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ADVANCED INORGANIC CHEMISTRY

A Comprehensive Text

FIFTH EDITION

ADVANCED INORGANIC CHEMISTRY

Fifth Edition

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. . . Chemistry, the most cosmopolitan of sciences,
the most secret of arts.
D'Arcy Wentworth Thompson

La Chimie crée son objet.
Marcelin Berthelot

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Preface to the Fifth Edition

The main purpose of this book is the same as that of previous editions: to provide the student with the background necessary to comprehend current research literature in inorganic and certain aspects of organometallic chemistry.

One of the most evident differences between this and earlier editions of the book is the absence of much theoretical material previously included. There are three reasons for this. From a practical point of view, the continuing rapid growth of the chemistry as such required the addition of important new facts to all of the descriptive material. Since we set great store by keeping this book in the format of one volume, something had to go. We found very little that could be omitted in the older descriptive material, and condensation has its limits if readability is to be maintained. Elimination of theoretical material, or at least severe reduction in the space devoted to it, seemed unavoidable.

Second, over the years, much of the theoretical background has found its way into textbooks used at a lower (American undergraduate) level, for example, our own *Basic Inorganic Chemistry,* 2nd edition (1987). This is true of ligand field theory, spectra and magnetism of transition metal complexes, and simple ideas about chemical bonds. Thus, removal of such material from this book can be regarded as the elimination of unnecessary repetition.

Third, in our own minds we have, over the years, become less persuaded of the value of certain types of theorizing. Theories come and go. Twenty-five years ago, when we began writing these books, there were widely accepted ideas about bonding that have by now fallen into disuse, and even disrepute. Thus we felt obliged to make space for facts at the expense of theoretical material.

We again thank those who have been kind enough to make suggestions for improvements and welcome any comments on this edition.

We remind readers of the guidelines under which references are supplied. These are largely from primary journals from mid-1979 to mid-1987. Many statements are documented by earlier references cited in earlier editions. Where there are two authors, both names are given; when more, the first starred author or in absence of a star, the first is given.

We have generally not quoted references to the appropriate sections of the authoritative handbooks namely, *Gmelin Handbook of Inorganic Chemistry,* Springer Verlag, Berlin, and the Pergamon Press *Comprehensive Treatises on Inorganic Chemistry, Coordination Chemistry, and Organometallic Chemistry,* which should be familiar to the dedicated student.

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Preface to the First Edition

It is now a truism that, in recent years, inorganic chemistry has experienced an impressive renaissance. Academic and industrial research in inorganic chemistry is flourishing, and the output of research papers and reviews is growing exponentially.

In spite of this interest, however, there has been no comprehensive textbook on inorganic chemistry at an advanced level incorporating the many new chemical developments, particularly the more recent theoretical advances in the interpretation of bonding and reactivity in inorganic compounds. It is the aim of this book, which is based on courses given by the authors over the past five to ten years, to fill this need. It is our hope that it will provide a sound basis in contemporary inorganic chemistry for the new generation of students and will stimulate their interest in a field in which trained personnel are still exceedingly scarce in both academic and industrial laboratories.

The content of this book, which encompasses the chemistry of all of the chemical elements and their compounds, including interpretative discussion in the light of the latest advances in structural chemistry, general valence theory, and, particularly, ligand field theory, provides a reasonable achievement for students at the B.Sc. honors level in British universities and at the senior year or first year graduate level in American universities. Our experience is that a course of about eighty lectures is desirable as a guide to the study of this material.

We are indebted to several of our colleagues, who have read sections of the manuscript, for their suggestions and criticism. It is, of course, the authors alone who are responsible for any errors or omissions in the final draft. We also thank the various authors and editors who have so kindly given us permission to reproduce diagrams from their papers: specific acknowledgements are made in the text. We sincerely appreciate the secretarial assistance of Miss C. M. Ross and Mrs. A. B. Blake in the preparation of the manuscript.

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Contents

PART ONE

Survey of Principles

PART TWO

The Chemistry of the Main Group Elements

PART THREE

The Chemistry of the Transition Elements

PART FOUR

Survey of Selected Areas: Metal Carbonyls, Metal–Metal Bonds and Clusters, Hydrides, Organometallic Compounds, Oxidative-Addition and -Insertion Reactions, Homogeneous Catalysis, Reaction Mechanisms, and Bioinorganic Chemistry

Appendices

Abbreviations in Common Use

1. Chemicals, Ligands, Radicals, etc.

Ac	acetyl, CH_3CO
acac	acetylacetonate anion
acacH	acetylacetone
AIBN	azoisobutyronitrile
am	ammonia (or occasionally an amine)
Ar	aryl or arene (ArH)
aq	aquated, H_2O
ATP	adenosine triphosphate
9-BBN	9-borabicyclo[3,3,1]nonane
bipy	2,2′-dipyridine, or bipyridine
Bu	butyl (*n*-, *i*-, *s*-, or *t*-: normal, iso, secondary, or tertiary butyl)
Bz	benzyl
C,*lmn*	cryptate ligand with *l*-, *m*- and *n*- membered bridges (cf. p. 52)
COD or cod	cycloocta-1,5-diene
COT or cot	cyclooctatetraene
Cp	cyclopentadienyl, C_5H_5
cy	cyclohexyl
dab or dad	1,4-diaza-1,3-butadienes, $RN{=}CH{-}CH{=}NR$
depe	1,2-bis(diethylphosphino)ethane
depm	1,2-bis(diethylphosphino)methane
diars	*o*-phenylenebisdimethylarsine, *o*-$C_6H_4(AsMe_2)_2$
dien	diethylenetriamine, $H_2N(CH_2CH_2NH)_2H$
diglyme	diethylene glycol dimethyl ether, $CH_3O(CH_2CH_2O)_2CH_3$
diop	{[2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis (methylene)]bis(diphenylphosphine)}
diphos	any chelating diphosphine, but usually 1,2-bis(diphenylphosphino)ethane, dppe
DME	dimethoxyethane (also glyme)
DMF or dmf	*N,N′*-dimethylformamide, $HCONMe_2$
dmg	dimethylglyoximate anion
$dmgH_2$	dimethylglyoxime
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	1,2-bis(dimethylphosphino)methane

DMSO or dmso	dimethyl sulfoxide, Me_2SO
dppe	1,2-bis(diphenylphosphino)ethane
DPPH	diphenylpicrylhydrazyl
dppm	bis(diphenylphosphino)methane
E	electrophile or element
$EDTAH_4$	ethylenediaminetetraacetic acid
$EDTAH_{4-n}^{n-}$	anions of $EDTAH_4$
en	ethylenediamine, $H_2NCH_2CH_2NH_2$
Et	ethyl
Fc	ferrocenyl (Fc′ for substituted Fc)
Fp	$Fe(CO)_2Cp$
glyme (= DME)	ethylene glycol dimethyl ether, $CH_3OCH_2CH_2OCH_3$
hfa	hexafluoroacetylacetonate anion
HMPA	hexamethylphosphoric triamide, $OP(NMe_2)_3$
L	ligand
M	central (usually metal) atom in compound
m-C-*n*	macrocyclic polyether with *m*-membered ring and *n* oxygen atoms (cf. p. 51)
Me	methyl
Mes	mesityl
Me_6tren	tris-(2-dimethylaminoethyl)amine, $N(CH_2CH_2NMe_2)_3$
NBD or nbd	norbornadiene
NBS	N-bromosuccinimide
np^2	bis-(2-diphenylphosphinoethyl)amine, $HN(CH_2CH_2PPh_2)_2$
np^3	tris-(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$
$NTAH_3$	nitrilotriacetic acid, $N(CH_2COOH)_3$
OAc	acetate anion
oep	octaethylporphyrin
ox	oxalate ion, $C_2O_4^{2-}$
Pc	phthalocyanine
Ph	phenyl, C_6H_5
phen	1,10-phenanthroline
pn	propylenediamine (1,2-diaminopropane)
PNP (= np^2)	bis-(2-diphenylphosphinoethyl)amine, $HN(CH_2CH_2PPh_2)_2$
porph	porphyrin (or any porphyrin)
pp^3	tris-(2-diphenylphosphinoethyl)phosphine, $P(CH_2CH_2PPh_2)_3$
PPN^+	$[(Ph_3P)_2N]^+$
Pr	propyl (*n*- or *i*-)
py	pyridine
pz	pyrazolyl

QAS	tris-(2-diphenylarsinophenyl)arsine, $As(o\text{-}C_6H_4AsPh_2)_3$
QP	tris-(2-diphenylphosphinophenyl)phosphine, $P(o\text{-}C_6H_4PPh_2)_3$
R	alkyl (preferably) or aryl group
R_F	perfluoro alkyl group
S	solvent
sal	salicylaldehyde
sal$_2$en or salen	bis-salicylaldehydeethylenediimine
TAN	tris-(2-diphenylarsinoethyl)amine, $N(CH_2CH_2AsPh_2)_3$
TAP	tris-(3-dimethylarsinopropyl)phosphine, $P(CH_2CH_2CH_2AsMe_2)_3$
TAS	bis-(3-dimethylarsinopropyl)methylarsine, $MeAs(CH_2CH_2CH_2AsMe_2)_2$
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
teen	*N*,*N*,*N'*,*N'*-tetraethylethylenediamine
terpy	terpyridine
TFA	trifluoroacetic acid
THF or thf	tetrahydrofuran
THT or tht	tetrahydrothiophene
tmen	*N*,*N*,*N'*,*N'*-tetramethylethylenediamine (also TMED, tmed)
tn	1,3-diaminopropane(trimethylenediamine)
tol	tolyl ($CH_3C_6H_4$)
TPN (= np^3)	tris-(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$
TPP	*meso*-tetraphenylporphyrin
tren	tris-(2-aminoethyl)amine, $N(CH_2CH_2NH_2)_3$
trien	triethylenetetraamine, $(\text{-}CH_2NHCH_2CH_2NH_2)_2$
triflate (ion)	$CF_3SO_3^-$
TSN	tris-(2-methylthiomethyl)amine, $N(CH_2CH_2SMe)_3$
TSP	tris-(2-methylthiophenyl)phosphine, $P(o\text{-}C_6H_4SMe)_3$
TSeP	tris-(2-methylselenophenyl)phosphine, $P(o\text{-}C_6H_4SeMe)_3$
TTA	2-thenoyltrifluoroacetone, $C_4H_3SCOCH_2COCF_3$
X	halogen or pseudohalogen

2. Miscellaneous

Å	angstrom unit, 10^{-10} m
asym	asymmetric or antisymmetric
bcc	body centered cubic
BM	Bohr magneton
bp	boiling point
ccp	cubic close packed
CFSE	crystal field stabilization energy
CFT	crystal field theory
CIDNP	chemically induced dynamic nuclear polarization

cm^{-1}	wave number
CT	charge transfer
dec	decomposes
d-	dextorotatory
ESCA	electron spectroscopy for chemical analysis (= XPE, X-ray photoelectron spectroscopy)
esr or epr	electron spin (or paramagnetic) resonance
eV	electron volt
FT	Fourier transform (for nmr or ir)
g	*g*-values
(g)	gaseous state
h	Planck's constant
hcp	hexagonal close packed
HOMO	highest occupied molecular orbital
Hz	hertz, s^{-1}
ICCC	International Coordination Chemistry Conference
ir	infrared
IUPAC	International Union of Pure and Applied Chemistry
l-	levorotatory
(l)	liquid state
LCAO	linear combination of atomic orbitals
LFSE	ligand field stabilization energy
LFT	ligand field theory
LUMO	lowest unoccupied molecular orbital
MAS nmr	magic angle spinning nmr
MO	molecular orbital
mp	melting point
NOE	nuclear Overhauser effect
nmr	nuclear magnetic resonance
PE	photoelectron (spectroscopy)
R	gas constant
(s)	solid state
SCE	saturated calomel electrode
SCF	self-consistent field
SCF-Xα-SW	self-consistent field, Xα, scattered wave (form of MO theory)
sp or *spy*	square pyramid(al)
str	vibrational stretching mode
sub	sublimes
sym	symmetrical
tbp	trigonal bipyramid(al)
U	lattice energy
uv	ultraviolet
VB	valence bond

Z	atomic number
ϵ	molar extinction coefficient
ν	frequency (cm^{-1} or Hz)
μ	magnetic moment in Bohr magnetons
χ	magnetic susceptibility
θ	Weiss constant

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1

SURVEY OF PRINCIPLES

Chapter One

Concepts in Stereochemistry and Bonding

1-1. Scope and Purpose of This Chapter

The inorganic chemist is called upon to correlate or rationalize an enormous range of factual data concerning the structures of molecules and extended solid arrays. A principal basis for such correlations is an understanding of chemical bonds. In a general sense, the more precisely and profoundly we can describe the electronic structures of compounds, the more fully and reliably we can predict their structures and properties. All chemists should therefore learn as much about molecular quantum mechanics and its applications as their time and talents permit. In practice, however, experimental chemists cannot approach the questions that arise every day in their experimental work from the point of view of rigorous theory. Rougher and readier approaches must be used.

In this chapter we shall very briefly survey some of the main, qualitative, generally accepted concepts that are useful in understanding and assimilating the wealth of factual material to follow in this book. This survey is not intended to provide an introduction of these topics for the uninitiated.

1-2. Structures of Solids

The great majority of solids of uniform purity and composition fall into one of the following categories:

1. *Molecular Solids.* These consist of discrete molecules making van der Waals contacts (perhaps also some hydrogen bonds) with one another. While the packing forces in the solid (or liquid) state undoubtedly cause minor perturbations to the structures of the molecules, it is usually satisfactory to ignore them and regard the molecule as an isolated entity. Thus, the solid state structure problem is not effectively different from the molecular structure problem.

2. *Metals.* These consist of close-packed arrays of atoms that have one or more relatively loosely bound electrons which become delocalized into energy bands. It is this type of delocalized electronic structure that accounts for the

characteristic physical properties of metals: good electrical and thermal conductivities, luster, strength, malleability (in many cases), and so on. From a chemical point of view, we shall note only one facet of the metallic state, namely, the existence in the close-packed structure of interstices, mainly tetrahedral and octahedral, into which small nonmetal atoms (H, B, C, N, etc.) can fit. When a given set of interstices is so occupied we have an *interstitial phase* or *interstitial compound,* such as Fe_3C, which is essential to the hardening of steel. These interstitial phases are usually less conducting but harder and more refractory than the parent metals.

3. *Covalent Infinite Arrays.* Substances of this kind are found among both elements and compounds. Elements that form extended covalent (as opposed to metallic) arrays are boron, all the Group IV (14) elements except lead, also phosphorus, arsenic, selenium, and tellurium. All other elements form either only metallic phases or only molecular ones. Some of these elements, of course, have allotropes of the metallic or molecular type in addition to the phase or phases that are extended covalent arrays. For example, tin has a metallic allotrope (white tin) in addition to that with the diamond structure (gray tin), and selenium forms two molecular allotropes containing Se_8 rings, isostructural with the rhombic form and the monoclinic form of sulfur. For tellurium we have a situation on the borderline of metallic behavior.

The structures of the principal allotropic forms of all the elements are discussed in detail as the chemistry of each element is treated. For illustrative purposes, we shall mention here only one such structure, the diamond structure, since this is adopted by several other elements and is a point of reference for various other structures. It is shown from two points of view in Fig. 1-1. The structure has a cubic unit cell with the full symmetry of the group T_d. However, for some purposes it can be viewed as a stacking of puckered infinite

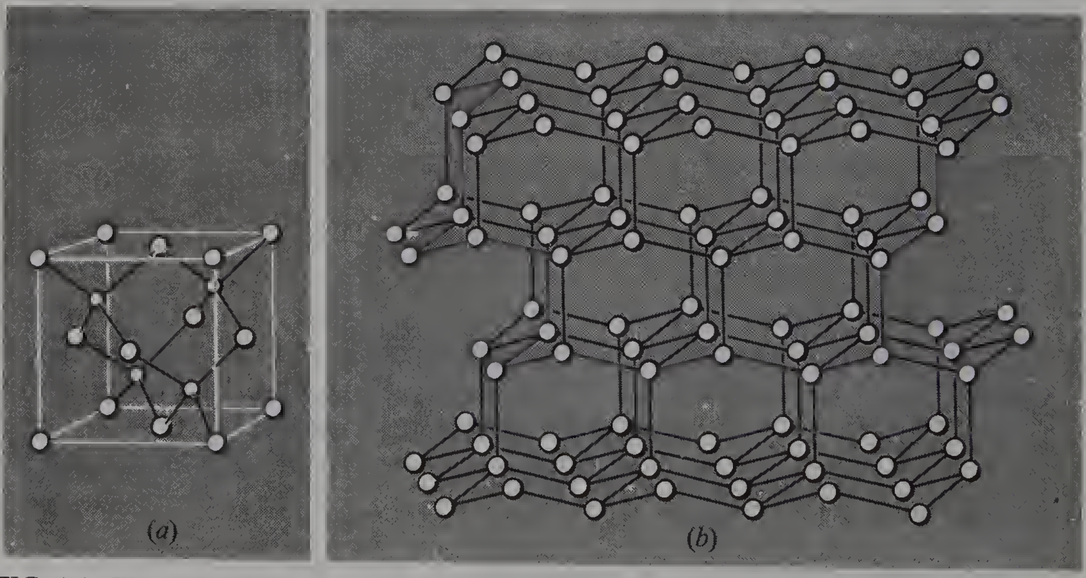
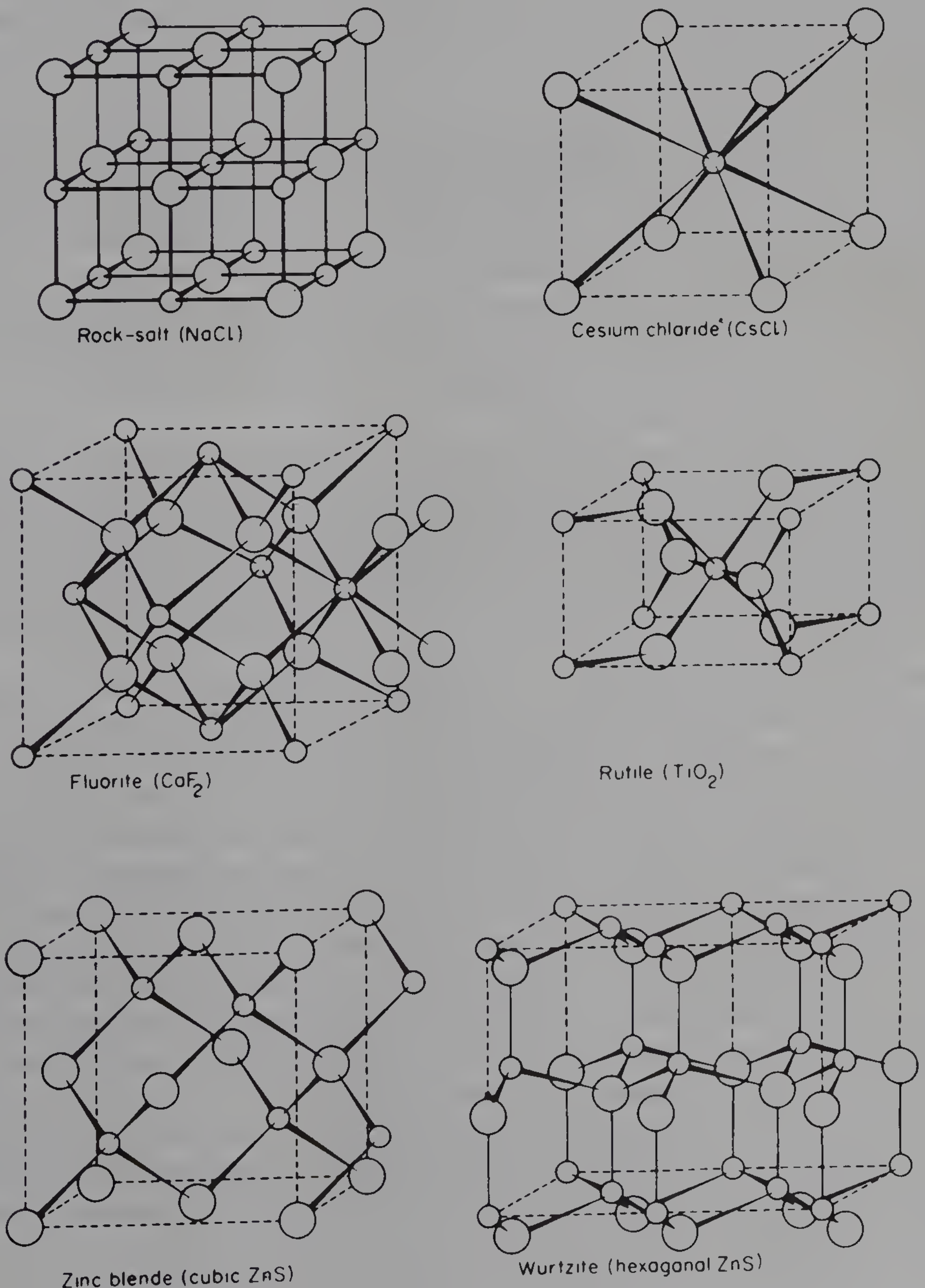


FIG. 1-1. The diamond structure seen from two points of view. (a) The conventional cubic unit cell. (b) A view showing how layers are stacked; these layers run perpendicular to the body diagonals of the cube.

layers. It will be noted that the zinc blende structure (Fig. 1-2) can be regarded as a diamond structure in which one half the sites are occupied by Zn^{2+} (or other cation) and the other half are occupied by S^{2-} (or other anion) in an ordered way. In the diamond structure itself all atoms are equivalent, each being surrounded by a perfect tetrahedron of four others. The electronic structure can be simply and fairly accurately described by saying that each atom forms a localized two-electron bond to each of its neighbors.



Rock-salt (NaCl)

Cesium chloride (CsCl)

Fluorite (CaF_2)

Rutile (TiO_2)

Zinc blende (cubic ZnS)

Wurtzite (hexagonal ZnS)

FIG. 1-2. Six important ionic structures. Small circles denote metal cations, large circles denote anions.

As soon as one changes from elements, where the adjacent atoms are identical and the bonds are necessarily nonpolar, to compounds, there enters the vexatious question of when to describe a substance as ionic and when to describe it as covalent. No attempt is made here to deal with this question in detail for the practical reason that, very largely, there is no need to have the answer—even granting, for the sake of argument only, that any such thing as "the answer" exists. Suffice it to say that bonds between unlike atoms all have some degree of polarity and (1) when the polarity is relatively small it is practical to describe the bonds as polar covalent ones, and (2) when the polarity is very high it makes more sense to consider that the substance consists of an array of ions.

4. *Ionic Structures.* No substance is perfectly ionic; there is always some sharing of electron density between adjacent positive and negative ions (i.e., some covalence). However, many substances can be understood in a practical way by employing the approximation that they consist essentially of arrays of oppositely charged ions. In discussing structures from this point of view it is necessary to have numerical values for the radii of the ions. Such radii can be estimated only by empirical and at least partially equivocal methods. Appendix 4 contains a set of radii that are widely used together with a few remarks on how they were derived.

Figure 1-2 shows six of the most important structures found among essentially ionic substances. In an ionic structure each ion is surrounded by a certain number of ions of the opposite sign; this number is called the *coordination number* of the ion. In the first three structures shown, namely, the NaCl, CsCl, and CaF_2 types, the cations have the coordination numbers 6, 8, and 8, respectively.

We now ask why a particular compound crystallizes with one or another of these structures. To answer this, we first recognize that ignoring the possibility of metastability, which seldom arises, the compound will adopt the arrangement providing the greatest stability, that is, the lowest energy. The factors that contribute to the energy are the attractive force between oppositely charged ions, which will increase with increasing coordination number, and the forces of repulsion, which will increase very rapidly if ions of the same charge are "squeezed" together. Thus the optimum arrangement in any crystal should be the one allowing the greatest number of oppositely charged ions to "touch" without requiring any squeezing together of ions with the same charge. The ability of a given structure to meet these requirements will depend on the relative sizes of the ions.

Let us analyze the situation for the CsCl structure. We place eight negative ions of radius r^- around a positive ion with the radius r^+ so that the M^+ to X^- distance is $r^+ + r^-$ and the adjacent X^- ions are just touching. Then the X^- to X^- distance, a, is given by

$$a = \frac{2}{\sqrt{3}}(r^+ + r^-) = 2r^-$$

or

$$\frac{r^-}{r^+} = 1.37$$

Now, if the ratio r^-/r^+ is > 1.37, the only way we can have all eight X^- ions touching the M^+ ion is to squeeze the X^- ions together. Alternatively, if r^-/r^+ is > 1.37, and we do not squeeze the X^- ions, they cannot touch the M^+ ion and a certain amount of electrostatic stabilization energy will be unattainable. Thus, when r^-/r^+ becomes equal to 1.37, the competition between attractive and repulsive forces is balanced, and any increase in the ratio may make the CsCl structure unfavorable relative to a structure with a lower coordination number, such as the NaCl structure.

In the NaCl structure, in order to have all ions just touching but not squeezed, with radius r^- for X^- and r^+ for M^+ we have

$$2r^- = \sqrt{2}(r^+ + r^-)$$

which gives for the critical radius ratio

$$\frac{r^-}{r^+} = 2.44$$

If the ratio r^-/r^+ exceeds 2.44, the NaCl structure becomes disfavored, and a structure with cation coordination number 4, for which the critical value of r^-/r^+ is 4.44, may be more favorable. To summarize, in this simple approximation, packing considerations lead us to expect the various structures to have the following ranges of stability in terms of the r^-/r^+ ratio:

CsCl and CaF_2 structures	$1 < r^-/r^+ < 1.37$
NaCl and rutile structures	$1.37 < r^-/r^+ < 2.44$
ZnS structures	$2.44 < r^-/r^+ < 4.44$

Obviously, similar reasoning may be applied to other structures and other types of ionic compounds.

The idea that crystal structures should be consistent with ionic size ratios, according to geometrical relationships such as those just examined, is a useful one, but it has only semiquantitative validity.[1] The radius ratio rules appear to hold about two-thirds of the time. Reasons for frequent failure are the flexibility of ions (i.e., the fact that even for a specified coordination number, the radius is not precisely defined), the role of lattice energies, as well as non-Coulombic factors such as ion polarizabilities and covalence.

The more common ionic crystal structures shown in Fig. 1-2 are mentioned repeatedly throughout the text. The *rutile structure,* named after one mineralogical form of TiO_2, is very common among oxides and fluorides of the MF_2 and MO_2 types (e.g., FeF_2, NiF_2, ZrO_2, and RuO_2), where the radius

---

[1] L. C. Nathan, *J. Chem. Educ.,* 1985, **62,** 215.

ratio favors coordination number 6 for the cation. Similarly, the *zinc blende* and *wurtzite structures,* named after two forms of zinc sulfide, are widely encountered when the radius ratio favors four coordination, and the *fluorite structure* is common when eight coordination of the cation is favored.

When a compound has stoichiometry and ion distribution opposite to that in one of the structures just mentioned, it may be said to have an *anti* structure. Thus compounds such as Li_2O, Na_2S, and K_2S, have the *antifluorite* structure in which the anions occupy the Ca^{2+} positions and the cations the F^- positions of the CaF_2 structure. The antirutile structure is sometimes encountered also.

Structures with Close Packing of Anions. Many structures of halides and oxides can be regarded as close-packed arrays of anions with cations in the octahedral and/or tetrahedral interstices. Even the NaCl structure can be thought of in this way (*ccp* array of Cl^- ions with all octahedral interstices filled), although this is not ordinarily useful. $CdCl_2$ also has *ccp* Cl^- ions with every other octahedral hole occupied by Cd^{2+}, and CdI_2 has *hcp* I^- ions with Cd^{2+} ions in half the octahedral holes. It is noteworthy that the $CdCl_2$ and CdI_2 structures (the latter appears in Fig. 1-3) are *layer structures.* The particular pattern in which cations occupy half the octahedral holes, is such as to leave alternate layers of direct anion–anion contact.

Corundum, the α form of Al_2O_3, has an *hcp* array of oxide ions with two-thirds of the octahedral interstices occupied by cations and is adopted by many other oxides (e.g., Ti_2O_3, V_2O_3, Cr_2O_3, Fe_2O_3, Ga_2O_3, and Rh_2O_3). The BiI_3 structure has an *hcp* array of anions with two-thirds of the octahedral

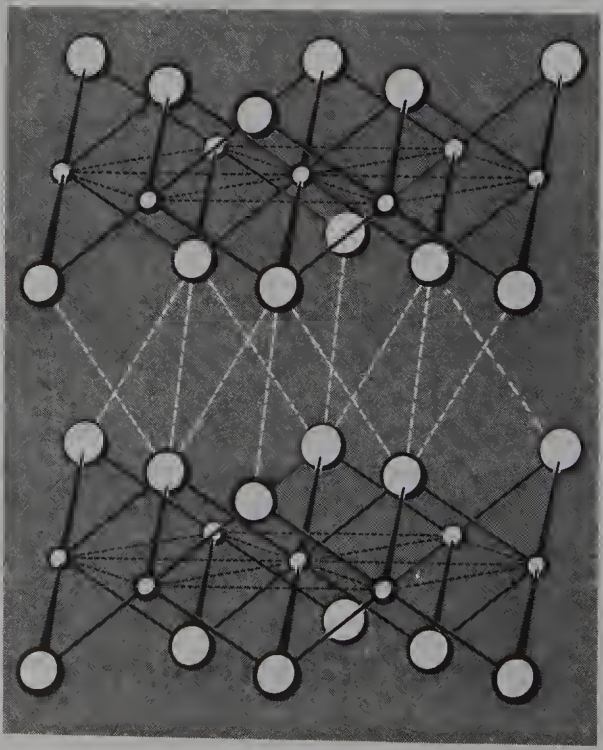


FIG. 1-3. A portion of the CdI_2 structure. Small spheres represent metal cations.

holes in each alternate pair of layers occupied by cations, and it is adopted by $FeCl_3$, $CrBr_3$, $TiCl_3$, VCl_3, and many other AB_3 compounds. As indicated, all the *structures* just mentioned are adopted by numerous *substances*. The structures are usually named in reference to one of these substances. Thus we speak of the NaCl, $CdCl_2$, CdI_2, BI_3, and corundum (or α-Al_2O_3) structures.

Some Mixed Oxide Structures. There is a vast number of oxides (and also some stoichiometrically related halides) having two or more different kinds of cation. Most of them occur in one of a few basic structural types, the names of which are derived from the first or principal compound shown to have that type of structure. Three of the most important such structures are now described.

1. *The Spinel Structure.* The compound $MgAl_2O_4$, which occurs in Nature as the mineral spinel, has a structure based on a *ccp* array of oxide ions. One-eighth of the tetrahedral holes (of which there are two per anion) are occupied by Mg^{2+} ions and one-half of the octahedral holes (of which there is one per anion) are occupied by Al^{3+} ions. This structure, or a modification to be discussed later, is adopted by many other mixed metal oxides of the type $M^{II}M_2^{III}O_4$ (e.g., $FeCr_2O_4$, $ZnAl_2O_4$, and $Co^{II}Co_2^{III}O_4$), by some of the type $M^{IV}M_2^{II}O_4$ (e.g., $TiZn_2O_4$ and $SnCo_2O_4$),and by some of the type $M_2^{I}M^{VI}O_4$ (e.g., Na_2MoO_4 and Ag_2MoO_4). This structure is often symbolized as $A[B_2]O_4$, where brackets enclose the ions in the octahedral interstices. An important variant is the *inverse spinel structure,* $B[AB]O_4$, in which half the B ions are in tetrahedral interstices and the A ions are in octahedral ones along with the other half of the B ions. This often happens when the A ions have a stronger preference for octahedral coordination than do the B ions. As far as is known, all $M^{IV}M_2^{II}O_4$ spinels are inverse (e.g., $Zn[ZnTi]O_4$), as are many of the $M^{II}M_2^{III}O_4$ ones (e.g., $Fe^{III}[Co^{II}Fe^{III}]O_4$, $Fe^{III}[Fe^{II}Fe^{III}]O_4$, and $Fe\,[NiFe]O_4$), as well.

There are also many compounds with *disordered spinel structures* in which only a fraction of the A ions are in tetrahedral sites (and a corresponding fraction in octahedral ones). This occurs when the preferences of both A and B ions for octahedral and tetrahedral sites do not differ markedly.

2. *The Ilmenite Structure.* This is the structure of the mineral ilmenite ($Fe^{II}Ti^{IV}O_3$). It is closely related to the corundum structure except that the cations are of two different types. It is adopted by ABO_3 oxides when the two cations, A and B, are of about the same size, but they need not be of the same charge so long as their total charge is +6. Thus in ilmenite itself and in $MgTiO_3$ and $CoTiO_3$ the cations have charges +2 and +4, whereas in α-$NaSbO_3$ the cations have charges of +1 and +5.

3. *The Perovskite Structure.* The mineral perovskite ($CaTiO_3$) has a structure in which the oxide ions and the large cation (Ca^{2+}) form a *ccp* array with the smaller cation (Ti^{4+}) occupying those octahedral holes formed exclusively by oxide ions, as shown in Fig. 1-4. This structure is often slightly distorted—in $CaTiO_3$ itself, for example. It is adopted by a great many ABO_3 oxides in

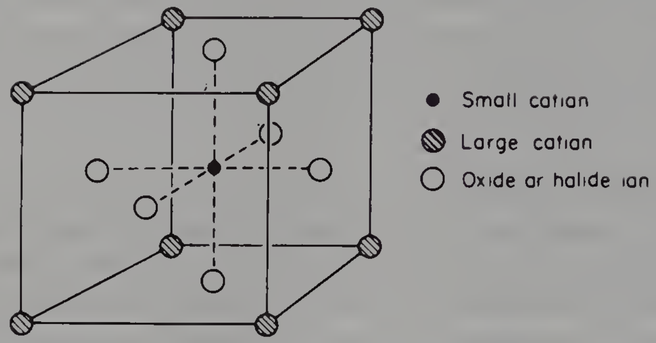


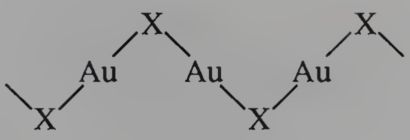
FIG. 1-4. The perovskite structure.

which one cation is comparable in size to O^{2-} and the other much smaller, with the cation charges variable so long as their sum is +6. It is found in $Sr^{II}Ti^{IV}O_3$, $Ba^{II}Ti^{IV}O_3$, $La^{III}Ga^{III}O_3$, and $Na^{I}Nb^{V}O_3$, and $K^{I}Nb^{V}O_3$, and also in some mixed fluorides (e.g., $KZnF_3$ and $KNiF_3$).

1-3. Coordination Numbers

The term coordination number normally refers to the number of anions (or ligands) that are nearest to a cation in an ionic solid, or a complex. For each coordination number, there are two or more geometrical arrangements. In this section we survey the important coordination numbers and geometries. We shall consider in detail coordination numbers 2 to 9, discussing under each the principal ligand arrangements. Higher coordination numbers will be discussed only briefly as they occur much less frequently.

Coordination Number 2. There are two geometric possibilities, linear and bent. If the two ligands are identical, the general types and their symmetries are linear, L—M—L, $D_{\infty h}$; bent, L—M—L, C_{2v}. This coordination number is, of course, found in numerous molecular compounds of divalent elements, but is relatively uncommon otherwise. In many cases where stoichiometry might imply its occurrence, a higher coordination number actually occurs because some ligands form "bridges" between two central atoms. In terms of the more conventional types of coordination compound—those with a rather metallic element at the center—it is restricted mainly to some complexes of Cu^{I}, Ag^{I}, Au^{I}, and Hg^{II}. Such complexes have linear arrangements of the metal ion and the two ligand atoms, and typical ones are $[ClCuCl]^-$, $[H_3NAgNH_3]^+$, and NCHgCN. The gold(I) halides present good examples of linear two coordination; they consist of zigzag chains of the type (1-I). The metal atoms in cations such as $[UO_2]^{2+}$, $[UO_2]^+$, and $[PuO_2]^{2+}$, which are linear, may also be said to have coordination number 2, but these oxo cations interact fairly strongly with additional ligands and their actual coordination numbers are much higher; it is true, however, that the central atoms



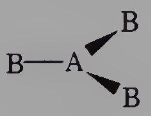
X = Cl, Br

(1-I)

have a specially strong affinity for the two oxygen atoms. Linear coordination also occurs in the several trihalide ions, such as I_3^- and $ClBrCl^-$.

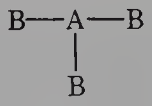
Coordination Number 3. The two most symmetrical arrangements are planar (1-IIa) and pyramidal (1-IIb), with D_{3h} and C_{3v} symmetry, respectively. Both these arrangements are found often among molecules formed by trivalent central elements. Among complexes of the metallic elements this is a rare coordination number; nearly all compounds or complexes of metal cations with stoichiometry MX_3 have structures in which sharing of ligands leads to a coordination number for M that exceeds three. There are, however, a few exceptions, such as the planar HgI_3^- ion that occurs in $[(CH_3)_3S^+][HgI_3^-]$, the MN_3 groups that occur in $Cr(NR_2)_3$ and $Fe(NR_2)_3$, where R = $(CH_3)_3Si$, and various gold(I) complexes, some of which are shown in Fig. 1-5, which are intermediate between two and three coordinate.

In a few cases (e.g., ClF_3 and BrF_3), a T-shaped form (1-III) of three coordination (symmetry C_{2v}) is found.



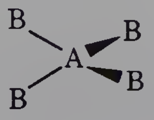
(1-IIa)

(1-IIb)

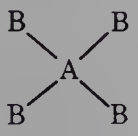


(1-III)

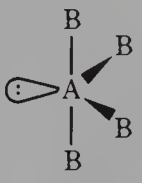
Coordination Number 4.[2] This is a highly important coordination number, occurring in hundreds of thousands of compounds, including, *inter alia,* most of those formed by the element carbon, essentially all those formed by silicon, germanium, and tin, and many compounds and complexes of other elements. There are three principal geometries. By far the most prevalent is tetrahedral geometry (1-IV), which has symmetry T_d when ideal. Tetrahedral complexes or molecules are almost the only kind of four-coordinate ones formed by non-



(1-IV)



(1-V)



(1-VI)

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[2] M. C. Favas and D. L. Kepert, *Prog. Inorg. Chem.*, 1980, **27**, 325.

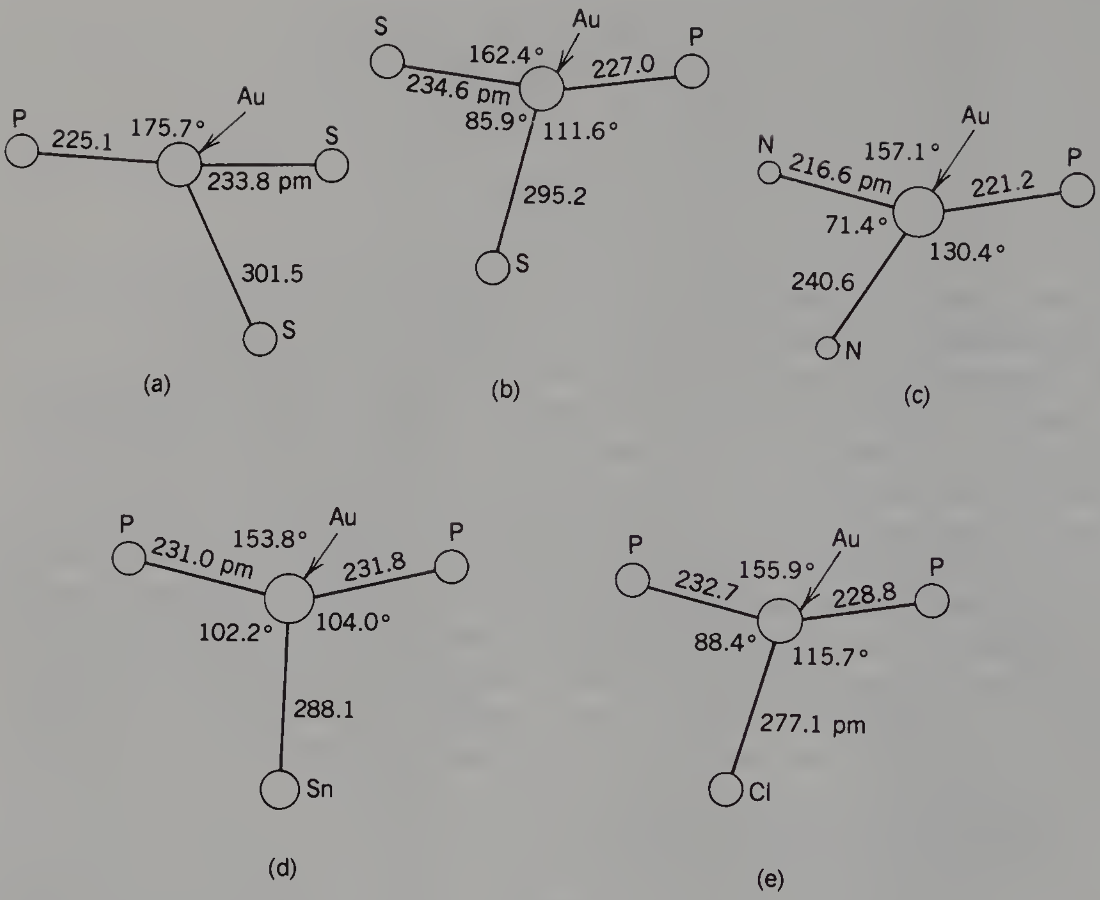
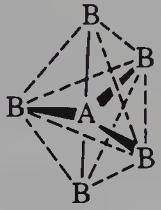


FIG. 1-5. Examples of irregular three coordination of Au^I. (a) $(Ph_3P)Au(S_2CNEt_2)$, best regarded as two coordinate; (b) $(Ph_3PAu)_2(C_4S_4)$ in which there are two identical Au environments per molecule; (c) $[(Ph_3P)Au(bipy)]^+$; (d) $(Me_2PhP)_2AuSnCl_3$; (e) $[CH_2(PPh_2)_2AuCl]_2$. [Reproduced by permission from P. G. Jones, *Gold Bull.*, 1981, **4**, 102.]

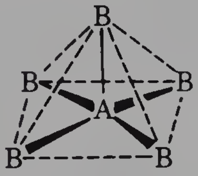
transition elements; whenever the central atom has no electrons in its valence shell orbitals except the four pairs forming the σ bonds to ligands, these bonds are disposed in a tetrahedral fashion. With many transition metal complexes, square geometry (1-V) occurs because of the presence of additional valence shell electrons and orbitals (i.e., partially filled *d* orbitals), although there are also many tetrahedral complexes formed by the transition metals. In some cases (e.g., with Ni^{II}, Co^{II}, and Cu^{II} in particular), there may be only a small difference in stability between the tetrahedral and the square arrangement and rapid interconversions may occur.

Square complexes are also found with nontransitional central atoms when there are two electron pairs present beyond the four used in bonding; these two pairs lie above and below the plane of the molecule. Examples are XeF_4 and $(ICl_3)_2$. Similarly, when there is one "extra" electron pair, as in SF_4, the irregular arrangement of symmetry C_{2v}(1-VI) is adopted.

Coordination Number 5. Though less common than numbers 4 and 6, coordination number 5 is still very important.[2,3] There are two principal geometries, and these may be conveniently designated by stating the polyhedra that are defined by the set of ligand atoms. In one case the ligand atoms lie at the vertices of a trigonal bipyramid (*tbp*) (1-VII), and in the other at the vertices of a square pyramid (*sp*) (1-VIII). The *tbp* belongs to the symmetry group D_{3h}; the *sp* belongs to the group C_{4v}. It is interesting and highly important that these two structures are similar enough to be interconverted without great difficulty. Moreover, a large fraction of the known five-coordinate complexes have structures that are intermediate between these two prototype structures. This ready deformability and interconvertibility gives rise to one of the most important types of stereochemical nonrigidity (cf. Section 29-12).



(1-VII)



(1-VIII)

On the whole the *tbp* seems to be somewhat more common than the *sp*, but there is no general predictive rule. For example the $[MCl_5]^{3-}$ ions (M = Cu, Cd, Hg) are *tbp*, but $[InCl_5]^{2-}$ and $[TlCl_5]^{2-}$ are *sp*, and there is one compound that contains both *tbp* and *sp* $[Ni(CN)_5]^{3-}$ ions in the same crystal.

Pentagonal planar coordination, as in $[Te(S_2COEt)_3]^-$ where two ligands are bidentate and one monodentate, is very unusual. It seems to be due to the presence of two stereochemically active lone pairs (see Section 1-5 for explanation).

Coordination Number 6. This is perhaps the most common coordination number, and the six ligands almost invariably lie at the vertices of an octahedron or a distorted octahedron. The very high symmetry, group O_h, of the regular octahedron, is discussed in detail in Appendix 5.

There are three principal forms of distortion of the octahedron. One is *tetragonal,* elongation or contraction along a single C_4 axis; the resultant symmetry is only D_{4h}. Another is *rhombic,* changes in the lengths of two of the C_4 axes so that no two are equal; the symmetry is then only D_{2h}. The third is a *trigonal* distortion, elongation or contraction along one of the C_3 axes so that the symmetry is reduced to D_{3d}. These three distortions are illustrated in Fig. 1-6.

The tetragonal distortion most commonly involves an elongation of one C_4 axis and, in the limit, two trans ligands are lost completely, leaving a

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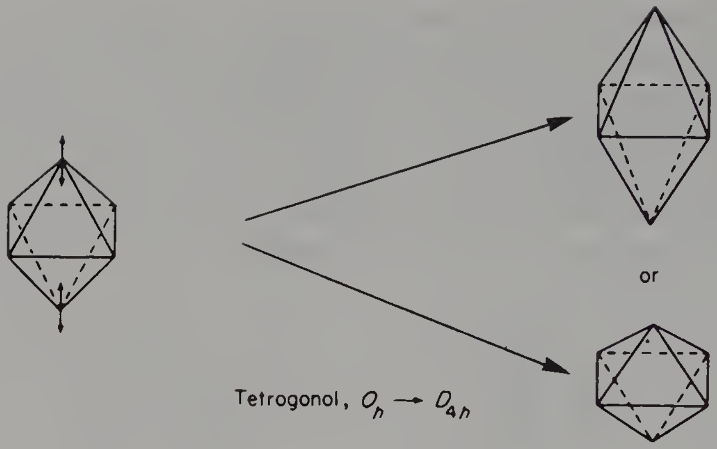
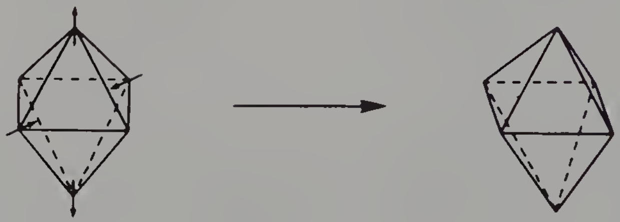
[3] R. R. Holmes, *Prog. Inorg. Chem.*, 1984, **32**, 119.



Tetragonal, $O_h \rightarrow D_{4h}$



Rhombic, $O_h \rightarrow D_{2h}$

Trigonal, $O_h \rightarrow D_{3d}$

FIG. 1-6. The three principal types of distortion found in real octahedral complexes.

square, four-coordinate complex. The trigonal distortion transforms the octahedron into a trigonal antiprism.

Another type of six-coordinate geometry, much rarer but nonetheless important, is that in which the ligands lie at the vertices of a trigonal prism; the ideal symmetry is D_{3h}. This arrangement has never been observed in a discrete ML_6 complex but only in complexes with chelating ligands and in a few metal sulfides, namely, MoS_2 and WS_2, where it was first seen many years ago, and more recently in MM'_3S_6 (M = Mn, Fe, Co, Ni; M' = Nb, Ta). The chelate complexes that best exemplify this type of coordination contain the 1,2-dithiolene or 1,2-diselenolene type ligands, RC(S)—C(S)R, RC(Se)—C(Se)R.

Structures lying between the extremes of trigonal prismatic and antiprismatic are sometimes found. As shown in Fig. 1-7, we may define the range of structures according to a twist angle ϕ, which is 0° for the prism and 60° for the antiprism. Ligands such as the dithiolenes (1-IX) and the tropolonato anion (1-X), which are somewhat inflexible and have too short a "bite" (the distance between the two atoms bonded to the metal atom) to reach across

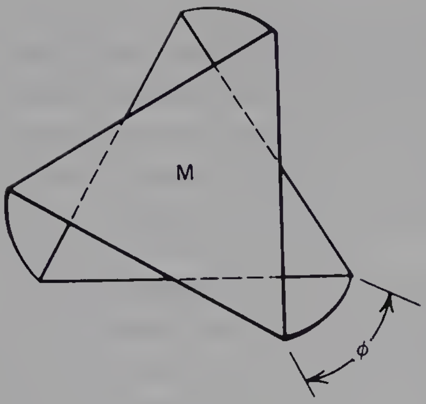
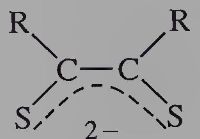
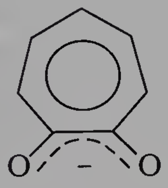


FIG. 1-7. A six-coordinate structure intermediate between the trigonal prism and antiprism projected down the threefold axis. The twist angle ϕ is measured in the plane of projection.

the distance between vertices of an octahedron, sometimes dictate a ϕ angle of $< 60°$.



(1-IX)



(1-X)

Coordination Number 7.[4] There are three important geometric arrangements, as shown in Fig. 1-8. Both experimental data and theory indicate that, except where a bias might arise from the requirements of a particular polydentate ligand, these three structures are of similar stability. Moreover, interconversions are not likely to be seriously hindered, so that seven-coordinate complexes should be prone to stereochemical nonrigidity, as is often observed.

Coordination Number 8.[5] There are three especially important idealized structures: the cube (O_h), the square antiprism (D_{4d}), and the triangulated

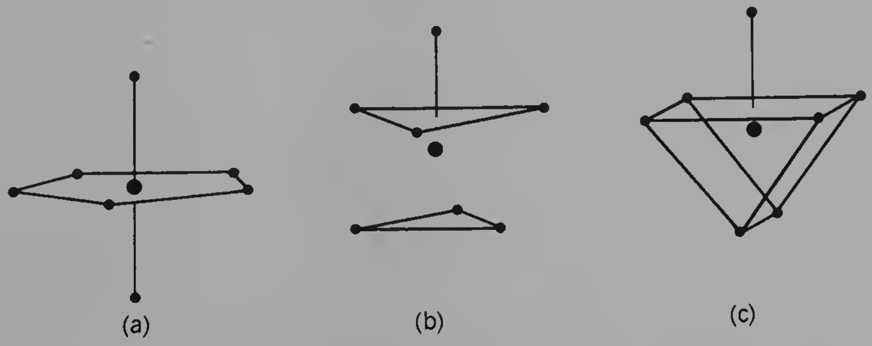


FIG. 1-8. The three important geometries for seven coordination. (a) Pentagonal bipyramid (D_{5h}); (b) Capped octahedron (C_{3v}); (c) Capped trigonal prism (C_{2v}).

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[4] D. L. Kepert, *Prog. Inorg. Chem.*, 1979, **25,** 41.

[5] D. L. Kepert, *Prog. Inorg. Chem.*, 1978, **24,** 179; J. K. Burdett *et al., Inorg. Chem.*, 1978, **17,** 2553.

dodecahedron (D_{2d}). All three are depicted in Fig. 1-9, which also shows how each of the latter two can be obtained by distortions of the cube. The cube occurs very infrequently in discrete complexes, although it is found in various solid arrays (e.g., the CsCl structure). Since each of the other two structures, which can be so easily obtained from it, allow the same close metal–ligand contacts while alleviating the ligand–ligand repulsions, their energetic superiority over the cube is understandable.

The dodecahedron can be viewed as a pair of interpenetrating tetrahedra: a flattened one defined by the B vertices and an elongated one defined by the A vertices. There are also several nonequivalent sets of edges, such as those marked *m* in Fig. 1-9. The *m* edges are generally those spanned when there are four bidentate ligands with a short bite.

Detailed analysis of the energetics of M—X and X—X interactions suggests that there will in general be little difference between the energies of the square antiprism and the dodecahedral arrangement, unless other factors, such as the existence of chelate rings, energies of partially filled inner shells, exceptional opportunities for orbital hydridization, or the like, come into play. Both arrangements occur quite commonly, and in some cases [e.g., the $M(CN)_8^{n-}$ (M = Mo or W; n = 3 or 4) ions] the geometry varies from one kind to the other with changes in the counterion in crystalline salts, on changing from crystalline to solution phases, and on changing the oxidation state of the metal atom [e.g., $TaCl_4(dmpe)_2$ is square antiprismatic while $TaCl_4(dmpe)_2^+$ is dodecahedral].[6a]

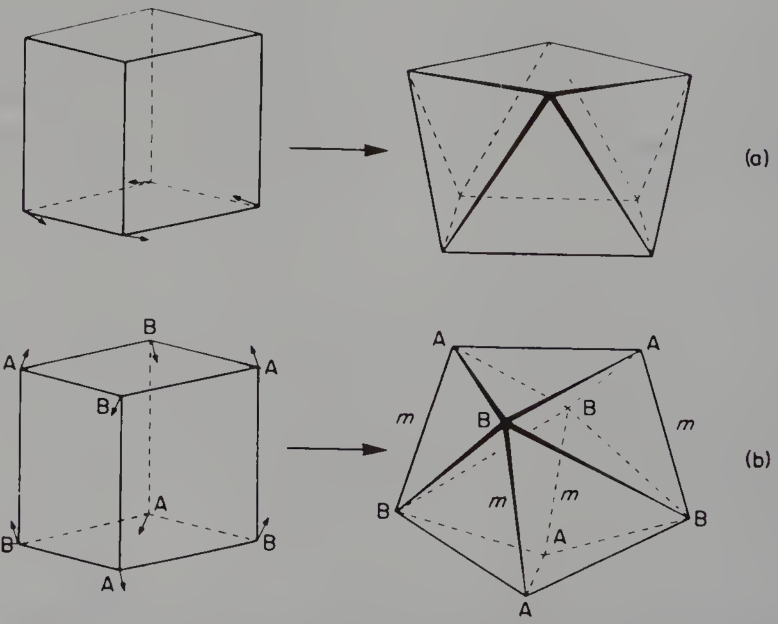
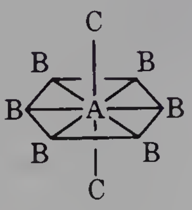


FIG. 1-9. The two most important ways of distorting the cube: (a) to produce a square antiprism; (b) to produce a dodecahedron.

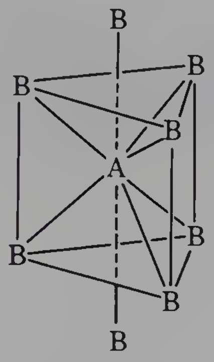
[6a] F. A. Cotton *et al., Inorg. Chem.*, 1983, **22**, 770.

A form of eight coordination, which is a variant of the dodecahedral arrangement, is found in several compounds containing bidentate ligands in which the two coordinated atoms are very close together (ligands said to have a small "bite"), such as NO_3^- and O_2^{2-}. In these, the close pairs of ligand atoms lie on the *m* edges of the dodecahedron (see Fig. 1-9*b*); these edges are then very short. Examples of this are the $Cr(O_2)_4^{3-}$ and $Co(NO_3)_4^{2-}$ ions and the $Ti(NO_3)_4$ molecule.

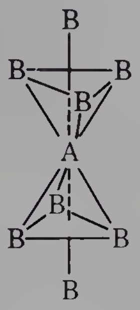
Three other forms of octacoordination, which occur much less often and are essentially restricted to actinide and lanthanide compounds, are the hexagonal bipyramid (D_{6h}) (1-XI), the bicapped trigonal prism (D_{3h}) (1-XII) and the bicapped trigonal antiprism (D_{3d}) (1-XIII). The hexagonal bipyramid is restricted almost entirely to the oxo ions, where an OMO group defines the axis of the bipyramid, though it is occasionally found elsewhere.



(1-XI)



(1-XII)



(1-XIII)

Although feasible, there is only one case of isolated geometric isomers. These are cis- and trans-$SmI_2[O(CH_2CH_2OMe]_2]_2$ where the cis has distorted dodecahedral and the trans, bicapped trigonal antiprismatic geometry.[6b]

Higher Coordination Numbers.[7] Of these, only nine displays appreciable regularity of form. The tricapped trigonal prism, shown in Fig. 1-10, is rather common, being found, for example, in the $[M(H_2O)_9]^{3+}$ ions of the lanthanides and $[ReH_9]^{2-}$. Another idealized structure, which is rarer, is that of a square antiprism capped on one rectangular face. Even higher coordination numbers, 10 to 12, are sometimes found for the largest metal ions. In general, these do not conform to any regular geometry, although for 10 coordination a bicapped square antiprism is sometimes found, for example, in $K_4[Th(O_2CCO_2)_4(H_2O)_2] \cdot 2H_2O$. A distorted icosahedral arrangement for 12 coordination is found in $[Ce(NO_3)_6]^{2-}$ and $[Pr(naph)_6]^{3+}$, where naph is 1,8-naphthyridine. The small bite of these bidentate ligands makes possible the high coordination number.

[6b] A. Sen *et al., Inorg. Chem.*, 1987, **26**, 1821.

[7] M. C. Favas and D. L. Kepert, *Prog. Inorg. Chem.*, 1981, **28**, 309.

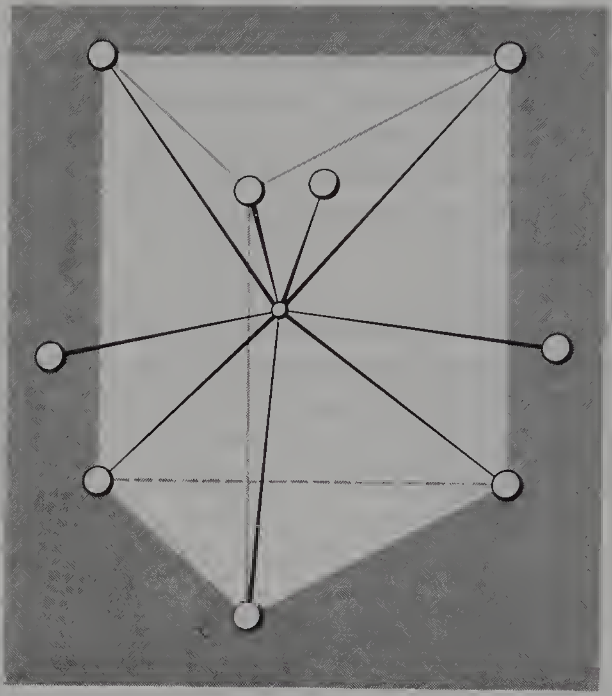


FIG. 1-10. The structure of many nine-coordinate complexes.

1-4. Cage and Cluster Structures

The formation of polyhedral cages and clusters is now recognized as an important and widespread phenomenon, and examples may be found in nearly all parts of the Periodic Table. This section mentions each of the principal polyhedra and gives illustrations. Further details may be found under the chemistry of the particular elements and especially in Chapter 23.

A cage or cluster is in a certain sense the antithesis of a complex; yet there are many similarities due to common symmetry properties. In each type of structure a set of atoms defines the vertices of a polyhedron, but in the one case—the complex—these atoms are each bound to one central atom and not to each other, whereas in the other—the cage or cluster—there is no central atom and the essential feature is a system of bonds connecting each atom directly to its neighbors in the polyhedron.

There are, however, some examples of clusters that also have a central atom, sometimes C or N and sometimes a metal atom. Examples of the former are discussed in Section 23-5, while examples of the latter are presented in Sections 23-8 and 19-I-8.

To a considerable extent the polyhedra found in cages and clusters are the same as those adopted by coordination compounds (e.g., the tetrahedron, trigonal bipyramid, and octahedron), but there are also others (see especially the polyhedra with six vertices), and cages with more than six vertices are far more common than coordination numbers > 6. It should be noted that triangular clusters, as in $[Re_3Cl_{12}]^{3-}$ or $Os_3(CO)_{12}$, though not literally polyhedra, are not essentially different from polyhedral species such as $Mo_6Cl_8^{4+}$ or $Ir_4(CO)_{12}$, respectively.

Just as all ligand atoms in a set need not be identical, so the atoms making up a cage or cluster may be different; indeed, to exclude species made up of more than one type of atom would be to exclude the majority of cages and clusters, including some of the most interesting and important ones.

Four Vertices. Tetrahedral cages or clusters have long been known for the P_4, As_4, and Sb_4 molecules and in more recent years have been found in polynuclear metal carbonyls such as $Co_4(CO)_{12}$, $Ir_4(CO)_{12}$, $[\eta^5\text{-}C_5H_5Fe(CO)]_4$, $RSiCo_3(CO)_9$, $Fe_4(CO)_{13}^{2-}$, $Re_4(CO)_{12}H_4$, and a number of others; B_4Cl_4 is another well-known example and doubtless many more will be encountered.

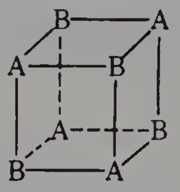
Five Vertices. Polyhedra with five vertices are the trigonal bipyramid (*tbp*) and the square pyramid (*sp*). Both are found among the boranes and carboranes (e.g., the *tbp* in $B_3C_2H_5$ and the *sp* in B_5H_9), as well as among the transition elements. Examples of the latter are $Os_5(CO)_{16}$ (*tbp*) and $Fe_3S_2(CO)_9$ (*sp*).

Six Vertices. Octahedral cages and clusters are numerous, especially among the transition metals. Examples are $Rh_6(CO)_{16}$ and $[Co_6(CO)_{14}]^{4-}$, as well as the metal halide type clusters, M_6X_8 and M_6X_{12}, for M = Nb, Ta, Mo, W, and Re. The $B_6H_6{}^{2-}$ and $B_4C_2H_6$ species are also octahedral, although B_6H_{10} is a pentagonal pyramid. Less regular geometries are also known such as the bicapped tetrahedron in $Os_6(CO)_{18}$ and capped square pyramid in $H_2Os_6(CO)_{18}$.

Seven Vertices. Such polyhedra are relatively rare. The isoelectronic $B_7H_7^{2-}$ and $B_5C_2H_7$ species have pentagonal bipyramidal (D_{5h}) structures. The $Os_7(CO)_{21}$ molecule has a capped octahedron of Os atoms with three CO groups on each Os.

Eight Vertices. Eight-atom polyhedral structures are very numerous. By far the most common polyhedron is the *cube;* this is in direct contrast to the situation with eightfold coordination, where a cubic arrangement of ligands is extremely rare because it is disfavored relative to the square antiprism and the triangulated dodecahedron in which ligand–ligand contacts are reduced. In the case of a cage compound, of course, it is the structure in which contacts between atoms are maximized that will tend to be favored (provided good bond angles can be maintained), since bonding rather than repulsive interactions exist between neighboring atoms.

The only known cases with eight *like* atoms in a cubic array are the hydrocarbon *cubane* (C_8H_8) and a few metal atom cluster species such as $Cu_8(i\text{-MNT})_6^{4-}$ ion [i-MNT = $S_2CC(CN)_2^{2-}$]. The other cubic systems all involve two different species of atom that alternate as shown in (1-XIV). In all cases either the A atoms or the B atoms or both have appended atoms or groups. The following list collects some of the many cube species, the elements at the alternate vertices of the cube being given in bold type.



(1-XIV)

A (and appended groups)	**B** (and appended groups)
Mn(CO)$_3$	SEt
Os(CO)$_3$	**O**
PtMe$_3$ or **Pt**Et$_3$	**Cl, Br, I, O**H
CH$_3$**Zn**	**O**CH$_3$
Tl	**O**CH$_3$
η^5-C$_5$H$_5$**Fe**	**S**
Me$_3$As**Cu**	**I**
Ph**Al**	**N**Ph
Co(CO)$_3$	**Sb**
FeSR	**S**
Mo(H$_2$O)$_3$	**S**

Although the polyhedron in cubane, or in a similar molecule, may have the full O_h symmetry of a cube, the A_4B_4-type structures can have at best tetrahedral, T_d, symmetry since they consist of two interpenetrating tetrahedra.

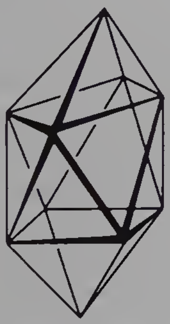
It must also be noted that only when the two interpenetrating tetrahedra happen to be exactly the same size will all the ABA and BAB angles be equal to 90°. Since the A and the B atoms differ, it is not in general to be expected that this will occur. In fact, there is, in principle, a whole range of bonding possibilities. At one extreme, represented by $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}]_4$, the members of one set of atoms (the Fe atoms) are so close together that they must be considered to be directly bonded, whereas the other set (the C atoms of the CO groups) are not at all bonded among themselves but only to those in the first set. In this extreme, it seems best to classify the system as having a tetrahedral cluster (of Fe atoms) supplemented by bridging CO groups.

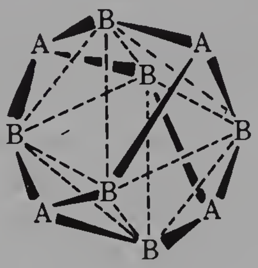
At the other extreme are the A_4B_4 systems in which all A—A and B—B distances are too long to admit of significant A—A or B—B bonding; thus the system can be regarded as genuinely cubic (even if the angles differ somewhat from 90°). This is true of most of the systems listed previously. The atoms, however, in the smaller of the two tetrahedra tend to have some amount of direct interaction with one another, thus blurring the line of demarcation between the *cluster* and *cage* types.

A relatively few species are known in which the polyhedron is, at least approximately, a triangulated dodecahedron (Fig. 1-9b). These are the boron species $B_8H_8^{2-}$, $B_6C_2H_8$, and B_8Cl_8.

Nine Vertices. Cages with nine vertices are rare. Representative ones are Bi_9^{5+} (in $Bi_{24}Cl_{26}$), $B_9H_9^{2-}$, and $B_7C_2H_9$, all of which have the tricapped trigonal prism structure (Fig. 1-10), and Sn_9^{4-}, which is a square antiprism capped on one square face.

Ten Vertices. Species with 10 vertices are well known. In $B_{10}H_{10}^{2-}$ and $B_8C_2H_{10}$ the polyhedron (1-XV) is a square antiprism capped on the square faces (symmetry D_{4d}). But there is a far commoner structure for 10-atom cages that is commonly called the *adamantane* structure after the hydrocarbon adamantane ($C_{10}H_{16}$), which has this structure; it is depicted in 1-XVI and consists of two subsets of atoms: a set of four (A) that lie at the vertices of a tetrahedron and a set of six (B) that lie at the vertices of an octahedron. The entire assemblage has the T_d symmetry of the tetrahedron. From other points of view it may be regarded as a tetrahedron with a bridging atom over each edge or as an octahedron with a triply bridging atom over an alternating set of four of the eight triangular faces.


(1-XV)

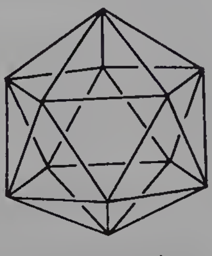


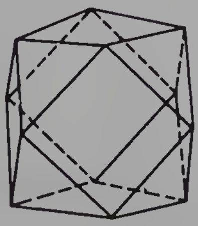
(1-XVI)

The adamantane structure is found in dozens of A_4B_6-type cage compounds formed mainly by the main group elements. The oldest recognized examples of this structure are probably the phosphorus(III) and phosphorus(V) oxides, in which we have P_4O_6 and $(OP)_4O_6$, respectively. Other representative examples include $P_4(NCH_3)_6$, $(OP)_4(NCH_3)_6$, $As_4(NCH_3)_6$, and $(MeSi)_4S_6$.

Eleven Vertices. Perhaps the only known eleven-atom cages are $B_{11}H_{11}^{2-}$ and $B_9C_2H_{11}$.

Twelve Vertices. Twelve-atom cages are not widespread but play a dominant role in boron chemistry. The most highly symmetrical arrangement is the icosahedron (1-XVII), which has 12 equivalent vertices and I_h symmetry. Icosahedra of boron atoms occur in all forms of elemental boron, in $B_{12}H_{12}^{2-}$, and in the numerous carboranes of the $B_{10}C_2H_{12}$ type. A related polyhedron, the cuboctahedron (1-XVIII) is found in several borides of stoichiometry MB_{12}.


(1-XVII)


(1-XVIII)

1-5. The Valence Shell Electron Pair Repulsion (VSEPR) Model[8]

In the VSEPR model the arrangement of bonds around a central atom is considered to depend on how many valence shell electron pairs, each occupying a localized one- or two-center orbital, are present, and on the relative sizes and shapes of these orbitals. The first rule is as follows:

Rule 1. *The pairs of electrons in a valence shell adopt that arrangement which maximizes their distance apart; that is, the electron pairs behave as if they repel each other.*[9]

Each electron pair is assumed to occupy a reasonably well-defined region of space, and other electrons are effectively excluded from this space. For electron pairs in the same valence shell, the arrangements that maximize their distance apart are listed in Table 1-1.

To apply rule 1 for the qualitative prediction of molecular shapes where only single bonds and unshared pairs are concerned, we compute the total number of electron pairs, bonding and nonbonding, select the appropriate arrangement in Table 1-1, and assign the electron pairs to it. In the cases of two, three, or four pairs, the results are immediately obvious as shown in Fig. 1-11. For example, an AB_4 molecule must be tetrahedral, an AB_3E molecule (E represents an unshared pair) must be pyramidal, and an AB_2E_2 molecule must be bent. There are no known exceptions to these predictions. Table 1-2 lists a few molecules and ions of the types AB_2E_2 and AB_3E, giving the angles.

Molecules with five electron pairs usually have trigonal bipyramidal structures, as predicted, but when some of these electron pairs are lone pairs (LP's) rather than bonding pairs (BP's), unambiguous prediction requires another rule.

TABLE 1-1
Predicted Arrangements of Electron Pairs in One Valence Shell

Number of pairs	Polyhedron defined
2	Linear
3	Equilateral triangle
4	Tetrahedron
5	Trigonal bipyramid
6	Octahedron
7	Monocapped octahedron
8	Square antiprism
9	Tricapped trigonal prism

[8] A. G. McKenna and J. F. McKenna, *J. Chem. Educ.*, 1984, **61**, 771; H. O. Desseyn *et al.*, *J. Chem. Educ.*, 1983, **60**, 220.

[9] L. S. Bartell and Y. Z. Barshad, *J. Am. Chem. Soc.*, 1984, **106**, 7700.

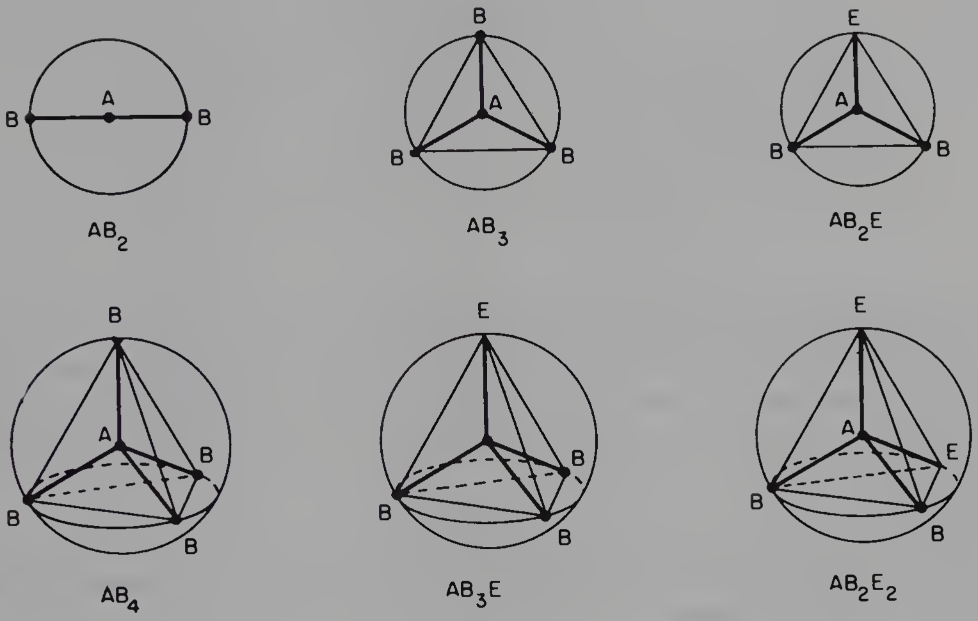


FIG. 1-11. Prediction of the shapes of molecules when the valence shell of the central atom contains two, three, or four electron pairs.

Rule 2. *A nonbonding pair occupies more space on the "surface" of the central atom than a bonding pair.*

This may also be expressed symbolically by writing LP-LP > LP-BP > BP-BP, meaning that the pair–pair repulsive forces decrease in that order. This is an understandable rule in the sense that the bonding pairs are drawn away from the surface of A by the other atom, B, and thus occupy a smaller solid angle.

With this rule we can deal with the AB_4E, AB_3E_2, and AB_2E_3 cases. Typical examples are shown in Fig. 1-12. The larger size of the LP's means that they rather than the BP's occupy the equatorial positions, because they are less crowded there. A secondary effect seen in these cases, as well as in the data of Table 1-2, is that B—A—B angles are always less than the ideal (i.e., 109.5, 120, 90°) ones because the LP-BP angles are prone to be larger.

For species with six pairs of valence shell electrons on the central atom

TABLE 1-2

Angles (deg) in Some AB_2E_2 and AB_3E Molecules

AB_2E_2		AB_3E					
Molecule	Angle	Molecule	Angle	Molecule	Angle	Molecule	Angle
H_2O	104.5	NH_3	107.3	NF_3	102.1		
H_2S	92.2	PH_3	93.3	PF_3	97.8	PCl_3	100.3
H_2Se	91	AsH_3	91.8	AsF_3	96.2	$AsCl_3$	98.7
H_2Te	89.5	SbH_3	91.3	SbF_3	88	$SbCl_3$	99.5
OF_2	103.2						
OCl_2	111						

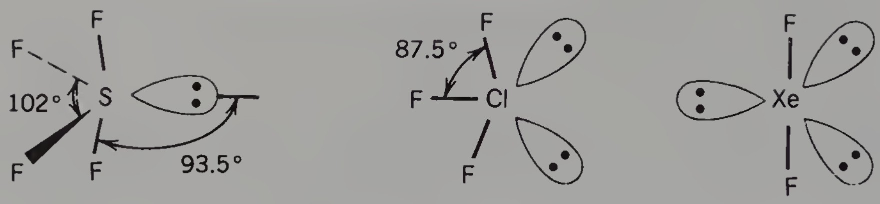


FIG. 1-12. Three molecules representing the AB_4E, AB_3E_2, and AB_2E_3 types.

the structures of AB_5E and AB_4E_2 type molecules can also be explained by invoking rule 2. In the AB_5E type the four equatorial B atoms make angles of <90° to the axial B atom and in AB_4E_2 type molecules the LP's occupy trans octahedral positions so that the molecule is square. Examples are shown in Fig. 1-13.

Two more rules[10] are sometimes used within the VSEPR model:

Rule 3. *The size of a bonding electron pair decreases with increasing electronegativity of the ligand.*

Rule 4. *The two electron pairs of a double bond (or the three electron pairs of a triple bond) take up more room than does the one electron pair of a single bond.*

Using rule 3 one can rationalize some of the trends in Table 1-2. For instance, the angles in NF_3 and F_2O are less than those in NH_3 and H_2O. Similarly, in a set of halo molecules AB_2E_2 or AB_3E, the BAB angles increase in the order F < Cl < Br ≈ I. There are, however, often exceptions when hydrides are considered, since the PH_3, AsH_3, and SH_2 angles are less than those in any trihalide of the same element.

Rule 4 accounts for the fact that angles in which multiple bonds are involved are generally larger than those involving only single bonds. A few representative examples are shown in Table 1-3. It should be noted that when the

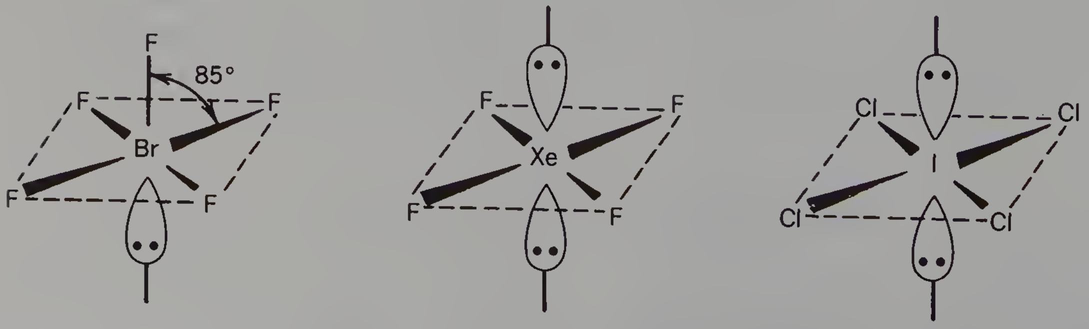


FIG. 1-13. Three examples of molecules or ions with six pairs of valence shell electrons.

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[10] Still other refinements have been proposed. Compare: K. O. Christe and H. Oberhammer, *Inorg. Chem.*, 1981, **20,** 296; I. Hargittai, *Inorg. Chem.*, 1982, **21,** 4334; J. L. Bills and S. P. Steed, *Inorg. Chem.*, 1983, **22,** 2401.

TABLE 1-3
Bond Angles in Some Molecules Containing a Double Bond

	Angles (°)		
Molecule	XCX	XCO	XCC
F_2CO	108	126	
Cl_2CO	111	124	
$(NH_2)_2CO$	118	121	
F_2SO	93	107	
Br_2SO	96	108	
$H_2C{=}CF_2$	110		125
$H_2C{=}CCl_2$	114		123
OPF_3	103		
$OPCl_3$	104		

double bond is to an atom less electronegative than those to which the single bonds are directed, the operation of rule 3 reinforces the effect of rule 4.

Predictions concerning relative lengths of bonds are also possible by using these rules. Thus for AB_5, AB_4E, AB_3E_2, and AB_5E molecules the nonequivalent bonds differ in length by about 0.1 Å. In the first three cases, in which there is a trigonal bipyramidal distribution of electron pairs, the axial bonds are longer. In AB_5E it is the four basal bonds that are longer. In the cases of five electron pairs with a *tbp* arrangement, the axial pairs have three neighboring pairs on lines at only 90° away, while the equatorial ones have only two such closely neighboring pairs; equilibrium is thus attained when the axial pairs move to a somewhat greater distance from the central atom, lengthening the axial bonds relative to the equatorial ones. In the case of AB_5E, the greater size of the lone pair will act more strongly on the bonding pairs cis to it, thus lengthening the set of basal bonds.

Shortcomings of the VSEPR Model. It is not surprising that such a simple model is not entirely adequate. In order that it not be misused, a few of its recognized shortcomings need to be stated.

1. In *very polar situations* an ionic picture is more accurate. Thus, Li_2O is linear not bent, as the AB_2E_2 classification would suggest. Two $+1$ ions riding on a spherical -2 ion would be expected to seek antipodal positions.

2. In the *alkaline earth, GroupIIA(2), dihalides,* the structures vary in a manner that neither the VSEPR nor any other simple model can completely account for. The facts are summarized in Table 1-4. The VSEPR model (as well as a purely ionic one) would predict linear structures throughout, as would a covalent model with *sp* hybrid orbitals. Use of pure *p* orbitals (or much *p* character in the hybrids) on the metal atom would predict bent molecules, but this is a purely *ad hoc* idea.

The pattern of deviations from linearity suggests that either, or both, of two factors need to be invoked. If a basically ionic model is used, polarization of the central cation by the anions must be considered. Such polarization, which might account for bending, would be greatest with the largest cations

TABLE 1-4
Structures of Group IIA(2) Halide Molecules[a]

	F	Cl	Br	I
Be	l	l	l	l
Mg	?(~160°?)	l	l	l
Ca	b(~140°)	l	l	l
Sr	b(~108°)	b(~120°)	l	l
Ba	b(~100°)	b(~100°)	b	b

[a] l = linear; b = bent, with estimated angle, where available, in parentheses.

and the smallest anions, which is consistent with the observed pattern of bending. Alternatively, it has been suggested that increasing participation of metal *d* orbitals as the metal atoms increase in atomic number could be added to a covalent picture of the bonding. It is by no means obvious, however, that this would need to occur in such a way as to cause bending.

3. There are molecules with *"inert" lone pairs.* There are a number of cases among compounds of the heavier main group elements (In^I, Tl^I, Sn^{II}, Pb^{II}, Sb^{III}, Bi^{III}, Te^{IV}, and Po^{IV}) where one pair of valence shell electrons appears to be strongly confined to the valence shell *s* orbital, where it is spherically distributed and plays no role in determining the arrangement of the ligand atoms. Thus, we have species such as $SeBr_6^{2-}$, $TeBr_6^{2-}$, $SbCl_6^{3-}$, and $BiCl_6^{3-}$, which have regular octahedral structures, although they are formally AB_6E cases. The molecule XeF_6 is a borderline case. The molecule does not have a regular octahedral structure but it is very flexible and has a near-zero force constant for changes in the F—Xe—F bond angles. In the solid state it forms complex polymeric species.

The stability of the oxidation states In^I and Tl^I is similarly attributed to the tendency of a ns^2 valence shell configuration to be stable. In some Sn^{II} compounds, for example, $SnCl_3^-$, the lone pair is stereochemically active, but sometimes, for example, in $SnCl_6^{2-}$, it is not.

4. In cases where *strong π bonding* may occur, this can neutralize the effect of a lone pair, as in the planar AB_3E species $C(CN)_3^-$. It is also notable that in amines generally, the energy difference between pyramidal and planar conformations is not great and in some cases, for example, $N(SiH_3)_3$, the preferred conformation is planar, perhaps because of π interactions (but see Section 1-8).

5. The VSEPR model fails completely to explain the gauche conformation of N_2H_4 and is ambiguous about H_2O_2. Clearly, if LP-LP repulsions are strongest, N_2H_4 should have an anti conformation, but in fact it has a gauche one.

1-6. Other Bonding Models: Hybridization and Three-Center Bonds

According to the hybridization model, bond directions are determined by a set of hybrid orbitals on the central atom which are used to form bonds to the ligand atoms and to hold unshared pairs. Thus AB_2 molecules are linear owing to the use of linear *sp* hybrid orbitals. AB_3 and AB_2E molecules should be equilateral triangular and angular, respectively, owing to use of trigonal sp^2 hybrids. AB_4, AB_3E, and AB_2E_2 molecules should be tetrahedral, pyramidal, and angular, respectively, because sp^3 hybrid orbitals are used. These cases are, of course, very familiar and involve no more than an octet of electrons.

For the AB_5, AB_4E, AB_3E_2, and AB_2E_3 molecules, the hybrids must now include *d* orbitals in their formation. The hybrid orbitals used must obviously be of the sp^3d type, but an ambiguity arises because there are two such sets, namely, $sp^3d_{z^2}$ leading to *tbp* geometry and $sp^3d_{x^2-y^2}$ leading to *sp* geometry. There is no way to predict with certainty which set is preferred, and doubtless the difference between them cannot be great. Since we know experimentally that AB_5 molecules nearly all have *tbp* structures, the same arrangement is assumed for the AB_4E cases, and so on. Even this *ad hoc* assumption does not solve all difficulties, since the position preferred by lone pairs must be decided and there is no simple physical model here (as there was in the VSEPR approach) to guide us. A preference by lone pairs for equatorial positions has to be assumed. With these assumptions, a consistent correlation of all the structures in this five-electron-pair class is possible.

For AB_6 molecules octahedral sp^3d^2 hybrids are used. AB_5E molecules must, naturally, be *sp*. For AB_4E_2 molecules there is nothing in the directed valence theory itself to show whether the lone pairs should be cis or trans. The assumption that they must be trans leads to consistent results.

The most fundamental problem with the hybridization model is that in all cases in which there are more than four electron pairs in the valence shell of the central atom it is necessary to postulate that at least one *d* orbital becomes fully involved in the bonding. There are both experimental and theoretical reasons for believing that this is too drastic an assumption. Some recent MO calculations and other theoretical considerations suggest that although the valence shell *d* orbitals make a significant contribution to the bonding in many cases, they never play as full a part as do the valence shell *p* orbitals. Fairly direct experimental evidence in the form of nuclear quadrupole resonance studies of the ICl_2^- and ICl_4^- ions shows that in these species, *d*-orbital participation is very small; this participation is probably greater in species with more electronegative ligand atoms, such as PF_5, SF_6, and $Te(OH)_6$, but not of equal importance with the contributions of the *s* and *p* orbitals.

Perhaps it is surprising that by going to the opposite extreme, namely, by omitting *all* consideration of *d* orbitals, but still adhering to the concept of directed orbitals, it is again possible to rationalize many of the principal features of the structures of main group compounds. This so-called three-center bond model is predicated on two main ideas: (1) that the use of outer *d* orbitals of the central atom is so slight that they may be neglected altogether, and (2) that the persistent recurrence of bond angles close to 90° and 180° in AB_n molecules suggests that orbitals perpendicular to one another, namely, *p* orbitals, are being used.

Two types of chemical bond are considered. First there is the ordinary two-center, two-electron (2*c*-2*e*) bond, formed by the overlap of a *p* orbital of the central atom with a σ orbital of an outer atom. Second, there is the linear three-center, four-electron (3*c*-4*e*) bond formed from a *p* orbital of the central atom and the σ orbitals of two outer atoms. In the 3*c*-4*e* bond only one pair of electrons occupies a bonding orbital while the other is in a non-bonding orbital. In a 3*c*-2*e* situation (not relevant here but important elsewhere, as in boron hydrides and bridged alkyls) only the bonding pair is present.

For molecules with an octet, or less, of electrons in the valence shell of the central atom, the hybridization theory, employing sp, sp^2, and sp^3 orbitals remains valid. This model was proposed for molecules in which five or more electron pairs on the central atom must be accounted for. Since it is, as we shall note later, undoubtedly too great a simplification, it will be applied only to a few illustrative cases. It is worth mentioning, however, since it has a certain heuristic value.

In molecules of the AB_4E type, the central atom is considered to use p_x and p_y orbitals to bind the four basal B atoms in 3*c*-4*e* bonds, while the axial B atom is bound through a regular 2*c*-2*e* bond employing the p_z orbital of A. The remaining electron pair is postulated to occupy a pure *s* orbital. In a similar way, an AB_3E_2 molecule is formulated as treating the two approximately "axial" A—B bonds as 3*c*-4*e* bonds formed by a single *p* orbital of atom A, the "equatorial" A—B bond formed as a normal 2*c*-2*e* bond using one of the other two *p* orbitals, while the lone pairs occupy the remaining *p* orbital and a stereochemically inert *s* orbital. This model is in good accord (qualitatively) with the difference in the types of A—B bond lengths in such molecules, since it assigns 2*c*-2*e* character to the shorter ones and 3*c*-4*e* character to the longer ones. It also explains straightforwardly the octahedral structures of such species as $SeCl_6^{2-}$.

The basic objection to the three-center bond model is that the *complete* omission of *s* and *d* character from all bonding orbitals is too much of a "ruthless approximation." It is moderately successful because the *ns* orbital is, in many cases, so much more stable than the *np* orbitals that it plays only a slight role and because outer *d* orbitals are seldom more than partly involved in bond formation. This model however, has only qualitative value. For example, in dealing with SF_4, it would imply that two of the S—F bonds are of the 2*c*-2*e* type and the other two are of the 3*c*-4*e* type. This corresponds to bond orders of 1.0 and 0.5; yet the bond lengths differ by only about 0.1 Å, albeit in the implied sense. Clearly, with such a small difference in bond lengths the bond orders cannot differ as greatly as this model would require.

1-7. MO Correlation (Walsh) Diagrams

Correlation diagrams were first applied to relatively simple cases many years ago by Walsh; the approach led to certain generalizations, called Walsh's rules, relating the shapes of triatomic molecules to their electronic structures.

The basic approach is to calculate, or estimate, the energies of molecular orbitals for two limiting structures, say, linear and bent (to 90°) for an AB_2 molecule, and draw a diagram showing how the orbitals of one configuration correlate with those of the other. Then, depending on which orbitals are occupied, one or the other structure can be seen to be preferred. By means of approximate MO theory, implemented by digital computers, this approach has been extended and generalized in recent years.

Triatomic Molecules. This case is elaborated in some detail to expound the method. Other cases then are treated more summarily. The coordinate system for the AB_2 molecule is shown in Fig. 1-14.

The AB_2 molecule has C_{2v} symmetry when it is bent and, when linear, $D_{\infty h}$ symmetry. To simplify notation, however, the linear configuration is considered to be simply an extremum of the C_{2v} symmetry; therefore the labels given to the orbitals through the range $90° \leqslant \theta < 180°$ are retained even when $\theta = 180°$. The symbols used to label the orbitals are derived from the orbital symmetry properties in a systematic way, but a detailed explanation is not given here.[11] For present purposes, these designations may be treated simply as labels.

The A atom of a AB_2 molecule will be assumed to have only s, p_x, p_y, and p_z orbitals in its valence shell, whereas each of the B atoms is allowed only a single orbital oriented to form a σ bond to A. In the linear configuration p_x^A and p_z^A are equivalent nonbonding orbitals labeled $2a_1$ and b_1, respectively. The orbitals s^A and p_y^A interact with σ_1^B and σ_2^B, the σ orbitals on the B atoms, to form one very strongly bonding orbital, $1a_1$, one less strongly bonding orbital, $1b_2$, and two antibonding σ orbitals, $3a_1$ and $2b_2$. The ordering of

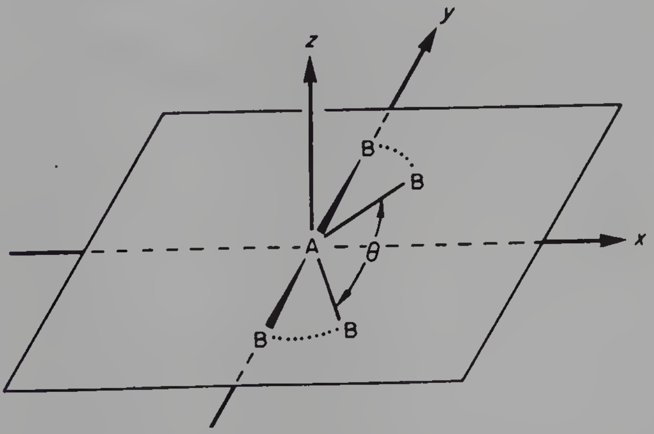

FIG. 1-14. The coordinate axes used for linear and bent AB_2 molecules.

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[11] For an explanation of the symbols, consult any introductory book on chemical or physical applications of group theory, for example, F. A. Cotton, *Chemical Applications of Group Theory*, 2nd ed., Wiley–Interscience, New York, 1971, p. 86, or H. H. Jaffé and M. Orchin, *Symmetry in Chemistry,* Wiley, New York, 1965, p. 61. See also the books by Gimarc, and by Albright, Burdett and Whangbo in the list of general references for details.

these orbitals and, in more detail, the approximate values of their energies can be estimated by an MO calculation. Similarly, for the bent molecule the MO energies may be estimated. Here only p_z^A is nonbonding; spacings and even the order of the other orbitals is a function of the angle of bending θ. The complete pattern of orbital energies, over a range of θ, as obtained with typical input parameters, is shown in Fig. 1-15. Calculations in the Hückel approximation are simple to perform and give the correct general features of the diagram but for certain cases (e.g., AB_2E_2, as noted later) very exact computations are needed for an unambiguous prediction of structure.

From the approximate diagram it is seen that an AB_2 molecule (one with no lone pairs) is more stable when linear than when bent. The $1b_2$ orbital drops steadily in energy from θ = 90 to 180°, while the energy of the $1a_1$ orbital is fairly insensitive to angle. For an AB_2E molecule the results are ambiguous, because the trend in the energy of the $2a_1$ orbital approximately offsets that of the $1b_2$ orbital. The correct result may be a sensitive function of the nature of A and B. Important examples of AB_2E molecules are carbenes CR_2, whose structures vary with changes in R. For AB_2E_2 molecules, the result should be the same as for AB_2E, since the energy of the b_1 orbital is independent (in this rough approximation) of the angle. Thus it is not clear in this approach that AB_2E_2 molecules should necessarily be bent, but all

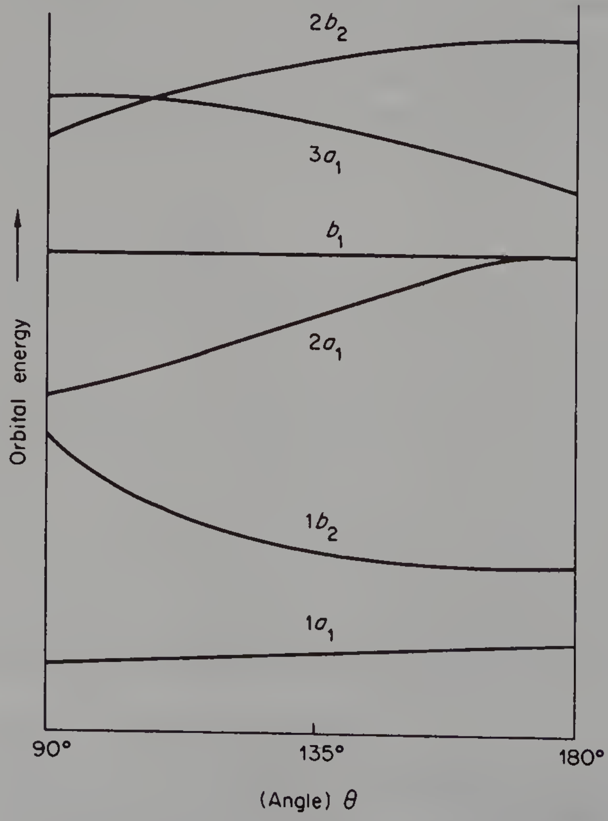

FIG. 1-15. Orbital correlation diagram for AB_2 triatomic molecules, where A uses only *s* and *p* orbitals.

known ones are. We shall return to this question because of the exceptional importance of one particular AB_2E_2 molecule, H_2O. For AB_2E_3 molecules the behavior of the $3a_1$ orbital would clearly favor a linear structure, and this is in accord with all known facts.

The H_2O Molecule. Because of its unique importance, this molecule has been subjected to more detailed study than any other AB_2E_2 molecule. A correlation diagram calculated specifically for H_2O is shown in Fig. 1-16. Although it differs in detail from the general AB_2E_2 diagram in Fig. 1-15, it is encouraging to see that the important qualitative features are the same. The general purpose diagram pertains to a situation in which there is only a small energy difference between the *ns* and the *np* orbitals of the central atom, and, as stated in discussing that general purpose diagram, it is not clear whether an AB_2E_2 molecule ought necessarily to be bent. In the diagram calculated expressly for H_2O the lowest level is practically pure 2*s* and its energy is essentially constant for all angles. It can be determined from this diagram that the energy is minimized at an angle of 106°, essentially in accord with the experimental value of 104.5°.

Just as important as the fact that Fig. 1-16 shows that even with simple methods (i.e., extended Hückel) this correlation diagram approach can yield reliable results for specific molecules (as well as general predictions) is some-

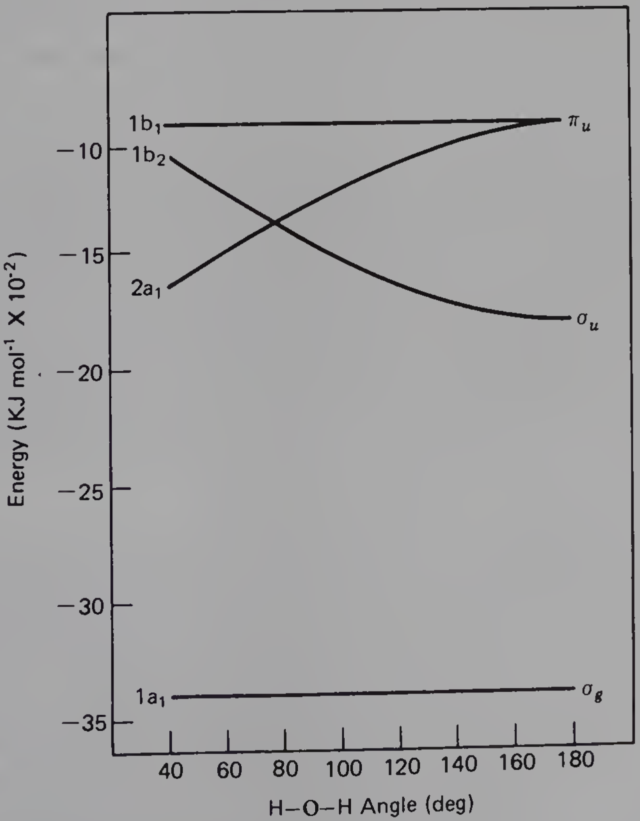

FIG. 1-16. A correlation diagram calculated by the extended Hückel method for H_2O. [Adapted from M. B. Hall, *Inorg. Chem.*, 1978, **17**, 2261.]

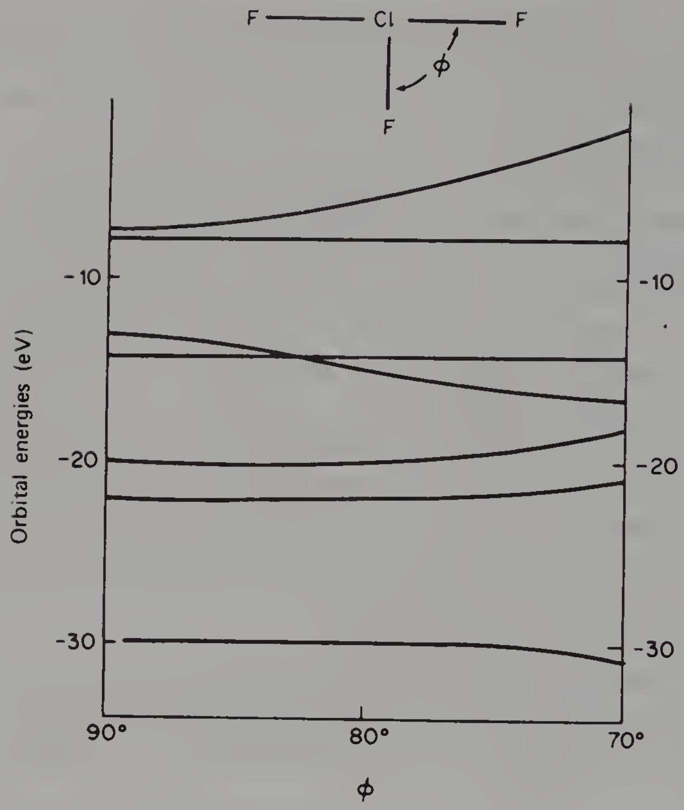

FIG. 1-17. Orbital energies (eV) as a function of angle for ClF_3 as calculated in the extended Hückel approximation. [Adapted from R. M. Gavin, Jr., *J. Chem. Educ.*, 1969, **46**, 413.]

thing else shown in Fig. 1-16. It can be seen that the assumption made in the VSEPR model that all valence shell electron pairs can be treated as having similar requirements for space on the surface of the central atom is not really justified, at least in this case. The electrons in the $1a_1$ orbital are essentially pure $2s$ electrons and have practically no influence on the shape of the molecule. The other lone pair is in a pure $2p$ orbital and the bonds are formed by essentially pure oxygen $2p$ orbitals. Thus, from this vantage point, and for this molecule, the assumption employed in the three-center bond approach, that pure p orbitals are the determinants of stereochemistry, is a very good one. In other cases, of course, it is not.

Tetraatomic Molecules. For AB_3E molecules with a C_3 axis of symmetry, very accurate calculations of energy as a function of angle have been made because of the relevance of this to the problem of barriers to inversion in pyramidal molecules. In the best of these calculations it is found that the relative energies of the pyramidal and the planar configurations are such that the pyramidal configuration is always the more stable, but the energy difference varies considerably (from ~25 kJ mol^{-1} for NH_3 to more than 150 kJ mol^{-1} for some AsX_3 and SbX_3 molecules). Also, interelectronic and internuclear repulsions as well as bond energies play an important role in determining the configurations.

For molecules with more than an octet of valence shell electrons on the central atom, the employment of correlation diagrams has been less systematic. Instead, some individual cases have been treated to see what distortions from assumed idealized geometries might be expected. For example, the T-shaped ClF_3 molecule has been treated as indicated in Fig. 1-17, where the results suggest that the angle ϕ should be $\sim 10° < 90°$, in semiquantitative agreement with observation.

1-8. $d\pi$-$p\pi$ Bonding

There are several structural phenomena that have traditionally been attributed to the formation of $d\pi$-$p\pi$ bonds, and until rather recently this type of explanation enjoyed wide though not universal favor. Recent work has raised more doubts. The phenomena in question are exemplified by:

1. The fact (already mentioned) that for amines such as $(R_3Si)_2NCH_3$, $(R_3Si)_3N$, and $(H_3Ge)_3N$, the central NSi_2C, NSi_3, and NGe_3 skeletons are planar.[12]

2. Many tetrahedral species such as SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, and ClO_4^- have bond lengths shorter than those predicted from conventional tables of single bond radii. In silicates the Si—O—Si units also show what were considered to be Si—O distances that are "too short," for single bonds.

Recent reexaminations of these phenomena by both theoretical[13] and experimental[14] methods together with earlier arguments now suggest that the $d\pi$-$p\pi$ contributions to these effects are at best small. Thus, in reading literature written prior to 1985, where such interactions are often accorded great importance, one should now be skeptical of all but the facts themselves.

This is not to say that $d\pi$-$p\pi$ bonding in main group compounds is never important. Probably in the case of —S—N=S— units, and in $F_3S{\equiv}N$, where the S—N distances are very short indeed, this type of bonding may be at work. However, it is always dangerous to attribute all structural effects to simple orbital overlaps, even if the explanation seems to fit, and the rise and fall of the $d\pi$-$p\pi$ overlap hypothesis is a case in point.

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[13] D. W. J. Cruickshank, *J. Mol. Struct.,* 1985, **130,** 1771.

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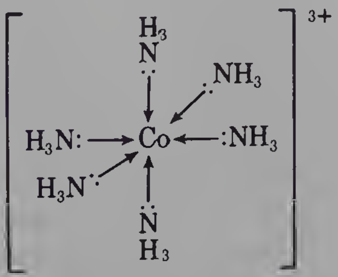
Chapter Two

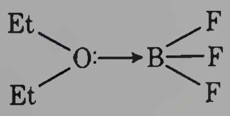
Introduction to Ligands and Complexes

GENERAL REMARKS

2-1. Introduction

It was known long before the Danish chemist S. M. Jørgensen (1837–1914) began his extensive studies on the synthesis of such "complex" compounds that the metal halides and other salts could give compounds with neutral molecules and that many of these compounds could easily be formed in aqueous solutions. The recognition of the true nature of "complexes" began with Alfred Werner (1866–1919) as set out in his classic work *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (1905)[1]; he received the Nobel Prize for this work in 1913. Werner showed that neutral molecules were bound directly to the metal so that complex salts such as $CoCl_3 \cdot 6NH_3$ were correctly formulated $[Co(NH_3)_6]^{3+}Cl_3^-$. He also demonstrated that there were profound stereochemical consequences of the assumption that the molecules or ions (ligands) around the metal occupied positions at the corners of an octahedron or a square. The stereochemical studies of Werner were later followed by the ideas of G. N. Lewis and N. V. Sidgwick, who proposed that a chemical bond required the sharing of an electron pair. This led to the idea that a neutral molecule with an electron pair (Lewis base) can donate these electrons to a metal ion or other electron acceptor (Lewis acid). Well-known examples are the following:





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[1] Braunschweig, 1905; English translation of second edition as *New Ideas on Inorganic Chemistry*, by E. P. Hedley, London, 1911.

We can now define a *ligand** as any molecule or ion that has at least one electron pair that can be so donated. Ligands may also be called Lewis bases; in the terms used in organic chemistry, they are nucleophiles. Metal ions or molecules such as BF_3 with incomplete valence electron shells are Lewis acids or electrophiles.

Although it is possible to regard even covalent compounds from the donor–acceptor point of view—for example, we could regard methane (CH_4) as composed of C^{4+} and four H^- ions—it is not a particularly profitable or realistic way of looking at such molecules. Nevertheless, in inorganic chemistry, ions such as H^-, F^-, Cl^-, NO_3^-, and SO_4^{2-}, and groups such as CH_3^- and $C_6H_5^-$, are commonly termed ligands even when they are bound in simple molecules by largely covalent bonds as in SF_6 or $W(CH_3)_6$. Although SiF_4 is normally called a molecule and SiF_6^{2-} a complex anion, the nature of the Si—F bonds in each species is essentially the same.

There are many ways of classifying ligands. One approach is based on the type of bonding interaction between the central atom and its neighbors. The bonding details are dealt with later, but the distinction between two major types of ligand can be illustrated by posing two questions.

1. Why do molecules like water or ammonia give complexes with ions of *both* main group and transition metals—for example, $[Al(OH_2)_6]^{3+}$ or $[Co(NH_3)_6]^{3+}$, while other types of molecules such as PF_3 or CO give complexes only with transition metals?

2. Although PF_3 and CO give neutral complexes such as $Ni(PF_3)_4$ or $Cr(CO)_6$, why do NH_3, amines, oxygen compounds, and so on, not give complexes such as $Ni(NH_3)_4$?

There are two main classes of ligands:

(*a*) *Classical* or *simple donor ligands* act as electron-pair donors to acceptor ions or molecules, and form complexes with all types of Lewis acids, metal ions, or molecules.

(*b*) *Nonclassical ligands, π-bonding* or *π-acid ligands,* form compounds largely if not entirely with transition metal atoms. This interaction occurs because of the special properties of both metal and ligand. The metal has *d* orbitals that can be utilized in bonding; the ligand has not only *donor* capacity but also has *acceptor* orbitals. This latter distinction is perhaps best illustrated by comparison of an amine, $:NR_3$, with a tertiary phosphine, $:PR_3$. Both can act as bases toward H^+, but the P atom differs from N in that it has vacant 3*d* orbitals of low energy, whereas in N the lowest energy *d* orbitals are at far too high an energy to use. Another example is that of CO, which has no measurable basicity to protons, yet readily reacts with metals like nickel that have high heats of atomization to give compounds like $Ni(CO)_4$.

Ligands may also be classified electronically, that is, according to the number of electrons that they contribute to a central atom when these ligands are regarded (sometimes artificially) as neutral species. Thus atoms or groups that can form a covalent bond are regarded as *one-electron* donors—examples

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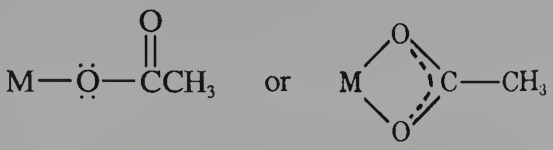
*For a history of the term, see W. H. Brock *et al., Polyhedron;* 1983, **2,** 1.

are F, SH, and CH_3. Any compound with an electron pair is a *two-electron donor* (e.g., $:NH_3$, $H_2O:$). Groups that can form a single bond and at the same time donate can be considered to be *three-electron donors.* For example, the acetate ion can be either a one- or a three-electron donor, namely,



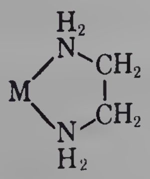
A molecule with two electron pairs (e.g., $H_2NCH_2CH_2NH_2$) can be regarded as a *four-electron donor,* and so on. This classification method is useful in that it is an aid in electron counting, particularly for transition metal complexes whose valence shells contain 18 electrons and whose stoichiometries correspond to what is called the *18-electron rule* or noble gas formalism. This is merely a phenomenological way of expressing the tendency of a transition metal atom to use all its valence orbitals, namely, the five *nd,* the $(n + 1)s$, and the three $(n + 1)p$ orbitals as fully as possible in metal-ligand bonding. The sum of the number of valence electrons in the gaseous atom plus the number of electrons from neutral ligands may attain a maximum value of 18.

This is illustrated by the following examples:

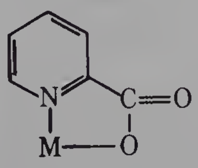
$$\begin{aligned} \mathrm{Cr} + 6\mathrm{CO} &= \mathrm{Cr(CO)_6} \\ 6 + (6 \times 2) &= 18 \\ \mathrm{Ru} + \mathrm{H} + \mathrm{CO_2CH_3} + 3\mathrm{PPh_3} &= \mathrm{RuH(CO_2Me)(PPh_3)_3} \\ 8 + 1 + 3 + (3 \times 2) &= 18 \end{aligned}$$

A third way of classifying ligands is *structurally,* that is, by the number of connections they make to the central atom. Where only one atom becomes closely connected (bonded) the ligand is said to be *unidentate* [e.g., the ligands in $Co(NH_3)_6^{3+}$, $AlCl_4^-$, $Fe(CN)_6^{3-}$]. When a ligand becomes attached by two or more atoms it is *bidentate, tridentate, tetradentate,* and so on, generally multidentate. Note that the Greek-derived corresponding prefixes (mono, ter, poly, etc.) are also used in the literature.

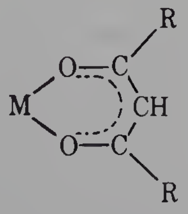
Bidentate ligands when bound entirely to one atom are termed *chelate,* as in (2-I), (2-II), and (2-III).



(2-I)

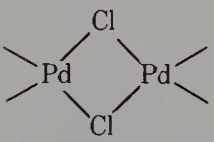


(2-II)

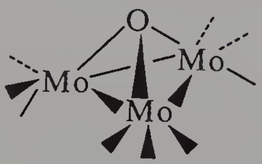


(2-III)

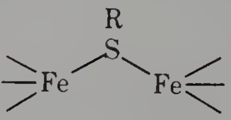
Another important role of ligands is as *bridging groups.* In many cases they serve as *unidentate* bridging ligands. This means that there is only *one* ligand atom that forms two (or even three) bonds to different metal atoms. For monoatomic ligands, such as the halide ions, and those containing only one possible donor atom, this *unidentate* form of bridging is, of course, the only possible one. A few examples are shown in (2-IV) to (2-VI). Ligands having more than one atom that can be an electron donor often function as *bidentate* bridging ligands. Examples are shown in (2-VII) and (2-VIII).



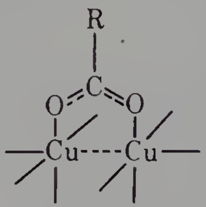
(2-IV)



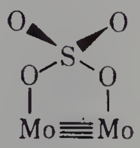
(2-V)



(2-VI)



(2-VII)



(2-VIII)

The standard notation for bridging ligands employs the descriptors η (eta) and μ (mu). The prefix η^n indicates that a ligand is using n of its atoms to form bonds to metal atoms (η is used also for nonbridging ligands, see Sections 2-10 to 2-12.), while the prefix μ implies that a ligand bridges two metal atoms. If a ligand bridges three, four, or more metal atoms, μ_3, or μ_4, and so on, are used. For example, in (2-IV), the chlorine atoms are μ-Cl, while in (2-V) the oxygen atom is μ_3-O. In (2-VII), the carboxylato ligand is μ,η^2 since it bridges two metal atoms (hence μ) employing two different oxygen atoms (hence η^2).

Some unidentate ligands have two or more different donor sites so that the possibility of *linkage isomerism* arises. Some important ligands of this type, which are called *ambidentate ligands,* are

$\left\{\begin{matrix}M—NO_2\\M—ONO\end{matrix}\right.$	Nitro Nitrito	$\left\{\begin{matrix}M—CN\\M—NC\end{matrix}\right.$	Cyano Isocyano
$\left\{\begin{matrix}M—SCN\\M—NCS\end{matrix}\right.$	*S*-Thiocyanato *N*-Thiocyanato	$R_2\underset{\underset{O}{\Vert}}{S} \rightarrow M$, $R_2SO \rightarrow M$	S and O-Bonded Dialkyl sulfoxide

The next sections discuss primarily the chemistry of simple donor ligands. Much of this chemistry applies equally well to main group metal ions (e.g., Na^+, Ca^{2+}, Ga^{3+}, or Cd^{2+}) and to transition metal ions. It is a chemistry largely of aqua ions, nitrogen donor ligands, such as ammonia or ethylenediamine, and halide ions, and it is chemistry of metal ions in positive oxidation states, usually 2+ and 3+.

Later sections consider complexes that have π-bonding ligands and also compounds that are called π *complexes,* which are those formed by unsaturated organic molecules. This is a chemistry largely of transition metals, often in formally low oxidation states such as -1, 0, and $+1$.

The borderline between π-bonding and non-π-bonding ligands is by no means clearly defined. Also the terms "nonclassical" versus "classical" are of limited validity, since Werner and his contemporaries studied complexes of cyanide ion and of tertiary phosphines; even pyridine, which they used extensively, is not solely a simple donor.

STABILITY OF COMPLEX IONS IN AQUEOUS SOLUTION

2-2. Aqua Ions

In a fundamental sense metal ions simply dissolved in water are already complexed—they have formed aqua ions. The process of forming in aqueous solution what we more conventionally call complexes is really one of displacing one set of ligands, which happen to be water molecules, by another set. Thus the logical place to begin a discussion of the formation and stability of complex ions in aqueous solution is with the aqua ions themselves.

From thermodynamic cycles the enthalpies of plunging gaseous metal ions into water can be estimated and the results, 2×10^2 to 4×10^3 kJ mol^{-1} (see Table 2-1), show that these interactions are very strong indeed. It is of importance in understanding the behavior of metal ions in aqueous solution to know how many water molecules each of these ions binds by direct metal-oxygen bonds. To put it another way, if we regard the ion as being an aqua complex $[M(H_2O)_x]^{n+}$, which is then further and more loosely solvated, we wish to know the coordination number x and also the manner in which the x water molecules are arranged around the metal ion. Classical measurements of various types—for example, ion mobilities, apparent hydrated radii, entropies of hydration—fail to give such detailed information because they cannot make any explicit distinction between those water molecules directly bonded to the metal—the x water molecules in the inner coordination sphere—and additional molecules that are held less strongly by hydrogen bonds to the water molecules of the inner coordination sphere. There are, however, ways of answering the question in many instances, ways depending, for the most

TABLE 2-1

Enthalpies of Hydration[a] of Some Ions (kJ mol^{-1})

H^+	−1091	Ca^{2+}	−1577	Cd^{2+}	−1807
Li^+	−519	Sr^{2+}	−1443	Hg^{2+}	−1824
Na^+	−406	Ba^{2+}	−1305	Sn^{2+}	−1552
K^+	−322	Cr^{2+}	−1904	Pb^{2+}	−1481
Rb^+	−293	Mn^{2+}	−1841	Al^{3+}	−4665
Cs^+	−264	Fe^{2+}	−1946	Fe^{3+}	−4430
Ag^+	−473	Co^{2+}	−1996	F^-	−515
Tl^+	−326	Ni^{2+}	−2105	Cl^-	−381
Be^{2+}	−2494	Cu^{2+}	−2100	Br^-	−347
Mg^{2+}	−1921	Zn^{2+}	−2046	I^-	−305

[a] Absolute values are based on the assignment of −1091 ± 10 kJ mol^{-1} to H^+ (cf. H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, 1963, **59**, 1126). Each value probably has an uncertainty of at least 10*n* kJ mol^{-1}, where *n* is the charge of the ion.

part, on modern physical and theoretical developments. A few illustrative examples will be considered here.

For the transition metal ions, the spectral and, to a lesser degree, magnetic properties depend on the constitution and symmetry of their surroundings. For example, the Co^{II} ion forms both octahedral and tetrahedral complexes. Thus we might suppose that the aqua ion could be either $[Co(H_2O)_6]^{2+}$ with octahedral symmetry, or $[Co(H_2O)_4]^{2+}$ with tetrahedral symmetry. It is found that the spectrum and the magnetism of Co^{II} in pink aqueous solutions of its salts with noncoordinating anions such as ClO_4^- or NO_3^- are very similar to the corresponding properties of octahedrally coordinated Co^{II} in general, and virtually identical with those of Co^{II} in such hydrated salts as $Co(ClO_4)_2 \cdot 6H_2O$ or $CoSO_4{\cdot}7H_2O$ where from X-ray studies octahedral $[Co(H_2O)_6]^{2+}$ ions definitely exist. Complementing this, the spectral and magnetic properties of the many known tetrahedral Co^{II} complexes, such as $[CoCl_4]^{2-}$, $[CoBr_4]^{2-}$, $[Co(NCS)_4]^{2-}$, and $[py_2CoCl_2]$, which are intensely green, blue, or purple, are completely different from those of Co^{II} in aqueous solution. Thus there is little doubt that aqueous solutions of otherwise uncomplexed Co^{II} contain predominantly* well-defined, octahedral $[Co(H_2O)_6]^{2+}$ ions, further hydrated, of course. Evidence of similar character can be adduced for many of the other transitional metal ions. For all the di- and tripositive ions of the first transition series, the aqua ions are octahedral $[M(H_2O)_6]^{2(\text{or } 3)+}$ species, although in those of Cr^{II}, Mn^{III}, and Cu^{II} there are definite distortions of the octahedra because of the Jahn–Teller effect.† Information on aqua ions of the second and third transition series, of which there are only a few, however, is not so certain. It is probable that the coordination is octahedral in many, but higher coordination numbers may occur. For the lanthanide ions, $M^{3+}(aq)$, it is certain that the coordination number is higher.

For ions that do not have partly filled *d* shells, evidence of the kind mentioned is lacking, since such ions do not have spectral or magnetic properties related in a straightforward way to the nature of their coordination spheres. We are therefore not sure about the state of aquation of many such ions, although nmr and other relaxation techniques have now supplied some such information. It should be noted that, even when the existence of a well-defined aqua ion is certain, there are vast differences in the average length of time that a water molecule spends in the coordination sphere, the so-called mean residence time. For Cr^{III} and Rh^{III} this time is so long that when a solution of $[Cr(H_2O)_6]^{3+}$ in ordinary water is mixed with water enriched in ^{18}O, many hours are required for complete equilibration of the enriched solvent water with the coordinated water. From a measurement of how many molecules of H_2O in the Cr^{III} and Rh^{III} solutions fail immediately to exchange with the enriched water added, the coordination numbers of these ions by water were shown to be 6. These cases are exceptional, however. Most other

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*However, there are also *small* quantities of tetrahedral $[Co(H_2O)_4]^{2+}$; see T. J. Swift, *Inorg. Chem.*, 1964, **3**, 526.

†This effect requires molecules to adopt geometries that do not lead to a degeneracy in valence level orbitals.

aqua ions are far more labile, and a similar equilibration would occur too rapidly to permit the same type of measurement. This particular rate problem is only one of several that are discussed more fully in Section 29-3.

Aqua ions are all more or less acidic; that is, they dissociate in a manner represented by the equation

$$[M(H_2O)_x]^{n+} = [M(H_2O)_{x-1}(OH)]^{(n-1)+} + H^+$$

$$K_A = \frac{[H^+][M(H_2O)_{x-1}(OH)]}{[M(H_2O)_x]}$$

The acidities vary widely, as the following K_A values show:

M in $[M(H_2O)_6]^{n+}$	K_A
Al^{III}	1.12×10^{-5}
Cr^{III}	1.26×10^{-4}
Fe^{III}	6.3×10^{-3}

Coordinated water molecules in other complexes also dissociate in the same way, for example,

$$[Co(NH_3)_5(H_2O)]^{3+} = [Co(NH_3)_5(OH)]^{2+} + H^+ \qquad K \approx 10^{-5.7}$$
$$[Pt(NH_3)_4(H_2O)_2]^{4+} = [Pt(NH_3)_4(H_2O)(OH)]^{3+} + H^+ \qquad K \approx 10^{-2}$$

2-3. Formation Constants of Complexes

The thermodynamic stability of a complex can be indicated by an equilibrium constant relating its concentration to the concentration of other species *when the system has reached equilibrium.* The kinetic stability of a species refers to the speed with which transformations leading to the attainment of equilibrium will occur. This section considers problems of thermodynamic stability, that is, the nature of equilibria once they are established.

If in a solution containing aquated metal ions M and unidentate ligands L, only soluble mononuclear complexes are formed, the system at equilibrium may be described by the following equations and equilibrium constants:

$$\begin{aligned}
M + L &= ML & K_1 &= \frac{[ML]}{[M][L]} \\
ML + L &= ML_2 & K_2 &= \frac{[ML_2]}{[ML][L]} \\
ML_2 + L &= ML_3 & K_3 &= \frac{[ML_3]}{[ML_2][L]} \\
&\vdots & &\vdots \\
ML_{N-1} + L &= ML_N & K_N &= \frac{[ML_N]}{[ML_{N-1}][L]}
\end{aligned}$$

There will be N such equilibria, where N represents the maximum coordination number of the metal ion M for the ligand L, and N may vary from one ligand to another. For instance, Al^{3+} forms $AlCl_4^-$ and AlF_6^{3-} and Co^{2+} forms $CoCl_4^{2-}$ and $Co(NH_3)_6^{2+}$, as the highest complexes with the ligands indicated.

Another way of expressing the equilibrium relations follows:

$$\begin{aligned}
&\mathrm{M} + \mathrm{L} = \mathrm{ML} && \beta_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}\\
&\mathrm{M} + 2\mathrm{L} = \mathrm{ML}_2 && \beta_2 = \frac{[\mathrm{ML}_2]}{[\mathrm{M}][\mathrm{L}]^2}\\
&\mathrm{M} + 3\mathrm{L} = \mathrm{ML}_3 && \beta_3 = \frac{[\mathrm{ML}_3]}{[\mathrm{M}][\mathrm{L}]^3}\\
&\qquad\vdots && \quad\vdots\\
&\mathrm{M} + N\mathrm{L} = \mathrm{ML}_N && \beta_N = \frac{[\mathrm{ML}_N]}{[\mathrm{M}][\mathrm{L}]^N}
\end{aligned}$$

Since there can be only N independent equilibria in such a system, it is clear that the K_i's and the β_i's must be related. The relationship is indeed rather obvious. Consider, for example, the expression for β_3. Let us multiply both numerator and denominator by $[ML][ML_2]$ and then rearrange slightly:

$$\begin{aligned}
\beta_3 &= \frac{[\mathrm{ML}_3]}{[\mathrm{M}][\mathrm{L}]^3}\cdot\frac{[\mathrm{ML}][\mathrm{ML}_2]}{[\mathrm{ML}][\mathrm{ML}_2]}\\
&= \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}\cdot\frac{[\mathrm{ML}_2]}{[\mathrm{ML}][\mathrm{L}]}\cdot\frac{[\mathrm{ML}_3]}{[\mathrm{ML}_2][\mathrm{L}]}
\end{aligned}$$

It is not difficult to see that this kind of relationship is perfectly general, namely,

$$\beta_k = K_1K_2K_3\cdots K_k = \prod_{i=1}^{i=k} K_i$$

The K_i's are called the *stepwise formation constants* (or stepwise stability constants), and the β_i's are called the *overall formation constants* (or overall stability constants); each type has its special convenience in certain cases.

In all of the previous equilibria we have written the metal ion without specifying charge or degree of solvation. The former omission is obviously of no importance, for the equilibria may be expressed as above whatever the charges. Omission of the water molecules is a convention that is usually convenient and harmless. It must be remembered when necessary. See, for example, the discussion of the chelate effect, in the next section.

With only a few exceptions, there is generally a slowly descending progression in the values of the K_i's in any particular system. This is illustrated by the data for the Cd^{II}–NH_3 system where the ligands are uncharged and by the Cd^{II}–CN^- system where the ligands are charged.

$$Cd^{2+} + NH_3 = [Cd(NH_3)]^{2+} \qquad K = 10^{2.65}$$

$$[Cd(NH_3)]^{2+} + NH_3 = [Cd(NH_3)_2]^{2+} \qquad K = 10^{2.10}$$

$$[Cd(NH_3)_2]^{2+} + NH_3 = [Cd(NH_3)_3]^{2+} \qquad K = 10^{1.44}$$

$$[Cd(NH_3)_3]^{2+} + NH_3 = [Cd(NH_3)_4]^{2+} \qquad K = 10^{0.93} \qquad (\beta_4 = 10^{7.12})$$

$$Cd^{2+} + CN^- = [Cd(CN)]^+ \qquad K = 10^{5.48}$$

$$[Cd(CN)]^+ + CN^- = [Cd(CN)_2] \qquad K = 10^{5.12}$$

$$[Cd(CN)_2] + CN^- = [Cd(CN)_3]^- \qquad K = 10^{4.63}$$

$$[Cd(CN)_3]^- + CN^- = [Cd(CN)_4]^{2-} \qquad K = 10^{3.65} \qquad (\beta_4 = 10^{18.8})$$

Thus, typically, as ligand is added to the solution of metal ion, ML is first formed more rapidly than any other complex in the series. As addition of ligand is continued, the ML_2 concentration rises rapidly, while the ML concentration drops, then ML_3 becomes dominant, ML and ML_2 becoming unimportant, and so forth, until the highest complex ML_N is formed, to the nearly complete exclusion of all others at very high ligand concentrations. These relationships are conveniently displayed in diagrams such as those shown in Fig. 2-1.

A steady decrease in K_i values with increasing i is to be expected, provided there are only slight changes in the metal-ligand bond energies as a function of i, which is usually the case. For example, in the Ni^{2+}–NH_3 system to be discussed next, the enthalpies of the successive reactions $Ni(NH_3)_{i-1} + NH_3 = Ni(NH_3)_i$ are all within the range 16.7 to 18.0 kJ mol^{-1}.

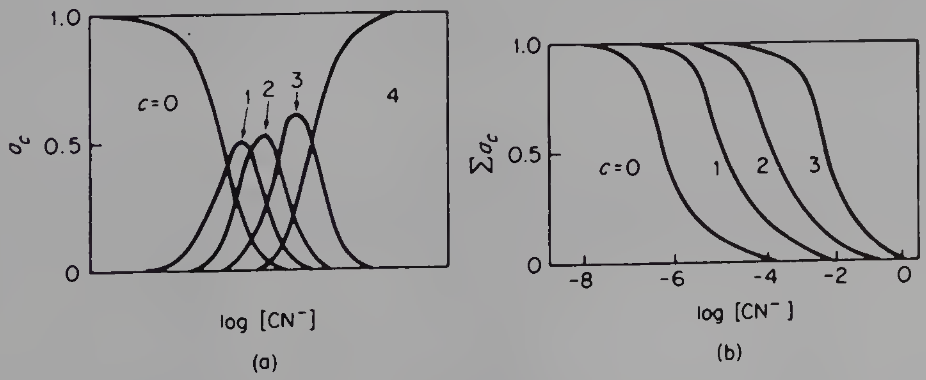

FIG. 2-1. Plots of the proportions of the various complexes $[Cd(CN)_c]^{(2-c)+}$ as a function of the ligand concentration.

$$\alpha_c = [Cd(CN)_c]/\text{total Cd} \qquad \Sigma\alpha_c = \sum_{c=0}^{4} [Cd(CN)_c]/\text{total Cd}$$

[Reproduced by permission from F. J. C. Rossetti, in *Modern Coordination Chemistry,* J. Lewis and R. G. Wilkins, Eds., Interscience, 1960, p. 10.

There are several reasons for a steady decrease in K_i values as the number of ligands increases: (1) statistical factors, (2) increased steric hindrance as the number of ligands increases if they are bulkier than the H_2O molecules they replace, (3) Coulombic factors, mainly in complexes with charged ligands. The statistical factors may be treated in the following way.[2] Suppose, as is almost certainly the case for Ni^{2+}, that the coordination number remains the same throughout the series $[M(H_2O)_N] \cdots [M(H_2O)_{N-n}L_n] \cdots [ML_N]$. The $[M(H_2O)_{N-n}L_n]$ species has n sites from which to lose a ligand, whereas the species $[M(H_2O)_{N-n+1}L_{n-1}]$ has $(N - n + 1)$ sites at which to gain a ligand. Thus the relative probability of passing from $[M(H_2O)_{N-n+1}L_{n-1}]$ to $[M(H_2O)_{N-n}L_n]$ is proportional to $(N - n + 1)/n$. Similarly, the relative probability of passing from $[M(H_2O)_{N-n}L_n]$ to $[M(H_2O)_{N-n-1}L_{n+1}]$ is proportional to $(N - n)/(n + 1)$. Hence on the basis of these statistical considerations alone, we expect

$$K_{n+1}/K_n = \frac{N - n}{n + 1} \div \frac{N - n + 1}{n} = \frac{n(N - n)}{(n + 1)(N - n + 1)}$$

In the Ni^{2+}–NH_3 system ($N = 6$), we find the comparison between experimental ratios of successive constants and those calculated from the previous formula to be as shown in Table 2-2. The experimental ratios are consistently smaller than the statistically expected ones, which is typical and shows that other factors are also of importance.

There are cases where the experimental ratios of the constants do not remain constant or change monotonically; instead, one of them is singularly large or small. There are several reasons for this: (1) an abrupt change in coordination number and hybridization at some stage of the sequence of complexes, (2) special steric effects that become operative only at a certain stage of coordination, and (3) an abrupt change in electronic structure of the metal ion at a certain stage of complexation. Each of these is now illustrated.

Values of K_3/K_2 are anomalously low for the halogeno complexes of mercury (II); HgX_2 species are linear, whereas $[HgX_4]^{2+}$ species are tetrahedral. Presumably the change from sp to sp^3 hybridization occurs on going from

TABLE 2-2
Comparison of Experimental and Statistical Formation Constants of Ni^{2+}–NH_3 Complexes

	Experimental	Statistical
K_2/K_1	0.28	0.417
K_3/K_2	0.31	0.533
K_4/K_3	0.29	0.562
K_5/K_4	0.36	0.533
K_6/K_5	0.2	0.417

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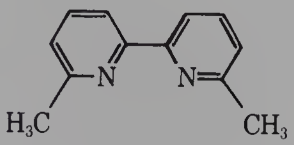
[2] For a more elaborate discussion see R. Pizer, *Inorg. Chem.*, 1984, **23**, 3027.

HgX_2 to $[HgX_3]^-$. K_3/K_2 is anomalously small for the ethylenediamine complexes of Zn^{II}, and this is believed to be due to the change from tetrahedral to octahedral coordination if it is assumed that $[Zn\ en_2]^{2+}$ is tetrahedral. For the Ag^+–NH_3 system $K_2 > K_1$, indicating that the linear structure is probably attained with $[Ag(NH_3)_2]^+$ but not with $[Ag(NH_3)(H_2O)_{3(\text{or } 5)}]^+$.

With 6,6′-dimethyl-2,2′-bipyridine (2-IX), many metal ions that form tris-2,2′-bipyridine complexes form only bis or mono complexes, or, in some cases, no isolable complexes at all, because of the steric hindrance between the methyl groups and other ligands attached to the ion.



(2-IX)

In the series of complexes of Fe^{II} with 1,10-phenanthroline (and also with 2,2′-bipyridine), K_3 is greater than K_2. This is because the tris complex is diamagnetic (i.e., the Fe^{2+} ion has the low-spin state t_{2g}^6) whereas in the mono and bis complexes, as in the aqua ion, there are four unpaired electrons. This change from the $t_{2g}^4e_g^2$ to the t_{2g}^6 causes the enthalpy change for addition of the third ligand to be anomalously large because the e_g electrons are antibonding.

2-4. The Chelate and Macrocyclic Effects[3]

The term "chelate effect" refers to the enhanced stability of a complex system containing chelate rings as compared to the stability of a system that is as similar as possible but contains none or fewer rings. As an example, consider the following equilibrium constants:

$$Ni^{2+}(aq) + 6NH_3(aq) = [Ni(NH_3)_6]^{2+}(aq) \qquad \log \beta = 8.61$$
$$Ni^{2+}(aq) + 3en(aq) = [Ni\ en_3]^{2+}(aq) \qquad \log \beta = 18.28$$

The system $[Ni\ en_3]^{2+}$ in which three chelate rings are formed is nearly 10^{10} times as stable as that in which no such ring is formed. Although the effect is not always so pronounced, such a chelate effect is a very general one.

To understand this effect, we must invoke the thermodynamic relationships:

$$\Delta G^\circ = -RT \ln \beta$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Thus β increases as ΔG° becomes more negative. A more negative ΔG° can result from making ΔH° more negative or from making ΔS° more positive.

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[3] J. J. R. Frausto da Silva, *J. Chem. Educ.*, 1983, **60**, 390.

As a very simple case, consider the reactions, and the pertinent thermodynamic data for them, given in Table 2-3. In this case the enthalpy difference is well within experimental error; the chelate effect can thus be traced entirely to the entropy difference.

In the example first cited, the enthalpies make a slight favorable contribution, but the main source of the chelate effect is still to be found in the entropies. We may look at this case in terms of the following metathesis:

$$[\mathrm{Ni(NH_3)_6}]^{2+}(\mathrm{aq}) + 3\,\mathrm{en(aq)} = [\mathrm{Ni\ en_3}]^{2+}(\mathrm{aq}) + 6\mathrm{NH_3(aq)} \qquad \log \beta = 9.67$$

for which the enthalpy change is -12.1 kJ mol^{-1}, whereas $-T\Delta S° = -55.1$ kJ mol^{-1}. The enthalpy change corresponds very closely to that expected from the increased crystal field stabilization energy of $[\mathrm{Ni\ en_3}]^{2+}$, which is estimated from spectral data to be -11.5 kJ mol^{-1} and can presumably be so explained.

As a final example, which illustrates the existence of a chelate effect despite an unfavorable enthalpy term, we may use the reaction

$$[\mathrm{Ni\ en_2(H_2O)_2}]^{2+}(\mathrm{aq}) + \mathrm{tren(aq)} = [\mathrm{Ni\ tren(H_2O)_2}]^{2+}(\mathrm{aq}) + 2\,\mathrm{en(aq)}$$
$$\log \beta = 1.88 \quad [\mathrm{tren} = \mathrm{N(CH_2CH_2NH_2)_3}]$$

For this reaction we have $\Delta H° = +13.0$, $-T\Delta S° = -23.7$, and $\Delta G° = -10.7$ (all in kJ mol^{-1}). The positive enthalpy change can be attributed both to greater steric strain resulting from the presence of three fused chelate rings in Ni tren, and to the inherently weaker M—N bond when N is a tertiary rather than a primary nitrogen atom. Nevertheless, the greater number of chelate rings (3 vs. 2) leads to greater stability, owing to an entropy effect that is only partially canceled by the unfavorable enthalpy change.

Probably the main cause of the large entropy increase in each of the three cases we have been considering is the net increase in the number of unbound molecules—ligands *per se* or water molecules. Thus although 6 $\mathrm{NH_3}$ displace 6 $\mathrm{H_2O}$, making no net change in the number of independent molecules, it takes only 3 en molecules to displace 6 $\mathrm{H_2O}$. Another more pictorial way to look at the problem is to visualize a chelate ligand with one end attached to the metal ion.[4] The other end cannot then get very far away, and the prob-

TABLE 2-3
Two Reactions Illustrating a Purely Entropy-Based Chelate Effect

$$\mathrm{Cd^{2+}(aq)} + 4\mathrm{CH_3NH_2(aq)} = [\mathrm{Cd(NH_2CH_3)_4}]^{2+}(\mathrm{aq}) \qquad \log \beta = 6.52$$
$$\mathrm{Cd^{2+}(aq)} + 2\mathrm{H_2NCH_2CH_2NH_2(aq)} = [\mathrm{Cd(en)_2}]^{2+}(\mathrm{aq}) \qquad \log \beta = 10.6$$

Ligands	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} deg^{-1})	$-T\Delta S°$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})
$4\mathrm{CH_3NH_2}$	-57.3	-67.3	20.1	-37.2
2 en	-56.5	$+14.1$	-4.2	-60.7

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[4] D. R. Rosseinsky, *J. Chem. Soc. Dalton Trans.*, **1979**, 732.

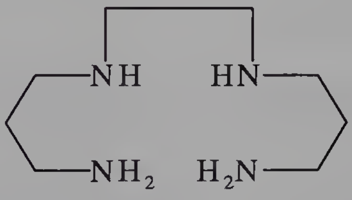
ability of it, too, becoming attached to the metal atom is greater than if this other end were instead another independent molecule, which would have access to a much larger volume of the solution.

The latter view provides an explanation for the decreasing magnitude of the chelate effect with increasing ring size, as illustrated by data such as those shown below for copper complexes of $H_2N(CH_2)_2NH_2$ and $H_2N(CH_2)_3NH_2$(tn):

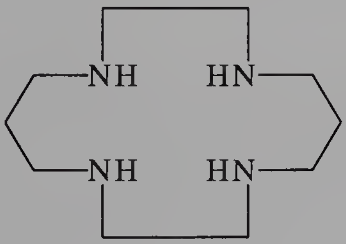
$$[\mathrm{Cu\ en_2}]^{2+}(aq) + 2\mathrm{tn}(aq) = [\mathrm{Cu\ tn_2}]^{2+}(aq) + 2\ \mathrm{en}(aq) \qquad \log \beta = -2.86$$

Of course, when the ring that must be formed becomes sufficiently large (seven membered or more), it becomes more probable that the other end of the chelate molecule will contact another metal ion than that it will come around to the first one and complete the ring. Table 2-4 summarizes the factors influencing the stabilities of complexes.

The Macrocyclic Effect. This term refers to the greater thermodynamic stability of a complex with a cyclic polydentate ligand when compared to the complex formed by a comparable noncyclic ligand. A representative comparison would be between the following pair:



L_1



L_2

The formation of zinc (II) complexes by these two ligands, that is, the reactions (2-1) have been shown[5] to have the following thermodynamic

$$\mathrm{Zn}^{2+}(aq) + L_i(aq) \longrightarrow \mathrm{Zn}L_i^{2+}(aq) \qquad (2\text{-}1)$$

parameters:

	L_1	L_2
log K	11.25	15.34
$-\Delta H°$ (kJ mol^{-1})	44.4	61.9
$\Delta S°$ (J deg^{-1} mol^{-1})	66.5	85.8

The gross macrocyclic effect is evident in the increase of 4.09 units in log K. It can be seen that the overall effect is of both enthalpic and entropic origin. The relative importance of these two contributions varies from case

[5] M. Micheloni and P. Paoletti, *Inorg. Chim, Acta,* 1980, **43,** 109.

TABLE 2-4
Factors Influencing Solution Stability of Complexes[a]

Enthalpy effects	Entropy effects
Variation of bond strength with electronegativities of metal ions and ligand donor atoms	Number of chelate rings Size of chelate ring
Ligand field effects	Changes of solvation on complex formation
Steric and electrostatic repulsion between ligands in complex	Arrangement of chelate rings
Enthalpy effects related to conformation of uncoordinated ligand	Entropy variations in uncoordinated ligands
Other Coulombic forces involving chelate ring formation	Effects resulting from differences in configurational entropies of the ligand in complex compound
Enthalpy of solution of ligands	Entropy of solution of ligands
Change in bond strength when ligand is charged (same donor and acceptor atom)	Entropy of solution of coordinated metal ions

[a] From R. T. Meyers, *Inorg. Chem.*, 1978, **17**, 952.

to case (see ref. 5 for a selection of comparisons), with enthalpy more often providing the dominant contribution.

Cryptate ligands afford a similar enhancement of stability in some cases, but the availability of many ligand conformations makes this a much more complicated situation.[6] Some cryptate selectivity effects for alkali and alkaline earth metal ions are mentioned in Chapters 4 and 5.

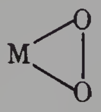
TYPES AND CLASSIFICATION OF LIGANDS

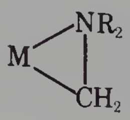
2-5. Multi- or Polydentate Ligands

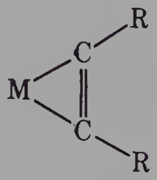
Regardless of whether π-bonding is involved, ligands can have various denticities, and we now illustrate some of the more important types.

Bidentate Ligands. These are very common and can be classified according to the size of the chelate ring formed as in the following examples:

Three-membered







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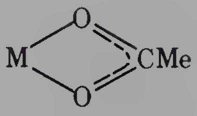
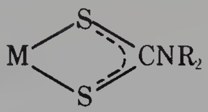
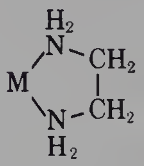
[6] H.-J. Buschmann, *Inorg. Chim. Acta*, 1985, **98**, 43; 1985, **102**, 95.

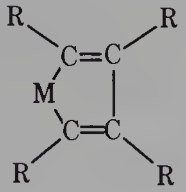
Four-membered



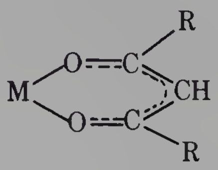


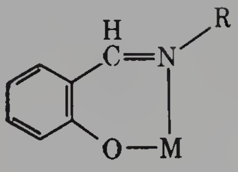
Five-membered



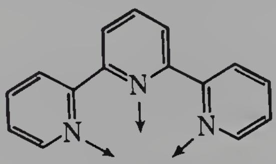


Six-membered

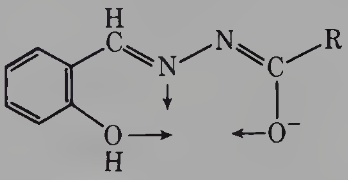




Tridentate Ligands. Some are *obligate planar* such as

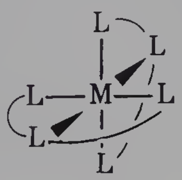


Terpyridine (terpy)

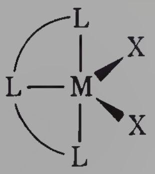


Acylhydrazones of salicylaldehyde

and many similar ones where maintenance of the π conjugation markedly favors planarity. Such ligands must form complexes of the types (2-X) or (2-XI).

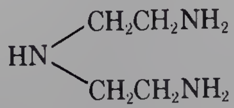


(2-X)



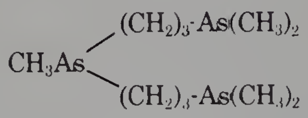
(2-XI)

There are also many flexible tridentate ligands such as



$HN(CH_2CH_2NH_2)_2$

Diethylenetriamine (dien)



$$CH_3As\begin{matrix}(CH_2)_3\text{-}As(CH_3)_2\\(CH_2)_3\text{-}As(CH_3)_2\end{matrix}$$

Bis(3-dimethylarsinylpropyl)methylarsine (triars)

which are about equally capable of meridional (2-X and 2-XI) and facial (2-XII) coordination.

(2-XII)

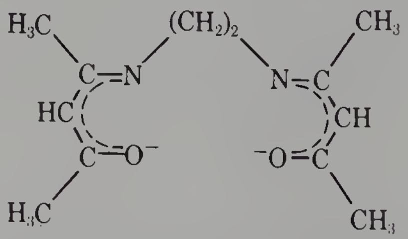
Quadridentate Ligands. There are four main types:

Open-Chain, Unbranched

$$H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$$

Triethylenetetramine (trien)

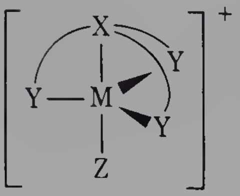
Schiff bases derived from acetylacetone, for example,



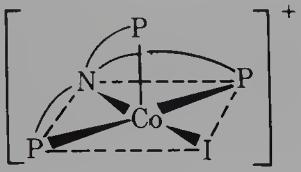
Tripod Ligands. These are of the type X(—Y)$_3$, where X is nitrogen, phosphorus, or arsenic, the Y groups are R_2N, R_2P, R_2As, RS, or RSe, and the connecting chains (—) are $(CH_2)_2$, $(CH_2)_3$, or *o*-phenylene. Some common ones are

$N(CH_2CH_2NH_2)_3$	tren
$N[CH_2CH_2N(CH_3)_2]_3$	Me$_6$tren
$N[CH_2CH_2P(C_6H_5)_2]_3$	*np*$_3$
P[*o*-$C_6H_4P(C_6H_5)_2]_3$	QP
$N(CH_2CH_2SCH_3)_3$	TSN
As[*o*-$C_6H_4As(C_6H_5)_2]_3$	QAS

The tripod ligands are used particularly to favor formation of trigonal-bipyramidal complexes of divalent metal ions, as shown schematically in (2-XIII), but they do not invariably give this result. For instance, whereas Ni(*np*$_3$)I_2 is trigonal-bipyramidal, Co(*np*$_3$)I_2 is square pyramidal (2-XIV).

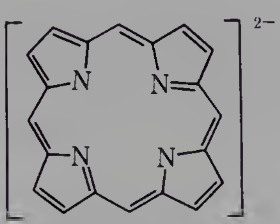


(2-XIII)

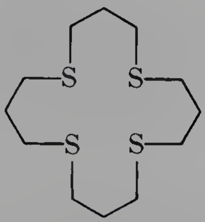


(2-XIV)

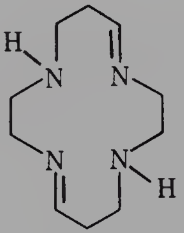
Macrocyclic. These may be (*a*) planar with unsaturated rings as in porphyrin (2-XV) and its derivatives, although, as discussed later in more detail (Section 10-12) the metal atom may be out of the plane of the nitrogen donor atoms, or (*b*) puckered with saturated rings as in the macrocycles (2-XVI) and (2-XVII).



(2-XV)

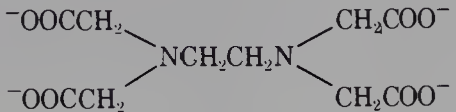


(2-XVI)



(2-XVII)

Pentadentate and Higher-Dentate Ligands. Perhaps the best known hexadentate ligand is ethylenediaminetetraacetate ($EDTA^{4-}$), which can also be pentadentate as $EDTAH^{3-}$.



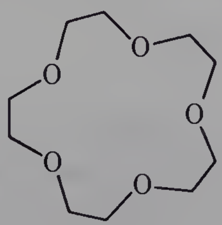
$$\begin{matrix}{}^{-}\mathrm{OOCCH_2}\\ {}^{-}\mathrm{OOCCH_2}\end{matrix}\rangle\mathrm{NCH_2CH_2N}\langle\begin{matrix}\mathrm{CH_2COO^-}\\ \mathrm{CH_2COO^-}\end{matrix}$$

$(EDTA)^{4-}$

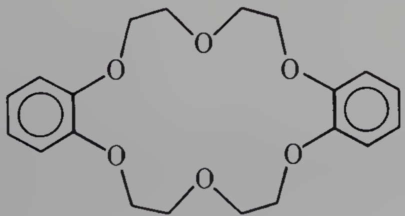
$$\begin{matrix}{}^{-}\mathrm{OOCCH_2}\\ {}^{-}\mathrm{OOCCH_2}\end{matrix}\rangle\mathrm{NCH_2CH_2N}\langle\begin{matrix}\mathrm{CH_2COOH}\\ \mathrm{CH_2COO^-}\end{matrix}$$

$(EDTAH)^{3-}$

Other important multidentate ligands are the *crown ethers and cryptates.* These are cyclic and polycyclic ligands that form their most important complexes with alkali and alkaline earth ions. The macrocyclic polyethers, commonly called *crown ethers,* are typified by (2-XVIII) and (2-XIX). Since the systematic names for such ligands are very unwieldy, a special nomenclature is used, in which (2-XVIII) and (2-XIX) are called, respectively, 15-crown-5 or 15-C-5 and dibenzo-18-crown-6. These examples should serve to show the rules for the simple nomenclature. Crown ethers with as many as 10 oxygens are known and several [e.g., (2-XIX)] are commercially available.

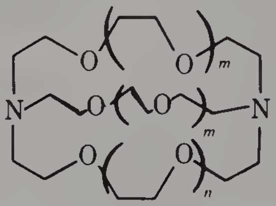


(2-XVIII)



(2-XIX)

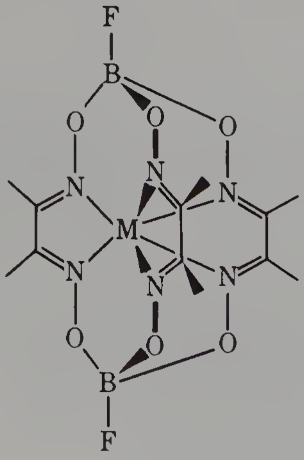
The cryptates are bicyclic species, most of which have the general formula (2-XX). Again a simplified code for naming them is a practical necessity. They are called "cryptate-*mmn,*" where *m* and *n* are as defined in (2-XX). One of the commonest is cryptate-222.



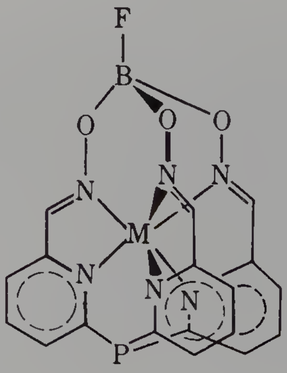
(2-XX)

These ligands have two characteristics that make them unusually interesting. Because they are chelating ligands of high denticity they give very high formation constants, and since the size of ion that will best fit the cavities can be predetermined by changing the ring size, these ligands can be designed to be selective.

In addition to the cryptates, which are synthesized apart from metal ions and then used to form complexes, there are other types of multicyclic ligand called *encapsulating ligands,* which are synthesized around the metal ion and cannot release it. Two of these are (2-XXI) and (2-XXII). An encapsulation complex allows studies to be carried out under extremely acidic or basic conditions since the metal ion, though it cannot be removed, can be oxidized or reduced. Such ligands also can enforce unusual coordination geometries; in the examples shown the coordination is much closer to trigonal prismatic than to octahedral.

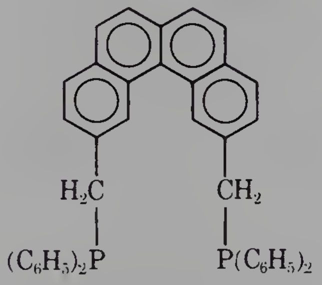


(2-XXI)



(2-XXII)

Ligands of Unusual Reach. Ordinarily bidentate ligands occupy cis positions around a metal ion. This is because two potential donor atoms separated by a chain long enough to be able to span two trans positions would have a very low probability of actually doing so. It would be more likely to form only one bond to a given metal atom, while using its second donor atom to coordinate to a different metal atom, or not at all. This is simply an inorganic example of the well-known problem in organic chemistry of synthesizing very large rings. By appropriately designing the connection between the donor atoms, however, ligands that span trans positions in a square complex or the two sites in a linear LML complex can be made. An example is (2-XXIII). Large chelate ring compounds[7] with 12 to 72 membered rings can be made from flexible bidentate ligands [e.g., $Me_2N(CH_2)_nNMe_2$ or $R_2P(CH_2)_nPR_2$].



(2-XXIII)

2-6. Conformation of Chelate Rings

Simple diagrams of chelate rings in which the ring conformation is ignored are adequate for many purposes. Indeed, in some cases, such as β-diketonate complexes, the rings are planar and no problem arises. The relative stabilities and certain spectroscopic properties of many chelate complexes, however, can be understood only by considering carefully the effects of the ring conformations, as in the important case of five-membered rings such as those formed by ethylenediamine.

Figure 2-2 shows three ways of viewing the puckered rings, and identifies the absolute configurations in the λ,δ notation. As indicated clearly in the figure, the chelate ring has as its only symmetry element a C_2 axis. It must therefore (see Appendix 5) be chiral, and the two forms of a given ring are enantiomorphs. When this source of enantiomorphism is combined with the two enantiomorphous ways, Λ and Δ of orienting the chelate rings about the metal atom (Fig. 2-3), a number of diastereomeric molecules become possible, specifically, the following eight:

Λ(δδδ)	Δ(λλλ)
Λ(δδλ)	Δ(λλδ)
Λ(δλλ)	Δ(λδδ)
Λ(λλλ)	Δ(δδδ)

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[7] L. M. Venanzi *et al.*, *Helv. Chim. Acta*, 1984, **67**, 65.

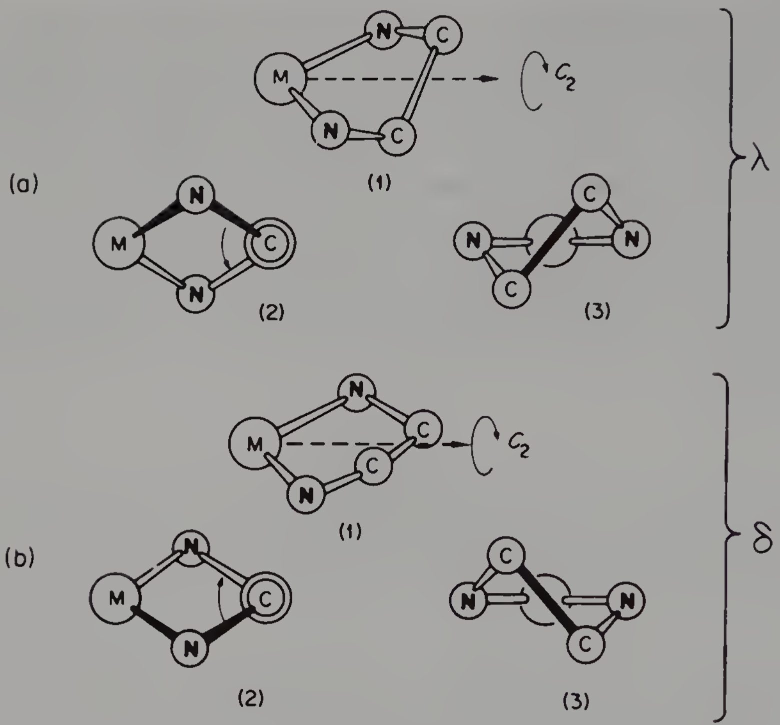

FIG. 2-2. Different ways of viewing the puckering of ethylenediamine chelate rings. The absolute configurations λ and δ are defined. [Reproduced by permission from C. J. Hawkins; see General References.]

The two columns are here arranged so as to place an enantiomorphous pair on each line. In the following discussion we shall mention only members of the Λ series; analogous energy relationships must of course exist among corresponding members of the Δ series.

The relative stabilities of the four diastereomers have been extensively investigated. First, it can easily be shown that the diastereomers must, in principle, differ in stability because there are different nonbonded (repulsive) interactions between the rings in each case. Figure 2-4 shows these differences for any two rings in the complex. When any reasonable potential function is used to estimate the magnitudes of the repulsive energies, it is concluded that

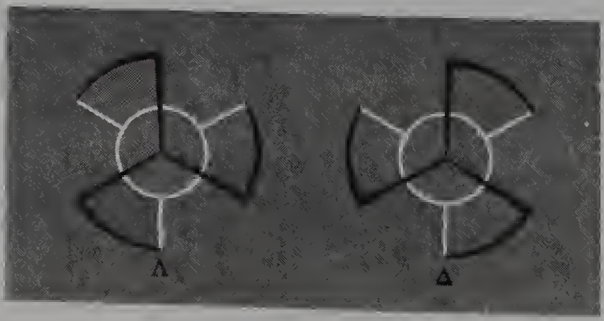

FIG. 2-3. Trischelate octahedral complexes (actual symmetry: D_3) showing how the absolute configurations Λ and Δ are defined according to the translation (twist) of the helices.

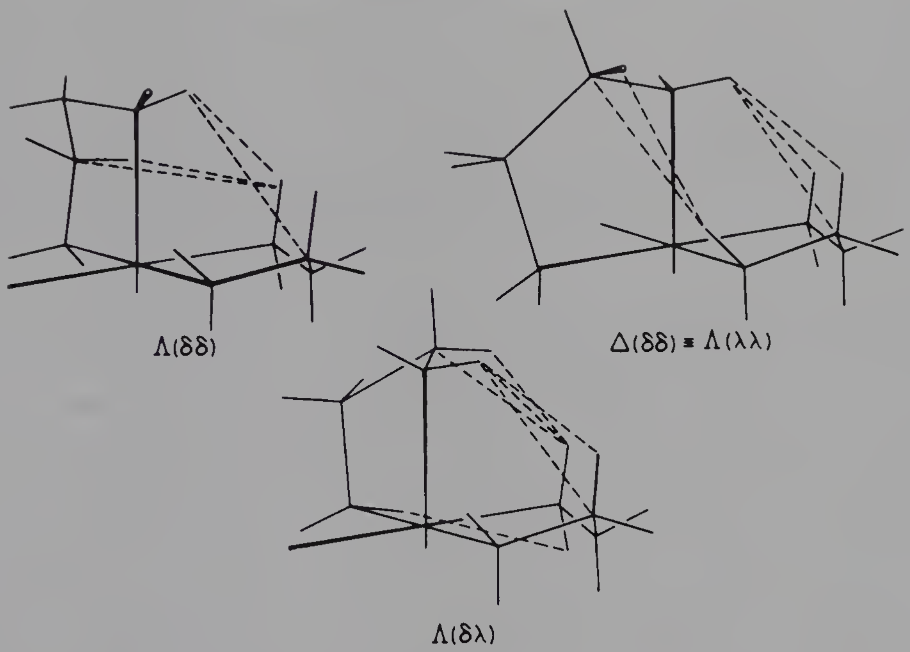

FIG. 2-4. The different sets of repulsive interactions that exist between the three different pairs of ring conformations in octahedral ethylenediamine complexes; broken lines represent the significant repulsive interactions. [Reproduced by permission from C. J. Hawkins; see General References.]

the order of decreasing stability is

$$\Lambda(\delta\delta\delta) > \Lambda(\delta\delta\lambda) > \Lambda(\delta\lambda\lambda) > \Lambda(\lambda\lambda\lambda)$$

This is not the actual order, however, because enthalpy differences between diastereomers are rather small (2–3 kJ mol^{-1}), and an entropy factor must also be considered. Entropy favors the δδλ and δλλ species because they are three times as probable as the δδδ and λλλ ones. Hence the best estimate of relative stabilities, which in fact agrees with all experimental data, becomes

$$\Lambda(\delta\delta\lambda) > \Lambda(\delta\delta\delta) \approx \Lambda(\delta\lambda\lambda) \gg \Lambda(\lambda\lambda\lambda)$$

In crystalline compounds, the Δ(δδδ) isomer (or its enantiomorph) has been found most often, but the other three have also been found. These crystallographic results probably prove nothing about the intrinsic relative stabilities, since hydrogen bonding and other intermolecular interactions can easily outweigh the small intrinsic energy differences.

Nuclear magnetic resonance studies of solutions of Ru^{II}, Pt^{IV}, Ni^{II}, Rh^{III}, Ir^{III}, and Co^{III} $[M\ en_3]^{n+}$ complexes have yielded the most useful data, and the general conclusions seem to be that the order of stability suggested here is correct and that ring inversions are very rapid. Both experiment and theory suggest that the barrier to ring inversion is only ~25 kJ mol^{-1}. Thus the four diastereomers of each overall form (Λ or Δ) are in labile equilibrium.

One of the interesting and important applications of the foregoing type of analysis is to the determination of absolute Δ or Λ configurations by using

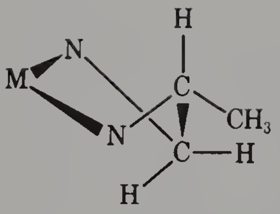

FIG. 2-5. The absolute configuration and expected conformation (i.e., with an equatorial CH_3 group) for an M(*l*-pn) chelate ring.

substituted ethylenediamine ligands of known absolute configuration. This is nicely illustrated by the $[Co(l\text{-pn})_3]^{3+}$ isomers. The absolute configuration of *l*-pn [pn = 1,2-diaminopropane, $NH_2CH(CH_3)—CH_2NH_2$] is known. It would also be expected from consideration of repulsions between rings in the tris complex (as indicated in Fig. 2-4) that pn chelate rings would always take a conformation that puts the CH_3 group in an equatorial position. Hence, an *l*-pn ring can be confidently expected to have the δ conformation shown in Fig. 2-5. Note that because of the extreme unfavorability of having axial CH_3 groups, only two tris complexes are expected to occur, namely, Λ(δδδ) and Δ(δδδ). But by the arguments already advanced for en rings, the Λ isomer should be the more stable of these two, by 5 to 10 kJ mol^{-1}. Thus we predict that the most stable $[Co(l\text{-pn})_3]^{3+}$ isomer must have the absolute configuration Λ about the metal.

In fact, the most stable $[Co(l\text{-pn})_3]^{3+}$ isomer is the one with + rotation at the sodium-D line, and it has the same circular dichroism spectrum, hence the same absolute configuration as $(+)\text{-}[Co\,en_3]^{3+}$. The absolute configuration of the latter has been determined, and it is indeed Λ. Thus the argument based on conformational analysis is validated.

