H_{46}N_2O_8$
$Mn_2(O_2CBu^t)_4(py)_2$, 43
$Mn_2C_{32}H_{28}N_4O_8$
$\{Mn(salen)O\}_2O_2$, 67
$Mn_2C_{36}H_{24}Cl_4N_4$
$Mn_2Cl_4(2,2'\text{-biquinolyl})_2$, 24
$Mn_2C_{40}H_{32}N_8O_2$
$Mn_2O_2(bipy)_4$, 103
$[Mn_2O_2(bipy)_4]^{3+}$, 84
$Mn_2C_{48}H_{32}N_8O_2$
$Mn_2O_2(phen)_4$, 103
$Mn_2C_{64}H_{36}N_{16}O$
$\{Mn(\text{phthalocyanine})\}_2O$, 76
$Mn_2C_{74}H_{42}N_{18}O$
$\{Mn(\text{phthalocyanine})(py)\}_2O$, 99
$Mn_2C_{88}H_{56}N_{14}O$
$\{Mn(N_3)(\text{tetraphenylporphyrin})\}_2O$, 98, 108
Mn_2ClO_4P
Mn_2ClPO_4, 45
Mn_2Cl_7
$[Mn_2Cl_7]^{3-}$, 58
Mn_2ErH_4
Mn_2ErH_4, 60
$Mn_2ErH_{4.6}$
$Mn_2ErH_{4.6}$, 60
Mn_2F_5
Mn_2F_5, 91
Mn_2F_9
$[Mn_2F_9]^-$, 107
$Mn_2H_3ClO_3$

$Mn_2(OH)_3Cl$, 35
$Mn_2K_2O_9S_3$
$K_2Mn_2(SO_3)_3$, 46
$Mn_2K_2O_{12}S_3$
$K_2Mn_2(SO_4)_3$, 46
Mn_2O_4Si
Mn_2SiO_4, 41
Mn_2O_6
$[Mn_2O_6]^{6-}$, 87, 109
Mn_2O_7
Mn_2O_7, 110
$Mn_2O_7P_2$
$Mn_2P_2O_7$, 45
$Mn_2O_9Se_3$
$Mn_2(SeO_3)_3$, 88
$Mn_2O_{12}S_3$
$Mn_2(SO_4)_3$, 87
Mn_2ScH_4
Mn_2ScH_4, 60
$Mn_2WC_4O_{11}$
$Mn_2(C_2O_4)_2WO_3$, 50
Mn_2ZrH_3
Mn_2ZrH_3, 60
$Mn_3BH_6O_4$
$Mn_3(OH)_2\{B(OH)_4\}$, 42
$Mn_3B_2O_6$
$Mn_3(BO_3)_2$, 42
$Mn_3C_{12}H_{10}O_{14}$
$Mn_3(citrate)_2$, 51
$Mn_3C_{16}H_{25}O_{17}$
$Mn_3O(OAc)_7(HOAc)$, 88
$Mn_3C_{27}H_{33}N_3O_{13}$
$Mn_3O(OAc)_6(py)_3$, 5
$[Mn_3O(OAc)_6(py)_3]^+$, 88
$Mn_3I_2O_{10}$
$Mn_3(IO_5)_2$, 47
Mn_3O_6Te
Mn_3TeO_6, 46
$Mn_3O_8P_2$
$Mn_3(PO_4)_2$, 45
$Mn_4C_{24}H_{60}N_{12}O_6$
$[Mn_4O_6\{HN(CH_2CH_2NH)_2CH_2CH_2\}_4]^{4+}$, 103
$Mn_4C_{60}H_{50}S_{10}$
$[Mn_4(SPh)_{10}]^{2-}$, 53
$Mn_4C_{112}H_{160}O_{16}$
$Mn_4(3,5\text{-}Bu^t_2\text{-}1,2\text{-}O_2C_6H_2)_8$, 106
$Mn_4Na_2O_{15}S_5$
$Na_2Mn_4(SO_3)_5$, 46
$Mn_5C_{28}H_{84}Cl_{10}O_{14}$
$Mn_5Cl_{10}(EtOH)_{14}$, 37
$Mn_5H_4O_{12}P_2$
$Mn_5(OH)_4(PO_4)_2$, 45
$Mn_7C_{18}H_{22}O_{56}$
$[Mn(H_2O)_2\{Mn_3O(HCO_2)_9\}_2]^{2-}$, 88
Mn_7O_{24}
$[Mn(MnO_4)_6]^{2-}$, 106
$Mn_{12}C_{32}H_{56}O_{48}$
$Mn_{12}O_{12}(OAc)_{16}(H_2O)_4$, 88
$MoAsCoFeWC_2H_6S$
$CoFeMoWS(AsMe_2)$, 832
$MoC_4N_4O_3$
$[MoO_3(CN)_4]^{2+}$, 780
$MoC_{54}H_{48}O_2P_4$
$[Mo(CO)_2(dppe)_2]^{2+}$, 31
$MoCoC_{10}H_2N_{10}O_4$
$[Co(CN)_5OOMoO(OH_2)(CN)_5]^{5+}$, 780
$MoCoFeC_{13}H_5O_8S$
$CoFeMoS(CO)_8Cp$, 832
$MoCoFeC_{22}H_{20}O_7S$
$CoFeMoS(CO)_7Cp(PMePrPh)$, 832
$MoCoH_{15}N_5O_4$
$[Co(NH_3)_5OMoO_3]^+$, 825
$MoFe_2Cl_4S_4$
$[MoFe_2S_4Cl_4]^{2-}$, 242
$MoFe_4C_{24}H_{27}O_6S_7$
$[MoFe_4S_4(SEt)_3(1,2\text{-}O_2C_6H_4)_3]^{3-}$, 241
$MoReC_{26}H_{36}Cl_6N_2P_3$
$ReNCl_2(PMe_2Ph)_3MoCl_4(NCMe)$, 189
$MoReC_{33}H_{47}Cl_5N_2OP_4$
$MoCl_4(OMe)\{(N_2)ReCl(PMe_2Ph)_4\}$, 133
$MoRe_2C_{64}H_{88}Cl_6N_4P_8$
$MoCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2$, 133
$MoRhC_{46}H_{42}P_2$
$Rh(PPh_3)_2(\mu\text{-}H)_2MoCp_2$, 1076
$MoRuC_{20}H_{16}N_4S_4$
$Ru(S_2MoS_2)(bipy)_2$, 352
$MoRu_2C_{40}H_{32}N_8S_4$
$[\{Ru(bipy)_2\}_2(MoS_4)]^{2+}$, 361
MoS_4
$[MoS_4]^{2-}$, 241
Mo_2FeS_8
$[Mo_2FeS_8]^{3-}$, 242
$Mo_2Fe_6C_{16}H_{40}S_{17}$
$[Mo_2Fe_6S_9(SEt)_8]^{3-}$, 1243
$Mo_2Fe_6C_{54}H_{45}S_{17}$
$[Mo_2Fe_6S_8(SPh)_9]^{3-}$, 1243
$Mo_2Fe_7C_{24}H_{60}S_{20}$
$[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$, 241
$Mo_6CoH_6O_{24}$
$[Co\{Mo_6O_{18}(OH)_6\}]^{3-}$, 827
$Mo_{10}Co_2H_4O_{38}$
$[Co_2\{Mo_{10}O_{34}(OH)_4\}]^{6-}$, 827

$Na_2Fe_2C_{34}H_{57}N_4O_7$
$Fe_2Na_2\{\{MeCOCHC(Me)=NCH_2\}_2\}_2(OEt)(THF)_2$, 1238
$Na_2MnO_8Se_2$
$Na_2Mn(SeO_4)_2$, 46
$Na_2Mn_4O_{15}S_5$
$Na_2Mn_4(SO_3)_5$, 46
$Nb_6CoCH_3NO_{22}$
$[Co(Nb_6O_{19})(CO_3)(NH_3)]^{7-}$, 826
$NiC_{54}H_{45}ClNOP_3$
$Ni(NO)Cl(PPh_3)_3$, 1067
NpO_2
$[NpO_2]^+$, 1053
$NpRhH_{10}O_7$
$[Rh(H_2O)_5ONpO]^{4+}$, 1053

$OsAlC_{33}H_{54}Cl_2N_2P_3$
$Os(NNAlMe_3)(PEt_2Ph)_3Cl_2$, 555
$OsAs_2C_{16}H_{22}Cl_4$
$Os(AsMe_2Ph)_2Cl_4$, 577
$OsAs_2C_{18}H_{42}Cl_4$
$Os(AsPr_3)_2Cl_4$, 577
$OsAs_2C_{25}H_{22}Cl_4$
$Os(dpam)Cl_4$, 579
$OsAs_2C_{34}H_{33}Cl_3P$
$Os\{PPh(CH_2CH_2AsPh_2)_2\}Cl_3$, 579
$OsAs_2C_{36}H_{30}Br_4$
$Os(AsPh_3)_2Br_4$, 577
$OsAs_2C_{36}H_{30}ClNO$
$Os(NO)Cl(AsPh_3)_2$, 550
$OsAs_3C_{24}H_{33}Cl_3$
$Os(AsMe_2Ph)_3Cl_3$, 577
$OsAs_3C_{27}H_{63}Cl_3$
$Os(AsPr_3)_3Cl_3$, 577
$OsAs_3C_{42}H_{49}$
$Os(AsEtPh_2)_3H_4$, 576
$OsAs_3C_{63}H_{67}Cl_2N_2$
$Os\{As(C_6H_4Me\text{-}4)_3\}_3Cl_2(N_2H_4)$, 556
$OsAs_3Hg_2C_{54}H_{45}Cl_5$
$Os(AsPh_3)_3Cl{\cdot}2HgCl_2$, 525
$OsAs_4C_{20}H_{32}ClNO$
$[Os(NO)(diars)_2Cl]^{2+}$, 547
$OsAs_4C_{20}H_{32}ClN_2$

$[Os(N_2)(diars)_2Cl]^+$, 555, 565
$OsAs_4C_{20}H_{32}ClN_3$
$Os(N_3)(diars)_2Cl$, 565
$OsAs_4C_{20}H_{32}Cl_2$
$[Os(diars)_2Cl_2]^{2+}$, 579
$OsAs_4C_{22}H_{32}N_2S_2$
$Os(diars)_2(SCN)_2$, 566
$OsAs_4C_{30}H_{40}N_2$
$[Os(bipy)(diars)_2]^{2+}$, 540
$OsAs_4C_{40}H_{62}$
$Os(AsEt_2Ph)_4H_2$, 576
$OsAs_4C_{52}H_{44}N_2S_2$
$Os(dpam)_2(SCN)_2$, 566
$OsAs_4C_{54}H_{42}Cl_2$
$Os\{As(C_6H_4AsPh_2\text{-}2)_3\}Cl_2$, 579
$OsAs_4C_{72}H_{60}Br_2$
$Os(AsPh_3)_4Br_2$, 577
$OsAs_6C_{75}H_{66}N_2S_2$
$Os(SCN)_2(dpam)_3$, 579
$OsBC_{36}H_{73}P_2$
$Os(BH_4)H_3\{P(C_6H_{11})_3\}_2$, 616
$OsB_{10}C_{20}H_{40}O_2P_2$
$OsB_{10}H_8(PMe_2Ph)_2(OEt)_2$, 616
$OsBr_4N$
$[OsNBr_4]^-$, 561
$OsBr_4O_2$
$[OsO_2Br_4]^{2-}$, 583
$OsBr_5N$
$[OsNBr_5]^{2-}$, 561
$OsBr_6$
$[OsBr_6]^-$, 615
$[OsBr_6]^{2-}$, 613, 614
$[OsBr_6]^{3-}$, 613
$OsCCl_5NS$
$[Os(NCS)Cl_5]^{2-}$, 566
$[Os(SCN)Cl_5]^{2-}$, 566
$OsCH_{12}N_6O$
$[Os(N_2)(NH_3)_4(CO)]^{2+}$, 555
$OsCH_{15}Cl_2N_5O$
$Os(NH_3)_5(CO)Cl_2$, 528
$OsCH_{15}F_3N_5O_3S$
$[Os(O_3SCF_3)(NH_3)_5]^{2+}$, 529, 600
$[Os(OSO_2CF_3)(NH_3)_5]^{2+}$, 536
$OsCH_{15}N_5O$
$[Os(NH_3)_5(CO)]^{2+}$, 529
$[Os(NH_3)_5(CO)]^{3+}$, 529
$[Os(NH_3)_5(CO)]^{4+}$, 528
$OsC_2Cl_4O_4$
$[Os(C_2O_4)Cl_4]^{2-}$, 601
$OsC_2H_2N_2O_4$
$[OsO_2(OH)_2(CN)_2]^{2-}$, 526
$OsC_2H_3Br_5N$
$[Os(NCMe)Br_5]^-$, 567
$OsC_2H_4NO_7$
$[OsN(C_2O_4)(OH)_2(H_2O)]^-$, 562
$OsC_2H_4N_2O_4$
$[Os(CN)_2(OH)_4]^{3-}$, 526
$OsC_2H_8Br_4N_4$
$Os(en)Br_4$, 530
$OsC_2H_8Cl_4N_2$
$Os(en)Cl_4$, 531
$[Os(en)Cl_4]^-$, 531
$OsC_2H_8N_4O_2S_2$
$[OsO_2(H_2NCSNH_2)_2]^{2+}$, 584
$OsC_2H_8O_8$
$[OsO_3(OH)_3(OCH_2CH_2OH)]^{2-}$, 593
$OsC_2H_{24}N_{10}O_2$
$[Os(N_2)(NH_3)_8(CO)_2]^{4+}$, 529
$OsC_3Cl_3O_5$
$[Os(C_2O_4)(CO)Cl_3]^{2-}$, 601
$OsC_4Cl_{12}N_2$
$[Os\{NC(CCl_3)NCClCCl_3\}Cl_5]$, 558
$OsC_4H_2NO_9$
$[OsN(C_2O_4)_2(H_2O)]^-$, 562
$OsC_4H_2N_4O_2$
$[Os(CN)_4(OH)_2]^{3-}$, 526
$OsC_4H_2N_5O$
$[OsN(CN)_4(H_2O)]^-$, 525, 562
$OsC_4H_8N_2O_6$
$OsO_2(Gly\text{-}O)_2$, 583
$OsC_4H_8O_5$
$OsO(O_2C_2H_4)_2$, 585
$OsC_4H_8O_6$
$[OsO_2(O_2C_2H_4)_2]^{2-}$, 585
$OsC_4H_9NO_3$
$OsO_3(NBu^t)$, 558
$OsC_4H_{10}Cl_2O_2Se_2$
$OsO_2Cl_2(MeSeCH_2CH_2SeMe)$, 609
$OsC_4H_{12}Cl_2O_2S_2$
$OsO_2Cl_2(SMe_2)_2$, 584
$OsC_4H_{12}N_{10}O_2$
$OsO_2\{HN{=}C(NH_2)NC(NH_2){=}NH\}_2$, 568
$OsC_4H_{12}O_6$
$[OsO_2(OMe)_4]^{2-}$, 580, 582, 585, 596
$OsC_4H_{14}NO_4S$
$[Os(SCH_2CH_2NMe_2)(OH)_4]^-$, 607
$OsC_4H_{14}N_{10}O_2$
$[OsO_2\{HN{=}C(NH_2)NHC(NH_2){=}NH\}_2]^+$, 568
$[OsO_2\{HN{=}C(NH_2)NHC(NH_2){=}NH\}_2]^{2+}$, 568
$OsC_4H_{14}N_{11}O$
$[OsON\{HN{=}C(NH_2)NHC(NH_2){=}NH\}_2]^{2-}$, 563
$OsC_4H_{16}ClN_6$
$[Os(\overline{N{=}CHCH{=}NCH{=}CH})(NH_3)_4Cl]^{2+}$, 535
$OsC_4H_{16}Cl_2N_4$
$[Os(en)_2Cl_2]^+$, 530, 531
$OsC_4H_{16}N_4O_2$
$[OsO_2(en)_2]^{2+}$, 583
$OsC_4H_{16}N_8$
$[Os(\overline{N{=}CHCH{=}NCH{=}CH})(N_2)(NH_3)_4]^{2+}$, 535
$OsC_4H_{16}N_8O_2S_4$
$[OsO_2(H_2NCSNH_2)_4]^{2+}$, 608
$OsC_4H_{18}N_4$
$[OsH_2(en)_2]^{2+}$, 530, 531
$OsC_4H_{19}N_7$
$[Os(\overline{N{=}CHCH{=}NCH{=}CH})(NH_3)_5]^{2+}$, 536
$[Os(\overline{N{=}CHCH{=}NCH{=}CH})(NH_3)_5]^{3+}$, 535
$OsC_4N_4O_2$
$[OsO_2(CN)_4]^{2-}$, 525, 526, 583
$OsC_4N_4S_4$
$[Os(NCS)_4]^{2-}$, 566
OsC_4O_{10}
$[OsO_2(C_2O_4)_2]^{2-}$, 582
$OsC_5H_5Cl_5N$
$[Os(py)Cl_5]^-$, 534
$OsC_5H_{20}N_6$
$[Os(py)(NH_3)_5]^{2+}$, 533, 534
$[Os(py)(NH_3)_5]^{3+}$, 534
OsC_5N_5
$[Os(CN)_5]^{4-}$, 525
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$[Os(NO)(CN)_5]^{2-}$, 546
$OsC_5N_6OS_5$
$[Os(NO)(NCS)_5]^{2-}$, 548, 566
$OsC_5N_6S_6$
$[Os(NS)(NCS)_5]^{2-}$, 553, 562, 566
$OsC_6H_4N_7S$
$[Os(H_2NCSNH_2)(CN)_5]^{2-}$, 608
$OsC_6H_4N_8OS$
$[Os(NO)(CN)_5(H_2NCSNH_2)]^{2-}$, 608
$OsC_6H_4O_{10}$
$[OsO_2(O_2CCH_2CO_2)_2]^{2-}$, 582
$OsC_6H_5Cl_4NO$
$[Os(py)(CO)Cl_4]^-$, 534
$OsC_6H_8H_2O_8$
$Os(en)(C_2O_4)_2$, 531
$OsC_6H_9O_8$

$[OsO_2(OAc)_3]^-$, 582, 585, 600
$OsC_6H_{10}O_6S_2$
$[Os(OH)_2\{O_2CCH(S)Me\}_2]^{2-}$, 617
$OsC_6H_{12}Cl_2N_2S_4$
$Os(S_2CNMe_2)_2Cl_2$, 605
$OsC_6H_{15}N_9O$
$[Os(N_2)_2(NH_3)_3(4\text{-}pyCONH_2)]^{2+}$, 555
$OsC_6H_{18}Cl_3O_3S_3$
$Os(DMSO)_3Cl_3$, 602
$OsC_6H_{18}Cl_4O_6P_2$
$Os\{P(OMe)_3\}_2Cl_4$, 575
$OsC_6H_{21}N_6$
$[Os(H_2NCH_2CH_2NH)_3]^+$, 532
$OsC_6H_{22}N_6$
$[Os(HN{=}CHCH_2NH_2)(en)_2]^{2+}$, 532
$[Os(H_2NCH_2CH_2NH)_2(en)]^+$, 532
$[Os(H_2NCH_2CH_2NH)_2(en)]^{2+}$, 532
$OsC_6H_{23}N_6$
$[Os(H_2NCH_2CH_2NH)(en)_2]^{2+}$, 530, 532
$[Os(H_2NCH_2CH_2NH)(en)_2]^{3+}$, 532
$[Os(H_2NCH_2CH_2NH)_2(en)]^{2+}$, 531
$OsC_6H_{24}I_2N_6$
$[Os(en)_3I_2]^{4+}$, 531
$OsC_6H_{24}N_6$
$[Os(en)_3]^{2+}$, 531
$[Os(en)_3]^{3+}$, 530, 531, 532
$OsC_6H_{24}N_{12}S_6$
$[Os(H_2NCSNH_2)_6]^{2+}$, 608
$[Os(H_2NCSNH_2)_6]^{3+}$, 608
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$[Os(CN)_6]^{3-}$, 525, 526
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$OsC_6N_6S_6$
$[Os(NCS)_6]^{3-}$, 566
$OsC_7H_{13}NO_4$
OsO_4(quinuclidine), 592
$OsC_8H_{17}NO_3$
$OsO_3\{N(CH_2)_7Me\}$, 558
$OsC_8H_{18}Cl_3S_3$
$Os\{S(CH_2CH_2CH_2SMe)_2\}Cl_3$, 603
$OsC_8H_{18}N_2O_2$
$OsO_2(NBu^t)_2$, 559
$OsC_8H_{24}N_6$
$Os(NH_3)_2(HN{=}CMeCMeNH)_2$, 533
$OsC_8H_{28}N_8$
$[Os(H_2NCH_2CH_2NH)_4]^{2+}$, 533
$OsC_8H_{29}N_8$
$[Os(H_2NCH_2CH_2NH)_3(en)]^{2+}$, 533
$OsC_9H_{27}P_3S_6$
$Os(PMe_3)_3S_6$, 603
$OsC_9H_{27}P_3S_7$
$Os(PMe_3)_3S_7$, 603
$OsC_{10}H_8Cl_4N_2$
$[Os(bipy)Cl_4]^-$, 541
$OsC_{10}H_{10}Cl_3N_3S$
$Os(NS)Cl_3(py)_2$, 553
$OsC_{10}H_{10}N_2O_3$
OsO_3py_2, 585, 595
$OsC_{10}H_{10}N_2O_4$
$OsO_4(py)_2$, 592
$OsC_{10}H_{13}N_2O_9$
$Os\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}(H_2O)$, 602
$OsC_{10}H_{14}Cl_2N_2O_8$
$[Os\{(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}Cl_2]^-$, 602
$OsC_{10}H_{14}Cl_2O_4$
$Os(acac)_2Cl_2$, 597
$OsC_{10}H_{14}N_2O_4$
$OsO_2(1,2\text{-}O_2C_6H_4)(py)_2$, 598
$OsC_{10}H_{15}N$
OsO_3(*N*-1-adamantyl), 558
$OsC_{12}H_8O_6$
$[OsO_2(1,2\text{-}O_2C_6H_4)_2]^{2-}$, 582, 597
$OsC_{12}H_{10}Cl_2N_2O_2$
$Os(py)_2(CO)_2Cl_2$, 533
$OsC_{12}H_{10}N_2O_4$
$OsO_2(OH)_2$(phen), 583
$OsC_{12}H_{12}Cl_2N_3O_2$
$Os(bipy)(Gly\text{-}O)Cl_2$, 602
$OsC_{12}H_{12}I_3N_6$
$Os(N{=}CHCH{=}NCH{=}CH)_3I_3$, 535
$OsC_{12}H_{14}N_7O_2$
$OsO_2\{HN{=}C(NH_2)NC(NH_2){=}NH\}(bipy)]^+$, 568
$OsC_{12}H_{20}N_4O_2$
$OsO_2\{NBu^tCH(CN)CH(CN)NBu^t\}$, 557
$OsC_{12}H_{24}O_5$
$OsO(O_2C_2Me_4)_2$, 585
$OsC_{12}H_{27}N_3O$
$OsO(NBu^t)_3$, 560
$OsC_{12}H_{30}Cl_3S_3$
$Os(SEt_2)_3Cl_3$, 603
$OsC_{12}H_{36}Cl_2P_4$
$Os(PMe_3)_4Cl_2$, 573
$[Os(PMe_3)_4Cl_2]^+$, 574
$OsC_{12}H_{36}NO_4Si_4$
$[OsN(OSiMe_3)_4]^-$, 562
$OsC_{12}H_{38}P_4$
$Os(PMe_3)_4H_2$, 571
$OsC_{12}H_{39}P_4$
$[Os(PMe_3)_4H_3]^+$, 571
$OsC_{12}N_6S_6$
$[Os\{S_2C_2(CN)_2\}_3]^{3-}$, 606
$OsC_{14}H_{10}O_6$
OsO_2(tropolonate)$_2$, 597
$OsC_{14}H_{12}O_5$
$\{OsO(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)_2\}_n$, 598
$OsC_{14}H_{16}N_4O_4$
$[Os(bipy)(Gly\text{-}O)_2]^+$, 602
$OsC_{14}H_{22}NOP_2S_4$
$Os(PMe_2Ph)_2(S_2CNMe_2)(S_2COEt)$, 605
$OsC_{14}H_{24}N_6$
$[Os(bipy)en_2]^{2+}$, 540
$OsC_{14}H_{26}N_2O_6$
$OsO_2\{NBu^tCH(CO_2Me)CH(CO_2Me)NBu^t\}$, 557
$OsC_{15}H_{12}N_3O_3$
OsO_2(terpy)(OH), 544
$OsC_{15}H_{15}Cl_3N_3$
$Os(py)_3Cl_3$, 534
$OsC_{15}H_{15}I_3N_3$
$Os(py)_3I_3$, 534
$OsC_{15}H_{16}N_4O_6$
OsO_2(thymine)py_2, 586
$OsC_{15}H_{21}O_6$
$Os(acac)_3$, 597
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$OsC_{15}H_{21}S_6$
$Os\{MeC(S)CHC(S)Me\}_3$, 606
$OsC_{15}H_{30}ClN_3S_6$
$Os(S_2CNEt_2)_3Cl$, 605
$OsC_{15}H_{30}N_3S_6$
$Os(S_2CNEt_2)_3$, 604
$[Os(S_2CNEt_2)_3]^-$, 604
$[Os(S_2CNEt_2)_3]^+$, 604
$OsC_{15}H_{30}N_3Se_6$
$Os(Se_2CNEt_2)_3$, 609
$OsC_{15}H_{45}O_{15}P_5$
$Os\{P(OMe)_3\}_5$, 575
$OsC_{16}H_8Cl_4N_2O_6$
$[OsO_2\{(2\text{-}O\text{-}3,5\text{-}Cl_2C_6H_2CONCH_2)_2\}]^{2-}$, 616
$OsC_{16}H_{12}Cl_4N_2O_6$
$[OsO_2\{(2\text{-}HO\text{-}3,5\text{-}Cl_2C_6H_2CONHCH_2)_2\}]_2^{-}$, 594
$OsC_{16}H_{15}Cl_2N_3O$
$Os(py)_3(CO)Cl_2$, 533
$OsC_{16}H_{18}N_4O_6$
OsO_2(1-methylthymine)py_2, 586
$OsC_{16}H_{22}Cl_3NP_2$
$OsN(PMe_2Ph)_2Cl_3$, 562

$OsC_{16}H_{22}Cl_3NP_2S$
$Os(NS)Cl_3(PMe_2Ph)_2$, 553
$OsC_{16}H_{22}Cl_4P_2$
$Os(PMe_2Ph)_2Cl_4$, 574
$OsC_{16}H_{27}P_2$
$[Os(PMe_2Ph)_2H_5]^+$, 571
$OsC_{16}H_{28}P_2$
$Os(PMe_2Ph)_2H_6$, 572
$OsC_{16}H_{38}N_2O_2S_2$
$Os(SCH_2CH_2NPr^i_2)(OH)_2$, 607
$OsC_{18}H_{12}O_6$
$Os(1,2\text{-}O_2C_6H_4)_3$, 597
$OsC_{18}H_{15}Cl_3N_9O_3$
$Os(benzotriazole)_3Cl_3$, 568
$OsC_{18}H_{15}Cl_5P$
$[Os(PPh_3)Cl_5]^-$, 568, 574
$OsC_{18}H_{18}N_9O_3$
$Os(benzotriazole)_3(OH)_3$, 568
$OsC_{18}H_{20}N_6$
$[Os(2\text{-}pyCH_2NH_2)(2\text{-}pyCH{=}NH_2)_2]^{2+}$, 535
$OsC_{18}H_{22}N_2O_4$
$OsO_2(O_2C_8H_{12})py_2$, 586
$OsC_{18}H_{22}N_6$
$[Os(2\text{-}pyCH_2NH_2)_2(2\text{-}pyCH{=}NH_2)]^{3+}$, 535
$OsC_{18}H_{24}N_6$
$[Os(2\text{-}pyCH_2NH_2)_3]^{3+}$, 535
$OsC_{18}H_{28}Cl_2P_3S_2$
$Os(PMe_2Ph)_2(S_2PMe_2)Cl_2$, 606
$OsC_{18}H_{28}P_3S_2$
$Os(PMe_2Ph)_2(S_2PMe_2)$, 605
$OsC_{18}H_{35}N_3O_5$
$OsO(NBu^t)\{NBu^tCH(CO_2Me)CH(CO_2Me)NBu^t\}$, 557
$OsC_{20}H_{16}ClN_5O$
$[Os(NO)(bipy)_2Cl]^+$, 548
$OsC_{20}H_{16}ClN_5O_2$
$Os(NO_2)(bipy)_2Cl$, 598
$OsC_{20}H_{16}Cl_2N_4$
$Os(bipy)_2Cl_2$, 537, 540
$[Os(bipy)_2Cl_2]^+$, 537, 541
$OsC_{20}H_{16}N_2O_8$
$[OsO_2(NO_3C_{10}H_8)_2]^{2+}$, 569
$OsC_{20}H_{16}N_4O_2$
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$OsC_{20}H_{18}Cl_4N_4O_4$
$Os\{(2\text{-}O\text{-}3,5\text{-}Cl_2C_6H_2CONCH_2)_2\}(py)_2$, 616
$OsC_{20}H_{18}N_2O_8$
$Os(NO_3C_{10}H_8)_2(OH)_2$, 569
$OsC_{20}H_{20}Cl_2N_4$
$Os(py)_4Cl_2$, 533
$OsC_{20}H_{20}N_4O_2$
$[Os(bipy)_2(H_2O)_2]^{2+}$, 541
$OsC_{20}H_{23}N_7O_8$
$OsO_2(adenosine)py_2$, 586
$OsC_{20}H_{30}Cl_4P_2$
$[Os(PEt_2Ph)_2Cl_4]^-$, 574
$OsC_{20}H_{32}Cl_2P_2$
$Os(PEt_2Ph)_2H_2Cl_2$, 570
$OsC_{20}H_{40}N_4S_8$
$Os(S_2CNEt_2)_4$, 604
$OsC_{20}H_{48}Cl_2P_4$
$Os(depe)_2Cl_2$, 579
$OsC_{20}H_{49}N_2P_4$
$[Os(N_2)H(Et_2PCH_2CH_2PEt_2)_2]^+$, 555
$OsC_{21}H_{12}Cl_3S_6$
$Os(4\text{-}S_2CC_6H_4Cl)_3$, 608
$OsC_{21}H_{15}O_6$
$Os(tropolonate)_3$, 597
$OsC_{21}H_{18}S_6$
$Os(3,4\text{-}S_2C_6H_3Me)_3$, 606
$[Os(3,4\text{-}S_2C_6H_3Me)_3]^-$, 606
$OsC_{22}H_{16}N_4O_4$
$Os(C_2O_4)(bipy)_2$, 601
$OsC_{22}H_{16}N_6$
$Os(CN)_2(bipy)_2$, 526
$[Os(CN)_2(bipy)_2]^+$, 526
$OsC_{22}H_{16}N_6S_2$
$Os(SCN)_2(bipy)_2$, 566
$OsC_{22}H_{18}Cl_2N_4$
$Os(2\text{-}pyN{=}NPh)_2Cl_2$, 535
$OsC_{22}H_{20}N_5O_2$
$[Os(bipy)_2(Gly\text{-}O)]^+$, 602
$OsC_{22}H_{34}N_2P_2S_4$
$Os(PMe_2Ph)_2(S_2CNMe_2)_2$, 604
$OsC_{24}H_{20}N_{12}O_3$
$[OsO_3(benzotriazole)_4]^{3-}$, 568
$OsC_{24}H_{22}Cl_2N_4$
$Os(2\text{-}pyN{=}NC_6H_4Me\text{-}3)_2Cl_2$, 535
$OsC_{24}H_{33}Cl_2F_3P_4$
$Os(PF_3)(PMe_2Ph)_3Cl_2$, 576
$OsC_{24}H_{33}Cl_2N_3P_3$
$Os(N_3)(PMe_2Ph)_3Cl_2$, 565
$OsC_{24}H_{33}Cl_3NP_3$
$Os(NPMe_2Ph)Cl_3(PMe_2Ph)_2$, 568
$OsC_{24}H_{33}Cl_3P_3$
$Os(PMe_2Ph)_3Cl_3$, 573
$OsC_{24}H_{34}ClN_2P_3$
$Os(N_2)(PMe_2Ph)_3HCl$, 555
$OsC_{24}H_{35}P_3$
$Os(PMe_2Ph)_3H_2$, 571
$OsC_{24}H_{37}Cl_2N_2P_3$
$Os(PMe_2Ph)_3Cl_2(N_2H_4)$, 556
$OsC_{24}H_{37}P_3$
$Os(PMe_2Ph)_3H_4$, 571
$OsC_{25}H_{19}ClN_5$
$[Os(terpy)(bipy)Cl]^+$, 543
$OsC_{25}H_{19}N_5O$
$[OsO(terpy)(bipy)]^{2+}$, 543
$OsC_{25}H_{19}N_6O$
$[Os(NO)(terpy)(bipy)]^{3+}$, 548
$OsC_{25}H_{19}N_6O_2$
$[Os(\overline{N{=}CHCH{=}NCH{=}C}CO_2)(bipy)_2]^+$, 536
$[Os(NO_2)(terpy)(bipy)]^+$, 598
$[Os(NO_2)(terpy)(bipy)]^{2+}$, 599
$OsC_{25}H_{20}N_5O$
$[Os(OH)(terpy)(bipy)]^{2+}$, 543
$OsC_{25}H_{21}ClN_5$
$[Os(bipy)_2Cl(py)]^+$, 540
$OsC_{25}H_{21}N_5O$
$[Os(terpy)(bipy)(H_2O)]^{2+}$, 543
$OsC_{25}H_{23}N_4O_2$
$[Os(bipy)_2(acac)]^+$, 540
$OsC_{25}H_{38}Cl_2NP_3$
$Os(PMe_2Ph)_3Cl_2(H_2NMe)$, 530
$OsC_{26}H_{16}N_4O_4$
$Os(C_2O_4)(phen)_2$, 601
$OsC_{26}H_{28}Cl_2P_2$
$Os(PMePh_2)_2H_2Cl_2$., 570
$OsC_{26}H_{38}Cl_2OP_3$
$Os(PMe_2Ph)_3Cl_2(OEt)$, 596
$OsC_{26}H_{39}ClP_4S_2$
$Os(PMe_2Ph)_3(S_2PMe_2)Cl$, 606
$OsC_{27}H_{18}N_3S_3$
$Os(8\text{-}quinolinothiolate)_3$, 617
$OsC_{27}H_{38}ClOP_3S_2$
$Os(PMe_2Ph)_3(S_2COEt)Cl$, 605
$OsC_{27}H_{39}ClNP_3S_2$
$Os(PMe_2Ph)_3(S_2CNMe_2)Cl$, 604
$OsC_{27}H_{39}Cl_2OP_3$
$[Os(PMe_2Ph)_3Cl_2(OCMe_2)]^+$, 598
$OsC_{28}H_{22}N_8$
$[Os(2,2'\text{-}bipyrimidine)(bipy)_2]^{2+}$, 537
$OsC_{28}H_{25}Cl_3N_2P$
$Os(py)_2(PPh_3)Cl_3$, 534
$[Os(py)_2(PPh_3)Cl_3]^+$, 534
$OsC_{28}H_{32}N_4O_8$
$Os_2O_4(O_4C_8H_{12})py_4$, 586

$OsC_{28}H_{56}Cl_2N_8S_4$
$Os(SCNEtCH_2CH_2NEt)_4Cl_2$, 607
$OsC_{29}H_{22}N_2O_4$
$OsO_2(O_2C_{19}H_{12})py_2$, 586
$OsC_{29}H_{44}NOP_3S_2$
$Os(PMe_2Ph)_3(S_2CNMe_2)(OEt)$, 596
$OsC_{30}H_{22}N_6$
$[Os(terpy)_2]^{2+}$, 537, 542
$[Os(terpy)_2]^{3+}$, 537, 543
$OsC_{30}H_{24}N_6$
$[Os(bipy)_3]^{2+}$, 537, 538
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$[Os(bipy)_3]^{4+}$, 539
$OsC_{30}H_{26}N_6$
$[Os(bipy)_2(py)_2]^{2+}$, 540
$OsC_{30}H_{33}ClF_5N_2P_3S$
$Os(N_2)(PMe_2Ph)_3Cl(SC_6F_5)$, 555
$OsC_{30}H_{36}N_6O_{24}$
$[Os\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}_3]^{10-}$, 602
$OsC_{30}H_{42}N_3P_3$
$[Os(NCMe)_3(PMe_2Ph)_3]^{2+}$, 567
$OsC_{30}H_{45}Cl_2N_2P_3$
$Os(N_2)(PEt_2Ph)_3Cl_2$, 555
$OsC_{30}H_{47}N_2P_3$
$Os(N_2)H_2(PEt_2Ph)_3$, 555
$OsC_{30}H_{49}P_3$
$Os(PEt_2Ph)_3H_4$, 571
$OsC_{30}H_{75}ClO_{15}P_5$
$[Os\{P(OEt)_3\}_5Cl]^+$, 575
$OsC_{32}H_{16}N_8$
$\{Os(phthalocyanine)\}_n$, 618
$OsC_{32}H_{16}N_8O_4S$
$\{Os(phthalocyanine)SO_4\}_n$, 619
$OsC_{32}H_{24}N_6$
$[Os(bipy)_2(phen)]^{2+}$, 537
$OsC_{32}H_{28}N_6$
$[Os(phen)(py)_4]^{2+}$, 540
$OsC_{32}H_{44}N_6P_4$
$Os(N_3)_2(PMe_2Ph)_4$, 565
$OsC_{32}H_{46}P_4$
$Os(PMe_2Ph)_4H_2$, 571
$OsC_{33}H_{30}Cl_2N_3P$
$Os(py)_3(PPh_3)Cl_2$, 534
$[Os(py)_3(PPh_3)Cl_2]^+$, 534
$[Os(py)_3(PPh_3)Cl_2]^{2+}$, 534
$OsC_{33}H_{48}Cl_3N_{15}$
$[Os(paludrine)_3]^{2+}$, 567
$[Os(paludrine)_3]^{3+}$, 568
$OsC_{34}H_{30}N_6$
$[Os(bipy)_2(4\text{-}pyCH{=}CH_2)_2]^{3+}$, 542
$OsC_{36}H_{24}N_6$
$[Os(phen)_3]^{2+}$, 537, 538
$[Os(phen)_3]^{3+}$, 537, 538
$[Os(phen)_3]^{4+}$, 539
$OsC_{36}H_{30}Cl_2F_6P_4$
$Os(PF_3)_2(PPh_3)_2Cl_2$, 576
$OsC_{36}H_{30}Cl_2NOP_2$
$Os(NO)Cl_2(PPh_3)_2$, 549
$OsC_{36}H_{30}Cl_2O_2P_2$
$OsO_2Cl_2(PPh_3)_2$, 584
$OsC_{36}H_{30}Cl_3NP_2S$
$Os(NS)Cl_3(PPh_3)_2$, 553
$OsC_{36}H_{30}Cl_3P_2$
$Os(PPh_3)_2Cl_3$, 574
$OsC_{36}H_{30}Cl_4P_2$
$Os(PPh_3)_2Cl_4$, 574
$OsC_{36}H_{30}N_2O_2P_2$
$Os(NO)_2(PPh_3)_2$, 547, 551
$OsC_{36}H_{30}N_2O_3P_2$
$Os(NO)(NO_2)(PPh_3)_2$, 550
$OsC_{36}H_{30}O_2P_2Se_2$
$Os(\eta^2\text{-}Se_2)(PPh_3)_2(CO)_2$, 609
$OsC_{36}H_{31}ClF_6P_4$
$Os(PF_3)_2(PPh_3)_2HCl$, 576
$OsC_{36}H_{31}Cl_4NP_2$
$Os(NHPPh_3)Cl_4(PPh_3)$, 568
$OsC_{36}H_{31}N_2O_2P_2$
$[Os(NO)_2H(PPh_3)_2]^+$, 551
$OsC_{36}H_{31}N_2O_3P_2$
$[Os(NO)_2(OH)(PPh_3)_2]^+$, 550
$OsC_{36}H_{32}Cl_2N_2O_2P_2$
$Os(NO)(NHOH)Cl_2(PPh_3)_2$, 557
$OsC_{36}H_{32}F_3P_3$
$Os(PF_3)(PPh_3)_2H_2$, 576
$OsC_{36}H_{33}Cl_3NP_2$
$Os(NH_3)Cl_3(PPh_3)_2$, 528, 529
$OsC_{36}H_{44}Br_2N_4$
Os(octaethylporphyrin)Br_2, 618
$OsC_{36}H_{44}Cl_2N_4$
Os(octaethylporphyrin)Cl_2, 618
$OsC_{36}H_{44}FN_5$
OsN(octaethylporphyrin)F, 562
$OsC_{36}H_{44}FN_5O$
Os(NO)F(octaethylporphyrin), 548
$OsC_{36}H_{44}N_4O_2$
OsO_2(octaethylporphyrin), 583, 618
$OsC_{36}H_{44}N_6O_2$
$Os(NO)_2$(octaethylporphyrin), 551
$OsC_{36}H_{90}O_{18}P_6$
$[Os\{P(OEt)_3\}_6]^{2+}$, 575
$OsC_{37}H_{30}ClNO_2P_2$
$Os(NO)(CO)Cl(PPh_3)_2$, 548, 550, 596
$OsC_{37}H_{30}Cl_2NO_2P_2$
$[Os(NO)(CO)Cl_2(PPh_3)_2]^+$, 548, 549
$OsC_{37}H_{31}Cl_2NO_2P_2$
$Os(HNO)Cl_2(CO)(PPh_3)_2$, 550, 551
$OsC_{37}H_{31}NO_2P_2$
$Os(NO)H(CO)(PPh_3)_2$, 550
$OsC_{37}H_{32}ClNO_3P_2$
$OsCl(NO)(CH_2SO_2)(PPh_3)_2$, 1165
$OsC_{37}H_{44}ClN_4O$
Os(octaethylporphyrin)(CO)Cl, 618
$OsC_{37}H_{47}N_5O_2$
Os(NO)(OMe)(octaethylporphyrin), 548
$OsC_{37}H_{67}ClO_3P_2$
$Os(O_2)(CO)HCl\{P(C_6H_{11})_3\}_2$, 596
$OsC_{38}H_{30}NO_3P_2$
$[Os(NO)(CO)_2(PPh_3)_2]^+$, 550
$OsC_{38}H_{30}O_2P_2S_2$
$Os(S_2)(PPh_3)_2(CO)_2$, 603
$OsC_{38}H_{30}O_4P_2$
$Os(O_2)(CO)_2(PPh_3)_2$, 596
$OsC_{38}H_{32}P_2S_4$
$Os(PPh_3)_2(S_2CH)_2$, 608
$OsC_{38}H_{33}Br_3NP_2$
$Os(NCMe)Br_3(PPh_3)_2$, 567
$OsC_{38}H_{33}Cl_3NP_2$
$Os(NCMe)Cl_3(PPh_3)_2$, 567
$OsC_{38}H_{36}Cl_2O_2P_2$
$Os(PPh_3)_2Cl_2(OMe)_2$, 596
$OsC_{38}H_{48}N_4O_2$
Os(octaethylporhyrin)(CO)(MeOH), 595
$OsC_{38}H_{50}N_4O_2$
Os(octaethylporphyrin)$(OMe)_2$, 618
$OsC_{38}H_{54}N_2O_4$
$OsO_2(O_2C_{28}H_{44})py_2$, 586
$OsC_{39}H_{33}O_2P_2S_2$
$[Os(CO)_2(PPh_3)_2(\eta^2\text{-}S_2Me)]^+$, 1121
$OsC_{39}H_{40}Cl_3P_3$
$Os(PMePh_2)_3HCl_3$, 570
$OsC_{40}H_{20}ClN_{10}$
Os(phthalocyanine)Cl$\{1,2\text{-}(NC)_2C_6H_4\}$, 619
$OsC_{40}H_{20}N_{10}$
OsO_2(phthalocyanine)$\{1,2\text{-}(NC)_2C_6H_4\}$, 619
$OsC_{40}H_{30}F_6N_2O_5P_2$
$Os(NO)(ON{=}COCF_3)(O_2CCF_3)(PPh_3)_2$, 547, 549