2-7. Second Sphere Coordination

The preceding discussion has dealt only with the ligands in direct contact with the metal ion—the *first coordination sphere* (FCS). Undoubtedly the next layer of molecules or ions—the *second coordination sphere* (SCS)—also displays a type of organization different from that in bulk solvent and dictated in part by its proximity to the metal ion and its FCS. In general, however, it is hard to establish any firm picture of the SCS, when it consists simply of a collection of solvent molecules. However, structured second coordination spheres formed by macrocyclic ligands can be often characterized in more detail, even by X-ray crystallography.

In many cases the major links between the two coordination spheres are hydrogen bonds between protic ligands (NH_3, en, and H_2O) in the FCS and the oxygen atoms of macrocyclic ethers that provide the SCS.[8] An example is provided by the "supercomplex" between $(COD)Rh(NH_3)_2$ and dibenzo-24-crown-8. Conversely, there may be hydrogen bonds between a surrounding

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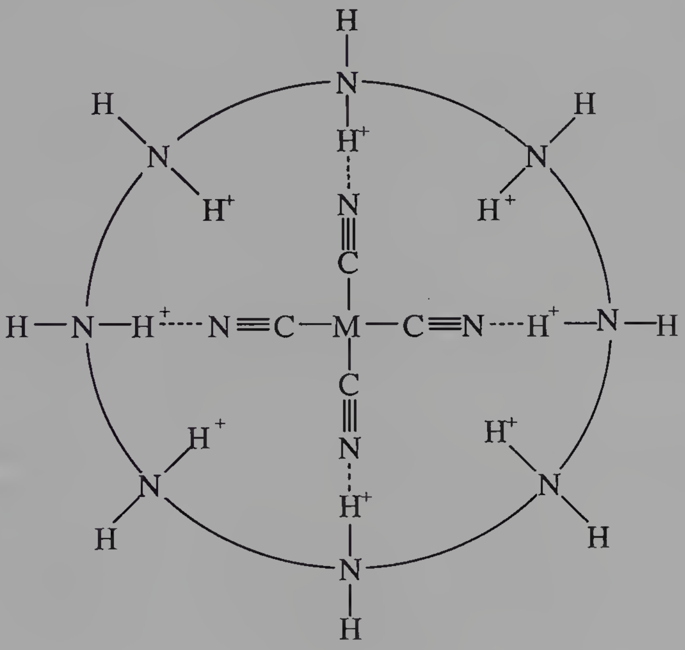
[8] H. M. Colquhoun *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 1939; *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 487 (review).

protonated amine macrocycle and a central anionic complex,[9] as shown schematically in (2-XXIV). In both of these types of "supercomplex" the H-bonding forces are supplemented by other noncovalent interactions, and it would appear that in some cases, as illustrated by the complexes of (COD)$PtCl_2$ and $[(COD)RhCl]_2$ with cyclodextrins,[10] the forces between the FCS and the SCS are entirely of the secondary types, namely, dipole–dipole, dipole–induced dipole, van der Waals, and so on.



(2-XXIV)

π-ACID OR π-BONDING LIGANDS: π COMPLEXES

The ligands for which π bonding is important are carbon monoxide, isocyanides, substituted phosphines, arsines, stibines or sulfides, nitric oxide, and various molecules with delocalized π orbitals. These include pyridine, 2,2′-bipyridine, 1,10-phenanthroline, and certain ligands containing 1,2-dithioketone or 1,2-dithiolene groups, such as the dithiomaleonitrile anion. Diverse complexes exist, ranging from binary molecular compounds such as $Cr(CO)_6$ or $Ni(PF_3)_4$ through mixed species such as $Co(CO)_3NO$ and $(C_6H_5)_3P\,Fe(CO)_4$, to complex ions such as $[Fe(CN)_5CO]^{3-}$, $[Mo(CO)_5I]^-$, $[Mn(CNR)_6]^+$, $[V\ phen_3]^+$, and $\{Ni[S_2C_2(CN)_2]_2\}^{2-}$.

In many of these complexes, the metal atoms are in low-positive, zero, or negative formal oxidation states. It is a characteristic of the ligands that they can stabilize low oxidation states. This property is associated with the fact

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[9] V. Balzani *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 55.

[10] A. Harada and S. Takahashi, *J. Chem. Soc. Chem. Commun.*, **1986,** 1229.

that in addition to lone pairs, these ligands possess *vacant π orbitals.* These vacant orbitals accept electron density from filled metal orbitals to form a type of π bonding that supplements the σ bonding arising from lone-pair donation; high electron density on the metal atom—of necessity in low oxidation states—thus can be delocalized onto the ligands. The ability of ligands to accept electron density into low-lying empty π orbitals can be called π *acidity,* the word "acidity" being used in the Lewis sense.

There are many unsaturated organic molecules and ions that are also capable of forming complexes with transition metals in low oxidation states, and these are called π *complexes.* There is a qualitative difference from π-acid ligands. The latter form bonds to the metal involving σ orbitals and π orbitals whose nodal planes include the axis of the σ bond. For the π-complexing ligands such as alkenes, arenes, and allyl groups, *both* the donation and back-acceptance (see next section) of electron density by the ligand are accomplished using ligand π orbitals. The metal is thus out of the molecular plane of the ligand, whereas with π-acid ligands the metal atom lies along the axes of the linear ligands or in the plane of planar ones.

In a third class of ligand that involves π bonding there are metal-oxygen or metal-nitrogen multiple bonds, as in $O{=}VCl_3$, MnO_4^-, and $N{\equiv}OsO_3^-$. Here the electron flow is in the opposite sense to that in the bonding of π-acid ligands (i.e., from *p* orbitals on O or N to the metal *d* orbitals).

We now survey the main classes of ligands that form π bonds to metal atoms. The chemical properties of metal carbonyls and metal complexes with the other π-bonding ligands will be presented in Chapter 22 and in sections dealing with the chemistry of NO, phosphorus (III) compounds, and so on.

2-8. π-Acid Ligands: CO as the Prototype

Ligands capable of accepting an appreciable amount of π-electron density, from the metal atoms into empty π or π* orbitals of their own are referred to as π-acceptor or π-acid ligands. Of these, carbon monoxide is the most important and the most extensively studied. We shall discuss the principal way in which it forms bonds to metals, namely, in a linear M—C—O fashion in detail here. In Chapter 22, the chemistry of metal carbonyls as a class (including the other forms of bonding in which CO engages) will be discussed. In Section 2-9 the way in which some similar ligands (such as RNC, N_2, NO) function as π-acid ligands will be compared with the behavior of CO.

The way in which CO (and many other π-acid ligands similarly) engages in bonding to a metal atom may be stated as follows:

1. Overlap of a filled carbon σ orbital with a σ-type orbital on the metal atom as in Fig. 2-6a. Electron flow C → M in such a dative overlap would lead to an unacceptable concentration of electron density on the metal atom when the latter is not a +2 or more highly charged ion. The metal therefore attempts to reduce this charge (Pauling's electroneutrality principle) by push-

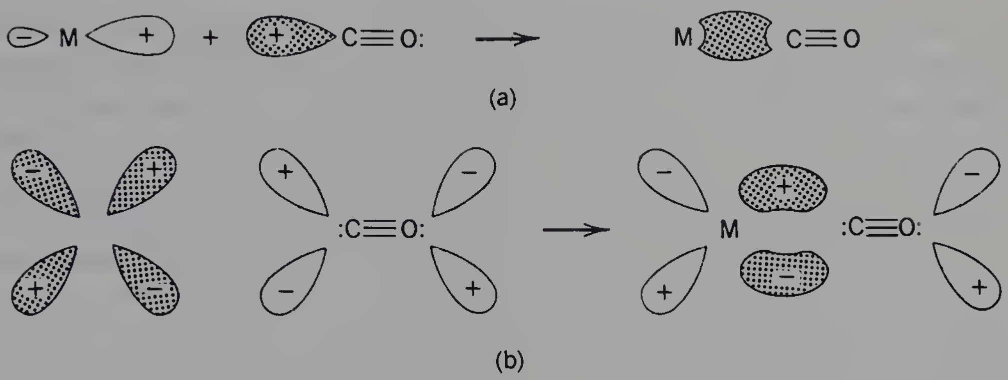

FIG. 2-6. (a) The formation of the metal ← carbon σ bond using an unshared pair on the C atom. (b) The formation of the metal → carbon π bond. The other orbitals on the CO are omitted for clarity.

ing electrons back to the ligand. This of course is possible *only* if the ligand has suitable acceptor orbitals.

2. A second dative overlap of a filled $d\pi$ or hybrid $dp\pi$ metal orbital with the empty, $p\pi$ orbital on carbon monoxide, which can act as a receptor of electron density (Fig. 2-6b).

This bonding mechanism is *synergic,* since the drift of metal electrons, referred to as "back-bonding", into CO orbitals, will tend to make the CO as a whole negative, hence to increase its basicity via the σ orbital of carbon; at the same time the drift of electrons to the metal in the σ bond tends to make the CO positive, thus enhancing the acceptor strength of the π orbitals. Thus up to a point the effects of σ-bond formation strengthen the π bonding, and vice versa. It may be noted here that dipole moment studies indicate that the moment of an M—C bond is only very low, about 0.5 D, suggesting a close approach to electroneutrality.

There have been many efforts to provide a detailed accounting of the relative importance of σ and π components of the bonding in metal carbonyls by means of molecular orbital calculations.[11] However, even for the simplest molecules, namely, $M(CO)_x$ ($x = 4, 5, 6$), it is not feasible to avoid making some important approximations, whose final effects on the results are uncertain. Hence, it is probably wiser to rely primarily on experimental evidence in attempting to understand the bonding in metal carbonyls and related complexes of π-acid ligands.

Two important and broadly useful lines of physical evidence showing the multiple nature of M—CO bonds are bond lengths and vibrational spectra. According to the preceding description of the bonding, as the extent of back-donation from M to CO increases, the M—C bond becomes stronger and the C≡O bond becomes weaker. Thus, the multiple bonding should be evidenced by shorter M—C and longer C—O bonds as compared to M—C single bonds

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[11] C. W. Bauschlicher, Jr., and P. S. Bagus, *J. Chem. Phys.*, 1984, **81,** 5889.

and $C{\equiv}O$ triple bonds, respectively. Actually very little information can be obtained from the CO bond lengths, because in the range of bond orders (2–3) concerned, CO bond length is relatively insensitive to bond order. The bond length in CO itself is 1.128 Å, while the bond lengths in metal carbonyl molecules are ~1.15 Å, a shift in the proper direction but of little quantitative significance owing to its small magnitude and the uncertainties (~0.02 Å) in the individual distances. For M—C distances, the sensitivity to bond order in the range concerned (1–2) is relatively high, probably ~0.3 to 0.4 Å per unit of bond order, and good evidence for multiple bonding can therefore be expected from such data. To do this we measure the lengths of M—CO bonds in the same molecule in which some other bond, M—X exists, such that this bond must be single. Then, using the known covalent radius for X, estimating the single bond covalent radius of C to be 0.70 Å when an *sp* hybrid orbital is used (the greater *s* character makes this ~0.07 Å shorter than that for sp^3 carbon), the length for a single M—CO bond *in this molecule* can be estimated and compared with the observed value.

Figure 2-7 shows some substitution products of $Cr(CO)_6$ in which three or four CO groups have been replaced by ligands such as aliphatic amine nitrogen, which has no capacity to compete with CO trans to it for π bonding or PH_3, which has very little capacity to do so. We see that in such cases the remaining CO groups have even shorter Cr—C bonds because of even more extensive development of Cr—C π-back-bonding. The shortening is greater in (b) than in (c), since there is slight π bonding to the phosphorus atoms of PH_3. The shortening is also greater in (d) than in (c) because there are only two CO groups in (d) to compete for the available $d\pi$ electrons of the chromium atom.

From the vibrational spectra of metal carbonyls, it is also possible to infer the existence and extent of M—C multiple bonding. This is most easily done by studying the CO stretching frequencies rather than the MC stretching frequencies, since the former give rise to strong sharp bands, well separated from all other vibrational modes of the molecules. The MC stretching frequencies, on the other hand, are in the same range with other types of vibration (e.g., MCO bends); therefore assignments are not easy to make, nor are the so-called MC stretching modes actually pure MC stretching motions. The inferring of M—C bond orders from the behavior of C—O vibra-

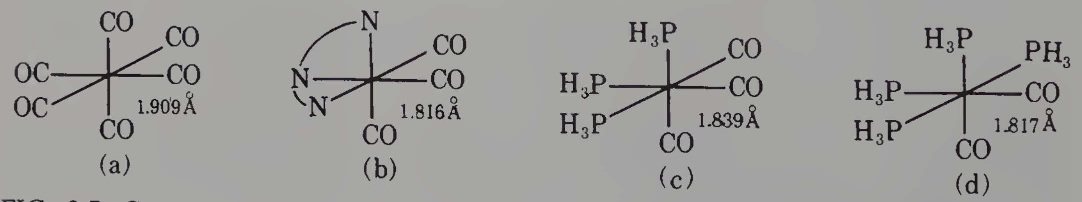

FIG. 2-7. Cr—C bond distances in (a) $Cr(CO)_6$, (b) *fac*-$[H_2N(CH_2)_2NH(CH_2)NH_2]Cr(CO)_3$, (c) *fac*-$(PH_3)_3Cr(CO)_3$, and (d) *cis*-$(PH_3)_4Cr(CO)_2$. [Data for (b) are from F. A. Cotton and D. C. Richardson, *Inorg. Chem.* 1966, **5,** 1851. Data for (a), (c), and (d) are from G. Huttner and S. Schelle, *J. Crystallogr. Mol. Struct.,* 1971, **1,** 69.]

tions depends on the assumption that the valence of C is constant, so that a given increase in the M—C bond order must cause an equal decrease in the C—O bond order; this, in turn, will cause a drop in the CO vibrational frequency.

From the direct comparison of CO stretching frequencies in carbonyl molecules with the stretching frequency of CO itself, certain useful qualitative conclusions can be drawn. The CO molecule has a stretching frequency of 2143 cm^{-1}. Terminal CO groups in neutral metal carbonyl molecules are found in the range 2125 to 1850 cm^{-1}, showing the reduction in CO bond orders. Moreover, when changes are made that should increase the extent of M—C back-bonding, the CO frequencies are shifted to even lower values. Thus if some CO groups are replaced by ligands with low or negligible back-accepting ability, those CO groups that remain must accept $d\pi$ electrons from the metal to a greater extent to prevent the accumulation of negative charge on the metal atom. Thus the frequencies for $Cr(CO)_6$ are ~2100, 2000, and 1985 cm^{-1} (exact values vary with phase and solvent) whereas, when three CO's are replaced by amine groups that have essentially no ability to back-accept, as $Crdien(CO)_3$ (Fig. 2-7b), there are two CO stretching modes with frequencies of ~1900 and 1760 cm^{-1}. Similarly, when we go from $Cr(CO)_6$ to the isoelectronic $V(CO)_6^-$, when more negative charge must be taken from the metal atom, a band is found at ~1860 cm^{-1} corresponding to the one found at ~2000 cm^{-1} in $Cr(CO)_6$. A series of these isoelectronic species illustrating this trend, with their infrared-active CO stretching frequencies (cm^{-1}) is $Ni(CO)_4$ (~2060); $Co(CO)_4^-$ (~1890); $Fe(CO)_4^{2-}$ (~1790). Conversely, a change that would tend to inhibit the shift of electrons from metal to CO π orbitals, such as placing a positive charge on the metal, should cause the CO frequencies to *rise,* and this effect has been observed in several cases, the following being representative:

$Mn(CO)_6^+$,~2090	$Mndien(CO)_3^+$,~2020,~1900
$Cr(CO)_6$,~2000	$Crdien(CO)_3$,~1900,~1760
$V(CO)_6^-$, ~1860	

To obtain semiquantitative estimates of M—C π bonding from vibrational frequencies, it is first necessary to carry out an approximate dynamical analysis of the CO stretching modes, thus to derive force constants for the CO groups. This procedure is discussed in Section 22-5.

The type of structural and spectroscopic evidence just noted, while persuasive, is nonetheless rather indirect. More direct evidence for M—CO π bonding has recently been obtained by photoelectron spectroscopy.[12] For $Cr(CO)_6$ and $W(CO)_6$ the photoionization of one of those electrons that must be responsible for whatever M—CO π bonding exists was carried out and the effect of removing such an electron on the frequency of the totally sym-

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[12] J. L. Hubbard and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1982, **104,** 2132.

metric M—C stretching vibration in the resulting $M(CO)_6^+$ ion measured. The frequency of this vibration was, in each case, found to be significantly lower than that of the corresponding vibration in the neutral $M(CO)_6$ molecule, that is, by 10% for $W(CO)_6^+$ and 15% for $Cr(CO)_6^+$. This unequivocally shows that the orbitals from which the electrons have been removed contribute importantly to the M—C bond strengths. By a further analysis of these same data it was shown that the loss of one such electron causes increases of ~0.14 and 0.10 Å in the Cr—C and W—C distances, respectively.

2-9. Other π-Acid Ligands

We shall specifically mention here the following CO-like π-acid ligands: RNC, N_2, CS, NO, and NS. The first three are isoelectronic with CO, while NO and NS have one more electron. The *chemistry* of compounds that contain these ligands is discussed in later sections (RNC and CS in Chapter 8; N_2, NO, and NS in Chapter 10) and we are concerned here only with discussing their ability to serve as π-acid ligands and how, in each case, it compares with that of CO.

Isocyanide Ligands. (See Section 8-11 for chemistry.) Isocyanides are capable of displaying as great π-acceptor capacity as CO when linked to a metal center capable of strong π donation, and this may be described using the same pattern of orbital overlaps as previously discussed for M—CO bonding. Both spectroscopic evidence (lowering of C—N stretching frequencies) and structural evidence [short M—C distances, such as 1.94 Å in $Cr(CNPh)_6$] demonstrate this. The important difference between CO and RNC is that the latter is not an *obligatory* π acid. That is, while CO is such a weak Lewis base that the stability of M—CO bonds requires the synergic participation of both σ donation and π acceptance, isocyanides are good Lewis bases and can form bonds to higher-valent metal ions where there is essentially only σ donation involved.

It may be noted here that the cyanide ion (CN^-) is also isoelectronic with CO and RNC, but its capacity to serve as a π acid is much lower and from the point of view of bonding it is perhaps best regarded as a pseudohalide rather than as a π-acid ligand. See Section 8-10 for the chemistry of CN^-.

Dinitrogen. Although N_2 is isoelectronic with CO and RNC, and isosteric with the former, it is far more inert and the first dinitrogen complex, $[Ru(NH_3)_5(N_2)]^{2+}$ was discovered only in 1965. Dinitrogen can be bound to metal atoms only in the presence of other ligands; there are no homoleptic complexes analogous to those formed by CO or RNC.

The bonding in *linear M—N—N groups* is qualitatively similar to that in terminal M—CO groups; the same two basic components, $M \leftarrow N_2$ σ donation and $M \rightarrow N_2$ π acceptance, are involved. The major quantitative differences, which account for the lower stability of N_2 complexes, appear to arise from small differences in the energies of the MO's of CO and N_2. For CO the σ-donor orbital is weakly antibonding, whereas the corresponding orbital for N_2 is of bonding character. Thus N_2 is a significantly poorer σ donor than is

CO. Now it is observed that in pairs of N_2 and CO complexes where the metal and other ligands are identical, the fractional lowerings of N_2 and CO frequencies are nearly identical. For the CO complexes, weakening of the CO bond, insofar as electronic factors are concerned, is due entirely to back-donation from metal $d\pi$ orbitals to CO π^* orbitals, with the σ donation slightly canceling some of this effect. For N_2 complexes, on the other hand, N≡N bond weakening results from both σ donation and π back-acceptance. The very similar changes in stretching frequencies for these two ligands suggest then that N_2 is weaker than CO in both its σ-donor and π-acceptor functions. This in turn would account for the poor stability of N_2 complexes in general. Terminal dinitrogen compounds have N—N stretching frequencies in the region 1930 to 2230 cm^{-1} (N_2 has ν = 2331 cm^{-1}). For discussion of chemistry, see Section 10-9.

The CS Ligand. Although the CS molecule cannot be isolated, complexes containing the M—CS unit are known (cf. Section 8-13). The synergic σ/π interactions in M—CS units are similar to those in M—CO units, but perhaps somewhat stronger.

The NO Ligand. The NO molecule is closely akin to the CO molecule except that it contains one more electron, which resides in a π^* orbital. Loss of this electron gives NO^+ which is isoelectronic with CO.

Just as the CO group reacts with a metal atom that presents an empty σ orbital and a pair of filled $d\pi$ orbitals, as illustrated in Fig. 2-6, to give a linear MCO grouping with a C → M σ bond and a significant degree of M → C π bonding, so the NO group engages in a structurally and electronically analogous reaction with a metal atom that may be considered, at least formally, to present an empty σ orbital and a pair of $d\pi$ orbitals containing only three electrons. The full set of four electrons for the $Md\pi \rightarrow \pi^*(NO)$ interactions is thus made up of three electrons from M and one from NO. In effect, NO contributes three electrons to the total bonding configuration under circumstances where CO contributes only two. Thus for purposes of formal electron "bookkeeping," the ligand NO can be regarded as a three-electron donor in the same sense as the ligand CO is considered a two-electron donor. This leads to the following very useful general rules concerning stoichiometry, which may be applied without specifically allocating the difference in the number of electrons to any particular (i.e., σ or π) orbitals:

1. Compounds isoelectronic with one containing an $M(CO)_n$ grouping are those containing $M'(CO)_{n-1}(NO)$, $M''(CO)_{n-2}(NO)_2$, and so on, where M′, M″, and so on, have atomic numbers that are 1, 2, . . . , and so on, <M. Some examples are (η-C_5H_5)CuCO, (η-C_5H_5)NiNO; $Ni(CO)_4$, $Co(CO)_3NO$, $Fe(CO)_2(NO)_2$, $Mn(CO)(NO)_3$; $Fe(CO)_5$, $Mn(CO)_4NO$.

2. Three CO groups can be replaced by two NO groups. Examples of pairs of compounds so related are

$Fe(CO)_5$	$Fe(CO)_2(NO)_2$
$Mn(CO)_4NO$	$Mn(CO)(NO)_3$
$Cr(CO)_6$	$Cr(NO)_4$

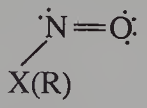
It may be noted that $Cr(NO)_4$ is the only known homoleptic metal nitrosyl complex. It is isoelectronic with $Ni(CO)_4$ and similarly has a tetrahedral structure, with a very short Cr—N distance (1.763 Å).[13] Claims for $Co(NO)_3$, $Fe(NO)_4$, and $Ru(NO)_4$ have never been confirmed.

It should be noted that the designation "linear MNO group" does not disallow a small amount of bending in cases where the group is not in an axially symmetric environment, just as with terminal MCO groups. Thus MNO angles of 161 to 175° may be found in "linear" MNO groups. Truly "bent MNO groups" have angles of 120 to 140°.

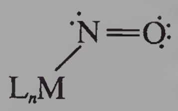
In compounds containing both MCO and linear MNO groups, the M—C and M—N bond lengths differ by a fairly constant amount, ~0.07 Å, approximately equal to the expected difference in the C and N radii, and suggest that under comparable circumstances M—CO and M—NO bonds are typically about equally strong. In a chemical sense the M—N bonds appear to be stronger, since substitution reactions on mixed carbonyl nitrosyl compounds typically result in displacement of CO in preference to NO. For example, $Co(CO)_3NO$ reacts with a variety of R_3P, X_3P, amine, and RNC compounds, invariably to yield the $Co(CO)_2(NO)L$ product.

The NO vibration frequencies for linear MNO groups substantiate the idea of extensive M—N π bonding, leading to appreciable population of NO π^* orbitals. Both the NO and O_2^+ species contain one π^* electron and their stretching frequencies are 1860 and 1876 cm^{-}, respectively. Thus the observed frequencies in the range 1800–1900 cm^{-1}, which are typical of linear MNO groups in molecules with small or zero charge, indicate the presence of approximately one electron pair shared between metal $d\pi$ and NO π^* orbitals.

Since nitrosyl halides (Section 10-8) and nitroso alkanes are bent, similar metal complexes can be anticipated:



and



A typical example is $IrCl_2(NO)(PPh_3)_2$ where the MNO angle is 123°. The NO here is best regarded as a 1*e* donor or as NO^-; π bonding is not involved. Bridging NO groups, where NO can be regarded as a 3*e* donor, are also known.

These aspects and reactions of coordinated NO are discussed in more detail in Section 10-10.

The sulfur analogues with M—NS bonds are discussed in Section 10-10.

2-10. π-Acid Ligands: Trivalent Phosphorus Compounds

Compounds of the type PX_3 (as well as AsX_3, SbX_3, SX_2, and SeX_2 species), especially when X is relatively electronegative, such as Ph, OR, Cl, or F, are important π-bonding ligands. This is particularly true of PF_3 which forms

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[13] K. Hedberg *et al., Inorg. Chem.*, 1985, **24**, 2776.

[14] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1985, **29**, 42.

many compounds comparable to those of CO,[14] for example, $Ni(PF_3)_4$ and $Cr(PF_3)_6$. Tertiary phosphines and phosphites, however, are also much better Lewis bases than CO and can form many complexes where π acidity plays little or no role. This is observed with the phosphine complexes of the early transition metals and with metal atoms of any kind in their higher oxidation states. In compounds such as $NbBr_4(PMe_2Ph)_3$ or $PtCl_4(PMePh_2)_2$ the M—P distances show no evidence of significant π bonding. Phosphorus ligands are discussed in Section 11-18.

In almost any CO-containing molecule, one or more CO groups can be replaced by a PX_3 or similar ligand. The ability of PR_3 ligands (R = Me, Et, or Bu) to compete with CO groups for metal $d\pi$ electrons can be studied in detail by photoelectron spectroscopy[15] and vibrational spectroscopy in $Mo(CO)_n(PR_3)_{6-n}$ species and similar ones. The significant σ-donor ability[16] and steric requirements[17] of such ligands is also important in regard to the structures of $M(CO)_x(PR_3)_y$ type molecules.

While the occurrence of $M \rightarrow P$ dative π bonding is a generally acknowledged fact, the explanation for it entails controversy. The classical, and still widely credited, picture is that shown in Fig. 2-8, in which phosphorus specifically employs a pair of its d orbitals to accept metal electrons. However, it has been proposed, on the basis of quantum mechanical calculations that phosphorus p orbitals and the P—X σ^* orbitals may play a major role in accepting metal $d\pi$ electrons, even to the complete exclusion of the phosphorus $d\pi$ orbitals.[18a] Experimental evidence for or against such ideas is lacking. Rotation about the M—P bond with relatively small barriers (32–38 kJ mol^{-1}) can be shown by nmr methods.[18b]

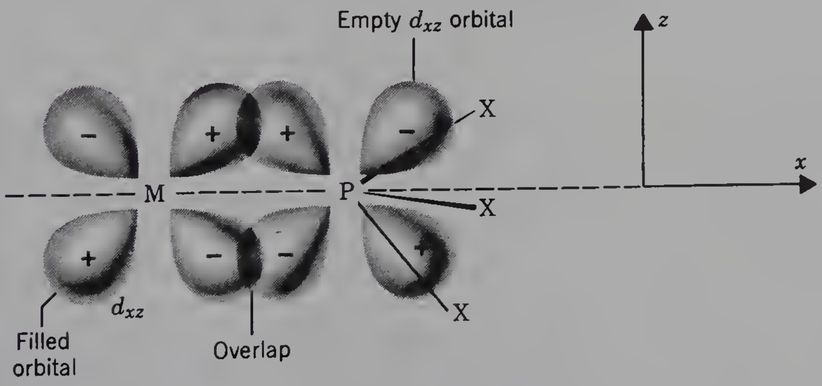

FIG. 2-8. The back-bonding from a filled metal d orbital to an empty phosphorus $3d$ orbital in the PX_3 ligand taking the internuclear axis as the x axis. An exactly similar overlap occurs in the xy plane using the d_{xy} orbitals.

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[15] B. E. Bursten *et al.*, *Inorg. Chem.*, 1984, **23,** 4361.

[16] F. W. B. Einstein *et al.*, *Inorg. Chem.*, 1985, **24,** 2777.

[17] F. A. Cotton *et al.*, *Inorg. Chem.*, 1982, **21,** 294.

[18a] W. C. Trogler *et al.*, *J. Am. Chem. Soc.*, 1983, **105,** 7033; D. S. Marynick, *J. Am. Chem. Soc.*, 1984, **106,** 4064; A. G. Orpen and N. G. Connelly, *J. Chem. Soc. Chem. Commun.*, **1985,** 1310; M. Braga, *Inorg. Chem.*, 1985, **24,** 2702.

[18b] G. Hunter *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987,** 1545.

Of course, the Lewis basicities of the PX_3 ligands vary considerably,[19] and not entirely predictably[20] with X. This must be taken into consideration because, as with other classes of ligands, the synergistic relationship between σ donation and π acceptance (regardless of the exact mechanism for the latter) is also a source of ambiguity in understanding this class of ligands.[21]

The extent of both donation from the lone pair on the P atom and back-donation depends on the nature of the groups attached to P. For PH_3 and $P(alkyl)_3$, π-acceptor ability is very low, but it becomes important with more electronegative groups. Analogous PX_3, AsX_3, and SbX_3 compounds differ very little, but the ligands having a nitrogen atom, which lacks π orbitals, cause significantly lower frequencies for the CO vibrations, as indicated by the CO stretching frequencies (cm^{-1}) in the following series of compounds:

$(PCl_3)_3Mo(CO)_3$	2040, 1991
$(AsCl_3)_3Mo(CO)_3$	2031, 1992
$(SbCl_3)_3Mo(CO)_3$	2045, 1991
dien $Mo(CO)_3$	1898, 1758

The pronounced effect of the electronegativity of the groups X is shown by the following CO stretching frequencies

$[(C_2H_5)_3P]_3Mo(CO)_3$	1937, 1841
$[(C_6H_5O)_3P]_3Mo(CO)_3$	1994, 1922
$[Cl_2(C_2H_5O)P]_3Mo(CO)_3$	2027, 1969
$(Cl_3P)_3Mo(CO)_3$	2040, 1991
$(F_3P)_3Mo(CO)_3$	2090, 2055

The most electronegative substituent, F in PF_3, will reduce very substantially the σ-donor character so that there will be less $P \rightarrow M$ electron transfer, and $Md\pi \rightarrow Pd\pi$ transfer should be aided. The result is that PF_3 and CO are quite comparable in their π-bonding capacity.

Attempts to order a large number of PX_3, AsX_3, and SbX_3 ligands according to their net π-accepting capacity have been made using $LNi(CO)_3$ compounds, and to a lesser extent others such as $LCr(CO)_5$. Both the CO stretching frequencies and the ^{13}C chemical shifts of the CO groups have been used as the indicative experimental parameter[22] and the two orderings are in general agreement. Based on these data some of the more common phosphorus li-

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[19] T. T. Derencsengi *Inorg. Chem.*, 1981, **20,** 665.

[20] G. M. Bancroft *et al., Inorg. Chem.*, 1986, **25,** 3675.

[21] W. P. Giering *et al., Organometallics,* 1985, **4,** 1981; see also R. V. Honeychuck and W. H. Hersh, *Inorg. Chem.*, 1987, **26,** 1826.

[22] G. M. Bodner *et al., Inorg. Chem.*, 1980, **19,** 1951; T. Bartik *et al., J. Organomet. Chem.*, 1984, **272,** 29.

gands come out in the following order (As and Sb ligands come very close to the corresponding P ligands):

$$PF_3 > PCl_3 > P(OAr)_3 > P(OR)_3 > P(Ar)_3 > PR(Ar)_2 > PR_2Ar > PR_3$$

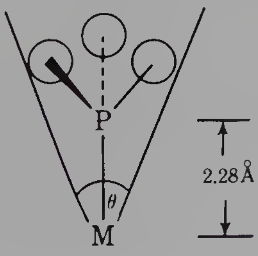
There is also structural evidence to support this general order.[23] For example, in $(PhO)_3PCr(CO)_5$ the P—Cr bond is 0.11 Å shorter than that in $Ph_3PCr(CO)_5$.

Of at least as great importance to the chemistry of PX_3 compounds as the electronic factors are *steric factors.*[24] Indeed these may be more important or even dominant in determining the stereochemistries and structures of compounds. Steric factors also affect rates and equilibria of dissociation reactions such as eq. 2-2 and the propensity of phosphine complexes to undergo oxidative–addition reactions, or form olefin complexes.[25]

$$Pd(PR_3)_4 \underset{+PR_3}{\overset{-PR_3}{\rightleftharpoons}} Pd(PR_3)_3 \underset{+PR_3}{\overset{-PR_3}{\rightleftharpoons}} Pd(PR_3)_2 \qquad (2\text{-}2)$$

The stereochemistry of phosphine ligands is the prime factor in many highly selective catalytic reactions of phosphine complexes, such as hydroformylation and asymmetric hydrogenation (Chapter 28).

The steric requirement of a PX_3 ligand is usually expressed by Tolman's cone angle, θ, as defined below. The cone in question is one that can just enclose the van der Waals surface of all ligand atoms over all rotational orientations about the M—P bond.* Triphenylphosphine has $\theta = 145°$ and $P(OCH_3)_3$ has $\theta = 107 \pm 2°$. It might have been expected that compounds with smaller cone angles would be better ligands, but since such compounds are stronger bases, it is not always easy to distinguish steric from electronic factors although some progress in this respect is being made[24]. However, increasing the cone angle by having bulky groups tends to favor (*a*) lower coordination numbers, (*b*) the formation of less sterically crowded isomers, and (*c*) increased rates and equilibria in dissociative reactions. An example



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[23] J. L. Atwood *et al., Organometallics,* 1985, **4,** 867.

[24] C. A. Tolman, *Chem. Rev.,* 1977, **77,** 313; see also W. P. Giering *et al., Organometallics,* 1987, **6,** 650 for discussion of steric and σ and π electronic effects and their separation.

[25] C. A. Tolman *et al., Organometallics,* 1983, **2,** 1391.

*More sophisticated definitions have been suggested but offer little practical advantage. See, for example, T. Bartik *et al., J. Organomet. Chem.,* 1984, **272,** 29.

of the latter effect is provided by the reactions

$$NiL_4 \overset{K}{=} NiL_3 + L$$

where K varies from >1 for L = PPh_3 (θ = 145°) to $<10^{-10}$ for L = $P(OEt)_3$ (θ = 109°).

2-11. Multiple Bonds from Ligands to Metals

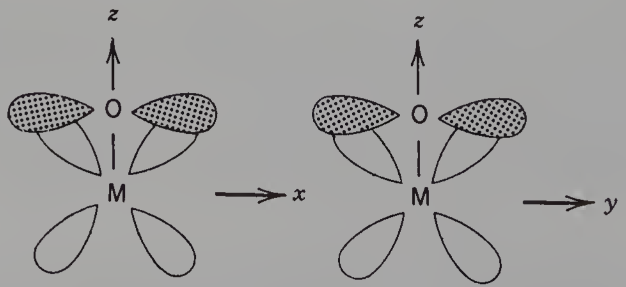
The concept of metal-ligand bonds as simple two-electron L → M donor bonds has broad applicability. As noted in Sections 2-8 through 2-10 a significant amount of M → L π bonding must be superimposed upon this for M—CO, M—NO, and other related ligands. Thus, these metal-ligand bonds have partial π character and bond orders >1 (but <1.5). However, there are many cases in which metal atoms form full double and triple bonds, either to nonmetal atoms (ligands) or to other metal atoms. The various multiple metal-metal bonds are discussed in Chapter 23.

We are concerned here with bonds of the types[26]

$$M{=}O \qquad M{=}S \qquad M{=}CR_2 \qquad M{=}NR \qquad M{\equiv}CR \qquad M{\equiv}N$$

as well as some M—X—M systems where multiple bond character is present in the M—X—M bonds. In all of these cases, overlap between ligand atom $p\pi$ orbitals and metal atom $d\pi$ orbitals must be invoked to account for bonding in addition to the M—X σ bonds.

M═O and M$\overset{\cdots}{—}$O$\overset{\cdots}{—}$M Bonds. The M═O bonds are extremely numerous. In general, the distances are very short, namely, 1.5 to 1.8 Å depending on oxidation numbers, other ligands, and so on. In many cases the bond order is probably significantly >2 because there are two filled $p\pi$ orbitals on the oxygen atom, both of which can engage in bonding to appropriately directed $d\pi$ orbitals on the metal atom, as shown in (2-XXV). There is no reason why, in many cases, that both of these interactions cannot proceed to the point where the sum of the two partial dative π bonds exceeds the bonding that would be provided by just one such interaction at its full extent. Thus, when a double bond, M═O is written, this should be regarded as a formalism and not an accurate specification of bond order.



(2-XXV)

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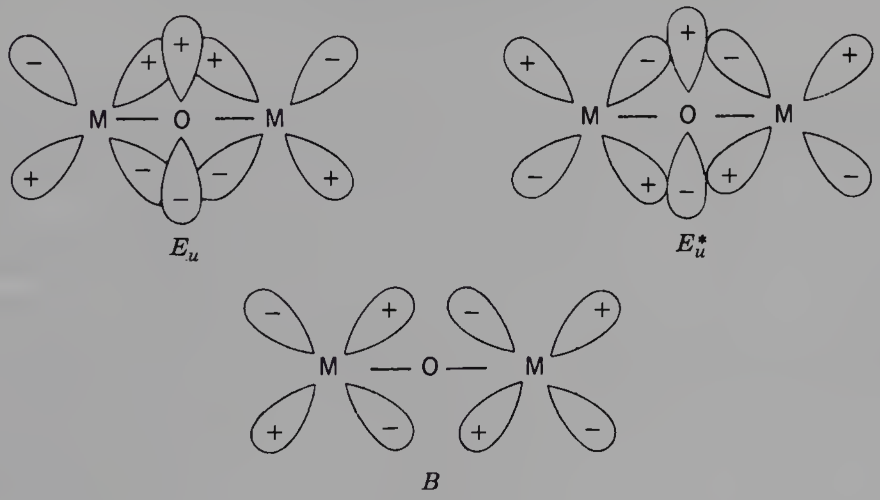
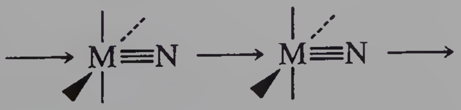
[26] W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 56.

There are also many examples of linear M—O—M units, and in these more delocalized π bonding occurs. The $[Cl_5MOMCl_5]^{n-}$ ions provide straightforward examples.[27] It may be assumed that by using a pair of *sp* hybrid orbitals on the oxygen atom a linear pair of M—O—M σ bonds is formed. There are then two orthogonal, occupied *p*π orbitals on the oxygen atom that can interact with suitable metal *d*π orbitals. Now, however, there is a total of four such *d*π orbitals and two sets of π interactions (2-XXVI) (one in the *xz* plane and the other just like it in the *yz* plane) will be established. With both of the two components of the E_u orbital occupied, there is a total of four σ electrons and four π electrons, and thus each M—O bond may be assigned (formally) a bond order of 2. This is consistent with the occurrence of M—O distances in the range of 1.75 to 1.90 Å for various M—O—M systems.[27]

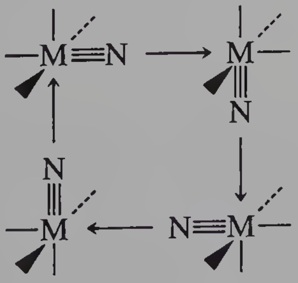


(2-XXVI)

Metal–Nitrogen Multiple Bonds.[28] As with oxygen there are two types, M≡N and M=N=M, but the former show a pronounced tendency towards association, either into linear chains (2-XXVII) or cycles (2-XVIII) as found in $MoNCl_3$. For discussion of chemistry, see Section 10-18.



(2-XXVII)



(2-XXVIII)

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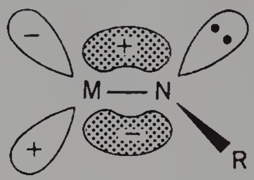
[27] F. A. Cotton and R. C. Najjar, *Inorg. Chem.*, 1981, **20,** 1866.

[28] R. Hoffmann *et al., J. Am. Chem. Soc.*, 1986, **108,** 5381.

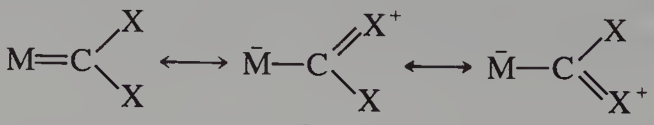
The types of orbital overlaps entailed in the formation of $M\equiv N$ and $M{=}N{=}M$ bonds are entirely analogous to those already discussed for the oxo cases. As full triple bonds, the $M\equiv N$ linkages are generally very short (e.g., 1.66 Å in $MoCl_4N^-$, and 1.58 Å in $ReCl_4N$), but the bonds ion $M{=}N{=}M$ systems are longer (~1.85 Å).

Metal to nitrogen double bonds[29] are found in the $M{=}NR$ compounds, sometimes called nitrenes (by analogy to carbenes), but better designated metal imides. Here the bonding can be described in very conventional terms with one σ bond, one π bond and a lone pair of electrons, as in (2-XXIX).



(2 = XXIX)

$M{=}CR_2$ and $M\equiv CR$ bonds. These play an enormous role in organometallic chemistry and will be discussed at length in Chapter 25. The nature of the M to C bonding is very much dependent on the nature of M and R.[30] At one extreme there are compounds in which M is in a high valence state and the R group(s) not of π-donor character. In these cases, the bonds are comparable to those just discussed for $M{=}NR$ and $M\equiv N$. For these types of compounds, the terms *alkylidene* ($M{=}CR_2$) and *alkylidyne* ($M\equiv CR$) have been favored. On the other hand, when the metal is in a low valence state and the substituents on carbon are π donors, the M—C bonds are *not* full double or triple bonds and the systems are rendered stable by the migration of charge from the substituents (such as OR or NR) on the carbon atom, as shown in resonance terms in (2-XXX). In these types of compounds it is customary to use the terms *carbene complex* and *carbyne complex*. The chemistry is qualitatively different for the two classes of each type (i.e., MCR_2 and MCR) of compound, as will be discussed in Chapter 25.



(2-XXX)

Heavier Ligand Atoms. We have just discussed the formation of M—X multiple bonds for the principal cases where X is an element from the first short period, namely, C, N, or O. It is to be noted that recently analogues for some of these, in which the heavier elements, Si, Ge, P, As, S, and Se occur, have been prepared, and doubtless this development will continue rapidly. As a first approximation the M—X bonding to the heavier X atoms

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[29] W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.

[30] E. A. Carter and W. A. Goddard, III, *J. Am. Chem. Soc.*, 1986, **108**, 4746.

can be described in the same ways as for the light X atoms, but it is possible that outer *d* orbitals may make some contribution for the heavier X atoms. The greater size of the heavier elements may also be important in some cases. Whatever the reasons, compounds such as linear $(C_5Me_5)(CO)_2Mn{=}Ge{=}Mn(CO)_2(C_5Me_5)$ and bent $(C_5Me_5)(CO)_2Mn{=}Te{=}Mn(CO)_2(C_5Me_5)$ have no C or O analogues; M=C=M bonds are found in some porphyrin complexes however (Section 8-9).

Another type of linkage formed only by the heavier elements is displayed by the compounds $Cp(CO)_2CrXCr(CO)_2Cp$, where X = S, Se but not O. The very short bonds (e.g., 2.20 Å for Cr—Se), together with other considerations, have been taken to imply that Cr≡X triple bonds exist.

π COMPLEXES OF UNSATURATED ORGANIC MOLECULES

Molecules that have multiple bonds (C=C, C≡C, C=O, C=N, S=O, N=O, etc.) can form what are called π *complexes* with transition metals. The chemistry of these is discussed in detail in Chapter 26.

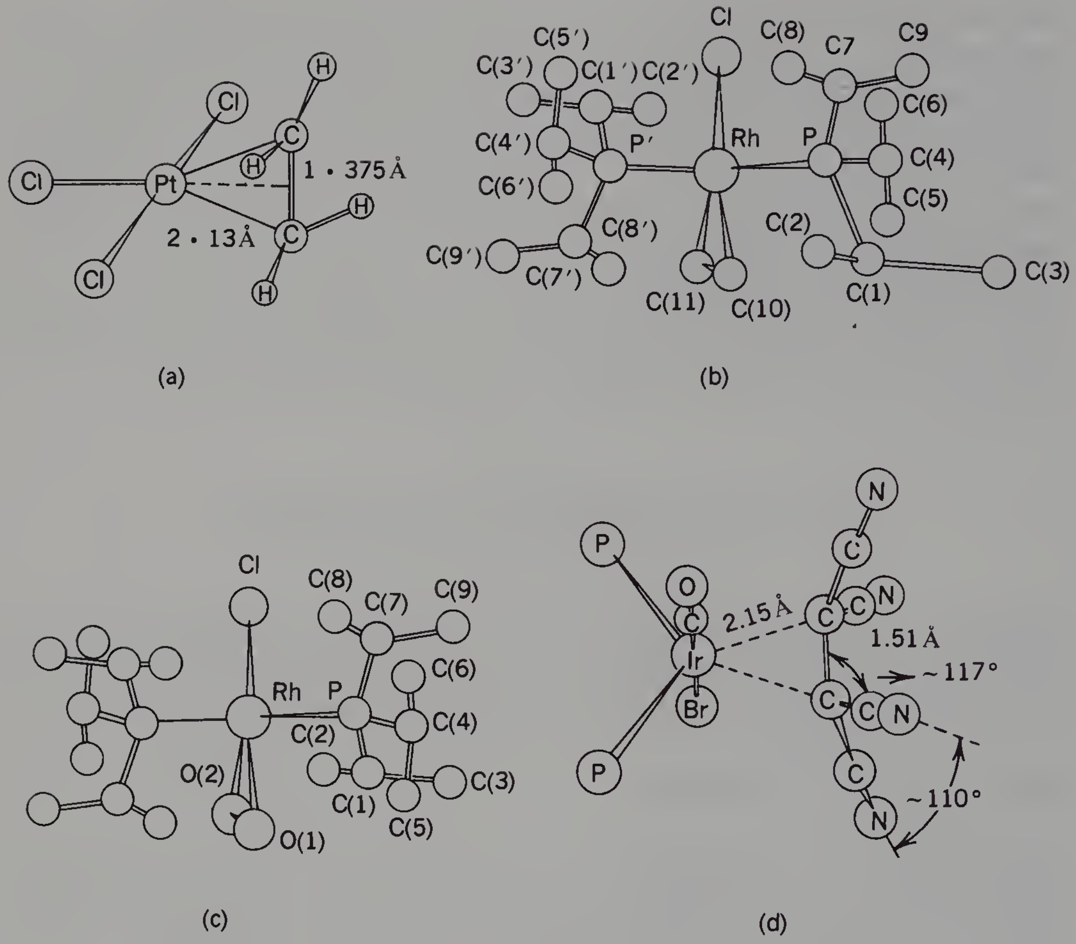
2-12. Alkenes and Alkynes

The most important π complexes are those of compounds with C=C bonds. The earliest known organotransition metal complex was discovered by W. C. Zeise in Copenhagen in about 1827, but the true constitution was not recognized until the 1950s. Zeise's salt, $K[Pt(C_2H_4)Cl_3]$, has ethylene bound to Pt as shown in Fig. 2-9a.

The key point is that the C=C axis of the coordinated alkene is perpendicular to one of the expected bond directions from the metal. The expected line of a bond orbital from the metal strikes the C=C bond at its midpoint (though for unsymmetrical alkenes, this need *not* be so).

Figure 2-9 shows several other examples of olefin complexes as well as a comparable dioxygen complex.

The most generally useful description of this type of bonding was developed for copper–alkene complexes by M. J. S. Dewar and later extended to other transition metals. Figure 2-10 illustrates the assumption that as with other π-bonding ligands like CO, there are *two* components to the total bonding: (*a*) overlap of the π-electron density of the olefin with a σ-type acceptor orbital on the metal atom and (*b*) a "back-bond" resulting from flow of electron density from filled metal d_{xz} or other $d\pi$–$p\pi$ hybrid orbitals into *antibonding* orbitals on the carbon atoms. This view is thus similar to that discussed for the bonding of carbon monoxide and similar weakly basic ligands and implies the retention of appreciable "double-bond" character in the olefin. Of course, the donation of π-bonding electrons to the metal σ orbital and the introduction of electrons into the π-antibonding orbital both weaken the π bonding in the



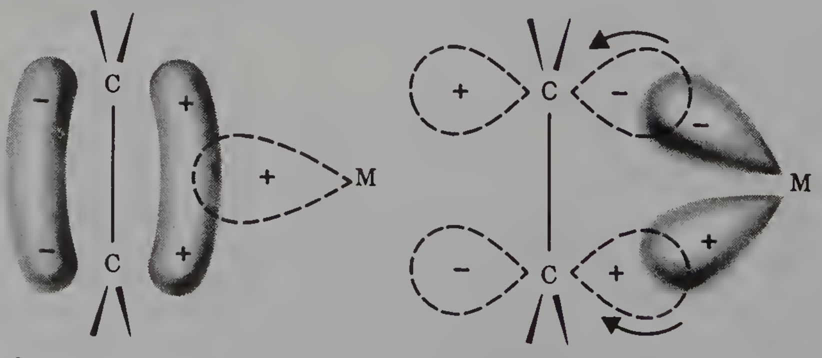
(a)

(b)

(c)

(d)

FIG. 2-9. (a) The structure of the ion in Zeise's salt. (b,c) The structures of ethylene and oxygen complexes, *trans*-RhClL(PPr$_3$)$_2$. (d) The structure of the tetracyanoethylene complex IrBr(CO)[(CN)$_2$C=C(CN)$_2$](PPh$_3$)$_2$.



Donation from filled π orbitals to vacant metal orbital

Back-bonding from filled metal orbital to acceptor π^* orbitals

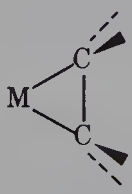
FIG. 2-10. The molecular orbital view of alkene–metal bonding according to Dewar.

olefin, and in every case except the anion of Zeise's salt there is significant lengthening of the olefin C—C bond.

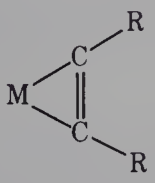
The important qualitative idea about metal–olefin bonding is that the bonding has dual character. There is donation of those electrons initially forming the C—C π bond into a metal orbital of suitable symmetry, and there is donation of electrons from filled metal orbitals of suitable symmetry back into the π-antibonding orbitals of the olefin. As in the CO case, the two components are synergically related. As one component increases, it tends to promote an increase in the other. On both theoretical and experimental grounds, it appears that the metal–alkene bond is essentially electroneutral, with donation and back-acceptance approximately balanced.

Although, as we have seen, the C—C axis of ethylene is perpendicular to the plane of the square coordination for Zeise's salt and other, similar complexes [Fig. 2-9(a) and (b)], this is not strongly demanded by the bonding. There is also a metal $d\pi$ orbital *in the plane,* and it too can interact with the olefin $p\pi^*$ orbital as shown in Fig. 2-10; the difference in stability between the perpendicular and in-plane orientations is thus not great on a bonding basis (although in-plane bonding is weaker) and may be mainly steric in origin. In any event, measurements of the barrier to rotation[31] of the olefin about an axis defined by a line from the metal atom to the midpoint of the olefin have given results of only 40–70 kJ mol^{-1} and there is one case where the in-plane orientation is found[32].

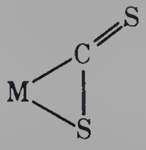
In complexes containing tetracyanoethylene (Fig. 2-9d) or $F_2C{=}CF_2$ the C—C bond is about as long as a normal single bond and the angles within the $C_2(CN)_4$ or C_2F_4 ligand suggest that the carbon atoms bound to the metal approach tetrahedral hybridization. Indeed, it is possible to formulate the bonding as involving two normal 2*c*-2*e* metal–carbon bonds in a metallacycle (2-XXXIa) with approximately sp^3 hybridized carbon. A number of other molecules that have multiple bonds and can be bound to metals in the η^2 fashion can be regarded as forming metallacycles (2-XXXIb) through (2-XXXIe).



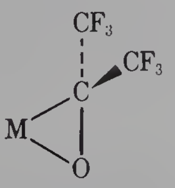
(2-XXXIa)



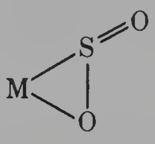
(2-XXXIb)



(2-XXXIc)



(2-XXXId)



(2-XXXIe)

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[31] S. Miya and K. Saito, *Inorg. Chem.*, 1981, **20,** 287.

[32] N. Kasai *et al.*, *J. Am. Chem. Soc.*, 1983, **105,** 2482; M. F. Rettig *et al.*, *Organometallics,* 1987, **6,** 1211.

Actually, the metallacycle view and the π-donor view are neither incompatible nor mutually exclusive but are complementary, with a smooth gradation of one description into the other. The one to be preferred in any given case depends on the extent to which the double bond of the ligand has been reduced to a single bond. From a formal point of view, however, the metallacycle view entails a problem with oxidation state. For example, a compound such as $Ni(C_2F_4)(CO)_3$ could be regarded as a nickel(II) rather than a nickel(0) complex. Clearly, in a compound such as $Pt(C_2H_4)_3$, it would be absurd to propose Pt^{VI}. It is best to regard molecules bound sideways as neutral ligands that do not alter the formal oxidation state.

Conjugated Alkenes. When two or more conjugated double bonds are engaged in bonding to a metal atom the interactions become more complex, though qualitatively the two types of basic, synergic components are involved. The case of the 1,3-butadiene unit is an important one and shows why it would be a drastic oversimplification to treat such cases as simply collections of separate monoolefin–metal interactions.

Two extreme formal representations of the bonding of 1,3-butadiene to a metal atom are possible (Fig. 2-11). The structure (b) would imply that bonds 1–2 and 3–4 should be longer than bond 2–3. In $C_4H_6Fe(CO)_3$ the bond lengths are approximately the same and $^{13}C—H$ coupling constants in the nmr spectra indicate that the hybridization at carbon still approximates to sp^2. However, in some other compounds of conjugated cyclic alkenes, the pattern is of the long–short–long type, indicating some contribution from this extreme structure.

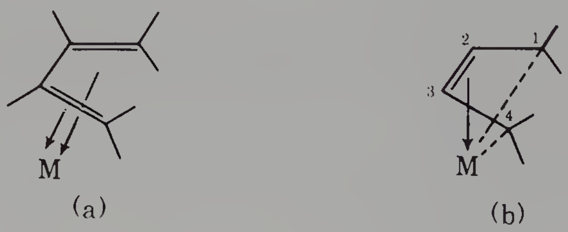


FIG. 2-11. Two extreme formal representations of the bonding of a 1,3-butadiene group to a metal atom: (a) implies that there are two more or less independent monoolefin metal interactions; (b) depicts σ bonds to C-1 and C-4 coupled with a monoolefin metal interaction to C-2 and C-3.

Alkynes. The presence of two mutually perpendicular π bonds in an alkyne makes for considerably more varied and complicated ligand behavior than that shown by alkenes. There is, of course, the simple use of one π bond and the associated π* orbital in exactly the same way as found in olefin complexes. This results in a lengthening of the C—C distance and a marked deviation from linearity. Typical results are shown schematically in Fig. 2-12(a).

An alkyne can also behave as a formal four-electron donor to one metal atom. In addition to the type of interaction just discussed, the other pair of π electrons may be partially donated to a metal $d\pi$ orbital lying perpendicular

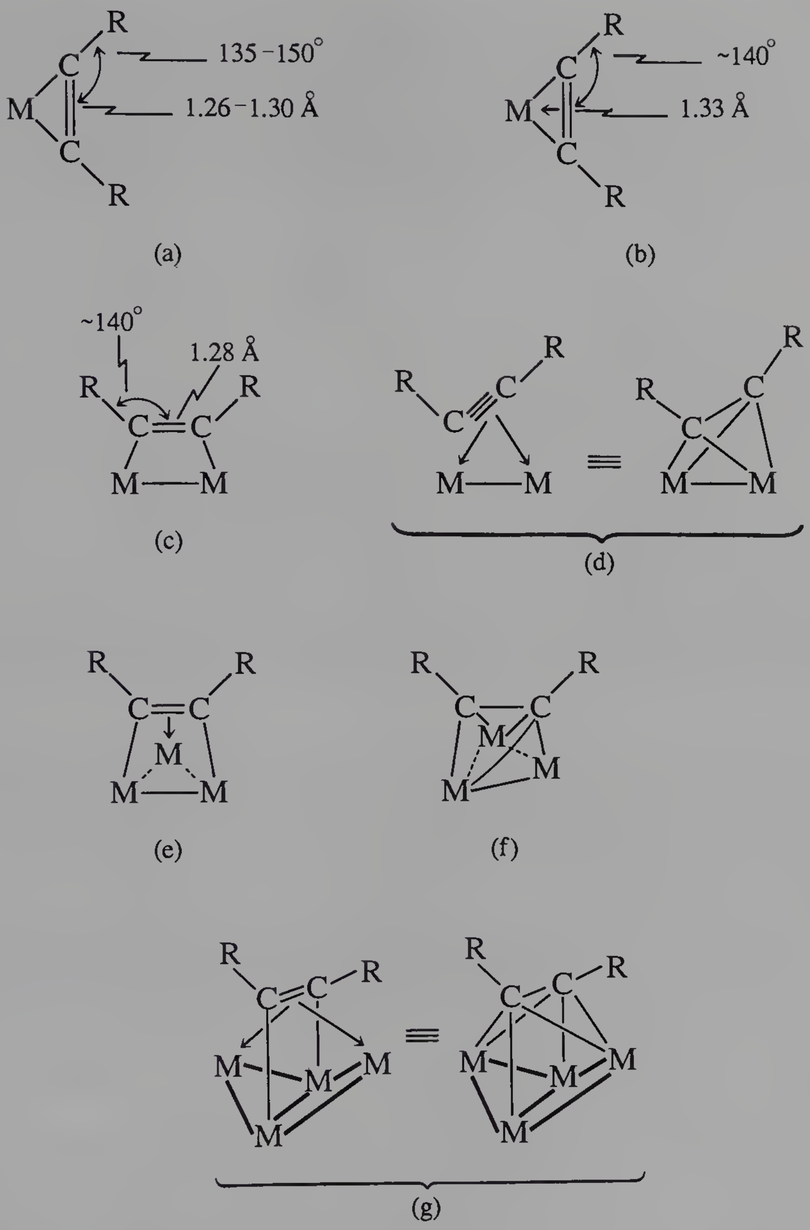
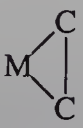


FIG. 2-12. Important modes of ligation of alkynes to single metal atoms and clusters of two, three, and four metal atoms.

to the plane of the three-membered  ring. Again, a synergistic back-donation may also occur if there is a filled *d* orbital perpendicular to *both* of those already used. This is shown in Fig. 2-13. This typically leads to even greater lengthening of the C—C distance. Figure 2-12(b) shows typical dimensions and indicates how an additional arrow is used to represent this four-electron bonding.

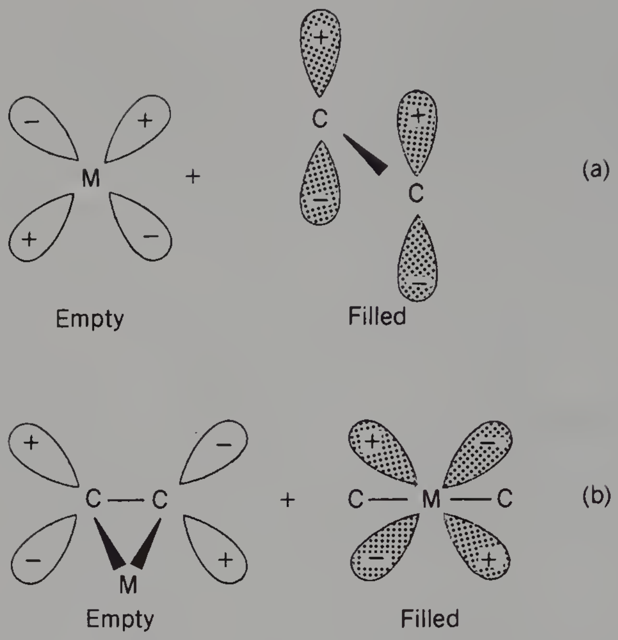


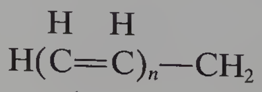
FIG. 2-13. The orbitals employed in the second synergic alkyne-to-metal bond.

When acting as a ligand toward two or more metal atoms, alkynes have a large repertoire of roles. With respect to a dimetal unit, there are two major types of structures, both describable as η^2, μ_2; they are shown in Fig. 2-12(c) and (d). In the planar structure of Fig. 2-12(c), the alkyne, is a two-electron donor. In structure (d), which is a distorted tetrahedral shape, the alkyne is a four-electron donor. The bonding in Fig. 2-12(d) can be envisioned as donation of one pair of π electrons to each metal atom (with appropriate back-donation) or as the formation of two single bonds to each metal atom. The latter view is certainly too extreme since the C—C distances in these cases are in the range 1.30 to 1.35 Å.

With trinuclear sets of metal atoms there are again two principal geometries, Fig. 2-12(e) and (f), in each of which the alkyne is a formal four-electron donor. Finally, we note that towards a tetranuclear set of metal atoms, the geometry shown in Fig. 2-12(g), where the metal atoms have the nonplanar "butterfly" arrangement is common. Here, again, the alkyne is a formal four-electron donor.

2-13. Enyl Ligands

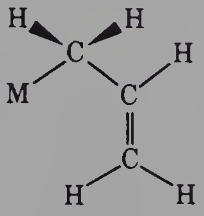
Groups of the formal type 2-XXXII can interact with a metal atom so as to serve as $(2n + 1)$-electron ligands. The two cases of greatest interest are the allyl and pentadienyl groups.



$$\mathrm{H}(\overset{\mathrm{H}}{\mathrm{C}}{=}\overset{\mathrm{H}}{\mathrm{C}})_n{-}\mathrm{CH_2}$$

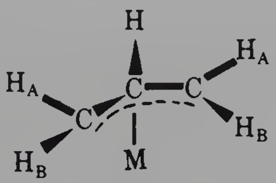
(2-XXXII)

The allyl system displays both η^1 (also often denoted σ behavior) (2-XXXIIIa) and η^3 behavior, (2-XXXIIIb). Note that (1) the η^3-allyl group is a three-electron donor, and (2) the hydrogen atoms of the methylene groups are not equivalent. There are *syn*-(H_A) and *anti*-(H_B) protons that can be distinguished by nmr. Many allyls show nonrigid behavior in solution (Section 29-15).



η^1 or σ-Allyl

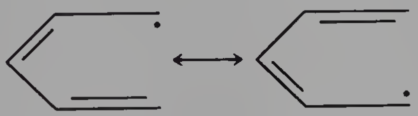
(2-XXXIIIa)



η^3 or π-Allyl

(2-XXXIIIb)

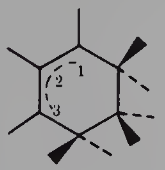
The η^5-pentadienyl ligand[33], as a five-electron donor in its semicircular, delocalised form represented schematically in 2-XXXIV is capable of forming a variety of metal complexes, including a so-called "open" ferrocene, $(C_5H_7)_2Fe$.



(2-XXXIV)

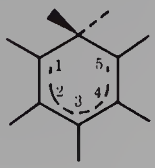
It may also be noted that η^3-allyl and η^5-pentadienyl units are often found within rings, especially six-membered rings, namely,

η-1-3-Cyclohexenyl



allylic

η-1-5-Cyclohexadienyl



dienylic

2-14. Aromatic Ring Systems

Just as the π electrons of alkenes can interact with metal *d* orbitals, so can certain of the delocalized π-electron ring systems of aromatic molecules overlap with d_{xz} and d_{yz} metal orbitals.

The first example of this type of complex was the molecule $Fe(C_5H_5)_2$, now

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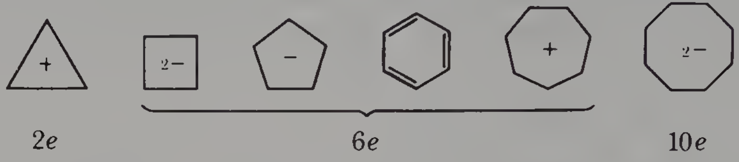
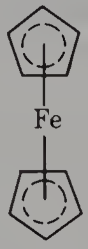
[33] R. D. Ernst, *Struct. Bonding* (*Berlin*), 1984, **57**, 1–53.

known as *ferrocene,* in which the 6π-electron system of the ion $C_5H_5^-$ is bound to the metal. Other aromatic systems with the "magic numbers" of 2, 6, and 10 for the aromatic electronic configuration are the carbocycles:



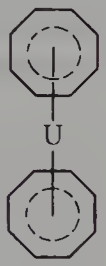
The C_5H_5, C_6H_6, and C_8H_8 rings are the most common in complexes, but the C_7H_7 and C_4H_4 systems also occur frequently. It should also be noted that for purposes of electron counting the ring system and the metal atom may be considered as neutral. For example, the total of 18 electrons in ferrocene can be regarded as 5 per C_5H_5 ring plus 8 from Fe.

Compounds are known that have only π-bonded rings such as ferrocene (2-XXXV), dibenzenechromium (2-XXXVI), or $(C_8H_8)_2U$ (2-XXXVII), but



(2-XXXV)

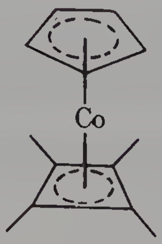
(2-XXXVI)



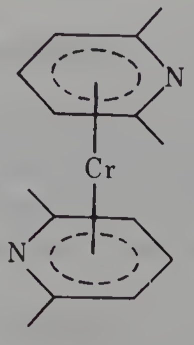
(2-XXXVII)

there are many compounds with one ring and other ligands such as halogens, CO, RNC, and R_3P. Examples are η-$C_5H_5Mn(CO)_3$ and η-$C_5H_5Fe(CO)_2Cl$. The symbol η is used to signify that all carbon atoms of the ring are bonded to the metal atom. There are also molecules in which two different types of arene ring are present, such that the total number of π electrons they provide, plus those possessed by the metal atom itself, add to 18. For example, in (2-XXXVIII), there are five π electrons from C_5H_5, four from C_4R_4, and nine from Co. Similarly, we have $(\eta$-$C_5H_5)(\eta$-$C_6H_6)Mn$.

It is also possible for heterocyclic arene rings to form complexes, examples being $(\eta$-$C_4H_4N)Mn(CO)_3$, $(\eta$-$C_4H_4S)Cr(CO)_3$, $(\eta$-$C_5H_5)(\eta$-$C_4H_4N)Fe$, $(\eta$-$C_5H_5)$-$(\eta$-$C_4H_4P)Fe$, and (2-XXXIX).



(2-XXXVIII)



(2-XXXIX)

The basic qualitative features of the bonding in ferrocene are well understood, and will serve to illustrate the basic principles for all (η-C_nH_n)M bonding, although for (C_8H_8)M systems there are a few additional points that are covered later.

The discussion of bonding does not depend critically on whether the preferred rotational orientation of the rings (see Fig. 2-14) in an (η-C_5H_5)$_2$M compound is staggered (D_{5d}) or eclipsed (D_{5h}); nor is that question unequivocally settled. It is experimentally certain that in ferrocenes the barrier to rotation is only about 8 to 20 kJ mol^{-1}*. The eclipsed configuration may be the more stable, but in condensed phases, especially crystals, where there are intermolecular energies of the same or greater magnitude than the barrier, either configuration may be found.

The bonding is best treated in the linear combination of atomic orbitals (LCAO–MO) approximation. A semiquantitative energy level diagram is given in Fig. 2-15. Each C_5H_5 ring, taken as a regular pentagon, has five π MO's, one strongly bonding (a), a degenerate pair that are weakly bonding (e_1), and a degenerate pair that are markedly antibonding (e_2), as shown in Fig. 2-16. The pair of rings taken together then has ten π orbitals and, if D_{5d} symmetry is assumed, so that there is a center of symmetry in the (η-C_5H_5)$_2$M molecule, there will be centrosymmetric (g) and antisymmetric (u) combinations. This is the origin of the set of orbitals shown on the left of Fig. 2-15. On the right are the valence shell ($3d$, $4s$, $4p$) orbitals of the iron atom. In the center are the MO's formed when the ring π orbitals and the valence orbitals of the iron atom interact.

For (η-C_5H_5)$_2$Fe, there are 18 valence electrons to be accommodated: 5 π-electrons from each C_5H_5 ring and 8 valence shell electrons from the iron atom. It will be seen that the pattern of MO's is such that there are exactly 9 bonding or nonbonding MO's and 10 antibonding ones. Hence the 18 electrons can just fill the bonding and nonbonding MO's, giving a closed configuration. Since the occupied orbitals are either of a type (which are each symmetric around the 5-fold molecular axis) or they are *pairs* of e_1 or e_2 type, which are also, *in pairs,* symmetrical about the axis, no intrinsic barrier to

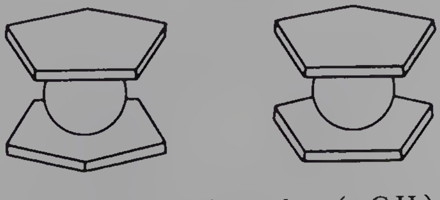


FIG. 2-14. Staggered and eclipsed configurations of an (η-C_5H_5)$_2$M compound. In crystalline ferrocene there are molecules of different orientations randomly distributed throughout the crystal (P. Seiler and J. D. Dunitz, *Acta Cryst.*, 1979, **B35,** 1068). Also, the H atoms of the rings are bent towards the metal (F. Takasagawa and J. F. Koetzle, *Acta Cryst.*, 1979, **B35,** 1074).

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*There are similar values for the rotation of rings in arene compounds; see J. Howard *et al., J. Chem. Soc. Dalton Trans.*, **1982,** 967, 977.

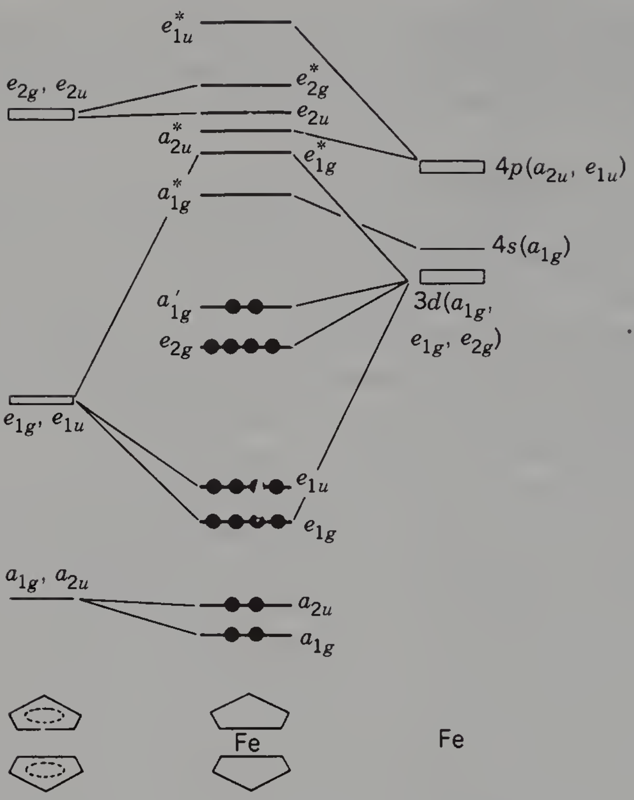

FIG. 2-15. An approximate MO diagram for ferrocene. Different workers often disagree about the exact order of the MO's; the order shown here, especially for the antibonding MO's, may be incorrect in detail, but the general pattern is widely accepted.

internal rotation is predicted. The very low barriers observed may be attributed to van der Waals forces directly between the rings.

Figure 2-15 indicates that among the principal bonding interactions is that giving rise to the strongly bonding e_{1g} and strongly antibonding e^*_{1g} orbitals. To give one concrete example of how ring and metal orbitals overlap, the nature of this particular important interaction is illustrated in Fig. 2-17. This particular interaction is in general the most important single one because the directional properties of the e_1-type d orbitals (d_{xz}, d_{yz}) give an excellent overlap with the e_1-type ring π orbitals, as Fig. 2-17 shows.

Systems containing only one η-C_5H_5 ring include (η-C_5H_5)$Mn(CO)_3$, (η-C_5H_5)$Co(CO)_2$, (η-C_5H_5)NiNO, and (η-C_5H_5)$CuPR_3$. The ring-to-metal bonding in these cases can be accounted for by a conceptually simple modification of the picture given previously for (η-C_5H_5)$_2$M systems. In each case a principal axis of symmetry can be chosen so as to pass through the metal atom and intersect the ring plane perpendicularly at the ring center; in other words, the C_5H_5M group is a pentagonal pyramid, symmetry C_{5v}. The single ring may then be considered to interact with the various metal orbitals in about the same way as do each of the rings in the sandwich system. The only difference is that opposite to this single ring is a different set of ligands which

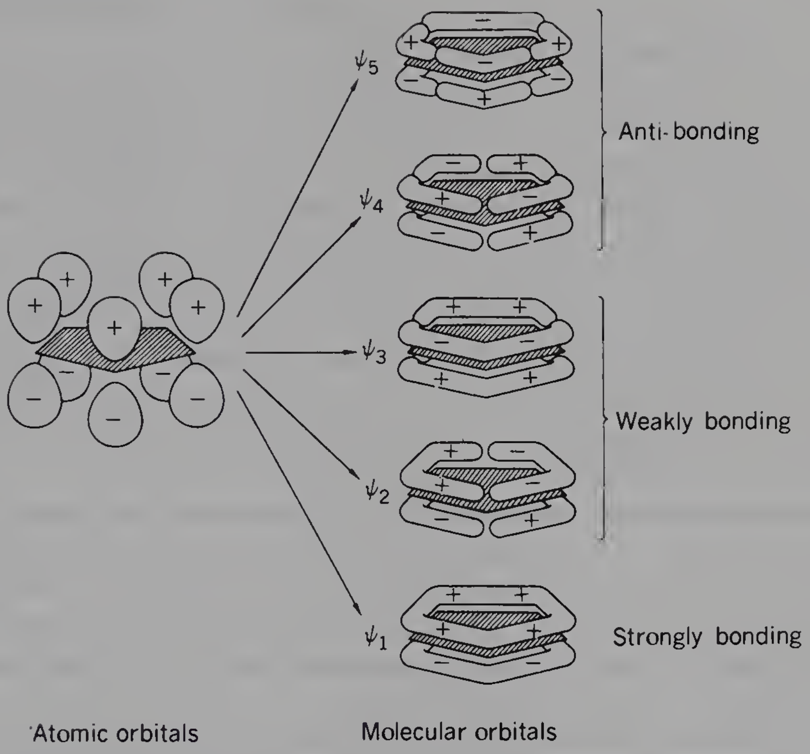

FIG. 2.16. The π molecular orbitals formed from the set of $p\pi$ orbitals of the C_5H_5 ring.

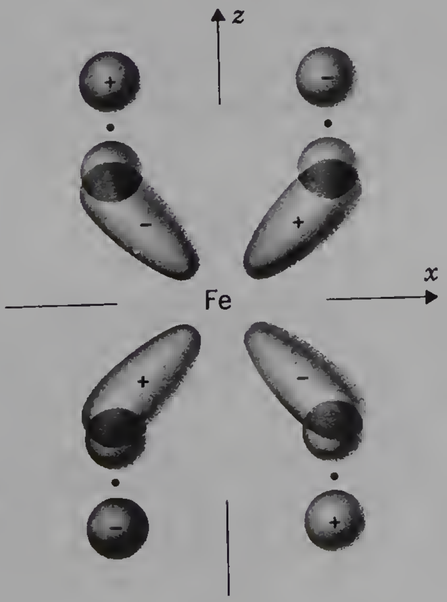

FIG. 2.17. Overlapping of one of the e_1-type d orbitals d_{xz} with an e_1-type π orbital to give a delocalized metal-ring bond: cross-sectional view taken in the xz plane.

interact with the opposite lobes of, for example, the *de*$_1$ orbitals, to form their own appropriate bonds to the metal atom.

The MO picture of ring-to-metal bonding just given for ferrocene is *qualitatively* but *not quantitatively* applicable to other $(\eta\text{-}C_5H_5)_2M$ compounds, and with obvious modifications, to other $(\eta\text{-arene})_2M$ molecules. Relative orbital energies can and do change as the metal is changed. Ferrocene itself has been treated by very elaborate MO calculations, and at the other extreme a ligand field model has also been applied to the $(\eta\text{-}C_5H_5)_2M$ compounds generally. Although it is clearly unrealistic to treat the bonding in these systems as electrostatic (i.e., M^{2+} and two negatively charged rings), this approach is of some utility in interpreting electronic absorption spectra.

It must also be noted that not all $(C_5H_5)_2M$ compounds are as simple structurally or electronically as might naively be expected. Those involving titanium and niobium have complex binuclear structures, as described in detail under the chemistry of these elements. In the case of $(\eta\text{-}C_5H_5)_2Ni$ there are two electrons in excess of those required for an 18-electron configuration; nonetheless, the molecule appears to have a structure with parallel rings and the two additional electrons have been assigned to the e_{1g}^* orbitals where they are appreciably delocalized onto the rings.

$(C_5H_5)_2Mn$ has a structure (Fig. 2-18) in which there are no discrete molecules until a transition occurs at 159°C, where it becomes isomorphous with ferrocene. However, there are five unpaired *d* electrons and the Mn to ring bonding is mainly ionic. $(CH_3C_5H_4)_2Mn(g)$ at 25°C is a roughly 2 to 1 mixture of ionic (high-spin) and covalent (low-spin) molecules with Mn—C distances of 2.42 and 2.14 Å, respectively, while $(C_5Me_5)_2Mn$ is molecular with one unpaired electron.

In many cases the rings are not parallel because additional ligands are present, for example, in $(C_5H_5)_2MX_2$ compounds with M = Ti, Zr, Mo and X = Cl, H, or R, or $(C_5H_5)_2MnPR_3$.[34] Bent molecules are also formed by tin and lead, where there is a stereochemically active lone pair.[35] Finally there

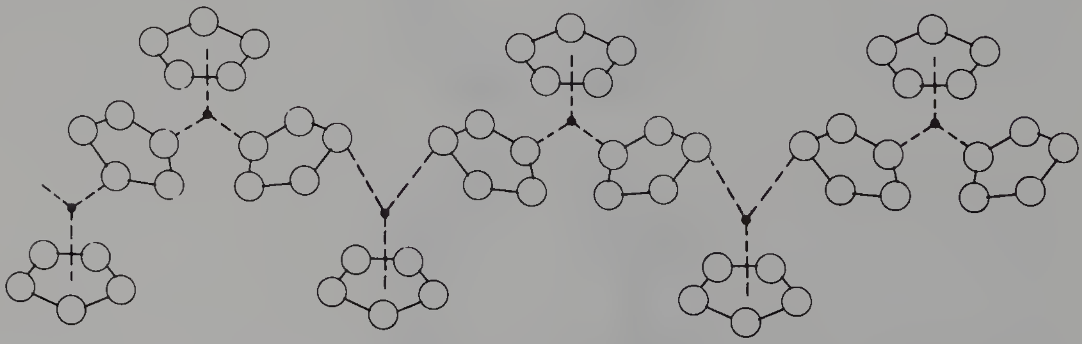

FIG. 2.18. The chain structure of $(C_5H_5)_2Mn$ in the low-temperature, antiferromagnetic crystal form.

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[34] G. Wilkinson *et al., J. Am. Chem. Soc.*, 1984, **106,** 2033.

[35] A. H. Cowley *et al., J. Am. Chem. Soc.*, 1982, **104,** 4064.

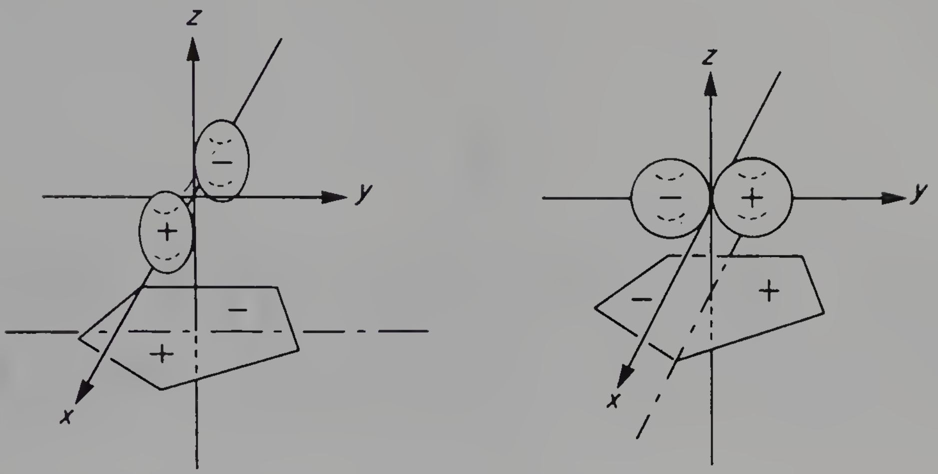

FIG. 2.19. Diagrams showing how p_x and p_y orbitals are symmetry adapted to overlap the e_1 π orbitals of a C_5H_5 ring.

can be "slippage" of the metal from the center to one side of the ring, which is probably important in the conversion of η^5 to η^1 species (Section 26-10).[36]

It is also possible to have covalent (η-C_5H_5)M groups even when the metal atom has no valence shell *d* orbitals, provided it has *p* orbitals of suitable energy and size. As shown in Fig. 2-19, a pair of p_x and p_y orbitals can overlap with the e_1 π orbitals of C_5H_5 in much the same way as do d_{xz} and d_{yz} orbitals. The C_5H_5In and C_5H_5Tl molecules are the best documented cases of this type of bonding.

Bonding in (η-C_8H_8)$_2$M Molecules. Although there are a few cases—for example, (η-C_8H_8)$ZrCl_2$(THF)—of one fully octagonal, planar C_8H_8 ring being symmetrically bonded to a *d*-block metal and it may be safely assumed that only metal *d* orbitals are used, the (η-C_8H_8)$_2$M compounds are formed only by metal atoms like uranium and thorium where the participation of *f* orbitals might reasonably be expected. However, at present, the role of the *f* orbitals is still not well defined. See Section 21-7 for further discussion and references.

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[36] J. W. Faller *et al., Organometallics,* 1985, **4,** 929; D. L. Lichtenberger *et al., Organometallics,* 1984, **3,** 1614, 1623.

2

THE CHEMISTRY OF THE MAIN GROUP ELEMENTS

Chapter Three

Hydrogen

GENERAL REMARKS

3-1. Introduction

Three isotopes of hydrogen are known: ^1H, ^2H (deuterium or D), and ^3H (tritium or T). Although isotope effects are greatest for hydrogen, justifying the use of distinctive names for the two heavier isotopes, the chemical properties of H, D, and T are essentially identical except in matters such as rates and equilibrium constants of reactions; in addition, diverse methods of isotope separation are known. The normal form of the element is the diatomic molecule: the various possibilities are H_2, D_2, T_2, HD, HT, and DT.*

Naturally occurring hydrogen contains 0.0156% deuterium, whereas tritium occurs naturally only in amounts of the order of 1 in 10^{17}.

Tritium is formed continuously in the upper atmosphere in nuclear reactions induced by cosmic rays; fast neutrons arising from cosmic ray reactions can produce tritium by the reaction $^{14}N(n,{}^3H)^{12}C$. Tritium is radioactive (β^-, 12.4 years) and is believed to be the main source of the minute traces of ^3He found in the atmosphere. It can be made in nuclear reactors by the thermal neutron reaction $^6Li(n,\alpha)^3H$, and is available for use as a tracer in studies of reaction mechanisms.

Deuterium as D_2O is separated from water by fractional distillation or electrolysis and by utilization of very small differences in the free energies of the H and D forms of different compounds, the H_2O–H_2S system being particularly favorable in large-scale use:

$$HOH(l) + HSD(g) = HOD(l) + HSH(g) \qquad K \approx 1.01$$

Deuterium oxide is available in ton quantities and is used as a moderator in nuclear reactors, both because it is effective in reducing the energies of fast fission neutrons to thermal energies and because deuterium has a much

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*Molecular H_2 (and D_2) have ortho and para forms in which the nuclear spins are aligned or opposed, respectively. This leads to very slight differences in bulk physical properties, and the forms can be separated by gas chromatography.

lower capture cross section for neutrons than has hydrogen, hence does not reduce appreciably the neutron flux. Deuterium is widely used in the study of reaction mechanisms and in spectroscopic studies.

Although the terrestrial abundance of H_2 is trivial, hydrogen in its compounds has one of the highest abundances. Hydrogen forms more compounds than any other element and hydrogen compounds of all elements excepting the noble gases are known.

Dihydrogen is a colorless, odorless gas (bp 20.28 K) virtually insoluble in water. In the laboratory it can be made by electrolysis of water or by action of dilute acids on zinc or iron. Industrially it is made by combustion of hydrocarbons, initially to give mixtures of CO and H_2, from which CO is removed in the "water gas shift reaction"

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Carbon dioxide is removed by scrubbing. For further discussion see Section 29-2.

Electrolysis of water is uneconomical except for production of D_2O. Although intensive efforts have been made to develop photochemical or catalytic cleavages of water to H_2 and/or O_2 none is yet practical. Representative systems studied are suspensions of platinum metal group complexes or oxides.[1]

Hydrogen is not exceptionally reactive, in part due to the highly endothermic dissociation:

$$H_2 = 2H \qquad \Delta H_0^0 = 434.1 \text{ kJ mol}^{-1}$$

Hydrogen burns in air to form water and will react with oxygen and the halogens explosively under certain conditions. At high temperatures the gas will reduce many oxides either to lower oxides or to the metal. In the presence of suitable catalysts and above room temperature it reacts with N_2 to form NH_3. With electropositive metals and most nonmetals it forms hydrides.

At high temperature, in arcs at high current density, in discharge tubes at low hydrogen pressure, or by ultraviolet irradiation of hydrogen, *atomic hydrogen* can be produced. It has a short half-life (~0.3 s). The heat of recombination is sufficient to produce exceedingly high temperatures, and atomic hydrogen has been used for welding metals. Atomic hydrogen is exceedingly reactive chemically, being a strong reducing agent.

Despite the high bond energy of H_2, the molecule is readily cleaved at low temperature and pressure by many transition metal complexes, when two metal-hydrogen bonds are formed, for example,

$$RhCl(PPh_3)_3 + H_2 \rightleftharpoons Rh(H)_2Cl(PPh_3)_3$$

[1] A. Mills and G. Williams, *J. Chem. Soc. Chem. Commun.*, **1987,** 606; M. Kaneko *et al.*, *ibid.*, **1987,** 227; W. Schumann *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1987, **25,** 241; A. L. Frank *et al.*, *J. Am. Chem. Soc.*, 1987, **109,** 3568.

These systems are discussed in detail in Chapters 24, 27, and 28 and their use in hydrogenation of organic substances described. Some transition metal complexes of *dihydrogen* are also known (Section 24-7).

In many chemical reactions, H_2 is evolved. Gas phase Raman spectroscopy provides an easy method for detection of H_2, HD, and D_2 in submicromolar quantities.[2]

3-2. The Bonding of Hydrogen

The chemistry of hydrogen depends mainly on three electronic processes:

1. *Loss of the Valence Electron.* The 1*s* valence electron may be lost to give the hydrogen ion H^+, which is merely the proton. Its small size ($r \sim 1.5 \times 10^{-13}$ cm) relative to atomic sizes ($r \sim 10^{-8}$ cm) and its small charge result in a unique ability to distort the electron cloud surrounding other atoms; the proton accordingly never exists as such, except in gaseous ion beams; in condensed phases it is invariably associated with other atoms or molecules.

2. *Acquisition of an Electron.* The hydrogen atom can acquire an electron, attaining the $1s^2$ structure of He, to form the hydride ion H^-. This ion exists as such essentially only in the saline hydrides formed by electropositive metals (Section 3-13).

3. *Formation of an Electron-Pair Bond.* The majority of hydrogen compounds contain an electron-pair bond. The number of carbon compounds of hydrogen is legion, and most of the less metallic elements form numerous hydrogen derivatives.

The chemistry of many of these compounds is highly dependent on the nature of the element (or the element plus its other ligands) to which hydrogen is bound. Particularly dependent is the degree to which compounds undergo dissociation in polar solvents and act as acids:

$$HX \rightleftharpoons H^+ + X^-$$

Also important for chemical behavior is the electronic structure and coordination number of the molecule as a whole. This is readily appreciated by considering the covalent hydrides BH_3, CH_4, NH_3, OH_2, and FH. The first not only dimerizes (to be discussed) but is a Lewis acid, methane is chemically unreactive and neutral, ammonia has a lone pair and is a base, water can act as a base or as a very weak acid, and FH is appreciably acidic in water.

Except in H_2 itself, where the bond is homopolar, all other H—X bonds possess polar character to some extent. The dipole may be oriented either way, and important chemical differences arise accordingly. Although the term "hydride" might be considered appropriate only for compounds with H negative, many compounds that act as acids in polar solvents are properly termed

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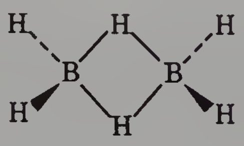
[2] R. J. H. Clark *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 2626.

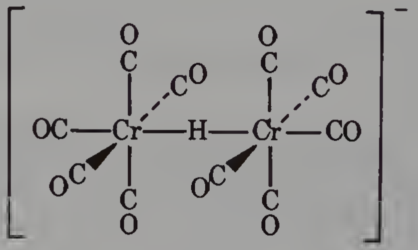
covalent hydrides. Thus although HCl and $HCo(CO)_4$ behave as strong acids in aqueous solution, they are gases at room temperature and are undissociated in nonpolar solvents.

4. *Unique Bonding Features.* The nature of the proton and the complete absence of any shielding of the nuclear charge by electron shells allow other forms of chemical activity that are either unique to hydrogen or particularly characteristic of it. Some of these are the following, which are discussed in some detail subsequently:

(a) The formation of numerous compounds, often nonstoichiometric, with metallic elements. They are generally called *hydrides* but cannot be regarded as simple saline hydrides.

(b) *Formation of hydrogen bridge bonds* in electron-deficient compounds such as in (3-I) or transition metal complexes as in (3-II).


(3-I)


(3-II)

The bridge bonds in boranes and related compounds are discussed in Chapter 6; the transition metal compounds are described in detail in Chapter 24.

(c) *The Hydrogen Bond.* This bond is important not only because it is essential to an understanding of much other hydrogen chemistry but also because it is one of the most intensively studied examples of intermolecular attraction. Hydrogen bonds dominate the chemistry of water, aqueous solutions, hydroxylic solvents, and OH-containing species generally, and they are of crucial importance in biological systems, being responsible *inter alia* for the linking of polypeptide chains in proteins and base pairs in nucleic acids.

THE HYDROGEN BOND, HYDRATES, HYDROGEN IONS, AND ACIDS

3-3. The Hydrogen Bond[3]

The concept of the hydrogen bond is due to Huggins, Latimer, and Rodebush in Berkeley in 1920. It is the term given to the relatively weak secondary

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[3] M. D Joesten, *J. Chem. Educ.*, 1982, **59**, 362 and references quoted; *Hydrogen Bonds*, P. Schuster, Ed., Springer, New York, 1983; A. C. Legon and D. J. Miller, *Acc. Chem. Res.*, 1987, **20**, 39 (gas phase dimers).

interaction between a hydrogen atom bound to an electronegative atom and another atom that is also generally electronegative and has one or more lone pairs enabling it to act as a base. We can thus refer to proton donors XH and proton acceptors Y and can give the following generalized representation of a hydrogen bond:

$$\overset{\delta-}{X}—\overset{\delta+}{H}\text{---}Y$$

Such interaction is strongest when both X and Y are first-row elements; the main proton donors are N—H, O—H, and F—H, and the most commonly encountered hydrogen bonds are O—H---O and N—H---O. It might be assumed that H bonding occurs in the direction of the lone pairs and this was confirmed for the NH---O═C bond in a survey of many structures.[4] However, this is not generally so, H bonds preferring linearity or near linearity. Lone pair directionality is more important in organic compounds for sp^2 rather than sp^3 lone pairs.[5]

Other groups such as P—H, S—H, Cl—H, and Br—H can also act as proton donors, and so even can C—H, provided the C—H bond is relatively polar as it is when the carbon is bound to electronegative groups as in $CHCl_3$ or the carbon atom is in an *sp*-hybridized state as in HCN or RC≡CH. The acceptor atoms can be N, O, F, Cl, Br, I, S, or P, but carbon never acts as an acceptor other than in certain π systems noted later.

It may be noted that in certain organometallic compounds of transition metals, interactions of the type C—H---M occur (Section 24-8).

Much of the earlier evidence for hydrogen bonding came from comparisons of the physical properties of hydrogen compounds. Classic examples are the apparently abnormally high boiling points of NH_3, H_2O, and HF (Fig. 3-1),

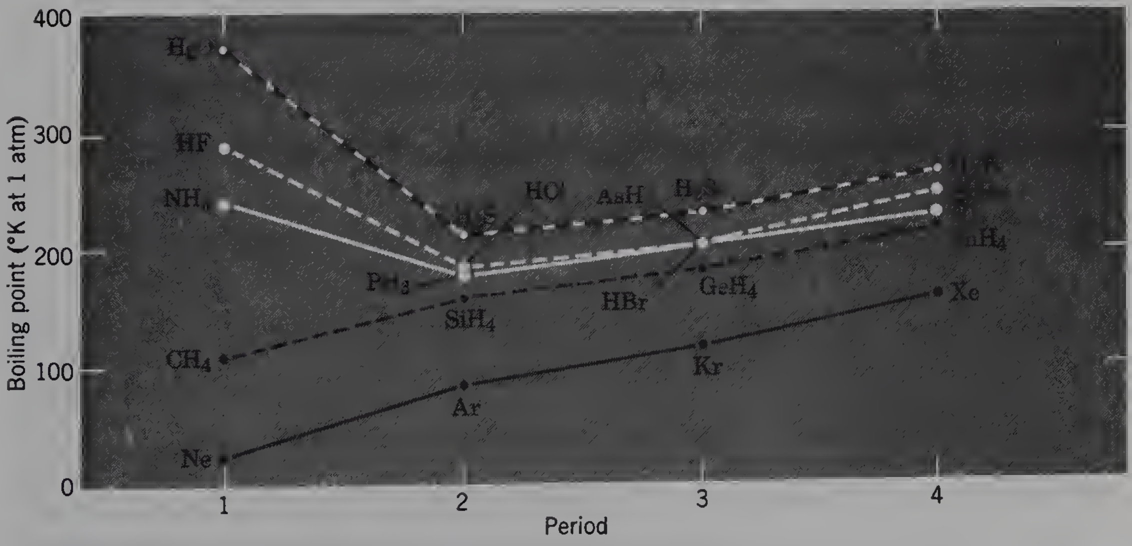

FIG. 3-1. Boiling points of some molecular hydrides.

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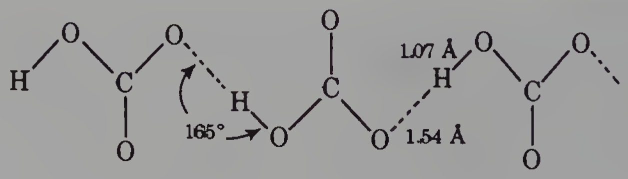
[4] R. Taylor *et al., J. Am. Chem. Soc.*, 1983, **105**, 5761.

[5] R. Taylor and O. Kennard, *Acc. Chem. Res.*, 1984, **17**, 320.

which imply association of these molecules in the liquid phase. Other properties such as heats of vaporization provided further evidence for association. Physical properties reflecting association are still useful in detecting H bonding, but the best evidence comes from X-ray and neutron diffraction crystallographic studies and from ir and nmr spectra.

Although H atoms are often observable in X-ray studies, their positions seldom can be ascertained with any accuracy. However, neutron diffraction data can usually give quite precise locations, because the scattering of neutrons of thermal energies is roughly similar for all nuclei, regardless of atomic number, whereas the scattering of X rays depends on electron density and is lowest for hydrogen. Even if accurate location of hydrogen atoms is not possible, the overall X—Y distance is significant. If X—Y distances are significantly shorter than normal van der Waals contacts for nonbonded atoms by, say, 0.2 Å, we can be fairly certain of the presence of a hydrogen bond. For O—H---O, distances below approximately 3 Å indicate hydrogen bonding. Thus for crystalline $NaHCO_3$ there are four kinds of O—O distance (between O's of different HCO_3^- ions) having values of 2.61, 3.12, 3.15, and 3.19 Å. The last three correspond to van der Waals contacts, but the first, 2.61 Å, corresponds to the H-bonded pair O—H---O.

The $NaHCO_3$ structure also serves to illustrate the results of a typical neutron diffraction study. As shown in (3-III), the HCO_3^- ions form infinite chains and the neutron results reveal the location of the proton. This example has two features that are entirely characteristic of most hydrogen bonds: (1) the X—H---Y chain is nearly (occasionally exactly) linear, and (2) the bond is unsymmetrical. The X—H distance is only a little (~0.1 Å) longer than for the isolated X—H bond, but the H---Y distance is far greater than the normal H—Y bond distance.



(3-III)

X ray and neutron diffraction are, of course, applicable only to crystalline solids. Spectroscopic methods are therefore valuable. Infrared and Raman spectra can detect H-bond formation because when an X—H bond participates in H-bond formation three main changes occur: (1) ν_{X-H} decreases, (2) the ν_{X-H} band becomes broader and its intensity increases, (3) the X—H wagging mode(s) increase in frequency. Proton nmr spectra give evidence of H-bond formation by showing a shift (usually to lower fields) of the proton involved.

The strengths of H bonds may be defined as the enthalpy of the process:

$$X—H---Y \longrightarrow X—H + Y$$

They vary from approximately zero when the overall X-to-Y distance is so long that it is about equal to the van der Waals contact distance for X—H with Y, to rather high values (>100 kJ mol^{-1}) for a few very short bonds. In general, such energies are rarely measurable and estimates of the relative strengths of H bonds are based on the magnitude of ir shifts and the shortness of the X-to-Y distances. Table 3-1 lists a few examples of H bonds and illustrates the ranges of certain properties.

The O—H---O bonds, which are the most common and have been most extensively studied, range from about 3.0 to 2.31 Å in length. Those from 3.0 to 2.8 Å are considered long and are relatively weak. The majority are in the range 2.8–2.6 Å and probably have energies in the range 15–40 kJ mol^{-1}. These are all unsymmetrical, like that shown in 3-III.

Very Short H Bonds.[6] These are found primarily in HF_2^-, $H(CO_2R)_2^-$, $H(ONO_2)_2^-$, and adducts like $KF\cdot CH_2(CO_2H)_2$. There are a few cases in which the bonds O---H---O and F---H---F (in KHF_2, 2.26 Å) are symmetrical but others are unsymmetrical and there appears to be no unique correlation between X---Y and X—H distances in X—H---Y; the entire environment has to be considered.

Multicenter H Bonds.[7] It is possible to have three-centered or bifurcated

TABLE 3-1
Some Parameters of Hydrogen Bonds

X—M---Y[a] Bond	Compound	Bond energy (kJ mol^{-1})[b]	Depression of stretching frequency (cm^{-1})	X---Y Bond distance[a] (Å)	X—H Distance (Å)
F---H---F[c]	KHF_2	~212	~2450	2.292(4)	1.145
F—H---F	HF(g)	~28.6	700	2.55	
O—H---O	$(HCO_2H)_2$	29.8	~460	2.67	
O—H---O	H_2O(s)	~21	~430	2.76	0.97
O—H---O	$B(OH)_3$			2.74	1.03
N—H---N	Melamine	~25	~120	3.00	
N—H---Cl	N_2H_5Cl		~460	3.12	
C—H---N	$(HCN)_n$		180	3.2	1.0

[a] For S—H---S bonds see B. Krebs, *Angew. Chem. Int. Ed. Engl.*, 1983, **22**, 113; for O—H---S, H. Meseitzer *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 1275; A. J. Williamson *et al.*, *Biochemistry*, 1983, **22**, 3581.

[b] For NHO, NHN, and OHO thermochemistry, see M. Meot-Ner, *J. Am. Chem. Soc.*, 1984, **106**, 1257.

[c] J. Emsley *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981**, 1219. For F---HOH see J. Emsley *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 313.

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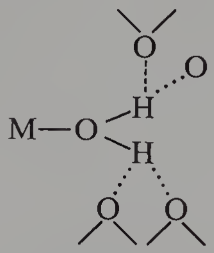
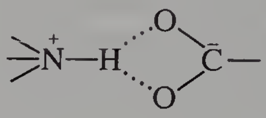
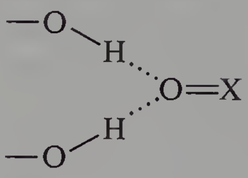
[6] J. Emsley, *Chem. Soc. Rev.*, **1980**, 91; S. H. Strauss *et al.*, *Inorg. Chem.*, 1986, **25**, 2806.

[7] J. Hine *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 7980; J. J. Zuckerman *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 7289; G. A. Jeffrey and J. Mitra, *J. Am. Chem. Soc.*, 1984, **106**, 5546; B. D. James and R. L. Davis, *Inorg. Chim. Acta*, 1985, **100**, L31.

hydrogen bonds of types such as:

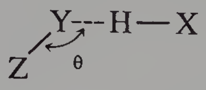






The statistical analysis of 1509 compounds with N—H---O=C bonds showed that ~20% were three-center but only six were found to be four-centered.[8]

Theory of H Bonds. For the majority of H bonds that are unsymmetrical and have medium to long overall lengths, the bonding force is mainly electrostatic, that is, the proton in a polar $X^{\delta-}$—$H^{\delta+}$ bond is attracted to the negative and/or polarizable atom Y. Given that the bond is essentially electrostatic, another question arises. If unshared electron pairs are concentrated along the direction of hybrid orbitals, will the proton approach the atom Y preferentially along these directions? In other words, does the proton see the atom Y as a structureless concentration of negative charge or as an atomic dipole? The answer to this question is not entirely clear-cut because in most cases where the angle θ in (3-IV) is in accord with the latter idea, it is possible to attribute this to steric requirements, as in carboxylic acid dimers or *o*-nitrophenol, or it can be equally well explained on the simpler theory as in the case of HCN polymers that are linear. However, the case of the $(HF)_n$ polymer (Fig. 3-2) and a few others seem to lend strong support to the hypothesis of preferred directions since there appears to be no other reason for the structure not to be linear.



(3-IV)

For the shortest H bonds, covalent forces doubtless are involved. Since the H atom cannot form two electron-pair bonds a 3*c*-2*e* bond picture must be used.

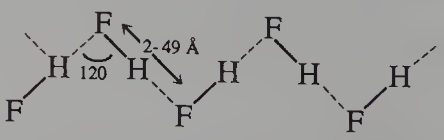


FIG. 3-2. The structure of crystalline hydrogen fluoride.

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[8] R. Taylor *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 244.

3-4. Ice and Water[9]

The structural nature of ice and, *a fortiori,* of water are very complex matters that can be treated but briefly here.

There are nine known modifications of ice, each stable over a certain range of temperature and pressure. Ordinary ice, ice I, which forms from liquid water at 0°C and 1 atm, has a rather open structure built of puckered, six-membered rings (Fig. 3-3). Each H_2O is tetrahedrally surrounded by the oxygen atoms of four neighboring molecules, and the whole array is linked by unsymmetrical hydrogen bonds. The O—H---O distance is 2.75 Å (at 100 K), and the H atom lie 1.01 Å from one oxygen and 1.74 Å from the other. Each oxygen atom has two near and two far hydrogen atoms, but there are six distinct arrangements, two being illustrated in Fig. 3-4, all equally probable. However, the existing arrangement at any one oxygen eliminates certain of these at its neighbors. A rigorous analysis of the probability of any given arrangement in an entire crystal leads to the conclusion that at the absolute zero ice I should have a disordered structure with a zero-point entropy of 3.4 J mol^{-1} deg^{-1}, in excellent agreement with experiment. This result in itself constitutes a good proof that the hydrogen bonds are unsymmetrical; if they were symmetrical, there would be a unique, ordered structure, hence no zero-point entropy. Entirely similar considerations confirm the presence of a network of unsymmetrical H bonds in KH_2PO_4 and $Ag_2H_3IO_6$, whereas the absence of zero-point entropy in K[FHF] accords with the symmetrical structure of the FHF^- ion.

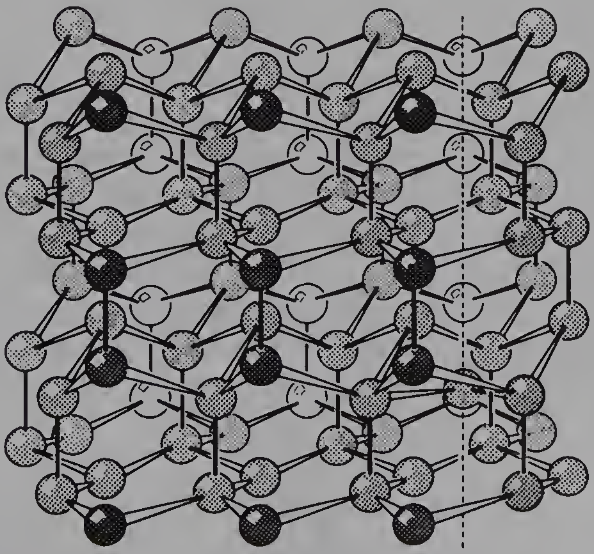

FIG. 3-3. The structure of ice I. Only the oxygen atoms are shown.

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[9] F. Franks, *Water,* Royal Society of Chemistry, London, 1984; E. W. Lang and H-D. Lüdemann, *Angew. Chem. Int. Ed. Engl.,* 1982, **21,** 315; V. L. Snoeyink and D. Jenkins, *Water Chemistry,* Wiley, New York, 1980 (mostly environmental aspects).

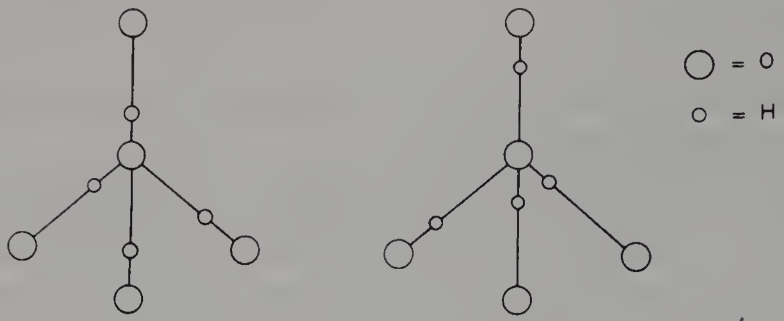

FIG. 3-4. Two possible configurations about an oxygen atom in ice.

The structure of *liquid water* is not random as in liquids with more or less spherical nonpolar molecules. It is highly structured but with fortuitous H-bonded links and species with four- to seven-membered rings, all of which are in rapid motion with the H bonds bending, stretching, and occasionally breaking.[10]

Alcohols, though similar to water in many respects, cannot form three-dimensional arrays and hence only linear or cyclic polymers exist.

3-5. Hydrates

Crystalline hydrates of metal ions and of organic substances, especially those with N—H and O—H bonds, are numerous. For metal ions, the oxygen is always bound to the metal and the lone pairs on it can be directed toward the metal and involved in bonding but can, however, also form H bonds. There is hence flexibility allowing stabilization in lattices of many different types of hydrated structure.

Some of the main structures are given in Fig. 3-5. It must be particularly noted that *gross distortions* from the angles of the ideal models shown are the *rule* and that large deviations from linearity of the H bonds also occur.

A number of organic molecules such as *p*-dihydroxybenzene, *p*-$C_6H_4(OH)_2$ when crystallized in the presence of small molecules such as Kr, CH_4, H_2S, and MeCN form H-bonded cages in which the molecule is trapped. These *clathrate compounds* are only one of a large class of *inclusion compounds* wherein small molecules are trapped in a lattice having holes of suitable size. Zeolites (Section 9-7) are probably the most useful of such compounds.

FIG. 3-5. Idealized structures for H-bonded coordinated water in hydrates. The metal M can also be replaced by HY in hydrates of organic compounds.

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[10] M. C. R. Symons, *Acc. Chem. Res.*, 1981, **14**, 179.

Similarly, water forms *gas hydrates*[11a] when water is frozen in the presence of Ar, Kr, Cl_2, SO_2, MeCl, and so on; the CH_4 hydrate occurs naturally.

There are two common structures. One has 46 water molecules connected to form 6 medium size and 2 small cages and is found for small molecules. Complete cage filling to give the composition $X \cdot 5.6\ H_2O$ is rare; medium cage filling gives $X \cdot 7.67\ H_2O$ and an actual example $Cl_2 \cdot 7.3\ H_2O$ approaches this. The second structure formed with larger molecules such as $CHCl_3$ or EtCl has 8 large and 16 smaller cages.

Salt hydrates are those formed when R_4N^+ or R_3S^+ salts crystallize from aqueous solution; examples are $[Bu_4N] \cdot PhCO_2 \cdot 39.5H_2O$ and $[Bu_3S]F \cdot 20H_2O$. The frameworks here are H-bonded water molecules, some H bonded to F^- or the oxygen of anions. The cations and parts of the anions (e.g., PhC of benzoate) occupy cavities randomly and incompletely. Clathrate hydrates of strong acids, for example, $HPF_6 \cdot 7.67H_2O$, $HBF_4 \cdot 5.75H_2O$, and $HClO_4 \cdot 5.5H_2O$ are also known.[11b]

It may be noted that there is some structural analogy between this type of hydrate and zeolites.[12] For example, $[Me_4N]OH \cdot 5H_2O$ is isostructural with the silicate sodalite and there are parallels between 12- and 17-Å gas hydrates and other zeolite structures.

3-6. Oxonium Ions

For the reaction

$$H(g) = H^+(g) + e$$

the ionization potential 13.59 eV (ΔH = 569 kJ mol^{-1}), is higher than the first ionization potential of xenon and is high by comparison with lithium or cesium and indeed many other elements. Hence with the possible exception of HF, bonds from hydrogen to other elements must be mainly covalent. For HF the bond energy is 5.9 eV. For a purely ionic bond the energy can be estimated as the sum of (1) 13.6 eV to ionize H, (2) -3.5 eV to place the electron on F, and (3) -15.6 eV as an upper limit on the electrostatic energy of the ion pair H^+F^- at the observed internuclear distance of HF. The sum of these terms is -5.5 eV as an upper limit, which is not too far below the actual bond energy. For HCl, on the other hand, the experimental bond energy is 4.5 eV, whereas for a purely ionic situation we would have the sum $+\ 13.6 - 3.6 - 11.3 = -1.5$ eV as an upper limit. Thus purely electrostatic bonding cannot nearly explain the stability of HCl.

Hydrogen can form the hydrogen ion *only* when its compounds are dissolved in media that *solvate* protons. The solvation process thus provides the energy required for bond rupture; a necessary corollary of this process is that the proton H^+ never exists in condensed phases, but occurs always as solvates (H_3O^+, R_2OH^+, etc.). The order of magnitude of these solvation energies

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[11a] E. Berecz, M. Balla-Achs, *Gas Hydrates,* Elsevier, Amsterdam, 1983.

[11b] D. Moorz *et al., J. Am. Chem. Soc.,* 1987, **109,** 1200.

[12] See G. T. Kokotailo *et al., J. Chem. Soc. Chem. Commun.,* **1984,** 1208.

can be appreciated by considering the solvation reaction in water (estimated from thermodynamic cycles):

$$H^+(g) + xH_2O = H^+(aq) \qquad \Delta H = -1091 \text{ kJ mol}^{-1}$$

Compounds that furnish solvated hydrogen ions in suitable polar solvents, such as water, are *protonic acids.*

The hydrogen ion in water is customarily referred to as "the hydrogen ion," implying H_3O^+. We shall usually write H^+ for the hydrogen ion and assume it to be understood that the ion is aquated since other ions, for example, Na^+ and Fe^{2+} are customarily so written although it is understood that the ions in solution are hydrated.

Water itself is weakly ionized:

$$2H_2O = H_3O^+ + OH^- \qquad \text{or} \qquad H_2O = H^+ + OH^-$$

Other cases of such *self-ionization* of a compound, where one molecule solvates a proton originating from another, are known; for example, in pure sulfuric acid

$$2H_2SO_4 = H_3SO_4^+ + HSO_4^-$$

and in liquid ammonia

$$2NH_3 = NH_4^+ + NH_2^-$$

In aqueous solutions, the hydrogen ion concentration is often given in terms of pH, defined as $-\log_{10}[H^+]$, where $[H^+]$ is the hydrogen ion activity, which may be considered to approximate to the molar concentration of H^+ ions in very dilute solutions.

At 25°C the ionic product of water is

$$K_w = [H^+][OH^-] = 1 \times 10^{-14} \, M^2$$

This value is significantly temperature dependent. When $[H^+] = [OH^-]$, the solution is neutral and $[H^+] = 1 \times 10^{-7} \, M$; that is, pH = 7.0. Solutions of lower pH are acidic; those of higher pH are alkaline.

The standard hydrogen electrode provides the reference for all other oxidation–reduction systems. The hydrogen half-cell or hydrogen electrode is

$$H^+(aq) + e = \tfrac{1}{2}H_2(g)$$

By definition, the potential of this system is zero ($E^0 = 0.000$ V) at all temperatures when an inert metallic electrode dips into a solution of hydrogen ions of unit activity (i.e., pH = 0) in equilibrium with H_2 at 1-atm pressure. The potentials of all other electrodes are then referred to this defined zero. However, the absolute potentials of other electrodes may be either greater or smaller; thus some must have positive and others negative potentials relative to the standard hydrogen electrode. This subject is not properly an aspect of the chemistry of hydrogen, but it is discussed briefly as a matter of convenience.

The difficulties that are sometimes caused by the so-called electrochemical sign conventions have arisen largely because the term "electrode potential" has been used to mean two distinct things:

1. *The Potential of an Actual Electrode.* For example, a zinc rod in an aqueous solution of zinc ions at unit activity ($a = 1$) at 25° has a potential of ~0.7627 V relative to the standard hydrogen electrode. There is no ambiguity about the sign because if this electrode and a hydrogen electrode were connected with a salt bridge, it would be necessary to connect the zinc rod to the negative terminal of a potentiometer and the hydrogen electrode to the positive terminal to measure the potential between them. Physically, the zinc electrode is richer in electrons than the hydrogen electrode.

2. *The Potential of a Half-Reaction.* Using the same chemical systems as an example, and remembering also that the Gibbs free energy of the standard hydrogen electrode is also defined as zero, we can write:

$$\begin{array}{lll} \mathrm{Zn} + 2\mathrm{H}^+(a = 1) \longrightarrow \mathrm{Zn}^{2+}(a = 1) + \mathrm{H}_2(\mathrm{g}) & \left.\begin{array}{l} \Delta G^0 = -147.5\ \mathrm{kJ} \\ E^0 = -\Delta G^0/nF = +0.7627\ \mathrm{V} \end{array}\right. \\ \mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+}(a = 1) + 2e^- & \\ \mathrm{Zn}^{2+}(a = 1) + \mathrm{H}_2(\mathrm{g}) \longrightarrow \mathrm{Zn} + 2\mathrm{H}^+(a = 1) & \left.\begin{array}{l} \Delta G^0 = +147.5\ \mathrm{kJ} \\ E^0 = -\Delta G^0/nF = -0.7627\ \mathrm{V} \end{array}\right. \\ \mathrm{Zn}^{2+}(a = 1) + 2e^- \longrightarrow \mathrm{Zn} & \end{array}$$

Since Zn dissolves in acid solutions under conditions specified in the definition of a standard electrode, the standard change in Gibbs free energy must be negative for the first pair of reactions and positive for the second pair. The potential of the Zn couple, defined by $\Delta G^0 = -nFE^0$ (n = number of electrons = 2, F = the Faraday), has to change sign accordingly. The half-reaction

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e^-$$

involves oxidation, and its potential is an *oxidation potential* whose sign is that of the so-called American sign convention. The half-reaction

$$\mathrm{Zn}^{2+} + 2e^- \longrightarrow \mathrm{Zn}$$

involves reduction, and its potential is a *reduction potential* associated with the European sign convention. There is no doubt about which potential is relevant, provided the half-reaction to which it refers is written out in full.

Inspection shows that the reduction potential has the same sign as the potential of the actual electrode. For this reason we adopt the IUPAC recommendation that *only reduction potentials be called electrode potentials.* Every half-reaction is therefore written in the form

$$\mathrm{ox} + ne^- \rightleftharpoons \mathrm{red}$$

and the Nernst equation for the electrode potential E is

$$E = E^0 + \frac{2.3026\,RT}{n\mathrm{F}} \log_{10} \frac{\text{activity of oxidant}}{\text{activity of reductant}} \tag{3-1}$$

where E^0 is the standard electrode potential, R the gas constant, and T the absolute temperature. Alternatively, we may sometimes speak of the electrode potential of a couple, for example, Fe^{3+}/Fe^{2+}, giving it the sign appropriate to the half-reaction written as a reduction.

For pure water, in which the H^+ activity is only 10^{-7} mol L^{-1} at 25°C the electrode potential, according to eq. 3-1 is more negative than the standard potential, that is, hydrogen becomes a better reductant:

$$H^+(aq)(10^{-7}\,M) + e = \tfrac{1}{2}H_2 \qquad E_{298} = -0.414\,V$$

In a basic solution, where the OH^- activity is 1 M, the potential is -0.83 V. In the absence of overvoltage (a certain lack of reversibility at certain metal surfaces), hydrogen is liberated from pure water by reagents whose electrode potentials are more negative than -0.414 V. Similarly, certain ions (e.g., the U^{3+} ion, for which the U^{4+}/U^{3+} standard potential is -0.61 V) will be oxidized by water, liberating hydrogen.

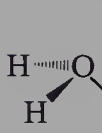
Many electropositive metals or ions, even if they do not liberate hydrogen from water, will be oxidized by a greater concentration of hydrogen ions—thus the reactions of Zn or Fe are normally used to prepare H_2 from dilute acids.

Finally a word on rates of acid–base reactions. All the protons in water are undergoing rapid migration from one oxygen atom to another, and the lifetime of an individual H_3O^+ ion in water is only approximately 10^{-13} s. The rate of reaction of H_3O^+ with a base such as OH^- in water is very fast but also is diffusion controlled. Reaction occurs when the solvated ions diffuse to within a critical separation, whereupon the proton is transferred by concerted shifts across one or more solvent molecules hydrogen bonded to the base.

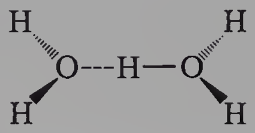
3-7. Structures of Hydrated H^+ and OH^- Ions

In crystalline compounds not only the hydroxonium ion (H_3O^+) but also more heavily solvated ions, for example, $H_5O_2^+$, and the hydrated hydroxyl ion ($H_3O_2^-$) have been characterized. In *acids* generally the proton is present as an oxonium ion, for example, in $H_2PtCl_6 \cdot 2H_2O$ or $HBF_4 \cdot nH_2O$, which cannot exist as HX, or it must be H bonded to some suitable atom in the acid molecule, for example, in H_2SO_4 (Section 3-12). However, for some acids such as $H_4Fe(CN)_6$ hydrated and anhydrous forms are known, the latter having MCN---H---NCM H-bonds (Section 8-10). There are also cases where no oxonium ion is present; $(CO_2H)_2 \cdot 2H_2O$ has a three-dimensional H-bonded structure while phosphoric acid hemihydrate is $2PO(OH)_3 \cdot H_2O$.

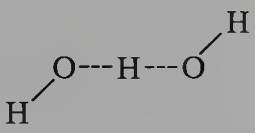
The structural role of H_3O^+ in a crystal often closely resembles that of NH_4^+; thus $H_3O^+ClO_4^-$ and $NH_4^+ClO_4^-$ are isomorphous. The important difference is that compounds of H_3O^+ and other oxonium ions generally have much lower melting points than have NH_4^+ salts. The structure of the H_3O^+ ion is that of a flat pyramid (3-V).[13a] In *p*-toluene sulfonic acid monohydrate for example the HOH angles are ~110° and the O—H distance ~1.01 Å. The $H_5O_2^+$ ion (3-VI) is quite common[13b]; in $HBr \cdot 2H_2O$ the proton is nearly centered but in other cases the O···H—O distances differ considerably. In all cases the H bonds are short.



(3-V)



(3-VI)



(3-VII)

The $H_7O_3^+$ and $H_9O_4^+$ ions are also characterized.[13c]

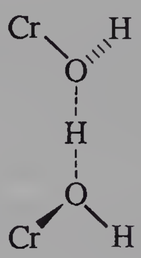
Analogues of hydroxonium ions are those derived from alcohols. Thus $[H(MeOH)_2]^+$, which is found in $[(MeOH)_2H]BF_4$ is the analogue of $H_5O_2^+$.

Solvated Anions. These are commonly found in crystals with short O—O bonds; typical are $[H(NO_3)_2]^-$, $[H(SO_3F)_2]^-$, and $[H(HCO_2)_2]^-$[14].

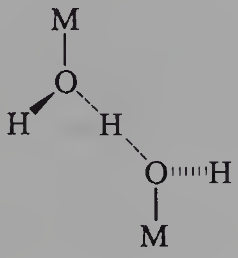
Solvation of the hydroxyl ion gives $H_3O_2^-$ (3-VII), which is isoelectronic with HF_2^- and similarly has a very short H bond, which may be almost symmetric in some cases with O···O ~2.3 Å.

Each oxygen can, of course, be additionally H bonded to two water molecules. The $H_3O_2^-$ ion is quite common in hydrated hydroxy complexes of metals,[15] originally considered to be of the type, for example, $[Cr(bipy)_2(H_2O)(OH)]^{2+}$. Such complexes are known to be dimers, $[(bipy)_2Cr(H_3O_2)_2Cr(bipyridine)_2]^{4+}$ with $H_3O_2^-$ bridges. These can be either gauche, (3-VIII) as in this chromium compound, or anti (3-IX) in some others.

Other anions are presumably also solvated but few have been character-



(3-VIII)



(3-IX)

[13a] See, for example, K. O. Christe, *Inorg. Chem.*, 1984, **23,** 3756.

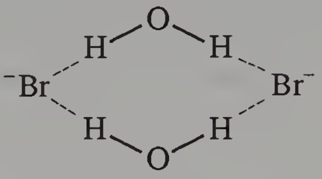
[13b] G. J. Kearly *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986,** 1801.

[13c] K. N. Raymond *et al.*, *Inorg. Chem.*, 1986, **25,** 1057.

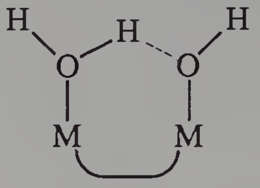
[14] E. Spinner, *J. Am. Chem. Soc.*, 1983, **105,** 756; R. D. Gillard *et al.*, *Polyhedron*, 1982, **1,** 528; C. Belin *et al.*, *J. Chem. Soc. Chem. Commun.*, **1981,** 1036.

[15] M. Ardon *et al.*, *Polyhedron*, 1987, **6,** 181; *J. Am. Chem. Soc.*, 1987, **109,** 1986.

ized, although $(H_2OBr^-)_2$ has been isolated using a large cation.[16a] It forms a cyclic polymer (3-Xa). Bridges of the type (3-Xb) have also been proposed.[16b]



(3-Xa)



(3-Xb)

STRENGTHS OF PROTONIC ACIDS

An important characteristic of hydrogen compounds (HX) is the extent to which they ionize in water or other solvents, that is, the extent to which they act as acids. The strength of an acid depends not only on the nature of the acid itself but very much on the medium in which it is dissolved. Thus CF_3CO_2H and $HClO_4$ are strong acids in water, whereas in 100% H_2SO_4 the former is nonacidic and the latter only a very weak acid. Similarly, H_3PO_4 is a base in 100% H_2SO_4. Although acidity can be measured in a wide variety of solvents, the most important is water, for which the pH scale was discussed previously.

It is convenient to note here that 1,8-bis(dimethylamino)naphthalene and related compounds are very strong bases and act as a *proton sponge* removing H^+ and forming N----H---N H-bonds that are symmetrical and nearly linear.[17]

3-8. Binary Acids

Although the intrinsic strength of H—X bonds is one factor, other factors are involved, as the following consideration of the appropriate thermodynamic cycles for a solvent system indicates. The intrinsic strength of H—X bonds and the thermal stability of covalent hydrides seem to depend on the electronegativities and size of the element X. The variation in bond strength in some binary hydrides is shown in Fig. 3-6. There is a fairly smooth *decrease* in bond strength with *increasing Z* in a periodic group and a general *increase across* any period.

For HX dissolved in water we may normally (but not always—see later) assume that dissociation occurs according to the equation:

$$HX(aq) = H^+(aq) + X^-(aq)$$

[16a] T. C. W. Mak, *Inorg. Chem.*, 1984, **23,** 620.
[16b] M. Loney *et al., Inorg. Chim. Acta.* 1986, **111,** 107.
[17] H. A. Staab *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 451; 1987, **26,** 460.

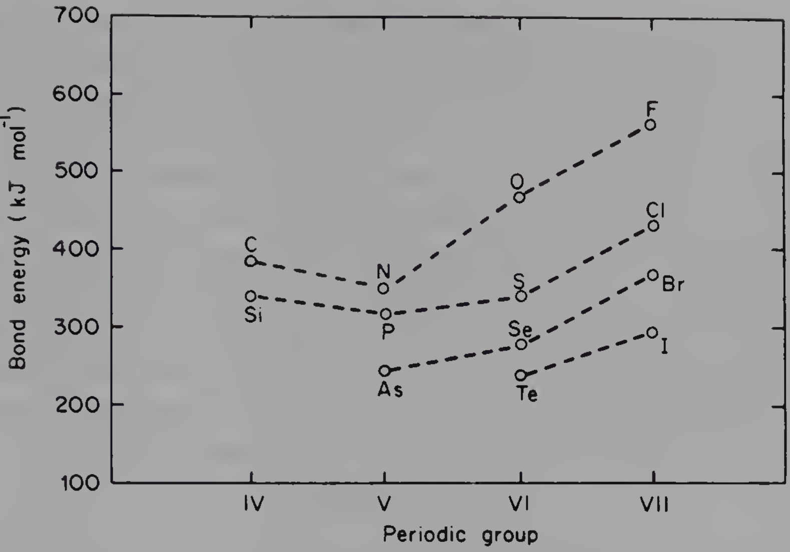


FIG. 3-6. Variation in mean H—X bond energies.

The dissociation constant K is related to the change in Gibbs free energy by the relation

$$\Delta G^0 = -RT \ln K \tag{3-2}$$

and the free energy change is in turn related to the changes in enthalpy and entropy via the relation

$$\Delta G = \Delta H - T\Delta S \tag{3-3}$$

in which R is the gas constant and T is the absolute temperature, which we shall take to be 298 K in the following discussion. The dissociation process may be considered to be the sum of several other reactions (i.e., as one step in a thermodynamic cycle). Table 3-2 summarizes the Gibbs free energy changes for these several steps.

Hydrogen fluoride in *dilute* aqueous solution is a very weak acid; the pK values for the halogen acids change only slightly (3 units overall) from HI to

TABLE 3-2
Free Energy Changes (kJ mol^{-1}) for Dissociation of HX Molecules in Water at 298 K

Process	HF	HCl	HBr	HI
$HX(aq) = HX(g)$	23.9	−4.2	−4.2	−4.2
$HX(g) = H(g) + X(g)$	535.1	404.5	339.1	272.2
$H(g) = H^+(g) + e$	1320.2	1320.2	1320.2	1320.2
$X(g) + e = X^-(g)$	−347.5	−366.8	−345.4	−315.3
$H^+(g) + X^-(g) = H^+(aq) + X^-(aq)$	−1513.6	−1393.4	−1363.7	−1330.2
$HX(aq) = H^+(aq) + X^-(aq)$	18.1	−39.7	−54.0	−57.3
$pK_A(= \Delta G^0/5.71)$	3.2	−7.0	−9.5	−10

HBr to HCl, but there is a precipitous change, by 10.2 units, on going to HF. The classic thermodynamic explanation for this is that the HF bond is so much stronger than those of the other HX molecules that even an unusually high free energy of solvation of F^- cannot compensate for it; thus most dissolved HF molecules remain undissociated. However, this is not correct. From ir studies of the four aqueous HX acids it was inferred that the H_3O^+ ion in aqueous HF is indeed present in large quantity but with a perturbed spectrum indicative of strong H bonding to F^-. In other words HF *is* dissociated, but tight ion pairs, $F^- {-}{-}{-} H^+{—}OH_2$, unique to F^-, which is a far better participant in H bonding than Cl^-, Br^-, or I^-, reduce the thermodynamic activity coefficient of H_3O^+. The ion pair $H_3O^+F^-$ increasingly dissociates on increasing the HF concentration with the formation of HF_2^-:

$$H_3O^+F^- + HF \rightleftharpoons H_3O^+ + HF_2^-$$

This view is confirmed by X-ray study of the crystalline hydrates $H_2O \cdot nHF$, $n = 1$, 2, and 4 which shows that these are $H_3O^+F^-$, $H_3O^+HF_2^-$, and $H_3O^+H_3F_4^-$.[18]

3-9. Oxo Acids

The second main class of acids are compounds with X—OH groups of the type H_nXO_m, for example, H_3PO_4, or better $O{=}P(OH)_3$.

For oxo acids certain generalizations may be made concerning (*a*) the magnitude of K_1 and (*b*) the ratios of successive constants, K_1/K_2, K_2/K_3, and so on. The value of K_1 seems to depend on the charge on the central atom. Qualitatively it is reasonable to suppose that the greater the positive charge, the more the process of proton loss will be favored on electrostatic grounds. If this positive charge is taken to be the so-called formal charge, semiquantitative correlations are possible. The formal charge in an oxo acid H_nXO_m is computed assuming the structure of the acid to be $O_{m-n}X(OH)_n$. Each X—(OH) bond is formed by sharing one X electron and one OH electron and is thus *formally* nonpolar. Each X—O bond is formed by using two X electrons and thus represents a net loss of one electron by X. Therefore the formal positive charge on X is equal to the number of X—O bonds, hence equal to $(m - n)$. The data in Table 3-3 show that with the exception of the acids listed in brackets, which are special cases to be discussed presently, the following relations between $m - n$ (or formal positive charge on X) and the values of K_1 hold:

For $m - n = 0$	$pK_1 \sim 8.5 \pm 1.0$	($K \sim 10^{-8}$ to 10^{-9})
For $m - n = 1$	$pK_1 \sim 2.8 \pm 0.9$	($K \sim 10^{-2}$ to 10^{-4})
For $m - n \geq 2$	$pK_1 \ll 0$ (the acid is very strong)	

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[18] D. Mootz, *Angew. Chem. Int. Ed. Engl.*, 1981, **20**, 791; see also G. T. Hefter, *Polyhedron*, 1984, **3**, 75.

TABLE 3-3
Strengths of Oxo Acids, H_nXO_m, in Water

$(m - n)$	Examples	$-\log K_1(\mathrm{p}K_1)$	$-\log K_2(\mathrm{p}K_2)$	$-\log K_3(\mathrm{p}K_3)$
0	HClO	7.50		
	HBrO	8.68		
	H_3AsO_3	9.22	?	?
	H_4GeO_4	8.59	13	?
	H_6TeO_6	8.80	?	?
	$[H_3PO_3]$	1.8	6.15	
	H_3BO_3	9.22	?	?
1	H_3PO_4	2.12	7.2	12
	H_3AsO_4	3.5	7.2	12.5
	H_5IO_6	3.29	6.7	~15
	H_2SO_3	1.90	7.25	
	H_2SeO_3	2.57	6.60	
	$HClO_2$	1.94		
	HNO_2	3.3		
	$[H_2CO_3]$	6.38 (3.58)	10.32	
2	HNO_3	Large neg. value		
	H_2SO_4	Large neg. value	1.92	
	H_2SeO_4	Large neg. value	2.05	
3	$HClO_4$	Very large neg. value		
	$HMnO_4$	Very large neg. value		
−1(?)	$[H_3PO_2]$	2	?	?

With very few exceptions, the difference between successive pK's is 4 to 5.

Phosphorous acid (H_3PO_3) obviously is out of line with the other acids having $m - n = 0$ and seems to fit fairly well in the group with $m - n = 1$. This is, in fact, where it belongs, since there is independent evidence (Section 11-16) that its structure is $OPH^*(OH)_2$ with H^* bonded directly to P. Similarly, H_3PO_2 has a pK_1 that would class it with the $m - n = 1$ acids where it, too, belongs, since its structure is $OP(H^*)_2(OH)$, with the two H^* hydrogen atoms directly bound to P.

Carbonic acid is exceptional in that the directly measured pK_1, 6.38, does not refer to the process

$$H_2CO_3 = H^+ + HCO_3^-$$

since CO_2 in solution is only partly in the form of H_2CO_3, but largely present as more loosely hydrated species CO_2(aq). When a correction is made for the equilibrium

$$CO_2(aq) + H_2O = H_2CO_3(aq)$$

the pK_1 value of 3.58 is obtained, which falls in the range for other $m - n = 1$ acids (see also Section 8-5).

Many metal ions whose solutions are acidic can be regarded as oxo acids.

Thus although the hydrolysis of metal ions is often written as shown here for Fe^{3+}:

$$Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$$

it is just as valid thermodynamically and much nearer to physical reality to recognize that the Fe^{3+} ion is coordinated by water molecules and to write:

$$[Fe(H_2O)_6]^{3+} = [Fe(H_2O)_5(OH)]^{2+} + H^+ \qquad K_{Fe^{3+}} \approx 10^{-3}$$

From this formulation it becomes clear why the Fe^{2+} ion, with a lower positive charge, is less acidic or, in alternative terms, less hydrolyzed than the Fe^{3+} ion:

$$[Fe(H_2O)_6]^{2+} = [Fe(H_2O)_5(OH)]^{+} + H^+ \qquad K_{Fe^{2+}} \ll K_{Fe^{3+}}$$

It should be noted that one cannot necessarily compare the acidity of the bivalent ion of one metal with that of the trivalent ion of *another* metal in this way, however. There appears to be no good general rule concerning the acidities of hydrated metal ions at the present time, although some attempts have been made at correlations.

3-10. Theory of Ratios of Successive Constants

It was shown many years ago by Niels Bjerrum that the ratios of successive acid dissociation constants could be accounted for in a nearly quantitative way by electrostatic considerations. Consider any bifunctional acid HXH:

$$HXH = HX^- + H^+ \qquad K_1$$

$$HX^- = X^{2-} + H^+ \qquad K_2$$

There is a purely statistical effect that can be considered in the following way. For the first process, dissociation can occur in two ways (i.e., there are two protons, either of which may dissociate), but recombination in only one; whereas in the second process dissociation can occur in only one way, but recombination in two (i.e., the proton has two sites to which it may return, hence twice the probability of recombining). Thus on purely statistical grounds one would expect $K_1 = 4K_2$. Bjerrum observed that for the dicarboxylic acids $HO_2C(CH_2)_nCO_2H$, the ratio K_1/K_2 was always >4 but decreased rapidly as n increased (see Table 3-4). He suggested the following explanation. When the two points of attachment of protons are close together in the molecule, the negative charge left at one site when the first proton leaves strongly

TABLE 3-4

K_1/K_2 Ratio for Dicarboxylic Acids, $HO_2C(CH_2)_nCO_2H$

n	1	2	3	4	5	6	7	8
K_1/K_2	1120	29.5	17.4	12.3	11.2	10.0	9.5	9.3

restrains the second one from leaving by electrostatic attraction. As the separation between the sites increases, this interaction should diminish.

By making calculations using Coulomb's law,* Bjerrum was able to obtain rough agreement with experimental data. The principal difficulty in obtaining quantitative agreement lies in a choice of dielectric constant, since some of the lines of electrostatic force run through the molecule ($D \sim 1$–10), others through neighboring water molecules (D uncertain), and still others through water having the dielectric constant (~82) of pure bulk water. Nearly quantitative agreement is obtained using more elaborate models that take into account the variability of the dielectric constant. The important point here for our purposes is to recognize the physical principles involved without necessarily trying to obtain quantitative results.

Thus the large separation in successive pK's for the oxo acids is attributable to the electrostatic effects of the negative charge left by the dissociation of one proton on the remaining ones. In bifunctional binary acids, where the negative charge due to the removal of one proton is concentrated on the very atom to which the second proton is bound, the separation of the constants is extraordinarily great: K_1 and K_2 for H_2S are $\sim 10^{-7}$ and 10^{-14}, respectively, whereas for water we have

$$H_2O = H^+ + OH^- \qquad K_1 = 10^{-14}$$

$$OH^- = H^+ + O^{2-} \qquad K_2 < 10^{-36} \text{(estimated)}$$

3-11. Pure Acids and Relative Acidities; Superacids[19]

The concepts of hydrogen ion concentration and pH discussed previously are meaningful only for dilute aqueous solutions of acids. A widely used means of gauging acidity in other media and at high concentrations is the Hammett acidity function H_0, which is defined in terms of the behavior of one or more indicator bases B, for which there is the protonation equilibrium

$$B + H^+ = BH^+$$

The acidity function is defined as

$$H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]}$$

In very dilute solutions

$$K_{BH^+} = \frac{[B][H^+]}{[BH^+]}$$

---

*$F \propto q_1 q_2 / Dr$, where F is the force; q_1 and q_2 the charges separated by r; and D the dielectric constant of the medium between them.

[19] G. A. Olah, G. K. S. Prakash, and J. Sommer, *Superacids*, Wiley, Chichester, 1985.

so that in water, H_0 becomes synonymous with pH. By using suitable organic bases (e.g., *p*-nitroaniline) and suitable indicators over various ranges of concentration and acidities or by nmr methods, it is possible to interrelate values of H_0 for strong acids extending from dilute solutions to the pure acid.

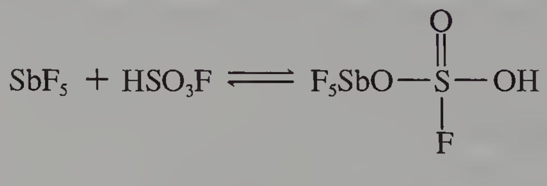
For a number of strong acids in aqueous solution up to concentrations about 8 M, the values of H_0 are very similar. This suggests that the acidity is independent of the anion. The rise in acidity with increasing concentration can be fairly well predicted by assuming that the hydrogen ion is present as $H_9O_4^+$, so that protonation can be represented as

$$H_9O_4^+ + B \rightleftharpoons BH^+ + 4H_2O$$

Values of H_0 for some pure liquid acids are given in Table 3-5. It is to be noted particularly that for HF the acidity can be very substantially increased by the additions of a Lewis acid or fluoride ion acceptor, for example:

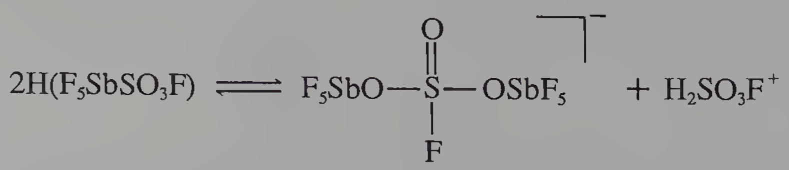
$$2HF + SbF_5 \rightleftharpoons H_2F^+ + SbF_6^-$$

but its acidity is decreased by addition of NaF owing to formation of the HF_2^- ion. Antimony pentafluoride is commonly used as the Lewis acid, since it is comparatively easy to handle, being a liquid, and is commercially available. However, other fluorides such as BF_3, NbF_5, and TaF_5 behave in a similar way. Acid media with $-H_0$ values above about six are often referred to as *superacids,*[19] since they are upward of 10^6 times as strong as a 1 M aqueous solution of a strong acid. The addition of SbF_5 to HSO_3F dramatically raises the $-H_0$ value from 15 for 0% SbF_5 to ~17 at 0.4 mol % SbF_5 and finally to 26.5 at 90 mol %, the latter being the highest $-H_0$ value known. The SbF_5—FSO_3H system, which is very complicated, has been thoroughly investigated by nmr and Raman spectra. The acidity is due to the formation of the $H_2SO_3F^+$ ion. The equilibria depend on the ratios of the components; with low ratios of SbF_5 to FSO_3H the main ones are the following:



$$SbF_5 + HSO_3F \rightleftharpoons F_5SbO-\overset{\overset{O}{\|}}{\underset{\underset{F}{|}}{S}}-OH$$

$$H(F_5SbSO_3F) + HSO_3F \rightleftharpoons [F_5SbOSO_2F]^- + H_2SO_3F^+$$



$$2H(F_5SbSO_3F) \rightleftharpoons \left[F_5SbO-\overset{\overset{O}{\|}}{\underset{\underset{F}{|}}{S}}-OSbF_5\right]^- + H_2SO_3F^+$$

At higher ratios the solutions appear to contain also the ions SbF_6^- and $[F_5Sb—F—SbF_5]^-$, which occur in solutions of SbF_5 in liquid HF, together

TABLE 3-5
The Hammett Acidity Function H_0 for Several Acids

Acid	$-H_0$	Acid	$-H_0$
$HSO_3F + SbF_5$ (14.1 mol %)	26.5	HF (100%)	11
$HF + SbF_5$ (0.6 mol %)	21.1	$HF + NaF$ (1 M)	8.4
HSO_3F	15	H_3PO_4	5.0
$H_2S_2O_7$	15	H_2SO_4 (63% in H_2O)	4.9
CF_3SO_3H	14.1	HCO_2H	2.2
H_2SO_4	12.1		

with HS_2O_6F and HS_3O_9F, which occur in SO_3—FSO_3H solutions. These are generated by the additional reactions

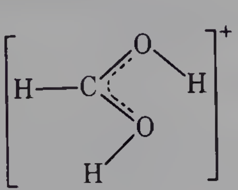
$$HSO_3F \rightleftharpoons HF + SO_3$$

$$3SbF_5 + 2HF \rightleftharpoons HSbF_6 + HSb_2F_{11}$$

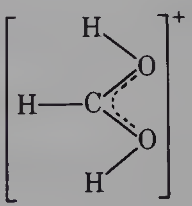
$$2HSO_3F + 3SO_3 \rightleftharpoons HS_2O_6F + HS_3O_9F$$

The SbF_5—HSO_3F solutions are very viscous and are normally diluted with liquid sulfur dioxide so that better resolution of nmr spectra is obtained. Although the equilibria appear not to be appreciably altered for molecular ratios $SbF_5{:}HSO_3F < 0.4$, in more concentrated SbF_5 solutions the additional equilibria noted here are shifted to the left by removal of SbF_5 as the stable complex $SbF_5{\cdot}SO_3$, which can be obtained crystalline. This results in a lowering of the acidity of the system; on the contrary, if SO_3 is added the acidity is increased by raising the concentration of $H_2SO_3F^+$, and the strongest known acid is SbF_5—$HSO_3F{\cdot}nSO_3$. The main species in HF—SbF_5 from 0 to 40 mol % SbF_5 is $H_3F_2^+$ but above 40% it is H_2F^+.[20]

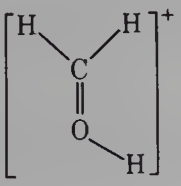
There has been extensive study of very strong acids especially FSO_3H—SbF_5—SO_2, HF—SbF_5, and HCl—Al_2Cl_6 for protonation of weak bases. Virtually all organic compounds react and the species can be characterized by nmr spectra. Thus formic acid at −60°C gives equal amounts of (3-XI) and (3-XII), formaldehyde (3-XIII), and fluorobenzene (3-XIV).



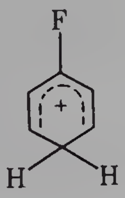
(3-XI)



(3-XII)



(3-XIII)



(3-XIV)

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[20] B. Bonnett and G. Mascherpa, *Inorg. Chem.*, 1980, **19**, 785.

Many metal carbonyl and organometallic complexes may be protonated on the metal or on the ligand (Chapters 24, 26 and 27), for example:

$$Fe(CO)_5 + H^+ \rightleftharpoons HFe(CO)_5^+$$

$$(\eta^5\text{-}C_5H_5)_2Fe + H^+ \rightleftharpoons (\eta^5\text{-}C_5H_5)_2FeH^+$$

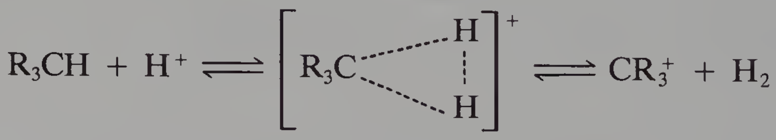
$$C_8H_8Fe(CO)_3 + H^+ \rightleftharpoons C_8H_9Fe(CO)_3^+$$

Even protonated carbonic acid, or more properly, the trihydroxycarbonium ion $C(OH)_3^+$, has been observed in solutions of carbonates or bicarbonates in $FSO_3H—SbF_5—SO_2$ solutions at −78°C; the ion is stable to 0°C in the absence of SO_2. It was suggested that $C(OH)_3^+$ might be involved even in biological systems at very acidic sites in enzymes such as carbonic anhydrase.

The superacid media can induce hydride abstraction, H—D exchange, C—C cleavage, and other reactions even with saturated hydrocarbons,[21] though CH_4 is rather unreactive. Carbonium ions are formed, some of which, notably the trimethylcarbonium ion, are quite stable:

$$Me_3CH \longrightarrow Me_3C^+ \longleftarrow CH_3CH_2CH_2CH_3$$

It is postulated that the attack by H^+ occurs on the electron density of the C—H and C—C single bonds and not on the C and H atoms themselves. The order of reactivity, qualitatively, is tertiary CH > C—C > secondary CH ⪢ primary CH. Even molecular H_2 may be protonated, since H_2–D_2 exchange is observed in the superacids, probably through a planar H_3^+ transition state. The reactions possibly involve *pentacoordinate* carbonium ions, for example, where the two hydrogen atoms are bound to carbon by closed three-center bonds.



$$R_3CH + H^+ \rightleftharpoons \left[R_3C\begin{matrix}\cdots H\\ \vdots\\ \cdots H\end{matrix}\right]^+ \rightleftharpoons CR_3^+ + H_2$$

The carbonium ions can undergo complex reactions. Thus methane can give carbonium ions with C—C bonds by condensation reactions of the type:

$$CH_4 \overset{H^+}{\rightleftharpoons} H_2 + CH_3^+ \xrightarrow{CH_4} C_2H_7^+ \rightleftharpoons H_2 + C_2H_5^+ \qquad \text{and so on}$$

CH_3^+ ions* have been detected by trapping with CO and subsequent hydrolysis of the acylium ion with water to give acetic acid, for example,

$$CH_3^+ + CO \longrightarrow CH_3CO^+ \xrightarrow{H_2O} CH_3CO_2H + H^+$$

The carbonylation of aromatics is also catalyzed by super acids.[22]

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[21] J. Deryck *et al., Chem. Rev.*, 1982, **82,** 591; M. Bassir *et al., New J. Chem.*, 1987, **11,** 437.

*$CH_3F—SbF_5$ in SO_2F_2 will methylate N_2O to give $CH_3O—N{=}N^+$ which is stable below −30°C. G. A. Olah *et al., J. Am. Chem. Soc.*, 1986, **108,** 2054.

[22] G. Olah *et al., J. Org. Chem.*, 1985, **50,** 1436.

The halogen-acid–Al_2X_6 systems are similar to HF—SbF_5.[23] Either can isomerize alkanes and catalyze hydrocarbon acetylation or alkylation.

3-12. Properties of Some Common Strong Acids

A collection of some properties of the more common and useful pure strong acids is found in Table 3-6.

Hydrogen Fluoride. The acid is made by the action of concentrated H_2SO_4 on CaF_2 and is the principal source of fluoride compounds (Chapter 14). It is available in steel cylinders, with purity approximately 99.5%; it can be purified further by distillation. Although liquid HF attacks glass rapidly, it can be handled conveniently in apparatus constructed either of copper or Monel metal or of materials such as polytetrafluoroethylene (Teflon or PTFE) and Kel-F (a chlorofluoro polymer).

The high dielectric constant is characteristic of hydrogen-bonded liquids. Since HF forms only a two-dimensional polymer, it is less viscous than water. In the vapor, HF is monomeric above 80°C, but at lower temperatures the physical properties are best accounted for by an equilibrium between HF and a hexamer, $(HF)_6$, which has a puckered ring structure. Crystalline $(HF)_n$ has zigzag chains (Fig. 3-2).

After water, liquid HF is one of the most generally useful solvents. Indeed in some respects it surpasses water as a solvent for both inorganic and organic compounds, which often give conducting solutions as noted previously; it can also be used for cryoscopic measurements.

The self-ionization equilibria in liquid HF are

$$2HF \rightleftharpoons H_2F^+ + F^- \qquad K \sim 10^{-10}$$

$$F^- + HF \rightleftharpoons HF_2^- \overset{HF}{\rightleftharpoons} H_2F_3^- \qquad \text{and so on}$$

TABLE 3-6
Properties of Some Strong Acids in the Pure State

Acid	mp (°C)	bp (°C)	κ[a] (temperature, °C)	ε[b] (temperature, °C)
HF	−83.36	19.74	1.6×10^{-6} (0)	84 (0)
HCl	−114.25	−85.09	3.5×10^{-9} (−85)	14.3 (−114)
HBr	−86.92	−66.78	1.4×10^{-10} (−84)	7.33 (−86)
HI	−50.85	−35.41	8.5×10^{-10} (−45)	3.57 (−45)
HNO_3	−41.59	82.6	3.77×10^{-2} (25)	
$HClO_4$	−112	(109°C extrap.)		
HSO_3F	−88.98	162.7	1.085×10^{-4} (25)	~120 (25)
H_2SO_4	10.3771	~270 d[c]	1.044×10^{-2} (25)	110 (20)

[a] Specific conductance ($ohm^{-1}\ cm^{-1}$). Values are often very sensitive to impurities.
[b] Dielectric constant divided by that of a vacuum.
[c] Constant-boiling mixture (338°C) contains 98.33% of H_2SO_4; d = with decomposition.

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[23] D. Fărcaşiu, *Acc. Chem. Res.*, 1982, **15**, 46.

The formation of the stable hydrogen-bonded anions accounts in part for the extreme acidity. In the liquid acid the fluoride ion is the conjugate base, and ionic fluorides behave as bases. Fluorides of M^+ and M^{2+} are often appreciably soluble in HF, and some such as TlF are very soluble.

The only substances that function as "acids" in liquid HF are those such as SbF_5 previously noted, which increase the concentration of H_2F^+. The latter ion appears to have an abnormally high mobility in such solutions.

Reactions in liquid HF are known that also illustrate amphoteric behavior, solvolysis, or complex formation. Although HF is waterlike; it is not easy, because of the reactivity, to establish an emf series, but a partial one is known.

In addition to its utility as a solvent system, HF as either liquid or gas is a useful fluorinating agent, converting many oxides and other halides into fluorides.

Hydrogen Chloride, Bromide, and Iodide. These acids are quite similar but differ from HF; they are normally pungent gases; in the solid state they have hydrogen-bonded zigzag chains and there is probably some hydrogen bonding in the liquid. Hydrogen chloride is made by the action of concentrated H_2SO_4 on concentrated aqueous HCl or NaCl; HBr and HI may be made by catalytic reaction of $H_2 + X_2$ over platinized silica gel or, for HI, by interaction of iodine and boiling tetrahydronaphthalene. The gases are soluble in a variety of solvents, especially polar ones. The solubility in water is not exceptional; in moles of HX per mole of solvent at 0°C and 1 atm the solubilities in water, 1-octanol, and benzene, respectively, are HCl, 0.409, 0.48, 0.39; HBr, 1.00, 1.30, 1.39; HI, 0.065, 0.173, 0.42.

The self-ionization is very small:

$$3HX \rightleftharpoons H_2X^+ + HX_2^-$$

Liquid HCl has been fairly extensively studied as a solvent, and many organic and some inorganic compounds dissolve giving conducting solutions:

$$B + 2HCl \rightleftharpoons BH^+ + HCl_2^-$$

The low temperatures required and the short liquid range are limitations, but conductimetric titrations are readily made.

Salts of the ion H_2Cl^+ have not been isolated, but salts of the HCl_2^- and HBr_2^- ions, which have X—H—X distances of 3.14 and 3.35 Å, respectively, are not uncommon. These distances, like that in HF_2 (2.26 A), are ~0.5 Å shorter than the sum of van der Waals radii and suggest that there are strong hydrogen bonds.

Nitric Acid.[24] Nitric acid is made industrially by oxidation of ammonia with air over platinum catalysts. The resulting nitric oxide (Section 10-6) is absorbed in water in the presence of air to form NO_2, which is then hydrated. The normal concentrated aqueous acid (~70% by weight) is colorless but

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[24] C. C. Addison, *Chem. Rev.*, 1980, **80**, 21.

often becomes yellow as a result of photochemical decomposition, which gives NO_2:

$$2HNO_3 \xrightarrow{h\nu} 2NO_2 + H_2O + \tfrac{1}{2}O_2$$

The so-called fuming nitric acid contains dissolved NO_2 in excess of the amount that can be hydrated to HNO_3 + NO.

Pure nitric acid can be obtained by treating KNO_3 with 100% H_2SO_4 at 0°C and removing the HNO_3 by vacuum distillation. The pure acid is a colorless liquid or white crystalline solid; the latter decomposes above its melting point according to the previous equation for the photochemical decomposition, hence must be stored below 0°C.

The acid has the highest self-ionization of the pure liquid acids. The initial protolysis

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$

is followed by rapid loss of water:

$$H_2NO_3^+ \rightleftharpoons H_2O + NO_2^+$$

so that the overall self-dissociation is

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

Pure nitric acid is a good ionizing solvent for electrolytes, but unless they produce the NO_2^+ or NO_3^- ions salts are sparingly soluble.

In dilute aqueous solution, nitric acid is approximately 93% dissociated at 0.1 *M* concentration. Nitric acid of concentration below 2 *M* has little oxidizing power. The concentrated acid is a powerful oxidizing agent and, of the metals, only Au, Pt, Ir, and Re are unattacked, although a few others such as Al, Fe, Cu are rendered *passive,* probably owing to formation of an oxide film; magnesium alone can liberate hydrogen and then only initially from dilute acid. The attack on metals generally involves reduction of nitrate. *Aqua regia* (~3 vol. of conc. HCl + 1 vol. of conc. HNO_3) contains free chlorine and ClNO, and it attacks gold and platinum metals, its action being more effective than that of HNO_3 mainly because of the complexing function of chloride ion. Red fuming nitric acid contains N_2O_4.[25] Some metals, notably tantalum, are quite resistant to HNO_3 but dissolve with extreme vigor if HF is added, to give TaF_6^- or similar ions. Nonmetals are usually oxidized by HNO_3 to oxo acids or oxides. The ability of HNO_3, especially in the presence of concentrated H_2SO_4, to nitrate many organic compounds, is attributable to the formation of the nitronium ion, NO_2^+ (Section 10-6).

Gaseous HNO_3 has a planar structure (Fig. 3-7), although hindered rotation of OH relative to NO_2 probably occurs.

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[25] M. F. A. Dove *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 2551.

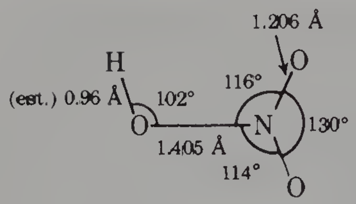

FIG. 3-7. The structure of nitric acid in the vapor.

Perchloric Acid. This is available in concentrations 70 to 72% by weight. The water azeotrope with 72.5% of $HClO_4$ boils at 203°C, and although some Cl_2 is produced, which can be swept out by air, there is no hazard involved. The anhydrous acid is best prepared by vacuum distillation of the concentrated acid in the presence of the dehydrating agent $Mg(ClO_4)_2$; it reacts explosively with organic material. The pure acid is stable at room temperature for only 3 to 4 days, decomposing to give $HClO_4 \cdot H_2O$ (84.6% acid) and Cl_2O_7.

The most important applications of aqueous $HClO_4$ involve its use as an oxidant. However, at concentrations below 50% and temperatures not exceeding 50 to 60°C, there is no release of O_2. The hot concentrated acid oxidizes organic materials vigorously or even explosively; it is a useful reagent for the destruction of organic matter, especially after pretreatment with, or in the presence of, H_2SO_4 or HNO_3. The addition of concentrated $HClO_4$ to organic solvents such as ethanol should be avoided where possible, even if the solutions are chilled.

Perchlorate salts of organic or organometallic cations or complexes with organic ligands must be handled with *extreme* caution; substitution of ClO_4^- by $CF_3SO_3^-$ is always advisable.

Sulfuric Acid. This is prepared on an enormous scale by the lead chamber and contact processes. In the former, SO_2 oxidation is catalyzed by oxides of nitrogen (by intermediate formation of nitrosylsulfuric acid, $HOSO_2ONO$); in the latter, heterogeneous catalysts such as Pt are used for the oxidation. Pure H_2SO_4 is a colorless liquid that is obtained from the commercial 98% acid by addition first of SO_3 or oleum and then titration with water until the correct specific conductance or melting point is achieved.

The phase diagram of the H_2SO_4–H_2O system is complicated, and eutectic hydrates such as $H_2SO_4 \cdot H_2O$ (mp 8.5°C) and $H_2SO_4 \cdot 2H_2O$ (mp −38°C) occur.

In pure crystalline H_2SO_4 there are SO_4 tetrahedra with S—O distances 1.42, 1.43, 1.52, and 1.55 Å, linked by strong H-bonds. There is also extensive H-bonding in the concentrated acid.

In the gas phase the structure is $O_2S(OH)_2$ which is essentially that in the liquid although the latter is extensively H-bonded.[26]

Pure H_2SO_4 shows extensive self-ionization resulting in high conductivity. The equilibrium

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^- \qquad K_{10^\circ C} = 1.7 \times 10^{-4}\ \mathrm{mol^2\ kg^{-2}}$$

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[26] R. D. Suenram *et al., J. Am. Chem. Soc.*, 1981, **103,** 2561.

is only one factor, since there are additional equilibria due to dehydration:

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^- \qquad K_{10°C} = 3.5 \times 10^{-5}\ \text{mol}^2\ \text{kg}^{-2}$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad K_{10°C} = 1\ \text{mol kg}^{-1}$$

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^- \qquad K_{10°C} = 7 \times 10^{-2}\ \text{mol kg}^{-1}$$

Estimates of the concentrations in 100% H_2SO_4 of the other species present, namely, H_3O^+, HSO_4^-, $H_3SO_4^+$, $HS_2O_7^-$, and $H_2S_2O_7$ can be made; for example, at 25°C, HSO_4^- is 0.023M.

Pure H_2SO_4 and dilute oleums have been greatly studied as solvent systems, but interpretation of the cryoscopic and other data is often complicated. Sulfuric acid is not a very strong oxidizing agent, although the 98% acid has some oxidizing ability when hot. The concentrated acid reacts with many organic materials, removing the elements of water and sometimes causing charring, for example, of carbohydrates. Many substances dissolve in the 100% acid, often undergoing protonation. Alkali metal sulfates and water also act as bases. Organic compounds may also undergo further dehydration reactions, for example:

$$C_2H_5OH \xrightarrow{H_2SO_4} C_2H_5OH_2^+ + HSO_4^- \xrightarrow{H_2SO_4} C_2H_5HSO_4 + H_3O^+ + HSO_4^-$$

Because of the strength of H_2SO_4, salts of other acids may undergo solvolysis, for example:

$$NH_4ClO_4 + H_2SO_4 \rightleftharpoons NH_4^+ + HSO_4^- + HClO_4$$

There are also examples of acid behavior. Thus H_3BO_3, which behaves initially as a base, gives quite a strong acid:

$$H_3BO_3 + 6H_2SO_4 \rightleftharpoons B(HSO_4)_3 + 3H_3O^+ + 3HSO_4^-$$

$$B(HSO_4)_3 + HSO_4^- \rightleftharpoons B(HSO_4)_4^-$$

The addition of SO_3 to H_2SO_4 gives what is known as *oleum* or fuming sulfuric acid $(SO_3)_n{\cdot}H_2O$; the constitution of concentrated oleums is controversial, but with equimolar ratios the major constituent is pyrosulfuric (disulfuric) acid ($H_2S_2O_7$). At higher concentrations of SO_3, Raman spectra indicate the formation of $H_2S_3O_{10}$ and $H_2S_4O_{13}$. Pyrosulfuric acid has higher acidity than H_2SO_4 and ionizes thus:

$$2H_2S_2O_7 \rightleftharpoons H_2S_3O_{10} + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_3O_{10}^-$$

The acid protonates many materials; $HClO_4$ behaves as a weak base, and CF_3CO_2H is a nonelectrolyte in oleum.

Fluorosulfuric Acid. Fluorosulfuric acid is made by the reaction:

$$SO_3 + HF = FSO_3H$$

or by treating KHF_2 or CaF_2 with oleum at ~250°C. When freed from HF by sweeping with an inert gas, it can be distilled in glass apparatus. Unlike

$ClSO_3H$, which is explosively hydrolyzed by water, FSO_3H is relatively slowly hydrolyzed.

Fluorosulfuric is one of the strongest of pure liquid acids. It is commonly used in the presence of SbF_5 as a protonating system, as noted (Section 3-11). An advantage over other acids is its ease of removal by distillation in vacuum. The self-ionization

$$2FSO_3H \rightleftharpoons FSO_3H_2^+ + FSO_3^-$$

is much lower than for H_2SO_4 and consequently interpretation of cryoscopic and conductometric measurements is fairly straightforward.

In addition to its solvent properties, FSO_3H is a convenient laboratory fluorinating agent. It reacts readily with oxides and salts of oxo acids at room temperature. For example, K_2CrO_4 and $KClO_4$ give CrO_2F_2 and ClO_3F, respectively.

Trifluoromethanesulfonic Acid. This very strong ($-H_0 = 15.1$), useful acid (CF_3SO_3H, bp 162°C) is often given the trivial name "triflic" acid and its salts called "triflates." It is very hygroscopic and forms the monohydrate $CF_3SO_3H \cdot H_2O$, mp 34°C. Its salts are similar to perchlorates but nonexplosive; the $CF_3SO_3^-$ ion is less likely than ClO_4^- to be found disordered in crystal structures. The ion is also a useful leaving group in many organic and inorganic syntheses.[27]

Related and most useful protonating acids are $(CF_3SO_2)_2CH_2$, $(CF_3SO_2)_2CHPh$, and $(CF_3SO_2)_2NH$ that also give noncoordinating anions like $CF_3SO_3^-$.[28]

Other Acids. Although "tetrafluoroboric" and "hexafluorophosphoric" acids do not exist as such but only in the form of oxonium salts, for example, $H_5O_2^+BF_4^-$, nevertheless in nonaqueous solvents such as carboxylic anhydrides or ethers there can be strong acid behavior. Tetrafluoroboric acid in diethyl ether is a useful strong acid, $[Et_2OH]^+BF_4^-$.

Finally it may be noted that there are some solids that behave as superacids with $H_0 \leq -16.0$. An example is the solid obtained by treating $Zr(OH)_4$ with concentrated H_2SO_4 and calcining the product at >500°C.[29a] They have uses in catalysis.[29b]

BINARY METALLIC HYDRIDES

Figure 3-8 represents a rough attempt to classify the various hydrides.

3-13. The Hydride Ion H^-; Saline Hydrides

The formation of the unipositive ion H^+ (or H_3O^+, etc.) suggests that hydrogen should be classed with the alkali metals in the Periodic Table. On the

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[27] See, for example, A. M. Sargeson *et al., Inorg. Chem.*, 1984, **23**, 2940.

[28] A. R. Siedle *et al., J. Am. Chem. Soc.*, 1984, **106**, 1510.

[29a] M. Hino and K. Arata, *J. Chem. Soc. Chem. Commun.*, **1985,** 112.

[29b] G. M. Kramer and G. B. McVicker, *Acc. Chem. Res.*, 1986, **19,** 78.

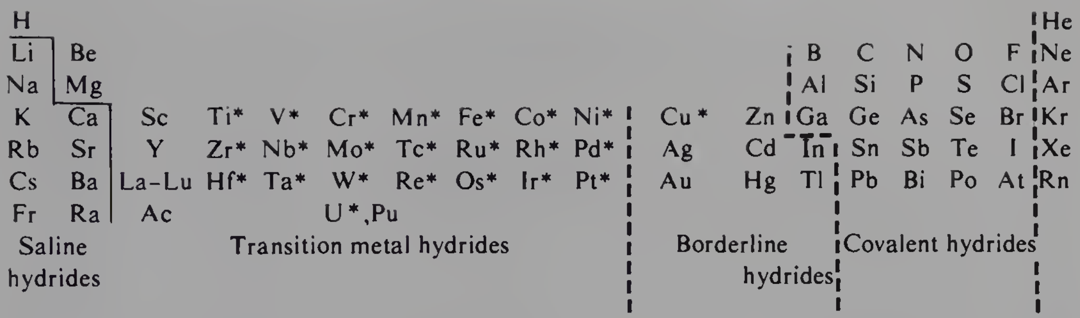


FIG. 3-8. A classification of hydrides. The starred elements are transition elements for which complex molecules containing M—M bonds are known.

other hand, the formation of the hydride ion might suggest an analogy with the halogens. Such attempts at classification of hydrogen with other elements can be misleading. The tendency of the hydrogen atom to form the negative ion is much lower than for the more electronegative halogen elements. This may be seen by comparing the energetics of the formation reactions:

$$\tfrac{1}{2}\mathrm{H_2(g)} \longrightarrow \mathrm{H(g)} \qquad \Delta H = 218 \text{ kJ mol}^{-1}$$

$$\tfrac{1}{2}\mathrm{Br_2(g)} \longrightarrow \mathrm{Br(g)} \qquad \Delta H = 113 \text{ kJ mol}^{-1}$$

$$\mathrm{H(g)} + e \longrightarrow \mathrm{H^-(g)} \qquad \Delta H = -67 \text{ kJ mol}^{-1}$$

$$\mathrm{Br(g)} + e \longrightarrow \mathrm{Br^-(g)} \qquad \Delta H = -345 \text{ kJ mol}^{-1}$$

$$\tfrac{1}{2}\mathrm{H_2(g)} + e \longrightarrow \mathrm{H^-(g)} \qquad \Delta H = +151 \text{ kJ mol}^{-1}$$

$$\tfrac{1}{2}\mathrm{Br_2(g)} + e \longrightarrow \mathrm{Br^-(g)} \qquad \Delta H = -232 \text{ kJ mol}^{-1}$$

Thus, owing to the endothermic character of the H^- ion, only the most electropositive metals—the alkalis and the alkaline earths—form saline or saltlike hydrides, such as NaH and CaH_2. The ionic nature of the compounds is shown by their high conductivities just below or at the melting point and by the fact that on electrolysis of solutions in molten alkali halides hydrogen is liberated at the *anode*.

X-ray and neutron diffraction studies show that in these hydrides the H^- ion has a crystallographic radius between those of F^- and Cl^-. Thus the electrostatic lattice energies of the hydride and the fluoride and chloride of a given metal will be similar. These facts and a consideration of the Born–Haber cycles lead us to conclude that *only* the most electropositive metals *can* form ionic hydrides, since in these cases relatively little energy is required to form the metal ion.

The hydrides and some of their physical properties are given in Table 3-7. The heats of formation compared with those of the alkali halides, which are about 420 kJ mol^{-1}, reflect the inherently small stability of the hydride ion.

For the relatively simple two-electron system in the H^- ion, it is possible to calculate an effective radius for the free ion, 2.08 Å. It is of interest to

TABLE 3-7
The Saltlike Hydrides and Some of Their Properties

Salt	Structure	Heat of formation $-\Delta H_f$(298 K)(kJ mol^{-1})	M—H distance (Å)	Apparent radius of H^-(Å)[a]
LiH	NaCl type	91.0	2.04	1.36
NaH	NaCl type	56.6	2.44	1.47
KH	NaCl type	57.9	2.85	1.52
RbH	NaCl type	47.4	3.02	1.54
CsH	NaCl type	49.9	3.19	1.52
CaH_2	Slightly distorted *hcp*	174.5	2.33[b]	1.35
SrH_2	Slightly distorted *hcp*	177.5	2.50	1.36
BaH_2	Slightly distorted *hcp*	171.5	2.67	1.34
MgH_2	Rutile type	74.5		1.30

[a] See text.

[b] Although half the H^- ions are surrounded by four Ca^{2+} and half by three Ca^{2+}, the Ca—H distances are the same.

compare this with some other values, specifically, 0.93 Å for the He atom, ~0.5 Å for the H atom, 1.81 Å for the crystallographic radius of Cl^-, and 0.30 Å for the covalent radius of hydrogen, as well as with the values of the "apparent" crystallographic radius of H^- given in Table 3-7. The values in the table are obtained by subtracting the Goldschmidt radii of the metal ions from the experimental M—H distances. The value 2.08 Å for the radius of free H^- is at first sight surprisingly large, being more than twice that for He. This results because the H^- nuclear charge is only half that in He and the electrons repel each other and screen each other (~30%) from the pull of the nucleus. Table 3-7 indicates that the apparent radius of H^- in the alkali hydrides never attains the value 2.08 Å and also that it decreases markedly with decreasing electropositive character of the metal. The generally small size is probably attributable in part to the easy compressibility of the rather diffuse H^- ion and partly to a certain degree of covalence in the bonds.

Preparation and Chemical Properties. The saline hydrides are prepared by direct interaction at 300 to 700°C. The rates are in the order Li > Cs > K > Na, largely because of the activation energy term in the Arrhenius equation.[30a] Extremely active hydrides[30b] of Li, Na, and K can be made by interaction of hydrogen with BuLi + TMEDA in hexane(LiH) or of BuLi + M(O*t*-Bu) + TMEDA in hexane (NaH and KH).

The saline hydrides are crystalline solids, white when pure but usually gray owing to traces of metal. They can be dissolved in molten alkali halides and on electrolysis of such a solution, for example, CaH_2 in LiCl + KCl at 360°C, hydrogen is released at the anode. They react instantly and completely with

[30a] S. E. Hill and R. J. Pulham, *J. Chem. Soc. Dalton Trans.*, **1982**, 217.

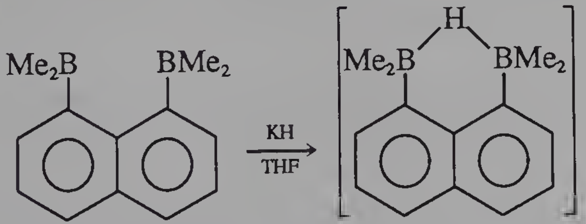
[30b] L. Brandsma *et al.*, *Angew, Chem. Int. Ed. Engl.*, 1986, **25**, 465.

even the weakest acids, such as water, according to the reaction

$$MH + H^+ = M^+ + H_2$$

The standard potential of the H_2/H^- couple has been estimated to be −2.25 V, making H^- one of the most powerful reducing agents known.

The hydrides of Rb, Cs, and Ba may ignite spontaneously in moist air. Thermal decomposition at high temperatures gives the metal and hydrogen. Lithium hydride alone can be melted (mp 688°C) and it is unaffected by oxygen below red heat or by chlorine or dry HCl; it is seldom used except for the preparation of the more useful complex hydride $LiAlH_4$ discussed in Section 7-9. Sodium hydride is available as a dispersion in mineral oil; although the solid reacts violently with water, the reaction of the dispersion is less violent. It is used extensively in organic synthesis and for the preparation of $NaBH_4$. Sodium hydride acts as a strong base for hydrogen abstractions but as a reducing agent it is slow and inefficient though improved by addition of nickel acetate as catalyst or by sodium *t*-amyloxide.[31] It is soluble in aqueous hexamethylphosphoramide giving a blue solution (cf. Section 4-3). Calcium hydride reacts smoothly with water and is a useful source of H_2 (1000 cm^3/g) as well as a convenient drying agent for gases and organic solvents. Finally it may be noted that the compound 1,8-naphthalenediylbis-(dimethylborane) (3-XV) reacts with KH in THF to give a bridged monohydride.[32] The compound also removes H^- from borohydride and other hydridic compounds and has been called a "hydride sponge" by analogy with a "proton sponge," which is similar but with NMe_2 instead of BMe_2 groups. It also gives a bridged anion with F^-.



(3-XV)

3-14. Hydrides of a More Covalent Nature

Beryllium and Mg hydrides can be made by thermal decomposition of $Be(CMe_3)_2$ and $MgEt_2$, respectively, but MgH_2 is best made by interaction of Mg with EtBr in THF containing anthracene followed by hydrogenation using a $CrCl_3(THF)_3$ catalyst with H_2 under pressure at 60 to 65°C.[33] Zinc hydride is similar.

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[31] P. Caubère, *Angew. Chem. Int. Ed. Engl.*, 1983, **22,** 599 (81 references to NaH in organic synthesis).

[32] H. E. Katz, *J. Am. Chem. Soc.*, 1985, **107,** 1420.

[33] B. Bogdanović *et. al.*, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 262.

Beryllium hydride (BeH_2) is difficult to obtain pure, but it is believed to have a polymeric structure with bridging hydrogen atoms as in the boranes (Chapter 6). Magnesium hydride has a rutile-type structure (Table 3-7) like MgF_2; it also has a low heat of formation and is less stable thermally than the true saline hydrides.

For aluminum there is evidence for AlH_3 and Al_2H_6 in the gas phase and AlH_3 (Section 7-9) forms at least six different solid phases, as well as solid etherates. The α-form, which appears to be the most stable solid form, has Al atoms octahedrally surrounded by H atoms in a structure very similar to that of AlF_3. Aluminum hydride (AlH_3) is a useful reducing agent in organic chemistry, and the products formed are significantly different from those of reduction by $LiAlH_4$. Nitriles can be reduced to amines via complex intermediates, and the reduction of alkyl halides is slower than with $LiAlH_4$ so that carboxyl or ester groups in compounds RCO_2H and RCO_2R' can be reduced preferentially in the presence of R″X.

There is no evidence for a comparable gallium hydride, but an unstable viscous oil that shows bands in the infrared spectrum due to Ga—H has been obtained by the reaction:

$$Me_3N{\cdot}GaH_3(s) + BF_3(g) \xrightarrow{-15^\circ C} GaH_3(l) + Me_3NBF_3(g)$$

There is also little evidence for hydrides of In and Tl.

3-15. Transition Metal Hydrides

The transition metals form a wide variety of compounds that have M—H bonds, including anions such as $[ReH_9]^{2-}$ and $[FeH_6]^{4-}$; these are discussed in detail in Chapter 24.

Hydrogen reacts with many transition metals or their alloys on heating, to give compounds commonly called hydrides even though in some cases they clearly do not contain hydride ions.[34] Many of these metal hydride systems are exceedingly complicated, showing the existence of more than one phase, often with wide divergences from stoichiometry. The most extensive studies have been made on the most electropositive elements, the lanthanides and actinides, and the titanium and vanadium groups of the *d*-block elements.

Satisfactory theoretical understanding of these substances has been slow to develop. Simple models emphasizing hydridic character, or protonic character or, again, covalent character for the hydrogen, have all been discussed. Only by elaborate band structure calculations can a true appreciation of their electronic structures and properties be obtained.

Lanthanide Hydrides. The metals such as lanthanum or neodymium react with H_2 at 1 atm and at or slightly above room temperature, to give black solids of graphite-like appearance. These products are pyrophoric in air and

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[34] *Hydrogen in Metals*, Vols. I, II (Topics in Applied Physics, Vols. 28, 29) G. Alefield and J. Völkl, Eds., Springer, 1978.

react vigorously with water. These are the phases MH_2 and MH_3 which are nonstoichiometric (e.g., $LaH_{2.87}$). Normally europium and ytterbium give only the dihydride phase, but higher ratios (e.g., $YbH_{2.55}$) can be obtained at 350°C under pressure.

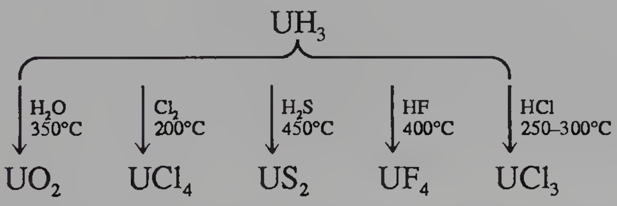
The hydrides appear to be predominantly ionic and to contain M^{3+} ions even in the MH_2 phase where the odd valence electron is probably located in a metallic conduction band as in the so-called dihalides such as LaI_2 (Chapter 20); in $YbH_{2.55}$ there is some evidence for both Yb^{2+} and Yb^{3+}.

Actinide Hydrides. Thorium and other actinides form complex systems with nonstoichiometric and stoichiometric phases. *Uranium hydride*[35] is of some importance chemically because it is often more suitable for the preparation of uranium compounds than is the massive metal. Uranium reacts rapidly and exothermically with hydrogen at 250 to 300°C to give a pyrophoric black powder. The reaction is reversible:

$$U + \tfrac{3}{2}H_2 = UH_3 \qquad \Delta H_f^0 = -129 \text{ kJ mol}^{-1}$$

The hydride decomposes at somewhat higher temperatures to give extremely reactive, finely divided metal. A study of the isostructural deuteride by X-ray and neutron diffraction shows that the deuterium atoms lie in a distorted tetrahedron equidistant from four uranium atoms; no U—U bonds appear to be present, and the U—D distance is 2.32 Å. The stoichiometric hydride UH_3 can be obtained, but the stability of the product with a slight deficiency of hydrogen is greater.

Some typical useful reactions are the following:



Hydrides of *d*-Block Transition Metals. Titanium, zirconium, and hafnium absorb hydrogen exothermically to give nonstoichiometric materials such as $TiH_{1.7}$ and $ZrH_{1.9}$. These and the similar hydrides of vanadium, niobium, and tantalum are grayish-black solids similar in appearance and reactivity to the finely divided metal. They are fairly stable in air but react when heated with air or acid reagents. The titanium and zirconium hydrides are used as reducing agents in metallurgical and other processes.

The affinity of many of the other *d*-block elements for hydrogen is small or zero with the exception of the following special cases.

A characteristic of palladium[36] and Pd–Ag or Pd–Au alloys is the absorption of H_2 and the high rate of diffusion of H_2 through a metal membrane

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[35] G. B. Deacon *et al., Inorg. Chim. Acta,* 1986, **111,** 193.

[36] F. A. Lewis, *Platinum Met. Rev.* 1982, **26,** 20, 70, 121.

compared to the rates for other metals such as Ni or Ir; various studies indicate the presence of palladium hydride phases.

An insoluble CuH with a wurtzite structure (Fig. 1-2) can be obtained by reduction of Cu^{2+} solutions by hypophosphorous acid. An amorphous hydride soluble in organic solvents such as pyridine or alkylphosphines results from the reaction of CuI and $LiAlH_4$ in pyridine.

There are numerous *mixed* hydrides such as Mg_2NiH_4, Li_2RhH_5, or Li_2RuH_6 some of which contain MH_n^{x-} ions as discussed in Chapter 24. These have been of particular interest as reversible, low volume storage materials for hydrogen, purification and separation of hydrogen, catalytic hydrogenations, and so on.[37] Interstitial hydrogen is also known in early transition metal and lanthanide halides, eg., $GdClH_{15}$.[38]

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[37] A. J. Fanelli *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 8.

[38] J. K. Burdett and G. L. Miller, *J. Am. Chem. Soc.,* 1987, **109,** 4092.

Chapter Four

The Group IA(1) Elements: Li, Na, K, Rb, Cs, Fr

GENERAL REMARKS

4-1. Introduction

The closely related elements lithium, sodium, potassium, rubidium, and cesium, often termed the alkali metals, have a single *s* electron outside a noble gas core. Some relevant data are listed in Table 4-1.

As a result of the low ionization enthalpies for the outer electrons and the sphericity and low polarizability of the resulting M^+ ions, the chemistry of these elements is principally that of their +1 ions. No other cations are known or, in view of the values of the second ionization enthalpies, expected. The ions M^-, where the *s* shell is filled, are discussed in Section 4-3.

The chemistry of the elements is mainly that of ionic salts in the solid state and solvated cations. Although some lithium and even sodium compounds are soluble in organic solvents, such compounds as $(LiCH_3)_4$ have essentially ionic Li^+; for sodium and potassium compounds close ion pairing can occur as discussed in later sections.

The gaseous diatomic molecules (M_2) are covalently bonded.

The element *francium* is formed in the natural radioactive decay series and in nuclear reactions. All its isotopes are radioactive with short half-lives. The ion behaves as would be expected from its position in the group.

Of all the groups in the Periodic Table, the Group IA(1) metals show most clearly and with least complication the effect of increasing size and mass on chemical and physical properties. Thus all of the following *decrease* through the series: (*a*) melting points and heats of sublimation of the metals; (*b*) lattice energies of all salts except those with the very smallest anions (because of irregular radius ratio effects); (*c*) effective hydrated radii and the hydration energies (see Table 4-2); (*d*) ease of thermal decomposition of nitrates and carbonates; (*e*) strength of the covalent bonds in the M_2 molecules; (*f*) heats of formation of fluorides, hydrides, oxides, and carbides (because of higher lattice energies with the smaller cations). Other trends also can readily be found.

TABLE 4-1
Some Properties of Group IA(1) Metals

			Ionization enthalpies (kJ mol^{-1})					
Element	Electronic configuration	Metal radius (Å)	1st	2nd $\times 10^{-3}$	mp (°C)	bp (°C)	E^{0a} (V)	$-\Delta H_{diss}{}^{b}$ (kJ mol^{-1})
Li	[He]2*s*	1.52	520.1	7.296	180.5	1326	−3.02	108.0
Na	[Ne]3*s*	1.86	495.7	4.563	97.8	883	−2.71	73.3
K	[Ar]4*s*	2.27	418.7	3.069	63.7	756	−2.92	49.9
Rb	[Kr]5*s*	2.48	402.9	2.640	38.98	688	−2.99	47.3
Cs	[Xe]6*s*	2.65	375.6	2.26	28.59	690	−3.02	43.6
Fr	[Rn]7*s*							

[a] For $M^+(aq) + e = M(s)$.
[b] Energy of dissociation of the diatomic molecule M_2.

The Li^+ ion is exceptionally small and hence has an exceptionally high charge–radius ratio comparable to that of Mg^{2+}. The properties of a number of *lithium compounds* are therefore anomalous (in relation to the other Group IA(1) elements) but resemble those of magnesium compounds. Many of the anomalous properties arise because the salts of Li^+ with small anions are exceptionally stable owing to their very high lattice energies, whereas salts with large anions are relatively unstable owing to poor packing of very large with very small ions. Lithium hydride is stable to approximately 900°C, but NaH decomposes at 350°C. Lithium nitride is stable, whereas Na_3N does not exist at 25°C. Lithium hydroxide decomposes at red heat to Li_2O, whereas the other hydroxides MOH sublime unchanged; LiOH is also considerably less soluble than the other hydroxides. The carbonate (Li_2CO_3) is thermally much less stable relative to Li_2O and CO_2 than are other alkali metal carbonates (M_2CO_3). The solubilities of Li^+ salts resemble those of Mg^{2+}. Thus LiF is sparingly soluble (0.27 g/100 g H_2O at 18°C) and can be precipitated from ammoniacal NH_4F solutions; LiCl, LiBr, LiI and, especially, $LiClO_4$ are soluble in solvents such as ethanol, acetone, and ethyl acetate, and LiCl is soluble in pyridine.

TABLE 4-2
Data on Hydration of Aqueous Group IA(1) Ions

	Li^+	Na^+	K^+	Rb^+	Cs^+
Crystal radii[a] (Å)	0.86	1.12	1.44	1.58	1.84
Approximate hydrated radii (Å)	3.40	2.76	2.32	2.28	2.28
Approximate hydration numbers[b]	25.3	16.6	10.5		9.9
Hydration energies (kJ mol^{-1})	519	406	322	293	264
Ionic mobilities (at ∞ dil., 18°C)	33.5	43.5	64.6	67.5	68

[a] Ladd radii.
[b] From transference data.

Sodium perchlorate ($NaClO_4$) is less soluble than $LiClO_4$ in various solvents by factors of 3 to 12, whereas $KClO_4$, $RbClO_4$, and $CsClO_4$ have solubilities only 10^{-3} of that of $LiClO_4$. Since the spherical ClO_4^- ion is virtually nonpolarizable and the alkali metal perchlorates form ionic crystals, the high solubility of $LiClO_4$ is mainly attributable to strong solvation of the Li^+ ion. Lithium bromide in hot concentrated solution has the unusual property of dissolving cellulose. Lithium sulfate does *not* form alums and is not isomorphous with the other sulfates.

Other ions that have chemical behavior closely resembling that of the Group IA(1) ions are:

1. Ammonium ions, NH_4^+, RNH_3^+, . . . , R_4N^+. Salts of NH_4^+ generally resemble those of K^+ quite closely in their solubilities and crystal structures.

2. The thallium(I) ion Tl^+ behaves in certain respects as an alkali metal ion (although in others more like Ag^+). Its ionic radius (1.54 Å) is comparable to that of Rb^+, although it is more polarizable. Thus TlOH is a water–soluble, strong base, which absorbs CO_2 from the air to form the carbonate. The sulfate and some other salts are isomorphous with the alkali metal salts.

3. Other unipositive, essentially spherical cations often behave like alkali ions of comparable size. For example, the very stable di(η-cyclopentadienyl)cobalt(III) ion and its analogues with similar "sandwich" structures (Chapter 26) have precipitation reactions similar to those of Cs^+, and $[(\eta\text{-}C_5H_5)_2Co]OH$ is a strong base that absorbs CO_2 from the air and forms insoluble salts with large anions.

THE ELEMENTS

4-2. Preparation and Properties

Sodium and K have high abundances (2.6 and 2.4%) in the lithosphere and occur in large deposits of rock salt, NaCl, and carnallite, $KCl{\cdot}MgCl_2{\cdot}6H_2O$. Lithium, Rb, and Cs have much lower abundances and occur mainly in a few silicate minerals.

Lithium and Na are obtained by electrolysis of fused salts or of low melting eutectics such as $CaCl_2 + NaCl$. Potassium, Rb, and Cs are made by treating molten MCl with Na vapor in a countercurrent fractionating tower; the metals are best purified by distillation. At the boiling point, the vapors have *ca.* 1% of M_2.

Lithium, Na, K, and Rb are silvery, but Cs has a golden-yellow appearance. In air, Li, Na, and K rapidly tarnish; Rb and Cs must be handled in argon.

Because there is only one valence electron per metal atom, the binding energies in the close-packed lattices are relatively weak and the metals hence soft with low melting points. Liquid sodium has been much studied in view of its use as a coolant in nuclear reactors and many reactions occur in the melt.[1] The most important alloys are the liquid Na—K ones where the eutectic with 77.2% K has mp -12.3°C. Lithium is immiscible with molten K, Rb, or Cs and with Na only over 380°C; the others are miscible in all proportions. The metals, usually Na or K, also dissolve in mercury with considerable vigor; sodium amalgam (Na/Hg) is liquid when Na poor ($\leq 7\%$) but solid when rich and is a useful reducing agent generally.

Lithium is relatively light (density 0.53 g/cm^3) and has the highest melting and boiling points and also the longest liquid range of all the alkali metals; it has also an extraordinarily high specific heat. These properties should make it an excellent coolant in heat exchangers, but it is also very corrosive—more so than other liquid metals—which is a great practical disadvantage; it is used to deoxidize, desulfurize, and generally degas copper and copper alloys.

Sodium metal may be dispersed by melting on various supporting solids (sodium carbonate, kieselguhr, etc.) or by high-speed stirring of a suspension of the metal in various hydrocarbon solvents held just above the melting point of the metal. Dispersions of the latter type may be poured in air, and they react with water only with effervescence. They are often used synthetically where sodium shot or lumps would react too slowly. Sodium and potassium, when dispersed on supports such as carbon, alumina, or silica[2] are often more reactive than the metals.

The high electrode potentials of the metals suggest potential use in batteries[3] and indeed several are known, for example, one with a Li anode, a polyvinylpyridine–I_2 cathode, and LiI as solid electrolyte; another with a liquid Na anode separated from a sulfur cathode by a β-Al_2O_3 solid electrolyte operates at 300°C.

The *chemical reactivity* of the metals toward all chemical reactants, except N_2, increases from Li to Cs. Usually the least reactive, lithium is only rather slowly attacked by water at 25°C, whereas sodium reacts vigorously, potassium inflames, and rubidium and cesium react explosively. With liquid Br_2, Li and Na barely react, whereas the others do so violently. Lithium does not replace the weakly acidic hydrogen in $C_6H_5C{\equiv}CH$, whereas the other alkali metals do so, yielding hydrogen gas. With N_2, however, Li is uniquely reactive to give a ruby-red crystalline nitride Li_3N (Mg also reacts to give Mg_3N_2); at 25°C this reaction is slow, but it is quite rapid at 400°C and has been studied in detail. Both Li and Mg can be used to remove nitrogen from other gases. When heated with carbon, both Li and Na react to form the *acetylides* Li_2C_2 and Na_2C_2. The heavier alkali metals also react with carbon, but give nonstoichiometric interstitial compounds where the metal atoms enter between the planes of carbon atoms in the lamellar graphite structure. This difference

[1] C. C. Addison, *The Chemistry of the Liquid Alkali Metals,* Wiley, New York, 1984.

[2] M. Rabinovitz *et al., Angew. Chem. Int. Ed. Engl.,* 1981, **20,** 1033.

[3] J. P. Gabano, Ed., *Lithium Batteries,* Academic Press, New York, 1983; R. J. Brodd, *Chem. Tech.,* 1985, 612; H. V. Venkatasetty, Ed., *Lithium Battery Technology,* Wiley, New York, 1984; J. L. Sudworth and A. R. Tilley, *The Sodium–Sulfur Battery,* Chapman & Hall, London, 1985.

may be attributed to size requirements for the metal, both in the ionic acetylides ($M_2^+C_2^{2-}$) and in the penetration of the graphite.

A particularly fundamental chemical difference between lithium and its congeners, attributable to cation size, is the reaction with oxygen. When the metals are burnt in air or oxygen at 1 atm, lithium forms the oxide Li_2O, with only a trace of Li_2O_2, whereas the other alkali oxides (M_2O) react further, giving as principal products the peroxides M_2O_2 and (from K, Rb, and Cs) the superoxides MO_2.

The reaction of the metals with H_2 was noted in Section 3-12. Lithium reacts with CO_2 to give $Li^+CO_2^{-\cdot}$ and $Li_2^+CO_2^{2-}$.[4]

The metals dissolve with reaction in alcohols to give the alkoxides. Sodium or K in ethanol or *tert*-butanol is commonly used in organic chemistry as a reducing agent and also provides a source of the nucleophilic alkoxide ions. The similar dialkylamides ($LiNR_2$), which are also widely useful synthetically, are best prepared indirectly by reaction of butyllithium (Sect. 4-7) with R_2NH.

4-3. Alkali Metals in Liquid Ammonia and Other Solvents[5a,b]

The metals, and to a lesser extent Ca, Sr, Ba, Eu, and Yb, are soluble in liquid ammonia and certain other solvents, giving solutions that are blue when dilute. These solutions conduct electricity *electrolytically* and measurements of transport numbers suggest that the main current carrier, which has an extraordinarily high mobility, is the solvated electron. Solvated electrons are formed in aqueous or other polar media by photolysis, radiolysis with ionizing radiations such as X rays, electrolysis, and probably some chemical reactions. The high reactivity of the electron and its short lifetime (in 0.75 *M* $HClO_4$, 6×10^{-11} s; in neutral water, $t_{1/2}$ *ca.* 10^{-4} s) make detection of such low concentrations difficult. Electrons can also be trapped in ionic lattices or in frozen water or alcohol when irradiated and again blue colors are observed.

In very pure liquid ammonia the lifetime of the solvated electron may be quite long (1% decomposition per day), but under ordinary conditions initial rapid decomposition occurs with water present, and with glass this is followed by a slower decomposition.

In *dilute solutions* the metal is dissociated into solvated metal ions (M^+) and electrons.

$$\text{M(s)(dispersed)} \rightleftharpoons \text{M(in solution)} \rightleftharpoons M^+ + e$$

$$2e \rightleftharpoons e_2$$

The broad absorption around 15,000 Å accounts for the common blue color; since the metal ions are colorless, this absorption must be associated with the

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[4] J. L. Margrave *et al.*, *J. Am. Chem. Soc.*, 1983, **105,** 3886.

[5a] J. L. Dye, *Progr. Inorg. Chem.*, 1984, **32,** 327.

[5b] D. Holton and P. P. Edwards, *Chem. Br.*, **1985,** 1007.

solvated electrons. Magnetic and esr studies show the presence of "free" electrons, but the decrease in paramagnetism with increasing concentration suggests that the ammoniated electrons can associate to form diamagnetic species containing electron pairs.

The electron is considered to be "smeared out" over a large volume so that the surrounding solvent molecules experience electronic and orientational polarization. The electron is trapped in the resultant polarization field, and repulsion between the electron and the electrons of the solvent molecules leads to the formation of a cavity within which the electron has the highest probability of being found. In ammonia this is estimated to be approximately 3 to 3.4 Å in diameter. This cavity concept is based on the fact that solutions are of much lower density than the pure solvent; that is, they occupy far greater volume than that expected from the sum of the volumes of metal and solvent. In methylamine, however, nmr studies suggest that most of the electron density is located on the N atoms of the solvent cavity.[6]

With increasing metal concentration the solutions become copper colored, have a metallic luster and high conductivity and contain M^- ions as discussed later.

X-ray and neutron diffraction studies of the Li–NH_3(l) system show that a golden-yellow solid $Li(NH_3)_4$ is formed[7]; three solid phases have a low vapor pressure compared to Na solvates but similar to solvates of Ca and other Ca group metals. Blue $Na(NH_3)_4$ is stable only at low temperatures.[8]

The metals are also soluble in a variety of other solvents such as $OP(NMe_2)_3$, amines, and ethers, to a greater or lesser extent depending on the dielectric constant and complexing ability of the solvent. The solubility in Me_2O or THF can be substantially increased by addition of cryptands, or crown ethers and liquid crown ethers, for example, 12-C-4 (mp 16°C) can be used.[9a]

The M^- Ions.[5,9a,b] Solutions of the metals except Li in ethers contain not only M^+_{solv} and e^-_{solv} but also the anion formed in the disproportionation reaction, which is driven by the solvation energy of the cation:

$$2M(s) \rightleftharpoons M^+_{solv} + M^-_{solv}$$

The reducing power of metals in amine solvents is probably due to M^- rather than to e^-. The use of cryptands or crown ethers not only drives the equilibrium towards Na^- formation but also provides sufficient stabilization to allow isolation of crystalline solids. There are two types: *alkalides* and *electrides.* Alkalides, which are the more kinetically and thermally stable, are yellow-bronze crystalline solids such as $[Na(C,2,2,2)]^+Na^-$. This has close-packed

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[6] P. P. Edwards *et al., J. Am. Chem. Soc.*, 1983, **105,** 2104.

[7] A. M. Stacy and M. J. Sienko, *Inorg. Chem.*, 1982, **21,** 2294.

[8] R. Winter and U. Schindewolf, *Ber. Bunsenges. Phys. Chem.*, 1982, **86,** 1093.

[9a] P. P. Edwards *et al., J. Am. Chem. Soc.*, 1986, **108,** 78; *J. Chem. Soc. Dalton Trans.*, **1986,** 323.

[9b] J. L. Dye *et al., J. Am. Chem. Soc.*, 1987, **109,** 3508; P. P. Edwards *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 1444.

$[Na(C,2,2,2)]^+$ ions with Na^- in octahedral holes between the cationic layers. Other examples are $[Rb(15\text{-}C\text{-}5)_2]^+Na^-$ and $[Cs(18\text{-}C\text{-}6)_2]^+e^-$ where the electron is trapped in a nearby spherical cavity radius ~2.4 Å.

Electrides, which contain trapped electrons, may be formed by addition of a second mole of complexing agent, that is,

$$M^- + L \rightleftharpoons ML + e^-_{solv}$$

$$ML \overset{L}{\rightleftharpoons} ML_2^+ + e^-_{solv}$$

but due to their extreme reactivity, isolation is more difficult. However, $[Cs(18\text{-}C\text{-}6)_2]^+e^-$ can be obtained as paramagnetic black crystals.

For the diamagnetic alkalides, magic angle nmr spectra of ^{23}Na and ^{133}Cs in, for example, $[Na(C,2,2,2)]^+Na^-$ and $[Cs(18\text{-}C\text{-}6)]^+Cs^-$ show separate peaks for M^+ and M^-, while the electride $[Cs(18\text{-}C\text{-}6)_2]^+e^-$ shows only a Cs^+ band. Nuclear magnetic resonance spectra for ^{23}Na and ^{37}Rb in liquid crown ether (12-C-4) or hexamethylphosphoramide solutions also give sharp signals for M^- suggesting that the anion is not solvated.

The ammonia and amine solutions of alkali metals are useful for preparing both organic and inorganic compounds. Thus Li in methylamine shows great selectivity in its reducing properties, but both this reagent and Li in ethylenediamine are quite powerful and can reduce aromatic rings to cyclic monoolefins. Sodium in liquid ammonia is probably the most widely used system for preparative purposes; the solution is moderately stable, but the decomposition reaction

$$Na + NH_3(l) = NaNH_2 + \tfrac{1}{2}H_2$$

can occur photochemically and is catalyzed by transition metal salts. Sodium amide can be conveniently prepared by treatment of Na with liquid ammonia in the presence of a trace of $FeCl_3$. Amines react similarly.

COMPOUNDS OF THE GROUP IA(1) ELEMENTS

4-4. Binary Compounds

The metals react directly with most nonmetals to give one or more binary compounds; they also form alloys and compounds with other metals such as Pb and Sn.

Oxides, are obtained by combustion of metal. Although Na normally gives Na_2O_2, it will take up further oxygen at elevated pressures and temperatures to form NaO_2. The per- and superoxides of the heavier alkalis can also be prepared by passing stoichiometric amounts of oxygen into their solutions in liquid ammonia, and ozonides (MO_3) are also known. The structures of the ions O_2^{2-}, O_2^-, and O_3^- and of their alkali salts are discussed in Sections 12-5 and 12-6. The increasing stability of the per- and superoxides as the size of the alkali ions increases is noteworthy and is a typical example of the stabilization of larger anions by larger cations through lattice energy effects.

Owing to the highly electropositive character of the metals, the various oxides (and also sulfides and similar compounds) are readily hydrolyzed by water according to the following equations:

$$M_2O + H_2O = 2M^+ + 2OH^-$$

$$M_2O_2 + 2H_2O = 2M^+ + 2OH^- + H_2O_2$$

$$2MO_2 + 2H_2O = O_2 + 2M^+ + 2OH^- + H_2O_2$$

The oxide Cs_2O has the *anti*-$CdCl_2$ structure and is the only known oxide with this type of lattice. An abnormally long Cs—Cs distance and a short Cs—O distance imply considerable polarization of the Cs^+ ion.

Rubidium and Cs form *suboxides* such as Rb_9O_2, $Rb_{12}O_2$, and $Cs_{11}O_3$ that are highly colored and often metallic in appearance. Their structures have metal clusters with M—M bonds; for example, in Rb_9O_2 there is a confacial bioctahedron of Rb atoms with an O atom in the center of each. Metal clusters M_4^{3+} have also been observed in zeolite cages[10] exposed to Na or K vapor.

The *hydroxides* (MOH) are white crystalline solids soluble in water and in alcohols. They can be sublimed unchanged at 350 to 400°C, and the vapors consist mainly of dimers $(MOH)_2$.

Measurements of the proton affinities of MOH in the gas phase show that the base strength increases from lithium to cesium, but this order need not be observed in aqueous or alcoholic solutions where the base strength of the hydroxide is reduced by solvent effects and hydrogen bonding. In suspension in nonhydroxylic solvents such as 1,2-dimethoxyethane, the hydroxides are exceedingly strong bases and can conveniently be used to deprotonate a wide variety of weak acids such as PH_3 ($pK \approx 27$) or C_5H_6 ($pK \approx 16$). The driving force for the reaction is provided by the formation of the stable hydrate:

$$2KOH(s) + HA = K^+A^- + KOH{\cdot}H_2O(s)$$

The alkali metals form a multitude of compounds with the elements of Groups IIIA–VIA (13–16) only a few of which can be thought of in *simple* ionic terms (i.e., in terms of M^+ ions and anions with complete octets, such as Na_2S, K_3P). The vast majority are far richer in the metalloidal element (e.g., NaP_7, $SrSi_2$, and LiGe) and contain complex polynuclear anionic structures. An example is $Li_{12}Si_7$, which contains both planar Si_5 and Si_4 rings.[11a] These materials are structurally and electronically transitional between ionic compounds and alloys. Most of them can be made either by direct reaction of the elements or by reaction of a liquid ammonia solution of the alkali metals with compounds of the metalloidal components.

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[10] P. P. Edwards *et al., J. Chem. Soc. Chem. Commun.,* **1984,** 982; U. Westphal and G. Geismar, *Z. Anorg. Allg. Chem.,* 1984, **508,** 165.

[11a] K.-F. Tebbe *et al., Angew. Chem. Int. Ed. Engl.,* 1980, **19,** 1033.

Zintl compounds[11b] or phases have anions that can often be isolated in crystalline solids by complexation of the alkali metal with cryptands or crowns; some are mentioned in other chapters but typical examples contain Sn_9^{4-}, $Sn_2Bi_2^{2-}$, or Pb_5^{2-} ions.

The red nitride Li_3N can be used as a reducing agent.[11c]

4-5. Ionic Salts and M$^+$ Ions in Solution

Salts of the bases MOH are crystalline, ionic solids, colorless except where the anion is colored. For the alkali metal ions the energies required to excite electrons to the lowest available empty orbitals could be supplied only by quanta far out in the vacuum ultraviolet (the transition $5p^6 \rightarrow 5p^5 6s$ in Cs^+ occurs at ~1000 Å). However, colored crystals of compounds such as NaCl are sometimes encountered. Color arises from the presence in the lattice of holes and free electrons, called color centers, and such chromophoric disturbances can be produced by irradiation of the crystals with X rays and nuclear radiation. The color results from transitions of the electrons between energy levels in the holes in which they are trapped. These electrons behave in principle similarly to those in solvent cages in the liquid ammonia solutions, but the energy levels are differently spaced and consequently the colors are different and variable. Small excesses of metal atoms produce similar effects, since these atoms form M^+ ions and electrons that occupy holes where anions would be in a perfect crystal.

The structures and stabilities of the ionic salts are determined in part by the lattice energies and by radius ratio effects, which have been discussed in Chapter 1. Thus the Li^+ ion is usually tetrahedrally surrounded by water molecules or negative ions, although $Li(H_2O)_6^+$ has also been found. On the other hand, the large Cs^+ ion can accommodate eight near-neighbor Cl^- ions, and its structure is different from that of NaCl, where the smaller cation Na^+ can accommodate only six near neighbors. The Na^+ ion appears to be six-coordinate in some nonaqueous solvents.

The salts generally have high melting points, electrical conductivity in melts, and ready solubility in water. They are seldom hydrated when the anions are small, as in the halides, because the hydration energies of the ions are insufficient to compensate for the energy required to expand the lattice. Owing to its small size, the Li^+ ion has a large hydration energy, and it is often hydrated in its solid salts when the same salts of other alkalis are unhydrated (namely, $LiClO_4 \cdot 3H_2O$). For salts of *strong* acids, the lithium salt is usually the *most* soluble in water of the alkali metal salts, whereas for *weak* acids the lithium salts are usually *less* soluble than those of the other alkalis.

The large size of the Cs^+ and Rb^+ ions frequently allows them to form

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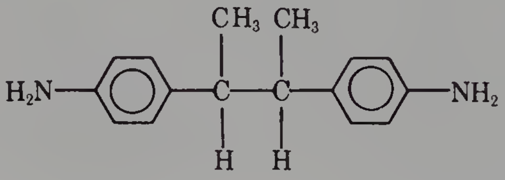
[11b] F. U. Axe and D. S. Marynick, *Inorg. Chem.*, 1987, **26**, 1658.

[11c] M. Kilner and G. Parkin, *J. Organomet. Chem.*, 1986, **302**, 181.

ionic salts with rather unstable anions, such as various polyhalide anions (Section 14-18) and the superoxides already mentioned.

Since few salts are sparingly soluble in water there are few *precipitation reactions* of the aqueous ions. Generally the larger the M^+ ion, the more numerous are its insoluble salts. Thus sodium has very few; the mixed Na–Zn and Na–Mg uranyl acetates [e.g., $NaZn(UO_2)_3(CH_3CO_2)_9 \cdot 6H_2O$], may be precipitated almost quantitatively under carefully controlled conditions from dilute acetic acid solutions. The perchlorates and hexachloroplatinates of K, Rb, and Cs are rather insoluble in water and virtually insoluble in 90% ethanol. These heavier ions may also be precipitated by the ion $[Co(NO_2)_6]^{3-}$ and various other large anions. Sodium tetraphenylborate $NaB(C_6H_5)_4$, which is moderately soluble in water, precipitates the tetraphenylborates of K, Rb, and Cs from neutral or faintly acid aqueous solutions.

Sodium chloride and some other MX salts can be precipitated from aqueous solution with the ligand (4-I) as, for example, NaL_3Cl, in which each Na^+ has distorted octahedral coordination by NH_2 groups from six different ligands.



(4-I)

The M^+ Ions in Solution. The primary hydration shell for Li^+ in aqueous solution is doubtless tetrahedral. Only tetrahydrated salts are formed except when there is also hydration of the anions. X-ray scattering studies show that the primary hydration number of K^+ is 4, and since Na^+ forms the stable $Na(NH_3)_4^+$ ion in liquid ammonia, it too presumably has a first coordination sphere of four water molecules. There is no direct evidence regarding Rb^+ or Cs^+, but a higher number, probably 6, seems likely.

In all cases electrostatic forces operate beyond the first shell, and additional water molecules are bound in layers of decreasing firmness. The larger the cation itself, the less it binds outer layers. Thus although the crystallographic radii *increase* down the group the hydrated radii *decrease* (Table 4-2). The hydration number of Li^+ is very large and Li^+ salt solutions generally deviate markedly from ideal solution behavior, showing abnormal colligative properties such as very low vapor pressures and freezing points. Also, hydration energies of the gaseous ions decrease. The decrease in size of the hydrated ions is manifested in various ways. The mobility of the ions in electrolytic conduction increases, and so generally does the strength of binding to ion-exchange resins.

The equilibria

$$A^+(aq) + [B^+R^-](s) = B^+(aq) + [A^+R^-](s)$$

where R represents the resin and A^+ and B^+ the cations, have been measured and the order of preference is usually $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, although irregular behavior does occur in some cases. The usual order may be explained if we assume that the binding force is essentially electrostatic and that under ordinary conditions the ions within the water-logged resin are hydrated approximately as they are outside it. Then the ion with the smallest hydrated radius (which is the one with the largest "naked" radius) will be able to approach most closely to the negative site of attachment and will hence be held most strongly according to Coulomb's law. The efficiency of separating alkali metal ions on cation exchangers can be increased significantly by adding chelating agents like EDTA to the eluting solution. These agents bind more strongly to the ions that are less strongly held to the resin, thus enhancing the separation factors.

4-6. Alkali Metal Complexes[12]

The M^+ ions are only very weakly complexed by simple anions, for example, F^- in 1 *M* fluoride solution, where the order falls Li → Cs.[13] Although lithium is an exception, as discussed later, chelation is usually essential to complex formation. Complexes are formed with β-diketones, nitrophenols, and so on; some, such as the hexafluoroacetylacetonates, are sublimable at 200°C, though the metal–ligand bonds are doubtless quite polar. The anhydrous β-diketonates are usually insoluble in organic solvents, indicating an ionic nature, but in the presence of additional coordinating ligands, including water, they may become soluble even in hydrocarbons; for example, sodium benzoylacetylacetonate dihydrate is soluble in toluene and tetramethylethylenediaminelithium hexafluoroacetylacetonate in benzene.

This behavior has allowed the development of solvent-extraction procedures for alkali metal ions. Thus not only can the trioctylphosphine oxide adduct $Li(PhCOCHCOPh)[OP(octyl)_3]_2$ be extracted from aqueous solutions into *p*-xylene, but also this process can be used to separate lithium from other alkali metal ions. Even Cs^+ can be extracted from aqueous solutions by 1,1,1-trifluoro-3-(2′ thenoyl)acetone (TTA) in $MeNO_2$–hydrocarbons.

Lithium forms a very wide range of complexes with amines, ethers, carboxylates, alkoxides, dialkylamides, and many other ligands whose structures are usually quite different from those of the other M^+ ions. Some of these are discussed in Section 4-8. However, we may note that in many of these compounds lithium can have coordination numbers 3–7.

Simple examples are LiNCS(16-C-4), which is tetragonal pyramidal while $LiI \cdot en_3$ has Li^+ in a distorted octahedron of N atoms. Chloride complex ions

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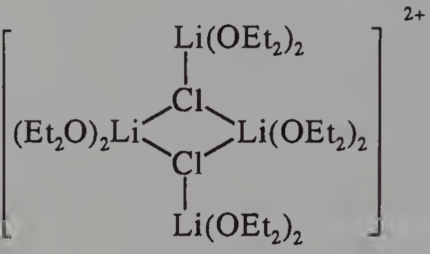
[12] N. S. Poonia and A. V. Bajaj, *Chem. Rev.*, 1979, **79,** 389; B. Dietrich, *J. Chem. Educ.*, 1985, **62,** 954 (with macrocycles).

[13] G. T. Hefter *et al., Polyhedron,* 1984, **3,** 845.

such as (4-II) have been characterized;



(4-II)

$LiBF_4[OP(NMe_2)_3]$ is soluble in benzene and has strong Li—F interactions[14a] and $LiNO_3$(diacetamide) is five-coordinate with η^1-NO_3.[14b]

The effectiveness of THF and dimethylethers of ethylene- and diethylene-glycols as media for reactions involving sodium metal may be due in part to slight solubility of Na but the driving force is undoubtably the complexation of Na^+ by the chelate ethers. The most important ethers are the crowns and cryptates[14c] (O, N) (Section 12-14), which bind M^+ strongly and often with high selectivity. The affinity of such a ligand for an ion is strongly dependent on how well the ion fits into the cavity that the ligand can provide for it. At the same time the strength of complexation and to some extent the selectivity also depend on the solvent. Illustrations of selectivity, provided by cryptate-221 and -222 are shown in Fig. 4-1.

For cryptate-222, for example, K^+ fits the cavity very well, but Li^+ and Na^+ are too small to make good contacts with the oxygen atoms and Rb^+ and Cs^+ are too large to enter without appreciable steric strain. An example

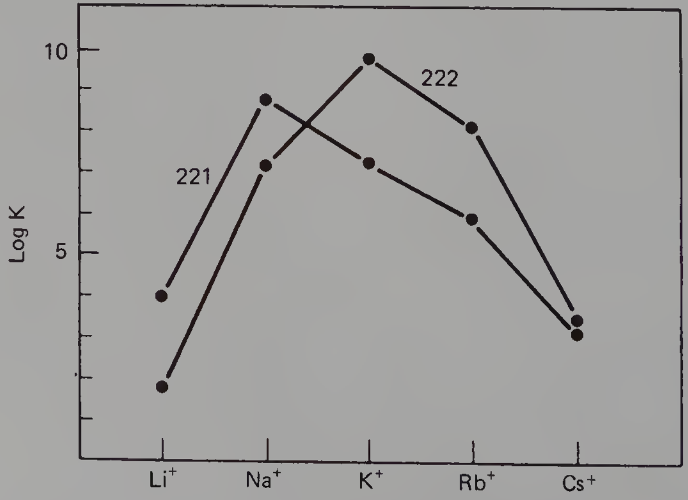


FIG. 4-1. Stability constants for cryptate-221 and -222 versus alkali ion in MeOH–H_2O = 95:5 [Adapted from J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, 1975, **97**, 6700.]

[14a] R. Snaith *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 127.
[14b] D. D. Bray and N. F. Bray, *Inorg. Chim. Acta,* 1986, **111,** 639.
[14c] D. Parker, *Adv. Inorg. Chem. Radiochem.*, 1983, **27,** 1.

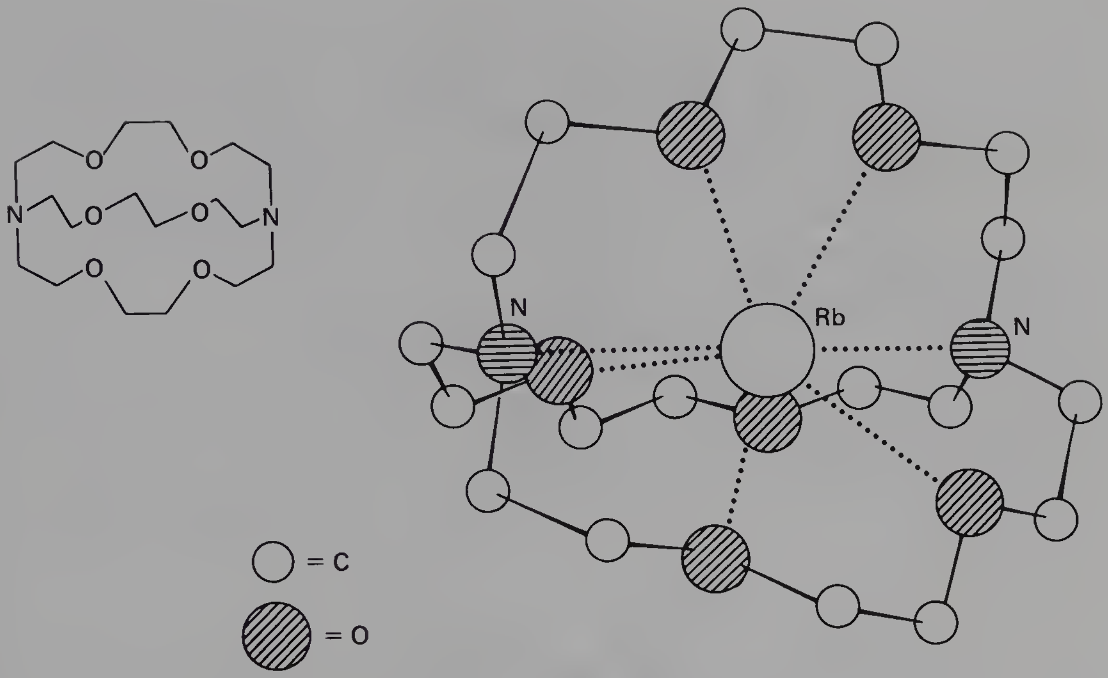
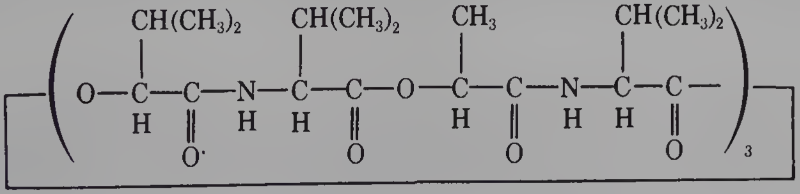


FIG. 4-2. The structure of the cation in the salt [$RbC_{18}H_{36}N_2O_6$]$SCN\cdot H_2O$. [Reproduced by permission from M. R. Truter, *Chem. Br.*, **1971,** 203.]

of an alkali cation (Rb^+) occupying the cavity in cryptate-222, and coordinated by the six oxygen and two nitrogen atoms, is presented in Fig. 4-2.

An 18-C-6 crown ether with a side chain terminating in an NH_2 group is selective for Na^+/K^+ in the transport of ions across a liquid membrane, thus mimicing natural ion-selective transport agents such as monensin.[15] Many of the natural agents are small polypeptides of which valinomycin (4-III) is another. The structures of two such complexes are shown in Fig. 4-3.



$$\left(O-\underset{H}{\overset{CH(CH_3)_2}{C}}-\underset{\underset{O}{\|}}{C}-\underset{H}{N}-\underset{H}{\overset{CH(CH_3)_2}{C}}-\underset{\underset{O}{\|}}{C}-O-\underset{H}{\overset{CH_3}{C}}-\underset{\underset{O}{\|}}{C}-\underset{H}{N}-\underset{H}{\overset{CH(CH_3)_2}{C}}-\underset{\underset{O}{\|}}{C}-\right)_3$$

(4-III)

Some ionophores with high preference for Li^+ are crown ethers with long aliphatic chains[16] and other macrocycles with functional groups may have utility for therapy in brain disorders for which Li^+ salts are used.

Open chain polyethers can also complex M^+ ions.[17]

Although few complex ions with only N donor ligands are stable for

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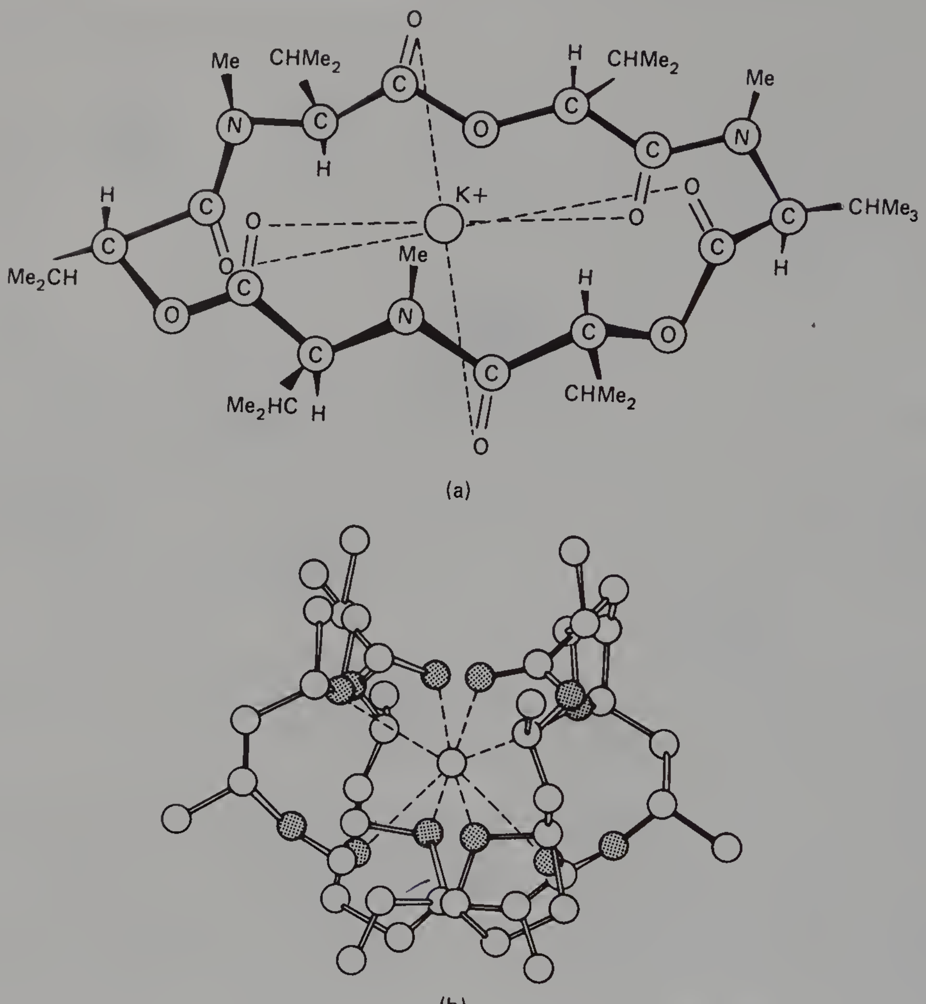
[15] W. Pangborn *et al., J. Am. Chem. Soc.,* 1987, **109,** 2163.

[16] T. Shono *et al., J. Am. Chem. Soc.,* 1984, **106,** 6978; A. Shanzar *et al., J. Am. Chem. Soc.,* 1983, **105,** 3815.

[17] D. L. Hughes and J. N. Wingfield, *J. Chem. Soc. Dalton Trans.,* **1984,** 1187.



(a)

(b)

FIG. 4-3. Structures of the K$^+$ salt of (a) [D-hydroxyisovaleric acid-*N*-methyl-L-valine]$_3$ or enniatin B and (b) nonactin. [Reproduced by permission from D. A. Fenton, *Chem. Soc. Rev.*, 1977, **6,** 325.]

Na$^+$—Cs$^+$, there are many of these for Li$^+$. Thus the effectiveness of $Me_2N(CH_2)_2NMe_2$ (tmen) in increasing the effectiveness of lithium alkyls (Section 4-7) is due to formation of $[Li(tmen)_2]^+$ with concomitant increase in nucleophilicity of the anion.

Rather unstable ammoniates such as $[Na(NH_3)_4]^+$ are obtained by the action of NH_3(l) on NaI.

Alkali Metal Salts of Complex Anions. The alkali metal salts of transition metal carbonylate anions such as $[Co(CO)_4]^-$ are discussed in detail in Chapter 22. However, it is relevant to note here that in such anions, ir spectra show that there is extensive ion-pair formation and that M$^+$ perturbs the CO or NO ligands on the metal.[18] As expected, Li$^+$ causes maximum perturbation

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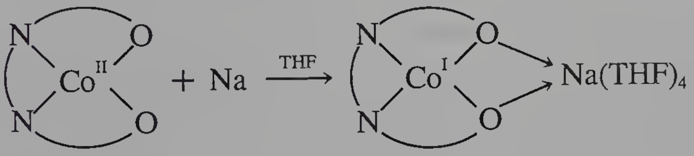
[18] M. Y. Darensbourg, *Progr. Inorg. Chem.*, 1985, **33,** 221.

and lowest CO stretching frequencies, via the M^+---O—C—Co or M^+---O—N—Fe interaction. No perturbation occurs with large cations of low charge density such as $[(Ph_3P)_2N]^+$ or $[\text{Na crypt}]^+$. In hydrido anions (Section 26-6) there is also Na^+---H—M interaction, which increases $CpV(CO)_3H^- < HFe(CO)_4^- < HCr(CO)_5^- < HW(CO)_5^- < HMo(CO)_4(PR_3)^-$, whereas the Na^+---OCM interaction is in the reverse order.

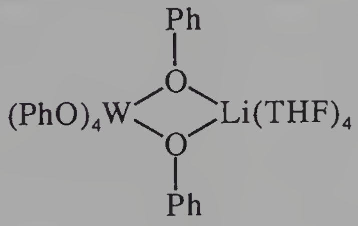
Exceptional compounds soluble in pentane despite being unsolvated by THF, tmen, and so on, are $K_2[Co(C_2H_4)_2(PMe_3)_3]_4$ and $Li_3[Co(C_2H_4)(PMe_3)_3]_3$ where, in the latter, Li^+ is bound both to Co and C_2H_4.[19] Many similar compounds, especially of Fe, Ni and Co are known, for example, $Li_2Fe(COD)_2$ and $Li(THF)_2Ni(C_4H_6)_3$.[20a] The "sandwich" ion $CpCo[P(O)(OEt)_2]_3^-$ (Section 26-14) acts as a tripod oxygen ligand giving pentane soluble $(NaL)_3{\cdot}2H_2O$.[20b]

The M^+ ions can also interact with oxygen atoms of other complexes such as those of Schiff bases like sal_2en[21]:



$$2VO\ sal_2en + NaBPh_4 \longrightarrow [(VOsal_2en)_2Na]^+BPh_4^-$$

Alkali metal complexes binding to the oxygen of alkoxides are also known,[22] for example (4-IV).



(4-IV)

Finally, some unusual species are the cation[23] $[Na_4(\mu\text{-}MeOH)_4(\mu\text{-}H_2O)_2(MeOH)]^{4+}$ found with $Mo_8O_{26}^{4-}$ and KZr_6I_{14} where the potassium is at the center of a Zr_6 cluster.[24] In $[Cs_9(18\text{-}C\text{-}6)_{14}]^{9+}$ in a rhodium cluster salt the Cs^+ ion is "sandwiched" between the crown ligands.[25]

[19] H.-F. Klein *et al., J. Chem. Soc. Chem. Commun.*, 1983, 231.

[20a] K. Jonas and C. Kruger, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 520.

[20b] W. Kläui *et al., J. Am. Chem. Soc.*, 1987, **109**, 164.

[21] C. Floriani *et al., J. Chem. Soc. Chem. Commun.*, **1987**, 183, 281; *Inorg. Chem.*, 1986, **25**, 4589.

[22] G. Wilkinson *et al., Polyhedron*, 1982, **1**, 641.

[23] E. M. McCarron, III, and R. L. Harlow, *Acta Cryst. (C)*, 1984, **40**, 1140.

[24] J. D. Smith and J. D. Corbett, *J. Am. Chem. Soc.*, 1984, **106**, 4618.

[25] J. L. Vidal *et al., Inorg. Chem.*, 1981, **20**, 227.

4-7. Organometallic Compounds[26]

Lithium Alkyls and Aryls. One of the largest uses for lithium metal is the synthesis of organolithium compounds, which are of great utility, generally resembling Grignard reagents, though usually more reactive.

They are commonly made by direct interaction of alkyl or aryl chloride in ether, benzene, or petroleum; ethers are slowly attacked, however, by LiR.

$$\mathrm{RCl + 2Li = RLi + LiCl}$$

In ether, MeLi gives complexes such as Li_4Me_3Br and Li_4Me_3I; *n*- or *t*-butyl lithium in hexane, benzene, or ethers may also be used in metal–hydrogen or metal–halogen exchanges, for example,

$$2n\text{-BuLi} + (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe} \longrightarrow (\eta^5\text{-C}_5\text{H}_4\text{Li})_2\text{Fe} + 2n\text{-C}_4\text{H}_{10}$$

$$n\text{-BuLi} + o\text{-Br(NO}_2)\text{C}_6\text{H}_4 \longrightarrow o\text{-Li(NO}_2)\text{C}_6\text{H}_4 + n\text{-BuBr}$$

Organolithiums are very reactive to water and to air, often being spontaneously flammable. They are soluble in hydrocarbons, have high volatility and may be sublimed in vacuum. Lithium alkyls are often considered to be carbanionic in reactions (although radicals are formed in some cases). However, although some solvated lithium compounds, for example, $Li(crown)_2CHPh_2$,[27] do have isolated planar carbanions, almost all lithium alkyls and aryls are associated in both the solid state and in solutions. There is accordingly a wide variation in reactivities depending on differences in aggregation and ion-pair interactions all of which are solvent dependent. Thus $LiCH_2Ph$, which is monomeric in THF reacts with a given substrate more than 10^4 times as fast as does $(LiMe)_4$. In noncoordinating solvents *t*-BuLi is hexameric while in THF there is an equilibrium[28]:

$$(t\text{-BuLi})_4 \rightleftharpoons 2(t\text{-BuLi})_2$$

$(PhLiEt_2O)_4$ is one of the few cases where solid and solution structures are similar.[29]

The addition of $Me_2N(CH_2)_2NMe_2$ to lithium reagents also increases the nucleophilicity remarkably by complexing the Li^+ ion.

The structures of the alkyls and related compounds are discussed in Section 4-8.

It may be noted that alkyls and aryls of main group and transition metals that are coordinately unsaturated have Lewis acid character (cf. the halides) and in alkylations of halides by LiR, in contrast to the use of MgR_2, *lithium*

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[26] J. L. Wardell, *Comprehensive Organometallic Chemistry,* Vol. 1, Chapter 2, Pergamon Press, Oxford, 1981; N. Jones, *Comprehensive Organic Chemistry,* Vol. 3, Chapter 15, Pergamon Press, Oxford, 1979.

[27] M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.,* 1985, **107,** 2174.

[28] J. F. McGarrity and C. A. Ugle, *J. Am. Chem. Soc.,* 1985, **107,** 1805, 1810.

[29] P. P. Power *et al., Organometallics,* 1984, **4,** 2117; L. M. Jackman and L. M. Scarmontos, *J. Am. Chem. Soc.,* 1984, **106,** 4627.

alkylate anions are often formed, for example,

$$Mo_2(O_2CMe)_4 + 8MeLi \xrightarrow{THF} [Li(THF)]_4[Mo_2Me_8]$$

$$MgPh_2 + 2PhLi \longrightarrow Li[MgPh_4]$$

$$WMe_6 + 2MeLi \longrightarrow Li_2[WMe_8]$$

The lithium alkylates of copper are of great utility in organic syntheses.

Polylithium Compounds. Compounds such as $(CH_2Li_2)_n$, Li_4C_3, and Li_4C can be made by the action of LiR on MeCN, MeC≡CH, and so on, or for $(CH_2Li_2)_n$ by thermal decomposition of MeLi.[30]

Organosodium and Potassium Compounds. These are essentially ionic, sparingly soluble if at all in hydrocarbons, and exceedingly air sensitive and reactive. Methyl potassium can be made by the reaction

$$Me_2Hg + 2K/Na \longrightarrow 2MeK + Na/Hg$$

It has the NiAs type structure (Fig. 13-4) and isolated methyl groups are probably rotating or disordered.

The Na and K compounds have little practical value due to their insolubility but interaction with $Mg(OCH_2CH_2OEt)_2$ gives benzene soluble species that can be used for arylations.[31] They can also be prepared from Na or K dispersed on an inert support, and such solids act as carbanionic catalysts for the cyclization, isomerization, or polymerization of alkenes. The so-called *alfin catalysts* for copolymerization of butadiene with styrene or isoprene to give rubbers consist of sodium alkyl (usually allyl) and alkoxide (usually isopropoxide) and NaCl, which are made simultaneously in hydrocarbons.

More important are the compounds formed by acidic hydrocarbons such as cyclopentadiene, indene, and acetylenes. These are obtained by reaction with sodium in liquid ammonia or, more conveniently, sodium dispersed in THF, glyme, diglyme, or dimethylformamide (DMF).

$$3C_5H_6 + 2Na \longrightarrow 2C_5H_5^-Na^+ + C_5H_8$$

$$RC{\equiv}CH + Na \longrightarrow RC{\equiv}C^-Na^+ + \tfrac{1}{2}H_2$$

Many aromatic hydrocarbons, as well as aromatic ketones, triphenylphosphine oxide, triphenylarsine, azobenzene, and so on, can form highly colored *radical anions* when treated at low temperatures with sodium or potassium in solvents such as THF. For the formation of such anions it must be possible to delocalize the negative charge over an aromatic system. Species such as the benzenide ($C_6H_6^-$), naphthalenide, or anthracenide ions can be detected and characterized spectroscopically and by esr. The sodium–naphthalene system $Na^+[C_{10}H_8]^-$ in an ether is widely used as a powerful reducing agent

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[30] R. J. Lagow *et al., Inorg. Chem.*, 1984, **23,** 3717; *J. Am. Chem. Soc.*, 1984, **106,** 3694. A. Maercker and M. Theis, *Angew. Chem. Int. Ed. Engl.*, 1984, **23,** 995.

[31] C. G. Screttas and M. M. Screttas, *Organometallics*, 1984, **3,** 904.

(e.g., in nitrogen-fixing systems employing titanium catalysts) and for the production of complexes in low oxidation states. The blue solution of sodium and benzophenone in THF, which contains the *ketyl* or radical ion, is a useful and rapid reagent for the removal of traces of oxygen from nitrogen.

4-8. Structures of Organolithiums and Related Lithium Compounds[32]

As well as the alkyls and aryls, lithium forms dialkylamides ($LiNR_2$); alkoxides (LiOR); dialkylphosphides ($LiPR_2$)[33]; thiolates (LiSR), and many other compounds most of which, as contrasted with their Na or K analogues, have exceptional solubility in organic solvents and with few exceptions are oligomers. Quite generally (*a*) the Li^+ ion is bound to the principal donor atom, for example, C in the alkyls or N in $LiNR_2$ by multicenter bonds and may also interact with other atoms such as H in the organic moiety; (*b*) lithium may have coordination numbers from 2 to 6 though four is most common; (*c*) lithium commonly is found in tetrahedra of lithium atoms, that is, Li_4 but other polyhedra occur. It is also found in rings such as $(LiN)_3$ that may, in certain cases, have hydrogen bridges between lithium and a metal $Li(\mu\text{-}H)_nM$.

Organolithium Compounds. The structure of the simplest, methyllithium, is shown in Fig. 4-4; that of $(EtLi)_4$ is similar. In both compounds the Li atoms are at the corners of a tetrahedron with the alkyl groups (μ_3) centered over the facial planes. Although the CH_3 group is symmetrically bound to three Li atoms, in the ethyl, the α carbon of CH_2CH_3 is closer to one Li atom than the other two.

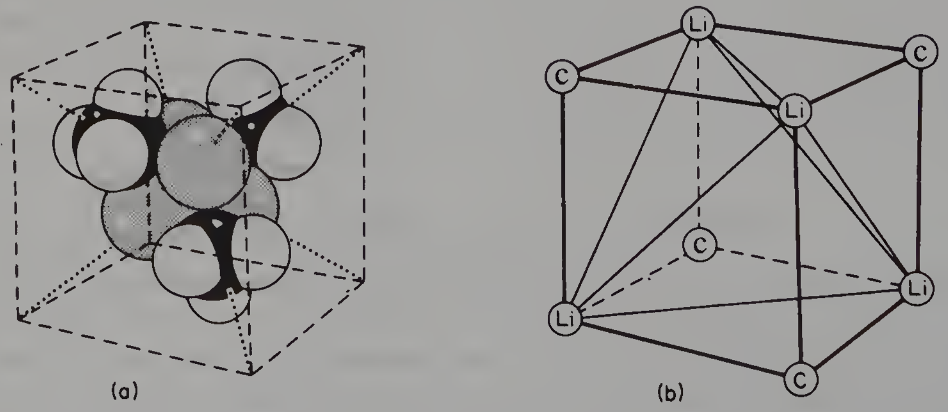

FIG. 4-4. The structure of $(CH_3Li)_4$. (a) Showing the tetrahedral Li_4 unit with the CH_3 groups located symmetrically above each face of the tetrahedron. [Adapted from E. Weiss and E. A. C. Lucken, *J. Organomet. Chem.*, 1964, **2**, 197.] The structure can also be regarded as derived from a cube (b).

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[32] W. N. Setzer and P. von R. Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 353 (an extensive review including compounds with Li—O, Li—N, Li—Si, etc., bonds).

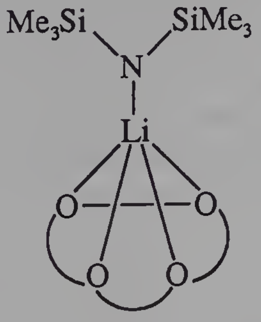
[33] See, for example, P. P. Power, *et al., Inorg. Chem.*, 1986, **25**, 1243; *J. Am. Chem. Soc.*, 1986, **108,** 6921.

Examples of other structures known are those of $Li_6(c\text{-}C_6H_{11})_6$, and $(LiPh\cdot OEt_2)_4$ as well as *ate* complexes such as $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$ and $Li_4[Mo_2Me_8]$.

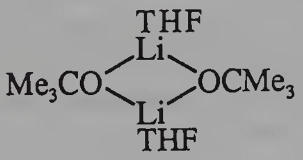
In all the oligomers, Li–Li bonding is not important although in a dimeric adduct of lithium cyclohexyl, the Li–Li distance, 2.34 Å is shorter than that in MeLi (2.57 Å) or in the Li_2 gas molecule (2.67 Å). Here too, as in other compounds where lithium interacts with alkenes, alkynes, and arenes, there is always a high degree of ionic character, despite the often high degree of solubility in alkanes. The precise degree and nature of the oligomerization is probably due to steric factors. The simpler alkyls usually give tetramers, for example, $(t\text{-BuLi})_4$,[34a] though even in a very bulky alkyl like $Li_4\{MnH(C_2H_4)[CH_2(Me)PCH_2CH_2PMe_2]_2\}_2\cdot 2Et_2O$[34b] there is a central Li_4 tetrahedron. In $(c\text{-}C_6H_{11}Li)_6\cdot 2C_6H_6$ there are Li_6 octahedra with cyclohexyl groups bridging on six of the eight faces and benzenes on the other two; $[Li(SiMe_3)]_6$ also has an octahedron of lithium atoms.

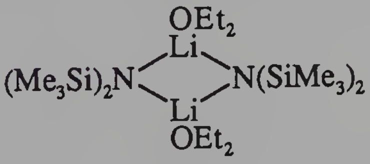
The oligomers are commonly cleaved by basic ligands like $Me_2N(CH_2)_2NMe_2$ or crown ethers.

The *dialkylamides* and *alkoxides* show similar features to unsolvated or solvated alkyls and aryls. Some examples of structures are the following.

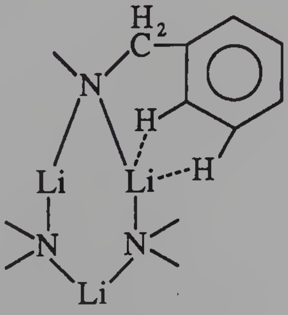


(12-C-4)





In the nonsolvated compound, $[LiN(CH_2Ph)_2]_3$, there is evidence of Li---HC interaction in the solid state[35] (4-V).



(4-V)

[34a] R. D. Thomas *et al., Organometallics,* 1987, **6,** 565.

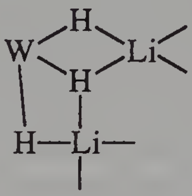
[34b] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 921.

[35] R. Snaith *et al., J. Chem. Soc. Chem. Commun.,* **1984,** 287.

Close Li–Me interactions are also found in $Li[MnN(SiMe_3)_2(OCt^-Bu_3)_2]$.[36]

It may be noted, however, that low C—H stretching frequencies in the ir spectra of transition metal species are not necessarily indicative of Li--H—C interactions as has sometimes been thought since these are observed not only in (4-V) but also in $[(PhCH_2)_2NLi(OEt_2)]_2$.

Another type of oligomeric lithium compound is $[LiWH_5(PMe_3)_3]_4$ (Section 24-5) that has a staggered ring of W and Li atoms that are linked by bridges of the type (4-VI).[37]



(4-VI)

Additional References

Bach, R. O., Ed., *Lithium: Current Applications in Science Medicine and Technology,* Wiley, New York, 1985.

Brandsma, L. and H. Verkruijsse, *Preparative Polar Organometallic Chemistry,* Vol. 1, B. M. Trost, Ed., Springer-Verlag, New York, 1986.

Organolithium Compounds. Solvated Electrons, *Top. Curr. Chem.,* **1986,** Vol 138. (polylithiated aliphatic hydrocarbons, lithiation reactions, electrochemistry of solvated electrons).

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[36] B. D. Murray and P. P. Power, *J. Am. Chem. Soc.,* 1984, **106,** 7011.

[37] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1987,** 837.

Chapter Five

The Group IIA(2) Elements: Be, Mg, Ca, Sr, Ba, Ra

GENERAL REMARKS

5-1. General Remarks

Some pertinent data for the elements are given in Table 5-1. Beryllium has unique chemical behavior with a predominantly covalent chemistry, although it forms a cation $[Be(H_2O)_4]^{2+}$. Magnesium has a chemistry intermediate between that of Be and the heavier elements, but it does not stand in as close relationship with the predominantly ionic heavier members as might have been expected from the similarity of Na, K, Rb, and Cs. It has considerable tendency to covalent bond formation, consistent with the high charge/radius ratio. For instance, like beryllium, its hydroxide can be precipitated from aqueous solutions, whereas hydroxides of the other elements are all moderately soluble, and it readily forms bonds to carbon.

The metal atomic radii are smaller than those of the Group I metals owing to the increased nuclear charge; the number of bonding electrons in the metals is twice as great, so that the metals have higher melting and boiling points and greater densities.

All are highly electropositive metals, however, as is shown by their high chemical reactivities, ionization enthalpies, standard electrode potentials and, for the heavier ones, the ionic nature of their compounds. Although the energies required to vaporize and ionize these atoms to the M^{2+} ions are considerably greater than those required to produce the M^+ ions of the Group I elements, the high lattice energies in the solid salts and the high hydration energies of the $M^{2+}(aq)$ ions compensate for this, with the result that the standard potentials are similar to those of the Li–Cs group.

The potential E^0 of beryllium is considerably lower than those of the other elements, indicating a greater divergence in compensation by the hydration energy, the high heat of sublimation, and the ionization enthalpy. As in Group IA(1), the smallest ion crystallographically (i.e., Be^{2+}) has the largest hydrated ionic radius.

All the M^{2+} ions are smaller and considerably less polarizable than the

TABLE 5-1
Some Physical Parameters for the Group IIA(2) Elements

Element	Electronic configuration	mp (°C)	Ionization enthalpies (kJ mol^{-1})		E^0 for M^{2+} (aq) + 2e = M(s) (V)	Ionic radius (Å)[a]	Charge / radius
			1st	2nd			
Be	[He]$2s^2$	1278	899	1757	-1.70[b]	0.31[b]	6.5
Mg	[Ne]$3s^2$	651	737	1450	-2.37	0.78	3.1
Ca	[Ar]$4s^2$	843	590	1146	-2.87	1.06	2.0
Sr	[Kr]$5s^2$	769	549	1064	-2.89	1.27	1.8
Ba	[Xe]$6s^2$	725	503	965	-2.90	1.43	1.5
Ra	[Rn]$7s^2$	700	509	979	-2.92	1.57	1.3

[a] Ladd radii.
[b] Estimated.

isoelectronic M^+ ions. Thus deviations from complete ionicity in their salts due to polarization of the cations are even less important. However, for Mg^{2+} and, to an exceptional degree for Be^{2+}, polarization of anions by the cations does produce a degree of covalence for compounds of Mg and makes covalence characteristic for Be. Accordingly only an estimated ionic radius can be given for Be^{2+}; the charge/radius ratio is greater than for any other cation except H^+ and B^{3+}, which again do not occur as such in crystals. The closest ratio is that for Al^{3+} and some similarities between the chemistries of Be and Al exist. Examples are the resistance of the metal to attack by acids owing to formation of an impervious oxide film on the surface, the amphoteric nature of the oxide and hydroxide, and Lewis acid behavior of the chlorides. However, Be shows just as many similarities to zinc, especially in the structures of its binary compounds (see Sections 16-6 to 16-8) and in the chemistry of its organic compounds. Thus BeS is insoluble in water, although Al_2S_3, CaS, and so on, are rapidly hydrolyzed.

Calcium, Sr, Ba, and Ra form a closely allied series in which the chemical and physical properties of the elements and their compounds vary systematically with increasing size in much the same manner as in Group IA(1), the ionic and electropositive nature being greatest for radium. Again the larger ions can stabilize certain large anions, e.g., the peroxide and superoxide ions, polyhalide ions, and so on. Some examples of systematic group trends in the series Ca–Ra are (*a*) hydration tendencies of the crystalline salts increase; (*b*) solubilities of sulfates, nitrates, chlorides, and so on (fluorides are an exception) decrease; (*c*) solubilities of halides in ethanol decrease; (*d*) thermal stabilities of carbonates, nitrates, and peroxides increase; (*e*) rates of reaction of the metals with hydrogen increase. Other similar trends can be found.

All isotopes of *radium* are radioactive, the longest-lived isotope being ^{226}Ra (α; ~1600 years). This isotope is formed in the natural decay series of ^{238}U and was first isolated by Pierre and Marie Curie from pitchblende. Once widely used in radiotherapy, it has largely been supplanted by radioisotopes made in nuclear reactors.

The elements zinc, cadmium, and mercury, which have two electrons outside filled penultimate *d* shells, are classed in Group IIB(12). Although the difference between the calcium and zinc subgroups is marked, zinc, and to a lesser extent cadmium, show some resemblance to beryllium or magnesium in their chemistry. We discuss these elements separately (Chapter 16), but note here that zinc, which has the lowest second ionization enthalpy in the Zn, Cd, Hg group, still has a value (1726 kJ mol^{-1}) similar to that of beryllium (1757 kJ mol^{-1}), and its standard potential (-0.76 V) is considerably less negative than that of magnesium.

There are a few ions with ionic radii and chemical properties similar to those of Sr^{2+} or Ba^{2+}, notably those of the $+2$ lanthanides (Section 20-14) and especially the europous ion (Eu^{2+}) and its more readily oxidized analogues Sm^{2+} and Yb^{2+}. Because of this fortuitous chemical similarity, europium is frequently found in Nature in Group II minerals, and this is a good example of the geochemical importance of such chemical similarity.

Although the differences between the first and second ionization enthalpies especially for beryllium might suggest the possibility of a stable $+1$ state, there is no evidence to support this. Calculations using Born–Haber cycles show that owing to the much greater lattice energies of MX_2 compounds, MX compounds would be unstable and disproportionate:

$$2MX \longrightarrow M + MX_2$$

There is some evidence for Be^{I} in fused chloride melts, for example

$$Be + Be^{II} = 2Be^{I}$$

but no Be^{I} compound has been isolated. Some studies of the dissolution of Be from anodes suggested Be^{+} as an intermediate, but subsequent work showed that disintegration of the metal occurs during dissolution, so that the apparent effect is one of the metal going into solution in the $+1$ state—too much metal is lost for the amount of current passed. The anode sludge, a mixture of Be and $Be(OH)_2$, had been considered to be due to disproportionation of Be^{+}, but photomicrography indicates that the beryllium in the sludge is due merely to spallation of the anode.

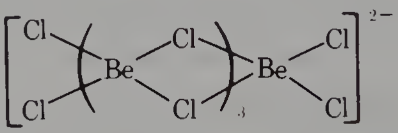
On the other hand, similar studies of anodic dissolution of Mg in pyridine and aqueous salt solutions do provide some evidence for transitory Mg^{+} ions, which would account for evolution of H_2 at or near the anode. Electrically generated Mg^{+} ions have been used to reduce organic compounds.

BERYLLIUM

5-2. Covalency and Stereochemistry for Beryllium

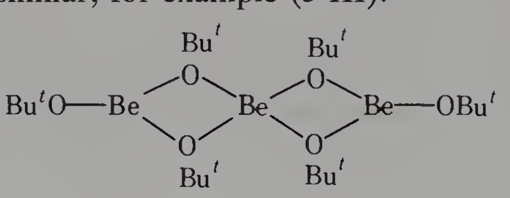
As a result of the small size, high ionization enthalpy, and high sublimation energy of beryllium, its lattice and hydration energies are insufficient to provide complete charge separation and the formation of simple Be^{2+} ions. In fact, in all compounds whose structures have been determined, even those of the most electronegative elements (i.e., BeO and BeF_2), there appears to be substantial covalent character in the bonding. On the other hand, to allow the formation of two covalent bonds —Be—, it is clear that unpairing of the two 2*s* electrons is required. Where free BeX_2 molecules occur, the Be atom is promoted to a state in which the two valence electrons occupy two equivalent *sp* hybrid orbitals and the X—Be—X system is linear. However, in such a linear molecule the Be atom has a coordination number of only 2 and there is a strong tendency for Be to achieve maximum (fourfold) coordination, or at least threefold coordination. Maximum coordination is achieved in several ways.

1. Polymerization may occur through bridging, as in solid $BeCl_2$ (Fig. 5-1). The coordination of Be is not exactly tetrahedral, since the ClBeCl angles are only 98.2° which means that the $BeCl_2Be$ units are somewhat elongated in the direction of the chain axis. In $(BeMe_2)_n$ the CBeC angle is 114°. These distortions from the ideal tetrahedral angle are related to the presence (or absence) of the lone pairs on the bridge group or atom that are available for bonding to the metal.[1] In the gas phase at high temperatures the chloride (and other halides) is linear, Cl—Be—Cl, but at lower temperatures there are appreciable amounts (~20% at 560°C) of a dimer in which Be is, presumably, three-coordinate. In the compounds of the type $M^IBe_2Cl_5$ (M^I = K, Rb, Tl, NO, NH_4) the anion (5-I) resembles a portion of the $(BeCl_2)_n$ chain.

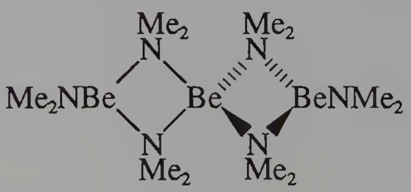


(5-I)

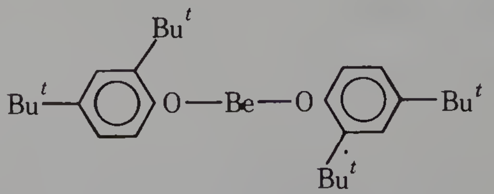
2. Alkoxides, $[Be(OR)_2]_n$, are usually associated with three- or four-coordinate Be. For example, $[Be(OMe)_2]_n$ is a high polymer, insoluble in hydrocarbon solvents. Even $[Be(O\text{-}t\text{-}Bu)_2]_3$, which is soluble, is trimeric (5-II). The compound $\{Be[OC(CF_3)_3]_2\}_2$ is a highly volatile dimer. The dialkylamides[2] are similar, for example (5-III).



(5-II)



(5-III)



(5-IV)

$(Me_3Si)_2N—Be—N(SiMe_3)_2$

(5-V)

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[1] E. Canadell and O. Eisenstein, *Inorg. Chem.*, 1983, **22**, 3856.

[2] H. Nöth and D. Schlosser, *Inorg. Chem.*, 1983, **22**, 2700.

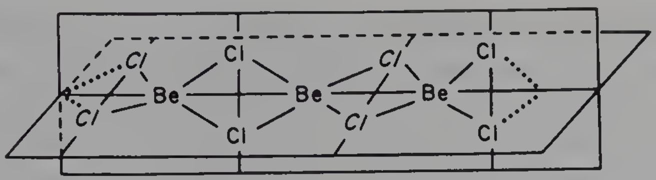

FIG. 5-1. The structure of polymeric $BeCl_2$ in the crystal. The structure of $Be(CH_3)_2$ is similar.

Only when there are bulky groups on O or N are monomers with two-coordinate Be such as (5-IV) and (5-V) obtained; these are isoelectronic with $B(OR)_2^+$ and $B(NR_2)_2^+$. Another example is Be(*t*-Bu)$_2$.

3. By functioning as Lewis acids, many beryllium compounds attain maximum coordination of the metal atom. Thus the chloride forms etherates $[Cl_2Be(OR_2)_2]$, and complex ions such as $[BeF_4]^{2-}$ and $[Be(H_2O)_4]^{2+}$ exist. In chelate compounds such as the acetylacetonate [Be(acac)$_2$], four approximately tetrahedral bonds are formed, with the C—O and Be—O bond lengths equivalent.

In addition to the tetrahedral $[BeF_4]^{2-}$ion, some substances of composition $M^IBe_2F_5$ contain infinite sheet anions (i.e., not the chains present in the previous chloro analogue) in which there are hexagonal rings of BeF_4 tetrahedra sharing corners, structurally analogous to the sheet silicate anions of empirical formula $Si_2O_5^{2-}$ (cf. Section 9-7).

The packing in crystals is almost invariably such as to give beryllium a coordination number of 4, with a tetrahedral configuration. In binary compounds, the structures are often those of the corresponding zinc compounds. Thus the low-temperature form of BeO has the wurtzite structure (Fig. 1-2); the most stable $Be(OH)_2$ polymorph has the $Zn(OH)_2$ structure, and BeS has the zinc blende structure (Fig. 1-2). Beryllium silicate (Be_2SiO_4) is exceptional among the orthosilicates of the alkaline earths, the rest of which have structures giving the metal ion octahedral coordination, in having the Be atoms tetrahedrally surrounded by oxygen atoms. It may be noted that Be with F gives compounds often isomorphous with oxygen compounds of silicon; thus $NaBeF_3$ is isomorphous with $CaSiO_3$, and there are five different corresponding forms of Na_2BeF_4 and Ca_2SiO_4.

In Be phthalocyanine the metal is perforce surrounded by four nitrogen atoms in a plane. This compound constitutes an example of a *forced configuration,* since the Be atom is held strongly in a rigid environment.

It is to be noted especially that beryllium compounds are *exceedingly poisonous,* particularly if inhaled, and great precautions must be taken in handling them.

5-3. Elemental Beryllium

The most important mineral is *beryl* $[Be_3Al_2(SiO_3)_6]$, which often occurs as large hexagonal prisms. The extraction from ores is complicated. The metal is obtained by electrolysis of $BeCl_2$, but since the melt has very low electrical conductivity (about 10^{-3} that of NaCl), sodium chloride is also added.

The gray metal is rather light (1.86 g/cm^3) and quite hard and brittle. Since the absorption of electromagnetic radiation depends on the electron density in matter, beryllium has the lowest stopping power per unit mass thickness of all suitable construction materials. It is used for "windows" in X-ray apparatus and has other special applications in nuclear technology. Like aluminum, metallic beryllium is rather resistant to acids unless finely divided or amalgamated, owing to the formation of an inert and impervious oxide film on the surface. Thus although the standard potential (-1.70 V) would indicate rapid reaction with dilute acids (and even H_2O), the rate of attack depends greatly on the source and fabrication of the metal. For the very pure metal the relative dissolution rates are $HF > H_2SO_4 \sim HCl > HNO_3$. The metal dissolves rapidly in 3*M* H_2SO_4 and in 5*M* NH_4F, but very slowly in HNO_3. Like aluminum, it also dissolves in strong bases, forming what is called the beryllate ion.

5-4. Binary Compounds

The white crystalline *oxide* BeO is obtained on ignition of beryllium or its compounds in air. It resembles Al_2O_3 in being highly refractory (mp 2570°C) and in having polymorphs; the high-temperature form (>800°C) is exceedingly inert and dissolves readily only in a hot syrup of concentrated H_2SO_4 and $(NH_4)_2SO_4$. The more reactive forms dissolve in hot alkali hydroxide solutions or fused $KHSO_4$.

Addition of the OH^- ion to $BeCl_2$ or other beryllium solutions gives the *hydroxide*. This is amphoteric, and in alkali solution the *beryllate* ion, probably $[Be(OH)_4]^{2-}$, is obtained. When these solutions are boiled, the most stable of several polymorphs of the hydroxide can be crystallized.

Beryllium halides, all four of which are known, are deliquescent and cannot be obtained from their hydrates by heating, since HX is lost as well as H_2O. The fluoride is obtained as a glassy hygroscopic mass by heating $(NH_4)_2BeF_4$. The glassy form has randomly oriented chains of $\cdots F_2BeF_2Be \cdots$ similar to those in $BeCl_2$ and $BeBr_2$ but disordered. Two crystalline modifications are known, which appear to be structurally analogous to the quartz and cristobalite modifications of SiO_2 (Section 9-7). At 555°C BeF_2 melts to a viscous liquid that has low electrical conductivity. The polymerization in the liquid may be lowered by addition of LiF, which forms the $[BeF_4]^{2-}$ ion.

Beryllium chloride is prepared by passing CCl_4 over BeO at 800°C. On a small scale the chloride and bromide are best prepared pure by direct interaction in a hot tube. The white crystalline chloride (mp 405°C) dissolves exothermically in water; from HCl solutions the salt $[Be(H_2O)_4]Cl_2$ can be obtained. Beryllium chloride is readily soluble in oxygenated solvents such as ethers. In melts with alkali halides, chloroberyllate ions $[BeCl_4]^{2-}$ may be formed, but this ion does not exist in aqueous solution.

On interaction of Be with NH_3 or N_2 at 900 to 1000°C the *nitride* Be_3N_2 is obtained as colorless crystals, readily hydrolyzed by water. The metal reacts with ethylene at 450°C to give BeC_2.

5-5. Complex Chemistry

Oxygen Ligands. In strongly acid solutions the *aqua ion* $[Be(H_2O)_4]^{2+}$ occurs, and crystalline salts with various anions can be readily obtained. The water in such salts is more firmly retained than is usual for aquates, indicating strong binding. Thus the sulfate is dehydrated to $BeSO_4$ only on strong heating, and $[Be(H_2O)_4]Cl_2$ loses no water over P_2O_5. Solutions of beryllium salts are acidic; this may be ascribed to the acidity of the aqua ion, the initial dissociation being

$$[Be(H_2O)_4]^{2+} \rightleftharpoons [Be(H_2O)_3(OH)]^+ + H^+$$

The addition of soluble carbonates to beryllium salt solutions gives only basic carbonates. Beryllium salt solutions also have the property of dissolving additional amounts of the oxide or hydroxide. This behavior is attributable to the formation of complex species with Be—OH—Be or Be—O—Be bridges. The rapidly established equilibria involved in the hydrolysis of the $[Be(H_2O)_4]^{2+}$ ion are very complicated and depend on the anion, the concentration, the temperature, and the pH. The main species, which will achieve four-coordination by additional water molecules, are considered to be $Be_2(OH)^{3+}$ and $Be_3(OH)_3^{3+}$ (probably cyclic).[3]

The $[Be_3(OH)_3]^{3+}$ ion predominates at pH 5.5 in perchlorate solution. Various crystalline hydroxo complexes have been isolated. In concentrated alkaline solution the main species is $[Be(OH)_4]^{2-}$.

Other complexes of oxygen ligands are mainly adducts of beryllium halides or alkyls with ethers, ketones, and so on [e.g., $BeCl_2(OEt_2)_2$]. There are also neutral complexes of β-diketones and similar compounds, of which the acetylacetonate is the simplest, and solvated cationic species such as $[Be(DMF)_4]^{2+}$. The most unusual complexes have the formula $Be_4O(O_2CR)_6$ and are formed by refluxing the hydroxide with carboxylic acids. These white crystalline compounds are soluble in organic solvents, even alkanes, but are insoluble in water and lower alcohols. They are inert to water but are hydrolyzed by dilute acids; in solution they are un-ionized and monomeric. They have the structures illustrated in Fig. 5-2. The central oxygen atom is tetrahedrally surrounded by the four beryllium atoms (this being one of the few cases, excepting solid oxides, in which oxygen is four-coordinate), and each beryllium atom is tetrahedrally surrounded by four oxygen atoms. Zinc also forms such complexes, as does the ZrO^{2+} ion, with benzoic acid. The zinc complexes are rapidly hydrolyzed by water, in contrast to those of beryllium. The acetate complex has been utilized as a means of purifying beryllium by solvent extraction from an aqueous solution into an organic layer. When $BeCl_2$

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[3] R. N. Sylva *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 2001.

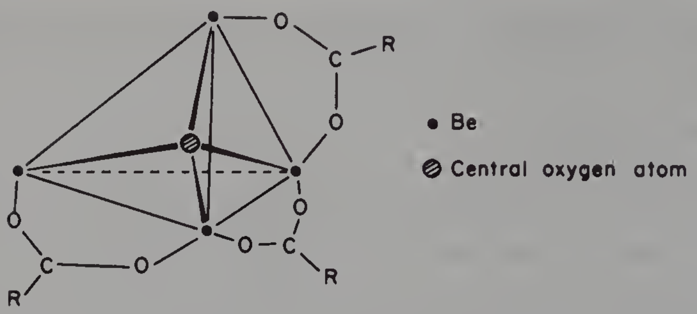

FIG. 5-2. The structure of the basic carboxylate complexes $Be_4O(O_2CR)_6$. Only three RCO_2 groups are shown.

is dissolved in N_2O_4 in ethyl acetate, crystalline $Be(NO_3)_2 \cdot 2N_2O_4$ is obtained. When heated at 50°C this gives $Be(NO_3)_2$, which at 125°C decomposes to N_2O_4 and volatile $Be_4O(NO_3)_6$. The structure of the latter appears to be similar to that of the acetate but with bridging nitrate groups. The basic nitrate is insoluble in nonpolar solvents.

The only halogeno complexes are the *tetrafluoroberyllates,* which are obtained by dissolving BeO or $Be(OH)_2$ in concentrated solutions or melts of acid fluorides such as NH_4HF_2. The tetrahedral ion has a crystal chemistry similar to that of SO_4^{2-}, and corresponding salts (e.g., $PbBeF_4$ and $PbSO_4$) usually have similar structures and solubility properties. Beryllium (II) fluoride (BeF_2) readily dissolves in water to give mainly $BeF_2(H_2O)_2$ according to ^9Be nmr spectra. In 1 *M* solutions of $(NH_4)_2BeF_4$ the ion BeF_3^- occurs from 15 to 20%.

The interaction between Cl^- and $[Be(H_2O)_4]^{2+}$ is very small and may be outer sphere in Nature.

Other Complexes. The stability of complexes with ligands containing nitrogen or other atoms is lower than those of oxygen ligands. Thus $[Be(NH_3)_4]Cl_2$ is thermally stable but is rapidly hydrolyzed in water. When $BeCl_2$ is treated with the Li salt of 2,2′-bipyridine, a green paramagnetic complex is formed, which is best regarded as a complex of Be^{2+} with the bipyridinyl radical anion.

Most of the other nitrogen complexes are derived from the hydride (Section 3-13) or organoberylliums, although compounds are known such as $[Be(NMe_2)_2]_3$, which have a central four-coordinate Be and terminal three-coordinate Be atoms with both bridge and terminal NMe_2 groups (5-III).

5-6. Organoberyllium Compounds[4]

Although beryllium alkyls can be obtained by the interaction of $BeCl_2$ with lithium alkyls or Grignard reagents, they are best made in a pure state by heating the metal and a mercury dialkyl, for example:

$$HgMe_2 + Be \xrightarrow{110^\circ C} BeMe_2 + Hg$$

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[4] N. A. Bell, *Comprehensive Organometallic Chemistry,* Vol. 1, Chapter 4, Pergamon Press, Oxford, 1981.

The alkyl can be collected by sublimation or distillation in a vacuum. On the other hand, the aryls are made by reaction of a lithium aryl in a hydrocarbon with $BeCl_2$ in diethyl ether in which the LiCl formed is insoluble, for example:

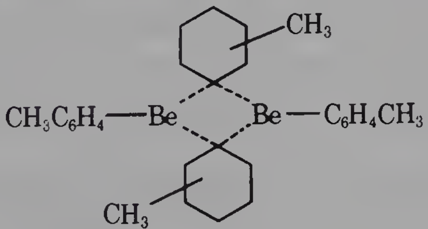
$$2LiC_6H_5 + BeCl_2 \longrightarrow 2LiCl\downarrow + Be(C_6H_5)_2$$

The alkyls are liquids or solids of high reactivity, spontaneously flammable in air and violently hydrolyzed by water. The bonding in polymers like $(BeMe_2)_n$ is of the $3c$-$2e$ type.

The aryls can be made by the reaction:

$$3BeEt_2 + 2B(aryl)_3 \longrightarrow 3Be(aryl)_2 + 2BEt_3$$

The *o*- and *m*-tolyl compounds are dimers, presumed to have structure (5-VI).



(5-VI)

The higher alkyls are progressively less highly polymerized; diethyl- and diisopropylberyllium are dimeric in benzene, but the *t*-butyl is monomeric; the same feature is found in aluminum alkyls.

As with several other elements, notably Mg and Al, there are close similarities between the alkyls and hydrides, especially in the complexes with donor ligands. For the polymeric alkyls, especially $BeMe_2$, strong donors such as Et_2O, Me_3N, or Me_2S are required to break down the polymeric structure. Mixed hydrido alkyls are known: thus pyrolysis of diisopropylberyllium gives a colorless, nonvolatile polymer:

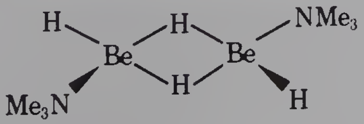
$$x(iso\text{-}C_3H_7)_2Be \xrightarrow{200°C} [(iso\text{-}C_3H_7)BeH]_x + xC_3H_6$$

However, above 100°C the *t*-butyl analogue gives pure BeH_2. With tertiary amines, reactions of the following types may occur:

$$BeMe_2 + Me_3N \longrightarrow Me_3N{\cdot}BeMe_2$$

$$2BeH_2 + 2R_3N \longrightarrow [R_3NBeH_2]_2$$

The trimethylamine hydrido complex appears to have structure (5-VII)



(5-VII)

Beryllium alkyls give colored complexes with 2,2′-bipyridine [e.g., bipy-$Be(C_2H_5)_2$, which is bright red]; the colors of these and similar complexes with aromatic amines given by beryllium, zinc, cadmium, aluminum, and gallium alkyls are believed to be due to electron transfer from the M—C bond to the lowest unoccupied orbital of the amine.

Beryllium forms cyclopentadienyl compounds, some of which have unorthodox structures because of the small size of the beryllium atom. In $(C_5H_5)BeX$ molecules, where X is an ordinary univalent atom or group (e.g., Cl, Br, $—CH_3$ or HC≡C—), the ring is attached to the metal in a symmetrical, pentahapto fashion giving the entire molecule C_{5v} symmetry. For the very air-sensitive $(C_5H_5)_2Be$, the structure has been more difficult to ascertain with certainty. A perfect D_{5d} or D_{5h} structure like that found for the transition metal compounds definitely does not occur, and in view of the size of the Be atom, could not be expected. One ring appears to be symmetrically bonded to Be and the other is variously described as σ bonded, "slipped," or ionically bonded. The beryllium atoms appear to be disordered in the crystals at both 25 and −120°C, making definitive interpretation impossible.

MAGNESIUM, CALCIUM, STRONTIUM, BARIUM, AND RADIUM

5-7. Occurrence; The Elements

Except for radium, the elements are widely distributed in minerals and in the sea. They occur in substantial deposits such as *dolomite* ($CaCO_3 \cdot MgCO_3$), *carnallite* ($MgCl_2 \cdot KCl \cdot 6H_2O$), and *barytes* ($BaSO_4$). Calcium is the third most abundant metal terrestrially.

Magnesium is produced in several ways. An important source is dolomite from which, after calcination, the calcium is removed by ion exchange using seawater. The equilibrium is favorable because the solubility of $Mg(OH)_2$ is lower than that of $Ca(OH)_2$:

$$Ca(OH)_2 \cdot Mg(OH)_2 + Mg^{2+} \longrightarrow 2Mg(OH)_2 + Ca^{2+}$$

The most important processes for preparation of magnesium are (*a*) the electrolysis of fused halide mixtures (e.g., $MgCl_2 + CaCl_2 + NaCl$) from which the least electropositive metal Mg is deposited, and (*b*) the reduction of MgO or of calcined dolomite ($MgO \cdot CaO$). The latter is heated with ferrosilicon:

$$CaO \cdot MgO + FeSi = Mg + \text{silicates of Ca and Fe}$$

and the magnesium is distilled out. Magnesium oxide can be heated with coke at 2000°C and the metal deposited by rapid quenching of the high-temperature equilibrium, which lies well to the right:

$$MgO + C \rightleftharpoons Mg + CO$$

Magnesium, which currently sells for about twice the price of aluminum, may in the long run replace it in many applications because the supply available in seawater is virtually unlimited.

Calcium and the other metals are made only on a relatively small scale, by the reaction:

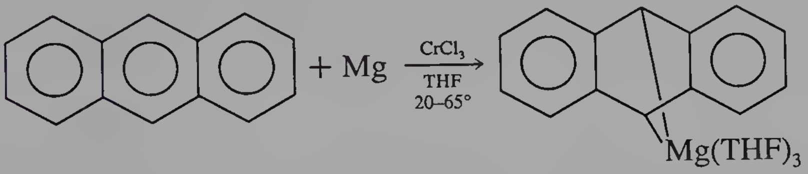
$$6CaO + 2Al \xrightarrow{1200°C} 3Ca + Ca_3Al_2O_6$$

or reduction of the halides with sodium.

Radium is isolated in the processing of uranium ores; after coprecipitation with barium sulfate, it can be obtained by fractional crystallization of a soluble salt.

Magnesium is a grayish-white metal with a surface oxide film that protects it to some extent chemically—thus it is not attacked by water, despite the favorable potential, unless amalgamated. It is readily soluble in dilute acids and is attacked by most alkyl and aryl halides in ether solution to give Grignard reagents.

Highly reactive Mg can be made in various ways for use in reductions, for example, by reduction of the halide with molten Na or K or more conveniently by interaction of the metal with anthracene and MeI in THF, which gives an orange "adduct" [5] (cf. synthesis of MgH_2, Section 3-14):



or by decomposition of MgH_2 at low pressure and 250°C.

Calcium and the other metals are soft and silvery, resembling sodium in their chemical reactivities, although somewhat less reactive. These metals are also soluble, though less readily and to a lesser extent than sodium, in liquid ammonia, giving blue solutions similar to those of the Group IA(1) metals (Section 4-3). These blue solutions are also susceptible to decomposition (with the formation of the amides) and have other chemical reactions similar to those of the Group IA(1) metal solutions. They differ, however, in that moderately stable metal ammines such as $Ca(NH_3)_6$ can be isolated on removal of solvent at the boiling point.

5-8. Binary Compounds

Oxides. These are white, high melting crystalline solids with NaCl type lattices. Calcium oxide,[6] mp 2570°C is made on a vast scale

$$CaCO_3 \rightleftharpoons CaO + CO_2(g) \qquad \Delta H°_{298} = 178.1 \text{ kJ mol}^{-1}$$

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[5] B. Bogdanović, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 262.

[6] K. W. Watkins, *J. Chem. Educ.*, 1983, **60,** 60; R. S. Boynton, *Chemistry and Technology of Lime and Limestone,* 2nd ed., Wiley, New York, 1980.

The oxide is relatively inert, especially after ignition at high temperatures, but the other oxides react with water, evolving heat, to form the hydroxides. They also absorb carbon dioxide from the air. Magnesium hydroxide is insoluble in water ($\sim 1 \times 10^{-4}$ g/L at 20°C) and can be precipitated from Mg^{2+} solutions; it is a much weaker base than the Ca–Ra hydroxides, although it has no acidic properties and unlike $Be(OH)_2$ is insoluble in an excess of hydroxide. The Ca–Ra hydroxides are all soluble in water, increasingly so with increasing atomic number [$Ca(OH)_2$, ~2g/L; $Ba(OH)_2$, ~60 g/L at ~20°C], and all are strong bases.

There is no optical transition in the electronic spectra of the M^{2+} ions, and they are all colorless. Colors of salts are thus due only to colors of the anions or to lattice defects. The oxides may also be obtained with defects, and BaO crystals with ~0.1% excess of metal in the lattice are deep red.

Halides. The anhydrous halides can be made by dehydration (Section 14-8) of the hydrated salts. For rigorous studies, however, magnesium halides are best made by the reaction

$$Mg + HgX_2 \xrightarrow{\text{boiling ether}} MgX_2(\text{solv}) + Hg$$

Magnesium and calcium halides readily absorb water. The tendency to form hydrates, as well as the solubilities in water, decrease with increasing size, and Sr, Ba, and Ra halides are normally anhydrous. This is attributed to the fact that the hydration energies decrease more rapidly than the lattice energies with the increasing size of M^{2+}.

The fluorides vary in solubility in the reverse order (i.e., $Mg < Ca < Sr < Ba$) because of the small size of the F^- relative to the M^{2+} ion. The lattice energies decrease unusually rapidly because the large cations make contact with one another without at the same time making contact with the F^- ions.

The alkaline earth halides are all typically ionic solids, but can be vaporized as molecules, the structures of which are not all linear (cf. Table 1-4). On account of its dispersion and transparency properties, CaF_2 is used for prisms in spectrometers and for cell windows (especially for aqueous solutions). It is also used to provide a stabilizing lattice for trapping lanthanide +2 ions.

Carbides. All the metals in the Ca–Ba series or their oxides react directly with carbon in an electric furnace to give the carbides MC_2. These are ionic acetylides whose general properties [hydrolysis to $M(OH)_2$ and C_2H_2, structures, etc.] are discussed in Chapter 8. Magnesium at ~500°C gives MgC_2 but, at 500 to 700°C with an excess of carbon, Mg_2C_3 is formed, which on hydrolysis gives $Mg(OH)_2$ and propyne and is presumably ionic, that is, $(Mg^{2+})_2(C_3^{4-})$.

Other Compounds. Direct reaction of the metals with other elements can lead to binary compounds such as borides, silicides, arsenides, and sulfides. Many of these are ionic and are rapidly hydrolyzed by water or dilute acids. At ~300°C, Mg reacts with N_2 to give colorless, crystalline Mg_3N_2 (resembling Li and Be in this respect). The other metals also react normally to form M_3N_2, but other stoichiometries are known. An interesting compound is Ca_2N, which has an *anti*-$CdCl_2$ type of layer structure, as does Cs_2O. In Ca_2N, however, there is one "excess" electron per formula unit. These excess electrons evidently occupy delocalized energy bands within metal atom layers, causing a lustrous, graphitic appearance.

The *hydrides* are discussed in Section 3-13; a complex salt $KMgH_3$ has been prepared.

5-9. Oxo Salts, Ions, and Complexes[7]

All the elements of Group IIA(2) form *oxo salts,* those of magnesium and calcium often being hydrated. The carbonates are all rather insoluble in water, and the solubility products decrease with increasing size of M^{2+}. The same applies to the sulfates; magnesium sulfate is readily soluble in water, and calcium sulfate has a hemihydrate $2CaSO_4 \cdot H_2O$ (plaster of Paris) that readily absorbs more water to form the very sparingly soluble $CaSO_4 \cdot 2H_2O$ (gypsum); Sr, Ba, and Ra sulfates are insoluble and anhydrous. The nitrates of Sr, Ba, and Ra are also anhydrous, and the last two can be precipitated from cold aqueous solution by addition of fuming HNO_3. Magnesium perchlorate is used as a drying agent.

For water, acetone, and methanol solutions, nmr studies have shown that the coordination number of Mg^{2+} is 6, although in liquid ammonia it appears to be 5. The $[Mg(H_2O)_6]^{2+}$ ion is not acidic and in contrast to $[Be(H_2O)_4]^{2+}$ can be dehydrated fairly readily; it occurs in a number of crystalline salts.

The complexity constants for Mg, Ca, Sr, and Ba vary greatly; there are three main groups.[8]

1. For small or highly charged anions and certain uni- and bidentate ligands, the constants decrease with increasing crystal radii, Mg > Ca > Sr > Ba.
2. For oxoanions like NO_3^-, SO_4^{2-}, and IO_4^-; the order accords with the hydrated radii, Mg < Ca < Sr < Ba.
3. For hydroxycarboxylic, polycarboxylic, and polyaminocarboxylic acids ligands the order is Mg < Ca > Sr > Ba.

The formation constants for cryptates, which show greatly enhanced stability and selectivity compared to crown ethers can be $\sim 10^6$ times greater than those of the ethers.[9] As for Na^+ and K^+, there are both synthetic and natural ligands with selective affinity for Ca^{2+}, the latter exercising a controlling effect in Ca^{2+} metabolism. One example is the antibiotic A_{23187}, a monocarboxylic acid that binds and transports Ca^{2+} across membranes. It is a tridentate and forms a seven-coordinate complex $Ca(N,O,O)_2(H_2O)$.[10]

Oxygen chelate compounds, among the most important being those of the ethylenediaminetetraacetate (EDTA) type, readily form complexes in alka-

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[7] N. S. Poonia and A. V. Bajag, *Chem. Rev.*, 1979, **79**, 389.

[8] R. Aruga, *Inorg. Chem.*, 1980, **19**, 2895.

[9] B. G. Cox *et al., J. Am Chem. Soc.*, 1984, **106**, 1273; C. K. Schauer and O. P. Anderson, *J. Am. Chem. Soc.*, 1987, **109**, 3646.

[10] G. D. Smith and W. L. Duax, *J. Am. Chem. Soc.*, 1976, **98**, 1578.

line aqueous solution, for example:

$$Ca^{2+} + EDTA^{4-} = [Ca(EDTA)]^{2-}$$

The complexing of calcium by EDTA and also by polyphosphates is of importance, not only for removal of calcium ions from water, but also for the volumetric estimation of calcium. In $Ca[CaEDTA]\cdot 7H_2O$ the coordination in the anion is 8.[11a] An L-aspartate complex[11b] is pharmacologically active for transport of Mg through membranes.

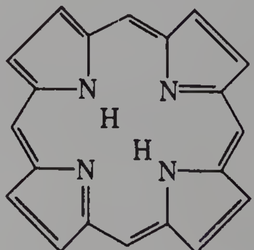
Unusual thermally stable and petroleum soluble complexes of Sr and Ba have been made[11c] by the reaction:

$$Ba(O\text{-}t\text{-}Bu)_2 + [Sn(O\text{-}t\text{-}Bu)_2]_2 \longrightarrow BaSn_2(O\text{-}t\text{-}Bu)_6$$

These have a "sandwich" type of structure (5-VIII) with an MO_6 group and trigonal planar oxygen atoms. Calcium is evidently too small to form such a species.

(5-VIII)

Ammonia and amines (other than cryptates) do not form complexes in solution but the halides give nonstoichiometric adducts, for example, $MCl_2\cdot nNH_3$. In liquid ammonia in the presence of anthracene, barium gives the green radical anion,[12] $Ba(NH_3)_2(anthracene_2)^{-\cdot}$. The only nitrogen complexes of significance are the magnesium tetrapyrroles, the parent compound of which is porphine (5-IX). These conjugated heterocycles provide a rigid planar environment for Mg^{2+} (and similar) ions. The most important of such derivatives are the *chlorophylls* and related compounds, which are of transcendental importance in photosynthesis in plants. The structure of chlorophyll-*a*, one of the many chlorophylls, is (5-X).



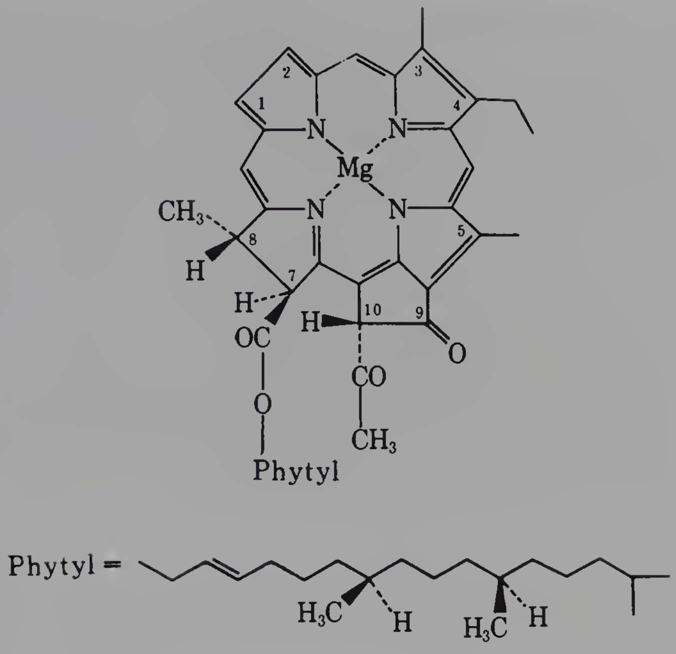
(5-IX)

[11a] B. L. Barnett and V. A Uchtman, *Inorg. Chem.*, 1979, **18,** 2674.

[11b] H. Schmidbaur *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 1013.

[11c] M. Veith *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 375.

[12] G. R. Stevenson and L. E. Schock, *J. Am. Chem. Soc.*, 1983, **105,** 3742.



(5-X)

In such porphine compounds the Mg atom is formally four-coordinate but further interaction with either water or other solvent molecules is a common, if not universal, occurrence; furthermore, in chlorophyll, interaction with the keto group at position 9 in *another* molecule is also established. It also appears that five-coordination is preferred over six-coordination as in the structure of magnesium tetraphenylporphyrin hydrate, where the Mg atom is out of the plane of the N atoms and is approximately square pyramidal. Although

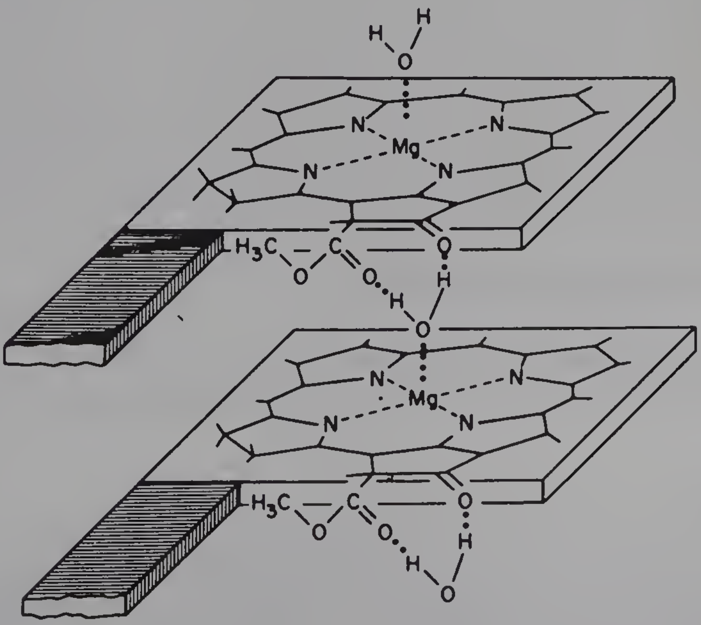
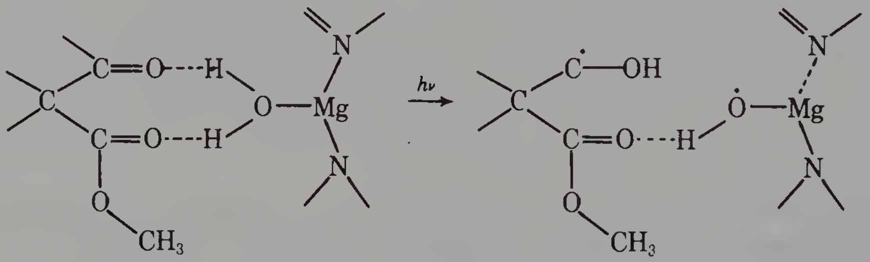


FIG. 5-3. Structure illustrating chlorophyll-*a*–water–chlorophyll-*a* interaction. The dimensions of the ring and the phytyl chain are not to scale. [Reproduced by permission from K. Ballschmiter and J. J. Katz, *J. Am. Chem. Soc.*, 1969, **91**, 2661].

Mg and other metalloporphyrins can undergo oxidation by one-electron changes, for Mg it is the macrocycle, not the metal, that is involved.

In chlorophylls hydrogen-bonding interactions lead to polymerization (Fig. 5-3); the hydrates may be monomeric or dimeric in benzene, but ordered aggregates of colloidal dimensions are formed in dodecane. Where a polar solvent is not present, association via coordination of the keto group at position 9 occurs as in solutions of anhydrous chlorophyll in alkanes.

The role of chlorophyll in the photosynthetic reduction of CO_2 by water in plants is to provide a source of electrons that may continue to be supplied for a time in the dark. Electron spin resonance studies of light-irradiated chlorophyll show that radicals are formed. These are probably of the type (5-XI). The electrons are transmitted through chlorophyll micelles to other intermediates involved in the reduction of CO_2.



(5-XI)

In tetraphenylporphyrin magnesium there can be weak binding, for example, by NCS^- in the octahedral positions.[13]

Halide Complexes. These are of magnesium and exist mainly in the solid state. Fusion of CsCl and $MgCl_2$ gives $CsMgCl_3$ where $MgCl_6$ is octahedral with opposite faces shared.[14] The halides $MgBr_2$, MgI_2, and $CaCl_2$ are soluble in alcohols and some other organic solvents, as is $Mg(ClO_4)_2$. Ether adducts such as $MgBr_2(THF)_4$ and $MgBr_2(OEt)_2)_2$ exist. The only simple anion is tetrahedral in $(Me_4N)_2MgCl_4$. However, other complex ions have been obtained.[15] Thus interaction of $MgCl_2(THF)_2$ and $TiCl_4(THF)_2$ gives $[(THF)_3Mg(\mu\text{-}Cl)_3Mg(THF)_3]^+[TiCl_5THF]^-$ while Ti, Zr, or Sn tetrachlorides give complexes such as $(EtOAc)_4Mg(\mu\text{-}Cl)_2TiCl_4$.

5-10. Organomagnesium Compounds[16]

The organo compounds of Ca, Sr, and Ba of the type RMI and $(\eta^5\text{-}C_5H_5)_2M$ can be prepared but are of little general utility compared to those of magnesium.

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[13] G. A. Rodley *et al.*, *Inorg. Chem.*, 1984, **23**, 4242.

[14] G. L. McPherson and L. A. Martin, *J. Am. Chem. Soc.*, 1984, **106**, 6884.

[15] P. Sobota *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 2077; *Z. Anorg. Allg. Chem.*, 1986, **533**, 215; D. Gordon and M. G. H. Wallbridge, *Inorg. Chim. Acta*, 1984, **88**, 15; H. J. de Liefde Meijer, *J. Organomet. Chem.*, 1984, **269**, 255.

[16] W. E. Lindsell, *Comprehensive Organometallic Chemistry*, Vol. 1, Chapter 4, Pergamon Press, Oxford, 1981 (also Ca, Sr, Ba); L. Brandsma and H. Verkruijsse, *Preparative Polar Organometallic Chemistry*, Vol. 1, B. M. Trost, Ed. Springer-Verlag, New York, 1986.

Grignard reagents (MgRX) are probably the most widely used of all organometallic compounds in both organic and organometallic synthesis. They are made by interaction of Mg with an organic halide in an ether.[17] The reaction is normally fastest with iodides and iodine can be used as an initiator for RCl or RBr. The *dialkyls* (R_2Mg) can be made by the dry reaction

$$HgR_2 + Mg(\text{excess}) = Hg + MgR_2$$

or by removal of MgX_2 from the Grignard by precipitation with dioxan and then recovery of R_2Mg from the solution. They can also be obtained directly from Mg, H_2, and alkene (cf. synthesis of AlR_3, Section 7-10).[5,18] This involves the catalyzed interaction using anthracene to give MgH_2 (Section 3-13) followed by reaction with alkene at 70 to 90°C catalyzed by 1% $ZrCl_4$:

$$MgH_2 + 2RCH{=}CH_2 \longrightarrow Mg(CH_2CH_2R)_2$$

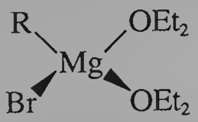
The useful sandwich cyclopentadienide, $Mg(C_5H_5)_2$, can be made by action of cyclopentadiene vapor on hot Mg or by thermal decomposition of C_5H_5MgBr, made in turn from the action of C_5H_6 on EtMgBr in ether.

The structures of Me_2Mg and Et_2Mg are linear polymers similar to Me_2Be with tetrahedral Mg and 3*c*-2*e* bridging alkyl groups.

Both R_2Mg and RMgX give stable tetrahedral adducts with donors such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED).

The Nature of Grignard Reagents. There has been prolonged controversy concerning the nature of Grignard reagents. Discordant results have often been obtained because of failure to eliminate impurities, such as traces of water or oxygen, which can aid or inhibit the attainment of equilibrium, and the occurrence of exchange reactions. Although recent work has given a reasonable understanding, the following discussion probably applies only to Grignard reagents prepared under strict conditions, not to those normally prepared without special precautions in the laboratory.

First, the structures of several crystalline Grignard reagents have been determined. In $PhMgBr(OEt_2)_2$ and $EtMgBr(OEt_2)_2$ the Mg atoms are essentially tetrahedral with structures of the form (5-XII). For less sterically demanding ethers such as THF, five-coordinate species may occur as in $MeMgBr(THF)_3$ (cf. $MgBr_2(OEt_2)_2$ versus $MgBr_2(THF)_4$). Thus it is clear that in *crystals* the basic Grignard structure is RMgX·*n*(solvent).



(5-XII)

The nature of Grignard reagents *in solution* is complex and depends critically on the alkyl and halide groups and on the solvent, concentration, and

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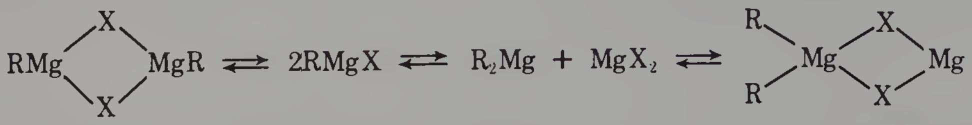
[17] Y.-H. Lai, *Synthesis,* **1981,** 585.

[18] B. Bogdanović, *Chem. Br.,* 1985, **21,** 711.

temperature. Quite generally, the Schlenck equilibria involved are of the type (5-XIII). Solvation (not shown) occurs and association is predominantly by halide rather than by carbon bridges, except for methyl compounds, where bridging by CH_3 groups may occur.



(5-XIII)

In dilute solutions and in more strongly donor solvents the monomeric species normally predominate; but in diethyl ether at concentrations exceeding 0.1 *M*, association occurs, and linear or cyclic polymers may be present. The behavior of several compounds is shown in Fig. 5-4, which includes the halides $MgBr_2$ and MgI_2.

Proton nmr spectra do not normally distinguish between R_2Mg and RMgX in solution because of rapid group exchange via transition states or intermediates of type (5-XIII). However, for perfluorophenyls the distinction can be made at 25°C and for Me_2Mg and MeMgBr at low temperature.

By ^{25}Mg nmr[19] all three species, RMgBr, R_2Mg, and $MgBr_2$ can be identified and for the equilibrium

$$2RMgBr \rightleftharpoons R_2Mg + MgBr_2$$

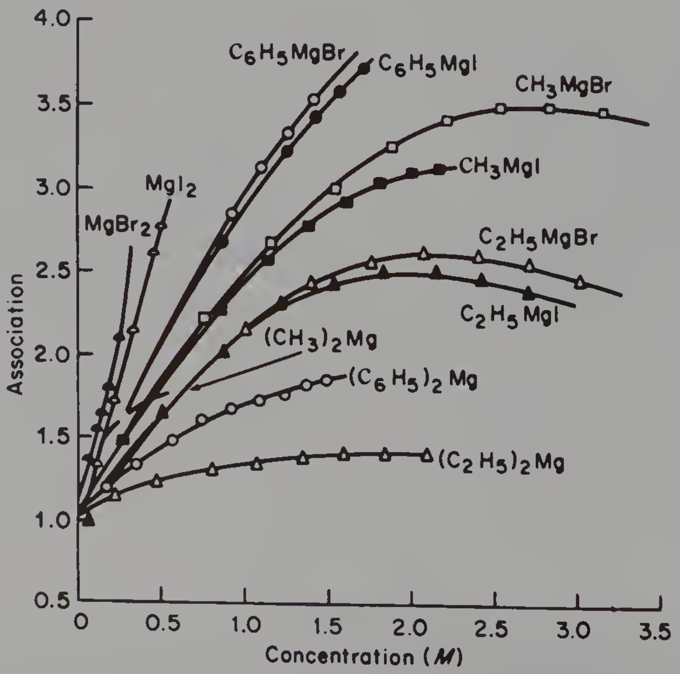


FIG. 5-4. Association of several alkyl and aryl magnesium bromides and iodides and related magnesium compounds in diethyl ether. [Reproduced by permission from F. W. Walker and E. C. Ashby, *J. Am. Chem. Soc.*, 1969, **91,** 3845].

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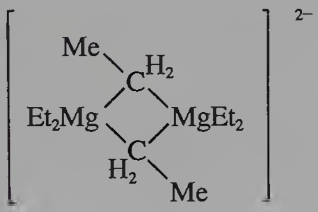
[19] R. Benn *et al.*, *Angew. Chem. Ind. Ed. Engl.*, 1984, **23,** 534.

$K \approx 30$ for R = CH_3 and ≈ 5 for R = Et. The effects of Lewis bases on the alkyl species can also be studied.

The actual formation of Grignards probably involves radicals and kinetic studies[20] suggest that the rate determining steps are halide abstraction from RX by Mg and electron transfer from Mg to RX. It is also possible that small clusters of Mg may be removed from the Mg surface and that $R(Mg_x)X$ clusters are formed.[21]

Finally, the alkylation of metal halides or other compounds in alkyl syntheses using R_2Mg or RMgX may well proceed via formation initially of alkyl bridges. Grignards can also act as single electron reducing agents, for example, in the reduction of ketones.[22a] Transition metal magnesium bonds can be made as in $(\eta^5\text{-}C_5H_5)(C_2H_4)Co(Ph)MgPh(THF)_2$.[22b]

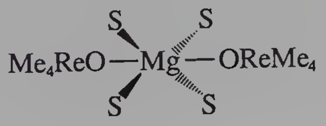
Other Organo Complexes. The interaction of Et_2Mg with a cryptate (L) gives the ato complex $[EtMgL]_2^+[Et_6Mg_2]^{2-}$ where the anion has the structure (5-XIV).[23] For the bulkier neopentyl the anion is the trigonal planar $[Mg(CH_2CMe_3)_3]^-$ while the cation has a pentagonal bipyramidal structure $[MgCH_2CMe_3L]^+$, which is also found in the $Mg(NCS)_2$(benzo-15-C-5) crown ether complex and $[MgEDTA(H_2O)]^{2-}$. There are also some compounds where solvated Mg is bound to a transition metal[24] (5-XV) or to the oxygen atom of an oxoalkylanion,[25] for example, (5-XVI).



(5-XIV)

$[Cp(CO)_2Fe]_2Mg(THF)_4$

(5-XV)



S = tetrahydrofuran

(5-XVI)

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Fenton, D., *Comprehensive Coordination Chemistry,* Vol. 3, Chapter 23, Pergamon Press, Oxford, 158 (complexes).

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[20] G. M. Whitesides *et al., J. Am. Chem. Soc.,* 1980, **102,** 217 *et seq.*

[21] Y. Imizu and K. J. Klabunde, *Inorg. Chem.,* 1984, **23,** 3602.

[22a] E. C. Ashby and A. B. Goel, *J. Am. Chem. Soc.,* 1981, **103,** 4983.

[22b] K. Jonas *et al., Angew. Chem. Int. Ed. Engl.,* 1986, **25,** 923.

[23] H. G. Richey, Jr. *et al., J. Am. Chem. Soc.,* 1985, **107,** 432.

[24] J. D. Atwood *et al., J. Am. Chem. Soc.,* 1980, **102,** 4529.

[25] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 2167.

Chapter Six

Boron: Group IIIA(13)

GENERAL REMARKS

6-1. Electronic Structure and Bonding

The first ionization potential of boron, 8.296 eV, is rather high, and the next two are much higher. Thus the total energy required to produce B^{3+} ions is far more than would be compensated by lattice energies of ionic compounds or by hydration of such ions in solution. Consequently, simple electron loss to form a cation plays no part in boron chemistry. Instead, covalent bond formation is of major importance, and boron compounds usually resemble those of other nonmetals, notably silicon, in their properties and reactions.

Despite the $2s^22p$ electronic structure, boron is always trivalent and never monovalent. This is because the total energy released in formation of three bonds in a BX_3 compound exceeds the energy of formation of one bond in a BX compound by more than enough to provide for promotion of boron to a hybridized valence state of the sp^2 type, wherein the three sp^2 hybrid orbitals lie in one plane at angles of 120°. It would therefore be expected, and is indeed found, without exception, that all monomeric, three-covalent boron compounds (trihalides, trialkyls, etc.) are planar with X—B—X bond angles of 120°. The covalent radius for trigonally hybridized boron is not well defined but probably lies between 0.85 and 0.90 Å. There are apparently substantial shortenings of many B—X bonds, and this has occasioned much discussion. For example, the estimated B—F, B—Cl, and B—Br distances would be ~1.52, 1.87, and 1.99 Å, whereas the actual distances in the respective trihalides are 1.310, 1.75, and 1.87 Å.

Three factors appear to be responsible for the shortness of bonds to boron:

1. Formation of $p\pi$–$p\pi$ bonds using filled $p\pi$ orbitals of the halogens and the vacant $p\pi$ orbital of boron. This is probably most important in BF_3, but of some significance in BCl_3 and BBr_3 as well.

2. Strengthening, hence shortening, of the B—X bonds by ionic–covalent resonance, especially for B—F and B—O bonds because of the large electronegativity differences. Evidence that this is important, in addition to the dative $p\pi$–$p\pi$ bonding, is afforded by the fact that even in BF_3 complexes

such as $(CH_3)_3NBF_3$ and BF_4^-, where the $p\pi$–$p\pi$ bond must be largely or totally absent, the B—F bonds are still apparently shortened.

3. Because of the incomplete octet in boron, repulsions between nonbonding electrons may be somewhat less than normal, permitting closer approach of the bonded atoms.

Elemental boron has properties that place it on the borderline between metals and nonmetals. It is a semiconductor, not a metallic conductor, and chemically it must be classed as a nonmetal. In general, boron chemistry resembles that of silicon more closely than that of aluminum, gallium, indium, and thallium. The main resemblances to Si and differences from Al are the following:

1. The similarity and complexity of the boric and silicic acids is notable. Boric acid, $B(OH)_3$, is weakly but definitely acidic, and not amphoteric, whereas $Al(OH)_3$ is mainly basic with some amphoteric behavior.

2. The hydrides of B and Si are volatile, spontaneously flammable, and readily hydrolyzed, whereas the only binary hydride of Al is a solid, polymeric material. However, structurally the boron hydrides are unique, having unusual stoichiometries and configurations and unusual bonding because of their *electron-deficient* nature.

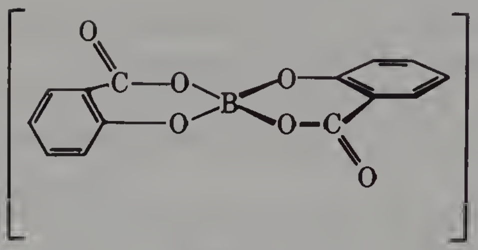
3. The boron halides (not BF_3), like the silicon halides, are readily hydrolyzed, whereas the aluminum halides are only partially hydrolyzed in water.

4. B_2O_3 and SiO_2 are similar in their acidic nature, as shown by the ease with which they dissolve metallic oxides on fusion to form borates and silicates, and both readily form glasses that are difficult to crystallize. Certain oxo compounds of B and Si are structurally similar, specifically the linear $(BO_2)_x$ and $(SiO_3)_x$ ions in metaborates and pyroxene silicates, respectively.

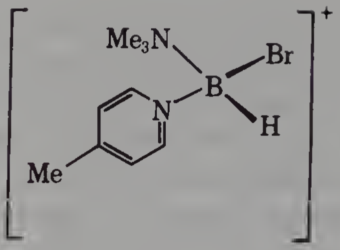
5. However, despite dimerization of the halides of Al and Ga and of the alkyls of Al, they behave as acceptors and form adducts similar to those given by boron halides and alkyls, for example, $Cl_3AlN(CH_3)_3$. Aluminum, like boron, also forms volatile alkoxides such as $Al(OC_2H_5)_3$, which are similar to borate esters $B(OR)_3$.

Although the BX_3 molecules in general do not dimerize [exceptions being BH_3 and $BH_2(CN)$], they do show a strong tendency to complete the octet in other ways. As will be discussed fully for the halides in Section 6-5, they are Lewis acids and behave as acceptors towards a wide variety of bases. In this way four-coordinate species with approximately tetrahedral structures are formed, examples being Me_3NBCl_3, Et_2OBF_3, Me_3PBH_3, and BF_4^-.

Boron also completes its octet by forming both anionic and cationic complexes. The former include such species as BF_4^-, BH_4^-, $B(C_6H_5)_4^-$, and $BH(OR)_3^-$, as well as chelates such as $[B(o\text{-}C_6H_4O_2)_2]^-$ and the salicylato complex (6-I), which has been partially resolved by fractional crystallization of its strychnine salt.



(6-I)



(6-II)

The cationic species[1a] are of three main types, some containing B—H bonds (see later) such as (6-II), but other types are known, for example,

$$(C_6H_5)_2BCl + \text{dipy} + AgClO_4 \xrightarrow{MeNO_2} [Ph_2B(\text{dipy})]^+ + ClO_4^- + AgCl$$

These cations have considerable hydrolytic stability, though they are attacked by base; 6-II has been resolved and is optically stable in acid at 25°C.

6-2. The Element

Boron is not an abundant element, but it occurs in some concentrated deposits in arid parts of California, and elsewhere, as *borax,* $Na_2B_4O_5(OH)_4 \cdot 8H_2O$ and *kernite,* $Na_2B_4O_5(OH)_4 \cdot 2H_2O$. *Tourmaline,* a nicely crystalline aluminosilicate, contains about 10% of boron.

Natural boron consists of two isotopes, ^{10}B (19.6%) and ^{11}B (80.4%). Isotopically enriched boron compounds can be made and are useful in spectroscopic and reaction mechanism studies. The boron nuclear spins (^{10}B, $S = 3$; ^{11}B, $S = \frac{3}{2}$) are also useful in structure elucidation (Fig. 6-11).

It is exceedingly difficult to prepare elemental boron in a state of high purity because of its high melting point and the corrosiveness of the liquid. It can be prepared in quantity but low purity (95–98%) in an amorphous form by reduction of B_2O_3 with magnesium, or by electrolytic reduction of KBF_4 in molten KCl/KF.

Methods that can be used to prepare pure boron cannot generally produce large quantities, although in some cases a kilogram scale is feasible. These methods include pyrolysis of boron hydrides and halides; perhaps the best methods involve reduction of BCl_3 or (better) BBr_3 with H_2 on a heated tantalum wire.[1b]

Boron is unique in not being a metal (because of its small size and high ionization enthalpies) but also not having as many electrons as it has valence shell orbitals. It therefore adopts unique—and very complex—structures in its several allotropes. All of them are dominated by the B_{12} icosahedron (see diagram 1-XVII). The most stable polymorph is the β-rhombohedral form (mp ~2180°C), which has perhaps the most complicated of all the structures; it is based on the icosahedral motif, but a full description would serve no

[1a] H. Nöth *et al., Inorg. Chem.,* 1982, **21,** 706; R. W. Parry *et al., Inorg. Chem.,* 1982, **21,** 716.
[1b] M. Vlasse *et al., J. Solid State Chem.,* 1979, **28,** 289.

useful purpose here. The α-rhombohedral form consists of nearly regular B_{12} icosahedra in a deformed cubic close packing. A β-tetragonal boron consists of layers of B_{12} icosahedra connected by single boron atoms, and there are other allotropes whose existence is definite but whose structures are only incompletely (or not at all) established. The so-called α-tetragonal form is not, apparently, a real allotrope. It was originally considered to be built of B_{12} icosahedra linked by B_2 units, but it is now believed that the linkages are C_2 or N_2 units.

Crystalline boron is extremely inert chemically. It is unaffected by boiling HCl or HF, only slowly oxidized by hot, concentrated nitric acid when finely powdered, and either not attacked or only very slowly attacked by many other hot concentrated oxidizing agents.

6-3. Borides

Compounds of boron with elements less electronegative than itself (i.e., metals) are called borides. Often compounds of boron with rather less metallic or metalloidal elements (e.g., P, As) are also termed borides. Borides of most but not all elements are known. They are generally hard, refractory substances and fairly inert chemically. They often possess very unusual physical and chemical properties. For example, the electrical and thermal conductivities of ZrB_2 and TiB_2 are ~10 times greater than those of the metals themselves, and the melting points are more than 1000°C higher. Some of the lanthanide hexaborides are among the best thermionic emitters known. The monoborides of phosphorus and arsenic are promising high-temperature semiconductors, and higher borides of some metalloids (e.g., AsB_6) are remarkably inert to chemical attack.

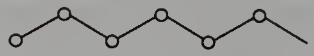
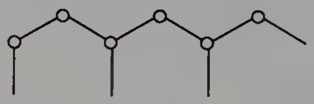
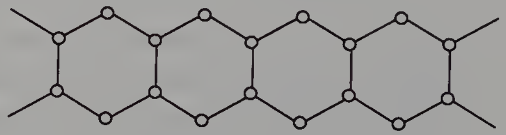
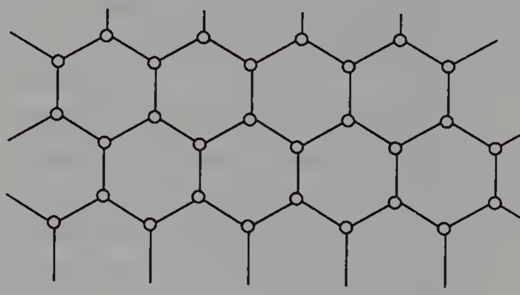
Borides may be prepared in a number of ways. On a small scale, direct combination of elemental boron with the metal, or with the metal oxide, may be used, but for industrial production metals or their oxides are reacted with B_2O_3 + C or with B_4C, whereby CO is evolved.

Boride compositions do not conform at all to the usual concepts of valence or stoichiometry. They range from the metal-rich borides (M_4B, M_3B, etc.) to the boron-rich borides (MB_4, MB_6, MB_{12}). The range of compositions together with some structural information is summarized in Table 6-1. Some pertinent comments on the structures are the following:

Borides with Isolated Boron Atoms. These are the most metal-rich borides. In some the boron atoms lie in triangular prismatic or square antiprismatic holes between multiple layers of metal atoms. In the others, the metal atoms are arranged in approximately close-packed arrays, with the boron atoms in triangular prismatic interstices.

Borides with Single and Double Chains of Boron Atoms. As the proportion of boron atoms increases, so do the possibilities for boron–boron linkages. In V_3B_2 there are pairs of boron atoms. In one modification of Ni_4B_3, two thirds of the boron atoms form infinite, zigzag chains, while one

TABLE 6-1
Examples of Metal Borides and Their Structures[a]

Formula	Examples	B—B bonds	Boron arrangements
M_4B M_3B M_2B	Mn_4B Ni_3B Be_2B	Isolated atoms	
M_3B_2	V_3B_2	Pairs	
MB	NiB FeB	Zigzag chains	
$M_{11}B_8$	$Ru_{11}B_8$	Branched chains	
M_3B_4	Ta_3B_4 Cr_3B_4	Double chains	
MB_2	CrB_2 TiB_2 MgB_2 ZrB_2 GdB_2	Two-dimensional network	
MB_4	LaB_4	Three-dimensional network	B_6 octahedron
MB_6	LaB_6		
MB_{12}	YB_{12}		B_{12} cubooctahedron
MB_{15}	NaB_{15}		B_{12} icosahedron
M_3B_{12}	B_4C		
MB_{66}	YB_{66}		$B_{12}(B_{12})_{12}$ giant icosahedron

[a] Adapted from J. Etourneau and P. Hagenmuller, *Philos. Mag. B,* 1985, **52,** 589.

third are isolated from other boron atoms; in another modification all the boron atoms are members of chains. The MB compounds all have structures with single chains, while in many M_3B_4 compounds there are double chains.

Borides with Two-Dimensional Nets. These are represented by MB_2 and M_2B_5 compounds and include some of the best electrically conducting, hardest, and highest melting of all borides. The crystal structures of the MB_2 compounds are unusually simple, consisting of alternating layers of close-packed metal atoms and "chicken wire" sheets of boron atoms, as shown in Table 6-1.

Borides with Three-Dimensional Boron Networks. The major types have formulas MB_4, MB_6, and MB_{12}. The MB_4 compounds may be of several types

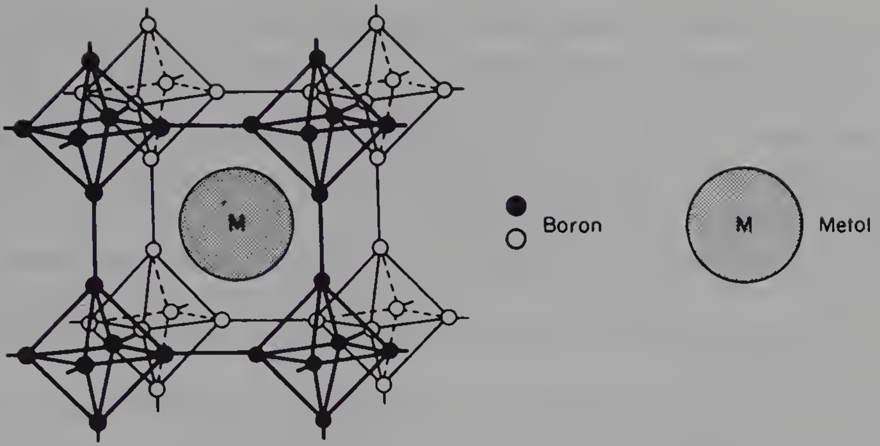
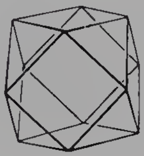


FIG. 6-1. Atomic arrangement in many MB_6 compounds.

insofar as structural details are concerned. ThB_4 and CeB_4 contain rather open networks of boron atoms interpenetrating a network of metal atoms. Perhaps as many as 20 other MB_4 compounds have the same structure. The MB_6 structure is fairly easy to visualize with the help of Fig. 6-1: It can be thought of as a CsCl structure, with B_6 octahedra in place of the Cl^- ions; however the B_6 octahedra are closely linked along the cube edges, so that the boron atoms constitute an infinite three-dimensional network. The MB_{12} compounds also have cubic structures consisting of M atoms and B_{12} cubooctahedra (6-III) packed in the manner of NaCl; again, the B_{12} polyhedra are closely linked to one another. Heating NaB_6 at 1000°C in argon converts it into NaB_{15}, in which there are icosahedra linked both directly and through B_3 chains.



(6-III)

6-4. Oxygen Compounds of Boron[2a]

The oxygen-containing substances are among the most important compounds of boron, comprising nearly all the naturally occurring forms of the element. The structures of such compounds consist mainly of trigonal BO_3 units with the occasional occurrence of tetrahedral BO_4 units. The B—O bond energies are 560 to 790 kJ, rivaled only by the B—F bond in BF_3 (640 kJ) in strength.

Boron Oxides. The principal oxide (B_2O_3) is obtained by fusing boric acid. It usually forms a glass and can be crystallized only with the greatest

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[2a] See, D. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry,* Supplement, Vol. 5, Part A, Longmans, London, 1980.

difficulty. This glass is believed to consist of randomly oriented B_3O_3 rings connected by bridging oxygen atoms.

B_2O_3 is acidic, reacting with water to give boric acid, $B(OH)_3$, and, when fused, dissolves many metal oxides to give borate glasses. Both the glassy and the crystalline substances contain infinite chains of triangular BO_3 units, interconnected by weaker B—O bonds.

An oxide that presumably contains B—B bonds (B_2O_2) is obtained by the reaction of B and B_2O_3 at 1300°C. By hydrolysis of alkoxides of the type $B_2(OR)_4$ (obtained from B_2Cl_4) $B_2(OH)_4$ is obtained and dehydration of this at 250°C gives $(BO)_x$.

Boron sulfide (B_2S_3) has a layer structure with both B_3S_3 and B_2S_2 rings linked by sulfur bridges; there is no resemblance to B_2O_3.

Boric Acid and Borate Ions in Solution. The hydrolysis of boron halides, hydrides, and so on, gives boric acid, $B(OH)_3$, or its salts. The acid is usually obtained from borax and it forms white, needlelike crystals in which $B(OH)_3$ units are linked together by hydrogen bonds to form infinite layers of nearly hexagonal symmetry; the layers are 3.18 Å apart, which accounts for the pronounced basal cleavage. Some reactions of boric acid are given in Fig. 6-2.

Since boric acid is moderately soluble in water, with a large negative heat of solution, the solubility increases markedly with temperature. It is a very

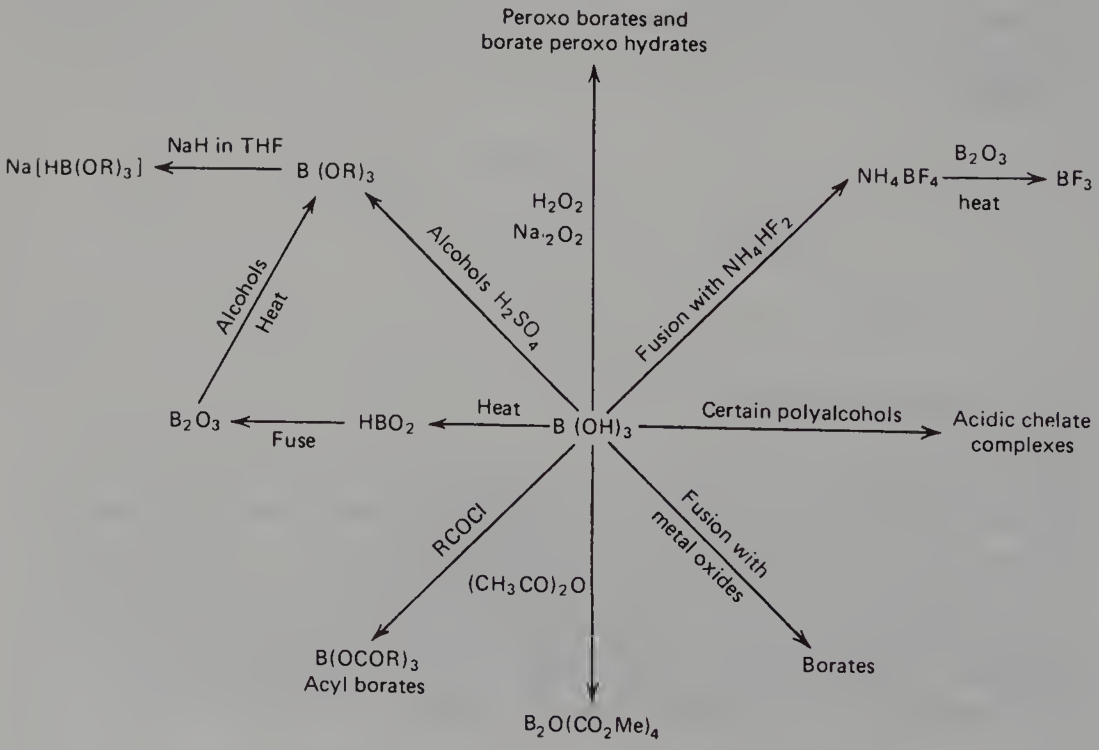


FIG. 6-2. Some reactions of boric acid.

weak and exclusively monobasic acid that acts not as a proton donor, but as a Lewis acid, accepting OH^-:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \qquad K = 6 \times 10^{-10}$$

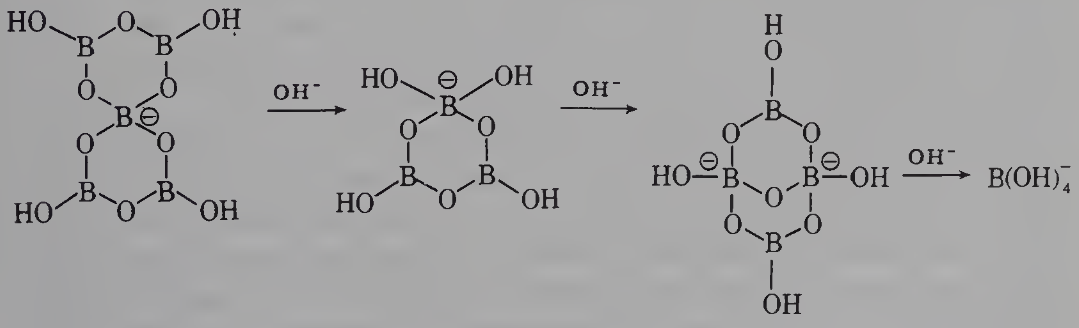
The $B(OH)_4^-$ ion occurs in several minerals. At concentrations $\leq 0.025\ M$, essentially only mononuclear species $B(OH)_3$ and $B(OH)_4^-$ are present. Boric acid–borate buffer mixtures serve as pH standards, and they occur in natural aqueous systems and in detergents.

In concentrated solutions polymeric ions are also present, for example,

$$2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O$$

Equilibrium between the various ions is rapidly established as shown by rapid exchange between $B(OH)_3$ labeled with ^{18}O and borates. The determination of the species in solution has been largely based on Raman spectra and comparison with the structures known for hydrated borates from X-ray diffraction.

The species $B_5O_6(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_4O_5(OH)_4^{2-}$ are formed successively with increasing pH. These ions, which can be designated (5.1), (3.1), (4.2), and so on, to indicate the number of B atoms and the charge (which corresponds to the number of four-coordinate B atoms) have the boroxine ring structures (6-IV), (6-V), and (6-VI), which have been confirmed in crystalline borates. With increasing pH, attack on neutral trigonal boron is favored, but there is a discontinuity when the number of BO_4 groups exceeds 50% so that tetraborate goes directly to $B(OH)_4^-$. In dilute solutions depolymerization rapidly occurs; thus the mononuclear species is formed when borax, which contains the ion (6-VI), is dissolved. Although the hydrated diborate ion $(HO)_3BOB(OH)_3^{2-}$ occurs in crystals, it does not occur in solution. However, a molecular compound with a B—O—B group does exist; this is the so-called boron acetate (Fig. 6-2), which has two acetato bridges, an oxo bridge, and unidentate acetates as end groups.



(6-IV) (6-V) (6-VI)

When heated, boric acid loses water stepwise:

$$B(OH)_3 \underset{H_2O}{\overset{heat}{\rightleftharpoons}} HBO_2 \underset{H_2O}{\overset{heat}{\rightleftharpoons}} B_2O_3$$

The intermediate substance, *metaboric acid* (HBO_2), exists in three modifications. If the $B(OH)_3$ is heated below 130°, HBO_2-III is formed. This has a layer structure in which B_3O_3 six rings are joined by hydrogen bonding between OH groups on the boron atoms. On continued heating of HBO_2-III at 130 to 150°C, HBO_2-II is formed; this has a more complex structure containing both BO_4 tetrahedra and B_2O_5 groups in chains linked by hydrogen bonds. Finally, on heating of HBO_2-II above 150°C, cubic HBO_2-I is formed in which all boron atoms are four-coordinate.

Crystalline Borates.[2b] Many borates occur naturally, usually in hydrated form. Anhydrous borates can be made by fusion of boric acid and metal oxides, and hydrated borates can be crystallized from aqueous solutions. The stoichiometry of borates—for example, $KB_5O_8 \cdot 4H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, CaB_2O_4, and $Mg_3B_7O_{13}Cl$—gives little idea of the structures of the anions, which are cyclic or linear polymers formed by linking together of BO_3 and/or BO_4 units by shared oxygen atoms. The main principles for determining these structures are similar to those for silicates, to which the borates are structurally and often physically similar in forming glasses.

In crystalline borates the most common structural units are those shown in Fig. 6-3. These skeletal units can be protonated to various degrees, and one or more of the boron atoms may have an OH^- ion added so as to make it tetrahedral rather than trigonal. The largest discrete borate anion known is the $B_{10}O_{21}^{12-}$ ion, which consists of two tetraborate units (Fig. 6-3) linked by two BO_3 triangles.

In anhydrous borates the BO_3^{3-} and $B_3O_6^{3-}$ ions, and the infinite chain anion, $(BO_2)_n^{n-}$, are quite common, as well as networks of $B_6O_{12}^{6-}$ and $B_3O_6^{3-}$ linked by shared oxygen atoms.[3]

Hydrated borates also contain polyanions in the crystal, but not all the known polyanions exist as such in solution (see above); only those containing one or more BO_4 groups appear to be stable. Important features of the structures are the following:

1. Both trigonal BO_3 and tetrahedral BO_4 groups are present, the ratio of BO_4 to total B being equivalent to the ratio of the charge on the anion to total boron atoms. Thus $KB_5O_8 \cdot 4H_2O$ has one BO_4 and four BO_3, whereas $Ca_2B_6O_{11} \cdot 7H_2O$ has four BO_4 and two BO_3 groups.
2. The basic structure is a six-atom boroxine ring whose stability depends on the presence of one or two BO_4 groups. Anions that do not have BO_4 groups, such as metaborate ($B_3O_6^{3-}$) or metaboric acid, $B_3O_3(OH)_3$, hydrate rapidly and lose their original structures. Certain complex borates can be precipitated or crystallized from solution, but this does not constitute evidence for the existence of such anions in solution, since other less complex anions can readily recombine during the crystallization process.
3. Other discrete and chain-polymer anions can be formed by linking of

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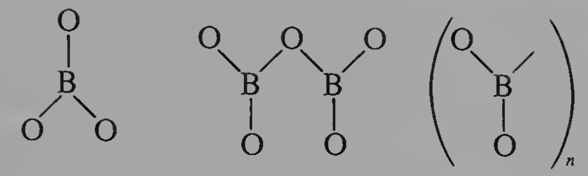
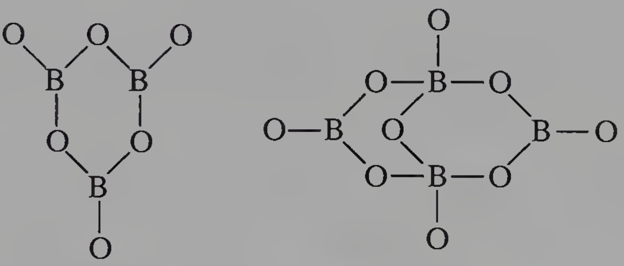
[2b] J. B. Farmer, *Adv. Inorg. Chem. Radiochem.*, 1982, **25**, 187.

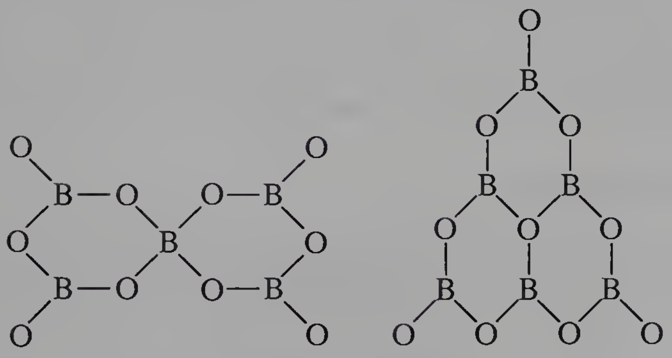
[3] J. Fayos *et al., Acta Cryst.*, 1985, **C41**, 1394, 1396.