$OsC_{40}H_{31}F_6NO_5P_2$
$Os(NO)H(PPh_3)_2(O_2CCF_3)_2$, 547
$OsC_{40}H_{36}Cl_4O_5P_2$
$Os_2O(OAc)_2Cl_4(PPh_3)_2$, 595
$[Os_2O(OAc)_2Cl_4(PPh_3)_2]^-$, 595
$OsC_{40}H_{37}Cl_2N_3O_3P_2$
$Os(N_2)\{N(OH)CHCO_2Et\}(PPh_3)_2Cl_2$, 555
$OsC_{40}H_{52}N_6O$
Os(octaethylporphyrin)(N_2)(THF), 618
$OsC_{40}H_{63}P_4$
$[Os(PEt_2Ph)_4H_3]^+$, 571
$OsC_{41}H_{39}Cl_4P_3$
Os(triphos)Cl_4, 579
$OsC_{42}H_{33}Cl_2P_3$
$Os\{PPh(C_6H_4PPh_2\text{-}2)_2\}_2Cl_2$, 579
$OsC_{42}H_{35}Cl_3N_2P_2$
$Os(N_2Ph)(PPh_3)_2Cl_3$, 551
$OsC_{42}H_{42}N_2P_2S_4$
$Os(PPh_3)_2(S_2CNMe_2)_2$, 604
$OsC_{42}H_{42}P_3S_6$
$Os\{S_2P(C_6H_4Me\text{-}4)_2\}_3$, 608
$OsC_{42}H_{45}Cl_3NO_3P_3$
$Os\{NP(OEt)Ph_2\}Cl_3\{P(OEt)Ph_2\}_2$, 568
$OsC_{42}H_{49}N_5O$
Os(octaethylporphyrin)(CO)py, 471, 617
$OsC_{42}H_{55}NS_4$
$Os(SC_6HMe_4\text{-}2,3,5,6)_4(NCMe)$, 607
$OsC_{42}H_{62}N_4O_6P_2$
Os(octaethylporphyrin)$\{P(OMe)_3\}_2$, 618
$OsC_{43}H_{35}Br_2O_2P_2$
$Os(O_2CPh)Br_2(PPh_3)_2$, 600
$OsC_{43}H_{35}Cl_3NP_2$
$Os(NCPh)Cl_3(PPh_3)_2$, 567
$OsC_{45}H_{36}O_3S_3$
$Os(SOC_{15}H_{12})_3$, 606
$OsC_{45}H_{37}N_2O_2P_2$
$[Os(NO)(CO)(CNC_6H_4Me\text{-}4)(PPh_3)_2]^+$, 550
$OsC_{46}H_{44}O_4P_2$
$Os(PPh_3)_2(acac)_2$, 597
$OsC_{46}H_{54}N_6$
Os(octaethylporphyrin)$(py)_2$, 618
$OsC_{48}H_{40}N_8O_2$
$[Os(bipy)_2(4\text{-}pyNHCOCH{=}CHPh)_2]^{2+}$, 542
$OsC_{48}H_{43}N_3P_2$
$OsH_3(PhNNNPh)(PPh_3)_2$, 565
$OsC_{48}H_{44}Cl_2P_4$
$Os(PHPh_2)_4Cl_2$, 573
$OsC_{50}H_{44}Cl_2P_4$
$Os(dppm)_2Cl_2$, 579
$OsC_{52}H_{44}Cl_2N_2P_2$
$Os(NCC_6H_4Me\text{–}4)_2(PPh_3)_2Cl_2$, 567
$OsC_{52}H_{48}Cl_2P_4$
$Os(dppe)_2Cl_2$, 579
$OsC_{52}H_{48}NOP_4$
$Os(NO)(dppe)_2$, 551
$[Os(NO)(dppe)_2]^-$, 550, 551
$[Os(NO)(dppe)_2]^+$, 550
$OsC_{52}H_{54}P_4$
$Os(PMePh_2)_4H_2$, 570
$OsC_{54}H_{36}N_6$
$[Os(2,2'\text{-biquinoline})_3]^{2+}$, 542
$OsC_{54}H_{45}ClNOP_3$
$Os(NO)Cl(PPh_3)_3$, 550
$OsC_{54}H_{45}Cl_2P_3$
$Os(PPh_3)_3Cl_2$, 572
$OsC_{54}H_{45}Cl_3NP_3$
$Os(NPPh_3)Cl_3(PPh_3)_2$, 568
$OsC_{54}H_{45}Cl_3P_3$
$Os(PPh_3)_3Cl_3$, 574
$OsC_{54}H_{46}ClP_3$
$Os(PPh_3)_3HCl$, 570
$OsC_{54}H_{46}NOP_3$
$Os(NO)H(PPh_3)_3$, 550
$OsC_{54}H_{47}F_3P_4$
$Os(PF_3)(PPh_3)_3H_2$, 576
$OsC_{54}H_{52}ClP_4$
$[Os\{Ph_2P(CH_2)_3PPh_2\}_2Cl]^+$, 579
$OsC_{56}H_{49}O_2P_3$
$Os(OAc)H(PPh_3)_3$, 600
$OsC_{56}H_{62}$
$Os(PEtPh_2)_4H_2$, 571
$OsC_{58}H_{46}N_6$
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$OsC_{60}H_{48}O_4S_4$
$Os(SOC_{15}H_{12})_4$, 607
$OsC_{60}H_{50}N_6P_2$
$Os(PhNNNPh)_2(PPh_3)_2$, 565
$OsC_{61}H_{50}Cl_2NOP_3$
$Os(PhCONPPh_3)Cl_2(PPh_3)_2$, 569
$OsC_{62}H_{95}NS_4$
$Os(SC_6H_2Pr^i_3\text{-}2,4,6)_4(NCMe)$, 607
$OsC_{72}H_{60}Br_2P_4$
$Os(PPh_3)_4Br_2$, 573
$OsC_{72}H_{60}Cl_2O_{12}P_4$
$Os\{P(OPh)_3\}Cl_2$, 575
$OsC_{72}H_{60}Cl_2P_4$
$Os(PPh_3)_4Cl_2$, 572
$OsClBrF_4$
$[OsF_4ClBr]^-$, 610
$OsClO_4$
$[OsO_4Cl]$, 592
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$[Os(SO_3)_5Cl]^{7-}$, 599
$OsCl_2F_4$
$[OsF_4Cl_2]^{2-}$, 610
$OsCl_2H_{12}N_6$
$[Os(N_2)(NH_3)_4Cl_2]^+$, 555
$OsCl_2O_3$
$[OsO_3Cl_2]^{2-}$, 583
$OsCl_2O_{12}S_4$
$[Os(SO_3)_4Cl_2]^{6-}$, 599
$OsCl_3F_3$
$[OsF_3Cl_3]^{2-}$, 610
$OsCl_3NO$
$\{Os(NO)Cl_3\}_n$, 546
$OsCl_3O_2P$
$OsO_2(PCl_3)$, 576
$OsCl_4F_2$
$[OsF_2Cl_4]^{2-}$, 610
$OsCl_4N$
$[OsNCl_4]^-$, 560
$OsCl_4NO$
$[Os(NO)Cl_4]^-$, 546, 548
$OsCl_4N_2S_2$
$Os(NS)_2Cl_4$, 553
$OsCl_4O$
$OsOCl_4$, 584
$OsCl_4O_2$
$[OsO_2Cl_4]^{2-}$, 583
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$[Os(SO_3)_4Cl_4]^{8-}$, 599
$OsCl_5N$
$[OsNCl_5]^{2-}$, 560
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$[Os(NO)Cl_5]^-$, 545
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$[Os(NS)Cl_5]^-$, 553
$OsCl_5N_2S_2$
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$[OsCl_6]^-$, 615
$[OsCl_6]^{2-}$, 613, 614
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$[OsOCl_6]^-$, 584
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$OsCl_3(PCl_3)$, 576
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$[OsO_4F]^-$, 592
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$OsF_{10}P_2$
$OsF_4(PF_3)_2$, 610
$OsF_{12}P_4$
$[Os(PF_3)_4]^{2-}$, 575
$OsF_{15}P_5$
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$OsFeC_4H_{26}N_4O_7$
$[Fe(H_2O)_5OOsO(en)_2]^{4+}$, 583
$OsHCl_5O$
$[OsCl_5(OH)]^{2-}$, 594, 615
$OsHNO_3$
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$[Os(NO)(OH)(NO_2)_4]^{2-}$, 546, 548, 598
$OsHO_5$
$[OsO_4(OH)]^-$, 591
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OsH_2Br_4NO
$[OsNBr_4(H_2O)]^{2-}$, 561
$OsH_2Cl_3O_3$
$[OsO_2Cl_3(H_2O)]^-$, 583
OsH_2Cl_4NO
$[OsNCl_4(H_2O)]^{2-}$, 561
OsH_2Cl_4NOS
$[Os(NS)Cl_4(H_2O)]^-$, 553
$OsH_2Cl_5NO_3S$
$[Os(NH_2SO_3)Cl_5]^{2-}$, 616
OsH_2Cl_5O
$[OsCl_5(H_2O)]^-$, 615
$OsH_2F_4NO_2$
$[Os(NO)F_4(H_2O)]^-$, 546
$OsH_2F_{12}P_4$
$Os(PF_3)_4H_2$, 576
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$[Os(SO_4)_2(OH)_2]^{2-}$, 599
$OsH_2O_{12}S_2$
$OsO_2(OH)_2(SO_4)_2$, 599
$OsH_2O_{16}S_5$
$[Os(SO_3)_5(H_2O)]^{6-}$, 599
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$[OsO_3(OH)_3]^-$, 592
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$OsH_4Cl_4O_2$
$OsCl_4(H_2O)_2$, 615
$OsH_4F_2NO_3$
$[OsNF_2(OH)_2(H_2O)]^-$, 562
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$OsH_6O_{12}S_3$
$[Os(SO_3)_3(H_2O)_3]^{4-}$, 599
$OsH_6O_{18}S_6$
$[Os(HSO_3)_6]^{4-}$, 600
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$RhCl_3(AsMePh_2)_3$, 1031
$RhAs_3C_{39}H_{40}Br$
$RhHBr(AsMePh_2)_3$, 1027
$RhAs_3C_{39}H_{40}Cl_2$
$RhHCl_2(AsMePh_2)_3$, 1026
$RhAs_3C_{45}H_{51}Cl_3$
$RhCl_3(AsPh_2Pr)_3$, 1031
$RhAs_3C_{45}H_{52}Cl_2$
$RhHCl_2(AsPh_2Pr)_3$, 1026
$RhAs_3C_{72}H_{61}P$
$RhH(AsPh_3)_3(PPh_3)$, 924
$RhAs_3HgC_{39}H_{39}Cl_2F$
$RhCl_2(HgF)(AsMePh_2)_3$, 1076
$RhAs_3HgC_{39}H_{39}Cl_3$
$RhCl_2(HgCl)(AsMePh_2)_3$, 1076
$RhAs_3HgC_{41}H_{42}Cl_2O_2$
$RhCl_2(HgOAc)(AsMePh_2)_3$, 1076
$RhAs_4C_{20}H_{32}ClNO_3$
$[RhCl(NO_3)(diars)_2]^+$, 1040
$RhAs_4C_{20}H_{32}Cl_2$
$[RhCl_2(diars)_2]^+$, 1039, 1040
$RhAs_4C_{20}H_{32}O_4S$
$[Rh(SO_4)(diars)_2]^+$, 1040
$RhAs_4C_{20}H_{33}Cl$
$[RhHCl(diars)_2]^+$, 1037
$RhAs_4C_{21}H_{35}ClO_2S$
$[RhCl(O_2SMe)(diars)_2]^+$, 1040
$RhAs_4C_{26}H_{36}ClNO_4S$
$[RhCl(4\text{-}O_2SC_6H_4NO_2)(diars)_2]$, 1040
$RhAs_4C_{26}H_{37}ClO_2S$
$[RhCl(O_2SPh)(diars)_2]^+$, 1040
$RhAs_4C_{27}H_{39}ClO_2S$
$[RhCl(4\text{-}O_2SC_6H_4Me)(diars)_2]^+$, 1040
$RhAs_4C_{52}H_{44}S_2$
$[RhS_2(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 1037
$RhAs_4C_{52}H_{45}Cl$
$[RhHCl(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 1037
$RhAs_4C_{52}H_{46}$
$[RhH_2(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 1037
$RhAs_4C_{53}H_{47}ClO_2S$
$[RhCl(O_2SMe)(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 1040
$RhAs_4C_{58}H_{49}ClO_2S$
$[RhCl(O_2SPh)(Ph_2AsCH{=}CHAsPh_2)_2]^+$, 1040
$RhAs_4C_{59}H_{55}ClO_2S$
$[RhCl[4\text{-}O_2SC_6H_4Me)(Ph_2AsCH_2CH_2AsPh_2)_2]^+$, 1040
$RhAs_6C_{34}H_{46}$
$[Rh\{MeAs(C_6H_4AsMe_2\text{-}2)_2\}_2]^{3+}$, 1044
$RhAuC_{18}H_{15}F_{12}P_5$
$Rh(PF_3)_4AuPPh_3$, 904
$RhBC_9H_{11}Cl_2N_6$
$[Rh\{HB(NN{=}CHCH{=}CH)_3\}Cl_2H]^-$, 1012
$RhBC_{10}H_{10}I_2N_6O$
$Rh\{HB(NN{=}CHCH{=}CH)_3\}COI_2$, 1012
$RhBC_{10}H_{14}Cl_2N_6O$
$Rh\{HB(NN{=}CHCH{=}CH)_3\}Cl_2(MeOH)$, 1012
$RhBC_{14}H_{25}F_2IN_4O_2$
$RhMeI(F_2BON{=}CEtCMe{=}N(CH_2)_3N{=}CEtCMe{=}NO)$, 1014
$RhBC_{36}H_{72}P_2$
$RhH_2(BH_4)\{P(C_6H_{11})_3\}_2$, 1022
$RhBC_{42}H_{36}ClO_2P_2$
$RhHCl(2\text{-}OC_6H_4OBH)(PPh_3)_2$, 1018
$RhBr_3Cl_3$
$[RhCl_3Br_3]^{3-}$, 1058
$RhBr_6$
$[RhBr_6]^{3-}$, 1057, 1058
$RhCH_{12}ClN_5$
$[Rh(NH_3)_4(CN)Cl]^+$, 986
$RhCH_{13}N_5O$
$[Rh(NH_3)_4(OH)(CN)]^+$, 964
$RhCH_{14}N_5O$
$[Rh(NH_3)_4(CN)(H_2O)]^{2+}$, 964, 986
$RhCH_{15}F_3N_5O_3S$
$[Rh(NH_3)_5(OSO_2CF_3)]^{2+}$, 956, 961
$RhCH_{15}N_5O_3$
$[Rh(NH_3)_5(CO_3)]^+$, 960
$RhCH_{15}N_6$
$[Rh(NH_3)_5(CN)]^{2+}$, 986
$RhCH_{15}N_6O$
$[Rh(NH_3)_5(NCO)]^{2+}$, 956, 962
$RhCH_{16}N_5O_2$
$[Rh(NH_3)_5(O_2CH)]^{2+}$, 960
$RhCH_{16}N_6$
$[Rh(NH_3)_5(HCN)]^{3+}$, 960

$RhCH_{19}N_7O$
$[Rh(NH_3)_5(H_2NCONH_2)]^{3+}$, 957, 960, 961
$RhC_2H_3Cl_5N$
$[RhCl_5(MeCN)]^{2-}$, 1005
$RhC_2H_{15}Cl_3N_5O_2$
$[Rh(NH_3)_5(O_2CCCl_3)]^{2+}$, 960
$RhC_2H_{15}F_3N_5O_2$
$[Rh(NH_3)_5(O_2CCF_3)]^{2+}$, 957, 959, 960
$RhC_2H_{15}N_5O_4$
$[Rh(NH_3)_5(C_2O_4)]^{+}$, 956
$RhC_2H_{16}F_2N_5O_2$
$[Rh(NH_3)_5(O_2CCHF_2)]^{2+}$, 960
$RhC_2H_{17}FN_5O_2$
$[Rh(NH_3)_5(O_2CCH_2F)]^{2+}$, 960
$RhC_2H_{18}N_5O_2$
$[Rh(NH_3)_5(OAc)]^{2+}$, 957, 959, 960
$RhC_2H_{20}N_6$
$[Rh(NH_3)_5(HN\overline{CH_2C}H_2)]^{3+}$, 964
$RhC_2H_{20}N_6O$
$[Rh(NH_3)_5(H_2NAc)]^{3+}$, 964
$RhC_3H_{10}Cl_4N_2$
$[Rh(pn)Cl_4]^{-}$, 981
$RhC_3H_{19}N_7$
$[Rh(NH_3)_5(imidazole)]^{3+}$, 964
$RhC_4Cl_2O_8$
$[Rh(C_2O_4)_2Cl_2]^{3-}$, 1049
$RhC_4H_3N_4O_3$
$[Rh(OOH)(CN)_4(H_2O)]^{2-}$, 1052
$RhC_4H_4O_{10}$
$[Rh(C_2O_4)_2(H_2O)_2]^{-}$, 1049
$RhC_4H_6Cl_4N_2$
$[RhCl_4(MeCN)_2]^{-}$, 1005
$RhC_4H_8Br_3N_2O$
$RhBr_3(MeCN)_2(H_2O)$, 1005
$RhC_4H_{10}Cl_3S_2$
$Rh(MeSCH_2CH_2SMe)Cl_3$, 1055
$RhC_4H_{10}Cl_4S_2$
$[Rh(MeSCH_2CH_2SMe)Cl_4]^{-}$, 1056
$RhC_4H_{12}Cl_4N_2$
$[Rh(H_2NCHMeCHMeNH_2)Cl_4]^{-}$, 981
$RhC_4H_{12}Cl_4O_2S_2$
$[Rh(DMSO)_2Cl_4]^{-}$, 1053
$RhC_4H_{16}BrClN_4$
$[Rh(cn)_2ClBr]^{+}$, 968
$RhC_4H_{16}BrIN_4$
$[Rh(en)_2BrI]^{+}$, 968
$RhC_4H_{16}Br_2N_4$
$[Rh(en)_2Br_2]^{+}$, 988
$RhC_4H_{16}ClIN_4$
$[Rh(en)_2ClI]^{+}$, 968
$RhC_4H_{16}ClN_5O_2$
$[Rh(en)_2(NO_2)Cl]^{+}$, 969
$RhC_4H_{16}ClN_7$
$[Rh(en)_2Cl(N_3)]^{+}$, 968
$RhC_4H_{16}Cl_2N_4$
$Rh(en)_2Cl_2$, 967
$[Rh(en)_2Cl_2]^{+}$, 966, 968, 972–974, 981, 982, 998, 1004, 1005
$RhC_4H_{16}N_5O_4$
$[Rh(en)_2(NO_2)(O_2)]^{+}$, 1052
$RhC_4H_{16}N_6O_4$
$[Rh(en)_2(NO_2)_2]^{+}$, 969, 970, 1052
$RhC_4H_{16}N_{10}$
$[Rh(en)_2(N_3)_2]^{+}$, 969
$RhC_4H_{17}ClN_4$
$[Rh(en)_2HCl]^{+}$, 969
$RhC_4H_{17}ClN_4O$
$[Rh(en)_2(Cl)(OH)]^{+}$, 968, 974
$RhC_4H_{18}ClN_4O$
$[Rh(en)_2Cl(H_2O)]^{-}$, 968
$[Rh(en)_2Cl(H_2O)]^{2+}$, 968, 972, 973, 978
$RhC_4H_{18}N_4$
$[Rh(en)_2H_2]^{+}$, 966, 969
$RhC_4H_{18}N_4O$
$[RhH(en)_2(OH)]^{+}$, 969, 1004
$RhC_4H_{18}N_4O_2$
$[Rh(en)_2(OH)_2]^{+}$, 969, 971, 978, 979, 1004
$RhC_4H_{18}N_4O_3$
$[Rh(en)_2(OH)(OOH)]^{+}$, 1004
$RhC_4H_{19}ClN_5$
$[Rh(en)_2(NH_3)Cl]^{2+}$, 969, 971, 972
$RhC_4H_{19}N_4O$
$[RhH(en)_2(H_2O)]^{2+}$, 1004
$RhC_4H_{19}N_4O_2$
$[Rh(en)_2(OH)(H_2O)]^{2+}$, 969, 971, 974, 979
$RhC_4H_{20}N_4O_2$
$[Rh(en)_2(H_2O)_2]^{3+}$, 967, 969, 971, 973, 974, 979, 988
$RhC_4H_{21}N_5O$
$[Rh(en)_2(NH_3)(OH_2)]^{3+}$, 969
$RhC_4H_{22}N_6$
$[Rh(en)_2(NH_3)_2]^{3+}$, 969, 971, 974
RhC_4O_{12}
$[Rh(CO_3)_4]^{4-}$, 938
RhC_5ClN_5
$[Rh(CN)_5Cl]^{3-}$, 952
RhC_5HN_5
$[Rh(CN)_5H]^{3-}$, 952
RhC_5HN_5O
$[Rh(CN)_5(OH)]^{3-}$, 952
$RhC_5H_2N_5O$
$[Rh(CN)_5(H_2O)]^{2-}$, 952
$RhC_5H_7F_6O_2P_2$
$Rh(acac)(PF_3)_2$, 910
$RhC_5H_{16}ClN_4O_3$
$Rh(cn)_2Cl(CO_3)$, 969, 978
$RhC_5H_{16}ClN_5S$
$[Rh(en)_2(NCS)Cl]^{+}$, 969
$RhC_5H_{16}N_4O_3$
$[Rh(en)_2(CO_3)]^{+}$, 977
$RhC_5H_{16}N_4O_6$
$[Rh(en)_2(OCO_2)_2]^{-}$, 969
$RhC_5H_{17}ClN_4O_3$
$Rh(en)_2Cl(CO_3H)$, 979
$RhC_5H_{17}N_4O_4$
$Rh(en)_2(CO_3)(OH)$, 969
$[Rh(en)_2(CO_3)(OH)]^{+}$, 979
$RhC_5H_{18}N_4O_4$
$[Rh(en)_2(CO_3)(H_2O)]^{+}$, 969, 978
$RhC_5H_{19}N_4O_4$
$[Rh(en)_2(CO_3H)(H_2O)]^{+}$, 978
$RhC_5H_{20}N_6$
$[Rh(NH_3)_5(py)]^{3+}$, 985
$RhC_5H_{24}N_5O_2$
$[Rh(NH_3)_5(O_2CBu^t)]^{2+}$, 957
$RhC_5H_{25}ClN_5$
$[Rh(NH_2Me)_5Cl]^{2+}$, 964, 965
$RhC_5H_{27}N_5O$
$[Rh(NH_2Me)_5(H_2O)]^{3+}$, 964
$RhC_5N_5S_5$
$[Rh(SCN)_5]^{2-}$, 1054
$RhC_6H_9ClN_4O$
$[Rh(NO)Cl(MeCN)_3]^{+}$, 1072
$RhC_6H_9Cl_3N_3$
$RhCl_3(MeCN)_3$, 1005
$RhC_6H_{10}NO_8$
$Rh\{N(CH_2CO_2)_3\}(H_2O)_2$, 1046
$RhC_6H_{12}N_3O_6$
$Rh(Gly\text{-}O)_3$, 1044
$RhC_6H_{15}Cl_3N_3$
$Rh(HN\overline{CH_2CH_2})_3Cl_3$, 964
$RhC_6H_{16}N_4O_4$
$[Rh(en)_2(C_2O_4)]^{+}$, 967, 970, 976
$RhC_6H_{16}N_4O_6$
$[Rh(en)_2(CO_3)_2]^{-}$, 978
$RhC_6H_{17}ClN_6$
$[Rh(en)_2(en\text{-}H)Cl]^{3+}$, 969

$RhC_6H_{18}Cl_2N_4$
$[Rh\{(H_2NCH_2CH_2NHCH_2)_2\}Cl_2]^+$, 989, 1003, 1005
$[Rh\{(H_2NCH_2CH_2)_3N\}Cl_2]^+$, 990, 991
$RhC_6H_{18}Cl_3O_3S_3$
$RhCl_3(DMSO)_3$, 1053
$RhC_6H_{18}Cl_3S_3$
$RhCl_3(SMe_2)_3$, 1054
$RhC_6H_{18}O_6P_3S_6$
$Rh\{S_2P(OMe)_2\}_3$, 1040
$RhC_6H_{19}ClN_4$
$[Rh\{(H_2NCH_2CH_2NHCH_2)_2\}HCl]^+$, 990
$RhC_6H_{20}ClN_4O$
$[Rh\{(H_2NCH_2CH_2)_3N\}Cl(H_2O)]^{2+}$, 992
$RhC_6H_{20}Cl_2N_4$
$[Rh(pn)_2Cl_2]^+$, 981
$[Rh\{H_2N(CH_2)_3NH_2\}_2Cl_2]^+$, 979, 985, 988
$RhC_6H_{20}N_5O_2$
$[Rh(en)_2(O\text{-}Gly)]^{2+}$, 970, 971
$RhC_6H_{20}N_6$
$[Rh(en-2H)(en-H)_2]^-$, 966
$RhC_6H_{21}ClN_4O$
$[Rh\{H_2N(CH_2)_3NH_2\}_2(OH)Cl]^+$, 980
$RhC_6H_{21}N_3O_3$
$[Rh(1,4,7\text{-triazacyclononane})(H_2O)_3]^{3+}$, 993
$RhC_6H_{21}N_6$
$Rh(en-H)_3$, 966
$RhC_6H_{22}ClN_4O$
$[Rh\{H_2N(CH_2)_3NH_2\}_2(H_2O)Cl]^{2+}$, 980
$RhC_6H_{22}N_4O_2$
$[Rh\{H_2N(CH_2)_3NH_2\}_2(OH)_2]^+$, 980
$RhC_6H_{22}N_6$
$[Rh(en-H)_2(en)]^+$, 966
$RhC_6H_{23}N_4O_2$
$[Rh\{H_2N(CH_2)_3NH_2\}_2(H_2O)(OH)]^{2+}$, 980
$RhC_6H_{24}N_4O_2$
$[Rh\{H_2N(CH_2)_3NH_2\}_2(H_2O)_2]^{3+}$, 979
$RhC_6H_{24}N_6$
$[Rh(en)_3]^{3+}$, 902, 965, 966, 970–972, 981, 985, 994, 995, 998
RhC_6N_6
$[Rh(CN)_6]^{3-}$, 952
$RhC_6N_6S_6$
$[Rh(SCN)_6]^{3-}$, 1055, 1056
$RhC_6N_6Sc_6$
$[Rh(SeCN)_6]^{3-}$, 1055, 1056
RhC_6O_{12}
$[Rh(C_2O_4)_3]^{3-}$, 964, 977, 1049, 1050
$RhC_7H_3N_6$
$[Rh(CN)_5(MeCN)]^{2-}$, 952
$RhC_7H_{16}O_4P$
$RhH(PMe_3)(OAc)_2$, 948
$RhC_7H_{20}Cl_2N_4$
$[Rh\{H_2NCH_2CH_2NH_2CH_2)_2CH_2\}Cl_2]^+$, 990, 991
$RhC_7H_{20}N_6$
$[Rh(NH_3)_5(NCPh)]^{3+}$, 960, 962
$RhC_7H_{22}N_6O$
$[Rh(NH_3)_5(H_2NCOPh)]^{3+}$, 964
$RhC_8H_6ClN_4S_4$
$Rh\{\overline{NC(S)CH{=}CHNHC}S\}_2Cl$, 1048
$RhC_8H_{10}N_2O_8$
$[Rh\{HN(CH_2CO_2)_2\}_2]^-$, 1046
$RhC_8H_{12}Cl_2N_4O_4$
$[Rh(DMG)_2Cl_2]^-$, 995
$RhC_8H_{12}N_5O$
$[Rh(NO)(MeCN)_4]^{2+}$, 1072
$RhC_8H_{14}Cl_2N_2O_4$
$[Rh(O_2CCH_2CH_2NHCH_2CH_2NHCH_2CH_2CO_2)Cl_2]^-$, 1047
$RhC_8H_{14}Cl_2N_4O_4$
$[Rh(HDMG)_2Cl_2]^-$, 1014
$RhC_8H_{14}Cl_2S_4$
$[Rh(S_2CPr)_2Cl_2]^-$, 1054
$RhC_8H_{15}Cl_2N_4O_4$
$Rh(H_2DMG)(HDMG)Cl_2$, 1014
$RhC_8H_{17}ClN_5O_4$
$Rh(HDMG)_2(HN_3)Cl$, 1014
$RhC_8H_{18}F_3O_8P_2$
$Rh(O_2CCF_3)\{P(OMe)_3\}_2$, 908
$RhC_8H_{20}Cl_2N_4$
$[Rh(\overline{HNCH_2CH_2})_4Cl_2]^-$, 964
$RhC_8H_{20}Cl_2S_4$
$[Rh(MeSCH_2CH_2SMe)_2Cl_2]^+$, 1055
$RhC_8H_{20}N_4O_4$
$[Rh\{H_2N(CH_2)_3NH_2\}_2(C_2O_4)]^+$, 979
$RhC_8H_{20}S_4$
$[Rh(MeSCH_2CH_2SMe)_2]^+$, 1056
$RhC_8H_{24}ClF_8N_4P_4$
$RhCl(PF_2NMe_2)_4$, 924
$RhC_8H_{24}Cl_2N_4$
$[Rh(H_2NCHMeCHMeNH_2)_2Cl_2]^+$, 981
$RhC_8H_{24}F_8N_4P_4$
$[Rh(PF_2NMe_2)_4]^-$, 905
$RhC_8H_{24}N_6$
$[Rh(dien-H)_2]^+$, 966
$RhC_8H_{24}P_4S_2$
$RhS_2(PMe_2)_4$, 1038
$RhC_8H_{26}N_6$
$[Rh(dien)_2]^{3+}$, 966
$RhC_8H_{28}N_6$
$[Rh(en)(en\text{-}Me)_2]^{3+}$, 970
$RhC_8H_{37}N_8O_3$
$[\{Rh(en)_2(H_2O)\}_2(\mu\text{-}OH)]^{5+}$, 970
$RhC_9H_{15}S_6$
$[Rh(S_2CEt)_3$, 1054, 1056
$RhC_9H_{17}Cl_3NS_2$
$Rh(py)(SMe_2)_2Cl_3$, 1054
$RhC_9H_{18}ClN_6O_4S$
$Rh(HDMG)_2Cl(H_2NCSNH_2)$, 1014
$RhC_9H_{18}N_3O_6$
$Rh\{O_2CCH(NH_2)Me\}_3$, 1044
$RhC_9H_{18}N_3S_6$
$Rh(S_2CNMe_2)_3$, 1054, 1063
$RhC_9H_{18}N_4OS_6$
$[Rh(NO)(S_2CNMe_2)_3]^+$, 1072
$RhC_9H_{19}N_4O_5$
$Rh(HDMG)_2(H_2O)(Me)$, 1014
$RhC_9H_{21}ClN_5$
$[Rh(en)_2Cl(py)]^{2+}$, 974
$RhC_9H_{27}ClP_3$
$RhCl(PMe_3)_3$, 917, 918
$RhC_9H_{27}Cl_3O_9P_3$
$RhCl_3\{P(CH_2OH)_3\}_3$, 1028
$RhC_9H_{27}Cl_3P_3$
$RhCl_3(PMe_3)_3$, 1028
$RhC_9H_{27}P_3$
$[Rh(PMe_3)_3]^+$, 921
$RhC_9H_{28}Cl_2P_3$
$RhHCl_2(PMe_3)_3$, 1027
$RhC_9H_{30}N_6$
$[Rh(en\text{-}Me)_3]^{3+}$, 970
$[Rh(pn)_3]^{3+}$, 980
$[Rh\{H_2N(CH_2)_3NH_2\}_3]^{3+}$, 980
$RhC_9H_{43}Cl_2P_2$
$RhHCl_2(PBu^t{}_2Me)_2$, 1018
$RhC_{10}H_8ClF_{12}O_7$
$RhCl(hfacac)_2(H_2O)_3$, 1051
$RhC_{10}H_{10}Cl_3N_2$
$Rh(py)_2Cl_3$, 995
$RhC_{10}H_{12}N_2O_8$
$[Rh\{O_2CCH_2CH(CO_2)NHCH_2CH_2NHCH(CO_2)\text{-}CH_2CO_2\}]^-$, 1045
$RhC_{10}H_{13}N_2O_9$
$[Rh\{O_2CCH_2CH(CO_2)NHCH_2CH_2NHCH(CO_2)\text{-}CH_2CO_2\}(OH)]^{2-}$, 1045
$RhC_{10}H_{14}Cl_2N_2O_8$
$[Rh(H_2edta)Cl_2]^-$, 1004

$[Rh\{H_2(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}Cl_2]^-$, 1044
$RhC_{10}H_{14}N_2O_8$
$[Rh\{MeN(CH_2CO_2)_2\}_2]^-$, 1046
$RhC_{10}H_{14}N_2O_9$
$[Rh\{O_2CCH_2CH(CO_2)NHCH_2CH_2NHCH(CO_2)CH_2CO_2\}(H_2O)]^-$, 1045
$[Rh\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}(H_2O)]^-$, 1044
$RhC_{10}H_{18}N_3O_6$
$Rh(O_2CCH_2CH_2NHCH_2CH_2NHCH_2CH_2CO_2)$-(Gly-O), 1046
$RhC_{10}H_{20}Cl_2S_4$
$[Rh(1,4,8,11\text{-tetrathiacyclotetradecane})Cl_2]^+$, 1056
$RhC_{10}H_{21}Cl_2N_4O_2$
$RhCl_2(ON{=}CMeCMe_2NH)(HON{=}CMeCMe_2NH)$, 1013
$RhC_{10}H_{22}N_4O_4$
$[Rh(O_2CCH_2CH_2NHCH_2CH_2NHCH_2CH_2CO_2)(en)]^+$, 1047
$RhC_{10}H_{24}Cl_2N_4$
$[Rh(1,4,7,10\text{-tetraazacyclotetradecane})Cl_2]^+$, 993
$[Rh(1,4,8,11\text{-tetraazacyclotetradecane})Cl_2]^+$, 991, 992
$RhC_{10}H_{24}N_6O_4$
$[Rh(1,4,8,11\text{-tetraazacyclotetradecane})(NO_2)_2]^+$, 993
$RhC_{10}H_{24}N_{10}$
$[Rh(1,4,8,11\text{-tetraazacyclotetradecane})(N_3)_2]^+$, 993
$RhC_{10}H_{25}ClN_4O$
$[Rh(1,4,8,11\text{-tetraazacyclotetradecane})(Cl)(OH)]^-$, 993
$RhC_{10}H_{25}ClN_5$
$[Rh(HNCH_2CH_2)_5Cl]^{2+}$, 964
$RhC_{10}H_{25}N_7O$
$[Rh(1,4,8,11\text{-tetraazacyclotetradecane})(N_3)(OH)]^-$, 993
$RhC_{10}H_{26}ClN_4O$
$[Rh(1,4,8,11\text{-tetraazacyclotetradecane})Cl(H_2O)]^+$, 993
$RhC_{10}H_{26}N_7O$
$[Rh(1,4,8,11\text{-tetraazacyclotetradecane})(N_3)(H_2O)]^+$, 993
$RhC_{10}H_{27}N_4O_2$
$[Rh(1,4,8,11\text{-tetraazacyclotetradecane})(OH)(H_2O)]^{2+}$, 993
$RhC_{11}H_{13}Cl_3N_3Se_2$
$Rh(SeCNCH_2CH_2NCSe)Cl_3(4\text{-}H_2NC_6H_4Me)$, 1057
$RhC_{11}H_{14}N_2O_8$
$[Rh\{O_2CCH_2)_2N(CH_2)_3N(CH_2CO_2)_2\}]^-$, 1045
$RhC_{11}H_{16}N_2O_9$
$[Rh\{O_2CCH_2)_2NCHMeCH_2N(CH_2CO_2)_2\}(H_2O)]^-$, 1045
$RhC_{11}H_{20}N_3O_6$
$Rh(O_2CCH_2CH_2NHCH_2CH_2NHCH_2CH_2CO_2)$-$\{O_2CCH(NH_2)Me\}$, 1046
$RhC_{11}H_{23}ClN_4O_4P$
$Rh(HDMG)_2Cl(PMe_3)$, 1014
$RhC_{11}H_{24}Cl_3S_3$
$RhCl_3\{MeC(CH_2SEt)_3\}$, 1054
$RhC_{12}H_8Cl_4N_2$
$[Rh(phen)Cl_4]^-$, 997
$RhC_{12}H_{10}ClN_2$
$Rh(py)_2(CN)_2Cl$, 952
$RhC_{12}H_{10}ClN_4$
$Rh(py)_2(CN)_2Cl$, 995
$RhC_{12}H_{14}N_2O_{12}$
$[Rh\{N(CH_2CO_2)_2CH_2CO_2H\}_2]^-$, 1046
$RhC_{12}H_{16}N_2O_8$
$[Rh\{O_2CCH_2CH_2N(CH_2CO_2)CH_2CH_2N(CH_2CO_2)CH_2CH_2CO_2\}]^-$, 1045
$RhC_{12}H_{21}Cl_3N_3$
$RhCl_3(Pr^iCN)_3$, 1005
$RhC_{12}H_{21}S_6$
$Rh(S_2CPr)_3$, 1054
$RhC_{12}H_{24}Cl_3O_3S_3$
$RhCl_3(SCH_2CH_2OCH_2CH_2)_3$, 1054, 1055
$RhC_{12}H_{24}N_6$
$[Rh(1,4,8,11\text{-tetraazacyclotetradecane})(CN)_2]^+$, 993
$RhC_{12}H_{24}N_6S_2$
$Rh(1,4,8,11\text{-tetraazacyclotetradecane})(NCS)_2]^+$, 993
$RhC_{12}H_{29}N_{12}$
$Rh(1,1,7,7\text{-}Et_4dien)(N_3)_3$, 991
$RhC_{12}H_{30}Cl_2NOP_2$
$Rh(NO)Cl_2(PEt_3)_2$, 1070
$RhC_{12}H_{30}Cl_3S_3$
$RhCl_3(SEt_2)_3$, 1054
$RhC_{12}H_{30}N_8$
$[Rh(sepulchrate)]^{2+}$, 994
$[Rh(sepulchrate)]^{3+}$, 994
$RhC_{12}H_{30}O_6P_3S_6$
$Rh\{S_2P(OEt)_2\}_3$, 1054
$RhC_{12}H_{31}P_2$
$RhH(PEt_3)_2$, 920
$RhC_{12}H_{32}Br_2P_4$
$[RhBr_2(Me_2PCH_2CH_2PMe_2)_2]^+$, 1035
$RhC_{12}H_{32}Cl_2P_4$
$[RhCl_2(Me_2PCH_2CH_2PMe_2)_2]^+$, 1035, 1039
$RhC_{12}H_{32}P_4S_2$
$[RhS_2(Me_2PCH_2CH_2PMe_2)_2]^+$, 1037, 1039
$RhC_{12}H_{32}P_4Se_2$
$[RhSe_2(Me_2PCH_2CH_2PMe_2)_2]^+$, 1037
$RhC_{12}H_{33}ClP_4$
$[RhHCl(Me_2PCH_2CH_2PMe_2)_2]^+$, 1036, 1037
$RhC_{12}H_{34}P_4$
$[RhH_2(Me_2PCH_2CH_2PMe_2)_2]^+$, 1036, 1037
$RhC_{12}H_{36}Br_2O_{12}P_4$
$[RhBr_2\{P(OMe)_3\}_4]^+$, 1034
$RhC_{12}H_{36}N_6$
$[Rh(H_2NCHMeCHMeNH_2)_3]^{3+}$, 981
$RhC_{12}H_{36}O_6S_6$
$[Rh(DMSO)_6]^{3+}$, 1053
$RhC_{12}H_{36}P_4$
$[Rh(PMe_3)_4]^+$, 920, 921, 926, 1041
$RhC_{12}H_{37}BrO_{12}P_4$
$[RhHBr\{P(OMe)_3\}_4]^+$, 1033
$RhC_{12}H_{37}P_4$
$RhH(PMe_3)_4$, 924
$RhC_{12}H_{38}O_{12}P_4$
$[RhH_2\{P(OMe)_3\}_4]^+$, 1032
$RhC_{12}N_6S_6$
$[Rh\{S_2C{=}C(CN)_2\}_3]^{2-}$, 1063
$RhC_{12}N_6Se_6$
$[Rh\{Se_2C_2(CN)_2\}_3]^{3-}$, 1057
$RhC_{13}H_{25}Cl_2N_4O_2$
$RhCl_2\{ON{=}CMeCMe_2N(CH_2)_3NCMe_2CMe{=}NOH\}$, 1013
$RhC_{13}H_{27}F_4N_2O_2P_2$
$Rh(acac)\{PF_2(NEt_2)\}_2$, 908
$RhC_{14}H_6N_2O_8$
$[Rh\{2,6\text{-}py(CO_2)_2\}_2]^-$, 1047
$RhC_{14}H_{10}Cl_4N_2$
$[RhCl_4(PhCN)_2]^-$, 1005
$RhC_{14}H_{29}ClP_3$
$RhCl(PMe_3)_2(PMe_2Ph)$, 920
$RhC_{15}H_3F_{18}O_6$
$Rh(hfacac)_3$, 1050, 1051
$RhC_{15}H_{12}F_9O_6$
$Rh(CF_3COCHCOMe)_3$, 1050, 1051, 1052
$RhC_{15}H_{15}Cl_3N_3$
$Rh(py)_3Cl_3$, 995, 1003
$RhC_{15}H_{18}N_3O_{12}$
$Rh\{MeCOC(NO_2)COMe\}_3$, 1050
$RhC_{15}H_{21}N_6O_3S_3$
$[Rh\{N{=}C(OH)CH{=}CMeNCS\}_3]^{3+}$, 1048
$RhC_{15}H_{21}O_6$
$Rh(acac)_3$, 1050, 1051
$RhC_{15}H_{21}S_6$
$Rh(MeCSCHCSMe)_3$, 1056
$RhC_{15}H_{30}N_3O_6S_3$
$Rh\{O_2CCH(NH_2)CH_2CH_2SMe\}_3$, 1044

$RhC_{15}H_{30}N_3S_6$
$Rh\{S_2CNEt_2\}_3$, 1054
$RhC_{15}H_{45}O_{15}P_5$
$[Rh\{P(OMe)_3\}_5]^+$, 929, 930, 1033
$RhC_{16}H_{14}N_2O_2$
Rh(salen), 943
$RhC_{16}H_{14}N_2O_4$
Rh(salen)O_2, 943
$RhC_{16}H_{17}N_6O$
$[Rh(NO)(MeCN)_3(bipy)]^{2+}$, 1072
$RhC_{16}H_{22}Cl_2NO_3P_2$
$RhCl_2(NO_3)(PMe_2Ph)_2$, 1022
$RhC_{16}H_{22}Cl_3N_2S$
$Rh(bipy)(SPr_2)Cl_3$, 1054
$RhC_{16}H_{22}Cl_4P_2$
$[RhCl_4(PMe_2Ph)_2]^-$, 1016
$RhC_{16}H_{24}Cl_2N_8$
$[Rh(MeNCH{=}NCH{=}CH)_4Cl_2]^+$, 996
$RhC_{16}H_{40}ClF_8N_4P_4$
$RhCl(PF_2NEt_2)_4$, 924
$RhC_{16}H_{40}IF_8N_4P_4$
$RhI(PF_2NEt_2)_4$, 924
$RhC_{17}H_{15}ClN_3O_4$
$Rh(py)_3(C_2O_4)Cl$, 995
$RhC_{18}H_{22}O_2P_2S_4$
$[Rh(S_2CO)_2(PMe_2Ph)_2]^-$, 1016
$RhC_{18}H_{28}Cl_2P_3S_2$
$RhCl_2(S_2PMe_2)(PMe_2Ph)_2$, 1022
$RhC_{18}H_{38}Cl_3N_2P_2$
$RhCl_3(PEt_3)_2(PhNHNH_2)$, 1029
$RhC_{18}H_{42}ClN_2P_2$
$RhCl(N_2)(PPr^i_3)_2$, 920
$RhC_{18}H_{42}Cl_2P_2$
$RhCl_2(PBu^t_2Me)_2$, 932
$RhC_{18}H_{42}Cl_3S_3$
$RhCl_3(SPr_2)_3$, 1054
$RhC_{18}H_{43}ClP_2$
$RhH_2Cl(PBu^t_2Me)_2$, 1018
$RhC_{18}H_{43}Cl_2P_2$
$RhHCl_2(PBu^t_2Me)_2$, 932
$RhC_{18}H_{43}N_2P_2$
$RhH(N_2)(PPr^i_3)_2$, 920
$RhC_{18}H_{43}P_2$
$RhH(PPr^i_3)_2$, 906
$RhC_{18}H_{45}Cl_3P_3$
$RhCl_3(PEt_3)_3$, 1028
$RhC_{18}H_{45}N_6O_3$
$[Rh_2(1,4,7\text{-}Me_3\text{-}1,4,7\text{-triazacyclononane})_2(\mu\text{-}OH)_3]^{3+}$, 993
$RhC_{18}H_{47}ClN_2P_2$
$RhCl(N_2)(PPr^i_3)_2$, 919
$RhC_{18}H_{47}ClO_2P_2S$
$RhCl(SO_2)(PPr^i_3)_2$, 920
$RhC_{18}H_{48}O_2P_2$
$[RhH_2(PPr^i_3)_2(H_2O)_2]^+$, 1033
$RhC_{19}H_{27}Cl_2OP_2S_2$
$RhCl_2(S_2COEt)(PMe_2Ph)_2$, 1022
$RhC_{19}H_{28}Cl_2NP_2S_2$
$RhCl_2(S_2CNMe_2)(PMe_2Ph)_2$, 1022
$RhC_{20}H_{16}Cl_2N_4$
$[Rh(bipy)_2Cl_2]^+$, 942, 981, 997–1000
$RhC_{20}H_{16}N_4$
$Rh(bipy)_2$, 1000
$[Rh(bipy)_2]^-$, 1000
$[Rh(bipy)_2]^+$, 1000, 1001
$RhC_{20}H_{17}N_4$
$[Rh(bipy)_2H]^{2+}$, 1001
$RhC_{20}H_{20}Br_2N_4$
$[Rh(py)_4Br_2]^+$, 996
$RhC_{20}H_{20}Cl_2N_4$
$[Rh(py)_4Cl_2]^+$, 995, 996, 998, 1003–1005, 1048
$RhC_{20}H_{21}Cl_2N_6O_6$
$[Rh(py)_4Cl_2][H(NO_3)_2]$, 996
$RhC_{20}H_{24}N_4O_2$
$[Rh(py)_4(H_2O)_2]^{3+}$, 995
$RhC_{20}H_{25}Br_4N_4O_2$
$[Rh(py)_4Br_2]Br{\cdot}HBr{\cdot}2H_2O$, 996
$RhC_{20}H_{27}O_2P_2S_4$
$Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2$, 1022
$RhC_{20}H_{36}N_5O$
$[Rh(NO)(Bu^tCN)_4]^{2+}$, 1072
$RhC_{20}H_{47}Cl_2P_2$
$RhHCl_2(PBu^tPr_2)_2$, 1018
$RhC_{21}H_{15}Cl_3N_3$
$RhCl_3(PhCN)_3$, 1005
$RhC_{21}H_{19}ClN_3O_2$
Rh(salen)pyCl, 1047
$RhC_{21}H_{19}N_3O_2$
Rh(salen)py, 943, 1047
$RhC_{21}H_{36}N_9S_3$
$Rh\{H_2NC(S)NN{=}\overline{C(CH_2)_5}\}_3$, 1048
$RhC_{21}H_{36}S_6$
$Rh\{MeC(SEt)CHCSMe\}_3$, 1056
$RhC_{21}H_{39}N_9S_3$
$[Rh\{H_2NC(S)NHN{=}\overline{C(CH_2)_5}\}_3]^{3+}$, 1048
$RhC_{22}H_{22}N_3O_2$
RhMe(salen)py, 1047
$[RhMe(salen)py]^+$, 1062
$RhC_{22}H_{50}Cl_2NP_2$
$RhHCl_2(PBu^tPr_2)_2(MeCN)$, 1027
$RhC_{23}H_{47}Cl_3NP_2$
$RhCl_3(PPr_3)_2(py)$, 1029
$RhC_{24}H_{16}Cl_2N_4$
$[Rh(phen)_2Cl_2]^+$, 997, 998
$RhC_{24}H_{16}N_4$
$[Rh(phen)_2]^+$, 982
$RhC_{24}H_{20}Cl_2N_4O_4$
$[Rh(4\text{-}pyCHO)_4Cl_2]^+$, 996
$RhC_{24}H_{24}Cl_2N_4$
$[Rh(3,3'\text{-}Me_2bipy)_2Cl_2]^+$, 999
$RhC_{24}H_{30}Cl_3S_3$
$RhCl_3(PhSEt)_3$, 1054
$RhC_{24}H_{33}BrCl_2P_3$
$RhCl_2Br(PMe_2Ph)_3$, 1029
$RhC_{24}H_{33}ClP_3$
$RhCl(PMe_3)_2(PPh_3)$, 920
$RhC_{24}H_{33}Cl_2NO_2P_3$
$RhCl_2(NO_2)(PMe_2Ph)_3$, 1029
$RhC_{24}H_{33}Cl_2N_3P_3$
$RhCl_2(N_3)(PMe_2Ph)_3$, 1029
$RhC_{24}H_{33}Cl_3P_3$
$RhCl_3(PMe_2Ph)_3$, 1028, 1030, 1034
$RhC_{24}H_{33}N_9P_3$
$Rh(N_3)_3(PMe_2Ph)_3$, 1029
$RhC_{24}H_{34}ClP_3$
$RhHCl_2(PMe_2Ph)_3$, 1026
$RhC_{24}H_{35}Cl_2OP_3$
$[RhCl_2(PMe_2Ph)_3(OH_2)]^+$, 1034
$RhC_{24}H_{55}N_2P_2$
$RhH(N_2)(PBu^t_3)_2$, 919, 920
$RhC_{24}H_{56}ClP_2$
$RhH_2Cl(PBu^t_3)_2$, 1018
$RhC_{24}H_{61}O_{12}P_4$
$RhH\{P(OEt)_3\}_4$, 921
$RhC_{25}H_{33}Cl_2NOP_3$
$RhCl_2(NCO)(PMe_2Ph)_3$, 1029
$RhC_{25}H_{33}Cl_2NP_3S$
$RhCl_2(NCS)(PMe_2Ph)_3$, 1029
$RhCl_2(SCN)(PMe_2Ph)_3$, 1029
$RhC_{25}H_{45}O_{15}P_5$
$[Rh\{P(OCH_2)_3CMe\}_5]^+$, 929
$RhC_{25}H_{49}ClNOP_2S$
$RhCl(PPr^i_3)_2(4\text{-}MeC_6H_4NSO)$, 920
$RhC_{26}H_{24}ClN_2O_3P_2$
Rh(NO)Cl(NO_2)(dppe), 1070
$RhC_{26}H_{24}Cl_2P_2$