Monoborate Diborate Polyborate



Triborate Tetraborate



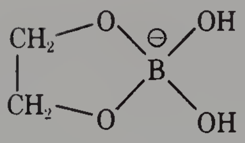
Pentaborate Hexaborate

FIG. 6-3. The commonest structural units found in crystalline borates.

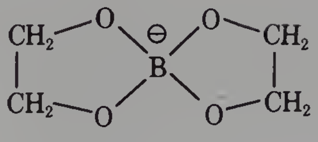
two or more rings by shared tetrahedral boron atoms, in some cases with dehydration [cf. metaborate (HBO_2)].

The most common hydrated triborate ion is $B_3O_3(OH)_5^{2-}$, often associated with Ca^{2+} or Mg^{2+}; this is similar to the $B_3O_3(OH)_4^-$ ion (6-V) mentioned previously. The $B_4O_5(OH)_4^{2-}$ ion (6-VI) is found in borax, in many other tetraborates, and in the so-called octaborates, $M_2^IM^{II}B_8O_{14}\cdot12H_2O$.

Borate Esters. Boric acid is readily converted to alkyl or aryl orthoborates, $B(OR)_3$, by action of alcohols and sulfuric acid. These compounds are usually colorless liquids. A common test for boron involves treating compounds with methanol and acid and observing the green color imparted to a flame by $B(OMe)_3$. With polyhydroxy alcohols or carboxylic acids that have *cis*-hydroxy groups, boric acid forms 1:1 or 1:2 chelate complexes, stepwise; these may be very stable [e.g., (6-VII) and (6-VIII)]. In the 1:1 complexes



(6-VII)



(6-VIII)

the acidity of the OH groups exceeds that in $B(OH)_3$, so that if glycerol is added to a boric acid solution, this can be titrated using aqueous NaOH.

Steric considerations are very critical in the formation of these complexes. Thus 1,2- and 1,3-diols in the cis form only, such as *cis*-1,2-cyclopentanediol, are active, and only *o*-quinols react. Indeed, the ability of a diol to affect the acidity of boric acid is a useful criterion of the configuration where cis–trans isomers are possible.

Peroxoborates. Treatment of borates with hydrogen peroxide or boric acid with sodium peroxide leads to products variously formulated as $NaBO_3 \cdot 4H_2O$ or $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$, which are extensively used in washing powders because they afford H_2O_2 in solution. The crystal structure has been found to contain $[B_2(O_2)_2(OH)_4]^{2-}$ units with two peroxo groups bridging the tetrahedral boron atoms. When this salt is heated, paramagnetic solids containing O_2^-, O_3^-, and a peroxoborate radical are formed. In solution there is the following equilibrium[4a]

$$[B(OH)_3(O_2H)]^- + H_2O = [B(OH)_4]^- + H_2O_2 \qquad K \approx 0.04$$

6-5. The Boron Trihalides

Compounds of the type BX_3 exist for all the halogens. The mixing of two halides leads to essentially a statistical equilibrium, for example

$$BF_3 + BCl_3 \rightleftharpoons BFCl_2 + BF_2Cl$$

These redistribution reactions presumably proceed through transitory dimers such as $F_2B(\mu\text{-}F)(\mu\text{-}Cl)BCl_2$, which may then dissociate to BF_2Cl and BCl_2F. While no mixed halide can be isolated, the PE (photoelectron), microwave, and nmr spectra of these molecules can be recorded on the mixtures.

The boron trihalides and some of their properties are listed in Table 6-2.

TABLE 6-2
The Boron Trihalides

Property	BF_3	BCl_3	BBr_3	BI_3
mp °C	−127.1	−107	−46	49.9
bp °C	−99.9	12.5	91.3	210
r(B—X)(Å)	1.30	1.75	1.87	2.10
ΔH_f^0 (298 K)(kJ mol^{-1})(gas)	−1123	−408	−208	
E(B—X)(kJ mol^{-1})	646	444	368	267

[4a] C. J. Adams and I. E. Clark, *Polyhedron,* 1983, **2,** 673.

Some reactions of the trihalides are summarized in Fig. 6-4. One of their most fundamental forms of chemical activity is to function as Lewis acids. Their ability to do this underlies much of the rest of their chemistry. However, the relative strengths of the boron halides as Lewis acids are in the order $BBr_3 > BCl_3 \geq BF_3$, which is the opposite to that expected either on steric grounds or from electronegativity. It can be explained, at least partially, in terms of boron-halogen π bonding. In an addition compound this π bonding

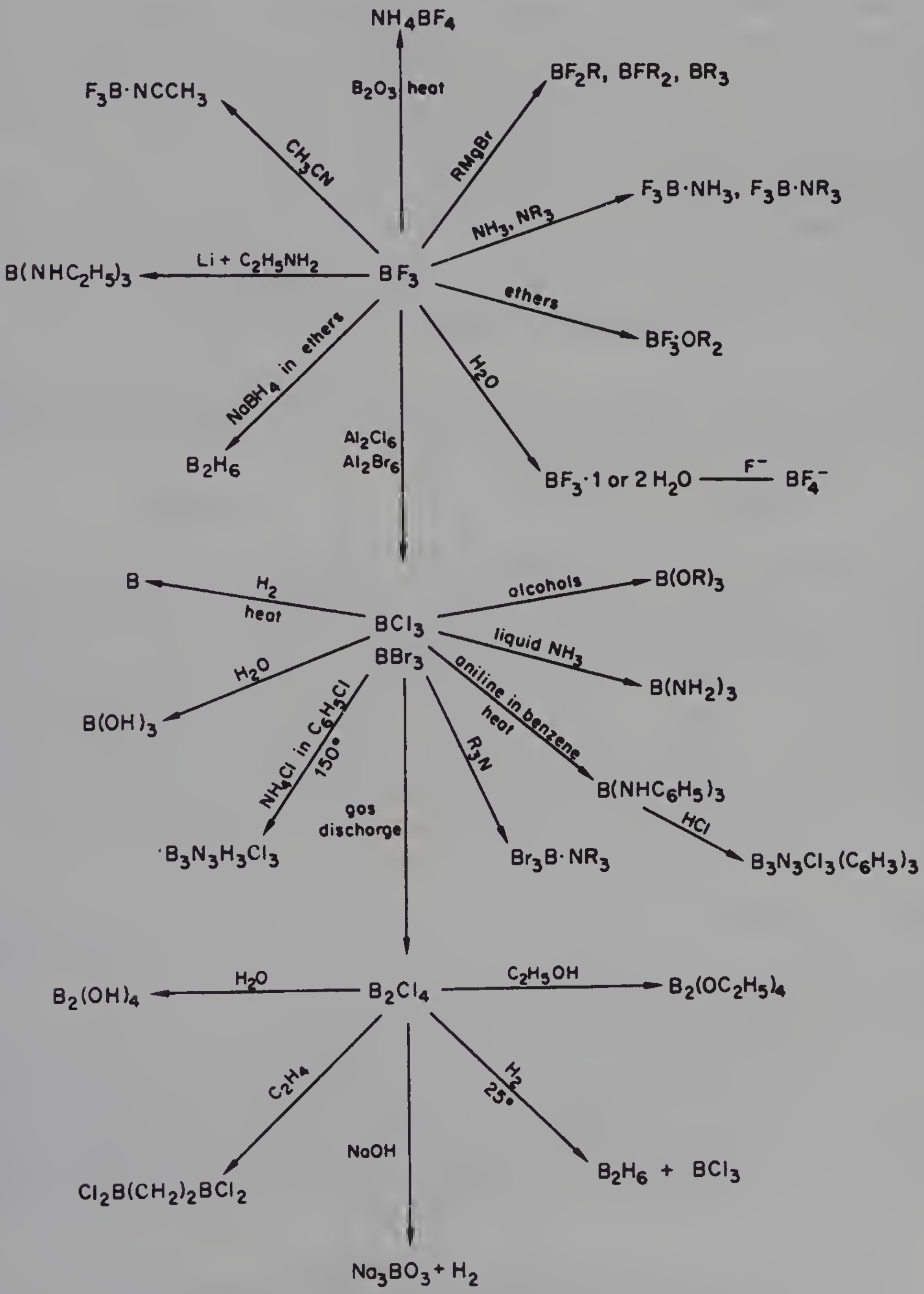


FIG. 6-4. Some reactions of the halides of boron.

is largely or completely lost, so that addition compounds of the trihalide with the strongest π bonding will be the most destabilized by loss of the energy of π bonding. There is good evidence that π bonding is strong in all of the boron trihalides, with a steady increase from BI_3 to BF_3.[4b] The Lewis acidity of the boron trihalides cannot, however, be entirely understood in terms of out-of-plane π bonding.[5] It is interesting to note that with CO, BF_3 interacts only weakly to give a "van der Waals" molecule, BF_3CO, in which BF_3 is still planar with a B—C distance of 2.89 Å.

Boron Trifluoride. This pungent, colorless gas is prepared by heating B_2O_3 with NH_4BF_4 or with CaF_2 and concentrated H_2SO_4. It reacts with water to form two *hydrates*, $BF_3{\cdot}H_2O$(mp 10.2°C) and $BF_3{\cdot}2H_2O$(mp 6.4°C). Each of these contains a quasitetrahedral H_2OBF_3 molecule; in the dihydrate an additional H_2O molecule is incorporated into the structure.[6]

Both hydrates partially dissociate into ions in their liquid phases, presumably as follows:

$$2(BF_3{\cdot}H_2O) \rightleftharpoons [H_3O\text{—}BF_3]^+ + [BF_3OH]^-$$

$$BF_3{\cdot}2H_2O \rightleftharpoons H_3O^+ + [BF_3OH]^-$$

Above about 20°C they decompose extensively, giving off BF_3. When relatively small amounts of BF_3 are passed into water, a solution of fluoroboric acid (see next reaction) is obtained:

$$4BF_3 + 6H_2O \longrightarrow 3H_3O^+ + 3BF_4^- + B(OH)_3$$

Boron trifluoride readily unites with water, ethers, alcohols, amines, phosphines, and so on to form adducts. Boron trifluoride is commonly available as its diethyletherate $(C_2H_5)_2OBF_3$. Because of its potency as a Lewis acid and its greater resistance to hydrolysis compared with BCl_3 and BBr_3, BF_3 is widely used to promote various organic reactions, such as (*a*) ethers or alcohols + acids → esters + H_2O or ROH; (*b*) alcohols + benzene → alkylbenzenes + H_2O; (*c*) polymerization of olefins and olefin oxides; and (*d*) Friedel–Crafts-like acylations and alkylations. In the first two cases, the effectiveness of BF_3 must depend on its ability to form an adduct with one or both of the reactants, thus lowering the activation energy of the rate-determining step in which H_2O or ROH is eliminated by breaking of C—O bonds. However, the exact mechanisms of these reactions are not known, nor are those of the olefin and olefin oxide polymerizations.

In the case of the Friedel–Crafts-like reactions, isolation of certain intermediates at low temperatures has provided a fairly definite idea of the function of the BF_3. Thus the ethylation of benzene by ethyl fluoride proceeds as in eq. 6-1. With benzene, HF, and BF_3, compound (6-IX) can be isolated at low temperatures. It will be seen that the BF_3 is not really "catalytic" but must

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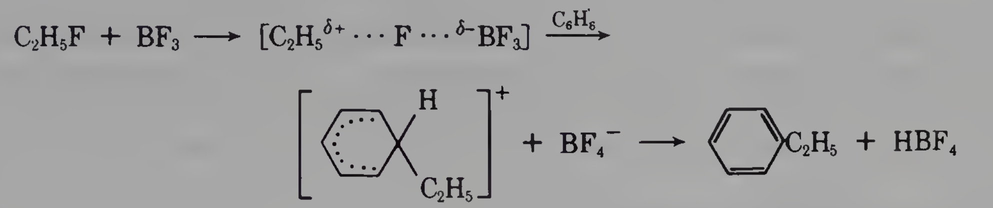
[4b] D. B. Beach and W. L. Jolly, *J. Phys. Chem.*, 1984, **88**, 4647.

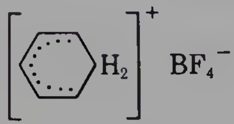
[5] G. A. Bowmaker *et al.*, *J. Chem. Soc. Faraday Trans. 2*, 1985, **81**, 1023.

[6] D. Mootz and M. Steffen, *Acta Cryst.*, 1981, **B37**, 1110.

be present in the stoichiometric amount, since it is consumed in the process of tying up the HF as HBF_4.



(6-1)



(6-IX)

Fluoroborate Anions. Fluoroboric acid does not exist, but there are solvates such as $HBF_4 \cdot Et_2O$ and $HBF_4 \cdot 2CH_3OH$ that contain oxonium ions,[7a] for example, $[CH_3OH_2][BF_4]$(mp −41°C). Solid salts, such as those of NH_4^+ of Na^+, are commercially available. Ammonium tetrafluoroborate is made by fusing NH_4HF_2 and B_2O_3.

The reaction of boric acid with aqueous HF to form the BF_4^- ion is slow except in strongly acid solution, and the major species is $[BF_3OH]^-$.

$$B(OH)_3 + 3F^- + 2H^+ = BF_3OH^- + 2H_2O$$

In aqueous solutions, $BF_2(OH)_2^-$ also occurs, and in concentrated solutions above pH 6.5, $B_3O_3F_6^{3-}$ is present. The BF_4^- ion is tetrahedral, and fluoroborates resemble the corresponding perchlorates in their solubilities and crystal structures. Although BF_4^- is normally a noncoordinating anion, in certain cases coordination does occur.[7b]

Other Trihalides. *Boron trichloride* is a liquid at room temperature under slight pressure (bp 12.5), and the *bromide* boils at 90°C. Both fume in moist air and are completely hydrolyzed by water, for example,

$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$$

The compounds are prepared by direct interaction of the elements at elevated temperatures.

The rapid hydrolysis by water could indicate that these halides are stronger Lewis acids than BF_3, and indeed, various studies have shown that the order of Lewis acidity is generally $BBr_3 > BCl_3 \approx BH_3 \geq BF_3 > BMe_3$.

The triiodide is prepared by the action of iodine on $NaBH_4$ or of HI on BCl_3 at red heat. It is an unstable white solid that polymerizes on standing, is explosively hydrolyzed by water, and acts as a Lewis acid.

Tetrachloroborates are obtained by addition of BCl_3 to alkali chlorides at

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[7a] D. Mootz and M. Steffen, *Angew. Chem. Int. Ed. Engl.*, 1981, **20,** 196.

[7b] W. Beck *et al., J. Organomet. Chem.,* 1983, **252,** 187.

high pressures, by cold milling at room temperatures, or by the reaction

$$[(C_2H_5)_4N]^+Cl^- + BCl_3 \xrightarrow{CHCl_3} [(C_2H_5)_4N]^+BCl_4^-$$

The stability of these salts and the corresponding tetrabromoborates and tetraiodoborates is greatest with the largest cations. With a given cation, the stability order is $MBCl_4 > MBBr_4 > MBI_4$, tetraiodoborates occurring only with the largest cations. Mixed ions such as BF_3Cl^- also exist.

6-6. Halides with B—B Bonds[8]

Diboron Tetrahalides (B_2X_4). These are known for X = F, Cl, Br, and I, but the last has been little studied. The B_2F_4 molecule has a planar structure in both crystalline and gaseous phases, whereas B_2Cl_4, though planar in the crystal has a D_{2d} structure in the vapor (as does B_2Br_4 also). The B—B distances are 1.70 to 1.75 Å consistent with these being a single, σ, B—B bond. The staggered structure is favored by the X···X nonbonded repulsions, but B—X π bond conjugation across the B—B unit may help to stabilize the planar structure. The two rotamers are not very different in stability (<10 kJ) in any case.

When BF_3 is passed over elemental B at 1850°C at low pressure BF molecules are formed. These react with BF_3 to generate B_2F_4 (mp −56°C; bp −34°C) as well as the very unstable $F_2BB(F)BF_2$ and B_8F_{12}.

The most studied of these compounds, B_2Cl_4, can be made by subjecting BCl_3 vapor to an electric discharge between mercury or copper electrodes, that is,

$$2BCl_3 + 2Hg \text{ (or } 2Cu) \longrightarrow B_2Cl_4 + Hg_2Cl_2 \text{ (or } 2CuCl)$$

B_2Cl_4 reacts with HCCH and H_2CCH_2 to add BCl_2 units across the C≡C and C=C bonds and with BBr_3 at −80°C to produce B_2Br_4. It is solvolyzed by H_2O and ROH to give $B_2(OH)_4$ and $B_2(OR)_4$, respectively.

Polyhedral B_nX_n Compounds. By thermolysis of B_2Cl_4 and B_2Br_4 the *closo*-halogenoboranes (B_nX_n) with $n = 4$, 8–12 for Cl and $n = 7$–10 for Br are obtained.[9] The B_9X_9 species, which have a tricapped trigonal prismatic structure are the most stable. Mass spectrographic evidence for B_nCl_n species with $n = 13$–20 has been reported,[10] and mixed species, $B_nCl_{n-x}Br_x$, are also known.

The remarkable thing about the B_nX_n molecules is that they have only $2n$ skeletal electrons, rather than $2n + 2$ as for the borane anions, carboranes, and so on (to be discussed later). Both photoelectron spectra and theoretical studies[11] have been made with a view to rationalizing this.

The B_4Cl_4 molecule is thermally unstable above ~70°C and has been studied

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[8] A. G. Massey, *Adv. Inorg. Chem. Radiochem.*, 1983, **26,** 1.

[9] T. Davan and J. A. Morrison, *Inorg. Chem.*, 1986, **25,** 2366.

[10] J. A. Morrison *et al., Inorg. Chem.*, 1983, **22,** 1821.

[11] P. R. LeBreton *et al., J. Am. Chem. Soc.*, 1986, **108,** 3937.

extensively. It has full tetrahedral symmetry and the bonding may be understood in terms of molecular orbitals that concentrate electron density on the faces of the central B_4 tetrahedron and in the four B—Cl bonds. Although most reactions of B_4Cl_4 disrupt the B_4 unit, reactions with LiR reagents afford B_4R_4 products.[12]

6-7. Diborane

Diborane (B_2H_6) is the point of departure, conceptually and in practice, for the chemistry of the higher boranes and their derivatives to which so much of this chapter will be devoted. It is also a useful reagent in organic chemistry.[13,14]

It can be prepared by action of 85% phosphoric acid on $NaBH_4$, but a convenient method is to drop boron trifluoride etherate into a solution of $NaBH_4$ in ethyleneglycol dimethylether (diglyme).

$$3NaBH_4 + 4BF_3 = 3NaBF_4 + 2B_2H_6$$

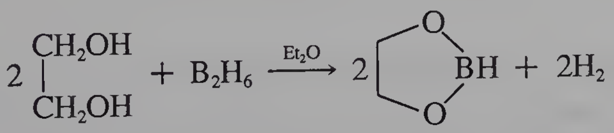
Diborane is available in cylinders and as various BH_3 solvates. The gas is highly toxic. When pure it does not react with oxygen at 25°C, but nevertheless it must be handled with care. It burns evolving much heat:

$$B_2H_6 + 3O_2 = B_2O_3 + 3H_2O \qquad \Delta H^0 = -2137.7 \text{ kJ mol}^{-1}$$

This reaction shows why boranes were once seriously considered as potential rocket fuels. The thermal decomposition of B_2H_6 is extremely complicated and the products depend on the conditions.

Borane (BH_3) can be obtained in the gas phase by thermal decomposition of $H_3B{\cdot}PF_3$ but cannot be isolated.

Some reactions of diborane are shown in Fig. 6-5. Although rapidly hydrolyzed by water, B_2H_6 reacts with alcohols in two stages, the last so slow that the intermediate compounds $(RO)_2BH$ can be isolated as adducts with NMe_3. With glycol, a dioxoborolane is formed:



Many types of reaction of B_2H_6 initially involve addition to Lewis bases to give unstable adducts (B_2H_6L). These can then undergo either symmetric cleavage to given borane adducts or unsymmetrical cleavage.

Many *borane adducts* ($H_3B{\cdot}L$) are known, and when the relative stabilities

[12] S. L. Emery and J. A. Morrison, *Inorg. Chem.*, 1985, **24,** 1612.

[13] H. C. Brown, *Organic Syntheses via Boranes,* Wiley, New York, 1975.

[14] L. H. Wong, in *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry,* Vol. 5, Suppl. 2, Part 3, Longmans, London, 1981, pp. 52–162.

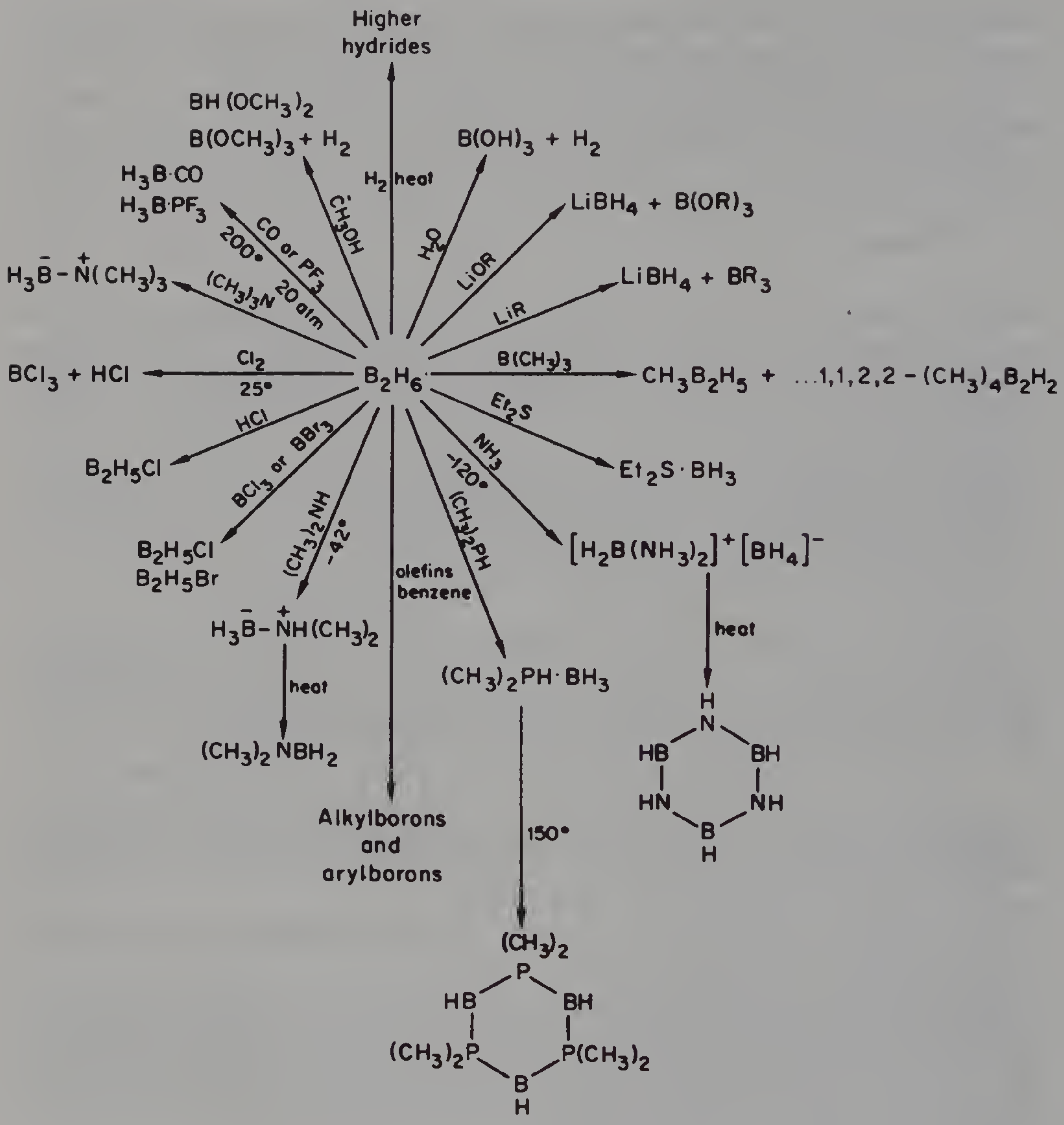


FIG. 6-5. Some reactions of diborane.

of these compounds are considered it is clear that BH_3 must be regarded as a stronger Lewis acid than BF_3. In the cases of BH_3CO and BH_3PF_3, there appears to be a small but real amount of π back-bonding in which B—H bonding electrons are partly shared with π acceptor orbitals of CO or PF_3, much as in metal carbonyls and PF_3 complexes,[15] but not nearly to the same extent.

With some Lewis bases (e.g., NH_3) the reaction can be complicated, but asymmetric cleavage of B_2H_6 occurs to give borohydride cations of the type $[L_2BH_2]^+BH_4^-$. Some adducts with amines and phosphines undergo further changes on heating to give cyclic compounds (Fig. 6-5).

[15] D. B. Beach and W. L. Jolly, *Inorg. Chem.*, 1985, **24**, 567.

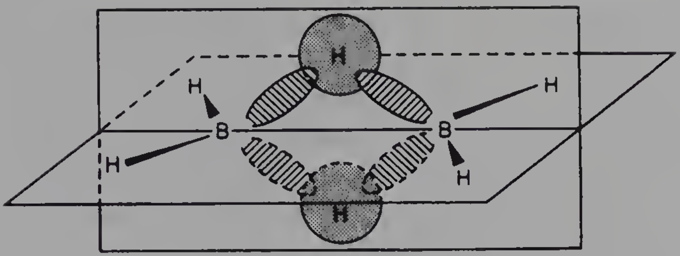


FIG. 6-6. The approach of two properly oriented BH_2 radicals and two H atoms leads to the formation of two 3*c*-2*e* B—H—B bonds.

Some of the most important uses of diborane are in the reduction of organic substances and in the hydroboration reaction discussed later (Section 6-14). Diborane differs from BH_4^- as a reductant for organic substances in that it attacks at electron-rich positions, whereas BH_4^- reacts by nucleophilic attack on an electrophilic center. Thus B_2H_6 will reduce both RCO_2H and $RCOOR'$; whereas $LiBH_4$ reduces only $RCOOR'$. Azo compounds, aldehydes, and nitriles are reduced by B_2H_6.

From the point of view of structure and bonding, diborane is of exceptional importance. It provides the prototypal example of three-center, two-electron (3*c*-2*e*) hydrogen bridge bonding. As shown in Fig. 6-6, the hydrogen atoms of B_2H_6 lie in two mutually perpendicular planes that intersect along the B to B line. The terminal B—H bonds may be regarded as conventional 2*c*-2*e* bonds. Thus each boron atom uses two electrons and two roughly sp^3 orbitals to form 2*c*-2*e* bonds to two hydrogen atoms. The boron atom in each BH_2 group still has one electron and two hybrid orbitals for further bonding. The plane of the two remaining orbitals is perpendicular to the BH_2 plane. When two such BH_2 groups approach each other as in Fig. 6-6, with hydrogen atoms also lying, as shown, in the plane of the four empty orbitals, two B—H—B 3*c*-2*e* bonds are formed. The total of four electrons required for these bonds is provided by the one electron carried by each H atom and by each BH_2 group.

6-8. Polyhedral Boranes—Preparation and Properties

In a remarkable series of papers from 1912 to 1936, Alfred Stock and his coworkers prepared and chemically characterized the following hydrides of boron (boranes): B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$. With the exception of diborane (B_2H_6), which was prepared by thermal decomposition of higher boranes, Stock prepared these hydrides by the action of acid on magnesium boride (MgB_2), obtaining in this way a mixture of volatile, reactive, and air-sensitive (some spontaneously flammable) compounds. To handle compounds with these properties, Stock developed the glass vacuum line and techniques for using it.

Preparative methods for the boranes are numerous and highly varied;

Stock's original method is now used only for B_6H_{10}. Most preparations begin with B_2H_6 and involve pyrolysis under a variety of conditions and often in the presence of H_2 or other reagents. The very important $B_{10}H_{14}$, for example, is obtained by pyrolysis of B_2H_6 at about 100°C, and B_5H_9 is formed on pyrolysis of B_2H_6 in the presence of hydrogen at 250°C. An electric discharge through B_2H_6 or other boranes is sometimes used, but this method gives only small yields. The best method for any given borane may be peculiar to it, for example, reaction of B_5H_{11} with the surface of crystalline hexamethylenetetramine to give B_9H_{15}, and the carefully controlled hydrolysis of the hydroxonium ion salt of $B_{20}H_{18}^{2-}$ to give a mixture of the isomers of $B_{18}H_{22}$.

Table 6-3 lists the better characterized boranes, most of whose structures are now known. Altogether, however, more than twenty-five B_nH_m compounds have been characterized. Some representative structures are shown in Fig. 6-7, which also gives the conventional numbering schemes.

The number of boron atoms is indicated by a latin prefix and the number of H atoms is given with an arabic number in parentheses: for example, pentaborane(9) is B_5H_9; pentaborane(11) is B_5H_{11}. If there is only one compound of B_n, the number can be omitted. Additional nomenclature is discussed later.

In addition to the general preparative routes that start with B_2H_6, many more specialized methods have been developed. Thus pentaborane(9) can be used to synthesize a number of higher boranes,[16] various borane anions can be subjected to hydride abstraction reactions,[17] and metal catalysts can cause hydrogen extrusion reactions, whereby *conjuncto*-boranes (to be defined later) are formed.[18]

The reactivity of the boranes is extremely diverse and can only be touched on briefly. Broad classes of chemical reactions are (*a*) acidity and the formation of borane anions, (*b*) substitution of H by halogens, organic groups, and so on, (*c*) adduct formation, (*d*) electron addition to give anions, and (*e*) skeletal additions and formation of compounds that have hetero atoms (C, Si, P, etc.) in the skeleton.

Two of the best studied boranes are B_5H_9 and $B_{10}H_{14}$.

Pentaborane(*9*) is a toxic liquid that can detonate in air. It can be halogenated exclusively in the apical position by halogens in the presence of aluminum halide catalysts. Interaction with alkenes at ~150°C gives alkyl derivatives.

Decaborane(*14*) has been made on a multiton scale as a rocket fuel by pyrolysis of B_2H_6 at 150°C in the presence of dimethylether. It is readily halogenated, and iodine gives 1- and 2-iododecaborane(14) and also 1,2-diiodo- and 2,4-diiododecaborane(14). Alkylation occurs with $AlCl_3$ and alkyl halides to give various substituted derivatives consistent with electrophilic

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[16] S. G. Shore *et al.*, *Inorg. Chem.*, 1986, **25**, 367.

[17] S. G. Shore *et al.*, *Inorg. Chem.*, 1982, **21**, 1952.

[18] E. W. Corcoran, Jr., and L. G. Sneddon, *Inorg. Chem.*, 1983, **22**, 182.

TABLE 6-3

The More Important Properties of Boranes[a]

Formula	Name	mp (°C)	bp (°C)	Reaction with air, at 25°C	Thermal stability	Reaction with water
B_2H_6	Diborane(6)[b]	−164.85	−92.59	Spontaneously flammable	Fairly stable at 25°C	Instant hydrolysis
B_4H_{10}	Tetraborane(10)[b]	−120	18	Not spontaneously flammable if pure	Decomposes fairly rapidly at 25°C	Hydrolysis in 24 h
B_5H_9	Pentaborane(9)[b]	−46.8	60	Spontaneously flammable	Stable at 25°C; slow decomposition 150°C	Hydrolyzed only on heating
B_5H_{11}	Pentaborane(11)[b]	−122	65	Spontaneously flammable	Decomposes very rapidly at 25°C	Rapid hydrolysis
B_6H_{10}	Hexaborane(10)[b]	−62.3	108	Stable	Slow decomposition at 25°C	Hydrolyzed only on heating
B_6H_{12}	Hexaborane(12)	−82.3	80–90		Liquid stable few hours at 25°C	Quantitative, to give B_4H_{10}, $B(OH)_3$, H_2
$B_{10}H_{14}$	Decaborane(14)[b]	99.5	213 (extrap.)	Very stable	Stable at 150°C	Slow hydrolysis
$B_{14}H_{18}$	Tetradecaborane(18)	liquid		Stable	Decomposes ~100°C	
$B_{14}H_{20}$	Tetradecaborane(20)	solid		Stable		
$B_{20}H_{16}$	Icosaborane(16)	196–199		Stable		Irreversibly gives $B_{20}H_{16}(OH)_2^{2-}$ and $2H^+$

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[a] *Other hydrides:* B_8H_{12}, B_8H_{14}, B_8H_{16}, B_8H_{18}, n-B_9H_{15}, i-B_9H_{15}, $B_{10}H_{16}$, $B_{13}H_{19}$, $B_{15}H_{23}$, $B_{16}H_{20}$, n-$B_{18}H_{22}$, i-$B_{18}H_{22}$, $B_{20}H_{26}$ (8 isomers, see G. M. Brown *et al.*, *Inorg. Chem.*, 1979, **18,** 1951. *Transient species detected in gas phase:* BH_3, B_2H_4, B_3H_7, B_4H_8, B_8H_{12}, B_9H_{13}.

[b] Structures of these boranes are shown in Fig. 6-7.

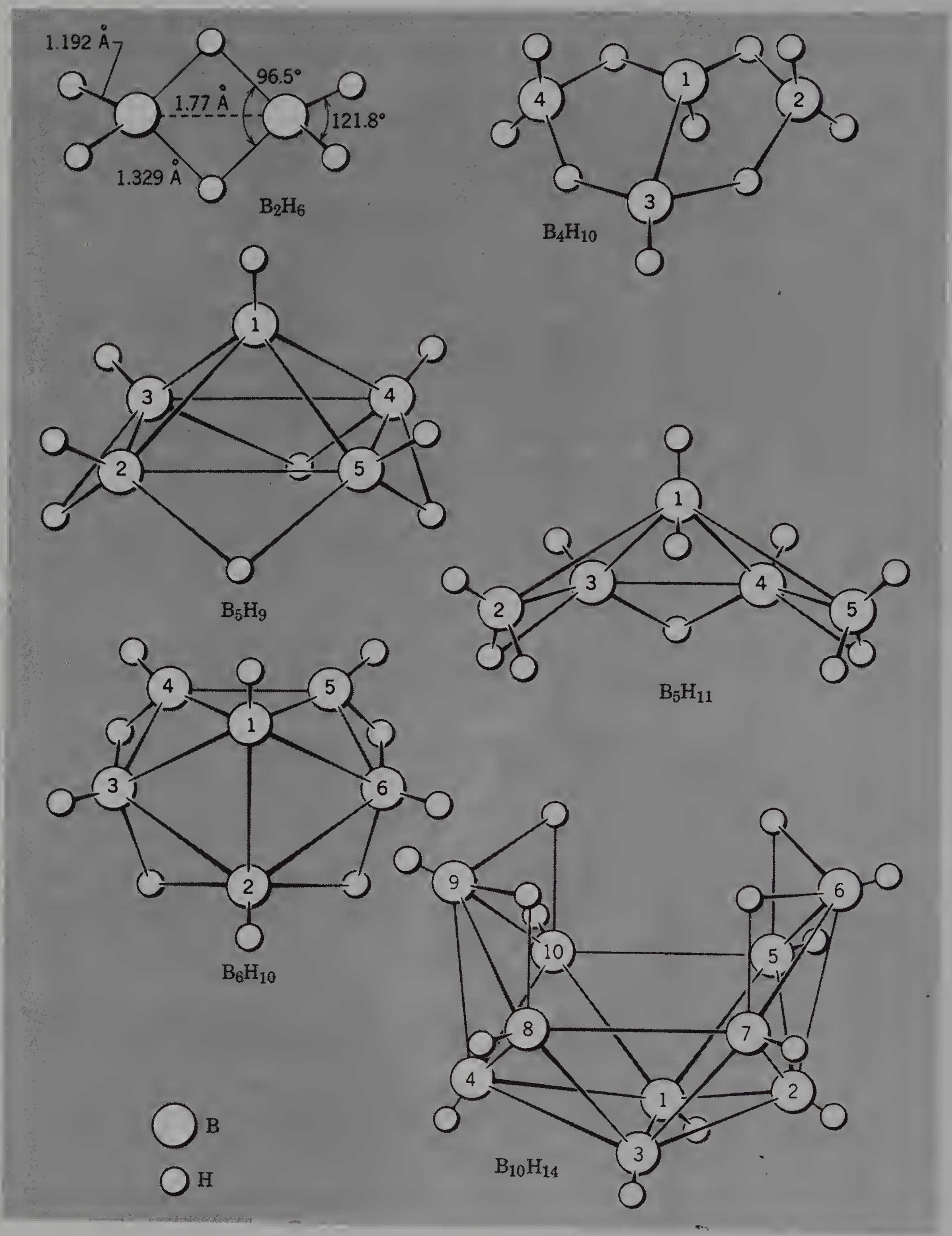


FIG. 6-7. Structures of some boranes.

attack at B atoms of highest electron density (i.e., 1, 3, 2, 4). Adducts are formed with neutral donors [e.g., $B_{10}H_{14}$ 6,9-$(CH_3CN)_2$] or with anions (e.g., $B_{10}H_{14}CN^-$, which readily loses H_2 to give $B_{10}H_{12}CN^-$).

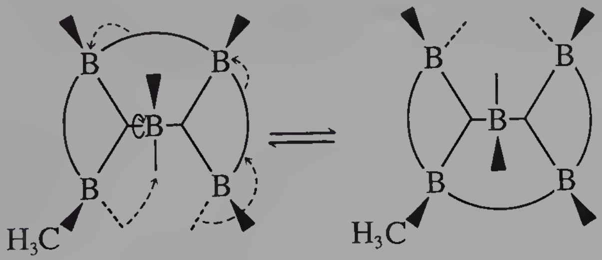
Many of the lower boranes function as monoprotic acids, and it is a *bridging H atom* that acts as the source of H^+. The conjugate base, a borane anion of the type discussed later, then has a B—B bond. This B—B bond is susceptible to insertion of electrophilic reagents; thus attack by BH_3 acting as an electrophile leads to *polyhedral expansion* of the boron framework. Some examples are

$$B_4H_{10} \xrightarrow{KH} B_4H_9^- \xrightarrow{BH_3} B_5H_{12}^- \xrightarrow{H^+} B_5H_{11}$$

$$B_5H_9 \xrightarrow{KH} B_5H_8^- \xrightarrow{BH_3} B_6H_{11}^- \xrightarrow{H^+} B_6H_{12}$$

Within a given class of boranes, the acidity increases with the size of the B framework. Thus we have the series $B_5H_9 < B_6H_{10} < B_{10}H_{14} < B_{16}H_{20} <$ *n*-$B_{18}H_{22}$, and $B_4H_{10} < B_5H_{11}$.

It may also be noted that boranes can display fluxional behavior or at least undergo rapid rearrangements because of the possibility of hydrogen atoms moving from terminal to bridging positions and vice versa. A recent example[19] is provided by the rapid equilibration of 2-$CH_3B_5H_{10}$ (6-X) and 3-$CH_3B_5H_{10}$ (6-XI), which presumably occurs by the process represented schematically here:



(6-X) (6-XI)

6-9. Polyhedral Boranes—Structures and Bonding

Structures. Because the boranes and their derivatives, for example, the polyhedral borane anions to be discussed in Section 6-11, have a variety of complex structures, a good deal of structural terminology that is mainly limited to this field has been devised. In presenting this terminology, we shall have to anticipate some of the borane anion chemistry. The main structural types of $B_nH_m^{x-}$ compounds are

Closo-boranes (a euphonious modification of the Greek *clovo,* cage) are complete (i.e., closed) polyhedra.

Nido-boranes (from Latin *nidus,* nest) have structures that may be described as polyhedra that lack one vertex.

Arachno-boranes (from the Greek word for a spiderweb) have structures describable as polyhedra from which two adjacent vertices are missing.

Hypho-boranes (from the Greek word for a net) have even more open

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[19] D. M. Ritter *et al., Inorg. Chem.,* 1986, **25,** 372.

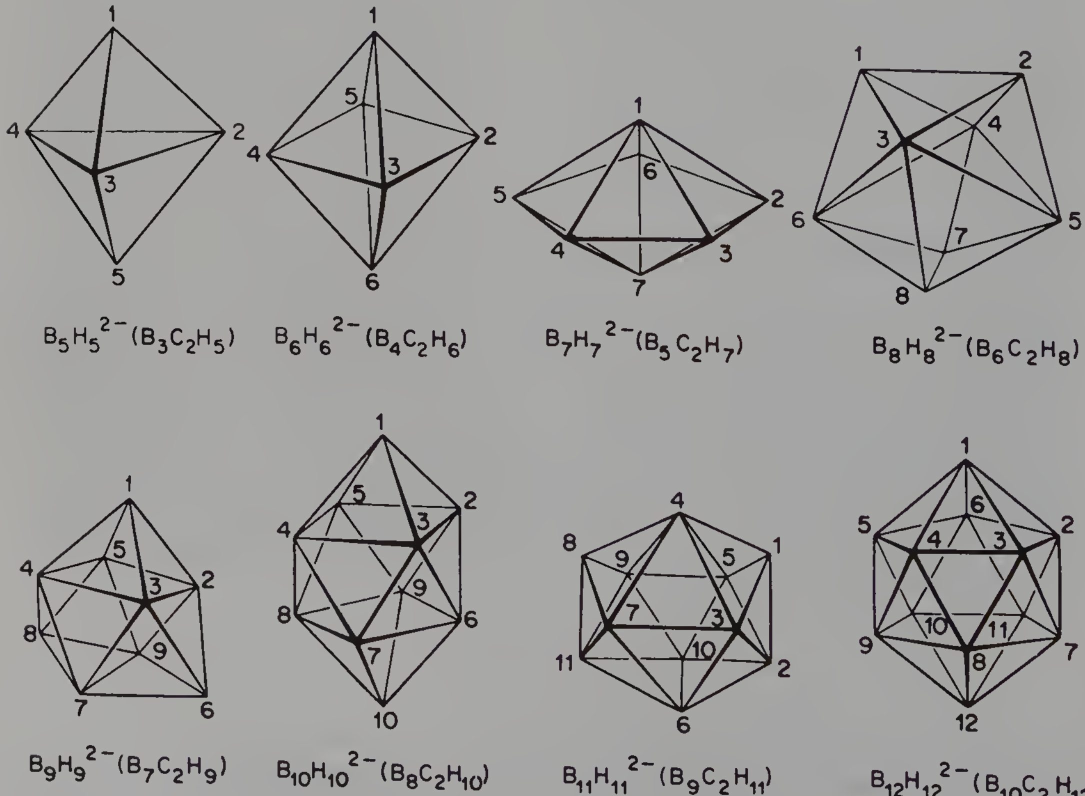
structures, often visualizable as polyhedral fragments formed by removal of three contiguous vertices of a complete polyhedron.

Conjuncto-boranes (from Latin implying the joining of subunits) have structures in which two or more of the preceding types are linked. For these the possibilities are very numerous[20] and nomenclatural problems can be formidable.[21] Linkage may be through a B—B bond, by way of one or more B—H—B bonds (3*c*-2*e*), or by having one or more boron atoms belong simultaneously to two subunits.

The *closo*-boranes are best represented by the polyhedral $B_nH_n^{2-}$ anions that we shall discuss in Section 6-11. Those from $B_5H_5^{2-}$ to $B_{12}H_{12}^{2-}$ are pictured in Fig. 6-8.

Several *nido*-boranes can be seen in Fig. 6-7. These are the ones having formulas of the type B_nH_{n+4}, namely:

B_2H_6, a triangle lacking one B
B_5H_9, an octahedron lacking one B
B_6H_{10}, a pentagonal bipyramid, lacking one apical B
$B_{10}H_{14}$, an 11-sided deltahedron, lacking one B



$B_5H_5^{2-}(B_3C_2H_5)$ $B_6H_6^{2-}(B_4C_2H_6)$ $B_7H_7^{2-}(B_5C_2H_7)$ $B_8H_8^{2-}(B_6C_2H_8)$

$B_9H_9^{2-}(B_7C_2H_9)$ $B_{10}H_{10}^{2-}(B_8C_2H_{10})$ $B_{11}H_{11}^{2-}(B_9C_2H_{11})$ $B_{12}H_{12}^{2-}(B_{10}C_2H_{12})$

FIG. 6-8. The triangulated-polyhedral structures of $B_nH_n^{2-}$ and $B_{n-2}C_2H_n$ species; conventional numbering schemes are indicated.

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[20] W. N. Lipscomb, *Inorg. Chem.*, 1980, **19,** 1415.

[21] W. H. Powell *et al., Inorg. Chem.*, 1984, **23,** 4132.

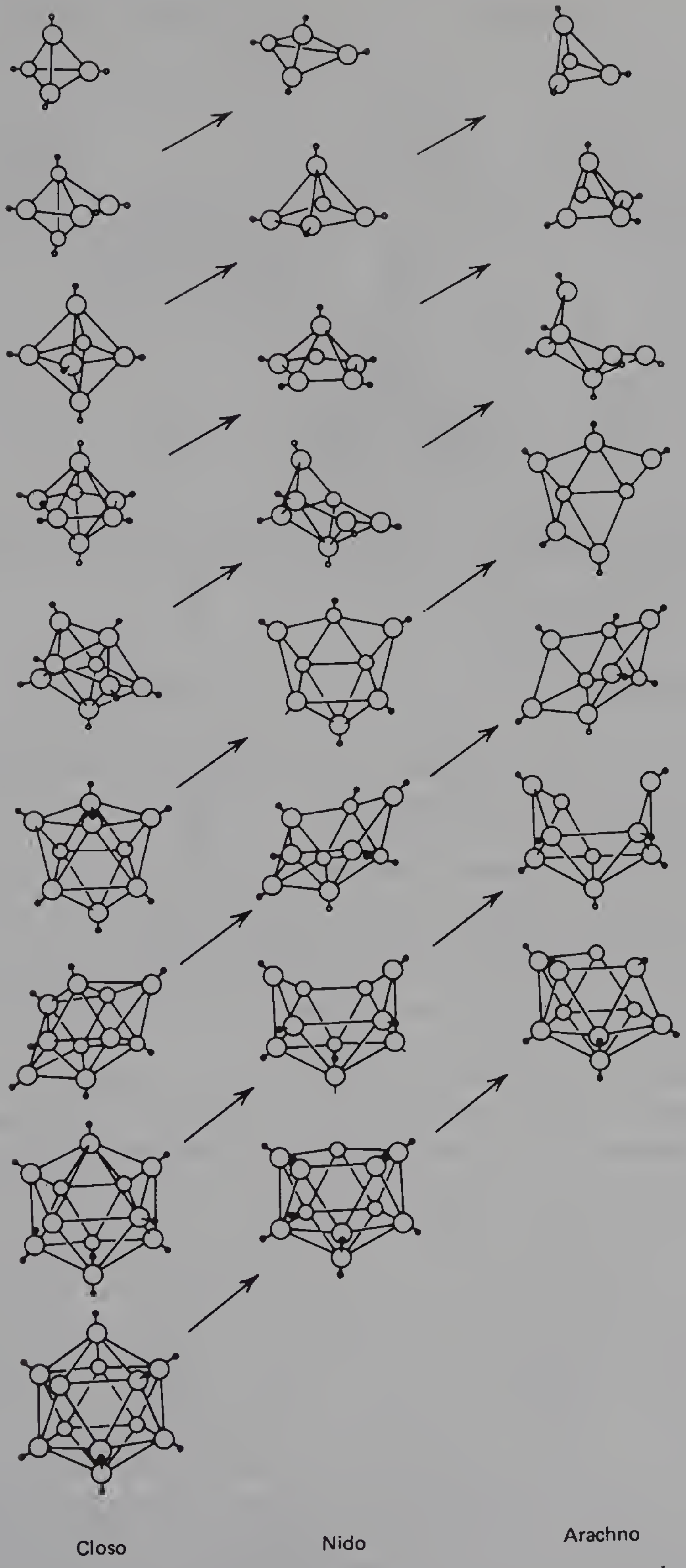


FIG. 6-9. Idealized polyhedral boron frameworks for *closo-*, *nido-*, and *arachno-*boranes and heteroboranes. Bridge hydrogens and BH_2 groups are not shown, but where appropriate they lie around the open face of the framework. The lines linking boron atoms merely illustrate cluster geometry. [Reproduced by permission from R. W. Rudolph, *Acc. Chem. Res.*, 1976, **9,** 446].

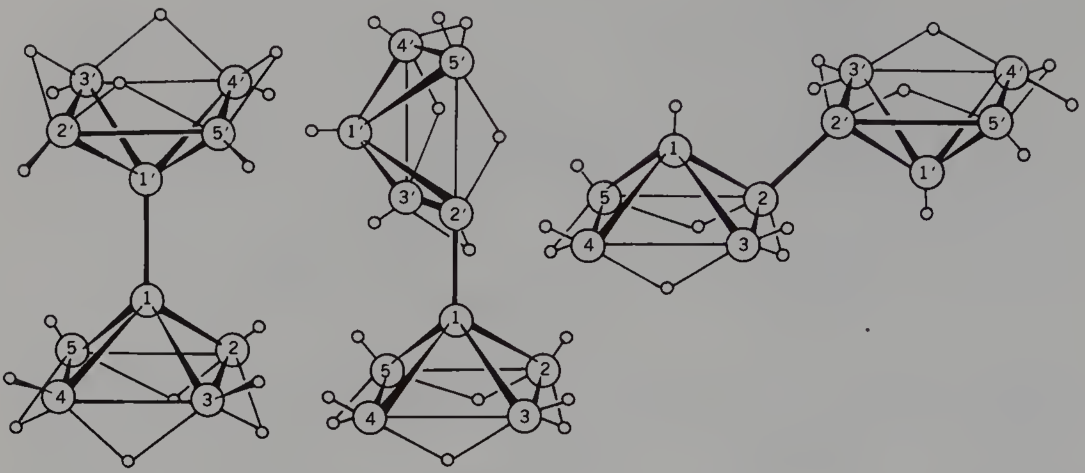


FIG. 6-10. The three isomers of the *conjuncto*-borane $B_{10}H_{16}$, formed by uniting B_5H_8 fragments of pentaborane(9).

Nido-structures are often found for the $B_nH_{n+3}^-$ ions, for example, $B_5H_8^-$ and $B_{10}H_{13}^-$.

There are two *arachno*-boranes shown in Fig. 6-7, namely, B_4H_{10} (an octahedron lacking two cis B atoms) and B_5H_{11} (a pentagonal bipyramid lacking one apical and one equatorial B atom).

The relationships of *closo, nido,* and *arachno* structures are illustrated generally in Fig. 6-9. *Hypho*-boranes are known only in the form of adducts such as $B_5H_9(PMe_3)_2$, and will not be discussed further.

Conjuncto-boranes may be illustrated by the three isomers of $(B_5H_8)_2$ in each of which there is a B—B bond replacing two B—H bonds of the original B_5H_9 units. These are shown in Fig. 6-10.

Structural Study by NMR. Though X-ray crystallography is the most precise source of structural information on boranes, nmr is an important adjunct, especially in elucidating the course of substitution reactions. This is particularly true with respect to the polyhedral borane anions and carboranes discussed in Sections 6-11 and 6-12. Primarily, it is the abundant ^{11}B isotope that is studied; proton-resonance spectra are rarely useful because the signals are broad, complex multiplets as a result of splitting by the ^{11}B and ^{10}B nuclei.

Figure 6-11 gives some general features of ^{11}B and ^{1}H nmr spectra, and Fig. 6-12 shows a specific example, that of $B_{10}H_{14}$, together with the assignment in terms of the conventional numbering scheme (Fig. 6-7). Each type of B atom is represented by a signal with intensity proportional to the number of such nuclei; the signals are all doublets because of splitting by the proton attached by a 2*c*-2*e* bond to each boron atom. Splitting by bridging protons is not resolved. The inset in Fig. 6-12 shows the principal difference (minor changes occur elsewhere in the spectrum) observed in the spectrum of 2-iododecaborane. It is quite clear that this molecule has the iodine substituent

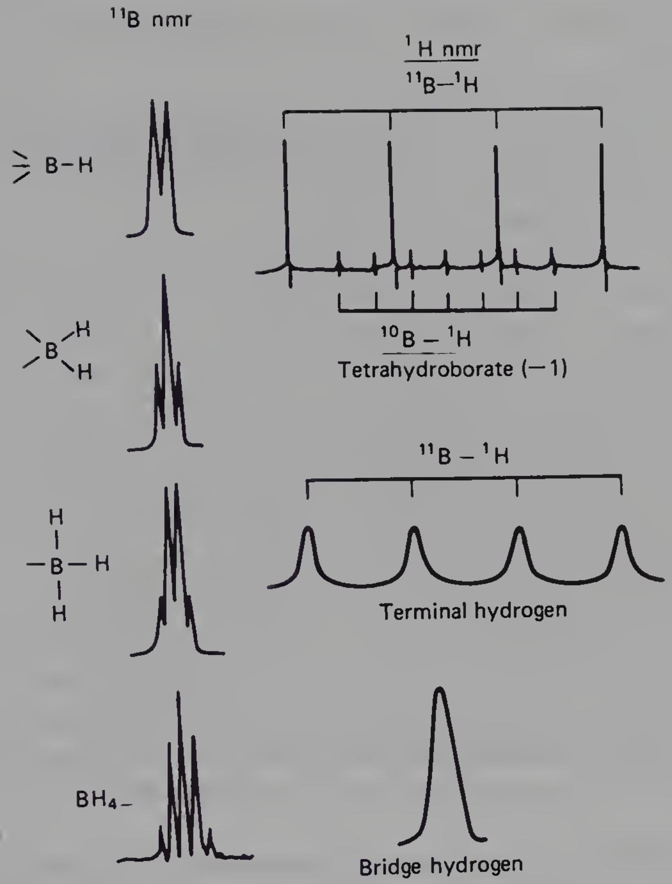


FIG. 6-11. Some general features of ^{11}B and ^{1}H nmr spectra. [Reproduced by permission from S. G. Shore, in *Boron Hydride Chemistry*, E. L. Muetterties, Ed., Academic Press, New York, 1975.]

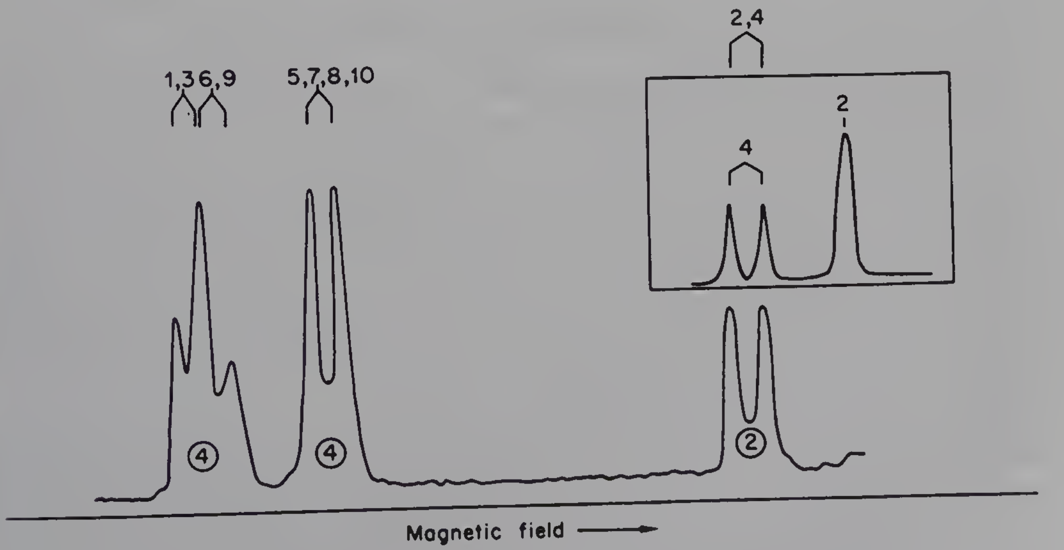


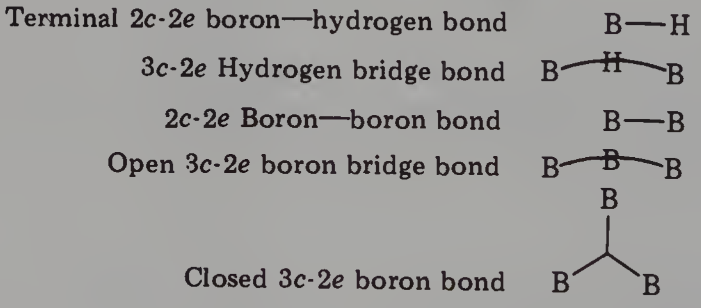
FIG. 6-12. The ^{11}B nmr spectrum of $B_{10}H_{14}$ at 64 MHz. The assignment is shown at the top and circled numbers give intensities of the multiplets. The inset is part of the spectrum of 2-$B_{10}H_{13}$I.

in the 2 (or 4)-position. Note the lack of splitting when no H is bonded to the boron atom.

Finally, it must be noted that many boron hydride compounds are fluxional in the sense that some or all hydrogen atoms are migrating. Consequently nmr spectra in solution may suggest higher symmetry than is consistent with known or presumed molecular structures.

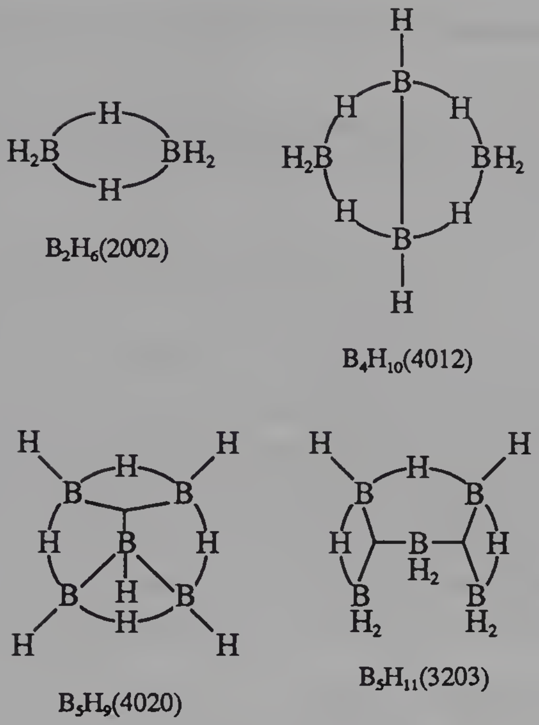
Bonding. The stoichiometries of the boranes, from the simplest B_2H_6 to the most complex, together with the number of electrons available, do not permit of structures or bonding schemes like those for hydrocarbons or other "normal" compounds of the lighter nonmetals. Not only are the structures unique, but in all of the boranes there is the problem of *electron deficiency,* that is, there are not enough electrons to permit the formation of conventional two-electron bonds (2*c*-2*e* bonds) between all adjacent pairs of atoms. To rationalize the structures in terms of acceptable bonding prescriptions, *multicenter bonding* of various sorts must be widely employed.

We have already seen that two structure-bonding elements are used in B_2H_6, namely, 2*c*-2*e* BH groups and 3*c*-2*e* BHB groups. To account for the structure and bonding of the higher boranes, these elements as well as three others are required. The three others are 2*c*-2*e* BB groups; 3*c*-2*e* open BBB groups; and 3*c*-2*e* closed BBB groups. These five structure-bonding elements may be conveniently represented in the following way:



For the boranes themselves the open 3*c*-2*e* boron bridge bond is not normally required, but it is utilized in some heterosystems. By using the other four elements in the previous list, the bonding in the boranes may be correlated with their structures. This way of formulating the bonding can be expressed in a shorthand or code, the so-called *styx* number, where these four letters denote the number of B—H—B, closed three-center B_3, two-center B—B and BH_2 groups, respectively. To illustrate this so-called *semitopological* method of representing the electronic structures, and their *styx* numbers, some examples are given in Fig. 6-13.

The semitopological scheme has its limitations. For the symmetrical *closo* structures and even for the larger and more symmetrical open structures it becomes difficult if not impossible to write simple, satisfactory structures of this sort. For B_5H_9, shown in Fig. 6-13, it is clear that the one picture shown is incompatible with the high (C_{4v}) symmetry of the molecule. In this case, which is still relatively simple, the difficulty is easily overcome by treating



$B_2H_6(2002)$

$B_4H_{10}(4012)$

$B_5H_9(4020)$

$B_5H_{11}(3203)$

FIG. 6-13. Some illustrations of the "semitopological" scheme for the bonding in boranes. *Styx* numbers are given in parentheses.

the structure shown as only one of four equivalent ones that together form a resonance hybrid. With increasing size and symmetry, however, this sort of approach becomes very cumbersome (since all canonical structures will not be equivalent) and it becomes desirable to employ an MO description, consistent with the full molecular symmetry and naturally incorporating delocalization.

Wade's Rules.[22] By combining empirical facts with the results of MO calculations, K. Wade derived a set of guidelines for relating the structures of boranes with their composition. These rules pertain to boranes of formula $B_nH_m^{x-}$, where $m \geq n$ and $x \geq 0$ (i.e., only neutral molecules or anions are considered).

Molecular orbital calculations have shown that independent of the value of n, if $m = n$ and the structure is *closo*, x will have to be 2 in order that all bonding orbitals be filled and all antibonding orbitals be empty. This means that there are $n + 1$ so-called framework electrons, that is, electrons in the central B_n polyhedron. The $B_6H_6^{2-}$ case may be used to illustrate this. Each B—H group supplies three orbitals (one having been used to form the B—H bond) and two electrons to the octahedral B_6 framework. The atomic orbitals combine to generate seven bonding MO's (not all of different energies since there are degeneracies) and eleven antibonding MO's. To fill all seven of the bonding MO's one more pair of electrons is required; hence the charge of

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[22] For a more complete development see K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18,** 1.

2−. Since the same general result is obtained for all *closo* boranes, we have the first of Wade's rules:

Rule 1. *For a* $B_nH_n^{x-}$ *species the preferred structure is a* closo *one (an n-vertex polyhedron) with a preferred charge of 2−. There are then n + 1 pairs of framework electrons.*

Next, we consider $B_nH_m^{x-}$ species where $m > n$. There are a number of these where $m = n + 4$ and $x = 0$, such as B_5H_9 and B_6H_{10}. If we remove $m - n$ protons from such a structure, we shall have $B_nH_n^{4-}$. Calculations suggest that such a species, which has $n + 2$ pairs of framework (i.e., non-BH) electrons, will have as its most stable structure the incomplete polyhedron obtained by removing one vertex from the polyhedron with $n + 1$ vertices. Thus we have a *nido* structure. The second of Wade's rules thus states:

Rule 2. *For a* B_nH_{n+4} *borane, where there are n + 2 pairs of framework electrons in the corresponding* $B_nH_n^{4-}$ *ion, a* nido *structure is preferred.*

In a similar way rules 3 and 4 are derived, which state:

Rule 3. *For a* B_nH_m *species based on a* $B_nH_n^{6-}$ *anion, an* arachno *structure derived from an (n + 2) vertex polyhedron is preferred.*

Rule 4. *For a* B_nH_m *species that derives from a* $B_nH_n^{8-}$ *anion, a* hypho *structure will be preferred.*

It is to be noted that these rules can be extended to carboranes (Section 6-12) by noting that a CH unit corresponds formally to BH^-. The applicability of these rules can be extensively illustrated by examining Fig. 6-9. As will be discussed in Chapter 23, with certain modifications (and with less rigor) Wade's rules also have some applicability to transition metal cluster compounds.

Finally, it may be noted that bonding in the boranes (as well as transition metal clusters) can be formulated by a model that treats the $B_nH_n^{n-}$ system as n B—H units distributed on a sphere. The boron orbitals (p_x, p_y, and an s–p_z hybrid) are then combined according to certain mathematical rules and relative energies estimated by the extended Hückel theory.[23] This gives rise to correlations between structures and electron counts that are consistent with Wade's rules and with experimental observations.

6-10. The Tetrahydridoborate (BH_4^-) Ion

This ion, also commonly called the borohydride ion (though that name is imprecise), can be considered to arise by Lewis acid behavior of BH_3 toward a hydride ion. In addition to the tetrahedral tetrahydridoborate ion itself, many substituted derivatives of it, such as $[BH_3CN]^-$ and $[BH(OMe)_3]^-$, are well known and all such species are reducing agents, often having quite specific

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[23] A. J. Stone, *Polyhedron,* 1984, **3,** 1299.

uses in organic and inorganic chemistry, where they may also be sources of H^- rather than simple reductants.

Typical preparative reactions are

$$4NaH + B(OCH_3)_3 \xrightarrow{\sim 250°C} NaBH_4 + 3NaOCH_3$$

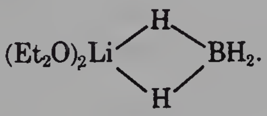
$$NaH + B(OCH_3)_3 \xrightarrow{THF} NaBH(OCH_3)_3$$

$$2LiH + B_2H_6 \xrightarrow{ether} 2LiBH_4$$

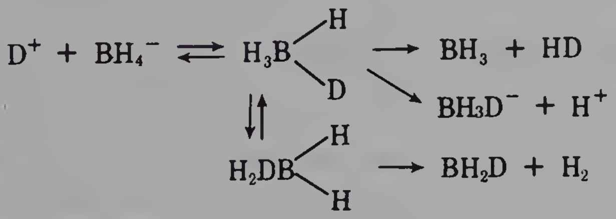
$$AlCl_3 + 3NaBH_4 \xrightarrow{heat} Al(BH_4)_3 + 3NaCl$$

$$UF_4 + 2Al(BH_4)_3 \longrightarrow U(BH_4)_4 + 2AlF_2BH_4$$

Sodium borohydride ($NaBH_4$) is representative of the alkali borohydrides, and it is the most common one. It is a white crystalline substance, stable in dry air and nonvolatile. Though insoluble in diethyl ether, it dissolves in water, THF, glymes (ethylene glycol ethers), and pyridine. Lithium borohydride is soluble in diethyl ether, but there is strong lithium–hydrogen interaction of the type



Aqueous solutions of BH_4^- slowly hydrolyze, though they are more stable when alkaline. Studies of the hydrolysis of BH_4^- in D_2O and of BD_4^- in H_2O provide good evidence that transient BH_5 (cf., CH_5^+) is a five-coordinate, fluxional intermediate of lifetime ~10^{-10} s. Thus much of the gas evolved from BH_4^- in D_2O is HD, and this and other observations can be accommodated by the scheme



Sodium borohydride reacts rapidly with methanol but rather slowly with ethanol, in which it is quite soluble. As a reducing agent for organic compounds, $NaBH_4$ has the limitation that it is insoluble in nonpolar solvents. However, phase transfer catalytic reductions can be made using cationic surfactants; alternatively, long-chain quaternary ammonium borohydrides can be used.

The cyanoborohydride (BH_3CN^-) has the advantage that it can be used in moderately acid solutions because it is more stable toward hydrolysis. There are also adducts of trialkylborons with LiH (e.g., $LiBHMe_3$). The compound $LiBHEt_3$ is an exceptionally powerful S_N2 nucleophile toward alkyl halides and the replacement of H by C_2H_5 increases the nucleophilicity of $LiBH_4$ by a factor of 10^5. This can be attributed to the greater ease of H transfer from the weaker Lewis acid BEt_3 than from BH_3.

The BH_4^- ion and also the BH_3Me^- ion are capable of serving as ligands, through M—H—B bridge bonds. This aspect of their chemistry, as well as that of other borane anions and aluminohydride anions is discussed in Section 24-10.

6-11. Polyhedral Borane Anions

There are many anionic boranes besides BH_4^- and its derivatives. A particularly important series are the polyhedral ones of general formula $B_nH_n^{2-}$ (already mentioned in Section 6-9). Those with n = 6–12 are well characterized. Some arise (as already noted) by acid dissociation of boranes, but many preparative methods exist.

Interaction of $NaBH_4$ and BF_3OEt_2 in diglyme or similar ether gives the ion $B_3H_8^-$

$$5BH_4^- + 4BF_3OEt_2 \longrightarrow 2B_3H_8^- + 3BF_4^- + 2H_2 + 4Et_2O$$

whereas the same reaction using excess BF_3 gives $B_{11}H_{14}^-$

$$17BH_4^- + 20BF_3OEt_2 \xrightarrow{105°C} 2B_{11}H_{14}^- + 15BF_4^- + 20H_2 + 20Et_2O$$

Pyrolysis of NaB_3H_8 at 200 to 230°C in vacuum gives salts of BH_4^-, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$, and air oxidation of $B_9H_9^{2-}$ in THF gives $B_8H_8^{2-}$ and $B_7H_7^{2-}$. The borane anions have full triangulated polyhedral *closo* structures (Fig. 6-8).

The ions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are hydrolytically stable and have been most thoroughly studied. The most useful syntheses are

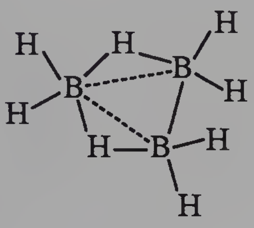
$$B_{10}H_{14} + 2R_3N \xrightarrow[\text{xylene}]{\text{boiling}} 2(R_3NH)^+ + B_{10}H_{10}^{2-} + H_2$$

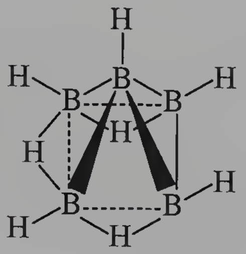
$$5B_2H_6 + 2NaBH_4 \xrightarrow[\text{diglyme}]{180°C} 2Na^+ + B_{12}H_{12}^{2-} + 13H_2$$

For these ions there is an enormous body of substitution chemistry, reminiscent of aromatic hydrocarbon chemistry. Attack by electrophilic reagents is the most important general reaction type. Representative attacking species are RCO^+, CO^+, $C_6H_5N_2^+$, and Br^+. These reactions proceed most readily in strongly acid media, and, in general, $B_{10}H_{10}^{2-}$ is much more susceptible to substitution than is $B_{12}H_{12}^{2-}$. Less reactive nucleophiles such as $C_6H_5N_2^+$ fail to attack $B_{12}H_{12}^{2-}$ and attack $B_{10}H_{10}^{2-}$ selectively at the apical (1, 10)-positions. Both $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ can be partially and completely halogenated; the rate of reaction of $B_{10}H_{10}^{2-}$ in aqueous or ethanolic solution with halogens decreases in the order $Cl_2 > Br_2 > I_2$ and also diminishes with increasing substitution. The perhalogeno ions have extremely high thermal stabilities and are also highly resistant to hydrolysis.

Oxidation of $B_{10}H_{10}^{2-}$ in aqueous solution by Fe^{3+} gives an ion $B_{20}H_{18}^{2-}$ that has two polyhedra linked by two three-center B—B—B bonds between the 6, 10 and 6′,10′ positions. This in turn is reduced by sodium in liquid ammonia to $B_{20}H_{18}^{4-}$, which has the polyhedra linked only by a B—B bond between the 10 positions. Isomers of $B_{20}H_{18}^{4-}$, can be made.

Other borane anions that are important but are not closed polyhedra are the $[H_3BHBH_3]^-$ ion,[24] $B_3H_8^-$ (6-XII) and $B_5H_8^-$ (6-XIII). The last two form many complexes with metal ions,[25a] and substitution products, for example, $B_3H_7X^-$.[25b] Both are fluxional because of rapid cycling of the bridging hydrogen atoms.


(6-XII)


(6-XIII)

6-12. Carboranes[26] and Other Heteroboranes

Carboranes (more formally and less commonly called carbaboranes) are polyhedral boranes that contain framework carbon atoms as well as boron atoms. The most important series are the *closo*-carboranes in which two BH^- units of a $B_nH_n^{2-}$ borane anion are replaced by the isoelectronic CH unit. These have been noted in Fig. 6-8. There are, however, many other carboranes, including those with 1, 3, or even 4 carbon atoms, and including *nido* and *arachno* as well as *closo* structures. The field is so large that only a few main features can be covered here.

In most cases isomers are possible and thus a suitable nomenclature is necessary. Briefly, the C_nB_m skeleton is numbered starting with an apex atom and then successive rings or belts of atoms are numbered in a clockwise direction. The C (or other hetero) atoms are given the lowest numbers possible within this scheme. The examples shown in Fig. 6-14 will illustrate the notation and also depict some of the species to be discussed here, where small italic numbers designate structures shown.

Preparative methods are numerous, but the *closo*-$C_2B_nH_{n+2}$ species are generally prepared by reactions of acetylene, RCCH or RCCR′ with a borane, either thermally or in a silent electric discharge:

$$B_5H_9 \xrightarrow[600°C]{C_2H_2} \underset{(i)}{1,5\text{-}C_2B_3H_5} + \underset{(ii)}{1,6\text{-}C_2B_4H_6} + \underset{(iii)}{2,4\text{-}C_2B_5H_7}$$

$$B_{10}H_{14} \xrightarrow[-H_2]{Et_2S} B_{10}H_{12}(SEt_2)_2 \xrightarrow[-2Et_2S]{RCCR'} \underset{(vii,\ R\ =\ R'\ =\ H)}{(CR)(CR')B_{10}H_{10}} + H_2$$

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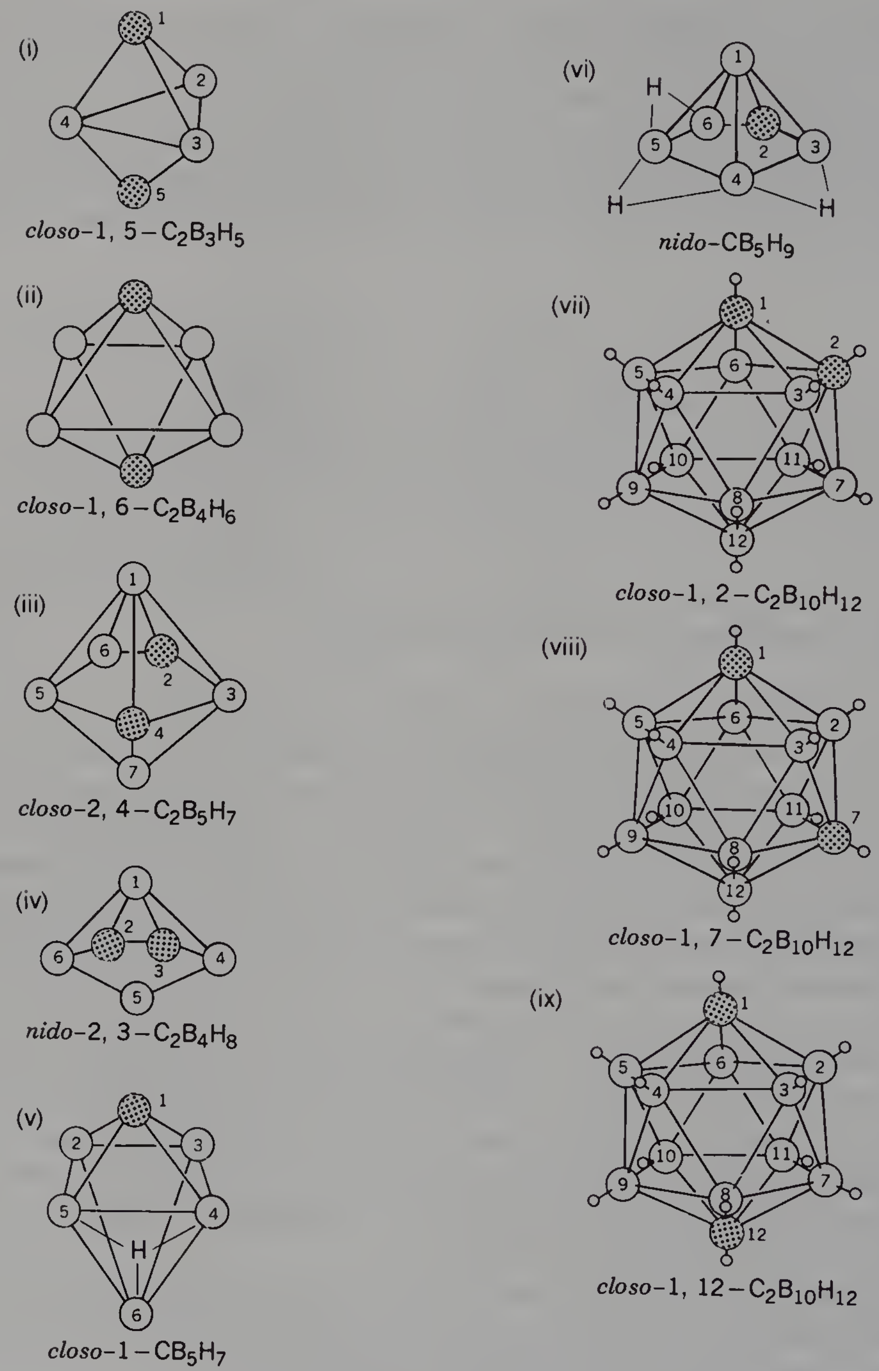
[24] R. Bau *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 1753.

[25a] R. N. Grimes, Ed., *Metal Interactions with Boron Clusters,* Plenum, New York, 1982.

[25b] S. J. Andrews and A. J. Welch, *Inorg. Chim. Acta,* 1985, **105,** 89.

[26] R. N. Grimes, *Adv. Inorg. Chem. Radiochem.*, 1983, **26,** 55.



(i) *closo*-1, 5-$C_2B_3H_5$

(ii) *closo*-1, 6-$C_2B_4H_6$

(iii) *closo*-2, 4-$C_2B_5H_7$

(iv) *nido*-2, 3-$C_2B_4H_8$

(v) *closo*-1-CB_5H_7

(vi) *nido*-CB_5H_9

(vii) *closo*-1, 2-$C_2B_{10}H_{12}$

(viii) *closo*-1, 7-$C_2B_{10}H_{12}$

(ix) *closo*-1, 12-$C_2B_{10}H_{12}$

FIG. 6-14. Some representative carboranes, showing numbering schemes.

Under mild conditions *nido*-carboranes can be obtained:

$$nido\text{-}B_5H_9 \xrightarrow[200°C]{C_2H_2} nido\text{-}2{,}3\text{-}C_2B_4H_8$$
$$\text{(iv)}$$

A common route to monocarboranes is by pyrolysis of methylboranes.

For example:

$$1,2\text{-}\mathrm{Me_2B_5H_7} \xrightarrow{500\text{–}600^\circ\mathrm{C}} \underset{\text{(i)}}{1,5\text{-}\mathrm{C_2B_3H_5}} + \begin{cases} 1\text{-}\mathrm{CB_5H_7} & \text{(v)} \\ \quad + & \\ 2\text{-}\mathrm{CB_5H_9} & \text{(vi)} \\ \quad + & \\ 3\text{-Me-}2\text{-}\mathrm{CB_5H_8} & \end{cases}$$

The action of strong base will not only generate anions, such as 1-$CB_5H_6^-$ from 1-CB_5H_7 (v), but can remove a boron atom (formally as BH^+) from the framework to generate anions. These *nido* or *arachno* anions can form metal complexes, as discussed in Section 6-13.

One of the most intensively studied carboranes is 1,2-$C_2B_{10}H_{12}$ (vii). It is an air-stable compound, readily prepared from $B_{10}H_{14}$ (by the reactions cited previously) in kilogram quantities. The C_2B_{10} framework is a distorted icosahedron. One of its interesting properties is that it can be isomerized by heating (470°C for several hours) or flash photolysis to the 1,7-isomer (viii). The 1,7-isomer can be isomerized (but only in very poor yield) to the 1,12-isomer (ix) by brief heating at 700°C. Since these isomerization processes appear to be intramolecular, they have been the subject of some interesting speculations. One proposal that can account for the 1,2 to 1,7 conversion, but not the 1,7 to 1,12 process, entails a cubooctahedron intermediate, as shown in Fig. 6-15. Other suggestions include a rotation of one triangular face [Fig. 6-16(a)] or twisting of one pentagonal pyramid within the icosahedron relative to the other [Fig. 6-16(b)].

This type of isomerization reaction is not limited to 1,2-$C_2B_{10}H_{12}$. The 1,6-$C_2B_8H_{10}$ molecule rearranges quantitatively to the 1,10-isomer at 350°C.

Carbon-substituted derivatives can be obtained using substituted acetylenes or by reaction sequences such as the following for 1,2-*closo*-$B_{10}H_{10}C_2H_2$ where a conventional and self-explanatory abbreviation is used for the $B_{10}C_2H_{10}$ group. The chemistry of *C*-substituted carboranes is quite similar to that of conventional carbon systems, and indeed organic-type reactions have led to the synthesis of thousands of carborane derivatives. A simple example is

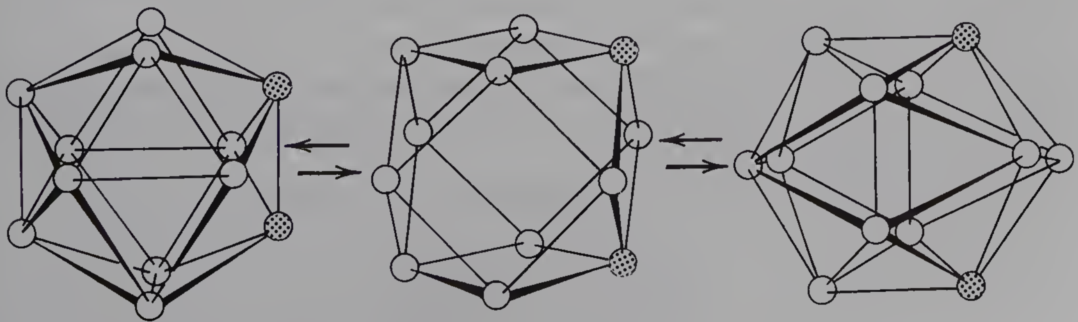


FIG. 6-15. The interconversion of 1,2- and 1,7-disubstituted icosahedral species through a cubooctahedral intermediate.

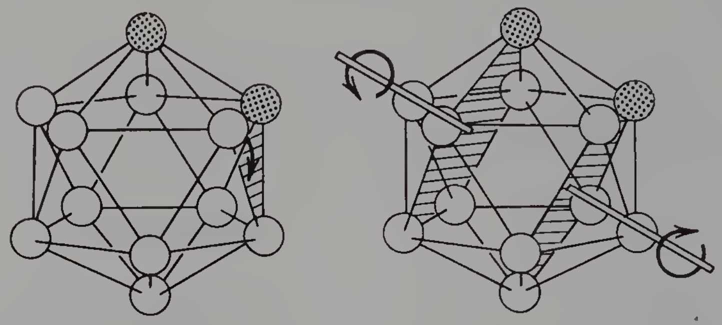
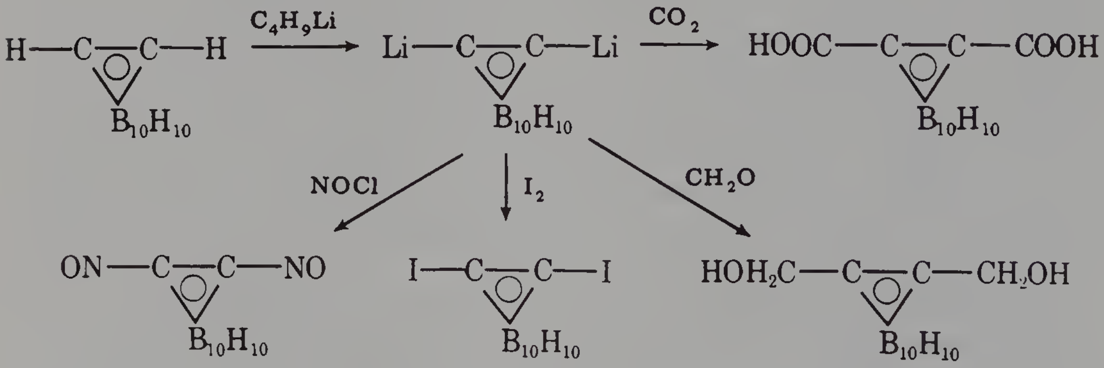

(a) (b)

FIG. 6-16. Two proposed ways of isomerizing 1,2-$C_2B_{10}H_{12}$. (a) By rotation of one triangular face. (b) By rotation of one pentagonal pyramid against another.

chlorination, where 1,2- and 1,7-$B_{10}H_{10}C_2H_2$ react at the most negative boron atoms (cf. $B_{10}H_{14}$) to give $B_{10}C_2H_{12-x}Cl_x$ molecules.



Molecular orbital calculations show that the carbon atoms in the $B_{10}C_2H_{12}$ molecules (and in carboranes in general) have considerable electron-withdrawing power; thus the most electron-deficient boron atoms are those *adjacent* to C, namely, those at positions 3 and 6 in 1,2-$B_{10}C_2H_{12}$ and those at positions 2 and 3 in 1,7-$B_{10}C_2H_{12}$. Therefore, the direct products of the reactions of the isomeric $B_{10}C_2H_{12}$ molecules and other carboranes with electrophilic reagents occur preferentially at the boron atoms most remote from the carbon atoms.

Boranes with Hetero Atoms Other than Carbon. Closely related to the carboranes are compounds with other atoms present, notably phosphorus, arsenic, and sulfur. The formalism for relating isoelectronic species is P ≡ BH^- and S ≡ BH^{2-}.

Typical examples with their "parent" boranes in parentheses are

1-SB_9H_9	($B_{10}H_{10}^{2-}$)
1-$SB_{11}H_{11}$	($B_{12}H_{12}^{2-}$)
1,2-$CPB_{10}H_{11}$	($B_{12}H_{12}^{2-}$)

As with carboranes, these substitutions lead to uneven charge distributions from which sites of electrophilic substitution can be predicted.[27]

6-13. Metal Complexes of Carboranes and Boranes[24,28–30]

Carborane Complexes. Carborane anions of the *nido* and *arachno* types have an enormous capacity to form complexes with transition metals. The seminal discovery in this field was Hawthorne's recognition that the *nido* anions (Fig. 6-17) obtained by the action of strong base on the 1,2- and 1,7-isomers of $C_2B_{10}H_{12}$ are capable of coordinating to metal atoms in much the same way as the cyclopentadienyl ion ($C_5H_5^-$) (Section 2-14). These $C_2B_9H_{11}^{2-}$ ions are commonly referred to as dicarbollide ions (from the Spanish *olla* meaning pot) to avoid the use of unwieldy systematic nomenclature.[31]

Solutions of the dicarbollide anions react with $FeCl_2$ in THF to form the iron(II) bis(dicarbollide) complexes $[Fe(C_2B_9H_{11})_2]^{2-}$ with the structure shown in Fig. 6-18(a). This complex is isoelectronic with ferrocene, and it too readily undergoes a one-electron oxidation. By employing a mixture of NaC_5H_5 and the dicarbollide anion the mixed sandwich compound [Fig. 6-18(b)] is obtained:

$$C_2H_9H_{11}^{2-} + C_5H_5^- + Fe^{2+} \xrightarrow{-e^-} Fe^{III}(C_2B_9H_{11})(C_5H_5)$$

This is only one example of the many mixed species, including complexes of

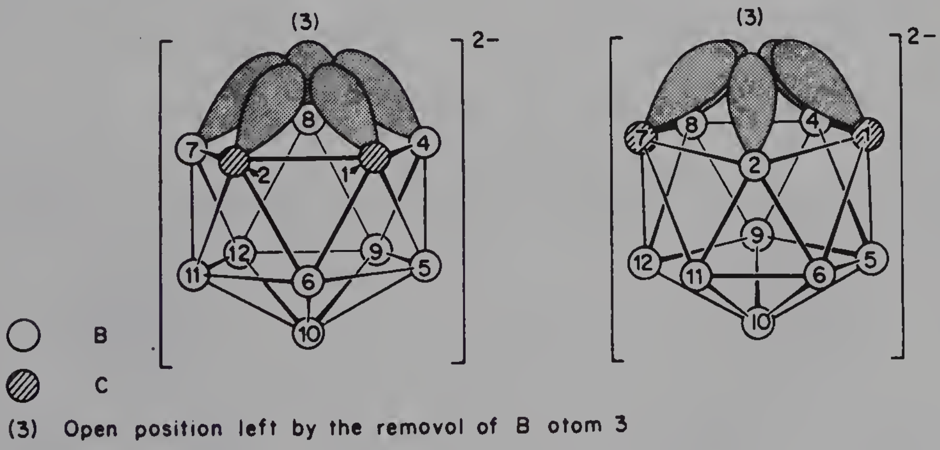


FIG. 6-17. Structures of the isomeric $B_9C_2H_{11}^{2-}$ ions.

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[27] T. R. Spalding *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 2591.

[28] N. N. Greenwood *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 1879.

[29] J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32,** 519; 1986, **34,** 212.

[30] R. N. Grimes *et al., Organometallics,* 1985, **4,** 882; *Comprehensive Organometallic Chemistry,* Vol. 1, Chap. 5.5, Pergamon Press, Oxford, 1982.

[31] As the chemistry of the metallaboranes and metallacarboranes continues to expand in both extent and complexity, the associated questions of notation, bonding descriptions, and so on, also become ever more difficult. See, for example, R. T. Baker, *Inorg. Chem.*, 1986, **25,** 109 and J. D. Kennedy, *Inorg. Chem.*, 1986, **25,** 111.

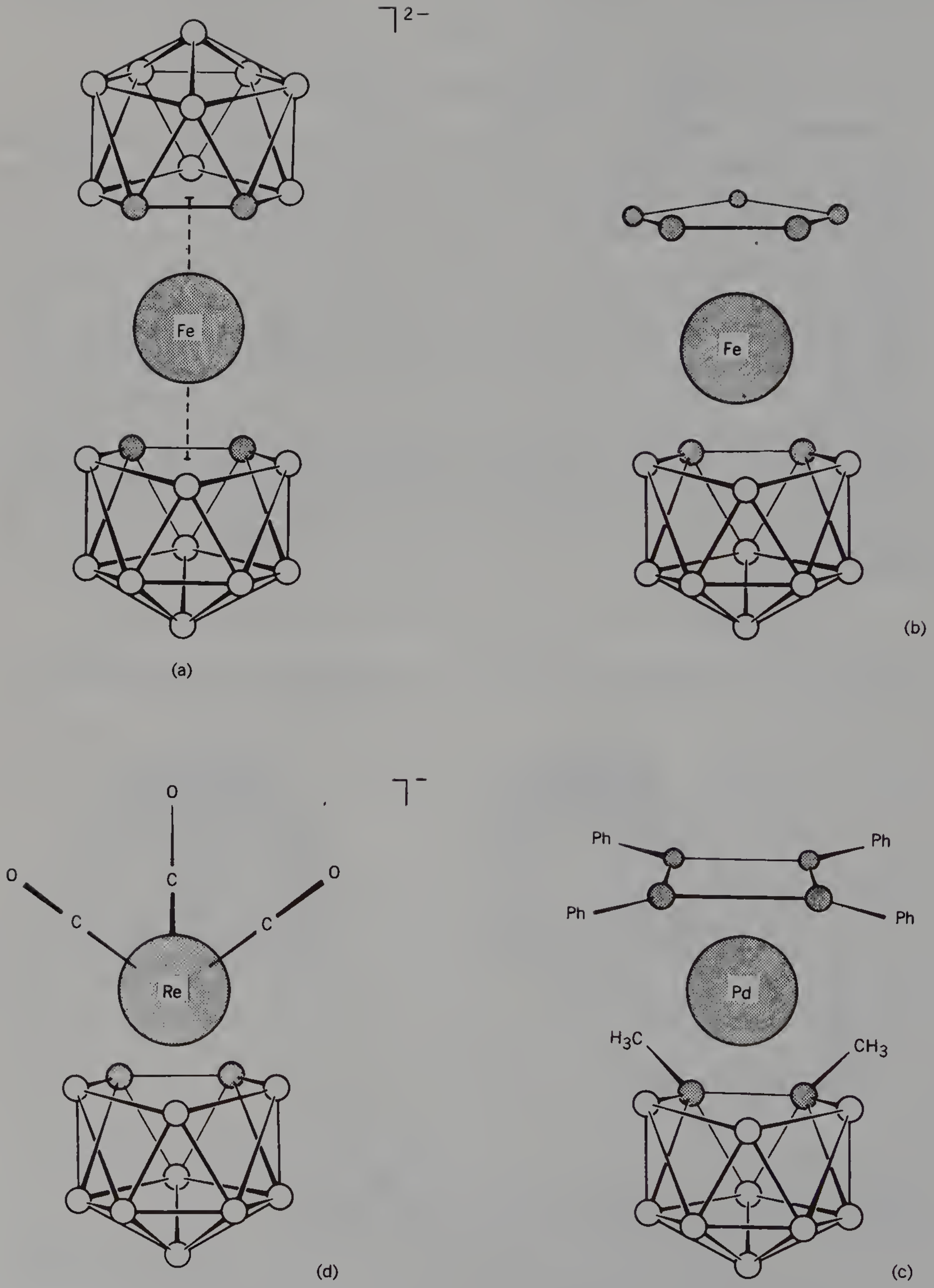

FIG. 6-18. Structures of some dicarbollide complexes mentioned in the text.

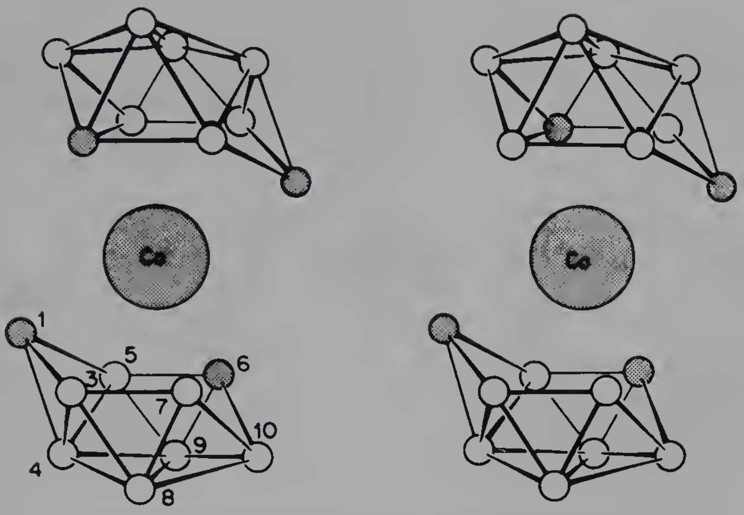

FIG. 6-19. Isomeric $[(C_2B_7H_9)_2Co]^-$ complexes.

various other metals. Some examples [See Fig. 6-18(c) and (d) also], are

$(C_2B_9H_{11})Mo(CO)_3^{2-}$
$(C_2B_9H_{11})Re(CO)_3^-$
$(C_2B_9H_{11})Co(C_5H_5)$
$[(MeC)_2B_9H_9]Pd(C_4Ph_4)$
$[(MeC)(PhC)B_9H_9]RhH(PPh_3)_2$

The last mentioned is one of various rhodium complexes that have catalytic activity in hydrogenation and other reactions.[32]

Other series of carborane complexes are known. For example, the anion $B_7C_2H_{11}^{2-}$ (which has isomers) gives the complex $[Co(B_7C_2H_9)_2]^-$, two of whose isomers are shown in Fig. 6-19.

Preparative methods for carborane complexes, in addition to the reaction of metal cations, or other suitable species, directly with the appropriate carborane anion include polyhedral contraction, illustrated in Fig. 6-20, a related type of process in which the deleted BH group is replaced by a metal atom, illustrated in Fig. 6-21, and reactions in which zero-valent metal precursors react with neutral carboranes, as, for example:

$$Pt(PR_3)_n + 2,3\text{-}(Me_2C)_2B_9H_9 \longrightarrow [2,4\text{-}(Me_2C)_2B_9H_9]Pt(PR_3)_2 + (n-2)PR_3$$

In addition to the compounds containing rather large carborane ligands, there are many that contain much smaller ones. This is illustrated in Fig. 6-22.

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[32] M. F. Hawthorne *et al., J. Am. Chem. Soc.,* 1984, **106,** 3011, 7444; *Organometallics,* 1985, **4,** 13.

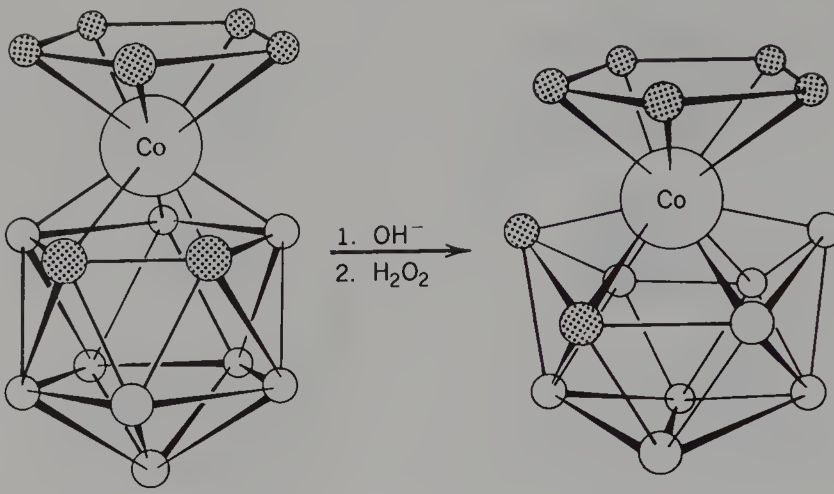
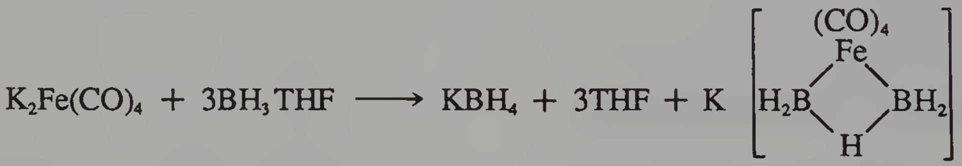


FIG. 6-20. A representative polyhedral contraction reaction for transforming one carborane complex into another.

Borane Complexes are of two types: those having only H to M bonds (which are discussed in Section 24-10) and those having direct B to M bonds, which will be discussed here. These range from what may be the simplest such compound, obtained by the reaction



$$K_2Fe(CO)_4 + 3BH_3THF \longrightarrow KBH_4 + 3THF + K\left[\begin{array}{ccc} & (CO)_4 & \\ & Fe & \\ H_2B & & BH_2 \\ & H & \end{array}\right]$$

to considerably more complex ions, such as that illustrated in Fig. 6-23(a), where there are both B—M and B—H—M bonds, and some that contain only B—M bonds, shown in Fig. 6-23(b) and (c). The latter may be regarded as, and named as, heteroboranes, just as were the carboranes.

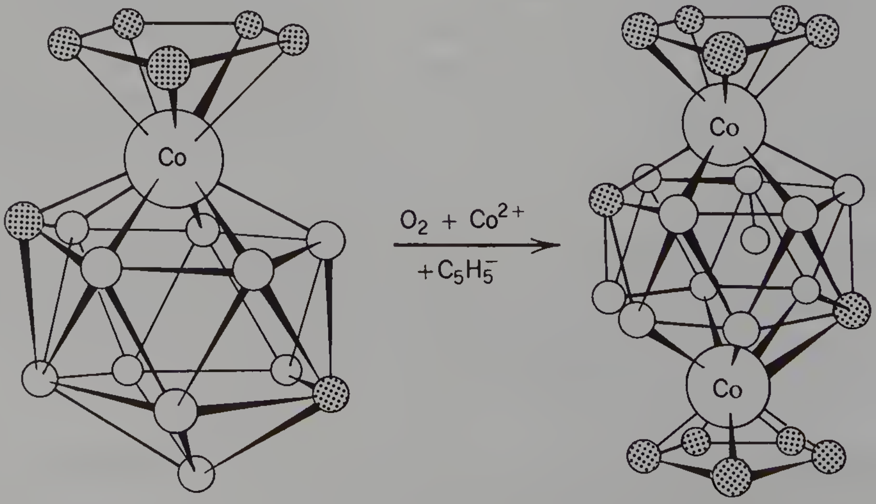


FIG. 6-21. A reaction for replacing a BH unit by another metal unit.

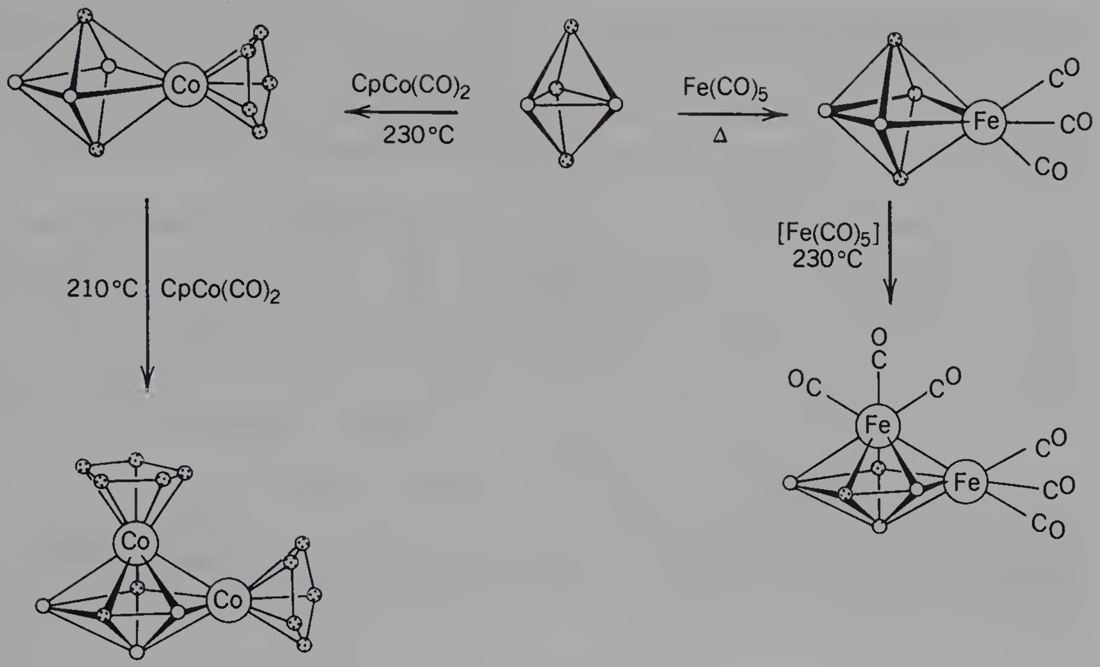


FIG. 6-22. Some illustrative examples of carborane complexes with small carborane moieties, and their preparation.

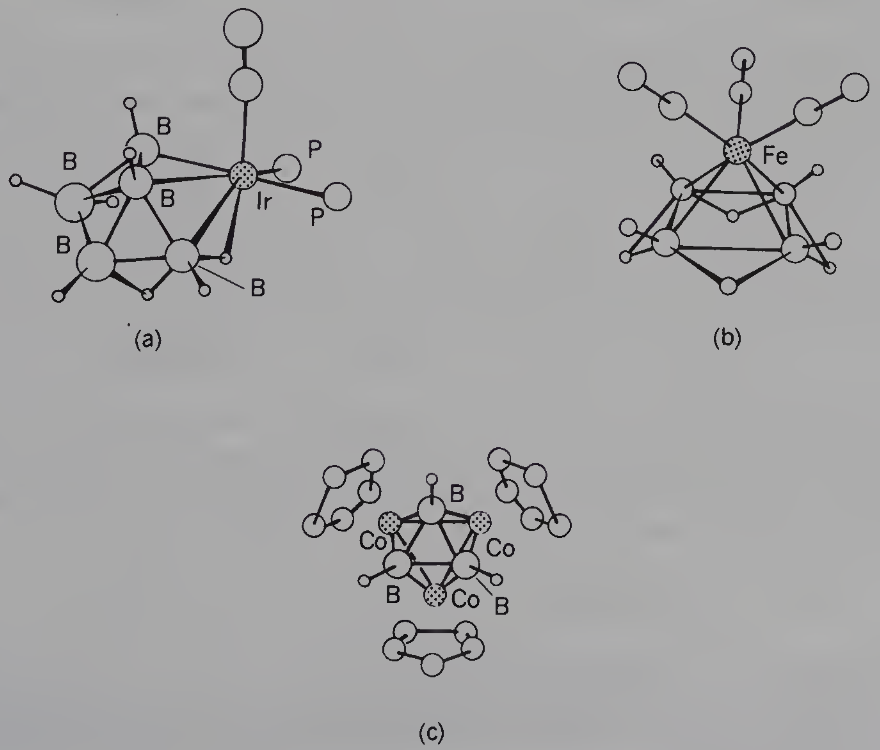


FIG. 6-23. Some borane complexes of transition metals that contain M—B bonds. (a) $(B_5H_8)Ir(CO)(PPh_3)_2$, (b) $(B_4H_8)Fe(CO)_3$, and (c) $(B_3H_3)Co_3(C_5H_5)_3$.

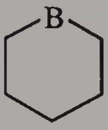
6-14. Organoboron Compounds[33]

Aside from the carboranes already discussed, there is a host of other compounds with B—C bonds, and organoboranes are reagents of special importance in organic synthesis.[14,34]

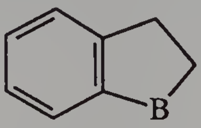
The alkyl and aryl borons can be made from the halides by conventional methods using lithium or Grignard reagents. The lower alkyls are reactive substances inflaming in air, but the aryls are stable. Compounds can be of the types R_3B, R_2BX, and RBX_2. Mixed compounds can be madė by reactions such as

$$R_3B + MeSH \xrightarrow{-MeR} R_2BSH \xrightarrow{Br_2} R_2BBr + RSSR$$

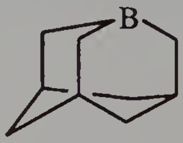
Boron can also be present in heterocyclic compounds of various types of which only a few leading examples can be mentioned here. There are numerous saturated compounds in which a BH (or BR) unit replaces a CH_2 unit, or B replaces CH. This class includes the species (6-XIV) to (6-XVI).



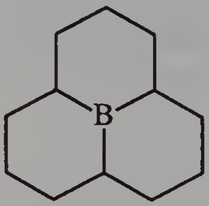
(6-XIV)



(6-XV)

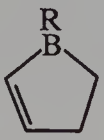


(6-XVI)

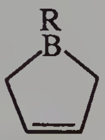


(6-XVII)

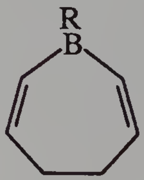
In (6-XVII) a boron atom replaces a CH unit. There are then unsaturated species[35] such as (6-XVIII), (6-XIX), and (6-XX). There are also systems in



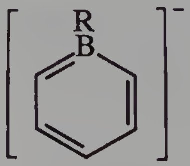
(6-XVIII)



(6-XIX)



(6-XX)



(6-XXI)

which, formally, a BR^- unit replaces a CH unit in an aromatic system, namely, (6-XXI). Such moieties can serve as arene ligands toward transition metals.[36]

Boronic and *boronous* acids, $RB(OH)_2$ and $R_2B(OH)$, and their esters and anhydrides, can be made by reactions such as

$$BF_3OEt_2 + C_6H_5MgBr \longrightarrow C_6H_5BF_2 \xrightarrow{H_2O} C_6H_5B(OH)_2$$

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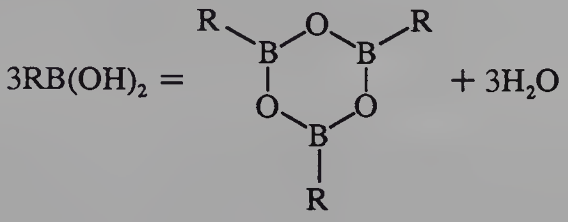
[33] See J. D. Odom *et al., Comprehensive Organometallic Chemistry,* Vol. 1, Pergamon, Oxford, 1982; K. Smith, *Organometallic Compounds of Boron,* Chapman and Hall, London, 1985.

[34] G. W. Kabalka, *J. Organomet. Chem.*, 1986, **298,** 1 (and previous annual reviews of organoboron chemistry in this journal).

[35] G. E. Herberich *et al., J. Organomet. Chem.*, 1983, **256,** C23.

[36] G. E. Herberich *et al., J. Organomet. Chem.*, 1985, **280,** 147.

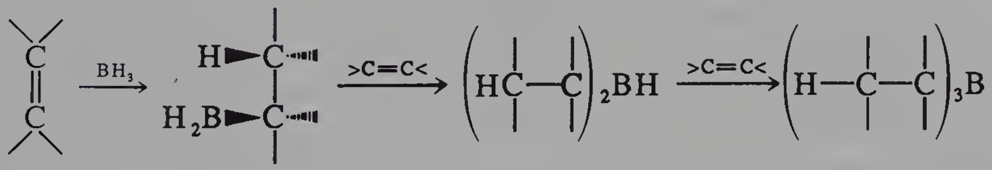
These stable and water-soluble compounds have acidities that depend on the R group. Dehydration of $RB(OH)_2$ by heating gives a *boroxine;*



the reaction is reversible. There are other ways to prepare boroxines and thence boronic acids,[37] namely,

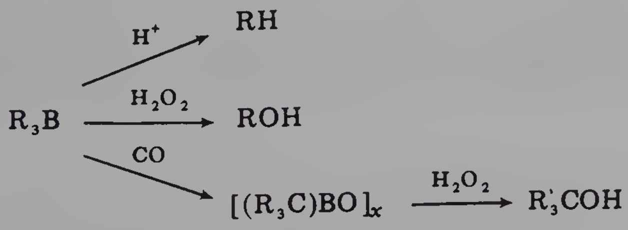
$$3BH_3{\cdot}SMe_2 + 3CO \longrightarrow (CH_3BO)_3 + 3Me_2S$$

Hydroboration. This reaction was discovered and has been developed by H. C. Brown and his students. It involves interaction of alkenes or alkynes with boranetetrahydrofuran, H_3BSMe_2 or B_2H_6 prepared *in situ,* to give, initially, alkylborons RBH_2, R_2BH, or R_3B. In effect, H and BH_2 groups are added anti-Markovnikov and cis, namely,



With simple unhindered alkenes the reaction proceeds to trialkylboron, but with trisubstituted and some disubstituted ones (e.g., cyclohexene) the reaction may be stopped at the R_2BH stage; tetrasubstituted alkenes react readily only to give RBH_2.

From the alkylborons so prepared, hydrocarbons, alcohols, ketones, and other compounds may be obtained by reaction with other reagents. The importance lies in the fact that the resulting hydration or hydrogenation products are anti-Markovnikov and cis.



With RBH_2 and R_2BH reactions with carbon monoxide followed by H_2O_2 lead to aldehydes and ketones, respectively. Polyenes may also undergo hy-

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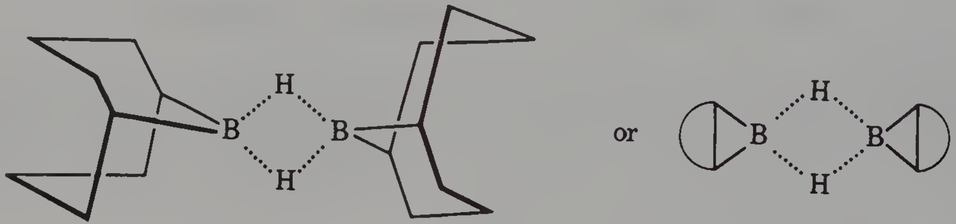
[37] H. C. Brown and T. E. Cole, *Organometallics,* 1985, **4,** 816.

droboration, for example,

A unique hydroboration reagent is 9-borobicyclo[3.3.1] nonane or 9-BBN (6-XXII). This liquid (bp 195°C, 12 Torr) is made by interaction of diborane and cycloocta-1,5-diene in THF. It is quite stable in absence of air and is commercially available. In the solid and in solution it is dimeric with hydrogen bridges.



(6-XXII)

9-BBN shows remarkable regioselectivity toward acyclic olefins; for example, hydroboration followed by oxidation converts hex-1-ene into hexan-1-ol in 99.9% yield. The organoboranes obtained using 9-BBN are also far more resistant to isomerization than most organoboranes. These undergo thermal isomerization in the presence of H^- ion at 75 to 160°C, (where boron evidently migrates along a carbon chain) to give a mixture of organoboranes approaching the thermodynamic equilibrium distribution. Again, this leads to high selectivity in reactions.

Tetraalkyl and -aryl Borates. When boron halides are treated with four equivalents of alkylating agent, the trialkyl or triaryl reacts further to form an anion of the type BR_4^-. The most important such compound is *sodium tetraphenylborate,* $Na[B(C_6H_5)_4]$; this is soluble in water and is stable in weakly acid solution; it gives insoluble precipitates with larger cations such as K^+, Rb^+, or Me_4N^+, that are suitable for gravimetric analysis. The ion can also act as a ligand wherein one phenyl ring is bound in an arene complex.

Polyboron Compounds. A few compounds of the type B_nR_n, R = alkyl[38] or aryl[39] are known. One example is $B_4(t\text{-}Bu)_4$ made by interaction of B_4Cl_4 and *t*-BuLi.

6-15. Boron–Nitrogen Compounds

The group —NR′—BR— is similar to —CR′=CR— and can replace it in many compounds. The analogy may be justified by assuming that the electron

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[38] J. A. Morrison *et al., J. Chem. Soc., Chem. Commun.,* **1981,** 250; *J. Am. Chem. Soc.,* 1982, **104,** 6790.

[39] W. Kucken and R. D. Brinkmann, *Z. Anorg. Allg. Chem.,* 1963, **325,** 255.

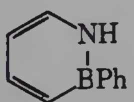
distribution in the N—B bond can be described by the resonance (6-XXIII a and b) whereby appreciable π bonding is introduced.

(a) (b)

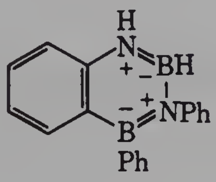
(6-XXIII)

There is evidence that such N—B bonds have appreciable π character, while at the same time they lack the polarity that would be engendered by 6-XXIII b. This apparent paradox is explained by the existence of considerable polarity in the σ bond, in a direction opposite to that in the π bond. Thus the net, or actual, polarity is only the difference between the two. The π bonding gives rise to rotational barriers[40] about these bonds in the range of 65 to 85 kJ mol^{-1}.

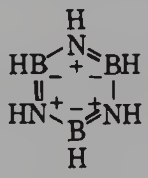
There are a number of heterocycles containing one or more —BR′—NR— units, such as (6-XXIV), (6-XXV), and (6-XXVI). The latter is called *borazine.*



(6-XXIV)



(6-XXV)



(6-XXVI)

Borazine has an obvious formal resemblance to benzene, and the physical properties of the two compounds are similar. Both MO calculations and experimental results for the transmission of substituent effects through the B_3N_3 ring indicate that the π electrons are partially delocalized.[41] Complete delocalization is not to be expected, since the nitrogen π orbitals should be of appreciably lower energy than the boron π orbitals. The planarity of the borazine molecule is shown by MO calculations to be stabilized by the π bonding, and the calculations also suggest that the N-to-B π-electron drift is actually outweighed by B to N σ drift, so that the nitrogen atoms are relatively negative.

The retention of negative charge by nitrogen means that chemically, borazine is not like benzene. It is much more reactive and, unlike benzene, readily undergoes addition reactions such as

$$B_3N_3H_6 + 3HX \longrightarrow (\text{—}H_2N\text{—}BHX\text{—})_3 \qquad (X = Cl, OH, OR, etc.)$$

Borazine decomposes slowly on storage and is hydrolyzed at elevated temperatures to NH_3 and $B(OH)_3$. It is of interest that borazine resembles benzene in forming arene–metal complexes (Section 26-11); thus the hexamethylbor-

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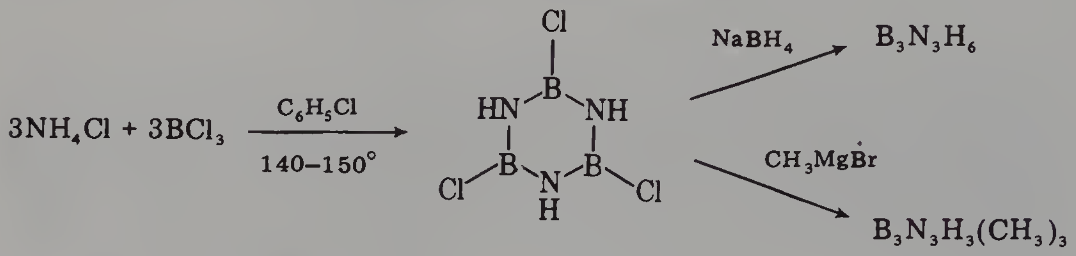
[40] C. Brown *et al., J. Organomet. Chem.*, 1985, **296,** C17.

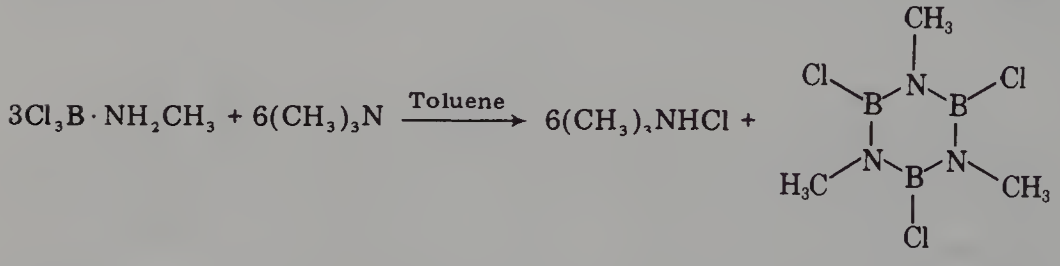
[41] R. J. Boyd *et al., Chem. Phys. Lett.*, 1984, **112,** 136.

azine complex, $B_3N_3(CH_3)_6Cr(CO)_3$ resembles $C_6(CH_3)_6Cr(CO)_3$ but is thermally less stable.

Reaction sequences by which borazine and substituted borazines may be synthesized are the following:



$$CH_3NH_2 + BCl_3 \xrightarrow[C_6H_5Cl]{\text{Boiling}} \begin{array}{l} Cl_3B\cdot NH_2CH_3 \\ \text{(m.p. 126–128°)} \end{array}$$

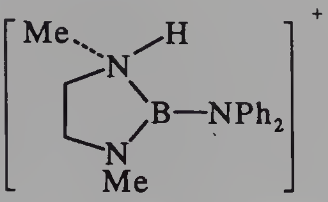


(m.p. 153–156°)

Another important boron–nitrogen compound is *boron nitride,* BN, a slippery white solid which exists in two polymorphs, analogous to graphite and diamond. The hexagonal form has a layer structure but with the significant difference from graphite that the layers are stacked in an eclipsed manner to give straight BNBN chains parallel to the *c* axis. Hexagonal BN is quite different from graphite in its physical properties (colorless and nonconducting) and chemically it is more stable although it reacts with F_2 (to give $BF_3 + N_2$) and HF (to give NH_4BF_4).

On heating at 1800°C under 85 katm of pressure, in the presence of catalysts, hexagonal BN is converted to a cubic modification comparable to diamond. The nitride is also made by interaction of B and NH_3 at high temperature; it is slowly hydrolysed by water.

Because of the ability of nitrogen atoms to form π donor bonds to boron atoms, it has been possible to stabilize planar, three-coordinate boron cations by surrounding the B atom with N atoms and employing an anion of minimal nucleophilicity (e.g., $CF_3SO_3^-$).[42] Thus, a cation such as 6-XXVII can be obtained.



(6-XXVII)

There is also an extensive chemistry of compounds similar to B—N compounds with B—P, B—As, B—S, and so on, bonds. There are simple adducts (e.g., H_3PBH_3) and also cyclic compounds such as $(Me_2PBH_2)_3$ with alternant B and P atoms. This compound and its arsenic analogue are extraordinarily stable and inert, a fact that has been attributed to a drift of electron density from the BH_2 groups into the *d* orbitals of P or As. This serves to reduce the hydridic nature of the hydrogen atoms, making them less susceptible to reaction with protonic reagents, and also to offset the B^-—P^+, B^-—As^+ polar character, which the σ bonding alone tends to produce. Another example is tribromoborthiin ($B_3S_3Br_3$), which has a six-membered BS ring with bromine atoms on B.

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Chapter Seven

The Group IIIA(13) Elements: Al, Ga, In, Tl

GENERAL REMARKS

7-1. Electronic Structures and Valences

The electronic structures and some other important fundamental properties of the Group IIIA(13) elements are listed in Table 7-1.

Although the first and smallest member of Group IIIA(13), namely, boron, has no cationic chemistry, the remaining four elements form cationic complexes such as $[Ga(H_2O)_6]^{3+}$; they also form many molecular compounds that are covalent.

While the main oxidation state is III, there are certain compounds in which the oxidation state is formally II. These, however, may have metal–metal bonds as in $[Cl_3Ga—GaCl_3]^{2-}$. The univalent state becomes progressively more stable as the group is descended and for thallium the Tl^{I}–Tl^{III} relationship is a dominant feature of the chemistry. This occurrence of an oxidation state two below the group valence is sometimes called the *inert pair* effect, which first makes itself evident here, although it is adumbrated in the low reactivity of mercury in Group IIB(12), and it is much more pronounced in Groups IVA(14) and VA(15). The term refers to the resistance of a pair of *s* electrons to be lost or to participate in covalent bond formation. Thus mercury is difficult to oxidize, allegedly because it contains only an inert pair ($6s^2$), Tl readily forms Tl^{I} rather than Tl^{III} because of the inert pair in its valence shell ($6s^26p$), and so on. The concept of the inert pair does not actually tell us anything about the ultimate reasons for the stability of certain lower valence states, but it is a useful label. The phenomenon is not due to intrinsic inertness, that is, unusually high ionization potential of the pair of *s* electrons, but rather to the decreasing strengths of bonds as a group is descended. Thus, for example, the sum of the second and third ionization enthalpies (kJ mol^{-1}) is lower for In (4501), than for Ga (4916), with Tl (4820), intermediate. There is, however, a steady decrease in the mean thermochemical bond energies, for example, among the trichlorides: Ga, 242; In, 206; Tl, 153 kJ mol^{-1}. The relative stabilities of oxidation states differing in the presence or absence of

TABLE 7-1
Some Properties of the Group IIIA(13) Elements

Property	Al	Ga	In	Tl
Electronic configuration	$[Ne]3s^23p$	$[Ar]3d^{10}4s^24p$	$[Kr]4d^{10}5s^25p$	$[Xe]4f^{14}5d^{10}6s^26p$
Ionization enthalpies ($kJ\ mol^{-1}$)				
1st	576.4	578.3	558.1	589.0
2nd	1814.1	1969.3	1811.2	1958.7
3rd	2741.4	2950.0	2689.3	2862.8
4th	11563.0	6149.7	5571.4	4867.7
mp (°C)	660	29.8	157	303
bp(°C)	2327	~2250	2070	1553
E^0 for $M^{3+} + 3e = M(s)$[a]	−1.66	−0.35	−0.34	0.72
Radius M^{3+} (Pauling)(Å)	0.50	0.62	0.81	0.95
Radius M^+ (Å)		1.13	1.32	1.40

[a] $In^+ + e = In$, $E^0 = -0.178$ V; $Tl^+ + e = Tl$, $E^0 = -0.3363$ V.

the inert pair are further discussed in connection with the Group IVA(14) elements (Chapter 9). Only where it can be shown that the electron pair has no stereochemical consequences is it reasonable to assume an s^2 pair. Recent theoretical work shows that relativistic effects make an important contribution to the inert pair effect.

In the trihalide, trialkyl, and trihydride compounds there are some resemblances to the corresponding boron chemistry. Thus MX_3 compounds behave as Lewis acids and can accept either neutral donor molecules or anions to

TABLE 7-2
Oxidation States and Stereochemistries of Group IIIA(13) Elements

Oxidation state	Coordination number[a]	Geometry	Examples
+1	6	Distorted octahedral	TlF
+2	4	Tetrahedral	$[Ga_2Cl_6]^{2-}$, $[In_2Cl_6]^{2-}$
+3	3	Planar	$In[Co(CO)_4]_3$, $Al(mesityl)_3$
	4	Tetrahedral	$[AlCl_4]^-$, $[GaH_4]^-$, $Al_2(CH_3)_6$, Ga_2Cl_6
	5	*tbp*	$AlCl_3(NMe_3)_2$, $[In(NCS)_5]^{2-}$ $Me_2GaCl(phen)$, $InCl_3(PPh_3)_2$
		sp	$[InCl_5]^{2-}$, EtAl (sal$_2$en) *p*-tolylTl$(S_2CNEt_2)_2$[b]
	6	Octahedral	$[Al(H_2O)_6]^{3+}$, $Ga(acac)_3$, $[AlF_6]^{3-}$, $[GaCl_2(phen)_2]^+$

[a] Coordination numbers for aluminum can be determined by ^{27}Al nmr spectra in solution or in solid state [magic-angle spinning (MAS)], see, for example, D. Müller *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 1277; L. B. Alemany and G. W. Kirker, *J. Am. Chem. Soc.*, 1986, **108**, 6158; A. R. Barron and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, **1986**, 287.

[b] C. L. Burschka, *Z. Anorg. Allg. Chem.*, 1982, **485**, 217.

give tetrahedral species; the acceptor ability generally decreases in the order $Al > Ga > In$, with the position of Tl uncertain. There are, however, notable distinctions from boron. These are in part due to the reduced ability to form multiple bonds and to the ability of the heavier elements to have coordination numbers exceeding four. Thus although boron gives $Me_2\overset{-}{B}{=}\overset{+}{N}Me_2$, Al, Ga, and In give dimeric species, for example, $[Me_2AlNMe_2]_2$, in which there is an NMe_2 bridging group and both the metal and nitrogen atoms are four-coordinate. Similarly, the boron halides are all monomeric, whereas those of Al, Ga, and In are all dimeric. The polymerization of trivalent Al, Ga, In, and Tl compounds to achieve coordination saturation is general, and four-membered rings appear to be a common way despite the valence angle strain implied. Second, compounds such as $(Me_3N)_2AlH_3$ have trigonal bipyramidal (*tbp*) structures, which of course are impossible for boron adducts.

The stereochemistries and oxidation states of Group IIIA(13) are summarized in Table 7-2.

THE ELEMENTS

7-2. Occurrence[1], Isolation, and Properties

Aluminum, the commonest metallic element in the earth's crust (8.8 mass %) occurs widely in Nature in silicates such as micas and feldspars, as the hydroxo oxide (*bauxite*), and as *cryolite* (Na_3AlF_6). The other elements are found only in trace quantities. Gallium and indium occur in aluminum and zinc ores, for example, in bauxite, but the richest sources contain <1% of Ga and still less In. Thallium is widely distributed and is usually recovered from flue dusts from the roasting of pyrites.

Aluminum is prepared on a vast scale. Bauxite is purified by dissolution in sodium hydroxide and reprecipitation using carbon dioxide. It is then dissolved in cryolite at 800 to 1000°C and the melt is electrolyzed. Aluminum is a hard, strong, white metal. Although highly electropositive, it is resistant to corrosion because a hard, tough film of oxide is formed on the surface. Thick oxide films, some with the proper porosity when fresh to trap particles of pigment, are often electrolytically applied to Al. Aluminum is soluble in dilute mineral acids, but is passivated by concentrated nitric acid. If the protective effect of the oxide film is overcome, for example, by scratching or by amalgamation, rapid attack even by water can occur. The metal is attacked under ordinary conditions by hot alkali hydroxides, halogens, and various nonmetals. Highly purified Al is quite resistant to acids and is best attacked by hydrochloric acid either containing a little $CuCl_2$, or in contact with Pt, some H_2O_2 also being added during the dissolution.

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[1] J. Haupin, *J. Chem. Educ.*, 1983, **60**, 279.

Gallium, indium, and *thallium* are usually obtained by electrolysis of aqueous solutions of their salts; for Ga and In this possibility arises because of large over voltages for hydrogen evolution on these metals. They are soft, white, comparatively reactive metals, dissolving readily in acids; however, thallium dissolves only slowly in sulfuric or hydrochloric acid, since the Tl^I salts formed are only sparingly soluble. Gallium, like Al, is soluble in sodium hydroxide. The elements react rapidly at room temperature, or on warming, with the halogens and nonmetals such as sulfur.

The exceptionally low melting point of Ga has no simple explanation. Since its boiling point (2070°C) is not abnormal, Ga has the longest liquid range of any known substance and finds use as a thermometer liquid.

CHEMISTRY OF THE TRIVALENT STATE

BINARY COMPOUNDS

7-3. Oxygen Compounds

Stoichiometrically there is only one oxide of aluminum, namely, *alumina* (Al_2O_3). This simplicity, however, is compensated by the occurrence of various polymorphs, hydrated species, and so on, the formation of which depends on the conditions of preparation. There are two forms of anhydrous Al_2O_3, namely, α-Al_2O_3 and γ-Al_2O_3. Other trivalent metals (Ga, Fe) form oxides that crystallize in the same two structures. In α-Al_2O_3 the oxide ions form a hexagonal close-packed array and the aluminum ions are distributed symmetrically among the octahedral interstices. The γ-Al_2O_3 structure is sometimes regarded as a "defect" spinel structure, that is, as having the structure of spinel with a deficit of cations (see below).

Alpha-Al_2O_3 is stable at high temperatures and also indefinitely metastable at low temperatures. It occurs in Nature as *corundum* and may be prepared by heating γ-Al_2O_3 or any hydrous oxide above 1000°C. Gamma-Al_2O_3 is obtained by dehydration of hydrous oxides at low temperatures (~450°C). Alpha-Al_2O_3 is very hard and resistant to hydration and attack by acids, whereas γ-Al_2O_3 readily takes up water and dissolves in acids. The Al_2O_3 that is formed on the surface of the metal has still another structure, namely, a defect rock salt structure; there is an arrangement of Al and O ions in the rock salt ordering with every third Al ion missing.

There are several important hydrated forms of alumina corresponding to the stoichiometries $AlO \cdot OH$ and $Al(OH)_3$. Addition of ammonia to a boiling solution of an aluminum salt produces a form of $AlO \cdot OH$ known as *boehmite,* which may be prepared in other ways also. A second form of $AlO \cdot OH$ occurs in Nature as the mineral *diaspore.* The true hydroxide $Al(OH)_3$ is obtained as a crystalline white precipitate when carbon dioxide is passed into alkaline "aluminate" solutions. It occurs in Nature as *gibbsite.* Materials sometimes referred to as β-aluminas have other ions such as Na^+ and Mg^{2+} present and a typical composition is $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$; these can act as ion exchangers, have high electrical conductivity, and are potential solid state electrolytes for batteries.[2]

Aluminas used in chromatography or as catalyst supports are prepared by heating hydrated oxide to various temperatures so that the surfaces may be partially or wholly dehydrated. The activity of the alumina depends critically on the treatment, subsequent exposure to moist air, and other factors.

The *gallium oxide* system is a similar system, affording a high-temperature α- and a low-temperature γ-Ga_2O_3. The trioxide is formed by heating the nitrate, the sulfate, or the hydrous oxides that are precipitated from Ga^{III} solutions by the action of ammonia. Beta-Ga_2O_3 contains both tetrahedrally and octahedrally coordinated gallium with Ga—O distances of 1.83 and 2.00 Å, respectively. The hydrous oxides GaOOH and $Ga(OH)_3$ are similar to their Al analogues.

Indium gives yellow In_2O_3, which is known in only one form, and a hydrated oxide $In(OH)_3$. *Thallium* has only the brown-black Tl_2O_3, which begins to lose oxygen at about 100°C to give Tl_2O. The action of NaOH on Tl^{III} salts gives what appears to be the oxide, whereas with Al, Ga, and In the initial products are basic salts.

Aluminum, gallium, and thallium form mixed oxides with other metals. First, there are aluminum oxides containing only traces of other metal ions. These include ruby (Cr^{3+}) and blue sapphire (Fe^{2+}, Fe^{3+}, and Ti^{4+}). Synthetic ruby, blue sapphire, and gem-quality corundum are now produced synthetically in large quantities. Second, there are mixed oxides containing macroscopic proportions of other elements, such as *spinel* ($MgAl_2O_4$) and *crysoberyl* ($BeAl_2O_4$). The spinel structure has been described and its importance as a prototype for many other $M^{II}M_2^{III}O_4$ compounds noted (Section 1-2).

Alkali metal compounds can be made by heating Al_2O_3 or Ga_2O_3 with sodium oxide at 1000°C; some have ionic lattices with anions composed of AlO_4 tetrahedra sharing corners. Examples are $Na_{14}Al_4O_{13}$ in which four tetrahedra share edges, $Na_{17}Al_5O_{16}$ that has chains, while $K_6Ga_2O_6$ has two GaO_4 sharing corners.[3]

It may also be noted that $AlPO_4$ and $GaPO_4$, made by heating the oxide with H_3PO_4, form frameworks similar to zeolites (Section 9-7) and are synthesized using amines as templates as in zeolite synthesis.[4] They are made up of tetrahedral AlO_4 and PO_4 units. Like zeolites they are active in catalytic

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[2] D. F. Shriver and G. C. Farringdon, *Chem. Eng. News,* 1985, May 20, p. 42 and references quoted; J. D. Barrie *et al., Solid State Ionics* 1986, **18–19**, 677.

[3] R. Hoppe *et al., Z. Anorg. Allg. Chem.,* 1983, **507**, 155; M. G. Barker *et al., J. Chem. Soc. Dalton Trans.,* **1984,** 1139.

[4] R. Kniep, *Angew. Chem. Int. Ed. Engl.,* 1986, **25**, 525; J. P. Parise, *Inorg. Chem.,* 1985, **24,** 4312, *J. Chem. Soc. Chem. Commun.,* **1985,** 606; N. J. Japp, *J. Chem Soc. Chem. Commun.,* **1985,** 1801; E. M. Flanigen *et al., Stud. Surf. Sci. Catal.,* 1986, **28,** 103.

reactions such as methanol conversion to hydrocarbons. Hydrated species like $[PrNH_3]^+[Ga_4(PO_4)_4OH]^-$ also are found.

7-4. Halides

All four halides of each element are known, with one exception. The compound TlI_3, obtained by adding iodine to thallous iodide, is not thallium(III) iodide, but rather thallium(I) triiodide $[Tl^I(I_3)]$. This situation may be compared with the nonexistence of iodides of other oxidizing cations such as Cu^{2+} and Fe^{3+}, except that here a lower-valent compound fortuitously has the same stoichiometry as the higher-valent one.

Although the $AlBr_3$ mass spectra show the ions $[AlBr_3]_n^+$, $n = 2, 4, 6$ in the gas phase,[5] monomers at high temperatures are probably planar like BX_3. Planarity has been confirmed in matrix isolation studies, though in an N_2 atmosphere a pyramidal species $N_2 \cdot AlCl_3$ was postulated.

The coordination numbers found in the crystalline halides are shown in Table 7-3. The fluorides of Al, Ga, and In are all high melting [1290, 950 (subl.), 1170°C, respectively], whereas the chlorides, bromides, and iodides have lower melting points. There is, in general, a good correlation between melting points and coordination number. Thus the three chlorides have the following melting points: $AlCl_3$, 193°C (at 1700 mm); $GaCl_3$, 78°C; $InCl_3$, 586°C.

The halides with coordination number 4 can be considered to consist of discrete dinuclear molecules (Fig. 7-1), and since there are no strong lattice forces, the melting points are low. In the vapor, aluminum chloride is also dimeric, so that there is a radical change of coordination number on vaporization, and these covalent structures persist in the vapor phase at temperatures not too far above the boiling points.

The halides dissolve readily in many nonpolar solvents such as benzene,

TABLE 7-3
Coordination Numbers of Metal Atoms in Group IIIA(13) Halides

	F	Cl	Br	I
Al	6	6	4	4[a]
Ga	6	4	4	4
In	6	6	6	4[b]
Tl	6	6	4	

[a] Chain structure with I bridges, $[I_2Al(\mu\text{-}I)_2]_n$, R. Kniep *et al., Angew. Chem. Int. Ed. Engl.*, 1982, **21**, 386.

[b] Yellow In_2I_6 gives red α form on storage; $AlBr_3$ is also dimorphic, R. Kniep and P. Blees, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 779. Indium tribromide and triiodide are dimeric but $InCl_3$ is monomeric in the gas phase. G. M. Bancroft, *et al., Inorg Chem.*, 1986 **25**, 2181.

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[5] T. P. Martin and J. Diefenbach, *J. Am. Chem. Soc.*, 1984, **106**, 623.

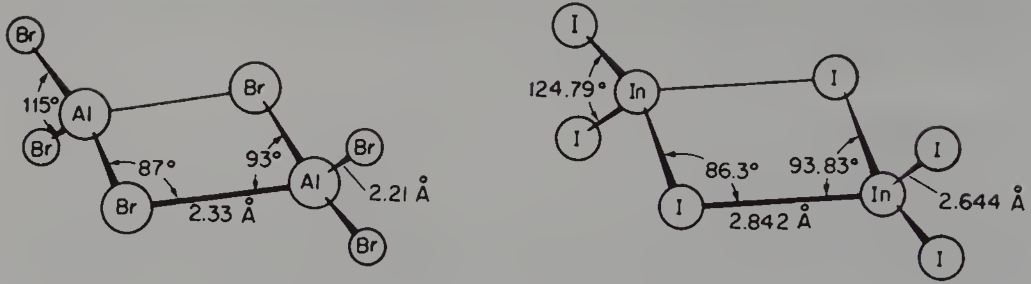

FIG. 7-1. The structures of Al_2Br_6 and In_2I_6.

in which they are dimeric. The enthalpies of dissociation, $Al_2X_6(g) = 2AlX_3(g)$ have been measured and are 46 to 63 kJ mol^{-1}. As Fig. 7-1 shows, the configuration of halogen atoms about each metal atom is far from exactly tetrahedral. The formation of such dimers is attributable to the tendency of the metal atoms to complete their octets. The dimers may be split by reaction with donor molecules, giving complexes such as R_3NAlCl_3. The halides dissolve in water, giving acidic solutions from which hydrates may be obtained. In acetonitrile dissociation occurs with the formation of $[Al(MeCN)_5Cl]^+$ and $AlCl_4^-$ ions.

Aluminum chloride–sodium chloride has been much used as a molten salt medium (mp 173°C) for electrolytic and other reactions (e.g., with S_8 and with metal halides). The equilibria involved at 175 to 300°C are[6]

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$$

$$3Al_2Cl_7^- \rightleftharpoons 2Al_3Cl_{10}^- + Cl^-$$

$$2Al_3Cl_{10}^- \rightleftharpoons 3Al_2Cl_6 + 2Cl^-$$

Interaction of $AlCl_3$ with *N*-butylpyridinium chloride or 1-methyl-3-ethylimidazolium chloride gives conducting *liquids* at room temperature that are good solvents for both organic and inorganic compounds.[7] The principal equilibrium is

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$$

but $Al_3Cl_{10}^-$, and Al_2Cl_6 may also be present depending on $AlCl_3$ concentration.

The interaction of trichlorides of Al, Ga, or In with other metal chlorides such as $CaCl_2$, $CrCl_3$, or UCl_5 leads to mixed halides with halogen bridges, for example, $Cl_4Nb(\mu\text{-}Cl)_2AlCl_2$, many of which are quite volatile.[8] Thus the vapor pressure of $NdCl_3$ is increased by a factor of 10^{13} at 600°C.

Thallium(III) Halides. The chloride, which is most commonly used, can

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[6] J. H. von Barner *et al.*, *Inorg. Chem.*, 1982, **21**, 402.

[7] R. A. Osteryoung *et al.*, *Inorg. Chem.*, 1985, **24**, 716; T. B. Scheffler and C. L. Hussey, *Inorg. Chem.*, 1984, **23**, 1926; T. Matsumoto and K. Ichikawa, *J. Am. Chem. Soc.*, 1984, **106**, 4316.

[8] T. Foosnaes and H. A. Øye, *Inorg. Chem.*, 1983, **22**, 3873; A. Justnes *et al.*, *Polyhedron*, 1982, **1**, 393; B. Krebs *et al.*, *Inorg. Chem.*, 1984, **23**, 164.

be prepared by the sequence:

$$\text{Tl, or TlCl, or } Tl_2CO_3 \xrightarrow{ClNO} TlCl_3{\cdot}NOCl \xrightarrow{heat} TlCl_3$$

Solutions of $TlCl_3$ and $TlBr_3$ in CH_3CN, which are useful for preparative work, are conveniently obtained by treating solutions of the monohalides with Cl_2 or Br_2. Solid $TlCl_3$ loses chlorine at about 40°C and above, to give the monochloride, and the tribromide loses bromine at even lower temperatures to give first $TlBr_2$, which is actually $Tl^I[Tl^{III}Br_4]$. The fluoride is stable to about 500°C.

7-5. Other Binary Compounds

The elements commonly form compounds such as carbides, nitrides, phosphides, and sulfides by direct interaction of the elements.

Aluminum carbide (Al_4C_3) is formed at temperatures of 1000 to 2000°C. It reacts instantly with water to produce methane, and since there are discrete carbon atoms (C—C = 3.16 Å) in the structure, it may be considered as a "methanide" with a C^{4-} ion, but this is doubtless an oversimplification.

The *nitrides* AlN, GaN, and InN are known. Only aluminum reacts directly with nitrogen; GaN is obtained on reaction of Ga or Ga_2O_3 at 600 to 1000°C with NH_3 and InN by pyrolysis of $(NH_4)_3InF_6$. All have a wurtzite structure (Fig. 1-2). They are fairly hard and stable, as might be expected from their close structural relationship to diamond and the diamond-like BN.

Aluminum and especially Ga and In form 1:1 compounds with Group VA(15) elements, the so-called III–V compounds, such as GaAs. These compounds have semiconductor properties similar to those of elemental Si and Ge, to which they are electronically and structurally similar. They can be obtained by reactions such as

$$Me_3Ga + AsH_3 \longrightarrow GaAs + 3CH_4$$

or by interaction of phosphorus and Ga_2O vapors at 900–1000°C.

COMPLEX COMPOUNDS

7-6. The Aqua Ions; Oxo Salts, Aqueous Chemistry

The elements form a wide variety of salts including hydrated chlorides, nitrates, sulfates, and perchlorates, as well as sparingly soluble phosphates.

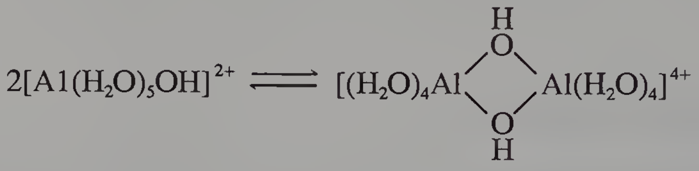
The *aqua ions,* $[M(H_2O)_6]^{3+}$, exist in both aqueous solutions and crystalline salts; $[Tl(H_2O)_6]^{3+}$ has two trans H_2O molecules that are more strongly bound than the others (cf. stability of $TlCl_2^+$ to follow). The ions are acidic,

$$[M(H_2O)_6]^{3+} \rightleftharpoons [M(H_2O)_5OH]^{2+} + H^+$$

and measured in the presence of noncomplexing anions, the constants K_A for Al, Ga, In, and Tl, respectively, are $\sim 10^{-5}$, 10^{-3}, 10^{-4}, and 10^{-1}. Salts of weak acids are extensively hydrolyzed by water. Indeed, $[Al(H_2O)_6]^{3+}$ will protonate the acetate ion:

$$[Al(H_2O)_6]^{3+} + MeCO_2^- \longrightarrow [Al(H_2O)_5OH]^{2+} + MeCO_2H$$

The $[Al(H_2O)_5OH]^{2+}$ ion has been detected in dilute solution[9a] but there is a very high constant for the dimerization[9b];



Over a wide pH range under physiological conditions[9c] in chloride solution the species appear to be $Al(OH)^{2+}$, $Al(OH)_3$, $Al(OH)_4^-$, $Al_3(OH)_{11}^{2-}$, $[Al_6(OH)_{15}]^{3+}$ and $[Al_8(OH)_{22}]^{2+}$.

The hydrolyzed species depend markedly on the exact conditions. Addition of Na_2CO_3 gives further condensation of the dimer to $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$,[10] whereas dissolving Al in aqueous $AlCl_3$ solution gives little of this Al_{13}^{7+} ion. Interaction of Na_4GeO_4 with aqueous $AlCl_3$ gives a similar ion $[GeO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{8+}$.[11]

The dimer has been characterized in several crystalline salts as has the Al_{13}^{7+} ion in $Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SO_4)_4 \cdot 13H_2O$.

Study of the substitution[12a] of the aluminum aqua ion by ligands such as SO_4^{2-}, citrate, and EDTA in dilute solutions, using ^{27}Al nmr spectroscopy, has been stimulated by the recognition of (*a*) the key role of Al^{3+} in acid lakes due to leaching from silicates by acid rain, (*b*) the toxicity of Al to aquatic life and the increased concentration of aluminosilicates in human brains in senile dementia (Alzheimer's disease);[12b,c] the latter is a consequence of the disease whose origin is a defective gene. An aluminum hydroxypyranone chelate is water soluble and very neurotoxic compared to other Al species.[12c]

Nuclear magnetic resonance spectra of ^{27}Al, both in solution and in the solid state,[13] allows determination of stereochemistry and coordination num-

[9a] J. W. Akitt and J. M. Elders, *J. Chem. Soc. Farady Trans. 1*, **1985**, 1923; *Bull. Soc. Chim. Fr.*, **1986**, 10.

[9b] J. W. Akitt *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 981.

[9c] M. Venturini and G. Berthou, *J. Chem. Soc. Dalton Trans.*, **1987**, 1145.

[10] See R. Bertram *et al.*, *Z. Anorg. Allg. Chem.*, 1985, **525**, 14; J. W. Akitt *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 1047.

[11] S. Schoenherr and H. Goerz, *Z. Anorg. Allg. Chem.*, 1983, **503**, 37.

[12a] G. L. Eichhorn *et al.*, *Inorg. Chem.*, 1983, **22**, 525; L-O. Öhman and S. Sjonberg, *J. Chem. Soc. Dalton Trans.*, **1983**, 2513.

[12b] *Chem. Br.*, 1987, April, p. 307; T. J. Crow, *Nature (London)*, 1986, **331**, 481.

[12c] C. Orvig, *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 4121; *Inorg. Chem.*, 1987, **26**, 2171.

[13] L. S. Glasser *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 23; J. J. Dechter *et al.*, *Inorg. Chem.*, 1985, **24**, 883.

ber since the absorption regions are characteristic for four, five, or six coordination numbers. For example, the Al_{13}^{7+} ion noted above has four-coordinate Al as have the aluminates (to be discussed).

Alcohol solvated ions such as $[Al(MeOH)_6]^{3+}$ and $[AlCl_2(MeOH)_4]^+$ as well as acetone and acetonitrile species are also established.[14]

Indium and Tl aqua ions readily form complexes with Cl^-, SO_4^{2-} and other anions and species such as $In(OH)(aq)^{2+}$ and $In(OH)_2^+$ are known.[15]

Alums, $M^IAl(SO_4)_2 \cdot 12H_2O$, where M^+ is almost any ion except Li^+, which is too small to be accommodated without loss in stability of the structure, give their name to a large number of analogous salts of +3 ions including those of Ti, V, Cr, Mn, Fe, Co, Ir, Ga, and In. There are three cubic structures consisting of $[M(H_2O)_6]^+$, $[M(H_2O)_6]^{3+}$, and two SO_4^{2-} ions, differing slightly in detail depending on the size of M^+.

Aluminates and Gallates. The hydroxides are amphoteric:

$$Al(OH)_3(s) = Al^{3+} + 3OH^- \qquad K \approx 5 \times 10^{-33}$$

$$Al(OH)_3(s) = AlO_2^- + H^+ + H_2O \qquad K \approx 4 \times 10^{-13}$$

$$Ga(OH)_3(s) = Ga^{3+} + 3OH^- \qquad K \approx 5 \times 10^{-37}$$

$$Ga(OH)_3(s) = GaO_2^- + H^+ + H_2O \qquad K \approx 10^{-15}$$

The oxides and the metals also dissolve in alkali bases as well as in acids. The oxides and hydroxides of In and Tl are, by contrast, basic; hydrated Tl_2O_3 is precipitated from solution even at pH 1 to 2.5. The nature of the aluminate and gallate solutions has been much studied by Raman and nmr spectra. The principal species in solution for Al is $[Al(OH)_4]^-$; only where Na^+ is the cation is there evidence for species in solution that may be related to solids that crystallize from aluminate solutions.[16] The latter contain dimeric anions with four-coordinate Al, $[(HO)_3AlOAl(OH)_3]^{2-}$, and others with octahedral Al^{3+}.

7-7. Halide Complexes and Adducts[17a]

Fluorides. The hydrated fluorides $AlF_3 \cdot nH_2O$ (n = 3 or 9) can be obtained by dissolving Al in aqueous HF. The nonahydrate is very soluble in water, and ^{19}F nmr spectra show the presence of $(H_2O)_3AlF_3$ as well as the ions AlF_4^-, $AlF_2(H_2O)_4^+$, and $AlF(H_2O)_5^{2+}$. At high fluoride concentrations and in crystalline solids the AlF_6^{3-} ion is also formed. The gallium system is similar.

The most important fluoro salt is *cryolite,* whose structure (Fig. 7-2) is adopted by many other salts containing small cations and large octahedral

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[14] J. W. Akitt *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 2639; Y. A. Buslaev and S. P. Petro-Synants, *Polyhedron,* 1984, **3,** 265.

[15] R. N. Sylva *et al., J. Chem. Soc. Dalton Trans.,* **1982,** 1911; K. Wieghardt *et al., Inorg. Chem.,* 1986, **25,** 1654.

[16] J. W. Akitt and W. Gessner, *J. Chem. Soc. Dalton Trans.,* **1984,** 147.

[17a] M. Dalibaut and J. Derouault, *Coord. Chem. Rev.* 1986, **74,** 1.

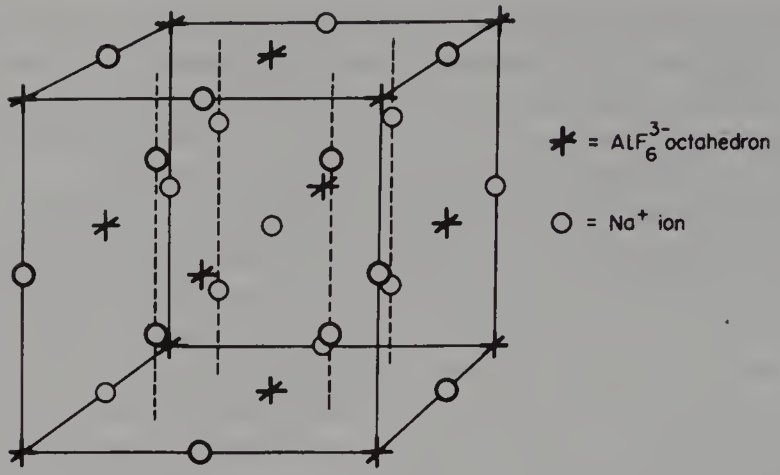


FIG. 7-2. The cubic structure of cryolite, Na_3AlF_6.

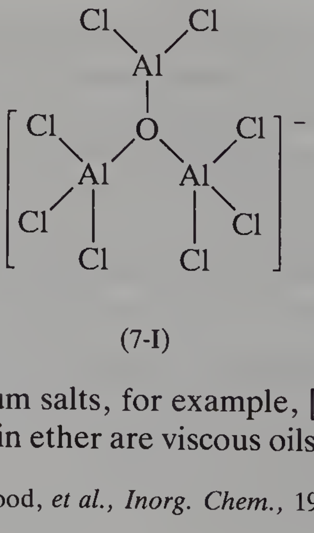
anions and, in its anti form, by many salts of the same type as $[Co(NH_3)_6]I_3$. It is closely related to the structures adopted by many compounds of the types $M_2^+[AB_6]^{2-}$ and $[XY_6]^{2+}Z_2^-$. The last two structures are essentially the fluorite (or antifluorite) structures (see Fig. 1-2) except that the anions (or cations) are octahedra whose axes are oriented parallel to the cube edges.

Chlorides. Aluminum and gallium form only the tetrahedral ions MCl_4^-. Crystalline salts can be obtained, for example, by action of Et_4NCl on M_2Cl_6 in an organic solvent. In THF^{17b}, aluminum forms $[AlCl_2(THF)_4]AlCl_4$.

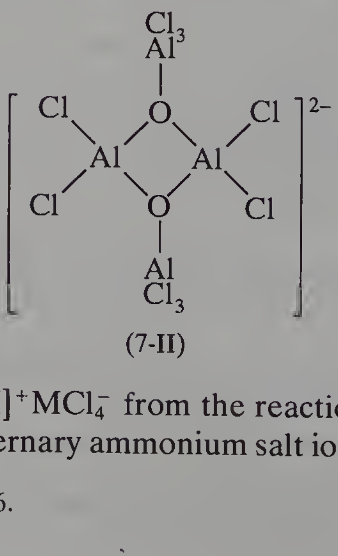
The tetrahaloaluminates are hydrolyzed by water, but gallium can be extracted from 8 *M* HCl solutions into ethers, where the ether phase contains $GaCl_4^-$ ions, so that at some point there is a change in coordination number:

$$[Ga(H_2O)_6]^{3+} \xrightleftharpoons{HCl} [GaCl_n(H_2O)_m]^{3-n} \xrightleftharpoons{HCl} [GaCl_4]^-$$

There are oxohalide ions $[Al_3(\mu_3\text{-}O)Cl_8]^-$ and $[Al_4O_2Cl_{10}]^{2-}$ with the structures (7-I) and (7-II).



(7-I)



(7-II)

Oxonium salts, for example, $[(Et_2O)_nH]^+MCl_4^-$ from the reaction of MCl_3 with HCl in ether are viscous oils (cf. quaternary ammonium salt ionic liquids,

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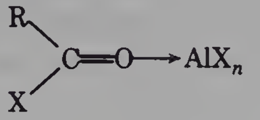
[17b] J. L. Atwood, *et al.*, *Inorg. Chem.*, 1987, **26**, 1466.

(Section 7-4). The formation of $AlCl_4^-$ and $AlBr_4^-$ ions is essential to the functioning of Al_2Cl_6 and Al_2Br_6 as Friedel–Crafts catalysts, since in this way the necessary carbonium ions are simultaneously formed. The spectra and structures of intermediates in the Friedel–Crafts reaction have been studied. There are two types, one molecular (7-III) the other ionic (7-IV) depending on the solvent. In CH_2Cl_2 only (7-III) is formed.



(7-III)

$$[R\text{—}C\text{—}O]^+[AlX_{n+1}]^-$$

(7-IV)

The oxocarbenium ion can then react further, for example,

$$RCO^+ + C_6H_6 \longrightarrow [RCOC_6H_6]^+ \longrightarrow RCOC_6H_5 + H^+$$

In addition to MCl_4^- there are 5 or 6 coordinate species,[18] $InCl_5^{2-}$, InF_6^{3-}, $TlCl_5^{2-}$, and $TlCl_6^{3-}$. Similar pseudohalide complexes, for example, $In(NCS)_5^{2-}$ and $In(NCS)_6^{3-}$ may also be obtained, depending on the size of the cation.

For TlI_4^-, the stability of iodide in contact with Tl^{III} is a result of the stability of the ion, since TlI_3 is itself unstable relative to $Tl^I(I_3)$. Thallium alone forms the ion $Tl_2Cl_9^{3-}$, which has the confacial bioctahedron structure.

Cationic Complexes. Apart from the aqua ions and partially substituted species such as $[GaCl(H_2O)_5]^{2+}$ noted previously, complexes with pyridine, bipyridine, or phenanthroline are known, for example, $[GaCl_2(phen)_2]$ and $[Ga(phen)_3]$. For thallium(III) complexes the best route appears to be oxidation of thallium(I) halide in acetonitrile solution by halogen, followed by addition of ligands to get complex ions.

Neutral Adducts. The trihalides (except the fluorides), and other R_3M compounds such as the trialkyls, triaryls, mixed R_2MX compounds and AlH_3, all function as Lewis acids, forming 1:1 adducts with a great variety of Lewis bases. This is one of the most important aspects of the chemistry of the Group IIIA(13) elements. The Lewis acidity of the AlX_3 groups (where X = Cl, CH_3, etc.) has been extensively studied thermodynamically, and basicity sequences for a variety of donors have been established.

As already indicated, the MX_3 molecules (X = halide) react with themselves to form dimeric molecules in which each metal atom has distorted tetrahedral coordination. Even in mixed organo halo compounds such as $(CH_3)_2AlCl$, this type of dimerization with *halogen atom bridges* occurs.

There are both four- and five-coordinate species. In the *tbp* complexes such as $MX_3(NMe_3)_2$ or $InCl_3(PPh_3)_2$ the halogen atoms are usually equatorial.

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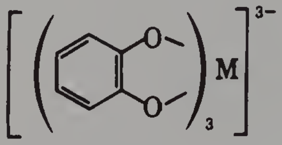
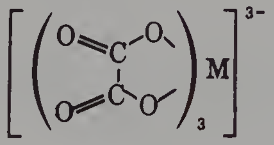
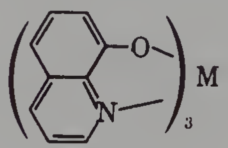
[18] J. Glaser *et al., Acta Chem. Scand.*, 1982, **36A,** 55, 125, 451.

7-8. Chelate and Other Complexes

The most important octahedral complexes of the Group IIIA(13) elements are those containing chelate rings. Typical are those of β-diketones, pyrocatechol (7-V), dicarboxylic acids (7-VI), and 8-quinolinol (7-VII). The neutral complexes dissolve readily in organic solvents, but are insoluble in water. The acetylacetonates have low melting points (<200°C) and vaporize without decomposition. The anionic complexes are isolated as the salts of large univalent cations. The 8-quinolinolates are used for analytical purposes. Tropone (T) gives an eight-coordinate anion of indium in $Na[InT_4]$.


(7-V)


(7-VI)


(7-VII)

Aluminum β-diketonates have been much studied by nmr methods because of their stereochemical nonrigidity (Chapter 29). The *carboxylates* of indium and thallium are obtained by dissolving the oxides in acid. Acetate and trifluoroacetate salts are used extensively as reagents in organic synthesis.[19] Certain other thallium compounds have been used also. The trifluoroacetate will directly "thallate" aromatic compounds to give aryl thallium di(trifluoroacetate), for example, $C_6H_5Tl(CO_2CF_3)_2$ (cf. aromatic mercuration, Section 16-18 and oxidize arenes to biaryls.

Sulfur complexes of Al, Ga, and In are uncommon, but the *trisdithiocarbamates*, $M(dtc)_3$, and thiolato anions, $Ga(SR)_4^-$, are known.

The gallium and In compounds differ structurally from most other trisdithiocarbamates in their close approach to a prismatic arrangement of S atoms.

Alkoxides. These are all polymeric even in solution in inert solvents. Only those of aluminum, particularly the isopropoxide, which is widely used in organic chemistry as a reducing agent for aldehydes and ketones, are of importance. They can be made by the reactions

$$Al + 3ROH \xrightarrow[\text{catalyst, warm}]{1\%\ HgCl_2\ \text{as}} (RO)_3Al + \tfrac{3}{2}H_2$$

$$AlCl_3 + 3RONa \longrightarrow (RO)_3Al + 3NaCl$$

The alkoxides hydrolyze vigorously in water. The *tert*-butoxide is a cyclic dimer (7-VIII) in solvents, whereas the isopropoxide is tetrameric (7-IX) at ordinary temperature according to ^1H, ^{13}C, and ^{27}Al nmr spectra, but trimeric at elevated temperatures. Terminal and bridging alkoxo groups can be distinguished by nmr spectra. Other alkoxides can exist also as dimers and

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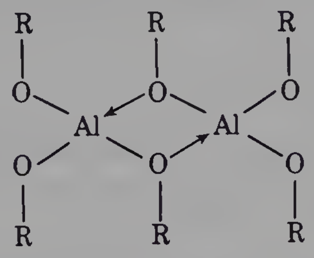
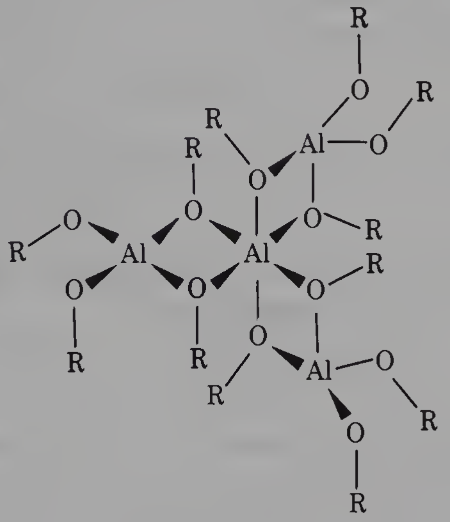
[19] S. Uemura, *Synthetic Reagents,* Vol. 5, J. S. Pizey, Ed., Wiley, New York, 1983; A. McKillop, *Comprehensive Organometallic Chemistry,* Vol. 7, Chapter 47, Pergamon Press, Oxford, 1982.

trimers. Mixed alkoxides, for example, $(MeOAlH_2)_n$ and $[MeOAlMe_2]_2$, are also known.



(7-VIII)



(7-IX)

Nitrato Complexes. Gallium and thallium form *nitrato* complexes by the reaction of N_2O_5 with $NO_2^+[GaCl_4]^-$ or $TlNO_3$, respectively. The gallium ion in $NO_2^+[Ga(NO_3)_4]^-$ appears to have unidentate NO_3 groups, by contrast with $[Fe(NO_3)_4]^-$, which has bidentate groups and is eight-coordinate, although the radius of Ga^{III} (0.62 Å) is only slightly smaller than that of Fe^{III} (0.64 Å)

7-9. Hydrides and Complex Hydrides

Aluminum hydride is obtained by interaction of $LiAlH_4$ with 100% H_2SO_4 in THF:

$$2LiAlH_4 + H_2SO_4 = 2AlH_3 + 2H_2 + Li_2SO_4$$

In the interaction of $LiAlH_4$ with $AlCl_3$, intermediates like $AlHCl_2$ are formed.

The white hydride is thermally unstable. It has a three-dimensional lattice isostructural with AlF_3. It is a useful reducing agent in organic chemistry, and the products formed are significantly different from those of reduction by $LiAlH_4$. There is little evidence for hydrides of In and Tl and $(GaH_3)_n$ is questionable, though a few hydride species such as $Me_2Ga(\mu\text{-}H)_2GaMe_2$, $(HGaCl_2)_2$, $GaH\textit{i}\text{-}Bu_2$[20a] and an organoindium species with bulky $C(SiMe_3)_3$ groups are known.[20b]

There is an extensive range of complex hydrides that can be regarded as

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[20a] P. L. Baxter *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 805.

[20b] C. Eaborn *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 988.

arising from Lewis acid behavior of MH_3. Thus adducts can be readily formed with donor molecules such as NR_3 and PR_3, or with H^- and other anions.

Hydride Anions. Both Al and Ga hydride anions are obtained by the reaction

$$4LiH + MCl_3 \xrightarrow{Et_2O} LiMH_4 + 3LiCl$$

However, for AlH_4^- the sodium salt can be obtained by direct interaction:

$$Na + Al + 2H_2 \xrightarrow[150°/2000\ psi/24h]{THF} NaAlH_4$$

The salt is obtained by precipitation with toluene and can be efficiently converted into the lithium salt:

$$NaAlH_4 + LiCl \xrightarrow{Et_2O} NaCl(s) + LiAlH_4$$

The most important compound is *lithium aluminum hydride,* a nonvolatile crystalline solid, stable below 120°C, that is explosively hydrolyzed by water. In the crystal there are tetrahedral AlH_4^- ions with an average Al—H distance of 1.55 Å. The Li^+ ions each have four near hydrogen neighbors (1.88–2.00 Å) and a fifth that is more remote (2.16 Å).

Lithium aluminum hydride is soluble in diethyl and other ethers and can be solubilized in benzene by crown ethers.[21a] In ethers, the Li^+, Na^+, and R_4N^+ salts of AlH_4^- and GaH_4^- tend to form three types of species depending on the concentration and on the solvent, namely, either loosely or tightly bound aggregates or ion pairs. Thus $LiAlH_4$ is extensively associated in diethyl ether, but at low concentrations in THF there are ion pairs. Nuclear magnetic resonance studies suggest that not only for AlH_4^- but also for ClO_4^- and I^- there is a solvated ion $Li(THF)_4^+$ since all three salts have an infrared band at 420 cm^{-1} associated with Li^+ in the solvent cage. Sodium aluminum hydride ($NaAlH_4$) is insoluble in diethyl ether.

Some reactions of $LiAlH_4$ are given in Fig. 7-3. Lithium aluminum hydride accomplishes many otherwise tedious and difficult reductions in organic chemistry as well as being a useful inorganic reductant. There may be differences in rates of reaction of different salts (e.g., Li^+ and Na^+), due not only to differences in the species in solution but to involvement of Li^+ in the reaction.

Related hydrido anions that are selective reducing agents are the benzene soluble "Red-Al", $Na[AlH(OMe)_2OEt]$, "Vitride"[21b] $Na[AlH_2(OCH_2CH_2OMe)_2]$, and $Li[AlH(Ot\text{-}Bu)_3]$.

Lithium and Na^+ salts of AlH_6^{3-} are best made by direct interaction of the metals under H_2 pressure, but can be made by the reaction

$$2NaH + NaAlH_4 \longrightarrow Na_3AlH_6$$

[21a] V. Gevorgyan and E. Lukevics, *J. Chem. Soc. Chem. Commun.*, **1985,** 1235.

[21b] O. Štrouf and B. Čásenský, *Sodium Dihydrido bis(2-methoxyethoxy)aluminate,* Elsevier, Amsterdam, 1985.

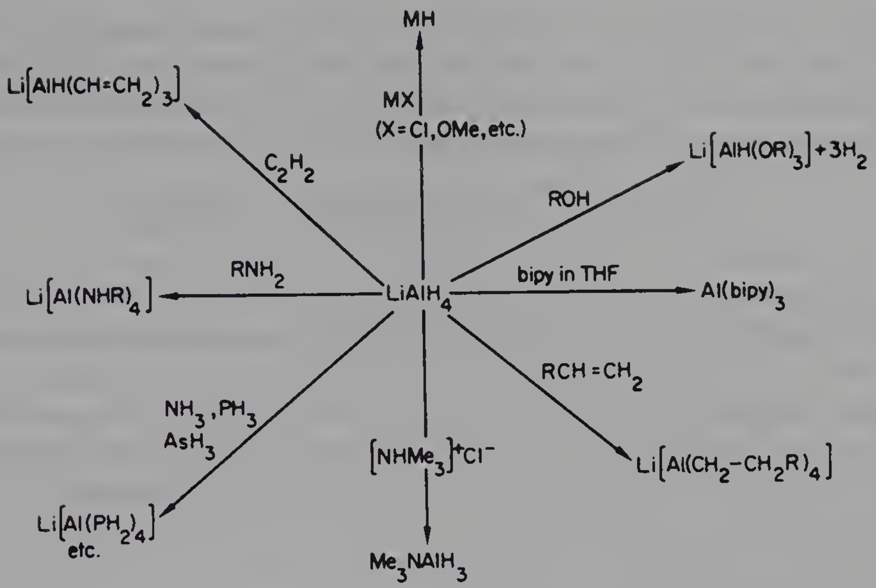

FIG. 7-3. Some reactions of lithium aluminum hydride.

Lithium gallium hydride decomposes slowly even at 25°C to give LiH, Ga, and H_2. Comparing the MH_4^- ions of B, Al, and Ga, the thermal and chemical stabilities vary according to the ability of MH_3 to act as an acceptor for H^-. The order, and also the M—H force constants of MH_4^-, are in the order $B > Al \gg Ga$.

Donor Adducts. These are similar to borane adducts, the stability order being $B > Al > Ga$ and also similar to adducts of the halides and alkyls, where the stability order is halides > alkyls > hydrides. The most studied adducts are the trialkylamine alanes (alane = AlH_3). Trimethylamine gives both 1:1 and 2:1 adducts, but the latter are stable only in the presence of an excess of amine:

$$Me_3NAlCl_3 + 3LiH \xrightarrow{Et_2O} Me_3NAlH_3 + 3LiCl$$

$$Me_3HN^+Cl^- + LiAlH_4 \xrightarrow[-60°C]{Et_2O} Me_3NAlH_3 + LiCl + H_2$$

$$3LiAlH_4 + AlCl_3 + 4NMe_3 \longrightarrow 4Me_3NAlH_3 + 3LiCl$$

$$Me_3NAlH_3 + Me_3N \rightleftharpoons (Me_3N)_2AlH_3$$

The monoamine is a white, volatile, crystalline solid (mp 75°C), readily hydrolyzed by water, which slowly decomposes to $(AlH_3)_n$. It is monomeric and tetrahedral. The bisamine is *tbp* with axial N atoms. Tetrahydrofuran also gives 1:1 and 2:1 adducts, but diethyl ether, presumably for steric reasons gives only the 1:1 compound, though a mixed THF–Et_2O adduct exists.

There are similar monoamine gallanes[22] where the Ga—H stretch at

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[22] A. J. Downs *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984,** 1755.

$\sim$1850 cm^{-1}, compared to $\sim$1790 cm^{-1} for the alane, suggests a stronger M—H bond, and indeed the gallanes are less sensitive to hydrolysis. The $(Me_3N)_2GaH_3$ compound is unstable above −60°C. Preparation of the gallanes illustrates a useful principle regarding the use of a weak donor as solvent:

$$\underset{\text{strong–weak}}{Me_3NGaH_3} + \underset{\text{strong}}{BF_3} \xrightarrow[\text{weak}]{Me_2S} \underset{\text{weak–weak}}{Me_2SGaH_3} + \underset{\text{strong–strong}}{Me_3NBF_3}$$

Because the weak–weak, strong–strong combination is favored over two weak–strong adducts, the net effect is to displace the strong donor Me_3N by the weaker one Me_2S.

Other Complexes. The AlH_4^- ion forms an extensive range of complexes with transition metals that are discussed in Section 24-10. The borohydrides $Al(BH_4)_3$, bp 44°C and $Me_2Al(BH_4)$ have $Al(\mu\text{-}H)_2BH_2$ bridges.

7-10. Organoaluminum Compounds[23]

Organoaluminum compounds may be made by the reaction:

$$2Al + 3R_2Hg \longrightarrow 2R_3Al(\text{or } [R_3Al]_2) + 3Hg$$

or by reaction of Grignard reagents with $AlCl_3$:

$$RMgCl + AlCl_3 \longrightarrow RAlCl_2, R_2AlCl, R_3Al$$

The lower alkyls are spontaneously flammable and extremely reactive liquids and all organoaluminums are sensitive to air and to water, alcohols, halocarbons and other compounds.

Direct methods for large-scale synthesis stemmed from studies by K. Ziegler that showed that aluminum hydride or $LiAlH_4$ reacts with olefins to give alkyls or alkyl anions—a reaction specific for B and Al hydrides:

$$AlH_3 + 3C_nH_{2n} \longrightarrow Al(C_nH_{2n+1})_3$$
$$LiAlH_4 + 4C_nH_{2n} \longrightarrow Li[Al(C_nH_{2n+1})_4]$$

Although $(AlH_3)_n$ cannot be made by direct interaction of Al and H_2, nevertheless in the presence of aluminum alkyl the following reaction to give the dialkyl hydride can occur:

$$Al + \tfrac{3}{2}H_2 + 2AlR_3 \longrightarrow 3AlR_2H$$

This hydride will then react with olefins:

$$AlR_2H + C_nH_{2n} \longrightarrow AlR_2(C_nH_{2n+1})$$

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[23] See *Comprehensive Organometallic Chemistry,* Pergamon Press, Oxford, 1982, J. J. Eisch, Vol. 1, Chapter 6, J. R. Zietz, Jr., *et al.,* Vol. 7, Chapter 46 (uses in organic synthesis). For (a) Ga and In and (b) Tl discussed only briefly here see (a) D. G. Tuck, Vol. 1, Chapter 7 and (b) H. Kurosawa, Vol. 1, Chapter 8; A. McKillop, Vol. 7, Chapter 47 (uses in organic synthesis).

The direct interaction of Al, H_2, and olefin (hydroalumination) is used to give either the dialkyl hydrides or the trialkyls.[24a]

It may be noted in connection with the direct synthesis of $NaAlH_4$ mentioned previously that, if ethylene (or other olefin) is present and $AlEt_3$ is used as catalyst, the direct interaction gives $Na[AlH_{4-n}Et_n]$.

Other technically important compounds are the *sesquichlorides* such as $Me_3Al_2Cl_3$ or $Et_3Al_2Cl_3$. These compounds can be made by direct interaction of Al or Mg—Al alloy with the alkyl chloride. This reaction fails for propyl and higher alkyls since the alkyl halides decompose in the presence of the alkyl aluminum halides to give HCl, alkenes, and so on.

The interaction of $AlCl_3$, Al, and ethylene at 100°C gives $Cl_2Al(CH_2)_2AlCl_2$ and $(Cl_2Al)_2CHMe$.[24b]

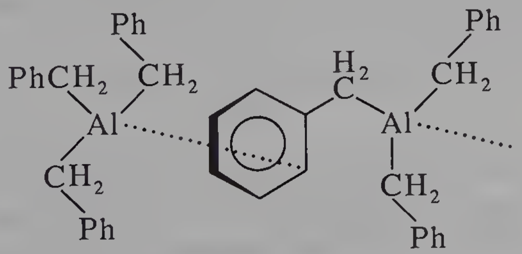
The *halides* (R_nAlCl_{3-n}) are always dimerized with Cl bridges and comparable alkoxides bridge through O, although $[Me_2Al(OCH_2OMe)]_2$ is unusual in having the ether oxygen coordinated[25] thus giving five-coordinate aluminum.

In condensed phases the lower alkyls and the aryls[26] are dimeric with the carbon atoms bridging and with *3c-2e* bonds supplemented in the aryls by additional interactions between π electrons and nonbonding metal orbitals.

For trimethylaluminum at −75°C the ^1H nmr spectrum exhibits separate resonances for the terminal and bridging methyl groups, but on warming, these begin to coalesce, and at room temperature only one sharp peak is observed. This indicates that the bridging and terminal methyl groups can exchange places across a relatively low energy barrier. The exchange process in Me_2Al_6 involves dissociation to monomer and reformation of the dimer:

$$Me_6Al_2 \rightleftharpoons 2Me_3Al$$

The extent of the dissociation for Al_2Me_6 is very small, 0.0047% at 20°C. Tribenzylaluminum is unique having a chain structure where there is interaction between Al, which has a vacant *p* orbital and a carbon atom of the phenyl ring *ortho* to the CH_2 group (7-X); trimesitylaluminum has planar three-coordinate Al both in the solid and in solution.[27]



(7-X)

[24a] U. M. Dzhemilev *et al., J. Organomet. Chem.*, 1986, **304,** 17; Y. Yamamoto *et al., J. Am. Chem. Soc.*, 1986, **108,** 6036.

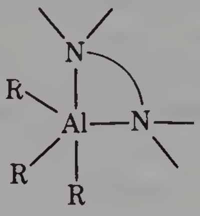
[24b] H. Martin. *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 311.

[25] R. Benn *et al., Angew. Chem. Int. Ed. Engl.*, 1983, **22,** 779.

[26] J. P. Oliver *et al., Organometallics*, 1982, **1,** 1307.

[27] J. P. Oliver *et al., Organometallics*, 1986, **5,** 1812.

The alkyls are Lewis acids, combining with donors such as amines, phosphines, ethers, and thioethers to give tetrahedral, four-coordinate species. Thus $Me_3N—AlMe_3$ in the gas phase has C_{3v} symmetry with staggered methyl groups. With tetramethylhydrazine and $(CH_3)_2NCH_2N(CH_3)_2$, five-coordinate species that appear to be of the kind shown in (7-XI) are obtained, although



(7-XI)

at room temperature exchange processes cause all methyl groups and all ethyl groups to appear equivalent in the proton nuclear resonance spectrum. With $(CH_3)_2NCH_2CH_2N(CH_3)_2$ a complex is formed that has an AlR_3 group bound to each nitrogen atom. Aluminum alkyls also combine with lithium alkyls:

$$(C_2H_5)_3Al + LiC_2H_5 \xrightarrow{\text{in benzene}} LiAl(C_2H_5)_4$$

The compound $LiAl(C_2H_5)_4$ has chains of alternating tetrahedral $Al(C_2H_5)_4^-$ and Li^+ in such a way that each lithium atom is tetrahedrally surrounded by four α-carbon atoms, close enough to indicate weak Li—C bonds.

Triethylaluminum, the sesquichloride $(C_2H_5)_3Al_2Cl_3$, and alkyl hydrides are used together with transition metal halides, alkoxides, or organometallic complexes as catalysts (e.g., Ziegler catalysts) for the polymerization of ethylene, propene, and a variety of other unsaturated compounds, as discussed in Chapter 28. They are also used widely as reducing and alkylating agents for transition metal complexes.

In alkylation of metal halides usually only *one* alkyl group is transferred, since the dialkyl aluminum halides are much less powerful alkylating agents than the trialkyls. The alkylaluminums react with compounds having acidic hydrogens to give the alkane; in some cases alkylation may occur, for example,

$$R_3COH \xrightarrow[\substack{\text{toluene} \\ 100\text{–}120°C}]{Me_3Al} R_3CMe$$

but in others, complex alkylaluminum compounds are obtained (e.g., with pyrazole, β-diketonates, phosphoric acid, or Schiff bases[28a]).

Some five-coordinate bridged compounds $R_2Al(\mu\text{-}X)_2AlR_2$, X = $OCH_2\text{-}2\text{-}C_5H_4N$ have been characterised by ^{27}Al nmr.[28b] Trimethylaluminum reacts with K_2SO_4, KNO_3, KCO_2Me, and so on, to give salts that have the oxygen of the anion bound to $AlMe_3$,[29a] examples being

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[28a] S. J. Dzugan and V. L. Goedken, *Inorg. Chem.*, 1986, **25**, 2858.

[28b] G. van Koten *et al., Organometallics,* 1985, **4,** 1701.

[29a] J. L. Atwood *et al., Organometallics,* 1985, **4,** 238.

$K_2[SO_4(AlMe_3)_4]$ and $K[NO_3(AlMe_3)_2]$. Similar reactions occur with KOPh to give $K[Me_3Al(\mu\text{-}OPh)AlMe_3]$ and, most remarkably, KO_2, which in toluene containing dibenzo-18-crown-6 gives a liquid clathrate of formula $[K\ crown][(Me_3Al)_2(\eta^1,\mu\text{-}O_2)]$[29b]; without the crown in benzene $K[Al_7(OMe)_3O_3Me_{13}]\cdot C_6H_6$ is formed. These *aluminoxanes*[30a] have Al_6O_6 open cages and are similar to the nitrogen-containing oligomers discussed later. Sodium hydride and Me_3Al in toluene with 15-C-5 give crown-free $Na[Me_3Al(\mu\text{-}H)AlMe_3]$ with a linear Al-H-Al bridge. Finally, there are phosphinomethyls, for example, $Me_2Al(\mu\text{-}CH_2PMe_2)_2AlMe_2$ with Al—P bonds.[30b]

The *trialkyls of Ga, In, and Tl* are less stable than those of Al, and, like those of boron, do *not* dimerize.

In the crystal Me_3In and Me_3Tl are tetramers, while bulkier alkyl groups like $CH(SiMe_3)_2$ give monomers with a rather flattened pyramidal structure.[31]

A number of dialkyl compounds of Ga, In, and Tl are well characterized and are stable even in aqueous solutions. Thus interaction of Me_2GaCl and ammonia gives $[Me_2Ga(NH_3)_2]^+Cl^-$, whereas partial hydrolysis of $Me_3Ga\cdot Et_2O$ gives crystals of the OH-bridged tetramer $[Me_2GaOH]_4$, which is soluble in acids to give the cation $[Me_2Ga(H_2O)_2]^+$ and in bases to give $[Me_2Ga(OH)_2]^-$. Thallium gives very stable ionic derivatives of the type R_2TlX (X = halogens, SO_4^{2-}, CN^-, NO_3^-, etc.), which resemble compounds R_2Hg in being unaffected by air and water. The ion $(CH_3)_2Tl^+$ in aqueous solution and in salts is linear, like R_2Hg and the ions Me_2Pb^{2+} and Me_2Sn^{2+}; the reason for the difference in structure of Me_2Ga^+ and Me_2Tl^+ is not obvious.

In crystals of thallium salts, as in dimethyltin salts (Section 9-11), the anions may act as bridges. Thus the sulfinate $(Me_2TlSO_2Me)_2$ is dimeric with sulfinate bridges. Additional coordination can certainly occur, and a complex $[Me_2Tl(py)]ClO_4$ has been isolated. The $[Me_2Tl(py)]^+$ ion appears to be T-shaped on the basis of spectroscopic measurements. Bis(pentafluorophenyl)thallium halides give what appear to be five-coordinate adducts such as $(C_6F_5)_2TlCl(bipy)$.

Organoaluminum Compounds with Al—N Bonds. The interaction of alkylaluminums or mixed alkyls such as $AlClEt_2$ with primary or secondary amines gives adducts initially. On heating, these adducts lose alkane to give oligomers that have Al—N—Al bonds, each Al becoming four-coordinate by interaction with a nitrogen atom lone pair:

$$2Et_2AlBr\cdot NH_2i\text{-}Bu \xrightarrow{120^\circ C} (EtBrAlNHi\text{-}Bu)_2 + 2C_2H_6$$

$$Me_3Al + H_2NMe \longrightarrow [MeAlNMe]_n + 2CH_4$$

The dimers have a four-membered Al_2N_2 ring (7-XII), which may have isomers if the groups are different. The tetramers have an Al_4N_4 cubic cage

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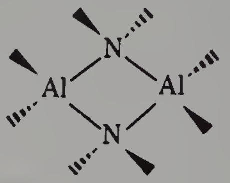
[29b] P. Fantucci and G. Pacchioni, *J. Chem. Soc. Dalton Trans.*, **1987**, 355.

[30a] J. L. Atwood *et al., J. Am. Chem. Soc.*, 1986, **108**, 1709.

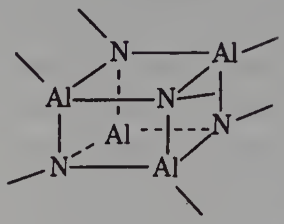
[30b] H. H. Karsch *et al., Organometallics,* 1987, **6,** 316.

[31] A. J. Carty *et al., Inorg. Chem.*, 1980, **19,** 3637.

(7-XIII) comparable to the C_8 cage in the hydrocarbon cubane. A more complex cage has been formed in the heptamer $(MeAlNMe)_7$.

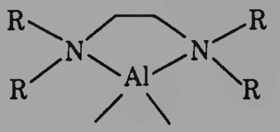


(7-XII)

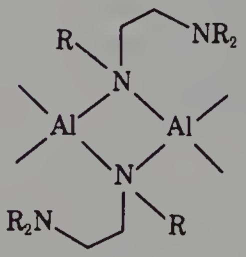


(7-XIII)

Chelate amines can give either monomers or dimers (7-XIV) and (7-XV), where steric factors of the alkyl groups appear to be most important in determining the nature of the product.



(7-XIV)

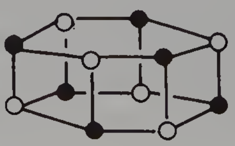


(7-XV)

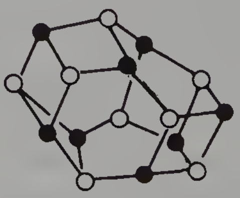
Similar *poly*(*N-alkylimino alanes*) are made by reactions such as

$$\left.\begin{array}{r} AlH_3NMe_3 + RNH_2 \longrightarrow \\ LiAlH_4 + RNH_3Cl \longrightarrow \\ Al + RNH_2 \longrightarrow \end{array}\right\} \frac{1}{n}(HAlNR)_n \left\{\begin{array}{l} + 2H_2 + Me_3N \\ +3H_2 + LiCl \\ + \frac{1}{2}H_2 \end{array}\right.$$

where n ranges from 2 to at least 35, but quite commonly takes values of 4, 6, or 8, giving compounds with the cage structures (7-XIII), (7-XVI), and (7-XVII).



(7-XVI)



(7-XVII)

● = AlH
○ = NR

The compounds have been used as reducing agents, for hydrogenation, and as polymerization catalysts. Polymers with Al—N backbones are obtained by interaction of R_3NAlH_3 with, for example, ethylenediamine or acetonitrile.

A gallium compound $[Me_2NGaH_2]_2$ has a structure of the type (7-XII).[32a] Some related phosphido species, for example, $(Me_2AlPMePh)_3$ exist.[32b]

[32a] A. J. Downs *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985,** 807.

[32b] O. T. Beachley Jr., and L. Victoriano, *Inorg. Chem.*, 1986, **25,** 1948.

7-11. Transition Metal Complexes[33]

The interaction of sodium salts of carbonylate ions, for example, $[Co(CO)_4]^-$, (see Chapter 22) with the metal chlorides, commonly gives compounds that are readily soluble in organic solvents. Examples are $AlCo_3(CO)_9$, $In[Mn(CO)_5]_3$, and $Tl[Co(CO)_4]_3$. These compounds have metal–metal bonds and are similar to those given, for example, by mercury(II). There are relatively few Al compounds of this type, but interaction of aluminum alkyls with metal carbonyls can give adducts that appear to have $M—C—O—AlR_3$ bonds. Where the elimination of alkane can occur, as with transition metal hydrides, more complicated compounds are formed (see Section 24-10).

THE CHEMISTRY OF OXIDATION STATES I AND II

Since the elements in Group IIIA(13) have the outer electron configurations ns^2np, it is natural to consider whether monovalent ions might exist. It may be recalled that there is no evidence for boron(I) under chemically important conditions.

7-12. Aluminum and Gallium(I, II)

No compounds containing Al^I exist at ordinary temperatures. Anodic oxidation of aluminum at high current densities evidently produces ephemeral lower-valent aluminum ions, either Al^I or Al^{II}, or both. *Gaseous* Al^I halide molecules exist at high temperatures, and the equilibrium:

$$AlCl_3(g) + 2Al(s) \rightleftharpoons 3AlCl(g)$$

has been thoroughly studied, and its use in purifying aluminum proposed. The reaction proceeds to the right at high temperatures, but reverses readily at low temperatures. Similarly, gaseous Al_2O and AlO molecules exist above 1000°C. No solid oxide containing lower-valent aluminum has been shown definitely to exist under ordinary conditions, although Al_2O and other M_2O species can be trapped in inert gas matrices at low temperatures.

An organo compound $Al_2i\text{-}Bu_4$ has an Al—Al bond.[34]

Gallium(I) Compounds. These are made by high temperature reactions such as

$$Ga_2O_3(s) + 4Ga(l) \xrightarrow{700°C} 3Ga_2O(g)$$

$$4Ga(l) + SiO_2(s) \rightleftharpoons Si(\text{in Ga}) + 2Ga_2O(g)$$

$$GaCl_3(g) \overset{1100°C}{\rightleftharpoons} GaCl(g) + Cl_2$$

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[33] S. K. Boocock and S. G. Shore, *Comprehensive Organometallic Chemistry*, Vol. 6, Chapter 41.2, Pergamon Press, Oxford, 1982.

[34] M. A. Miller and E. P. Schram, *Organometallics*, 1985, **4**, 1362.

Although GaCl has not been isolated pure, Ga_2O and Ga_2S have been, but the latter solid is nonstoichiometric. The best-known compounds are the "dihalides" GaX_2; these are known to have the saltlike structure $Ga^I[Ga^{III}X_4]$; the Ga^I ion can also be obtained in other salts such as $Ga[AlCl_4]$. Fused $GaCl_2$ is a typical conducting molten salt. These halides are prepared by the reaction

$$2GaX_3 + 4Ga \xrightarrow[60°C]{benzene} 3Ga_2X_2$$

With X = I, a stoichiometric amount of Ga must be used, otherwise Ga_4I_6 is obtained; this is thought to be $(Ga^+)_2(Ga_2I_6^{2-})$. Salts of the type $[GaL_4]$-$[GaCl_4]$ have been obtained with sulfur, selenium, and arsenic donors (L). Gallium chloride and $GaBr_2$ dissolve in aromatic solvents to give bis arene species $[Ar_2Ga^I(\mu\text{-}Ga^{III}Cl_4)]_2$;[35] there are also thallium analogs.

Gallium(II) Compounds. The anodic dissolution of Ga in 6 *M* HCl or HBr at 0°C followed by addition of Me_4NX precipitates white crystalline salts of the ion $[Ga_2X_6]^{2-}$ that are stable and diamagnetic. In the staggered ethanelike ions there is a Ga—Ga bond of 2.39 Å for X = Cl and 2.41 Å when X = Br, so that formally, gallium is in the II oxidation state. The treatment of $GaCl_2$ with dioxane gives a crystalline solvate $(diox)Cl_2Ga—GaCl_2(diox)$, in which each Ga atom has a distorted tetrahedral configuration and the Ga—Ga distance is 2.406(1) Å. The chalcogenides GaS, GaSe, and GaTe, obtained by direct interaction, also have Ga—Ga units in the structure.

7-13. Indium(I, II)[36]

Indium(I) can be obtained in low concentration in aqueous solution by using an indium metal anode in 0.01*M* perchloric acid. It is rapidly oxidized by both H^+ ion and by air, and is also unstable to disproportionation:

$$In^{3+} + 3e = In \qquad E^0 = -0.343 \text{ V}$$

$$In^{3+} + 2e = In^+ \qquad E^0 = -0.426 \text{ V}$$

$$In^+ + e = In \qquad E^0 = -0.178 \text{ V}$$

The extremely reactive In^{2+} aquated ion is formed in the reduction of In^{3+} with hydrated electrons. The halides InX (X = Cl, Br, and I) are all isostructural with the low-temperature form of TlI. These compounds as well as InO, In_2S, and In_2Se are obtained by solid state reactions: they are unstable to water. In^I is more stable in acetonitrile, and it is possible to isolate ClO_4^-, BF_4^-, and PF_6^- salts of In^+ by reaction of In/Hg with silver salts in acetonitrile.

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[35] H. Schmidbauer, *et al., Organometallics,* 1986, **5,** 1647.

[36] D. G. Tuck *et al., Inorg. Chim. Acta,* 1985, **97,** 73.

The *dihalides,* that is, $In^{I}[InX_4]$, are made by refluxing indium with halogen in xylene:

$$2In + 3X_2 = 2InX_3$$

$$2InX_3 + In = 3InX_2$$

while In^{II} complexes can be made by the reaction

$$2R_4NX + 2InX_2 \xrightarrow{\text{xylene}} (R_4N)_2[In_2X_6]$$

Unlike $[Ga_2X_6]^{2-}$ the $[In_2X_6]^{2-}$ ions disproportionate in nonaqueous solvents to give $In^{I}X_2^-$ and $In^{III}X_4^-$.

Pentamethylcyclopentadienyl indium is a hexamer, $(^*CpIn)_6$ with an octahedral In_6 core.[37]

7-14. Thallium(I, II)

The unipositive state is quite stable; in aqueous solution it is distinctly more stable than Tl^{III}:

$$Tl^{3+} + 2e = Tl^+$$

$$E^0 = +1.25\ \text{V}\ [E_f = +0.77,\ 1\ M\ \text{HCl};\ +1.26,\ 1\ M\ \text{HClO}_4]$$

The Tl^+ ion is not very sensitive to pH, although the Tl^{3+} ion is extensively hydrolyzed to $TlOH^{2+}$ and the colloidal oxide even at pH 1 to 2.5; the redox potential is hence very dependent on pH as well as on the presence of complexing anions. Thus as indicated by the previously listed potentials, the presence of Cl^- stabilizes Tl^{3+} more (by formation of complexes) than Tl^+ and the potential is thereby lowered.

The colorless Tl^+ ion has a radius of 1.54 Å, which can be compared with those of K^+, Rb^+, and Ag^+ (1.44, 1.58, and 1.27 Å). In its chemistry this ion resembles either the alkali or silver(I) ions.

The Tl^+ ion has been proposed as a probe for the behavior of K^+ in biological systems. The two isotopes ^{203}Tl and ^{205}Tl (70.48%) both have nuclear spin, and nmr signals are readily detected both in solutions and in solids; also the Tl^{I} (and Tl^{III}) resonances are very sensitive to the environment and have huge solvent-dependent shifts. For Tl^+ it is possible to correlate shifts with solvating ability, hence the utility as a probe in biological systems.

In crystalline salts, the Tl^+ ion is usually six- or eight-coordinate. The yellow hydroxide is thermally unstable, giving the black oxide Tl_2O at about 100°C. The latter and the hydroxide are readily soluble in water to give strongly basic solutions that absorb carbon dioxide from the air; TlOH is a weaker base than KOH, however. Many Tl^+ salts have solubilities somewhat lower than those of the corresponding alkali salts, but otherwise are similar

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[37] O. T. Beachley *et al., J. Am. Chem. Soc.,* 1986, **108,** 4666.

to and quite often isomorphous with them. Examples of such salts are the cyanide, nitrate, carbonate, sulfate, phosphates, perchlorate, and alums.

Thallium(I) sulfate, nitrate, and acetate are moderately soluble in water, but—except for the very soluble TlF—the halides are sparingly soluble. The chromate and the black sulfide Tl_2S, which can be precipitated by hydrogen sulfide from weakly acid solutions, are also insoluble. Thallium(I) chloride also resembles silver chloride in being photosensitive; it darkens on exposure to light. Incorporation of Tl^I halides into alkali halides gives rise to new absorption and emission bands, because complexes of the type that exist also in solutions (most notably TlX_2^- and TlX_4^{3-}) are formed; such thallium-activated alkali halide crystals are used as phosphors (e.g., for scintillation radiation detectors). Thallium(I) chloride is insoluble in ammonia, unlike AgCl.

Thallium(I) fluoride is essentially ionic, with layers held together by $Tl \cdots F$ interactions. The ion is octahedral, with two cis fluorines at longer distances. It is also found that the Tl^+ ion is far from being spherical.

With the exception of those with halide, oxygen, and sulfur ligands, Tl^I gives rather few complexes. The dithiocarbamates $Tl(S_2CNR_2)$, made from aqueous Tl_2SO_4 and the sodium dithiocarbamates, are useful reagents for the synthesis of other metal dithiocarbamates from the chlorides in organic solvents, since the Tl dithiocarbamate is soluble and TlCl is precipitated on reaction. The structure of the *n*-propyl complex shows that it is polymeric with $[TlS_2CNPr_2]_2$ dimeric units linked by Tl—S bonds.

Electron-exchange reactions in the Tl^I—Tl^{III} system have been intensively studied and appear to be two-electron transfer processes; various Tl^{III} complexes participate under appropriate conditions.

When oxygen, nitrogen, and sulfur bound to organic groups are also bound to Tl^I, the Tl—X bond appears to be more covalent than the bond to alkali metal ions in similar compounds. Thallium compounds tend to be polymeric rather than ionic. Thus the acetylacetonate is a linear polymer with four-coordinate Tl. The alkoxides, which are obtained by reactions such as

$$4Tl + 4C_2H_5OH \longrightarrow (TlOC_2H_5)_4 + 2H_2$$

are liquids with the exception of the crystalline methoxide. All are tetramers[38] and the methoxide has a distorted cube structure, with the Tl and O atoms at corners of regular tetrahedra of different size, so that oxygen is four-coordinate. Vibrational studies indicate that there are weak direct $Tl \cdots Tl$ interactions in these molecules.

Thallium(I) forms compounds with transition metals as in $TlCo(CO)_4$ that are mainly "salts" of carbonylate anions and tend to be ionic. Metal-metal bonds may be cleaved, for example,

$$[(\eta\text{-}C_5H_5)(CO)_3Mo]_2 + 2Tl = 2TlMo(CO)_3(\eta\text{-}C_5H_5)$$

[38] R. W. Mathews *et al.*, *J. Chem. Soc. Dalton Trans.*, **1980,** 1439.

Thallium(I) forms the insoluble C_5H_5Tl on addition of aqueous TlOH to C_5H_6; it can be used to make other cyclopentadienyl compounds (Chapter 26). No stable compounds of *thallium(II)* exist. The Tl^{2+} ion has been proposed to occur in reactions involving Tl^+ with one-electron oxidants and Tl^{3+} with reductants, and has been detected in flash photolyses where it has a half-life of only 0.5 ms:

$$H_2O + Tl^{3+} \xrightarrow{h\nu} Tl^{2+} + OH\cdot + H^+$$

Redox and disproportionation reactions can be studied and estimates made for the couples Tl^{3+}/Tl^{2+}, $E = 0.33$ V and Tl^{2+}/Tl^+, $E = 2.22$ V.

All thallium compounds are *exceedingly* poisonous.

Further References

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Smith I. C. *et al., Indium. Trace Metals in the Environment,* Vol. 5, Ann Arbor Scientific Publishers, Ann Arbor, Michigan, 1978 (contains much information on In chemistry).

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Chapter Eight

Carbon: Group IVA(14)

GENERAL REMARKS

There are more compounds of carbon than of any other element except hydrogen, and most of them are best regarded as organic chemicals.

The electronic structure of the C atom in its ground state is $1s^2 2s^2 2p^2$, with the two $2p$ electrons unpaired, following Hund's rule. To account for the normal four-covalence we must consider that it is promoted to a valence state based on the configuration $2s2p_x2p_y2p_z$. The ion C^{4+} does not arise in any normal chemical process, but something approximating to the C^{4-} ion may possibly exist in some carbides. In general, however, carbon forms covalent bonds.

In organic reactions there is abundant evidence for transient carbonium ions (R_3C^+), carbanions (R_3C^-), and carbenes ($:CR_2$). Some stable carbonium ions like Ph_3C^+ and carbanions like $C(CN)_3^-$ can be isolated as well as radicals like $Ph_3C^\cdot$. In most of these cases the charge or the electron must be delocalized over the entire system for stability. Transition metal complexes with carbene or carbyne ligands, $L_nM{=}CR_2$ and $L_nM{\equiv}CR$ are discussed in Chapter 25.

Coordination Numbers. In virtually all its stable compounds carbon forms four bonds and has coordination numbers of 2 ($\equiv$C— or =C=), 3 (=C), or 4, with linear, triangular (planar), and tetrahedral geometries, respectively; CO has coordination number 1. In interstitial carbides (Section 8-3) and certain metal cluster compounds (Chapter 23) carbon atoms are found with coordination numbers of 5 or 6. Coordination number 5 is also found in compounds with bridging alkyls such as Al_2Me_6, in some carboranes (Section 6-12) and in reactive intermediates.[1]

Catenation. The unusual stability of catenated carbon compounds, compared with those of silicon and sulfur, can be appreciated by considering the bond-energy data shown in Table 8-1. Thus the simple *thermal* stability of —C_n— chains is high because of the intrinsic strength of C—C bonds. The relative stabilities toward oxidation follow from the fact that C—C and C—O bonds are of comparable stability, whereas for Si, and probably also for S,

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[1] G. A. Olah and G. K. S. Prakash, *Chem. Br.*, 1983, 916.

TABLE 8-1
Some Bond Energies Involving Carbon, Silicon, and Sulfur

Bond	Energy (kJ mol^{-1})	Bond	Energy (kJ mol^{-1})
C—C	356	C—O	336
Si—Si	226	Si—O	368
S—S	226	S—O	~330

the bond to oxygen is considerably stronger. Thus, given the necessary activation energy, compounds with a number of Si—Si links are converted very exothermically into compounds with Si—O bonds.

THE ELEMENT

Carbon has the isotopic composition ^{12}C 98.89% and ^{13}C 1.11%. Only ^{13}C has nuclear spin ($S = \frac{1}{2}$); with Fourier transform nmr, spectroscopic measurements can be made using natural abundance.

The radioisotope ^{14}C (β^-, 5570 years), which is widely used as a tracer, is made by thermal neutron irradiation of Li or Al nitride, $^{14}N(n,p)^{14}C$. It is available not only as CO_2 or carbonates but also in numerous labeled organic compounds. Its formation in the atmosphere and absorption of CO_2 by living organisms provide the basis of radiocarbon dating.

8-1. Allotropy of Carbon: Diamond; Graphite

Diamond and graphite differ in their physical and chemical properties because of differences in the arrangement and bonding of the carbon atoms. Diamond is denser than graphite (3.51 vs. 2.22 g cm^{-3}), but graphite is the more stable, by 2.9 kJ mol^{-1} at 300 K and 1-atm pressure. From the densities it follows that to transform graphite into diamond, pressure must be applied, and from the thermodynamic properties of the two allotropes it can be estimated that they would be in equilibrium at 300 K under a pressure of ~15,000 atm. Of course, equilibrium is attained extremely slowly at this temperature, and this property allows the diamond structure to persist under ordinary conditions.

The energy required to vaporize graphite to a monoatomic gas is an important quantity, since it enters into the estimation of the energies of all bonds involving carbon. It is not easy to measure directly because even at very high temperatures, the vapor contains appreciable fractions of C_2, C_3, and so on. However, the exact value is now known to be 716.9 kJ mol^{-1} at 300 K; in using older tables of bond energies, the heat of sublimation of graphite may have been taken as ~520 or 574 kJ mol^{-1}.

Diamond. This form of carbon is almost invariably found with the cubic structure (see Fig. 1-1). There is also a hexagonal form (lonsdaleite) found in certain meteorites and also available synthetically, in which the puckered layers are stacked in an ABAB· · · pattern instead of the ABCABC· · · pattern. The hexagonal form is probably unstable toward the cubic, since unlike the cubic, it contains some eclipsed bonds.

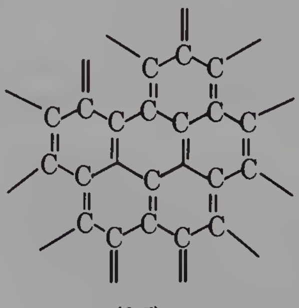
Diamond is the hardest solid known. It has a high density and index of refraction, the highest mp (~4000°C),[2] thermal conductivity, and lowest molar entropy (2.4 J $mol^{-1}K^{-1}$) of any element.

Although graphite can be directly converted into diamond at temperatures of ~300 K and pressures above 125 kbar, in order to obtain useful rates of conversion, a transition metal catalyst such as Cr, Fe, or Pt is used.[3a] It appears that a thin film of molten metal forms on the graphite, dissolving some and reprecipitating it as diamond, which is less soluble; about 40% of the world's supply of industrial-quality diamonds are now synthetic. Even gem-quality stones up to ~5 mm in diameter can be obtained, although these are not economically competitive with natural diamonds. By accidental or deliberate introduction of trace impurities, colored stones can be produced—nitrogen causes a yellow coloration, and boron gives blue.

The graphite–diamond conversion has been treated theoretically, the conclusion being that hexagonal graphite cannot easily be converted to diamond and that the process is more complicated than the models used indicate.[3b]

The chemical reactivity of diamond is much lower than that of carbon in the form of macrocrystalline graphite or the various amorphous forms. Diamond can be made to burn in air by heating it to 600 to 800°C.

Graphite. Hexagonal graphite has a layer structure as indicated in Fig. 8-1. The separation of the layers is 3.35 Å, which is about equal to the sum of van der Waals radii and indicates that the forces between layers should be relatively slight. Thus the observed softness and particularly the lubricity of graphite can be attributed to the easy slippage of these layers over one another. It will be noted that within each layer each carbon atom is surrounded by only three others. After forming one σ bond with each neighbor, each carbon atom would still have one electron and these are paired up into a system of π bonds (8-I). Resonance with other structures having different but



(8-I)

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[2] W. A. Bassett, *Science,* 1984, **225,** 921.

[3a] M. M. Bindel *et al., Indian J. Pure Appl. Phys.,* 1986, **24,** 173; Z. Shen *et al., Physica,* 1986, **139–140,** 642; K. Higashi and A. Onodera, *Physica,* 1986, **139–140,** 813.

[3b] M. Kertesz and R. Hoffmann, *J. Solid State Chem.,* 1984, **54,** 313.

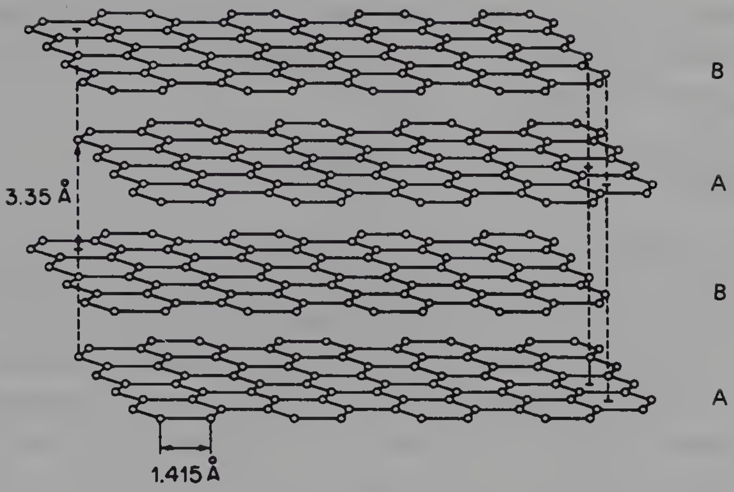

FIG. 8-1. The normal structure of graphite.

equivalent arrangements of the double bonds makes all C—C distances equal at 1.415 Å. This is a little longer than the C—C distance in benzene, where the bond order is 1.5, and agrees with the assumption that the bond order in graphite is ~1.33.

Actually two modifications of graphite exist, differing in the order of the layers. In no case do all the carbon atoms of one layer lie directly over those in the next layer, but, in the structure shown in Fig. 8-1, carbon atoms in every other layer are superposed. This type of stacking, which may be designated (ABAB· · ·), is apparently the most stable and exists in the commonly occurring hexagonal form of graphite. There is also a rhombohedral form, frequently present in naturally occurring graphite, in which the stacking order is (ABCABC· · ·); that is, every third layer is superposed. It seems that local areas of rhombohedral structure can be formed by mechanical deformation of hexagonal crystals and can be removed by heat treatment.

Laser vaporization of graphite and mass spectrometer study suggests the formation of a C_{60}^+ cluster,[4] which can possibly bind to La in $C_{60}La^+$.

Amorphous carbons, carbon black, soot, charcoals, and so on, are all microcrystalline forms of graphite. The physical properties depend on the nature and magnitude of the surface area. They show electrical conductivity, have high chemical reactivity due to oxygenated groups on the surface and readily intercalate other molecules (see later). Graphites and amorphous carbons as supports for Pd, Pt, and other metals are widely used in catalysis.

Strong graphite fibers are made by pyrolysis, at 1500°C or above, of oriented organic polymer fibers (e.g., those of polyacrylonitrile, polyacrylate esters, or cellulose). When incorporated into plastics the reinforced materials are light and very strong. Other forms of graphite such as foams, foils, or whiskers can also be made.

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[4] D. M. Cox *et al., J. Am. Chem. Soc.,* 1986, **108**, 2457; D. J. Klein *et al., J. Am. Chem. Soc.,* 1986, **108,** 1301; M. D. Newton and R. E. Stanton, *J. Am. Chem. Soc.,* 1986, **108,** 2469.

Other Forms. At least four other forms—"carbon III," a very rare mineral called chaoite, and other cubic and hexagonal forms, all rare and poorly understood—are also known.

8-2. Intercalation Compounds of Graphite[5]

The layered structure of graphite allows molecules and ions to penetrate between the layers, forming interstitial or lamellar compounds. There are two basic types; those in which the graphite becomes nonconducting and those in which high electrical conductivity remains or is enhanced. Only two substances of the first type are known, namely, graphite oxide and graphite fluoride. *Graphite "oxide"* is obtained by treating graphite with strong aqueous oxidizing agents such as fuming nitric acid or HNO_3 + $KClO_3$. The idealized stoichiometry is C_8O_2OH and there are $—C{=}O$ and $—C—OH$ groups in the material, which is fairly acidic.

Graphite fluoride is obtained by fluorination.[6] At 2-atm pressure in liquid HF at 20°C a material C_xF, $5 > x > 2$ is first obtained, which then forms $C_{12}^+HF_2^-$; electrolysis of alkali fluoride melts with C anodes also gives C_xF. At high temperatures, 400–600°C, fluorination gives white $(CF)_n$.

Electrically conducting intercalation compounds, also called lamellar compounds, are formed by insertion of various atoms, molecules, or ions between the layers of graphite. The intercalates can be made by spontaneous reaction with alkali metals, or halides like $FeCl_3$ or ReF_6.[7]

Electrochemical intercalation is cleaner and controllable

$$C_n + M^+ + e^- \rightleftharpoons M^+ + C_n^-$$

$$C_n + X^- - e^- \rightleftharpoons C_n^+ + X^-$$

The guest ions penetrate during cathodic reduction or anodic oxidation of graphite. Solvent may also be incorporated into the layers as in $K(THF)C_{24}$ or $C_n(MeNO_2)_2PF_6$. Among the earliest lamellar compounds were those of alkali metals of initial composition C_8M (Cs, Rb, K) but C_6Li. Sodium does not form a material more concentrated than $C_{64}Na$. All these materials ignite in air and react explosively with water. They have high electrical conductivity.

Generally for any given guest species there is a whole series of stoichiometric compositions obtainable, each corresponding to a "stage." This term refers to the frequency with which the layers of the graphite host are invaded, as shown in Fig. 8-2. For a stage *n* compound every *n*th layer contains guest species, so that the highest concentration of guest occurs in the stage 1 compound.

[5] H. Selig and L. B. Ebert, *Adv. Inorg. Chem. Radiochem.*, 1980, **23,** 281; J. O. Besenhard and H. P. Fritz, *Angew. Chem. Int. Ed. Engl.*, 1983, **22,** 950 (review, 509 references); *Intercalated Materials,* F. Levy, Ed., Reidel, Dordrecht, 1979.

[6] T. Mallouk and N. Bartlett, *J. Chem. Soc. Chem. Commun.*, **1983,** 103.

[7] H. Selig *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 1689.

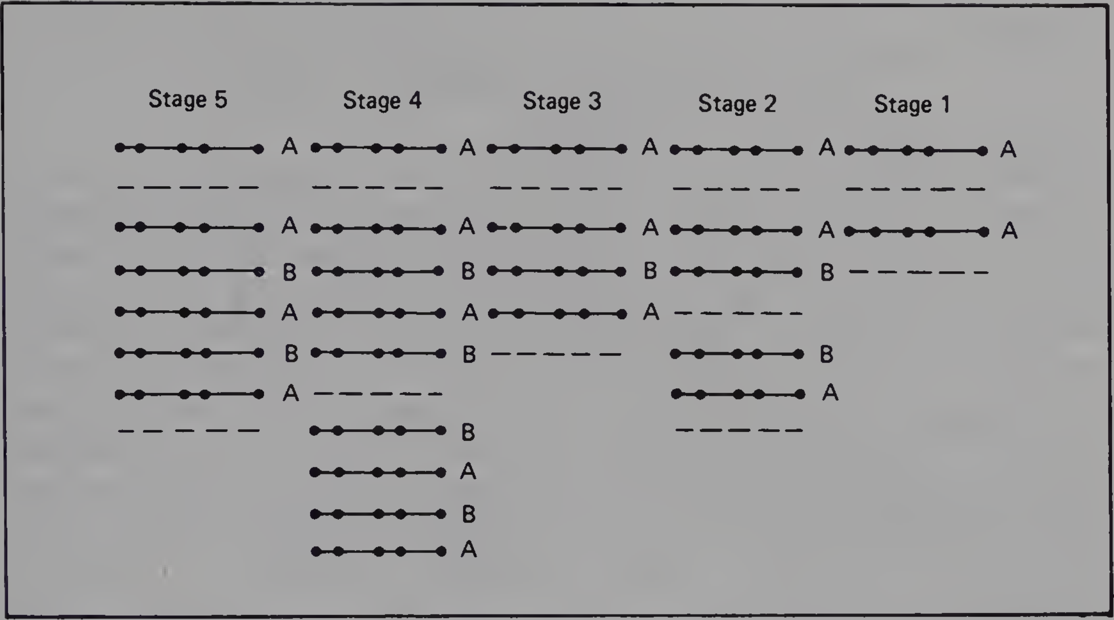

FIG. 8-2. The various stages of graphite intercalation compounds. The letters A and B refer to the stacking pattern of carbon layers, and the two carbon layers flanking a guest layer are always equivalent, that is, have their carbon atoms superposed.

NONMOLECULAR COMPOUNDS

8-3. Carbides

Only compounds in which carbon is combined with elements of similar or lower electronegativity are called carbides.

Preparative methods for carbides of all types include: (*a*) direct union of the elements at high temperature (2200°C and above); (*b*) heating a compound of the metal, particularly the oxide, with carbon; and (*c*) heating the metal in the vapor of a suitable hydrocarbon. Carbides of Cu, Ag, Au, Zn, and Cd, also commonly called acetylides, are prepared by passing acetylene into solutions of the metal salts; with Cu, Ag, and Au, ammoniacal solutions of salts of the unipositive ions are used to obtain Cu_2C_2, Ag_2C_2, and Au_2C_2 (uncertain), whereas for Zn and Cd the acetylides ZnC_2 and CdC_2 are obtained by passing acetylene into petroleum solutions of dialkyl compounds. The Cu and Ag acetylides are explosive, being sensitive to both heat and mechanical shock.

1. *Saltlike Carbides.* The most electropositive metals form carbides having physical and chemical properties indicating that they are essentially ionic. The colorless crystals are hydrolyzed by water or dilute acids at ordinary temperatures, and hydrocarbons corresponding to the anions $C^{4-}(CH_4)$, C_2^{2-} (C_2H_2), and C_3^{4-} (C_3H_4) are formed. For example, Be_2C and Al_4C_3 are methides, the former having an antifluorite structure. Al_4C_3 hydrolyzes ac-

cording to

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

Lithium carbides are noted in Section 4-2.

There are many carbides that contain C_2^{2-} ions, or anions that can be so written to a first approximation. For the M_2^I compounds, where M^I may be one of the alkali metals or one of the coinage metals, and for the $M^{II}C_2$ compounds where M^{II} may be an alkaline earth metal, Zn, or Cd and for $M_2^{III}(C_2)_3$ compounds in which M^{III} is Al, La, Pr, or Tb, this description is probably a very good approximation. In these cases, the postulation of C_2^{2-} ions requires that the metal ions be in their normal oxidation states. In those instances where accurate structural parameters are known, the C—C distances lie in the range 1.19 to 1.24 Å. The compounds react with water and the C_2^{2-} ions are hydrolyzed to give acetylene only, for example,

$$Ca^{2+}C_2^{2-} + 2H_2O \longrightarrow HCCH + Ca(OH)_2$$

There are, however, a number of carbides that have the same structures as those discussed previously, meaning that the carbon atoms occur in discrete pairs, but they cannot be satisfactorily described as C_2^{2-} compounds. These include YC_2, TbC_2, YbC_2, LuC_2, UC_2, Ce_2C_3, Pr_2C_3, and Tb_2C_3. For these MC_2 compounds neutron-scattering experiments show that (*a*) the metal atoms are essentially trivalent and (*b*) the C—C distances are 1.28 to 1.30 Å for the lanthanide compounds and 1.34 Å for UC_2. These facts and other details of the structures are consistent with the view that the metal atoms lose not only the electrons necessary to produce C_2^{2-} ions (which would make them M^{2+} ions) but also a third electron, mainly to the antibonding orbitals of the C_2^{2-} groups, thus lengthening the C—C bonds (cf. C—C = 1.19 Å in CaC_2). There are actually other, more delocalized, interactions among the cations and anions in these compounds, since they have metallic properties. The M_2C_3 compounds have the metals in their trivalent states, C—C distances of 1.24 to 1.28 Å, and also direct metal-metal interactions. These carbides, which cannot be represented simply as aggregates of C_2^{2-} ions and metal atoms in their normal oxidation states, are hydrolyzed by water to give only 50 to 70% of HCCH, while C_2H_4, CH_4, and H_2 are also produced. There is no detailed understanding of these hydrolytic processes.

Most of the MC_2 acetylides have the CaC_2 structure which is derived from the NaCl structure with the $[C—C]^{2-}$ ions lying lengthwise in the same direction along the cell axes, thus causing a distortion from cubic symmetry to tetragonal symmetry with one axis longer than the other two. In thorium carbide the C_2^{2-} ions are lying flat in parallel planes in such a way that two axes are equally lengthened with respect to the third. These structures are shown in Fig. 8-3. Li_2C_2 has a structure similar to that of CaC_2.

2. *Interstitial Carbides.* These have characteristically very high melting points, great hardness, and metallic conductivity.

3. *Covalent Carbides.* Although other carbides (e.g., Be_2C) are at least partially covalent, the two elements that approach carbon closely in size and

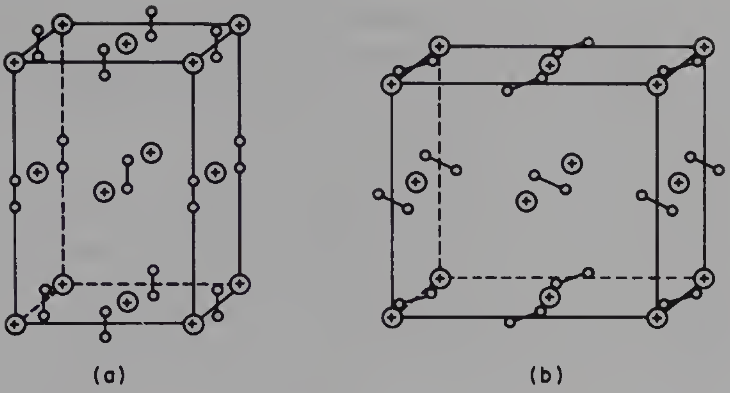

FIG. 8-3. The structures of (a) CaC_2 and (b) ThC_2 (the latter somewhat simplified).

electronegativity, namely, silicon and boron, give completely covalent compounds. Silicon carbide (SiC), known as carborundum, is an extremely hard, infusible, and chemically stable material made by reducing SiO_2 with carbon in an electric furnace. It has three structural modifications, in all of which there are infinite three-dimensional arrays of Si and C atoms, each tetrahedrally surrounded by four of the other kind. No evidence has been obtained for a germanium carbide.

Boron carbide (B_4C) is also an extremely hard, infusible, and inert substance, made by reduction of B_2O_3 with carbon in an electric furnace, and has a very unusual structure. The C atoms occur in linear chains of 3, and the boron atoms in icosahedral groups of 12 (as in crystalline boron itself). These two units are then packed together in a sodium chloride-like array. There are, of course, covalent bonds between C and B atoms as well as between B atoms in different icosahedra. A graphite-like boron carbide (BC_3) has been made by interaction of benzene and BCl_3 at 800°C.[8a]

Finally, a salt of composition $[C_{48}H_{51}]^+[C_{61}H_{39}]^-$ as greenish-black crystals has been isolated by mixing solutions of bulky substituted cyclopropenylium ion ($C_3R_3^+$) with a bulky carbanion.[8b]

SIMPLE MOLECULAR COMPOUNDS

Some of the more important inorganic carbon compounds and their properties are listed in Table 8-2.

8-4. Carbon Halides

Carbon tetrafluoride is an extraordinarily stable compound. It is the end product in the fluorination of any carbon-containing compound. A laboratory preparation involves the fluorination of silicon carbide. The SiF_4 also formed is removed easily by passing the mixture through 20% NaOH solution. The

[8a] N. Bartlett *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 1758.
[8b] K. Okamoto, *J. Chem. Soc. Chem. Commun.*, **1985**, 173.

TABLE 8-2
Some Simple Compounds of Carbon

Compound	mp (°C)	bp (°C)	Remarks
CF_4	−185	−128	Very stable
CCl_4	−23	76	Moderately stable
CBr_4	93	190	Decomposes slightly on boiling
CI_4	171		Decomposes before boiling; can be sublimed under low pressure
COF_2	−114	−83	Easily decomposed by H_2O
$COCl_2$	−118	8	"Phosgene"; highly toxic
$COBr_2$		65	Fumes in air; $COBr_2 + H_2O \rightarrow CO_2 + 2HBr$
$CO(NH_2)_2$	132		Isomerized by heat to NH_4NCO
CO	−205	−190	Odorless and toxic
CO_2	−57 (5.2 atm)	−79	
C_3O_2		6.8	Evil-smelling gas
COS	−138	−50	Flammable; slowly decomposed by H_2O
CS_2	−109	46	Flammable and toxic
$(CN)_2$	−28	−21	Very toxic; colorless; water soluble
HCN	−13.4	25.6	Very toxic; high dielectric constant (116 at 20°C) for the associated liquid

CF_4 is unaffected, whereas the SiF_4 is immediately hydrolyzed; the difference exists because in CF_4 carbon is coordinately saturated, whereas silicon in SiF_4 has 3*d* orbitals available for coordination of OH^- ions in the first step of the hydrolysis reaction.

Carbon tetrachloride is a common solvent; it is fairly readily photochemically decomposed and also quite often readily transfers chlorine to various substrates, CCl_3 radicals often being formed simultaneously at high temperatures (300–500°C). It is often used to convert oxides into chlorides. Although it is thermodynamically unstable with respect to hydrolysis, the absence of acceptor orbitals on carbon makes attack very difficult. The halocarbons CCl_4 and $CHCl_3$ have high liver toxicity[9] while others like DDT are powerful insecticides. Such compounds may act by forming dihalocarbenes, which have been trapped by iron porphyrin-type macrocycles (Chapter 25).

Carbon tetrabromide, a pale yellow solid at room temperature, is insoluble in water and other polar solvents but soluble in some nonpolar solvents such as benzene.

Carbon tetraiodide is a bright red, crystalline material, possessing an odor like that of iodine. Both heat and light cause decomposition to iodine and tetraiodoethylene. The tetraiodide is insoluble in water and alcohol, though attacked by both at elevated temperatures, and soluble in benzene. It may be prepared by the reaction:

$$CCl_4 + 4C_2H_5I \xrightarrow{AlCl_3} CI_4 + 4C_2H_5Cl$$

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[9] G. H. Loew, *J. Am. Chem. Soc.*, 1983, **105**, 3434.

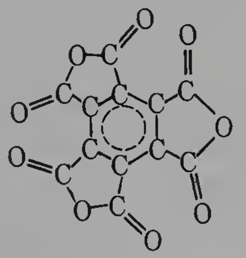
The increasing instability, both thermal and photochemical, of the carbon tetrahalides with increasing weight of the halogen correlate with a steady decrease in the C—X bond energies:

C—F 485 C—Cl 327 C—Br 285 C—I 213 kJ mol^{-1}

The *carbonyl halides* (X_2CO: X = F, Cl, Br), or mixed (e.g., ClBrCO) are hydrolytically unstable compounds. Urea [$(NH_2)_2CO$] is related but more stable. They all have longer CO bonds than do simple ketones because of partial double bonding of X to C, which weakens the carbon-to-oxygen π bonding.

8-5. Carbon Oxides

There are four stable oxides of carbon: CO, CO_2, C_3O_2, and $C_{12}O_9$. The last is the anhydride of mellitic acid (8-II) and not discussed, nor are unstable oxides such as C_2O, C_2O_3, and CO_3. *Tricarbon monoxide,*[10] which is a cumulene C=C=CO, can be made by pyrolysis of fumaroyl dichloride, Cl(O)CCH=CHC(O)Cl, and studied spectroscopically.


(8-II)

Carbon monoxide is formed when carbon is burned with a deficiency of oxygen. The following equilibrium exists at all temperatures, but is not rapidly attained at ordinary temperatures:

$$2CO(g) \rightleftharpoons C(s) + CO_2(g)$$

Carbon monoxide is made industrially on a huge scale, together with hydrogen as "synthesis gas," and is used for a variety of large-scale organic syntheses (Section 28-2). Although CO is an exceedingly weak Lewis base, one of its most important properties is the ability to act as a donor ligand toward transition metals (Section 2-8). Nickel metal reacts with CO to form $Ni(CO)_4$, and Fe reacts under more forcing conditions to give $Fe(CO)_5$. Metal carbonyls are discussed in detail in Chapter 22.

Carbon monoxide is very toxic, rapidly giving a bright red complex with the hemoglobin of blood. Carbon monoxide reacts with alkali metals in liquid ammonia to give the alkali metal *carbonyls;* these white solids contain the $[OCCO]^{2-}$ ion.

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[10] R. D. Brown *et al., J. Am. Chem. Soc.,* 1985, **107,** 7877, 4112.

Carbon dioxide[11] is obtained in combustion of carbon and hydrocarbons, calcination of $CaCO_3$, and so on. It forms complexes with transition metals (Section 8-12) and inserts into MH and other bonds (Section 27-7). Liquid CO_2 at pressures up to 400 bar is a solvent for some organic compounds and is used to extract caffeine from coffee beans.[12a]

The gas is very soluble in ethanolamines, which are used to scrub CO_2 from gas streams.[12b]

Many attempts have been made to find economically feasible ways of reducing CO_2 to CO or to organic compounds, but photosynthesis in green plants is still the only large scale way.

Electrochemical reduction[13] can give CO and $C_2O_4^{2-}$. For example, CO is produced[14] in aqueous media:

$$CO_2 + 2e^- + 2H^+ \longrightarrow CO + H_2O$$

while $C_2O_4^{2-}$ is produced in organic solvents such as DMF:

$$2CO_2^{\dot{-}} \longrightarrow C_2O_4^{2-}$$

Carbon dioxide has also been reduced to methanol, formate, oxalate, methane, and carbon monoxide by electrolysis mediated by either transition metal complexes such as $[Ru(bpy)_2(CO)_2]^{2+}$, palladium porphyrins and phosphine complexes, or by powdered solids of various sorts like platinized TiO_2.[15]

Other electrochemical methods involve trapping of CO_2 by radicals $^{\cdot}CH_2CN$ in a rhodium complex system to give cyanoacetate $NCCH_2CO_2^-$.[16]

Bicarbonate ion can also be reduced on palladium supported on a polymer electrode[17]:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

$$HCO_3^- + 2e + 2H^+ \longrightarrow HCO_2^- + H_2O$$

Carbon suboxide (C_3O_2), an evil-smelling gas, is formed by dehydrating malonic acid with P_2O_5 in vacuum at 140 to 150°C, or better, by thermolysis of diacetyltartaric anhydride. The molecule is linear and can be represented

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[11] D. A. Palmer and R. van Eldik, *Chem. Rev.*, 1983, **83**, 651 (extensive review on CO_2, CO_3^{2-}, and reactions thereof); S. Inoue and N. Yamazaki, Eds., *Organic and Bioorganic Chemistry of Carbon Dioxide*, Wiley, New York, 1982.

[12a] Z. Alwani, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 623.

[12b] P. M. M. Blauwhoff *et al., Chem. Eng. Sci.*, 1983, **38**, 1411.

[13] K. Ogura and H. Uchida, *J. Chem. Soc. Dalton Trans.*, **1987**, 1377.

[14] M. Beley *et al., J. Chem. Soc. Chem. Commun.*, **1984**, 1315; C. M. Lieber and N. S. Lewis, *J. Am. Chem. Soc.*, 1984, **106**, 5033; see also T. J. Meyer, *J. Chem. Soc. Chem. Commun.*, **1985**, 1414, 1416; L. O. Spreer *et al., J. Chem. Soc. Dalton Trans.*, **1987**, 2105.

[15] T. Tanaka *et al., Organometallics*, 1987, **6**, 181; *J. Chem. Soc. Chem. Commun.*, **1987**, 131; D. L. Dubois and A. Miedaner, *J. Am. Chem. Soc.*, 1987, **109**, 113; K. Ogura and K. Takamagari, *J. Chem. Soc. Dalton Trans.*, **1986**, 1519; J-P. Sauvage *et al., J. Am. Chem. Soc.*, 1986, **108**, 7461.

[16] S. Slater and J. W. Wagenknecht, *J. Am. Chem. Soc.*, 1984, **106**, 5367.

[17] M. S. Wrighton *et al., J. Am. Chem. Soc.*, 1984, **106**, 3673.

by the structural formula O═C═C═C═O. It is stable at −78°C, but at 25°C it polymerizes, forming yellow to violet products. Photolysis of C_3O_2 gives C_2O, which will react with olefins:

$$C_2O + CH_2{=}CH_2 \longrightarrow CH_2CCH_2 + CO$$

It reacts but slowly with water to give malonic acid, of which it is the anhydride, but more rapidly with stronger nucleophiles:

$$C_3O_2 + 2H_2O \longrightarrow HO_2CCH_2CO_2H$$

$$C_3O_2 + 2NHR_2 \longrightarrow R_2NCOCH_2CONR_2$$

Carbonic Acid. Though CO is formally the anhydride of formic acid, its solubility in water and bases is slight. It will give formates when heated with alkalis, however. As just noted, C_3O_2 gives malonic acid. However, CO_2 is by far the most important carbonic acid anydride, combining with water to give *carbonic acid,* for which the following equilibrium constants are conventionally written:

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.16 \times 10^{-7}$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.84 \times 10^{-11}$$

The equilibrium quotient in the first equation is not really correct. It assumes that all CO_2 dissolved and undissociated is present as H_2CO_3, which is not true. In fact, the greater part of the dissolved CO_2 is only loosely hydrated, so that the correct first dissociation constant, using the "true" activity of H_2CO_3, has a value of about 2×10^{-4}, which is more nearly in agreement with expectation for an acid with the structure $(HO)_2CO$.

The rate at which CO_2 comes into equilibrium with H_2CO_3 and its dissociation products when passed into water is measurably slow, and this indeed is what has made possible an analytical distinction between H_2CO_3 and the loosely hydrated CO_2 (aq). This slowness is of great importance physiologically and in biological, analytical, and industrial chemistry.

The slow reaction can easily be demonstrated by addition of a saturated aqueous solution of CO_2 on the one hand and of dilute acetic acid on the other to solutions of dilute NaOH containing phenolphthalein indicator. The acetic acid neutralization is instantaneous, whereas with the CO_2 neutralization it takes several seconds for the color to fade.

The neutralization of CO_2 occurs by two paths. For pH < 8 the principal mechanism is direct hydration of CO_2

$$\begin{aligned} CO_2 + H_2O &= H_2CO_3 && \text{(slow)} \\ H_2CO_3 + OH^- &= HCO_3^- + H_2O && \text{(instantaneous)} \end{aligned} \qquad (8\text{-}1)$$

The rate law is pseudo-first order,

$$-d[CO_2]/dt = k_{CO_2}[CO_2] \qquad k_{CO_2} = 0.03\ s^{-1}$$

At pH > 10 the predominant reaction is direct reaction of CO_2 and OH^-:

$$\begin{aligned} CO_2 + OH^- &= HCO_3^- && \text{(slow)} \\ HCO_3^- + OH^- &= CO_3^{2-} + H_2O && \text{(instantaneous)} \end{aligned} \tag{8-2}$$

where the rate law is

$$-d[CO_2]/dt = k_{OH}[OH^-][CO_2] \qquad k_{OH} = 8500\ s^{-1}\ (mol/L)^{-1}$$

This can be interpreted, of course, merely as the base catalysis of eq. (8-1). In the pH range 8 to 10 both mechanisms are important. For each hydration reaction (8-1 and 8-2) there is a corresponding dehydration reaction:

$$H_2CO_3 \longrightarrow H_2O + CO_2 \qquad k_{H_2CO_3} = k_{CO_2} \times K \qquad = 20\ s^{-1}$$

$$HCO_3^- \longrightarrow CO_2 + OH^- \qquad k_{HCO_3^-} = k_{OH} \times KK_w/K_A = 2 \times 10^{-4}\ s^{-1}$$

Hence for the equilibrium

$$H_2CO_3 \rightleftharpoons CO_2 + H_2O$$

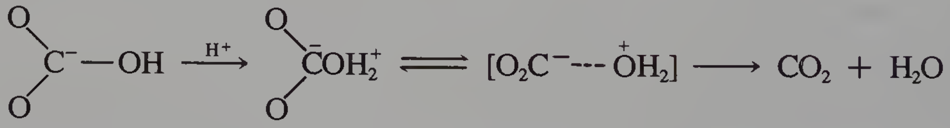
$$K = [CO_2]/[H_2CO_3] = k_{H_2CO_3}/k_{CO_2} = {\sim}600 \tag{8-3}$$

It follows from eq. 8-3 that K_A, the true ionization constant of H_2CO_3, is greater than the apparent constant, as noted previously.

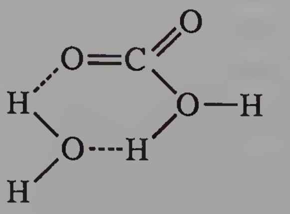
Kinetic studies of the protonation[18]

$$H_3O^+ + HCO_3^- \longrightarrow 2H_2O + CO_2$$

show a stepwise reaction via a zwitterion:



Theoretical considerations of the $H_2O—CO_2$ reaction also suggest that the initial hydrated species is a six-membered, H-bonded ring[19a] (8-III), and that



(8-III)

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[18] P. Paneth and M. H. O'Leary, *J. Am. Chem. Soc.*, 1985, **107**, 7381.

[19a] M. T. Nguyen and T. K. Ha, *J. Am. Chem. Soc.*, 1984, **106**, 599.

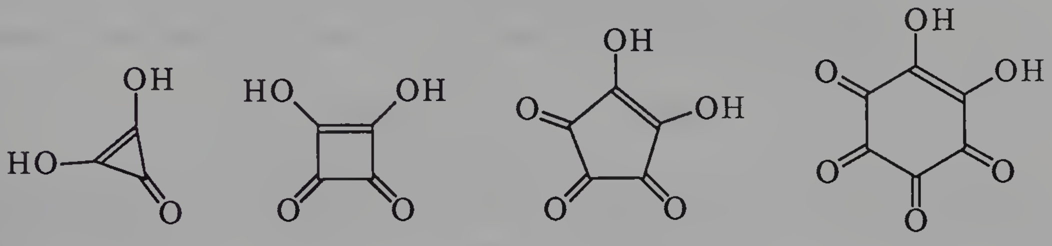
this plays an essential role in the orientation of the reactants in the carbonic anhydrase catalyzed hydration (Chapter 30).

An etherate of H_2CO_3 is obtained by interaction of HCl with Na_2CO_3 at low temperatures in dimethyl ether. The resultant white crystalline solid (mp -47°C), which decomposes at about 5°C, is probably $OC(OH)_2 \cdot O(CH_3)_2$.

Thermal decomposition of NH_4HCO_3 gives H_2CO_3 in the gas phase.[19b]

8-6. Oxocarbon Anions[20]

Oxo carbon anions that have aromatic character are derived from the hydroxy acids (8-IVa–d). They are made relatively easily. Electrochemical reduction of CO, which proceeds via radical ions[21] gives $C_4O_4^{2-}$; interaction of K and CO at 170°C gives $K_6C_6O_6$. Cyclization reactions of acetylenic ethers, for example, t-BuOC$\equiv$COt-Bu by $Co_2(CO)_8$ and treatment of the resulting butoxides with CF_3CO_2H also gives the anions.



(a) (b) (c) (d)

(8-IV)

8-7. Compounds with C—N Bonds; Cyanides and Related Compounds

An important area of "inorganic" carbon chemistry is that of compounds with C—N bonds. The most important species are the cyanide, cyanate, and thiocyanate ions and their derivatives. We can regard many of these compounds as being pseudohalogens or pseudohalides, but the analogies, although reasonably apt for cyanogen, $(CN)_2$, are not especially valid in other cases.

1. *Cyanogen.* This flammable gas (Table 8-2) is stable even though it is unusually endothermic ($\Delta Hf^\circ_{298} = 297$ kJ mol^{-1}). It can be prepared by oxidation of HCN using (*a*) O_2 with a silver catalyst, (*b*) Cl_2 over activated carbon or silica, or (*c*) NO_2 over calcium oxide-glass; the last reaction allows the NO produced to be recycled:

$$2HCN + NO_2 \longrightarrow (CN)_2 + NO + H_2O$$

Cyanogen can also be obtained from the cyanide ion by aqueous oxidation

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[19b] H. Schwartz *et al., Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 354.

[20] F. Serratosa, *Acc. Chem. Res.*, 1983, **16,** 170; *Oxocarbons,* R. West, Ed., Academic Press, New York, 1980; A. H. Schmidt, *Chem. Unserer Zeit.*, 1982, **16,** 47.

[21] See P. W. Lednor and P. C. Versloot, *J. Chem. Soc. Chem. Commun.*, **1983,** 284.

using Cu^{2+} (cf. the Cu^{2+}–I^- reaction):

$$Cu^{2+} + 2CN^- \longrightarrow CuCN + \tfrac{1}{2}(CN)_2$$

or acidified peroxodisulfate. A better procedure for dry $(CN)_2$ employs the reaction

$$Hg(CN)_2 + HgCl_2 \longrightarrow Hg_2Cl_2 + (CN)_2$$

The cyanogen molecule, $N{\equiv}C{-}C{\equiv}N$, is linear. It dissociates into CN radicals, and, like RX and X_2 compounds, it can oxidatively add to lower-valent metal atoms giving dicyano complexes, for example,

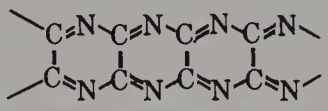
$$(Ph_3P)_4Pd + (CN)_2 \longrightarrow (Ph_3P)_2Pd(CN)_2 + 2Ph_3P$$

A further resemblance to the halogens is the disproportionation in basic solution:

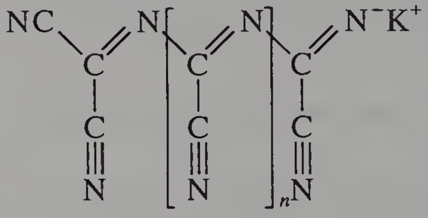
$$(CN)_2 + 2OH^- \longrightarrow CN^- + OCN^- + H_2O$$

Thermodynamically this reaction can occur in acid solution, but it is rapid only in base. Cyanogen has a large number of reactions, some of which are shown in Fig. 8-4. A stoichiometric mixture of O_2 and $(CN)_2$ burns, producing one of the hottest flames (~5050 K) known from a chemical reaction.

Impure $(CN)_2$ can polymerize on heating to give a polymer, paracyanogen (8-Va), which will depolymerize above ~850°C. Interaction of KCN and ICN gives a linear polycyanogen (8-Vb).[22]



(8-Va)



(8-Vb)

2. *Hydrogen Cyanide.* Like the hydrogen halides, HCN is a covalent, molecular substance, but is a weak acid on aqueous solution pK 9.0.

Proton transfer studies, however, show that as with normal protonic acids direct proton transfer to base B

$$B\!: + HCN \longrightarrow BH^+ + CN^-$$

occurs without participation of water.[23a]

The colorless gas is extremely toxic (though much less so than H_2S); it is formed on addition of strong acids to cyanides and on a large scale industrially by the reaction.[23b]

$$CH_4 + NH_3 \xrightarrow[Pt]{1200^\circ C} HCN + 3H_2 \qquad \Delta H = -247 \text{ kJ mol}^{-1}$$

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[22] Z. Tòth *et al.*, *Inorg. Chim. Acta*, 1986, **113**, 67.
[23a] R. A. Bednar and W. P. Jencks, *J. Am. Chem. Soc.*, 1985, **107**, 7117, 7126, 7135.
[23b] M. P. Suarez and D. G. Loffler, *J. Catal.*, 1986, **97**, 240.

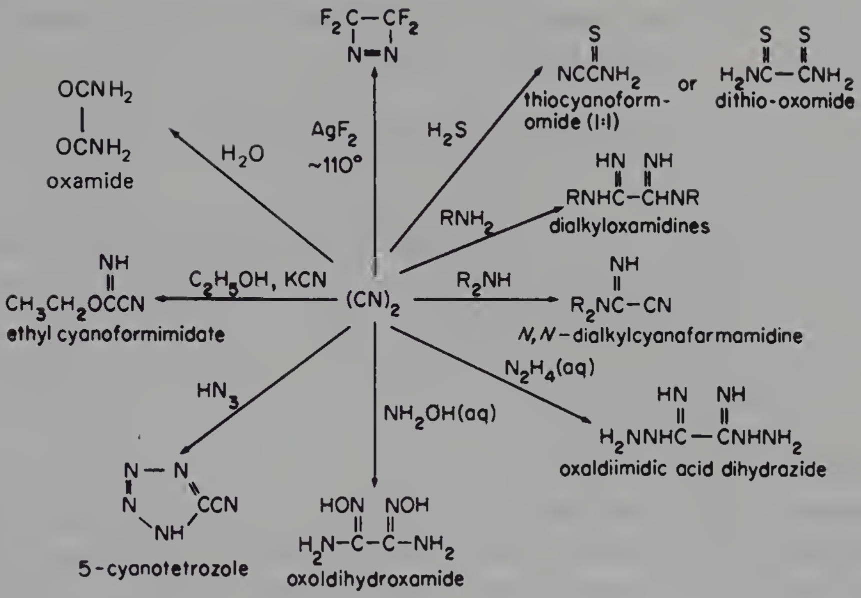

FIG. 8-4. Some reactions of cyanogen. Other products may also be obtained by fluorination (e.g., $CF_3N{=}NCF_3$).

HCN condenses at 25.6°C to a liquid with a very high dielectric constant (107 at 25°C). Here, as in similar cases, such as water, the high dielectric constant is due to association of intrinsically very polar molecules by hydrogen bonding. Liquid HCN is unstable and can polymerize violently in the absence of stabilizers: in aqueous solutions polymerization is induced by ultraviolet light.

Hydrogen cyanide is thought to have been one of the small molecules in the earth's primeval atmosphere and to have been an important source or intermediate in the formation of biologically important chemicals.[23c] Among the many polymerized products of HCN are the trimer, aminomalononitrile, $HC(NH_2)(CN)_2$, the tetramer, diaminomalononitrile, and polymers of high molecular weight. Furthermore, under pressure with traces of water and ammonia, HCN pentamerizes to adenine,[24] and HCN can also act as a condensing agent for amino acids to give polypeptides.

Industrial uses of HCN are for synthesis of methyl methacrylate and to form adiponitrile (for adipic acid and nylon) by addition to 1,3-butadiene in the presence of nickel(0) phosphite complexes (Section 28-12). Waste HCN is also oxidatively hydrolyzed to give oxamide for use as fertilizer.

3. *Cyanides.* Sodium cyanide is made by absorbing gaseous HCN in NaOH or Na_2CO_3 solution. It used to be made by the reaction of molten sodium with ammonia first to give $NaNH_2$, which reacts with carbon to give sodium

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[23c] J. P. Ferris, *Chem. Eng. News,* 1984, Aug. 27, p. 36 and references quoted; B. Vennesland, Ed., *Cyanide in Biology,* Academic Press, New York, 1981; C. Wentrup *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 916.

[24] See A. B. Boet and A. W. Schwartz, *Bioorg. Chem.,* 1983, **12,** 8.

cyanamide Na_2NCN and finally NaCN according to the stoichiometry

$$NaNH_2 + C = NaCN + H_2$$

In crystalline alkali cyanides at normal temperatures the CN^- ion is rotationally disordered and is thus effectively spherical with a radius of 1.92 Å. Hence NaCN has the NaCl structure.

The main use of NaCN is in the extraction of gold and silver from their ores by the formation of cyano complexes (Section 8-10). The ions Ag^+, Hg_2^{2+}, and Pb^{2+} give insoluble cyanides.

Calcium cyanamide (CaNCN) is made in an impure form, largely for fertilizer use, by the reaction

$$CaC_2 + N_2 \xrightarrow{\sim 1100°C} CaNCN + C \qquad \Delta H = -297 \text{ kJ mol}^{-1}$$

The cyanamide ion is linear and is isostructural and isoelectronic with CO_2.

Cyanamide (H_2NCN), a crystalline solid (mp 45°C), is prepared by hydrolysis of CaNCN:

$$CaNCN + H_2O + CO_2 = CaCO_3 + H_2NCN$$

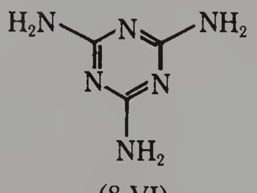
In alkaline solution at 80°C cyanamide dimerizes to dicyandiamide

$$2H_2NCN = (H_2N)_2C{=}NCN$$

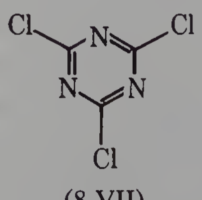
and this in turn may be converted to *melamine* (8-VI), the cyclic trimer of cyanamide, by heating in NH_3. Melamine is more easily made from urea,

$$6NH_2CONH_2 \xrightarrow{100 \text{ atm, } 300°C} C_3N_3(NH_2)_3 + 6NH_3 + 3CO_2$$

and the CO_2 and NH_3 formed can be recycled to give urea. Melamine is used for polymers and plastics.



(8-VI)



(8-VII)

4. *Cyanogen Halides.* The most important compound is *cyanogen chloride* (bp 13°C), which is obtained by the action of Cl_2 on HCN, by electrolysis of aqueous solutions of HCN and NH_4Cl, and in other ways. It may be polymerized thermally to *cyanuric chloride,* which has the cyclic triazine structure (8-VII) similar to that of melamine. The chlorine atoms in $C_3N_3Cl_3$ are labile and there is an extensive organic chemistry of triazines, since these compounds are widely used in herbicides and dye stuffs.

Fluorination of $C_3N_3Cl_3$ gives $C_3N_3F_3$, which can be cracked to give FCN. Although this is stable as a gas (bp −46°C), it polymerizes at 25°C. Cyanogen bromide is similar to ClCN. Cyanogen iodide is made by treating $Hg(CN)_2$ with I_2.

The cyanogen halides generally behave like other halogenoids.

Compounds between CN and other halogenoid radicals are known, such as NCN_3 formed by the reaction

$$BrCN + NaN_3 = NaBr + NCN_3$$

5. *Cyanate and Its Analogous S, Se, and Te Ions.* The linear ion OCN^- is obtained by mild oxidation of aqueous CN^-, for example:

$$PbO(s) + KCN(aq) \longrightarrow Pb(s) + KOCN(aq)$$

The free acid, $K = 1.2 \times 10^{-4}$, decomposes in solution to NH_3, H_2O, and CO_2. There is little evidence for $(OCN)_2$, but covalent compounds such as $P(NCO)_3$ and some metal complexes are known. The compounds are usually prepared from halides by interaction with AgNCO in benzene or NH_4OCN in acetonitrile or liquid SO_2. In such compounds or complexes, either the O or N atoms of OCN can be bound to other atoms and this possibility exists also for SCN. In general most nonmetallic elements seem to be N-bonded.

Thiocyanates are obtained by fusing alkali cyanides with sulfur; the reaction of S with KCN is rapid and quantitative, and S in benzene or acetone can be titrated with KCN in 2-propanol with bromothymol blue as indicator. Thiocyanate is the product of detoxification of CN^- in living systems. The removal of CN^- contamination in aqueous solutions by use of rhodium–cadmium sulfide suspension in aqueous alkaline sulfide solution has been studied.[25]

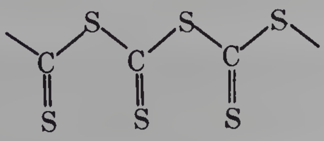
Thiocyanogen is obtained by MnO_2 oxidation

$$2SCN^- = (SCN)_2 + 2e \qquad E^\circ = -0.77 \text{ V}$$

but since it is rapidly decomposed by water it is best made by action of Br_2 on AgSCN in an inert solvent. In the free state $(SCN)_2$ rapidly and irreversibly polymerizes to brick red polythiocyanogen, but it is most stable in CCl_4 or CH_3CO_2H solution, where it exists as NCSSCN.

8-8. Compounds with C—S Bonds

Carbon Disulfide. This compound is produced by the direction interaction of C and S at high temperatures. A similar yellow liquid CSe_2 is made by the action of CH_2Cl_2 on molten selenium; it has a worse smell than CS_2 but, unlike it, is nonflammable. The selenide slowly polymerizes spontaneously, but CS_2 does so only under high pressures, to give a black solid having structure (8-VIII).



(8-VIII)

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[25] N. Serpone *et al., Inorg. Chem.*, 1986, **25**, 2135.

In addition to its high flammability in air, CS_2 is a very reactive molecule and has an extensive chemistry.[26a] It is used to prepare carbon tetrachloride industrially:

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

Important reactions of CS_2 involve nucleophilic attacks on carbon by the ions SH^- and OR^- and by primary or secondary amines, which lead, respectively, to thiocarbonates, xanthates, and dithiocarbamates, for example,

$$SCS + :SH^- \longrightarrow S_2CSH^- \xrightarrow{OH^-} CS_3^{2-}$$

$$SCS + :OCH_3^- \longrightarrow CH_3OCS_2^-$$

$$SCS + :NHR_2 \xrightarrow{OH^-} R_2NCS_2^-$$

The molecule readily undergoes insertion reactions, for example,

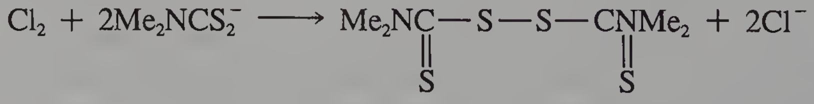
$$M(NR_2)_4 + 4CS_2 \longrightarrow M(S_2CNR_2)_4$$

The monosulfide, COS, is generally similar in its reactions.[26b]

Thiocarbonates. Thiocarbonates are readily formed by the action of SH^- on CS_2 in alkaline solution, and numerous yellow salts containing the planar ion are known. Heating CS_3^{2-} with S affords orange tetrathiocarbonates, which have the structure $[S_3C{-}S{-}S]^{2-}$. The free acids can be obtained from both these ions as red oils, stable at low temperatures.

Dithiocarbamates; Thiuram Disulfides. Dithiocarbamates are normally prepared as alkali metal salts by the action of primary or secondary amines on CS_2 in the presence of, say, NaOH. The zinc, manganese, and iron dithiocarbamates are extensively used as agricultural fungicides, and zinc salts as accelerators in the vulcanization of rubber. Alkali metal dithiocarbamates are usually hydrated and are dissociated in aqueous solution. When anhydrous, they are soluble in organic solvents in which they are associated.

On oxidation of aqueous solutions by H_2O_2, Cl_2, or $S_2O_8^{2-}$, *thiuram disulfides,* of which the tetramethyl is the commonest, are obtained:



$$Cl_2 + 2Me_2NCS_2^- \longrightarrow Me_2N\underset{\underset{\displaystyle S}{\|}}{C}{-}S{-}S{-}\underset{\underset{\displaystyle S}{\|}}{C}NMe_2 + 2Cl^-$$

Thiuram disulfides, which are strong oxidants, are also used as polymerization initiators (for, when heated, they give radicals) and as vulcanization accelerators.

Tetraethylthiuram disulfide is "Antabuse" the agent for rendering the body allergic to ethanol.

[26a] M. Yokoyama and T. Imamoto, *Synthesis,* **1984,** 797 (organic reactions of CS_2).

[26b] K. K. Pandey and H. L. Nigam, *Rev. Inorg. Chem.*, 1984, **6,** 69 (111 references).

CARBON AND CARBON COMPOUNDS AS LIGANDS

The most important complexes involving carbon-containing ligands in which carbon is bound to the metal are discussed separately; those of carbon monoxide in Chapters 22 and 23, organometallic compounds of transition elements in Chapters 25 and 26, and organometallic compounds of the main group elements in the respective chapters.

The bonding of CO and some organic molecules has been discussed in Chapter 2.

In this chapter we discuss carbon and other C-bonded ligands.

8-9. Carbon

Carbon is found in a number of cluster compounds of carbon monoxide, being derived from the latter by cleavage of the C—O bond (Chapter 23). Interstitial carbon is also found in the cluster $Gd_{10}Cl_{18}C_4$.[27] A number of complexes with M—C—M bridges[28a] are known, mainly in porphyrin compounds. Thus reduction of the tetraphenylporphyrin (tpp)FeCl by $NaBH_4$ in CH_2Cl_2 gives (tpp)Fe, which in turn with CI_4 gives $[(tpp)Fe]_2C$ as dark purple crystals. Mössbauer spectra indicate that this has Fe^{IV} so that we have (tpp) Fe═C═Fe (tpp); resonance Raman spectra also indicate Fe═C bonding.[28b] The complex can undergo both oxidation and reduction to give species with charges from −2 to +4.

8-10. Cyanide Ion

The CN^- ion can form complexes in aqueous solution with transition metal ions and particularly strong complexes with Zn^{2+}, Cd^{2+}, and Hg^{2+}.

Complexes can be formed in both low and high oxidative states, for example, $K_4[Ni^0(CN)_4]$, $K_3[Fe^{III}(CN)_6]$. Probably only in *d* metal complexes such as the Ni^0 is there any appreciable π bonding, and since CN^- is a strong nucleophile, π bonding need not be invoked to explain the stability of complexes in high oxidation states and the negative charge on the ion would decrease π acceptor behavior compared to say CO.[29a] Cyanide ion occupies a high position in the spectrochemical series, gives rise to a large nephelauxetic effect, and produces a large trans effect.

In the low oxidation states of metals, calculations suggest that the 5σ MO interacts with metal *d* orbitals, but that 4σ, 1π, and 2π MO's also participate.[29b]

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[27] S. Satpathy and O. K. Anderson, *Inorg. Chem.*, 1985, **24**, 2604.

[28a] W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 56.

[28b] D. Lançon and K. M. Kadish, *Inorg. Chem.*, 1984, **23**, 3942; T. G. Spiro *et al.*, *Inorg. Chem.*, 1984, **22**, 3987.

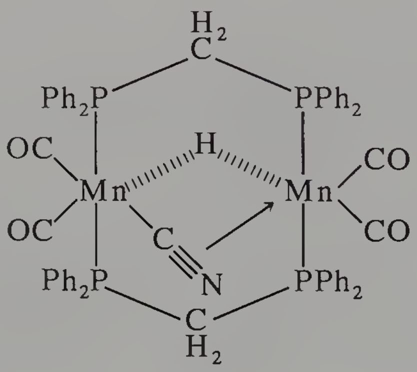
[29a] J. Murgich and T. Oja, *J. Chem. Soc. Dalton Trans.*, **1987**, 1637.

[29b] M. Sano *et al.*, *Inorg. Chem.*, 1982, **21**, 3837.

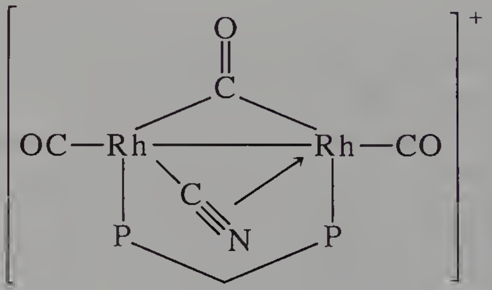
Unidentate CN^- always binds through C, but since the N atom has a lone pair (see later) cyanide can act as a bridge giving M—C—N—M links. Such bridges are found in many crystalline cyanides such as AuCN, $Zn(CN)_2$, or $Cd(CN)_2$, all of which are polymeric with chain structures. Many complex compounds such as the Prussian blues (Section 18-E-6), have linear MCNM bridges[30]; mixed metal bridges M′CNM″ can be formed. Cyanide bridge complexes can also be made by reactions of cyano complex anions,[31] for example,

$$Cp_2ZrI_2 + K_2Pt(CN)_4 \longrightarrow \{Cp_2ZrPt(CN)_4\}_n$$

A second type of bridge is that where CN acts as a 4*e* donor as in (8-IXa) and (8-IXb)[32]



(8-IXa)



(8-IXb)

In $[Cp_2Mo_2(CO)_4\mu\text{-}CN]^-$ nmr study shows that the CN group exchanges its position by a "windscreen wiper" effect similar to that involved in exchanges via semibridging CO groups (Chapter 22).

Most cyano complexes have the general formula $[M^{n+}(CN)_x]^{(x-n)-}$ and are anionic, but mixed complexes such as $[M(CN)_5X]^{n-}$, X = H_2O, NH_3, CO, NO, H, or halogen are common. Certain cyano complexes can be obtained in different oxidation states with the same geometry $M(CN)_x^{n-}$, $M(CN)_x^{(n+1)-}$, $M(CN)_x^{(n+2)-}$ thus resembling bipyridyl (Section 12-11) and dithiolene (Section 13-16) complexes. Some compounds, for example, $Zn_3[Co(CN)_6]_2$ behave like molecular sieves and absorb small molecules.[33]

The *anhydrous acids* can often be isolated, for example, $H_3[Rh(CN)_6]$ and $H_4[Fe(CN)_6]$. These differ from those of other complex ions such as $[PtCl_6]^{2-}$ or $[SiF_6]^{2-}$ that are invariably hydrated and are H_3O^+ salts.

The hydrogen atoms in the cyanides are H-bonded M—CN---H---NC—M[34] and different types of structure arise depending on the stoichiometry. For example, in $H[Au(CN)_4]$ there are sheets. For octahedral anions

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[30] L. P. Michiels *et al., Inorg. Chim. Acta,* 1985, **100,** 211; C. A. Bignozzi and F. Scandol, *Inorg. Chem.,* 1984, **23,** 1540; R. E. Hester and E. M. Nour, *J. Chem. Soc. Dalton Trans.,* **1981,** 939.

[31] W. M. Risen *et al., Inorg. Chem.,* 1981, **20,** 4447.

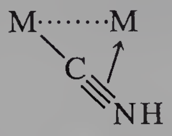
[32] A. J. Deeming *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 2669; S. P. Deraniyagala and K. R. Grundy, *Inorg. Chim. Acta,* 1984, **84,** 205.

[33] G. Boxhoorn *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 1305.

[34] See W. Beck *et al., Angew. Chem. Int. Ed. Engl.,* 1984, **23,** 377 for references.

there is a difference in structure depending on whether the number of protons equals half the number of cyanide ions. For $H_3[M(CN)_6]$ compounds an infinite, regular three-dimensional array is formed in which the hydrogen bonds are perhaps symmetrical, whereas in other cases the structures appear to be more complicated.

The formation of linear bridges implies basicity on the N atom of a MCN group and indeed methylation or protonation can occur to give isocyano groups, MCNMe, or MCNH[35a] as in $W(CO)_5CNH$; bridging cyanides of the (8-IX) type can also be protonated to μ, η^2-HNC groups (8-X).[35b]



(8-X)

The formation of complexes with Lewis bases,[35c] especially BPh_3, that is, $MCNBPh_3$, is of importance in the hydrocyanation of alkenes by nickel complexes (Section 28-12).

Finally, *cyanogen* can act as a ligand:

$$(AgAsF_6)_n + Zn(CN)_2 \longrightarrow \{Ag[(CN)_2]_2\}_n(AgF_6)_n$$

where there is an AgNC—CNAg group.[36]

8-11. Isocyanides[37]

Isocyanides (RNC) are stronger σ donors than CO although CF_3NC is a much better π acceptor than other isocyanides. Like CN^-, they form complexes in both low oxidation states, for example $Cr(CN\textit{t}\text{-}Bu)_6$, as well as in positive oxidation states, for example $[Mn(CNR)_6]^{2+}$, where CO analogues are not known and π bonding is of little significance. Table 8-3 shows that the extent to which the CN stretching frequencies in $Cr(CNAr)_6$ and $Ni(CNAr)_4$ molecules are lowered relative to the frequencies of the free CNAr molecules exceeds that by which the CO modes of the corresponding carbonyls lie below the frequency of CO. The difference between CO and RNC is also shown by the possibility of oxidations as with $Cr(CNPh)_6$, which can be obtained with charges 0, +1, +2 and +3 and for which no chromium carbonyl analogues exist.[38]

[35a] W. P. Fehlhammer *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 863.

[35b] A. J. Deeming and S. Donovan-Mtonzi, *J. Chem. Soc. Dalton Trans.*, **1985,** 1609.

[35c] C. Woodcock and D. F. Shriver *Inorg. Chem.*, 1986, **25,** 2137.

[36] H. W. Roesky *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 417.

[37] E. Singleton and H. E. Oosthuizen, *Adv. Organomet. Chem.*, 1983, **22,** 209; Y. Yamamoto, *Coord. Chem. Rev.*, 1980, **32,** 193; M. D. Rausch *et al., Organometallics*, 1986, **5,** 2465 (Ti, Zr, Hf); H. Fischer *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 744 ($CNCR_2$ types).

[38] D. A. Bohling and K. R. Mann, *Inorg. Chem.*, 1984, **23,** 1426.

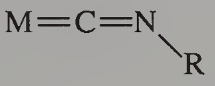
TABLE 8-3
Lowering of CO and CN Frequencies in Analogous Compounds, Relative to Values for Free CO and CNAr[a]

Molecule[b]	$\Delta\upsilon$ (cm^{-1}) for each fundamental mode		
$Cr(CO)_6$	43	123	160
$Cr(CNAr)_6$	68	140	185
$Ni(CO)_4$	15	106	
$Ni(CNAr)_4$	70	125	

[a] Ar represents C_6H_5 and p-$CH_3OC_6H_4$.

[b] Data for isonitriles from F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, 1961, **83,** 351.

Although terminal MCNR groups are normally close to linear with CNC angles of 165 to 179°, *bent isocyanides* with angles ~130 to 135° are known.[39] This situation is thus similar to other linear/bent systems like M—NO or MNNR (Section 10-20). The bending can be accounted for by a contribution of (8-XIa) to (8-XIb), both representing extreme forms:


$M{=}C{=}N{-}R$

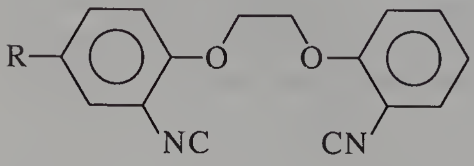
(8-XIa)

$M{-}C{\equiv}NR$

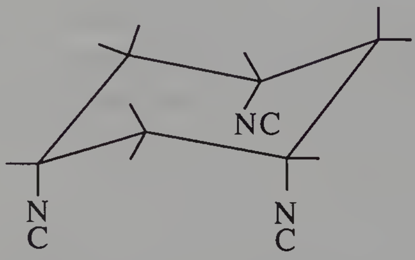
(8-XIb)

In $Ru(CN\textit{t}\text{-}Bu)_4PPh_3$, for example, the PPh_3 and bent *t*-BuNC groups are equatorial with the almost linear *t*-BuNC groups in axial positions. The ir bands for bent groups are in the 1830 to 1870-cm^{-1} region compared to bands ~1960 cm^{-1} for linear RNC groups.

Diisocyanides[40] such as $CN(CH_2)_nNC$ and $CNC(Me)_2(CH_2)_2C(Me)_2NC$ give chelate octahedral complexes of Cr, Mn, Fe, and Co in 0 to +3 oxidation states and square Rh^I cations. They can also act as bridges between metal atoms in Ni, Pd, Pt, or Rh complexes such as $[Rh_2(\mu\text{-}L)_4]^{2+}$. Other isocyanides are



and



but the *cis,cis,*1,3,5-tricyanocyclohexane does not act as a tridentate to a triangle of metals.

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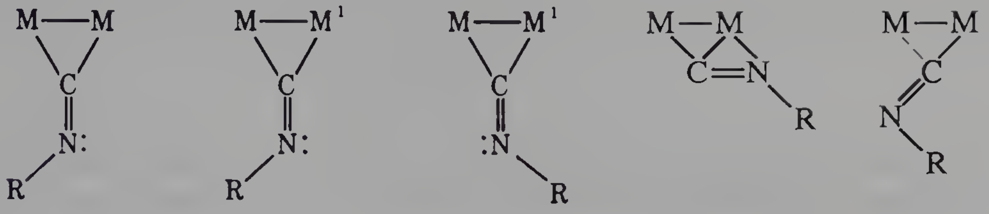
[39] F. G. A. Stone *et al., J. Chem. Soc. Dalton Trans.,* **1980,** 1779.

[40] H. B. Gray *et al., Inorg. Chem.,* 1984, **23,** 2572; R. J. Angelici *et al., J. Organomet. Chem.,* 1984, **260,** 347.

Bridging isocyanides[41] are of several types:



The CNC bonds are greatly bent with angles ~120°C. There may also be exchange between terminal and bridge groups as in $Fe_2(\mu\text{-}CNEt)_3(CNEt)_6$[42a] possibly via semibridged species.[42b] Triply bridging isocyanides are rare but one example[43] is $Cp_3Co_3(\mu_3\text{-}NCR)(\mu_3\text{-}S)$.

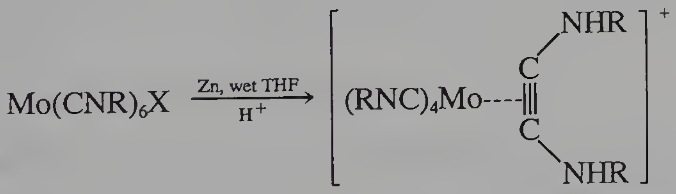
Isocyanide complexes may be obtained by substitution of metal carbonyls but high temperatures are required and photolytic methods are preferable.[44] They can also be made from halides and by electrophilic attacks[45] on cyanide complexes as just noted, generally

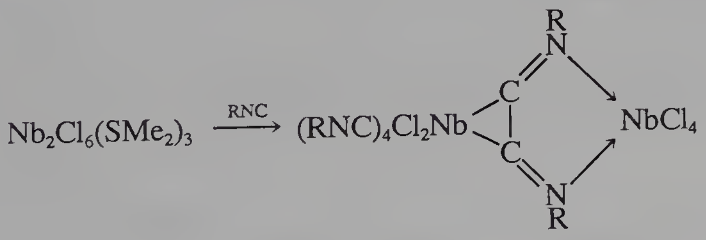
$$L_nMCN \xrightarrow{RX} L_nMCNR^+ + X^-$$

Reactions of Isocyanide Complexes. Isocyanide complexes undergo many types of reaction. Some of the more important are the following:

1. *Coupling Reactions,*[39,46] which lead to C—C bond formation.

Some examples are





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[41] Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, 1986, **25**, 3327; N. A. Bailey *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 341.

[42a] J. M. Bassett *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981**, 219.

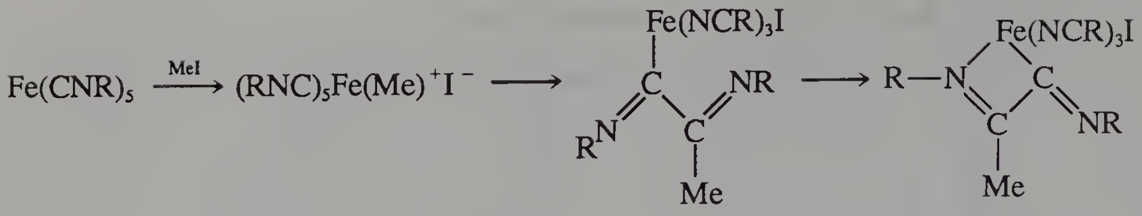
[42b] C. P. Kubiak *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 754.

[43] A. R. Manning *et al.*, *J. Chem. Soc. Chem. Commun.*, **1983**, 1071.

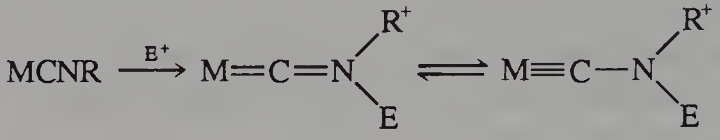
[44] N. J. Colville *et al.*, *J. Chem. Soc. Dalton Trans.*, **1982**, 1069.

[45] See, for example, G. J. Baird and S. G. Davies, *J. Organomet. Chem.*, 1984, **262**, 215; A. Bell and D. A. Edwards, *J. Chem. Soc. Dalton Trans.*, **1984**, 1317.

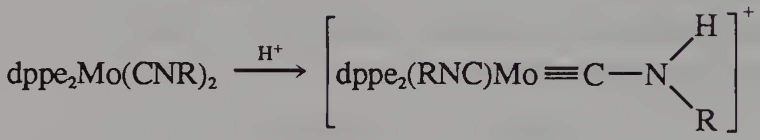
[46] S. Warner and S. J. Lippard, *Organometallics*, 1986, **5**, 1716; D. Lentz, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 525; R. D. Adams *et al.*, *J. Am. Chem. Soc.*, 1980, **102**, 7476; F. A. Cotton *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 6987.



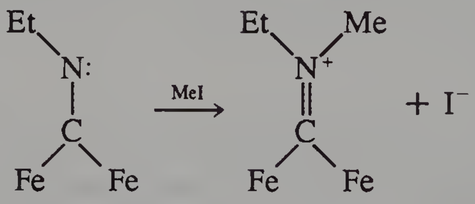
2. *Electrophilic attacks*[42,47] can give alkylidyne compounds (Chapter 25)



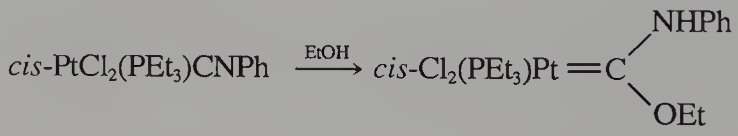
a specific example being

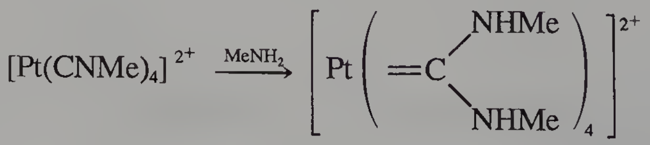


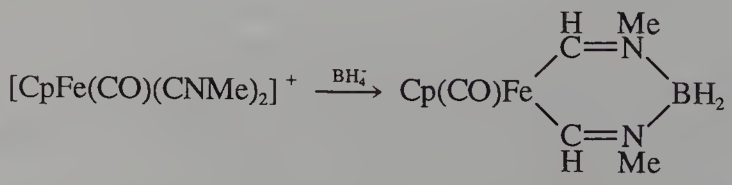
while bridging isocyanides have high nucleophilicity and are readily attacked, for example,



3. *Nucleophilic attacks* either at C or at N can give alkylidene complexes (Section 25-9), for example,







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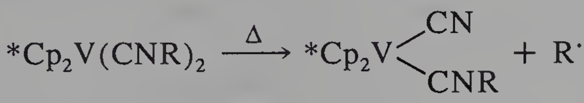
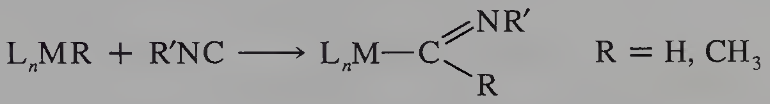
[47] A. R. Manning and P. Murray, *J. Chem. Soc. Dalton Trans.*, **1986**, 2399; R. L. Richards *et al.*, *J. Chem. Soc. Dalton Trans.*, **1980**, 492.

4. *Dealkylation*[48] also can occur in some reactions to give a cyano complex:



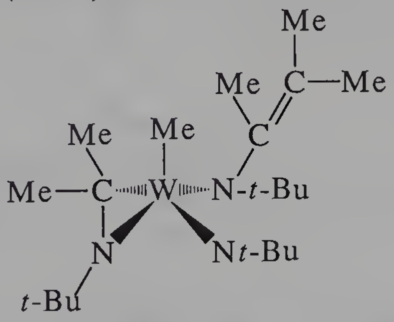
$$*Cp_2V(CNR)_2 \xrightarrow{\Delta} *Cp_2V(CN)(CNR) + R^{\cdot}$$

Finally, although not a reaction of isocyanide complexes as such, except as labile intermediates, it can be noted that metal hydrido or alkyl compounds can undergo *insertion reactions* (Chapter 27) to give *acylimidoyl* complexes[49a]:



$$L_nMR + R'NC \longrightarrow L_nM{-}C({=}NR')R \qquad R = H, CH_3$$

More complicated reactions can follow as in the rection of WMe_6 with *t*-BuNC, which results in (8-XII).

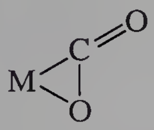


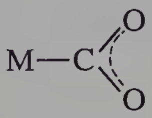
(8-XII)

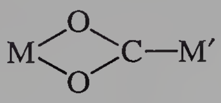
Isocyanide complexes are involved in catalytic hydrogenations (Chapter 28) of isocyanides.[49b]

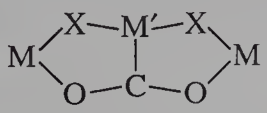
8-12. Carbon Dioxide, Carbon Disulfide[50]

Carbon Dioxide.[51] The three cumulenes, CO_2, CS_2, and COS, X=C=X, react in rather similar ways to give complexes but those of CO_2 have been best studied because of the hope of direct conversion of CO_2 into organic chemicals. In early studies, some complexes believed to be of CO_2 were found to be carbonates, due to interaction with traces of oxygen, but authentic compounds of the following types[52] are known:









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[48] C. Floriani *et al.*, *Inorg. Chem.*, 1984, **23**, 1739; S. J. Lippard *et al.*, *Organometallics*, 1982, **1**, 142.

[49a] See, for example, I. P. Rothwell *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 390; J. E. Bercaw *et al.*, *Organometallics*, 1986, **5**, 443.

[49b] S. T. McKenna *et al.*, *Organometallics*, 1986, **5**, 2233.

[50] J. A. Ibers, *Chem. Soc. Rev.*, **1982**, 57; C. Mealli *et al.*, *Inorg. Chem.*, 1984, **23**, 56.

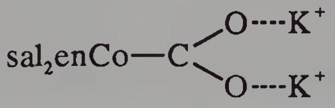
[51] D. J. Darensbourg and R. A. Kudaroski, *Adv. Organomet. Chem.*, 1983, **22**, 129; D. A. Palmer and R. van Eldik, *Chem. Rev.*, 1983, **83**, 651.

[52] E. Carmona *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 2286; T. Herskovitz *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 5914; K. G. Caulton *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 8309; C. T. Tso and A. R. Cutter, *J. Am. Chem. Soc.*, 1986, **108**, 6069.

The η^2 compounds are best characterized and a good example is *trans*-$Mo(CO_2)_2(PMe_3)_4$. These have ir bands at ~1660 and 1630 cm^{-1}, whereas η^1 compounds absorb at ~1550 and 1220 cm^{-1}.

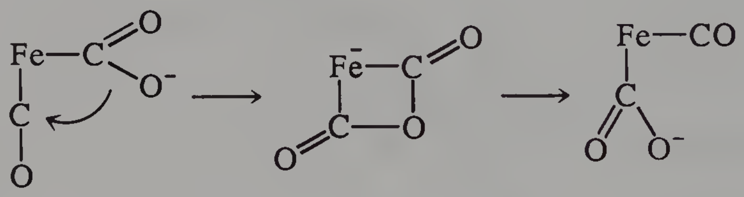
Examples of the η^1 type are $Cl(diars)Rh(\eta^1\text{-}CO_2)$ and $[(CO)_5WCO_2]^-$.

η^1-Complexes are also formed by Schiff base compounds of alkali metals (Section 4-6) where part of the stability is probably attributable to O----K^+ interaction[53a]:

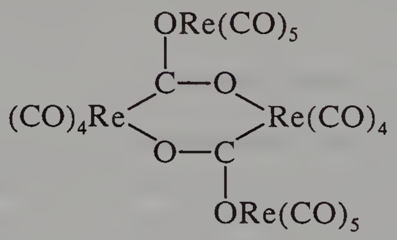


and also by Co and Ni azamacrocycles.[53b]

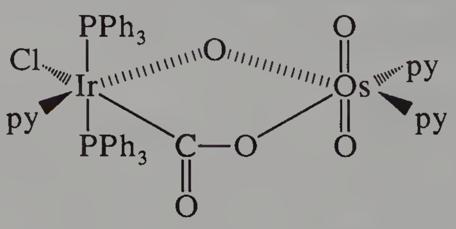
η^1-Species have been invoked in intramolecular exchanges to oxygen in carbon monoxide in $CpFe(CO)_2CO_2^-$



Bridged CO_2 compounds have been characterized in clusters (Chapter 23) and in compounds such as (8-XIIIa and b)



(8-XIIIa)



(8-XIIIb)

Carbon dioxide readily undergoes insertion reactions[51] (Chapter 27) probably via initial CO_2 complexing, with metal alkoxides, dialkylamides, and metal

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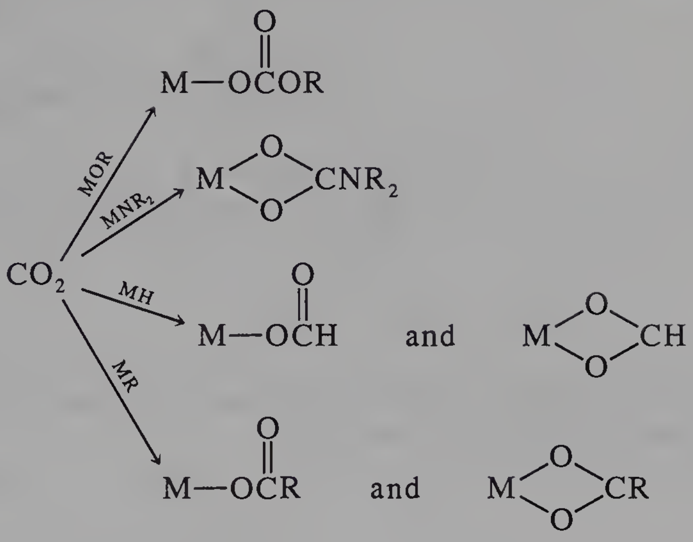
[53a] C. Floriani *et al.*, *J. Am. Chem. Soc.*, 1982, **104,** 5082.

[53b] D. A. Gangi and R. R. Durand, *J. Chem. Soc. Chem. Commun.*, **1986,** 697.

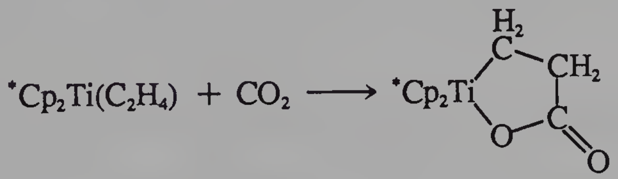
hydrides and alkyls:



There are a number of reactions of CO_2 with metal complexes in which prior coordination is likely. With complexes of oxophilic metals like Ti or Zr, deoxygenation to CO may occur while in others disproportionation to give CO and CO_3^{2-} occurs[54]; an example of the latter reaction is

$$2Ru(CO)_4^{2-} + 2CO_2 \longrightarrow Ru_2(CO)_8^{2-} + CO + CO_3^{2-}$$

The formation of strong Ti—O bonds also provides the driving force for the reaction[55]



The electron rich metal center in *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ also reacts with CO_2 to give a complex where H is transferred from ethylene to give an acrylic acid complex corresponding to the insertion at Mo[56]:

$$CH_2{=}CH_2 + CO_2 \longrightarrow CH_2{=}CH{-}CO_2H$$

Carbon Disulfide. Carbon disulfide is a very versatile ligand that gives a wide variety of complexes which, apart from η^1-CS_2 compounds all involve

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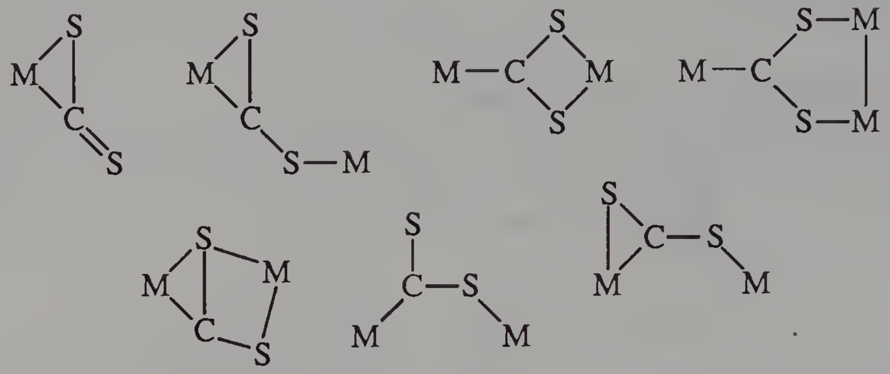
[54] C. Bianchini *et al.*, *Inorg. Chem.*, 1984, **23**, 2731; G. R. Lee and N. J. Cooper, *Organometallics*, 1985, **4**, 1467; S. G. Shore *et al.*, *Organometallics*, 1985, **4**, 1483.

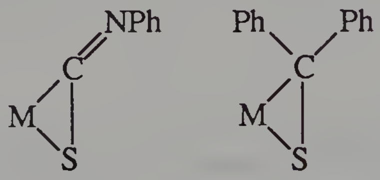
[55] S. A. Cohen and J. E. Bercaw, *Organometallics*, 1985, **4**, 1006.

[56] E. Carmona *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 5529.

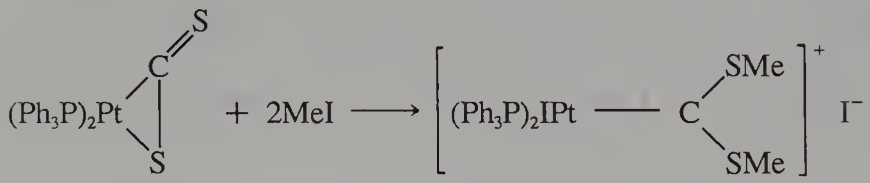
bonding to carbon[57]:

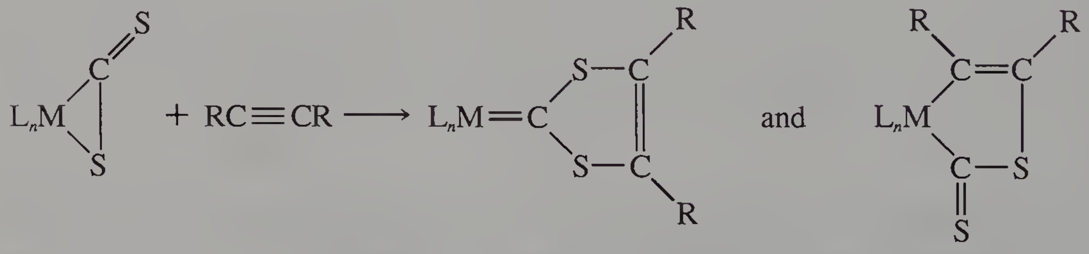


Not only COS but CSSe and CSe_2 give similar species,[58] as well as thiocyanates, cyanates, Ph_2CS, and so on,[59]

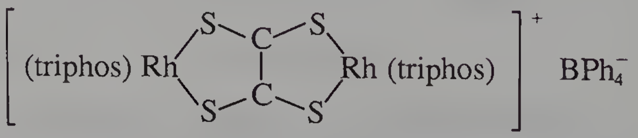


The coordinated CS_2 is very reactive and a large number of reactions are known.[60] A few are the following:





$[RhCl(C_2H_4)_2]_2 + CS_2 + \text{(triphos)} + NaBPh_4 \longrightarrow$



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[57] J. A. Ibers *et al., Inorg. Chem.*, 1983, **22,** 411; D. H. Farrer *et al., Inorg. Chem.*, 1984, **23,** 3258; R. A. Andersen *et al., Inorg. Chem.*, 1986, **25,** 1756; C. Bianchini *et al.*, in *Stereochemistry of Organometallic and Inorganic Compounds,* I. Bernal, Ed. Elsevier, Amsterdam, 1986.

[58] See, for example, D. Kolb and H. Werner, *J. Organomet. Chem.*, 1984, **268,** 49.

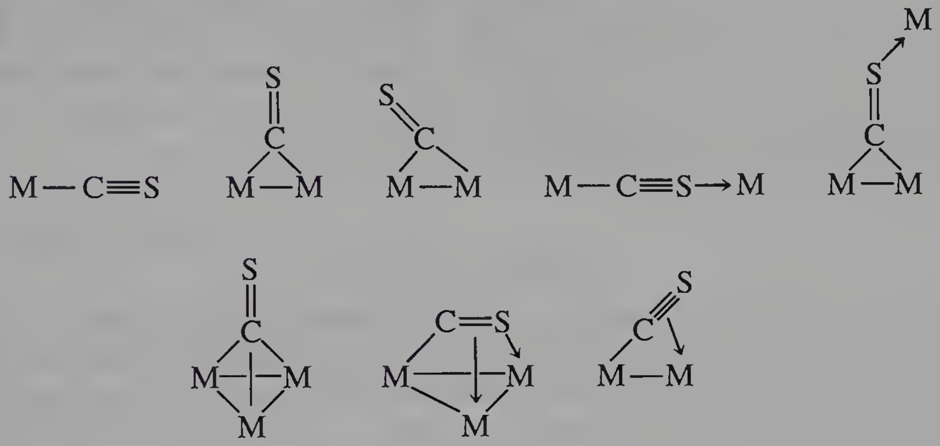
[59] C. Floriani *et al., Inorg. Chem.*, 1984, **23,** 3532; C. Bianchini *et al., Organometallics,* 1983, **2,** 1834.

[60] C. Bianchini *et al., Organometallics,* 1986, **5,** 1733; R. Colton *et al., Inorg. Chem.*, 1984, **23,** 720; A. Walker *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 2595; L. F. Dahl *et al., J. Am. Chem. Soc.*, 1987, **109,** 4739.

Like CO_2, CS_2 undergoes insertion reactions with M—H, M—R, and so on, bonds (Chapter 27).[61]

8-13. Thiocarbonyl Compounds[62]

Although unlike CO, CS is not stable, polymerizing above −160°C,[63] many MCS compounds can be made. The types of bonding are similar to those of CO:



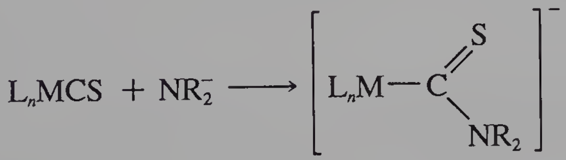
In general, linear CS is a stronger σ donor and π acceptor than CO, but this depends on the electron richness of the metal and in some cases the reverse is true.[64]

The compounds are often made by desulfurization of CS_2 complexes but they can also be made by interaction of $CSCl_2$ with, for example, $Fe(CO)_4^{2-}$, and in other ways such as[65]:

$$(Me_3P)_2(CO)_2Fe(\eta^2\text{-}CS_2Me) \xrightarrow{Na/Hg} Fe(CS)(CO)_2(PMe_3)_2$$

The CS group can undergo a wide variety of reactions including electrophilic attack at sulfur and nucleophilic attack at C, for example,

$$L_nMCS + MeI \longrightarrow [L_nMCSMe]^+I^-$$



$$L_nMCS + NR_2^- \longrightarrow \left[L_nM\text{—}C\begin{matrix}{=S}\\{\text{—}NR_2}\end{matrix} \right]^-$$

[61] See, for example, C. Bianchini *et al., Organometallics,* 1985, **4,** 1014.

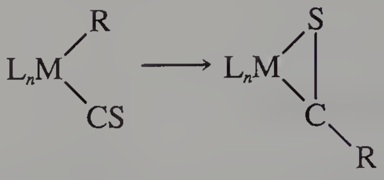
[62] P. V. Broadhurst, *Polyhedron,* 1985, **4,** 1801 (155 references and much data); R. J. Angelici *et al., J. Am. Chem. Soc.,* 1986, **108,** 5154; S. Lotz *et al., Inorg. Chem.,* 1986, **25,** 3053; L. Busetto *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 1791.

[63] K. J. Klabunde *et al., J. Am. Chem. Soc.,* 1984, **106,** 267.

[64] R. A. Jacobsen *et al., Inorg. Chem.,* 1987, **26,** 452.

[65] D. Touchard *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 37.

and intramolecular transfers:



8-14. Other C-Bonded Ligands

Acetonitrile (Section 10-15), although usually bonded through nitrogen, is acidic and can give species with (H)M—CH_2CN groups while CH_3NO_2 similarly can give (H)M—CH_2NO_2 groups.[66] Carbon bonded *acetylacetonates* are noted in Section 12-15; C-bonded dipyridyls and cyclo metallated *N*-compounds are discussed in Section 27-9.

Additional References

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Craig, P., Ed., *Organometallic Compounds in the Environment,* Pitmans, London 1986 (Hg, Sn, Pb, As, Si etc.,).

Ito, T., and A. Yamamoto, in *Organic and Bioinorganic Chemistry of Carbon Dioxide,* S. Inoue and N. Yamazaki, Eds., Kodasha Ltd., Tokyo, 1982.

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[66] J. P. Fackler *et al., Organometallics,* 1984, **3,** 1312; L. Randaccio *et al., Inorg. Chem.,* 1981, **20,** 2722.

Chapter Nine

The Group IVA(14) Elements: Si, Ge, Sn, Pb

GENERAL REMARKS

9-1. Group Trends

There is no more striking example of an enormous discontinuity in general properties between the first- and the second-row elements followed by a relatively smooth change toward more metallic character thereafter than in Group IVA(14). Little of the chemistry of silicon can be inferred from that of carbon. Carbon is strictly nonmetallic; Si is essentially nonmetallic; germanium is metalloid; tin and especially lead are metallic. Some properties of the elements are given in Table 9-1.

Catenation. Though not as extensive as in carbon chemistry, catenation is an important feature of Group IVA(14) chemistry in certain types of compounds. Extensive chains occur in Si and Ge hydrides (up to Si_6H_{14} and Ge_9H_{20}), in Si halides (only Ge_2Cl_6 is known), and in certain organo compounds. For Sn and Pb catenation occurs only in organo compounds. Lead and Sn form compounds such as Na_4Pb_9 and Na_2Sn_5 that contain polyhedral clusters of metal atoms. Silicon also forms a few cluster anions such as the Si_4 ion in $BaSi_2$.

However, there is a general if not entirely smooth decrease in the tendency to catenation in the order $C \gg Si > Ge \approx Sn \gg Pb$, which may be ascribed partly to diminishing strength of the C—C, Si—Si, Ge—Ge, Sn—Sn, and Pb—Pb bonds (Table 9-2).

Bond Strengths. The strengths of single covalent bonds between Group IVA(14) atoms and other atoms (Table 9-2) generally decrease from Si to Pb. In some cases there is an initial rise from C to Si followed by a decrease. These energies do not, of course, reflect the ease of heterolysis of bonds, which is the usual way in chemical reactions; thus, for example, in spite of the high Si—Cl or Si—F bond energies, compounds containing these bonds are highly reactive. Since the charge separation in a bond is a critical factor, the bond ionicities must also be considered when interpreting the reactivities

TABLE 9-1
Some Properties of the Group IVA(14) Elements

Element	Electronic structure	mp (°C)	bp (°C)	Ionization enthalpies ($kJ\ mol^{-1}$)				Electro-negativity	Covalent radius[a] (Å)
				1st	2nd	3rd	4th		
C	$[He]2s^22p^2$	>3550[b]	4827	1086	2353	4618	6512	2.5–2.6	0.77
Si	$[Ne]3s^23p^2$	1410	2355	786.3	1577	3228	4355	1.8–1.9	1.17
Ge	$[Ar]3d^{10}4s^24p^2$	937	2830	760	1537	3301	4410	1.8–1.9	1.22
Sn	$[Kr]4d^{10}5s^25p^2$	231.9	2260	708.2	1411	2942	3928	1.8–1.9	1.40[c]
Pb	$[Xe]4f^{14}5d^{10}6s^26p^2$	327.5	1744	715.3	1450	3080	4082	1.8	1.44[d]

[a] Tetrahedral (i.e., sp^3 radii).

[b] Diamond.

[c] Covalent radius of Sn^{II}, 1.63 Å.

[d] Ionic radius of Pb^{2+}, 1.33 (CN 6); of Pb^{4+}, 0.775 Å.

toward nucleophilic reagents. Thus Si—Cl bonds are much more reactive than Si—C bonds because, though stronger, they are more polar, $Si^{\delta+}$—$Cl^{\delta-}$, rendering the silicon more susceptible to attack by a nucleophile such as OH^-.

It may be noted also that (*a*) there is a steady decrease in M—C and M—H bond energies; (*b*) M—H bonds are stronger than M—C bonds.

Electronegativities. The electronegativities of the Group IVA(14) elements have been a contentious matter. Although C is generally agreed to be the most electronegative element, certain evidence, some of it suspect, has been interpreted as indicating that Ge is more electronegative than Si or Sn. It is to be remembered that electronegativity is a very qualitative matter, and it seems most reasonable to accept a slight progressive decrease Si → Pb.

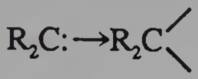
It can be noted that Zn in HCl reduces only germanium halides to the hydrides, which suggests a higher electronegativity for Ge than for Si or Sn. Also, dilute aqueous NaOH does not affect GeH_4 or SnH_4, but SiH_4 is rapidly hydrolyzed by water containing a trace of OH^-. This is consistent with, though not necessarily indicative of, the Ge—H or Sn—H bonds either being nonpolar or having the positive charge on hydrogen. Finally, germanium halides are hydrolyzed in water only slowly and reversibly.

TABLE 9-2
Approximate Average Bond Energies[a]

Group IVA(14) element	Energy of bond ($kJ\ mol^{-1}$) with							
	Self	H	C	F	Cl	Br	I	O
C	356	416		485	327	285	213	336
Si	210–250	323	250–335	582	391	310	234	368
Ge	190–210	290	255	465	356	276	213	
Sn	105–145	252	193		344	272	187	

[a] For thermodynamic data, bond distances and some other properties of Si compounds see M. J. S. Dewar *et al.*, *Organometallics,* 1986, **5,** 375.

The Divalent State. The term "lower valence" indicates the use of fewer than four electrons in bonding. Thus although the *oxidation state* of carbon in CO is usually formally taken to be 2, this is only a formalism, and carbon uses more than two valence electrons in bonding. True divalence is found in carbenes and the Si, Ge, and Sn analogues (MR_2) discussed later; the high reactivity of carbenes may result from the greater accessibility of the sp^2 hybridized lone pair in the smaller carbon atom. The stable divalent compounds of the other elements can be regarded as carbenelike in the sense that they are bent with a lone pair and undergo the general type of carbene reactions to give new bonds to the element, that is,



However, the divalent state becomes increasingly stable down the group and is dominant for lead.

Inspection of Table 9-1 clearly shows that this trend cannot be explained exclusively in terms of ionization enthalpies, since these are essentially the same for all the elements Si–Pb. The "inert pair" concept (Section 1-5) probably holds only for lead ion Pb^{2+}_{aq} where there could be a $6s^2$ configuration.[1] In more covalent Pb^{II} compounds and most Sn^{II} compounds there are stereochemically active lone pairs—indeed some MX_2 and MR_2 compounds of Ge and Sn can act as donor ligands.

Other factors that undoubtedly govern the relative stabilities of the oxidation states are promotion energies, bond strengths for covalent compounds, and lattice energies for ionic compounds. Taking first the promotion energies, it is rather easy to see why the divalent state becomes stable if we remember that the M—X bond energies generally decrease in the order Si—X, Ge—X, Sn—X, Pb—X(?). (The factor that stabilizes CH_4 relative to $CH_2 + H_2$ despite the much higher promotional energy required in forming CH_4, is the great strength of the C—H bonds and the fact that two more of these are formed in CH_4 than in CH_2.) Thus if we have a series of reactions $MX_2 + X_2 = MX_4$ in which the M—X bond energies are decreasing, it is obviously possible that this energy may eventually become too small to compensate for the $M^{II} \rightarrow M^{IV}$ promotion energy and the MX_2 compound becomes the more stable. The progression is illustrated by ease of addition of chlorine to the dichlorides:

$$GeCl_2 + Cl_2 \longrightarrow GeCl_4 \qquad \text{(very rapid at 25°C)}$$

$$SnCl_2 + Cl_2 \longrightarrow SnCl_4 \qquad \text{(slow at 25°C)}$$

$$PbCl_2 + Cl_2 \longrightarrow PbCl_4 \qquad \text{(only under forcing conditions)}$$

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[1] P. G. Harrison *et al.*, *J. Chem. Soc. Dalton Trans.*, **1983,** 1845.

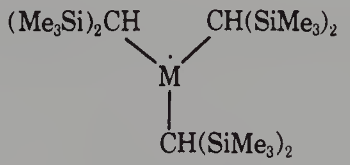
Note that even $PbCl_4$ decomposes except at low temperatures, while $PbBr_4$ and PbI_4 do not exist, probably owing to the reducing power of Br^- and I^-. For ionic compounds matters are not so simple but, since the sizes of the (real or hypothetical) ions, M^{2+} and M^{4+}, increase down the group, it is possible that lattice energy differences no longer favor the M^{4+} compound relative to the M^{2+} compound in view of the considerable energy expenditure required for the process

$$M^{2+} \longrightarrow M^{4+} + 2e$$

Of course, there are few compounds of the types MX_2 or MX_4 that are entirely covalent or ionic (almost certainly no ionic MX_4 compounds), so that the previous arguments are oversimplifications, but they indicate roughly the factors involved. For solutions no simple argument can be given, since Sn^{4+} and Pb^{4+} probably have no real existence.

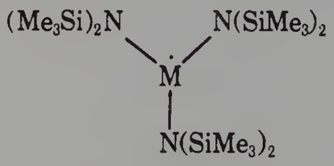
It should be noted that compounds appearing from their stoichiometries to contain Group IVA(14) elements in formal oxidation states between II and IV are generally mixed valence compounds. For example, Ge_5F_{12} consists of four Ge^{II} and one Ge^{IV} suitably coordinated and linked by fluorine atoms. Similarly Sn_3F_8 is built of octahedral $Sn^{IV}F_6$ and pyramidally coordinated $Sn^{II}F_3$ in 1:2 ratio, linked by shared F atoms.

The only authentic stable compounds of Group IVA(14) elements with formal oxidation number III are of the types (9-I) and (9-II). Type (9-Ia) has a half-life of only ~10 min, but the others have lives of 3 to 12 months. The stability of these radicals is due to the great steric hindrance to attack resulting from the bulk of the ligands.



a. M = Si
b. M = Ge
c. M = Sn

(9-I)



a. M = Ge
b. M = Sn

(9-II)

Tin, like iron, is an element for which Mössbauer spectroscopy can be broadly useful. Using the Sn^{119m} nucleus, isomer shift (IS) measurements allow one to determine oxidation number and to some extent to estimate structural and bonding features.[2] The IS values are usually in the order $Sn^{II} > Sn^0 > Sn^{IV}$, though this cannot be trusted absolutely.

Multiple Bonding. In the early 1960s, unstable transient intermediates

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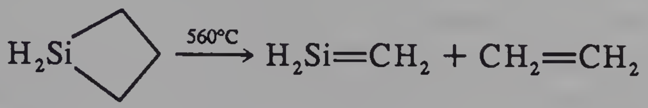
[2] See, for example, R. Barbieri and A. Silvestri, *J. Chem. Soc. Dalton Trans.*, **1984,** 1239 (112 compounds of five-coordinate Sn).

with Si═C, $p\pi$–$p\pi$ bonding were discovered in reactions such as

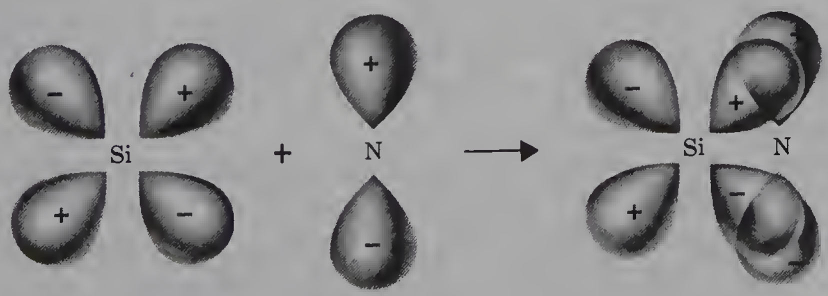


Compounds $R_2Si{=}CR'_2$ and $R_2M{=}MR'_2$ for Si, Ge, and Sn have now been isolated provided that bulky groups are used as discussed in Section 9-13.

Although stoichiometric similarities occur, for example, CO_2 and SiO_2, Me_2CO, and Me_2SiO, there is no structural or chemical similarity. Also, reactions that might have been expected to yield a carbonlike product do not do so—thus dehydration of silanols, $R_2Si(OH)_2$, produces $(R_2SiO)_n$ and $R_2(OH)SiOSi(OH)R_2$.

Multiple bonding of the $d\pi$–$p\pi$ type for Si is quite well established, especially in bonds to O and N. It is important to note, however, that this does not necessarily lead to conjugation in the sense usual for carbon multiple bond systems. Observations of the following types provide evidence for $d\pi$–$p\pi$ bonding.

1. Trisilylamine $(H_3Si)_3N$ differs from $(H_3C)_3N$ in being planar rather than pyramidal[3a] and in being a very weak Lewis base; $(H_3Si)_2NH$ is also planar while H_3SiNCO has a linear Si—N—C—O chain in the vapor phase, although there is some bending with $\angle$Si—N—C = 158° and $\angle$N—C—O = 176° in the crystalline solid. These observations can be explained by supposing that nitrogen forms dative π bonds to the Si atoms. In the planar state of $(H_3Si)_3N$, the nonbonding electrons of N would occupy the $2p_z$ orbital, if we assume that the N—Si bonds are formed using sp_xp_y trigonal hybrid orbitals of nitrogen. Silicon has empty $3d$ orbitals, which are of low enough energy to be able to interact appreciably with the nitrogen $2p_z$ orbital. Thus the N—Si π bonding is due to the kind of overlap indicated in Fig. 9-1. It is the additional bond strength to be gained by this $p\pi$–$d\pi$ bonding that causes the NSi_3



Empty $3d$ orbital of Si

Filled $2p_z$ orbital of N

Overlap

FIG. 9-1. Formation of a $d\pi$–$p\pi$ bond between Si and N in trisilylamine.

[3a] P. Livant *et al.*, *Inorg. Chem.* 1983, **22**, 895.

skeleton to take up a planar configuration, whereas with $N(CH_3)_3$, where the carbon has no low-energy d orbitals, the σ bonding alone determines the configuration, which is pyramidal as expected.

$(H_3Si)_3P$ is pyramidal, however, indicating that the second-row atom P is less able to contribute a p orbital to $d\pi$–$p\pi$ bonding than is nitrogen.

Similarly, H_3GeNCO is *not* linear in the gas phase. Evidently effective π bonding in the linear structure occurs only for Si—N and not Ge—N bonds.

2. The disilyl ethers $(R_3Si)_2O$ all have large angles at oxygen (140–180°), and both electronic and steric explanations have been suggested. Electronically, overlap between filled oxygen $p\pi$ orbitals and silicon $d\pi$ orbitals would improve with increasing angle and in the limit might favor linearity.[3b] When $R = C_6H_5$ the angle at oxygen is 180°, but there may also be a strong steric factor here because of the very large R groups.

3. Silanols, such as Me_3SiOH, are stronger acids than the carbon analogues and form stronger hydrogen bonds; for Ph_3MOH the acidities are in the order $C \approx Si \gg Sn$. The hydrogen bonding can be ascribed to Si—O π bonding involving one of the two unshared pairs of the silanol oxygen and the $3d$ orbital of Si to give a situation somewhat similar electronically to that of the nitrogen atom in an imine $R_2C{=}NH$. One unshared pair still remains on the oxygen, which is consistent with the failure of the *base* character of the silanol to be much lowered, in spite of its stronger acidity, compared with the analogous alcohol; the base order is $C \approx Si < Ge < Sn$.

A similar situation arises with the acid strength of R_3MCO_2H, where the order is $Si \geq Ge > C$; in this case the $d\pi$–$p\pi$ bonding probably acts to stabilize the anion. The order of π bonding, $C > Si > Ge \geq Sn > Pb$, is obtained from hydrogen bonding and nmr studies on amines. Thus $(Me_3Si)_3N$ is virtually nonbasic, the germanium compound is about as basic as a tertiary amine, and the tin compound is more basic than any organic amine. The same order is found in RMX_3 when X = alkyl, but when X = halogen it is $C < Si < Ge < Sn$.

Silicon-29 nmr spectra in both solids and solutions can be correlated with bonding types,[4] namely, all σ bonds as in Me_4Si, $\sigma + \pi$ types as in $Me\ddot{O}\overset{\curvearrowright}{-}Si(OMe)_3$ and those where there are both types as in $H_2Si\overset{\curvearrowleft}{-}\ddot{F}_2$.

Stereochemistry.[5] The stereochemistries of the Group IVA(14) compounds are given in Table 9-3.

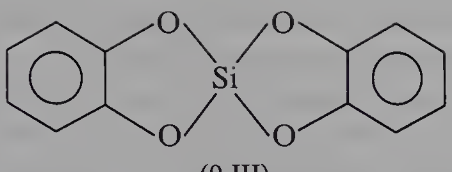
IV-Oxidation State. All the elements form tetrahedral compounds and some chiral compounds such as GeHMePh(α-napthyl) are known. It was first believed that planar SiO_4 groups occurred in complexes of the type (9-III) but this is not so, although distorted SiO_4 tetrahedra do occur.[6]

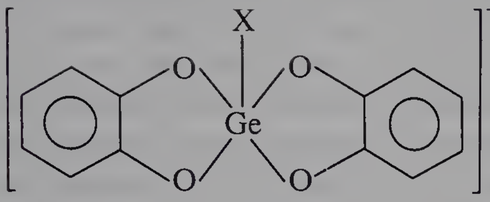
[3b] See N. Janes and E. Oldfield, *J. Am. Chem. Soc.*, 1986, **108**, 5743 for SiOSi $d\pi$–$p\pi$ bonding.

[4] N. Janes and E. Oldfield, *J. Am. Chem. Soc.*, 1985, **107**, 6769.

[5] M. G. Gielen, *Topics in Inorganic and Organometallic Stereochemistry*, G. Geoffroy, Ed., Wiley, New York, 1981 (Sn, Ge).

[6] J. J. Zuckerman *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1983, **22**, 501.


(9-III)


(9-IV)

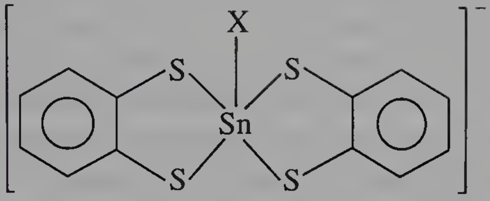

(9-V)

TABLE 9-3
Valence and Stereochemistry of Group IVA(14) Elements

Valence	Coordination number	Geometry	Examples
II	2	ψ-Trigonal (angular)	$Ge(N\textit{t}\text{-}Bu_2)_2$, $Pb(C_5H_5)_2$
	3	Pyramidal	$SnCl_2 \cdot 2H_2O$, $SnCl_3^-$, $Pb(SPh)_3^-$, $Sn[CH(PPh_2)_2]_2$[a]
	4	ψ-*tbp*	Pb^{II} in Pb_3O_4, $Sn(S_2CNR_2)_2$, Sn(β-dike)$_2$
	5	ψ-Octahedral	SnO (blue-black form)
	6	Octahedral	PbS (NaCl type), GeI_2 (CaI_2 type)
	7	Complex	$[SC(NH_2)_2]_2PbCl$, $(18\text{-}C\text{-}6)SnCl^+$
	6, 7	ψ-Pentagonal bipyramidal + complex ψ-8-coordination	$Sn^{II}[Sn(EDTA)H_2O] \cdot H_2O$
	9, 10	Complex	$Pb(NO_3)_2$(semicarbazone)[b], $Pb(O_2CMe)_2 \cdot 3H_2O$
IV	3	Trigonal	Ph_3Si^+[c]
	4	Tetrahedral	SiO_2, $SiCl_4$, GeH_4, $PbMe_4$
	5[d]	*tbp*	$Me_3SnCl(py)$, $SnCl_5^-$, SiF_5^-, $RSiF_4^-$
	5[e]	*sp*	$[XSi(O_2C_6H_4)_2]^-$
	6	Octahedral	SiF_6^{2-}, $[Si(acac)_3]^+$, $[Si(ox)_3]^{2-}$, GeO_2, $PbCl_6^{2-}$, *trans*-$GeCl_4(py)_2$, $Sn(S_2CNEt_2)_4$
	7[f]	Pentagonal bipyramidal	$Ph_2Sn(NO_3)_2(OPPh_3)$
	8	Dodecahedral	$Sn(NO_3)_4$, $Pb(O_2CMe)_4$

[a] A. L. Balch and D. E. Oram, *Organometallics*, 1986, **5**, 2159.

[b] See G. J. Palenik *et al.*, *Inorg. Chim. Acta*, 1986, **111**, L53.

[c] J. B. Lambert *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 2482.

[d] See G. Klebe *et al.*, *J. Chem. Soc. Dalton Trans.*, 1985, **1**, 5 (Si).

[e] See R. R. Holmes *et al.*, *Organometallics*, 1984, **3**, 750; *Inorg. Chem.*, 1987, **26**, 760.

[f] See G. Pelizzi *et al.*, *J. Chem. Soc. Dalton Trans.* **1985**, 487.

Since valence shell expansion by utilization of outer *d* orbitals can occur 5 and 6 coordinate species are common.

Pentacoordination is found mainly (*a*) in ions MX_5^- and $R_nMX_{5-n}^-$ stabilized in lattices by large cations, that are usually trigonal bipyramidal; (*b*) spiro compounds with O, S, and N chelates such as 9-IV and 9-V that are usually square pyramidal.[7] The distortion to square pyramidal structures in the solid tends to increase with decreasing electronegativity of the central atom; (*c*) adducts of halides or substituted halides with donor ligands, for example, MX_4L; (*d*) for Sn, polymeric compounds R_3SnX where X acts as a bridge.

Octahedral coordination is common for all the elements, although for ions and adducts, whether a compound will be five- or six-coordinate depends on delicate energy balances and cannot be predicted.

II-Oxidation State. As noted previously in virtually all divalent compounds, there is a lone rather than *inert* pair.[8a] Thus in Ge_5F_{12} the Ge^{II} atoms are square pyramidal with the lone pair occupying the sixth position and the same is true in the blue-black form of SnO and of PbO where there are MO_5 ψ-octahedra.

In many Sn^{II} compounds there are atoms at three corners of a tetrahedron and a lone pair of electrons at the fourth. Thus $SnCl_2 \cdot 2H_2O$ has a pyramidal $SnCl_2OH_2$ molecule, the second H_2O not being coordinated (it is readily lost at 80°C), while $K_2SnCl_4 \cdot H_2O$ consists of ψ-tetrahedral $SnCl_3^-$ ions and Cl^- ions. The ψ-tetrahedral SnF_3^- ion is also known, and the $Sn_2F_5^-$ ion consists of two SnF_3^- ions sharing a fluorine atom. Other Sn^{II} compounds such as $SnCl_2$ or SnS similarly involve three coordination but with a bridge group between the metal atoms.

For lead with its relatively large radius, higher coordination numbers have been established but in some of these there is no evidence for stereochemically active lone pairs as in the 10-coordinate $Pb(\eta^2\text{-}NO_3)_2$(semicarbazone).[8b]

However, in the 1,4,7-triazacyclononane complex, $LPb(NO_3)_2$, the electron pair *is* stereochemically active.[8c]

THE ELEMENTS

9-2. Occurrence, Isolation, and Properties

Silicon is second only to oxygen in weight percentage of the earth's crust (~28%) and is found in an enormous diversity of silicate minerals. Germanium, Sn, and Pb are relatively rare elements ($\sim 10^{-3}$ wt %), but they are well known because of their technical importance and the relative ease with which Sn and Pb are obtained from natural sources.

[7] See, for example, R. R. Holmes *et al.*, *Inorg. Chem.*, 1986, **25**, 600, 607.
[8a] S-W. Ng and J. J. Zuckerman, *Adv. Inorg. Chem. Radiochem.*, 1985, **29**, 297 (178 references).
[8b] G. J. Palenik *et al.*, *Inorg. Chim. Acta*, 1986, **111**, L53.
[8c] K. Wieghardt *et al.*, *Inorg. Chem.*, 1986, **25**, 1647.

Silicon is obtained in the ordinary commercial form by reduction of SiO_2 with carbon or CaC_2 in an electric furnace. Similarly, Ge is prepared by reduction of GeO_2 with C or H_2. Silicon and Ge are used as semiconductors in transistors and for microcircuitry. Exceedingly high purity is essential, and special methods are required to obtain usable materials; these include fractional distillation of halides, $SiHCl_3$, and so on, reduction of halides by H_2 or thermal decomposition of SiH_4 to give the element, then zone refining of the latter. Thin films of semi-insulating polycrystalline Si on Si single crystals for integrated circuits can be made by interaction of SiH_4 and N_2O.[9]

Tin and Pb are obtained from the ores in various ways, commonly by reduction of their oxides with carbon. Further purification is usually effected by dissolving the metals in acid and depositing the pure metals electrolytically.

Silicon is rather unreactive. It is attacked by halogens giving tetrahalides, and by alkalis giving solutions of silicates. It is not attacked by acids except HF; presumably the stability of SiF_6^{2-} provides the driving force here. Highly reactive Si, prepared by the reaction,

$$3CaSi_2 + 2SbCl_3 \longrightarrow 6Si + 2Sb + 3CaCl_2$$

reacts with water to give SiO_2 and hydrogen.

Germanium is somewhat more reactive than Si and dissolves in concentrated H_2SO_4 and HNO_3. Tin and Pb dissolve in several acids and are rapidly attacked by halogens. They are attacked slowly by cold alkali, rapidly by hot, to form stannates and plumbites. Lead often appears to be much more noble and unreactive than would be indicated by its standard potential of -0.13 V. This low reactivity can be attributed to a high overvoltage for hydrogen and also in some cases to insoluble surface coatings. Thus Pb is not dissolved by dilute H_2SO_4 and concentrated HCl.

9-3. Allotropic Forms

Silicon and Ge are normally isostructural with diamond. By use of very high pressures, denser forms with distorted tetrahedra have been produced. The graphite structure (Section 8-1) which requires the formation of $p\pi$–$p\pi$ bonds is unique to carbon.

Tin has two crystalline modifications, with the equilibria

$$\underset{\text{"gray"}}{\alpha\text{-Sn}} \xrightleftharpoons{18^\circ\text{C}} \underset{\text{"white"}}{\beta\text{-Sn}} \xrightleftharpoons{232^\circ\text{C}} \text{Sn(l)}$$

α-Tin, or gray Sn (density at 20°C = 5.75), has the diamond structure. The metallic form, β or white Sn (density at 20°C = 7.31), has a distorted close-packed lattice. The approach to ideal close packing accounts for the considerably greater density of the β metal compared with the diamond form.

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[9] J. Wong *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 359.

Lead exists only in a *ccp*, metallic form. This is a reflection both of its preference for divalence rather than tetravalence and of the relatively low stability of the Pb—Pb bond.

COMPOUNDS OF THE GROUP IVA(14) ELEMENTS

9-4. Anions and Binary Compounds

The reduction by alkali metals of Ge, Sn and Pb salts in liquid ammonia or in the presence of hexamethylphosphoramide or cryptands has allowed the isolation of many stable anions such as Ge_9^{4-}, Sn_5^{2-}, Sn_9^{3-}, Pb_5^{2-}, and mixed ions of various sorts such as $Sn_2Bi_2^{2-}$, $SnTe_4^{4-}$.[10] It may be noted that the M_4^{4-} ions are 20*e* species and isoelectronic with P_4, As_4, or Sb_4 and are similarly tetrahedral. The anion in (K crypt)$_3$$Sn_9^{3-}$ has a tricapped trigonal prismatic structure and is paramagnetic with 21 skeletal electrons.

While interactions of alkali metals or magnesium with elemental silicon and germanium (or their oxides) can give various silicides or germanides, most of these products do not contain true anions and some are semiconductors.[11a] However, in $Li_{12}Si_7$ there are Si_5 rings and trigonal planar Si-centered Si_4 units in the lattice.[11b]

Dibarium silicide (Ba_2Si) has an *anti*-$PbCl_2$ structure with Si^{4-} octahedrally coordinated by Ba atoms; Si_4 tetrahedra also occur in K_3LiSi_4.[11c]

Finally, there are binary compounds such as SiS_2 and GeS_2 that have chains of tetrahedral MS_4 linked by S bridges. Tin disulfide has a CaI_2 lattice, each Sn having six S neighbors. Silicon nitride (Si_3N_3) is the end product of heating $Si(NH_2)_4$ made by interaction of $SiCl_4$ and NH_3. There are various polymorphs of silicon carbide made by high temperature interaction; some have wurtzite (ZnS) or diamond structures.[12]

THE TETRAVALENT STATE

9-5. Hydrides

All the hydrides, Table 9-4, are colorless.

Silanes. Monosilane (SiH_4) is best prepared on a small scale by heating SiO_2 and $LiAlH_4$ at 150 to 170°C. On a larger scale SiO_2 or alkali silicates

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[10] L. L. Lohr *et al., Inorg. Chem.*, 1986, **25,** 1535; J. D. Corbett, *Chem. Rev.*, 1985, **85,** 383.

[11a] J. Evers *et al., Angew. Chem. Int. Ed. Engl.*, 1984, **23,** 528.

[11b] H. G. von Schering *et al., Chem. Ber.*, 1986, **119,** 3576.

[11c] H. G. von Schnering *et al., Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 349.

[12] J. S. Hartman, *J. Chem. Soc. Chem. Commun.*, **1985,** 159.

TABLE 9-4
Tetravalent Hydrides and Halides of Group IVA(14) Elements

Hydrides[a]		Fluorides and chlorides[b]		
$\mathrm{MH_4}$	Other[c]	$\mathrm{MF_4}$	$\mathrm{MCl_4}$	Other[d]
$\mathrm{SiH_4}$ bp −112°C	$\mathrm{Si_2H_6 \rightarrow Si_6H_{14}}$ bp −145°C	$\mathrm{SiF_4}$ bp −86°C	$\mathrm{SiCl_4}$ bp −57.6°C	$\mathrm{Si_2Cl_6 \rightarrow Si_6Cl_{14}}$ bp −145°C $\mathrm{Si_2F_6 \rightarrow Si_{16}F_{34}}$ bp −18.5°C
$\mathrm{GeH_4}$ bp −88°C	$\mathrm{Ge_2H_6 \rightarrow Ge_9H_{20}}$ bp −29°C	$\mathrm{GeF_4}$ mp −37°C	$\mathrm{GeCl_4}$ bp 83°C	$\mathrm{Ge_2Cl_6}$ mp 40°C
$\mathrm{SnH_4}$ bp −52.5°C	$\mathrm{Sn_2H_6}$	$\mathrm{SnF_4}$ subl. 704°C	$\mathrm{SnCl_4}$ bp 114.1°C	
$\mathrm{PbH_4}$		$\mathrm{PbF_4}$	$\mathrm{PbCl_4}$ d. 105°C	

[a] There are mixed Si—Ge hydrides and *cyclo* silanes as well as isomers that may be separable by g.l.c.

[b] All $\mathrm{MX_4}$ compounds except $\mathrm{PbBr_4}$ and $\mathrm{PbI_4}$ are known, as well as mixed halides of Si (e.g., $\mathrm{SiF_3I}$ and $\mathrm{SiFCl_2Br}$) and even SiFClBrI.

[c] For discussion of aromaticity of $\mathrm{Si_6H_6}$, see A. Sax and R. Janoschek, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 651.

[d] $\mathrm{Si_2Br_6}$ mp 90.8°C; B. S. Suresh and D. K. Padma, *J. Chem. Soc. Dalton Trans.*, **1984**, 1779.

are reduced by an NaCl—$\mathrm{AlCl_3}$ eutectic (mp 120°C) containing Al metal, or with hydrogen at 400 atm and 175°C. The original Stock procedure of acid hydrolysis of magnesium silicide gives a mixture of silanes. Chlorosilanes may also be reduced by $\mathrm{LiAlH_4}$.

Higher silanes can also be made by photolysis of $\mathrm{SiH_4}$–$\mathrm{H_2}$ mixtures and $\mathrm{SiH_2}$ may be an intermediate.[13]

Only $\mathrm{SiH_4}$ and $\mathrm{Si_2H_6}$ are indefinitely stable at 25°C; the higher silanes decompose giving $\mathrm{H_2}$ and mono- and disilane, possibly indicating $\mathrm{SiH_2}$ as an intermediate.

The hydridic reactivity of the Si—H bond in silanes and substituted silanes may be attributed to charge separation $\mathrm{Si^{\delta+}—H^{\delta-}}$ that results from the greater electronegativity of H than of Si. Silanes are spontaneously flammable in air, for example,

$$\mathrm{Si_4H_{10}} + \tfrac{13}{2}\mathrm{O_2} \longrightarrow 4\mathrm{SiO_2} + 5\mathrm{H_2O}$$

Although silanes are stable to water and dilute mineral acids, rapid hydrolysis occurs with bases;

$$\mathrm{Si_2H_6} + (4+n)\mathrm{H_2O} \longrightarrow 2\mathrm{SiO_2}\cdot n\mathrm{H_2O} + 7\mathrm{H_2}$$

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[13] G. Olbrich *et al.*, *Organometallics*, 1984, **3**, 1267.

The silanes are strong reducing agents. With halogens they react explosively at 25°C, but controlled replacement of H by Cl or Br may be effected in the presence of AlX_3 to give halogenosilanes such as SiH_3Cl.

Monogermane together with Ge_2H_6 and Ge_3H_8 can be made by heating GeO_2 and $LiAlH_4$ or by addition of $NaBH_4$ to GeO_2 in acid solution. Higher germanes are made by electric discharge in GeH_4. Germanes are less flammable than silanes, although still rapidly oxidized in air, and the higher germanes increasingly so. The germanes are resistant to hydrolysis, and GeH_4 is unaffected by even 30% NaOH.