$RhCl_2$(dppe), 929, 933
$RhC_{26}H_{27}ClN_4O_4P$
$Rh(DMG)_2(PPh_3)Cl$, 950
$RhC_{26}H_{29}ClN_4O_4P$
$Rh(HDMG)_2Cl(PPh_3)$, 1014
$RhC_{26}H_{29}ClN_4O_4Sb$
$Rh(HDMG)_2Cl(SbPh_3)$, 1014
$RhC_{26}H_{29}ClO_4P$
$RhCl(acac)_2(PPh_3)$, 1017
$RhC_{26}H_{30}ClN_4O_4P$
$[Rh(HDMG)(H_2DMG)Cl(PPh_3)]^+$, 1014
$RhC_{26}H_{30}N_4O_4P$
$Rh(HDMG)_2H(PPh_3)$, 1014
$RhC_{26}H_{39}Cl_2P_4S_2$
$RhCl_2(S_2PMe_2)(PMe_2Ph)_3$, 1030
$RhC_{27}H_{24}ClOP_2$
RhCl(CO)(dppe), 926
$RhC_{27}H_{33}N_3O_3P_3$
$Rh(NCO)_3(PMe_2Ph)_3$, 1029
$RhC_{27}H_{33}N_3P_3S_3$
$Rh(SCN)_3(PMe_2Ph)_3$, 1029
$RhC_{27}H_{39}Cl_2NP_3S_2$
$RhCl_2(S_2CNMe_2)(PMe_2Ph)_3$, 1030
$RhC_{27}H_{63}Cl_3O_3P_3$
$RhCl_3(PBu_3)_2\{P(OMe)_3\}$, 1028
$RhC_{27}H_{63}Cl_3P_3$
$RhCl_3(PPr_3)_3$, 1029
$RhC_{28}H_{32}Cl_2P_3S_2$
$RhCl_2(S_2PPh_2)(PMe_2Ph)_2$, 1022
$RhC_{28}H_{32}O_2P_2$
$[Rh(dppe)(MeOH)_2]^+$, 1075
$RhC_{28}H_{53}O_{12}P_4$
$RhH\{P(OCH_2)_3CPr\}_4$, 921
$RhC_{29}H_{38}Cl_2NP_3$
$[RhCl_2(PMe_2Ph)_3(py)]^+$, 1034
$RhC_{29}H_{63}Cl_3P_3$
$RhCl_3\{Bu^tCH_2P\{CH_2CH_2P(CH_2Bu^t)_2\}_2\}$, 1042
$RhC_{30}H_{22}N_6$
$[Rh(terpy)_2]^{3+}$, 997
$RhC_{30}H_{24}N_6$
$[Rh(bipy)_3]^{2+}$, 930, 1000, 1001
$[Rh(bipy)_3]^{3+}$, 997–1001
$RhC_{30}H_{38}BO_6P_2$
$[Rh(BPh_4)\{P(OMe)_3\}_2]$, 930
$RhC_{30}H_{45}Cl_3P_3$
$RhCl_3(PEt_2Ph)_3$, 1028
$RhC_{30}H_{45}O_6P_4S_6$
$Rh\{S_2P(OEt)_2\}_3(PPh_3)$, 1017
$RhC_{30}H_{46}Cl_2P_3$
$RhHCl_2(PEt_2Ph)_3$, 1026
$RhC_{30}H_{62}Cl_3N_2P_2$
$RhCl_3(PBu_3)_2(PhNHNH_2)$, 1029
$RhC_{30}H_{70}Cl_2P_3$
$RhHCl_2(PBu^tPr_2)_3$, 1027
$RhC_{30}H_{75}O_{15}P_5$
$[Rh\{P(OEt)_3\}_5]^+$, 929
$RhC_{31}H_{33}Cl_2F_5NP_3$
$[RhCl_2(PMe_2Ph)_3(NCC_6F_5)]^+$, 1034
$RhC_{32}H_{16}ClN_8$
Rh(phthalocyanine)Cl, 1011
$RhC_{32}H_{24}N_6$
$[Rh(bipy)_2(phen)]^{3+}$, 999
$RhC_{32}H_{28}N_4$
$[Rh(CNC_6H_4Me\text{-}4)_4]^+$, 943
$RhC_{32}H_{34}Cl_2O_4P_2$
$[RhCl_2(Ph_2PCH_2CO_2Et)_2]^+$, 1039
$RhC_{32}H_{34}Cl_3O_4P_2$
$RhCl_3(Ph_2PCH_2CO_2Et)_2$, 1023
$RhC_{32}H_{38}O_2P_2S_2$
$[RhO_2(Ph_2PCH_2CH_2SEt)_2]^+$, 1037
$RhC_{32}H_{40}Cl_2P_4$
$[RhCl_2(PhMePCH_2CH_2PMePh)_2]^+$, 1039
$RhC_{32}H_{40}O_2P_4$
$[RhO_2(PhMePCH_2CH_2PMePh)_2]^+$, 1038
$RhC_{32}H_{40}O_4P_4S$
$[Rh(O_2SO_2)(PhMePCH_2CH_2PMePh)_2]^+$, 1038
$RhC_{32}H_{40}O_6N_2P_4$
$[Rh(ONO_2)_2(PhMePCH_2CH_2PMePh)_2]^+$, 1038
$RhC_{32}H_{41}NO_4P_4$
$[Rh(OH)(NO_3)(PhMePCH_2CH_2PMePh)_2]^+$, 1039
$RhC_{32}H_{44}Cl_2P_4$
$[RhCl_2(PMe_2Ph)_4]^+$, 1034
$RhC_{32}H_{44}O_2P_4$
$[Rh(O_2)(PMe_2Ph)_4]^+$, 1034
$RhC_{32}H_{46}Cl_2P_2$
$RhCl_2(PhC{\equiv}CPBu^t_2)_2$, 932
$RhC_{33}H_{20}ClN_8O$
Rh(phthalocyanine)(MeOH)Cl, 1011
$RhC_{33}H_{43}ClO_2P_4S$
$[RhCl(O_2SMe)(PhMePCH_2CH_2PMePh)_2]^+$, 1039
$RhC_{33}H_{45}O_6$
Rh{3-(hydroxymethylene)camphorate}$_3$, 1053
$RhC_{33}H_{48}Cl_3N_{15}$
$[Rh\{4\text{-}ClC_6H_4NHC(=NH)NHC(=NH)NHPr^i\}_3]^{4+}$, 1063
$RhC_{34}H_{24}N_6$
$[Rh(bipy)(phen)_2]^{3+}$, 999
$RhC_{36}H_{24}N_6$
$[Rh(phen)_3]^{2+}$, 1000
$[Rh(phen)_3]^{3+}$, 998, 999, 1001
$RhC_{36}H_{30}BrClNOP_2$
$Rh(NO)ClBr(PPh_3)_2$, 1070
$RhC_{36}H_{30}Br_2NOP_2$
$Rh(NO)Br_2(PPh_3)_2$, 1069
$RhC_{36}H_{30}Br_2NO_7P_2$
$Rh(NO)Br_2\{P(OPh)_3\}_2$, 1069
$RhC_{36}H_{30}Br_2O_6P_2$
$RhBr_2\{P(OPh)_3\}_2$, 1070
$RhC_{36}H_{30}Br_4P_2$
$[RhBr_4(PPh_3)_2]^-$, 1016
$RhC_{36}H_{30}ClF_3P_3$
$RhCl(PF_3)(PPh_3)_2$, 910, 918
$RhC_{36}H_{30}ClN_2O_3P_2$
$Rh(NO)Cl(NO_2)(PPh_3)_2$, 1070, 1071
$RhC_{36}H_{30}ClN_2P_2$
$RhCl(N_2)(PPh_3)_2$, 919
$RhC_{36}H_{30}ClO_2P_2$
$RhCl(O_2)(PPh_3)_2$, 1021
$RhC_{36}H_{30}ClO_2P_2S$
$RhCl(SO_2)(PPh_3)_2$, 911, 918
$RhC_{36}H_{30}ClP_2$
$RhCl(PPh_3)_2$, 906
$RhC_{36}H_{30}ClP_6$
$RhCl(P_4)(PPh_3)_2$, 920
$RhC_{36}H_{30}Cl_2NOP_2$
$Rh(NO)Cl_2(PPh_3)_2$, 1067, 1068, 1069, 1073
$RhC_{36}H_{30}Cl_2NP_2S$
$Rh(NS)Cl_2(PPh_3)_2$, 1067, 1074
$RhC_{36}H_{30}Cl_4P_2$
$[RhCl_4(PPh_3)_2]^-$, 1016
$RhC_{36}H_{30}I_2NOP_2$
$Rh(NO)I_2(PPh_3)_2$, 1070
$RhC_{36}H_{30}NOP_2$
Rh(5-methyl-8-quinolinolate)($Ph_2PCH{=}CHPPh_2$), 914
$Rh(NO)(PPh_3)_2$, 1068
$RhC_{36}H_{30}NO_3P_2S$
$Rh(NO)(PPh_3)_2(SO_2)$, 1067, 1068
$RhC_{36}H_{30}NO_5P_2S$
$Rh(NO)(SO_4)(PPh_3)_2$, 1068, 1070
$RhC_{36}H_{30}N_2O_2P_2$
$[Rh(NO)_2(PPh_3)_2]^+$, 1067, 1073, 1074
$RhC_{36}H_{30}N_3O_7P_2$
$Rh(NO)(NO_3)_2(PPh_3)_2$, 1067, 1070
$RhC_{36}H_{30}P_3S_6$
$Rh(S_2PPh_2)_3$, 1055
$RhC_{36}H_{31}Cl_2P_2$

$RhHCl_2(PPh_3)_2$, 1018
$RhSb_2C_{36}H_{31}Cl_2$
$RhHCl_2(SbPh_3)_2$, 1018
$RhGeC_{36}H_{31}Cl_4P_2$
$RhHCl(GeCl_3)(PPh_3)_2$, 1020
$RhC_{36}H_{31}P_2$
$RhH(PPh_3)_2$, 920
$RhC_{36}H_{32}ClP_2$
$RhH_2Cl(PPh_3)_2$, 1018
$RhC_{36}H_{32}ClP_2S$
$RhHCl(HS)(PPh_3)_2$, 1018
$RhC_{36}H_{33}Cl_3P_3$
$RhCl_3(PHPh_2)_3$, 1028, 1029
$RhC_{36}H_{36}N_6$
$[Rh(3,3'\text{-}Me_2bipy)_3]^{3+}$, 999
$RhC_{36}H_{37}ClO_2P_3$
$Rh(O_2)Cl\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1042
$RhC_{36}H_{37}ClO_2P_3S$
$RhCl(SO_2)\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1041
$RhC_{36}H_{37}ClO_4P_3S$
$Rh(SO_4)Cl\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1042
$RhC_{36}H_{37}ClP_3$
$RhCl\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1041
$RhC_{36}H_{37}ClP_3S_2$
$Rh(S_2)Cl\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1042
$RhC_{36}H_{37}Cl_3P_3$
$RhCl_3\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1043
$RhC_{36}H_{37}NOP_3$
$Rh(NO)\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1067
$RhC_{36}H_{38}ClP_3$
$RhHCl\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1043
$RhC_{36}H_{38}Cl_2P_3$
$RhHCl_2\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1042
$RhC_{36}H_{39}ClP_3$
$RhH_2Cl\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1042
$RhC_{36}H_{44}ClN_4$
Rh(octaethylporphyrin)Cl, 1007, 1009
$RhC_{36}H_{44}ClN_5O$
Rh(octaethylporphyrin)Cl(NO), 1007
$RhC_{36}H_{44}N_4$
[Rh(octaethylporphyrin)]$^-$, 1007
$RhC_{36}H_{44}N_4O_2$
Rh(octaethylporphyrin)(O_2), 1007, 1052
$RhC_{36}H_{44}N_5O$
Rh(octacthylporhyrin)(NO), 1007
$RhC_{36}H_{44}N_6O_2$
Rh(octaethylporphyrin)$(NO)_2$, 1008
$RhC_{36}H_{45}N_4$
RhH(octaethylporphyrin), 943, 1007
$RhC_{36}H_{50}N_6$
$[Rh(Me_2NH)_2(etioporphyrin\ I)]^+$, 1007
$RhC_{36}H_{51}O_6$
Rh(3-acetylcamphorate)$_3$, 1053
$RhC_{36}H_{57}Cl_3P_3$
$RhCl_3(PPhPr_2)_3$, 1028
$RhC_{36}H_{61}ClP_3$
$RhCl\{PhP\{CH_2CH_2CH_2P(C_6H_{11})_2\}_2\}$, 1041
$RhC_{36}H_{66}ClN_2P_2$
$RhCl\{P(C_6H_{11})_3\}_2N_2$, 907, 918
$RhC_{36}H_{66}ClO_2P_2S$
$RhCl(SO_2)\{P(C_6H_{11})_3\}_2$, 907
$RhC_{36}H_{66}ClP_2$
$RhCl\{P(C_6H_{11})_3\}_2$, 907
$RhC_{36}H_{66}Cl_2P_2$
$RhCl_2\{P(C_6H_{11})_3\}_2$, 929, 932
$RhC_{36}H_{66}FP_2$
$RhF\{P(C_6H_{11})_3\}_2$, 906
$RhC_{36}H_{67}BrClP_2$
$RhHClBr\{P(C_6H_{11})_3\}_2$, 1018
$RhC_{36}H_{67}Cl_2P_2$
$RhHCl_2\{P(C_6H_{11})_3\}_2$, 1018
$RhC_{36}H_{67}N_2P_2$
$RhH(N_2)\{P(C_6H_{11})_3\}_2$, 907
$RhC_{36}H_{67}P_2$
$RhH\{P(C_6H_{11})_3\}_2$, 907
$RhC_{36}H_{68}ClP_2$
$RhH_2Cl\{P(C_6H_{11})_3\}_2$, 1018
$RhC_{36}H_{80}Cl_2P_4$
$[RhCl_2(Bu^t{}_2PCH_2CH_2PBu^t{}_2)_2]^+$, 1039
$RhC_{36}H_{81}Br_3P_3$
$RhBr_3(PBu_3)_3$, 1031
$RhC_{36}H_{81}Cl_3P_3$
$RhCl_3(PBu_3)_3$, 1025, 1029
$RhC_{37}H_{30}NO_2P_2$
$Rh(CN)(O_2)(PPh_3)_2$, 1021
$[Rh(NO)(CO)(PPh_3)_2]^{2+}$, 1073
$RhC_{37}H_{32}NP_2$
$RhH_2(CN)(PPh_3)_2$, 1018
$RhC_{37}H_{33}Cl_2O_2P_2S$
$RhCl_2(SO_2Me)(PPh_3)_2$, 1022
$RhC_{37}H_{33}I_2P_2$
$RhMe(PPh_3)_2I_2$, 1007
$RhC_{37}H_{37}ClO_3P_3$
$Rh(CO_3)Cl\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1042
$RhC_{37}H_{47}N_4$
RhMe(octaethylporphyrin), 1007, 1009
$RhC_{38}H_{30}N_3OP_2S_2$
$Rh(NO)(CNS)_2(PPh_3)_2$, 1070
$Rh(NO)(NCS)_2(PPh_3)_2$, 1067
$RhC_{38}H_{30}N_3P_2S_3$
$Rh(NCS)_3(PPh_3)_2$, 1022
$RhC_{38}H_{32}ClN_2P_2$
$RhHCl(CN)(PPh_3)_2(HCN)$, 1022
$RhC_{38}H_{33}ClNP_2$
$RhCl(PPh_3)_2(MeCN)$, 920
$RhC_{38}H_{33}ClN_2OP_2$
$[Rh(NO)Cl(MeCN)(PPh_3)_2]^-$, 1072
$RhC_{38}H_{38}Cl_2N_2P_2$
$[RhCl_2(PEtPh_2)_2(bipy)]^+$, 1034
$RhC_{38}H_{39}ClN_2P_2$
$[RhHCl(PEtPh_2)_2(bipy)]^+$, 1033
$RhC_{38}H_{40}NP_3$
$[Rh(MeCN)\{PhP(CH_2CH_2CH_2PPh_2)_2\}]^+$, 1041
$RhC_{38}H_{44}ClNO_4P_4S$
$[RhCl(4\text{-}O_2SC_6H_4NO_2)(PhMePCH_2CH_2PMePh)_2]^+$, 1039
$RhC_{38}H_{44}N_4O_4$
Rh(mesoporphyrin IX diethylester), 1006
$RhC_{39}H_{30}F_6NP_2$
$Rh\{N{=}C(CF_3)_2\}(PPh_3)_2$, 907
$RhC_{39}H_{36}NO_2P_2S_2$
$Rh(O_2)(S_2CNMe_2)(PPh_3)_2$, 1021
$RhC_{39}H_{39}Cl_3P_3$
$RhCl_3(PMePh_2)_3$, 1029
$RhC_{39}H_{39}NOP_3$
$Rh(NO)(PMePh_2)_3$, 1067
$RhGeC_{39}H_{40}ClP_2$
$RhHCl(GeMe_3)(PPh_3)_2$, 1020
$RhC_{39}H_{40}Cl_2P_3$
$RhHCl_2(PMePh_2)_3$, 1026
$RhC_{39}H_{47}ClO_2P_4S$
$[RhCl(4\text{-}O_2SC_6H_4Me)(PhMePCH_2CH_2PMePh)_2]^+$, 1039
$RhC_{40}H_{30}F_6NO_5P_2$
$Rh(NO)(O_2CCF_3)_2(PPh_3)_2$, 1070
$RhC_{40}H_{30}N_4P_2S_4$
$[Rh(NCS)_4(PPh_3)_2]^-$, 1016
$[Rh(SCN)_4(PPh_3)_2]^-$, 1015
$RhC_{40}H_{36}NO_5P_2$
$Rh(NO)(OAc)_2(PPh_3)_2$, 1070, 1071
$RhC_{40}H_{36}N_3OP_2$
$[Rh(NO)(MeCN)_2(PPh_3)_2]^{2+}$, 1072
$RhC_{40}H_{38}Cl_2N_2P_2$
$[RhCl_2(PEtPh_2)_2(phen)]^+$, 1034
$RhC_{40}H_{38}N_2P_2$
$[RhH_2(PPh_3)_2(MeCN)_2]^+$, 1032

$RhC_{40}H_{38}O_2P_2S_2$
$[RhO_2(Ph_2PCH_2CH_2SPh)_2]^+$, 1037
$RhC_{40}H_{39}ClN_2P_2$
$[RhHCl(PEtPh_2)_2(phen)]^+$, 1033
$RhC_{40}H_{44}O_2P_2$
$[RhH_2(PPh_3)_2(EtOH)_2]^+$, 1032
$RhC_{40}H_{60}ClO_8P_4$
$RhCl\{PPh(OEt)_2\}_4$, 924
$RhC_{40}H_{61}O_8P_4$
$RhH\{PPh(OEt)_2\}_4$, 923
$RhC_{40}H_{74}N_2P_2$
$[RhH_2\{P(C_6H_{11})_3\}_2(MeCN)_2]^+$, 1032
$RhC_{41}H_{37}ClO_4P_2$
$Rh(PPh_3)_2(OH)Cl(acac)$, 1051
$RhC_{41}H_{37}O_2P_2$
$Rh(acac)(PPh_3)_2$, 908
$RhC_{41}H_{37}O_8P_2$
$Rh(acac)\{P(OPh)_3\}_2$, 908
$RhC_{41}H_{38}ClO_4P_2$
$Rh(PPh_3)_2(OOH)Cl(acac)$, 1051
$RhC_{41}H_{39}Cl_3P_3$
$RhCl_3\{MeC(CH_2PPh_2)_3\}$, 1043
$RhC_{41}H_{39}NOP_3$
$Rh(NO)\{MeC(CH_2PPh_2)_3\}$, 1068
$RhC_{41}H_{40}N_2OP_2S_2$
$[Rh(NO)(S_2CNEt_2)(PPh_3)_2]^+$, 1072
$RhC_{41}H_{72}Cl_2NP_2$
$RhHCl_2\{P(C_6H_{11})_3\}_2(py)$, 1019
$RhC_{42}H_{30}Cl_8O_2P_2$
$RhCl(C_6Cl_4O_2)(PPh_3)_2$, 1022
$RhC_{42}H_{35}Cl_2N_2P_2$
$RhCl_2(N_2Ph)(PPh_3)_2$, 1022
$RhC_{42}H_{35}OP_2$
$Rh(OPh)(PPh_3)_2$, 907
$RhC_{42}H_{36}Cl_3N_3P_3$
$RhCl_3(Ph_2PCH_2CN)_3$, 1023
$RhC_{42}H_{36}N_6$
$[Rh(4,4'\text{-}Me_2phen)_3]^{3+}$, 1002
$RhC_{42}H_{39}N_4OP_2$
$[Rh(NO)(MeCN)_3(PPh_3)_2]^{2+}$, 1073
$RhC_{42}H_{40}NO_5P_2$
$Rh(NO)(O_2CEt)_2(PPh_3)_2$, 1071
$RhC_{42}H_{42}ClN_2P_3$
$Rh(N_2Ph)Cl\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 1043
$RhC_{42}H_{42}Cl_2NOP_2$
$Rh(NO)(Cl_2)\{P(C_6H_4Me\text{-}4)_3\}_2$, 1068
$RhC_{42}H_{42}Cl_2P_2$
$RhCl_2\{P(C_6H_4Me\text{-}2)_3\}_2$, 932
$RhC_{42}H_{42}N_3O_2P_2S_2$
$Rh(O_2)\{Me_2NC(S)NC(S)NMe_2\}(PPh_3)_2$, 1021
$RhC_{42}H_{44}O_2P_2$
$[RhH_2(PPh_3)_2(Me_2CO)_2]^+$, 1032
$RhC_{42}H_{45}Cl_3P_3$
$RhCl_3(PEtPh_2)_3$, 1027, 1029
$RhC_{42}H_{46}Cl_2P_3$
$RhHCl_2(PEtPh_2)_3$, 1026, 1027
$RhC_{42}H_{47}ClP_3$
$RhH_2Cl(PEtPh_2)_3$, 1026
$RhC_{42}H_{69}Cl_3P_3$
$RhCl_3(PBu_2Ph)_3$, 1028
$RhC_{43}H_{35}ClNO_2P_2$
$Rh(NO)Cl(PhCO)(PPh_3)_2$, 1067, 1070
$RhC_{43}H_{37}Cl_2O_2P_2S$
$RhCl_2(O_2SC_6H_4Me\text{-}4)(PPh_3)_2$, 1022
$RhC_{43}H_{38}ClP_2S$
$RhHCl(4\text{-}SC_6H_4Me)(PPh_3)_2$, 1018
$RhC_{44}H_{24}N_4O_{12}S_4$
$Rh\{tetra\text{-}(4\text{-}sulfonatophenyl)porphyrin\}$, 1008
$RhC_{44}H_{26}N_4O_{13}S_4$
$[Rh\{tetra\text{-}(4\text{-}sulfonatophenyl)porphyrin\}(H_2O)]^{3-}$, 1007
$RhC_{44}H_{26}N_4O_{14}S_4$
$[Rh\{tetra\text{-}(4\text{-}sulfonatophenyl)porphyrin\}(OH)_2]^{5-}$, 1008
$RhC_{44}H_{28}ClN_4$
$Rh(tetraphenylporphyrin)Cl$, 1007
$RhC_{44}H_{28}N_4O_2$
$Rh(O_2)(tetraphenylporphyrin)$, 1052
$RhC_{44}H_{28}N_4O_{14}S_4$
$[Rh\{tetra\text{-}(4\text{-}sulfonatophenyl)porphyrin\}(H_2O)_2]^{3-}$, 1008, 1009
$RhC_{44}H_{28}N_5O$
$Rh(tetraphenylporphyrin)(NO)$, 1007
$RhC_{44}H_{34}N_5O$
$Rh(tetraphenylporphyrin)(CONEt_2)$, 1009
$RhC_{44}H_{40}F_6N_3P_2$
$Rh\{N{=}C(CF_3)_2\}\{C(NMeCH_2)_2\}(PPh_3)_2$, 907
$RhC_{44}H_{43}ClNP_2$
$RhH_2Cl(PPh_3)(PhCHMeNH_2)$, 1026
$RhC_{45}H_{28}ClN_4O$
$Rh(tetraphenylporphyrin)Cl(CO)$, 1009
$RhC_{45}H_{39}ClP_2S_2$
$RhCl(SSCH_2CPhCH_2)(PPh_3)_2$, 1022
$RhC_{45}H_{41}N_2O_2P_2S$
$Rh(O_2)\{SC(NPh)NMe_2\}(PPh_3)_2$, 1021
$RhC_{45}H_{51}Cl_3P_3$
$RhCl_3(PPh_2Pr)_3$, 1029
$RhC_{46}H_{30}Cl_7S_2P_2$
$RhCl(C_{10}Cl_6S_2)(PPh_3)_2$, 1022
$RhC_{46}H_{40}N_2P_2$
$[RhH_2(PPh_3)_2(bipy)]^+$, 1032, 1033
$RhC_{46}H_{43}N_7OP$
$Rh(NO)(4\text{-}MeC_6H_4NNNC_6H_4Me\text{-}4)_2(PPh_3)$, 1071
$RhC_{47}H_{33}N_4O_2$
$Rh(tetraphenylporphyrin)(CO_2Et)$, 1009
$RhC_{48}H_{40}I_2O_2P_2S_2$
$RhI_2\{S_2P(OPh)_2\}(PPh_3)_2$, 1022
$RhC_{48}H_{40}O_2P_3S_2$
$Rh\{S_2P(OPh)_2\}(PPh_3)_2$, 908
$RhC_{48}H_{41}ClP_3S$
$RhHCl(2\text{-}SC_6H_4PHPh)(PPh_3)_2$, 1022
$RhC_{48}H_{42}N_3P_2$
$RhH_2(PhNNNPh)(PPh_3)_2$, 1022
$RhC_{48}H_{44}P_4$
$[Rh(PHPh_2)_4]^+$, 925
$RhC_{48}H_{52}I_2P_3S_2$
$RhI_2\{S_2P(C_6H_{11})_2\}(PPh_3)_2$, 1022
$RhC_{48}H_{52}P_3S_2$
$Rh\{S_2P(C_6H_{11})_2\}(PPh_3)_2$, 908
$RhC_{48}H_{57}Cl_3P_3$
$RhCl_3(PBuPh_2)_3$, 1029
$RhC_{48}H_{110}P_4$
$[RhH_2(PBu_3)_4]^+$, 1032
$RhC_{50}H_{30}F_{10}NO_5P_2$
$Rh(NO)(O_2CC_6F_5)_2(PPh_3)_2$, 1070
$RhC_{50}H_{33}ClN_4$
$RhPh(tetraphenylporphyrin)Cl$, 1007, 1063
$RhC_{50}H_{38}Cl_2NO_5P_2$
$Rh(NO)(4\text{-}O_2CC_6H_4Cl)_2(PPh_3)_2$, 1071
$RhC_{50}H_{38}N_3O_9P_2$
$Rh(NO)(4\text{-}O_2CC_6H_4NO_2)_2(PPh_3)_2$, 1071
$RhC_{50}H_{44}O_2P_4$
$[RhO_2(dppm)_2]^+$, 1037
$RhC_{50}H_{45}ClP_4$
$[RhHCl(dppm)_2]^+$, 1037
$RhC_{51}H_{41}ClO_2P_2$
$RhCl(PhCOCHCOPh)(PPh_3)_2$, 1022
$RhC_{52}H_{44}NO_5P_2$
$Rh(NO)(4\text{-}O_2CC_6H_4Me)_2(PPh_3)_2$, 1070, 1071
$RhC_{52}H_{44}P_4$
$[Rh(Ph_2PCH{=}CHPPh_2)_2]^+$, 928
$RhC_{52}H_{45}ClP_4$
$[RhHCl(Ph_2PCH{=}CHPPh_2)_2]^+$, 1037
$RhC_{52}H_{48}Cl_2P_4$
$[RhCl_2(dppe)_2]^+$, 1039

$RhC_{52}H_{48}NOP_4$
$[Rh(NO)(dppe)_2]^{2+}$, 1072
$RhC_{52}H_{48}O_2P_4$
$[RhO_2(dppe)_2]^+$, 1037, 1038
$[RhO_2(Ph_2PCHMePPh_2)_2]^+$, 1037
$RhC_{52}H_{48}P_4$
$Rh(dppe)_2$, 906
$[Rh(dppe)_2]^+$, 906, 924, 926, 928
$RhC_{52}H_{48}P_4S_2$
$[RhS_2(dppe)_2]^+$, 1037
$RhC_{52}H_{49}ClP_4$
$[RhHCl(dppe)_2]^+$, 1037, 1039
$[RhHCl(Ph_2PCHMePPh_2)_2]^+$, 1037
$RhC_{52}H_{49}P_4$
$RhH(dppe)_2$, 906, 924
$RhC_{52}H_{53}ClO_4P_4$
$[RhHCl\{PPh_2(OMe)\}_4]^+$, 1033
$RhC_{52}H_{53}P_4$
$RhH(PPh_2Me)_4$, 921, 924
$RhC_{54}ClF_{45}P_3$
$RhCl\{P(C_6F_5)_3\}_3$, 915
$RhC_{54}H_{36}F_9NOP_3$
$Rh(NO)\{P(C_6H_4F\text{-}4)_3\}_3$, 1066
$RhC_{54}H_{40}P_3$
RhH(1-phenyldibenzophosphole)$_3$, 924
$RhC_{54}H_{45}BrP_3$
$RhBr(PPh_3)_3$, 917
$RhC_{54}H_{45}ClNOP_3$
$[Rh(NO)Cl(PPh_3)_3]^+$, 1072
$RhC_{54}H_{45}ClNO_2P_3$
$[RhCl(NO_2)(PPh_3)_3]^+$, 1034
$RhC_{54}H_{45}ClO_2P_3$
$RhCl(O_2)(PPh_3)_3$, 1030
$RhC_{54}H_{45}ClO_9P_3$
$RhCl\{P(OPh)_3\}_3$, 916
$RhC_{54}H_{45}ClP_3$
$RhCl(PPh_3)_3$, 903, 905, 906, 913, 914, 916–918, 920, 1017, 1021, 1026, 1030, 1041
$RhC_{54}H_{45}Cl_3P_3$
$RhCl_3(PPh_3)_3$, 1029
$RhC_{54}H_{45}NOP_3$
$Rh(NO)(PPh_3)_3$, 1066–1068
$RhC_{54}H_{45}NO_2P_3S$
$Rh(O_2)\{SC(=NPh)PPh_2\}(PPh_3)_2$, 1021
$RhC_{54}H_{45}P_3$
$[Rh(PPh_3)_3]^+$, 914
$RhC_{54}H_{45}P_4S_6$
$Rh(S_2PPh_2)_3(PPh_3)$, 1017
$RhC_{54}H_{46}Cl_2P_3$
$RhHCl_2(PPh_3)_3$, 1026
$RhC_{54}H_{46}F_3P_4$
$RhH(PPh_3)_3(PF_3)$, 921
$RhC_{54}H_{46}O_9P_3$
$[RhH\{P(OPh_3\}_3]^-$, 923
$RhC_{54}H_{46}P_3$
$RhH(PPh_3)_3$, 916–918
$RhC_{54}H_{47}ClP_3$
$RhH_2Cl(PPh_3)_3$, 1026
$RhC_{54}H_{52}O_2P_4$
$[Rh\{HOCH_2CH(PPh_2)CH_2PPh_2\}_2]^+$, 928
$[RhO_2\{Ph_2P(CH_2)_3PPh_2\}_2]^+$, 1037
$RhC_{54}H_{53}ClP_4$
$[RhHCl\{Ph_2P(CH_2)_3PPh_2\}_2]^+$, 1037
$RhC_{54}H_{54}P_4$
$[RhH_2\{PH_2P(CH_2)_3PPh_2\}_2]^+$, 1037
$RhC_{54}H_{99}Cl_3P_3$
$RhCl_3\{P(C_6H_{11})_3\}_3$, 1029
$RhC_{55}H_{45}NOP_3S$
$Rh\{SC(=NPh)P(O)Ph_2\}(PPh_3)_2$, 1021
$RhC_{55}H_{45}NO_3P_3S$
$Rh(O_2)\{SC(=NPh)P(O)Ph_2\}(PPh_3)_2$, 1021
$RhC_{55}H_{45}NP_3S$
$Rh\{SC(=NPh)PPh_2\}(PPh_3)_2$, 1021
$RhC_{56}H_{48}O_2P_3$
$Rh(OAc)(PPh_3)_3$, 916
$RhC_{60}H_{50}ClN_6P_2$
$RhCl(PhNNNPh)_2(PPh_3)_2$, 1017
$RhC_{60}H_{135}O_{15}P_5$
$[Rh\{P(OBu)_3\}_5]^+$, 929
$RhC_{61}H_{50}O_2P_3$
$Rh(O_2CPh)(PPh_3)_3$, 916, 917
$RhC_{62}H_{65}O_4P_4$
$RhH(diop)_2$, 925
$RhC_{62}H_{66}O_4P_4$
$[RhH_2(diop)_2]^+$, 1037
$RhC_{63}H_{63}NOP_3$
$Rh(NO)\{P(C_6H_4Me\text{-}4)_3\}_3$, 1067, 1068
$RhC_{66}H_{55}N_4OP_3$
$Rh(NO)(PhNNNPh)(PPh_3)_3$, 1067
$RhC_{72}H_{53}P_4$
RhH(1-phenyldibenzophosphole)$_4$, 924
$RhC_{72}H_{61}O_{12}P_4$
$RhH\{P(OPh)_3\}_4$, 923
$RhC_{72}H_{61}P_4$
$RhH(PPh_3)_4$, 921–923, 1019
$RhC_{72}H_{88}N_8O_2$
$\{Rh(octaethylporphyrin)\}_2O_2$, 1008
$RhC_{144}H_{120}P_8$
$\{Rh(PPh_3)_4\}_2$, 905
$RhClN_2O_2$
$\{RhCl(NO)_2\}_n$, 1066
$RhCl_2F_6P_2$
$[RhCl_2(PF_3)_2]^-$, 906
$RhCl_3I_3$
$[RhCl_3I_3]^{3-}$, 1058
$RhCl_6$
$[RhCl_6]^{2-}$, 1061, 1062
$[RhCl_6]^{3-}$, 964, 1057–1060
$RhCl_{18}H_{42}ClO_2P_2S$
$RhCl(SO_2)(PPr^i_3)_2$, 920
RhF_4
RhF_4, 1062, 1065
RhF_5
RhF_5, 1063
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RhF_6, 1064, 1065
$[RhF_6]^-$, 1063
$[RhF_6]^{2-}$, 1061
$[RhF_6]^{3-}$, 1058
$RhF_6P_3S_6$
$Rh(S_2PF_2)_3$, 1055
RhF_9NOP_3
$Rh(NO)(PF_3)_3$, 1066
$RhF_{12}P_4$
$[Rh(PF_3)_4]^-$, 904, 923
$RhFeC_9H_{19}N_4O_5$
$[Rh(HDMG)(HDMG\text{-}Fe)(H_2O)Me]^{2+}$, 1015
$RhGe_6Cl_{18}$
$[Rh(GeCl_3)_6]^-$, 1019
$RhHF_{12}P_4$
$RhH(PF_3)_4$, 904, 921, 922, 923
RhH_2Cl_5O
$[RhCl_5(H_2O)]^{2-}$, 1058–1060
$RhH_4Cl_4O_2$
$[RhCl_4(H_2O)_2]^-$, 1058–1060
$RhH_4O_{11}P_3$
$Rh(H_2O)(H_2P_3O_{10})$, 1053
$RhH_6Cl_3O_3$
$RhCl_3(H_2O)_3$, 1058–1060
$RhH_8Cl_2O_4$
$[RhCl_2(H_2O)_4]^+$, 1058–1060
$RhH_8O_{12}P_2$
$[Rh(H_2O)_4(PO_4)_2]^{3+}$, 1053
$RhH_{10}ClO_5$
$[RhCl(H_2O)_5]^+$, 943, 948
$[RhCl(H_2O)_5]^{2+}$, 1058–1060

$RhH_{11}O_6$
$[Rh(H_2O)_5(OH)]^{2+}$, 1049
$RhH_{12}ClN_7$
$[Rh(NH_3)_4(N_3)Cl]^+$, 987
$RhH_{12}Cl_2N_4$
$[Rh(NH_3)_4Cl_2]^-$, 954, 959, 987, 988
$RhH_{12}I_2N_4$
$[Rh(NH_3)_4I_2]^+$, 982
$RhH_{12}O_6$
$[Rh(H_2O)_6]^{3+}$, 948, 1049, 1053, 1058–1060
$RhH_{14}ClN_4O$
$[RhCl(H_2O)(NH_3)_4]^{2+}$, 964, 988
$RhH_{14}N_4O_2$
$[Rh(NH_3)_4(OH)_2]_2^{+}$, 964
$RhH_{15}BrN_5$
$[Rh(NH_3)_5Br]^{2+}$, 958, 959, 964, 981, 982, 985
$RhH_{15}ClN_5$
$[RhCl(NH_3)_5]^+$, 930
$[RhCl(NH_3)_5]^{2+}$, 902, 948, 953, 954, 956–958, 960, 965, 982, 985, 988, 995
$RhH_{15}IN_5$
$[RhI(NH_3)_5]^{2+}$, 958, 982
$RhH_{15}N_4O_2$
$[Rh(NH_3)_4(OH)(H_2O)]^{2+}$, 963
$RhH_{15}N_5O_4S$
$[Rh(NH_3)_5(SO_4)]^+$, 957, 960
$RhH_{15}N_6O_2$
$[Rh(NH_3)_5(NO_2)]^{2+}$, 957, 959–961
$[Rh(NH_3)_5(ONO)]^{2+}$, 961
$RhH_{15}N_6O_3$
$[Rh(NH_3)_5(NO_3)]^{2+}$, 957, 959, 960
$RhH_{15}N_8$
$[Rh(NH_3)_5(N_3)]^{2+}$, 959, 960, 986
$RhH_{16}N_4O_2$
$[Rh(NH_3)_4(H_2O)_2]^{3+}$, 964
$RhH_{16}N_5$
$[Rh(NH_3)_5H]^{2+}$, 954, 963
$RhH_{16}N_5O$
$[Rh(NH_3)_5(OH)]^{2+}$, 960, 963
$RhH_{17}N_5O$
$[Rh(NH_3)_5(H_2O)]^{3+}$, 954, 957, 958, 960, 964, 985, 986
$RhH_{17}N_6Cl$
$[Rh(NH_3)_5(NH_2Cl)]^{3+}$, 956
$RhH_{18}N_6$
$[Rh(NH_3)_6]^{3+}$, 956, 962, 984
$RhHgC_{24}H_{33}Cl_5P_3$
$RhCl_3(PMe_2Ph)_3(HgCl_2)$, 1076
$RhHgCl_5(PMe_2Ph)_3$, 1076
$RhIrC_{24}H_{63}ClP_4$
$IrH_2(PEt_3)_2(\mu\text{-}Cl)(\mu\text{-}H)Rh(PEt_3)_2$, 1074, 1151, 1164
$RhIrC_{44}H_{70}P_4$
$Rh(dppe)(\mu\text{-}H)_2IrH_2(PPr^i_3)_2$, 1074, 1151
$RhIrC_{44}H_{71}ClP_5$
$[IrH(PEt_3)_3(\mu\text{-}Cl)(\mu\text{-}H)Rh(dppe)]^+$, 1164
$RhIrC_{44}H_{72}P_5$
$[Rh(dppe)(\mu\text{-}H)_3Ir(PEt_3)_3]^+$., 1075, 1151
$RhMoC_{46}H_{42}P_2$
$Rh(PPh_3)_2(\mu\text{-}H)_2MoCp_2$, 1076
RhN_6O_{12}
$[Rh(NO_2)_6]^{3-}$, 1012
$RhNpH_{10}O_7$
$[Rh(H_2O)_5ONpO]^{4+}$, 1053
RhO
$[RhO]^{3+}$, 1063
RhO_2
RhO_2, 1062
$[RhO_2]^+$, 1063
RhO_3
RhO_3, 1065
$[RhO_3]^-$, 1063
$[RhO_3]^{2-}$, 1062
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$[RhO_4]^{2-}$, 1064, 1065
$[RhO_4]^{3-}$, 1063
RhO_6
$[RhO_6]^{8-}$, 1062
$RhO_{16}S_4$
$[Rh(SO_4)_4]^{4-}$, 944
$RhOsC_4H_{34}N_{12}$
$[Rh(NH_3)_5(\mu\text{-}N{=}CHCH{=}NCH{=}CH)Os(NH_3)_5]^{6+}$, 535, 956
$RhRuC_{51}H_{44}ClOP_4$
$RuRhCl(\mu\text{-}CO)(dppm)_2$, 373
$RhRuC_{52}H_{46}ClO_2P_4$
$RuRhH_2Cl(\mu\text{-}CO)(CO)(dppm)_2$, 462
$RhRuC_{72}H_{60}Cl_5P_4$
$RhCl(PPh_3)_2(\mu\text{-}Cl)_3RuCl(PPh_3)_2$, 1076
$RhSbC_{21}H_{21}Cl_2$
$RhCl_2\{Sb(C_6H_4Me\text{-}2)_3\}$, 933
$RhSbSnC_{54}H_{45}Cl_5$
$RhCl_2(SnCl_3)(SbPh_3)_3$, 1032
$RhSb_2C_{36}H_{32}Cl$
$RhH_2Cl(SbPh_3)_2$, 1018
$RhSb_3C_{54}H_{45}Cl_3$
$RhCl_3(SbPh_3)_3$, 1032
$RhSb_3C_{55}H_{45}Cl_2NS$
$RhCl_2(NCS)(SbPh_3)_3$, 1032
$RhAs_2SiC_{42}H_{46}ClO_3$
$RhHCl\{Si(OEt)_3\}(AsPh_3)_2$, 1020
$RhSiC_{36}H_{31}Cl_4P_2$
$RhHCl(SiCl_3)(PPh_3)_2$, 1020
$RhSiC_{37}H_{34}Cl_3P_2$
$RhHCl(SiCl_2Me)(PPh_3)_2$, 1020
$RhSiC_{38}H_{37}Cl_2P_2$
$RhHCl(SiClMe_2)(PPh_3)_2$, 1020
$RhSiC_{39}H_{40}ClP_2$
$RhHCl(SiMe_3)(PPh_3)_2$, 1020
$RhSiC_{39}H_{41}O_3P_2$
$RhH_2\{Si(OMe)_3\}(PPh_3)_2$, 1018
$RhSiC_{40}H_{43}P_2$
$RhH_2(SiHEt_2)(PPh_3)_2$, 1018
$RhSiC_{42}H_{46}ClO_3P_2$
$RhHCl\{Si(OEt)_3\}(PPh_3)_2$, 1020
$RhSiC_{42}H_{46}ClP_2$
$RhHCl(SiEt_3)(PPh_3)_2$, 1020
$RhSiC_{54}H_{46}ClP_2$
$RhHCl(SiPh_3)(PPh_3)_2$, 1020
$RhSi_2C_{33}H_{45}NP_3$
$Rh\{N(SiMe_2CH_2PPh_2)_2\}(PMe_3)$, 1041
$RhSi_2C_{42}H_{48}NP_2$
$Rh\{N(SiMe_3)_2\}(PPh_3)_2$, 907
$RhSi_2C_{48}H_{51}NP_3$
$Rh\{N(SiMe_2CH_2PPh_2)_2\}(PPh_3)$, 1041
$RhSnC_{18}H_{15}F_{12}P_4$
$Rh(PF_3)_4SnPh_3$, 904
$RhSnC_{43}H_{49}ClP_2Si_2$
$RhCl(PPh_3)_2Sn\{CH(SiMe_3)_2\}$, 920
$RhSn_2Cl_{10}$
$[RhCl_4(SnCl_3)_2]^3$, 953
$RhSn_3Cl_{12}$
$[RhCl_3(SnCl_3)_3]^{3-}$, 953
$RhSn_7H_8F_{19}O_4$
$[Rh\{SnF_2(H_2O)_2\}_2(Sn_4F_{15})]^-$, 953
$RhWC_{46}H_{42}P_2$
$Rh(PPh_3)_2(\mu\text{-}H)_2WCp_2$, 1076
$Rh_2As_4C_{24}H_{60}Cl_6$
$\{RhCl_3(AsEt_3)_2\}_2$, 1025
$Rh_2As_4C_{51}H_{44}Cl_2O$
$Rh_2Cl_2(\mu\text{-}CO)(dpam)_2$, 941
$Rh_2As_4C_{51}H_{45}Cl_3O$
$Rh_2Cl_3(\mu\text{-}H)(\mu\text{-}CO)(dpam)_2$, 941
$Rh_2As_4C_{52}H_{44}Cl_2I_2O_2$
$Rh_2(CO)_2Cl_2I_2(dpam)_2$, 941
$Rh_2As_4C_{52}H_{44}Cl_2O_2$
$Rh_2(CO)_2Cl_2(dpam)_2$, 941
$Rh_2As_6C_{78}H_{72}Cl_6$