Stannane (SnH_4) is best obtained by interaction of $SnCl_4$ and $LiAlH_4$ in ether at $-30°C$. It decomposes rapidly when heated and yields β-tin at 0°C. Although it is stable to dilute acids and bases, 2.5*M* NaOH causes decomposition to Sn and some stannate. Stannane is easily oxidized and can be used to reduce organic compounds (e.g., C_6H_5CHO to $C_6H_5CH_2OH$, and $C_6H_5NO_2$ to $C_6H_5NH_2$). With concentrated acids at low temperatures, the solvated stannonium ion is formed by the reaction

$$SnH_4 + H^+ \longrightarrow SnH_3^+ + H_2$$

Plumbane (PbH_4) is said to be formed in traces when Mg–Pb alloys are hydrolyzed by acid or when Pb^{2+} salts are reduced cathodically, but its existence is doubtful.

All the elements form stable organohydrides (R_nMH_{4-n}); they are readily made by reduction of the corresponding chlorides with $LiAlH_4$. There are also a number of compounds of transition metals with silyl groups [e.g., $H_3SiCo(CO)_4$].

Perhaps the most important reaction of compounds with an Si—H bond, such as Cl_3SiH or Me_3SiH, and one that is of commercial importance is the Speier or *hydrosilation* reaction of alkenes, for example:

$$RCH{=}CH_2 + HSiCl_3 \longrightarrow RCH_2CH_2SiCl_3$$

which is discussed in Section 28-11. The reaction may involve the oxidative addition (Chapter 27) of Si—H bonds across a transition metal.[14]

SiH_4 and GeH_4 react with K to form H_3SiK and H_3GeK, which have NaCl type structures.

The unusual reducing properties of $SiHCl_3$ are discussed in Section 9-6.

9-6. Halides

The more important halides are given in Table 9-4.

Fluorides. These are obtained by fluorination of the other halides or by direct interaction; GeF_4 is best made by heating $BaGeF_6$. Tetrafluorides of

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[14] R. P. Corriu *et al.*, *Organometallics*, 1984, **3**, 1272.

Si and Ge are hydrolyzed by an excess of water to the hydrous oxides; the main product from SiF_4 and H_2O in the gas phase is $F_3SiOSiF_3$. In an excess of aqueous HF, the hexafluoro anions (MF_6^{2-}) are formed. Tin tetrafluoride is polymeric, with Sn octahedrally coordinated by four bridging and two nonbridging F atoms. Lead tetrafluoride is made by the action of F_2 on PbF_2; a supposed preparation by the action of HF on $Pb(O_2CMe)_4$ in $CHCl_3$ at 0°C gives the much more reactive $Pb(O_2CMe)_2F_2$.

Silicon Chlorides. Silicon tetrachloride is made by chlorination of Si at red heat. Hexachlorodisilane (Si_2Cl_6) can be obtained by interaction of $SiCl_4$ and Si at high temperatures or, along with $SiCl_4$ and higher chlorides, by chlorination of a silicide such as that of calcium. The higher members, which have highly branched structures, can also be obtained by amine-catalyzed reactions such as

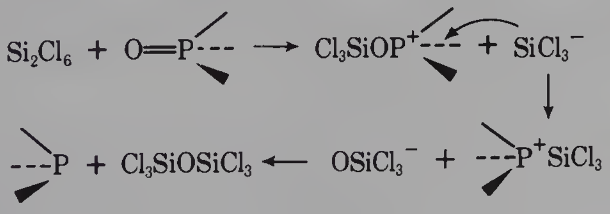
$$5Si_2Cl_6 \longrightarrow Si_6Cl_{14} + 4SiCl_4$$

$$3Si_3Cl_8 \longrightarrow Si_5Cl_{12} + 2Si_2Cl_6$$

and by photolysis of $SiHCl_3$. The products are separated by fractional distillation.

All the chlorides are immediately and completely hydrolyzed by water, but careful hydrolysis of $SiCl_4$ gives $Cl_3SiOSiCl_3$ and $(Cl_3SiO)_2SiCl_2$.

Hexachlorodisilane is a useful reducing agent for compounds with oxygen bound to S, N, or P; under mild conditions, at 25°C in $CHCl_3$ chlorooxosilanes are produced. It is particularly useful for converting optically active phosphine oxides $R^1R^2R^3PO$ into the corresponding phosphine. Since the reduction is accompanied by configurational inversion, the intermediacy of a highly nucleophilic $SiCl_3^-$ ion (cf. PCl_3) has been proposed:



The postulation of $SiCl_3^-$ can also accommodate the equally useful, clean, selective reductions by trichlorosilane (bp 33°C) and also the formation of C=C and Si—C bonds by reaction of $SiHCl_3$ with CCl_4, RX, RCOCl, and other halogen compounds in the presence of amines. In these cases the hypothetical $SiCl_3^-$ could be generated by the reaction

$$HSiCl_3 + R_3N \rightleftharpoons R_3NH^+ + SiCl_3^-$$

followed by

$$SiCl_3^- + Cl_3C{-}CCl_3 \longrightarrow SiCl_4 + Cl^- + Cl_2C{=}CCl_2$$

$$SiCl_3^- + RX \longrightarrow [R^- + XSiCl_3] \longrightarrow RSiCl_3 + X^-$$

There is some precedent for the postulation of the $SiCl_3^-$ ion, since trisubstituted organosilanes (R_3SiH), react with bases to give silyl ions (R_3Si^-).

Chloride Oxides. A variety of chlorooxosilanes, both linear and cyclic, is known. Thus controlled hydrolysis of $SiCl_4$ with moist ether, or interaction of Cl_2 and O_2 on hot silicon, gives $Cl_3SiO(SiOCl_2)_nSiCl_3$, where $n = 1$ to 4.

Germanium Tetrachloride. This differs from $SiCl_4$ in that only partial hydrolysis occurs in aqueous 6 to $9M$ HCl and there are equilibria involving species of the type $[Ge(OH)_nCl_{6-n}]^{2-}$; the tetrachloride can be distilled and separated from concentrated HCl solutions of GeO_2.

Tin and Lead Tetrachlorides. These are also hydrolyzed completely only in water; in the presence of an excess of acid they form chloroanions, as discussed in Section 9-9.

9-7. Oxygen Compounds of Silicon[15]

Silica. Pure SiO_2 occurs in only two forms, *quartz* and *cristobalite.* The silicon is always tetrahedrally bound to four oxygen atoms, but the bonds have considerable ionic character. In cristobalite the Si atoms are placed as are the C atoms in diamond with the O atoms midway between each pair. In quartz there are helices, so that enantiomorphic crystals occur, and these may be easily recognized and separated mechanically.

The interconversion of quartz and cristobalite on heating requires breaking and re-forming of bonds, and the activation energy is high. However, the rates of conversion are profoundly affected by the presence of impurities, or by the introduction of alkali metal oxides or other "mineralizers," and amorphous silica can also be converted to crystalline quartz in the presence of Mg^{2+} or Ca^{2+}.[16]

What was believed to be a third form of SiO_2 "tridymite" is probably a solid solution of mineralizer and silica.

Slow cooling of molten silica or heating any form of solid silica to the softening temperature gives an amorphous material that is glassy in appearance and is indeed a glass in the general sense, that is, a material with no long-range order but rather a disordered array of polymeric chains, sheets, or three-dimensional units.

Dense forms of SiO_2, called coesite and stishovite, were first made under drastic conditions (250–1300°C at 35–120 katm), but they were subsequently identified in meteor craters where the impact conditions were presumably similar; stishovite has the rutile structure. Both are chemically more inert than normal SiO_2 to which they revert on heating.

Silica is relatively unreactive towards Cl_2, H_2, acids, and most metals at

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[15] F. Liebau, *Structural Chemistry of Silicates,* Springer, New York, 1985.

[16] O. Yamaguchi *et al., J. Chem. Soc. Dalton Trans.,* **1982,** 1005.

ordinary or slightly elevated temperatures, but it is attacked by fluorine, aqueous HF, alkali hydroxides, fused carbonates, and so on.

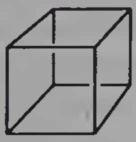
Amorphous silica, silica "gel," can be made by hydrolysis of alkoxides such as $Si(OEt)_4$; it is used, when dehydrated, as a drying agent, and chromatographic and catalyst support material. It appears to contain $Si(OSi{\equiv})_4$, $Si(OSi{\equiv})_3OH$, and $Si(OSi{\equiv})_2(OH)_2$ groups. The nmr studies on ^{29}Si indicate that silica found in plants, flagellates, and other biological systems has the same type of structure as silica gel.[17]

Silicates. There is an enormous variety of silicates, including rock forming and synthetic minerals. Only the briefest survey can be given. The basic unit in all silicates is the SiO_4 tetrahedron; these occur singly or by sharing O atoms in small groups that may be linear or cyclic, in infinite chains and sheets.

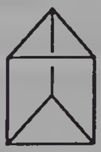
Although silicate structures have been determined mainly by X-ray diffraction, magic-angle spinning nmr using ^{29}Si and ^{27}Al is useful for microcrystalline and amorphous solids and glasses.[18] In aluminosilicates such spectra can distinguish between tetrahedral and octahedral Al.

Alkali Silicates; Silicate Solutions. Sodium silicates are made on a large scale by fusion of SiO_2 and Na_2CO_3 at ~1500°C for detergent and other uses.[19]

Aqueous solutions of silicates have been studied by Raman and ^{29}Si nmr spectra. The free SiO_4^{4-} ion has a lifetime of only milliseconds,[20] and silicate anions are polymeric. Many species have been identified by trimethylsilation of hydroxy groups and glc (gas–liquid chromatography) analysis of the products. The solutions contain linear, cyclic, and cage polymeric ions in proportions depending on the pH, concentration, and temperature. For alkali ions, most of the Si is in ions with charge $>10^-$ but for Me_4N^+ in solutions below 50°C the major ion is the anion $[Si_8O_{20}]^{8-}$, which in the crystal has a double ring (9-VI). Silicon-29 nmr of Ge substituted species confirm that in solution there are both double-four and double-three rings (9-VI and 9-VII).[21] The sort of species actually isolated after silation are of the type $Si_6O_{15}(SiMe_3)_6$, $Si_6O_{18}(SiMe_3)_{12}$, and $Si_8O_{12}(OMe)_8$.[22]



(9-VI)



—— = Si—O—Si

(9-VII)

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[17] S. Mann *et al., J. Chem. Soc. Chem. Commun.,* **1983,** 168.

[18] See J. M. Thomas *et al., Angew. Chem. Int. Ed. Engl.* 1983, **22,** 259.

[19] L. S. D. Glasser, *Chem. Br.,* **1982,** 33. *Soluble Silicates:* J. S. Falcone, Jr., Ed. (ACS Symposium Series No. 194), American Chemical Society, Washington, DC, 1981.

[20] G. Engelhardt and D. Hoebbel, *J. Chem. Soc. Chem. Commun.,* **1984,** 514.

[21] E. Oldfield *et al., J. Am. Chem. Soc.,* 1986, **108,** 30.

[22] See, for example, V. W. Day *et al., J. Am. Chem. Soc.,* 1985, **107,** 8262.

The alkaline silicate species are commonly in dynamic equilibrium and on undergoing pH changes or dilution, equilibria may be quite rapidly established, within hours. However, for Me_4N^+ solutions, which are important in zeolite synthesis (see next section) approaches to equilibrium can take days or weeks.[23]

Simple Orthosilicates. Some crystalline silicates contain discrete SiO_4^{4-} ions; since the cations are coordinated by the O atoms the nature of the structure depends on the coordination number of the cation. In *phenacite* (Be_2SiO_4) and *willemite* (Zn_2SiO_4) the cations are surrounded by a tetrahedrally arranged set of four oxygen atoms. There are a number of compounds of the type M_2SiO_4, where M^{2+} is Mg^{2+}, Fe^{2+}, Mn^{2+}, or some other cation with a preferred coordination number of 6, in which the SiO_4^{4-} anions are so arranged as to provide interstices with six oxygen atoms at the apices of an octahedron in which the cations are found. In *zircon* ($ZrSiO_4$) the Zr^{4+} ion is eight-coordinate, although not all Zr—O distances are equal. It may be noted that, although the M—O bonds are probably more ionic than the Si—O bonds, there is doubtless some covalent character to them, and these substances should not be regarded as literally ionic in the sense $[M^{2+}]_2[SiO_4^{4-}]$ but rather as somewhere between this extreme and the opposite one of giant molecules. There are also other silicates containing discrete SiO_4 tetrahedra.

Other Discrete, Noncyclic Silicate Anions. The simplest of the condensed silicate anions—that is, those formed by combining two or more SiO_4 tetrahedra by sharing of oxygen atoms—is the pyrosilicate ion ($Si_2O_7^{6-}$). This ion occurs in *thortveitite* ($Sc_2Si_2O_7$), *hemimorphite* $[Zn_4(OH)_2Si_2O_7]$, and in at least three other minerals. It is interesting that the Si—O—Si angle varies from 131 to 180° in these substances. In the lanthanide silicates ($M_2O_3 \cdot 2SiO_2$) there are $O_3SiOSi(O)_2OSiO_3^{6-}$ ions.

Cyclic Silicate Anions. The structures of two such cyclic ions are shown schematically in Fig. 9-2. It should be clear that the general formula for any such ion must be $Si_nO_{3n}^{2n-}$. The ion $Si_3O_9^{6-}$ occurs in *benitoite* ($BaTiSi_3O_9$) and probably in $Ca_2BaSi_3O_9$. The ion $Si_6O_{18}^{12-}$ occurs in *beryl* ($Be_3Al_2Si_6O_{18}$).

Infinite Chain Anions. The two main types of infinite chain anions are the *pyroxenes,* which contain single-strand chains of composition $(SiO_3^{2-})_n$ (Fig. 9-3) and the *amphiboles,* which contain double-strand, cross-linked chains or bands of composition $(Si_4O_{11}^{6-})_n$. Note that the general formula of the anion in a pyroxene is the same as in a silicate with a cyclic anion. Silicates with this general stoichiometry are often called "metasilicates," especially in older literature. There is actually neither metasilicic acid not any discrete metasilicate anion. With the exception of the few "metasilicates" with cyclic anions, such compounds contain infinite chain anions.

Examples of pyroxenes are *enstatite* ($MgSiO_3$), *diopside* $[CaMg(SiO_3)_2]$, and *spodumene* $[LiAl(SiO_3)_2]$, the last being an important lithium ore. In the

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[23] E. Oldfield *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 66.

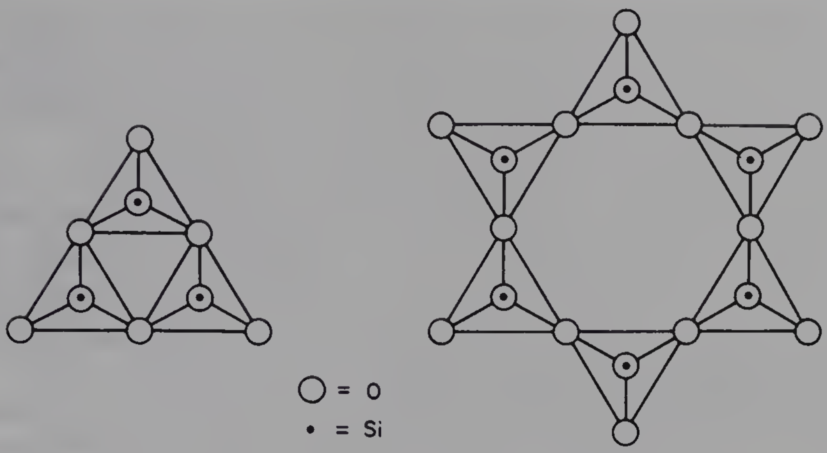

FIG. 9-2. Examples of cyclic silicate anions; $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$.

latter there is one unipositive and one tripositive cation instead of two dipositive cations. Indeed, the three compounds cited illustrate very well the important principle that within rather wide limits, *the specific cations or even their charges are unimportant as long as the total positive charge is sufficient to produce electroneutrality.* This may be easily understood in terms of the structure of the pyroxenes in which the $(SiO_3)_n$ chains lie parallel and are held together by the cations that lie between them. Obviously the exact identity of the individual cations is of minor importance in such a structure.

A typical amphibole is *tremolite,* $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$. Although it would not seem to be absolutely necessary, amphiboles apparently always contain some hydroxyl groups attached to the cations. Aside from this, however, they are structurally similar to the pyroxenes, in that the $(Si_4O_{11}^{6-})_n$ bands lie parallel and are held together by the metal ions lying between them. Like the pyroxenes and for the same reason, they are subject to some variability in the particular cations incorporated.

Because of the strength of the $(SiO_3)_n$ and $(Si_4O_{11})_n$ chains in the pyroxenes and amphiboles, and also because of the relative weakness and lack of strong directional properties in the essentially electrostatic forces between them via the metal ions, we might expect such substances to cleave most readily in directions parallel to the chains. This is in fact the case, dramatically so in the various *asbestos* minerals.[24] Asbestos is an imprecise commercial term

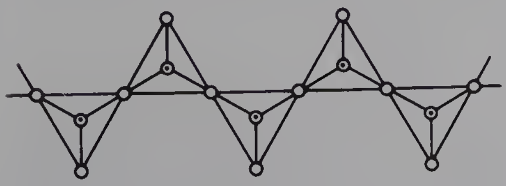

FIG. 9-3. A linear chain silicate anion.

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[24] S. S. Chissick *et al.*, Eds., *Asbestos: Properties Applications and Hazards,* Vol. 1, 1979, Vol. 2, 1983, Wiley, New York.

referring to fibrous silicates such as *chrysotile,* white serpentine, $Mg_6Si_4O_{10}(OH)_8$ and *crocidolite,* blue amphibole, $Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2$. These materials, though frequently used in the past, are now considered dangerous and exposure to fibers in air can initiate a rare form of lung cancer.

Infinite Sheet Anions. When SiO_4 tetrahedra are linked into infinite two-dimensional networks as shown in Fig. 9-4, the empirical formula for the anion is $(Si_2O_5^{2-})_n$. Many silicates have such sheet structures with the sheets bound together by the cations that lie between them. Such substances might thus be expected to cleave readily into thin sheets, and this expectation is confirmed in the micas, which are silicates of this type.

Framework Minerals. The next logical extension in this progression from simple SiO_4^{4-} ions to larger and more complex structures would be to three-dimensional structures in which every oxygen is shared between two tetrahedra. The empirical formula for such a substance would be simply $(SiO_2)_n$; that is, we should have silica. However, if some silicon atoms in such a three-dimensional framework structure are replaced by aluminum the framework must be negatively charged and there must be other cations uniformly distributed through it.

Aluminosilicates of this type are the feldspars, zeolites, and ultramarines, which (except for the last) are among the most widespread, diverse, and useful silicate minerals in Nature. Moreover, many synthetic zeolites have been made in the laboratory, and have important uses. The feldspars are the major constituents of igneous rocks and include such minerals as *orthoclase* ($KAlSi_3O_8$), which may be written $K[(AlO_2)(SiO_2)_3]$ to indicate that one fourth of the oxygen tetrahedra are occupied by Al atoms and *anorthite* {$CaAl_2Si_2O_8$ or $Ca[(AlO_2)_2(SiO_2)_2]$}, in which half the tetrahedra are AlO_4 and half are SiO_4.

A semiprecious deep-blue gem *lapis lazuli* has been known from ancient times and is available in synthetic forms under the name *ultramarine*. These

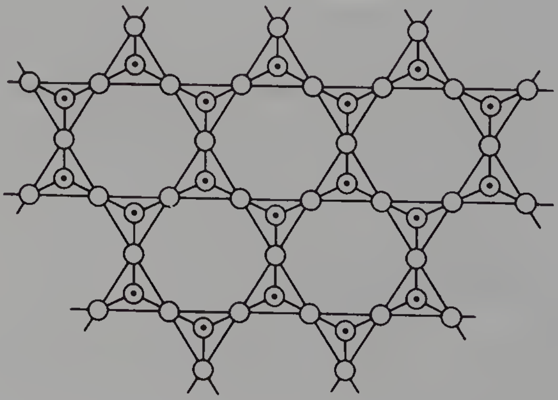

FIG. 9-4. Sheet silicate anion structure idealized. [For a real example, see A. K. Pant, *Acta Crystallogr. B*, 1968, **24**, 1077.]

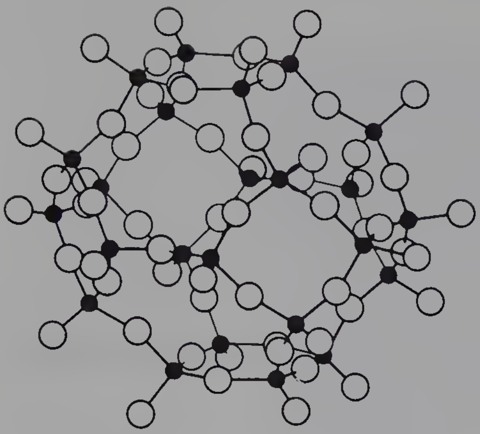

FIG. 9-5. The arrangement of AlO_4 and SiO_4 tetrahedra that gives the cubooctahedral cavity in some zeolites and felspathoids; dot represents Si or Al.

are aluminosilicates of the sodalite type that contain sulfur in the form of the radical anions S_3^- and S_2^-. The former, always present, causes a deep-blue color, and when S_2^- is also present a green hue is produced.

Zeolites.[25] Zeolites, sometimes called *porotectosilicates,* are the most important framework silicates. A zeolite may be defined as an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration. The framework consists of an open arrangement of corner-sharing tetrahedra where SiO_4 are partially replaced by AlO_4 tetrahedra, which requires sufficient cations to achieve electroneutrality. The cavities are occupied by H_2O molecules. An idealized formula is $M^{n+}_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot nH_2O$. Magic-angle nmr spectra show that there are five distinct $Si(OAl)_n(OSi)_{4-n}$ structures, $n = 0$–4 corresponding to the tetrahedral SiO_4. There is a rule (Loewenstein's) that there is an alternation of Al and Si on the tetrahedral sites, that is, two Al atoms cannot be adjacent and there are no Al—O—Al links. Some typical cavities occurring in zeolites are shown in Figs. 9-5 and 9-6. A representative formula for a naturally occurring zeolite is that of *faujasite,* $Na_{13}Ca_{11}Mg_9KAl_{55}Si_{137}O_{384}\cdot 235H_2O$.

There are some 37 natural and over 100 synthetic zeolites, the latter all made by hydrothermal synthesis. The main uses are as molecular sieves, catalysts, and catalyst supports for platinum group and other metals.

Molecular sieves is the term first given to zeolites dehydrated by heating

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[25] B. Držaj *et al., Zeolites,* Elsevier, Amsterdam, 1986, (symposium proceedings); R. M. Barrer, *Hydrothermal Chemistry of Zeolites,* Academic Press, New York, 1982; *Zeolites,* 1980, Vol. 1, Butterworth London; M. S. Spencer, *Crit. Rep. Appl. Chem.,* 1985, **12,** 65 [catalysis by zeolites (93 references)]; F. R. Ribeivo *et al.,* Eds., *Zeolites: Science and Technology,* Reidel, Dordrecht, 1984; G. Gottardi and E. Galli, *Natural Zeolites,* Springer, New York, 1985; J. M. Thomas *et al., Angew. Chem. Int. Ed. Engl.,* 1983, **22,** 259; 1984, **23,** 671.

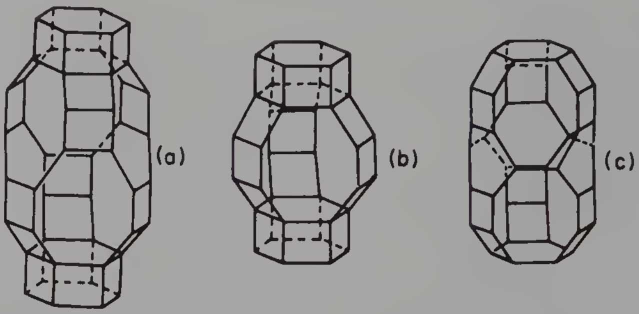

FIG. 9-6. Cavities of different dimensions in (a) chabazite ($Ca_6Al_{12}Si_{24}O_{72}\cdot H_2O$), (b) gmelinite [$(Na_2Ca)_4Al_8Si_{16}O_{48}\cdot 24H_2O$], and (c) erionite, ($Ca_{4.5}Al_9Si_{27}O_{72}\cdot 27H_2O$).

in vacuum at about 350°C. However, there are now other materials,[26] such as phosphorus substituted zeolites, microporous silicas, and $AlPO_4$ frameworks made hydrothermally in the presence of quaternary ammonium salts, like zeolites.

Dehydration of the synthetic zeolite Linde *A*, $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$ leaves cubic microcrystals in which the AlO_4 and SiO_4 tetrahedra are linked together to form a ring of eight O atoms on each face of the unit cube and an irregular ring of six O atoms across each corner. In the center of the unit cell is a large cavity about 11.4 Å in diameter, which is connected to six identical cavities in adjacent unit cells by the eight-membered rings, which have inner diameters of ~4.2 Å. In addition, the large cavity is connected to eight smaller cavities, ~6.6 Å in diameter, by the six-membered rings, which provide openings ~2.0 Å in diameter. In the hydrated form all the cavities contain water molecules. In the anhydrous state the same cavities may be occupied by other molecules brought into contact with the zeolite, provided such molecules are able to pass through the apertures connecting cavities. Molecules within the cavities then tend to be held there by attractive forces of electrostatic and van der Waals types. Thus the zeolite will be able to absorb and strongly retain molecules just small enough to enter the cavities. It will not absorb at all those too big to enter, and it will absorb weakly very small molecules or atoms that can enter but also leave easily. For example, zeolite *A* will absorb straight chain but not branched chain or aromatic hydrocarbons.

High silica zeolites are exemplified by ZSM-5 (Mobil Oil) and silicalite (Union Carbide); these zeolites are also made hydrothermally using large tetraalkyl ammonium ions as templates for crystal growth; soluble double five-membered ring silicates are possible intermediates.[27] Subsequent heating

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[26] B. M. Lok *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 6092; J. B. Parise, *J. Chem. Soc. Chem. Commun.*, **1984,** 1449; R. Kniep, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 525 (Al_2O_3—P_2O_5—H_2O).
[27] P. A. Jacobs and J. Martens, *Synthesis of High Silica Zeolites*, Elsevier, Amsterdam, 1987.

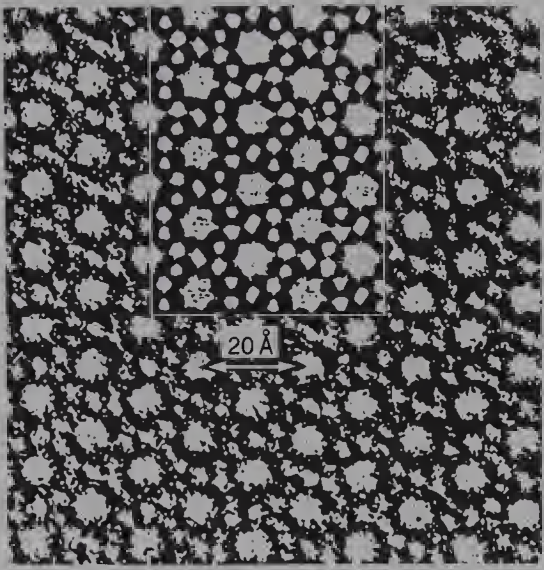


FIG. 9-7. Ultra high resolution electron microscope photograph of ZSM-5 looking along the 5.5-Å diameter channels. The inserted rectangle shows a computed image. The distance between the arrowheads is 20 Å. The 10-, 6-, and 5-membered rings can be seen. [Reproduced by kind permission of Prof. J. M. Thomas, Cambridge University (see also *J. Chem. Soc. Chem. Commun.*, **1982,** 1380).]

of the microcrystalline product removes organic matter and water. Magic-angle spinning nmr spectra show that there are AlO_4 tetrahedra and the general formula is $H_x[(AlO_2)_x(SiO_2)_{96-x}]\cdot 16H_2O$ where x is normally ~3 and the pore diameters about 5.5 Å. In Fig. 9-7 a high resolution microscopic picture of ZSM-5 is shown. The main feature of these zeolites and other zeolites is that due to the dimensions and geometry of the channels only certain reactants can enter and diffuse leading to shape selectivity in catalytic reactions.[28]

Since the catalytic, sorption and ion-exchange properties are strongly dependent on the Al–Si ratio it is important to be able to vary this. The Al content can be decreased, for example, by treatment with $SiCl_4$, which removes Al as $AlCl_3$. It can be increased in high silica zeolites by $AlCl_3$ vapor:

$$(SiO_2)_x + 4AlCl_3 \longrightarrow Al^{3+}[(AlO_2)_3(SiO_2)_{x-3}] + 3SiCl_4$$

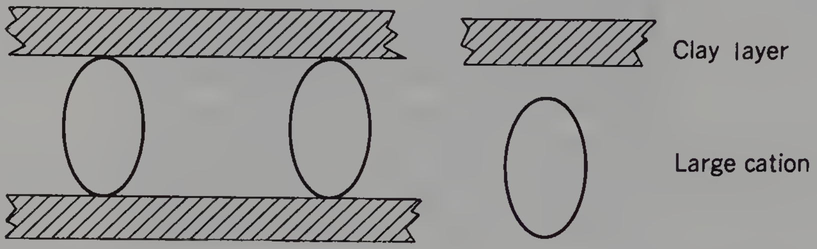
or aqueous KOH treatment.[29a] Use of sodium gallate also allows replacement of Si by Ga. Much information on zeolite and other silicate structures can now be obtained by MAS nmr of ^{27}Al, ^{29}Si, or ^{17}O.[29b]

[28] S. M. Csicsery, *Chem. Br.*, **1985,** 473; C. J. Plank, *Chem. Tech.*, **1984,** 243.

[29a] J. Klinowski *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 582.

[29b] E. Oldfield *et al., J. Am. Chem. Soc.*, 1987, **109,** 1632; E. Lippman *et al., J. Am. Chem. Soc.*, 1986, **108,** 1730; J. M. Newsam, *J. Chem. Soc. Chem. Commun.*, **1987,** 123.

Clays.[30] Among the infinite sheets previously noted are clay minerals such as *montmorillonite, kaolin,* and *talc* that are ubiquitous in Nature. All are hydrous with layered structure and can accordingly intercalate molecules and ions. Like zeolites they have ion-exchange properties, often with high selectivity. They have a wide range of uses including catalytic ones where transition metal ions may be intercalated.[31a] *Pillared clays*[31a,b] are clays in which very large cations such as $Nb_6Cl_{12}^{2+}$ or $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ are intercalated to form "pillars" (9-VIII); this leads to expanded layers, improved diffusion, sorption, and catalytic properties. After heating, such pillared clays have holes or cavities and zeolite-like behavior; an advantage is their cheapness.



(9-VIII)

9-8. Oxygen Compounds of Germanium, Tin, and Lead

Oxides and Hydroxides. Germanium dioxide is known in the quartz, stishovite, and crystobalite structures analogous to those of SiO_2 and transformations are catalyzed by ions[32] such as Na^+. SnO_2 exists in three different modifications of which the rutile form (in the mineral *cassiterite*) is most common; PbO_2 shows only the rutile structure. The basicity of the dioxides appears to increase from Si to Pb. Silicon dioxide is purely acidic, GeO_2 is less so and in concentrated HCl gives $GeCl_4$, SnO_2 is amphoteric, though when made at high temperatures, or by dissolving Sn in hot concentrated HNO_3 it is, like PbO_2, remarkably inert to chemical attack.

There is little evidence that there are true hydroxides, $M(OH)_4$, and the products obtained by hydrolysis of hydrides, halides, alkoxides, and so on, are best regarded as hydrous oxides. Thus the addition of OH^- to Sn^{IV} solutions gives a white gelatinous precipitate that when heated is dehydrated through various intermediates and gives SnO_2 at 600°C.

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[30] W. T. Reichle, *Chem. Tech.*, **1986**, 58; J. M. Thomas *et al.*, *J. Mol. Catal.*, 1984, **27**, 157; B. K. G. Theng, *Chemistry of Clay Organic Reactions*, Wiley, New York, 1974; L. Fowden *et al.*, Eds., *Philos. Trans. R. Soc.*, 1984, **A311**, 219.

[31a] T. J. Pinnavaia *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 4783, 7223; *Inorg. Chem.*, 1985, **24**, 1222; S. L. Suibe *et al.*, *Inorg Chem.*, 1986, **25**, 4217; P. Laszlo *et al.*, *Synthesis*, **1986**, 655.

[31b] R. Burch, C. I. Warburton, *J. Catal.*, 1986, **97**, 511, *J. Chem. Soc. Chem. Commun.*, **1987**, 117.

[32] G. Schmidt and R. Gruehn, *Z. Anorg. Allg. Chem.*, 1984, **512**, 193.

Oxo Anions. The known chemistry of germanates is much less extensive than that of silicates. Although there are many similarities, there are some structural differences because Ge more readily accepts higher coordination numbers. In $K_2Ge_8O_{17}$, for example, six of the Ge atoms are in GeO_4 tetrahedra but two are five-coordinate, as silicon never is under normal conditions. Germanates containing the $Ge(OH)_6^{2-}$ ion are also known.

In dilute aqueous solutions the major germanate ions appear to be $[GeO(OH)_3]^-$, $[GeO_2(OH)_2]^{2-}$, and $\{[Ge(OH)_4]_8(OH)_3\}^{3-}$. Fusion of SnO_2 or PbO_2 with K_2O gives K_2MO_3, which has chains of edge-shared MO_5 square pyramids. Crystalline alkali metal stannates and plumbates can be obtained as trihydrates, for instance, $K_2SnO_3{\cdot}3H_2O$. Such materials contain the octahedral anions $Sn(OH)_6^{2-}$ and $Pb(OH)_6^{2-}$.

9-9. Complexes of Group IVA(14) Elements

Most of the complexes of germanium, tin, and lead in the IV oxidation state contain halide ions or donor ligands that are oxygen, nitrogen, sulfur, or phosphorus compounds.

Anionic Species. In aqueous solution the only fluoroanion[33] is SiF_6^{2-}, whose high stability accounts for the incomplete hydrolysis of SiF_4 in water:

$$2SiF_4 + 2H_2O \longrightarrow SiO_2 + SiF_6^{2-} + 2H^+ + 2HF$$

The ion is usually made by attack of HF on hydrous silica and is stable even in basic solution. Although the salts that crystallize are normally those of the SiF_6^{2-} ion, the pentafluorosilicate ion is found in compounds such as $[Ph_4As][SiF_5]$. Typical reactions producing SiF_5^- salts are

$$SiO_2 + HF(aq) + [R_4N]Cl \xrightarrow{CH_3OH} [R_4N]SiF_5$$

$$SiF_4 + [R_4N]F \xrightarrow{CH_3OH} [R_4N]SiF_5$$

Several GeF_5^- salts are known.[34] The nmr data for the SiF_5^- ion and also for the similar species, $RSiF_4^-$ and $R_2SiF_3^-$, indicate *tbp* structures, but above −60°C exchange processes are occurring; in phenyl compounds, the Ph groups are equatorial.[35]

Germanium, tin and lead also form hexafluoro anions; for example, dissolution of GeO_2 in aqueous HF followed by the addition of KF at 0°C gives crystals of K_2GeF_6. The Ge and Sn anions are hydrolyzed by bases, but the Pb salts are hydrolyzed even by water. Many tin species, $SnF_{6-n}X_n^{2-}$, $X = OH^-, Cl^-, Br^-$, and so on have been studied by nmr.[36] Anhydrous

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[33] R. E. Mesmer *et al., Inorg. Chem.*, 1980, **19**, 758.

[34] N. Bartlett, *et al., Inorg Chem.*, 1984, **23**, 3167.

[35] D. Schomberg and R. Krebs, *Inorg. Chem.*, 1984, **23**, 1378.

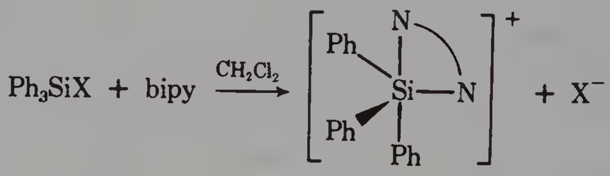
[36] K. B. Dillon and A. Marshall, *J. Chem. Soc. Dalton Trans.*, **1984**, 1245.

hexafluorostannates can be made by dry fluorination of the stannates ($M^{I}_2SnO_3\cdot 3H_2O$).

The hexachloro ions of Ge and Sn are normally made by the action of HCl or $M^{I}Cl$ on MCl_4. The thermally unstable yellow salts of $PbCl_6^{2-}$ are obtained by the action of HCl and Cl_2 on $PbCl_2$. Under certain conditions, pentachloro complexes of Ge and Sn may be stabilized, for example, by the use of $(C_6H_5)_3C^+$ as the cation or by the interaction of MCl_4 and $Bu_4N^+Cl^-$ in $SOCl_2$ solution.

Other anionic species include the ions $[Ge(SO_3F)_6]^{2-}$ and $[Sn(SO_3F)_5]^-$ formed by oxidation of the element with $S_2O_6F_2$ in HSO_3F,[37] and the nitrate $[Sn(NO_3)_6]^{2-}$. There are also distorted *tbp* spirocyclic oxygen or sulfur chelated anions (e.g., 9-IV and 9-V) that are nonrigid in solution,[7] oxalates $[M(ox)_3]^{2-}$, and other carboxylates.

Cationic Species. There are comparatively few cationic complexes, the most important being the octahedral β-diketonates and tropolonates (T) of Si and Ge such as $[Ge(acac)_3]^+$ and SiT_3^+. "Siliconium" ions can also be formed by reactions such as



or by oxidation of $SiCl_2(bipy)_2$ to *cis*-$[SiCl_2(bipy)_2]^{2+}$.

Neutral Species. These are numerous and quite varied in type. The majority are six-coordinate, examples being *trans*-$SnCl_2(\beta\text{-dike})_2$, $SnCl_2(S_2CNEt_2)_2$, and $Sn[(OC_2H_4)_2N(C_2H_4OH)]_2$. Both lower and higher coordination numbers also occur, examples being five in $PhSi(o\text{-}C_6H_4O_2)_2$ and presumably seven or eight in $Sn(S_2CNEt_2)_4$.

Adducts. The tetrahalides are prone to add neutral ligands to form adducts that are usually six-coordinate. Typical examples are *trans*-$SiF_4(py)_2$, *cis*-$SiF_4(bipy)$, $SiCl_4L_2$ (L = py, PMe_3), and numerous *cis*-SnX_2(L—L) and *cis* or *trans*-SnX_4L_2 compounds.[38]

The Lewis acid order is $SnCl_4 > SnBr_4 > SnI_4$.

9-10. Alkoxides, Carboxylates, and Oxo Salts

All four elements form *alkoxides*, but those of silicon, for example, $Si(OC_2H_5)_4$, often called *silicate esters*, are the most important; the surface of glass or silica can also be alkoxylated. Alkoxides are normally obtained by the standard method:

$$MCl_4 + 4ROH + 4\text{ amine} \longrightarrow M(OR)_4 + 4\text{ amine}\cdot HCl$$

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[37] F. Aubke, *et al., Inorg. Chem.*, 1984, **23**, 653.

[38] See, for example, A. E. Merbach *et al., J. Chem. Soc. Dalton Trans.*, **1984**, 804.

Silicon alkoxides are rapidly hydrolyzed by water, eventually to hydrous silica, but polymeric hydroxo alkoxo intermediates occur.

Of the *carboxylates, lead tetraacetate*[39] is the most important because it is used in organic chemistry as a strong but selective oxidizing agent. It is made by dissolving Pb_3O_4 in hot glacial acetic acid or by electrolytic oxidation of Pb^{II} in acetic acid. In oxidations the attacking species is generally considered to be $Pb(O_2CMe)_3^+$, which is isoelectronic with the similar oxidant $Tl(O_2CMe)_3$, but this is not always so, and some oxidations are known to be free radical in nature. The trifluoroacetate is a white solid, which will oxidize even heptane to give the CF_3CO_2R species, from which the alcohol ROH is obtained by hydrolysis; benzene similarly gives phenol.

The tetraacetates of Si, Ge, Sn, and Pb also form complex anions such as $[Pb(O_2CMe)_6]^{2-}$ or $[Sn(O_2CMe)_5]^-$. For $M(O_2CMe)_4$, Si and Ge are four-coordinate with unidentate acetate; Pb has only bidentate acetates, whereas the smaller Sn has a very distorted dodecahedron.

Tin(IV) sulfate, $Sn(SO_4)_2 \cdot 2H_2O$, can be crystallized from solutions obtained by oxidation of Sn^{II} sulfate; it is extensively hydrolyzed in water.

Tin(IV) nitrate is obtained as a colorless volatile solid by interaction of N_2O_5 and $SnCl_4$; it contains bidentate NO_3^- groups giving dodecahedral coordination. The compound reacts with organic matter.

9-11. Organo Compounds[40]

The general formula is $R_{4-n}MX_n$ (n = 0 to 3), where R is alkyl or aryl and X is any of a wide variety of atoms or groups (H, halogen, OR′, NR_2', SR′, $Mn(CO)_5$, etc.). The elements may also form part of a heterocyclic ring, for example $(R_2MO)_3$.

For a given class of compounds, members with C—Si and C—Ge bonds have higher thermal stability and lower reactivity than those with bonds to Sn and Pb. In catenated compounds similarly, Si—Si and Ge—Ge bonds are more stable and less reactive than Sn—Sn and Pb—Pb bonds; for example, Si_2Me_6 is very stable, but Pb_2Me_6 blackens in air and decomposes rapidly in CCl_4, although it is fairly stable in benzene.

The bonds to carbon are usually made via interaction of lithium, mercury, or aluminum alkyls or RMgX and the Group IV halide, but there are many special synthetic methods, some of which are noted later.

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[39] G. M. Rubottom, In *Oxidation in Organic Chemistry,* W. H. Tranhowsky, Ed., Academic Press, New York, 1982.

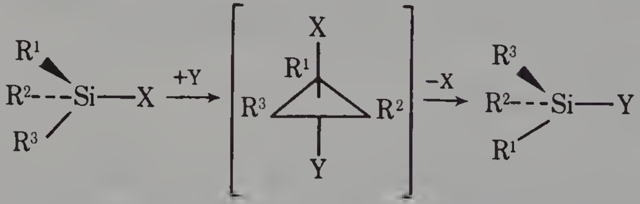
[40] H. Sakurai, Ed., *Organosilicon and Bioorganic Silicon Chemistry,* Ellis Horwood, Chichester, 1985.
For Si—D. A. Armitage; T. J. Barton, *et al.;* R. West, in *Comprehensive Organometallic Chemistry,* Pergamon, Oxford, 1982, Vol. 2, Chapters 9.1–9.4.
For Ge—P. Riviére, *et al., ibid,* Chapter 10.
For Sn—A. G. Davies, *ibid,* Chapter 11.
For Pb—P. G. Harrison, *ibid,* Chapter 12.

Silicon and Germanium. The organo compounds of Si and Ge are very similar in their properties, although Ge compounds have been less extensively studied. We discuss only Si compounds.

Silicon–carbon bond dissociation energies are less than those of C—C bonds but are still quite high, in the region 250 to 335 kJ mol^{-1}. The tetraalkyls and -aryls are hence thermally quite stable; $Si(C_6H_5)_4$, for example, boils unchanged at 530°C.

The chemical reactivity of Si—C bonds is generally greater than that of C—C bonds because (*a*) the greater polarity of the bond $Si^{\delta+}—C^{\delta-}$ allows easier nucleophilic attack on Si and electrophilic attack on C than for C—C compounds, and (*b*) displacement reactions at silicon are facilitated by its ability to form five-coordinate transition states by utilization of *d* orbitals.

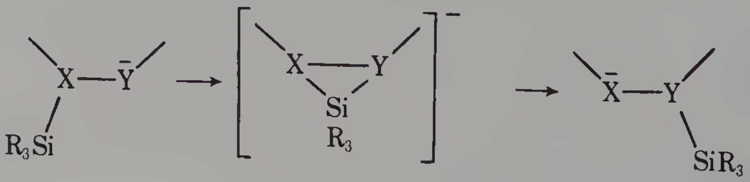
The reactions of Si compounds have no mechanism analogous to S_N1 reactions at carbon and are generally complicated.[41a] Substitution reactions at four-coordinate silicon characteristically proceed via an associative mechanism involving five-coordinate transition states. Retention or inversion of stereochemistry may occur depending on the nature of the entering or leaving groups, namely,



With the same leaving group, both retention and inversion can be observed; hard nucleophiles tend to attack equatorially to give retention, soft ones, apically leading to inversion.

Finally, mechanisms depend crucially on the solvent used. If this has donor ability like DMF or DMSO it may attack first to form the five-coordinate species and is then displaced by an incoming nucleophile.

A characteristic feature of organosilicon (and -germanium) chemistry, setting it strikingly apart from carbon chemistry, is the great ease with which R_3Si (and R_3Ge) groups migrate; a factor of up to 10^{12} as compared to analogous carbon compounds is typical. Among the best studied migration reactions are anionic 1,2-shifts, represented generally by the equation:



[41a] See, for example, R. J. P. Corriu *et al.*, *Angew, Chem. Int. Ed. Engl.*, 1986, **25**, 473; J. A. Deiters and R. R. Holmes, *J. Am. Chem. Soc.*, 1987, **109**, 1686, 1692.

where X—Y may be N—N, O—N, or S—C. As indicated, a transition state involving five-coordinate Si is postulated; since carbon has no valence shell *d* orbitals, it cannot form such a transition state easily, and such 1,2-shifts are "forbidden" in the Woodward–Hoffmann sense.

Radicals are less important in silicon than in carbon chemistry. However, silicon radicals have been detected in solution by esr and have been isolated in matrices. They are made by hydrogen abstraction with *t*-butoxy and other radicals generated photochemically, for example,

$$R_3SiH + Me_3CO^{\cdot} \longrightarrow R_3Si^{\cdot} + Me_3COH$$

The stable $R_3Si\cdot$ radicals with extremely bulky R groups have been isolated.

A comparison of the rates of reactions such as

$$p\text{-}XC_6H_4MR_3 + H_2O \longrightarrow R_3MOH + C_6H_5X$$

in aqueous-methanolic $HClO_4$ gives the order $Si(1) < Ge(36) \ll \ll Sn(3 \times 10^5) \ll Pb(2 \times 10^8)$, which suggests that with increasing size, there is increased availability of outer orbitals, which allows more rapid initial solvent coordination to give the five-coordinated transition state.

Alkyl- and Arylsilicon Halides. These compounds are of special importance because of their hydrolytic reactions. They may be obtained by normal Grignard procedures from $SiCl_4$, or, in the case of the methyl derivatives, by the Rochow process, in which methyl chloride is passed over a heated, copper-activated silicon:

$$CH_3Cl + Si(Cu) \longrightarrow (CH_3)_nSiCl_{4-n}$$

The halides are liquids that are readily hydrolyzed by water, usually in an inert solvent. In certain cases, the silanol intermediates R_3SiOH, $R_2Si(OH)_2$, and $RSi(OH)_3$ can be isolated, but the diols and triols usually condense under the hydrolysis conditions to siloxanes that have Si—O—Si bonds. The exact nature of the products depends on the hydrolysis conditions and linear, cyclic, and complex cross-linked polymers of varying molecular weights can be obtained. They are often referred to as silicones; the commercial polymers usually have R = CH_3, but other groups may be incorporated for special purposes.

Controlled hydrolysis of the alkyl halides in suitable ratios can give products of particular physical characteristics. The polymers may be liquids, rubbers, or solids, which have in general high thermal stability, high dielectric strength, and resistance to oxidation and chemical attack.

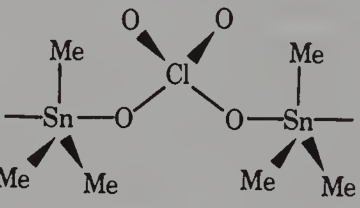
Examples of simple siloxanes are $Ph_3SiOSiPh_3$ and the cyclic trimer or tetramer $(Et_2SiO)_{3(\text{or } 4)}$; linear polymers contain —SiR_2—O—SiR_2—O— chains, whereas the cross-linked sheets have the basic unit $RSi(O—)_3$.

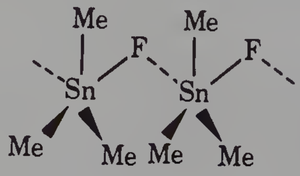
The Me_3SiX compounds and Lewis acids give adducts, for example, $Me_3SiBr^{\delta-}\rightarrow Al^{\delta+}Br_3$ but no R_3Si^+ ions are formed.[41b]

[41b] G. A. Olah *et al.*, *Organometallics*, 1984, **3**, 1337.

Tin. Where the compounds of tin differ from those of Si and Ge they do so mainly because of a greater tendency of Sn^{IV} to show coordination numbers >4 and because of ionization to give cationic species (or, as in the case of $Li^+[SnMe_5]^-$ a *tbp* anion[42a]) and octahedral species of the type $R_4Sn(bipy)$.[42b]

Trialkyltin compounds of the type R_3SnX, of which the best studied are the CH_3 compounds ($X = ClO_4$, F, NO_3, etc.), are of interest in that they are always associated in the solid by anion bridging (9-IX and 9-X); the coordination of the tin atom is close to *tbp* with planar $SnMe_3$ groups. When X is RCO_2 the compounds may in addition be monomeric with unidentate or bidentate carboxylate groups.


(9-IX)


(9-X)

The R_3SnX (and also R_3PbX) compounds also form 1:1 and 1:2 adducts with Lewis bases, and these also generally appear to contain five-coordinate Sn, with the alkyl groups axial. The highly specific action of R_3SnX compounds in biological systems where toxicity is independent of X is probably due to dissociation.[43] In water the trimethyl perchlorate gives $[Me_3Sn(H_2O)_2]^+$.

Dialkyltin compounds (R_2SnX_2) have behavior similar to that of the trialkyl compounds. Thus the fluoride Me_2SnF_2 is again polymeric, with bridging F atoms, but Sn is octahedral and the Me—Sn—Me group is linear. However, the chloride and bromide have low melting points (90 and 74°C) and are essentially molecular compounds, only weakly linked by halogen bridges. The nitrate $Me_2Sn(NO_3)_2$ is strictly molecular with bidentate nitrate groups.

The halides also give conducting solutions in water and the aqua ion has the linear C—Sn—C group characteristic of the dialkyl species (cf. the linear species Me_2Hg, Me_2Tl^+, Me_2Cd, and Me_2Pb^{2+}), probably with four water molecules completing octahedral coordination. The linearity in these species appears to result from maximizing of *s* character in the bonding orbitals of the metal atoms. The ions Me_2SnCl^+ and Me_2SnOH^+ also exist, and in alkaline solution *trans*-$[Me_2Sn(OH)_4]^{2-}$ occurs.

Catenated linear and cyclic organotin compounds are relatively numerous and stable. For example, the reaction of sodium in liquid ammonia with $Sn(CH_3)_2Cl_2$ gives $[Sn(CH_3)_2]_n$, which consists mainly of linear molecules with

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[42a] H. J. Reich and N. H. Phillips, *J. Am. Chem. Soc.*, 1986, **108**, 2102.
[42b] V. G. K. Das *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 129.
[43] R. R. Holmes *et al.*, *Inorg. Chem.*, 1984, **23**, 3147.

chain lengths of 12 to 20 (and perhaps more), as well as at least one cyclic compound, $[Sn(CH_3)_2]_6$. There is no evidence for branching of chains. Similar results have been obtained with other alkyl and aryl groups; for example, the cyclic hexamer and nonamer of Et_2Sn, the cyclic pentamer and hexamer of Ph_2Sn, and the cyclic tetramer of t-Bu_2Sn have been isolated, as well as linear species. In some cases the terminal groups of the linear species are SnR_2H. The structure of $[Ph_2Sn]_6$ has an Sn_6 ring in a chair configuration, with the Sn—Sn bonds of about the same length as those in gray tin. Macrocycles such as $[Ar_2Sn(CH_2)_n]_4$ are also known.[44]

Organotin hydrides (R_3SnH), which can be made by $LiAlH_4$ reduction of the halide or in other ways, are useful reducing agents in organic chemistry; some of the reactions are known to proceed by free-radical pathways. The hydrides undergo additional reactions with alkenes or alkynes similar to the hydrosilation reaction, which provides a useful synthetic method for organotin compounds containing functional groups.

$$R_3SnH + R_2C{=}CR'_2 \longrightarrow R_3SnCR_2CR'_2H$$

Unlike hydrosilation (Section 28-11), hydrostannation proceeds via radical chains propagated by $R_3Sn\cdot$ radicals; intermediate radicals $R_3SnCR_2CR'_2\cdot$ have been characterized.[45]

Organotin compounds are widely used as marine antifouling compounds, wood preservatives, stabilizers for poly(vinyl chloride), antihelmintics, and so on.

Tin sulfide in marine sediments can react with CH_3I—a ubiquitous biogenic molecule in sea water—to give tin methyls[46]

$$SnS + 4MeI \longrightarrow MeSnI_3 + Me_3SI$$

Lead. There is an extensive organolead chemistry, but the most important compounds are $PbMe_4$ and $PbEt_4$. These compounds were made in large quantities for use as antiknock agents in gasoline, although their use is now being phased out in favor of nonpolluting or less polluting oxygenates such as methyl t-butyl ether, dimethyl carbonate, and MeOH.

The major commercial synthesis is by the interaction of a sodium–lead alloy with CH_3Cl or C_2H_5Cl in an autoclave at 80 to 100°C, without solvent for C_2H_5Cl but in toluene at a higher temperature for CH_3Cl. The reaction is complicated and not fully understood, and only a quarter of the lead appears in the desired product:

$$4NaPb + 4RCl \longrightarrow R_4Pb + 3Pb + 4NaCl$$

[44] Y. Azuma and M. Newcomb, *Organometallics*, 1984, **3**, 9.

[45] M. J. S. Dewar *et al., J. Am. Chem. Soc.*, 1984, **106**, 6773.

[46] W. F. Manders *et al., J. Chem. Soc. Chem. Commun.*, **1984**, 538.

The required recycling of the lead is disadvantageous, and electrolytic procedures have been developed. One process involves electrolysis of $NaAlEt_4$ with a lead anode and mercury cathode; the sodium formed can be converted into NaH and the electrolyte regenerated:

$$4NaAlEt_4 + Pb \longrightarrow 4Na + PbEt_4 + 4AlEt_3$$

$$4Na + 2H_2 \longrightarrow 4NaH$$

$$4NaH + 4AlEt_3 + 4C_2H_4 \longrightarrow 4NaAlEt_4$$

The alkyls are nonpolar, highly toxic liquids. The tetramethyl begins to decompose around 200°C and the tetraethyl around 110°C, by free-radical mechanisms.

THE DIVALENT STATE

9-12. Halides, Oxides, Salts, and Complexes

Silicon. Divalent Si^{II} species[47a] are thermodynamically unstable under normal conditions but the SiX_2 species occur in high temperature reactions and have been trapped by rapid chilling to liquid nitrogen temperature.

At ~1150°C and low pressures SiF_4 and Si react to give SiF_2 in ~50% yield:

$$SiF_4 + Si \rightleftharpoons 2SiF_2$$

The compound is stable for a few minutes at *ca.* 10^{-6} atm. pressure, whereas CF_2 has $t_{1/2} \approx 1$ s and GeF_2 is a stable solid at room temperature. It is diamagnetic and the molecule is angular, with a bond angle of 101° both in the vapor and in the condensed phase. The reddish-brown solid gives an esr spectrum and presumably also contains $^{\cdot}SiF_2(SiF_2)_nSiF_2^{\cdot}$ radicals. When warmed it becomes white, cracking to give fluorosilanes up to $Si_{16}F_{34}$.

In the gas phase SiF_2 reacts with oxygen but is otherwise not very reactive. Allowing the solid to warm in the presence of various compounds (e.g., CF_3I, H_2S, GeH_4, or H_2O) yields insertion products such as $SiF_2H(OH)$ and H_3GeSiF_2H.

Silicon dichloride[47b] has been made by the reaction

$$Si_2Cl_6 \xrightarrow[1450°C]{KSi} 3SiCl_2$$

and in various other ways.

Some polymeric, formally divalent iodides have been made by treating $(SiPh_2)_n$ with HI and $AlCl_3$; these are Si_4I_8, Si_5I_{10}, and Si_6I_{12}.[48]

[47a] L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, 1979, **79,** 529.

[47b] H. Bock *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 205; I. Hargittai, *J. Am. Chem. Soc.*, 1983, **105,** 2895; E. A. Chernyshev *et al., J. Organomet. Chem.*, 1984, **271,** 129.

[48] E. Hengge and D. Kovar, *Angew. Chem. Int. Ed. Engl.*, 1981, **20,** 678.

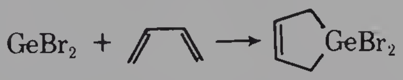
Germanium. The germanium dihalides[49] are quite stable. Germanium (II) fluoride (GeF_2), a white crystalline solid (mp 111°C), is formed by the action of anhydrous HF on Ge in a bomb at 200°C or by the reaction of Ge and GeF_4 above 100°C. It is a fluorine-bridged polymer, the Ge atom having a distorted trigonal bipyramid arrangement of four atoms and an equatorial lone pair. The compound reacts exothermically with solutions of alkali metal fluorides to give the hydrolytically stable ion GeF_3^-; in fluoride solutions the ion is oxidized by air, and in strong acid solutions by H^+, to give GeF_6^{2-}. The vapors of GeF_2 contain oligomers $(GeF_2)_n$ where $n = 1$ to 3.

The other dihalides are less stable than GeF_2 and similar to each other. They can be prepared by the reactions

$$Ge + GeX_4 \longrightarrow 2GeX_2$$

In the gas phase or isolated in noble gas matrices, they are bent with angles of 90 to 100°C. The solids react to complete their octets (e.g., with donors, to produce pyramidal $LGeX_2$ molecules), or with butadiene:

$$GeI_2 + R_3P \longrightarrow R_3PGeI_2$$



Other divalent germanium compounds include salts of $GeCl_3^-$, the sulfide GeS, and a white to yellow hydroxide of no definite stoichiometry that is converted by NaOH to a brown material that has Ge—H bonds.

Germanium and tin form stable, diamagnetic β-diketonato complexes such as $M(acac)_2$ and $M(acac)X$, where M is Ge, Sn, and X is Cl or I. The $M(dike)_2$ types can be distilled or sublimed; they are soluble and monomeric in benzene and other hydrocarbon solvents.

Tin. The fluoride and chloride are obtained by reaction of Sn with gaseous HF or HCl. Tin(II) bromide ($SnBr_2$) is obtained by dissolving tin in aqueous HBr, distilling off constant boiling HBr/H_2O, and cooling. The tin atoms are nine- and eight-coordinate in $SnCl_2$ and $SnBr_2$, respectively. Tin(II) fluoride (SnF_2) has a unique structure with an eight-membered ring of alternating Sn and F atoms and one terminal F on each trigonal pyramidal Sn atom. Water hydrolyzes the halides, but they dissolve in solutions containing excess halide ion to give SnX_3^- ions. With the fluoride, SnF^+ and $Sn_2F_5^-$ can also be detected, and the latter is known in crystalline salts. The SnF_2 forms $[SnF]^+[SbF_6]^-$ and similar compounds with F^- acceptors. Tin(II) fluoride is used in toothpastes, presumably as a source of fluoride to harden dental enamel.

Many salts of the ion $SnCl_3^-$ are known but few for the ψ-*tbp* $SnCl_4^{2-}$ ion[50]

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[49] S. M. van der Kirk *et al., Polyhedron,* 1983, **2**, 509.

[50] P. G. Harrison *et al., Inorg. Chim. Acta,* 1983, **75**, 265.

and various solid phases (for example, Cs_4SnCl_6) have been characterized.[51]

The halides dissolve in donor solvents such as acetone, pyridine, or DMSO to give pyramidal adducts SnX_2L.

The air-sensitive tin(II) ion (Sn^{2+}) occurs in acid perchlorate solutions, which may be obtained by the reaction

$$Cu(ClO_4)_2 + Sn/Hg = Cu + Sn^{2+} + 2ClO_4^-$$

The only salt of a bare Sn^{2+} ion appears to be $Sn^{2+}(SbF_6^-)_2(AsF_3)_2$ which is formed when SnF_2 and SbF_5 are dissolved in AsF_3. The ion is nine-coordinate with six F atoms from SbF_6^- and three F atoms from AsF_3 but there is distortion due to effects of the lone pair.[52]

In aqueous solutions at pH 2.7 to 3.7, $3M$ in $NaClO_4$, the main hydrolytic reactions are

$$Sn^{2+} + H_2O = Sn(OH)^+ + H^+ \qquad \log K = -3.7$$

$$3Sn^{2+} + 4H_2O = Sn_3(OH)_4^{2+} + 4H^+ \qquad \log K = -6.8$$

The trimeric, probably cyclic, ion appears to provide the nucleus of several basic tin(II) salts obtained from aqueous solutions at fairly low pH. Thus the nitrate appears to be $Sn_3(OH)_4(NO_3)_2$ and the sulfate $Sn_3(OH)_2OSO_4$, which contains the cyclic $[Sn_3O(OH)_2]^{2+}$ ion. All Sn^{II} solutions are readily oxidized by oxygen and, unless stringently protected from air, normally contain some Sn^{IV}. The chloride solutions are often used as mild reducing agents:

$$SnCl_6^{2-} + 2e = SnCl_3^- + 3Cl^- \qquad E^0 = \sim 0.0\text{ V } (1M\text{ HCl}, 4M\text{ Cl}^-)$$

The addition of aqueous ammonia to Sn^{II} solutions gives the white hydrous oxide that is dehydrated to black SnO when heated in suspension at 60 to 70 °C in $2M$ NH_4OH. It disproportionates above ~250°C to give Sn and Sn_3O_4 and over 500°C Sn and SnO_2 are formed.[53]

A true tin(II) hydroxide[54] has been made by the anhydrous reaction

$$2R_3SnOH + SnCl_2 \longrightarrow Sn(OH)_2 + 2R_3SnCl$$

as a white, amorphous solid. The anhydrous oxide is amphoteric and dissolves in alkali hydroxide to give solutions of *stannites,* which may contain the ion $[Sn(OH)_6]^{4-}$. These solutions are quite strong reducing agents; on storage they deposit SnO, and at 70 to 100°C they disproportionate slowly to β-tin and Sn^{IV}. The only characterized oxostannite is the deep yellow $K_2Sn_2O_3$ made by direct interaction at 550°C; it has a perovskite structure with half the anions missing.

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[51] J. D. Donaldson *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 767.

[52] A. J. Edwards and K. I. Khallow, *J. Chem. Soc. Chem. Commun.,* **1984,** 50.

[53] F. Gauzzi *et al., Inorg. Chim. Acta,* 1985, **104,** 1.

[54] W-W. du Mont and B. Neudart, *Angew. Chem. Int. Ed. Engl.,* 1980, **19,** 553.

Other Sn^{II} compounds include carboxylates and carboxylato anion complexes[55] such as $Sn(O_2CCF_3)_2$ and $[Sn(O_2CMe)_3]^-$. There are also some mixed valence carboxylates made by the interaction of Sn_2Ph_6 with carboxylic acids. Examples are $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2 \cdot C_6H_6$ and $[Sn^{II}Sn^{IV}O(O_2CR)_4\{O(OCR)_2\}]_2$; the latter has μ_3-O and μ-O_2CR groups.[56]

The thiolate ion $[Sn(SPh)_3]^-$ is pyramidal[57] like the Pb analogue, while a rare phosphine complex $Sn[C(PMe_2)_3]_2$ has two P atoms of the anion $C(PMe_2)_3^-$ coordinated in a ψ *tbp* structure.[58]

Some Sn^{II} (and also Pb^{II}) chalcogenide, halide, and mixed compounds (e.g., $CsSnBr_3$ and Pb_4Cl_6S) are intensely colored, even black, the color becoming more intense as the atomic number of the chalcogen or halogen increases. These appear to have unusual structures and bonding. For example, $CsSnBr_3$ has an ideal perovskite structure (no stereochemically active lone pair) and is a semiconductor; the halide and chalcogenide ions may use outer *d* orbitals to form energy bands that are partially populated by the 5*s* or 6*s* electrons of Sn^{II} or Pb^{II}.

Lead. Lead has a well-defined cationic chemistry. There are several crystalline salts most of which are insoluble ($PbSO_4$, $PbCrO_4$) or sparingly soluble (PbF_2, $PbCl_2$) in water. The soluble ones,[59] $Pb(ClO_4)_2 \cdot 3H_2O$, $Pb(NO_3)_2$, and $Pb(O_2CMe)_2 \cdot 3H_2O$ give the hydrated ions Pb^{2+}, $PbNO_3^+$, and $Pb(O_2CMe)^+$, respectively, in solution.[60] The halides, unlike those of Sn are always anhydrous and have distorted close-packed halogen lattices.

The *oxide* has two forms: litharge, red with a layer structure, and massicott, yellow with a chain structure. The oxide Pb_3O_4 (red lead), which is made by heating PbO or PbO_2 in air, behaves chemically as a mixture of PbO and PbO_2, but the crystal contains $Pb^{IV}O_6$ octahedra linked in chains by sharing of opposite edges, the chains being linked by Pb^{II} atoms each bound to three oxygen atoms. In all Pb^{II} oxides and mixed oxides the stereochemical influence of the lone pair is apparent.[61a]

The lead(II) ion is partially hydrolyzed in water.[61b] In perchlorate solutions the first equilibrium appears to be[61a]

$$Pb^{2+} + H_2O = PbOH^+ + H^+ \qquad \log K \approx -7.9$$

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[55] S. M. Grimes *et al., J. Chem. Soc. Dalton Trans.,* **1984,** 1965; T. Birchall *et al., J. Chem. Soc. Dalton Trans.,* **1987,** 1675.

[56] T. Birchall and J. P. Johnson, *Inorg. Chem.,* 1982, **21,** 3724.

[57] P. A. W. Dean *et al., Can. J. Chem.,* 1985, **63,** 394.

[58] H. H. Karsch *et al., Organometallics,* 1986, **5,** 1664; A. L. Balch and D. Oram, *Inorg. Chem.,* 1987, **26,** 1906; cf. also A. H. Cowley *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 1446 for $Li(thf)M(PBu_2)_3$, M = Sn, Pb.

[59] M. C. Etter *et al., Inorg. Chem.,* 1984, **23,** 3580.

[60] P. G. Harrison *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 1845.

[61a] C. Casales and I. Rasines, *J. Chem. Soc. Dalton Trans.,* **1986,** 1247.

[61b] R. N. Sylva and P. L. Brown, *J. Chem. Soc. Dalton Trans.,* **1980,** 1577.

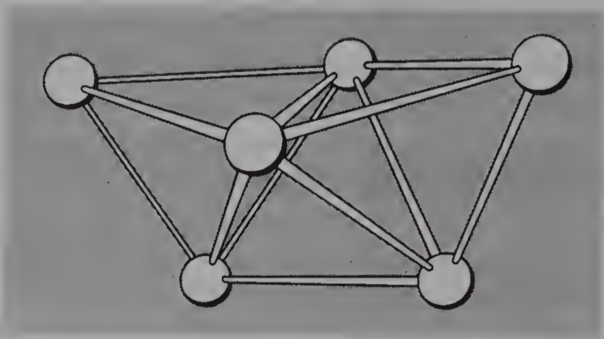

FIG. 9-8. The three face-sharing tetrahedra of Pb atoms in the $Pb_6O(OH)_6^{4+}$ cluster. The middle tetrahedron has an O atom at its center. The end tetrahedra have μ_3-OH groups.

but the main aqueous species is $Pb_4(OH)_4^{4+}$, which has a cubane structure with μ_3-OH bridges in crystalline salts.

Another polymeric ion obtained by dissolving PbO in $HClO_4$ and adding an appropriate amount of base has a structure shown in Fig. 9-8. A μ_4-O unit in the center of a Pb_4O_4 cube also occurs in $Pb_4O(OSiPh_3)_6$ which is formed by the action of Ph_3SiOH on Cp_2Pb,[62] while $Pb_9O_4Br_{10}$ has a Pb_4O_4 cube with each O atom bound to an additional Pb giving a $Pb_4(OPb)_4$ unit.[63]

Addition of base to lead solutions gives the hydrous oxide, which dissolves in an excess of base to give the plumbate ion. If aqueous ammonia is added to a lead acetate solution, a white precipitate of a basic acetate is formed. On suspension in warm aqueous ammonia and subsequent drying it yields a very pure lead oxide, which is most stable in the tetragonal red form.

Lead(II) also forms numerous complexes that are mostly octahedral, although a phosphorodithioate, $Pb(S_2Pi\text{-}Pr_2)_2$, is polymeric, with six Pb—S bonds and a stereochemically active lone pair. Interaction of the nitrate and NaSPh allows isolation of $[Ph_4As][Pb(SPh)_3]$, which provided the first clear example of trigonal pyramidal Pb^{II}.[64]

9-13. Silenes and Other Organo Compounds[65]

Compounds of stoichiometry GeR_2 or SnR_2, known for a long time, proved to be cyclogermanes or stannanes[66] such as $(Me_2Sn)_6$ or various other polymers with M^{II}—M^{II} bonds. Similarly, silicon compounds made by reduction of

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[62] P. G. Harrison *et al.*, *J. Chem. Soc. Chem. Commun.*, **1980,** 1251.

[63] H-L. Keller, *Angew. Chem. Int. Ed. Engl.*, 1983, **22,** 324.

[64] G. Christou *et al.*, *Polyhedron*, 1984, **2,** 1247; P. A. W. Dean *et al.*, *Inorg. Chem.*, 1984, **23,** 4232.

[65] A. H. Cowley and N. C. Norman, *Progr. Inorg. Chem.*, 1986, **34,** 1; M. Veith and O. Recktenwald, in *Organotin Compounds, Topics in Current Chemistry*, No. 104, Springer, New York, 1982; G. Raabe and J. Michl, *Chem. Rev.*, 1985, **85,** 419 (Multiple bonds to Si, 435 references; A. G. Brook and K. M. Baines, *Adv. Organomet. Chem.*, 1986, **25,** 1.

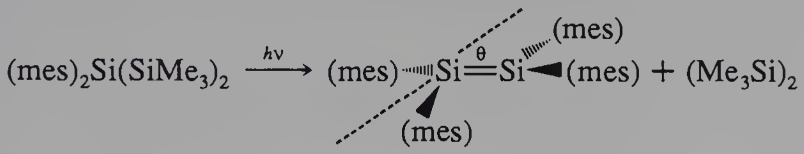
[66] See, for example, W. P. Neuman *et al.*, *Organometallics*, 1985, **4,** 1954; S. Masamune and L. R. Sita, *J. Am. Chem. Soc.*, 1985, **107,** 6390.

R_2SiCl_2 by Li or Na/K in THF where R is *not* a bulky ligand are cyclic polymers. These compounds are often similar to hydrocarbons[67] but differ in having large Si—Si—Si angles ~115°.

However, when the alkyl or aryl groups are very bulky, monomers (MR_2) or dimers ($R_2M{=}MR_2$) can be isolated. The simplest silene (Me_2Si) can be obtained only in the gas phase or in solution by the reaction[68]

$$c\text{-}(Me_2Si)_6 \xrightarrow{\Delta} c\text{-}(Me_2Si)_5 + Me_2Si$$

Silenes. The first isolable compound, the yellow tetramesityl disilene (9-XI) was made by R. West via the reaction

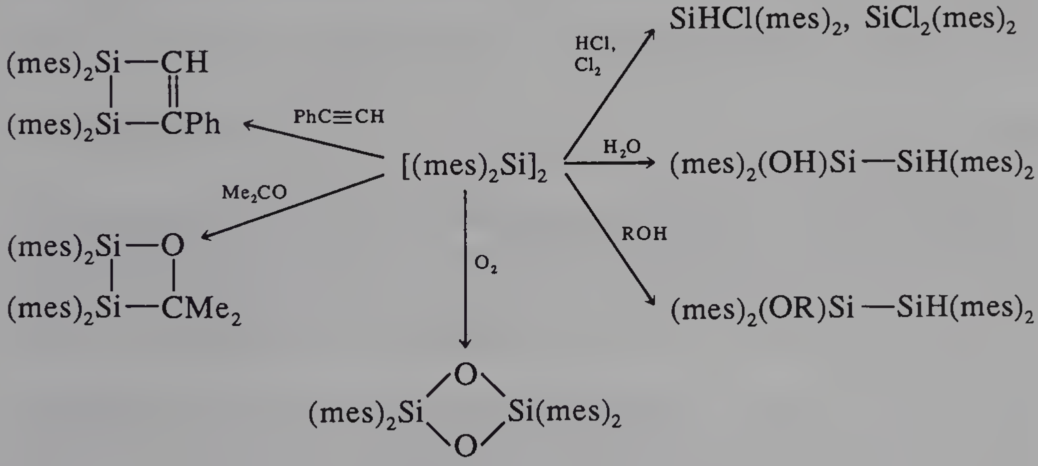


(9-XI)

It is an air sensitive but reasonably thermally stable solid with a slightly bent trans structure θ = 18°. The Si═Si bond (2.16 Å) is ~9% shorter than a Si—Si bond.

Many other disilenes are made by reduction of R_2SiCl_2 with Li or Li naphthalenide.[69] Some compounds have cis and trans isomers for which activation energies of isomerization are known.[70a]

Some reactions of the mesityl are given in Fig. 9-9. The oxo compound[70b] (9-XII) has a nearly planar $Si(\mu\text{-}O)_2Si$ ring. The Si—Si distance is also shorter



(9-XII)

FIG. 9-9. Reactions of tetramesitylsilene (mes = mesityl).

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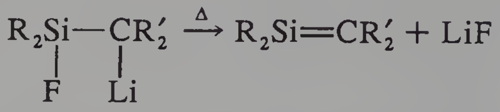
[67] R. West *et al.*, *Organometallics*, 1985, **4,** 1664; *J. Am. Chem. Soc.*, 1986, **108,** 5478.
[68] W. P. Weber *et. al.*, *J. Am. Chem. Soc.*, 1984, **106,** 7267.
[69] S. Masamune *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1987, **26**, 584.
[70a] R. West *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 4239.
[70b] R. West *et al.*, *J. Am. Chem. Soc.*, 1987, **109,** 4116.

than normal in $(\mu\text{-}O)_2$ compounds suggesting that the oxygen breaks only the π and not the σ component of the Si═Si bond.

There are similar compounds, $R_2Si{=}CR_2$, with Si═C bonds[71] that can be made by elimination reactions of the type



$$\underset{\textstyle F}{R_2Si}-\underset{\textstyle Li}{CR'_2} \xrightarrow{\Delta} R_2Si{=}CR'_2 + LiF$$

A representative example is $Me_2Si{=}C(SiMe_3)(SiMe\textit{t}\text{-}Bu_2)$ where the $C_2Si{=}CSi_2$ skeleton is planar with a Si═C bond distance of 1.702 Å. Finally, compounds with Si═N, Si≡N, Si═P, and Si═O bonds are now known,[72] an example being $\textit{t}\text{-}Bu_2Si{=}NSi\textit{t}\text{-}Bu_3$.

The air sensitive $(Me_5C_5)_2Si$ has two forms[73a] in the solid state one with parallel rings, the other bent like Cp_2Sn; $Si(\eta^5\text{-}C_2B_9H_{11})_2$ has a sandwich structure.[73b]

Germanium, Tin, and Lead. The *germenes*,[74a] which can be made by the action of Grignard reagents on $GeCl_2$·dioxan in ether, are less stable than silenes. Thus $Ge_2[CH(SiMe_3)_2]_4$ behaves chemically as a very reactive singlet, $:GeR_2$, indicating the lability of the Ge—Ge bond. It dissociates in the vapor to the angular[74b] GeR_2 and gives carbenelike compounds (Chapter 25) such as $(CO)_5CrGeR_2$. A stable compound with a Ge═C bond is known.[74c]

Tin[74a] and *lead* form highly colored monomers or dimers but in Sn_2R_4 the Sn—Sn distance 2.76 Å is closer to that of a Sn—Sn single bond. Theoretical studies[45] indicate that π bonding does not occur and that tin is pyramidal sp^3 with conjugative interaction leading to some sort of Sn—Sn bond or possibly

There are also Ge and Sn compounds of the type $R_2M{=}\ddot{P}{-}R'$ where R′ is 2,4,6-tri-*t*-butyl phenyl.[75]

Another class of divalent compounds are the η^5 cyclopentadienyls $(\eta^5\text{-}C_5R_5)_2M$, M = Ge, Sn, and Pb.[76] With the exception of the decaphenyl, all

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[71] N. Wiberg *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 229; H. F. Schaefer III, *Acc. Chem. Res.*, 1982, **15**, 283.

[72] M. Hesse and U. Klingebiel, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 649; N. Wiberg *et al., J. Chem. Soc. Chem. Commun.*, **1986**, 591; R. West *et al., J. Am. Chem. Soc.*, 1986, **108**, 4241; C. N. Smit and F. Bickelhaupt, *Organometallics*, 1987, **6**, 1156.

[73a] P. Jutzi *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 164.

[73b] M. F. Hawthorne *et al., J. Am. Chem. Soc.*, 1986, **108**, 5369.

[74a] M. F. Lappert *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 2387.

[74b] A. Haaland *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 1551.

[74c] C. Couret *et al., J. Am. Chem. Soc.*, 1987, **109**, 4411.

[75] J. Escudie *et al., J. Am. Chem. Soc.*, 1985, **107**, 3378; C. Couret *et al., J. Am. Chem. Soc.*, 1985, **107**, 8280.

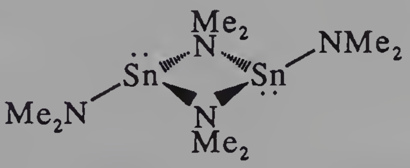
[76] H. Schumann *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 773; H. F. Schaefer III, *et al., J. Am. Chem. Soc.*, 1985, **107**, 7239; P. Jutzi and B. Hielscher, *Organometallics*, 1986, **5**, 1201, 2511.

are angular (~30–50°C) in the gas phase and in solution with stereochemically active lone pairs. In the crystal, $(C_5H_5)_2Pb$ has a zigzag chain with alternately bridging and nonbridging C_5H_5 groups.

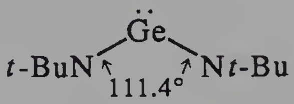
The decaphenyl analogue, $(\eta^5\text{-}Ph_5C_5)_2Sn$ has a nonangular, ferrocenelike structure; the bright yellow color, high stability, and low basicity suggest that the lone-pair electrons are delocalized over the aromatic, electron-withdrawing system.[77]

9-14. Dialkylamides and Alkoxides

These are somewhat similar to the alkyl or aryl compounds being monomeric with bulky ligands and dimeric with less bulky ones.[78] Examples are (9-XIII) and (9-XIV).



(9-XIII)



(9-XIV)

The orange $Ge(Nt\text{-}Bu_2)_2$ is stable but the maroon tin analogue is thermo- and photosensitive.

The *t*-butoxide $[Ge(OCMe_3)_2]_2$ made by the action of *t*-butanol on Cp_2Ge is trans dimeric but the bulkier $Ge(OCt\text{-}Bu_3)_2$ is a monomer. There is a similar compound $[Sn(Ot\text{-}Bu)_2]_2$ and salts $M[Sn(Ot\text{-}Bu)_3]$, bulky thiolates $M(SR)_2$, and more complicated species like the cubane $Sn_4(\mu\text{-}NR)_4$.[79]

THE ELEMENTS AND THEIR COMPOUNDS AS LIGANDS

9-15. The Elements

There is a variety of compounds that have Si bound to transition metals in relatively simple molecules[80] such as $Si[Re(CO)_5]_4$ or in clusters[81] (Chapter 23) such as $[Co_9(\mu_8\text{-}Si)(CO)_{21}]^{2-}$. Germanium, tin, and lead also form clusters such as $[Co_5Ge(CO)_{16}]^-$, $Co_4Pb(CO)_{16}(PR_3)_4$, and $[Fe_4Pb(CO)_{16}]^{2-}$.[82]

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[77] J. J. Zuckerman *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 4259.

[78] M. F. Lappert *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985,** 51; *J. Chem. Soc. Chem. Commun.*, **1985,** 548; M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1984, **23,** 413. M. Veith, *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 14.

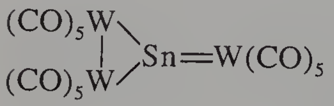
[79] M. Veith *et al.*, *Angew, Chem. Int. Ed. Engl.*, **1986,** 375; F. Fjeldberg *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985,** 939; W-W. du Mont, *Angew. Chem. Int. Ed. Engl.*, 1984, **23,** 61; P. P. Hitchcock *et al.*, *J. Chem. Soc. Chem. Commun.*, **1983,** 1492.

[80] B. J. Aylett *et al.*, *J. Organomet. Chem.*, 1983, **249,** 55.

[81] K. M. Mackay *et al.*, *J. Chem. Soc. Chem. Commun.*, **1984,** 1276.

[82] P. Hackett and A. R. Manning, *Polyhedron,* 1982, **1,** 45; B. K. Nicholson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1982,** 1023; K. M. Mackay and B. K. Nicholson, *Comprehensive Organometallic Chemistry,* Vol. 6, Chapter 43, Pergamon Press, Oxford, 1982; K. H. Whitmire *et al.*, *Inorg. Chem.*, 1986, **25,** 2080.

In addition, however, there are compounds such as (9-XV), (9-XVI), and (9-XVII).[83]



(9-XV)

$Ge[W(CO)_5]_4$

(9-XVI)

$Cp(CO)_2Mn{=}Pb{=}Mn(CO)_2Cp$

(9-XVII)

The latter is made by photolyzing $CpMn(CO)_3$ and $PbCl_2$ in THF.

In (9-XV) the W_3Sn group is planar.

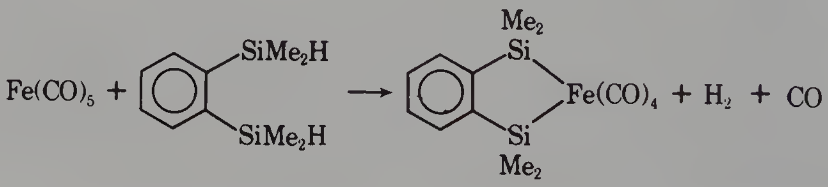
9-16. Silicon, Germanium, and Tin(IV)

The major types of complex containing Si, Ge, or Sn ligands are those with SiR_3, GeR_3, and SnR_3 groups that are similar in stoichiometry to those of carbon compounds. They can be obtained by reactions such as

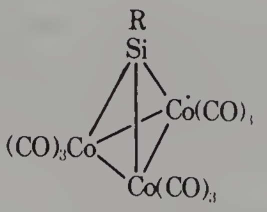
$$(\eta\text{-}C_5H_5)(CO)_3WNa + ClSiMe_3 = (\eta\text{-}C_5H_5)(CO)_3WSiMe_3 + NaCl$$

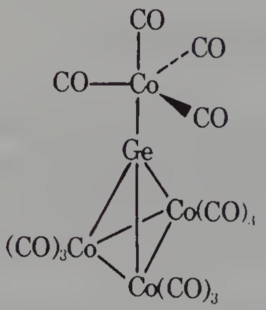
or, for Si, by oxidative–addition reactions (Chapter 27) of silanes, for example,

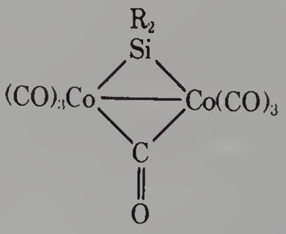
$$trans\text{-}Ir^{I}Cl(CO)(PPh_3)_3 + Me_3SiH = Ir^{III}Cl(H)(SiMe_3)(CO)(PPh_3)_2$$

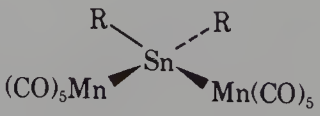


The SiR_3 groups have a very high trans effect. There are also compounds with bridging groups such as the following:









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[83] G. Huttner *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 428; *J. Organomet. Chem.*, 1985, **282,** 331; W. A. Herrmann *et al., J. Am. Chem. Soc.*, 1987, **109,** 2508.

Non-transition metal compounds are Li or Mg ones such as $[Mg(SiMe_3)_2]_2(tmen)$,[84] which can be used to synthesize other compounds.

9-17. Divalent Compounds

Most of the divalent compounds of Ge, Sn, and Pb^{II} have a lone pair and hence can act as donors. Examples are neutral compounds like Cp_2Sn, $Sn(acac)_2$, $Sn[CH(SiMe_3)_2]_2$, or $Sn(NR_2)_2$.[78] Some anionic species are, for example, $GeCl_3^-$ and $SnCl_3^-$. As well as acting as donors, the MX_2 compounds may behave as reducing agents or insert into metal halogen bonds, for example,

$$(CO)_5MnBr + Sn(NR_2)_2 \longrightarrow (CO)_5MnSnBr(NR_2)_2$$

$$[(BuNC)_6MoCl]^+ + SnCl_2 \longrightarrow [(BuNC)_6MoSnCl_3]^+$$

Tin compounds have been most studied, especially those of the $SnCl_3^-$ ion, by ^{119}Sn nmr and Mössbauer spectra.[85] The $SnCl_3^-$ ligand has a high trans effect and trans influence but has a rather low nucleophilicity. Thus in contrast to N, P, and As donors, $SnCl_2$ will not cleave halide bridges in compounds with, for example, $Pt(\mu\text{-}Cl)_2Pt$ bridges.

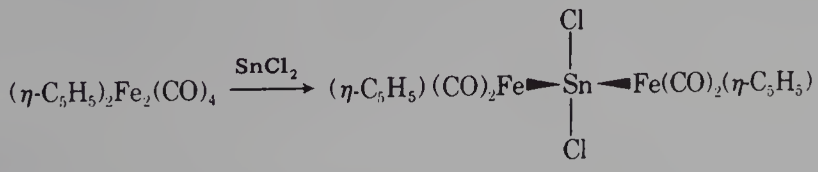
The $SnCl_3^-$ ion can generally displace Cl^-, CO, and more weakly bound ligands, for example,

$$[PtCl_4]^{2-} \xrightarrow{2SnCl_3^-} [PtCl_2(SnCl_3)_2]^{2-} \xrightarrow{3SnCl_3^-} [Pt(SnCl_3)_5]^{3-}$$

Typical complexes are $[RuCl_2(SnCl_3)_4]^{4-}$, $[Os(SnCl_3)_6]^{4-}$, $[PtH(SnCl_3)_2(PEt_3)_2]^-$, and *cis*- or *trans*-$[Pt(CO)Cl_2(SnCl_3)]^-$.[86]

The $SnCl_3^-$ ligand is a good leaving group and can thus provide a site for substrate coordination in catalytic reactions[87]; platinum metal systems will catalyze hydrogenation or hydroformylation of alkenes, water-gas shift and other reactions, (Chapter 28) in solutions or in melts of quaternary salts ($R_4N^+ SnCl_3^-$).

Some metal–metal bonded complexes react with $SnCl_2$ in a type of *insertion reaction,* (Chapter 27) where $SnCl_2$ could be considered to be showing carbenelike behavior, but the resulting compounds are clearly compounds of tin(IV):



$$(\eta\text{-}C_5H_5)_2Fe_2(CO)_4 \xrightarrow{SnCl_2} (\eta\text{-}C_5H_5)(CO)_2Fe\text{—}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Sn}}\text{—}Fe(CO)_2(\eta\text{-}C_5H_5)$$

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[84] J. P. Oliver *et al., Organometallics,* 1983, **2,** 746.

[85] See, for example, J. H. Nelson *et al., Inorg. Chem.,* 1984, **23,** 449; P. S. Pregosin *et al., J. Chem. Soc. Dalton Trans.,* **1984,** 2329; *J. Organomet. Chem.,* 1986, **308,** 373; K. R. Koch *et al., Polyhedron,* 1987, **6,** 71; Y. Saito *et al., Inorg. Chem.,* 1987, **26,** 3347.

[86] See, for example, I. R. Herbert *et al., Inorg. Chim. Acta,* 1986, **112,** 29.

[87] See, for example, H. C. Clark *et al., Organometallics,* 1982, **1,** 64.

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Chapter Ten

Nitrogen: Group VA(15)

GENERAL REMARKS

10-1. Introduction

The electronic configuration of the nitrogen atom in its ground state (^4S) is $1s^22s^22p^3$, with the three $2p$ electrons distributed among the p_x, p_y, and p_z orbitals with spins parallel. Nitrogen forms an exceedingly large number of compounds, most of which are to be considered organic rather than inorganic. It is one of the most electronegative elements, only oxygen and fluorine exceeding it in this respect.

The nitrogen atom may complete its octet in several ways:

1. *Electron Gain to Form the Nitride Ion, N^{3-}.* This ion occurs only in the saltlike nitrides of the most electropositive elements, for example, Li_3N. Many nonionic nitrides exist and are discussed later in this chapter.

2. *Formation of Electron-Pair Bonds.* The octet can be completed either by the formation of three single bonds, as in NH_3 or NF_3, or by multiple-bond formation, as in nitrogen itself ($:N{\equiv}N:$) azo compounds ($-\ddot{N}{=}\ddot{N}-$), nitro compounds (RNO_2), and so on.

3. *Formation of Electron-Pair Bonds with Electron Gain.* The completed octet is achieved in this way in ions such as the amide ion NH_2^- and the imide ion NH^{2-}.

4. *Formation of Electron-Pair Bonds with Electron Loss.* Nitrogen can form four bonds, provided an electron is lost, to give positively charged ions R_4N^+ such as NH_4^+, $N_2H_5^+$, and $(C_2H_5)_4N^+$. The ions may sometimes be regarded as being formed by protonation of the lone pair:

$$H_3N: + H^+ \longrightarrow [NH_4]^+$$

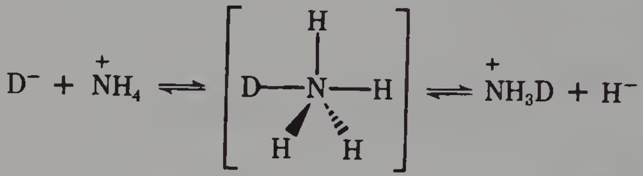
or generally

$$R_3N: + RX \longrightarrow R_4N^+ + X^-$$

Failure to Complete the Octet. There are a few relatively stable species in which, *formally,* the octet of nitrogen is incomplete. The classic examples are NO and NO_2 together with nitroxides R_2NO and the ion $(O_3S)_2NO^{2-}$; all have one unpaired electron. Nitroxide radicals are used as *spin labels,* since they can be attached to proteins, membranes, and so on, and inferences about their environment drawn from the characteristics of the observed esr signals.

Expansion of Octet. Normally, no expansion of the octet is permissible, but there are reactions that may indicate pentacoordinate nitrogen intermediates, or more likely, transition states.

Thus when molten ammonium trifluoroacetate (mp 130°C) is treated with LiH, deuteration studies show isotopic scrambling. Although it could be that D^- impinges only on the hydrogen of NH_4^+, another possibility is



Also, the synthesis of NF_4^+ from NF_3, F_2, and AsF_5 could involve an NF_5 species, though this seems unlikely (see Section 10-8).

Formal Oxidation Numbers. Classically, formal oxidation numbers ranging from -3 (e.g., in NH_3) to $+5$ (e.g., in HNO_3) have been assigned to nitrogen; though useful in balancing redox equations, they have no physical significance.

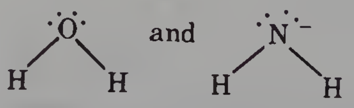
10-2. Types of Covalence in Nitrogen; Stereochemistry

In common with other first-row elements, nitrogen has only four orbitals available for bond formation, and a maximum of four 2*c*-2*e* bonds may be formed. However, since formation of three electron-pair bonds completes the octet $:N(:R)_3$, and the nitrogen atom then possesses a lone pair of electrons, four 2*c*-2*e* bonds can only be formed either (*a*) by coordination, as in donor–acceptor complexes, for example, $F_3B^-—N^+(CH_3)_3$, or in amine oxides, for example, $(CH_3)_3N^+—O^-$, or (*b*) by loss of an electron, as in ammonium ions (NH_4^+ and NR_4^+). This loss of an electron gives a valence state configuration for nitrogen (as N^+) with four unpaired electrons in sp^3 hybrid orbitals analogous to that of neutral carbon, while, as noted previously, gain of an electron (as in NH_2^-) leaves only two electrons for bond formation. In this case the nitrogen atom (as N^-) is isoelectronic with the neutral oxygen atom, and angular bonds are formed. We can thus compare, sterically, the following isoelectronic species;

Tetrahedral

NH_4^+ and CH_4
(also BH_4^-)

Angular



It may be noted that the ions NH_2^-, OH^-, and F^- are isoelectronic and have comparable sizes. The amide, imide, and nitride ions, which can be considered to be members of the isoelectronic series NH_4^+, NH_3, NH_2^-, NH^{2-}, and N^{3-}, occur as discrete ions only in salts of highly electropositive elements.

In all nitrogen compounds where the atom forms two or three bonds, there remain, respectively, two pairs or one pair of nonbonding or lone-pair electrons. The lone pairs have a profound effect on stereochemistry and are also responsible for the donor properties of the atom possessing them. To illustrate the important chemical consequences of nonbonding electron pairs, we consider one of the most important types of molecule, namely NR_3, as exemplified by NH_3 and amines.

Three-Covalent Nitrogen. Molecules of this type are invariably pyramidal, except in special cases to be discussed later. The bond angles vary according to the groups attached to the nitrogen atom. Pyramidal molecules of the kind NRR′R″ should be chiral. No optical isomers have ever been isolated, however, because molecules of this type execute a motion known as inversion, in which the nitrogen atom oscillates through the plane of the three R groups much as an umbrella can turn inside out. As the nitrogen atom crosses from one side of the plane to the other [from one equilibrium position, say $+r_0$, to the other, $-r_0$, in Fig. 10-1(a)], the molecule goes through a state of higher potential energy, as shown in the potential energy curve [Fig. 10-1(b)]. This "potential energy barrier" to inversion, however, is only 23.4 kJ mol^{-1}, and the frequency of the oscillation is 2.387013×10^{10} Hz in NH_3. Generally, in simple alkylamines, barriers are in the range of 16 to 40 kJ mol^{-1}; thus isolation of optical isomers can never be expected. However, heteroatom substitution and incorporation of N into strained rings raises the barrier, and in some cases invertomers have been separated. For the heavier elements (P, As, Sb, Bi), the inversion barriers of XH_3 are much higher.

Multiple Bonding in Nitrogen and Its Compounds. Like its neighbors carbon and oxygen, nitrogen readily forms multiple bonds, and many compounds for which there are no analogues among the heavier elements. Thus, whereas P, As, and Sb form tetrahedral molecules P_4, As_4, and Sb_4, nitrogen forms the multiple-bonded diatomic molecule :N≡N:, with an extremely short internuclear distance (1.094 Å) and very high bond strength. Nitrogen

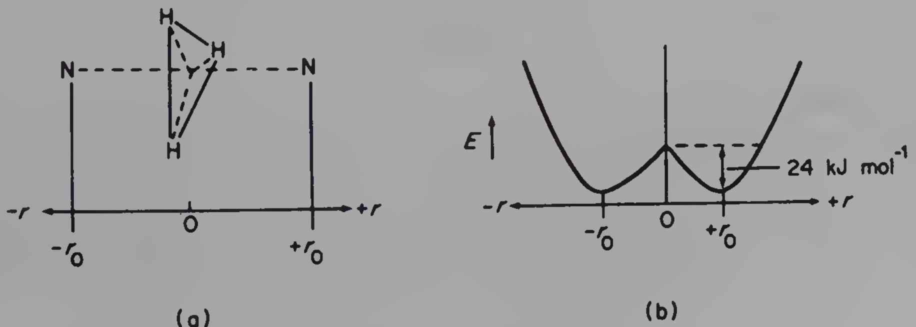
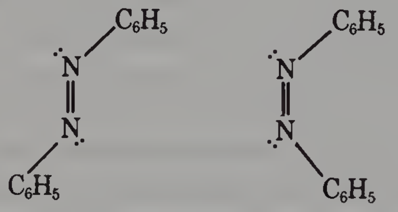


FIG. 10-1. Diagrams illustrating the inversion of NH_3 (see text).

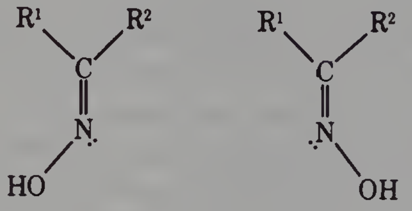
also forms triple bonds to other elements including carbon ($H_3CC{\equiv}N$), sulfur ($F_3S{\equiv}N$), and some transition metals (O_3OsN^-).

In compounds where nitrogen forms one single and one double bond, the grouping $X\text{—}\ddot{N}{=}Y$ is nonlinear. This can be explained by assuming that nitrogen uses a set of sp^2 orbitals, two of which form σ bonds to X and Y, while the third houses the lone pair. A π bond to Y is then formed using the nitrogen p_z orbital. In certain cases stereoisomers result from the nonlinearity, for example, *cis*-, and *trans*-azobenzenes (10-Ia and b) and the oximes (10-IIa and b). These are interconverted more easily than are *cis*- and *trans*-olefins, but not readily.



(a) (b)

(10-I)



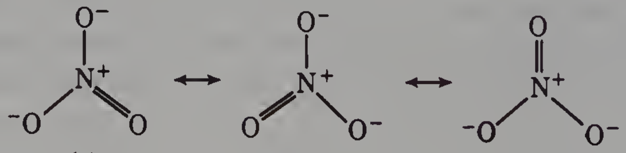
(a) (b)

(10-II)

Multiple bonding occurs also in oxo compounds. For example, NO_2^- (10-III) and NO_3^- (10-IV) can be regarded as resonance hybrids in the valence bond approach. From the MO viewpoint, one considers the existence of a π MO extending symmetrically over the entire ion and containing the two π electrons.

(a) (b)

(10-III)



(a) (b) (c)

(10-IV)

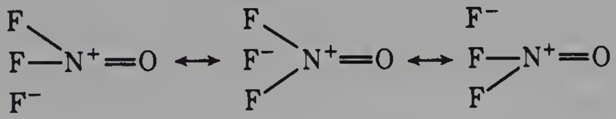
Planar Three-Coordinate Nitrogen. Structures of this type can exist in a few compounds where π bonding is involved as in silicon derivatives such as $N(SiH_3)_3$, $N_2(SiH_3)_4$, and $NMe_2(SiMe_3)$.[1] In condensed phases there can be slight deviations from nonplanarity and, for example, although $NMe_2(SiH_3)$ is monomeric in the vapor it has N—Si interaction leading to formation of a cyclic pentamer in the crystal.

The complex $[Ir_3N(SO_4)_6(H_2O)_3]^{6-}$ ion (Section 10-18) also has a planar

[1] D. W. H. Rankin and H. E. Robertson, *J. Chem. Soc. Dalton Trans.*, **1987**, 785.

NIr_3 group while $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)Fe]_3N$ which is nonbasic has an almost planar NC_3 group.[2]

Donor Properties of Three-Covalent Nitrogen; Four-Covalent Nitrogen. As noted previously, the formation of approximately tetrahedral bonds to nitrogen occurs principally in ammonium cations (R_4N^+), amine oxides ($R_3N^+—O^-$), and in Lewis acid–base adducts (e.g., $R_3N^+—B^-X_3$). In the amine oxides and these adducts, the bonds must have considerable polarity; in the amine oxides, for instance, N → O donation cannot be effectively counterbalanced by any back-donation to N. In accord with this, the stability of amine oxides decreases as the R_3N basicity decreases, since the ability of N to donate to O is the major factor. Similarly, $R_3N \rightarrow BX_3$ complexes have stabilities that are roughly parallel to R_3N basicity for given BX_3. When R is fluorine, basicity is minimal and $F_3N \rightarrow BX_3$ compounds are unknown. It is, therefore, curious that F_3NO is an isolable compound (Section 10-8). Evidently the extreme electronegativity of fluorine coupled with the availability of $p\pi$ electrons on oxygen allows the structures in (10-V) to contribute to stability.



(10-V)

Catenation and N—N Single-Bond Energies. Unlike carbon and a few other elements, nitrogen has little tendency for catenation, primarily owing to the weakness of the N—N single bond. If we compare the approximate single-bond energies in $H_3C—CH_3$, $H_2N—NH_2$, HO—OH, and F—F (~350, 160, 140, and 150 kJ mol^{-1}, respectively), it is clear that there is a profound drop between C and N. This difference is most probably attributable to the effects of repulsion between nonbonding lone-pair electrons. The strength of the N—N bond, and also of the O—O bond, decreases with increasing electronegativity of the attached groups; increasing electronegativity would perhaps have been expected to reduce repulsion between lone pairs, but it obviously will also weaken any homonuclear σ bond.

There are a few types of compound containing chains of three or more nitrogen atoms with some multiple bonds such as $R_2N—N{=}NR_2$, $RN{=}N—NR—NR_2$, $RN{=}N—NR—N{=}NR$, and $RN{=}N—NR—N{=}N—NR—N{=}NR$, where R represents an organic radical (some R groups may be H, but known compounds contain only a few H atoms). There are also cyclic compounds containing rings with up to five consecutive nitrogen atoms. Many of these compounds are not particularly stable, and all are traditionally in the realm of organic chemistry.[3]

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[2] M. Herberhold *et al., Angew. Chem. Int. Ed. Engl.,* 1982, **21,** 74.

[3] F. R. Benson, *The High Nitrogen Compounds,* Wiley, New York, 1984.

Hydrogen Bonding. Since it is one of the most electronegative elements, nitrogen, along with oxygen, fluorine and, to a lesser extent, chlorine, enters extensively into hydrogen-bond formation in its hydrogen compounds, both as a proton donor (N—H---X) and as a proton receptor (N---H—X).

THE ELEMENT

10-3. Occurrence and Properties

Nitrogen occurs in Nature mainly as dinitrogen (N_2), an inert diatomic gas (mp 63.1 K, bp 77.3 K) that comprises 78% by volume of the earth's atmosphere. Naturally occurring nitrogen consists of ^{14}N and ^{15}N with an absolute ratio $^{14}N/^{15}N = 272.0 \pm 0.3$. The isotope ^{15}N is useful as a tracer and especially for nmr studies.[4] There is a wide range of chemical shifts (~900 ppm) compared to ^1H and ^{13}C; the abundance (0.375%) is low and the sensitivity is only $\sim 10^{-3}$ that of ^1H but spectra can be quite readily obtained. Nitrogen-14 has a quadrupole moment but sharp lines can be observed in certain cases such as NH_4^+, NF_4^+, MeCN, NO_3^-, and NO_2^+ since high local symmetry enables sufficiently slow relaxation of the electric quadrupole and hence of nuclear spin.

Nitric acid containing up to 99.8% ^{15}N can be obtained by efficient fractionation of the system

$$^{15}NO(g) + H^{14}NO_3(aq) = {}^{14}NO(g) + H^{15}NO_3(aq) \qquad K = 1.055$$

The $H^{15}NO_3$ produced can be used to prepare any desired ^{15}N-labeled nitrogen compound.

The N—N bond distance in N_2 is 1.097 Å in the gas and 1.15 Å in the solid. The heat of dissociation is extremely large:

$$N_2(g) = 2N(g) \qquad \Delta H = 944.7 \text{ kJ mol}^{-1} \qquad K_{25°C} = 10^{-120}$$

Because the reaction is endothermic, the equilibrium constant increases with increasing temperature, but still, even at 3000°C and ordinary pressures, there is no appreciable dissociation. The great strength of the N≡N bond is principally responsible for the chemical inertness of N_2 and for the endothermicity of most simple nitrogen compounds, even though they may contain strong bonds. Thus $E(N{\equiv}N) \approx 6E(N{-}N)$, whereas $E(C{\equiv}C) \approx 2.5E(C{-}C)$. Dinitrogen is notably unreactive in comparison with isoelectronic, triply bonded systems such as X—C≡C—X, :C≡O:, X—C≡N:, and X—N≡C:. Both —C≡C— and —C≡N groups are known to serve as donors by using their π electrons. The lower ability of N_2 to form stable linkages in this way may be attributed to its electron configuration, which is . . . $(\pi)^4(\sigma_2)^2$; that is, the

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[4] W. von Philipsborn and R. Müller, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 383 (184 references); K. Kanamori and J. D. Roberts, *Acct. Chem. Res.*, 1983, **16**, 35.

π-bonding electrons are even more tightly bound than the σ-bonding electrons, and the latter are themselves tightly bound ($\Delta H_{\text{ion}} = 1496$ kJ mol^{-1}). In acetylene, on the other hand, the electron configuration is . . . $(\sigma_g)^2(\pi_u)^4$, and the ΔH_{ion} of the π_u electrons is only 1100 kJ mol^{-1}.

Dinitrogen is obtained commercially by liquefaction and fractionation of air; it usually contains some argon and, depending on the quality, upwards of ~30 ppm of oxygen. The oxygen may be removed by passing the gas over Cr^{2+} on silica gel, through sodium benzophenone ketyl in THF, aqueous V^{2+}, and so on. Spectroscopically pure N_2 is made by heating NaN_3 or $Ba(N_3)_2$.

Although generally nonreactive except at elevated temperatures, N_2 will react at room temperature with Li to give Li_3N and with a variety of transition metal complexes to give the $M(N_2)$ species. It is utilized directly by nitrogen fixing bacteria either free living or symbiotic on root nodules of clover, peas, beans, and so on. Despite extensive study on mild conversions of N_2 to NH_3, N_2H_4 and other compounds, no economic catalytic way has yet been discovered. However, coordinated dinitrogen can be attacked (Section 10-9) and some solutions such as a $V(OH)_2$—$Mg(OH)_2$ suspension will reduce the gas[5]:

$$2V(OH)_2 + N_2 + 2H_2O = N_2H_4 + 2VO(OH)_2$$

At elevated temperatures N_2 becomes more reactive, especially when catalyzed, typical reactions being

$$N_2(g) + 3H_2(g) = 2NH_3(g) \qquad K_{25^\circ C} = 10^3 \text{ atm}^{-2}$$

$$N_2(g) + O_2(g) = 2NO(g) \qquad K_{25^\circ C} = 5 \times 10^{-31}$$

$$N_2(g) + 3Mg(s) = Mg_3N_2(s)$$

$$N_2(g) + CaC_2(s) = C(s) + CaNCN(s)$$

Active Nitrogen. When N_2 is subjected to an electrical discharge under suitable conditions, a very reactive form is generated, accompanied by a yellow afterglow that may persist for several seconds after the discharge has been terminated. The high reactivity is largely due to the presence of ground state (^4S) nitrogen atoms. These have a relatively long lifetime in a vessel suitably "poisoned" to minimize wall recombination. The ternary collision process

$$2N(^4S) + X \longrightarrow N_2 + X$$

where X is molecular or atomic nitrogen, is at least partially responsible for populating the excited molecular states, which in turn lead to the afterglow. The afterglow is due mainly to emission of the first positive band system, $N_2(B^3\pi_g) \rightarrow N_2(A^3\Sigma_u^+)$ of the molecular nitrogen spectrum, though some other band systems also contribute.

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[5] A. E. Shilov, in *Energy Resources Through Photochemistry and Catalysis*, Chapter 16, Academic Press, New York, 1983; G. N. Schrautzer *et al.*, *Inorg. Chem.*, 1984, **23**, 2772.

NITROGEN COMPOUNDS

10-4. Nitrides

As with carbides, there are three general classes. Ionic nitrides are formed by Li, Mg, Ca, Sr, Ba, Zn, and some others. Their formulas correspond to what would result from combination of the normal metal ions with N^{3-} ions. They are all essentially ionic and are properly written as $(Ca^{2+})_3(N^{3-})_2$, $(Li^+)_3N^{3-}$, and so on. Nitrides of the M_3N_2 type are often antiisomorphous with oxides of the M_2O_3 type. This does not in itself mean that, like the oxides, they are ionic. However, their ready hydrolysis to NH_3 and the metal hydroxides makes this seem likely. The ionic nitrides are prepared by direct union of the elements or by loss of ammonia from amides on heating, for example,

$$3Ba(NH_2)_2 \longrightarrow Ba_3N_2 + 4NH_3$$

Lithium nitride, which has a hexagonal ionic structure, has a low solubility in THF but can be used as a reducing agent, for example, Ti^{IV} to Ti^{III}.[6]

There are various covalent *nitrides* (BN, S_4N_4, P_3N_5, etc.), and their properties vary greatly depending on the element with which nitrogen is combined. Such substances are therefore discussed under the appropriate element.

The transition metals form nitrides that are analogous to the transition metal borides and carbides in their constitution and properties. The nitrogen atoms often occupy interstices in the close-packed metal lattices. These nitrides are often not exactly stoichiometric (being N deficient), and they are metallic in appearance, hardness, and electrical conductivity, since the electronic band structure of the metal persists. Like the borides and carbides, they are chemically very inert, extremely hard, and have very high melting points. They are usually prepared by heating the metal in NH_3 at 1100 to 1200°C. A representative compound VN melts at 2570°C and has a hardness between 9 and 10.

10-5. Nitrogen Hydrides

Ammonia.[7] Anhydrous NH_3 is made on a large scale by the Haber process,[8] in which the reaction

$$N_2(g) + 3H_2(g) = 2NH_3(g) \qquad \Delta H = -46 \text{ kJ mol}^{-1}$$

$$K_{25°C} = 10^3 \text{ atm}^{-2}$$

is carried out in the presence of a catalyst at pressures of 10^2 to 10^3 atm and temperatures of 400 to 550°C. Although the equilibrium is most favorable at low temperature, elevated temperatures are invariably required to obtain

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[6] M. Kilner and G. Parkin, *J. Organomet. Chem.*, 1986, **302,** 181.

[7] R. Jayaraman, *Synthetic Reagents,* Vol. 5, J. S. Pizey, Ed., Horwood–Wiley, New York, 1983.

[8] J. S. Merriam and K. Atwood, *Appl. Ind. Catal.,* 1984, **3,** 113.

satisfactory rates. The usual catalyst is α iron containing some oxide to widen the lattice and enlarge the active interface, but Ru on carbon or MgO on Al_2O_3 activated by alkali metal oxides can also be used.[9]

Ammonia is a colorless pungent gas with a normal boiling point of -33.35°C and a freezing point of -77.7°C. The liquid has a large heat of evaporation ($1.37\ kJ\ g^{-1}$ at the boiling point) and is therefore fairly easily handled in ordinary laboratory equipment. Liquid ammonia resembles water in its physical behavior, being highly associated because of the polarity of the molecules and strong hydrogen bonding. Its dielectric constant (~22 at -34°C; cf. 81 for H_2O at 25°C) is sufficiently high to make it a fair ionizing solvent and electrochemical studies can be made in the liquid near the critical pressure (133°C, 112.5 atm)[10]:

$$2NH_3 = NH_4^+ + NH_2^-$$

$$K_{-50°C} = [NH_4^+][NH_2^-] = \sim 10^{-30}$$

Liquid ammonia has lower reactivity than H_2O toward electropositive metals, which may dissolve giving blue solutions (Section 4-3).

Because $NH_3(l)$ has a much lower dielectric constant than water, it is a better solvent for organic compounds but generally a poorer one for ionic inorganic compounds. Exceptions occur when complexing by NH_3 is superior to that by water. Thus AgI is exceedingly insoluble in water but $NH_3(l)$ at 25°C dissolves 207 g/100 cm^3. Primary solvation numbers of cations in $NH_3(l)$ appear similar to those in H_2O (e.g., 5.0 ± 0.2 and 6.0 ± 0.5 for Mg^{2+} and Al^{3+}, respectively), but there may be some exceptions. Thus Ag^+ appears to be primarily linearly two-coordinate in H_2O but tetrahedrally coordinated as $[Ag(NH_3)_4]^+$ in $NH_3(l)$. It has also been suggested that $[Zn(NH_3)_4]^{2+}$ may be the principal species in $NH_3(l)$ as compared to $[Zn(H_2O)_6]^{2+}$ in H_2O.

Reactions of Ammonia. Ammonia reacts with oxygen as in eq. 10-1.

$$4NH_3(g) + 3O_2(g) = 2N_2(g) + 6H_2O(g) \qquad K_{25°C} = 10^{228} \qquad (10\text{-}1)$$

However, ammonia can be made to react as in eq. 10-2.

$$4NH_3 + 5O_2 = 4NO + 6H_2O \qquad K_{25°C} = 10^{168} \qquad (10\text{-}2)$$

even though the process of eq. 10-1 is thermodynamically much more favorable, by carrying out the reaction at 750 to 900°C in the presence of a platinum or platinum–rhodium catalyst. This can easily be demonstrated in the laboratory by introducing a piece of glowing platinum foil into a jar containing gaseous NH_3 and O_2; the foil will continue to glow because of the heat of reaction 10-2, which occurs only on the surface of the metal, and brown fumes will appear owing to the reaction of NO with the excess of O_2 to produce NO_2. Industrially the mixed oxides of nitrogen are then absorbed in water to

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[9] K-I. Aika, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 559.

[10] A. J. Bard *et al., J. Am. Chem. Soc.*, 1984, **106**, 6851.

form nitric acid:

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO \qquad \text{and so on}$$

Thus the sequence in industrial utilization of atmospheric nitrogen is

$$N_2 \xrightarrow[\substack{\text{Haber}\\ \text{process}}]{H_2} NH_3 \xrightarrow[\substack{\text{Ostwald}\\ \text{process}}]{O_2} NO \xrightarrow{O_2 + H_2O} HNO_3(aq)$$

Ammonia is extremely soluble in water and gives *hydrates*.[11] The hydrates $NH_3{\cdot}H_2O$, $NH_3{\cdot}2H_2O$, and $2NH_3{\cdot}H_2O$ have NH_3 and H_2O molecules linked by H bonds; no NH_4^+ or OH^- ions or NH_4OH molecules exist in the hydrates. The hydrate $NH_3{\cdot}H_2O$ has chains of H_2O molecules linked by H bonds (2.76 Å); these chains are cross linked by NH_3 into a three-dimensional lattice by O—H---N (2.78 Å) and O---H—N bonds (3.21–3.29 Å). In aqueous solution ammonia is probably hydrated in a similar manner. Although aqueous solutions are commonly referred to as solutions of the weak base NH_4OH, called "ammonium hydroxide," there is reason to believe that it probably does not exist. Solutions of ammonia are best described as $NH_3(aq)$, with the equilibrium[12] written as

$$NH_3(aq) + H_2O = NH_4^+ + OH^-$$

$$K_{25°C} = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.77 \times 10^{-5}\ (pK_b = 4.75)$$

In an odd sense NH_4OH might be considered a *strong* base, since it is completely dissociated in water. A 1 *M* solution of NH_3 is only 0.0042 *M* in NH_4^+ and OH^-.

Nuclear magnetic resonance measurements show that the hydrogen atoms of NH_3 rapidly exchange with those of water by the process

$$H_2O + NH_3 = OH^- + NH_4^+$$

but there is only slow exchange between NH_3 molecules in the vapor phase or in the liquid if water is completely removed.

Ammonium Salts. There are many rather stable crystalline salts of the tetrahedral NH_4^+ ion; most of them are water soluble. Salts of strong acids are fully ionized, and the solutions are slightly acidic:

$$NH_4Cl = NH_4^+ + Cl^- \qquad K \approx \infty$$

$$NH_4^+ + H_2O = NH_3 + H_3O^+ \qquad K_{25°C} = 5.5 \times 10^{-10}$$

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[11] J. E. Bertie and M. R. Shehata, *J. Chem. Phys.*, 1984, **81,** 27.

[12] J. M. W. Scott *et al., J. Am. Chem. Soc.*, 1981, **103,** 5923.

Thus a 1 *M* solution will have a pH of ~4.7. The constant for the second reaction is sometimes called the hydrolysis constant; however, it may also be considered the acidity constant of the cationic acid NH_4^+, and the system regarded as an acid–base system in the following sense:

$$\underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{H_2O} = \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{NH_3(aq)}$$

Ammonium salts generally resemble those of K^+ and Rb^+ in solubility and, except where hydrogen-bonding effects are important, in structure, since the three ions are of comparable (Pauling) radii: $NH_4^+ = 1.48$ Å, $K^+ = 1.33$ Å, $Rb^+ = 1.48$ Å.

Many ammonium salts volatilize with dissociation around 300°C, for example,

$$NH_4Cl(s) = NH_3(g) + HCl(g) \qquad \Delta H = 177 \text{ kJ mol}^{-1} \quad K_{25^\circ C} = 10^{-16}$$
$$NH_4NO_3(s) = NH_3(g) + HNO_3(g) \quad \Delta H = 171 \text{ kJ mol}^{-1}$$

Some salts that contain oxidizing anions decompose when heated, with oxidation of the ammonia to N_2O or N_2 or both. For example,

$$(NH_4)_2Cr_2O_7(s) = N_2(g) + 4H_2O(g) + Cr_2O_3(s) \qquad \Delta H = -315 \text{ kJ mol}^{-1}$$
$$NH_4NO_3(l) = N_2O(g) + 2H_2O(g) \qquad \Delta H = -23 \text{ kJ mol}^{-1}$$

Ammonium halides are very useful for conversion of oxides to halides, oxohalides, or ammonium salts of halogeno anions at elevated temperatures.[13]

Ammonium nitrate volatilizes reversibly at moderate temperatures; at higher temperatures, irreversible decomposition occurs exothermically, giving mainly N_2O. This is the reaction by which N_2O is prepared commercially. At still higher temperatures, the N_2O itself decomposes into nitrogen and oxygen. Ammonium nitrate can be caused to detonate when initiated by another high explosive, and mixtures of ammonium nitrate with TNT or other high explosives are used for bombs. The decomposition of liquid ammonium nitrate can also become explosively rapid, particularly when catalyzed by traces of acid and chloride; there are instances of disastrous explosions of ammonium nitrate in bulk following fires. Ammonium perchlorate is important as an oxidizer in solid propellants for rocket fuels, and its thermal decomposition has been studied in detail.

Tetraalkylammonium ions (R_4N^+), prepared generally by the reaction

$$R_3N + RI = R_4N^+I^-$$

are often of use in inorganic chemistry when large univalent cations are required. Various R_4N radicals in the form of apparently crystalline amalgams

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[13] G. Meyer *et al., Inorg. Chem.*, 1985, **24**, 3504.

($\sim$12 Hg/NR_4) can be obtained electrolytically or by reduction of R_4NX with Na/Hg in media where the resulting NaX is insoluble.

Hydrazine[14a] (N_2H_4) may be thought of as derived from NH_3 by replacement of an H atom by the —NH_2 group. It might, therefore, be expected to be a base, but somewhat weaker than NH_3, which is the case. It is a bifunctional base:

$$N_2H_4(aq) + H_2O = N_2H_5^+ + OH^- \qquad K_{25°C} = 8.5 \times 10^{-7}$$

$$N_2H_5^+(aq) + H_2O = N_2H_6^{2+} + OH^- \qquad K_{25°C} = 8.9 \times 10^{-16}$$

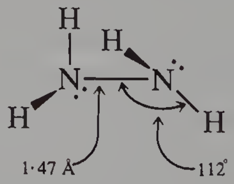
and two series of hydrazinium salts are obtainable. Those of $N_2H_5^+$ are stable in water, and those of $N_2H_6^{2+}$ are, as expected from the foregoing equilibrium constant, extensively hydrolyzed. Salts of $N_2H_6^{2+}$ can be obtained by crystallization from aqueous solution containing a large excess of the acid, since they are usually less soluble than the monoacid salts.

As another consequence of its basicity, hydrazine, like NH_3, can form coordination complexes with both Lewis acids and metal ions. Just as with respect to the proton, electrostatic considerations (and, in these cases, steric considerations) militate against bifunctional behavior.

Anhydrous N_2H_4 (mp 2°C, bp 113.5°C), a fuming colorless liquid with a high dielectric constant (ϵ = 52 at 25°C), is surprisingly stable in view of its endothermic nature (ΔH_f^0 = 50 kJ mol^{-1}). It will burn in air, however, with considerable evolution of heat, which accounts for interest in it and certain of its alkylated derivatives as potential rocket fuels:

$$N_2H_4(l) + O_2(g) = N_2(g) + 2H_2O(l) \qquad \Delta H^0 = 622 \text{ kJ mol}^{-1}$$

At 25°C N_2H_4 is 100% in the gauche form 10-VI (cf. N_2F_4, to follow).



(10-VI)

Aqueous hydrazine is a powerful reducing agent in basic solution; in many of such reactions diimine (see below) is an intermediate. One reaction, which is quantitative with some oxidants (e.g., I_2), is

$$N_2 + 4H_2O + 4e = 4OH^- + N_2H_4(aq) \qquad E^0 = -1.16 \text{ V}$$

However, NH_3 and HN_3 are also obtained under various conditions. Air and

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[14a] E. W. Eckhardt, *Hydrazine and its Derivatives: Preparation, Properties and Applications*, Wiley, New York, 1984; P. A. Smith, *Derivatives of Hydrazine and Other Hydronitrogens with N—N Bonds*, Benjamin–Cummings, Menlo Park, California, 1982; F. Cardula, *J. Chem. Educ.* **1983,** 505.

O_2, especially when catalyzed by multivalent metal ions in basic solution, produce H_2O_2:

$$2O_2 + N_2H_4(aq) \longrightarrow 2H_2O_2(aq) + N_2$$

but further reaction occurs in the presence of metal ions:

$$N_2H_4 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$$

In acid solution hydrazine can reduce halogens:

$$N_2H_4(aq) + 2X_2 = 4HX + N_2$$

The following potential indicates that in acid solution $N_2H_5^+$ is not oxidized by air.

$$N_2H_5^+ = N_2 + 5H^+ + 4e \qquad E^0 = +0.23\ V$$

Hydrazine is made in quantity by the Raschig synthesis, or a variant thereof. The overall reaction, carried out in aqueous solution, is

$$2NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$$

The reaction proceeds in two steps; the first being nearly quantitative at 0°C with a 3:1 NH_3 to OCl^- ratio:

$$NH_3 + NaOCl \longrightarrow NaOH + NH_2Cl \qquad \text{(fast)}$$

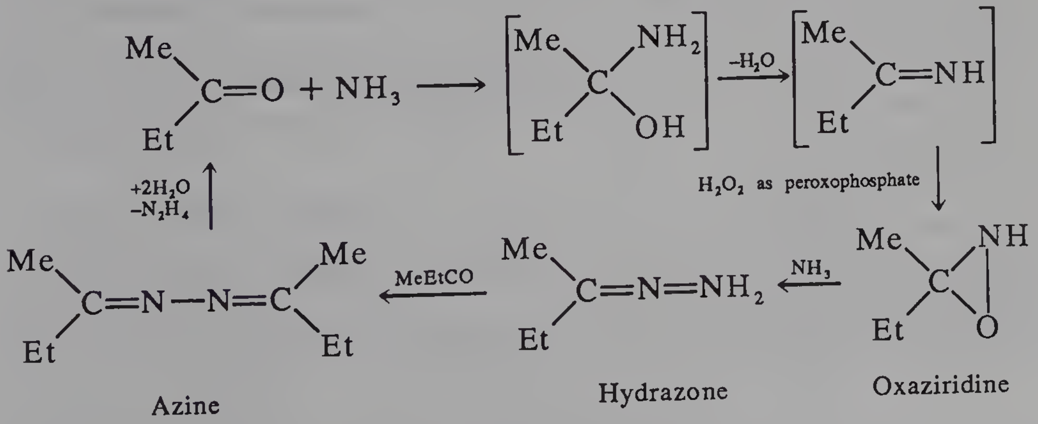
$$NH_3 + NH_2Cl + NaOH \longrightarrow N_2H_4 + NaCl + H_2O$$

However, there is a competing and parasitic reaction that is rather fast once some N_2H_4 has been formed:

$$2NH_2Cl + N_2H_4 \longrightarrow 2NH_4Cl + N_2$$

Addition of gelatine is said to suppress this reaction by scavenging heavy metal ions.

An improved process,[14b] which avoids the use of NaOCl and disposal of NaCl involves the sequence



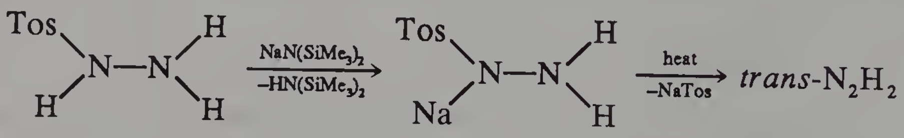
[14b] *Chem. Eng. News*, 1981, Nov. 2, p. 32.

Catalytic quantities of phosphate are used to serve as a carrier via a peroxo-anion for oxidation of the intermediate imine. The azine is insoluble in the aqueous medium and is hydrolyzed separately.

Aqueous solutions when concentrated are inflammable; anhydrous N_2H_4 can be obtained by distillation of the hydrate over NaOH.

The main uses for N_2H_4 are for synthesis of herbicides and pesticides, blowing agents for foam rubber and plastics, for rocket fuel, and for removal of O_2 in boilers.

Diazene (Diimide, N_2H_2)[15] and Other Nitrogen Hydrides. Diazene can be obtained with NH_3, by microwave discharge in gaseous N_2H_4, and in the pure state by the reaction (Tos = *p*-toluenesulfonate)



The diamagnetic yellow compound is unstable above −180°C, decomposing mainly to N_2, H_2, and N_2H_4. Thermolysis of the potassium salt gives the cis isomer, and the cesium salt gives $N{=}NH_2$ (isodiazene); both are very unstable. Both *cis*- and *trans*-$CH_3N{=}NCH_3$ and *trans*-$CH_3N{=}NH$ are known.

Diazene also has a transient existence in solution during oxidations of N_2H_4 by two-electron oxidants (O_2, peroxides, chloramine-T, etc.):

$$N_2H_4 \xrightarrow{-2H} N_2H_2$$

It is also formed in alkaline cleavage of chloramine:

$$H_2NCl \xrightarrow{OH^-} HNCl^-$$

$$HNCl^- + H_2NCl \xrightarrow{-Cl^-} H(Cl)N{-}NH_2 \xrightarrow{-HCl} HN{=}NH$$

The existence of N_2H_2 has been shown by, among other things, the stereospecific cis-hydrogenation of C=C bonds by hydrazine and an oxidant.

Some other unstable hydrides (e.g., N_4H_2 and N_4H_4) are known, and interaction of NH_3 on a silver zeolite produces Ag^+ complexes of triazane (N_3H_5) and cyclotriazane (N_3H_3).

Hydrazoic Acid and Azides. Although HN_3 is a hydride of nitrogen in a formal sense, it has no essential relationship to NH_3 and N_2H_4. The sodium salt is prepared by the reactions

$$3NaNH_2 + NaNO_3 \xrightarrow{175^\circ C} NaN_3 + 3NaOH + NH_3$$

$$2NaNH_2 + N_2O(g) \xrightarrow{190^\circ C} NaN_3 + NaOH + NH_3$$

and the free acid can be obtained in solution by the reaction

$$N_2H_5^+ + HNO_2 \xrightarrow{\text{aq. soln.}} HN_3 + H^+ + 2H_2O$$

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[15] R. A. Back, *Rev. Chem. Intermed.*, 1984, **5**, 293 (151 references).

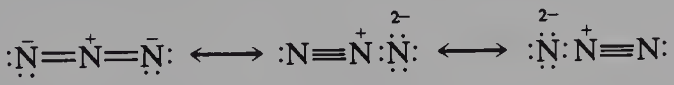
Many other oxidizing agents attack N_2H_4 to form small amounts of HN_3 or azides. Hydrazoic acid ($pK_A^{25} = 4.75$), obtainable pure by distillation from aqueous solutions, is a colorless liquid (bp 37°C) and dangerously explosive. Azides of many metals are known; those of heavy metals are generally explosive; lead, mercury, and barium azides explode on being struck sharply and are used in detonation caps.

Azides of electropositive metals are not explosive and decompose smoothly and quantitatively when heated to 300°C or higher, for example,

$$2NaN_3(s) = 2Na(l) + 3N_2(g)$$

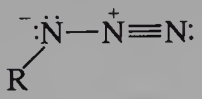
In general, N_3^- behaves rather like a halide ion and is commonly considered to be a pseudohalide.

The ion is symmetrical and linear (N—N, 1.16 Å), and its electronic structure may be represented in valence bond theory as

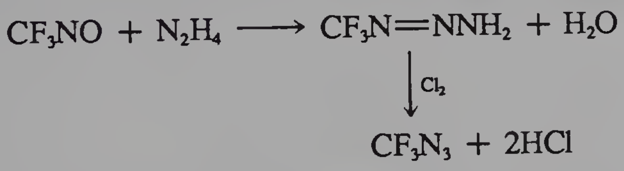


$$:\overset{-}{\underset{..}{N}}=\overset{+}{N}=\overset{-}{\underset{..}{N}}: \longleftrightarrow :N\equiv\overset{+}{N}:\overset{2-}{\underset{..}{\ddot{N}}}: \longleftrightarrow :\overset{2-}{\underset{..}{\ddot{N}}}:\overset{+}{N}\equiv N:$$

In covalent azides[16] such as HN_3, MeN_3, or CF_3N_3 the N—N distances become unequal with a resonance contribution from



Organic azides are reasonably stable. Trifluoromethyl azide (CF_3N_3), mp −152°C, explodes only at 330°C. It is made by the reaction



$$\begin{array}{l} CF_3NO + N_2H_4 \longrightarrow CF_3N{=}NNH_2 + H_2O \\ \qquad\qquad\qquad\qquad\quad \downarrow Cl_2 \\ \qquad\qquad\qquad\qquad\quad CF_3N_3 + 2HCl \end{array}$$

There are also halogen azides that are unstable and/or explosive.[17]

Hydroxylamine. Since N_2H_4 may be thought of as derived from ammonia by replacement of one hydrogen by NH_2, so NH_2OH is obtained by replacement of H by OH. Hydroxylamine is a weaker base than NH_3:

$$NH_2OH(aq) + H_2O = NH_3OH^+ + OH^- \qquad K_{25°C} = 6.6 \times 10^{-9}$$

Hydroxylamine is prepared by reduction of nitrates or nitrites either electrolytically or with SO_2, under closely controlled conditions. It is also made, in 70% yield, by H_2 reduction of NO in dilute H_2SO_4 solution with platinized active charcoal as catalyst.[18] Free hydroxylamine is a white solid (mp 33°C) that must be kept at 0°C to avoid decomposition. It is normally encountered

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[16] K. O. Christe *et al.*, *Inorg. Chem.*, 1984, **23**, 4283.
[17] K. Dehnicke, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 169.
[18] G. R. Jauszik and P. Crocetta, *Appl. Catal.*, 1985, **7**, 1.

as an aqueous solution and as salts, for example, $[NH_3OH]Cl$, $[NH_3OH]NO_3$, and $[NH_3OH]_2SO_4$, which are stable, water soluble, white solids. Although hydroxylamine can serve as either an oxidizing or a reducing agent, it is usually used as the latter.

The reaction

$$4Fe^{3+} + 2NH_3OH^+ = 4Fe^{2+} + N_2O + 6H^+ + H_2O$$

is quantitative but mechanistically complex.

10-6. Oxides of Nitrogen[19]

The oxides of nitrogen are listed in Table 10-1, and their structures are shown in Fig. 10-2.

Dinitrogen Oxide (Nitrous Oxide). This is obtained by thermal decomposition of ammonium nitrate in the melt at 250 to 260°C:

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

The contaminants are NO, which can be removed by passage through an iron(II) sulfate solution and 1 to 2% of N_2. The NH_4NO_3 must be free from Cl^-, since this catalytically causes decomposition to N_2. However, heating HNO_3 or H_2SO_4 solutions of NH_4NO_3 with small amounts of Cl^- gives almost pure N_2O. The gas is also produced in the reduction of nitrites and nitrates under certain conditions and by decomposition of hyponitrites.

Nitrous oxide is relatively unreactive, being inert to the halogens, alkali metals, and ozone at room temperature. It will oxidize some low-valent transition metal complexes such as Cp_2V and $Cp_2Ti(CO)_2$ to oxo species[20] and

TABLE 10-1
Oxides of Nitrogen

Formula	Name	Color	Temperatures (°C)	Remarks
N_2O	Nitrous oxide	Colorless	mp −90.8; bp −88.5	Rather unreactive
NO	Nitric oxide	Colorless	mp −163.6; bp −151.8	Moderately reactive
N_2O_3	Dinitrogen trioxide	Dark blue	fp −100.6; dec. 3.5	Extensively dissociated as gas
NO_2	Nitrogen dioxide	Brown		Rather reactive
N_2O_4	Dinitrogen tetroxide	Colorless	bp 21.15 fp −11.2	Extensively dissociated to NO_2 as gas and partly as liquid
N_2O_5	Dinitrogen pentoxide	Colorless	mp 30; dec. 47	Unstable as gas; ionic solid
NO_3; N_2O_6				Not well characterized and quite unstable

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[19] J. Laane and J. R. Olsen, *Progr. Inorg. Chem.*, 1980, **27**, 466 (vibrational spectra).

[20] F. Bottomley *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 5651; *J. Chem. Soc. Dalton Trans.*, **1983**, 399; G. L. Hillhouse *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 5538.

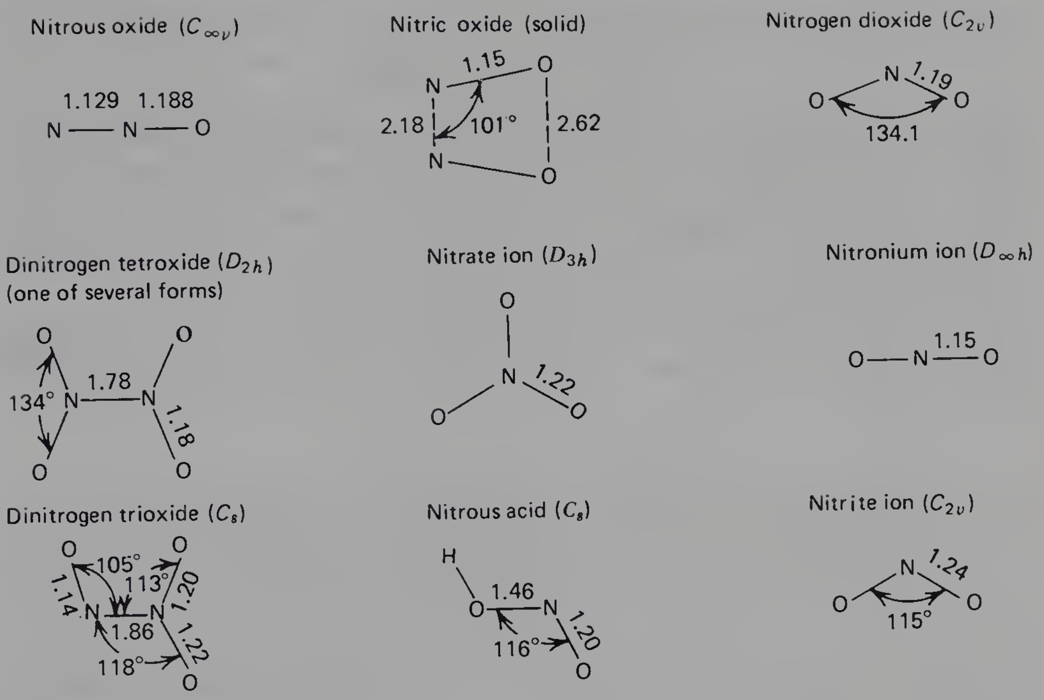

FIG. 10-2. The structures and point group symmetries of some nitrogen oxides and anions (angles in degrees; bond lengths in Å). Note that the N—NO_2 bond length in N_2O_4 and N_2O_3 is very long compared to the single bond radius in, for example, $H_2N—NH_2$ of 1.47 Å.

forms the complex $[Ru(NH_3)_5N_2O]^{2+}$. At elevated temperatures it decomposes to nitrogen and oxygen, reacts with alkali metals and many organic compounds, and supports combustion. Apart from its anesthetic role, its chief commercial use is as an aerosol propellant.

Nitric Oxide. This is formed in many reactions involving reduction of nitric acid and solutions of nitrates and nitrites. For example, with 8 *M* nitric acid,

$$8HNO_3 + 3Cu \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Reasonably pure NO is obtained by the aqueous reactions

$$2NaNO_2 + 2NaI + 4H_2SO_4 \longrightarrow I_2 + 4NaHSO_4 + 2H_2O + 2NO$$

$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$$

or dry,

$$3KNO_2(l) + KNO_3(l) + Cr_2O_3(s) \longrightarrow 2K_2CrO_4(s,l) + 4NO$$

Commercially it is obtained by catalytic oxidation of ammonia as already noted. Direct combination of the elements occurs only at very high temperatures, and to isolate the small amounts so formed (a few volume percent at 3000°C) the equilibrium mixture must be rapidly chilled. Though much studied, this reaction has not been developed into a practical commercial synthesis.

Nitric oxide reacts instantly with O_2:

$$2NO + O_2 \longrightarrow 2NO_2$$

It also reacts with F_2, Cl_2, and Br_2 to form the nitrosyl halides XNO (Section 10-8) and with CF_3I to give CF_3NO and I_2. It is oxidized to nitric acid by several strong oxidizing agents; the reaction with permanganate is quantitative and provides a method of analysis. It is reduced to N_2O by SO_2 and to NH_2OH by chromium(II) ion, in acid solution in both cases.

Nitric oxide is thermodynamically unstable at 25°C and 1 atm and under pressure readily decomposes in the range 30 to 50° and reacts chemically as NO_2 or N_2O_3[21a]:

$$3NO \longrightarrow N_2O + NO_2$$

Over Cu^{2+}–ZSM-5 zeolite disproportionation to N_2 and O_2 occurs.[21b]

The NO molecule has the electron configuration $(\sigma_1)^2(\sigma_1^*)^2(\sigma_2, \pi)^6(\pi^*)$. The unpaired π^* electron renders the molecule paramagnetic and partly cancels the effect of the π-bonding electrons. Thus the bond order is 2.5, consistent with an interatomic distance of 1.15 Å, which is intermediate between the triple-bond distance in NO^+ (see later) of 1.06 Å and representative double-bond distances of ~1.20 Å.

Nitric oxide dimerizes in the solid state (Fig. 10-2). Dimers persist in the vapor at the boiling point where the structure is similar but the N—N distance is longer (2.237 Å) and the ONN angle is 99.6°.[21c] The binding energy of the dimer, ~16 kJ mol^{-1} is consistent with the long N—N bond. The dimer has no unpaired spins but feeble intrinsic temperature-independent paramagnetism. Unstable forms can be isolated in matrices.

The electron in the π^* orbital is relatively easily lost (ΔH_{ion} = 891 kJ mol^{-1}), to give the *nitrosonium ion* (NO^+), which has an extensive and important chemistry. Because the electron removed comes out of an antibonding orbital, the bond is stronger in NO^+ than in NO: the bond length decreases by 0.09 Å and the vibration frequency rises from 1840 cm^{-1} in NO to 2150 to 2400 cm^{-1} (depending on environment) in NO^+. Numerous ionic compounds of NO^+ are known.

When N_2O_3 or N_2O_4 is dissolved in concentrated sulfuric acid, the ion is formed:

$$N_2O_3 + 3H_2SO_4 = 2NO^+ + 3HSO_4^- + H_3O^+$$

$$N_2O_4 + 3H_2SO_4 = NO^+ + NO_2^+ + 3HSO_4^- + H_3O^+$$

The isolable compound $NO^+HSO_4^-$ (nitrosonium hydrogen sulfate) was an important intermediate in the old lead-chamber process for manufacture of

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[21a] G. Wilkinson *et al., Polyhedron,* 1985, **41,** 1941.

[21b] M. Iwamoto *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 1272.

[21c] S. G. Kukolich, *J. Am. Chem. Soc.,* 1982, **104,** 4715.

sulfuric acid. Its saltlike constitution has been shown by electrolysis, conductivity studies, and cryoscopic measurements. The compounds $NO^+ClO_4^-$ and $NO^+BF_4^-$, both isostructural with the corresponding ammonium and H_3O^+ compounds, are known; many others such as $(NO)_2PtCl_6$, $NOFeCl_4$, $NOAsF_6$, $NOSbF_6$, and $NOSbCl_6$ may be made in the following general ways:

$$NO + MoF_6 \longrightarrow NO^+MoF_6^-$$

$$ClNO + SbCl_5 \longrightarrow NO^+SbCl_6^-$$

All such salts are readily hydrolyzed,

$$NO^+ + H_2O \longrightarrow H^+ + HNO_2$$

and they must be prepared and handled under anhydrous conditions.

In alkaline solution at 0°C, SO_3^{2-} reacts with NO to give a white crystalline solid, potassium *N*-nitrosohydroxylamine-*N*-sulfonate ($K_2SO_3N_2O_2$):

$$ON^{\cdot} + :SO_3^{2-} = [ON^{\cdot} \longleftarrow SO_3]^{2-}$$

$$[ON^{\cdot}SO_3]^{2-} + N^{\cdot}O = [O{=}N(\mu\text{-}NO)SO_3]^{2-}$$

Other species with N_2O_2 groups are obtained by interaction of amines with NO.

The NO^+ ion is isoelectronic with CO, and, like CO, will form bonds to transition metals (Section 10-10). The compound responsible for the brown ring in the test for nitrates is a complex of iron whose formula is $[Fe(H_2O)_5NO]^{2+}$.

Dinitrogen Trioxide.[22] This oxide is best obtained by interaction of stoichiometric quantities of NO and O_2 or NO and N_2O_4 as an intensely blue liquid and a pale blue solid. The dissociation

$$N_2O_3 = NO + NO_2$$

begins to be significant above −30°C. There appears to be some self-ionization in the liquid:

$$N_2O_3 \rightleftharpoons NO^+ + NO_2^-$$

The molecule is polar in the sense $ON^{\delta+}{-}NO_2^{\delta-}$. The stable structure in the solid has a long N—N bond, and this structure persists in the liquid and gas (Fig. 10-2).

Nitrogen trioxide is formally the anhydride of nitrous acid:

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

It is blue in water, and in nonpolar solvents. Dissolution of $NO + NO_2$ in aqueous alkali solution gives NO_2^-. In strongly acid media, $HN_2O_3^+$ may be formed. It is a powerful nitrosating agent for organic compounds.[23]

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[22] S. E. Schwartz *et al., Inorg. Chem.*, 1981, **20,** 445.

[23] D. L. H. Williams, *Adv. Phys. Org. Chem.*, 1983, **19,** 381.

Nitrogen Dioxide and Dinitrogen Tetroxide. These two oxides exist in a strongly temperature-dependent equilibrium[24]

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad K = 1.4 \times 10^{-5}\ \text{mol dm}^{-3}\ (303\ \text{K})$$

The dissociation energy of N_2O_4 in the gas phase is 57 kJ mol^{-1}. In the solid, the oxide is entirely the colorless diamagnetic molecule N_2O_4. Partial dissociation occurs in the liquid; it is pale yellow at the freezing point and contains 0.01% of NO_2, which increases to 0.1% in the deep red-brown liquid at the boiling point, 21.15°C. In the vapor at 100°C the composition is NO_2 90%, N_2O_4 10%, and dissociation is complete above 140°C. Molecular beam mass spectrometric studies indicate that trimers and tetramers occur, but there is no evidence for such species under normal conditions.

The monomer NO_2 has an unpaired electron and its properties, red-brown color, and ready dimerization to colorless and diamagnetic N_2O_4, are not unexpected for such a radical. Nitrogen dioxide can also lose its odd electron fairly readily ($\Delta H_{\text{ion}} = 928$ kJ mol^{-1}) to give NO_2^+, the *nitronium ion,* discussed later.

Although other forms can exist in inert matrices, the most stable form of N_2O_4 is that shown in Fig. 10-2. This molecule has unusual features, namely, the planarity and the long N—N bond. Molecular orbital calculations suggest that although the bond is of a σ type, it is long because of delocalization of the electron pair over the whole molecule, with large repulsion between doubly occupied MO's of NO_2. The coplanarity results from a delicate balance of forces favoring the skew and planar forms. The barrier to rotation about the N—N bond is estimated to be ~9.6 kJ mol^{-1}.

The mixed oxides are obtained by heating metal nitrates, by oxidation of NO in air, and by reduction of nitric acid and nitrates by metals and other reducing agents. The gases are highly toxic and attack metals rapidly. They react with water,

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

the nitrous acid decomposing, particularly when warmed:

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

The thermal decomposition

$$2NO_2 \rightleftharpoons 2NO + O_2$$

begins at 150°C and is complete at 600°C.

The oxides are fairly strong oxidizing agents in aqueous solution, comparable in strength to bromine:

$$N_2O_4 + 2H^+ + 2e = 2HNO_2 \qquad E^0 = +1.07\ \text{V}$$

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[24] A. Boughriet *et al., Nouv. J. Chim.,* 1985, **9,** 651.

The mixed oxides, "nitrous fumes," are used in organic chemistry as selective oxidizing agents; the first step is hydrogen abstraction,

$$RH + NO_2 = R^{\cdot} + HONO$$

and the strength of the C—H bond generally determines the nature of the reaction.

Nitrogen dioxide and NO, commonly referred to as NO_x, are both of concern in atmospheric pollution, being produced in combustion.[25] There has been consequently intensive study of catalytic reactions involving reduction or decomposition of the oxides. Dinitrogen tetroxide undergoes self-ionization[26a] endothermically

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad K = 7.1 \times 10^{-8}\ \text{mol dm}^{-3} \quad (303\ \text{K})$$

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^- \qquad K = 10^{-22}\ \text{mol dm}^{-3} \quad (303\ \text{K})$$

It has been used as a solvent[26b] and forms molecular addition compounds with a great variety of nitrogen, oxygen, and aromatic donor compounds. Systems involving liquid N_2O_4 mixed with an organic solvent are often very reactive; for example, they dissolve relatively noble metals to form nitrates, often solvated with N_2O_4. Thus Cu reacts vigorously with N_2O_4 in ethyl acetate to give crystalline $Cu(NO_3)_2{\cdot}N_2O_4$, from which anhydrous, volatile (at 150–200°C) Cu^{II} nitrate is obtained. Some of the compounds obtained in this way are nitrosonium salts, for example, $Zn(NO_3)_2{\cdot}2N_2O_4$ is $(NO^+)_2[Zn(NO_3)_4]^{2-}$, and $Cu(NO_3)_2{\cdot}N_2O_4$ consists of NO^+ ions and polymeric nitrato anions. The complex $Fe(NO_3)_3(1.5N_2O_4)$ also appears to have a nitrato anion $[Fe(NO_3)_4]^-$, but with a cation $N_4O_6^{2+}$ that can be regarded as NO_3^- bound to three NO^+ groups.

In anhydrous acids N_2O_4 dissociates ionically and in anhydrous HNO_3 dissociation is almost complete:

$$N_2O_4 = NO^+ + NO_3^-$$

The dissociation in H_2SO_4 is complete in dilute solution; at higher concentrations undissociated N_2O_4 is present, and at very high concentrations HNO_3 is formed:

$$N_2O_4 + 3H_2SO_4 = NO^+HSO_4^- + HNO_3 + HSO_4^- + SO_3 + H_3O^+$$

The $NOHSO_4$ actually crystallizes out. The detailed mechanism and intermediates are undoubtedly complex.

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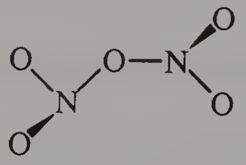
[25] D. F. Church *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 211; B. Harrison *et al.*, *Catalysis,* Vol. 5, p. 127, Royal Society of Chemistry, London, 1982; B. Harrison *et al.*, *Platinum Metals Rev.*, 1985, **29,** 50.

[26a] See A. Boughriet *et al.*, *Can. J. Chem.*, 1986, **64,** 5.

[26b] C. C. Addison, *Chem. Rev.*, 1980, **80,** 21.

Dinitrogen Pentoxide. The oxide N_2O_5 has the structure (10-VII) in the gas phase at −11°C but in the solid, the stable form is $NO_2^+NO_3^-$.



N—O(bridge) = 1.498 Å
N—O(terminal) = 1.188 Å
$\widehat{NON} = 111.8°$
$\widehat{ONO} = 133.2°$

(10-VII)

The oxide is obtained by dehydration of HNO_3 with P_2O_5 or by interaction of FNO_2 and $LiNO_3$[27]; it is not too stable (sometimes exploding) and is distilled in a current of ozonized O_2:

$$2HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5$$

It is, conversely, the anhydride of nitric acid:

$$N_2O_5 + H_2O = 2HNO_3$$

It is deliquescent, readily producing nitric acid by this reaction.

As with N_2O_4, ionic dissociation occurs in anhydrous H_2SO_4, HNO_3, or H_3PO_4 to produce NO_2^+, for instance,

$$N_2O_5 + 3H_2SO_4 \rightleftharpoons 2NO_2^+ + 3HSO_4^- + H_3O^+$$

Many gas phase reactions of N_2O_5 depend on dissociation to NO_2 and NO_3, with the latter then reacting further as an oxidizing agent. These reactions are among the better understood complex inorganic reactions.

In the N_2O_5-catalyzed decomposition of O_3, the steady state concentration of NO_3 can be high enough to allow its absorption spectrum to be recorded.

Nitrosylazide, Nitrylazide. Although they have the stoichiometry of nitrogen oxides (i.e., N_4O and N_4O_2), these unstable compounds are azides of NO^+ and NO_2^+, respectively. They are obtained in solution by the action of NO^+ and NO^{2+} salts (e.g., of BF_4^-) with sodium azide in an organic solvent but have not been isolated. Decomposition occurs at −50°C for N_4O and above −10°C for N_4O_2.

10-7. Oxo Acids and Anions of Nitrogen

Hyponitrous Acid. Sodium hyponitrite ($Na_2N_2O_2$) can be made by Na/Hg reduction of aqueous $NaNO_2$. The salt can be extracted with water and crystallized by addition of ethanol. The silver salt, which is insoluble in water, is used in syntheses of alkyl hyponitrites.

The anion is stable but on addition of H^+ is destabilized by protonation on oxygen,[28] whereas the $N_2O_3^{2-}$ (see later) is protonated at nitrogen.

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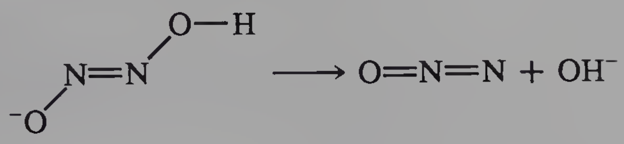
[27] W. W. Wilson and K. O. Christe, *Inorg. Chem.*, 1987, **26,** 1631.
[28] F. T. Bonner *et al., Inorg. Chem.*, 1985, **24,** 1934.

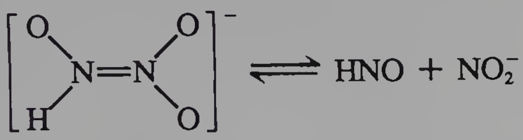
$HN_2O_2^-$ decomposes without N—N cleavage to give N_2O



In acid solution, $(NOH)_2$ is present and is more stable than $HN_2O_2^-$.

Hyponitrites undergo various oxidation–reduction reactions but usually act as reducing agents. An isomer of hyponitrous acid is *nitramide*, $H_2N—NO_2$, which is a weak acid ($K_{25°C} = 2.6 \times 10^{-7}$).

The Trioxodinitrate(II) Ion.[29] The interaction of NH_2OH and an alkylnitrate in methanol containing NaOMe at 0°C gives the salt $Na_2N_2O_3$, which is stable but decomposes in neutral or alkaline media:



$$2HNO \longrightarrow N_2O + H_2O$$

Nitrous Acid. Solutions of the weak acid HNO_2 ($pK_A^{25°C} = 5.22$) are made by acidifying solutions of nitrites. The aqueous solution can be obtained free of salts by the reaction

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow 2HNO_2 + BaSO_4(s)$$

The acid is unknown in the liquid state, but it can be obtained in the vapor phase; the trans form (Fig. 10-2) has been shown to be more stable than the cis form by ~2.1 kJ mol⁻¹. In the gas phase the following equilibrium is rapidly established:

$$NO + NO_2 + H_2O = 2HNO_2 \qquad K_{20°C} = 1.56 \text{ atm}^{-1}$$

Aqueous solutions of nitrous acid are unstable and decompose rapidly when heated:

$$3HNO_2 \rightleftharpoons H^+ + NO_3^- + H_2O + 2NO$$

Nitrous acid can behave both as an oxidant, for example, toward I^-, Fe^{2+}, or $C_2O_4^{2-}$:

$$HNO_2 + H^+ + e = NO + H_2O \qquad E^0 = 1.0 \text{ V}$$

and as a reducing agent:

$$NO_3^- + 3H^+ + 2e = HNO_2 + H_2O \qquad E^0 = 0.94 \text{ V}$$

Nitrites of the alkali metals are best prepared by heating the nitrates with

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[29] F. T. Bonner *et al., Inorg. Chem.,* 1986, **25**, 4635; M. N. Hughes *et al., Inorg. Chem.,* 1986, **25**, 2676.

a reducing agent such as carbon, lead, or iron. The salt $PPN^+NO_2^-$ is a useful mild nitrosylating agent.

The NO_2^- ion can be reduced by formic acid in the presence of $MoO(dtc)_2$ to N_2O in DMF solution or electrocatalytically mediated by water soluble iron porphyrins to NH_2OH and NH_3; nitrate ion can similarly be reduced to NH_3 using Mo/Fe modified electrodes.[30]

The yellow *peroxonitrite* ion, which is stable for hours in 0.1 *M* base, is made by one of the few examples of radical couplings involving O_2^- at pH 12 to 13[31]

$$O_2^- + NO \longrightarrow {}^-OONO$$

Nitric Acid and Nitrates. The acid has already been discussed (Section 3-11). Nitrates of almost all metallic elements are known. They are frequently hydrated and most are soluble in water. Many metal nitrates can be obtained anhydrous, and a number of these, for example, $Cu(NO_3)_2$, sublime without decomposition.

Anhydrous nitrates often have high solubility in organic solvents and are best regarded as covalent. Alkali metal nitrates sublime in vacuum at 350 to 500°C, but decomposition occurs at higher temperatures to yield nitrites and oxygen or above 700°C to yield oxides or peroxides.[32a] Ammonium nitrate gives N_2O and H_2O on heating.

Nitrate ion can be reduced only with difficulty. Aluminum or Zn in NaOH solution gives NH_3, and a few transition metal complex ions, for example, of Mo^{III}, allow reduction to NO_2^-; electrochemical reduction in the presence of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ proceeds via NO_2^- and NH_2OH.[32b]

Peroxonitric acid ($HOONO_2$) is unstable but can be obtained by interaction of HNO_3 and 90% H_2O_2[33] and the gas removed in an argon stream.

The Nitronium Ion. This ion (NO_2^+) is directly involved, not only in the dissociation of HNO_3 itself, but also in nitration reactions and in solutions of nitrogen oxides in HNO_3 and other strong acids.

Detailed kinetic studies on the nitration of aromatic compounds first led to the idea that the attacking species was the NO_2^+ ion generated by ionizations of the following types:

$$2HNO_3 = NO_2^+ + NO_3^- + H_2O$$

$$HNO_3 + H_2SO_4 = NO_2^+ + HSO_4^- + H_2O$$

The importance of the first type is reflected in the fact that addition of ionized nitrate salts to the reaction mixture will retard the reaction. The actual ni-

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[30] M. D. Ryan, *Inorg. Chem.*, 1986, **25**, 2606; T. Tanaka *et al.*, *Inorg. Chem.*, 1986, **25**, 3018; T. J. Meyer *et al.*, *J. Am. Chem Soc.*, 1986 **108**, 5876.

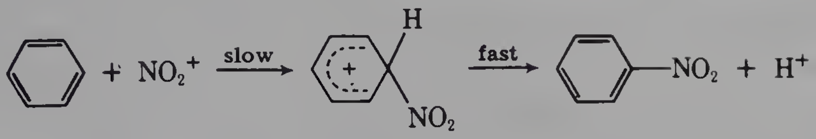
[31] N. V. Blough and O. C. Zafirion, *Inorg. Chem.*, 1985, **24**, 3502.

[32a] D. A. Nissen and D. A. Mecker, *Inorg. Chem.*, 1983, **22**, 716.

[32b] T. Tanaka, *J. Chem. Soc. Chem. Commun.*, **1986**, 135.

[33] R. A. Kenley *et al.*, *J. Am. Chem. Soc.*, 1981, **103**, 2203.

tration process can then be formulated as



The dissociation of HNO_3 in various media is shown by cryoscopic studies, and nitrogen oxides have also been found to dissociate to produce nitronium ions as noted previously. Spectroscopic studies have confirmed the presence of the various ions in such solutions. For example, the NO_2^+ ion can be identified by a Raman line at about 1400 cm^{-1}.

Crystalline *nitronium salts* can be made by reactions such as

$$N_2O_5 + HClO_4 \longrightarrow [NO_2^+ClO_4^-] + HNO_3$$

$$N_2O_5 + FSO_3H \longrightarrow [NO_2^+FSO_3^-] + HNO_3$$

$$HNO_3 + 2SO_3 \longrightarrow [NO_2^+HS_2O_7^-]$$

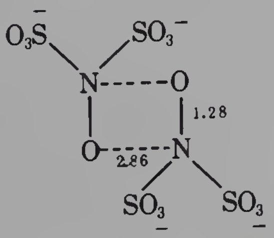
The first two of these reactions are really just metatheses, since N_2O_5 in the solid and in anhydrous acid solution is $NO_2^+NO_3^-$. The other reaction is one between an acid anhydride, SO_3, and a base(!) ($NO_2^+OH^-$).

Nitronium salts are thermodynamically stable, but very reactive chemically. They are rapidly hydrolyzed by moisture; in addition, $NO_2^+ClO_4^-$, for example, reacts violently with organic matter, but it can actually be used to carry out nitrations in nitrobenzene solution.

The Hydroxylamine-*N,N*-Disulfonate and Nitroso Disulfonate Ions. The interaction of nitrite and bisulfite ions gives the hydroxylamine-*N,N*-disulfonate ion,[34a] $HON(SO_3)_2^{2-}$, or, in base, $ON(SO_3)_2^{3-}$:

$$2HSO_3^- + HNO_2 \longrightarrow HON(SO_3)_2^{2-} \xrightarrow{OH^-} ON(SO_3)_2^{3-}$$

In $Na_3[ON(SO_3)_2]\cdot H_2O$ the N atom is pyramidal and bound to O and to two S atoms. The ion can undergo 1*e* oxidation, for example, by air,[34b] to give the *nitrosodisulfonate* ion $\cdot ON(SO_3)_2^{2-}$. The ion in solution and in salts of large cations is paramagnetic but the potassium salt (Fremy's salt) is dimorphic with yellow and orange-brown forms. The yellow monoclinic version, though nearly diamagnetic, has a thermally accessible triplet state. The triclinic form is paramagnetic with magnetic interaction between neighboring ions, which are arranged:



[34a] E. Narita *et al., Ind. Eng. Chem. Proc. Res. Dev.*, 1984, **23**, 262.

[34b] H. Willner *et al., Inorg. Chem.*, 1987, **26**, 2137.

10-8. Halogen Compounds of Nitrogen

Binary Halides. These are NF_3, N_2F_2, N_2F_4, NF_2Cl, $NFCl_2$, and NCl_3, and the halogen azides XN_3 (X = F[35], Cl, Br, or I). With the exception of NF_3 the halides are reactive, potentially hazardous substances. Some of them like $NFCl_2$ are explosive, others not. Only the fluorides are important.

Nitrogen Trifluoride. The electrolysis of NH_4F in anhydrous HF yields NF_3 plus small amounts of N_2F_2, whereas electrolysis of molten NH_4F constitutes a preferred preparative method for N_2F_2. Other synthetic methods are

$$2NF_2H \xrightarrow[\text{pH 1–2}]{\text{FeCl}_3\text{(aq)}} N_2F_4 \qquad (\sim 100\%)$$

$$NH_3 + F_2 \text{ (diluted by } N_2\text{)} \xrightarrow[\text{reactor}]{\text{copper packed}} \begin{cases} NF_3 \\ N_2F_4 \\ N_2F_2 \\ NHF_2 \end{cases}$$

(Predominant product depends on conditions, especially the F_2/NH_3 ratio.)

$$2NF_2H + 2KF \longrightarrow 2KHF_2 + N_2F_2$$

Dinitrogen difluoride may also be prepared by photolysis of N_2F_4 in the presence of Br_2.

Nitrogen trifluoride (bp −129°C) is a very stable gas that normally is reactive only at ~250 to 300°C but reacts readily with $AlCl_3$ at 70°C:

$$2NF_3 + 2AlCl_3 \longrightarrow N_2 + 3Cl_2 + 2AlF_3$$

It is unaffected by water or most other reagents at room temperature and thermally stable in the absence of reducing metals; when heated in the presence of fluorine acceptors such as Cu, the metal is fluorinated and N_2F_4 is obtained. The NF_3 molecule has a pyramidal structure but a very low dipole moment, and it appears to be devoid of donor properties. The interaction of NF_3, F_2, and a strong Lewis acid (such as BF_3, AsF_5, or SbF_5) under pressure, uv irradiation at low temperatures, or glow discharge in a sapphire apparatus, gives salts of the *tetrafluoroammonium* ion (NF_4^+), for example,

$$NF_3 + F_2 + BF_3 \xrightarrow{h\nu} NF_4BF_4$$

$$NF_3 + F_2 + AsF_5 \longrightarrow NF_4AsF_6$$

The NF_4^+ salts are hydrolyzed giving NF_3, H_2O_2, O_2 and HF.

The unstable difluoroammonium ion can be made from the explosive NHF_2 by the reaction

$$NHF_2 + HF + AsF_5 \xrightarrow{-78°C} NH_2F_2AsF_6$$

Tetrafluorohydrazine. This gas (bp −73°C), is best prepared by the reaction of NF_3 with Cu as seen previously. Its structure is similar to that of

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[35] T. Ozawa and T. Kwan, *J. Chem. Soc. Chem. Commun.*, **1985**, 54.

hydrazine, but differs in having comparable amounts of gauche and anti forms, the latter being slightly more stable, by ~2 kJ mol^{-1}. Tetrafluorohydrazine dissociates readily in the gas and liquid phases according to the equation[36]

$$N_2F_4 = 2NF_2 \qquad \Delta H_{298^\circ C} = 78 \pm 6 \text{ kJ mol}^{-1}$$

which accounts for its high reactivity. The esr and electronic spectra of the difluoroamino radical $^{\cdot}NF_2$ indicate that it is bent (cf. OF_2, O_3^-, SO_2^-, ClO_2) with the odd electron in a relatively pure π MO.

Since N_2F_4 dissociates so readily, it shows reactions typical of free radicals; thus it abstracts hydrogen from thiols,

$$2NF_2 + 2RSH \longrightarrow 2HNF_2 + RSSR$$

and undergoes other reactions such as

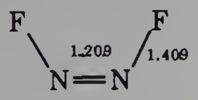
$$N_2F_4 + Cl_2 \xrightarrow{h\nu} 2\,NF_2Cl \qquad K_{25^\circ C} = 1 \times 10^{-3}$$

$$RI + NF_2 \xrightarrow{h\nu} RNF_2 + \tfrac{1}{2}I_2$$

$$RCHO + N_2F_4 \longrightarrow RCONF_2 + NHF_2$$

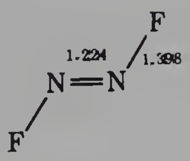
It reacts explosively with H_2 in a radical chain reaction. It also reacts at 300°C with NO and rapid chilling in liquid nitrogen gives the unstable purple nitrosodifluoroamine ($ONNF_2$). Tetrafluorohydrazine is hydrolyzed by water, but only after an inhibition period. In HF(l) it reacts with SbF_5 to give $N_2F_3^+SbF_6^-$.

Difluorodiazene (Dinitrogen Difluoride). This gas (N_2F_2) consists of two isomers (10-VIII) and (10-IX).



b.p. − 105.7°

(10-VIII)



b.p. − 111.4°

(10-IX)

The cis isomer predominates (~90%) at 25°C and is the more reactive. Isomerization to the equilibrium mixture is catalyzed by stainless steel. The pure trans form can be obtained in ~45% yield by the reaction

$$2N_2F_4 + 2AlCl_3 \longrightarrow N_2F_2 + 3Cl_2 + 2AlF_3 + N_2$$

Nitrogen Trichloride, Tribromide, and Triiodide. The chloride (NCl_3) is formed in the chlorination of the slightly acid solutions of NH_4Cl (see next section) and may be continuously extracted into CCl_4. When pure, it is a pale yellow oil (bp ~71°C). It is endothermic ($\Delta H_f^0 = 232$ kJ mol^{-1}), explosive,

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[36] P. B. Davis *et al.*, *J. Chem. Soc. Chem. Commun.*, **1982,** 690.

photosensitive, and, generally, very reactive. The vapor has been employed in bleaching flour. The molecule is pyramidal, with N—Cl = 1.753 Å and Cl—N—Cl = 107° 47′.

Nitrogen tribromide is similar to NCl_3 and is hydrolyzed in base:

$$2NBr_3 + 3OH^- = N_2 + 3Br^- + 3HOBr$$

Concentrated aqueous ammonia reacts with I_2 at 23°C to give black, explosive crystals of $(NI_3{\cdot}NH_3)_n$ that contains zigzag chains of NI_4 tetrahedra sharing corners, with NH_3 molecules lying between the chains and linking them together; $NI_3{\cdot}3NH_3$ is similar.

Haloamines. These are compounds of the type H_2NX and HNX_2, where H may be replaced by an alkyl radical. Only H_2NCl (chloramine), HNF_2, and H_2NF have been isolated; $HNCl_2$, H_2NBr, and $HNBr_2$ probably exist but are quite unstable.

Chloramine, fp −66°C, is formed in the gas phase reaction

$$2NH_3 + Cl_2 \longrightarrow NH_2Cl_{(g)} + NH_4Cl_{(s)}$$

It is stable as a gas or in solutions but the liquid and solid are explosive. The chlorination of aqueous NH_3 has been studied in detail[37] and NH_2Cl is readily obtained by interaction of NH_3 and OCl^- at pH > 8. At pH 3 to 5 $NHCl_2$, and at pH < 3, NCl_3 is formed according to the reactions

$$2NH_2Cl + H^+ \rightleftharpoons NHCl_2 + NH_4^+$$

$$3NHCl_2 + H^+ \longrightarrow 2NCl_3 + NH_4^+$$

Difluoroamine, a colorless, explosive liquid (bp 23.6°C), can be obtained as just described or by H_2SO_4 acidification of fluorinated aqueous solutions of urea; the first product H_2NCONF_2, gives HNF_2 on hydrolysis. It can be converted into chlorodifluoroamine ($ClNF_2$) by the action of Cl_2 and KF. Unlike NF_3, NHF_2 is a weak donor:

$$NHF_2(g) + BF_3(g) = HF_2NBF_3(s) \qquad \Delta H = -88 \text{ kJ mol}^{-1}$$

Oxo Halides. The compounds and some of their properties are listed in Table 10-2.

The *nitrosyl halides* are formed by direct union of the halogens with NO and also in other ways. They are increasingly unstable in the series FNO, ClNO, and BrNO. The ClNO is always slightly impure, decomposing (to Cl_2 and NO) to the extent of about 0.5% at room temperature, and BrNO is decomposed to ~7% at room temperature and 1 atm.

All three are reactive and are powerful oxidizing agents, able to attack many metals. All decompose on treatment with water producing HNO_3, HNO_2, NO, and HX.

The only known *nitryl halides,* which may be regarded as derivatives of

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[37] See V. C. Hand and D. W. Margerum, *Inorg. Chem.,* 1983, **22,** 1449.

TABLE 10-2
Physical Properties of Nitrosyl Halides (XNO) and Nitryl Halides (XNO_2)

Property	FNO[a]	ClNO	BrNO	FNO_2[a]	$ClNO_2$
Color of gas	Colorless	Orange-yellow	Red	Colorless	Colorless
Melting point (°C)	−133	−62	−56	−166	−145
Boiling point (°C)	−60	−6	~0	−72	−15
Structure	Bent	Bent	Bent	Planar[b]	Planar[b]
X—N distance (Å)	1.52	1.95 ± 0.01	2.14 ± 0.02	1.35	1.840 ± 0.002
N—O distance (Å)	1.13	1.14 ± 0.02	1.15 ± 0.04	1.23	1.202 ± 0.001
X—N—O angle (deg)	110	116 ± 2	114		
O—N—O angle (deg)				125 (assumed)	130.6 ± 0.2

[a] Uncertainties in structure parameters not known.
[b] Molecular symmetry, C_{2v}.

HNO_3 where a halogen atom replaces OH, are FNO_2 and $ClNO_2$. The former is prepared by the reaction

$$N_2O_4 + 2CoF_3(s) \xrightarrow{300°C} 2FNO_2 + 2CoF_2(s)$$

Nitryl chloride ($ClNO_2$) is not obtainable by the direct reaction of NO_2 and Cl_2, but is made by the reaction

$$ClSO_3H + HNO_3 \text{ (anhydrous)} \xrightarrow{0°C} ClNO_2 + H_2SO_4$$

Both compounds are quite reactive and are decomposed by water:

$$XNO_2 + H_2O = HNO_3 + HX$$

Reaction of NO_2 and F_2 at −30°C gives *nitrosyl hypofluorite* (ONOF).

Interaction of NCl_3, $SOCl_2$, and $SbCl_5$ in CCl_4 gives the yellow salt $[ONCl_2]^+SbCl_6^-$, which is stable to 145°C.

Halogen Nitrates. Two of these highly reactive substances are known: $ClONO_2$ (bp 22.3°C) and $FONO_2$ (bp −46°C). Chlorine nitrate ($ClONO_2$) is not known to be intrinsically explosive, but it reacts explosively with organic matter; $FONO_2$ is liable to explode. The best preparative reactions appear to be

$$ClF + HNO_3 \longrightarrow ClONO_2 + HF$$

$$F_2 + HNO_3 \longrightarrow FONO_2 + HF$$

Trifluoramine Oxide. This stable, toxic, and oxidizing gas (bp −87.6°C), which is resistant to hydrolysis, can be prepared by the reaction

$$2NF_3 + O_2 \xrightarrow[\text{discharge}]{\text{electric}} 2F_3NO$$

$$FNO + F_2 \xrightarrow{h\nu\ 25°C} F_3NO$$

It reacts with strong F^- acceptors such as AsF_5 and SbF_5 to give salts of NF_2O^+ and also with olefins[38]; with NO it reacts rapidly to give FNO.[39]

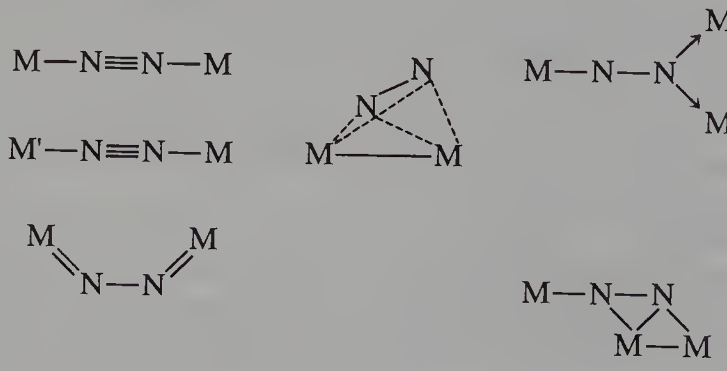
DINITROGEN AND NITROGEN COMPOUNDS AS LIGANDS

Dinitrogen and NO are particularly important ligands toward transition metals; the bonding is discussed in Section 2-9. Almost any compound containing nitrogen that has lone pairs can act as a ligand and we consider later the most important classes of ligands.

10-9. Dinitrogen[40]

Although CO and N_2 are isoelectronic the first N_2 complex was discovered only in 1965 by Allan and Senoff by the interaction of hydrazine with $RuCl_3(aq)$ to give $[Ru(N_2)(NH_3)_5]^{2+}$. Dinitrogen compounds are commonly obtained by reduction under N_2 of complex halides by chemical or electrochemical reduction.[41] Typical examples are $Cr(N_2)_2(dmpe)_2$, and $HCo(N_2)(PPh_3)_3$. The Mo and W complexes with phosphine ligands have been much studied as models for hydrogenation of N_2 to NH_3 or N_2H_4.

Although end-on η^1 binding is most common, η^2 bonding as with C_2H_4 is known and a variety of *bridging modes* that differ from those of CO (Chapter 22) in part due to the donor ability of the lone pair, MNN:→, and the possibility of using NN π bonds.[42]



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[38] K. O. Christe *et al.*, *Inorg. Chem.*, 1983, **22,** 1355.

[39] S. A. Kinkead and J. M. Shreeve, *Inorg. Chem.*, 1984, **23,** 4174.

[40] J. Chatt *et al.*, *Chem. Rev.*, 1978, **78,** 589; P. Pelikán and R. Boca, *Coord. Chem. Rev.*, 1984, **55,** 55, *J. Mol. Catal.*, 1985, **31,** 289; R. A. Henderson *et al.*, *Adv. Inorg. Chem. Radiochem.*, 1983, **27,** 198; H. M. Colquhoun, *Acc. Chem. Res.*, 1984, **17,** 23; G. J. Leigh, *Trans. Met. Chem.*, 1986, **11,** 118.

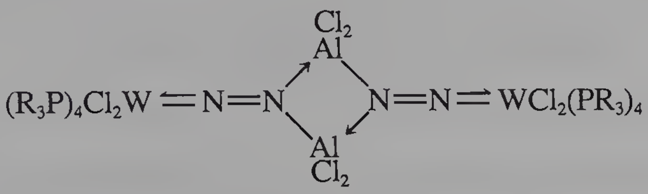
[41] See, for example, T. I. Al-Salih and C. J. Pickett, *J. Chem. Soc. Dalton Trans.*, **1985,** 1255; R. L. Richards *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986,** 245.

[42] M. Hidai *et al.*, *J. Am. Chem. Soc.*, 1983, **105,** 1680; R. J. H. Clark *et al.*, *J. Chem. Soc. Dalton Trans.*, **1983,** 2005; M. R. Churchill and Y. J. Li, *J. Organomet. Chem.*, 1986, **301,** 49.

The linear symmetric bridges[43] are most common with bond distances 1.124 to 1.298 Å. However, in certain W and Ta compounds, for example, $[(dme)Cl_2(Ph_2C_2)W]_2\mu\text{-}N_2$ the bond length is long, 1.292 Å, and the bonding could involve N_2^{4-}, that is, $M\overset{\longleftarrow}{=}\ddot{N}-\ddot{N}\overset{\longrightarrow}{=}M$ which would explain the quantitative hydrolysis of the compounds to N_2H_4 and reactivity towards ketones.[44]

$$L_nM\mu(N_2)ML_n + 2R_2CO \longrightarrow R_2C{=}N{-}N{=}CR_2 + 2L_nMO$$

The donor properties of coordinated N_2 are illustrated by the complex



Reactivity of Bound N_2.[45] Although the mechanism of reduction of N_2 in biological systems is by no means clear, the reactions of coordinated N_2 in simple systems are reasonably well understood. The principal types of reaction sequence involve *hydrazido, imido,* and *nitrido* species, to be discussed later, in a cycle of the type

$$\begin{tikzcd}
MN_2 \arrow[r, "H^+", "e"'] & MNNH \arrow[r, "H^+", "e"'] & M{=}NNH_2 \arrow[d, "e"', "H^+ - NH_3"] \\
M{-}NH_3 \arrow[u, "\substack{+N_2\\-NH_3}"] & M{=}NH \arrow[l, "2H^+"', "2e"] & M{\equiv}N \arrow[l, "H^+"', "e"]
\end{tikzcd}$$

Electrophilic attack[46] by H^+ or other electrophiles can lead to N—H or N—C bond formation and in some cases to NH_3 and N_2H_4. Examples are

$$(PhMe_2P)_4Mo(N_2)_2 + 2HX \longrightarrow [(PhMe_2P)_4XMoNNH_2]X + N_2$$

$$(diphos)_2W(N_2)_2 + RCOCl \longrightarrow (diphos)_2ClWNNC(O)Ph + N_2$$

For some compounds, and depending on the nature of the acid and of the solvent, there can be formation of (*a*) NH bonds, (*b*) MH bonds, (*c*) the complex is oxidized with loss of N_2 and of H_2, and (*d*) oxidative addition of

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[43] C. P. Powell and M. B. Hall, *Inorg. Chem.*, 1984, **23,** 4619; R. L. Richards *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2429.

[44] M. R. Churchill *et al., Inorg. Chem.*, 1984, **23,** 4472; A. K. Rappé *et al., Inorg. Chem.*, 1984, **23,** 995.

[45] M. Hidai in T. G. Spiro, Ed., *Molybdenum Enzymes,* Wiley, New York, 1985.

[46] A. M. Colquhoun, *Acc. Chem. Res.*, 1984, **17,** 23; T. A. George *et al., Inorg. Chem.*, 1985, **24,** 3568, *J. Am. Chem. Soc.*, 1985, **107,** 5157; R. A. Henderson, *J. Chem. Soc. Dalton Trans.*, **1984,** 2259; R. H. Morris *et al., Inorg. Chem.*, 1986, **25,** 3926; S. N. Anderson *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 1591.

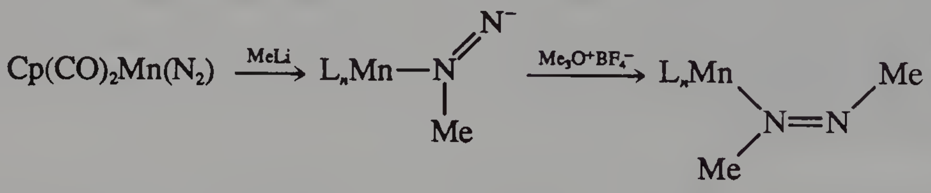
HX (Chapter 27) occurs, for example,

$$\begin{tikzcd}
 & & \mathrm{MoH_2Cl_2(diphos)} \\
\mathrm{(diphos)_2Mo(N_2)_2} \arrow[r, "\mathrm{HCl, THF}"] & \mathrm{[(diphos)_2MoH(N_2)_2]^+} \arrow[ur, "\substack{\mathrm{HCl} \\ +\mathrm{Cl}^-}"] \arrow[dr, "\mathrm{HCl}"'] & \\
 & & \mathrm{[Mo(NNH_2)Cl(diphos)]^+}
\end{tikzcd}$$

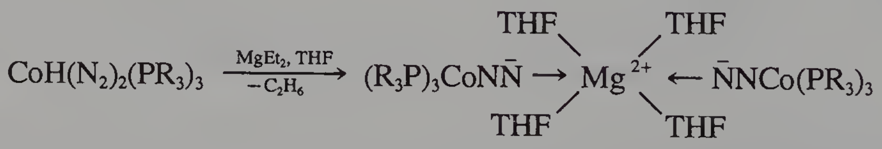
Addition of alkyl halides[47] can lead to C—X bond cleavage and *radical reactions:*

$$\begin{tikzcd}
\mathrm{(diphos)_2Mo(N_2)_2} \arrow[r, "\mathrm{RX}", "-\mathrm{N_2}"'] & \mathrm{(diphos)_2Mo(RX)N_2} \arrow[d] \\
\mathrm{(diphos)_2MoX(NNR)} & \mathrm{(diphos)_2MoX(N_2)} + \mathrm{R} \arrow[l]
\end{tikzcd}$$

Nucleophilic attack is also possible as in the reaction



Alkyl magnesiums can react[48]:



Finally, MN_2 species can act as simple donors to Lewis acids such as $AlCl_3$ or $AlMe_3$.[49]

10-10. Nitrogen Monoxide[50]

Nitric oxide compounds and some of their reactions such as

$$[Fe(CN)_5NO]^{2-} + 2OH^- \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + H_2O$$

have long been known. The compounds have mainly one NO group but di- and tri-nitrosyls, for example, $Fe(CO)_2(NO)_2$ and $Mn(CO)(NO)_3$ exist. The

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[47] M. Hidai *et al., J. Organomet. Chem.,* 1984, **272,** 155; see also W. Hussain *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 1473.

[48] A. Yamamoto *et al., Organometallics,* 1983, **2,** 1429.

[49] R. L. Richards *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 2429.

[50] J. A. McCleverty, *Chem. Rev.,* 1979, **79,** 37; R. D. Feltham and J. H. Enemark, in *Topics in Inorganic and Organometallic Stereochemistry,* G. Geoffroy, Ed., Wiley-Interscience, New York, 1981; K. K. Pandy, *Coord. Chem. Rev.,* 1983, **51,** 69 (NO in organic synthesis).

only pure nitrosyl is $Cr(NO)_4$.[51] The complexes can be made from carbonyls by NO substitution, from $NOPF_6$, by reductive processes[52] from NO_2^- or NO_3^-, or by interaction of oxo species with hydroxylamine.[53] Some representative syntheses are

$$Co_2(CO)_8 + 2NO \longrightarrow 2Co(NO)(CO)_3 + 2CO$$

$$Cp_2Ni + NO \longrightarrow CpNiNO + ?$$

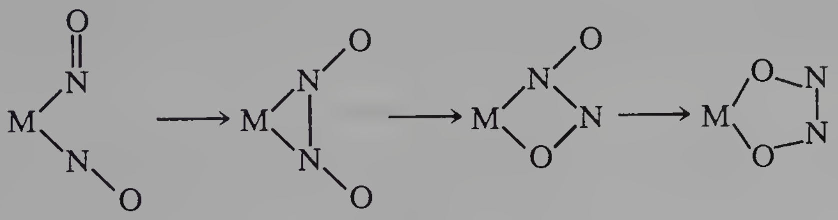
$$Fe(CO)_5 + PPN^+NO_2^- \xrightarrow{MeCN} [Fe(CO)_3NO]^- + CO_2$$

$$OsO_4 \xrightarrow[NCS^-]{NH_2OH \cdot HCl} [OsNO(NCS)_5]^{2-}$$

$$RhCl(CO)(PPr_3)_2 \xrightarrow{NOBF_4} [RhCl(NO)(CO)(PPr_3)_2]\ BF_4$$

The reaction with OsO_4 is similar to a common reaction of oxo anions such as VO_4^{3-} or ReO_4^- in alkaline or acidic solution containing coordinating anions with hydroxylamine; intermediates with partially deprotonated ligands H_2NO and HNO may be isolated.[54] Nitric acid can also act as a source of NO,[55] especially for ruthenium, any of whose solutions treated with HNO_3 can be assumed to contain Ru(NO) species.

Finally, it may be noted that interaction of NO with some low-valent compounds, for example, $Pt(PPh_3)_3$ can give *hyponitrite* complexes probably via a nitrosyl (10-X) with one M—NO bent (see next section) and the sequence.[56]



(10-X)

Bonding Modes. The three principal modes are

(a) terminal linear M—NO groups in which the NO is *formally* regarded as binding as a 2*e* donor NO^+ with transfer of the odd electron to the metal, thus lowering its oxidation state. Overall, NO is hence a 3*e* donor. In many cases the MNO angle is below 180°, especially where the group is not in an axially symmetrical environment and "slightly bent" MNO groups may have angles between ~160 to 180°.

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[51] I. H. Hillier *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 438.

[52] See, for example, R. Stevens and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1982, **104,** 6454.

[53] See, for example, K. Wieghardt *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 2493.

[54] R. Bhattacharyya *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2085; K. Wieghardt *et al., Inorg. Chem.*, 1983, **22,** 1221.

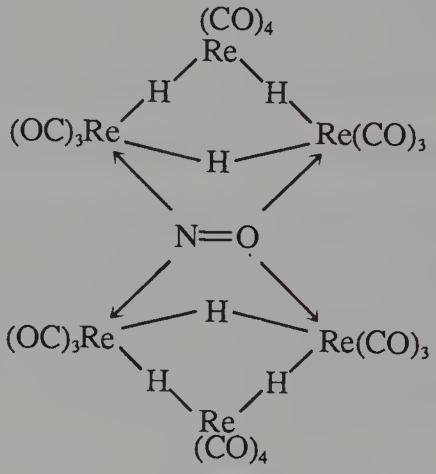
[55] K. Wieghardt *et al., Inorg. Chem.*, 1984, **23,** 427.

[56] F. Mares *et al., Inorg. Chem.*, 1983, **22,** 960.

(b) Truly bent MNO groups have angles between ~120 to 140°. The NO can be considered as a 1*e* donor and compared with compounds like ClNO or *t*-BuNO with a X—N single bond.

(c) Bridging NO groups bound through N may be symmetric or asymmetric or μ_3 in clusters.[57] Thus in $Cp_3Mn_3(NO)_4$ there are three μ_2 and one μ_3 bridges and NO again functions as a 3*e* donor.

An unusual μ_4, η^2 bridge where NO is formally bound as NO^- is (10-XI).



(10-XI)

For *mononitrosyls,* the stoichiometries and properties can be accounted for by considering the $\{MNO\}^n$ unit as a functional group, *n* being the number of *d* electrons on the metal M *plus* the number of NO electrons in excess of those on NO^+.[58] Examples are

$$\{MNO\}^5 = [Cr^I(NO)(CN)_5]^{3-}$$

$$\{MNO\}^8 = Mn^{-1}(NO)(CO)_4,\ Ir^I(NO)Cl_2(PR_3)_3$$

Whether the MNO group is linear or bent depends on

1. The coordination geometry and number.
2. The value of *n*.
3. The nature of the one-electron MO's.

Thus for $n \leqslant 6$ all $\{MNO\}^n$ groups are linear or nearly so in octahedral coordination but bent if $n \geqslant 7$.

For five-coordination MNO is linear for $n \leqslant 6$; $\{MNO\}^8$ is linear for *tbp* but bent in *sp*. For four-coordination, $n = 10$, tetrahedral has linear but planar has bent MNO.

Infrared spectra allow a distinction between "linear" and bent groups, the former generally having $\nu > 1610\ cm^{-1}$; bridged species have ν NO for μ_2

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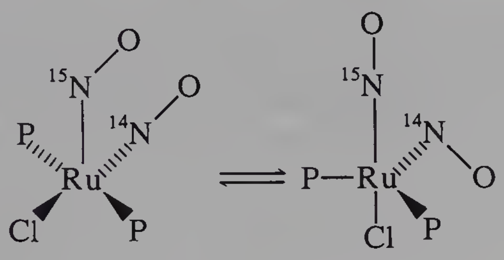
[57] F. Bottomley, *Inorg. Chem.*, 1983, **22,** 2656; L. F. Dahl *et al., Organometallics,* 1985, **4,** 2221; G. Pilloni *et al., Organometallics,* 1987, **6,** 597.

[58] J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 1974, **13,** 329; T. W. Hawkins and M. B. Hall, *Inorg. Chem.*, 1980, **19,** 1735.

1480 to 1510 cm^{-1} and for μ_3 ~ 1320 cm^{-1}. There is some overlap in the ir regions, however, and a better spectroscopic criterion is the ^{15}N nmr spectrum.[59] Linear MNO groups have shifts (relative to MeNO$_2$, high frequency positive) near to the value for NO$^+$ (δ −5) in the region −75 to +180 ppm and slightly bent nitrosyls (angles 160–180°) are slightly deshielded relative to linear ones. For bent species, there is a very substantial deshielding, increasing with the degree of bending of ~500 to 800 ppm (*cf. t*-BuNO, δ 594). Magic-angle nmr of solids also show a large chemical shift anisotropy for bent MNO. Specific examples are [Ru(NO)(NH$_3$)$_5$]Cl$_3$, ⟨RuNO = 172.8°, δ −29 and Co(NO)sal$_2$en, ⟨CoNO = 127.0°, δ 725.4.

Compounds that have *both* bent and linear groups can be obtained, one example being [RuCl(NO)$_2$(PPh$_3$)$_2$]$^+$. The nmr studies show that the ion is nonrigid with a linear–bent exchange giving isomers in solution:



In the solid the square pyramidal ion has bent apical and linear basal NO groups.

The linear–bent transition probably requires little energy and may well be involved in reactions of dinitrosyl intermediates in reactions such as that noted previously leading to a hyponitrite complex or in reactions of NO and CO to give N$_2$O and CO$_2$ catalyzed by nitrosyl complexes.

Increasing the electron density on the metal may also lead to a linear → bent transition. This can be done by addition of a donor ligand[60] or by reduction[61] as in the conversion of CpM(CO)$_2$NO to CpM(CO)$_2$NO$^{\cdot -}$.

Reactions of Coordinated NO.[50,62] In view of the differences between the electronic structures of linear, bent, and bridged NO groups, considerable differences in their chemical reactivity can be expected. Generally, linear MNO groups are attacked by nucleophiles while bent ones with, in effect, a lone pair on N, are susceptible to electrophilic attack, but this is by no means a rule and there are many exceptions. A few of the more common reactions of nitrosyls are now described.

Nucleophilic Attack. Interaction of linear NO complexes with nucleophiles such as OH$^-$, OR$^-$, SR$^-$, and NH$_2$R usually occurs at the N atom[63] but

[59] J. Mason *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 444; *Inorg. Chem.*, 1984, **23,** 3629.

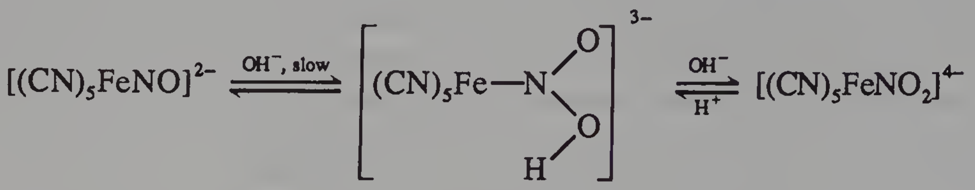
[60] D. W. Meek *et al., Inorg. Chem.*, 1980, **19,** 85.

[61] W. E. Geiger *et al., J. Am. Chem. Soc.*, 1984, **106,** 7000.

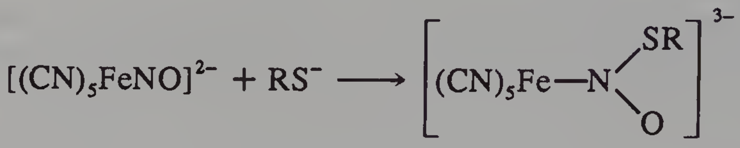
[62] For references see S. R. Stobart *et al., J. Am. Chem. Soc.*, 1985, **107,** 8258.

[63] M. D. Johnson and R. G. Williams, *Inorg. Chem.*, 1984, **23,** 231.

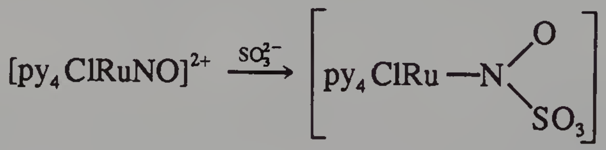
attacks on O may also occur. A classic example is that of nitroprusside with hydroxide ion to give a nitro complex



and with thiols to give a red coloration, a reaction long used for detection of RS$^-$



The reaction of nitroprusside with sulfite may indeed be the first example of the reaction of a coordinated ligand (Boedeker, 1861). The type of red unstable species is probably indicated by the stable ruthenium complex:

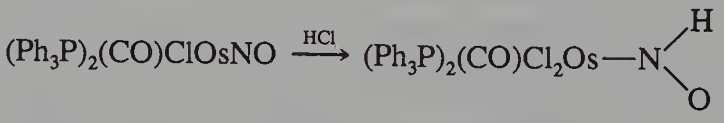


where the unusual nitrosylsulfito ligand has a long, (1.82 Å) weak N—S bond[64]

This type of ruthenium complex also illustrates a further type of reaction probably proceeding via nucleophilic attack, namely, condensation and elimination of water:

$$[\mathrm{bipy_2\,ClRuNO}]^{2+} + \mathrm{H_2NPh} \longrightarrow [\mathrm{bipy_2\,ClRuN{=}NPh}]^{2+} + \mathrm{H_2O}$$

Electrophilic Attacks. Attacks by H$^+$ or Me$^+$ may be at either N or O,[65] for example,



Bridged NO species can also be attacked, for example,

$$[\mathrm{Ru_3(CO)_{10}}\mu\text{-}\mathrm{NO}]^- \xrightarrow{\mathrm{CF_3SO_3Me}} [\mathrm{Ru_3(CO)_9}(\mu_3\text{-}\mathrm{CO})\mu\text{-}\mathrm{NOMe}]$$

In the reaction of a manganese cluster [$M_3\mu_3$-NO] where M = (η^5-C_5H_4MeMnNO) the first, hydroximido product can undergo further reaction

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[64] F. Bottomley *et al., J. Chem. Soc. Dalton Trans.*, **1983,** 2465.

[65] R. E. Stevens and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1982, **104,** 6452.

with HBF_4 to give μ_3-NH.[66] This is similar to attacks on M—CO that lead to CH_4 (Section 28-3).

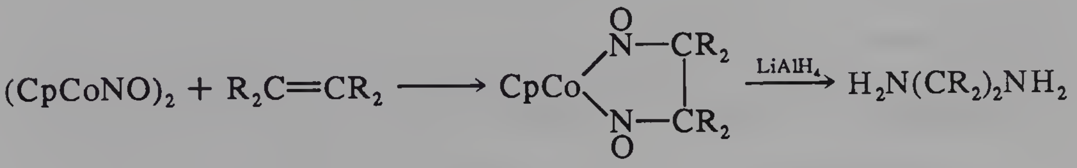
$$M_3(\mu_3\text{-}NO) \underset{Et_3N}{\overset{H^+}{\rightleftharpoons}} M_3(\mu_3\text{-}NOH)^+ \xrightarrow[2e]{2H^+} M_3(\mu_3\text{-}NH)^+$$

Oxygenation. Some NO complexes react with O_2

$$L_nMNO + \tfrac{1}{2}O_2 = L_nMNO_2$$

Since the nitro complexes can be reduced to MNO, for example, by alkenes, there is the possibility of oxidation reactions that are catalytic. These O-transfer reactions are discussed in Section 28-23.

Alkene Reactions. The stoichiometric reactions of μ-NO species with alkenes can provide a route to amines[67]:



Reductions. Reduction of L_nMNO by boro- or aluminohydrides or other reducing agents can give species with H—M—NO units that can be further reduced,[68] for example,

$$FeCl(NO)_3 \xrightarrow{\text{Red-Al}} Fe_2(NO)_4(\mu\text{-}NH_2)_2$$

$$[RuClpy_4NO]^{2+} \xrightarrow{Zn,\ H^+} [RuClpy_4NH_3]^+ + H_2O$$

Many NO species can, of course undergo reversible one-electron reductions[69] such as

$$(Et_2NCS_2)_2Mo(NO)_2 \overset{e}{\rightleftharpoons} [(Et_2NCS)_2Mo(NO)_2]^-$$

Intermolecular Transfers. Exchanges of NO between complexes is possible especially where coordinately unsaturated complexes can form bridged NO intermediates:

$$RhNO(PPh_3)_3 + CoCl(PPh_3)_3 \rightleftharpoons CoNO(PPh_3)_3 + RhCl(PPh_3)_3$$

Reactions possibly involving nitrosyl intermediates have been noted previ-

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[66] P. Legzdins *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 3727; *cf*, also B. F. G. Johnson *et al.*, *J. Chem. Soc. Chem. Commun.*, **1984**, 186.

[67] R. G. Bergman *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 2985; N. G. Connelly *et al.*, *J. Chem. Soc. Dalton Trans.*, **1983**, 295.

[68] M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, 1981, **105**, 5577; P. Legzdins *et al.*, *Inorg. Chem.*, 1980, **19**, 3626; W. P. Fang and C. H. Cheng, *J. Chem. Soc. Chem. Commun.*, **1986**, 503.

[69] J. A. Broomhead *et al.*, *Inorg. Chem.*, 1982, **21**, 103.

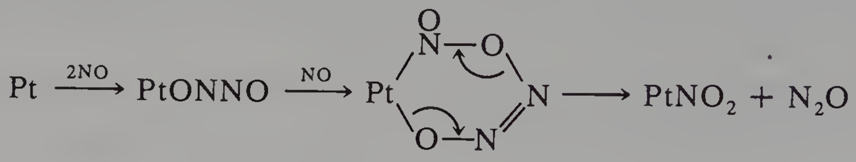
ously; another example[70] is

$$(Cp_2TiCl)_2 + 2NO \longrightarrow (Cp_2TiCl)_2\mu\text{-}O + N_2O$$

The insertion of NO into M—C bonds is considered in Chapter 27. In certain cases, however, disproportionation occurs instead,[71] for example,

$$(Et_3P)_2PtMe_2 + 6NO \longrightarrow (Et_3P)_2PtMe_2(NO_2)_2 + 2N_2O$$

a reaction that may proceed by the sequence



Thionitrosyls.[72] Relatively few compounds with MNS groups are known. They have been made by reactions involving attack on M≡N by S_8 or SCl_2, or by reactions involving KCNS, $(NSCl)_3$, or NS^+.[73] Some examples are

$$(Et_2NCS_2)_2Mo{\equiv}N + \tfrac{1}{8}S_8 \longrightarrow (Et_2NCS_2)_3MoNS$$

$$Na[CpCr(CO)_3] + \tfrac{1}{3}S_3N_3Cl_3 \longrightarrow CpCr(CO)_2NS + CO + NaCl$$

$$[CpFe(CO)_2SO_2]AsF_6 + NSAsF_6 \longrightarrow [CpFe(CO)_2NS]^{2+} + 2AsF_6^- + SO_2$$

Although ir spectra suggest that, like NO, NS can give linear, bent, and bridged species, the only X-ray diffraction studies have been on compounds with linear or almost linear groups. The π-acceptor ability of NS compared to NO depends on the charge density in the complex.[74]

A related complex, *trans*-$Rh(CO)(NSO)(PPh_3)_2$ has been made by interaction of $CsNSO_2$ with $RhH(CO)(PPh_2)_3$ in MeCN.[75]

Other Nitrogen Oxides. Nitrogen dioxide, which has an unpaired electron like NO readily loses this to form the nitrite anion, which can be bound either through N or through O; NO_2^- complexes are discussed in Section 12-16.

Dinitrogen monoxide complexes may be intermediates in some reactions of N_2O that give oxo metal species and N_2 but only $[Ru(NH_3)_5N_2O]^{2+}$ has been characterized. It is still uncertain whether there is bonding through N or through O.[76]

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[70] F. Bottomley and I. J. B. Lin, *J. Chem. Soc. Dalton Trans.*, **1981,** 271.

[71] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1982,** 663.

[72] H. W. Roesky and K. K. Pandey, *Adv. Inorg. Chem. Radiochem.*, 1983, **26,** 337; H. L. Nigam *et al., Proc. Indian Nat. Sci. Acad.*, 1982, **48A,** 16. K. Dehnicke *et al., Z. Naturforschg.*, 1986, **41B,** 560; *Z. Anorg. Allg. Chem.*, 1986, **532,** 175.

[73] D. J. Woolins *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 1043; G. Hartman and R. Mews, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 202; D. L. Lichtenberger *et al., Inorg. Chem.*, 1984, **23,** 2721; J. W. Bats *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2081.

[74] D. L. Lichtenberger and J. L. Hubbard, *Inorg. Chem.*, 1985, **24,** 3835; H. W. Roesky *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 719; J. Baldas *et al., Austral. J. Chem.*, 1984, **37,** 751.

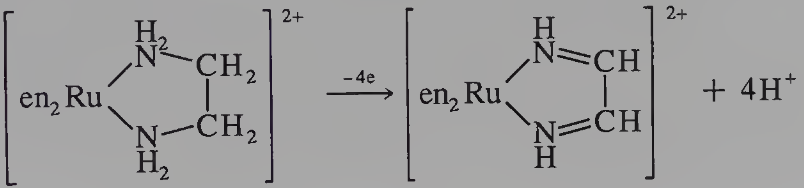
[75] H. W. Roesky *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2271.

[76] D. F-T. Tuan and R. Hoffmann, *Inorg. Chem.*, 1985, **24,** 871.

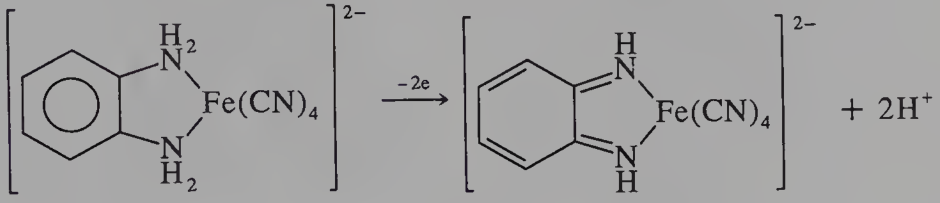
10-11. Ammonia and Amines

Ammonia complexes are among the longest known and most intensively studied. As well as classical complexes such as $[Co(NH_3)_6]^{3+}$ many metal halides form adducts with NH_3 or amines.

Coordinated NH_3 and amine ligands can undergo oxidation and condensation reactions. Thus the trisethylenediamine complex $[Ruen_3]^{2+}$ may be oxidized, probably initially to a Ru^{III} complex, whereupon intramolecular oxidative dehydrogenation of the ligand occurs, to give an α-*diimine complex:*



There is also a similar reaction for *o*-phenylenediamine complexes:



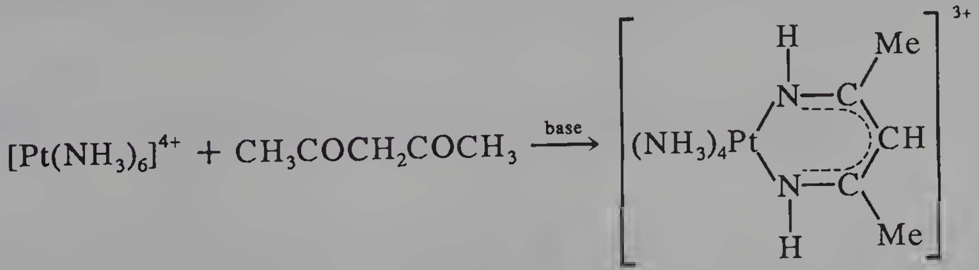
o-Benzoquinonediimine complex

Diimine complexes can also be obtained in other ways—for example, by reductive coupling of nitriles. Diimine complexes are discussed later.

Finally, amine complexes may be oxidized to give nitrile complexes:

$$[(NH_3)_5RuNH_2CH_2R]^{3+} \longrightarrow [(NH_3)_5RuN{\equiv}CR]^{2+}$$

Examples of condensation reactions are given later in this chapter when discussing template synthesis, but one example is the interaction of NH_3 complexes with β-diketones in basic solution to give nitrogen ligands that are comparable to β-diketonates (Section 10-14):



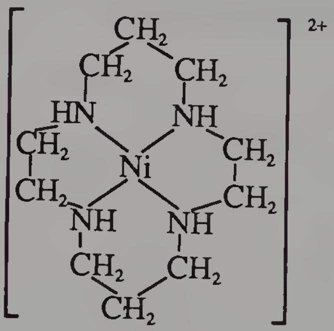
Macrocyclic Amine Ligands. The large ring compounds whose structures are such that several donor atoms can bind to a metal are most commonly nitrogen donors. However, mixed N,O; N,S; N,O,S; N,O,P; and so on, donors are known. Depending on the donor atoms, these can be designated N_4, N_2O_2, O_4, and so on. The heterocycles can be broadly classed into those without and those with conjugated π systems; the latter are discussed later.

Macrocyclic complexes have the following characteristics[77a]

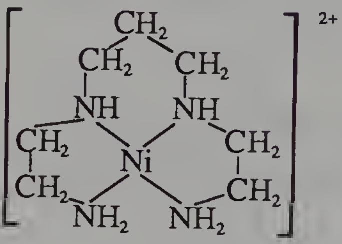
1. A marked kinetic inertness both to the formation of the complexes from the ligand and metal ion, and to the reverse, the extrusion of the metal ion from the ligand.

2. They can stabilize high oxidation states[77b] that are not normally readily attainable, such as Cu^{III} or Ni^{III}.

3. They have high thermodynamic stability—the formation constants for N_4 macrocycles may be orders of magnitude greater than the formation constants for nonmacrocyclic N_4 ligands. Thus for Ni^{2+} the formation constant for the macrocycle cyclam (10-XII) is about five orders of magnitude greater than that for the nonmacrocycle tetradentate (10-XIII):



(10-XII)

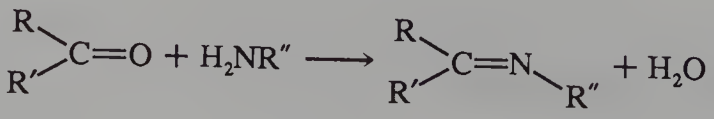


(10-XIII)

This *macrocyclic effect* has been discussed thermodynamically in Section 2-4.

The size of the hole greatly influences the properties of the complex relative to those of open chain analogues and cavity sizes can now be related to ligand structure for both nonconjugated and conjugated ligands.[78]

Macrocycles that are saturated or have double bonds in only one part of the ring can be made independently or can be made by *template synthesis*[79] where the presence of a metal ion controls the ligand synthesis. An important route is the Schiff base condensation reaction (eq. 10-3),



$$R(R')C{=}O + H_2NR'' \longrightarrow R(R')C{=}N{-}R'' + H_2O \qquad (10\text{-}3)$$

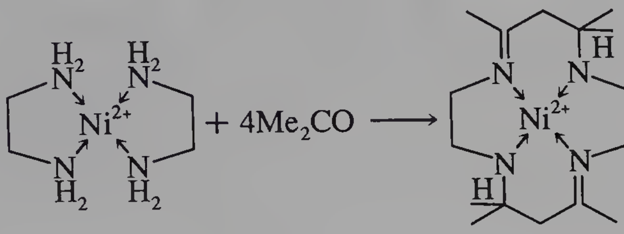
[77a] See R. M. Clay *et al., Inorg. Chem.*, 1985, **24**, 3330; R. D. Hancock *et al., Inorg. Chem.*, 1985, **24**, 3378.

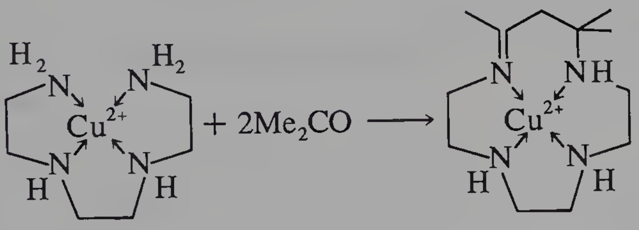
[77b] L. Fabbrizzi, *Comments Inorg. Chem.*, 1985, **4**, 33.

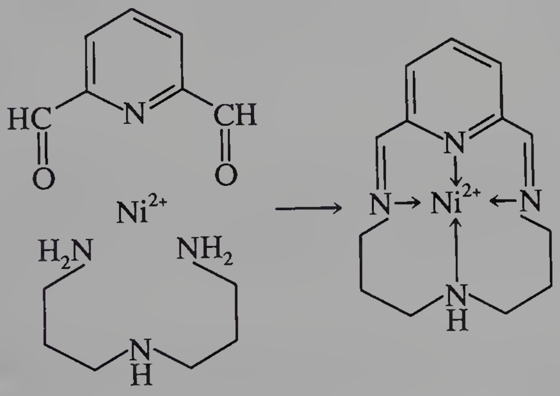
[78] K. Henrick, P. A. Tasker, and L. F. Lindoy, *Prog. Inorg. Chem.*, 1985, **33**, 1.

[79] See, for example, B. A. Anderson and S. C. Jackels, *Inorg. Chem.*, 1986, **25**, 1085; T. W. Bell and F. Guzzo, *J. Chem. Soc. Chem. Commun.*, **1986**, 769 (a Sr^{2+} nitrogen crown).

often (but not necessarily) with a metal ion as template, and with subsequent hydrogenation to obtain a saturated system not subject to hydrolytic degradation by reversal of reaction 10-3. Some representative preparative reactions are eqs. 10-4 to 10-6.

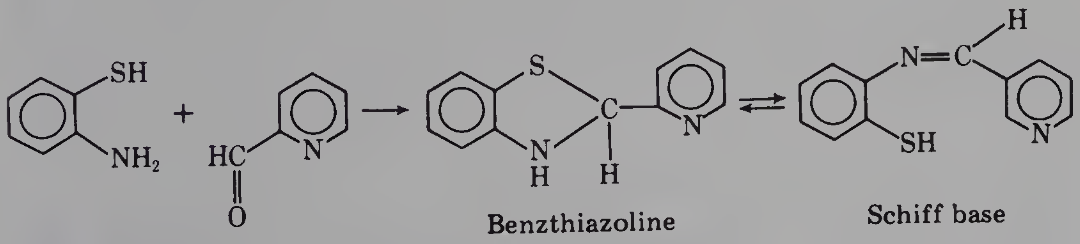

(10-4)


(10-5)


(10-6)

Other examples are as follows:

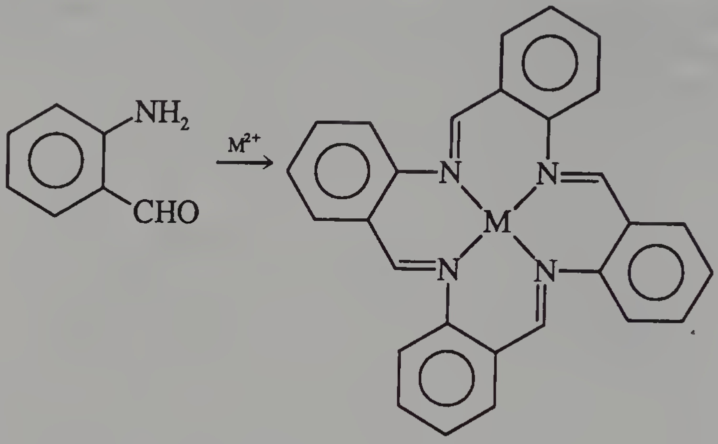
1. The condensation of *o*-aminothiophenol with pyridine-1-carboxaldehyde gives benzthiaazoline in the absence of metal ions:



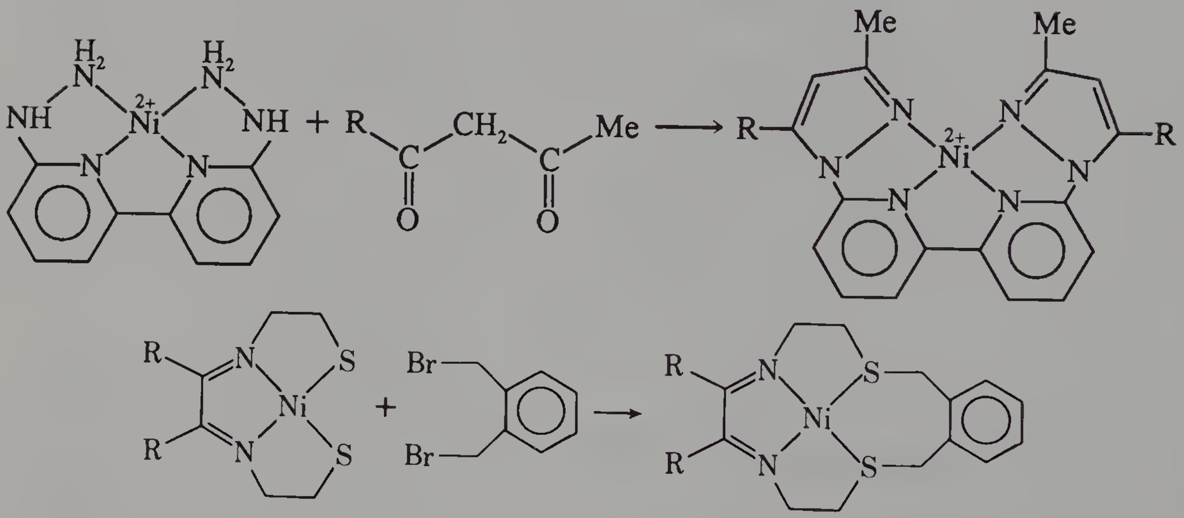
In the presence of metal ions, any small amount of the Schiff base that may be in equilibrium with benzthiazoline will be removed to give a metal complex.

2. The self-condensation of *o*-aminobenzaldehyde in the presence of $BF_3 \cdot OEt_2$ in acetic acid gives a macrocycle and when metal ion is also present,

a complex is formed, for example,

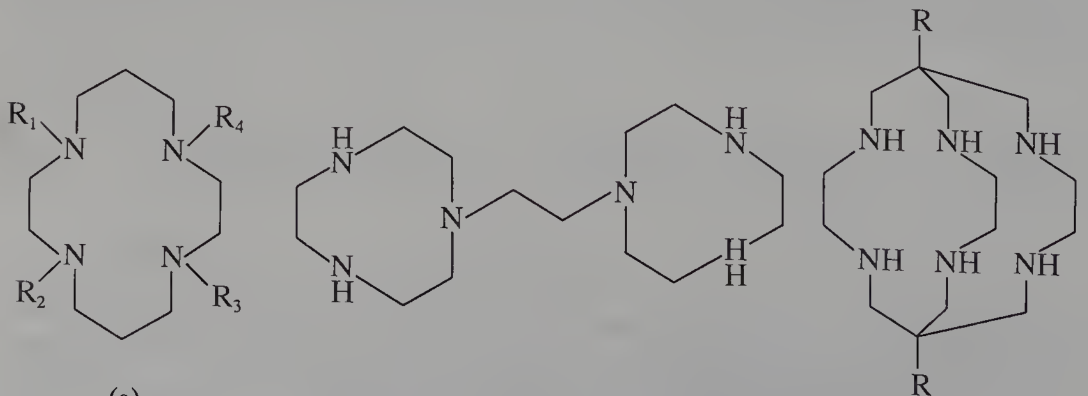


3. The reaction of chelate complexes as follows:



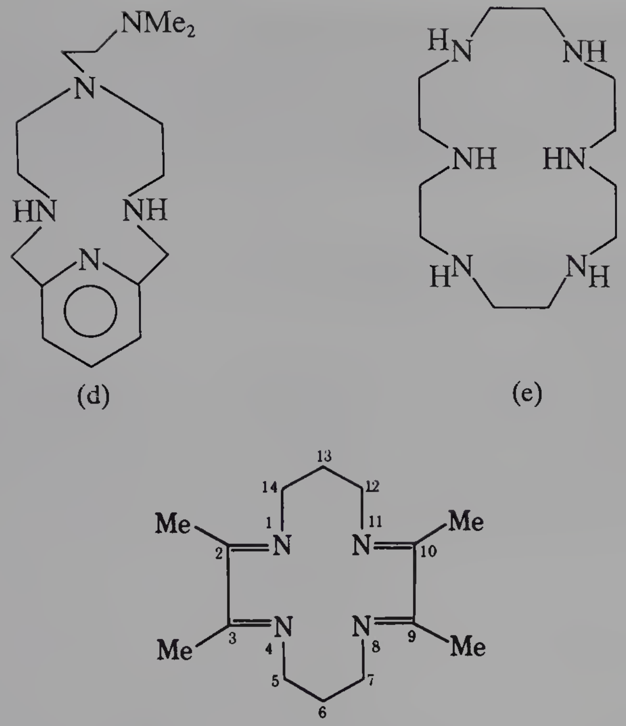
Finally, note that there must be *some* control of the reaction by the size of the metal used. If the ion is too small or too large, no macrocyclic complex may be formed.

Other examples of macrocyclic amines are of the types (10-XIVa–f)



(a) (b) (c)

(10-XIV)



(d)

(e)

Me4[14]-1,4,8,11-tetraene-N4

(f)

(10-XIV) (*Continued*)

In ligands of type 10-XIVa the redox and spectral properties of complexes can be altered by varying the R_1–R_4 groups, thus altering the N-donor behavior.[80] In N_4 macrocycles the hole sizes and best fit for metals depends on the configuration which is commonly nonplanar. Metals can also be bound out of the N_4 donor plane (cf. porphyrins to follow).[81]

Compound 10-XIVb is a hexadentate bimacrocycle, 1,4-bis(1,4,7-triaza-1-cyclononyl)ethane (dtne) that can form mononuclear as well as oligomeric complexes,[82] one example being $[\mathrm{Mn}_4^{\mathrm{IV}}(\mu\text{-O})_6(\mathrm{dtne})_6]^{4+}$. Compound (10-XIVc) is an *encapsulating ligand* sometimes called a "sepulchrate," where three of the NH groups can be replaced by S and the apical C by N.[83] Compound (10-XIVd) is a pentadentate with a *pendant arm*.[84] The ligand (10-XIVe) is an N_6 macrocycle (hexacyclen) L that when protonated (H_4L^{4+}) will form a 1:1 complex with *anions* such as $PhSO_3^-$, ClO_4^-, or IO_3^-, although the anions are believed not to occupy the cavity.[85]

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[80] E. K. Barefield *et al.*, *Inorg. Chem.*, 1984, **23**, 3092; N. W. Alcock *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 2813.

[81] R. D. Hancock *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 3198, 5947.

[82] K. Wieghardt *et al.*, *Inorg. Chem.*, 1985, **24**, 3067; 1,4,7-triazacyclononane (tacn) is also a useful ligand, K. Wieghardt *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 187.

[83] A. M. Sargeson *et al.*, *Inorg. Chem.*, 1984, **23**, 4369.

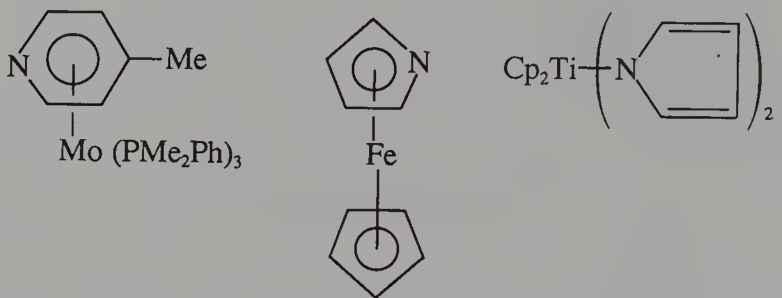
[84] P. Moore *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 545.

[85] R. I. Gelb *et al.*, *Inorg. Chem.*, 1986, **25**, 1527.

The macrocyclic *cryptates* are discussed in Section 10-14.

Aromatic Amines.[86] Pyridines generally give complexes that are more stable than those of aliphatic amines. A few cases are known where pyridines are found η^6 as arenes (Chapter 26). Thus (10-XVa) is obtained from $(R_3P)_4Mo(N_2)_2$ via a η^1 pyridine intermediate $(R_3P)_3Mo(N_2)_2$ py, which then loses N_2.[87]

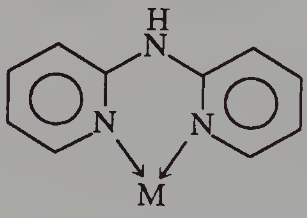
Other π-bonded *N*-heterocycles such as the pyrollyl (10-XVb) are known as well as η^1-pyrrolyls like (10-XVc).



(a) (b) (c)

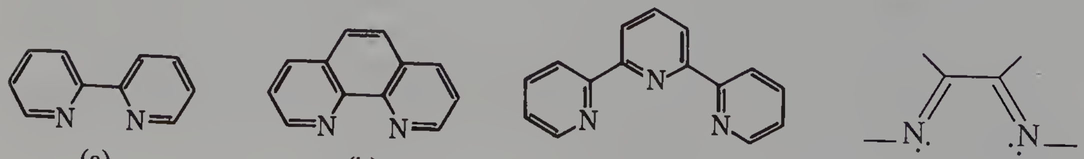
(10-XV)

Di-2-pyridylamine gives six-membered nonplanar rings (10-XVI) where the NH proton is still acidic and can be deprotonated by strong bases.[88a]



(10-XVI)

Polyimines. The aromatic amines such as 2,2′-bipyridine, 1,10-phenanthroline, and terpyridine (10-XVIIa–c) are best considered as α-*diimines*[88b] with the group (10-XVIId)



(a) (b) (c) (d)

(10-XVII)

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[86] P. Tomasik and Z. Ratajewicz, *The Chemistry of Heterocyclic Compounds, Vol. 14, Part 6. Pyridine Metal Complexes*, Wiley, New York, 1985. E. C. Constable, *Adv. Inorg. Chim. Radiochem.*, 1986, **30**, 69 (ter- and oligopyridines).

[87] R. H. Morris and J. E. Ressner, *J. Chem. Soc. Chem. Commun.*, **1983**, 909.

[88a] M. K. De Armond *et al.*, *Inorg. Chem.*, 1984, **23**, 3010.

[88b] S. Ernst and W. Kaim, *J. Am. Chem. Soc.*, 1986, **108**, 3578.

This shows their relationship to other imine systems such as those noted above, formed by oxidation of chelated amines.

A characteristic feature is that such ligands can form metal complexes in a wide range of oxidation states as in the redox series

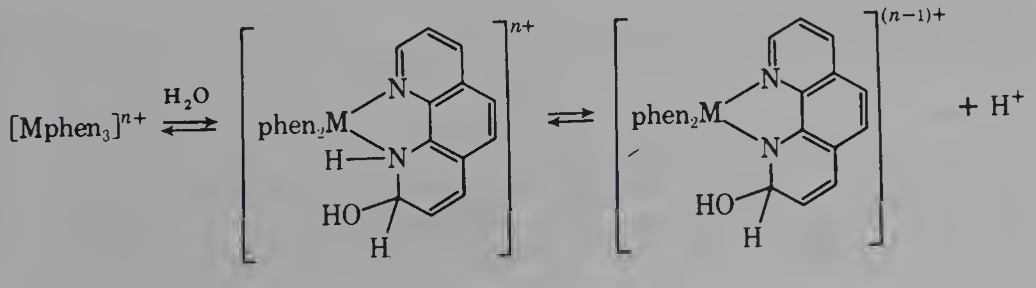
$$[\mathrm{Cr\ bipy_3}]^{3+} \rightleftharpoons [\mathrm{Cr\ bipy_3}]^{2+} \rightleftharpoons [\mathrm{Cr\ bipy_3}]^{+} \rightleftharpoons [\mathrm{Cr\ bipy_3}]^{0} \rightleftharpoons [\mathrm{Cr\ bipy_3}]^{-1}$$

For metal ions in "normal" oxidation states, the interaction of metal $d\pi$ orbitals with the ligand π^* orbitals is significant, but not exceptional. However, these ligands can stabilize metal atoms in very low formal oxidation states and in such complexes it is believed that there is extensive occupation of the ligand π^* orbitals, so that the compounds can often be best formulated as having radical anion ligands $L\dot{-}$. Most work has been carried out on bipy complexes, but it is apparent that phen and terpy afford very similar complexes.

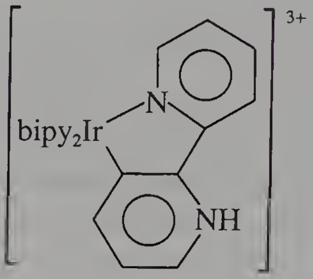
The low-valent metal complexes are invariably colored, usually intensely so. For those containing transition metals, the bands responsible are believed to be mainly $d \rightarrow \pi^*$ charge-transfer bands. In other cases $\pi \rightarrow \pi^*$ ligand bands may also be active. For the ML_2 complexes of Be, Mg, Ca, and Sr, esr spectra show the presence of a ground, or low-lying excited, state that is a spin triplet. This can be best explained by postulating the M^{2+} cation and two radical anion ligands $L\dot{-}$. Also, for the *tris*-bipy complexes $[\mathrm{Cr(bipy)_3}]^+$, $[\mathrm{V(bipy)_3}]$, and $[\mathrm{Ti(bipy)_3}]^-$, esr data indicate that there is strong σ interaction with metal 4*s* orbitals, while the unpaired electrons are extensively delocalized on the ligands.

Although 2,2′-bipyridine and 1,10-phenanthroline usually give chelate complexes, *unidentate complexes* can be formed as in $[\mathrm{PtCl(PEt_3)_2(\eta^1\text{-}phen)}]^+$; in solution they are fluxional and the platinum atom moves from one nitrogen atom to the other. This is so also for unidentate pyridazine and 1,8-naphthyridine complexes (see below).

Aqueous solutions of aromatic amine complexes such as $[\mathrm{Fe(phen)_3}]^{3+}$ or $[\mathrm{PtCl_2(py)_4}]^{2+}$ often show unexpected kinetic, equilibrium, and spectral behavior in the presence of nucleophiles like OH^-, CN^-, or OR^-. Since certain heterocyclic amines—*not* py, bipy, or phen, however—can undergo attack at C by OH^- or H_2O, and so on, it was suggested that when phen or similar ligands were *activated* by complexation, they too could be attacked at carbon:



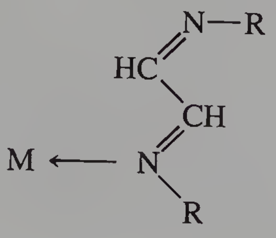
The situation is complicated and not fully resolved and it is not certain in octahedral species whether the interaction is with the ligand or with the metal.[89] What *has* been confirmed[90] is that in some Ir and Ru compounds, for example, $[Ir(bipy)_3(H_2O)]^{3+}$, there are C^3, N^1 *orthometallated rings* (10-XVIII) (see Section 27-9).



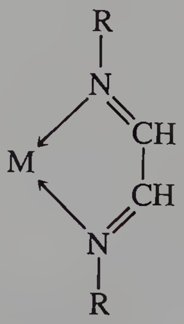
(10-XVIII)

Azadienes and Related Compounds.[91] There is an extensive chemistry of α-diimines related to bipyridine-type complexes of which the most important are the 1,4-diaza-1,3-butadienes (dab or dad) (RN=CH—CH=NR) and monoazadienes ($RN{=}CH_2{-}CH{=}CHR$), which are intermediate between diazadienes and dienes. These complexes are made by substitution of CO, C_2H_4, and so on, by dab, or by interaction with halides alone or in the presence of reducing agents.

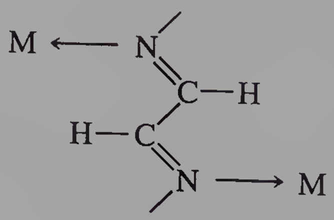
Due to the flexibility of the dab skeleton, and the strong N σ-donor and π-acceptor behavior, coupled with the wide possibilities for different substituents on N or C, there is a variety of bonding modes. The ligands can act as 2, 4, 6, or 8 electron donors; in the 8*e* donor the πC=N orbitals are used for η^2-C,N bonding.[92] We have, for example, the following modes.



$(R_3P)PdCl_2(dab)$



$Ni(dab)_2$



$[(Bu_3P)PtCl_2]_2(dab)$

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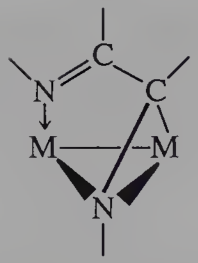
[89] E. C. Constable, *Polyhedron,* 1983, **2,** 551; N. Serpone, *Coord. Chem. Rev.,* 1983, **50,** 209; G. Nord, *Comments Inorg. Chem.,* 1985, **4,** 193; R. D. Gillard, *Comments Inorg. Chem.,* 1986, **5,** 175.

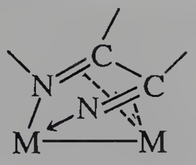
[90] R. J. Watts *et al., J. Am. Chem. Soc.,* 1984, **106,** 6647, *Inorg. Chem.,* 1983, **22,** 4060; W. R. Cherry *et al., Inorg. Chem.,* 1985, **24,** 4078.

[91] H. tom Dieck *et al., Nouv. J. Chim.,* 1985, **9,** 289; *Organometallics,* 1986, **5,** 1449. G. van Koten and K. Vrieze, *Adv. Organomet. Chem.,* 1982, **21,** 151.

[92] K. Vrieze *et al., Organometallics,* 1985, **4,** 1306.

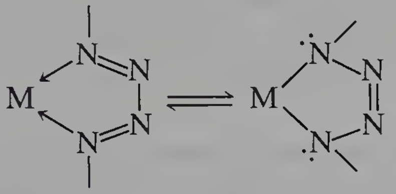


$Fe_2(CO)_6(dab)$

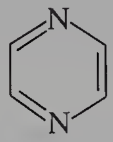


$Mn_2(CO)_6(dab)$

Tetrazabutadienes do not exist but can be generated as ligands at a metal atom, for example, by interaction of organoazides (RN_3) with $CpCo(CO)_2$ or $Ni(COD)_2$.[93] They are best regarded as neutral π-acid ligands with π delocalization that can stabilize an electron-rich system (10-XIX)



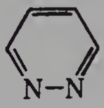
(10-XIX)



(10-XX)

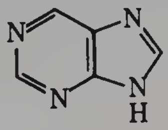
1,4-Diazenes (10-XX) can act as η^1 or bridging ligands.[94]

Other Nitrogen Heterocycles. Some of the more important are



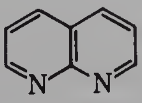
Pyridazine

Pyrimidine

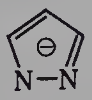


Purine

Pyrazine



1,8-Naphthyridine



Pyrazolate

Imidazolate

Pyrazolates have been much used; they normally form bridges with both N atoms bound to the metals, which may be linked by M—M bond(s). Most have only two bridges, for examples, $[Ir(COD)\mu\text{-}pz]_2$[95] (10-XXI), and so far only one case of a tetra bridged complex, $Rh_2^{II}(pz)_4$, is known.[96]

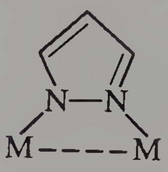
---

[93] M. J. Maroney and W. C. Trogler, *J. Am. Chem. Soc.*, 1984, **106**, 4144.

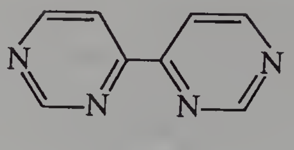
[94] W. Kaim, *Angew. Chem. Int. Ed. Engl.*, 1983, **22**, 171.

[95] S. R. Stobart *et al.*, *Organometallics*, 1985, **4**, 1107.

[96] G. Wilkinson *et al.*, *Polyhedron*, 1985, **3**, 1103.



(10-XXI)



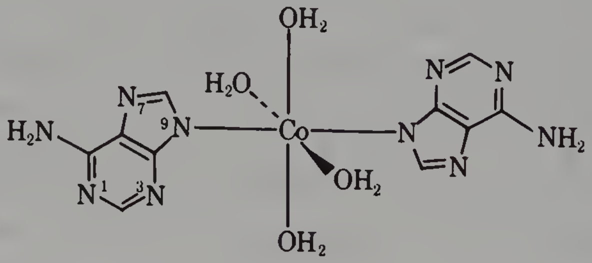
(10-XXII)

1,8-Naphthyridine complexes are mostly chelate[97] but there are some bridged complexes.

The 4,4′-bipyrimidine (10-XXII) has high π-acceptor ability and can chelate N,N′, or η^1 through the end N atoms.[98]

Nucleotides, purines, and *pyrimidines*[99] have been studied as ligands largely on account of their presence in nucleic acids. The action of certain metal complexes, notably *cis*-$PtCl_2(NH_3)_2$, as anticancer agents, is believed to arise through binding to nucleic acids. Other aspects of the binding of metals to nucleic acid include the attachment of lanthanide ions as shift reagents and fluorescent probes and the use of heavy metals to assist in X-ray structural determinations.

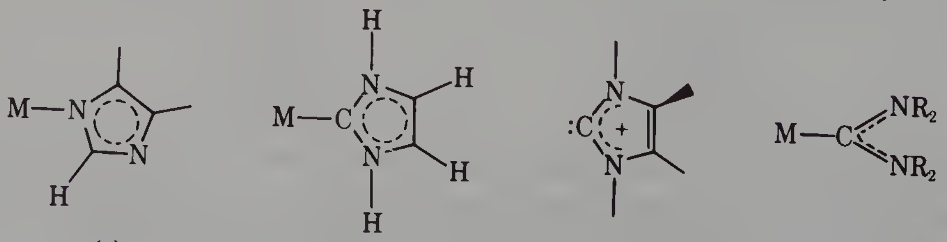
For unsubstituted *purines,* the most probable site for coordination is the imidazole nitrogen (N-9), which is protonated in the free neutral ligand. An example is the cobalt complex of adenine, $[Co(ad)_2(H_2O)_4]^+$ (10-XXIII).



(10-XXIII)

If the 9-position is blocked, the other imidazole nitrogen, N-7, is coordinated. Binding appears somewhat less likely through N-1 than through N-7; there is also binding with both N-1 and N-7.

Imidazoles have been widely studied. Although the binding is usually through



(a) (b) (c) (d)

(10-XXIV)

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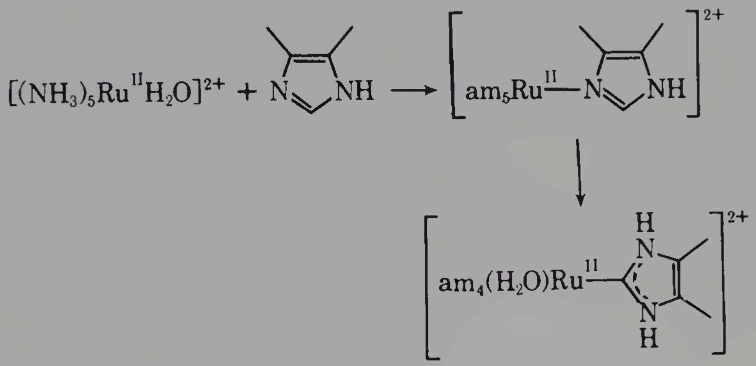
[97] W. C. Kaska, *Inorg. Chem.*, 1984, **23,** 3633.

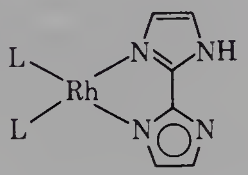
[98] S. Ernst and W. Kaim, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 430.

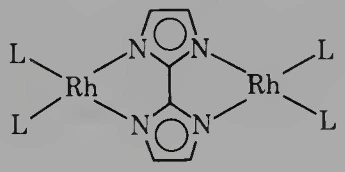
[99] R. B. Martin, *Acc. Chem. Res.*, 1985, **18,** 32; T. G. Spiro, *Nucleic Acid Metal Interactions,* Vol. 1, Wiley, New York, 1980; H. Pezzano and F. Podo, *Chem. Rev.*, 1980, **80,** 365.

the N atom (10-XXIVa), in some Ru^{II}, Ru^{III}, Fe^0, and Cr^0 complexes it is possible to have C-bonded groups[100] (10-XXIVb). The C-bonded entity can be regarded as a carbene (10-XXIVc) (see Chapter 25) or as a C-bound amidine (10-XXIVd). An example of a C-bonded species is the ruthenium(II) complex obtained as follows:



The N-bonded imidazolate mono anion forms bridges.[101] Biimidazoles can act as mono- or dianion, for example, in the complexes





10-12. Macrocyclic Ligands with Conjugated π Systems

There is often a very substantial difference between the conjugated and saturated macrocycles with regard to the rates of substitution reactions, which may be up to 10^{12} times greater for the conjugated systems. The enormous rate enhancement can be correlated with the lifetime of the leaving ligand in the inner coordination sphere of the metal complex. This profound difference presumably explains why biologically active metal systems invariably have highly unsaturated macrocyclic ligands.

Phthalocyanines.[102] These were one of the earliest classes of synthetic N_4 macrocycles to be discovered. They are obtained by interaction of phthalonitrile with metal halides in which the metal ion plays an essential role as a template. Complexes such as 10-XXV characteristically have exceptional thermal stabilities, subliming in vacuum around 500°C. They are also intensely

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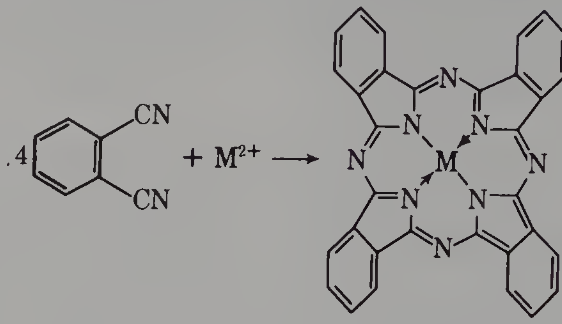
[100] M. F. Tweedle and H. Taube, *Inorg. Chem.*, 1982, **21**, 3361.

[101] S. J. Lippard *et al.*, *Inorg. Chem.*, 1981, **20**, 2933.

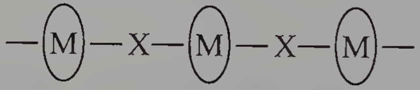
[102] F. H. Moser and A. L. Thomas, Eds., *The Phthalocyanins*, Vols. I and II, CRC Press, Boca Raton, Florida, 1983; M. Kasuga and M. Tsutsui, *Coord. Chem. Rev.*, 1980, **32**, 67.

colored and are an important class of commercial pigments. The solubility is usually very low, but sulfonated derivatives are soluble in polar solvents.



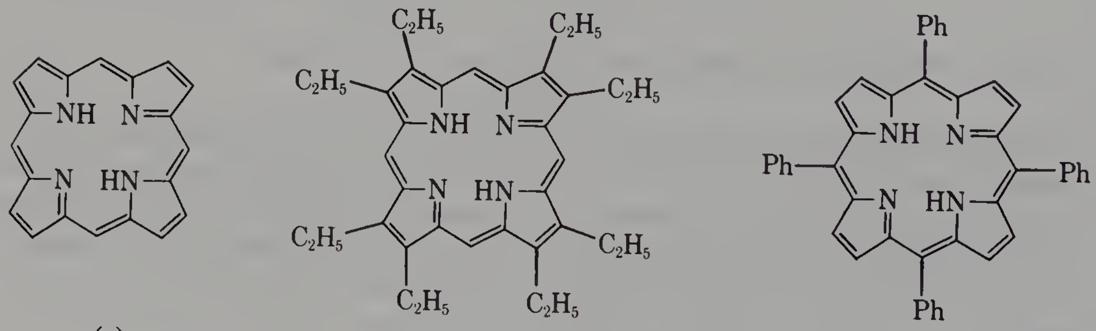
(10-XXV)

Polymers of the type (10-XXVI) can be made where metal phthalocyanines are linked in chains by CN^- or by ligands such as pyrazines.[103]



(10-XXVI)

Porphyrins.[104] These ligands are derivatives of porphine (10-XXVIIa). They are especially important because many naturally occurring metal-containing natural products (chlorophylls, heme, cytochromes, etc.) contain related macrocyclic ligands; metallaporphyrins are also found in petroleum, bitumens, and so on, where they derived from chlorophylls.



(a) (b) (c)

(10-XXVII)

Almost every metal in the Periodic Table can be coordinated to a porphyrin. The most widely used synthetic ligands apart from porphine itself are octaethylporphyrin (H_2OEP) (10-XXVIIb) and *meso*-tetraphenylporphyrin (H_2TPP) (10-XXVIIc); in the latter the phenyl rings are free to rotate.

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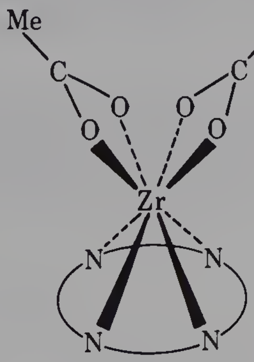
[103] M. Hanack *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 3207.

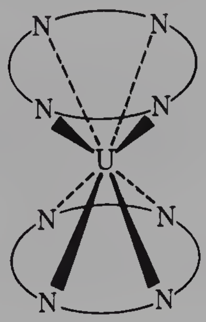
[104] D. Dolphin, Ed., *The Porphyrins*, Academic Press, New York, 1978. (an authoritative reference in seven volumes); D. K. Lavallee, *Coord. Chem. Rev.*, 1985, **61**, 55; P. J. Brothers and J. P. Collman, *Acc. Chem. Res.*, 1986, **19**, 209 (organometallic aspects).

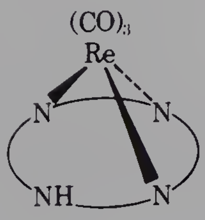
Although the most common form of coordination is that with a metal atom in the center of the plane and bound to four nitrogen atoms, nevertheless porphyrins can act as bi-, tri-, or tetra- ligands in which the metal atom lies out of the N_4 plane, as discussed later.

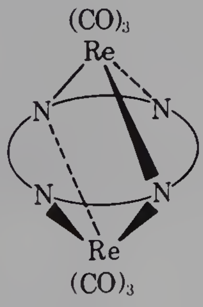
Complexes of synthetic porphyrins can be made by interaction of the ligand with a metal salt in a common solvent, usually DMF. Although H_2OEP has high solubility in organic solvents, H_2TPP is less soluble but sulfonated derivatives are soluble in both water and methanol. Complexes can also be obtained by interaction of H_2porph with metal carbonyls, acetylacetonates, alkyls, hydrides, and so on.

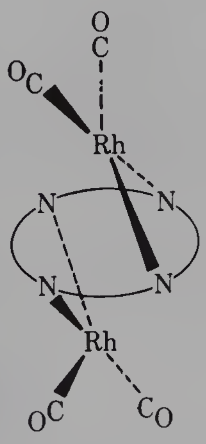
The radius of the central hole is, of course, fixed, although it can be altered to some extent by puckering of the rings, and it lies between 1.929 and 2.098 Å. This means that many metal atoms cannot fit *in* the hole and must form out-of-plane complexes. Some examples are











It will be noted that the porphyrin can act as a bi- or tridentate ligand and this situation can also be achieved by linking two of the N positions by a bridge such as N—CR_2—N.[105] Porphyrin complexes commonly can undergo reversible redox reactions.[106a] However, in certain systems, the transfer of a

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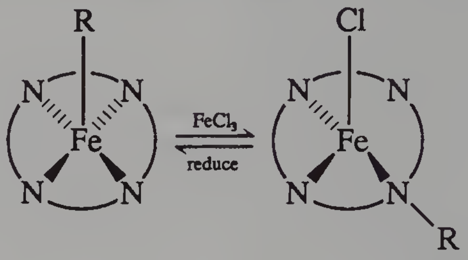
[105] R. Weiss *et al.*, *J. Am. Chem. Soc.*, 1982, **104,** 1272.

[106a] T. K. M. Kadish, *Progr. Inorg. Chem.*, 1986, **34,** 435.

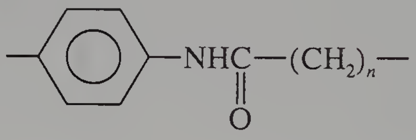
group from the metal to a N atom can occur, and this again leads to tridentate binding,[106b] namely,



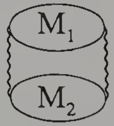
These types of slipped or skewed porphyrins, as well as those with linear bridges of the types M—O—M, M—N—M, and M—C—M have been treated theoretically.[107]

Alkylidene complexes, for example, (porph)Fe$=$CCl$_2$ may be formed in reactions of metalloporphyrin with halogenated solvents and such species may be responsible for the toxicity of halogenated insecticides and solvents like CCl$_4$.[108]

Quite complicated porphyrin systems have been constructed with the object of modeling natural systems with biological functions (Chapter 30). Some have holes, pockets, and protection for the metal from oxidation by O$_2$.[109] Some, shown diagramatically are the following, where ∿∿∿ designates a chain such as

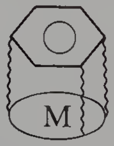


$-C_6H_4-NH\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_n-$

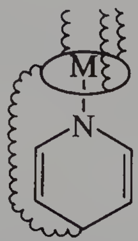


Strati or
face to face

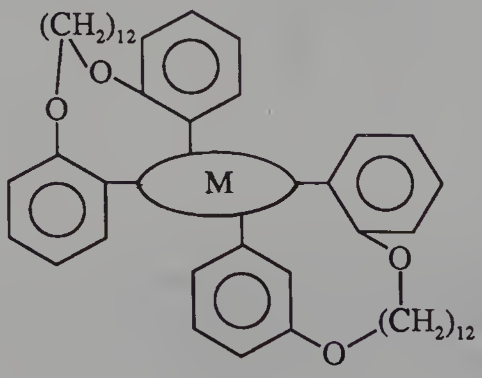
Strapped
or crowned



Pocket or capped



Picket fence



Basket handle

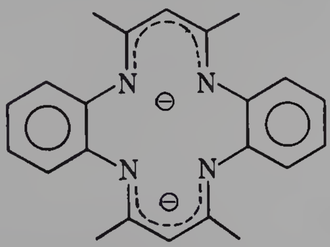
[106b] D. Mansuy *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 6159.

[107] R. Hoffmann *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 2222.

[108] D. Mansuy *et al.*, *Inorg. Chem.*, 1982, **21**, 2056.

[109] See J-M. Savéant *et al.*, *Inorg. Chem.*, 1986, **25**, 4857, 4294; K. S. Suslick *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 7281; F. A. Walker *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 2659.

Other important conjugated macrocycles are the *corrins,* which occur in vitamin B_{12} (Section 30-10). Conjugated systems such as dibenzotetraaza-[14]-annulene (10-XXVIII) have a smaller coordination radius than porphyrins and usually form out-of-plane complexes.

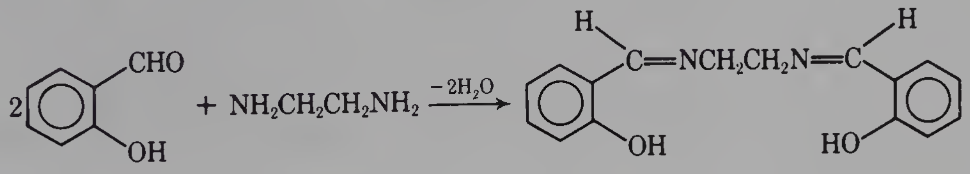


(10-XXVIII)

10-13. Schiff Base Ligands

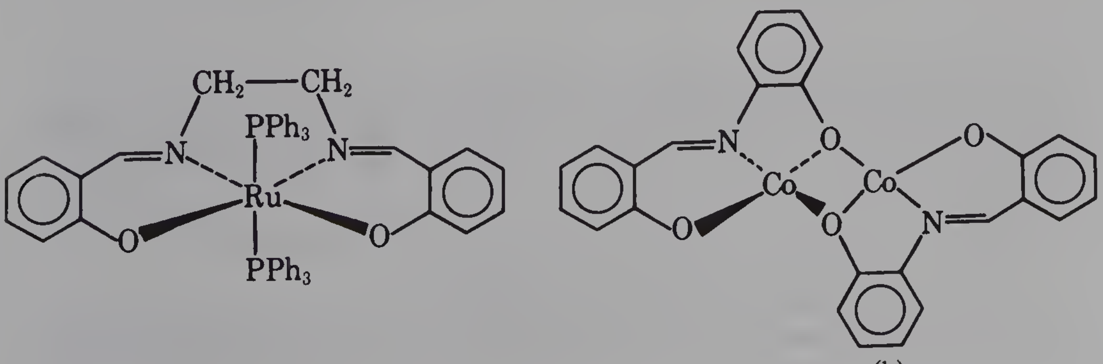
These diverse ligands usually contain both N and O donor atoms although purely N as well as N, S donors exist.

One of the best known Schiff base ligands is bis(salicylaldehyde)ethylenediimine (sal_2en):



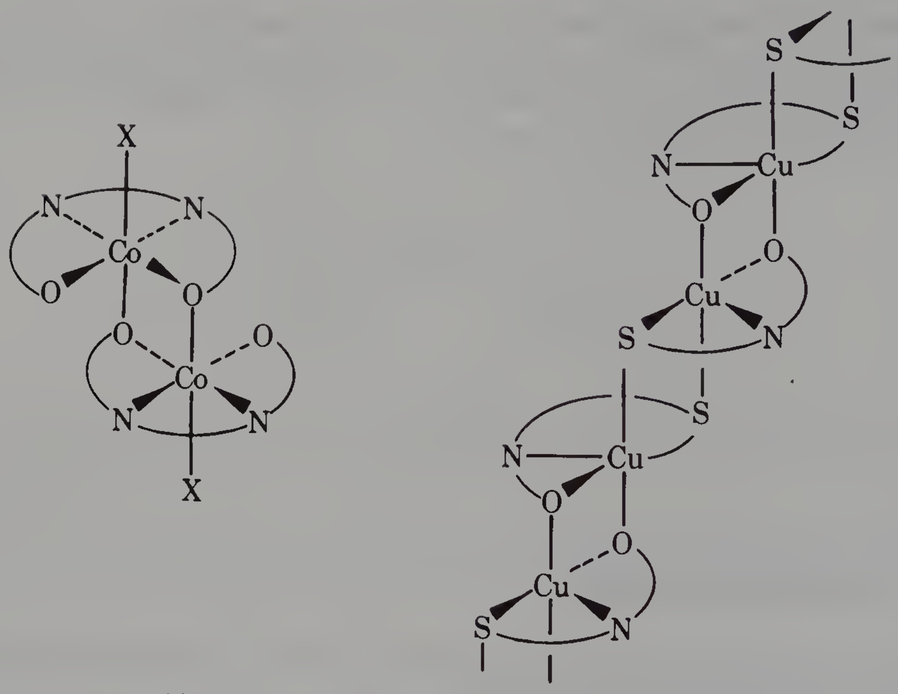
This is an acidic (two OH groups), tetradentate (2N, 2O) ligand. Other Schiff bases can be mono-, di-, or tetrafunctional and can have denticities of six or more with various donor atom combinations (e.g., for quinquedentate, N_3O_2; N_2O_3; N_2O_2P; N_2O_2S). Complexes of un-ionized or partly ionized Schiff bases are also known [e.g., $LaCl_3sal_2enH_2{\cdot}aq$].

Some representative types of complex that illustrate not only the formation of mononuclear but of binuclear and polymeric species are (10-XXIXa–d).



(a) (b)

(10-XXIX)

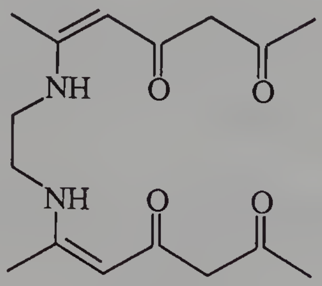


(c) (d)

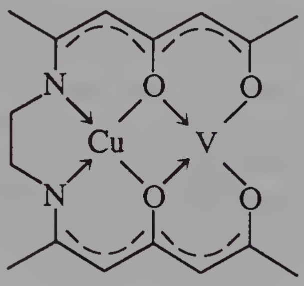
(10-XXIX) (*Continued*)

Like the porphyrin ligands noted earlier, face-to-face Schiff base ligands can be constructed to hold two metals such as Mn^{II}, Mn^{II} or Mn^{II}, Mn^{III}.[110]

A type of ligand that can hold metals side by side is called *compartmental*.[111] They can be made by condensing 1,3,5 triketones with α,ω alkanediamines. An example is (10-XXX) which can be used to bind two metals as in (10-XXXI).



(10-XXX)



(10-XXXI)

Unsymmetrical Schiff bases can also be made.[112]

A related type of ligand that is very resistant to oxidation and consequently useful for complexing metals in high oxidation states, for example Ru^{VI}, is (10-XXXII).[113]

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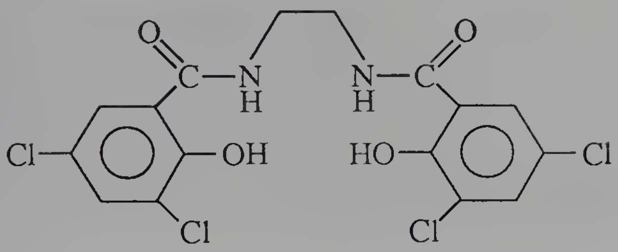
[110] H. Okawa *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 59.

[111] N. A. Bailey *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 1471.

[112] E. Sinn *et al., Inorg. Chem.*, 1985, **24,** 127.

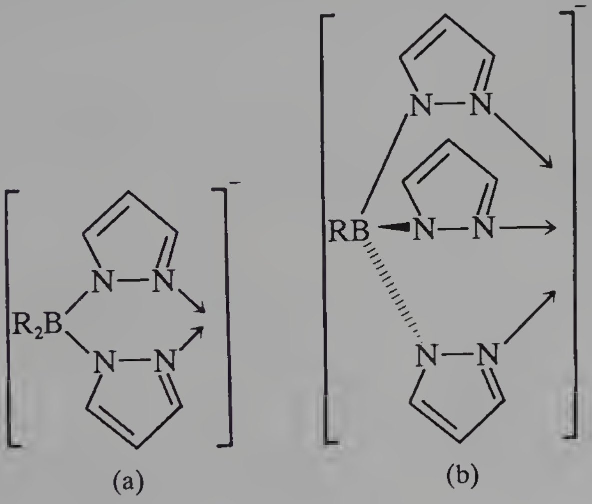
[113] T. J. Collins *et al., J. Am. Chem. Soc.*, 1986, **108,** 6593; C-M. Che and W-K. Cheng, *J. Chem. Soc. Chem. Commun.*, **1986,** 1443.



(10-XXXII)

10-14. Polypyrazolylborate Ligands[114]

The interaction of pyrazole and sodium borohydride or alkyl-substituted borohydrides leads to anionic ligands of the type (10-XXXIIIa, b), designated $R_2Bpz_2^-$ and $RBpz_3^-$, respectively. The boron atom is tetrahedral, and bonding to metal is through only one of each of the pyrrole ring N atoms as shown.



(10-XXXIII)

The dipyrazolyl anions $R_2Bpz_2^-$ have a formal analogy to the β-diketonate ions (Section 12-15) and, like them, form complexes of the type $(R_2Bpz_2)_2M$. However, because of the much greater steric requirements of the $R_2Bpz_2^-$ ligand, such compounds are always strictly monomeric. For steric reasons it appears to be difficult to make tris complexes; one example is the anion $[V(H_2Bpz_2)_3]^-$.

The $RBpz_3^-$ ligands give a number of unusual complexes.[115a] These ligands themselves are unique in being the only trigonally tridentate, uninegative ligands. They form trigonally distorted octahedral complexes, $(RBpz_3)_2M^{0,+}$, with di- and trivalent metal ions, most of which are exceptionally stable. At least to a degree, an analogy can be made between RB pz_3^- and the cyclopentadienyl anion $C_5H_5^-$; both are six-electron, uninegative

[114] S. Trofimenko, *Progr. Inorg. Chem.*, 1986, **34**, 115.

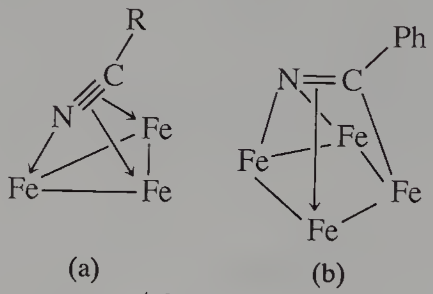
[115a] J. S. Thompson *et al.*, *Inorg. Chem.*, 1987, **26**, 1507; M. Cocivera *et al.*, *Organometallics*, 1982, **1**, 1139.

ligands. There are some mono-$RBpz_3^-$ complexes that bear considerable resemblance to half-sandwich complexes ($C_5H_5ML_x$) (see Chapter 26); thus $Mo(CO)_6$ reacts with $Na(RBpz_3)$ and NaC_5H_5 to give, respectively, $(RBpz_3)Mo(CO)_3^-$ and $(\eta\text{-}C_5H_5)Mo(CO)_3^-$; another example is $Rh(C_2H_4)_2(HBpz_3)$ that can be compared to $Rh(CO)_2(\eta\text{-}C_5H_5)$. The compound $Yb(HBpz_3)_3$ has two tri- and one bidentate ligand.[115b]

10-15. Nitriles[116]

Nitriles are good donors and bonding is usually η^1 through the N atom. However, a few cases of η^2-C, N binding have been confirmed,[117] as in $Cp_2W(\eta^2\text{-}MeCN)$ where the C—N stretching frequencies are depressed below the normal region ~2000 cm^{-1}. The M—NC angles in linear compounds vary little from 180° but one case, that of $(Me_3CCN)_3SmI_2$, has a MNC angle of 151.3.[118] Complexes with bis nitriles acting as chelates are known.[119a] Cyano complexes such as $(bipy)_2Ru(CN)_2$ can also act as ligands,[119b] although the result is merely a bridging cyanide M—CN—M′.

Bridging nitriles are known only for cluster complexes.[120] Thus in $Fe_3(CO)_9(RCN)$ the nitrile is a 6*e*, μ_3,η^2 ligand (10-XXXIVa), while in $Fe_4(CO)_{12}(PhCN)$ the nitrile is μ_4,η^2 (10-XXXIVb).


(a) (b)

(10-XXXIV)

Nitriles may reduce halides in higher oxidation states [e.g., interaction of $ReCl_5$ or WCl_6 gives $ReCl_4(MeCN)_2$ and $WCl_4(MeCN)_2$, respectively] together with chlorinated organic N compounds.

Nitrile complexes of copper are important in copper hydrometallurgy; those of ruthenium are involved in the catalytic dimerization of acrylonitrile.

[115b] M. V. Stanier and J. Takats, *Inorg. Chem.*, 1982, **21**, 4050.

[116] B. N. Storhoff and H. C. Lewis, Jr., *Coord. Chem. Rev.*, 1977, **23**, 1; K. Wade *et al., Coord. Chem. Rev.*, 1982, **44**, 149 (acrylonitrile); C. M. Jensen and W. C. Trogler, *J. Am. Chem. Soc.*, 1986, **108**, 723.

[117] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 2017.

[118] A. Sen *et al., Inorg. Chem.*, 1985, **24**, 3082.

[119a] R. J. Angelici *et al., Inorg. Chem.*, 1983, **22**, 4063.

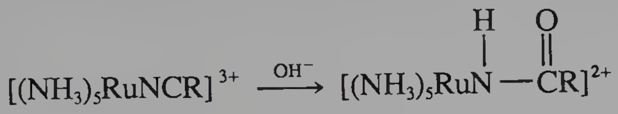
[119b] C. Bartocci *et al., Inorg. Chim. Acta.*, 1983, **76**, L119.

[120] H. D. Kaesz *et al., J. Am. Chem. Soc.*, 1979, **101**, 7260; E. Keller and D. Wolters, *Chem. Ber.*, **1984**, 1572.

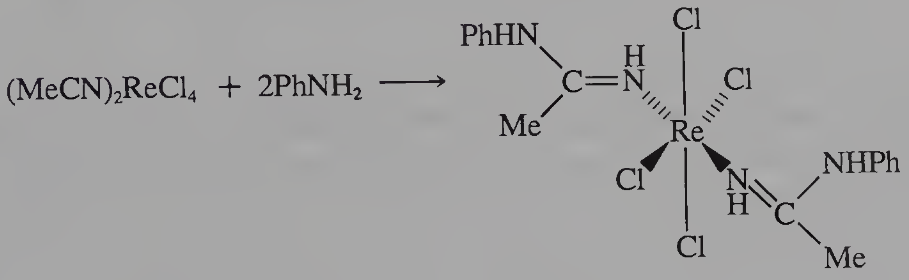
Complexes such as $[Pd(MeCN)_4]^{2+}$ or $[Mo(NO)_2(MeCN)_4]^{2+}$ catalyze polymerization of alkenes.[121]

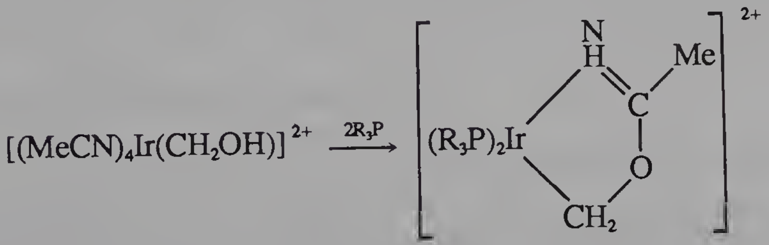
Nitrile complexes undergo a wide variety of reactions, the most important being the following.

Nucleophilic attacks at C.[122] The hydrolysis of MeCN and other nitriles is strongly catalyzed by complexing with a metal that withdraws electron density from the nitrile and the C atom is then attacked readily, for example,

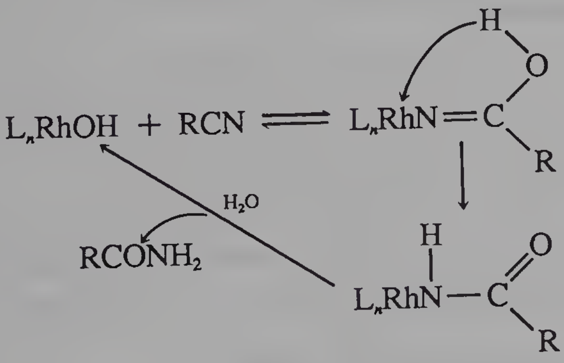


$$[(NH_3)_5RuNCR]^{3+} \xrightarrow{OH^-} [(NH_3)_5Ru\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}R]^{2+}$$





The catalytic *hydration* of nitriles[123] to amides probably proceeds by cycles involving hydridometal intermediates, and oxidative addition of H_2O (Chapter 27), for example,



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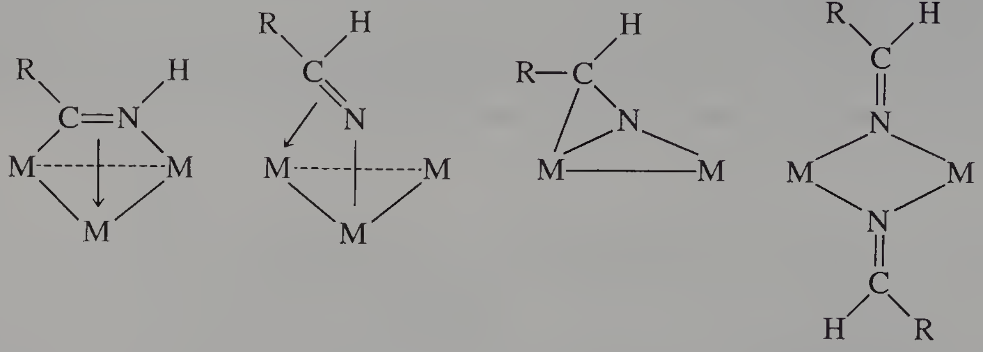
[121] A. Sen *et al., J. Am. Chem. Soc.,* 1986, **108,** 4096.

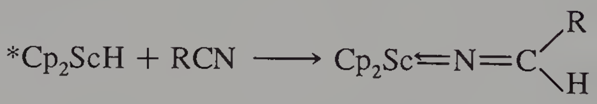
[122] G. Natile *et al., J. Am. Chem. Soc.,* 1986, **108,** 1180; B. Anderes and D. K. Lavallee, *Inorg. Chem.,* 1983, **22,** 3724; D. L. Thorn and J. C. Calabrese, *J. Organomet. Chem.,* 1984, **272,** 283; P. Paul and K. Nag, *Inorg. Chem.,* 1987, **26,** 1586.

[123] C. M. Jensen and W. C. Trogler, *J. Am. Chem. Soc.,* 1986, **108,** 723; M. Lovey *et al., Inorg. Chim. Acta,* 1986, **111,** 107.

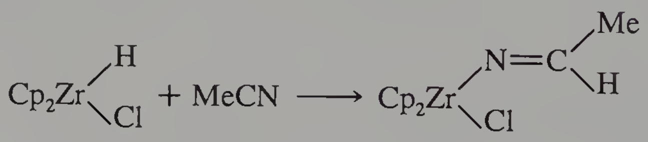
Reduction. Nitriles can be reduced by hydrido complexes of various sorts and intermediate complexes of the following types have been isolated.[124a]



Hydride transfer giving an alkylideneamido group occurs in the reactions[124b,125]



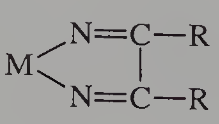
$$*Cp_2ScH + RCN \longrightarrow Cp_2Sc \Leftarrow N{=}C(R)(H)$$

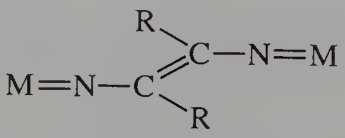


$$Cp_2Zr(H)(Cl) + MeCN \longrightarrow Cp_2Zr(N{=}C(Me)(H))(Cl)$$

Catalytic reductions, for example, of CH_3CN to $CH_3CH_2NH_2$ can also be achieved by use of phosphine complexes[126] such as $[diphos_2Ru(NCMe)_2]^{2+}$ or $RhH(PPr)_3$ and by $*Cp_2ScR$[124a] under hydrogen pressure.

Coupling. Reductive coupling of nitriles can occur when nitrile complexes, or metal halides in the presence of nitriles are reduced. These reactions give species with the groupings[127]





or, for CF_3CN, which is more reactive, complexes in which hydrogen has also been abstracted from solvents[128]:

[124a] J. E. Bercaw *et al., Organometallics,* 1986, **5,** 443.

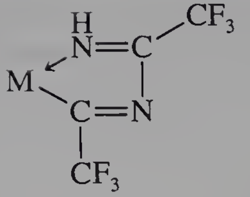
[124b] J. J. Evans *et al., J. Am. Chem. Soc.,* 1984, **106,** 1291; P. M. Lausorot, *J. Organometal. Chem.,* 1985, **291,** 221. See also M. R. Du Bois *et al., J. Am. Chem. Soc.,* 1987, **109,** 283 for reduction with C—N cleavage.

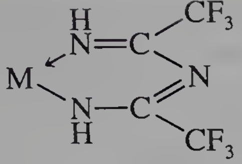
[125] G. Erker *et al., J. Organometal. Chem.,* 1985, **280,** 343.

[126] For references see G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1987,** 2947.

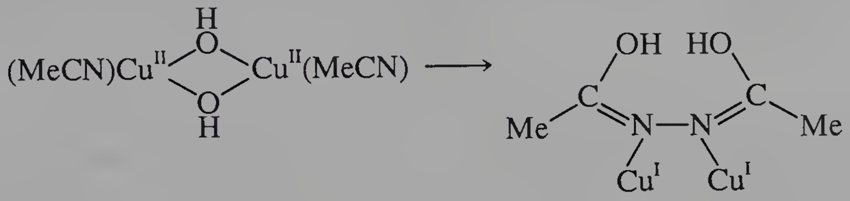
[127] A. P. Sattelberger *et al., J. Am. Chem. Soc.,* 1980, **102,** 7111.

[128] P. Woodward *et al., J. Chem. Soc. Dalton Trans.,* **1981,** 1169.





Oxidative coupling occurs in the reaction of a Cu_2^I macrocyclic complex with MeCN, O_2, and water via a Cu^{II} hydroxy bridged species, which under-



goes intramolecular nucleophilic attack and coupling.[129]

It may be noted finally that acetonitrile is weakly acidic, $pK_A \approx 25$[130] and, like CH_3NO_2, can undergo oxidative–addition reactions (Chapter 27) to give the H—M—CH_2CN species,[131] while similar C—H cleavage can occur on surfaces.[132] In addition, C—N bond cleavage can occur as in the reaction

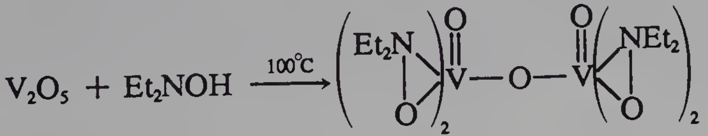
$$W_2(Ot\text{-}Bu)_6 + RCN \longrightarrow (t\text{-}BuO)_3W{\equiv}N + (t\text{-}BuO)_3W{\equiv}CR$$

10-16. Hydroxylamine and its Derivatives

Hydroxylamine (H_2NOH) or substituted hydroxylamines, can give neutral unidentate complexes with Co^{III}, Pt^{II}, or Ni^{II}, but the deprotonated species, *hydroxylamido(1 −)*(H_2NO^-) *hydroxylamido(2 −)*(HNO), and their alkyl or aryl substituted analogues are more important. Fully dehydrogenated H_2NOH is, of course NO, and indeed NO complexes can often be obtained by reactions of NH_2OH in basic solution in addition to deprotonated species, for example,

$$MoO_4^{2-} + SCN^- + NH_2OH \longrightarrow [MoNO(\eta^2\text{-}H_2NO)(NCS)_4]^{2-}$$

This type of reaction of oxoanions is the usual way to make hydroxylamido(2 −) complexes,[133] for example,



$$MoO_4^{2-} + 2MeH_2NOH^+ \longrightarrow cis\text{-}MoO_2(\eta^2\text{-}MeHNO)_2 + 2H_2O$$

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[129] M. G. B. Drew *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985,** 262.

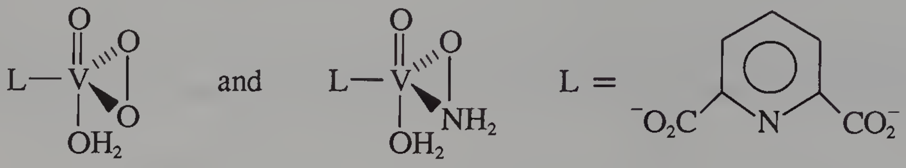
[130] J. E. Ellis *et al.*, *J. Am. Chem. Soc.*, 1983, **105,** 2301.

[131] S. D. Ittel *et al.*, *J. Am. Chem. Soc.*, 1978, **100,** 7577; E. L. Muetterties *et al.*, *J. Am. Chem. Soc.*, 1981, **103,** 767.

[132] D. M-T. Chan *et al.*, *Inorg. Chem.*, 1986, **25,** 4170.

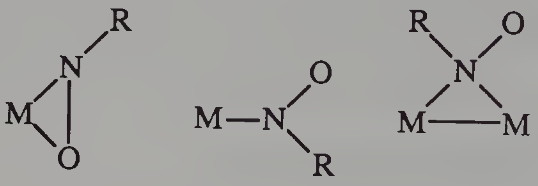
[133] K. Wieghardt *et al.*, *Inorg. Chem.*, 1983, **22,** 1221; C. D. Garner *et al.*, *J. Chem. Soc. Dalton Trans.*, **1983,** 2495; A. Müller *et al.*, *Z. Anorg. Allg. Chem.*, 1983, **503,** 22.

The R_2NO^- complexes are generally side-on, η^2. Since H_2NOH is isoelectronic with H_2O_2 there is some formal similarity between H_2NO^- and HOO^- and there are structural similarities as in the pentagonal bipyramidal complexes (10-XXXV)[134]



(10-XXXV)

Complexes with the RNO ligand can be derived either by deprotonation of the substituted hydroxylamine, that is, hydroxylamido (2−) or directly from nitrosoalkanes $(RNO)_2$ or nitroso arenes. They are sometimes called *nitrosoalkane or arene complexes* or, more systematically *metallaoxaziridines* when they are η^2-bound as is common.[135] Other bonding forms[136] are η^1 and μ.



Examples of synthetic methods[137] are

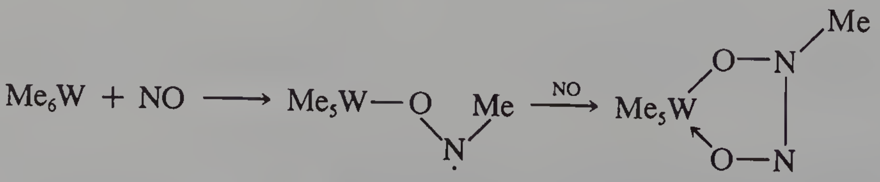
$$dtc_2MoO_2 + RHNOH \longrightarrow dtc_2(O)Mo(\eta^2\text{-}ONR)$$

$$dtc_2Mo(CO)_2 + PhNO_2 \longrightarrow dtc_2(O)Mo(\eta^2\text{-}ONPh)$$

$$(Ph_3P)_2Pt(C_2H_4) + PhNO \longrightarrow (Ph_3P)_2Pt(\eta^2\text{-}ONPh)$$

$$(Ph_3P)_2Cl_3ReNPh + O_2 \longrightarrow Cl_3Re(\eta^1\text{-}ONPh)(OPPh_3)_2$$

The RNO compounds are important intermediates in the insertion of NO into metal alkyls (Chapter 27) but these can react further depending on whether the initial product is paramagnetic, in which case an *N*-methyl-*N*-nitroso-hydroxylaminato chelate is formed by N—N bond formation,



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[134] K. Wieghardt *et al., Inorg. Chem.*, 1981, **20,** 3436.

[135] See, for example, C. Cenini *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 355.

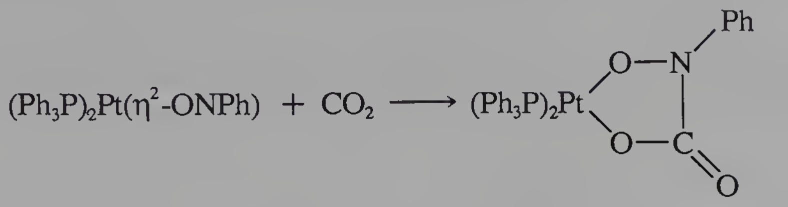
[136] R. G. Bergman *et al., J. Am. Chem. Soc.*, 1981, **103,** 3613; D. Mansuy *et al., J. Am. Chem. Soc.*, 1983, **105,** 455.

[137] J. McCleverty *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 401.

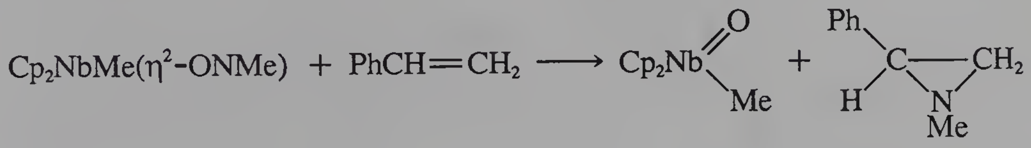
or is diamagnetic, in which case MeN is transferred to NMe and azomethane eliminated:

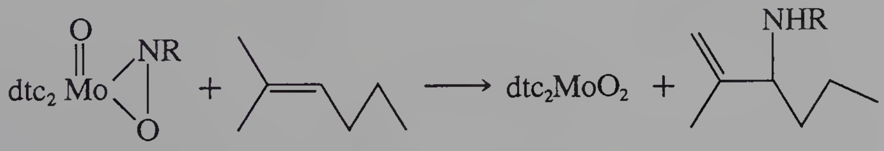
$$\mathrm{2ReOMe_4 + 2NO \longrightarrow 2ReO(ONMe)Me_3 \longrightarrow 2Me_3ReO_2 + MeN{=}NMe}$$

RNO compounds can undergo insertions such as



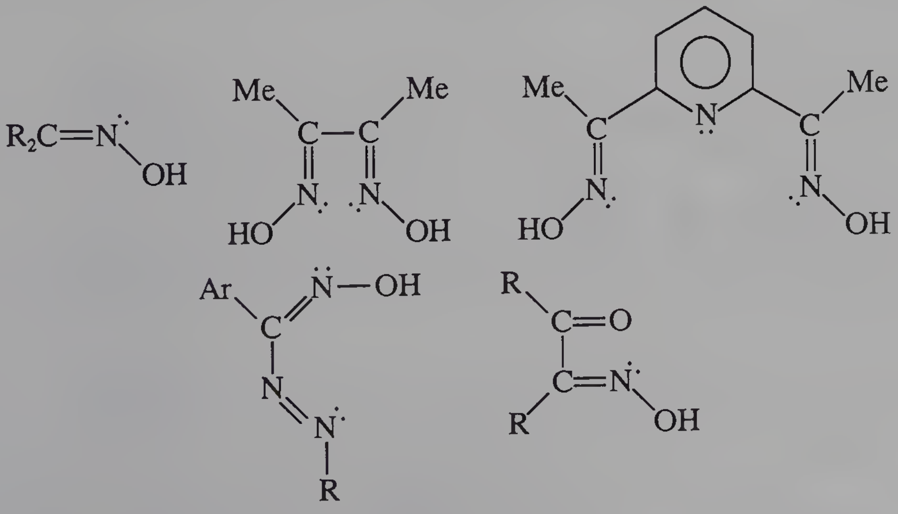
and facile N—O bond cleavages, whereby NR groups can be transferred to alkenes or other organic molecules, for example,





10-17. Oximes and C-Nitroso Compounds[138]

Oximes made by condensation of hydroxylamines with aldehydes or ketones can be of the types



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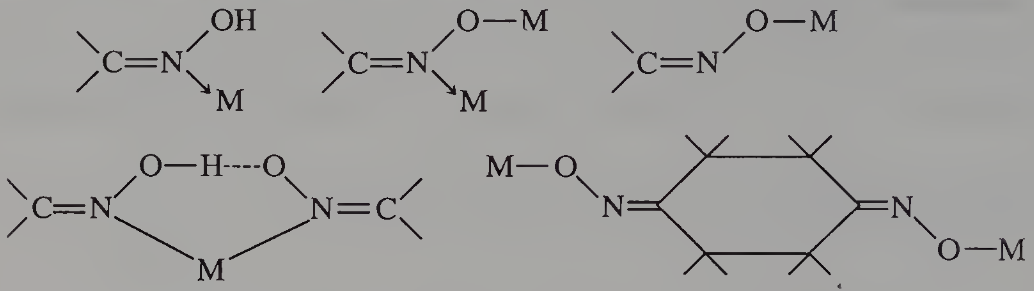
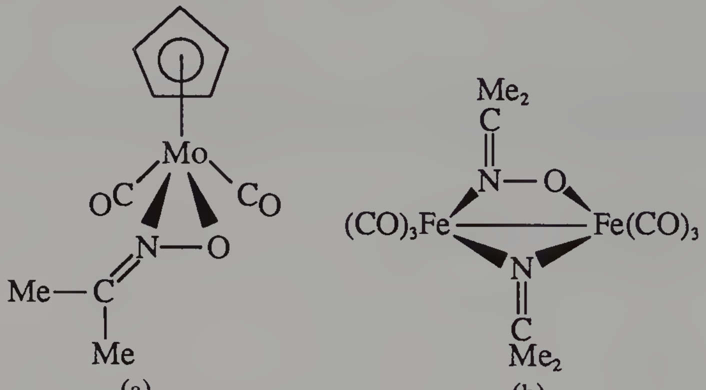
[138] K. Osseo-Assare *et al.*, *Coord. Chem. Rev.*, 1984, **59**, 141 (hydroxy oximes).

They can bind in several ways,[139] namely,



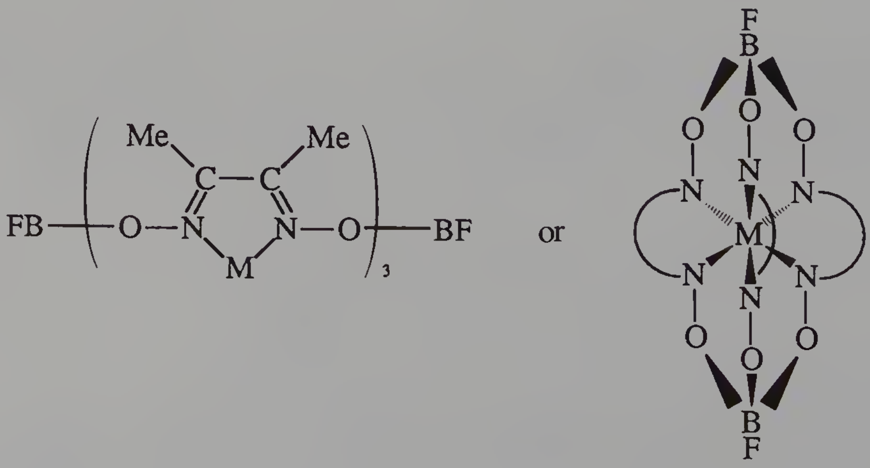
Monooximes of the type $R_2C{=}NOH$ can be bound also in different ways (10-XXXVIa and b); in type (a) the ligand can be regarded as a 3*e* donor


(a) (b)

(10-XXXVI)

The oxime function is usually a poor donor ligand unless it is part of a chelating system. Complexes of *cis*-dioximes such as the well-known red nickel complex (Section 18-G) are examples. Apart from N_4 binding, important features are the strong O—H---O hydrogen bonds and the stacking of such planar units in columns in the crystal.

Oxime complexes have formed the basis for the construction of *clathro-*



(10-XXXVII)

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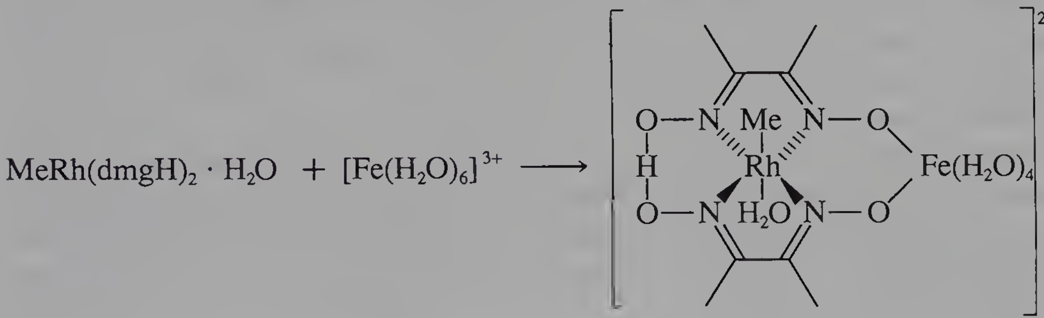
[139] See, for example, A. Chakravorty *et al., Inorg. Chem.*, 1985, **24,** 1250.

chelate or *encapsulating* ligands[140] in which three O atoms of oxime ligands are capped by a group such as BF (10-XXXVII).

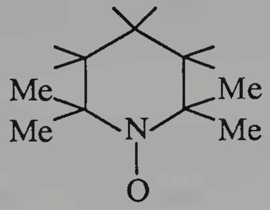
Such compounds can be obtained by interaction of dimethylglyoxime with a metal salt in the presence of BF_3 or $B(OH)_3$; an example is $Fe(dmg)_3(BOH)_2$. Some of these clathrochelates, for example, $FB(O\dot{N}CHC_5H_3\dot{N})_3P^-$, impose trigonal prismatic geometry. Instead of BF capping, clathrochelates with a *metal complex cap* [e.g., diethylenetriaminechromium(III)] can also be made.

The O—H---O hydrogen bridge of dimethylglyoxime complexes can also be replaced[141] by O—BF_2—O or O—M—O as in the reaction



Oxime complexes are used commercially for extraction of metals such as copper by complexing and solvent extraction.

Other C—NO Complexes. Apart from those of RNO discussed previously, others include those of nitroxide radicals such as *t*-Bu_2NO and 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo) (10-XXXVIII) used as probes in biological systems. The bonding[142] can be η^1—O or η^2—N,O where the ligand is bound as R_2NO^-.



(10-XXXVIII)

10-18. Ligands Derived by Deprotonation of Ammonia and Amines; Amido, Imido, and Nitrido Complexes

Amido and Dialkylamido Ligands.[143] Ammonia can be deprotonated by alkali metals to give the anions NH_2^-, NH^{2-}, and N^{3-}, and all of these species can act as ligands.

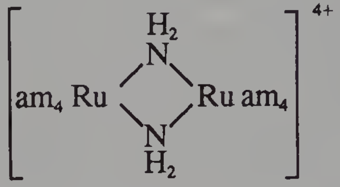
[140] See, for example, J. J. Grzybowski *et al., Inorg. Chem.*, 1985, **24**, 3381; A. M. Sargeson *et al., Inorg. Chem.*, 1986, **25**, 384; D. N. Hendrickson *et al., J. Am. Chem. Soc.*, 1985, **107**, 4202.

[141] J. H. Espenson and R. C. McHatton, *Inorg. Chem.*, 1981, **20**, 3090.

[142] D. Gatteschi *et al., Inorg. Chem.*, 1984, **23**, 798; *J. Am. Chem. Soc.*, 1984, **106**, 5813; D. N. Hendrickson *et al., J. Am. Chem. Soc.*, 1984, **106**, 5273.

[143] M. F. Lappert, A. R. Sanger, R. C. Shrivaster, and P. P. Power, *Metal and Metalloidal Amides*, Horwood-Wiley, New York, 1979.

There are numerous examples of the *amido* ligand NH_2 acting as a bridge, as in the ruthenium complex



However, dialkyl or aryl amido ligands are more important. The complexes are usually made from the halides by interaction with $LiNR_2$. They are closely related to alkoxides (Section 12-11) and alkyls (Chapter 25) and often have similar stoichiometries, volatilities, and structures, for example, $Cr(NEt_2)_4$, $Cr(OtBu)_4$, and $Cr(CH_2SiMe_3)_4$.

The use of bulky alkyl or aryl groups, as in the case of alkyls and alkoxides, prevents dimerization or polymerization and gives complexes with unusually low coordination numbers, for example, $Fe[N(SiMe_3)_2]_2$; similar PR_2 compounds (Section 11-18), for example, $Mo(P(cy)_2)_4$ are known, but NR_2 is a stronger π donor than PR_2.[144a]

For a series of $M[N(SiMe_3)_2]_n$, compounds, photoelectron spectra indicate that the ionization energies for the N lone pair and M—N π bonds increase with the positive charge on the metal and decrease with the size.[144b] This indicates that the lone pair interacts with silicon $\dot{N}\overset{\rightarrow}{-}Si$ rather than with the transition metal.

However, $M\overset{\leftarrow}{-}\ddot{N}$ π bonding has been invoked to explain the planarity of some $M(NR_2)_3$ species, for example of V and Fe, although others of Nd, Eu, Yb, and Sc are pyramidal. Core binding energies of homoleptic NMe_2 species of Ti^{IV}, Zr^{IV}, Ta^{V}, and W^{VI} do, however, indicate that $Np\pi \rightarrow Md\pi$ bonding is significant.[145]

In the $M(NR_2)_3$ compounds, rotation of NR_2 about the M—N axis may be restricted and lead to inequivalence of the R groups in certain cases, as shown by nmr spectra.

Alkylamido (MNHR) compounds are less common than the dialkylamido ones and also generally less stable towards intermolecular elimination

$$2L_nMNHR \longrightarrow (L_nM)_2(\mu\text{-}NR) + RNH_2$$

As for dialkylamides, use of bulky groups such as 2,4,6-tri-*t*-butylphenyl allows isolation, for example, of $Sn(NHR)_2$ compounds.[146] Examples of transition metal alkylamides[147] are $Re(NHPh)(N_2)(PMe_3)_4$ and $(BuN)_2W(NHt\text{-}Bu)_2$. A

[144a] M. H. Chisholm *et al., J. Am. Chem. Soc.*, 1987, **109**, 905.

[144b] J. C. Green *et al., J. Chem. Soc. Dalton Trans.*, **1982,** 887.

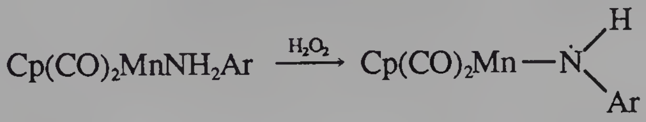
[145] W. L. Jolly *et al., Inorg. Chem.*, 1985, **24**, 4741.

[146] B. Cetinkaya *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 148.

[147] H. E. Bryndza *et al., Organometallics*, 1985, **3**, 939; G. Wilkinson *et al., Polyhedron*, 1982, **1**, 37; G. L. Hillhouse and J. E. Bercaw, *Organometallics*, 1982, **1**, 1025; C. J. Jones *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 1525.

unique compound $[TaCl(\mu\text{-}Cl)(N\textit{t}\text{-}Bu)(NH\textit{t}\text{-}Bu)(NH_2\textit{t}\text{-}Bu)]_2$ has three different types of ligand.[148]

Another complex with an NHR group actually has a bound iminyl radical[149]:



$$Cp(CO)_2MnNH_2Ar \xrightarrow{H_2O_2} Cp(CO)_2Mn{-}\dot{N}(H)(Ar)$$

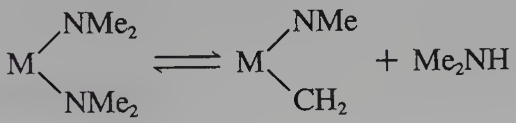
Dialkylamides can undergo insertion reactions with CO_2 or CS_2 to give carbamates or dithiocarbamates:

$$Me_3Ta(NMe_2)_2 + 2CS_2 \longrightarrow Me_3Ta(S_2CNMe_2)_2$$

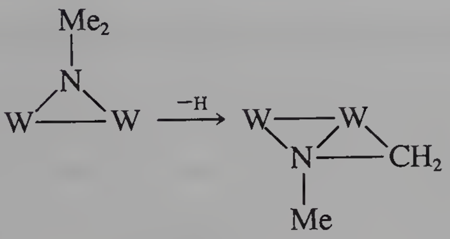
They can also undergo β or γ hydride transfer elimination reactions[150] (cf., Section 25-5), for example,

$$R_2Zr[N(SiMe_3)_2]_2 \xrightarrow{\Delta} 2RH + \{Zr\overline{CHSiMe_2N}SiMe_3[N(SiMe_3)_2]\}_2$$

cyclometallation,[151a] and bridge formation to give the μ, η^2, η^1 ligand[151b]



$$M(NMe_2)_2 \rightleftharpoons M(NMe)(CH_2) + Me_2NH$$



Imido, Alkylimido, or Nitrene Complexes.[152] Deprotonation of NH_2^- gives NH^{2-}, which is isoelectronic with O^{2-}; compounds with M—NH groups are, however, much less common than those with NR groups. The latter can be referred to as *nitrene* (RN:) species comparable to carbene (R_2C:) species. Complexes with NH or NR groups are believed to be intermediates in catalytic reactions such as the synthesis of acrylonitrile from propene, NH_3 and O_2 (Chapter 28), and reduction of N_2.

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[148] A. J. Nielsen *et al., J. Chem. Soc. Chem. Commun.*, **1984**, 205.

[149] D. Sellman *et al., Angew. Chem. Int. Ed. Engl.*, 1982, **21,** 691.

[150] R. A. Andersen *et al., Organometallics*, 1982, **2,** 16.

[151a] W. A. Nugent and R. M. Zubyk, *Inorg. Chem.*, 1986, **25,** 4604.

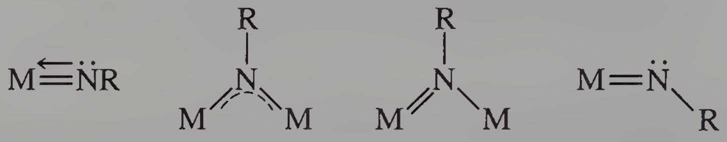
[151b] M. H. Chisholm *et al., J. Am. Chem. Soc.*, 1986, **108,** 989.

[152] W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31,** 123; K. Dehnicke and J. Strähle, *Angew. Chem. Int. Ed. Engl.*, 1981, **20,** 413; E. A. Maatte *et al., Inorg. Chem.*, 1986, **25,** 822; R. Hoffmann *et al., J. Am. Chem. Soc.*, 1986, **108,** 5382.

The M—NH complexes can undergo the H-transfer reactions[153]

$$L_nMNH_2 \xleftarrow{+H} L_nM{=}NH \xrightarrow{-H} L_nM{\equiv}N$$

The ligands (H or R) can be bound as follows[154a]



as well as μ_3 or μ_4 in cluster compounds,[154b] for example, $Ru_4(\mu_4\text{-}NH)(CO)_{11}$.

The *linear* complexes may have slightly bent groups and the M—N distances in transition metal compounds suggest that NR is a 4*e* donor with N → M π donation. The $M\overset{\leftarrow}{\equiv}NR$ stretch is in the region 850 to 1150 cm^{-1}. In the bent species, NR is a 2*e* donor, so that the linear-bent system is similar to that for linear and bent M—NO groups. An example is $dtc_2Mo(NPh)_2$ where there is one severely bent Mo—NPh since with two linear groups the Mo atom would have 20*e*.

The compounds can be made in various ways, one, commonly involving oxidation of amines,[155] for example,

$$Me_3SiOReO_3 + 3t\text{-}Bu(SiMe_3)NH \longrightarrow Me_3SiORe(Nt\text{-}Bu)_3 + 3Me_3SiOH$$

$$CrO_3 + t\text{-}Bu(Me_3Si)NH \longrightarrow (Me_3SiO)_2Cr(Nt\text{-}Bu)_2$$

Others include action of organic azides or isocyanates,[156] for example,

$$^*Cp_2V + PhN_3 \longrightarrow {}^*Cp_2VNPh + N_2$$

$$OWCl_4 + RNCO \longrightarrow RNWCl_4 + CO_2$$

and exchanges with alkylidene complexes[157]

$$Me_3CC(H){=}TaCl_3(THF)_2 \xrightarrow{RN{=}CHPh} RNTaCl_3(THF)_2 + Me_3CCH{=}CHPh$$

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[153] R. A. Henderson, *J. Chem. Soc. Dalton Trans.*, **1983,** 51; R. A. D. Wentworth, *Inorg. Chem.*, 1980, **19,** 2006.

[154a] M. L. Blohm and W. L. Gladfelter, *Organometallics,* 1986, **5,** 1049; G. L. Geoffroy *et al., J. Am. Chem. Soc.*, 1985, **107,** 729; M. H. Chisholm *et al., Inorg. Chem.*, 1985, **24,** 796; W. Clegg *et al., Acta Cryst.*, 1984, **C40,** 927; S. Bhaduri *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 1765; G. V. Goedken and B. L. Haymore, *Inorg. Chem.*, 1983, **22,** 157.

[154b] See, for example, L. F. Dahl *et al., J. Am. Chem. Soc.*, 1986, 5924–5942; J. A. Smieja and W. L. Gladfelter, *Inorg. Chem.*, 1986, **25,** 2667; G. L. Geoffroy *et al., J. Am. Chem. Soc.*, 1987, **109,** 3936.

[155] W. A. Nugent, *Inorg. Chem.*, 1983, **22,** 965.

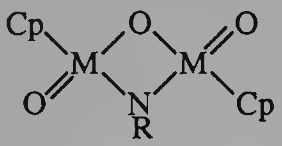
[156] A. L. Rheingold *et al., J. Am. Chem. Soc.*, 1985, **107,** 7945; D. C. Bradley *et al., J. Chem. Soc. Dalton Trans.*, **1983,** 2651; L. G. Hubert-Pfalzgraf and G. Aharonian, *Inorg. Chim. Acta,* 1985, **100,** L21; J. H. Osborne and W. C. Trogler, *Inorg. Chem.*, 1985, **24,** 3098. M. L. H. Green and K. J. Moynihan, *Polyhedron,* 1986, **5,** 921; A. J. Nielson *et al., Polyhedron,* 1987, **6,** 1657.

[157] S. M. Rocklage and R. R. Schrock, *J. Am. Chem. Soc.*, 1982, **104,** 3077.

and deoxygenation of PhNO or $PhNO_2$,[158] for example,

$$W_2(OCMe_3)_6 + PhNO \longrightarrow (RO)_2(PhN)W(\mu\text{-}O)(\mu\text{-}OR)W(NPh)(OR)_2$$

$[Cp_2(CO)_2M]_2 + ArNO_2 \longrightarrow$

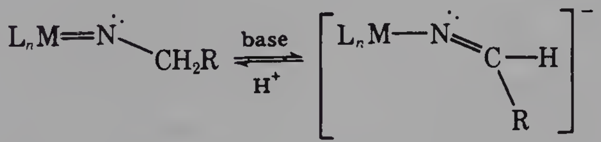


and condensations, especially for rhenium species.

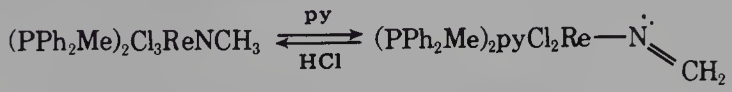
$$OReCl_3(PPh_3)_2 + ArNH_2 \longrightarrow ArNReCl_3(PPh_3)_2 + H_2O$$

Just as there are chemical differences between linear and bent M—NO groups, there are similar differences in reactivity of linear and bent MNR groups, the former being electrophilic due to the increased M—N triple bonding and the latter nucleophilic due to the lone pair on N.

Methyleneamido(amino) complexes can arise by base attack on bent MNR species, that is,

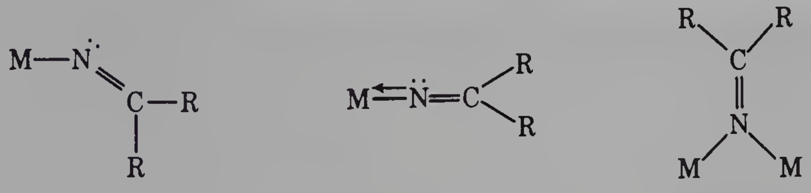


for example,



$$(PPh_2Me)_2Cl_3ReNCH_3 \underset{HCl}{\overset{py}{\rightleftharpoons}} (PPh_2Me)_2pyCl_2Re—\ddot{N}{=}CH_2$$

The ligand so formed (—N=CH_2) methyleneamido, or the substituted groups (—N=CR_2) can be considered to resemble NO, since they can act not only as one-electron ligands but as three-electron ligands giving linear π-bonded groups. The bonding modes are thus



Bent Linear Bridged

There are a number of compounds with symmetrical bridges.

In addition to the deprotonation reactions mentioned previously, there is a more general method of synthesis involving reaction of metal complex halides with LiN=CR_2, which are in turn obtained from compounds such as Ph_2C=NH or t-Bu_2C=NH by action of n-BuLi.

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[158] F. A. Cotton and E. S. Shamshoum, *J. Am. Chem. Soc.*, 1984, **106**, 3222; H. Alper *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 1701.

Nitrido Complexes.[159] The nitride ion is one of the strongest of π donors ($\mathrm{M{\equiv}N}$, 1.6–1.8 Å) and the compounds are rather similar to those containing $\mathrm{M}\overset{\leftarrow}{=}\dot{\underset{..}{\mathrm{N}}}\mathrm{R}$ or $\mathrm{M{=}O}$ groups; the $\mathrm{M{\equiv}N}$ infrared stretch is in the region 950 to 1200 $\mathrm{cm^{-1}}$. The relative bond strengths are probably $\mathrm{M{\equiv}N} > \mathrm{M{=}O} > \mathrm{M}\overset{\leftarrow}{=}\dot{\underset{..}{\mathrm{N}}}\mathrm{R}$. Typical nitrido complexes are $\mathrm{OsNBr_4}$, $\mathrm{TcN(dtc)_2}$, and TPPMnN. They are usually made by reactions[160] involving oxidation of ammonia,

$$\mathrm{OsO_4 + OH^- + NH_3 \longrightarrow OsO_3N^- + 2H_2O}$$

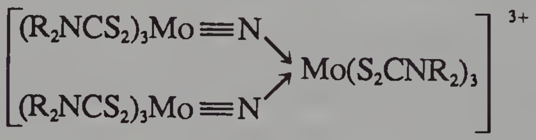
$$\mathrm{ClMn(TPP) + PhIO + NH_3 \longrightarrow NMn^{V}(TPP)}$$

or photolysis or thermal decomposition of azides

$$\mathrm{(porph)CrN_3 \xrightarrow{h\nu} (porph)CrN + N_2}$$

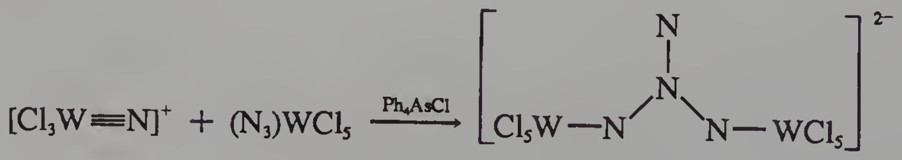
The nitrido ligand changes its basicity depending on the nature of the trans groups and itself has a strong trans-labilizing effect.

The nitrogen atom in some of these compounds can be attacked. Thus tertiary phosphines react with $\mathrm{OsNCl_3(AsPh_3)_2}$ to give phosphine imidate complexes ($\mathrm{R_3PClOs{-}N{=}PR_3}$) in which there is $d\pi$-$p\pi$-$d\pi$ bonding. The formation of a thionitrosyl complex with an $\mathrm{Mo{-}N{=}S}$ group by attack of $\mathrm{S_8}$ has been mentioned earlier. An exceptional case of interaction is with another metal atom as in the complex (10-XXXIX), where the $\mathrm{Mo{\equiv}N}$ distance (~1.65 Å) is similar to that in $\mathrm{N{\equiv}Mo(dtc)_3}$, whereas the $\mathrm{{\equiv}N \rightarrow Mo}$ distance is 2.12 to 2.14 Å.



(10-XXXIX)

An even more unusual nucleophilic attack gives a complex with a unique planar $\mathrm{N_4}$ bridge.[161]



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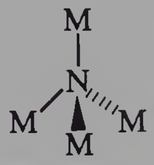
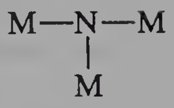
[159] K. Dehnicke and J. Strähle, *Angew. Chem. Int. Ed. Engl.*, 1981, **20,** 413; W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 56; D. M-T. Chan *et al.*, *Inorg. Chem.*, 1986, **25,** 4170.
[160] See, for example, J. W. Buchler *et al.*, *Chem. Ber.*, **1984,** 2261.
[161] K. Dehnicke *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1984, **23,** 149.

Bridged nitrido species. These are of the types

$$\mathrm{M}\!\stackrel{\cdots}{-}\!\mathrm{N}\!\stackrel{\cdots}{-}\!\mathrm{M'} \qquad \mathrm{M}\!\equiv\!\mathrm{N}\!\longrightarrow\!\mathrm{M'}$$



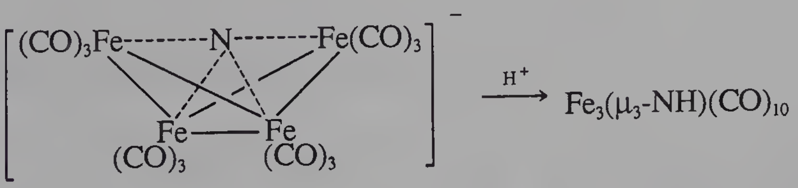


Symmetrical single bridges[162] are found in $[Ru_2NCl_8(H_2O)_2]^{3-}$, $[Ru_2N(en)_5]^{5+}$, and porphyrin or phthalocyanin compounds $(LM)_2N$. The tetraphenylporphin $(TPPFe)_2N$ differs from the comparable antiferromagnetic $(TPPFe)_2O$ in having spin $\frac{1}{2}$; it can also exist with + or − charges where the species are best regarded as having oxidation states of 3,3(−1), 3.5,3.5(0), and 4,4(+1).[163]

Asymmetric bridges occur in $[ReN(CN)_4]_n^{2-}$, $[(RO)_3MoN]_n$, and $[NMoCl_3(OPCl_3)]_4$, but no bent MNM bridges are known, unlike bent MOM. The essential linearity results from MNM π bonding. Only two examples of T-shaped μ_3-N are known, one being $Mo_4(\mu_3\text{-}N)_2(\mu\text{-}OPr)_2(OPr)_{10}$.[164]

The *triangular,* planar *N*-centered species are much less common than M_3O ones (Section 12-9). The metal atoms may be bridged by groups such as SO_4^{2-} or RCO_2^- and the charge on the complex depends on the anion. Since NM_3^{III} has a +6 charge, we can have complexes like $[Ir_3N(SO_4)_6(H_2O)_3]^{6-}$.[165] The latter is obtained by heating Ir salts in $H_2SO_4 + (NH_4)_2SO_4$. The ion can undergo reversible redox cycles.

Tetrabridged (μ_4) species can be regarded as a type of quaternary ammonium ion. Examples[166] are $(MeHg)_4N^+$ and $(Ph_3PAu)_4N^+$. However, several cluster complexes[167] with central N atoms are known, examples being $[Fe_4N(CO)_{12}]^-$, $[Ru_6N(CO)_{16}]^-$, and $[Co_6N(CO)_{15}]^-$. They may be obtained from polynuclear carbonyls by interaction with NO^+, N_3^-, or $Fe(CO)_3NO^-$. The N atom in the open-sided cluster $[Fe_4N(CO)_{12}]^-$ can be protonated with disruption of the cluster:



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[162] W. P. Griffith *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 434; V. L. Goedken and C. Ercolani, *J. Chem. Soc. Chem. Commun.*, **1984,** 378.

[163] L. A. Bottomley *et al., Inorg. Chem.*, 1985, **24,** 3733; D. F. Bocian *et al., Inorg. Chem.*, 1982, **21,** 2885.

[164] M. H. Chisholm *et al., J. Am. Chem. Soc.*, 1985, **107,** 3722.

[165] A. C. Skapski *et al., J. Chem. Soc. Chem. Commun.*, **1971,** 876; A. C. Sykes *et al., Inorg. Chem.*, 1986, **25,** 3144.

[166] Y. L. Slovokhotov and Y. T. Struckhov, *J. Organomet. Chem.*, 1984, **277,** 143.

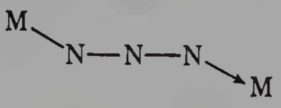
[167] W. L. Gladfelter *et al., Organometallics*, 1986, **5,** 1049; *J. Am. Chem. Soc.*, 1986, **108,** 2301; C. E. Anson *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 1715; B. F. G. Johnson *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 1526.

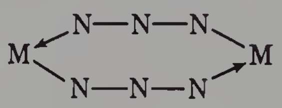
10-19. Simple Anionic Nitrogen-Containing Ligands

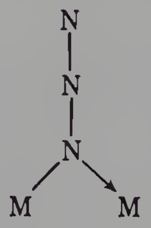
Thiocyanate[168] **and Cyanate.** The NCS^- ion is ambidentate, binding through N or S or as a bridge M—NCS—M.[169] The distinction[170] between N and S bonding can be made by ^{14}N nuclear quadrupole studies and by MAS nmr ^{13}C spectra. The bonding depends on the metal, steric factors, and the nature of other ligands present. Heavier metals are commonly S-bonded and in such cases M—SCN is usually bent[171] with an angle ~110° but N-bonded species may also have nonlinear M—N—C groups.

Cyanates are generally similar.[172]

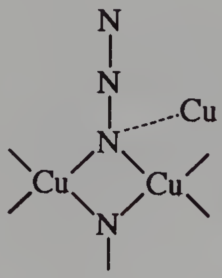
Azide.[173] The azide ion can give η^1 and bridged species of the types



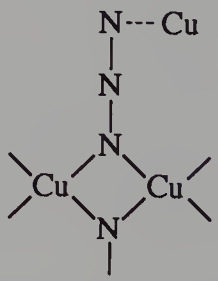




In the unidentate complexes the a bond in $M{-}N\overset{a}{-}N\overset{b}{-}N$ is commonly longer than b. In polymeric $Cu(N_3)_2$, the chains are linked by interactions of the type



and



1,3-Triazenido.[174] The compounds ArNNN(H)Ar are acidic and the anions

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[168] J. L. Burmeister, in *The Chemistry and Biochemistry of Thiocyanic Acid,* A. A. Newman, Ed., Academic Press, New York, 1975.

[169] W. M. Reiff *et al., Inorg. Chem.,* 1983, **22,** 150.

[170] N. Zumbulyadis and H. J. Gysling, *J. Am. Chem. Soc.,* 1982, **104,** 3246.

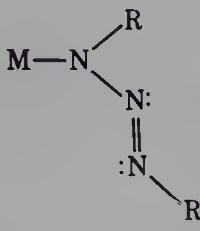
[171] W. R. Scheidt *et al., J. Am. Chem. Soc.,* 1982, **104,** 3367.

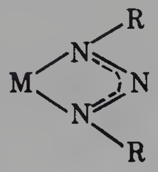
[172] See, for example, T. Schönherr, *Inorg. Chem.,* 1986, **25,** 171.

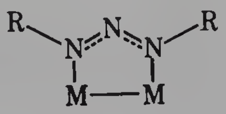
[173] J. Straehle, *Comments Inorg. Chem.,* 1985, **4,** 295; Z. Dori and R. F. Ziolo, *Chem. Rev.,* 1973, **73,** 247; P. Chaudhuri *et al., Inorg. Chem.,* 1986, **25,** 2818.

[174] R. Rossi *et al., J. Chem. Soc. Dalton Trans.,* **1982,** 1949; G. L. Hillhouse and J. E. Bercaw, *Organometallics,* 1982, **1,** 1025; J. Lewis *et al., J. Chem. Soc. Dalton Trans.,* **1982,** 2085; G. Wilkinson *et al., Polyhedron,* 1983, **2,** 79; E. Pfeiffer *et al., Transition Met. Chem.,* 1977, **2,** 240; D. S. Moore and S. D. Robinson, *Adv. Inorg. Chem. Radiochem.,* 1986, **30,** 1 (review).

can function as unidentate, chelate, or bridging ligands where the structures resemble those of the more important carboxylates (Section 12-16).







Although the compounds can be made by substitution reactions, for example,

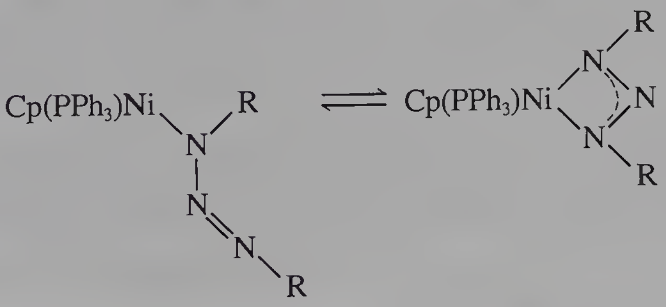
$$ReOCl_3(PPh_3)_3 + LiArN_3Ar \xrightarrow{PPh_3} ReCl_2(\eta^2\text{-}ArN_3Ar)(PPh_3)_2 + OPPh_3 + LiCl$$

they can also be made by insertion reactions of organic azides:

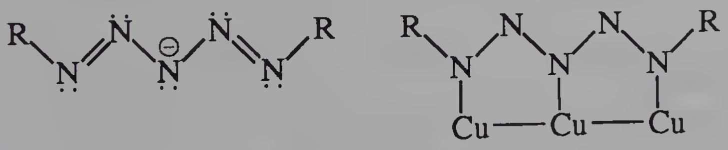
$$^*Cp_2HfH_2 + RN_3 \longrightarrow {}^*Cp_2Hf(H)(\eta^2\text{-}HNNNR)$$

$$(Me_3P)_3CoMe_3 + ArN_3 \longrightarrow (Me_3P)_3CoMe_2(\eta^2\text{-}MeN_3Ar)$$

The η^1 and η^2 species may be in equilibrium in certain cases, for example,



Related complexes[175] can be formed from 1,5 substituted 1,4-pentaazadiene-3-ide (10-XLa) as in (10-XLb)



(a) (b)

(10-XL)

Amidinato and Sulfurdiiminato Ligands. If the central N atom in RN_3R^- is replaced by CR′, (R′ = H, Me, etc.) we obtain *N,N′* disubstituted for-

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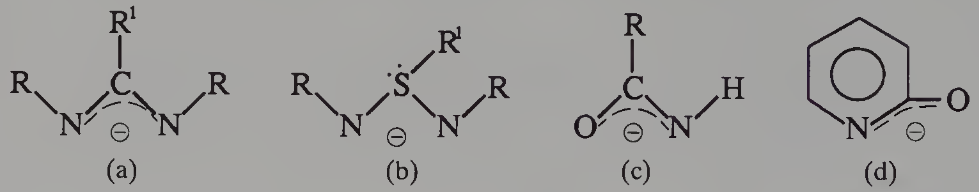
[175] J. Beck and J. Strähle, *Z. Naturforsch.*, 1986, **41B,** 4.

mamidinato or alkyl or aryl*aminidinato* ligands (10-XLIa); we obtain the *sulfurdiiminato* (10-XLIb) ligands on replacement with SR′.



(a) (b) (c) (d)

(10-XLI)

These ligands can be η^1, η^2 (with π-type or N—M σ bonding) or μ[176a]; amidinato ligands have been studied for asymmetric catalytic systems.[176b] Related are substituted *amidato*[177] ligands derived from amides and 2-hydroxopyridinato[178] ones (10-XLIc, d) both of which tend to give bridged species.

10-20. Hydrazine and Related Ligands with N—N Bonds[179]

There is a large number of complexes of ligands with N—N bonds. They have been greatly studied in recent years because of their relationship, real or imagined, to the problem of the conversion of dinitrogen to ammonia or hydrazine and the reactions of coordinated N_2. The relationship between these ligands and others such as NH has been noted above (p. 335).

Hydrazine. Hydrazine usually acts as a reducing agent but some compounds of N_2H_4 such as $Zn(N_2H_4)_2Cl_2$ or $Cp(CO)_2ReN_2H_4$ have one coordinated N atom.

Substitution by alkyl or aryl groups (RNHNHR′ or NH_2NR_2) may sterically inhibit coordination of the substituted atom but complexes such as $Mo(CO)_5$(RNHNHR) and $[RuH(COD)(NH_2NMe_2)_3]^+$ have been made.[180a] Hydrazinium $(N_2H_5)^+$ can also act as a η^1 ligand. An example of η^2 coordination on vanadium involves $H_2NNMePh$.[180b]

Both N atoms in N_2H_4 and Me_2NNH_2 can bridge in certain cases. An unusual example of a μ-η^1,η^1 hydrazine with a μ-η^2,η^2, hydrazido(2−) ligand is (10-XLIIa) made by interaction of N_2H_4 with $PhNWMe_4$, while a hydrazido (1−)

[176a] M. Kilner *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 1359; L. A. Oro *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 1487.

[176b] H. Brunner, *Angew. Chem. Int. Ed. Engl.,* 1983, **25** 987.

[177] F. A. Cotton *et al., Inorg. Chim. Acta,* 1985, **101,** 185.

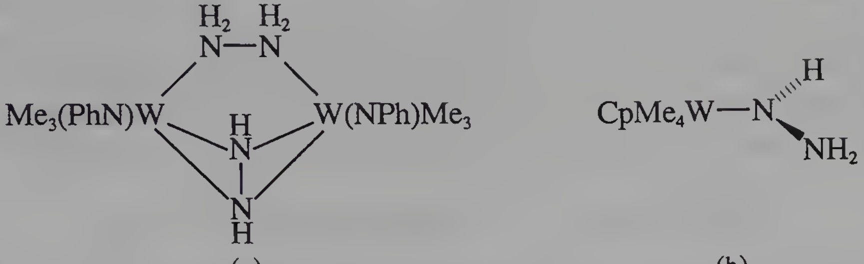
[178] W. Clegg *et al., Inorg. Chem.,* 1982, **21,** 1897; for 2-thiolato pyridine complexes see P. K. Mascharak *et al., Inorg. Chem.,* 1986, **25,** 2109.

[179] R. A. Henderson, G. J. Leigh, and C. J. Pickett, *Adv. Inorg. Chem. Radiochem.,* 1983, **27,** 198.

[180a] M. N. Ackermann *et al., Organometallics,* 1986, **5,** 966; E. Singleton *et al., J. Organomet. Chem.,* 1984, **272,** C25; K. C. Patel *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 119.

[180b] L. F. Larkworthy *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 1748.

complex is (10-XLIIb).[181] The latter decomposes with loss of CH_4 to give $^*CpMe_3W{=}NNH_2$.



(a) (b)

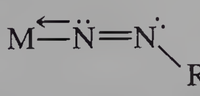
(10-XLII)

Diazenido Complexes.[182] The ligand NNR has been referred to in the literature as aryl (or alkyl) azo, diazo, or diazenato. The aryl compounds are commonest; they can be obtained from diazonium compounds (ArN_2^+) and from hydrazines such as $PhNNH_2$ or ArC(O)NNH. They are also formed by electrophilic or nucleophilic attacks on dinitrogen compounds (Section 10-9); for example,

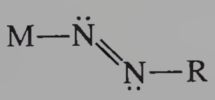
$$(\text{diphos})_2\text{Mo}(N_2) + \text{RCOCl} + \text{HCl} \xrightarrow{\text{NEt}_3} (\text{diphos})_2\text{ClMo}(N_2\text{COR})$$

$$\eta\text{-}C_5H_5(CO)_2MnN_2 \xrightarrow{\text{LiPh}} \text{Li}[\eta\text{-}C_5H_5(CO)_2MnN_2Ph]$$

The ligand can be regarded as RN_2^+ (the analogue of NO^+), or as RN_2^-, (the analogue of NO^-), or as neutral RN_2 (the analogue of CO), and there has been the same type of discussion concerning the extent of metal-ligand π bonding. As with NO compounds, the N=N stretches vary widely from ~2095 cm^{-1} (indicating M—N π bonding) down to ~1440 cm^{-1} in bridging species. The main distinction is between the following types of complex:



(a) Linear or single bent



(b) Double bent

Type (a), of which $ArN_2RuCl_3(PPh_3)_2$ is an example, can be regarded as derived from RN_2^+. The M—N—N bonds are almost but not quite linear, the M—N—N angle usually being ~170°. There is considerable M—N π bonding, but the π character appears to be less than that in M—NO compounds. Type (b), of which $[ArN_2RhCl(\text{triphos})]^+$ is an example, show con-

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[181] R. R. Schrock *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 8316; 1985, **107**, 4557. For hydrazide (2−), NH_2^{2-} see J. D. Lane and R. A. Henderson, *J. Chem. Soc. Dalton Trans.*, **1987**, 197.

[182] See G. J. Leigh *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 377, 385; M. Hidai *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 1562; E. Bordignon *et al.*, *Inorg. Chem.*, 1986, **25**, 950. W. Hussain *et al.*, *J. Chem, Soc. Dalton Trans.*, **1986**, 1473.

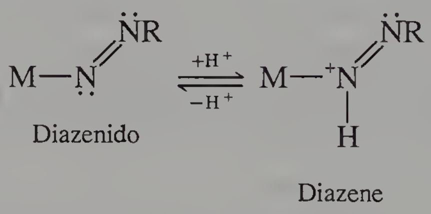
siderable variation in angles, but M—N—N is usually ~120°. They can be considered to be derived from RN_2^-.

There are some iridium complexes of the *neutral* group $C_5Cl_4N_2$ acting as a two-electron donor [e.g., $IrCl(N_2C_5Cl_4)(PPh_3)_2$], which can be compared with $IrCl(CO)(PPh_3)_2$; these also have a type (a) bent structure.[183]

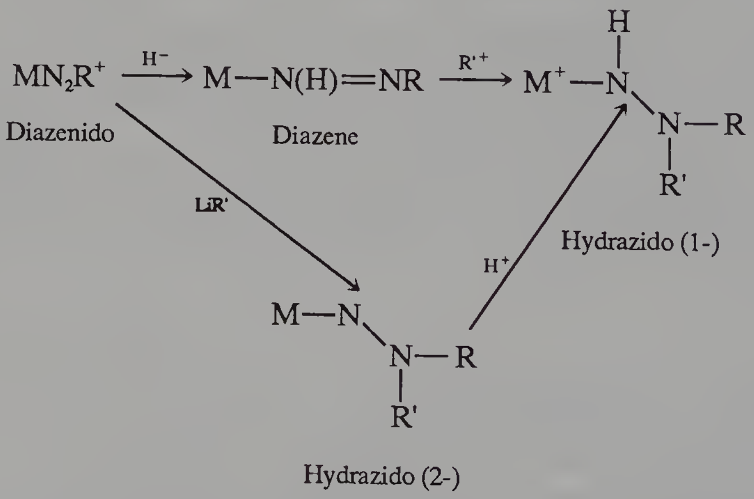
η^2-bonding is found in $CpTiCl_2(\eta^2\text{-NNPh})$. The RN_2 compounds undergo a number of reactions, thus hydrogenation to a hydrazino complex:

$$[(Ph_3P)_2PtN_2Ar]^+ \xrightarrow{H_2} [(Ph_3P)_2Pt(H)NH_2NHAr]^+$$

More important, however, is attack by electrophiles, especially H^+, which shows that diazenido complexes are related to diazene complexes discussed here by the acid–base equilibrium



There is also the sequence (*cf.*, p. 335)[184]



which models a sequence for protonation and reduction of N_2, that is, $M(N_2) \rightarrow MN_2H \rightarrow MN_2H_2 \rightarrow MN_2H_3$.

1,2-Diazenes or Azo Compounds (RN=NR′). These usually utilize one or both of the lone pairs on N as σ donors to give η^1 or bridged compounds[185a]:

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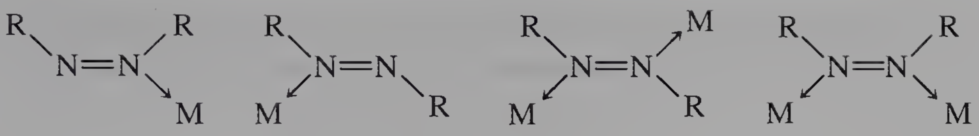
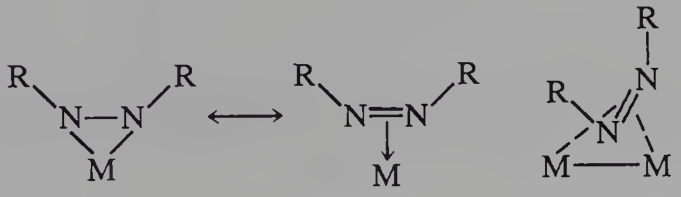
[183] K. D. Schram and J. A. Ibers, *J. Am. Chem. Soc.*, 1980, **102**, 2441.

[184] D. Sutton *et al.*, *Inorg. Chem.*, 1984, **23**, 363.