$Rh_2Cl_6(Ph_2AsCH_2CH_2AsPh_2)_3$, 1025

$Rh_2B_2C_{18}H_{20}Cl_4N_{12}$
$\{RhCl\{HBNN{=}CHCH{=}CH)_3\}\}_2(\mu\text{-}Cl)_2$, 1012

$Rh_2C_4Cl_2O_4$
$\{Rh(CO)_2Cl\}_2$, 952, 1003

$Rh_2C_4Cl_2O_{12}$
$[Rh_2(O_2CO)_4Cl_2]^{6-}$, 935

$Rh_2C_4H_4O_8$
$Rh_2(O_2CH)_4$, 944, 945

$Rh_2C_4H_4O_{14}$
$[Rh_2(O_2CO)_4(H_2O)_2]^{4-}$, 935

$Rh_2C_4H_6O_4$
$[Rh_2(OAc)_2]^{2+}$, 948

$Rh_2C_4H_8O_{10}$
$Rh_2(O_2CH)_4(H_2O)_2$, 935, 944

$Rh_2C_4H_{10}O_8P_2$
$Rh_2(O_2CH)_4(PH_3)_2$, 946

$Rh_2C_4O_{12}$
$[Rh_2(CO_3)_4]^{4-}$, 944

$Rh_2C_6H_9O_6$
$[Rh_2(OAc)_3]^{+}$, 948

$Rh_2C_8F_{12}O_8$
$Rh_2(O_2CCF_3)_4$, 947

$Rh_2C_8H_4F_{12}N_4O_4$
$Rh_2(HNCOCF_3)_4$, 940, 949

$Rh_2C_8H_4F_{12}O_{10}$
$Rh_2(O_2CCF_3)_4(H_2O)_2$, 937

$Rh_2C_8H_6F_6O_8$
$Rh_2(OAc)_2(O_2CCF_3)_2$, 948

$Rh_2C_8H_8Cl_6N_4Se_4$
$Rh_2(SeCNCH_2CH_2NCSe)_2Cl_6$, 1057

$Rh_2C_8H_{12}Cl_2O_8$
$[Rh_2(OAc)_4Cl_2]^{2-}$, 945

$Rh_2C_8H_{12}N_2O_{10}$
$\{Rh(OAc)_2(NO)\}_2$, 1066

$Rh_2C_8H_{12}N_2O_{11}$
$Rh_2(OAc)_4(NO)(NO_2)$, 934

$Rh_2C_8H_{12}O_8$
$[\{Rh(OAc)_2\}_2]^{+}$, 949,1065
$Rh_2(OAc)_4$, 934–936, 941, 945–951
$[Rh_2(OAc)_4]^{+}$, 948

$Rh_2C_8H_{13}NO_7$
$Rh_2(OAc)_3(HNCOMe)$, 950

$Rh_2C_8H_{14}O_4$
$[Rh_2(O_2CPr)_2]^{2+}$, 948

$Rh_2C_8H_{15}N_3O_5$
$Rh_2(OAc)(HNCOMe)_3$, 950

$Rh_2C_8H_{16}N_4O_4$
$Rh_2(HNCOMe)_4$, 950

$Rh_2C_8H_{16}O_{10}$
$Rh_2(OAc)_4(H_2O)_2$, 934, 944, 945

$Rh_2C_8H_{18}Cl_6N_2O_2$
$[Rh_2Cl_6(Me_2NCOMe)_2]^{2-}$, 944

$Rh_2C_8H_{20}Cl_6S_4$
$Rh_2(MeSCH_2CH_2SMe)_2Cl_6$, 1056

$Rh_2C_8H_{32}Cl_2N_8O_2$
$[\{Rh(en)_2Cl\}_2(\mu\text{-}O_2)]^{3+}$, 1052

$Rh_2C_8H_{32}N_{10}O_6$
$[\{Rh(en)_2(NO_2)\}_2(\mu\text{-}O_2)]^{3+}$, 1052

$Rh_2C_8H_{34}N_8O_2$
$[\{Rh(en)_2\}_2(\mu\text{-}OH)_2]^{4+}$, 970, 975

$Rh_2C_8H_{36}N_8O_4$
$[\{Rh(en)_2(H_2O)\}_2(\mu\text{-}O_2)]^{5+}$, 1005, 1052

$Rh_2C_8H_{72}O_8$
$Rh_2(OAc)_4$, 948

$Rh_2C_{10}H_{12}O_{10}$
$Rh_2(OAc)_4(CO)_2$, 938

$Rh_2C_{10}H_{20}O_{10}$
$Rh_2(OAc)_4(MeOH)_2$, 934, 945

$Rh_2C_{12}H_{12}F_{12}O_{10}$
$Rh_2(O_2CCF_3)_4(EtOH)_2$, 937

$Rh_2C_{12}H_{12}F_{12}O_{10}S_2$
$Rh_2(O_2CCF_3)_4(DMSO)_2$, 937

$Rh_2C_{12}H_{12}F_{12}O_{12}S_2$
$Rh_2(O_2CCF_3)_4(O_2SMe_2)_2$, 937

$Rh_2C_{12}H_{18}N_2O_8$
$Rh_2(OAc)_4(MeNC)_2$, 938

$Rh_2C_{12}H_{24}O_{10}S_2$
$Rh_2(OAc)_4(DMSO)_2$, 934

$Rh_2C_{12}H_{28}Cl_2F_8O_4P_2$
$\{RhCl\{PF_2(OPr)\}_2\}_2$, 909

$Rh_2C_{12}H_{32}N_4O_{10}$
$[Rh_2(O_2CCH_2CH_2NH_3)_4(H_2O)_2]^{2+}$, 935

$Rh_2C_{12}H_{33}N_6O_3$
$[Rh_2(1,4,7\text{-triazacyclononane})_2(\mu\text{-}OH)_3]^{3+}$, 994

$Rh_2C_{12}H_{34}N_6O_4$
$[Rh_2\{1,4,7\text{-triazacyclononane})_2(\mu\text{-}OH)_2(OH)_2]^{2+}$, 994

$Rh_2C_{12}H_{36}Cl_2O_{12}P_4$
$\{RhCl\{P(OMe)_3\}_2\}_2$, 909

$Rh_2C_{12}H_{36}Cl_6P_4$
$\{RhCl_3(PMe_3)_2\}_2$, 1025

$Rh_2C_{12}H_{36}N_6O_4$
$[Rh_2(1,4,7,\text{-triazacyclononane})_2(H_2O)_2(\mu\text{-}OH)_2]^{4+}$, 993

$Rh_2C_{13}H_{32}N_6O_5$
$[Rh_2(1,4,7\text{-triazacyclononane})_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]^{2+}$, 994

$Rh_2C_{14}H_{16}N_2O_8$
$Rh_2(OAc)_4(4\text{-pyCN})$, 946

$Rh_2C_{14}H_{20}O_8$
$Rh_2(OAc)_2(acac)_2$, 942

$Rh_2C_{14}H_{22}N_4O_8$
$Rh_2(OAc)_4$(4-amino-5-aminomethyl-2-methylpyrimidine), 937

$Rh_2C_{14}H_{35}N_6O_4$
$[Rh_2(1,4,7\text{-triazacyclononane})_2(\mu\text{-}OH)_2(\mu\text{-}OAc)]^{3+}$, 993

$Rh_2C_{15}H_{30}N_5S_{10}$
$[Rh_2(S_2CNMe_2)_5]^{+}$, 1054, 1063

$Rh_2C_{16}H_{24}I_2N_8$
$[Rh_2(MeNC)_8I_2]^{2+}$, 943

$Rh_2C_{16}H_{24}N_8O_8$
$Rh_2(DMG)_4$, 942

$Rh_2C_{16}H_{28}O_8$
$Rh_2(O_2CPr)_4$, 948

$Rh_2C_{16}H_{32}O_{10}S_2$
$Rh_2(O_2CEt)_4(DMSO)_2$, 935

$Rh_2C_{19}H_{18}N_3O_6$
$[Rh_2(OAc)_3\{2\text{-}(2\text{-pyridyl})\text{-}1,8\text{-naphthyridine}\}]^{+}$, 941

$Rh_2C_{20}H_{12}Cl_4N_4O_4$
$Rh_2(\overline{N{=}CClCH{=}CHCH{=}CO})_4$, 939

$Rh_2C_{20}H_{24}Cl_2N_8$
$[Rh_2(CNCH_2CH_2CH_2NC)_4Cl_2]^{2-}$, 943

$Rh_2C_{20}H_{24}N_8$
$[Rh_2(CNCH_2CH_2CH_2NC)_4]^{2-}$, 943

$Rh_2C_{20}H_{31}N_4O_{10}S$
$Rh_2(OAc)_4$(thiamine)(H_2O), 937

$Rh_2C_{20}H_{36}O_8$
$Rh_2(O_2CBu^t)_4$, 946

$Rh_2C_{20}H_{40}O_{10}$
$Rh_2(O_2CBu^t)_4(H_2O)_2$, 935

$Rh_2C_{22}H_{18}F_4N_4O_5S$
$Rh_2(\overline{N{=}CFCH{=}CHCH{=}CO})(DMSO)$, 939

$Rh_2C_{22}H_{28}N_8O_{12}$
$Rh_2(OAc)_4$(theophylline)$_2$, 936

$Rh_2C_{23}H_{16}Cl_4N_6O_4$
$Rh_2(\overline{N{=}CClCH{=}CHCH{=}CO})_4$(imidazole), 939

$Rh_2C_{23}H_{28}N_4O_8$
$Rh_2(OAc)_2(\overline{N{=}CMeCH{=}CHCH{=}CO})_2$(imidazole), 941

$Rh_2C_{24}H_{20}Cl_2F_6N_4P_2$
$Rh_2Cl_2(PF_3)_2(PhNNPh)_2$, 909

$Rh_2C_{24}H_{21}N_4O_6$
$[Rh_2(OAc)_3\{2,7\text{-bis}(2\text{-pyridyl})\text{-}1,8\text{-naphthyridine}\}]^{+}$, 941

$Rh_2C_{24}H_{24}N_4O_4$
$Rh_2(\overline{N{=}CMeCH{=}CHCH{=}CO})_4$, 939

$Rh_2C_{24}H_{30}N_2O_{10}S_2$

$Rh_2(OAc)_4\{PhNHC(OMe)S\}_2$, 934

$Rh_2C_{24}H_{32}N_8O_{12}$
$Rh_2(OAc)_4(caffeine)_2$, 936

$Rh_2C_{24}H_{36}Cl_2N_4$
$[Rh_2(1,8\text{-diisocyanomenthane})_2Cl_2]^{2+}$, 943

$Rh_2C_{24}H_{46}ClN_8O_4$
$Rh_2Cl(ON{=}CMeCMe_2NCH_2CH_2\text{-}NCMe_2CMe{=}NOH)_2$, 1013

$Rh_2C_{24}H_{60}Cl_6P_4$
$\{RhCl_3(PEt_3)_2\}_2$, 1025

$Rh_2C_{24}H_{76}N_{12}P_4$
$\{RhH_2\{P(NMe_2)_3\}_2\}_2$, 1065

$Rh_2C_{26}H_{18}Cl_2N_4O_4$
$Rh_2(O_2CH)_2(phen)_2Cl_2$, 942

$Rh_2C_{26}H_{27}N_5O_4$
$Rh_2(\overline{N{=}CMeCH{=}CHCH{=}CO})_4(MeCN)$, 939

$Rh_2C_{26}H_{36}Cl_3OP_3$
$Rh_2Cl_3(COMe)(PMe_2Ph)_3$, 953

$Rh_2C_{26}H_{36}F_{12}N_2O_{10}$
$Rh_2(O_2CCF_3)_4\{Me_2\overline{C(CH_2)_3CMe_2NO}\}_2$, 937, 938

$Rh_2C_{27}H_{28}N_6O_4$
$Rh_2(\overline{N{=}CMeCH{=}CHCH{=}CO})_4(imidazole)$, 939

$Rh_2C_{28}H_{20}Cl_2N_4S_4$
$\{RhCl(benzothiazole)_2\}_2$, 911

$Rh_2C_{28}H_{20}O_8$
$Rh_2(O_2CPh)_4$, 948

$Rh_2C_{28}H_{22}Cl_2N_4O_4$
$Rh_2(phen)_2(OAc)_2Cl_2$, 950

$Rh_2C_{28}H_{24}N_4O_4$
$Rh_2(HNCOPh)_4$, 940

$Rh_2C_{28}H_{54}Cl_4N_8O_4$
$Rh_2Cl_4\{ON{=}CMeCMe_2N(CH_2)_4NCMe_2\text{-}CMe{=}NOH\}_2$, 1013

$Rh_2C_{30}H_{24}N_6O_4$
$[Rh_2(OAc)_2\{2\text{-}(2\text{-pyridyl})\text{-}1,8\text{-naphthyridine}\}_2]^{2+}$, 941

$Rh_2C_{30}H_{28}O_{14}$
$Rh_2(O_2CC_6H_4OH\text{-}2)_4(EtOH)(H_2O)$, 935, 936

$Rh_2C_{30}H_{31}N_5O_5$
$Rh_2(\overline{N{=}CMeCH{=}CHCH{=}CO})_4(\overline{HNCMe{=}CHCH{=}CHCO})$, 939

$Rh_2C_{32}H_{24}N_8$
$[Rh_2(1,8\text{-naphthyridine})_4]^{4+}$, 941

$Rh_2C_{32}H_{32}N_4O_4$
$Rh_2(PhNCOMe)_4$, 950

$Rh_2C_{32}H_{32}O_{14}$
$Rh_2\{O_2CCH(OH)Ph\}_4(H_2O)_2$, 935

$Rh_2C_{32}H_{40}Cl_2P_4$
$\{RhCl\{2\text{-}(2\text{-}Me_2PC_6H_4)C_6H_4PMe_2\}\}_2$, 913

$Rh_2C_{34}H_{32}N_4O_4$
$\{Rh\{2\text{-}OC_6H_4CH{=}NCH_2)_2CH_2\}\}_2$, 943

$Rh_2C_{36}H_{28}O_8$
$Rh_2(O_2CCH{=}CHPh)_4$, 935

$Rh_2C_{36}H_{30}Cl_4N_2P_2S_2$
$\{Rh(NS)Cl_2(PPh_3)\}_2$, 1074

$Rh_2C_{36}H_{81}Cl_6P_3$
$Rh_2Cl_6(PBu_3)_3$, 1025

$Rh_2C_{36}H_{86}N_2P_4$
$\{RhH(PPr^i{}_3)_2\}_2(N_2)$, 920

$Rh_2C_{36}H_{88}O_{12}P_4$
$\{RhH_2\{P(OPr^i)_3\}_2\}_2$, 1065

$Rh_2C_{38}H_{30}N_2O_8$
$Rh_2(O_2CPh)_4(py)_2$, 935

$Rh_2C_{39}H_{27}Cl_2N_9$
$[Rh_2\{2\text{-}(2\text{-pyridyl})\text{-}1,8\text{-naphthyridine}\}_3Cl_2]^{2+}$, 941

$Rh_2C_{40}H_{28}N_4O_4$
$\{Rh(1,2\text{-}(2\text{-}OC_6H_4CH{=}N)_2C_6H_4)\}_2$, 943

$Rh_2C_{40}H_{32}Cl_2N_8O_2$
$[\{Rh(bipy)_2Cl\}_2(\mu\text{-}O_2)]^{3+}$, 1052

$Rh_2C_{40}H_{32}Cl_2N_{10}O_6$
$\{Rh(bipy)_2Cl(NO_3)\}_2$, 942

$Rh_2C_{40}H_{40}Cl_2N_8O_2$
$[\{Rh(py)_4Cl\}_2(\mu\text{-}O_2)]^{3+}$, 1052

$Rh_2C_{44}H_{30}F_{12}O_8P_2$
$Rh_2(O_2CCF_3)_4(PPh_3)_2$, 937

$Rh_2C_{44}H_{30}F_{12}O_{14}P_2$
$Rh_2(O_2CCF_3)_4\{P(OPh)_3\}_2$, 937

$Rh_2C_{46}H_{68}O_{10}$
$Rh_2(O_2C\text{-}1\text{-adamantane})_4(MeOH)_2$, 935

$Rh_2C_{48}H_{42}Cl_5O_4P_4$
$Rh_2Cl_5\{(Ph_2PO)_2H\}_2$, 1025

$Rh_2C_{48}H_{42}N_2O_8$
$Rh_2(OAc)_2(O_2CCPh_3)_2(MeCN)_2$, 941

$Rh_2C_{48}H_{48}N_4O_8P_2$
$Rh_2(OAc)_2(DMG)_2(PPh_3)_2$, 942

$Rh_2C_{48}H_{72}N_8$
$[Rh_2(1,8\text{-diisocyanomenthane})_4]^{2+}$, 943

$Rh_2C_{48}H_{108}Cl_6P_4$
$\{RhCl_3(PBu_3)_2\}_2$, 1025

$Rh_2C_{50}H_{44}Cl_2O_2P_4S$
$Rh_2Cl_2(SO_2)(dppm)_2$, 1040

$Rh_2C_{52}H_{48}Cl_2P_4$
$\{RhCl(dppe)\}_2$, 913

$Rh_2C_{52}H_{52}Cl_6P_4$
$\{RhCl_3(PMePh_2)_2\}_2$, 1025

$Rh_2C_{52}H_{54}N_8O_8P_2$
$Rh_2(DMG)_4(PPh_3)_2$, 942, 950

$Rh_2C_{53}H_{50}Cl_2N_2O_9P_4$
$Rh_2(CO)\{(PhO)_2PNEtP(OPh)_2\}_2Cl_2$, 951

$Rh_2C_{56}H_{90}Cl_6P_4$
$\{RhCl_3(PEtPh_2)_2\}_2$, 1025

$Rh_2C_{62}H_{64}Cl_2O_4P_4$
$\{RhCl(diop)\}_2$, 913

$Rh_2C_{64}H_{64}Cl_2P_6$
$Rh_2Cl_2\{1,4\text{-}\{(Ph_2PCH_2CH_2)_2PCH_2\}_2C_6H_4\}$, 1044

$Rh_2C_{64}H_{64}Cl_4P_6$
$[Rh_2Cl_4\{1,4\text{-}\{(Ph_2PCH_2CH_2)_2PCH_2\}_2C_6H_4\}]^{2+}$, 1044

$Rh_2C_{72}Cl_2F_{60}P_4$
$\{RhCl\{P(C_6F_5)_3\}_2\}_2$, 906, 910

$Rh_2C_{72}Cl_6F_{60}P_4$
$\{RhCl_3\{P(C_6F_5)_3\}_2\}_2$, 1025

$Rh_2C_{72}H_{56}Cl_2P_4$
$\{RhCl\{2\text{-}(2\text{-}Ph_2PC_6H_4)C_6H_4PPh_2\}\}_2$, 913

$Rh_2C_{72}H_{60}ClO_4P_4S_2$
$\{Rh(PPh_3)_2\}_2(\mu\text{-}SO_2)_2(\mu\text{-}Cl)$, 911

$Rh_2C_{72}H_{60}Cl_2O_4P_4$
$\{RhCl(O_2)(PPh_3)_2\}_2$, 1021, 1030

$Rh_2C_{72}H_{60}Cl_2O_4P_4S_2$
$\{RhCl(SO_2)(PPh_3)_2\}_2$, 911

$Rh_2C_{72}H_{60}Cl_2O_{12}P_4$
$\{RhCl\{P(OPh)_3\}_2\}_2$, 909, 911

$Rh_2C_{72}H_{60}Cl_2P_4$
$\{RhCl(PPh_3)_2\}_2$, 909, 910

$Rh_2C_{72}H_{88}N_8$
$\{Rh(octaethylporphyrin)\}_2$, 943, 951, 1007

$Rh_2C_{72}H_{132}Cl_6P_4$
$\{RhCl_3\{P(C_6H_{11})_3\}_2\}_2$, 1025

$Rh_2C_{74}H_{64}P_6$
$\{Rh(PPh_2)(dppm)\}_2$, 913

$Rh_2C_{76}H_{68}P_6$
$\{Rh(PPh_2)(dppe)\}_2$, 913

$Rh_2C_{80}H_{72}N_2P_6$
$Rh_2(CN)_2(dppe)_3$, 928

$Rh_2C_{81}H_{75}O_3P_5$
$Rh_2(CO_3)(PPh_3)_5$, 922

$Rh_2C_{88}H_{64}P_4$
$[Rh_2\{2,2'\text{-}(Ph_2P)_2\text{-}1,1'\text{-binaphthyl}\}_2]^{2+}$, 912

$Rh_2Cl_2F_{12}P_4$
$\{RhCl(PF_3)_2\}_2$, 904, 909–910

Rh_2Cl_9
$[Rh_2Cl_9]^{3-}$, 944, 1057, 1058

$Rh_2F_{22}P_8$
$\{Rh(PF_2)(PF_3)_3\}_2$, 922

$Rh_2F_{24}P_8$
$Rh_2(PF_3)_8$, 904, 905

$Rh_2H_4O_{18}S_4$
$[Rh_2(SO_4)_4(H_2O)_2]^{4-}$, 939

$Rh_2H_{12}O_{18}P_4$
$Rh_2\{O_2P(OH)_2\}_4(H_2O)_2$, 935
$Rh_2H_{20}O_{10}$
$[Rh_2(H_2O)_{10}]^{4+}$, 943
$Rh_2H_{20}O_{12}$
$[\{Rh(H_2O)_5\}_2(\mu\text{-}O_2)]^{4+}$, 948
$Rh_2H_{26}N_8O_2$
$[\{Rh(NH_3)_4\}_2(\mu\text{-}OH)_2]^{4+}$, 963
$Rh_2HgC_8H_{32}N_8$
$[\{Rh(en)_2\}_2Hg]^{4+}$, 1004
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Rh_2O_3, 1053
$Rh_2O_{16}S_4$
$[Rh_2(SO_4)_4]^{4-}$, 939
$Rh_2Sb_{12}C_{150}H_{132}Cl_6$
$\{RhCl_3(Ph_2SbCH_2SbPh_2)_3\}_2$, 1025
$Rh_2Sn_4Cl_{14}$
$[\{RhCl(SnCl_3)_2\}_2]^{4-}$, 906
$Rh_3C_{12}H_{24}O_{16}$
$[Rh_3(\mu\text{-}O)(OAc)_6(H_2O)_3]^{+}$, 948, 951
$Rh_3C_{18}H_{57}O_{18}P_6$
$\{RhH\{P(OMe)_3\}_2\}_3$, 911
$Rh_3F_{27}P_9$
$Rh_3(PF_3)_9$, 905
$Rh_{20}H_{20}Cl_2N_4$
$[Rh(py)_4Cl_2]^{+}$, 995
$RuAsC_{22}H_{15}O_4$
$Ru(CO)_4(AsPh_3)$, 371
$RuAsC_{36}H_{30}Cl_2P$
$\{RuCl_2(AsPh_3)(PPh_3)\}_n$, 379
$RuAsC_{38}H_{31}ClN_4$
$[RuCl(bipy)_2(AsPh_3)]^{+}$, 392
$RuAsF_9$
$RuF_4{\cdot}AsF_5$, 447
$RuAs_2C_{36}H_{30}ClNO$
$RuCl(NO)(AsPh_3)_2$, 368, 394
$RuAs_2C_{36}H_{30}Cl_2$
$\{RuCl_2(AsPh_3)_2\}_n$, 379
$RuAs_2C_{36}H_{30}Cl_3NO_2$
$RuCl_3(NO)(AsPh_3)(OAsPh_3)$, 394
$RuAs_2C_{36}H_{30}Cl_3NP_2$
$RuCl_3N(PPh_3)_2$, 419
$RuAs_2C_{36}H_{31}Br_2$
$RuHBr_2(AsPh_3)_2$, 461, 462
$RuAs_2C_{37}H_{34}Cl_3O$
$RuCl_3(AsPh_3)_2(MeOH)$, 379, 416
$RuAs_2C_{38}H_{36}Br_3OS$
$RuBr_3(AsPh_3)_2(DMSO)$, 439
$RuAs_2C_{40}H_{43}ClO_2P_2S_2$
$RuHCl(DMSO)_2(AsPh_3)_2$, 458
$RuAs_2C_{40}H_{43}N_2O_2S_2$
$[RuH(N_2)(DMSO)_2(AsPh_3)_2]^{+}$, 459
$RuAs_2C_{41}H_{30}F_6OP_2S_2$
$Ru\{S_2C_2(CF_3)_2\}(CO)(AsPh_3)_2$, 406
$RuAs_2C_{62}H_{55}ClP_2$
$RuHCl(PPh_3)_2(Ph_2AsCH_2CH_2AsPh_2)$, 453
$RuAs_2C_{72}H_{74}N_4$
$[Ru(octaethylporphyrin)(AsPh_3)_2]^{+}$, 471
$RuAs_3C_{24}H_{33}Cl_3$
$RuCl_3(AsMe_2Ph)_3$, 379
$RuAs_3C_{39}H_{39}Cl_2NO$
$RuCl_2(NO)(AsMePh_2)_3$, 374
$RuAs_3C_{43}H_{52}N_2O_2S_2$
$[RuH(N_2)(DMSO)_2(AsMePh_2)_3]^{+}$, 459
$RuAs_3C_{54}H_{45}Cl_2O_2$
$RuCl_2(AsPh_3)_3(O_2)$, 416
$RuAs_3C_{54}H_{45}Cl_3$
$RuCl_3(AsPh_3)_3$, 379, 416
$RuAs_3C_{54}H_{45}Cl_3O$
$RuCl_3(AsPh_3)_2(OAsPh_3)$, 416
$RuAs_4C_{20}H_{31}ClN$
$[RuCl(NH_3)(diars)_2]^{+}$, 391
$RuAs_4C_{20}H_{32}ClNO$
$[RuCl(NO)(diars)_2]^{2+}$, 394
$RuAs_4C_{20}H_{32}ClNO_2$
$RuCl(NO_2)(diars)_2$, 394
$RuAs_4C_{20}H_{32}ClN_2$
$[RuCl(N_2)(diars)_2]^{+}$, 391, 394
$RuAs_4C_{20}H_{32}ClN_3$
$RuCl(N_3)(diars)_2$, 394
$RuAs_4C_{20}H_{32}Cl_2$
$RuCl_2(diars)_2$, 379
$[RuCl_2(diars)_2]^{+}$, 418
$RuAs_4C_{20}H_{32}INO$
$[RuI(NO)(diars)_2]^{2+}$, 394
$RuAs_4C_{20}H_{32}N_6$
$Ru(N_3)_2(diars)_2$, 394
$RuAs_4C_{21}H_{35}Cl$
$RuClMe(diars)$, 386
$RuAs_4C_{24}H_{44}P_2S_4$
$Ru(S_2PMe_2)_2(diars)_2$, 405
$RuAs_4C_{32}H_{44}Cl_2$
$RuCl_2(AsMe_2Ph)_4$, 379
$RuAs_4C_{50}H_{44}Cl_3NO$
$RuCl_3(NO)(dpam)_2$, 393
$RuAs_4C_{52}H_{44}Cl_2$
$RuCl_2(Ph_2AsCH{=}CHAsPh_2)_2$, 379
$RuAs_4C_{52}H_{44}Cl_2O_2$
$RuCl_2(CO)_2(dpam)_2$, 383
$RuAs_4C_{52}H_{49}Cl$
$RuHCl(Ph_2AsCH_2CH_2AsPh_2)_2$, 453
$RuAs_4C_{54}H_{42}Br_2$
$RuBr_2\{As(C_6H_4AsPh_2\text{-}2)_3\}$, 380
$RuAs_4C_{54}H_{44}N_2$
$Ru(CN)_2(Ph_2AsCH{=}CHAsPh_2)_2$, 282
$RuAs_4C_{64}H_{64}ClP_2$
$[RuCl\{1,4\text{-}(Ph_2AsCH_2CH_2)_2PCH_2\}_2C_6H_4\}]^{+}$, 377
$RuAs_6C_{75}H_{66}Cl_2P_6$
$RuCl_2(Ph_2AsCH_2AsPh_2)_3$, 380
$RuBCH_{18}N_6$
$[Ru(BH_3CN)(NH_3)_5]^{+}$, 282
$[Ru(BH_3CN)(NH_3)_5]^{2+}$, 282
$RuBC_9H_{32}P_3$
$[RuH(\eta^2\text{-}BH_4)(PMe_3)_3$, 454
$RuBC_{18}H_{18}N_8$
$[Ru\{B(\overline{NN{=}CHCH{=}CH})_4\}(C_6H_6)]^{+}$, 356
$RuBC_{26}H_{31}P_2$
$RuH(\eta^2\text{-}BH_4)(PMePh_2)_2$, 454
$RuBC_{36}H_{42}P_3$
$RuH(\eta^2\text{-}BH_4)\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 454
$RuBC_{37}H_{71}OP_2$
$RuH(BH_4)\{CO\}\{P(C_6H_{11})_3\}_2$, 457
$RuBC_{39}H_{30}NO_2P_2$
$RuH(BH_3CN)(CO)_2$(5-Ph-dibenzophosphole)$_2$, 457
$RuBC_{54}H_{50}P_3$
$RuH(BH_4)(PPh_3)_3$, 454
$RuBC_{55}H_{50}OP_3$
$RuH(BH_4)(CO)(PPh_3)_3$, 457
$RuB_{10}C_{56}H_{61}N_2P_3S$
$RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$, 451
$RuBr_6$
$[RuBr_6]^{2-}$, 447
$[RuBr_6]^{3-}$, 445
$RuCBrO$
$\{RuBr(CO)\}_n$, 440
$RuCCl_5O$
$[RuCl_5(CO)]^{2-}$, 292, 443, 446
$RuCHCl_5O_2$
$[RuCl_5(O_2CH)]^{3-}$, 429
$RuCH_2Cl_4O_2$
$[RuCl_4(CO)(OH_2)]^{2-}$, 292, 443
$RuCH_3Cl_4O_3$
$[RuCl_4(O_2CH)(OH_2)]^{2-}$, 429
$RuCH_{12}N_5$
$\{Ru(CN)(NH_3)_4\}_n^{n+}$, 282
$RuCH_{12}N_6O_2$

$[Ru(NCO)(NO)(NH_3)_4]^{2+}$, 298
$RuCH_{14}N_4O_2$
$[Ru(CO)(NH_3)_4(OH_2)]^{2+}$, 292
$RuCH_{15}F_3N_5O_3S$
$[Ru(O_3SCF_3)(NH_3)_5]^{2-}$, 304, 305, 307
$RuCH_{15}N_5O$
$[Ru(CO)(NH_3)_5]^{2+}$, 291
$RuCH_{15}N_6$
$[Ru(CN)(NH_3)_5]^{+}$, 282
$RuCH_{15}N_6O$
$[Ru(NCO)(NH_3)_5]^{2+}$, 301, 303
$RuCH_{15}N_6S$
$[Ru(NCS)(NH_3)_5]^{2-}$, 301, 318
$[Ru(SCN)(NH_3)_5]^{-}$, 301, 318
$RuCH_{16}N_6$
$[Ru(NCH)(NH_3)_5]^{+}$, 282
$RuCH_{17}N_7$
$[Ru(NH_3)_5(\overline{N{=}NCH_2})]^{2+}$, 299
$RuCH_{18}N_6O_2$
$[Ru(H_2NCO_2H)(NH_3)_5]^{3+}$, 303
$RuCH_{21}N_5OS$
$[Ru(NH_3)_5(DMSO)]^{2+}$, 306
$RuC_2Cl_2O_2$
$\{RuCl_2(CO)_2\}_n$, 443
$RuC_2Cl_3NO_5$
$[RuCl_3(C_2O_4)(NO)]^{2-}$, 429
$RuC_2Cl_4O_2$
$[RuCl_4(CO)_2]^{2-}$, 443
$RuC_2H_7N_2O_6$
$[Ru(OH)_3(Gly\text{-}O)(NO)]^{-}$, 362, 466
$RuC_2H_8O_8$
$[Ru(C_2O_4)(OH_2)_4]^{+}$, 429
$RuC_2H_{12}N_4O_4$
$[Ru(C_2O_4)(NH_3)_4]^{+}$, 305, 306, 308
$RuC_2H_{12}N_6S_2$
$[Ru(NCS)_2(NH_3)_4]^{+}$, 301
$RuC_2H_{13}N_4O_4$
$[Ru(C_2O_4H)(NH_3)_4]^{2+}$, 306
$RuC_2H_{14}N_5O_3$
$[Ru(NH_3)_4(O_2CCONH_2)]^{2+}$, 311
$RuC_2H_{15}N_5O_3$
$[Ru(OAc)(NO)(NH_3)_4]^{2+}$, 298
$RuC_2H_{17}ClN_5O_2$
$[Ru(O_2CCH_2Cl)(NH_3)_5]^{2+}$, 306
$RuC_2H_{17}N_6O_3$
$[Ru(NH_3)_5(HNCOCO_2H)]^{2+}$, 303
$RuC_2H_{18}N_5O_2$
$[Ru(OAc)(NH_3)_5]^{2+}$, 306
$RuC_2H_{18}N_6$
$[Ru(NH_3)_5(NCMe)]^{2+}$, 301
$[Ru(NH_3)_5(NCMe)]^{3+}$, 302
$RuC_2H_{20}N_6O_2$
$[Ru(NH_3)_5(NH_2CH_2CO_2H)]^{2+}$, 310
$[Ru(NH_3)_5(O_2CCH_2NH_3)]^{3+}$, 310
$RuC_2H_{21}N_5OS$
$[Ru(NH_3)_5(DMSO)]^{2+}$, 307, 439
$RuC_2H_{21}N_5S$
$[Ru(NH_3)_5(HSEt)]^{2-}$, 307
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$[Ru(NH_3)_5(SMe_2)]^{3+}$, 308
$RuC_2I_2O_2$
$\{RuI_2(CO)_2\}_n$, 440
$RuC_3Cl_3O_3$
$[RuCl_3(CO)_3]^{-}$, 443
$RuC_3F_3O_3$
$RuF_3(CO)_3$, 442
$[RuF_3(CO)_3]^{-}$, 446
$RuC_3H_5O_7$
$[Ru(O_2CH)_3(OH_2)]^{-}$, 426
$RuC_3H_7Cl_5NO$
$[RuCl_5(DMF)]^{-}$, 447
$RuC_3H_9Cl_2N_5O_2S$
$RuCl_2\{MeNHCSNC(=NH)NH_2\}(OH_2)(NO)$, 468
$RuC_3H_{16}ClN_6$
$[RuCl(NH_3)_4(\overline{HNCH{=}NCH{=}CH})]^{2+}$, 296
$RuC_3H_{16}N_5O_5S$
$Ru(NO_2)\{H_2NCSNC(=NH)NH_2\}(OH_2)_3$, 468
$RuC_3H_{19}N_7$
$[Ru(NH_3)_5(\overline{N{=}CHNHCH{=}CH})]^{2+}$, 295
$RuC_3H_{21}N_5O$
$[Ru(NH_3)_5(OCMe_2)]^{2+}$, 292, 297, 318
$RuC_4BrCl_3O_4Si$
$RuBr(SiCl_3)(CO)_4$, 285
$RuC_4Br_2O_4$
$RuBr_2(CO)_4$, 443
RuC_4ClNO_9
$[RuCl(C_2O_4)_2(NO)]^{2-}$, 429
$RuC_4Cl_6O_4Si_2$
$Ru(SiCl_3)_2(CO)_4$, 285
$RuC_4H_2O_4$
$RuH_2(CO)_4$, 452
$RuC_4H_3N_6O_{10}$
$[Ru(OH)(NO_2)_2(ON{=}\overline{CCONHCONHCO})(NO)]^{-}$, 464
$RuC_4H_3O_4$
$\{Ru(\mu\text{-}OAc)(CO)_2\}_n$, 425
$RuC_4H_4O_{10}$
$[Ru(C_2O_4)_2(OH_2)_2]^{-}$, 429
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$[Ru(NCS)_2(SCN)_2(NH_3)_2]^{-}$, 301
$RuC_4H_6O_2S_2$
$\{Ru(SMe)_2(CO)_2\}_n$, 431
$RuC_4H_{10}Cl_2N_8S_2$
$[RuCl_2\{H_2NCSNC(=NH)NH_2\}_2]^{+}$, 468
$RuC_4H_{10}Cl_3S_2$
$RuCl_3(MeSCH_2CH_2SMe)$, 432
$RuC_4H_{10}Cl_4S_2$
$[RuCl_4(MeSCH_2CH_2SMe)]^{-}$, 433
$RuC_4H_{12}Cl_3NO_3S_2$
$RuCl_3(NO)(DMSO)_2$, 439
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$[RuCl_4(DMSO)_2]^{-}$, 439
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$[Ru(NH_3)_4\{HN{=}CMeC(Me){=}NH\}]^{2+}$, 303
$RuC_4H_{16}Cl_2N_4$
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$[Ru(N_3)_2(en)_2]^{+}$, 323
$RuC_4H_{18}ClN_4O$
$[RuCl(en)_2(OH_2)]^{2+}$, 323
$RuC_4H_{18}N_6O$
$[Ru(N_2)(en)_2(OH_2)]^{2+}$, 323
$RuC_4H_{19}N_5O_4$
$[Ru(NH_3)_5(HO_2CCH{=}CHCO_2H)]^{2+}$, 292
$RuC_4H_{19}N_7$
$[Ru(NH_3)_5(\overline{N{=}CHCH{=}NCH{=}CH})]^{2+}$, 293, 295, 296, 317
$[Ru(NH_3)_5(\overline{N{=}CHCH{=}NCH{=}CH})]^{3+}$, 295, 296
$RuC_4H_{20}N_4O_2$
$[Ru(en)_2(OH_2)_2]^{2+}$, 323
$[Ru(en)_2(OH_2)_2]^{3+}$, 323
$RuC_4H_{20}N_6O_2$
$[Ru(NH_3)_5(NCCO_2Et)]^{2+}$, 303
$RuC_4H_{20}N_7$
$[Ru(NH_3)_5(\overline{HN{=}CHCH{=}NCH{=}CH})]^{2+}$, 326
$RuC_4H_{21}N_6O_3$
$[Ru(NH_3)_5(HNCOCO_2Et)]^{2+}$, 303
$RuC_4H_{23}N_5S_2$
$[Ru(NH_3)_5\{\overline{S(CH_2)_4S}\}]^{2+}$, 308
$[Ru(NH_3)_5\{\overline{S(CH_2)_4S}\}]^{3+}$, 308

$RuC_4H_{24}N_5S_2$
$[Ru(NH_3)_5\{S(CH_2)_4SH\}]^{2+}$, 308
$RuC_4H_{24}N_6O_2$
$[Ru(NH_3)_5(NH_2CH_2CO_2Et)]^{3+}$, 310
$RuC_4H_{25}N_5S_2$
$[Ru(NH_3)_5\{HS(CH_2)_4SH\}]^{2+}$, 308
$RuC_4H_{25}N_6O_2$
$[Ru(NH_3)_5\{OC(OEt)CH_2NH_3\}]^{3+}$, 310
$RuC_4I_2N_2O_2$
$[Ru(CN)_2I_2(CO)_2]^{2-}$, 283
$RuC_4I_2O_4$
$RuI_2(CO)_4$, 442
$RuC_4N_2O_2S_2$
$\{Ru(NCS)_2(CO)_2\}_n$, 326
RuC_4O_{10}
$[RuO_2(C_2O_4)_2]^{2-}$, 429
$RuC_5H_6Cl_2O_4$
$RuCl_2(CO)_3(EtOH)$, 443
$RuC_5H_{11}Cl_2O_4$
$Ru(acac)Cl_2(OH_2)_2$, 424
$RuC_5H_{12}Cl_3OS_2$
$[RuCl_3(CO)(SMe_2)_2]^-$, 432
$RuC_5H_{17}N_5$
$[Ru(NH_3)_4(py)]^{2+}$, 294, 295
$RuC_5H_{17}N_5O_4S$
$[Ru(SO_4)(NH_3)_4(py)]^+$, 307
$RuC_5H_{19}N_9O$
$[Ru(NH_3)_5(hypoxanthine)]^{3+}$, 296
$RuC_5H_{20}ClN_{10}S_5$
$[RuCl(H_2NCSNH_2)_5]^{2+}$, 437
$RuC_5H_{20}N_6$
$[Ru(NH_3)_5(py)]^{2+}$, 293, 294, 300
$[Ru(NH_3)_5(py)]^{3+}$, 289, 296, 297
$[Ru(NH_3)_5(py)]_4^{+}$, 297
$RuC_5H_{21}N_7$
$[Ru(NH_3)_5(4\text{-}pyNH_2)]^{2+}$, 293
$RuC_5H_{22}N_7$
$[Ru(NH_3)_5(4\text{-}pyNH_3)]^{3+}$, 293, 294
$RuC_5H_{22}N_7OS$
$[Ru\{NSC(NH_2)_2\}(en)_2(OH_2)]^{3+}$, 323
$RuC_5H_{22}N_8O$
$[Ru(NH_3)_5(1\text{-methylcytosine})]^{2+}$, 296
$RuC_5H_{26}N_5O$
$[Ru(OH)(NH_2Me)_5]^{2+}$, 323
RuC_5N_6O
$[Ru(CN)_5(NO)]^{2-}$, 281, 282, 362
$RuC_5N_6OS_5$
$[Ru(NCS)_5(NO)]^{2-}$, 362
$RuC_5N_6O_2$
$[Ru(CN)_5(NO_2)]^{4-}$, 281, 282
RuC_6HN_6
$[RuH(CN)_6]^{3-}$, 281
$RuC_6H_2N_6$
$[RuH_2(CN)_6]^{2-}$, 282
$RuC_6H_6O_2S_6$
$Ru(S_2CSMe)_2(CO)_2$, 435
$RuC_6H_8N_2O_8$
$[Ru(C_2O_4)_2(en)]^-$, 324
$RuC_6H_9Cl_3N_3$
$RuCl_3(MeCN)_3$, 432
$RuC_6H_{10}O_2S_2$
$\{Ru(SEt)_2(CO)_2\}_n$, 431
$RuC_6H_{12}ClN_3OS_4$
$RuCl(S_2CNMe_2)_2(NO)$, 435
$RuC_6H_{12}I_2O_2S_4$
$RuI_2(CO)_2(HSCH_2CH_2SH)_2$, 433
$RuC_6H_{12}N_4O_3S_4$
$Ru(S_2CNMe_2)_2(NO_2)(NO)$, 362
$RuC_6H_{16}N_4O_4$
$[Ru(C_2O_4)(en)_2]^+$, 324, 429
$RuC_6H_{18}ClN_6O$
$[RuCl(NH_3)_4(4\text{-}pyCONH_2)]^{2+}$, 296
$RuC_6H_{18}Cl_2N_4$
$[RuCl_2\{(H_2NCH_2CH_2NHCH_2)_2\}]^+$, 323
$RuC_6H_{18}Cl_3O_3S_3$
$RuCl_3(DMSO)_3$, 439
$[RuCl_3(DMSO)_3]^-$, 438
$RuC_6H_{18}IN_6O$
$[RuI(NH_3)_4(4\text{-}pyCONH_2)]^{2+}$, 309
$RuC_6H_{18}N_6O$
$[Ru(NH_3)_4(4\text{-}pyCONH_2)]^{3+}$, 296
$RuC_6H_{18}N_6O_5S$
$[Ru(SO_4)(NH_3)_4(4\text{-}pyCONH_2)]^+$, 304, 309, 319
$RuC_6H_{18}N_{10}$
$[Ru(N_3)_2\{(H_2NCH_2CH_2NHCH_2)_2\}]^+$, 323
$RuC_6H_{20}Cl_3O_4S_3$
$RuCl_3(DMSO)_3(OH_2)$, 438
$RuC_6H_{20}N_5Se$
$[Ru(SePh)(NH_3)_5]^{2+}$, 440
$RuC_6H_{20}N_6O$
$[Ru(NH_3)_4(CO)\{\overline{CNHC(Me)=CMeNH}\}]^{2+}$, 295
$[Ru(N_2)\{(H_2NCH_2CH_2NHCH_2)_2\}(OH_2)]^{2+}$, 323
$RuC_6H_{20}N_6O_2$
$[Ru(NH_3)_4(4\text{-}pyCONH_2)(OH_2)]^{2+}$, 293, 304, 309
$[Ru(NH_3)_4(4\text{-}pyCONH_2)(OH_2)]^{3+}$, 308
$RuC_6H_{21}N_7$
$[Ru(NH_3)_5\{HN=\overline{CCH=CHC(=NH)CH=CH}\}]^{2+}$, 303
$RuC_6H_{21}N_7O$
$[Ru(NH_3)_5(4\text{-}pyCONH_2)]^{2+}$, 293
$[Ru(NH_3)_5(4\text{-}pyCONH_2)]^{3+}$, 296, 297
$RuC_6H_{21}N_9O$
$[Ru(NH_3)_5(7\text{-methylhypoxanthine})]^{3+}$, 296
$RuC_6H_{24}N_6$
$[Ru(en)_3]^{2+}$, 321–323
$[Ru(en)_3]^{3+}$, 321, 322, 324
$RuC_6H_{24}N_{12}S_6$
$[Ru(H_2NCSNH_2)_6]^{3+}$, 437
$RuC_6H_{25}ClN_6$
$[RuCl(enH)(en)_2]^{2+}$, 324
$[RuCl(enH)(en)_2]^{3+}$, 324
$RuC_6H_{25}N_5$
$[Ru(NH_3)_5(EtC{\equiv}CEt)]^{2+}$, 292
$RuC_6H_{25}N_7$
$Ru(NH_3)_5\{\overline{N=NC(CH_2)_5}\}$, 301
$RuC_6H_{27}N_6O$
$[Ru(enH)(en)_2(OH_2)]^{3+}$, 323, 324
$RuC_6H_{29}N_4O_4P$
$Ru(NH_3)_4(OH_2)\{P(OEt)_3\}$, 391
$[Ru(NH_3)_4(OH_2)\{P(OEt)_3\}]^{2+}$, 304
$RuC_6H_{30}N_6$
$[Ru(NH_2Me)_6]^{2+}$, 321, 323
$RuC_6I_4O_6$
$\{RuI_2(CO)_3\}_2$, 443
$RuC_6N_4O_2S_4$
$[Ru(NCS)_4(CO)_2]^{2-}$, 365
RuC_6N_6
$[Ru(CN)_4(NC)_2]^{5-}$, 281
$[Ru(CN)_5(NC)]^{5-}$, 281
$[Ru(CN)_6]^{3-}$, 284, 476
$[Ru(CN)_6]^{4-}$, 281, 283, 362, 476, 526
RuC_6N_6O
$[Ru(CN)_5(CNO)]^{4-}$, 284
$RuC_6N_6O_3$
$[Ru(CN)_4(CNO)_2(O)]^{3-}$, 284
$RuC_6N_6S_6$
$[Ru(NCS)_5(SCN)]^{3-}$, 365
$[Ru(NCS)_6]^{3-}$, 365
$[Ru(SCN)_6]^{4-}$, 365
$RuC_6O_6S_6$
$Ru(S_2C_2O_2)_3$, 436
RuC_6O_{12}
$[Ru(C_2O_4)_3]^{2-}$, 429
$[Ru(C_2O_4)_3]^{3-}$, 324, 327, 429, 476
$RuC_7H_8Cl_2$
$\{RuCl_2(nbd)\}_n$, 347

$RuC_7H_9BrO_4Si$
$RuBr(SiMe_3)(CO)_4$, 285
$RuC_7H_9O_7P$
$Ru(CO)_4\{P(OMe)_3\}$, 371
$RuC_7H_{18}N_7O$
$[Ru(CN)(NH_3)_4(4\text{-}pyCONH_2)]$, 282
$RuC_7H_{19}N_5O$
$[Ru(NH_3)_4(2\text{-}pyCoMe)]^{2+}$, 311
$RuC_7H_{20}N_6$
$[Ru(NH_3)_5(NCPh)]^{3+}$, 302
$RuC_7H_{21}N_5O$
$[Ru(NH_3)_4(2\text{-}pyCHMeOH)]^{2+}$, 311
$RuC_8H_4ClN_7O_9$
$RuCl(ON{=}\overline{CCONHCONHCO})_2(NO)$, 465
$RuC_8H_4Cl_2N_6O_8$
$[RuCl_2(ON{=}\overline{CCONHCONHCO})_2]^-$, 465
$RuC_8H_5Cl_2NO_3$
$RuCl_2(CO)_3(py)$, 326
$RuC_8H_5N_7O_{10}$
$Ru(OH)(ON{=}\overline{CCONHCONHCO})_2(NO)$, 464
$RuC_8H_8Cl_3O$
$[RuCl_3(nbd)(CO)]^-$, 345
$RuC_8H_{12}Cl_2N_4$
$RuCl_2(NCMe)_4$, 365
$RuC_8H_{12}N_2O_2S_4$
$Ru(S_2CNMe_2)_2(CO)_2$, 435
$RuC_8H_{18}Cl_3S_3$
$RuCl_3\{S(CH_2CH_2CH_2SMe)_2\}$, 433
$RuC_8H_{19}Cl_2N_7O_2$
$[Ru(caffeine)(NH_3)_3Cl_2]^+$, 937
$RuC_8H_{20}Br_3NOS_2$
$RuBr_3(SEt_2)_2(NO)$, 362
$RuC_8H_{20}N_8$
$[Ru(NH_3)_4(\overline{N{=}CHCH{=}NCH{=}CH})_2]^{2+}$, 295
$RuC_8H_{21}N_5O$
$[Ru(CNCH_2Ph)(NH_3)_4(OH_2)]^{2+}$, 291
$RuC_8H_{21}N_8$
$[Ru(\overline{N{=}CHCH{=}NHCH{=}CH})(NH_3)_4(\overline{N{=}CHCH{=}NCH{=}CH})]^{3+}$, 295
$RuC_8H_{22}N_6$
$[Ru(CNCH_2Ph)(NH_3)_5]^{2+}$, 291
$[Ru(CNCH_2Ph)(NH_3)_5]^{3+}$, 291
$RuC_8H_{24}Br_2O_4S_4$
$RuBr_2(DMSO)_4$, 437, 439
$RuC_8H_{24}Cl_2O_4S_4$
$RuCl_2(DMSO)_4$, 350, 353, 437–439, 463
$RuC_8H_{24}Cl_2S_4$
$RuCl_2(SMe_2)_4$, 432
$RuC_8H_{24}I_2O_4S_4$
$RuI_2(DMSO)_4$, 437
$RuC_8H_{28}N_8$
$[Ru(cod)(NH_2NH_2)_4]^{2+}$, 364
$RuC_9H_4N_7$
$[Ru(CN)_5(\overline{N{=}CHCH{=}NCH{=}CH})]^{3-}$, 282
$RuC_9H_5N_2O_9$
$[Ru(C_2O_4)_2(NO)(py)]^-$, 429
$RuC_9H_5N_7$
$[Ru(CN)_5(\overline{HN{=}CHCH{=}NCH{=}CH})]^{2-}$, 326
$RuC_9H_5O_3S$
$\{Ru(SPh)(CO)_3\}_n$, 431
$RuC_9H_{10}O_3S$
$\{RuS(CO)_3(C_6H_{10})\}_n$, 430
$RuC_9H_{18}ClN_3S_5$
$RuCl(S_2CNMe_2)_2(\eta^2\text{-}SCNMe_2)$, 434
$RuC_9H_{18}ClN_3S_6$
$RuCl(S_2CNMe_2)_3$, 434
$RuC_9H_{18}I_3N_3S_6$
$Ru(S_2CNMe_2)_3I_3$, 434
$RuC_9H_{18}N_3S_6$
$Ru(S_2CNMe_2)_3$, 362, 433
$RuC_9H_{18}N_4OSe_6$
$Ru(Se_2CNMe_2)_3(NO)$, 440
$RuC_9H_{21}ClO_2P_2$
$RuCl(Me)(CO)_2(PMe_3)_2$, 386
$RuC_9H_{21}N_7$
$[Ru(NH_3)_4(py)(\overline{N{=}CHCH{=}NCH{=}CH})]^{2+}$, 295
$RuC_{10}H_3ClO_5S_5$
$[Ru(DMSO)_5Cl]^{2+}$, 439
$RuC_{10}H_7N_8O_9$
$[Ru(ON{=}\overline{CCONHCONHCO})_2(MeCN)(NO)]^+$, 465
$RuC_{10}H_8Cl_2N_2O_2$
$Ru(O)_2Cl_2(bipy)$, 352, 422
$RuC_{10}H_8Cl_3N_2$
$RuCl_3(bipy)$, 347
$RuC_{10}H_8Cl_4N_2$
$RuCl_4(bipy)$, 357
$[RuCl_4(bipy)]^-$, 353, 357
$[RuCl_4(bipy)]^{2-}$, 353
$RuC_{10}H_8N_2O_4$
$RuO_4(bipy)$, 352
$RuC_{10}H_{10}Cl_2N_2O_2$
$RuO_2Cl_2(py)_2$, 327
$RuC_{10}H_{10}Cl_2N_2S_2$
$\{RuCl_2(2\text{-}pySH)_2\}_n$, 431
$RuC_{10}H_{10}Cl_3N_2O$
$RuCl_3(bipy)(OH_2)$, 353
$RuC_{10}H_{10}Cl_3N_6$
$RuCl_3\{HC(\overline{NN{=}CHCH{=}CH})_3\}$, 357
$RuC_{10}H_{10}Cl_4N_2$
$[RuCl_4(py)_2]^-$, 327
$RuC_{10}H_{10}N_2O_4$
$RuO_4(py)_2$, 327
$RuC_{10}H_{12}Cl_2N_2O_8$
$[RuCl_2\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}]^{2-}$, 467
$RuC_{10}H_{12}F_6N_2S_6$
$Ru(S_2CNMe_2)_2\{S_2C_2(CF_3)_2\}$, 435
$RuC_{10}H_{12}N_4O_8$
$[Ru\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}(N_2)]^{2-}$, 467
$RuC_{10}H_{13}ClN_2O_8$
$[RuCl\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)\text{-}CH_2CO_2\}]^-$, 467
$RuC_{10}H_{13}N_2O_9$
$[Ru(OH)\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}]^{2-}$, 466
$RuC_{10}H_{14}ClNOS_4$
$RuCl(MeCSCHCSMe)_2(NO)$, 362, 436
$RuC_{10}H_{14}ClNO_5$
$Ru(acac)_2(Cl)(NO)$, 362, 464
$RuC_{10}H_{14}ClN_2O_8$
$RuCl\{O_2CCH_2N(CH_2CO_2H)CH_2CH_2N(CH_2CO_2H)\text{-}CH_2CO_2\}$, 467
$RuC_{10}H_{14}Cl_2N_2O_8$
$[RuCl_2\{O_2CCH_2N(CH_2CO_2H)CH_2CH_2N(CH_2CO_2H)\text{-}CH_2CO_2\}]^-$, 467
$RuC_{10}H_{14}N_2O_9$
$[Ru\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}(OH_2)]^-$, 466
$[Ru\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}(OH_2)]^{2-}$, 466
$RuC_{10}H_{15}Cl_2N_2O_8$
$RuCl_2\{O_2CCH_2N(CH_2CO_2H)CH_2CH_2N\text{-}(CH_2CO_2H)_2\}$, 467
$RuC_{10}H_{20}Cl_2S_4$
$RuCl_2$(1,4,8,11-tetrathiacyclotetradecane), 477
$RuC_{10}H_{20}Cl_3S_4$
$RuCl_3$(1,4,8,11-tetrathiacyclotetradecane), 477
$RuC_{10}H_{20}N_6$
$[Ru(bipy)(NH_3)_4]^{2+}$, 297
$[Ru(bipy)(NH_3)_4]^{3+}$, 297
$RuC_{10}H_{22}N_6$
$[Ru(NH_3)_4(py)_2]^{2+}$, 295
$[Ru(NH_3)_4(py)_2]^{3+}$, 295
$RuC_{10}H_{22}N_8$
$[Ru(en)_2$(diimidazole)$]^{2+}$, 322
$RuC_{10}H_{24}Cl_2N_4$
$[RuCl_2$(1,4,8,11-tetraazacyclotetradecane)$]^+$, 476
$RuC_{10}H_{25}N_2O_6S_3$
Ru(Gly-Gly)$(DMSO)_3$, 466
$RuC_{10}H_{30}ClO_5S_5$

$[RuCl(OSMe_2)_2(SOMe_2)_3]^+$, 438

$RuC_{10}H_{30}F_{10}N_5P_5$
$Ru(PF_2NMe_2)_5$, 366

$RuC_{10}H_{31}N_6O_3P$
$Ru(NH_3)_4\{P(OEt)_3\}(\overline{N{=}CHCH{=}NCH{=}CH})$, 391

$RuC_{11}H_{10}Cl_3N_2O$
$[RuCl_3(CO)(py)_2]^-$, 326

$RuC_{11}H_{11}Cl_3P$
$RuCl_3$(3-Me-1-Ph-phosphole), 418

$RuC_{11}H_{12}N_2O_9$
$[Ru\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}(CO)]^{2-}$, 466

$RuC_{11}H_{15}Cl_2NO$
$RuCl_2(CO)$(cod)(NCMe), 365

$RuC_{11}H_{19}Cl_3NS_2$
$RuCl_3(EtSCH_2CH_2SEt)$(py), 432

$RuC_{11}H_{20}N_2OS_4$
$Ru(S_2CNEt_2)_2(CO)$, 435

$RuC_{11}H_{23}Cl_2N_5O_3S_3$
$RuCl_2$(adenine)$(DMSO)_3$, 439

$RuC_{11}H_{24}Cl_3S_3$
$RuCl_3\{MeC(CH_2SEt)_3\}$, 433

$RuC_{12}H_6N_9O_{12}$
$[Ru(\overline{ON{=}CCONHCONHCO})_3]^-$, 464, 465

$RuC_{12}H_6N_{10}O_{13}$
$Ru(\overline{ON{=}CCONHCONHCO})_3(NO)$, 465

$RuC_{12}H_8ClN_3O$
$[RuCl(NO)(phen)]^{2+}$, 348

$RuC_{12}H_8Cl_4N_2$
$RuCl_4$(phen), 353
$[RuCl_4(phen)]^-$, 353

$RuC_{12}H_{10}ClN_3O_5$
$RuCl(C_2O_4)(NO)(py)_2$, 429

$RuC_{12}H_{10}Cl_2N_2O_2$
$RuCl_2(CO)_2(py)_2$, 326

$RuC_{12}H_{14}O_6$
$Ru(acac)_2(CO)_2$, 424

$RuC_{12}H_{16}Cl_2N_8S_2$
$[RuCl_2(2\text{-}pyNHCSNHNH_2)_2]$, 468

$RuC_{12}H_{18}N_6$
$[Ru(CNMe)_6]^{2+}$, 282
$[Ru(NCMe)_6]^{2+}$, 365

$RuC_{12}H_{20}N_2O_2S_4$
$Ru(S_2CNEt_2)_2(CO)_2$, 435

$RuC_{12}H_{20}N_6$
$[Ru(phen)(NH_3)_4]^{2+}$, 297

$RuC_{12}H_{21}N_8O_2$
$[Ru(NH_3)_4$(10-methylisoalloxazine)$]^{2+}$, 311

$RuC_{12}H_{24}Cl_2OS_3$
$RuCl_2(CO)\{MeC(CH_2SEt)_3\}$, 433

$RuC_{12}H_{24}Cl_2OS_4$
$RuCl_2(CO)\{MeC(CH_2SEt)_3\}$, 433

$RuC_{12}H_{24}N_8O_2$
$[Ru(NH_3)_4(4\text{-}pyCONH_2)_2]^{2+}$, 295
$[Ru(NH_3)_4(4\text{-}pyCONH_2)_2]^{3+}$, 297

$RuC_{12}H_{24}P_2S_4$
$Ru(S_2PMe_2)_2$(cod), 405

$RuC_{12}H_{30}Cl_3S_3$
$RuCl_3(SEt_2)_3$, 432

$RuC_{12}H_{30}P_3S_6$
$Ru(S_2PEt_2)_3$, 436

$RuC_{12}H_{32}Cl_2P_4$
$RuCl_2(Me_2PCH_2CH_2PMe_2)_2$, 379, 386

$RuC_{12}H_{32}P_4$
$Ru(Me_2PCH_2CH_2PMe_2)_2$, 367

$RuC_{12}H_{34}P_4$
$Ru(CH_2PMe_2)_2(PMe_3)_2$, 389

$RuC_{12}H_{35}ClP_4$
$RuCl(CH_2PMe_2)(PMe_3)_3$, 389

$RuC_{12}H_{35}IP_4$
$RuI(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3$, 389

$RuC_{12}H_{36}ClP_4$
$[RuCl(PMe_3)_4]^+$, 376

$RuC_{12}H_{36}Cl_2O_{12}P_4$
$RuCl_2\{P(OMe)_3\}_4$, 366

$RuC_{12}H_{36}N_6P_4$
$Ru(N_3)_2(PMe_3)_4$, 394

$RuC_{12}H_{36}O_6P_3S_6$
$Ru\{S_2P(OEt)_2\}_3$, 436

$RuC_{12}H_{36}O_6S_6$
$[Ru(DMSO)_6]^{2+}$, 438
$[Ru(DMSO)_6]^{3+}$, 439

$RuC_{12}H_{36}P_4$
$RuH(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3$, 367

$RuC_{12}H_{37}ClP_4$
$RuHCl(PMe_3)_4$, 452

$RuC_{12}H_{38}P_4$
$RuH_2(PMe_3)_4$, 451

$RuC_{12}H_{42}N_4O_6P_2$
$[Ru(NH_3)_4\{P(OEt)_3\}_2]^{2+}$, 304, 391

$RuC_{12}N_6S_6$
$[Ru\{S_2C{=}C(CN)_2\}_3]^{3-}$, 436

$RuC_{13}H_{10}O_2Se$
$Ru(SePh)(CO)_2Cp$, 439

$RuC_{13}H_{13}Cl_2NO$
$RuCl_2(CO)$(nbd)(py), 326

$RuC_{13}H_{33}NP_4$
$RuH(CN)(Me_2PCH_2CH_2PMe_2)_2$, 282

$RuC_{13}H_{39}ClP_4$
$RuClMe(PMe_3)_4$, 386

$RuC_{13}H_{40}P_4$
$RuHMe(PMe_3)_4$, 453

$RuC_{14}H_6N_2O_8$
$[Ru\{2,6\text{-}py(CO_2)_2\}_2]^-$, 466
$[Ru\{2,6\text{-}py(CO_2)_2\}_2]^{2-}$, 466

$RuC_{14}H_8O_2S_4$
$[Ru(S_2C_6H_4)_2(CO)_2]^{2-}$, 436

$RuC_{14}H_9Cl_2N_2O_2$
$[Ru\{2\text{-}(PhN{=}N)C_6H_4\}(Cl_2)(CO)_2]^-$, 353

$RuC_{14}H_{10}N_4O_2S_2$
$Ru(NCS)_2(CO)_2(py)_2$, 326

$RuC_{14}H_{10}O_2S_2$
$\{Ru(SPh)_2(CO)_2\}_n$, 431

$RuC_{14}H_{12}N_2O_2S_2$
$Ru(SC_6H_4NH_2\text{-}2)_2(CO)_2$, 431

$RuC_{14}H_{14}Cl_2N_2O_2$
$RuCl_2(CO)_2(NH_2Ph)_2$, 324

$RuC_{14}H_{16}Cl_2O_2S_2$
$\{RuCl_2(OSPhMe)_2\}_n$, 439

$RuC_{14}H_{16}N_2O_4$
$Ru(OAc)_2(py)_2$, 426

$RuC_{14}H_{21}ClN_3$
$[RuCl(cod)(NCMe)_3]^+$, 365

$RuC_{14}H_{22}N_3$
$[RuH(cod)(NCMe)_3]^+$, 365

$RuC_{14}H_{25}N_7O$
$[Ru(CNCH_2Ph)(NH_3)_4(4\text{-}pyCONH_2)$, 291

$RuC_{14}H_{28}N_8$
$[Ru(CNMe)_4\{C(NHMe)_2\}_2]^{2+}$, 282

$RuC_{14}H_{32}Cl_2N_4$
$[RuCl_2(1,4,8,11\text{-}Me_4\text{-}1,4,8,11\text{-}$
$\text{tetraazacyclotetradecane})]^+$, 476

$RuC_{14}H_{34}N_4O_2$
$[RuO(1,4,8,11\text{-}Me_4\text{-}1,4,8,11\text{-}tetraazacyclotetradecane)\text{-}$
$(OH_2)]^{2+}$, 476

$RuC_{14}H_{37}N_6$
$[RuH(NH_2NMe_2)_3(cod)]^+$, 460

$RuC_{14}H_{37}P_4$
$[RuH(Me_2PCH_2CH_2CH_2PMe_2)_2]^+$, 459

$RuC_{14}H_{39}ClO_2P_4$
$Ru(Cl)(\eta^2\text{-}OAc)(PMe_3)_4$, 402

$RuC_{14}H_{40}P_4$
$Ru(PMe_3)_4(C_2H_4)$, 367

$RuC_{14}H_{42}P_4$
$RuMe_2(PMe_3)_4$, 386

$RuC_{15}H_8F_6N_2O_7S_2$
$Ru(O_3SCF_3)_2(CO)$(phen), 345

$RuC_{15}H_{10}O_3S_2$
{Ru(SPh)$_2$(CO)$_3$}$_n$, 431
$RuC_{15}H_{11}Cl_3N_3$
RuCl$_3$(terpy), 356, 357
$RuC_{15}H_{11}Cl_3N_4O$
[RuCl$_2$(NO)(terpy)]$^-$, 357
$RuC_{15}H_{15}Cl_3N_3$
RuCl$_3$(py)$_3$, 327
$RuC_{15}H_{20}NO_7$
Ru(acac)$_2${MeCOC(=NO)COMe}, 464
$RuC_{15}H_{20}N_4$
[Ru(nbd)(NCMe)$_4$]$^{2+}$, 350, 365
$RuC_{15}H_{20}N_6$
[Ru(NH$_3$)$_5$(py)]$^{4+}$, 297
[Ru(NH$_3$)$_3$(terpy)]$^{3+}$, 297
$RuC_{15}H_{21}NO_7$
Ru(acac)$_2${ONCH(COMe)$_2$}, 362
$RuC_{15}H_{21}O_6$
Ru(acac)$_3$, 423
[Ru(acac)$_3$]$^-$, 424
$RuC_{15}H_{21}S_6$
Ru(MeCSCHCSMe)$_3$, 362, 436
$RuC_{15}H_{24}N_3O_3S_6$
Ru(S$_2$CNCH$_2$CH$_2$OCH$_2$CH$_2$)$_3$, 433
$RuC_{15}H_{25}N_3O$
[Ru(cod)(NCMe)$_3$(MeOH)]$^{2+}$, 365
$RuC_{15}H_{30}N_3S_6$
Ru(S$_2$CNEt$_2$)$_3$, 433
[Ru(S$_2$CNEt$_2$)$_3$]$^+$, 434
$RuC_{15}H_{30}N_3Se_6$
Ru(Se$_2$CNEt$_2$)$_3$, 440
$RuC_{15}H_{30}N_4OS_6$
Ru(S$_2$CNEt$_2$)$_3$(NO), 362, 434
$RuC_{15}H_{39}N_9$
[Ru(CNBu^t)$_3$(NH$_2$NH$_2$)$_3$]$^{2+}$, 364
$RuC_{15}H_{42}O_2P_4$
Ru(η^1-OAc)(Me)(PMe$_3$)$_4$, 386, 402
$RuC_{15}H_{45}ClO_{15}P_5$
[RuCl{P(OMe)$_3$}$_5$]$^+$, 376
$RuC_{15}H_{45}O_{15}P_5$
RuMe{P(OMe)$_3$}$_4${P(O)(OMe)$_2$}, 366, 386
Ru{P(OMe)$_3$}$_5$, 366, 371
$RuC_{15}H_{50}N_5S_{10}$
Ru$_2$(S$_2$CNEt$_2$)$_5$, 434
$RuC_{15}N_7$
[Ru(NH$_3$)$_5$(N$_2$)]$^{2+}$, 300
$RuC_{16}H_{10}Cl_2N_2O_2$
RuCl$_2$(CO)$_2$(NCPh)$_2$, 365
$RuC_{16}H_{11}Cl_2N_3O$
RuCl$_2$(CO)(terpy), 356, 392
$RuC_{16}H_{12}Cl_2N_8$
RuCl$_2$(2,2′-bipyrazine)$_2$, 335
$RuC_{16}H_{14}I_2O_2Se_2$
RuI$_2$(CO)$_2${PhSeCH$_2$CH$_2$SePh}, 440
$RuC_{16}H_{14}N_4O_5$
Ru(ONO)(salen)(NO), 463
$RuC_{16}H_{16}N_2O_6$
Ru(OAc)$_2$(CO)$_2$(py)$_2$, 326
$RuC_{16}H_{16}N_4O_2$
[Ru(CO)$_2$(NCMe)$_2$(py)$_2$]$^{2+}$, 326, 345
$RuC_{16}H_{18}I_2N_2O_2$
RuI$_2$(CO)$_2$(4-H$_2$NC$_6$H$_4$Me)$_2$, 381
$RuC_{16}H_{24}N_4$
[Ru(cod)(NCMe)$_4$]$^{2+}$, 365
$RuC_{16}H_{26}N_6$
[Ru(CNCH$_2$Ph)$_2$(NH$_3$)$_4$]$^{2+}$, 291
$RuC_{16}H_{27}O_4P$
Ru(CO)$_4$(PBu$^t_3$), 371
$RuC_{16}H_{38}N_2P_2$
RuH$_2$(CNBu^t)$_2$(PMe$_3$)$_2$, 452
$RuC_{16}H_{42}P_4$
RuEt$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$, 386
$RuC_{16}H_{46}P_4Si$
Ru{(CH$_2$)$_2$SiMe$_2$}(PMe$_3$)$_4$, 388
$RuC_{16}H_{47}ClP_5$
[RuCl(CH$_2$PMe$_3$)(PMe$_3$)$_4$]$^+$, 376, 386
$RuC_{16}H_{48}O_{15}P_5$
[RuMe{P(OMe)$_3$}$_5$]$^+$, 376, 386
$RuC_{17}H_{11}Cl_2N_3O_2$
RuCl$_2$(CO)$_2$(terpy), 356
$RuC_{17}H_{16}Cl_2N_2$
RuCl$_2$(nbd)(bipy), 347
$RuC_{17}H_{22}O_4$
Ru(acac)$_2$(nbd), 424
$RuC_{17}H_{30}Cl_2N_2$
RuCl$_2$(nbd){HN(CH$_2$)$_5$}$_2$, 324
$RuC_{17}H_{46}P_4$
Ru{(CH$_2$)$_2$CMe$_2$}(PMe$_3$)$_4$, 388
$RuC_{18}H_{13}Cl_2N_3O$
RuCl$_2$(CO)(py)(phen), 345
$RuC_{18}H_{14}N_2O_4$
Ru(salen)(CO)$_2$, 463
$RuC_{18}H_{15}ClN_9$
[RuCl(2,2′-bipyrazine)$_2$(NCMe)]$^+$, 335
$RuC_{18}H_{15}F_{12}P_5$
Ru(PF$_3$)$_4$(PPh$_3$), 367
$RuC_{18}H_{15}O_6Se_3$
Ru(O$_2$SePh)$_3$, 440
$RuC_{18}H_{15}S_3$
Ru(SPh)$_3$, 431
$RuC_{18}H_{18}O_2S_4$
Ru(2,3,8,9-dibenzo-1,4,7,10-tetrathiacyclodecane)-(CO)$_2$, 436
$RuC_{18}H_{23}ClN_2$
RuHCl(cod)(py)$_2$, 326
$RuC_{18}H_{26}O_4$
Ru(acac)$_2$(cod), 424
$RuC_{18}H_{27}O_3S_6$
Ru(EtOSCHCSMe)$_3$, 436
$RuC_{18}H_{29}ClN_2O_2P$
[RuCl(NH=NPh)(CO)$_2$(PBu^{t}Pr$_2$)]$^+$, 395
$RuC_{18}H_{31}N_3S$
[Ru(MeCN)$_3$(SEt$_2$)(cod)]$^{2+}$, 432
$RuC_{18}H_{34}N_{10}O_4S_4$
[Ru(adenine)$_2$(DMSO)$_4$]$^{2+}$, 438
$RuC_{18}H_{35}ClN_2$
RuHCl{HN(CH$_2$)$_5$}$_2$(cod), 457
$RuC_{18}H_{38}P_4$
RuH(η^1-Ph)(Ph$_2$PCH$_2$PPh$_2$)$_2$, 453
$RuC_{18}H_{43}O_5P$
[Ru(OH$_2$)$_5${P(C$_6$H$_{11}$)$_3$}]$^+$, 463
$RuC_{19}H_{14}Cl_2NO_2P$
RuCl$_2$(CO)$_2$(2-pyPPh$_2$), 409
$RuC_{19}H_{16}N_2O_5$
Ru(CO)$_3$(4-MeOC$_6$H$_4$N=CHCH=NC$_6$H$_4$OMe-4), 364
$RuC_{19}H_{22}Cl_2N_2$
RuCl$_2$(nbd)(H$_2$NPh)$_2$, 324
$RuC_{19}H_{26}Cl_2OP_2$
RuCl$_2$(CO)(PMe$_2$Ph)$_2$(C$_2$H$_4$), 390
$RuC_{19}H_{26}Cl_3OS_2$
RuCl$_3$(SPhPr^i)$_2$(MeOH), 432
$RuC_{19}H_{42}OP_4$
Ru(2-CH$_2$OC$_6$H$_4$)(PMe$_3$)$_4$, 389
$RuC_{19}H_{42}P_4$
Ru(2-CH$_2$C$_6$H$_4$)(PMe$_3$)$_4$, 389
$RuC_{20}H_{12}N_2O_4$
Ru(8-quinolinolate)$_2$(CO)$_2$, 465
$RuC_{20}H_{15}I_3O_2P$
[RuI$_3$(CO)$_2$(PPh$_3$)]$^-$, 383
$RuC_{20}H_{16}ClN_4S$
[RuCl(bipy)$_2$S]$^-$, 348, 349
$RuC_{20}H_{16}ClN_5O$
[RuCl(NO)(bipy)$_2$]$^+$, 348, 349
[RuCl(NO)(bipy)$_2$]$^{2-}$, 348–350, 354, 357
$RuC_{20}H_{16}ClN_5O_2$
RuCl(NO$_2$)(bipy)$_2$, 348, 349

$[RuCl(NO_2)(bipy)_2]^+$, 348

$RuC_{20}H_{16}ClN_5O_3$
$[RuCl(NO_3)(bipy)_2]^+$, 348

$RuC_{20}H_{16}ClN_5O_4S$
$RuCl\{N(O)SO_3\}(bipy)_2$, 350

$RuC_{20}H_{16}Cl_2N_4$
$RuCl_2(bipy)_2$, 323, 346, 348–353, 359–361
$[RuCl_2(bipy)_2]^+$, 348, 353, 361

$RuC_{20}H_{16}I_2N_4$
$RuI_2(bipy)_2$, 348

$RuC_{20}H_{16}N_4$
$[Ru(bipy)_2]^+$, 1001

$RuC_{20}H_{16}N_4O_2$
$[Ru(bipy)_2(O)_2]^{2+}$, 352

$RuC_{20}H_{16}N_6O_3$
$[Ru(NO_2)(NO)(bipy)_2]^{2+}$, 349

$RuC_{20}H_{16}N_6O_4$
$Ru(NO_2)(bipy)_2$, 349

$RuC_{20}H_{16}N_6S_2$
$[Ru(bipy)_2(S_2)]^{2+}$, 346

$RuC_{20}H_{16}N_8O$
$Ru(N_3)(NO)(bipy)_2$, 349

$RuC_{20}H_{16}N_8O_2$
$Ru(N_3)(NO_2)(bipy)_2$, 349

$RuC_{20}H_{16}N_{10}$
$Ru(N_3)_2(bipy)_2$, 350

$RuC_{20}H_{17}ClN_5O_2$
$[RuCl(NO_2H)(bipy)_2]^-$, 350

$RuC_{20}H_{17}N_4O_2$
$[Ru(bipy)_2(O)(OH)]^{2+}$, 352

$RuC_{20}H_{17}N_5O_2$
$[Ru(NO)(OH)(bipy)_2]^{2+}$, 348

$RuC_{20}H_{17}N_{10}O$
$[Ru(OH)(\overline{N{=}CHCH{=}CHN{=}CC{=}NCH{=}CHCH{=}N})_2(\overline{N{=}CHN{=}CHCH{=}CH})]^+$, 335

$RuC_{20}H_{18}ClN_4O$
$[RuCl(bipy)_2(OH_2)]^+$, 346, 353
$[RuCl(bipy)_2(OH_2)]^{2+}$, 353

$RuC_{20}H_{18}N_4O$
$[Ru(bipy)_2(OH_2)]^{2-}$, 352

$RuC_{20}H_{18}N_4O_2$
$[Ru(bipy)_2(O)(OH_2)]^{2+}$, 352

$RuC_{20}H_{19}Cl_3N_2P$
$[RuCl_3(phen)(PMe_2Ph)]^-$, 392

$RuC_{20}H_{19}N_4O_2$
$[Ru(OH)(OH_2)(bipy)_2]^{2-}$, 351, 352

$RuC_{20}H_{20}ClN_5O$
$[RuCl(NO)(py)_4]^{2+}$, 326

$RuC_{20}H_{20}ClN_5O_4S$
$RuCl\{N(O)SO_3\}(py)_4$, 326

$RuC_{20}H_{20}ClN_6$
$[RuCl(N_2)(py)_4]^-$, 326

$RuC_{20}H_{20}ClN_7$
$RuCl(N_3)(py)_4$, 326

$RuC_{20}H_{20}Cl_2N_4$
$RuCl_2(py)_4$, 327, 392

$RuC_{20}H_{20}N_4O_2$
$[Ru(bipy)_2(OH_2)_2]^{2+}$, 284, 347, 350, 351, 353
$[Ru(bipy)_2(OH_2)_2]^{3+}$, 345, 351

$RuC_{20}H_{20}N_6O_4$
$Ru(NO_2)_2(py)_4$, 326, 327

$RuC_{20}H_{21}N_5O_2$
$[Ru(OH)(NO)(py)_4]^{2-}$, 326

$RuC_{20}H_{22}ClF_3O_2P_2$
$RuCl(\eta^1\text{-}CF{=}CF_2)(CO)_2(PMe_2Ph)_2$, 386

$RuC_{20}H_{22}ClN_4O$
$[RuCl(py)_4(OH_2)]^+$, 326

$RuC_{20}H_{22}N_5O_2$
$[Ru(NO)(py)_4(OH_2)]^{2+}$, 326

$RuC_{20}H_{22}N_6$
$[Ru(bipy)_2(NH_3)_2]^{2+}$, 297, 349
$[Ru(bipy)_2(NH_3)_2]^{3+}$, 297

$RuC_{20}H_{23}ClN_5$
$[RuCl(NH_3)(py)_4]^+$, 326

$RuC_{20}H_{24}N_4O_2$
$[Ru(py)_4(OH_2)_2]^{2+}$, 327

$RuC_{20}H_{24}N_4O_8$
$[Ru\{O_2CCH_2N(CH_2CO_2H)CH_2CH_2N(CH_2CO_2H)\text{-}CH_2CO_2\}(py)_2]$, 467

$RuC_{20}H_{24}N_6O_{16}$
$[Ru\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}_2(N_2)]^{4-}$, 467

$RuC_{20}H_{25}ClO_3P_2$
$RuCl(COMe)(CO)_2(PMe_2Ph)_2$, 386

$RuC_{20}H_{25}Cl_3NS_2$
$RuCl_3(SPhPr^i)_2(MeCN)$, 432

$RuC_{20}H_{26}N_6$
$[Ru(NH_3)_2(py)_4]^{2+}$, 295

$RuC_{20}H_{28}O_2P_2$
$RuMe_2(CO)_2(PMe_2Ph)_2$, 386, 388

$RuC_{20}H_{31}Cl_2N_2OP$
$RuCl_2(CO)(py)_2(PBu^t{}_2Me)$, 392

$RuC_{20}H_{40}N_5S_8$
$[Ru_2N(S_2CNEt_2)_4]^+$, 435

$RuC_{20}H_{42}Cl_2N_2$
$RuCl_2(cod)\{H_2N(CH_2)_5Me\}_2$, 324

$RuC_{20}H_{44}N_8$
$[Ru(CNBu^t)_4(NH_2NH_2)_2]^{2+}$, 364

$RuC_{20}H_{48}O_2P_2Si_2$
$Ru(SiMe_3)_2(CO)_2(PEt_3)_2$, 286

$RuC_{21}H_{12}N_3S_6$
Ru(benzothiazole-2-thiolate)$_3$, 431

$RuC_{21}H_{15}Cl_2O_2PS$
$RuCl_2(CO)_2(CS)(PPh_3)$, 383

$RuC_{21}H_{15}Cl_6O_3PSi_2$
$Ru(SiCl_3)_2(CO)_3(PPh_3)$, 285

$RuC_{21}H_{15}O_3PS_2$
$Ru(S_2CO)(CO)_2(PPh_3)$, 406

$RuC_{21}H_{16}ClN_4O$
$[RuCl(CO)(bipy)_2]^+$, 346

$RuC_{21}H_{16}N_4O_3$
$Ru(CO_3)(bipy)_2$, 323, 350, 351, 353

$RuC_{21}H_{17}N_4O$
$[RuH(CO)(bipy)_2]^+$, 346, 459

$RuC_{21}H_{17}O_3P$
$RuH_2(CO)_3(PPh_3)$, 452

$RuC_{21}H_{18}N_4O_2$
$[Ru(CO)(bipy)_2(OH_2)]^{2+}$, 346

$RuC_{21}H_{19}F_6O_7PSi$
$Ru(Ph_2PCH_2SiMe_2OH)(CO)_2(O_2CCF_3)_2$, 286

$RuC_{21}H_{28}O_3P_2$
$RuMe(COMe)(CO)_2(PMe_2Ph)_2$, 386

$RuC_{21}H_{34}OP_4S_4$
$Ru(S_2PMe_2)_2(CO)(PMe_2Ph)_2$, 405

$RuC_{21}H_{47}ClOP_2$
$RuHCl(CO)(PBu^t{}_2Et)_2$, 457

$RuC_{21}H_{51}N_9$
$[Ru(CNBu^t)_3(NH_2NMe_2)_3]^{2+}$, 364

$RuC_{22}H_{15}O_4P$
$Ru(CO)_4(PPh_3)$, 368, 370, 371, 452

$RuC_{22}H_{16}Cl_2N_4O_2$
$RuCl_2(CO)_2(bipy)_2$, 357

$RuC_{22}H_{16}N_4O_2$
$[Ru(CO)_2(bipy)_2]^{2+}$, 346

$RuC_{22}H_{16}N_4O_4$
$Ru(C_2O_4)(bipy)_2$, 345, 353

$RuC_{22}H_{16}N_6$
$Ru(CN)_2(bipy)_2$, 282, 345
$[Ru(CN)_2(bipy)_2]^+$, 284

$RuC_{22}H_{16}N_6S_2$
$Ru(NCS)_2(bipy)_2$, 350
$Ru(SCN)_2(bipy)_2$, 284

$RuC_{22}H_{17}Cl_2O_2P$
$RuCl_2(CO)_2(2\text{-}CH_2{=}CHC_6H_4PPh_2)$, 390

$RuC_{22}H_{19}ClN_5$
$RuCl(bipy)_2(NCMe)$, 349
$[RuCl(bipy)_2(NCMe)]^+$, 349, 353

$RuC_{22}H_{19}N_3O_3$
Ru(salen)(CO)(py), 463
$[Ru(salen)(CO)(py)]^+$, 463
$RuC_{22}H_{19}N_6O$
$[Ru(NO)(bipy)_2(NCMe)]^{2+}$, 348
$[Ru(NO)(bipy)_2(NCMe)]^{3+}$, 348
$RuC_{22}H_{19}N_8$
$Ru(N_3)(bipy)_2(NCMe)$, 350
$RuC_{22}H_{20}N_4O_4$
$Ru(C_2O_4)(py)_4$, 327
$RuC_{22}H_{20}N_6S_2$
$Ru(NCS)_2(py)_4$, 327
$RuC_{22}H_{22}ClN_4OS$
$[RuCl(bipy)_2(DMSO)]^+$, 350
$RuC_{22}H_{22}N_4O_2$
$R(OMe)_2(bipy)_2$, 351
$RuC_{22}H_{24}N_5$
$[Ru(bipy)_2(en)]^{2+}$, 351
$RuC_{22}H_{24}N_6$
$[Ru(bipy)_2(en)]^{2+}$, 322
$RuC_{22}H_{26}N_6$
$[Ru(bipy)(en)(py)_2]^{2+}$, 322
$RuC_{22}H_{27}Cl_2O_2PS_2$
$RuCl_2(DMSO)_2(PPh_3)$, 408
$RuC_{22}H_{28}O_4P_2$
$Ru(COMe)_2(CO)_2(PMe_2Ph)_2$, 386
$RuC_{22}H_{39}ClP_4$
Ru(2-np)(Cl)($Me_2PCH_2CH_2PMe_2$)$_2$, 386
$RuC_{22}H_{40}N_6$
$[Ru(bipy)(TMEDA)_2]^{3+}$, 322
$RuC_{22}H_{40}P_4$
RuH(2-np)($Ph_2PCH_2PPh_2$)$_2$, 453
$RuC_{22}H_{47}ClO_2P_2$
$RuHCl(CO)_2(PBu^tPr_2)_2$, 457
$RuC_{23}H_{17}Cl_2O_3P$
$RuCl_2(CO)_3(2\text{-}CH_2{=}CHC_6H_4PPh_2)$, 390
$RuC_{23}H_{17}O_3P$
$Ru(CO)_3(2\text{-}H_2C{=}CHC_6H_4PPh_2)$, 372
$RuC_{23}H_{19}ClN_4O$
$[RuCl(bipy)_2(OCMe_2)]^+$, 357
$RuC_{23}H_{19}Cl_2O_3PS$
$RuCl_2(CO)_3(Ph_2PCH_2CH_2SPh)$, 409
$RuC_{23}H_{22}ClN_4O$
$[RuCl(bipy)_2(OCMe_2)]^+$, 349, 360
$RuC_{23}H_{22}N_2O_2$
Ru(salen)(nbd), 463
$RuC_{23}H_{24}Cl_6O_5PSi_2$
$Ru(SiCl_3)_2(CO)_2(PPh_3)\{P(OMe)_3\}$, 286
$RuC_{23}H_{41}O_6P_3S_2$
$[Ru(S_2CH)(PMe_2Ph)_2\{P(OMe)_3\}_2]^+$, 406
$RuC_{23}H_{50}ClNOP_2$
$RuHCl(CO)(CNMe)(PBu^t{}_2Et)_2$, 457
$RuC_{24}H_{16}Cl_2N_4$
$RuCl_2(phen)_2$, 353
$RuC_{24}H_{17}N_4O_2$
$[Ru\{2\text{-}(PhN{=}N)C_6H_4\}(CO)_2(bipy)]^+$, 353
$RuC_{24}H_{18}N_{12}$
$[Ru(2,2'\text{-bipyrazine})_3]^+$, 334
$[Ru(2,2'\text{-bipyrazine})_3]^{2+}$, 334, 335, 347
$[Ru(2,2'\text{-bipyrazine})_3]^{3+}$, 334
$RuC_{24}H_{20}ClN_6$
$[RuCl(bipy)_2(\overline{N{=}CHCH{=}NCH{=}CH})]^+$, 348, 359
$RuC_{24}H_{20}N_4O_2$
$Ru(PhN{=}NPh)_2(CO)_2$, 468
$RuC_{24}H_{21}F_8NO_4P_2$
$Ru(\eta^2\text{-}O_2CCF_3)_2(PF_2NMe_2)(PPh_3)$, 402
$RuC_{24}H_{22}N_6$
$[Ru(bipy)_2(NCMe)_2]^{2+}$, 334, 348, 361
$RuC_{24}H_{23}N_6OS$
$[Ru(NCS)(bipy)_2(DMF)]^+$, 350
$RuC_{24}H_{26}N_4O_2$
$[Ru(bipy)_2(DME)]^{2+}$, 351
$RuC_{24}H_{26}N_4O_4$
$Ru(OAc)_2(py)_4$, 426
$RuC_{24}H_{28}N_4O_2$
$[Ru(bipy)_2(EtOH)_2]^{2+}$, 353
$RuC_{24}H_{33}N_2O_6P_3$
$Ru(NO_3)_2(PMe_2Ph)_3$, 401
$RuC_{24}H_{37}Cl_2N_2P_3$
$RuCl_2(NH_2NH_2)(PMe_2Ph)_3$, 391
$RuC_{24}H_{42}N_4O_4$
$Ru(OAc)_2(Bu^tNC)_4$, 426
$RuC_{24}H_{42}P_4S_4$
$Ru(S_2PEt_2)_2(PMe_2Ph)_2$, 405
$RuC_{24}H_{60}Cl_2O_{12}P_4$
$RuCl_2\{P(OEt)_3\}_4$, 378
$RuC_{25}H_{19}ClN_5$
$[RuCl(bipy)(terpy)]^+$, 356, 357
$RuC_{25}H_{19}N_5O$
$[Ru(O)(terpy)(bipy)]^{2+}$, 357
$RuC_{25}H_{19}N_6O$
$[Ru(NO)(terpy)(bipy)]^{3+}$, 356
$RuC_{25}H_{19}N_6O_2$
$[Ru(NO_2)(terpy)(bipy)]^+$, 356
$RuC_{25}H_{19}N_6O_3$
$[Ru(NO_3)(terpy)(bipy)]^{2+}$, 356
$RuC_{25}H_{20}N_5O$
$[Ru(OH)(terpy)(bipy)]^{2+}$, 357
$RuC_{25}H_{21}ClN_5$
$[RuCl(bipy)_2(py)]^+$, 348, 350, 357
$[RuCl(bipy)_2(py)]^{2+}$, 357
$RuC_{25}H_{21}N_5O$
$[Ru(O)(bipy)_2(py)]^{2+}$, 351, 352
$[Ru(terpy)(bipy)(OH_2)]^{2+}$, 356, 357
$[Ru(terpy)(bipy)(OH_2)]^{3+}$, 357
$RuC_{25}H_{21}N_6O$
$[Ru(NO)(bipy)_2(py)]^{3+}$, 349, 350
$RuC_{25}H_{21}N_6O_2$
$[Ru(NO_2)(bipy)_2(py)]^+$, 348, 349
$RuC_{25}H_{21}N_6O_3$
$[Ru(NO_3)(bipy)_2(py)]^+$, 349
$RuC_{25}H_{22}N_5O$
$[Ru(OH)(bipy)_2(py)]^{2+}$, 351
$RuC_{25}H_{22}N_6$
$[Ru(terpy)(bipy)(NH_3)]^{2+}$, 356
$[Ru(terpy)(bipy)(NH_3)]^{3+}$, 297
$RuC_{25}H_{23}ClN_5$
$[RuCl(bipy)(py)_3]^+$, 348
$RuC_{25}H_{23}N_5O$
$[Ru(bipy)_2(py)(OH_2)]^{2+}$, 350–352
$[Ru(bipy)_2(py)(OH_2)]^{3+}$, 351
$RuC_{25}H_{24}N_6$
$[Ru(bipy)_2(py)(NH_3)]^{2+}$, 349
$RuC_{25}H_{27}N_2OPS_4$
$Ru(S_2CNMe_2)_2(CO)(PPh_3)$, 405
$RuC_{25}H_{33}ClNO_4P_3$
$RuCl(NO_3)(CO)(PMe_2Ph)_3$, 401
$RuC_{25}H_{33}Cl_2OP_3$
$RuCl_2(CO)(PMe_2Ph)_3$, 381
$RuC_{25}H_{33}Cl_2O_6P_3S$
$RuCl_2(CS)\{P(OMe)_2Ph\}_3$, 383
$RuC_{25}H_{37}NO_2P_2$
$RuMe(COMe)(CO)(CNBu^t)(PMe_2Ph)_2$, 387
$RuC_{25}H_{46}N_5$
$[RuH(CNBu^t)_5]^+$, 458
$RuC_{25}H_{50}N_5S_{10}$
$[Ru(S_2CNEt_2)_5]^+$, 1055
$RuC_{26}H_{12}N_2O_{10}$
$Ru_3(CO)_8$(8-quinolinolate)$_2$, 465
$RuC_{26}H_{15}F_{12}PS_4$
$[Ru\{S_2C_2(CF_3)_2\}_2(PPh_3)]$, 406
$[Ru\{S_2C_2(CF_3)_2\}_2(PPh_3)]^-$, 406
$RuC_{26}H_{16}N_4O_2$
$[Ru(CO)_2(phen)_2]^{2+}$, 345
$RuC_{26}H_{16}N_6$
$Ru(CN)_2(phen)_2$, 282

$RuC_{26}H_{18}N_4O_2S_4$
Ru(benzothiazole-2-thiolate)$_2$(py)$_2$(CO)$_2$, 431
$RuC_{26}H_{19}F_3N_5O_3S$
[Ru(O_3SCF_3)(terpy)(bipy)]$^+$, 357
[Ru(O_3SCF_3)(terpy)(bipy)]$^{2+}$, 357
$RuC_{26}H_{20}N_6$
[Ru(bipy)$_2$(N=CCH=CHCH=CHC=N), 335
$RuC_{26}H_{20}O_2P_2S_4$
Ru(S_2PPh_2)$_2$(CO)$_2$, 436
$RuC_{26}H_{21}ClN_5O_2$
[RuCl{N(O)C_6H_4OH}(bipy)$_2$]$^+$, 349
$RuC_{26}H_{21}N_7O_3$
[Ru(NO_2)(4-pyCONH$_2$)(bipy)$_2$]$^+$, 348
$RuC_{26}H_{22}Cl_2N_6O_2$
$RuCl_2$(HON=CPhN=NPh)$_2$, 364
$RuC_{26}H_{22}N_6$
[Ru(bipy)$_2${(NH)$_2C_6H_4$}]$^{2+}$, 335
$RuC_{26}H_{22}N_8$
Ru(bipy)$_2$(NCH=NCH=CH)$_2$, 359
$RuC_{26}H_{24}ClNO_2P$
RuCl(η^1-C_3H_5)(CO)$_2$(PPh_3)(η^2-MeCH=CN), 390
$RuC_{26}H_{24}N_6$
[Ru(phen)$_2$(en)]$^{2+}$, 322
$RuC_{26}H_{26}ClI_2NOP_2$
$RuClI_2$(NO)($PMePh_2$)$_2$, 394
$RuC_{26}H_{26}ClNOP_2$
RuCl(NO)($PMePh_2$)$_2$, 394
$RuC_{26}H_{26}Cl_3NOP_2$
$RuCl_3$(NO)($PMePh_2$)$_2$, 393
$RuC_{26}H_{28}N_4O_2$
[Ru(bipy)$_2$($OCMe_2$)$_2$]$^{2+}$, 351, 359
$RuC_{26}H_{30}Cl_2N_2P_2$
$RuCl_2$(bipy)(PMe_2Ph)$_2$, 392
$RuC_{26}H_{30}O_3P_2$
RuPh(COMe)(CO)$_2$(PMe_2Ph)$_2$, 386
$RuC_{26}H_{39}Cl_2OP_3$
$RuCl_2$(EtOH)(PMe_2Ph)$_3$, 399
$RuC_{27}H_{23}ClN_6$
[RuCl(4-$N_2C_6H_4$Me)(bipy)$_2$]$^{2+}$, 349, 353
$RuC_{27}H_{23}N_6O_3$
[Ru{N(O)C_6H_4Me}(NO_2)(bipy)$_2$]$^+$, 350
$RuC_{27}H_{24}N_4$
[Ru(nbd)(bipy)$_2$]$^{2+}$, 347
$RuC_{27}H_{24}N_6$
[Ru(bipy)$_2${2-pyC(Me)=NH}]$^{2+}$, 336
[Ru(bipy)$_2$(py)(MeCN)]$^{2+}$, 352
$RuC_{27}H_{26}N_6$
[Ru(bipy)$_2$(2-pyCHMeNH_2)]$^{2+}$, 336
$RuC_{27}H_{27}P_4$
[RuH($Ph_2PCH_2CH_2CH_2PPh_2$)$_2$]$^+$, 459
$RuC_{27}H_{36}N_9O_3$
Ru{ON(Et)=NNC_6H_4Me-4}$_3$, 467
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RuH{C_6H_4OP(OPh)$_2$}{P(OMe)$_3$}$_3$, 456
$RuC_{27}H_{54}O_3P_2$
Ru(CO)$_3$(PBu^t_3)$_2$, 371
$RuC_{28}H_{20}Cl_2N_4$
$RuCl_2${2-(2′-pyridyl)quinoline}$_2$, 353
$RuC_{28}H_{21}Cl_2N_2O_4$
$RuCl_2${PhCOC(Ph)=NOH}{PhCOC(Ph)=NO}, 464
$RuC_{28}H_{23}N_4O$
[Ru(CO)(η^1-CH_2Ph)(bipy)$_2$]$^+$, 347
$RuC_{28}H_{25}N_6$
[Ru($NCMe_2$)(terpy)(bipy)]$^{3+}$, 356
$RuC_{28}H_{26}O_2P_2$
RuH_2(CO)$_2$(dppe), 452
$RuC_{28}H_{28}Cl_3S_4$
$RuCl_3$(PhSCH_2CH_2SPh)$_2$, 432
$RuC_{28}H_{28}N_6$
[Ru(terpy)(bipy)(NH_2Pr^i)]$^{2+}$, 356
$RuC_{28}H_{30}ClN_2P_2$
[RuCl(phen)(PMe_2Ph)$_2$]$^+$, 392
$RuC_{28}H_{30}Cl_2N_2P_2$
$RuCl_2$(phen)(PMe_2Ph)$_2$, 392
$RuC_{28}H_{32}ClOP$
RuCl(Me)(cod){PPh_2(C_6H_4OMe-2)}, 409
$RuC_{28}H_{32}Cl_3P_2$
$RuCl_2$(PPh_3){Bu^tPCH=CMeC(Me)=CH}$_2$, 378
$RuC_{28}H_{32}N_4$
[Ru(cod)(py)$_4$]$^{2+}$, 326
$RuC_{28}H_{36}ClNOP_2$
RuCl(Ph)(CO)($CNBu^t$)(PMe_2Ph)$_2$, 384
$RuC_{28}H_{43}O_3P_4S_2$
[Ru(S_2CH)(PMe_2Ph)$_3${P(OMe)$_3$}]$^+$, 406
$RuC_{29}H_{17}F_{12}O_5P$
Ru(hfacac)$_2$(CO)(PPh_3), 400
$RuC_{29}H_{24}O_3P_2$
Ru(CO)$_3$(dppe), 370
$RuC_{29}H_{36}ClN_2OP_2$
[RuCl(bipy)(PMe_2Ph)$_2$($OCMe_2$)]$^+$, 392
$RuC_{29}H_{67}ClN_8O_9P_3$
[RuCl(MeNCH_2CH_2NMeC=CNMeCH_2CH_2NMe)$_2$-{P(OMe)$_3$}$_3$]$^+$, 385
$RuC_{30}H_{22}N_6$
[Ru(terpy)$_2$]$^{2+}$, 354
[Ru(terpy)$_2$]$^{3+}$, 354
$RuC_{30}H_{22}N_8$
[Ru(phen)$_2$(diimidazole)]$^{2+}$, 322
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$RuC_{30}H_{26}N_6$
[Ru(bipy)$_2$(py)$_2$]$^+$, 348
[Ru(bipy)$_2$(py)$_2$]$^{2+}$, 347, 352
[Ru(bipy)$_2$(py)$_2$]$^{3+}$, 348
$RuC_{30}H_{27}P_2$
[RuH_2(PPh_2)(PPh_3)]$^-$, 460
$RuC_{30}H_{28}N_6$
[Ru(bipy)(py)$_4$]$^{2+}$, 322, 347, 353
$RuC_{30}H_{30}N_6$
[Ru(py)$_6$]$^{2+}$, 325
$RuC_{30}H_{32}O_2P_2S_2$
Ru(SOCPh)$_2$(PMe_2Ph)$_2$, 407
$RuC_{30}H_{34}ClP$
RuHCl(PPh_3)(η-C_6Me_6), 457
$RuC_{30}H_{36}ClO_3P$
RuCl(Me)(cod){P(C_6H_4OMe-2)$_3$}, 409
$RuC_{30}H_{39}NO_2P_2$
RuPh(COMe)(CO)($CNBu^t$)(PMe_2Ph)$_2$, 387
$RuC_{30}H_{45}Cl_3NP_3$
$RuCl_3$($NPEt_2Ph$)(PEt_2Ph)$_2$, 419
$RuC_{30}H_{45}Cl_3P_3$
[$RuCl_3$(PEt_2Ph)$_3$]$^-$, 410
$RuC_{30}H_{45}N_2P_3S_4$
Ru(S_2CNMe_2)$_2$(PMe_2Ph)$_3$, 405
$RuC_{30}H_{46}N_2O_2P_2$
Ru{C(Me)=NBu^t}(COMe)(CO)($CNBu^t$)(PMe_2Ph)$_2$, 388
$RuC_{31}H_{30}Cl_2OP_2$
$RuCl_2$(CO)($Ph_2PCH_2CH_2CH$=$CHCH_2CH_2PPh_2$), 390
$RuC_{31}H_{31}Cl_2O_2P_2$
$RuCl_2$(acac)(dppe), 417
$RuC_{31}H_{31}N_9$
Ru{HC(NN=CHCH=CH)$_3$}{4-pyCH=CH_2)$_3$]$^{2+}$, 357
$RuC_{31}H_{45}Cl_2OP_3$
$RuCl_2$(CO)(PEt_2Ph)$_3$, 381
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$RuC_{32}H_{16}N_8$
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$RuC_{32}H_{20}F_6O_3P_2$
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$RuC_{32}H_{24}N_6$
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$RuC_{32}H_{26}N_6$
[Ru(bipy)(phen)(py)$_2$]$^{2+}$, 348
$RuC_{32}H_{28}ClN_2O_4P$
RuCl(2-HOC$_6$H$_4$CH=NOH)(2-HOC$_6$H$_4$CH=NO)(PPh$_3$), 398
$RuC_{32}H_{28}N_2O_2S_4$
[Ru{S$_2$CN(CH$_2$Ph)$_2$}$_2$(CO)$_2$]$^{+}$, 435
$RuC_{32}H_{32}Cl_2N_4O_4$
RuCl$_2$(4-MeOC$_6$H$_4$N=CHCH=NC$_6$H$_4$OMe-4)$_2$, 364
$RuC_{32}H_{35}ClO_2P_2$
RuCl(CO)(4-MeC$_6$H$_3$COC$_6$H$_4$Me-4)(PMe$_2$Ph)$_2$, 388
$RuC_{32}H_{40}N_2O_2P_2S_2$
Ru(SOCPh)$_2$(en)(PMe$_2$Ph)$_2$, 407
$RuC_{32}H_{47}P_4$
[RuH$_3$(PMe$_2$Ph)$_4$]$^{+}$, 462
$RuC_{33}H_{16}N_8O$
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$RuC_{33}H_{25}N_6O$
[Ru{2-OC$_6$H$_4$)benzimidazole)(bipy)$_2$]$^{+}$, 354
$RuC_{33}H_{26}Cl_2N_3P$
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$RuC_{33}H_{30}Cl_2N_3P$
RuCl$_2$(py)$_3$(PPh$_3$), 391
$RuC_{33}H_{30}N_3O_2P$
[Ru(terpy)(OH$_2$)$_2$(PPh$_3$)]$^{2+}$, 356
$RuC_{33}H_{34}Cl_2P_2$
RuCl$_2$(PMePh$_2$)$_2$(nbd), 390
$RuC_{33}H_{45}P_4S_2$
[Ru(S$_2$CHPMe$_2$Ph)(PMe$_2$Ph)$_3$]$^{+}$, 406
[Ru(S$_2$CH)(PMe$_2$Ph)$_4$]$^{+}$, 406
$RuC_{33}H_{49}OP_4$
[RuH(MeOH)(PMe$_2$Ph)$_4$]$^{+}$, 399, 458
$RuC_{33}H_{51}O_3P_3$
[Ru(Me$_2$CO)$_3$(PMe$_2$Ph)$_3$]$^{2+}$, 399
$RuC_{34}H_{24}N_6$
[Ru(bipy)(phen)$_2$]$^{2+}$, 335, 345
$RuC_{34}H_{26}N_6$
[Ru(phen)$_2$(py)$_2$]$^{2+}$, 347, 348, 353
$RuC_{34}H_{28}Cl_2N_2P_2$
RuCl$_2$(2-pyPPh$_2$)$_2$, 409
$RuC_{34}H_{29}N_2O_2P$
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$RuC_{34}H_{30}N_6$
[Ru(CNCH$_2$Ph)$_2$(bipy)$_2$]$^{2+}$, 351
$RuC_{34}H_{30}N_6O_2$
[Ru{N(O)C$_6$H$_4$Me}$_2$(bipy)$_2$]$^{2+}$, 349
$RuC_{34}H_{33}ClP_3$
[RuCl{PhP(CH$_2$CH$_2$PPh$_2$)$_2$}]$^{+}$, 380
$RuC_{34}H_{34}OP_2$
Ru(CO)(dppm)(cod), 372
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[RuCl{2-(Ph$_2$PCH$_2$CH$_2$)py}$_2$]$^{+}$, 408
$RuC_{34}H_{36}Cl_2N_2P_2$
RuCl$_2$(2-(Ph$_2$PCH$_2$CH$_2$)py}$_2$, 408
$RuC_{34}H_{41}ClN_2P_3$
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RuCl(Ph$_2$PCH$_2$CH$_2$CH$_2$PMe$_2$)$_2$, 376
$RuC_{34}H_{47}O_2P_4$
[Ru(η^2-OAc)(PMe$_2$Ph)$_4$]$^{+}$, 403
$RuC_{34}H_{47}O_3P_4$
[Ru(O$_2$COMe)(PMe$_2$Ph)$_4$]$^{+}$, 404
$RuC_{34}H_{56}N_4O_8P_4$
[Ru(NH$_2$NHMe)$_2$(P(OMe)$_2$Ph}$_4$]$^{2+}$, 391
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[RuCl$_2$(PhCN)(bipy)(PPh$_3$)]$^{+}$, 417
$RuC_{35}H_{30}N_5PS_2$
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$RuC_{35}H_{34}O_2P_2$
Ru(CO)$_2$(dppm)(cod), 372
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Ru(phthalocyanine)(CO)(NCMe), 475
$RuC_{35}H_{49}O_2P_4S$
[Ru(SOCOEt)(PMe$_2$Ph)$_4$]$^{+}$, 407
$RuC_{35}H_{50}NO_2P_4$
[Ru(O$_2$CNMe$_2$)(PMe$_2$Ph)$_4$]$^{-}$, 404
$RuC_{35}H_{50}NP_4S_2$
[Ru(S$_2$CNMe$_2$)(PMe$_2$Ph)$_4$]$^{+}$, 405
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{Ru(phthalocyanine)(N=CHCH=NCH=CH)}, 474
$RuC_{36}H_{22}N_{10}$
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[Ru(phen)$_3$]$^{2+}$, 328
$RuC_{36}H_{28}Cl_2N_2O_2P_2$
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$RuC_{36}H_{28}N_8O_2S_2$
Ru(phthalocyanine)(DMSO)$_2$, 474
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RuCl$_3$(NO){P(OPh)$_3$}$_2$, 394
$RuC_{36}H_{30}Cl_3NP_2S$
RuCl$_3$(NS)(PPh$_3$)$_2$, 394
$RuC_{36}H_{30}Cl_4N_6$
{Ru(PhN=NPh)Cl$_2$}$_2$(μ-PhN=NPh), 468
$RuC_{36}H_{30}F_9P_5$
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$RuC_{36}H_{31}N_2O_3P_2$
[Ru(OH)(NO)$_2$(PPh$_3$)$_2$]$^{-}$, 368
$RuC_{36}H_{32}O_7P_2S_2$
Ru(OH$_2$)(PPh$_3$)$_2$(SO$_2$)(SO$_4$), 399, 401, 408
$RuC_{36}H_{32}P_2$
[RuH$_3$(PPh$_3$)$_2$]$^{-}$, 460
$RuC_{36}H_{34}O_2P_2$

$RuH(OH)(OH_2)(PPh_3)_2$, 399
$RuC_{36}H_{35}ClN_2O_2P_2$
$RuCl(NH_2O)(NH_2OH)(PPh_3)_2$, 364
$RuC_{36}H_{35}P_2$
$[RuH_5(PPh_3)_2]^-$, 460
$RuC_{36}H_{36}P_2$
$RuH_6(PPh_3)_2$, 463
$RuC_{36}H_{37}Cl_2P_3$
$\{RuCl_2[PhP(CH_2CH_2CH_2PPh_2)_2]\}_n$, 380
$RuC_{36}H_{39}Cl_3P_3$
$RuCl_3$(3,4-Me_2-1-Ph-phosphole)$_3$, 416
$RuC_{36}H_{46}N_2O_2P_2S_2$
$Ru(SOCPh)_2(HNCMeCH_2CMe_2NH_2)(PMe_2Ph)_2$, 407
$RuC_{36}H_{61}Cl_2P_3$
$RuCl_2\{PhP[CH_2CH_2CH_2P(C_6H_{11})_2]_2\}$, 380
$RuC_{36}H_{72}P_2$
$RuH_6\{P(C_6H_{11})_3\}_2$, 463
$RuC_{37}H_{29}ClOP_2$
$\underline{RuCl(C_6H_4PPh_2)}(CO)(PPh_3)$, 389
$RuC_{37}H_{30}BrNO_2P_2$
$RuBr(CO)(NO)(PPh_3)_2$, 368
$RuC_{37}H_{30}ClNO_2P_2$
$RuCl(CO)(NO)(PPh_3)_2$, 368
$RuC_{37}H_{30}Cl_3OP_2$
$RuCl_3(CO)(PPh_3)_2$, 383
$RuC_{37}H_{30}Cl_3P_2S$
$[RuCl_3(CS)(PPh_3)_2]^-$, 383
$RuC_{37}H_{30}N_2O_3P_2$
$Ru(CO)_3(Ph_2Ppy)_2$, 370
$RuC_{37}H_{30}N_2O_7P_2$
$Ru(NO_3)_2(CO)(PPh_3)_2$, 401
$RuC_{37}H_{31}NO_4P_2$
$RuH(NO_3)(CO)(PPh_3)_2$, 401
$RuC_{37}H_{32}Cl_2OP_2S$
$RuCl_2(OH_2)(CS)(PPh_3)_2$, 383, 399
$RuC_{37}H_{32}Cl_2O_2P_2$
$RuCl_2(OH_2)(CO)(PPh_3)_2$, 399
$RuC_{37}H_{34}Cl_3OP_2$
$RuCl_3(PPh_3)_2$(MeOH), 377
$RuC_{37}H_{37}Cl_2OP_3$
$RuCl_2(CO)\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 383
$RuC_{37}H_{39}OP_3$
$RuH_2(CO)\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 451
$RuC_{37}H_{39}O_3P_2$
$[RuH(H_2O)_2(MeOH)(PPh_3)_2]^+$, 399, 459
$RuC_{37}H_{44}BrN_4O$
Ru(octaethylporphyrin)(Br)(CO), 471
$RuC_{37}H_{44}N_4O$
Ru(octaethylporphyrin)(CO), 469, 471, 472
[Ru(octaethylporphyrin)(CO)]$^+$, 471
$RuC_{37}H_{47}N_5O_2$
Ru(octaethylporphyrin)(OMe)(NO), 473
$RuC_{37}H_{61}Cl_2OP_3$
$RuCl_2(CO)\{PHP\{CH_2CH_2CH_2P(C_6H_{11})_2\}_2\}$, 383
$RuC_{37}H_{66}Cl_2OP_2$
$RuCl_2(CO)\{P(C_6H_{11})_3\}_2$, 381
$RuC_{37}H_{67}ClOP_2$
$RuHCl(CO)\{P(C_6H_{11})_3\}_2$, 457
$RuC_{37}H_{67}ClO_3P_2S$
$RuHCl(CO)\{P(C_6H_{11})_3\}_2(SO_2)$, 408, 457
$RuC_{38}H_{21}N_9O$
Ru(phthalocyanine)(CO)(py), 475
$RuC_{38}H_{28}O_2P_2$
$RuH_2(CO)_2$(5-Ph-dibenzophosphole)$_2$, 452
$RuC_{38}H_{30}ClN_2O_2P_2S_2$
$[RuCl(S_2N_2)(CO)_2(PPh_3)_2]^+$, 398
$RuC_{38}H_{30}Cl_2OPS$
$RuCl_2(CO)(CS)(PPh_3)$, 383
$RuC_{38}H_{30}Cl_2OP_2S$
$RuCl_2(CO)(CS)(PPh_3)_2$, 383
$RuC_{38}H_{30}Cl_2OP_2Se$
$RuCl_2(CO)(CSe)(PPh_3)_2$, 383
$RuC_{38}H_{30}Cl_2O_2P_2$
$RuCl_2(CO)_2(PPh_3)_2$, 381, 409
$RuCl_2\{PPh_2(C_6H_4CHO\text{-}2)\}_2$, 409
$RuC_{38}H_{30}Cl_4OP_2$
$RuCl_2(CCl_2)(CO)(PPh_3)_2$, 386
$RuC_{38}H_{30}I_2O_2P_2Se_2$
$RuI_2(CO)_2(SePPh_3)_2$, 440
$RuC_{38}H_{30}N_2O_6P_2$
$Ru(ONO)_2(CO)_2(PPh_3)_2$, 367
$RuC_{38}H_{30}N_2O_8P_2$
$Ru(NO_3)_2(CO)_2(PPh_3)_2$, 401
$RuC_{38}H_{30}N_2P_2S_2$
$\{Ru(NCS)_2(PPh_3)_2\}_n$, 397
$RuC_{38}H_{30}N_{10}O_2$
Ru(phthalocyanine)$(DMF)_2$, 475
$RuC_{38}H_{30}O_2P_2$
$RuI_2(CO)_2(PPh_3)_2$, 382
$RuC_{38}H_{30}O_2P_2S_3$
$Ru(CO)_2(SPPh_3)_2S$, 404
$RuC_{38}H_{30}O_6P_2S$
$Ru(SO_4)(CO)_2(PPh_3)_2$, 402
$RuC_{38}H_{30}O_6P_2S_2$
$Ru(CO)_2(PPh_3)_2(OSOSO_2)$, 371
$RuC_{38}H_{31}ClOP_2S_2$
$RuCl(S_2CH)(CO)(PPh_3)_2$, 406
$RuC_{38}H_{31}ClO_2P_2$
$RuHCl(CO)_2(PPh_3)_2$, 457
$RuC_{38}H_{31}ClO_2P_2S$
$RuCl(\eta^2\text{-}OCOH)(CS)(PPh_3)_2$, 383, 402
$RuC_{38}H_{31}F_9O_2P_4$
$RuH(O_2CCF_3)(PF_3)_2(PPh_3)_2$, 455
$RuC_{38}H_{31}IO_2P_2Se$
$RuI(OH)(CO)(CSe)(PPh_3)_2$, 383
$RuC_{38}H_{31}N_5O_2P$
$[Ru(NO_2)(bipy)_2(PPh_3)]^+$, 392
$RuC_{38}H_{32}O_2P_2$
$RuH_2(CO)_2(PPh_3)_2$, 371, 451
$RuC_{38}H_{32}P_2S_4$
$Ru(S_2CH)_2(PPh_3)_2$, 406
$RuC_{38}H_{33}ClN_2OP_2$
$RuCl(CN)(NH_3)(CO)(PPh_3)_2$, 283, 391
$RuC_{38}H_{33}O_3P_2$
$RuH(H_2O)(CO)_2(PPh_3)_2$, 459
$[RuH(H_2O)(CO)_2(PPh_3)_2]^+$, 399
$RuC_{38}H_{33}P_2$
$[\underline{Ru(C_6H_4PPh_2)}(PPh_3)(C_2H_4)]^-$, 460
$RuC_{38}H_{34}Cl_2OP_2S$
$RuCl_2(CS)(MeOH)(PPh_3)_2$, 383, 399
$RuC_{38}H_{34}Cl_2O_2P_2$
$RuCl_2(CO)(MeOH)(PPh_3)_2$, 399
$RuCl_2\{PPh_2(C_6H_4OMe\text{-}2)\}_2$, 408
$[RuCl_2\{PPh_2(C_6H_4OMe\text{-}2)\}_2]^+$, 418
$RuC_{38}H_{35}NP_2$
$RuH_2(MeCN)(PPh_3)_2$, 452
$RuC_{38}H_{37}O_2P_3$
$Ru(CO)_2\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 372
$[Ru(CO)_2\{PhP(CH_2CH_2CH_2PPh_2)_2\}]^{2+}$, 383
$RuC_{38}H_{38}F_6NP_4$
$RuH_2(PF_3)(PF_3NMe_2)(PPh_3)_2$, 451
$RuC_{38}H_{38}O_3P_4S_2$
$Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}$, 405
$RuC_{38}H_{41}F_3NP_4$
$[RuH(MeCN)(PF_3)\{PhP(CH_2CH_2CH_2PPh_2)_2\}]^+$, 460
$RuC_{38}H_{43}O_2P_3S_2$
$Ru(SOCPh)_2(PMe_2Ph)_3$, 407
$RuC_{38}H_{44}N_4O_2$
Ru(octaethylporphyrin)$(CO)_2$, 469
$RuC_{38}H_{44}N_6$
[Ru(octaethylporphyrin)$(CN)_2]^-$, 473
$RuC_{38}H_{47}N_5O_2$
Ru(octaethylporphyrin)(O_2)(NCMe), 473
$RuC_{38}H_{51}N_4P$
$Ru(CNBu^t)_4(PPh_3)$, 371
$RuC_{38}H_{62}O_2P_3$

$[RuH(CO)_2\{PhP\{CH_2CH_2CH_2P(C_6H_{11})_2\}_2\}]^+$, 460
$RuC_{38}H_{66}O_2P_3$
$Ru(CO)_2\{PhP\{CH_2CH_2CH_2P(C_6H_{11})_2\}_2\}$, 372
$RuC_{38}H_{70}P_2$
$[RuH\{C_6H_{10}P(C_6H_{11})_2\}\{P(C_6H_{11})_3\}(C_2H_4)]$, 463
$RuC_{39}H_{30}ClF_3O_2P_2$
$RuCl(CF_3)(CO)_2(PPh_3)_2$, 386
$RuC_{39}H_{30}ClNO_2P_2$
$RuCl(CN)(CO)_2(PPh_3)_2$, 283
$RuC_{39}H_{30}IO_3P_2$
$[RuI(CO)_3(PPh_3)_2]^+$, 280, 382
$RuC_{39}H_{30}O_2P_2S_2$
$Ru(CS_2)(CO)_2(PPh_3)_2$, 383
$RuC_{39}H_{30}O_3P_2$
$Ru(CO)_3(PPh_3)_2$, 370, 371, 463
$RuC_{39}H_{30}O_3P_2S$
$Ru(CO)_2(PPh_3)_2(\eta^2\text{-COS})$, 371
$RuC_{39}H_{30}O_3P_2S_2$
$Ru(S_2CO)(CO)_2(PPh_3)_2$, 371
$RuC_{39}H_{31}O_3P_2$
$[RuH(CO)_3(PPh_3)_2]^+$, 459
$RuC_{39}H_{33}IO_2P_2$
$RuI(\eta^2\text{-COMe})(CO)(PPh_3)_2$, 387
$RuC_{39}H_{34}ClNO_2P_2$
$RuCl(CO)(NO)(PPh_2CH_2Ph)_2$, 368
$RuC_{39}H_{34}Cl_2O_2P_2$
$RuCl_2(CO)\{PPh_2(C_6H_4OMe\text{-}2)\}_2$, 408
$RuC_{39}H_{34}O_2P_2S_2$
$RuH(S_2COMe)(CO)(PPh_3)_2$, 406
$RuC_{39}H_{34}O_3P_2$
$Ru(\eta^2\text{-}O_2CH)(Me)(CO)(PPh_3)_2$, 403
$RuC_{39}H_{35}NOP_2$
$Ru(NO)(PPh_3)_2(\eta\text{-}C_3H_5)$, 368
$RuC_{39}H_{36}Cl_2OP_2$
$\{RuCl_2(Me_2CO)(PPh_3)_2\}_n$, 399
$RuC_{39}H_{43}O_3P_4$
$RuH_2\{P(OMe)_3\}\{PhP(CH_2CH_2CH_2PPh_2)_2\}$, 451
$RuC_{39}H_{49}OP_4S$
$[Ru(SOCPh)(PMe_2Ph)_4]^+$, 407
$RuC_{39}H_{50}N_4O_2$
Ru(octaethylporphyrin)(CO)(EtOH), 469
$RuC_{40}H_{30}N_2O_2P_2S_2$
$Ru(NCS)_2(CO)_2(PPh_3)_2$, 397
$RuC_{40}H_{30}N_2O_2P_2Se_2$
$Ru(NCSe)_2(CO)_2(PPh_3)_2$, 440
$RuC_{40}H_{32}O_3P_2S_2$
$Ru(SOCH)_2(CO)_2(PPh_3)_2$, 407
$RuC_{40}H_{33}NOP_2S_2$
$Ru(CN)(\eta_2\text{-}CS_2Me)(CO)(PPh_3)_2$, 283
$RuC_{40}H_{33}O_2P_2S_2$
$[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]^+$, 406
$RuC_{40}H_{34}Cl_2O_4P_2$
$RuCl_2(CO)_2\{PPh_2(C_6H_4OMe\text{-}2)\}_2$, 409
$RuC_{40}H_{34}Cl_2P_2$
$RuC_{12}(2\text{-}CH_2{=}CHC_6H_4PPh_2)_2$, 390
$RuC_{40}H_{35}ClO_2P_2$
$RuCl(COEt)(CO)(PPh_3)_2$, 387
$RuC_{40}H_{36}Cl_2N_2P_2$
$RuCl_2(MeCN)_2(PPh_3)_2$, 396
$RuC_{40}H_{36}O_4P_2$
$Ru(\eta^2\text{-}OAc)_2(PPh_3)_2$, 402
$RuC_{40}H_{37}Cl_2NOP_2S$
$RuCl_2(CS)(PPh_3)_2(DMF)$, 399
$RuC_{40}H_{37}Cl_2NO_2P_2$
$RuCl_2(CO)(DMF)(PPh_3)_2$, 383, 399
$RuCl_2(HONCMeCOMe)(PPh_3)_2$, 397
$RuC_{40}H_{38}Cl_2N_2O_2P_2$
$RuCl_2(H_2DMG)(PPh_3)_2$, 397
$RuC_{40}H_{38}Cl_2P_2S_2$
$\{RuCl_2(Ph_2PCH_2CH_2SPh)_2\}_n$, 409
$RuC_{40}H_{38}N_2OP_2$
$[Ru(OH_2)(MeCN)_2(PPh_3)_2]^{2+}$, 397
$RuC_{40}H_{39}ClO_3P_3S$
$[RuCl(CS)\{P(OMe)Ph_2\}_3]^+$, 383
$RuC_{40}H_{39}ClO_4P_3$
$[RuCl(CO)\{P(OMe)Ph_2\}_3]^+$, 382
$RuC_{40}H_{39}Cl_2OP_3$
$RuCl_2(CO)(PMePh_2)_3$, 390
$RuC_{40}H_{39}Cl_2O_4P_3$
$RuCl_2(CO)\{P(OMe)Ph_2\}_3$, 381
$RuC_{40}H_{39}N_2O_7P_3$
$Ru(NO_3)_2(CO)(PMePh_2)_3$, 401
$RuC_{40}H_{40}Cl_2N_2P_2$
$RuCl_2\{PPh_2(C_6H_4NMe_2)\}_2$, 408
$RuC_{40}H_{40}Cl_2OP_4$
$RuCl_2\{1,2\text{-}(MePhP)_2C_6H_4\}\{2\text{-}(MePhP)C_6H_4P(O)MePh\}$, 380
$RuC_{40}H_{41}OP_3$
$RuH_2(CO)(PMePh_2)_3$, 451
$RuC_{40}H_{42}P_4S_4$
$Ru(S_2PMe_2)_2(PPh_3)_2$, 405
$RuC_{40}H_{47}O_4P_4$
$[RuH(CO)\{P(OMe)_3\}\{PhP(CH_2CH_2CH_2PPh_2)_2\}]^+$, 460
$RuC_{40}H_{49}ClN_2P_3$
$[RuCl(3,4,7,8\text{-}Me_4phen)(PMe_2Ph)_3]^+$, 392
$RuC_{40}H_{55}NO_3P_5$
$[Ru(NO_3)(PMe_2Ph)_5]^+$, 401
$RuC_{40}H_{56}P_5$
$[RuH(PMe_2Ph)_5]^+$, 458
$RuC_{40}H_{62}O_8P_4$
$RuH_2\{P(OEt)_2Ph\}_4$, 451
$RuC_{40}H_{80}ClF_3N_{16}P$
$[RuCl(MeNCH_2CH_2NMeC{=}CNMeCH_2CH_2NMe)_4(PF_3)]^+$, 385
$RuC_{41}H_{30}F_6OP_2S_2$
$Ru\{S_2C_2(CF_3)_2\}(CO)(PPh_3)_2$, 406
$RuC_{41}H_{33}ClN_5$
$[RuCl(terpy)(pyCH{=}CHPh)_2]^+$, 356
$RuC_{41}H_{33}N_3OP$
$[Ru(\eta\text{-}CH_2Ph)(CO)(PPh_3)(terpy)]^+$, 356, 392
$RuC_{41}H_{34}OP_2$
$Ru(CO)(2\text{-}H_2C{=}CHC_6H_4PPh_2)_2$, 372
$RuC_{41}H_{35}ClOP_2$
$Ru(2\text{-}CHMeC_6H_4PPh_2)Cl(CO)(2\text{-}CH_2{=}CHC_6H_4PPh_2)$, 390
$RuC_{41}H_{35}Cl_3NP_2$
$RuCl_3(PPh_3)_2(py)$, 416
$RuC_{41}H_{36}N_2OP_2S_2$
$Ru(S_2CNMe)(CNMe)(CO)(PPh_3)_2$, 406
$RuC_{41}H_{36}O_3P_2S_2$
$Ru(SOCMe)_2(CO)(PPh_3)_2$, 407
$RuC_{41}H_{36}O_5P_2$
$Ru(OAc)_2(CO)(PPh_3)_2$, 402
$RuC_{41}H_{36}P_2$
$RuH(PPh_3)_2Cp$, 457
$RuC_{41}H_{37}N_2OP_2$
$[RuH(CO)(MeCN)_2(PPh_3)_2]^+$, 459
$RuC_{41}H_{38}Cl_2OP_2S_2$
$RuCl_2(CO)(Ph_2PCH_2CH_2SPh)_2$, 410
$RuC_{41}H_{39}Cl_2NO_2P_2$
$RuCl_2(CO)(AcNMe_2)(PPh_3)_2$, 399
$RuC_{41}H_{39}NP_2$
$RuH(\eta\text{-}C_3H_5)(MeCN)(PPh_3)_2$, 457
$RuC_{41}H_{39}OP_2$
$RuH(CO)(PPh_3)_2(THF)$, 399
$RuC_{41}H_{49}BrN_5$
Ru(octaethylporphyrin)(Br)(py), 472
$RuC_{41}H_{52}N_4O_2$
Ru(octaethylporphyrin)(CO)(THF), 470
$RuC_{42}H_{20}Cl_2NP_2S$
$RuCl_2(CS)(py)(PPh_3)_2$, 392
$RuC_{42}H_{26}N_{10}$
Ru(phthalocyanine)$(py)_2$, 475
$RuC_{42}H_{30}Cl_6O_2P_2$
$RuCl_2(C_6Cl_4O_2)(PPh_3)_2$, 400

$RuC_{42}H_{30}S_6$
$Ru(S_2C_2Ph_2)_3$, 436
$RuC_{42}H_{32}F_6O_3P_2$
$RuH(hfacac)(CO)(PPh_3)_2$, 400
$RuC_{42}H_{34}Cl_2O_2P_2$
$RuCl_2(CO)_2(2\text{-}CH_2{=}CHC_6H_4PPh_2)_2$, 390
$RuC_{42}H_{34}O_2P_2$
$Ru(CO)_2(2\text{-}H_2C{=}CHC_6H_4PPh_2)_2$, 372
$Ru(CO)_2(2\text{-}Ph_2PC_6H_4CH{=}CHCHMeC_6H_4PPh_2\text{-}2)$, 372
$RuC_{42}H_{36}N_4P_2S_2$
$Ru(NCS)_2(MeCN)_2(PPh_3)_2$, 397
$RuC_{42}H_{37}ClO_3P_2$
$RuCl(acac)(CO)(PPh_3)_2$, 400
$RuC_{42}H_{37}NO_6P_2$
$Ru(NO_3)(acac)(CO)(PPh_3)_2$, 400
$RuC_{42}H_{38}Cl_2O_2P_2S_2$
$RuCl_2(CO)_2(Ph_2PCH_2CH_2SPh)_2$, 409
$RuC_{42}H_{38}O_3P_2$
$RuH(acac)(CO)(PPh_3)_2$, 400
$RuC_{42}H_{38}P_2$
$RuH(PPh_3)_2(\eta\text{-}C_6H_6)$, 457
$RuC_{42}H_{39}Cl_2O_3P_3S$
$RuCl_2(CO)(SO_2)(triphos)$, 382
$RuC_{42}H_{40}Cl_2F_4P_4$
$\{RuCl_2(PF_2CH_2CH{=}CH_2)_2(PPh_3)_2\}_n$, 378
$RuC_{42}H_{41}NP_2$
$RuH(\eta^3\text{-}C_4H_7)(MeCN)(PPh_3)_2$, 457
$RuC_{42}H_{42}ClP_4$
$[RuCl\{(Ph_2PCH_2CH_2PPhCH_2)_2\}]^+$, 377
$RuC_{42}H_{42}Cl_2NP_3$
$RuCl_2\{N(CH_2CH_2PPh_2)_3\}$, 380
$RuC_{42}H_{42}N_7P_3$
$Ru(N_3)_2\{N(CH_2CH_2PPh_2)_3\}$, 394
$RuC_{42}H_{42}O_3P_3$
$[Ru(\eta^2\text{-}OAc)(CO)(PMePh_2)_3$, 403
$RuC_{42}H_{43}Cl_2NOP_2$
$RuCl_2(HON{=}CMeBu^t)(PPh_3)_2$, 397
$RuC_{42}H_{44}Cl_2N_2O_2P_2$
$RuCl_2(HON{=}CMe_2)_2(PPh_3)_2$, 397
$RuC_{42}H_{44}P_4$
$RuH_2(PMePh_2)_4$, 451
$RuC_{42}H_{45}P_3$
$RuH\{\eta\text{-}C_3H_5)(PMePh_2)_3$, 457
$RuC_{42}H_{49}NP_2Si_2$
$RuH\{N(SiMe_3)_2\}(PPh_3)_2$, 457
$RuC_{42}H_{49}N_5O$
Ru(octaethylporphyrin)(CO)(py), 471–473
$[Ru(octaethylporphyrin)(CO)(py)]^{2+}$, 471
$RuC_{42}H_{49}N_5S$
Ru(octaethylporphyrin)(CS)(py), 473
$RuC_{42}H_{49}N_6$
Ru(octaethylporphyrin)(CN)(py), 473
$RuC_{42}H_{55}F_3O_2P_5$
$[Ru(\eta^1\text{-}O_2CCF_3)(PMe_2Ph)_5]^+$, 403
$RuC_{42}H_{56}O_6P_5$
$[RuH\{P(OMe)_3\}_2\{PhP(CH_2CH_2CH_2PPh_2)_2\}]^+$, 459
$RuC_{42}H_{66}N_6O_6$
$[Ru(CNCMe_2CH_2COMe)_6]^{2+}$, 282
$RuC_{42}H_{72}ClNOP_2$
$RuHCl(CO)(py)\{P(C_6H_{11})_3\}_2$, 457
$RuC_{43}H_{30}Cl_4N_2O_2P_2$
$Ru(CO)_2(PPh_3)_2(N_2C_5Cl_4)$, 371
$RuC_{43}H_{35}Cl_2FN_2OP_2$
$RuCl_2(N_2HC_6H_4F\text{-}4)(CO)(PPh_3)_2$, 364
$RuC_{43}H_{35}Cl_2O_2P_2$
$RuCl_2(O_2CPh)(PPh_3)_2$, 417
$RuC_{43}H_{36}ClO_2P_2$
$RuCl(2\text{-}pyCH_2O)(CO)(PPh_3)_2$, 389
$RuC_{43}H_{36}N_2OP_2$
$RuH(NNPh)(CO)(PPh_3)_2$, 395
$RuC_{43}H_{36}N_5O$
$[Ru(bipy)_2(py)(OPPh_3)]^{2+}$, 352
$RuC_{43}H_{37}Cl_2N_2OP_2$
$\{RuCl_2(NNC_6H_4OMe\text{-}4)(PPh_3)_2\}_n$, 395
$RuC_{43}H_{37}Cl_3N_2P_2$
$RuCl_3(NNC_6H_4Me\text{-}4)(PPh_3)_2$, 394
$RuC_{43}H_{38}Cl_2P_2$
$RuCl_2(PPh_3)_2(nbd)$, 390
$RuC_{43}H_{39}ClO_2P_3$
$[RuCl(CO)_2(triphos)]^+$, 383
$RuC_{43}H_{39}ClO_5P_2$
$RuCl(MeO_2CCH_2CHCO_2Me)(CO)(PPh_3)_2$, 389
$RuC_{43}H_{39}ClP_2$
$RuHCl(PPh_3)_2(nbd)$, 457
$RuC_{43}H_{39}O_2P_3$
$Ru(CO)_2(triphos)$, 372
$RuC_{43}H_{40}NOP_2S_3$
$[Ru(S_2CNEt_2)(CO)(CS)(PPh_3)_2]^+$, 406
$RuC_{43}H_{45}Cl_2P_3S_2$
$RuCl_2(S_2CPEtPh_2)(PEtPh_2)_2$, 407
$RuC_{43}H_{47}OP_3$
$RuH_2(CO)(PEtPh_2)_3$, 451
$RuC_{43}H_{52}N_6$
Ru(octaethylporphyrin)(NCMe)(py), 472
$[Ru(octaethylporphyrin)(NCMe)(py)]^+$, 472
$RuC_{44}H_{30}Cl_4O_4P_2$
$Ru(2\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2$, 401
$[Ru(2\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2]^+$, 418
$RuC_{44}H_{30}F_{12}P_2S_4$
$Ru\{S_2C_2(CF_3)_2\}_2(PPh_3)_2$, 406
$RuC_{44}H_{33}O_2P_3$
$Ru(CO)_2\{PhP(C_6H_4PPh_2\text{-}2)_2\}$, 372
$RuC_{44}H_{34}Cl_3NOP_2$
$RuCl_2(CO)(CNC_6H_4Cl\text{-}4)(PPh_3)_2$, 384
$RuC_{44}H_{35}ClO_3P_2$
$RuCl(\eta^2\text{-}O_2CPh)(CO)(PPh_3)_2$, 387, 403
$RuC_{44}H_{35}FIN_2O_2P_2$
$[RuI(N_2HC_6H_4F\text{-}4)(CO)_2(PPh_3)_2]^+$, 364
$RuC_{44}H_{36}ClN_2O_2P_2$
$[RuCl(NH{=}NPh)(CO)_2(PPh_3)_2]^+$, 395
$RuC_{44}H_{36}N_2O_2P_2$
$RuH(NNPh)(CO)_2(PPh_3)_2$, 395
$RuC_{44}H_{37}F_3O_5P_2$
$Ru(O_2CCF_3)(acac)(CO)(PPh_3)_2$, 400
$RuC_{44}H_{37}N_2O_2P_2$
$[RuH(NH{=}NPh)(CO)_2(PPh_3)_2]^-$, 395
$RuC_{44}H_{38}ClNOP_2$
$RuCl(2\text{-}pyCH_2CH_2)(CO)(PPh_3)_2$, 389
$RuC_{44}H_{42}N_2O_4P_2$
$Ru(OAc)_2(CNMe)_2(PPh_3)_2$, 384
$RuC_{44}H_{43}ClN_2OP_2$
$RuCl\{CH_2{=}C(Me)NCHNPr\}(CO)(PPh_3)_2$, 395
$RuC_{44}H_{43}NOP_2S_4$
$[Ru(S_2CNEt_2)(\eta^1\text{-}CS_2Me)(CO)(PPh_3)_2$, 406
$RuC_{44}H_{46}O_2P_2$
$RuH(C_6H_4PPh_2)(PPh_3)(THF)_2$, 454
$RuC_{44}H_{48}ClOP_4S$
$[RuCl(DMSO)\{(Ph_2PCH_2CH_2PPhCH_2)_2\}]^+$, 377
$RuC_{44}H_{48}O_2P_2Si_2$
$Ru(SiMe_3)_2(CO)_2(PPh_3)_2$, 286
$RuC_{44}H_{49}ClOP_3S_2$
$[RuCl(MeOH)(S_2CPEtPh_2)(PEtPh_2)_2]^+$, 407
$RuC_{45}H_{28}ClN_4O$
Ru(tetraphenylporphyrin)Cl(CO), 469
$RuC_{45}H_{28}N_4O$
Ru(tetraphenylporphyrin)(CO), 472
$RuC_{45}H_{28}N_4O_{13}S_4$
$Ru\{(4\text{-}O_3SC_6H_4)_4porphyrin)\}(CO)]^{4-}$, 472
$RuC_{45}H_{37}ClN_9P_3$
$RuHCl\{(2\text{-}py)_3P\}_3$, 409
$RuC_{45}H_{37}ClO_2P_2$
$RuCl(2\text{-}MeCOC_6H_4)(CO)(PPh_3)_2$, 389
$RuCl(COC_6H_4Me\text{-}4)(CO)(PPh_3)_2$, 387
$RuC_{45}H_{37}IO_2P_2$
$RuI(\eta^2\text{-}COC_6H_4Me\text{-}4)(CO)(PPh_3)_2$, 387

$RuC_{45}H_{37}NO_3P_2$
Ru(CO)(CNC$_6$H$_4$Me-4)(O$_2$)(PPh$_3$)$_2$, 371
$RuC_{45}H_{38}O_3P_2$
Ru(η^2-O$_2$CH)(C$_6$H$_4$Me-2)(CO)(PPh$_3$)$_2$, 403
$RuC_{45}H_{39}NO_2P_3$
[Ru(CO)(NO)(PPh$_3$)(dppe)]$^+$, 370
$RuC_{45}H_{51}Cl_2O_2P_3S_2$
RuCl$_2$(DMSO)$_2$(triphos), 408
$RuC_{45}H_{52}ClO_2P_3S_2$
RuHCl(DMSO)$_2$(triphos), 458
$RuC_{45}H_{54}O_2P_2$
RuHMe(PPh$_3$)$_2$(Et$_2$O)$_2$, 454
$RuC_{46}H_{37}NO_2P_2$
Ru(CO)$_2$(CNC$_6$H$_4$Me-4)(PPh$_3$)$_2$, 371
$RuC_{46}H_{37}NO_4P_2$
Ru(CO$_3$)(CO)(CNC$_6$H$_4$Me-4)(PPh$_3$)$_2$, 371, 384, 402
$RuC_{46}H_{38}ClNO_3P_2$
RuCl(CO)$_2$(CONHC$_6$H$_4$Me-4)(PPh$_3$)$_2$, 391
$RuC_{46}H_{38}Cl_2N_2P_2$
[RuCl$_2$(bipy)(PPh$_3$)$_2$]$^+$, 417
$RuC_{46}H_{38}N_2P_2$
RuH(C$_6$H$_4$PPh$_2$)(bipy)(PPh$_3$), 455
$RuC_{46}H_{38}N_2P_2S_2$
Ru(2-pyS)$_2$(PPh$_3$)$_2$, 431
$RuC_{46}H_{40}Cl_2N_2P_2$
RuCl$_2$(py)$_2$(PPh$_3$)$_2$, 391
$RuC_{46}H_{40}N_2P_2$
RuH$_2$(bipy)(PPh$_3$)$_2$, 452
$RuC_{46}H_{40}N_4P_2$
[Ru(bipy)$_2$(dppe)]$^{2+}$, 351
$RuC_{46}H_{41}Cl_2NOP_2$
RuCl$_2$(CO)(HCNMeC$_6$H$_4$Me-4)(PPh$_3$)$_2$, 384
$RuC_{46}H_{44}O_4P_2$
Ru(acac)$_2$(PPh$_3$)$_2$, 400
$RuC_{46}H_{54}N_6$
Ru(octaethylporphyrin)(py)$_2$, 471–473
[Ru(octaethylporphyrin)(py)$_2$]$^+$, 471
$RuC_{47}H_{34}N_4O_2$
Ru(tetraphenylporphyrin)(CO)(EtOH), 469
$RuC_{47}H_{41}NO_3P_2$
Ru(CO)(OAc)(HC=NC$_6$H$_4$Me-4)(PPh$_3$)$_2$, 384
$RuC_{47}H_{42}ClNO_3P_2$
RuCl(CO)(OAc)(HCNHC$_6$H$_4$Me-4)(PPh$_3$)$_2$, 384
$RuC_{47}H_{42}NO_3P_2$
[Ru(CO)(OAc)(HCNHC$_6$H$_4$Me-4)(PPh$_3$)$_2$]$^+$, 384
$RuC_{47}H_{43}NP_2$
RuH(η^3-C$_3$H$_4$Ph)(MeCN)(PPh$_3$)$_2$, 457
$RuC_{48}H_{30}N_{10}$
Ru(phthalocyanine)(CNCH$_2$Ph)$_2$, 475
$RuC_{48}H_{38}Cl_2N_2P_2$
RuCl$_2$(phen)(PPh$_3$)$_2$, 392
$RuC_{48}H_{39}N_4O_2$
{Ru(tetraphenylporphyrin)(OEt)(HOEt), 473
$RuC_{48}H_{40}N_4O_2$
Ru(tetraphenylporphyrin)(HOEt)$_2$, 473
$RuC_{48}H_{41}N_5P_2$
RuH(N$_2$)(PhNNNPh)(PPh$_3$)$_2$, 458
$RuC_{48}H_{42}N_2O_2P_2$
Ru(PPh$_3$)$_2$(N=CMeCH=CHCH=CO)$_2$, 466
$RuC_{48}H_{44}Cl_2P_4$
RuCl$_2$(PHPh$_2$)$_4$, 378
$RuC_{48}H_{44}NO_3P_2$
Ru(CO)(OAc)(HCNMeC$_6$H$_4$Me-4)(PPh$_3$)$_2$, 384
$RuC_{48}H_{45}ClP_4$
RuHCl(PHPh$_2$)$_4$, 452
$RuC_{48}H_{45}O_2P_3S_2$
Ru(SOCPh)$_2$(dppe)(PMe$_2$Ph), 408
$RuC_{48}H_{46}P_4$
RuH$_2$(PHPh$_2$)$_4$, 451
$RuC_{48}H_{48}Cl_2N_2O_4$
RuCl$_2$(2-MeC$_6$H$_4$CN)$_2$(Ph$_2$PCH$_2$CO$_2$Et)$_2$, 397
$RuC_{48}H_{48}N_2O_2P_2$
Ru{(OCMeCHCMeNCH$_2$)$_2$}(PPh$_3$)$_2$, 398
$RuC_{48}H_{48}N_6O_6$
Ru(4-MeOC$_6$H$_4$N=CHCH=NC$_6$H$_4$OMe-4)$_3$, 364
[Ru(4-MeOC$_6$H$_4$N=CHCH=NC$_6$H$_4$OMe-4)$_3$]$^{2+}$, 364
$RuC_{48}H_{51}Cl_2O_6P_3$
RuCl$_2${PPh$_2$(CH$_2$CO$_2$Et)}$_3$, 409
$RuC_{48}H_{51}NOP_3$
[RuMe(CO)(CNBu^t)(triphos)]$^+$, 382
$RuC_{48}H_{51}O_3P_4S_2$
[Ru(S$_2$CHPMe$_2$Ph){P(OMe)Ph$_2$}$_3$]$^+$, 406
$RuC_{48}H_{60}P_5$
[Ru(PhC≡C)(PMe$_2$Ph)$_5$]$^+$, 376
$RuC_{49}H_{38}N_2O_6P_2$
Ru(CO)(2-OC$_6$H$_4$NO)(2-OC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$, 398
$RuC_{49}H_{42}O_7P_2$
Ru{MeO$_2$CCH=CC(CO$_2$Me)=CHC(CO$_2$Me)=CH}-(CO)(PPh$_3$)$_2$, 404
$RuC_{50}H_{29}Cl_2N_2O_2P_2$
RuCl$_2$(4-pyCOMe)$_2$(PPh$_3$)$_2$, 392
$RuC_{50}H_{40}Cl_2N_2P_2$
RuCl$_2$(CNPh)$_2$(PPh$_3$)$_2$, 384
$RuC_{50}H_{40}O_2P_2S_2$
Ru(SOCPh)$_2$(PPh$_3$)$_2$, 407
$RuC_{50}H_{41}P_2$
[RuH(PPh$_3$)$_2$(anthracene)]$^-$, 460
$RuC_{50}H_{42}Cl_2NO_2P_2$
RuCl$_2$(HONCPhCPhOH)(PPh$_3$)$_2$, 397
$RuC_{50}H_{42}N_2O_4P_2$
Ru(2-OC$_6$H$_4$CH=NOH)$_2$(PPh$_3$)$_2$, 398
$RuC_{50}H_{42}N_4OP_2$
RuH(PhN=NCH=NNPh)(CO)(PPh$_3$)$_2$, 396
$RuC_{50}H_{44}Cl_2P_4$
RuCl$_2$(dppm)$_2$, 379, 380
[RuCl$_2$(dppm)$_2$]$^+$, 417
$RuC_{50}H_{46}P_4$
RuH$_2$(dppm)$_2$, 461
$RuC_{50}H_{47}N_2OP_2S_2$
Ru(S$_2$CNEt$_2$)(CNC$_6$H$_4$Me-4)(CO)(PPh$_3$)$_2$, 406
$RuC_{50}H_{47}OP_4$
[RuH(OH$_2$)(dppm)$_2$]$^+$, 459
$RuC_{50}H_{48}Cl_2N_2P_2$
RuCl$_2$(NH$_2$CH$_2$Ph)$_2$(PPh$_3$)$_2$, 391
$RuC_{50}H_{48}N_2OP_2S_2$
Ru(CO)(S$_2$CNEt$_2$)(HC=NC$_6$H$_4$Me-4)(PPh$_3$)$_2$, 384
$RuC_{50}H_{50}Cl_2O_4P_2$
RuCl$_2${PPh$_2$(C$_6$H$_4$COCHCOBu^t-2)}$_2$H$_2$, 409
$RuC_{50}H_{50}P_2$
RuH(PPh$_3$)$_2$(PhCH=CH$_2$)(1-3-η-C$_6$H$_{11}$), 457
$RuC_{51}H_{41}ClN_3P_2$
[RuCl(PPh$_3$)$_2$(terpy)]$^+$, 356, 392
$RuC_{51}H_{44}ClOP_4$
[RuCl(CO)(dppm)$_2$]$^+$, 383
$RuC_{51}H_{45}N_3OP_2$
RuH(4-MeC$_6$H$_4$NNNC$_6$H$_4$Me-4)(CO)(PPh$_3$)$_2$, 395
$RuC_{51}H_{45}OP_4$
[RuH(CO)(dppm)$_2$]$^+$, 383
$RuC_{52}H_{37}ClNOP_2$
RuCl(CO)(4-MeC$_6$H$_4$NCC$_6$H$_4$Me-4)(PPh$_3$)$_2$, 384
$RuC_{52}H_{44}N_2O_2P_2$
Ru(salen)(PPh$_3$)$_2$, 397
$RuC_{52}H_{45}O_2P_4$
[Ru(CHO)(CO)(dppm)$_2$]$^-$, 383
[RuH(CO)$_2$(dppm)$_2$]$^+$, 383
$RuC_{52}H_{46}N_2OP_2$
RuH(4-MeC$_6$H$_4$NCHNC$_6$H$_4$Me-4)(CO)(PPh$_3$)$_2$, 395
$RuC_{52}H_{48}NOP_4$
[Ru(NO)(dppe)$_2$]$^+$, 370
$RuC_{52}H_{48}P_4$
RuH(C$_6$H$_4$PPhCH$_2$CH$_2$Ph)(dppe), 456
$RuC_{52}H_{50}P_4$
RuH$_2$(dppe)$_2$, 451, 461
$RuC_{52}H_{51}P_4$
[RuH$_3$(dppe)$_2$]$^+$, 462
$RuC_{52}H_{52}ClO_4P_4$

$[RuCl\{P(OMe)Ph_2\}_4]^-$, 376, 410

$RuC_{53}H_{44}N_2O_3P_2$
Ru(4-MeC$_6$H$_4$NCONC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)$_2$, 396

$RuC_{53}H_{46}N_2O_2P_2$
Ru{(2-OC$_6$H$_4$CH=NCH$_2$)$_2$CH$_2$}(PPh$_3$)$_2$, 398

$RuC_{53}H_{48}OP_4$
Ru(CO)(dppe)$_2$, 372

$RuC_{53}H_{49}OP_4$
$[RuH(CO)(dppe)]^+$, 383

$RuC_{54}H_{38}N_6$
Ru(tetraphenylporphyrin)(py)$_2$, 472
$[Ru(tetraphenylporphyrin)(py)_2]^+$, 472

$RuC_{54}H_{43}P_3$
RuH$_4$(S-Ph-dibenzophosphole)$_3$, 462

$RuC_{54}H_{44}ClP_3$
RuCl(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$, 389

$RuC_{54}H_{45}Br_2P_3$
RuBr$_2$(PPh$_3$)$_3$, 378

$RuC_{54}H_{45}Cl_2P_3$
RuCl$_2$(PPh$_3$)$_3$, 287, 356, 364, 377, 401, 416, 463

$RuC_{54}H_{45}Cl_3NP_3$
RuCl$_3$(NPPh$_3$)(PPh$_3$)$_2$, 419

$RuC_{54}H_{45}Cl_3P_3$
RuCl$_3$(PPh$_3$)$_3$, 416

$RuC_{54}H_{45}P_3$
$[RuH_2(C_6H_4PPh_2)(PPh_3)_2]^-$, 456

$RuC_{54}H_{45}P_3S$
RuH(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$S, 455

$RuC_{54}H_{46}ClP_3$
RuHCl(PPh$_3$)$_3$, 452, 453, 462, 463

$RuC_{54}H_{46}NOP_3$
RuH(NO)(PPh$_3$)$_3$, 370

$RuC_{54}H_{46}P_3$
$[RuH_2(C_6H_4PPh_2)(PPh_3)_2]^-$, 460
$[RuH(PPh_3)_3]^+$, 458

$RuC_{54}H_{47}N_2P_3$
RuH$_2$(N$_2$)(PPh$_3$)$_3$, 451

$RuC_{54}H_{47}P_3$
RuH$_2$(PPh$_3$)$_3$, 450

$RuC_{54}H_{48}P_3$
$[RuH_3(PPh_3)_3]$, 460
$[RuH_3(PPh_3)_3]^+$, 463

$RuC_{54}H_{49}N_4P$
Ru(octaethylporphryin)(PPh$_3$), 473

$RuC_{54}H_{49}O_2P_4$
$[Ru(CHO)(CO)(dppe)_2]^+$, 383

$RuC_{54}H_{49}P_3$
RuH$_4$(PPh$_3$)$_3$, 462

$RuC_{54}H_{50}O_4P_4$
Ru(OAc)$_2$(dppm)$_2$, 428

$RuC_{54}H_{52}ClP_4$
RuCl(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)$_2$, 374
$[RuCl(Ph_2PCH_2CH_2CH_2PPh_2)_2]^-$, 374

$RuC_{54}H_{52}ClP_4O$
$[RuCl(dppm)_2(THF)]^+$, 376

$RuC_{54}H_{52}NOP_4$
$[Ru(NO)\{Ph_2P(CH_2)_3PPh_2\}_2]^+$, 370, 374

$RuC_{54}H_{52}O_3P_4$
RuH{C$_6$H$_4$OP(OPh)$_2$}{PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$}, 456

$RuC_{54}H_{52}P_4$
RuH(C$_6$H$_4$PPhCH$_2$CH$_2$CH$_2$PPh$_2$)-(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$), 456

$RuC_{54}H_{55}OP_4$
$[RuH(EtOH)(dppe)_2]^+$, 399, 459

$RuC_{54}H_{59}BrN_4P$
Ru(octaethylporphyrin)Br(PPh$_3$), 473

$RuC_{54}H_{59}N_4P$
Ru(octaethylporphyrin)(PPh$_3$), 473

$RuC_{55}H_{44}ClO_{10}$
RuCl{2-C$_6$H$_4$OP(OPh)$_2$}(CO){P(OPh)$_3$}$_2$, 389

$RuC_{55}H_{45}ClP_3$
RuHCl(PPh$_3$)$_3$, 399

$RuC_{55}H_{45}Cl_2OP_3$
RuCl$_2$(CO)(PPh$_3$)$_3$, 381

$RuC_{55}H_{45}Cl_2P_3S_2$
RuCl$_2$(S$_2$CPPh$_3$)(PPh$_3$)$_2$, 411

$RuC_{55}H_{45}NO_2P_3$
$[Ru(CO)(NO)(PPh_3)_3]^+$, 370

$RuC_{55}H_{45}OP_3$
RuH(C$_6$H$_4$PPh$_2$)(CO)(PPh$_3$)$_2$, 456

$RuC_{55}H_{45}O_7P_3$
RuH{C$_6$H$_4$OP(OPh)$_2$}(CO)(PPh$_3$){P(OPh)$_3$}, 456

$RuC_{55}H_{45}O_{10}P_3$
RuH{C$_6$H$_4$OP(OPh)$_2$}(CO){P(OPh)$_3$}$_2$, 456

$RuC_{55}H_{46}ClOP_3$
RuHCl(CO)(PPh$_3$)$_3$, 377, 456, 459, 463

$RuC_{55}H_{46}ClP_3S$
RuHCl(CS)(PPh$_3$)$_3$, 383, 456

$RuC_{55}H_{47}OP_3$
RuH$_2$(CO)(PPh$_3$)$_3$, 451

$RuC_{55}H_{47}O_2P_3$
RuH(O$_2$CH)(PPh$_3$)$_3$, 455

$RuC_{55}H_{47}P_3$
RuMe(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$, 389

$RuC_{55}H_{48}ClP_3$
RuClMe(PPh$_3$)$_3$, 386

$RuC_{55}H_{48}NO_2P_3$
RuH(CH$_2$NO$_2$)(PPh$_3$)$_3$, 458

$RuC_{55}H_{48}O_2P_3$
$[RuH(H_2O)(CO)(PPh_3)_3]^+$, 459

$RuC_{56}H_{42}N_2P_4$
Ru(CN)$_2${P(C$_6$H$_4$PPh$_2$-2)$_3$}, 282

$RuC_{56}H_{44}N_4OP_2$
Ru{2-C$_6$H$_4$N=NC(Ph)=NNPh}(CO)(PPh$_3$)$_2$, 396

$RuC_{56}H_{45}O_2P_3$
Ru(CO)$_2$(PPh$_3$)$_3$, 371

$RuC_{56}H_{46}N_4P_2$
$[Ru(bipy)_2(PPh_3)_2]^{2+}$, 347, 392

$RuC_{56}H_{46}O_2P_3$
$[RuH(CO)_2(PPh_3)_3]^+$, 459

$RuC_{56}H_{48}ClO_2P_3$
Ru(Cl)(η^2-OAc)(PPh$_3$)$_3$, 402

$RuC_{56}H_{48}NP_3$
RuH(C$_6$H$_4$PPh)(MeCN)(PPh$_3$)$_2$, 455

$RuC_{56}H_{49}O_2P_3$
RuH(OAc)(PPh$_3$)$_3$, 454

$RuC_{56}H_{49}O_{11}P_3S_3$
RuH(OAc)(Ph$_2$PC$_6$H$_4$SO$_3$H)$_3$, 455

$RuC_{56}H_{49}P_3$
RuH(C$_6$H$_4$PPh$_2$)(PPh$_3$)$_2$(C$_2$H$_4$), 455

$RuC_{56}H_{50}NP_3$
RuH$_2$(MeCN)(PPh$_3$)$_3$, 451

$RuC_{56}H_{50}O_3P_3$
$[Ru(OAc)(OH_2)(PPh_3)_3]^+$, 399
$[Ru(\eta^2\text{-}OAc)(OH_2)(PPh_3)_3]^+$, 403

$RuC_{56}H_{51}Cl_2O_{10}P_3S$
RuCl$_2$(DMSO){P(OPh)$_3$}$_3$, 408

$RuC_{56}H_{99}ClOP_3S_2$
$[RuCl\{S_2CP(C_6H_{11})_3\}(CO)\{P(C_6H_{11})_3\}_2]^+$, 407

$RuC_{56}H_{100}OP_3S_2$
$[RuH\{S_2CP(C_6H_{11})_3\}(CO)\{P(C_6H_{11})_3\}_2]^+$, 407, 459

$RuC_{57}H_{49}O_4P_3$
RuH(O$_2$CCH$_2$CO$_2$H)(PPh$_3$)$_3$, 455

$RuC_{57}H_{52}NO_2P_3$
RuH(O$_2$CNMe$_2$)(PPh$_3$)$_3$, 404, 455

$RuC_{57}H_{58}NP_4$
$[RuH(CNBu^t)(dppe)_2]^+$, 459

$RuC_{58}H_{48}N_4P_2$
Ru(2-pyNPh)$_2$(PPh$_3$)$_2$, 392

$RuC_{58}H_{51}NO_2P_3$
$[Ru(OAc)(MeCN)(PPh_3)_3]^+$, 397

$RuC_{58}H_{52}N_2P_3$
$[RuH(MeCN)_2(PPh_3)_3]^+$, 459

$RuC_{58}H_{55}P_3$
RuH$_2$(PPh$_3$)$_3$(THF), 451

$RuC_{58}H_{60}Cl_2P_6$

$[RuCl_2\{(Ph_2PCH_2CH_2)_2PCH_2CH_2P(CH_2CH_2PPh_2)_2\}]^+$, 418

$RuC_{59}H_{50}NP_3$
$RuH(C_6H_4PPh_2)(py)(PPh_3)_2$, 455

$RuC_{59}H_{51}N_2P_3$
$RuH(2\text{-}pyNH)(PPh_3)_3$, 457

$RuC_{59}H_{57}P_3$
$RuH_2(PPh_3)_3(\eta^2\text{-}C_5H_{10})$, 451

$RuC_{60}H_{42}N_6$
Ru(tetraphenylporphyrin)$(CNCH_2Ph)_2$, 473

$RuC_{60}H_{44}O_4S_4$
$Ru(PhCSCHCOPh)_4$, 437

$RuC_{60}H_{50}N_6P_2$
$Ru(PhNNNPh)_2(PPh_3)_2$, 394

$RuC_{60}H_{51}N_2P_3$
$Ru\{2\text{-}C_6H_4(NH)_2\}(PPh_3)_3$, 391

$RuC_{60}H_{57}Cl_2P_5$
$RuCl_2(PPh_3)\{P(CH_2CH_2PPh_2)_3\}$, 380

$RuC_{60}H_{62}IO_3P_3Si$
$RuH_2I\{Si(OEt)_3\}(PPh_3)_3$, 287

$RuC_{60}H_{98}N_4P_2$
$[Ru(octaethylporphyrin)(PBu_3)_2]^+$, 471

$RuC_{61}H_{50}P_3S$
$RuH(SPh)(PPh_3)_3$, 404

$RuC_{61}H_{54}P_4$
$RuH_2(dppm)(PPh_3)_2$, 451

$RuC_{62}H_{50}O_2P_4S_4$
$Ru(S_2PPh_2)_2(CO)_2(PPh_3)_2$, 405

$RuC_{62}H_{51}N_2P_3$
$RuH_2\{C_6H_4(CN)_2\}(PPh_3)_3$, 452

$RuC_{62}H_{51}O_3P_3$
$RuH(2\text{-}O_2CC_6H_4CHO)(PPh_3)_3$, 455

$RuC_{62}H_{65}ClO_4P_4$
$RuHCl(diop)_2$, 453

$RuC_{63}H_{52}NOP_3$
$Ru(CO)(CNC_6H_4Me\text{-}4)(PPh_3)_3$, 371
$RuH(8\text{-}quinolinolate)(PPh_3)_3$, 457

$RuC_{64}H_{54}N_2O_2P_2$
$Ru(2\text{-}OC_6H_4CH{=}NCH_2Ph)_2(PPh_3)_2$, 398

$RuC_{64}H_{64}P_6$
$[Ru\{1,4\text{-}\{(Ph_2PCH_2CH_2)_2PCH_2\}_2C_6H_4\}]^{2+}$, 377

$RuC_{65}H_{64}ClOP_6$
$[RuCl(CO)\{1,4\text{-}\{(Ph_2PCH_2CH_2)_2PCH_2\}_2C_6H_4\}]^+$, 377

$RuC_{66}H_{55}ClN_2P_3$
$Ru(PhN{=}NPh)Cl(PPh_3)_3$, 468

$RuC_{66}H_{56}N_3P_3$
$RuH(PhNNNPh)(PPh_3)_3$, 396

$RuC_{68}H_{66}Cl_2P_6$
$RuCl_2\{PhP(CH_2CH_2PPh_2)_2\}_2$, 380

$RuC_{70}H_{77}N_9O$
$Ru\{4\text{-}Et_2NC_6H_4\}_4porphyrin\}(CO)(4\text{-}pyBu^t)$, 471

$RuC_{72}H_{58}O_{12}P_4$
$Ru\{2\text{-}C_6H_4OP(OPh)_2\}_2\{P(OPh)_3\}_2$, 389

$RuC_{72}H_{59}ClO_{12}P_4$
$RuCl\{2\text{-}C_6H_4OP(OPh)_2\}\{P(OPh)_3\}_3$, 389

$RuC_{72}H_{60}Cl_2P_4$
$RuCl_2(PPh_3)_4$, 367, 377

$RuC_{72}H_{61}P_4$
$[RuH(PPh_3)_4]^+$, 458

$RuC_{72}H_{62}P_4$
$RuH_2(PPh_3)_4$, 450, 462, 463

$RuC_{72}H_{63}P_4$
$[RuH_3(PPh_3)_4]^+$, 463

$RuC_{72}H_{71}P_4$
$[RuH(PPh_3)_4]^-$, 458

$RuC_{72}H_{74}N_4P_2$
Ru(octaethylporphyrin)$(PPh_3)_2$, 473

$RuC_{73}H_{60}OP_4$
$Ru(CO)(PPh_3)_4$, 372

$RuC_{74}H_{63}NP_3$
$RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$, 367

$RuC_{74}H_{63}NP_4$
$Ru(\eta^2\text{-}MeCN)(PPh_3)_4$, 367

$RuC_{80}H_{58}N_4P_2$
Ru(tetraphenylporphyrin)$(PPh_3)_2$, 473

$RuC_{80}H_{80}O_2P_4$
$\{RuH(OH)(PPh_3)_2(THF)\}_2$, 399

$RuC_{82}H_{78}Cl_2P_6$
$RuCl_2(triphos)_2$, 380

$RuC_{92}H_{66}N_8O_3$
$\{Ru(tetraphenylporphyrin)(OEt)\}_2O$, 473

$RuC_{94}H_{72}N_4P_4$
Ru(tetraphenylporphyrin)$(dppm)_2$, 473

$RuCl_3$
$RuCl_3$, 308, 444, 463
$[RuCl_3]^-$, 441

$RuCl_3C_6H_{21}Cl_3O_6P_2$
$RuCl_3(NH_3)\{P(OMe)_3\}_2$, 416

$RuCl_3NO$
$RuCl_3(NO)$, 323, 362

$RuCl_3O_2$
$[RuO_2Cl_3]^-$, 422

$RuCl_4$
$RuCl_4$, 446
$[RuCl_4]^{2-}$, 441

$RuCl_4N$
$[RuNCl_4]^-$, 364

$RuCl_4O$
$[RuOCl_4]^{2-}$, 448

$RuCl_4O_2$
$[RuO_2Cl_4]^{2-}$, 450

$RuCl_4S$
$(RuCl_4S)_n$, 430

$RuCl_5$
$[RuCl_5]^{2-}$, 445

$RuCl_5NO$
$[RuCl_5(NO)]^-$, 357, 363
$[RuCl_5(NO)]^{2-}$, 298, 348, 362–364

$RuCl_6$
$[RuCl_6]^{2-}$, 289, 327, 447
$[RuCl_6]^{3-}$, 444

$RuCoC_3H_{31}N_{11}O_4S$
$[Co(NH_3)_5(\mu\text{-}HNCH{=}NCH{=}CH)Ru(NH_3)_4(SO_4)]^{2+}$, 696

$RuCoC_{10}H_{19}N_{11}$
$[Co(en)_2(NH_3)(\mu\text{-}NC)Ru(CN)_5]$, 283

$RuCoC_{10}H_{41}N_{11}O$
$[Co(NH_3)_4(H_2O)\{NCC(CH_2CH_2)_3CCN\}Ru(NH_3)_5]^{5+}$, 679

$RuCoC_{16}H_{11}ClO_4P$
$RuCoHCl(\mu\text{-}PPh_2)(CO)_4$, 373

$RuCoC_{18}H_{16}N_{12}O_4$
$Co\{L\text{-}O_2CCH(NH_2)CH_2C{=}CHNHCH{=}N\}_2(\mu\text{-}NC)Ru(CN)_5]^{3-}$, 283

$RuCoC_{19}H_{10}O_7P$
$RuCo(\mu\text{-}PPh_2)(CO)_7$, 373

$RuCoC_{36}H_{25}O_6P_2$
$RuCo(\mu\text{-}PPh_2)(CO)_6(PPh_3)$, 373

$RuCoC_{53}H_{40}O_5P_3$
$RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)$, 373

$RuCrH_{25}N_5O_6$
$[Ru(NH_3)_4(OH_2)(\mu\text{-}NH)Cr(OH_2)_5]^{5+}$, 299

RuF_3O_4P
RuO_4PF_3, 420

RuF_4O
$RuOF_4$, 449

RuF_6
RuF_6, 449
$[RuF_6]^-$, 448
$[RuF_6]^{2-}$, 447, 448
$[RuF_6]^{3-}$, 444

$RuF_6O_4P_2$
$RuO_4(PF_3)_2$, 420

RuF_7P
$\{RuF_4(PF_3)\}_n$, 447

RuF_8

RuF_8, 450
$RuF_{12}P_4$
$[Ru(PF_3)_4]^{2-}$, 366, 451
$RuF_{15}P_5$
$Ru(PF_3)_5$, 366, 371
$RuFeC_8H_{18}Cl_5O_2P_2$
$RuCl(FeCl_4)(CO)_2(PMe_3)_2$, 382
$RuFeC_9H_{19}N_{12}$
$[Fe(CN)_5(\mu\text{-}N{=}CHCH{=}NCH{=}CH)Ru(NH_3)_5]^-$, 317
$RuFeC_{11}H_{24}N_6$
$[Ru(NH_3)_5(FcCN)]^{2+}$, 317
$RuFeC_{13}H_{26}N_6$
$[Ru(NH_3)_5(FcCH{=}CHCN)]^{2+}$, 317
$RuFe_2C_8H_{18}Cl_8O_2P_2$
$Ru(FeCl_4)_2(CO)_2(PMe_3)_2$, 382
$RuFe_4C_6N_6$
$Fe_4[Ru(CN)_6]$, 281
$RuGeC_7H_9O_4$
$[Ru(GeMe_3)(CO)_4]^-$, 287
$RuGe_2C_4Cl_6O_4$
$Ru(GeCl_3)_2(CO)_4$, 287
$RuGe_2C_{10}H_{18}O_4$
$Ru(GeMe_3)_2(CO)_4$, 287
$RuGe_2C_{12}H_{18}O_6$
$Ru_2(\mu\text{-}GeMe_2)_3(CO)_6$, 287
$RuGe_2C_{44}H_{48}O_2P_2$
$Ru(GeMe_3)_2(CO)_2(PPh_3)_2$, 287
$RuHCl_4NO_2$
$[RuCl_4(OH)(NO)]^{2-}$, 363
$RuHCl_5O$
$[RuCl_5(OH)]^{2-}$, 353
$RuHF_{12}P_4$
$[RuH(PF_3)_4]^-$, 451, 461
$RuHN_5O_{10}$
$[Ru(OH)(NO_2)_4(NO)]^{2-}$, 361
RuH_2Br_5O
$[RuBr_5(OH_2)]^{2-}$, 445
$RuH_2Cl_4O_2$
$[RuCl_4(OH)_2]^{2-}$, 448
RuH_2Cl_5O
$[RuCl_5(H_2O)]^{2-}$, 289, 299, 308, 324, 445, 446
$RuH_2F_{12}P_4$
$RuH_2(PF_3)_4$, 451
RuH_3O_5
$[RuO_2(OH)_3]^-$, 422
$[RuO_2(OH)_3]^{2-}$, 422
$RuH_4Cl_3NO_3$
$RuCl_3(NO)(OH_2)_2$, 362, 363
$RuH_4Cl_4O_2$
$[RuCl_4(OH_2)_2]^-$, 445, 446
$RuH_4N_4O_{11}$
$Ru(NO_2)(NO_3)_2(NO)(OH_2)_2$, 361
$RuH_4N_4O_{12}$
$Ru(NO_3)_3(NO)(OH_2)_2$, 361
RuH_5NO
$[Ru(NH_3)(OH_2)]^{3+}$, 299
RuH_6
$[RuH_6]^{4-}$, 460
$RuH_6Cl_2O_4$
$RuCl_2(OH)_2(OH_2)_2$, 448
$RuH_6Cl_3O_3$
$RuCl_3(OH_2)_3$, 445
$[RuCl_3(OH_2)_3]^-$, 442
$RuH_6N_3O_9$
$[Ru(NO_2)(NO_3)(NO)(OH_2)_3]^+$, 361
RuH_6S_6
$[Ru(SH)_6]^{3-}$, 430
$RuH_8Cl_2O_4$
$RuCl_2(OH_2)_4$, 442
$[RuCl_2(OH_2)_4]^+$, 446
$RuH_9Cl_3N_3$
$RuCl_3(NH_3)_3$, 308
$RuH_{10}ClO_5$
$[RuCl(OH_2)_5]^+$, 442
$[RuCl(OH_2)_5]^{2+}$, 446
$RuH_{10}NO_6$
$[Ru(NO)(OH_2)_5]^{3+}$, 362
$RuH_{10}N_2O_5$
$[Ru(N_2)(OH_2)_5]^{2+}$, 421
$RuH_{11}O_6$
$[Ru(OH)(OH_2)_5]^{2+}$, 421
$RuH_{12}BrN_5O$
$[RuBr(NO)(NH_3)_4]^{2+}$, 298
$RuH_{12}Br_2N_4$
$[RuBr_2(NH_3)_4]^+$, 309
$RuH_{12}ClN_4O_2S$
$[RuCl(NH_3)_4(SO_2)]^+$, 292, 296, 306, 307, 316, 320
$RuH_{12}ClN_5O$
$[RuCl(NO)(NH_3)_4]^{2+}$, 298
$RuH_{12}Cl_2N_4$
$[RuCl_2(NH_3)_4]^+$, 292, 295, 299, 307–309
$RuH_{12}N_4O_2$
$[Ru(O)_2(NH_3)_4]^{2+}$, 305
$RuH_{12}N_8$
$[Ru(NH_3)_4(N_2)_2]^{2+}$, 300
$RuH_{12}N_8O$
$[Ru(N_3)(NO)(NH_3)_4]^{2+}$, 298
$RuH_{12}O_6$
$[Ru(H_2O)_6]^{2+}$, 325, 327, 420, 421, 442
$[Ru(H_2O)_6]^{3+}$, 420, 421
$[Ru(H_2O)_6]^{4+}$, 421
$RuH_{13}ClN_4O$
$[RuCl(OH)(NH_3)_4]^+$, 309
$RuH_{13}N_5O_2$
$[Ru(OH)(NO)(NH_3)_4]^{2+}$, 298, 548
$RuH_{14}ClN_4O$
$[RuCl(NH_3)_4(OH_2)]^{2+}$, 309
$RuH_{14}N_4O_2$
$Ru(NH_3)_4(OH)_2$, 298
$[Ru(NH_3)_4(OH_2)_2]^{2+}$, 305
$RuH_{14}N_4O_3S$
$[Ru(NH_3)_4(OH_2)(SO_2)]^{2+}$, 307
$RuH_{14}N_4O_4S$
$Ru(SO_3)(NH_3)_4(OH_2)$, 295, 304, 307, 316
$RuH_{14}N_4O_6S_2$
$Ru(HSO_3)_2(NH_3)_4$, 306
$RuH_{14}N_5O_2$
$[Ru(NO)(NH_3)_4(OH_2)]^{3+}$, 298
$RuH_{14}N_6O$
$[Ru(NH_3)_4(N_2)(OH_2)]^{2+}$, 299, 300
$[Ru(NO)(NH_2)(NH_3)_4]^{2+}$, 298
$RuH_{15}BrN_5$
$[RuBr(NH_3)_5]^{2+}$, 298
$RuH_{15}ClN_5$
$[RuCl(NH_3)_5]^+$, 305, 308
$[RuCl(NH_3)_5]^{2+}$, 280, 289–292, 294, 298, 299, 302, 304–306, 308, 309, 312, 317
$RuH_{15}N_4O_4S$
$[Ru(HSO_3)(NH_3)_4(OH_2)]^+$, 307
$RuH_{15}N_5O_2S$
$[Ru(NH_3)_5(SO_2)]^{2+}$, 306, 307
$RuH_{15}N_5O_3S$
$Ru(SO_3)(NH_3)_5$, 306
$RuH_{15}N_5O_3S_2$
$[Ru(S_2O_3)(NH_3)_5]^+$, 307, 318
$RuH_{15}N_6O$
$[Ru(NO)(NH_3)_5]^{3+}$, 297–299, 301, 302, 317
$RuH_{15}N_6O_2$
$[Ru(NO_2)(NH_3)_5]^+$, 298
$RuH_{15}N_7$
$Ru(NH_3)_5(N_2)$, 299
$[Ru(NH_3)_5(N_2)]^+$, 299
$[Ru(NH_3)_5(N_2)]^{2+}$, 289, 295, 298–301, 306, 317, 318, 321
$[Ru(NH_3)_5(N_2)]^{3+}$, 301
$RuH_{15}N_7O$

$[Ru(NH_3)_5(N_2O)]^{2+}$, 299, 301
$RuH_{15}N_8$
$[Ru(N_3)(NH_3)_5]^{2+}$, 299, 303, 317
$RuH_{16}N_4O_2$
$[Ru(NH_3)_4(OH_2)_2]^{2+}$, 296, 297, 310
$[Ru(NH_3)_4(OH_2)_2]^{3+}$, 297, 305, 310
$RuH_{16}N_5O$
$[Ru(OH)(NH_3)_5]^{2+}$, 290, 301, 305, 306, 309
$RuH_{16}N_6$
$[Ru(NH_3)_5(NH)]^{3+}$, 303
$RuH_{16}N_6O_3S$
$[Ru(NH_3)_5(NHSO_3)]^{+}$, 303
$RuH_{17}N_5O$
$[Ru(NH_3)_5(OH_2)]^{2+}$, 290, 291, 293, 294, 297, 299, 301, 304–308, 312, 317, 318
$[Ru(NH_3)_5(OH_2)]^{3+}$, 297, 304, 305
$RuH_{17}N_5S$
$[Ru(NH_3)_5(SH_2)]^{2+}$, 307
$[Ru(NH_3)_5(SH_2)]^{3+}$, 307
$RuH_{17}N_6$
$[Ru(NH_2)(NH_3)_5]^{2+}$, 290
$RuH_{17}N_6O_3S$
$[Ru(NH_3)_5(NH_2SO_3)]^{2+}$, 303
$RuH_{18}N_6$
$[Ru(NH_3)_6]^{2+}$, 289, 290, 294, 296, 298, 299, 301, 304–306, 308, 319
$[Ru(NH_3)_6]^{3+}$, 289, 290, 297–299, 302, 303, 308, 311, 317
$[Ru(NH_3)_6]^{4+}$, 290
$[Ru(NH_3)_6]^{5+}$, 290
$RuH_{30}N_{10}O$
$[\{Ru(NH_3)_5\}_2O]^{4+}$, 318
$RuH_{30}N_{12}$
$[\{Ru(NH_3)_5\}_2(N_2)]^{4+}$, 299
$RuHgC_8H_5Cl_2NO_3$
RuCl(HgCl)(CO)$_3$py, 280
$RuHgC_{39}H_{30}ClO_3P_2$
$[Ru(HgCl)(CO)_3(PPh_3)_2]^{+}$, 280
$RuHgC_{40}H_{30}F_3O_3P_2$
$[Ru(HgCF_3)(CO)_3(PPh_3)_2]^{+}$, 280
$RuHgC_{40}H_{30}F_6O_2P_2$
$Ru(HgCF_3)(CF_3)(CO)_2(PPh_3)_2$, 280
RuI_2NO
$RuI_2(NO)$, 326
$RuLi_2C_{47}H_{60}O_2P_4$
$RuHMe(PPh_3)_2(LiMeOEt_2)_2$, 454
$RuMnC_{54}H_{40}O_6P_2$
$RuMn(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$, 373
$RuMnC_{55}H_{44}ClO_5P_4$
$RuMnCl(\mu\text{-dppm})_2(\mu\text{-}CO)_2(CO)_3$, 373
$RuMoC_{20}H_{16}N_4S_4$
$Ru(S_2MoS_2)(bipy)_2$, 352
RuO_4
RuO_4, 352, 360, 423
$[RuO_4]^{-}$, 422
$[RuO_4]^{2-}$, 421–423
$[RuO_4]^{3-}$, 421
$RuO_{10}S_4$
$Ru(S_2O_5)_2$, 430
$RuOsC_8BrCl_3O_8Si$
$Os(CO)_4BrRu(SiCl_3)(CO)_4$, 285
$Os(CO)_5\{RuBr(SiCl_3)(CO)_3\}$, 285
$RuOsC_{24}H_{36}Cl_2N_{10}$
$[OsRu(\overline{N{=}CHCH{=}NCH{=}CH})(bipy)_4Cl_2]^{2+}$, 537
$RuOsC_{25}H_{35}N_{10}O_2$
$[OsRu(\overline{N{=}CHCH{=}NCH{=}CCO_2})(bipy)_4]^{2+}$, 537
$RuOsC_{48}H_{38}N_{12}$
$[OsRu(2,2'\text{-bipyrimidine})(bipy)_4]^{4+}$, 537
$RuOsC_{73}H_{60}Cl_4OP_4$
$Ru(CO)(PPh_3)_2(\mu\text{-}Cl)_2OsCl(PPh_3)_2$, 411
$RuOsC_{76}H_{88}N_8$
$OsRu(octaethylporphyrin)_2$, 618
$RuOsH_{29}N_{11}O$
$[Os(NH_3)_5(N_2)Ru(NH_3)_4(H_2O)]^{4+}$, 556
$[Ru(NH_3)_4(H_2O)(\mu\text{-}N_2)Os(NH_3)_5]^{4+}$, 318
$RuPb_2C_{10}H_{18}O_4$
$Ru(PbMe_3)_2(CO)_4$, 289
$RuPtC_{26}H_{29}N_9$
$[Ru(CN)(bipy)_2(\mu\text{-}CN)Pt(dien)]^{2+}$, 283
$RuPt_2C_{26}H_{24}Cl_4N_6$
$Ru(CN)_2(bipy)_2\{PtCl_2(C_2H_4)\}_2$, 283
$RuPt_2C_{30}H_{42}N_{12}$
$[Pt(dien)(NC)\{Ru(bipy)_2(CN)Pt(dien)\}]^{4+}$, 283
$RuPt_2C_{76}H_{60}O_{16}P_4$
$RuPt_2(CO)_4\{P(OPh)_3\}_4$, 374
$RuRhC_{51}H_{44}ClOP_4$
$RuRhCl(\mu\text{-}CO)(dppm)_2$, 373
$RuRhC_{72}H_{60}Cl_5P_4$
$RhCl(PPh_3)_2(\mu\text{-}Cl)_3RuCl(PPh_3)_2$, 1076
$RuSbC_{22}H_{15}O_4$
$Ru(CO)_4(SbPh_3)$, 371
$RuSbC_{36}H_{30}Cl_3NOP$
$RuCl_3(NO)(PPh_3)(SbPh_3)$, 393
$RuSb_2C_{36}H_{30}Cl_3NO$
$RuCl_3(NO)(SbPh_3)_2$, 394
$RuSb_3C_{54}H_{45}Cl_2$
$\{RuCl_2(SbPh_3)_3\}_n$, 379
$RuSb_3C_{55}H_{45}Cl_2O$
$RuCl_2(CO)(SbPh_3)_3$, 383
$RuSb_4C_{72}H_{60}Br_2$
$RuBr_2(SbPh_3)_4$, 379
$RuSnC_2Cl_8O_2$
$[RuCl_2(SnCl_3)_2(CO)_2]^{2-}$, 288
$RuSnC_4Cl_4O_4$
$RuCl(SnCl_3)(CO)_4$, 288
$RuSnC_7H_9ClO_4$
$RuCl(SnMe_3)(CO)_4$, 288
$RuSnC_{14}H_{30}Cl_3O_2S_3$
$[Ru(SnCl_3)(CO)_2(SEt_2)_3]^{+}$, 289, 432
$RuSnC_{39}H_{30}I_4O_3P_2$
$[RuI(CO)_3(PPh_3)_2]SnI_3$, 289
$RuSnC_{40}H_{36}Cl_4O_2P_2$
$RuCl(SnCl_3)(CO)(PPh_3)_2(OCMe_2)$, 288
$RuSnC_{42}H_{40}Cl_4N_2P_2$
$RuCl(SnCl_3)(CNEt)_2(PPh_3)_2$, 289, 384
$RuSnC_{48}H_{45}Cl_3P_4$
$RuH(SnCl_3)(PHPh_2)_4$, 289, 452
$RuSn_2C_4Cl_6O_4$
$Ru(SnCl_3)_2(CO)_4$, 288
$RuSn_2C_8H_{24}Cl_6O_4S_4$
$Ru(SnCl_3)_2(DMSO)_4$, 289
$RuSn_2C_{10}H_{18}O_4$
$Ru(SnMe_3)_2(CO)_4$, 288
$RuSn_2C_{12}H_{20}Cl_6N_4$
$Ru(SnCl_3)_2(CNEt)_4$, 289
$RuSn_2Cl_9NO$
$[RuCl_3(SnCl_3)_2(NO)]^{2-}$, 288
$RuSn_4Cl_{14}$
$[RuCl_2(SnCl_3)_4]^{4-}$, 288
$RuSn_5ClF_{15}$
$[RuCl(SnF_3)_5]^{4-}$, 288
$RuSn_5Cl_{16}$
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$Ru_2As_3C_{63}H_{63}Cl_6$
$[Ru_2Cl_6\{As(C_6H_4Me\text{-}4)_3\}_3]^{-}$, 415
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$Ru_2Cl_5(Ph_2AsCH_2CH_2AsPh_2)_2$, 415
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$Ru_2As_4C_{54}H_{48}Cl_4O_2$
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$Ru_2C_4Cl_4O_4$
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$[\{RuCl(en)_2\}_2(\mu\text{-}OH)]^{3+}$, 325
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$[\{Ru(NH_3)_4(\overline{HN{=}CHCH{=}NCH{=}CH})\}_2(\overline{N{=}CHCH{=}NCH{=}CH})]^{6+}$, 316
$Ru_2C_{12}H_{40}N_{15}$
$[\{Ru(NH_3)_4(\overline{N{=}CHCH{=}NCH{=}CH})\}_2(NH_3)(\overline{HN{=}CHCH{=}NCH{=}CH})]^{5+}$, 320
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$[\{Ru\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}\}_2O]^{4-}$, 467
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$\{Ru(PMe_3)_3\}_2(\mu\text{-}CH_2)_3$, 419
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$Ru_2(CO)_6(4\text{-}MeOC_6H_4N{=}CHCH{=}NC_6H_4OMe\text{-}4)$, 364
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$\{Ru(S_2CNEt_2)_2(CO)\}_2$, 435
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$Ru_2O(OAc)_3(CO)(PPh_3)$, 428
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$[Ru(NH_3)_5(\mu\text{-}\overline{N{=}CHCH{=}NCH{=}CH})Ru(NCMe)(bipy)_2]^{5+}$, 316
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$Ru_2C_{28}H_{54}Cl_2O_4P_2$
$\{Ru(\mu\text{-}Cl)(CO)_2(PBu^t_3)\}_2$, 375
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$Ru_2Cl_4(bipy)_3$, 361
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$\{Ru(\mu\text{-}OMe)(CO)_2(PBu^t_3)\}_2$, 375
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$RuCl_2(PEt_2Ph)(\mu\text{-}Cl)_3Ru(PEt_2Ph)_3$, 415
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$Ru_2C_{32}H_{60}O_8P_2$
$\{Ru(\mu\text{-}OAc)(CO)_2(PBu^t_3)\}_2$, 375
$Ru_2C_{34}H_{28}N_4O_6$
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$\{Ru(CO)_3(Ph_2PCH_2SiMe_2)\}_2$, 286
$Ru_2C_{38}H_{30}Cl_4O_2P_2S_2$
$\{RuCl_2(SPPh_3)(CO)\}_2$, 408
$Ru_2C_{38}H_{46}F_9O_7P_4$
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$\{RuCl_2(CO)_2(PPh_3)\}_2$, 413
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$\{Ru(\mu\text{-}I)(CO)_2(PPh_3)\}_2$, 375
$Ru_2C_{40}H_{30}O_4P_2S_2$
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$Ru_2C_{40}H_{32}Cl_2N_8$
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$[\{RuCl(bipy)_2\}_2O]^{2+}$, 360
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$Ru_2C_{40}H_{32}N_{10}O_5$
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$[\{Ru(bipy)_2(H_2O)\}_2O]^{2+}$, 360
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$Ru_2C_{40}H_{37}I_4O_2NP_2Se_2$
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$Ru_2C_{40}H_{60}Cl_5P_4$
$[Ru_2Cl_5(PEt_2Ph)_4]^+$, 418
$Ru_2C_{42}H_{30}Cl_4N_6$
$\{RuCl_2(NCPh)_3\}_2$, 365
$Ru_2C_{42}H_{32}N_8O_4$
$[\{Ru(bipy)_2\}_2(C_2O_4)]^{2+}$, 360
$Ru_2C_{42}H_{38}I_2N_2O_2P_2S_2$
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$Ru_2C_{44}H_{36}Cl_2N_{10}$
$[\{RuCl(bipy)_2\}_2(\overline{N{=}CHCH{=}NCH{=}CH})]^{2+}$, 359
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$Ru_2C_{46}H_{38}N_{12}$
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$Ru_2C_{46}H_{52}N_{12}P_2$
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$Ru_2C_{47}H_{42}ClN_{10}O$
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$Ru_2C_{48}H_{66}Cl_3P_6$
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$[Ru_2Cl_3(PEt_2Ph)_6]^{2+}$, 415
$Ru_2C_{48}H_{69}O_3P_6$
$[Ru_2(OH)_3(PMe_2Ph)_6]^-$, 400
$Ru_2C_{48}H_{69}P_6$
$[Ru_2H_3(PMe_2Ph)_6]^+$, 461
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$\{RuCl(PBu_3)_2\}_2(\mu\text{-}Cl)_3$, 415
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$Ru_2C_{55}H_{45}Cl_4F_3OP_4$
Ru_2Cl_4(CO)(PF_3)(PPh_3)$_3$, 412
$Ru_2C_{56}H_{45}Cl_4O_2P_3$
Ru_2Cl_4(CO)$_2$(PPh_3)$_3$, 411
$Ru_2C_{56}H_{48}Cl_2N_8$
[Ru_2Cl_2(2,9-Me_2phen)$_4$]$^{2+}$, 392
$Ru_2C_{58}H_{56}O_8P_4$
Ru_2(OAc)$_4$(dppm)$_2$, 428
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$Ru_2C_{60}H_{90}Cl_3P_6$
[{Ru(PEt_2Ph)$_3$}$_2$(μ-Cl)$_3$]$^+$, 410
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$Ru_2C_{64}H_{52}N_4O_4P_2$
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Ru_2Cl_4(MeNCH$_2$CH$_2$NMeC=CNMeCH$_2$CH$_2$NMe)(PPh_3)$_2$, 413
$Ru_2C_{68}H_{59}Cl_3N_4O_2P_3$
[Ru_2Cl_3(NNC_6H_4OMe-4)$_2$(PPh_3)$_3$]$^+$, 395
$Ru_2C_{72}H_{58}Cl_2P_4$
{RuCl($C_6H_4PPh_2$)(PPh_3)}$_2$, 389
$Ru_2C_{72}H_{60}Cl_4F_3P_5$
Ru_2Cl_4(PF_3)(PPh_3)$_4$, 412
$Ru_2C_{72}H_{60}Cl_4N_2P_4$
RuCl(PPh_3)$_2$(μ-Cl)$_3$Ru(N_2)(PPh_3)$_2$, 412
$Ru_2C_{72}H_{60}Cl_4P_4$
{$RuCl_2$(PPh_3)$_2$}$_2$, 377
$Ru_2C_{72}H_{60}Cl_4P_4S_2$
{$RuCl_2$(SPPh_3)(PPh_3)}$_2$, 408
$Ru_2C_{72}H_{60}Cl_5P_4$
[Ru_2Cl_5(PPh_3)$_4$]$^-$, 411
$Ru_2C_{72}H_{60}O_{12}P_4S_4$
{Ru(SO_4)(SO_2)(PPh_3)$_2$}$_2$, 402
$Ru_2C_{72}H_{62}O_2P_4$
[Ru(OH)$_2$(PPh_3)$_4$]$^+$, 400
$Ru_2C_{72}H_{63}Cl_3P_4$
$Ru_2H_3Cl_3$(PPh_3)$_4$, 462
$Ru_2C_{72}H_{64}N_2P_4$
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{RuCl(OH)(OH_2)(PPh_3)$_2$}$_2$, 399
$Ru_2C_{72}H_{66}N_2P_4$
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$Ru_2C_{72}H_{88}Cl_2N_8O$
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Ru_2H_6{P(C_6H_{11})$_3$}$_4$, 463
$Ru_2C_{73}H_{60}Cl_3P_4S$
Ru(CS)(PPh_3)$_2$(μ-Cl)$_3$RuCl(PPh_3)$_2$, 411
$Ru_2C_{73}H_{60}Cl_4OP_4$
[Ru_2Cl_4(CO)(PPh_3)$_4$]$^+$, 415
$Ru_2C_{73}H_{60}Cl_4P_4S$
Ru(CS)(PPh_3)$_2$(μ-Cl)$_3$RuCl(PPh_3)$_2$, 392
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$Ru_2C_{76}H_{66}Cl_4N_2P_4$
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$Ru_2C_{76}H_{69}Cl_4NOP_4$
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$Ru_2C_{78}H_{60}N_6P_4S_6$
{Ru(NCS)$_3$(PPh_3)$_2$}$_2$, 418
$Ru_2C_{78}H_{76}O_4P_4$
{RuH(OH)($OCMe_2$)(PPh_3)$_2$}$_2$, 399
$Ru_2C_{78}H_{78}Cl_3O_6P_6$
[Ru_2Cl_3{P(OMe)Ph_2}$_6$]$^+$, 410
$Ru_2C_{79}H_{72}Cl_4OP_4$
Ru(CO)(PPh_3)$_2$(μ-Cl)$_3$RuCl{P(C_6H_4Me)$_3$}$_2$, 411
$Ru_2C_{80}H_{68}Cl_2N_2O_2P_4$
{RuCl(CHMeCN)(CO)(PPh_3)$_2$}$_2$, 386
$Ru_2C_{80}H_{84}O_4P_4$
{RuH(OH)(Bu^tOH)(PPh_3)$_2$}$_2$, 399
$Ru_2C_{82}H_{74}Cl_2O_4P_4$
{RuCl(acac)(PPh_3)$_2$}$_2$, 400
$Ru_2C_{84}H_{84}Cl_4P_6$
Ru_2Cl_4(dppb)$_3$, 414
$Ru_2C_{84}H_{88}Cl_2P_4$
{RuH_2Cl{P(C_6H_4Me-4)$_3$}$_2$}$_2$, 462
$Ru_2C_{86}H_{90}Cl_2O_8P_6$
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$Ru_2C_{90}H_{74}O_6P_4$
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$Ru_2C_{92}H_{76}Cl_2N_4P_4$
[{RuCl(bipy)(PPh_3)$_2$}$_2$]$^{2+}$, 392
$Ru_2C_{92}H_{78}Cl_2N_4P_4$
{RuHCl(bipy)(PPh_3)$_2$}$_2$, 458
$Ru_2C_{92}H_{78}Cl_2N_4P_4S_4$
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$Ru_2C_{92}H_{83}Cl_2N_7O_2P_4$
[Ru_2Cl_2(MeCN)$_3$(NNC_6H_4OMe-4)$_2$(PPh_3)$_4$]$^{2+}$, 395
$Ru_2C_{93}H_{96}Cl_4O_6P_6$
Ru_2Cl_4(diop)$_3$, 414
$Ru_2C_{96}H_{86}Cl_4P_8$
{$RuCl_2$(PPh_3)}$_2${1,4-{($Ph_2PCH_2CH_2$)$_2$$PCH_2$}$_2$$C_6H_4$}, 414
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{Ru(tetraphenylporphyrin)(CO)}$_2$(4,4′-bipy), 472
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[{Ru(SC_6F_5(bipy)(PPh_3)$_2$}$_2$]$^{2+}$, 404
$Ru_2C_{104}H_{92}F_{10}N_4P_4S_2$
[{Ru(SC_6F_5)(bipy)(PPh_3)$_2$}$_2$]$^{2+}$, 392
$Ru_2C_{108}H_{92}Cl_2P_6$
{RuHCl(PPh_3)$_3$}$_2$, 461, 463
$Ru_2C_{108}H_{102}O_4P_8$
[{Ru(dppe)$_2$}$_2$(μ-OAc)$_2$]$^{2+}$, 428
$Ru_2C_{112}H_{120}Cl_2O_8P_8$
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$[\{Ru(NH_3)_5\}_2\{Fe(CN)_2\}]^{4+}$, 320
$Ru_2FeC_{44}H_{30}Cl_2O_8P_2$
$\{Ru(CO)_2(PPh_3)\}_2(\mu\text{-}Cl)_2\{\mu\text{-}Fe(CO)_4\}$, 413
$Ru_2FeC_{44}H_{32}O_9P_2$
$\{Ru(CO)_2(PPh_3)\}_2(\mu\text{-}H)(\mu\text{-}OH)\{\mu\text{-}Fe(CO)_4\}$, 413
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$[\{Ru(OH_2)_5\}_2(N_2)]^{4+}$, 421
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$[\{RuCl(NO)(NH_3)_4\}_2(N_2)]^{4+}$, 318
$Ru_2H_{28}N_{10}$
$[\{Ru(NH_3)_4\}_2(\mu\text{-}NH_2)_2]^{4+}$, 311
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$[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]^{4+}$, 301, 318
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$[\{Ru(NH_3)_5\}_2(N_2)]^{4+}$, 301, 317, 318
$[\{Ru(NH_3)_5\}_2(N_2)]^{5-}$, 318
$Ru_2H_{30}N_{12}O$
$[\{Ru(NH_3)_5\}_2(N_2O)]^{4+}$, 318
$Ru_2HgC_{26}H_{78}P_8$
$\{RuMe(PMe_3)_4\}_2Hg$, 281
$Ru_2MoC_{40}H_{32}N_8S_4$
$[\{Ru(bipy)_2\}_2(MoS_4)]^{2+}$, 361
$Ru_2PtC_{34}H_{24}O_8P_2$
$Ru_2Pt(CO)_8(dppe)$, 374
$Ru_2SbC_6Cl_7O_6$
$\{RuCl_2(CO)_3\}_2(SbCl_3)$, 443
$Ru_2SnC_5Cl_6O_5$
$Ru_2Cl_3(SnCl_3)(CO)_5$, 288
$Ru_2SnC_{56}H_{45}Cl_6O_2P_3$
$Ru(SnCl_3)(CO)(PPh_3)(\mu\text{-}Cl)_3Ru(CO)(PPh_3)_2$, 288
$Ru_2Sn_2C_{12}H_{12}O_8$
$\{Ru(\mu\text{-}SnMe_2)(CO)_4\}_2$, 288
$Ru_2Sn_2Cl_{12}N_2O_2$
$[Ru_2Cl_6(SnCl_3)_2(NO)_2]^{4-}$, 288
$Ru_2Sn_4C_{16}H_{30}O_6$
$\{Ru(\mu\text{-}SnMe_2)(SnMe_3)(CO)_3\}_2$, 288
$Ru_2Zn_2C_{111}H_{99}ClP_6$
$\{RuHMe(C_6H_4PPh_2)(PPh_3)_2\}_2Zn_2ClMe$, 455
$Ru_2Zr_2C_{94}H_{84}Cl_4P_4$
$\{ZrCp_2(\mu\text{-}Cl)(\mu\text{-}CH_2)Ru(PPh_3)_2\}_2(\mu\text{-}Cl)_2$, 414
$Ru_3C_4H_{46}N_{14}O_2$
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$Ru_3H_2(\mu_3\text{-}S)(CO)_9$, 430
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$Ru_3H_2(\mu_3\text{-}Se)(CO)_9$, 439
$Ru_3C_9H_3O_9S$
$Ru_3H_3(\mu\text{-}S)(CO)_9$, 430
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$Ru_3Cl_6(CO)_{12}$, 443
$Ru_3C_{12}H_4O_{12}S$
$Ru_3H(\mu\text{-}SCH_2CO_2H)(CO)_{10}$, 431
$Ru_3C_{12}H_6O_{10}S$
$Ru_3H(\mu\text{-}SEt)(CO)_{10}$, 431
$Ru_3C_{12}H_7O_{10}S$
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$Ru_3C_{12}H_{12}Cl_6O_9Si_3$
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$Ru_3C_{12}H_{24}O_{15}$
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$Ru_3C_{12}H_{24}O_{16}$
$Ru_3O(OAc)_6(OH_2)_3$, 427
$[Ru_3O(OAc)_6(OH_2)_3]^{-}$, 427
$Ru_3C_{12}H_{48}N_{18}O_8S_2$
$[\{Ru(NH_3)_4(\overline{N{=}CHCH{=}NCH{=}CH})\}_3](SO_4)_2]^{4+}$, 320
$Ru_3C_{12}O_{12}$
$Ru_3(CO)_{12}$, 373
$Ru_3C_{14}H_8O_6S$
$Ru_3(\mu_3\text{-}S)(CO)_6(\mu_3\text{-}\eta^8\text{-}C_8H_8)$, 432
$Ru_3C_{15}H_{26}O_{16}$
$Ru_3O(OAc)_6(CO)(MeOH)_2$, 428
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$Ru_3C_{16}H_{18}O_{16}P_2$
$Ru_3(CO)_{10}\{P(OMe)_3\}_2$, 373
$Ru_3C_{17}H_{28}N_2O_{14}$
$Ru_3O(OAc)_6(NCMe)_2(MeOH)$, 428
$Ru_3C_{18}H_{27}O_9P_3$
$Ru_3(CO)_9(PMe_3)_3$, 373
$Ru_3C_{19}H_{37}N_3O_{14}$
$[Ru_3HO(OAc)_5(DMF)_3]^{+}$, 428
$Ru_3C_{20}H_{58}N_{22}$
$[\{Ru(\overline{NH_3})_4(\overline{N{=}CHCH{=}NCH{=}CH})\}_3(\overline{HN{=}CHCH{=}NCH{=}CH})_2]^{8+}$, 320
$Ru_3C_{23}H_{28}N_2O_{14}$
$Ru_3O(OAc)_6(CO)(py)_2$, 428
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$Ru_3(CO)_8$(4-$MeOC_6H_4N{=}CHCH{=}NC_6H_4OMe$-4), 364
$Ru_3C_{26}H_{32}N_4O_{13}$
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$Ru_3C_{28}H_{19}O_8P$
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$Ru_3C_{28}H_{80}P_8$
$[\{Ru(PMe_3)_4(\mu\text{-}CH_2)_2\}_2Ru]^{2+}$, 419

$Ru_3C_{29}H_{33}O_{11}P$
$Ru_3(CO)_{11}\{P(C_6H_{11})_3\}$, 373

$Ru_3C_{32}H_{22}O_8P_2$
$Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8$, 462

$Ru_3C_{33}H_{33}O_{12}P_3$
$Ru_3(CO)_9(PMe_3)(PPh_3)\{P(OMe)_3\}$, 373

$Ru_3C_{33}H_{60}Cl_2N_6O_3S_{12}$
$\{Ru(S_2CNEt_2)_2(CO)\}_3Cl_2$, 435

$Ru_3C_{34}H_{57}O_9SiP_3$
$Ru_3(CO)_9\{(Bu_2P)_3SiMe\}$, 373

$Ru_3C_{35}H_{22}O_{10}P_2$
$Ru_3(CO)_{10}(dppm)$, 373

$Ru_3C_{35}H_{70}N_5S_{10}$
$[Ru_2(S_2CNPr^i_2)_5]^+$, 434

$Ru_3C_{38}H_{33}O_9P_3$
$Ru_3(CO)_9(PMe_3)(dppe)$, 373

$Ru_3C_{42}H_{30}O_6S_6$
$\{Ru(SPh)_2(CO)_2\}_3$, 431

$Ru_3C_{43}H_{33}O_7P_3$
$Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_7(PHPh_2)$, 462

$Ru_3C_{44}H_{30}N_2O_{10}P_2$
$Ru_3(CO)_8(NO)_2(PPh_3)_2$, 372

$Ru_3C_{48}H_{48}NO_{14}P_2$
$Ru_3O(OAc)_6(NO)(PPh_3)_2$, 428

$Ru_3C_{54}H_{45}Cl_3P_3S_2$
$Ru_3Cl_3S_2(PPh_3)_3$, 404

$Ru_3C_{66}H_{63}O_{13}P_3$
$Ru_3O(OAc)_6(PPh_3)_3$, 427

$Ru_3C_{68}H_{56}Cl_2N_{16}$
$[Ru_3Cl_2(bipy)_6(\overline{N{=}CHCH{=}NCH{=}CH})_2]^{4+}$, 359

$Ru_3C_{72}H_{60}Cl_3O_4P_4S_2$
$Ru_3Cl_3(PPh_3)_4(SO_2)_2$, 408

$Ru_3C_{126}H_{135}Cl_5O_9P_9$
$[Ru_3Cl_5\{P(OEt)Ph_2\}_9]^+$, 410

Ru_3Cl_{12}
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$Ru_3Ge_3C_{15}H_{18}O_9$
$\{Ru(\mu\text{-}GeMe_2)(CO)_3\}_3$, 287

$Ru_3H_{35}N_{10}O_6$
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$Ru_3H_{42}N_{14}O_2$
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$Ru_3Sb_3C_{63}H_{45}O_9$
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$Ru_3SnC_{12}Cl_4O_{12}$
$Ru_3(CO)_{12}SnCl_4$, 288

$Ru_4C_6F_{14}O_6$
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$Ru_4C_6H_{60}N_{24}$
$[\{Ru(NH_3)_5\}_4(TCNE)]^{8+}$, 320

$Ru_4C_{12}F_8O_{12}$
$\{RuF_2(CO)_3\}_4$, 442

$Ru_4C_{12}H_3O_{12}$
$[Ru_4H_3(CO)_{12}]^-$, 461

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$[Ru_4H(CO)_{13}]^-$, 461

$Ru_4C_{16}H_{64}N_{24}O_8S_2$
$[\{Ru(NH_3)_4(\overline{N{=}CHCH{=}NCH{=}CH})\}_4(SO_4)_2]^{6+}$, 320

$Ru_4C_{18}H_{28}N_2O_8$
$\{Ru_2(\mu\text{-}OAc)(CO)_2\{HN(\overline{CH_2})_5\}\}_2$, 425

$Ru_4C_{24}H_{74}N_{28}$
$[\{Ru(NH_3)_4(\overline{N{=}CHCH{=}NCH{=}CH})\}_4(HN{=}\overline{CHCH{=}NCH{=}CH})_2]^{10+}$, 320

$Ru_4C_{40}H_{32}N_4O_{12}$
$Ru_4(CO)_8(4\text{-}MeOC_6H_4N{=}CHCH{=}NC_6H_4OMe\text{-}4)_2$, 364

$Ru_4C_{40}H_{56}N_4O_{20}$
$\{Ru(acac)_2(NO)\}_4$, 362, 464

$Ru_4C_{40}H_{66}O_{16}P_2$
$Ru_4(OAc)_4(CO)_8(PBu_3)_2$, 375

$Ru_4C_{44}H_{47}O_{15}P_2$
$Ru_4H_4(CO)_9(PMe_2Ph)\{P(OC_6H_4Me\text{-}4)_3\}\{P(OCH_2)_3CEt\}$, 462

$Ru_4C_{48}H_{40}Cl_4N_4O_4P_4$
$\{Ru(\mu\text{-}Cl)(NO)(\mu\text{-}PPh_2)\}_4$, 372

$Ru_4C_{66}H_{120}O_{16}P_4$
$Ru_4\{O_2C(CH_2)_3CO_2\}_2(CO)_8(PBu_3)_4$, 375

$Ru_4C_{84}H_{66}N_{24}$
$[\{Ru(bipy)_2(2,2'\text{-bipyrimidine})\}_3Ru]^{8+}$, 359

$Ru_4C_{92}H_{76}Cl_2N_{22}$
$[Ru_4Cl_2(bipy)_8(\overline{N{=}CHCH{=}NCH{=}CH})_3]^{6+}$, 359

$Ru_4C_{140}H_{128}O_6P_8$
$Ru_4H_4(OH)_2(PPh_2)_2(CO)_2(Me_2CO)_2(PPh_3)_6$, 400

Ru_4F_{20}
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$Ru_4H_4O_4$
$[Ru_4(OH)_4]^{8+}$, 421

$Ru_4H_{12}O_{12}$
$[Ru_4(OH)_{12}]^{4+}$, 421

Ru_5Cl_{12}
$[Ru_5Cl_{12}]^{2-}$, 441

$Ru_6C_{18}HO_{18}$
$[Ru_6H(CO)_{18}]^-$, 461

$Ru_6C_{19}H_{12}O_{15}S_2$
$Ru_6H_2(SEt)_2(CO)_{15}$, 432

$Ru_6C_{22}H_{16}O_{15}S_3$
$Ru_6HC(SEt)_3(CO)_{15}$, 432

$Ru_6C_{47}H_{22}O_{22}P_2$
$\{Ru_3(CO)_{11}\}_2(dppm)$, 373

$Ru_6C_{48}H_{60}N_6O_{26}$
$[\{Ru_3O(OAc)_6(py)_2\}_2(\mu\text{-}\overline{N{=}CHCH{=}NCH{=}CH})]^{2+}$, 429

$Ru_6C_{102}H_{108}O_{26}P_6$
$Ru_6O_2(OAc)_{12}(dppe)_3$, 428

$Ru_9C_{65}H_{82}N_8O_{40}$
$[\{Ru_3O(OAc)_6(py)_2(\overline{N{=}CHCH{=}NCH{=}CH})\}_2\{Ru_3O(OAc)_6(CO)\}]^{2+}$, 429

$Ru_{40}H_{33}NOP_2S_2$
$Ru(CN)(\eta^2\text{-}CS_2Me)(CO)(PPh_3)_2$, 406

$SbRhC_{21}H_{21}Cl_2$
$RhCl_2\{Sb(C_6H_4Me\text{-}2)_3\}$, 933

$SbRhSnC_{54}H_{45}Cl_5$
$RhCl_2(SnCl_3)(SbPh_3)_3$, 1032

$SbRuC_{22}H_{15}O_4$
$Ru(CO)_4(SbPh_3)$, 371

$SbRuC_{36}H_{30}Cl_3NOP$
$RuCl_3(NO)(PPh_3)(SbPh_3)$, 393

$SbRu_2C_6Cl_7O_6$
$\{RuCl_2(CO)_3\}_2(SbCl_3)$, 443

$Sb_2OsC_{36}H_{30}Cl_4$
$Os(SbPh_3)_2Cl_4$, 577

$Sb_2ReC_{36}H_{30}Cl_2N_2O_2$
$Rc(NO)_2Cl_2(SbPh_3)_2$, 204

$Sb_2RhC_{36}H_{32}Cl$
$RhH_2Cl(SbPh_3)_2$, 1018

$Sb_2RuC_{36}H_{30}Cl_3NO$
$RuCl_3(NO)(SbPh_3)_2$, 394

$Sb_3IrC_{56}H_{45}O_2$
$[Ir(CO)_2(SbPh_3)_3]^+$, 1111

$Sb_3OsC_{54}H_{45}Br_3$
$Os(SbPh_3)_3Br_3$, 577

$Sb_3OsC_{54}H_{45}Cl_3$
$Os(SbPh_3)_3Cl_3$, 577

$Sb_3RhC_{54}H_{45}Cl_3$
$RhCl_3(SbPh_3)_3$, 1032

$Sb_3RhC_{55}H_{45}Cl_2NS$
$RhCl_2(NCS)(SbPh_3)_3$, 1032
$Sb_3RuC_{54}H_{45}Cl_2$
$\{RuCl_2(SbPh_3)_3\}_n$, 379
$Sb_3RuC_{55}H_{45}Cl_2O$
$RuCl_2(CO)(SbPh_3)_3$, 383
$Sb_3Ru_3C_{63}H_{45}O_9$
$Ru_3(CO)_9(SbPh_3)_3$, 373
$Sb_4OsC_{72}H_{60}Cl_2$
$Os(SbPh_3)_4Cl_2$, 577
$Sb_4RuC_{72}H_{60}Br_2$
$RuBr_2(SbPh_3)_4$, 379
$Sb_{12}Rh_2C_{150}H_{132}Cl_6$
$\{RhCl_3(Ph_2SbCH_2SbPh_2)_3\}_2$, 1025
$ScMn_2H_4$
Mn_2ScH_4, 60
$SiAs_2RhC_{36}H_{31}Cl_4$
$RhHCl(SiCl_3)(AsPh_3)_2$, 1020
$SiAs_2RhC_{42}H_{46}ClO_3$
$RhHCl\{Si(OEt)_3\}(AsPh_3)_2$, 1020
$SiCoC_7H_9O_4$
$Co(SiMe_3)(CO)_4$, 657
$SiCoC_{60}H_{62}O_3P_3$
$CoH_2\{Si(OEt)_3\}(PPh_3)_3$, 655
$SiFeF_6$
$FeSiF_6$, 1236
$SiIrC_{16}H_{32}Cl$
$IrH_2Cl(C_5Me_5)(SiEt_3)$, 1166
$SiIrC_{35}H_{35}OP_2$
$Ir(CO)(PPh_2CH_2CH_2SiMe_2)(PPh_3)$, 1164
$SiRhC_{36}H_{31}Cl_4P_2$
$RhHCl(SiCl_3)(PPh_3)_2$, 1020
$SiRhC_{37}H_{34}Cl_3P_2$
$RhHCl(SiCl_2Me)(PPh_3)_2$, 1020
$SiRhC_{38}H_{37}Cl_2P_2$
$RhHCl(SiClMe_2)(PPh_3)_2$, 1020
$SiRhC_{39}H_{40}ClP_2$
$RhHCl(SiMe_3)(PPh_3)_2$, 1020
$SiRhC_{39}H_{41}O_3P_2$
$RhH_2\{Si(OMe)_3\}(PPh_3)_2$, 1018
$SiRhC_{40}H_{43}P_2$
$RhH_2(SiHEt_2)(PPh_3)_2$, 1018
$SiRhC_{42}H_{46}ClO_3P_2$
$RhHCl\{Si(OEt)_3\}(PPh_3)_2$, 1020
$SiRhC_{42}H_{46}ClP_2$
$RhHCl(SiEt_3)(PPh_3)_2$, 1020
$SiRhC_{54}H_{46}ClP_2$
$RhHCl(SiPh_3)(PPh_3)_2$, 1020
$Si_2IrC_{22}H_{47}$
$IrH_2(C_5Me_5)(SiEt_3)_2$, 1166
$Si_2IrC_{31}H_{37}INP_2$
$IrI(Me)\{N(SiMe_2CHPPh_2)_2\}$, 1161
$Si_2IrC_{32}H_{40}ClP_2$
$IrCl(PPh_2CH_2CH_2SiMe_2)_2$, 1164
$Si_2RhC_{33}H_{45}NP_3$
$Rh\{N(SiMe_2CH_2PPh_2)_2\}(PMe_3)$, 1041
$Si_2RhC_{42}H_{48}NP_2$
$Rh\{N(SiMe_3)_2\}(PPh_3)_2$, 907
$Si_2RhC_{48}H_{51}NP_3$
$Rh\{N(SiMe_2CH_2PPh_2)_2\}(PPh_3)$, 1041
$Si_3IrC_{13}H_{39}INOP_2$
$IrHI\{SiH_2N(SiH_3)_2\}(CO)(PEt_3)_2$, 1126
$Si_3IrC_{13}H_{39}IOP_3$
$IrHI\{SiH_2P(SiH_3)_2\}(CO)(PEt_3)_2$, 1126
$Si_3Ir_2C_{26}H_{69}I_2NO_2P_4$
$\{IrHI(SiH_2)(CO)(PEt_3)_2\}_2(NSiH_3)$, 1126
$Si_3Ir_3C_{39}H_{99}I_3O_3P_7$
$\{IrHI(SiH_2)(CO)(PEt_3)_2\}_3P$, 1126
$Si_5Ir_2C_{26}H_{73}I_2O_2P_5$
$\{IrHI(SiH_2)_2(CO)(PEt_3)_2\}_2(PSiH_3)$, 1126
$Si_6FeC_{18}H_{54}N_3$
$Fe\{N(SiMe_3)_2\}_3$, 1183
$SnFeC_{12}H_{36}Cl_4O_{12}P_4$
$Fe(SnCl_3)Cl\{P(OMe)_3\}_4$, 1233
$SnFeC_{15}H_{45}C_{13}O_{15}P_5$
$Fe(SnCl_3)\{P(OMe)_3\}_5$, 1233
$SnFeC_{20}H_{15}Cl_3NO_3P$
$Fe(SnCl_3)(CO)_2(NO)(PPh_3)$, 1189
$SnIrC_{24}H_{24}O_3P$
$Ir(CO)_3(SnMe_3)(PPh_3)$, 1103
$SnIrC_{36}H_{31}Cl_4P_2$
$IrHCl(SnCl_3)(PPh_3)_2$, 1103
$SnIrC_{36}H_{32}Cl_4OP_2$
$IrH_2(SnCl_3)(CO)(PPh_3)_2$, 1103
$SnIrC_{37}H_{30}Cl_3OP_2$
$IrCl(SnCl_2)(CO)(PPh_3)_2$, 1103
$SnIrC_{37}H_{30}Cl_5OP_2$
$IrCl(SnCl_4)(CO)(PPh_3)_2$, 1128
$SnIrC_{37}H_{31}Cl_4OP_2$
$IrHCl(SnCl_3)(CO)(PPh_3)_2$, 1103, 1127
$SnIrC_{37}H_{32}Cl_3OP_2$
$IrH_2(SnCl_3)(CO)(PPh_3)_2$, 1127
$SnIrC_{38}H_{33}Cl_4OP_2$
$IrCl(SnCl_3)Me(CO)(PPh_3)_2$, 1128
$SnIrC_{39}H_{30}O_3P$
$Ir(CO)_3(SnPh_3)(PPh_3)$, 1103
$SnIrC_{39}H_{34}Cl_3OP_2$
$Ir(SnCl_3)(C_2H_4)(CO)(PPh_3)_2$, 1103
$SnIrC_{54}H_{46}Cl_4P_3$
$IrHCl(SnCl_3)(PPh_3)_3$, 1127
$SnIr_2C_{42}H_{30}Cl_2O_6P_2$
$\{Ir(CO)_3(PPh_3)\}_2(SnCl_2)$, 1103
$SnIr_2C_{44}H_{36}O_6P_2$
$\{Ir(CO)_3(PPh_3)\}_2(SnMe_2)$, 1103
$SnOsC_{54}H_{45}Cl_5P_3$
$Os(SnCl_3)(PPh_3)_3Cl_2$, 527
$SnOsCl_8$
$[Os(SnCl_3)Cl_5]^{4-}$, 527
$SnRhC_{18}H_{15}F_{12}P_4$
$Rh(PF_3)_4SnPh_3$, 904
$SnRhSbC_{54}H_{45}Cl_5$
$RhCl_2(SnCl_3)(SbPh_3)_3$, 1032
$SnRuC_2Cl_8O_2$
$[RuCl_2(SnCl_3)_2(CO)_2]^{2-}$, 288
$SnRuC_4Cl_4O_4$
$RuCl(SnCl_3)(CO)_4$, 288
$SnRuC_7H_9ClO_4$
$RuCl(SnMe_3)(CO)_4$, 288
$SnRuC_{14}H_{30}Cl_3O_2S_3$
$[Ru(SnCl_3)(CO)_2(SEt_2)_3]^+$, 289, 432
$SnRuC_{39}H_{30}I_4O_3P_2$
$[RuI(CO)_3(PPh_3)_2]SnI_3$, 289
$SnRuC_{40}H_{36}Cl_4O_2P_2$
$RuCl(SnCl_3)(CO)(PPh_3)_2(OCMe_2)$, 288
$SnRuC_{42}H_{40}Cl_4N_2P_2$
$RuCl(SnCl_3)(CNEt)_2(PPh_3)_2$, 289, 384
$SnRuC_{48}H_{45}Cl_3P_4$
$RuH(SnCl_3)(PHPh_2)_4$, 289, 452
$SnRu_2C_5Cl_6O_5$
$Ru_2Cl_3(SnCl_3)(CO)_5$, 288
$SnRu_2C_{56}H_{45}Cl_6O_2P_3$
$Ru(SnCl_3)(CO)(PPh_3)(\mu\text{-}Cl)_3Ru(CO)(PPh_3)_2$, 288
$SnRu_3C_{12}Cl_4O_{12}$
$Ru_3(CO)_{12}SnCl_4$, 288
Sn_2IrBr_{10}
$[IrBr_4(SnBr_3)_2]^-$, 1127
Sn_2OsCl_9NO
$[Os(NO)Cl_3(SnCl_3)_2]^{2-}$, 548
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$Sn_2RuC_4Cl_6O_4$
$Ru(SnCl_3)_2(CO)_4$, 288
$Sn_2RuC_8H_{24}Cl_6O_4S_4$
$Ru(SnCl_3)_2(DMSO)_4$, 289
$Sn_2RuC_{10}H_{18}O_4$
$Ru(SnMe_3)_2(CO)_4$, 288
$Sn_2RuC_{12}H_{20}Cl_6N_4$

$Ru(SnCl_3)_2(CNEt)_4$, 289

Sn_2RuCl_9NO
$[RuCl_3(SnCl_3)_2(NO)]^{2-}$, 288

$Sn_2Ru_2C_{12}H_{12}O_8$
$\{Ru(\mu\text{-}SnMe_2)(CO)_4\}_2$, 288

$Sn_2Ru_2Cl_{12}N_2O_2$
$[Ru_2Cl_6(SnCl_3)_2(NO)_2]^{4-}$, 288

$Sn_4Rh_2Cl_{14}$
$[\{RhCl(SnCl_3)_2\}_2]^{4-}$, 906

Sn_4RuCl_{14}
$[RuCl_2(SnCl_3)_4]^{4-}$, 288

$Sn_4Ru_2C_{16}H_{30}O_6$
$\{Ru(\mu\text{-}SnMe_2)(SnMe_3)(CO)_3\}_2$, 288

Sn_5OsBr_{16}
$[Os(SnBr_3)_5Br]^{4-}$, 527

Sn_5OsCl_{15}
$[Os(SnCl_3)_5]^{4-}$, 527

Sn_5OsCl_{16}
$[Os(SnCl_3)_5Cl]^{2-}$, 527
$[Os(SnCl_3)_5Cl]^{4-}$, 527

Sn_5RuClF_{15}
$[RuCl(SnF_3)_5]^{4-}$, 288

Sn_5RuCl_{16}
$[RuCl(SnCl_3)_5]^{4-}$, 288

Sn_6OsCl_{18}
$[Os(SnCl_3)_6]^{4-}$, 527

Sn_6RuCl_{18}
$[Ru(SnCl_3)_6]^{4-}$, 288

Sn_6RuF_{18}
$[Ru(SnF_3)_6]^{4-}$, 288

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Sr_2FeO_4, 266

$TiReC_{36}H_{52}Cl_5N_2OP_4$
$TiCl_4(THF)\{(N_2)ReCl(PMe_2Ph)_4\}$, 133

$TiRe_2C_{36}H_{54}Cl_7N_2O_2P_4$
$Ti_2OCl_6(Et_2O)\{(N_2)ReCl(PMe_2Ph)_4\}$, 133

$TiRe_2C_{64}H_{88}Cl_6N_4P_8$
$TiCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2$, 133

$WAsCoFeMoC_2H_6S$
$CoFeMoWS(AsMe_2)$, 832

$WIrC_{46}H_{42}P_2$
$[IrH(PPh_3)_2(\mu\text{-}H)_2(\eta\text{-}\sigma\text{:}1\text{-}5\text{-}\eta\text{-}C_5H_4WCp]^+$, 1152

$WIrC_{54}H_{40}O_6P_3$
$IrW(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$, 1163

$WIrC_{66}H_{51}O_5P_4$
$IrWH(CO)_5(\mu\text{-}PPh_2)_2(PPh_3)_2$, 1163

$WMn_2C_4O_{11}$
$Mn_2(C_2O_4)_2WO_3$, 50

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$[WO_4]^{2-}$, 825

$WRhC_{46}H_{42}P_2$
$Rh(PPh_3)_2(\mu\text{-}H)_2WCp_2$, 1076

$W_{11}MnH_2O_{44}P$
$[PMnW_{11}O_{39}(OH_2)]^{5-}$, 47

$W_{11}ReO_{40}P$
$[RePW_{11}O_{40}]^{4-}$, 192

$W_{12}CoO_{40}$
$[CoW_{12}O_{40}]^{5-}$, 827

$W_{17}MnH_2O_{62}P_2$
$[P_2MnW_{17}O_{61}(OH_2)]^{8-}$, 47

$Zn_2Ru_2C_{111}H_{99}ClP_6$
$\{RuHMe(C_6H_4PPh_2)(PPh_3)_2\}_2Zn_2ClMe$, 455

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Mn_2ZrH_3, 60

$Zr_2Ru_2C_{94}H_{84}Cl_4P_4$
$\{ZrCp_2(\mu\text{-}Cl)(\mu\text{-}CH_2)Ru(PPh_3)_2\}_2(\mu\text{-}Cl)_2$, 414