[185a] D. Mansuy, *J. Am. Chem. Soc.*, 1983, **105**, 1399; C. Floriani *et al.*, *J. Chem. Soc. Dalton Trans.*, **1983**, 1515; T. B. Rauchfuss *et al.*, *J. Am Chem. Soc.*, 1984, **106**, 7801; M. N. Ackermann *et al.*, *Organometallics*, 1986, **5**, 966; E. Bordignon *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 6627 (ArN=NH).



However, olefinlike η^2 bonding is known, for example, in $Cp_2Ti(\eta^2\text{-}Ph_2N_2)$ and $(tol_3P)_3Ni(\eta^2\text{-}Ph_2N_2)$ and π bonds may also be used in bridging (cf. $RC{\equiv}CR'$).

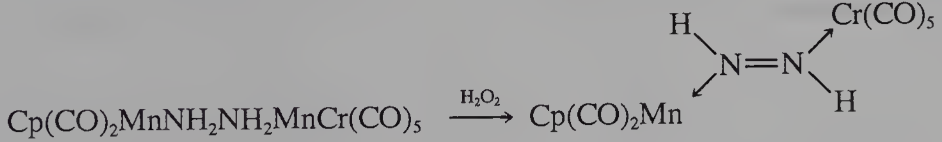


For $CpRe(CO)_2(Ph_2N_2)$ in solution there is an equilibrium between η^1 and η^2 species.[185b] Binding as a hydrazido(2−) ligand[186] is comparable to the bonding of N_2 as $M \leftarrow :N{\equiv}N: \rightarrow M$ or as the hypothetical ion N_2^{4-}. Azo compounds can, in certain reactions, cleave to give M=NR compounds in a type of metathesis reaction[187] (Section 28-16):

$$Nb{=}Nb + PhN{=}NPh \longrightarrow 2Nb{=}NPh$$

A specific example is the synthesis of $Ta_2Cl_6(NPh)_2(Me_2S)_2$. An important feature of the aromatic azo compounds is the reactivity to C—H cleavage of the ortho position. These so-called cyclometallation reactions are discussed in detail in Section 27-9.

Diazene compounds can be made directly from R_2N_2 or by oxidation of hydrazine and substituted hydrazine complexes, for example,



There are fewer examples of N,N disubstituted diazenes or isodiazenes, NNR_2, hydrazido(2−). Hydrogen compounds can be made by protonation[188]:

$$(diphos)_2Mo(N_2)_2 \xrightarrow{HBF_4} [(diphos)_2FMoNNH_2]^+$$

Diazoalkanes or Alkylidenehydrazido(2−). Complexes of the ligands $R_2C{=}N{=}N$[189a] can be made from the free ligands, and by condensation of L_nMNNH_2 with aldehydes or ketones.

[185b] D. Sutton *et al.*, *Inorg. Chem.*, 1987, **26**, 111.

[186] M. R. Churchill *et al.*, *Organometallics*, 1984, **3**, 109; D. Sellman *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 981.

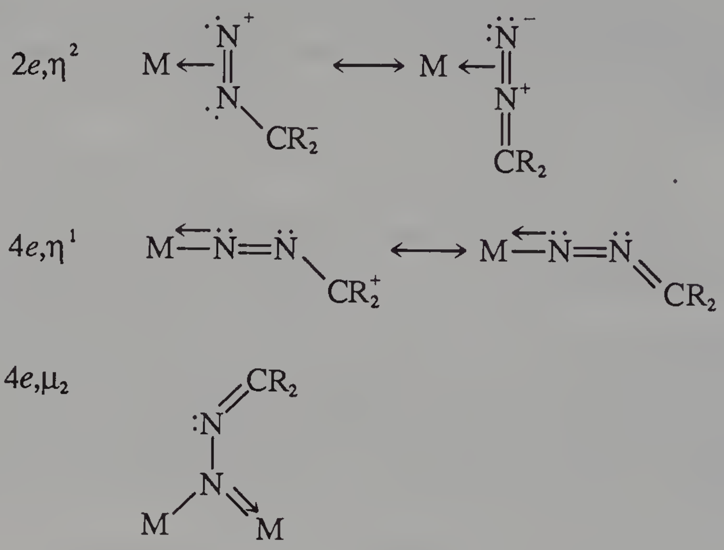
[187] F. A. Cotton *et al.*, *Polyhedron*, 1986, **5**, 895; W. L. Gladfelter *et al.*, *Organometallics*, 1987, **6**, 1311.

[188] See, for example, J. Zubieta *et al.*, *Inorg. Chem.*, 1986, **25**, 405.

[189a] See for example, J. Schwartz *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 1322; C. Woodcock and R. Eisenberg, *Organometallics*, 1985, **4**, 4; M. Cowie *et al.*, *Organometallics*, 1986, **5**, 860.

Diazoalkanes also provide a route to alkylidene complexes by loss of N_2 (Section 25-8). The ligands can act as 2, 4, or 6*e* donors, for example,

$$2e,\ \eta^1 \qquad M \longleftarrow N{\equiv}\overset{+}{N}{=}CR_2$$

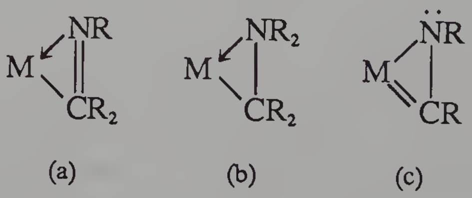


Some representative examples are $Cp_2V(\eta^2\text{-}Ph_2CN_2)$ and $(dtc)_2(CO)W(\eta^1\text{-}N_2CMe_2)$.

Azalkenylidenes[189b] with the group $M{=}N{=}CR_2^+$ are similar to the compounds with $M\overset{\leftarrow}{=}\ddot{N}{=}CR_2$ groups (p. 371).

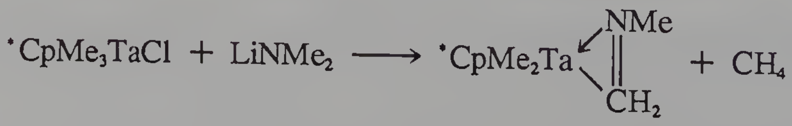
10-21. Nitrogen Ligands Binding by N and C

Metallaaziranes. These ligands, usually η^2, have N and C bonds:



(a) (b) (c)

Those of type (a) may be formed in reactions of dialkylamides, for example,



$$^{*}CpMe_3TaCl + LiNMe_2 \longrightarrow {}^{*}CpMe_2Ta\begin{smallmatrix}\swarrow NMe\\ \| \\ \diagdown CH_2\end{smallmatrix} + CH_4$$

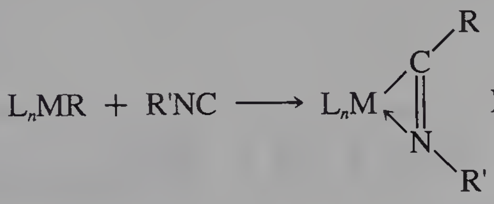
where a β-H transfer from a CH_3 group of an intermediate with a $Ta(NMe_2)$ group leads to elimination of methane.[190a] The *aminomethyls,* type (b) can be made by reactions of sodium salts of carbonylate anions $Na^+[M(CO)_n]^-$ with $CH_2{=}NR_2^+Cl$ and in other ways.[190b]

[189b] H. Werner *et al., Angew Chem. Int. Ed. Engl.,* 1987, **26,** 248.

[190a] J. E. Bercaw *et al., J. Am. Chem. Soc.,* 1983, **105,** 2651.

[190b] See I. Bernal *et al., Inorg. Chim. Acta,* 1981, **51,** 201.

Compounds of type (c) are *iminoacyls* that can be formed by insertion reaction of isocyanides with transition metal alkyls[191]:



R = H, Me, etc.

Carbodiimides. These cumulenes RN═C═NR, like other cumulenes can bind in several ways but usually η^1 through N donation, and η^2-C,N.

Additional References

Chivers, T. and F. Edelmann, *Polyhedron,* 1986, **5,** 1661 (S, N ligands).

Dehnicke, K., *Adv. Inorg. Chem. Radiochem.,* 1983, **26,** 169 (halogen azides).

Dutta, R. L. and M. N. Hossain, *J. Sci. Ind. Res.,* 1985, **44,** 635 (hydrazones as ligands; 227 references).

Golub, A. M., H. Köhler and V. V. Skopenko, Eds., *Chemistry of Pseudohalides,* Elsevier, Amsterdam, 1986 (N_3^-, CN^-, NCO^-, $C(CN)_3^-$).

Kelly, P. F. and J. D. Woollins, *Polyhedron,* 1986, **5,** 607 (S, N ligands).

Wilkinson, G., R. D. Gillard and J. A. McCleverty, Eds., *Comprehensive Coordination Chemistry,* Pergamon Press, Oxford, 1987, Vol. 2.

[191] See, for example, I. P. Rothwell *et al., Organometallics,* 1985, **4,** 1896; E. K. Barefield *et al., Organometallics,* 1987, **6,** 454.

Chapter Eleven

The Group VA(15) Elements: P, As, Sb, Bi

GENERAL REMARKS

11-1. Group Trends and Stereochemistry

The electronic structures and some other properties of the elements in Group VA(15) are listed in Table 11-1. The valence shells have a structure formally similar to that of nitrogen, but beyond the stoichiometries of some of the simpler compounds—NH_3, PH_3, NCl_3, $BiCl_3$, for example—there is little resemblance between the characteristics of these elements and those of nitrogen.

The only naturally occurring isotope of phosphorus (^{31}P) has a nuclear spin of $\frac{1}{2}$ and a large magnetic moment. Nuclear magnetic resonance spectroscopy has accordingly played an extremely important role in the study of phosphorus compounds. For antimony, the isotope ^{121}Sb is suitable for Mössbauer spectroscopy.

The elements P, As, Sb, and Bi show a considerable range in chemical behavior. There are fairly continuous variations in certain properties and characteristics, although in several instances there is no regular trend, for example, in the ability of the pentoxides to act as oxidizing agents. Phosphorus, like nitrogen, is essentially covalent in all its chemistry, whereas As, Sb, and Bi show increasing tendencies to cationic behavior. Although the electronic structure of the next noble gas could be achieved by electron gain, considerable energies are involved (e.g., ~1450 kJ mol^{-1} to form P^{3-} from P); thus significantly ionic compounds such as Na_3P are few. The loss of valence electrons is similarly difficult to achieve because of the high ionization enthalpies. The 5+ ions do not exist, but for trivalent antimony and bismuth cationic behavior does occur. Bismuth trifluoride seems predominantly ionic, and salts such as $Sb_2(SO_4)_3$ and $Bi(NO_3)_3 \cdot 5H_2O$, as well as salts of the oxo ions SbO^+ and BiO^+, exist.

Some of the more important tends are shown by the oxides, which change from acidic for phosphorus to basic for bismuth, and by the halides, which have increasingly ionic character: PCl_3 is instantly hydrolyzed by water to

TABLE 11-1
Some Properties of P, As, Sb, and Bi

Property	P	As	Sb	Bi
Electronic structure	$[Ne]3s^23p^3$	$[Ar]3d^{10}4s^24p^3$	$[Kr]4d^{10}5s^25p^3$	$[Xe]4f^{14}5d^{10}6s^26p^3$
Sum of 1st three ionization enthalpies $[(kJ\ mol^{-1})/10^3]$	5.83	5.60	5.05	5.02
Electronegativity[a]	2.06	2.20	1.82	1.67
Radii (Å)				
Ionic	$2.12(P^{3-})$		$0.92(Sb^{3+})$	$1.08(Bi^{3+})$
Covalent[b]	1.10	1.21	1.41	1.52
Melting point (°C)	44.1 (α-form)	814 (36 atm)	630.5	271.3

[a] Allred–Rochow type.

[b] For trivalent state.

$HPO(OH)_2$, and the other trihalides give initially clear solutions that hydrolyze to As_2O_3, SbOCl, and BiOCl, respectively. There is also an increase in the stability of the lower oxidation state with increasing atomic number; thus Bi_2O_5 is the most difficult to prepare and the least stable pentoxide.

Although oxidation states or oxidation numbers can be, and often are, assigned to these elements in their compounds, they are of rather limited utility except in the formalities of balancing equations. The important valence features concern the number of covalent bonds formed and the stereochemistries. The general types of compound and stereochemical possibilities are given in Table 11-2.

The differences between the chemistries of N and P, which are due to the

TABLE 11-2
Major Stereochemical Patterns for Compounds of Group VA(15) Elements

Formal valence	Number of bonds formed	Geometry	Examples
1	3	Trigonal plane	$PhP[Mn(CO)_2Cp]_2$
3	2	Angular	PH_2^-, $(Me_2N)_2P^+$, $R_2N-P=NR$, $R-P=CR_2$
	3	Pyramidal	PH_3, $AsCl_3$, $SbPh_3$
	4	Tetrahedral	PH_4^+, $P(CH_2OH)_4^+$, $AsPh_4^+$
		ψ *tbp*	KSb_2F_7, $SbCl_3(PhNH_2)$, $K_2[Sb_2(tart)_2]\cdot 3H_2O$, SbOCl
	5	ψ octahedral	SbF_5^{2-}, $[Sb_4F_{16}]^{4-}$, Sb_2S_3, $SbCl_3(PhNH_2)_2$
	6	Octahedral	$[Bi_6O_6(OH)_3]^{3+}$, $[SbBr_6]^{3-}$
5	3	Planar	$P[N(SiMe_3)_2](NSiMe_3)_2$
	4	Tetrahedral	PCl_4^+, $(RO)_3PO$, $RPO(OH)_2$
	5	*tbp*	PF_5, AsF_5, $SbCl_5$, $AsPh_5$
		sp	$SbPh_5$
	6	Octahedral	PF_6^-, $Sb(OH)_6^-$, $SbBr_6^-$

same factors that are responsible for the C—Si and O—S differences, can be summarized as follows:

Nitrogen	Phosphorus
(a) Very strong $p\pi$–$p\pi$ bonds	Weak $p\pi$–$p\pi$ bonds
(b) $p\pi$–$d\pi$ bonding is rare	Weak to moderate but important $d\pi$–$p\pi$ and $d\pi$–$d\pi$ bonding
(c) No valence expansion	Valence expansion

Point (a) leads to facts such as the existence of $P(OR)_3$ but not of $N(OR)_3$, nitrogen giving instead $O{=}N(OR)$, and the marked differences between the oxides and oxo acids of nitrogen on the one hand and those of phosphorus on the other.

Point (b) is associated with rearrangements such as

and with the existence of phosphonitrilic compounds $(PNCl_2)_n$. Furthermore, although PX_3, AsX_3, and SbX_3 (X = halogen, alkyl, or aryl), like NR_3 compounds, behave as donors owing to the presence of lone pairs, there is one major difference; the nitrogen atom can have no function other than simple donation, because no other orbital is accessible; but P, As, and Sb have empty *d* orbitals of fairly low energy. Thus when the atom to which the P, As, or Sb donates has electrons in orbitals of the same symmetry as the empty *d* orbitals, back-donation resulting in overall multiple-bond character may result. This factor is especially important for the stability of complexes with transition elements where $d\pi$–$d\pi$ bonding contributes substantially to the bonding and has been discussed in detail in Section 2-10.

The consequences of vacant *d* orbitals are also evident on comparing the amine oxides (R_3NO) on the one hand, with R_3PO or R_3AsO on the other. In the *N*-oxide the electronic structure can be represented by the single canonical structure $R_3N^+{—}O^-$, whereas for the others the bonds to oxygen have multiple character and are represented as resonance hybrids:

$$R_3P^+{—}O^- \longleftrightarrow R_3P{=}O \longleftrightarrow R_3P^-{\equiv}O^+$$

These views are substantiated by the shortness of the P—O bonds (~1.45 as compared with ~1.6 Å for the sum of the single-bond radii) and by the normal bond lengths and high polarities of N—O bonds. The amine oxides are also more chemically reactive, the P—O bonds being very stable indeed, as would be expected from their strength, ~500 kJ mol^{-1}.

Point (c) is responsible for the phenomena such as the Wittig reaction (Section 11-12) and for the existence of compounds such as $P(C_6H_5)_5$, $P(OR)_5$, $[P(OR)_6]^-$, and $[PR_4]^+[PR_6]^-$ in which the coordination number is 5 or 6. The extent to which hybridization employing 3*d* orbitals is involved is somewhat uncertain, since the *d* levels are rather high for full utilization and the higher states may be stabilized in part by electrostatic forces; it is significant that the higher coordination numbers for P^V are most readily obtained with more electronegative groups such as halogens, OR, or phenyl.

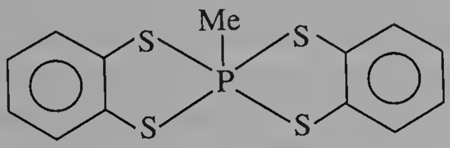
Stereochemistry with Formal Valence Three. The overwhelming majority of compounds having these elements in formal valence state three have three pyramidally directed single bonds, with a lone pair occupying the fourth *tetrahedral* position. The tetrahedron can be completed by "quaternization" (formal addition of R^+ or H^+) to give cations, for example, PR_4^+.

There are a few examples of two-coordination with phosphorus, as in PH_2^-, $(R_2N)_2P^+$, and others listed in Table 11-2.

With higher coordination numbers, the question of the stereochemical activity of the lone pair arises. In many cases ψ-*tbp* and ψ-octahedral species are observed, but in some cases the lone pair seems to occupy an *s* orbital and not compete with the bonding pairs for a position in the coordination sphere (see Section 11-6).

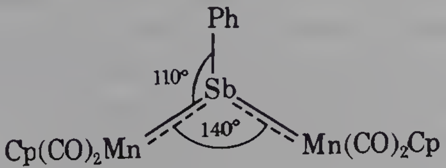
Stereochemistry with Formal Valence Five. A complicating feature in the stereochemistry of the five-valent compounds is that the *tbp* and *sp* configurations for the five-connected species differ very little in energy. The *tbp* is nearly always the more stable, but not by a great deal, for EX_5 molecules in which all X are separate groups (i.e., not connected to give rings). As a general rule[1] *sp* structures are favored by the presence of two unsaturated five-membered rings (11-I). The similar energies of the *tbp* and *sp* configurations provide a pathway for stereochemical nonrigidity, via the Berry pseudorotation path (Section 29-12).

One general rule for mixed species (EX_nY_{5-n}) with *tbp* structures is that the more electronegative groups prefer the axial sites.

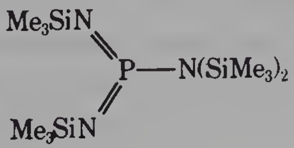


(11-I)

Planar P, As, and Sb Compounds. There are unusual compounds in which the elements, formally in the I oxidation state, form trigonal planar compounds of type (11-II); $d\pi$–$p\pi$ interaction is doubtless involved in the bonding. In the second (11-III), phosphorus is formally pentavalent.



(11-II)



(11-III)

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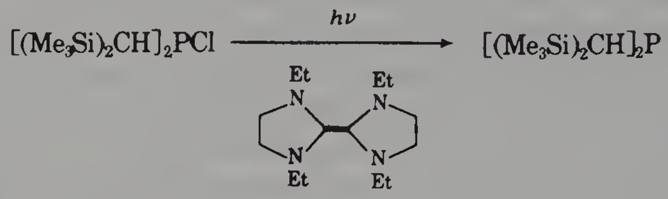
[1] R. R. Holmes, *Prog. Inorg. Chem.*, 1984, **32**, 119.

Phosphorus Radicals. The action of light in the presence of an activated alkene as halogen acceptor leads to R_2P radicals, namely,



$$[(Me_3Si)_2CH]_2PCl \xrightarrow{h\nu} [(Me_3Si)_2CH]_2P$$

The stability of the radical is connected with the bulk of the bis(trimethylsilyl) methyl group.

11-2. The Elements

All are found in Nature as compounds except for minute amounts of elemental arsenic and bismuth. Their abundances decrease in order of increasing atomic number with phosphorus being considerably more abundant than all of the others combined. Though >200 phosphate minerals are known only those of the apatite type, for example, fluoroapatite, $[3Ca_3(PO_4)_2 \cdot Ca(F, Cl)_2]$, are commercial sources. Arsenic and antimony are commonly associated with sulfide minerals, particularly those of copper, lead, and silver. The main bismuth ores are Bi_2O_3 and various sulfides.

Phosphorus. Currently, commercial production is by reduction of phosphate rock with coke and silica in an electric furnace. The element volatilizes out and is condensed under water as white phosphorus, a soft, white, waxy solid (mp 44.1°C, bp 280°C):

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 6CaSiO_3 + 10CO$$

Most of the phosphorus produced is converted to phosphoric acid for use in making fertilizer, or in other commercial processes. Since the conversion of the element to P_2O_5 or H_3PO_4 is very exothermic, a more economic process[2] in which the heat from this second step is used in place of electricity to heat the kiln in which the reduction is carried out has been developed. Another process has been proposed to go directly from phosphate rock to P_2O_5 and H_3PO_4 without an intermediate reduction step.

There are three main forms of phosphorus—white, black, and red—but there are numerous allotropes, some of dubious validity.

White phosphorus in the liquid and solid forms consists of tetrahedral P_4 molecules ($P—P = 2.21$ Å), which persist in the vapor phase up to 800°C where measurable dissociation to P_2 molecules ($P\equiv P = 1.89$ Å) begins. The process $P_4(g) = 2P_2(g)$ is endothermic (217 kJ/mol). It proceeds cleanly in a unimolecular fashion without intermediates or other fragments.[3]

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[2] *Chem. Eng. News,* October 21, 1985, p. 23.

[3] H. Bock and H. Müller, *Inorg. Chem.,* 1984, **23,** 4365.

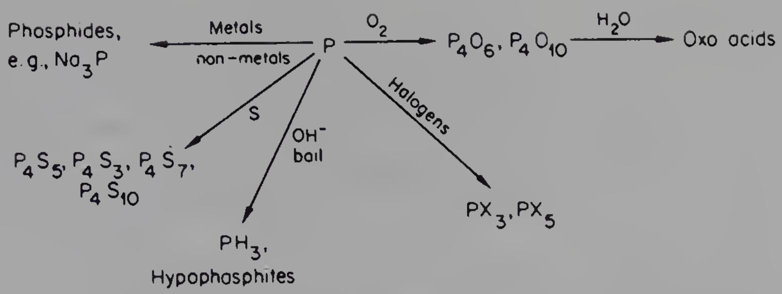

FIG. 11-1. Some typical and important reactions of red and white phosphorus.

White phosphorus is the least stable solid allotrope, but all others revert to it when melted. It is highly reactive and toxic, and is commonly stored under water to protect it from air. It is soluble in organic solvents such as CS_2 and benzene and by virtue of the lone pairs projecting from each P atom, the P_4 molecule can serve as a kind of phosphine ligand (Section 11-18). Some reactions of white (and red, *vide infra*) phosphorus are shown in Fig. 11-1.

Since by simple criteria the tetrahedral molecule might appear strained in comparison to a cubic P_8 structure, there has been much theoretical study of why P_8 is not observed. Clearly the $2P_4 \rightarrow P_8$ transformation is entropically disfavored and it has also been argued that there is so high a barrier to the transformation that at temperatures sufficiently high to achieve a detectable rate of conversion, P_8 would be entropically disfavored and P_2 would be more stable than either P_4 or P_8.[4] However, in contradiction to intuitive feelings about strain in P_4, several recent electronic structure calculations have led to the conclusion that the $2P_4 \rightarrow P_8$ conversion is in fact enthalpically disfavored.[5]

Orthorhombic black phosphorus, the most thermodynamically stable and least reactive form, is obtained by heating white phosphorus under pressure. It has a graphitic appearance and consists of double layers as shown in Fig. 11-2(a). When subjected to pressures above 12 kbar the orthorhombic form transforms successively to the rhombohedral and cubic forms, Fig. 11-2 (b) and (c).

Red phosphorus is of intermediate reactivity and is used commercially. Ordinarily it is amorphous but various crystalline forms have been isolated. It is easily obtained by heating white phosphorus in a sealed vessel at ~400°C. It is thought to consist of polymers resulting from partial opening of the P_4 tetrahedra.

Arsenic, Antimony, and Bismuth. Extractive methods are varied depending on the ore. For arsenic, industrial scale recovery is by thermolysis of the ore FeAsS to FeS and As. For antimony, a typical process is reaction of Sb_2S_3 with Fe to give FeS + Sb.

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[4] E. A. Halevi *et al., Inorg. Chem.*, 1984, **23,** 4376.

[5] M. W. Schmidt and M. S. Gordon, *Inorg. Chem.*, 1985, **24,** 4503; G. Trinquier *et al., J. Am. Chem. Soc.*, 1985, **107,** 7210; R. Ahlrichs *et al., J. Am. Chem. Soc.*, 1985, **107,** 7260; K. Raghavachari *et al., Chem. Phys. Lett.*, 1985, **122,** 219.

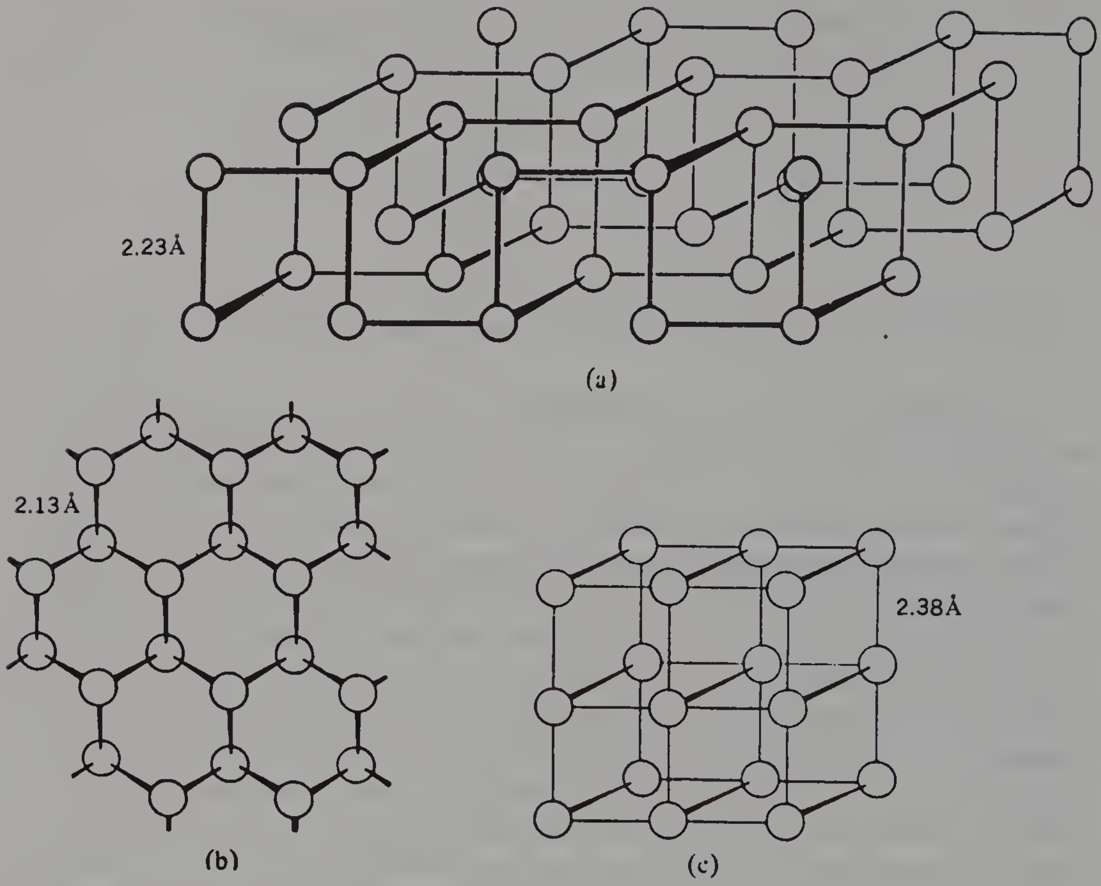

FIG. 11-2. Three forms of black phosphorus. (a) The orthorhombic form (one double layer). (b) The rhombohedral form. (c) The cubic form.

These elements have fewer allotropic forms than phosphorus. For As and Sb unstable yellow allotropes comparable to white phosphorus are obtainable by rapid condensation of vapors. They readily transform to the bright, "metallic" α-rhombohedral forms similar to rhombohedral black phosphorus. This is also the commonest form for bismuth. Other allotropes are not well characterized.

The elements, like phosphorus, all combine readily with O_2, and they react readily with halogens and some other nonmetals. They are unaffected by dilute nonoxidizing acids, but with nitric acid As gives arsenic acid, Sb gives the trioxide, and Bi dissolves to form the nitrate.

BINARY COMPOUNDS

11-3. Phosphides, Arsenides, Antimonides, and Bismuthides

The Group VA(15) elements (E) form binary compounds with virtually every metallic element in the periodic table. The compounds vary enormously in their chemical and physical properties, and their structures range from simple ones (e.g., many ME compounds have the zinc blende structure) to very elaborate ones containing chains, sheets, spirals, and polyhedra formed by the nonmetallic element. There are some compounds that have formulas consistent with the presence of E^{3-} ions (e.g., Sr_3P_2 and Na_3As) but their physical properties indicate that they are metallic rather than ionic in character.

The most common method for preparing all of these compounds, regardless of their physical, chemical, or structural nature, is simply by reaction of stoichiometric quantities of the elements, although other methods are sometimes used.

We can do no more here than mention a few conspicuous aspects of this vast field. The transition metals generally form compounds that have compositions ME_n, where $n = 1, 2,$ or 3. There are hundreds known and they vary in properties, but most of them are hard, insoluble, relatively unreactive, and semiconducting. Three of the principal structural types are represented by: (*a*) $CoAs_3$ (skutterudite), which has a cubic structure in which square As_4 rings are found; (*b*) NiAs, in which each As is in a trigonal prism of Ni atoms while each Ni atom is in the center of a hexagonal bipyramid of six As and two Ni atoms. This type of structure has a pronounced tendency to be nonstoichiometric and phases with compositions approaching ME_2 can be obtained.

For As, Sb, and Bi, there is an important series of compounds formed with the Group IIIA(13) elements. These are commonly called III–V compounds (based on the traditional group numbering in the periodic table) and they have important applications as semiconductors. To illustrate, GaAs is isoelectronic to silicon, but a greater range of properties can be achieved because composition can be more easily varied. The disadvantage of III–V compounds relative to silicon based semiconductors is that they are reactive towards moisture and must be encapsulated (see also Section 9-5).

Zintl Phases. The Group VA(15) elements all react with alkali and alkaline earth elements to form a considerable number of these which contain E_n^{m-} anions. Characterization of the E_n^{m-} ions has for the most part been accomplished by dissolving the solids in liquid NH_3 or $H_2NCH_2CH_2NH_2$ and adding 2,2,2-crypt to complex the cations. The resulting crystalline materials, such as $[K(2,2,2\text{-crypt})]_2Bi_4$, can then be examined by X-ray crystallography. In this way, it has been shown that the following principal types of Zintl anions exist.

1. Square E_4^{2-} for As, Sb, and Bi (Fig. 11-3).
2. The E_7^{3-} ions (Fig. 11-3). Note that P_4S_3 is isostructural and isoelectronic with P_7^{3-}. The Bi_7^{3-} ion, though reported, may not exist.
3. As_5^{3-}, As_6^{4-}, P_{11}^{3-}, and As_{11}^{3-} are all known.[6]

It has recently been shown that structural information can be obtained

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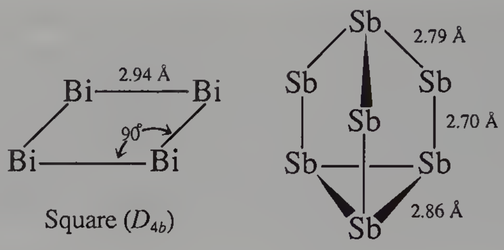
[6] C. N. E. Belin, *J. Am. Chem. Soc.*, 1980, **102,** 6063.



Square (D_{4h})

Capped trigonal prism (C_{3v})

FIG. 11-3. The structures of two important Zintl anions formed by Group VA(15) elements. (a) The Bi_4^{2-} ion (cf. A. Cisar and J. D. Corbett, *Inorg. Chem.*, 1977, **16,** 2482). (b) The Sb_7^{3-} ion (cf. J. C. Corbett *et al., J. Am. Chem. Soc.*, 1976, **98,** 7234).

directly on solutions of the Zintl phases by EXAFS (extended X-ray absorption fine structure).[7a]

11-4. Hydrides[7b]

The gases MH_3 can be obtained by treating phosphides or arsenides of electropositive metals either with acids or by reduction of sulfuric acid solutions of arsenic, antimony, or bismuth with an electropositive metal or electrolytically. The stability falls rapidly down the group, so the SbH_3 and BiH_3 are very unstable thermally, the latter having been obtained only in traces. The average bond energies are in accord with this trend in stabilities: E_{N-H}, 391; E_{P-H}, 322; E_{As-H}, 247; and E_{Sb-H}, 255 kJ mol^{-1}.

Phosphine (PH_3) is readily obtained by the action of dilute acid on calcium or aluminum phosphide, by pyrolysis of H_3PO_3 or, in a purer state, by the action of KOH in PH_4I. On a large scale, PH_3 is made by the action of NaOH on white phosphorus, which also forms sodium hypophosphite (Section 11-16).

The molecule is pyramidal with an HPH angle of 93.7°. Phosphine, when pure, is not spontaneously flammable, but often inflames owing to traces of P_2H_4 or P_4 vapor. It is readily oxidized by air when ignited, and explosive mixtures may be formed. It is also exceedingly poisonous. Unlike NH_3, it is not associated in the liquid state and it is only sparingly soluble in water; pH measurements show that the solutions are neither basic nor acidic—the acid constant is $\sim 10^{-29}$ and the base constant $\sim 10^{-26}$. However, it does react with some acids to give phosphonium salts (Section 11-10), and in basic solution we have

$$\tfrac{1}{4}P_4 + 3H_2O + 3e = PH_3 + 3OH^- \qquad E^0 = -0.89 \text{ V}$$

[7a] J. Roziére *et al., Inorg. Chem.*, 1985, **24,** 3710.
[7b] M. Baudler, *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 419.

The proton affinities of PH_3 and NH_3 (eq. 11-1) differ considerably.

$$EH_3(g) + H^+(g) = EH_4^+(g) \qquad (11\text{-}1)$$

$$\Delta H^0 = 770 \text{ kJ mol}^{-1} \text{ for E} = \text{P}$$

$$\Delta H^0 = 866 \text{ kJ mol}^{-1} \text{ for E} = \text{N}$$

Also, the barrier to inversion for PH_3 is 155 kJ mol^{-1} as compared with only 24 kJ mol^{-1} for NH_3. Quite generally the barriers for R_3P and R_3N compounds differ by about this much. Like other PX_3 compounds, PH_3 (and also AsH_3) forms complexes with transition metals [e.g., *cis*-$Cr(CO)_3(PH_3)_3$].

Arsine (AsH_3) is extremely poisonous. Its ready thermal decomposition to arsenic, which is deposited on hot surfaces as a mirror, is utilized in tests for arsenic, for example, the well-known Marsh test, where arsenic compounds are reduced by zinc in HCl solution.

Stibine is very similar to arsine but even less stable.

All these hydrides are strong reducing agents and react with solutions of many metal ions, such as Ag^I and Cu^{II}, to give the phosphides, arsenides, or stibnides, or a mixture of these with the metals.

Phosphorus alone forms other hydrides. *Diphosphine* (P_2H_4) is obtained along with phosphine by hydrolysis of calcium phosphide and can be condensed as a yellow liquid. It is spontaneously flammable and decomposes on storage to form polymeric, amorphous yellow solids, insoluble in common solvents and of stoichiometry approximating to, but varying around, P_2H. Unlike N_2H_4, diphosphine has no basic properties. On photolysis it gives P_3H_5. It exists mainly in the gauche form (cf. hydrazine, Section 10-5).

11-5. Halides

The major types are the trihalides (EX_3), the pentahalides (EX_5), and the dielement tetrahalides (E_2X_4). We shall discuss them in that order. All trihalides except PF_3 are best obtained by direct halogenation, keeping the element in excess, whereas the pentahalides may all be prepared by reaction of the elements with excess halogen. Special methods are used for E_2X_4 compounds.

Trihalides. These are listed in Table 11-3; all 16 are known, but only a few merit discussion.

All the trihalides are rapidly hydrolyzed by water and are rather volatile. The gaseous molecules have pyramidal structures, and some form molecular lattices. The iodides AsI_3, SbI_3, and BiI_3 crystallize in layer lattices with no discrete molecules. Bismuth trifluoride has an ionic lattice, and SbF_3 has an intermediate structure in which SbF_3 molecules (Sb—F = 1.92 Å) are linked through F bridges (Sb···F, 2.61 Å) to give each Sb^{III} a very distorted octahedral environment.

Mixed trihalides can be detected in mixtures, but it is not certain, despite

TABLE 11-3
The Trihalides of the Group VA(15) Elements (mp and bp in °C)

Fluorides		Chlorides		Bromides		Iodides	
PF_3	bp −101.8	PCl_3	bp 76.1	PBr_3	bp 173.2	PI_3	mp 61.2
AsF_3	bp 62.8	$AsCl_3$	bp 103.2	$AsBr_3$	mp 31.2 bp 221.0	AsI_3	mp 140.0
SbF_3	mp 292.0	$SbCl_3$	mp 73.17	$SbBr_3$	mp 97.0	SbI_3	mp 171.0
BiF_3	mp 725.0	$BiCl_3$	mp 233.5	$BiBr_3$	mp 219.0	BiI_3	mp 408.6

some older claims, that any can be isolated in pure form since the equilibria, for example,

$$PCl_3 + PBr_3 \rightleftharpoons PCl_2Br + PClBr_2$$

are labile.

Phosphorus trifluoride is a colorless gas, best made by fluorination of PCl_3. It forms complexes with transition metals similar to those formed by carbon monoxide (Section 2-8). Like CO, it is highly poisonous because of the formation of a hemoglobin complex. Unlike the other trihalides, PF_3 is hydrolyzed only slowly by water, but it is attacked by alkalis.

Phosphorus trichloride has an extensive chemistry (see Fig. 11-4) and is made on an industrial scale. In addition to the reactions shown in Fig. 11-4, PCl_3 reacts with the AgCN to give $P(CN)_3$.

Phosphorus triiodide has been shown[8a] to be a useful oxygen atom abstracting agent converting R_2SO to R_2S and RCH_2NO_2 to RCN, for example.

Arsenic, antimony, and bismuth trihalides comprise 12 compounds that

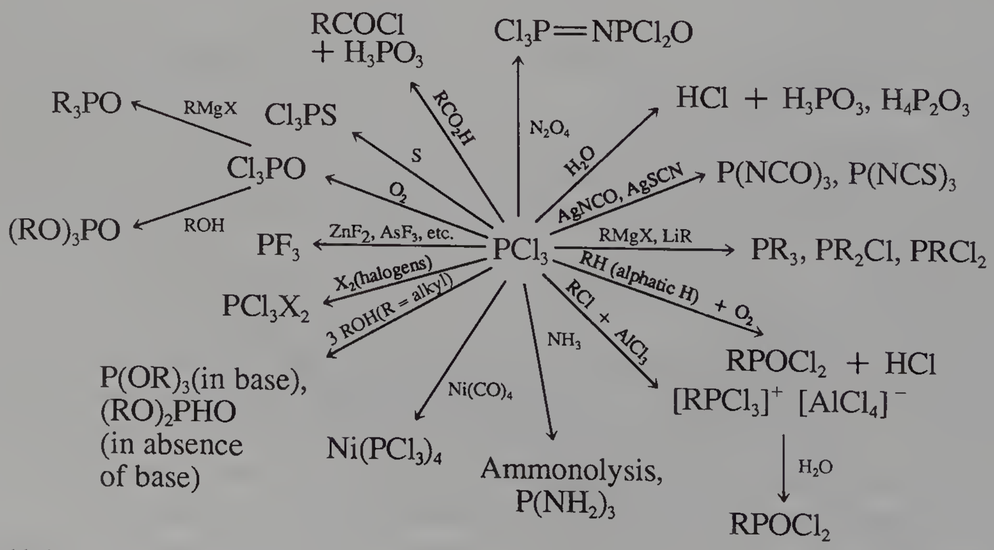


FIG. 11-4. Some important reactions of PCl_3. Many of these are typical for other MX_3 compounds as well as for MOX_3 compounds.

[8a] J. N. Denis and A. Krief, *J. Chem. Soc. Chem. Commun.*, **1980**, 544.

exhibit diversity in their physical and chemical properties, as well as considerable variations in their structures. Some, such as AsF_3, $AsCl_3$, $AsBr_3$, $SbCl_3$, and $SbBr_3$ are essentially molecular, and they give pyramidal EX_3 molecules readily in the vapor phase. For the iodides, the solids have close-packed arrays of I atoms with E atoms in octahedral interstices but located off-center so that incipient EI_3 molecules can be considered to exist.

Bismuth trichloride also has a quasimolecular structure in the solid, but with significant distortion. It differs from other EX_3 compounds in being readily hydrolyzed by water to BiOCl, but this redissolves in concentrated aqueous HCl, and $BiCl_3$ is recovered on evaporation. Antimony trichloride has somewhat similar behavior.[8b] Bismuth trifluoride has an ionic type of structure (like that of YF_3), with nine-coordination of the bismuth.

Arsenic trifluoride and especially SbF_3 (called the Swarts reagent) are very useful reagents for fluorination of various nonmetallic substrates, as indicated by the following conversions:

$$RCl \longrightarrow RF$$

$$SiCl_4 \longrightarrow SiCl_3F,\ SiCl_2F_2,\ SiClF_3$$

$$R_3PS \longrightarrow R_3PF_2$$

Arsenic trichloride and $SbCl_3$ also have some utility as nonaqueous solvents.[8c] It is doubtful that they undergo significant self-ionization (although this has been proposed, namely, to $ECl_2^+ + ECl_4^-$) but they have low viscosities, high dielectric constants, liquid ranges of ~150°C, and are good media for Cl^- transfer reactions.

Pentahalides. As indicated in Table 11-4, the four pentafluorides are all well known. Phosphorus pentafluoride, which may be prepared by fluorinating PCl_5 with AsF_3 or CaF_2 is molecular, with a *tbp* structure under all conditions. It is a colorless gas (bp −102°C), which reacts readily with Lewis bases such as amines and ethers, as well as F^-, to form six-coordinate complexes.[9] The fluxional character of the molecule, whereby the axial and equatorial F atoms change places rapidly on the NMR time scale is well known and is generally explained in terms of the Berry pseudorotation process (see Section 29-12).

Arsenic pentafluoride is generally similar to PF_5, but SbF_5 is markedly different. It is associated through F bridges even in the gas phase.[10] In the liquid state it is extremely viscous due to the formation of linear polymers believed to be as shown in (11-IV) and in the solid there are cyclic tetramers (11-V). Bismuth pentafluoride forms white needle crystals built of infinite

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[8b] J. F. Sawyer and R. J. Gillespie, *Progr. Inorg. Chem.*, 1986, **34**, 65 (review on Sb^{III} halides).

[8c] G. P. Smith *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 654.

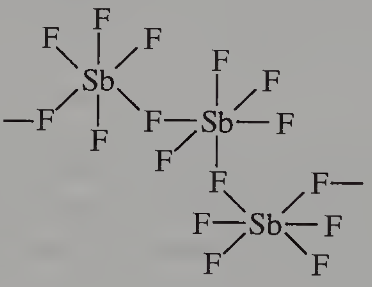
[9] R. R. Holmes, ACS Monographs, Nos. 175 and 176, 1980.

[10] J. Passmore, *J. Chem. Soc. Dalton Trans.*, **1985**, 9.

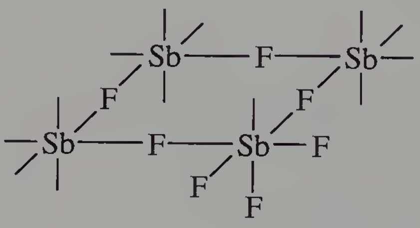
TABLE 11-4
Pentahalides of the Elements P, As, Sb, and Bi

Fluorides	Chlorides	Bromide	Iodide
	A. Binary		
PF_5	PCl_5	PBr_5	PI_5
AsF_5	$AsCl_5$		
SbF_5	$SbCl_5$		
BiF_5			
	B. Mixed		
PCl_4F	PCl_3F_2	PBr_2F_3	
		$[AsCl_4][AsF_6]$	
$SbCl_4F$	$SbCl_3F_2$	$SbCl_2F_3$	

linear chains of BiF_6 octahedra linked by trans bridges. The three heavier pentafluorides, especially BiF_5, are powerful fluorinating and oxidizing agents.



(11-IV)



(11-V)

Arsenic pentafluoride and SbF_5, and, to a lesser extent PF_5, are potent fluoride ion acceptors, forming MF_6^- ions or more complex species. The PF_6^- ion is a common and convenient *noncomplexing* anion, which has even less coordinating ability than ClO_4^- or BF_4^-.

In liquid HF, PF_5 is a nonelectrolyte, but AsF_5 and SbF_5 give conducting solutions, presumably because of the reactions

$$2HF + 2AsF_5 \longrightarrow H_2F^+ + As_2F_{11}^- \text{ (can be isolated as } Et_4N^+ \text{ salt)}$$

$$2HF + SbF_5 \longrightarrow H_2F^+ + SbF_6^-$$

The strong X^- acceptor capacity of the SbX_5 compounds leads to their use as Friedel–Crafts catalysts[11a] and to the ability of SbF_5 to enhance the acidities of HF(l) and HSO_3F(l) (Section 3-11).

The other pentahalides all have complex structural behavior centering around the existence of fairly stable EX_4^+ ions. Not all of the possible binary pentahalides are known, but there are quite a few mixed pentahalides. All of the binary ones and the better known mixed ones are listed in Table 11-4.

[11a] G. G. Yakobsen and G. G. Furin, *Synthesis*, **1980,** 345.

Some of the important structural features are the following:

Phosphorus pentachloride is molecular in the gas and liquid phases; when dissolved in nonpolar solvents, it may dimerize to a certain extent in some of them. However, it crystallizes to form $[PCl_4^+][PCl_6^-]$, and when dissolved in polar solvents (e.g., MeCN and $PhNO_2$) there are two forms of ionization whose relative importance depends in an obvious way on concentration:

$$2PCl_5 = [PCl_4^+] + [PCl_6^-]$$

$$PCl_5 = [PCl_4^+] + Cl^-$$

There is also a metastable solid form consisting of $[PCl_4^+]_2[PCl_6^-]Cl^-$. Compounds containing the PCl_4^+ and PCl_6^- ions form under other circumstances as well, for example, in the PCl_5–$TiCl_4$ system one can obtain $[PCl_4]_3[TiCl_6][PCl_6]$.[11b]

Phosphorus pentabromide appears to be wholly dissociated to $PBr_3 + Br_2$ in the gas phase and no liquid is known. The solid normally consists of $[PBr_4^+]Br^-$, but a form consisting of $[PBr_4^+][Br_3^-]PBr_3$ has been made by rapidly cooling the vapor at 15 K. The pentaiodide is not well known; it appears to be $[PI_4^+]I^-$ in solution.

Arsenic pentachloride can be prepared at low temperature but decomposes above ~ -50°C. Antimony pentachloride is made by reaction of Cl_2 with $SbCl_3$ and is stable up to ~140°C. The solid (mp 4°C) contains $Cl_4Sb(\mu\text{-}Cl)_2SbCl_4$ dimers. The curious instability of $AsCl_5$ relative to PCl_5 and $SbCl_5$ has been attributed to a stabilization of the $4s^2$ electron pair in all the elements immediately following the first transition series. Other consequences of this stabilization are found in the chemistry of Ga, Ge, Se, and Br, generally having to do with lower stability of the highest oxidation states.

The nonexistence of $BiCl_5$ and of EBr_5 and EI_5 compounds other than those of phosphorus can be attributed to the inability of the formally uninegative halogens to coexist with the oxidation state +5 of the Group VA(15) elements (cf. the nonexistence of FeI_3, CuI_2, TlI_3, etc.). There are many mixed halides, which are often ionic in nature. The halide PCl_4F has both a molecular and an ionic form, that is, $[PCl_4^+][PCl_4F_2^-]$. In the PCl_xF_{5-x} molecules, the chlorine atoms always prefer the equatorial and the fluorine atoms the axial positions,[12] in line with the general rule that the more electronegative groups prefer the axial positions in PX_xY_{5-x} molecules.

In strong acid media mixed halo cations $[PX_nY_{4-n}]^+$ can be generated by reactions of PX_3 with Y_2.[13]

Lower Halides. For P, As, and Sb, these are of the stoichiometry E_2X_4, and only some are known. The halides P_2Cl_4 and P_2Br_4 are least well characterized, while P_2F_4, P_2I_4, As_2I_4, and Sb_2I_4 are well defined. They all have

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[11b] J. Shamir, *Inorg. Chim. Acta,* 1986, **111,** 141.

[12] K. Hedberg *et al., Inorg. Chem.,* 1985, **24,** 2774.

[13] K. B., Dillon *et al., J. Chem. Soc. Dalton Trans.,* **1979,** 1591.

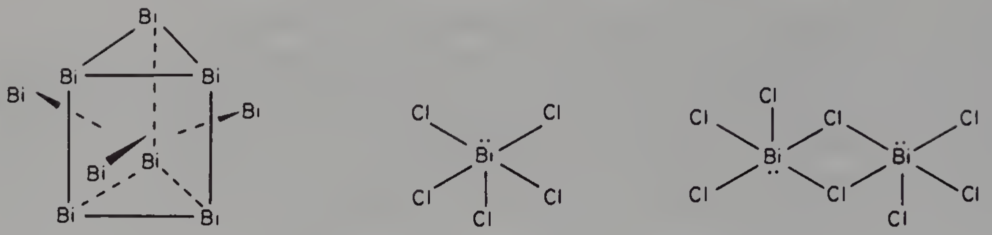

FIG. 11-5. The structures of the species present in BiCl, which is, in fact, $Bi_{24}Cl_{28}$.

an $X_2E—EX_2$ type of structure, and all are reactive. Arsenic tetraiodide and Sb_2I_4 decompose on standing to $EX_3 + E$.

No Bi_2X_4 compound is known, but it has long been known that when metallic bismuth is dissolved in molten $BiCl_3$ a black solid of approximate composition BiCl can be obtained. This solid is $Bi_{24}Cl_{28}$, and it has an elaborate constitution, consisting of four $BiCl_5^{2-}$, one $Bi_2Cl_8^{2-}$, and two Bi_9^{5+} ions, the structures of which are depicted in Fig. 11-5. The electronic structure of the Bi_9^{5+} ion, a metal atom cluster, has been treated in terms of delocalized molecular orbitals. Other low-valent species present in various molten salt solutions are Bi^+, Bi^{3+}, Bi_5^{3+}, and Bi_8^{2+}. The last, in $Bi_8(AlCl_4)_2$ has a square antiprismatic structure.[14]

Several intermediate antimony halides, that is, $(SbF_3)_x(SbF_5)_y$, with $x = y = 1$; $x = 6$ and $y = 5$; $x = 2$ and $y = 1$; $x = 3$ and $y = 1$ are known. Their existence, and their structures, depend on the high fluoride ion affinity of SbF_5, whereby SbF_6^- ions and complex polymeric cations, such as $(Sb_3F_8^+)_\infty$ are formed.[15]

11-6. Complexes of the Halides

Oxidation State III. Phosphorus trihalides have virtually no Lewis basicity, though a PBr_4^- ion has been observed.

Arsenic(III) halides display limited but significant Lewis basicity and form the $As_2Cl_8^{2-}$, $As_2Br_8^{2-}$ and $(AsBr_4^-)_n$ anions. The first two consist of AsX_5 square pyramids sharing an edge (similar to $Bi_2Cl_8^{2-}$ as shown in Fig. 11-5), and the last is an infinite chain similar to that in $pyHSbCl_4$ to be discussed later.

It is with Sb^{III} and Bi^{III} that really extensive complex formation occurs. Antimony trichloride forms complexes with neutral donors; those with $PhNH_2$ have structures showing that the N—Sb bonds are relatively weak and that the lone pair is stereochemically active, as illustrated in Fig. 11-6. The variations in Sb—Cl distances are in very good accord with the three-center bond model discussed in Section 1-6. Antimony trichloride also forms 2:1 and 1:1

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[14] B. Krebs *et al., Angew. Chem. Int. Ed. Engl.*, 1982, **21,** 445.
[15] J. Passmore *et al., J. Chem. Soc. Dalton Trans.*, **1983,** 619.

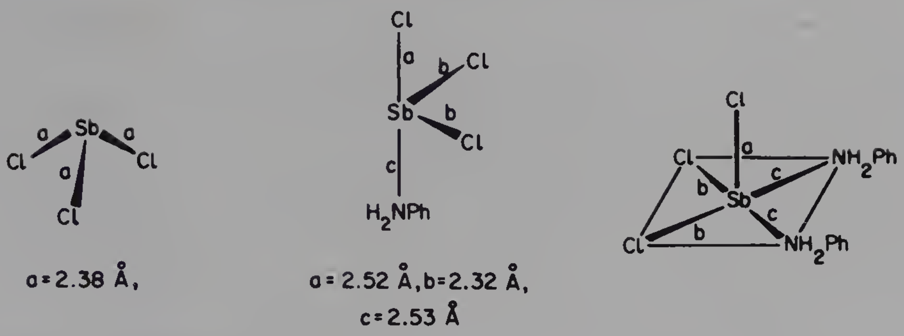


FIG. 11-6. The structures of $SbCl_3$ and two of its aniline complexes.

complexes with aromatic hydrocarbons such as naphthalene or *p*-xylene, where weak interaction between $SbCl_3$ and the π cloud occurs.

There are some EX_4^- containing compounds, where the EX_4^- ions have the same type of ψ-*tbp* structure as isoelectronic molecules such as SeF_4. On the other hand, it is very common for compounds whose formulas (e.g., $KSbF_4$) might suggest the presence of discrete EX_4^- ions to have much more complex anions resulting from association via μ-X groups. Similarly, while a few discrete MX_5^- ions are found (with ψ-octahedral structures, like IF_5), association into larger, X-bridged aggregates is very common. Some representative examples are shown in Figs. 11-7 and 11-8.

There are also EX_6^{3-} complexes, and many of them have been shown to have regular octahedral structures, despite the fact that they have an "extra" pair of valence shell electrons, that is, a total of 14 rather than 12. Examples are $(NH_4)_2SbBr_6$, which is *not* an Sb^{IV} compound, but rather consists of $(NH_4)_4(Sb^{III}Br_6)(Sb^{V}Br_6)$ and $(Me_2NH_2)_3BiBr_6$, in which there is only a slight distortion (quite possibly attributable to packing forces) from octahedral symmetry. The usual explanation for this lack of a stereochemical effect due to the extra pair of electrons is that they occupy the *ns* orbital and do not play a direct role in bonding. There are also a number of $E_2X_9^{3-}$ species with confacial bioctahedral structures, for example, in compounds such as the cesium salts $Cs_3E_2Cl_9$ (E = Sb and Bi).

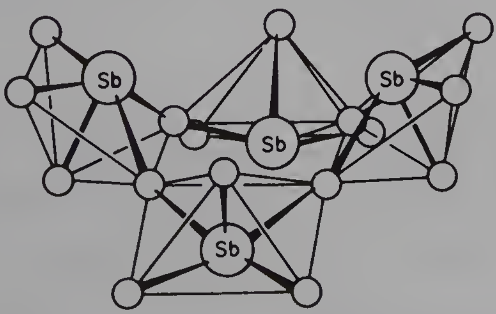
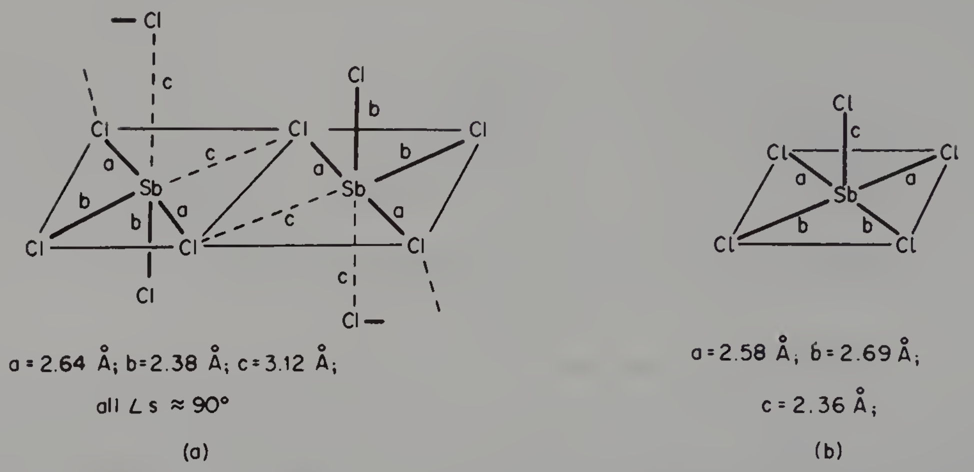


FIG. 11-7. The structure of the $Sb_4F_{16}^{4-}$ ion in $KSbF_4$.



(a) (b)

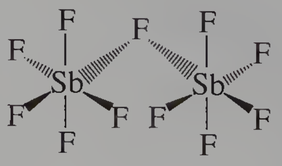
FIG. 11-8. (a) A portion of the anion chain in $(pyH)SbCl_4$. (b) The $SbCl_5^{2-}$ ion found in $(NH_4)_2SbCl_5$.

It is not easy to forecast when there will be a stereochemically active lone pair in these E^{III} complexes, but the following general trends can be noted. Stereochemical activity of the lone pair decreases with (1) increasing coordination numbers, (2) increasing atomic number of the halogen, and (3) increasing atomic number of E (i.e., As > Sb > Bi).

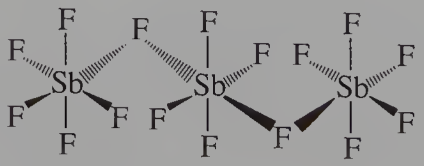
Oxidation State V. Here the behavior is a bit less complex; the overwhelming tendency is for the EX_5 molecules to interact with an electron donor (L) to give octahedral or distorted octahedral complexes, $EX_5L^{0,-}$.[16] When L = X, which is perhaps the most important case, the hexahalo anions (EX_6^-), which are strictly octahedral, are obtained.

The PF_6^- ion is important in preparing compounds where an anion of very low coordinating power is required; along with BF_4^- and $CF_3SO_3^-$ it affords a safe alternative to ClO_4^-, which should be avoided because of its tendency to give explosive compounds. The PCl_6^- and PBr_6^- ions are also known.

Complexes of Sb^V with fluorine and chlorine are numerous. The simple SbF_6^- and $SbCl_6^-$ ions are well characterized and occur with a great variety of cations, including some very exotic ones such as O_2^+, S_2N^+, and polyhalogeno cations such as ICl_2^+ or IBr_2^+.[17] More elaborate anions can be formed by association through F bridges. Thus, the $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$ ions (11-VI and 11-VII) are known. The angle at the μ-F atom of the $Sb_2F_{11}^-$ ion varies somewhat but is generally 150 to 160°.



(11-VI)



(11-VII)

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[16] L. Riesel and M. Kant, *Z. Anorg. Allg. Chem.*, 1985, **530**, 207.
[17] T. Birchall and R. D. Meyers, *Inorg. Chem.*, 1983, **22**, 1751.

11-7. Oxides

The following are the established oxides; those in [ ] are poorly characterized:

P_4O_6	$As_4O_6(As_2O_3)$	$Sb_4O_6(Sb_2O_3)$	Bi_2O_3
P_4O_7			
P_4O_8		Sb_2O_4	
P_4O_9			
P_4O_{10}	As_2O_5	Sb_2O_5	$[Bi_2O_5]$
$[P_2O_6]$			

Phosphorus Oxides. The five well-characterized ones form a structurally homologous series.[18a] The structures of the end members, P_4O_6 and P_4O_{10} are shown in Fig. 11-9. The intermediate ones have 1, 2, or 3 exo oxygen atoms added to the P_4O_6 structure. Preparative methods for the intermediate members are varied and not simple and will not be given here.

The *pentoxide,*[18b] P_4O_{10}, so-called for historical reasons, is usually the main product of burning phosphorus; conditions can be optimized to make it the sole product. It is a white, crystalline solid that sublimes at 360°C (1 atm) and this affords a good method of purifying it from its commonest impurities, which are nonvolatile products of incipient hydrolysis. The hexagonal crys-

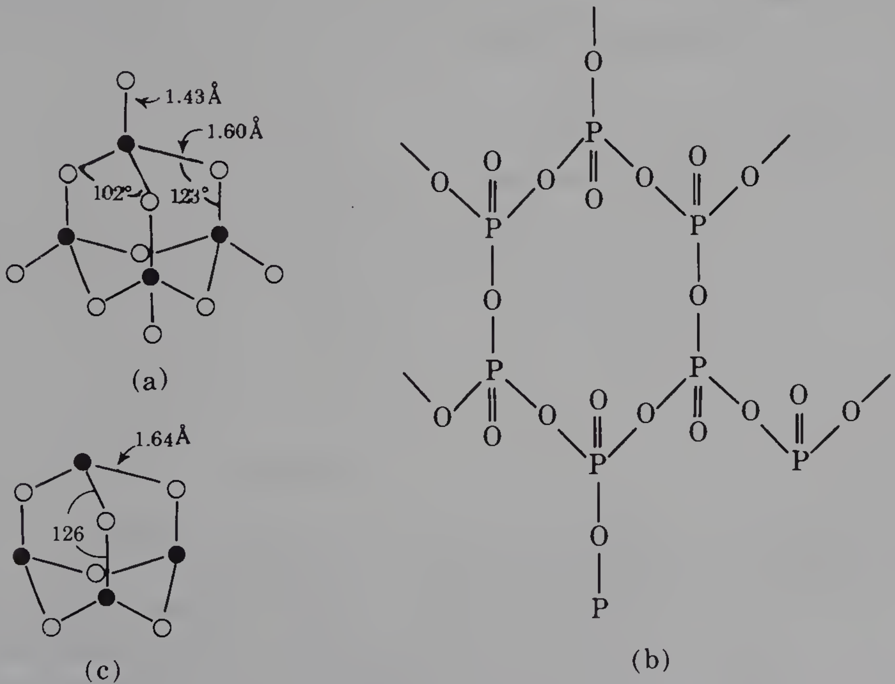


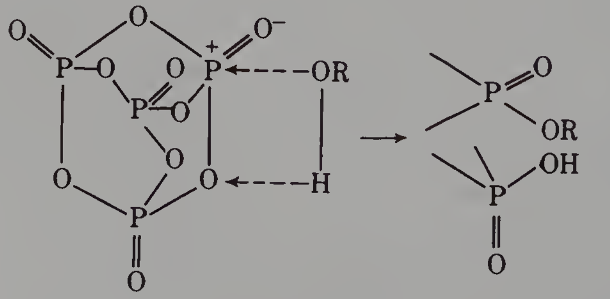
FIG. 11-9. The structures of (a) P_4O_{10} molecules (T_d); (b) P_4O_{10} sheets; (c) P_4O_6 molecules (T_d).

[18a] M. Jansen and M. Moebs, *Inorg. Chem.*, 1984, **23,** 4486.
[18b] B. D. Sharma, *Inorg. Chem.*, 1987, **26,** 454.

talline form (H form) obtained on sublimation contains P_4O_{10} molecules [Fig. 11-9(a)] in which a P_4 tetrahedron has six edge-bridging(br) oxygen atoms and four terminal(t) ones. These molecules, which persist in the gas phase, have full tetrahedral (T_d) symmetry, and the P—O(br) and P—O(t) distances are 1.604 and 1.429 Å, respectively, by gas phase electron diffraction. Other crystalline and glassy forms, obtained by heating the H form, have infinite sheets [Fig. 11-9(b)]; note that the local environment of each phosphorus atom is the same as that in the P_4O_{10} molecule.

The most important chemical property of P_4O_{10} is its avidity for water. It is one of the most effective drying agents known at temperatures below 100°C. It reacts with water to form a mixture of phosphoric acids whose composition depends on the quantity of water and other conditions. It will even extract the elements of water from many other substances themselves considered good dehydrating agents; for example, it converts pure HNO_3 into N_2O_5 and H_2SO_4 into SO_3. It also dehydrates many organic compounds (e.g., converting amides into nitriles). With alcohols it gives esters of simple and polymeric phosphoric acids depending on reaction conditions.

The breakdown of P_4O_{10} with various reagents (alcohols, water, phenols, ethers, alkyl phosphates, etc.) is a very general one and is illustrative also of the general reaction schemes for the breakdown of P_4S_{10} and for the reaction of P_4 with alkali to give PH_3, hypophosphite, and so on. The reaction initially involves breaking a P—O—P bridge. Thus an alcohol reacts with P_4O_{10} as in eq. 11-2, followed by further reaction at the next most anhydridelike linkage, until eventually products containing only one P atom are produced (eq. 11-3).



(11-2)

$$P_4O_{10} + 6\,ROH \longrightarrow 2\,(RO)_2PO{\cdot}OH + 2\,RO{\cdot}PO(OH)_2 \qquad (11\text{-}3)$$

The fusion of P_4O_{10} with basic oxides gives solid phosphates of various types, their nature depending on experimental conditions.

The *trioxide,* P_4O_6, again so named for historical reasons, has a structure of tetrahedral symmetry similar to that of P_4O_{10} except that the four terminal oxygen atoms are not present [Fig. 11-9(c)], and the P—O(br) distances, 1.638 Å, are slightly longer. It is a colorless, volatile (mp 23.8°C, bp 175°C) compound formed in ~50% yield when white phosphorus is burned in an oxygen-deficient atmosphere. It is difficult to separate by distillation from traces of unchanged phosphorus, but irradiation with uv light changes the white phosphorus into red, from which the P_4O_6 can be separated by dissolution in organic solvents. The chemistry of P_4O_6 is not well known, but it appears to be complex.

When heated above 210°C, P_4O_6 decomposes into red P and other oxides (PO_x). It reacts vigorously with chlorine and bromine to give the oxo halides and with iodine in a sealed tube to give P_2I_4. It is stable to oxygen at room temperature. When it is shaken vigorously with an excess of cold water, it is hydrated exclusively to phosphorous acid (H_3PO_3), of which it is formally the anhydride; P_4O_6 apparently cannot be obtained by dehydration of phosphorous acid. The reaction of phosphorus trioxide with *hot* water is very complicated, producing among other products PH_3, phosphoric acid, and elemental P; it may be noted in partial explanation that phosphorous acid itself, and all trivalent phosphorus acids generally, are thermally unstable, for example,

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

Arsenic Oxides. *Arsenic trioxide* (As_4O_6), formed on burning the metal in air, has in the ordinary form the same structure as P_4O_6. In another crystalline form there are AsO_3 pyramids joined through oxygen atoms to form layers. The ordinary form is soluble in various organic solvents as As_4O_6 molecules and in water to give solutions of "arsenious acid," which is probably $As(OH)_3$ though it has never been firmly characterized. The As_2O_3 dissolves in aqueous bases to give arsenite ions such as $[AsO(OH)_2]^-$, $[AsO_2(OH)]^{2-}$, and $[AsO_3]^{3-}$.

Arsenic pentoxide cannot be obtained by direct reaction of arsenic with oxygen. It is prepared by oxidation of As with nitric acid followed by dehydration of the arsenic acid hydrates so obtained. It readily loses oxygen when heated to give the trioxide. It is very soluble in water, giving solutions of arsenic acid. It has a structure similar to that of β-Ga_2O_3 with cations in adjacent tetrahedral and octahedral oxygen environments.

Antimony Oxides. Antimony *trioxide* is obtained by direct reaction of the element with oxygen. In the vapor and in the solid below 570°C it consists of P_4O_6-type molecules; the high-temperature solid form is polymeric. It is insoluble in water or dilute nitric and sulfuric acids, but soluble in hydrochloric and certain organic acids. It dissolves in bases to give solutions of antimonates(III). The yellow *pentoxide* is made mainly by the action of oxygen at high pressure and temperature on Sb_2O_3; it has a structure similar to that of Nb_2O_5 with octahedral SbO_6 groups. Treatment of elemental Sb with concentrated HNO_3 gives a mixture of Sb_2O_3 and $Sb_4O_4(OH)_2(NO_3)_2$; the latter decomposes on heating at 135°C in air to Sb_2O_3.[19a]

When either the tri- or the pentoxide is heated in air at about 900°C, a white insoluble powder of composition SbO_2 is obtained. Both α- and β-forms are recognized, and the former has been shown to consist of Sb^V in octahedral interstices and $Sb^{III}O_4$ pyramidal units.

Bismuth Oxides. The only well-established oxide of bismuth is Bi_2O_3, a

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[19a] F. J. Berry and M. E. Brett, *Inorg. Chim. Acta*, 1984, **83**, 167.

yellow powder soluble in acids to give bismuth salts; being insoluble in alkalis, however, it has no acidic character. From solutions of bismuth salts, alkali, or ammonium hydroxide precipitates a *hydroxide,* $Bi(OH)_3$. Like the oxide, this compound is completely basic. *Bismuth(V) oxide* is extremely unstable and has never been obtained in pure form. The action of extremely powerful oxidizing agents on Bi_2O_3 gives a red-brown powder that rapidly loses oxygen at 100°C.

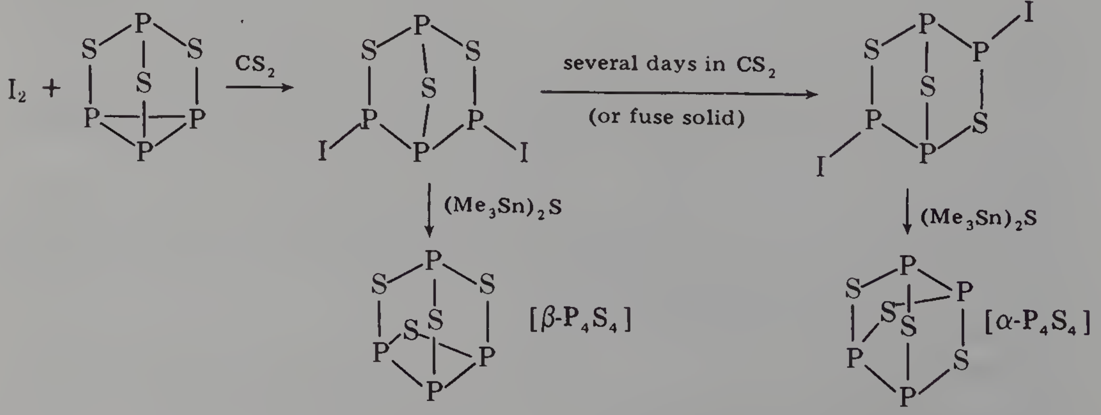
The oxides of the Group VA(15) elements clearly exemplify two important trends that are manifest to some extent in all main groups of the Periodic Table: (1) the stability of the higher oxidation state decreases with increasing atomic number, and (2) in a given oxidation state the metallic character of the elements, therefore the basicity of the oxides, increase with increasing atomic number. Thus P^{III} and As^{III} oxides are acidic, Sb^{III} oxide is amphoteric, and Bi^{III} oxide is strictly basic.

11-8. Sulfides and Other Chalcogenides

Like the oxides, sulfides[19b] and other chalcogenides are mostly based structurally on a tetrahedral array of P or As atoms with bridging S or Se atoms and, less commonly, terminal S or Se, but the details differ a good deal. We shall discuss in detail only the phosphorus sulfides. The known structures are shown in Fig. 11-10. In many cases these structures are known quantitatively from X-ray crystallography, but for some only the qualitative structure is available from ^{31}P nmr.

The molecular sulfides P_4S_3, P_4S_7, P_4S_9, and P_4S_{10} are prepared by heating together red phosphorus and sulfur in the formula ratios. Melts of composition intermediate between P/S = 4:3 and P/S = 4:7 contain at least five other molecular phosphorus sulfides. These cannot be efficiently separated, but may be prepared separately in other ways.

α- and β-P_4S_4. Iodine adds across a P—P bond in P_4S_3 to give β-$P_4S_3I_2$, which slowly isomerizes to α-$P_4S_3I_2$. The latter may also be obtained directly by heating the elements together. The following scheme shows the quantitative conversion of α- and β-$P_4S_3I_2$ to α- and β-P_4S_4 by bis(trimethytin)sulfide in CS_2:



[19b] M. Meisel, *Z. Chem.*, 1985, **23,** 117.

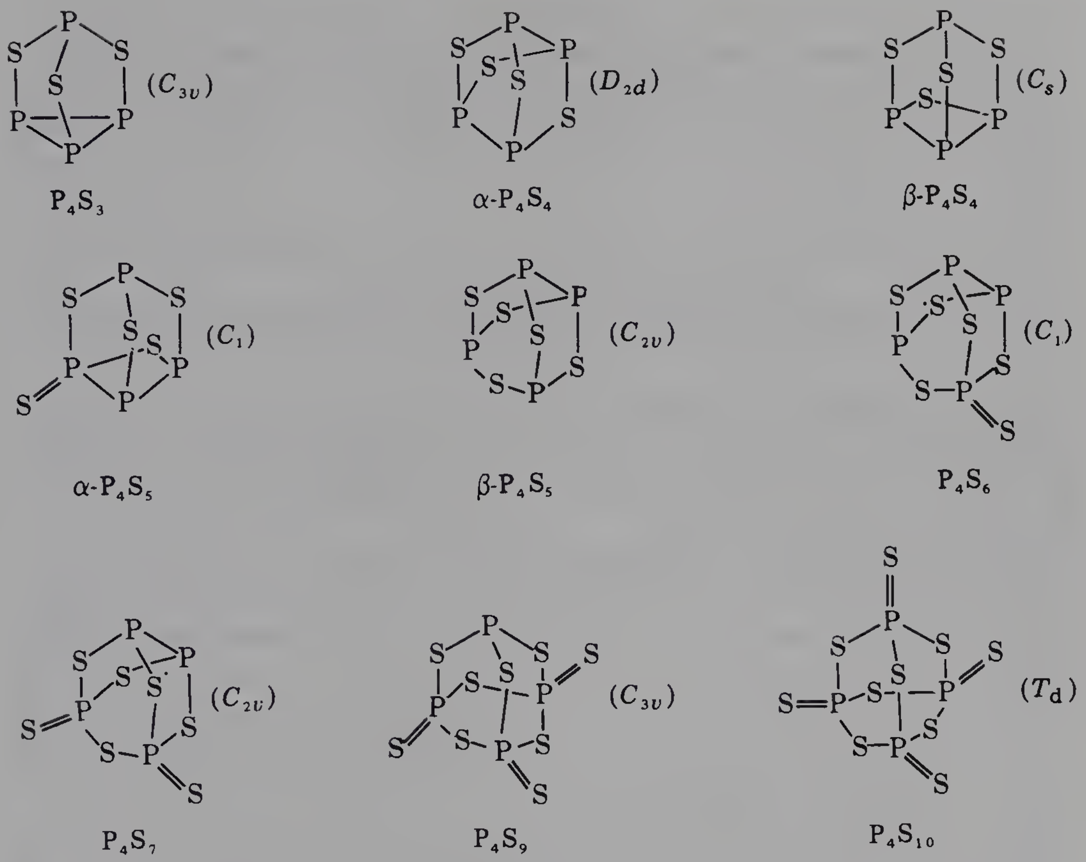

P_4S_3 α-P_4S_4 β-P_4S_4 α-P_4S_5 β-P_4S_5 P_4S_6 P_4S_7 P_4S_9 P_4S_{10}

FIG. 11-10. Structures of P_4S_n molecules.

α- and β-P_4S_5 are obtained by the following reactions:

$$5P_4S_3 + 12Br_2 \longrightarrow 3\alpha\text{-}P_4S_5 + 8PBr_3$$

$$P_4S_7 + 2Ph_3P \longrightarrow \beta\text{-}P_4S_5 + 2Ph_3PS$$

In the second reaction P_4S_6 is an intermediate, but has not been isolated pure as it forms mixed crystals with P_4S_7. Its structure is inferred from those of P_4S_7 and β-P_4S_5. Triphenyl phosphine is a general reagent for removal of terminal S and can also be used to prepare P_4S_9 from P_4S_{10} and β-P_4S_4 from α-P_4S_5.

All the P_4S_n compounds are stable in CS_2 solution except for P_4S_4, which slowly disproportionates into α-P_4S_5 and P_4S_3. All structures derive from a P_4 tetrahedron by replacement of P—P units by P—S—P and by addition of terminal S atoms. The sulfide P_4S_3 is industrially used in making "strike-anywhere" matches, while P_4S_{10} is used in organic chemistry to convert organic CO, CO_2H, CONH, and OH groups to their sulfur analogues, and in the preparation of industrial lubricant additives. All of these sulfides are more or less readily hydrolyzed to H_3PO_4 or other oxo acids.

There are other Group VA(15) chalcogenides that conform to the structural pattern of the phosphorus sulfides. These are displayed in Table 11-5. In addition to these, arsenic forms As_2S_3 and As_2Se_3, which have layer structures,

TABLE 11-5

Structurally Analogous Group VA(15) Molecular Chalcogenides

P_4S_3[a]	α-P_4S_4	β-P_4S_4	α-P_4S_5	P_4S_7	P_4S_{10}
P_4Se_3	P_4Se_4		P_4Se_5	P_4Se_7	P_4Se_{10}
As_4S_3	α-,β-As_4S_4[b]	γ-As_4S_4	As_4S_5		As_4S_{10}
As_4Se_3	As_4Se_4				

[a] P_7^{3-} and As_7^{3-} have the same type of structure, as do P_7H_3 and P_7R_3 compounds, where PH or PR replaces S.

[b] α- and β-As_4S_4 have the same molecular structure but a different crystal packing (cf. F. J. Porter and G. M. Sheldrick, *J. Chem. Soc. Dalton Trans.*, **1972**, 1347).

and As_2S_5 (of unknown structure). The sulfides As_2S_3 and As_2S_5 can be precipitated from aqueous solutions of As^{III} and As^V by H_2S. They are insoluble in water but acidic enough to dissolve in alkali sulfide solutions to form thio anions.

Antimony forms Sb_2S_3 either by direct combination of the elements or by precipitation with H_2S from Sb^{III} solutions; it dissolves in an excess of sulfide to give anionic thio complexes, probably mainly SbS_3^{3-}. Antimony(III) sulfide (Sb_2S_3), as well as Sb_2Se_3 and Bi_2S_3, have a ribbonlike polymeric structure in which each Sb atom and each S atom is bound to three atoms of the opposite kind, forming interlocking SbS_3 and SSb_3 pyramids (see Section 13-7). So-called antimony(V) sulfide (Sb_2S_5) is not a stoichiometric substance and according to Moßbauer spectroscopy contains only Sb^{III}.

Bismuth gives dark brown Bi_2S_3 on precipitation of Bi^{III} solutions by H_2S; it is not acidic. A sulfide BiS_2 is obtained as gray needles by direct interaction at 1250°C and 50 kbar; its structure is unknown but may be $Bi^{3+}[BiS_4]^{3-}$.

OTHER COMPOUNDS

11-9. Oxo Halides

The most important oxo halides are the *phosphoryl halides* (X_3PO), in which X may be F, Cl, Br, or I. The commonest (Cl_3PO) is obtained by the reactions

$$2PCl_3 + O_2 \longrightarrow 2Cl_3PO$$

$$P_4O_{10} + 6PCl_5 \longrightarrow 10Cl_3PO$$

The reactions of Cl_3PO are much like those of PCl_3 (Fig. 11-4). The halogens can be replaced by alkyl or aryl groups by means of Grignard reagents, and by alkoxo groups by means of alcohols; hydrolysis by water yields phosphoric acid. Phosphoryl chloride (Cl_3PO) also has donor properties toward metal ions, and many complexes are known. Distillation of the Cl_3PO complexes of $ZrCl_4$ and $HfCl_4$ can be used to separate zirconium and hafnium, and the very strong $Cl_3PO—Al_2Cl_6$ complex has been utilized to remove Al_2Cl_6 from adducts with Friedel–Crafts reaction products.

All X_3PO molecules have a pyramidal PX_3 group, with the oxygen atom occupying the fourth position to complete a distorted tetrahedron. The P—O bond lengths are about 1.55 Å, consistent with the existence of double bonds. Several mixed phosphoryl halides, phosphoryl pseudohalides, as well as X_3PS and X_3PSe compounds are also known. All of these compounds are prone to ready hydrolysis.

Some more complex oxohalides are known, of which the *pyrophosphoryl halides,* $X_2P(O)—O—P(O)X_2$, X = Cl, F are best known.

There are no definite, analogous X_3EO compounds except Cl_3AsO, which is unstable above −25°C. There are, however, some polymeric As and Sb compounds with μ-O atoms, such as $As_2O_3Cl_4$ (not isostructural with its P analogue), $Sb_4O_5Cl_2$, $Sb_8O_{11}Cl_2$, and Sb_8OCl_{22}. There are also some oxohalo anionic species, such as $[F_5EOEF_5]^{2-}$, E = As, Sb, and $[F_4As(\mu\text{-}O)_2AsF_4]^{2-}$.

Antimony and *bismuth* form the important oxo halides SbOCl and BiOCl, which are insoluble in water. They are precipitated when solutions of Sb^{III} and Bi^{III} in concentrated HCl are diluted. They have quite different but complicated, layer structures.

11-10. Phosphonium Compounds

Although organic derivatives of the type $[MR_4]^+X^-$ are well known for M = P, As, Sb and Bi, only phosphorus gives the prototype PH_4^+, and this does not form any very stable compounds. As noted in Section 11-4, the proton affinity of PH_3 is substantially less than that of NH_3. The PH_4^+ ion is tetrahedral, with P—H = 1.414 Å as compared to P—H = 1.44 Å in PH_3. The best-known phosphonium salt is the iodide, which is formed as colorless crystals on mixing of gaseous HI and PH_3. The chloride and bromide are even less stable; the dissociation pressure of PH_4Cl into PH_3 and HCl reaches 1 atm below 0°C. The estimated basicity constant of PH_3 in water is about 10^{-26}, and phosphonium salts are completely hydrolyzed by water, releasing the rather insoluble gas PH_3

$$PH_4I(s) + H_2O \longrightarrow H_3O^+ + I^- + PH_3(g)$$

The gas PH_3 dissolves in very strong acids such as $BF_3{\cdot}H_2O$ and $BF_3{\cdot}CH_3OH$ where it is protonated to PH_4^+.

The most readily produced compound is tetra(hydroxymethyl)phosphonium chloride obtained by the interaction of phosphine with formaldehyde in hydrochloric acid solution:

$$PH_3 + 4CH_2O + HCl \longrightarrow [P(CH_2OH)_4]^+Cl^-$$

It is a white crystalline solid, soluble in water and it is available commercially. On addition of base it forms $P(CH_2OH)_3$.

Phosphorus and, to a lesser extent, arsenic form many quaternary cations (R_4E^+) in which R may be alkyl, aryl, R_2N, halogen, and alkoxy, or mixtures thereof. The tetraalkyl and tetraaryl cations are common and easily made by the quaternization reaction.

$$R_3E + RX \longrightarrow [R_4E]^+X^-$$

For bismuth, only the Ph_4Bi^+ ion is known.

11-11. Phosphorus–Nitrogen Compounds

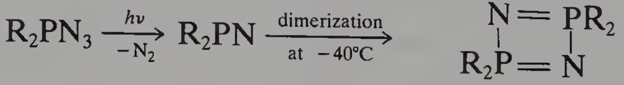
There is a very extensive chemistry of compounds with P—N and P═N bonds, but for the most part the molecules are oligomeric or polymeric. Among the few relatively simple ones are $(Me_2N)_3P$ and $(Me_2N)_3PO$ (hexamethylphosphoramide), several $X_2P—NMe_2$ (X = Cl, F, and CF_3) and $PF_3(NH_2)_2$ (which has equatorial NH_2 groups.[20a] The so-called PNP^+ (sometimes PPN^+) ion ($Ph_3PNPPh_3^+$) is widely used to isolate large anions in crystalline form or to give organic soluble reagents for use in synthesis.[20b]

Actually, the PNP cation is but one special example of a group of compounds called *phosphazenes*. Monophosphazenes ($R_3P{=}NR'$), diphosphazenes ($R_3P{=}N{-}PR_2'$), and polyphosphazenes ($R_3P{=}N{-}(PR_2{=}N)_n\cdots PR_2'$) are all known. Hundreds of monophosphazenes alone have been characterized, and a general synthetic route is

$$R_3PCl_2 + R'NH_2 \longrightarrow R_3P{=}NR' + 2HCl$$

However, it is the cyclophosphazenes and long-chain polyphosphazenes that have recently attracted the greatest attention.

Cyclophosphazenes. The simplest type, cyclodiphosphazenes, are scarcely known, the first one having only recently been reported.[21] This was obtained as shown in eq. 11-4.



(11-4)

$$R = Me_2HC—$$

The molecule is planar with essentially equal P—N distances (1.65 ± 0.01 Å), indicative of a delocalized π bond system. It is thermodynamically stable (mp 110°C) and not air sensitive. Presumably, other cyclodiphosphazenes will now be made.

The best known cyclophosphazenes are the trimeric and tetrameric ones, (11-VIII) and (11-IX), but much larger rings are well known. For $(NPMe_2)_n$ those with n from 3 to 12 are all fully characterized, including crystal structures.[22] The alternating sets of single and double bonds written in (11-VIII)

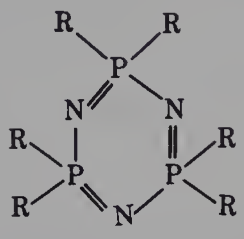
[20a] K. Hedberg *et al., Inorg. Chem.*, 1984, **23,** 3659.

[20b] W. L. Gladfelter and R. E. Stevens, *Inorg. Chem.*, 1983, **22,** 2034.

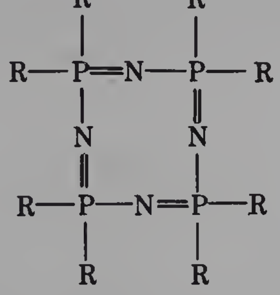
[21] G. Bertrand *et al., J. Am. Chem. Soc.*, 1984, **106,** 6088.

[22] N. L. Paddock *et al., J. Am. Chem. Soc.*, 1985, **107,** 6923.

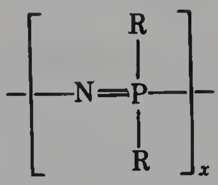
to (11-X) for convenience should not (see following structures) be taken literally.



(11-VIII)



(11-IX)



(11-X)

Hexachlorocyclotriphosphazene $(NPCl_2)_3$, is a key intermediate in the synthesis of many other phosphazenes and is readily prepared as follows:

$$n\mathrm{PCl_5} + n\mathrm{NH_4Cl} \xrightarrow{\text{in } C_2H_2Cl_4 \text{ or } C_6H_5Cl} (\mathrm{NPCl_2})_n + 4n\mathrm{HCl}$$

This reaction produces a mixture of $[NPCl_2]_n$ species, but under selected conditions high yields of the trimer and tetramer can be obtained. These can be readily separated. The trimer, a white crystalline solid (mp 113°C) that sublimes readily in vacuum at 50°C is commercially available; it is the source for synthesis of linear polymers discussed below.

The majority of phosphazene reactions involve replacement of halogen atoms by other groups to give partially or fully substituted derivatives, for example,

$$(\mathrm{NPCl_2})_3 + 6\mathrm{NaF} \xrightarrow{\mathrm{MeCN}} (\mathrm{NPF_2})_3 + 6\mathrm{NaCl}$$

$$(\mathrm{NPCl_2})_3 + 6\mathrm{NaOR} \longrightarrow [\mathrm{NP(OR)_2}]_3 + 6\mathrm{NaCl}$$

$$[\mathrm{NP(OR)_2}]_3 + x\mathrm{RNH}^- \longrightarrow \mathrm{N_3P_3(OR)}_{6-x}(\mathrm{NHR})_x + x\mathrm{OR}^-$$

The mechanism of these reactions, especially with organometallic reagents, is not fully understood, but they appear to proceed by S_N2 attack on P by the nucleophile.

In partially substituted molecules, many isomers are of course possible. These isomers can usually be separated and characterized (e.g., by nmr spectroscopy).

The rings in $(NPF_2)_x$ where $x = 3$ or 4 are planar but larger rings are not planar. For other $(NPX_2)_n$ compounds the six rings are planar or nearly so, but larger rings are generally nonplanar with NPN angles of ~120° and PNP angles of ~132°. Figure 11-11 shows the structures of $(NPCl_2)_3$ and $(NPClPh)_4$. The P—N distances, which are generally equal or very nearly so in these ring systems, lie in the range 1.55 to 1.61 Å; they are thus shorter than the expected single-bond length of ~1.75 to 1.80 Å. Considerable attention has been paid to the nature of the P—N π bonding, which the P—N distances indicate is appreciable, but the matter is still subject to controversy. The main question

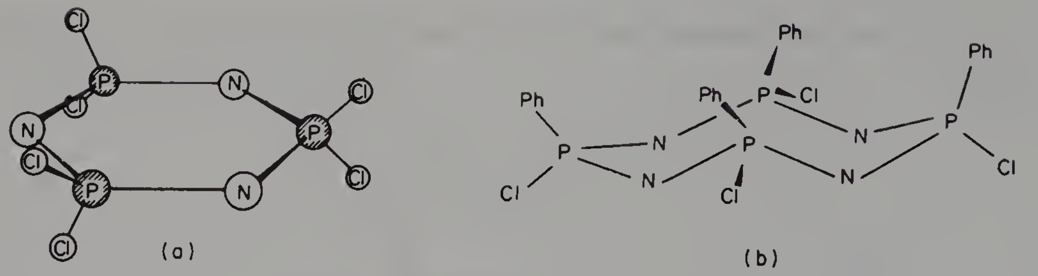
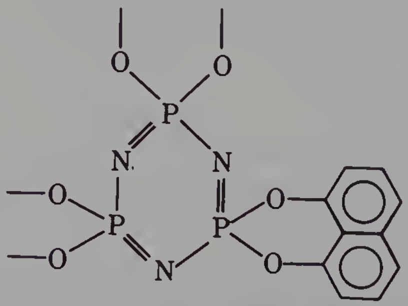


FIG. 11-11. The structures of two representative cyclic phosphazenes: (a) $(NPCl_2)_3$; (b) all-*cis*-$(NPClPh)_4$.

concerns the extent of delocalization, that is, whether there is complete delocalization all around the rings to give them a kind of aromatic character, or whether there are more localized "islands" within the NPN segments. Of course there may be considerable differences between the essentially planar rings and those that are puckered. The problem is a complicated one owing to the large number of orbitals potentially involved and to the general lack of ring planarity, which means that rigorous assignment of σ and π character to individual orbitals is impossible.

These rings are conformationally flexible, and π bonding is only one of many factors that influence the conformations. However, satisfactory force fields for use in molecular mechanics type calculations have not yet been developed.

Compared to the linear phosphazenes, the cyclophosphazenes have few uses, but spiro compounds such as (11-XI) crystallize with channels and can act as tunnel clathrates for aromatic molecules, olefins, and so on.[23]



(11-XI)

Linear Polyphosphazenes. The polymerization of molten $(NPCl_2)_3$ above 230°C to high molecular weight materials was first reported by Stokes in 1897; above 350°C, the linear polymers fragment and form small cyclic species. In general there are polymers that may be represented by the general formula (11-X) and R may be halogen (F, Cl, and Br), alkyl, aryl, and alkoxy. Those with large, hydrophobic R groups are resistant to hydrolysis and thus useful.

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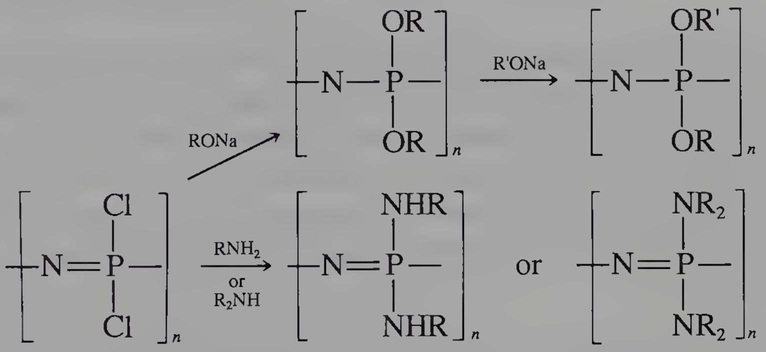
[23] H. R. Allcock *et al.*, *Inorg. Chem.*, 1986, **25**, 41.

To prepare them it is necessary to first prepare $(NPCl_2)_3$ that is rigorously free of PCl_5 and then convert this to $(NPCl_2)_x$ polymer. Failure to eliminate all PCl_5 leads to cross-linked, insoluble polymer that cannot be successfully used to replace all Cl by the desired side chains. Using highly linear, soluble polymers, with $n \geq 15{,}000$, the following substitution types of reactions can be carried out:

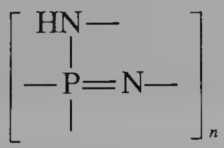


The trimer $(NPF_2)_3$ may also be polymerized and F atoms then substituted. A wide range of physical properties can be achieved by different combinations of substituents; glasses, rubbers or tough, flexible solids. Some can be fabricated into fibers, and there are others that remain flexible to −90°C. Biodegradable polymers in which $R = NHCH_2CO_2Et$ hydrolyze slowly to harmless products and find surgical applications, for example, in sutures.

A material known as *phospham,* produced by the reaction

$$4NH_3(g) + 2P(\text{red}) \xrightleftharpoons{500^\circ C} 2PN_2H(s) + 5H_2$$

is a highly cross-linked polyphosphazene (11-XII)



(11-XII)

Other P—N Compounds. In the large and important class of compounds called phosphazenes we are formally dealing with P^V and N^{III}. There are other P—N compounds that are formally P^{III}—N^{III} types. In these the P—N bonds are all nominally single, but, of course, partial double-bond character arises by $Np\pi$–$Pd\pi$ donor bonding, indicated as follows in resonance terms:

$$\text{P—}\ddot{\text{N}} \longleftrightarrow \overset{-}{\text{P}}\text{=}\overset{+}{\text{N}}$$

The *aminophosphanes,* $(R_2N)_nPX_{3-n}$, are monomeric, but the aminoiminophosphanes (R_2N—P=NR′) may be either monomers when the R and R′ groups are bulky, or dimers (11-XIII) with less bulky substituents.[24]

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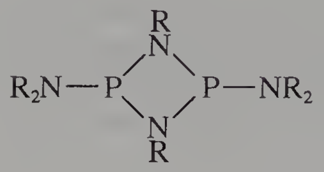
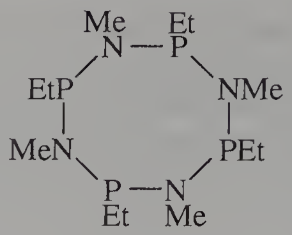
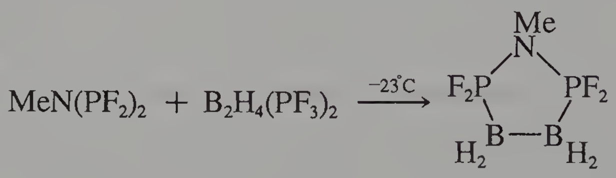
[24] O. J. Sherer and H. Conrad, *Z. Naturforsch.*, 1981, **36b**, 515.

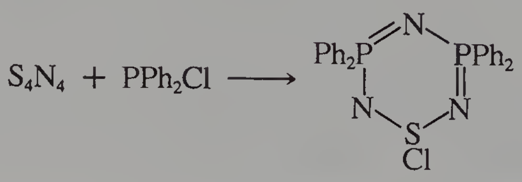

(11-XIII)


(11-XIV)

There are also compounds with larger rings, such as (11-XIV). The cyclic dimers have essentially planar rings, but the substituents on the phosphorus atoms (which have overall pyramidal sets of bonds) can adopt either cis or trans relationships relative to the ring plane.[25]

A variety of rings with still other elements included can be made, as in the following examples (where, again, we have formally P^{V}):


(a)


(b)

Finally, there are polycyclic P—N compounds such as those shown in Fig. 11-12. Note that (a) which has an adamantane-type structure and (c) are isomers; when R = Me, the adamantane structure is thermally stable, but

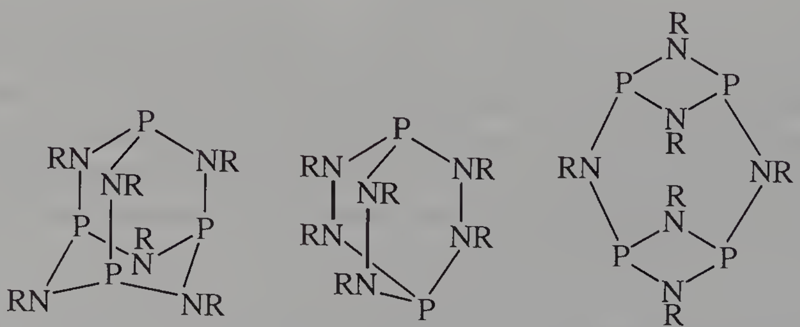

(a) (b) (c)

FIG. 11-12. Three polycyclic types of P—N compounds.

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[25] A. D. Norman *et al.*, *Inorg. Chem.*, 1985, **24,** 4725.

when R = Me_2HC, the (a) structure converts to the (c) structure on heating for 12 days at 157°C.[26]

It is noteworthy that in monaminophosphanes ($R_2PNR'_2$) quaternization reactions occur preferentially at the phosphorus atom, for example,

$$Me_2PNMe_2 + MeI \longrightarrow [Me_3\overset{+}{P}NMe_2]I^-$$

11-12. Organic Compounds

There is a vast chemistry of organophosphorus compounds, and even for arsenic, antimony, and bismuth, the literature is voluminous. Consequently only a few topics can be discussed here. It must also be noted that we discuss only the compounds that have P—C bonds. Many compounds sometimes referred to as organophosphorus compounds that are widely used as insecticides, nerve poisons, and so on, as a result of their anticholinesterase activity, do *not,* in general, contain P—C bonds. They are usually organic esters of phosphates or thiophosphates; examples are the well-known malathion, and parathion, which is $(EtO)_2P^V(S)(OC_6H_4NO_2)$. Compounds with P—C bonds are almost entirely synthetic, though a few rare examples occur in Nature.

With a few exceptions, mentioned at the end of this section, the organo derivatives are compounds with only three or four bonds to the central atom. They may be prepared in a great variety of ways, the simplest being by treatment of halides or oxo halides with Grignard reagents:

$$(O)MX_3 + 3RMgX \longrightarrow (O)MR_3 + 3MgX_2$$

Trimethylphosphine is spontaneously flammable in air, but the higher trialkyls are oxidized more slowly. The phosphine oxides (R_3MO), which may be obtained from the oxo halides as shown here or by oxidation of the corresponding R_3M compounds by H_2O_2 or air, are all very stable.

The P—O bonds are very short (e.g., 1.483 Å in Ph_3PO), suggesting a bond order >2. In R_3PS compounds the P—S values are close to the double-bond values.

There are good methods for preparing optically pure dissymmetric phosphine oxides, abcPO, for example, $(CH_3)(C_3H_7)(C_6H_5)PO$. It is then possible to reduce these to optically pure phosphines with either retention or inversion. The reductant $HSiCl_3$ (Section 9-6) accomplishes this with either retention or inversion, depending on the base used in conjunction with it. Hexachlorodisilane reduces with inversion, and to account for this the following mechanism has been proposed:

$$abcPO + Si_2Cl_6 \longrightarrow abcP^+OSiCl_3 + SiCl_3^-$$

$$SiCl_3^- + abcP^+OSiCl_3 \longrightarrow Cl_3SiP^+abc + SiCl_3O^- \text{ (inversion)}$$

$$Cl_3SiP^+abc + SiCl_3O^- \longrightarrow Cl_3SiOSiCl_3 + Pabc$$

(attack of Cl_3SiO^- on $SiCl_3$)

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[26] O. J. Sherer *et al., Angew. Chem. Int. Ed. Engl.,* 1980, **19**, 571.

Interestingly, the same reagent removes S from abcPS with retention; it is presumed that the first step is similar, but that $SiCl_3^-$ then attacks sulfur, rather than phosphorus:

$$abcPS + Si_2Cl_6 \longrightarrow abcP^+SSiCl_3 + SiCl_3^-$$

$$abcPSSiCl_3 + SiCl_3^- \longrightarrow abcP + Cl_3SiSSiCl_3$$

Trialkyl- and triarylphosphines, -arsines, and -stibines, and chelating di- and triphosphines and -arsines are widely used as π-acid ligands (Section 11-18).

Toward trivalent boron compounds, gas phase calorimetric studies of the reactions (E = P, As, and Sb)

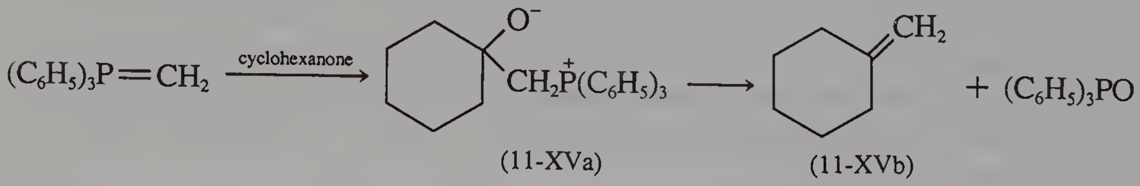
$$Me_3E(g) + BX_3(g) = Me_3EBX_3(s)$$

show that the order of base strength is P > As > Sb.

Triphenylphosphine, a white crystalline solid (mp 80°C), is a particularly important ligand for transition metal complexes and is used industrially in the rhodium-catalyzed hydroformylation process (Section 28-8). It is also widely used in the *Wittig reaction* for olefin synthesis.[27a] This reaction involves the formation of alkylidenetriphenylphosphoranes from the action of butyllithium or other base on the quaternary halide, for example,

$$[(C_6H_5)_3PCH_3]^+Br^- \xrightarrow{n\text{-butyllithium}} (C_6H_5)_3P{=}CH_2$$

This intermediate reacts very rapidly with aldehydes and ketones to give zwitterionic compounds (11-XVa), which eliminate triphenylphosphine oxide under mild conditions to give olefins (11-XVb):



There are a few radical species ($R_2P^\cdot$) and their complexes.[27b] These exist only when R is very bulky, for example, $(Me_3Si)_2N$— or $(Me_3Si)_2CH$—.

Alkylidene Phosphoranes.[28] In addition to the important Wittig reagent ($Ph_3P{=}CH_2$) there are many other $R_3P{=}CR'R''$ compounds in which (usually) R′ or both R′ and R″ are hydrogen. Examples are $Me_3P{=}CH_2$, $Et_3P{=}CH_2$, $Me_2EtP{=}CH_2$, and $Et_3P{=}CHMe$, all of which are colorless liquids, stable for long periods in an inert atmosphere. There are arsenic analogues of these compounds.

The P=C distances range from 1.66 to 1.74 Å, clearly indicative of considerable, if not full double-bond character, and in general their electronic

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[27a] M. Schlosser *et al., Phosphorus and Sulfur,* 1983, **18,** 171.

[27b] M. F. Lappert *et al., J. Chem. Soc. Dalton Trans.,* **1980,** 2428; A. H. Cowley *et al., J. Am. Chem. Soc.,* 1982, **104,** 331.

[28] H. Schmidbaur *et al., Phosphorus and Sulfur,* 1983, **18,** 167.

structures may be represented in resonance terms as follows:

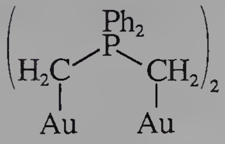
$$R_3P{=}CR'_2 \longleftrightarrow R_3\overset{+}{P}{-}\overset{-}{C}R'_2$$

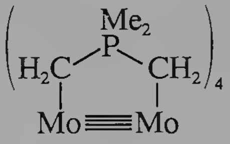
These compounds, which are often called phosphine ylides, are prepared by deprotonation of a quaternary phosphonium ion, namely,

$$Me_4PBr + NaNH_2 \xrightarrow{\text{reflux}} Me_3P{=}CH_2 + NaBr + NH_3$$

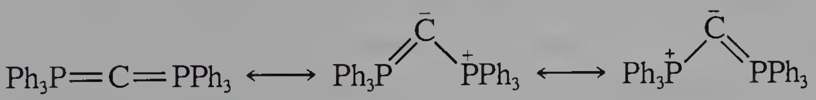
$$Ph_2Me_2PBr + KH \xrightarrow{\text{THF}} Ph_2MeP{=}CH_2 + KBr + H_2$$

These molecules can be further deprotonated to give the ylide anions, $Me_2P(CH_2)_2^-$ and $Ph_2P(CH_2)_2^-$ that can serve as bridging ligands, as in (11-XVI) and (11-XVII).

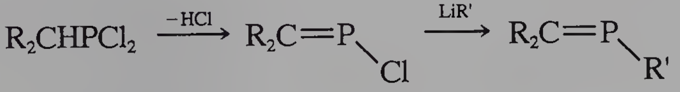

(11-XVI)


(11-XVII)

An unusual, cumulenelike phosphine ylide is $Ph_3P{=}C{=}PPh_3$, prepared by dehydrobromination of $[Ph_3PCH_2PPh_3]Br_2$ with potassium in diglyme. Somewhat surprisingly, the P—C—P angle is 137°, suggesting that again there are polar contributions to the electronic structure:

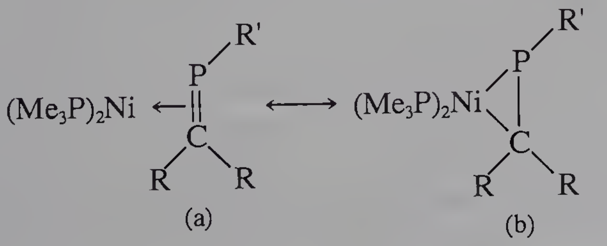


Phosphaalkenes.[29] Not to be confused with the phosphine ylides, these are compounds of the general formula $R_2C{=}P{-}R'$. They are accessible by the following general route:



R,R' = Me_3Si, 2,4,6-*t*-$Bu_3C_6H_2$, mesityl, and so on

The molecules are bent (~110°C), with P=C distances of ~1.68 Å. They can form complexes similar to those formed by olefins in which the bonding arises by donation of the π electrons, as in (11-XVIII).


(a) (b)

(11-XVIII)

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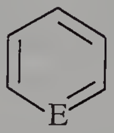
[29] A. H. Cowley *et al., J. Am. Chem. Soc.*, 1984, **106**, 7015; *J. Chem. Soc. Chem. Commun.*, **1987**, 780; T. A. van der Knaap and F. Bickelhaupt, *Phosphorus and Sulfur*, 1983, **18**, 47.

There is also a cumulenelike molecule,[30] (2,4,6-*t*-$Bu_3C_6H_2$)P=C=P(2,4,6-*t*-$Bu_3C_6H_2$), which, however, is nearly linear (~173°C), in contrast to the previously mentioned diylide; there are also phosphaalkynes, RC≡P.

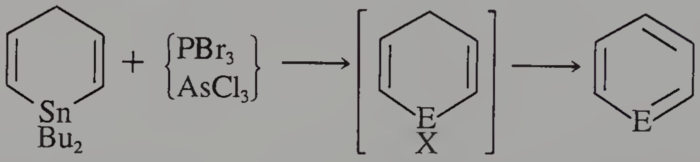
Pyridine Analogues (heterobenzenes). These molecules (11-XIX) are known for all four elements, although the bismuth compound is extremely



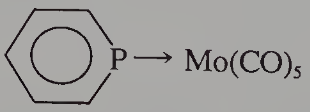
E = P, As, Sb, and Bi

(11-XIX)

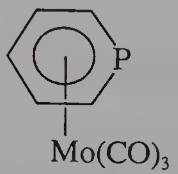
unstable, and stibabenzene (C_5H_5Sb) rapidly polymerizes at room temperature. Phosphabenzene and arsabenzene are thermally stable (distillable) and can be prepared by the reactions



Derivatives of both, such as 2,4,6-$Ph_3C_5H_2E$, and as well as 1-arsanaphthalene and 9-arsaanthracene are also known. Both C_5H_5P and C_5H_5As have planar structures with C—C and C—E bond lengths indicative of aromatic-type delocalization of the π electrons, although they have not yet demonstrated an extensive aromatic organic chemistry comparable to that of pyridine. Phosphabenzene and its derivatives can form both σ- and η^6-type complexes, for example, (11-XX) and (11-XXI).



(11-XX)



(11-XXI)

Pentavalent Compounds (R_5M). These tend to be more stable with the heavier elements, whereas the corresponding R_3M compounds become less stable. In general the pentaaryls are far more stable than pentaalkyls. Thus, for arsenic Me_5As is the only known alkyl, while pentaaryls are numerous.[31a] The pentaphenyl compounds Ph_5M are perhaps the best characterized pure organic derivatives, but a host of mixed compounds, especially of antimony, of the types Ph_4SbX and Ph_3SbX_2 (X = OH, OR, or halogen) are known. In all but two cases these molecules have *tbp* structures, with the more electronegative ligands at axial positions. A configuration closer to *sp* has been

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[30] H. H. Karsch *et al., Angew. Chem. Int. Ed. Engl.,* 1984, **23,** 618.
[31a] R. Bohra and H. W. Roesky, *Adv. Inorg. Radiochem.,* 1984, **28,** 203.

found for crystalline Ph_5Sb, and an *sp* configuration has been postulated on spectroscopic evidence for penta(cyclopropyl)antimony. However, since $(p\text{-tolyl})_5Sb$ has a *tbp* structure in the crystal, though it is nonrigid in solution except at −130°C, it seems likely that the *sp* structure in crystalline Ph_5Sb is occasioned by packing interactions and is not inherently preferred.

The mixed chloroalkyl phosphoranes,[31b] PR_nCl_{5-n} behave as Lewis acids, for example,

$$PMeCl_4 + R_4NCl \longrightarrow [R_4N][PMeCl_5]$$

but can also react as Cl^- donors, namely,

$$PMeCl_4 \xrightarrow{SbCl_5} [PMeCl_3][SbCl_6] \xrightarrow{(bipy)} [PMeCl_3bipy][SbCl_6].$$

Although alkyl compounds are well characterized for antimony, phosphorus and arsenic alkyls are unstable, and attempts to make pentamethylphosphorane by the same method as succeeds for Ph_5P gives the ylid, namely,

$$Ph_4PBr + PhLi \longrightarrow Ph_5P + LiBr$$

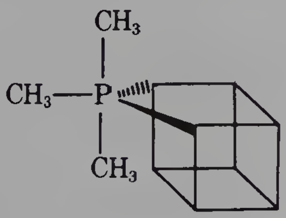
but

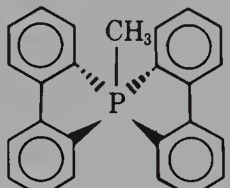
$$Me_4PI + MeLi \longrightarrow Me_3P{=}CH_2 + CH_4 + LiI$$

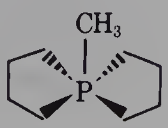
and

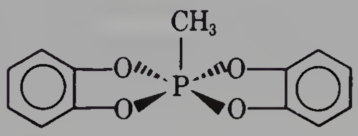
$$Ph_4PBr + MeLi \longrightarrow Ph_3P{=}CH_2 + C_6H_6 + LiBr$$

However, the formation of ylids can be prevented by incorporation of P into heterocycles as in the following examples:









The spirophosphoranes and phosphorus(V) esters are approximately square pyramidal.

The antimony compounds $Me_3Sb(NO_3)_2$ and $Me_3Sb(ClO_4)_2$, which appear to be molecular with *tbp* structures in the solid, dissolve in water and ionize, apparently to give the planar cation $(CH_3)_3Sb^{2+}$.

[31b] R. M. K. Deng and K. B. Dillon, *J. Chem. Soc. Dalton Trans.*, **1984**, 1911, 1917.

11-13. Compounds with Element–Element Single Bonds

The elements themselves as well as the halides (E_2X_4) and the hydrogen compounds (H_2PPH_2 and P_3H_5) have already been mentioned. Also, previously noted (Section 11-3) are the many Zintl anions, which contain E—E bonds that are approximately single bonds, although perhaps better discussed in terms of a delocalized picture. There is, finally, a very large number of molecular compounds containing organic groups together with one or more E—E bonds, and it is to these that we now turn.

The simplest are the $R_2E—ER_2$ molecules, formed by all four elements. A general method of preparation is by coupling identical R_2EX units, for example,

$$2Ph_2BiCl + 2Na \xrightarrow{NH_3(l)} Ph_2Bi—BiPh_2 + 2NaCl$$

The *diphosphines* (R_2PPR_2) readily react with O_2 or S_n to give the $R_2P(O)P(O)R_2$ and $R_2P(S)P(S)R_2$ molecules but the latter, also available in other ways, can be desulfurized as a way of preparing R_2PPR_2 compounds.

Among the *diarsines* ($R_2As—AsR_2$) the methyl compound (Me_2As_4) is called dicacodyl and its Me_2AsX derivatives are called cacodyls, for example, cacodyl chloride (Me_2AsCl).

Distibines ($R_2Sb—SbR_2$)[32] *and Dibismuthines* ($R_2Bi—BiR_2$)[32,33] with a wide variety of R groups are known. All of them have a yellow or orange color when melted, but those with small R groups give solids that are orange, red, blue, or violet. It is believed that these changes in color are due to intermolecular association into ---E—E---E—E--- chains in the solid. The $Ph_2E—EPh_2$ compounds, which show no such chains remain yellow as solids, whereas the solid $Me_2E—EMe_2$ compounds are blue.

Other classes of compounds containing one P—P bond are the $(RO)_2PP(OR)_2$ and $(RO)_2P(O)P(O)(OR)_2$ types, as well as RClPPClR[34] and $(R_2N)ClPPCl(NR_2)$.[35] On mixing Me_2EEMe_2 and $Me_2E'E'Me_2$, the $Me_2EE'Me_2$ compounds are formed in equilibrium with the homonuclear ones.[36]

Organocyclophosphanes $(PR)_n$, *and -arsanes* $(AsR)_n$, with $n = 3$ to 6, are well known. Ring size preference is largely determined by the size or electronegativity of the R groups. Small alkyl substituents as well as phenyl favor $(PR)_5$, whereas bulky groups favor $(PR)_4$ and even $(PR)_3$.[37] The compounds

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[32] A. J. Ashe, III, *et al., Organometallics*, 1983, **2**, 1573, 1859.

[33] F. Calderazzo *et al., J. Chem. Soc. Chem. Commun*, **1983**, 507.

[34] M. Baudler *et al., Chem. Ber.*, 1982, **489**, 11.

[35] R. B. King *et al., J. Chem. Soc. Chem. Commun.*, **1983**, 477.

[36] A. J. Ashe, III, and E. G. Ludwig, Jr., *J. Organomet. Chem.*, 1986, **303**, 197.

[37] M. Baudler, *Pure Appl. Chem.*, 1980, 755; *Angew. Chem. Int. Ed. Engl.*, 1982, **21**, 492; *Phosphorus Sulfur*, 1983, **18**, 57.

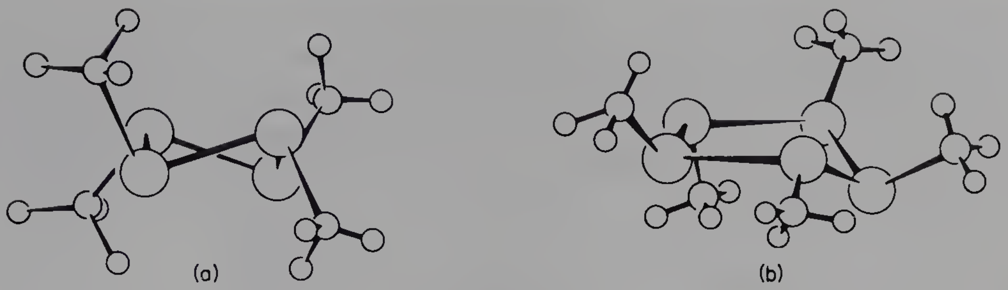


FIG. 11-13. The structures of (a) $(CF_3P)_4$ and (b) $(CF_3P)_5$. Large, medium, and small circles represent P, C, and F atoms, respectively.

are thermally stable though reactive and typical preparative reactions are

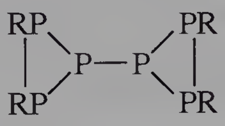
$$5CH_3PCl_2 + 10LiH \longrightarrow (PCH_3)_5 + 10LiCl + 5H_2$$

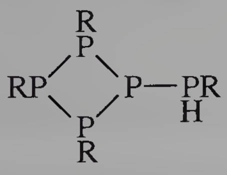
$$3Me_3CPCl_2 + 3Mg \longrightarrow (PCMe_3)_3 + 3MgCl_2$$

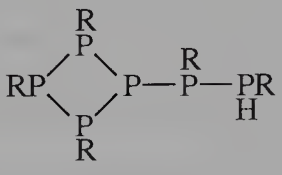
$$nRAsO_3Na_2 + (\text{excess})\ H_3PO_2 \longrightarrow (RAs)_n$$

The larger rings are, as expected, puckered (Fig. 11-13), while in $(PR)_3$ compounds only two of the R groups lie on one side of the ring plane.

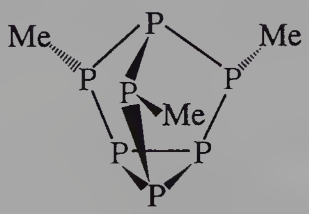
There are also linear triphosphines containing CF_3 groups, such as $(CF_3)P[P(CF_3)_2]$, and $CH_3P[P(CF_3)_2]_2$, and other partly cyclic species such as (11-XXII), (11-XXIII), and (11-XXIV) (where R = Me_3C):

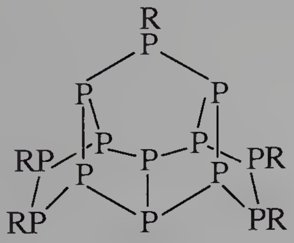

(11-XXII)

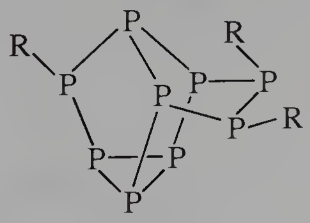

(11-XXIII)


(11-XXIV)

Even larger molecules, for which polycyclic structures have been proposed but not yet proved [(11-XXV)–(11-XXVII) where R = Me_2HC] are known.[38]


(11-XXV)


(11-XXVI)


(11-XXVII)

11-14. Compounds with Element–Element Double Bonds[39a]

While N=N bonds abound, until recently other Group VA(15) E=E bonds were unknown. Today, however, there are stable compounds that contain

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[38] M. Baudler *et al.*, *Z. Naturforsch.*, 1983, **B38**, 428, 955; *Angew. Chem. Int. Ed. Engl.*, 1983, **22,** 1002.

[39a] A. H. Cowley and N. C. Norman, *Progr. Inorg. Chem.*, 1986, **34,** 1; M. Yoshifuji *et al.*, *Phosphorus Sulfur,* 1983, **18,** 11.

TABLE 11-6
Structures of RE=E′R′ Compounds

E	E′	R	R′	E=E′ distance (Å)	Sum of double bond radii (Å)
P	P	Ar[a]	Ar[a]	2.034(2)	2.00
P	P	$(Me_3Si)_3C$	$(Me_3Si)_3C$	2.014(6)	2.00
				2.004(6)	2.00
P	P	$(Me_3Si)BuN$	$(Me_3Si)BuN$	2.034	2.00
P	As	Ar	$(Me_3Si)_2CH$	2.124(2)	2.11
As	As	Ar	$(Me_3Si)_2CH$	2.224(2)	2.22
As	As	$(Me_3Si)_3C$	$(Me_3Si)_3C$	2.244	2.22

[a] Ar = 2,4,6-$(Me_3C)C_6H_2$.

P=P, P=As and As=As bonds, although E=E or E=E′ bonds involving Sb or Bi are still unknown. The best calculations show that the π bond strengths of HN=NH and HP=PH are 256 and 150 kJ mol^{-1}, respectively. Thus, while much weaker than the N—N π bond, the P—P π bond has considerable strength.[39b]

The basic difficulty in obtaining stable compounds that contain E=E′ bonds is thermodynamic. Compounds with such bonds are unstable relative to cyclic oligomers of the type discussed in Section 11-13, that is, $(RP)_n$ or $(RAs)_n$. It has been found that oligomerization can be thwarted by employing large R groups. This strategy is mainly a kinetic one (the compounds are relatively unreactive in other ways as well) but may have a thermodynamic element as well in that cyclic $(RE)_n$ molecules are doubtless destabilized when R is very large.

The known RE=E′R′ molecules are listed in Table 11-6 along with their E=E′ bond lengths. It can be seen that these bond lengths are all ~0.20 Å

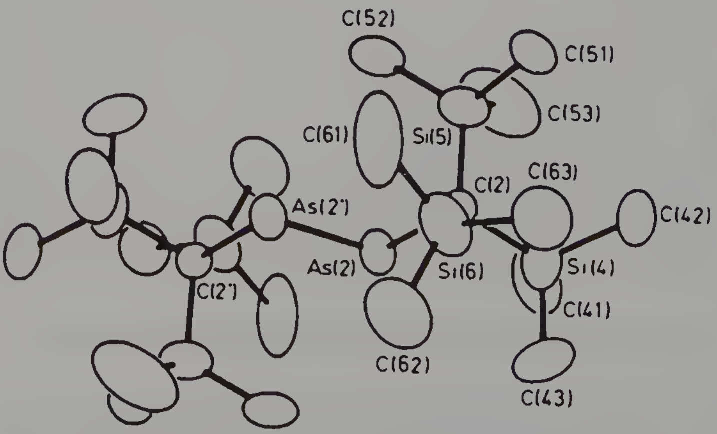


FIG. 11-14. The structure of $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ (from A. H. Cowley *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 383).

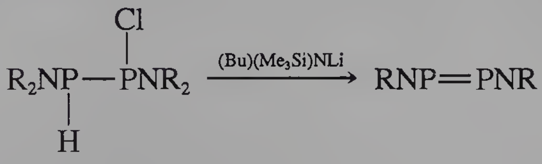
[39b] M. W. Schmidt and M. S. Gordon, *Inorg. Chem.*, 1986, **25**, 248.

shorter than the corresponding E—E′ lengths and in good accord with estimates from Pauling's double-bond radii. The molecules are all essentially, or exactly, planar in their central X—E=E—X portions. The structure of $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ is shown in Fig. 11-14.

Methods of preparation are mainly the following, although others are known:[40,41]

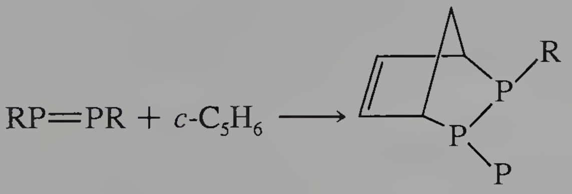
$$2RPCl_2 + 2Mg \longrightarrow RP{=}PR + 2MgCl_2$$

$$RECl_2 + H_2E'R' \xrightarrow{\text{base}} RE{=}E'R'$$

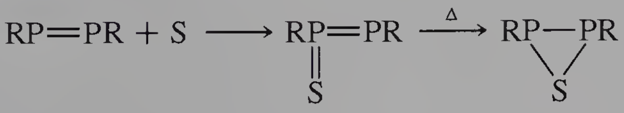


$$R_2N\underset{\displaystyle H}{P}-\overset{\displaystyle Cl}{P}NR_2 \xrightarrow{(Bu)(Me_3Si)NLi} RNP{=}PNR$$

Just as the large R groups inhibit oligomerization, they also inhibit other forms of reactivity. Some of the reactions that have been observed are

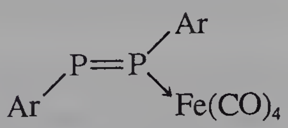


$$RP{=}PR + HCl \longrightarrow RP(Cl){-}P(H)R$$

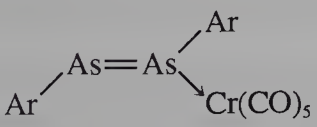


$$RP{=}PR + S \longrightarrow \underset{\displaystyle \overset{\|}{S}}{RP}{=}PR \xrightarrow{\Delta} RP{-}PR\ (\text{bridged by } S)$$

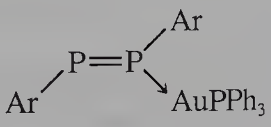
There are also reactions with metal-centered Lewis acids, whereby a lone pair on P or As is employed to form a donor bond; compounds such as (11-XXVIII)–(11-XXX) are thus known [Ar = $2,4,6\text{-}(Me_3C)C_6H_2$].



(11-XXVIII)



(11-XXIX)



(11-XXX)

11-15. Cationic Chemistry

The formation of quaternary cations has been discussed (Section 11-10). There are a few other forms of cationic behavior, although only for Sb and Bi is there aqueous cationic behavior.

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[40] P. P. Power *et al., J. Am. Chem. Soc.,* 1983, **105,** 7460.

[41] J. Escudie *et al., J. Chem. Soc. Chem. Commun.,* **1984,** 1621.

Phosphorus forms a series of two-coordinate cations, called phosphenium ions.[42] The general method of preparation is illustrated in eq. 11-5.

$$RR'PCl + \tfrac{1}{2}Al_2Cl_6 \longrightarrow [RR'P][AlCl_4] \qquad (11\text{-}5)$$

R and R′ groups may be R_2N, $(Me_3Si)_2N$, *t*-Bu, Cl, and Cp′. For arsenic and antimony there are only a few analogous species, for example, the $[Cp'_2E]BF_4$ compounds. A compound $[Ph_3PPPh_3][AlCl_4]$ has also been reported that formally contains a complexed P^+ ion.[43a]

There is little if any evidence for the existence of P or As cationic species under aqueous conditions, although the following reactions may occur to some slight extent.

$$H_2O + OH^- + AsO^+ \longleftarrow As(OH)_3 \longrightarrow As^{3+} + 3OH^-$$

Antimony has some definite cationic chemistry, but only in the trivalent state, the basic character of Sb_2O_5 being negligible. Cationic compounds of Sb^{III} are mostly of the "antimonyl" ion SbO^+, although some of the "Sb^{3+}" ion, such as $Sb_2(SO_4)_3$, are known. Antimony salts readily form complexes with various acids in which the antimony forms the nucleus of an anion.

In sulfuric acid from 0.5 to 12 *M*, Sb^V appears to be present as the $[Sb_3O_9]^{3-}$ ion. For Sb^{III} in sulfuric acid, the species present vary markedly with the acid concentration, namely,

$$SbO^+ \text{ and/or } Sb(OH)_2^+ \qquad <1.5\ M\ H_2SO_4$$

$$SbOSO_4^-,\ Sb(SO_4)_2^- \qquad \sim 1.0 \text{ to } 18\ M\ H_2SO_4$$

In salts the $Sb(C_2O_4)_3^{3-}$ ion has a ψ-pentagonal bipyramid structure [Fig. 11-15(a)] with a lone pair at one axial position.

The tartrate complex of antimony(III), *tartar emetic,* $K_2[Sb_2(d\text{-}C_4O_6H_2)_2]\cdot 3H_2O$, has been known in medicine for over 300 years and is used for treatment of schistosomiasis and leishmaniasis; the toxic side effects can be mediated by penicillamine. In the salts the ion has a binuclear structure [Fig. 11-15(b)] and the Sb atom has ψ-*tbp* geometry. This coordination is also found in the complex $K[As(C_6H_4O_2)_2]$ derived from catechol (*o*-dihydroxybenzene).

Only for bismuth can it be said that there is an extensive true cationic chemistry. Aqueous solutions contain well-defined hydrated cations, but there is no evidence for the simple aqua ion $[Bi(H_2O)_n]^{3+}$. In neutral perchlorate solutions the main species is $[Bi_6O_6]^{6+}$ or its hydrated form, $[Bi_6(OH)_{12}]^{6+}$, and at higher pH $[Bi_6O_6(OH)_3]^{3+}$ is formed. The $[Bi_6(OH)_{12}]^{6+}$ species contains an octahedron of Bi^{3+} ions with an OH^- bridging each edge. Vibrational analysis suggests some weak bonding directly between the Bi atoms.

There is considerable evidence for the association of Bi^{3+} ion with nitrate

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[42] A. H. Cowley and R. A. Kemp, *Chem. Rev.*, 1985, **85**, 367.

[43a] A. Schmidpeter *et al., Phosphorus and Sulfur,* 1983, **18**, 23.

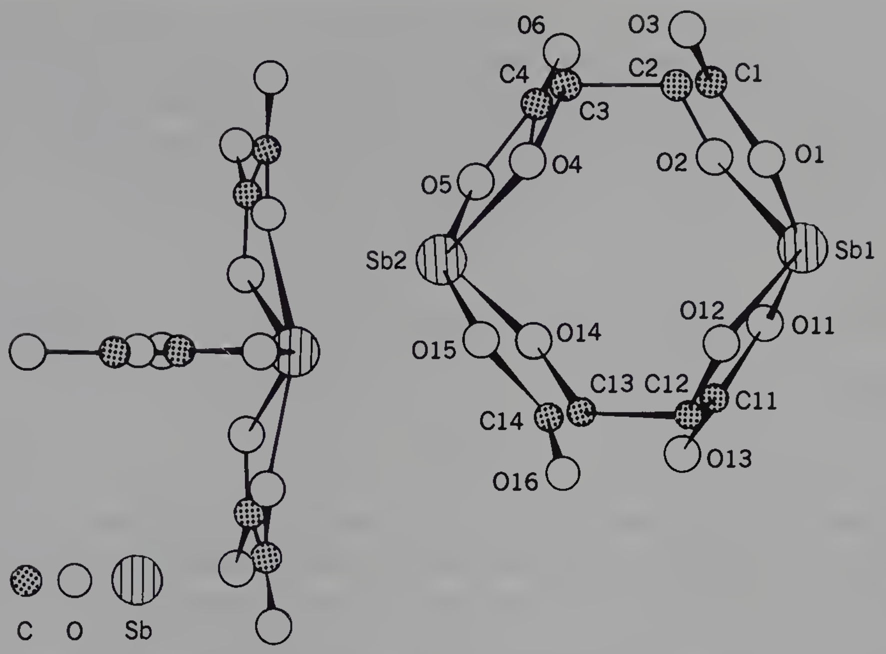

FIG. 11-15. The structures of two antimony(III) complexes. (a) The $Sb(C_2O_4)_3^{3-}$ ion. (b) The $Sb_2(d\text{-}C_4H_2O_6)_2^{2-}$ anion in the tartrate complex called tartar emetic (by permission from M. E. Gress and R. A. Jacobsen, *Inorg. Chem. Acta,* 1974, **8,** 209).

ions in aqueous solution. The nitrate ions appear to be mainly bidentate, and all members of the set $Bi(NO_3)(H_2O)_n^{2+}$---$Bi(NO_3)_4^-$ appear to occur. From acid solution various hydrated crystalline salts such as $Bi(NO_3)_3 \cdot 5H_2O$, $Bi_2(SO_4)_3$, and double nitrates of the type $M_3^{II}[Bi(NO_3)_6]_2 \cdot 24H_2O$ can be obtained. Treatment of Bi_2O_3 with HNO_3 gives basic salts such as $BiO(NO_3)$ and $Bi_2O_2(OH)(NO_3)$. Similar salts, generally insoluble in water, are precipitated on dilution of strongly acid solutions of Bi compounds. The nitrate $Bi_6O_4(OH)_4(NO_3)_6H_2O$ has a Bi_6 octahedron with face-bridging μ_3-oxo groups, and the $[Bi_6O_4(OH)_4]^{6+}$ unit is known to persist in solution.[43b]

THE OXO ANIONS

The oxo anions in both lower and higher states are a very important part of the chemistry of phosphorus and arsenic and comprise the only real aqueous chemistry of these elements. For the more metallic antimony and bismuth, oxo anion formation is less pronounced, and for bismuth only ill-defined "bismuthates" exist.

11-16. Oxo Acids and Anions of Phosphorus

All phosphorus oxo acids have POH groups in which the hydrogen atom is ionizable; hydrogen atoms in P—H groups are not ionized. There is a vast

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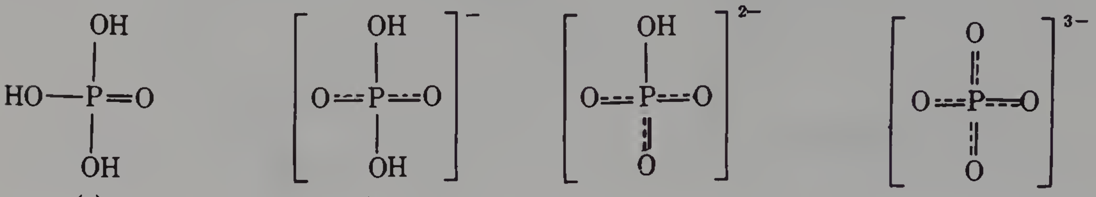
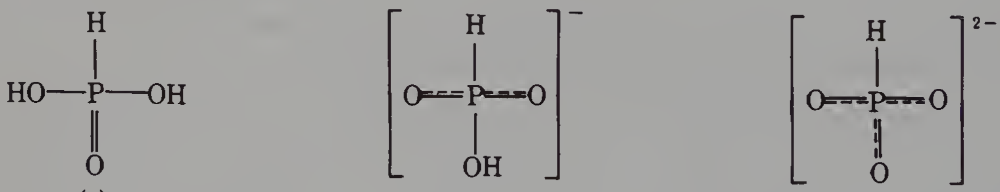
[43b] B. Sundvall, *Acta Chem. Scand.*, 1980, **A34,** 93.

number of oxo acids or ions, some of them of great technical importance, but we can attempt to deal only with some structural principles, and some of the more important individual compounds. The *oxo anions* are of main importance, since in many cases the free acid cannot be isolated, though its salts are stable. Both lower (P^{III}) and higher (P^{V}) acids are known.


(a) (b) (c) (d)

(11-XXXI)

The principal higher acid is orthophosphoric acid (11-XXXIa) and its various anions (11-XXXIb)–(11-XXXId), all of which are tetrahedral. The phosphorus(III) acid, which might naively have been considered to be $P(OH)_3$, has in fact the four-connected tetrahedral structure (11-XXXIIa); it is only difunctional, and its anions are (11-XXXIIb) and (11-XXXIIc). Only in the triesters of phosphorous acid [$P(OR)_3$] do we encounter three-connected phosphorus, and even these, as will be seen later, have a tendency to rearrange to four-connected species.


(a) (b) (c)

(11-XXXII)

Similarly, the acid of formula H_3PO_2 (hypophosphorous acid) also has a four-connected structure (11-XXXIIIa), as does its anion (11-XXXIIIb).


(a) (b)

(11-XXXIII)

Lower Acids

Hypophosphorous Acid. The salts of $PH_2(O)(OH)$ are usually prepared by boiling white phosphorus with alkali or alkaline earth hydroxide. The main reactions appear to be

$$P_4 + 4OH^- + 4H_2O \longrightarrow 4H_2PO_2^- + 2H_2$$

$$P_4 + 4OH^- + 2H_2O \longrightarrow 2HPO_3^{2-} + 2PH_3$$

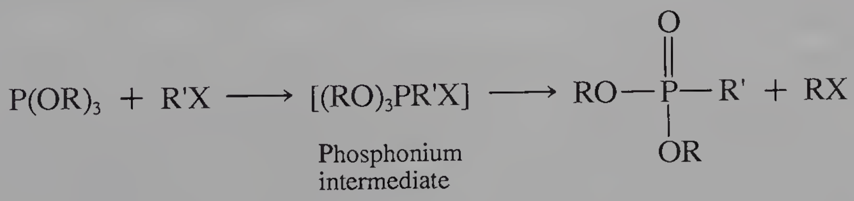
The calcium salt is soluble in water, unlike that of phosphite or phosphate; the free acid can be made from it or obtained by oxidation of phosphine with iodine in water. Both the acid and its salts are powerful reducing agents, being oxidized to orthophosphate. The pure white crystalline solid is a monobasic acid (pK = 1.2). The more correct, though rarely used name of this acid is phosphinic acid. When the H—P bonds are replaced by R—P bonds, however, to give $R_2P(O)OH$, acids, these are regularly called phosphinous acids and their salts phosphinates.

Phosphorous Acid. This acid, $PH(O)(OH)_2$, is obtained by treating PCl_3 or P_4O_6 with water; when pure, it is a deliquescent colorless solid (mp 70.1°C, pK = 1.8). It is oxidized to orthophosphate by halogen, sulfur dioxide, and other agents, but the reactions are slow and complex. The mono-, di-, and triesters can be obtained from reactions of alcohols or phenols with PCl_3 alone or in the presence of an organic base as hydrogen chloride acceptor. They can also be obtained directly from white phosphorus by the reaction

$$P_4 + 6OR^- + 6CCl_4 + 6ROH = 4P(OR)_3 + 6CHCl_3 + 6Cl^-$$

The systematic but little used name for this acid is phosphonic acid. When the P—H bond is replaced by a P—R bond, to give $RP(O)(OH)_2$, these acids are regularly called phosphonic acids and their salts phosphonates.

Although compounds of composition $P(OR)_3$ are well known and are useful as ligands (Section 11-18) and in other ways, they are subject to the *Michaelis–Arbusov* reaction[44] with alkyl halides, which converts them to diesters of phosphonic acids:

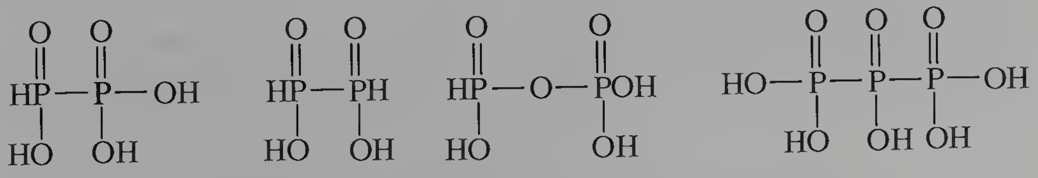


$$P(OR)_3 + R'X \longrightarrow \underset{\substack{\text{Phosphonium}\\ \text{intermediate}}}{[(RO)_3PR'X]} \longrightarrow RO-\underset{\mathrm{OR}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{P}}}}-R' + RX$$

The methyl ester easily undergoes spontaneous isomerization to the dimethyl ester of methylphosphonic acid:

$$P(OCH_3)_3 \longrightarrow CH_3PO(OCH_3)_2$$

There are also a number of di- and polyacids of phosphorus in lower formal oxidation states, in which there are P—H or P—P bonds, or both. A few examples, which we shall not discuss further, are the following:



$$H\underset{\mathrm{HO}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{P}}}}-\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{P}}}}-OH \qquad H\underset{\mathrm{HO}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{P}}}}-\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{P}}}}H \qquad H\underset{\mathrm{HO}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{P}}}}-O-\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{P}}}}OH \qquad HO-\underset{\mathrm{HO}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{P}}}}-\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{P}}}}-\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\overset{\|}{\underset{|}{P}}}}-OH$$

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[44] A. K. Bhattacharya and G. Thyagarajan, *Chem. Rev.*, 1981, **81**, 415.

Higher Acids.

Orthophosphoric Acid. The acid H_3PO_4 or $PO(OH)_3$, commonly called phosphoric acid, is one of the oldest known and most important phosphorus compounds. It is made in vast quantities, usually as 85% syrupy acid, by the direct reaction of ground phosphate rock with sulfuric acid and also by the direct burning of phosphorus and subsequent hydration of the oxide P_4O_{10}. The pure acid is a colorless crystalline solid (mp 42.35°C). It is very stable and has essentially no oxidizing properties below 350 to 400°C. At elevated temperatures it is fairly reactive toward metals and is reduced; it will also then attack quartz. Fresh molten H_3PO_4 has appreciable ionic conductivity suggesting autoprotolysis:

$$2H_3PO_4 \rightleftharpoons H_4PO_4^+ + H_2PO_4^-$$

Pyrophosphoric acid is also produced:

$$2H_3PO_4 \longrightarrow H_2O + H_4P_2O_7$$

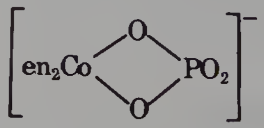
but this conversion is temperature dependent and is slow at room temperature.

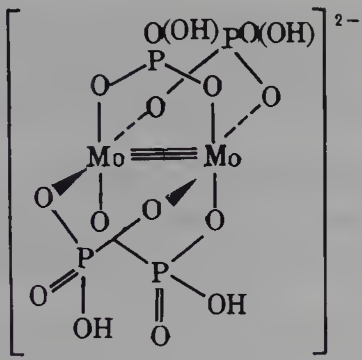
The acid is tribasic: at 25°C, $pK_1 = 2.15$, $pK_2 = 7.1$, $pK_3 \approx 12.4$. The pure acid and its crystalline hydrates have tetrahedral PO_4 groups connected by hydrogen bonds. These persist in the concentrated solutions and are responsible for the syrupy nature. For solutions of concentration $< \sim 50\%$, the phosphate anions are hydrogen bonded to the liquid water rather than to other phosphate anions.

Phosphates of most metal ions and other cations are known. Some of these are of enormous commercial and practical importance, for example, ammonium phosphate fertilizers, and alkali phosphate buffers. Natural phosphate minerals are *all* orthophosphates, the major one being fluorapatite; hydroxoapatites, partly carbonated, make up the mineral part of teeth. The role of traces of F^- in strengthening dental enamel is presumably connected with these structural relationships, but a detailed explanation of the phenomenon is still lacking.

Orthophosphoric acid and phosphates form complexes with many transition metal ions. The precipitation of insoluble phosphates from fairly concentrated acid solution (3–6 *M* HNO_3) is characteristic of 4+ cations such as those of Ce, Th, Zr, U, and Pu. Phosphates of B, Al, Zr, and so on, are used industrially as catalysts for a variety of reactions.

The phosphate ions, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} are well known as ligands, of monodentate, chelating, or bridging types; examples of the last two are

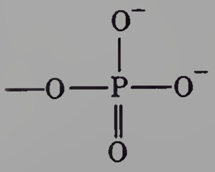




Although the majority of phosphate esters have four-connected phosphorus, there are a few in which five or even six oxygen atoms surround phosphorus, for example, $[P(OMe)_6]^-$ and $[P(o\text{-}C_6H_4O_2)_3]^-$.

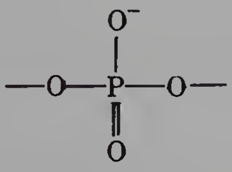
Condensed Phosphates. Condensed phosphates are those containing more than one P atom and having P—O—P bonds. We may note that the *lower* acids can also give condensed species. We shall deal here only with a few examples of phosphates.

There are three main building units in condensed phosphates: the end unit (11-XXXIV), the middle unit (11-XXXV), and the branching unit (11-XXXVI).



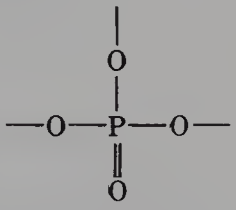
$-O-\overset{O^-}{\underset{O}{\overset{|}{\underset{\|}{P}}}}-O^-$

(11-XXXIV)



$-O-\overset{O^-}{\underset{O}{\overset{|}{\underset{\|}{P}}}}-O-$

(11-XXXV)

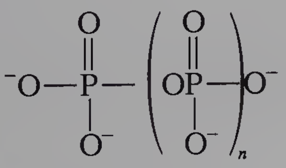


$-O-\overset{\overset{|}{O}}{\underset{O}{\overset{|}{\underset{\|}{P}}}}-O-$

(11-XXXVI)

These units can be distinguished by chemical reactivity differences (branch points are rapidly hydrolyzed) and by ^{31}P nmr spectra. Combinations of these units can give rise to four main types of polyphosphates:

1. Polyphosphates (11-XXXVII), which have been isolated pure with $n = 1$ to 16 and general formula $[P_nO_{3n+1}]^{(n+2)-}$.
2. Infinite chain *metaphosphates,* $[(PO_3)_n]^{n-}$.
3. Cyclic metaphosphates, $[(PO_3)_n]^{n-}$, with $n = 3$ to 10, or more.
4. Ultraphosphates, which contain branching units. The ultimate ultraphosphate is P_4O_{10}, consisting entirely of branch units.



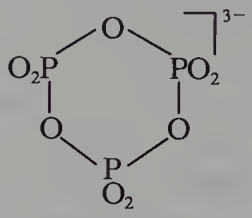
$^-O-\overset{O}{\underset{O^-}{\overset{\|}{\underset{|}{P}}}}-\left(O\overset{O}{\underset{O^-}{\overset{\|}{\underset{|}{P}}}}\right)_n-O^-$

(11-XXXVII)

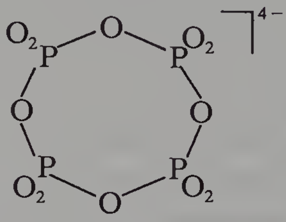
Some representative linear polyphosphates are the alkali salts $M^I_4P_2O_7$ (pyrophosphates) and $M^I_5P_3O_{10}$ (tripolyphosphates). Many detergents contain

$Na_5P_3O_{10}$, and it has other industrial uses. In detergents the triphosphate serves to sequester Ca^{2+} and Mg^{2+} ions. Using Ln^{3+} ions as models, the mode of complexation was shown by nmr to involve attachment of two tetradentate $P_3O_{10}^{5-}$ ions.[45a]

An infinite chain metaphosphate is $Li_2(NH_4)P_3O_9$. The most common type of metaphosphates are the cyclotriphosphates ($M_3P_3O_9$) and cyclic tetraphosphates, which contain the anions (11-XXXVIII) and (11-XXXIX). The



(11-XXXVIII)



(11-XXXIX)

$P_3O_9^{3-}$ rings have chair conformations; the $P_4O_{12}^{4-}$ rings are puckered but conformations vary from compound to compound. An efficient synthesis of a cyclotriphospate is by the following[45b] reaction:

$$2(MeO)_3PO + (Me_2N)_3PO \longrightarrow [Me_4N]_3(P_3O_9)$$

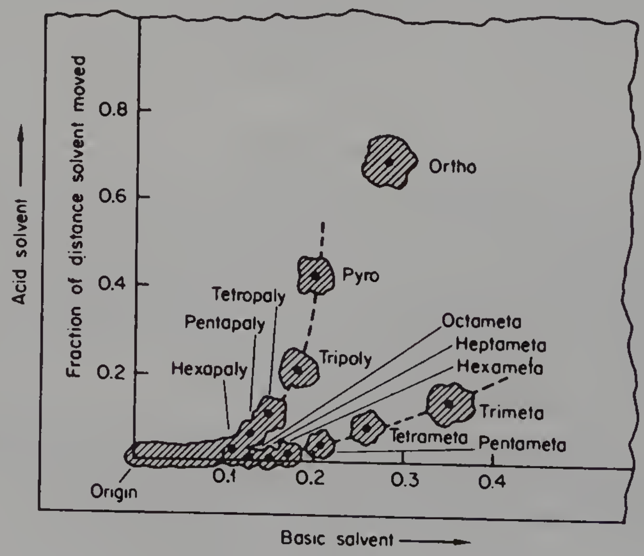


FIG. 11-16. Chromatographic separation of complex phosphate mixtures. Corner of a two-dimensional paper chromatogram, showing the positions of the pentameta- through octametaphosphate rings in relation to the positions of the well-known ring and chain phosphates. The basic solvent traveled 23 cm in 24 h, whereas the acid solvent traveled 11.5 cm in 5.5 h.

[45a] M. S. Nieuwenhuizen *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 12.
[45b] F. Seel *et al.*, *Z. Anorg. Allg. Chem.*, 1984, **516,** 177.

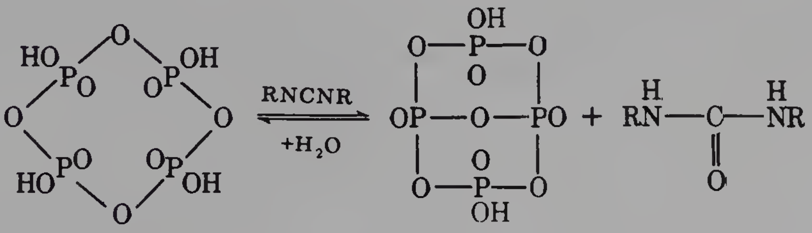
Condensed phosphates are usually prepared by dehydration of orthophosphates under various conditions of temperature (300–1200°C) and also by appropriate hydration of dehydrated species, as, for example,

$$(n - 2)NaH_2PO_4 + 2Na_2HPO_4 \xrightarrow{\text{heat}} \underset{\text{Polyphosphate}}{Na_{n+2}P_nO_{3n+1}} + (n - 1)H_2O$$

$$nNaH_2PO_4 \xrightarrow{\text{heat}} \underset{\text{Metaphosphate}}{n(NaPO_3)_n} + nH_2O$$

They can also be prepared by controlled addition of water or other reagents to P_4O_{10}, by treating chlorophosphates with silver phosphates, and so on. The complex mixtures of anions that can be obtained are separated by using ion-exchange or chromatographic procedures as illustrated in Fig. 11-16.

Carbodiimides in solvents such as DMSO or tetramethyl urea can dehydrate H_3PO_4, polyphosphoric acids, or ring acids to the bicyclic ultraphosphonic acid ($H_2P_4O_{11}$), as illustrated by the following reaction:



Tetrametaphosphoric 1,5-μ-Oxotetrametaphosphoric

Polyphosphoric acids[45c] are obtained by reaction of P_4O_{10} with water or by heating H_3PO_4 to remove water. A P_4O_{10}/H_2O mixture containing 72.42% P_4O_{10} corresponds to pure H_3PO_4, but the usual commercial grades of the acid contain more water. As the P_4O_{10} content increases $H_4P_2O_7$, *pyrophosphoric acid,* forms along with the P_3 through P_8 polyphosphoric acids. Equilibria are achieved only slowly, and half-lives for the formation or hydrolysis of P—O—P linkages when catalysts are excluded can be of the order of years. That is why enzymes called phosphorylases or nucleases are so important in biochemistry, to achieve needed interconversions of mono-, di-, tri-, and polyphosphate esters.

Phosphate Esters in Biology. Many of the most essential chemicals in life processes are phosphate esters. These include the genetic substances DNA and RNA [representative fragments of the chains appear as (11-XL) and (11-XLI), respectively], as well as cyclic AMP (adenosine monophosphate), (11-XLII). In addition, the transfer of phosphate groups between ATP and ADP (eq. 11-6), is of fundamental importance in the energetics of biological systems. All the biological reactions involving formation and hydrolysis of these and other phosphate esters, and polyphosphates are effected by enzyme cat-

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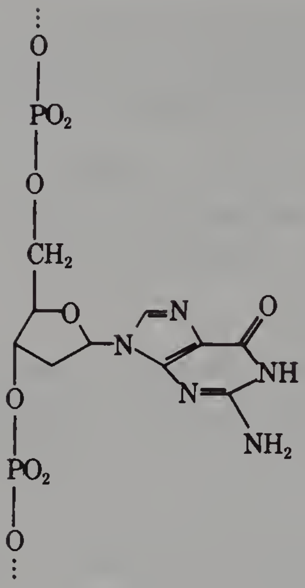
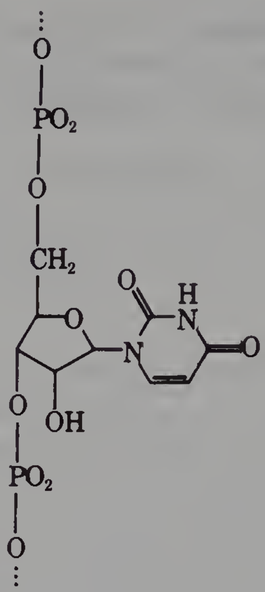
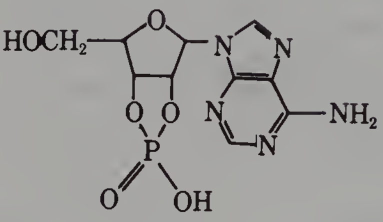
[45c] See J. S. Pizey, ed., *Synthetic Reagents,* Horwood-Wiley, Chichester, 1985.



(11-XL)

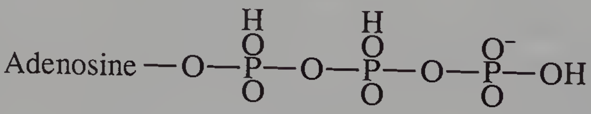


(11-XLI)



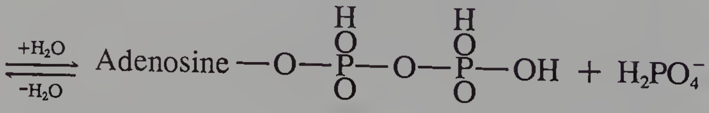
(11-XLII)

alysts, many of which contain metal ions as parts of their structure, or require them as coenzymes.



$$\text{Adenosine}-O-\underset{O}{\overset{\overset{H}{O}}{P}}-O-\underset{O}{\overset{\overset{H}{O}}{P}}-O-\underset{O}{\overset{O^-}{P}}-OH$$

ATP



$$\underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} \text{Adenosine}-O-\underset{O}{\overset{\overset{H}{O}}{P}}-O-\underset{O}{\overset{\overset{H}{O}}{P}}-OH + H_2PO_4^- \qquad (11\text{-}6)$$

ADP

In no small measure because of the importance of such substances and processes as those just mentioned, the hydrolysis of phosphate esters has received much fundamental study. Triesters are attacked by OH^- at phosphorus and by H_2O at carbon, as shown in eq. 11-7. Diesters, which are

$$OP(OR)_3 \begin{array}{l} \xrightarrow{^{18}OH^-} OP(OR)_2(^{18}OH) + RO^- \\ \xrightarrow[H_2{}^{18}O]{} OP(OR)_2(OH) + R^{18}OH \end{array} \qquad (11\text{-}7)$$

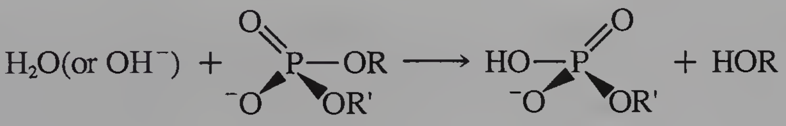
strongly acidic (eq. 11-8), are completely in the anionic form at normal (and physiological) pH's:

$$R'O-\overset{\overset{\large O}{\|}}{\underset{\underset{\large OH}{|}}{P}}-OR \rightleftharpoons R'OPO_2OR^- + H^+ \qquad K \approx 10^{-1.6} \tag{11-8}$$

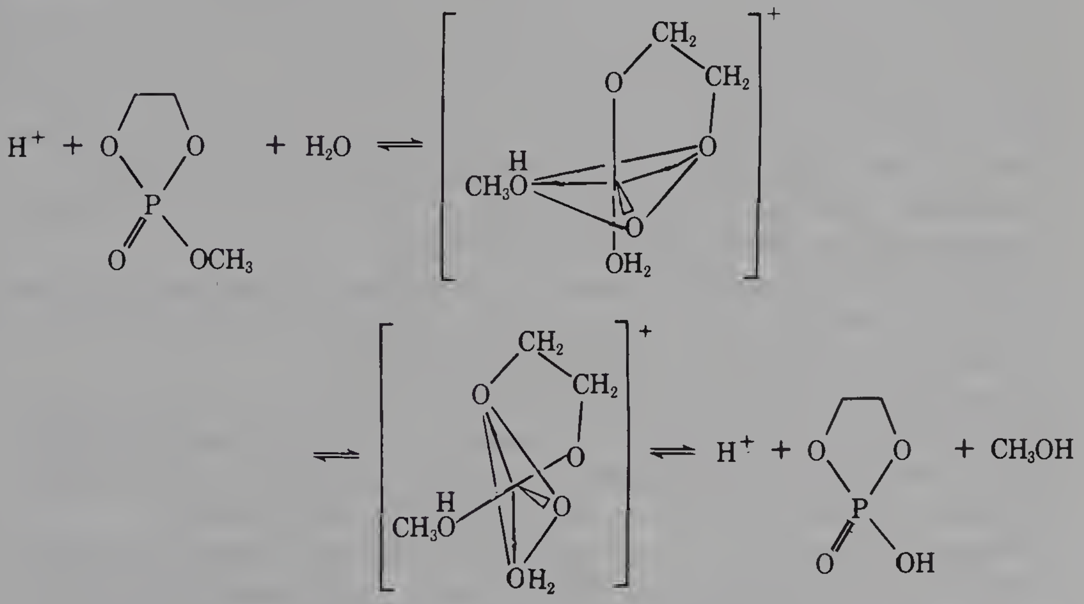
They are thus relatively resistant to nucleophilic attack by either OH^- or H_2O, and this is why enzymic catalysis is indispensable to achieve useful rates of reaction.

Three major pathways have been discussed for phosphate ester hydrolyses:

1. One-step nucleophilic displacement (S_N2) with inversion:



2. Nucleophilic attack in which a cyclic five-coordinate intermediate is formed, which then pseudorotates (cf. Section 29-13):



3. The somewhat controversial "metaphosphate" path, which entails release of a short-lived PO_3^- ion, which is rapidly converted by H_2O to $H_2PO_4^-$. The PO_3^- ion has been shown to be very stable and unreactive in the gas phase,[46] and it appears likely that this pathway may occur in aprotic solvents (e.g., CH_3CN), but its occurrence in aqueous media remains unproved.[47]

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[46] M. Henchman *et al., J. Am. Chem. Soc.,* 1985, **107,** 1453.

[47] J. M. Friedman and J. R. Knowles, *J. Am. Chem. Soc.,* 1985, **107,** 6126; F. Ramirez *et al., J. Am. Chem. Soc.,* 1986, **108,** 348.

11-17. Oxo Acids and Anions of As, Sb, and Bi

Arsenic. Arsenic acid (H_3AsO_4) is obtained by treating arsenic with concentrated nitric acid to give white crystals, $H_3AsO_4 \cdot \frac{1}{2}H_2O$, or by catalyzed treatment of As_2O_3 with air and H_2O under pressure.[48] Unlike phosphoric acid, it is a moderately strong oxidizing agent in acid solution, the potentials being

$$H_3AsO_4 + 2H^+ + 2e = HAsO_2 + 2H_2O \qquad E^0 = 0.559 \text{ V}$$

$$H_3PO_4 + 2H^+ + 2e = H_3PO_3 + H_2O \qquad E^0 = -0.276 \text{ V}$$

Arsenic acid is tribasic but somewhat weaker ($pK_1 = 2.3$) than phosphoric acid. The arsenates generally resemble orthophosphates and are often isomorphous with them.

Condensed arsenic anions are much less stable than the condensed phosphates and, owing to rapid hydrolysis, do not exist in aqueous solution. Dehydration of KH_2AsO_4 gives three forms, stable at different temperatures, of metaarsenate; one form is known to contain an infinite chain polyanion, and another contains the cyclotriarsenate ion, $[As_3O_9]^{3-}$.

Raman spectra show that in acid solutions of As_4O_6 the only detectable species is the pyramidal $As(OH)_3$. In basic solutions ($[OH^-]/[As^{III}]$ ratios of 3.5–15) the four pyramidal species $As(OH)_3$, $As(OH)_2O^-$, $As(OH)O_2^{2-}$, and AsO_3^{3-} appear to be present. In solid salts the arsenite ion is known in the AsO_3^{3-} form, as well as in more complex ones. Alkali metal arsenites are very soluble in water while those of heavy metals are more or less insoluble.

Antimony. No lower acid is known, but only the hydrated oxide, $Sb_2O_3(aq)$; the antimonites are well-defined salts, however.

Addition of dilute alkali hydroxide to $SbCl_5$ gives solutions containing the $[Sb^V(OH)_6]^-$ ion, which can be obtained in crystalline salts; the sodium salt is unusual in being the least soluble of the alkali salts.

There do not appear to be finite SbO_4^{3-} ions under any circumstances. Some "antimonates" obtained by heating oxides, for example, M^ISbO_3, $M^{III}SbO_4$, and $M_2^{II}Sb_2O_7$, contain SbO_6 octahedra and differ only in the manner of linking in the lattice. They are best regarded as mixed oxides.

Bismuth. When $Bi(OH)_3$ in strongly alkaline solution is treated with chlorine or other strong oxidizing agents, "bismuthates" are obtained, but never in a state of high purity. They can be made, for example, by heating Na_2O_2 and Bi_2O_3, which gives $NaBi^VO_3$. This yellow-brown solid dissolves in 0.5 M $HClO_4$ to give a solution that is stable in absence of light for several days. The Bi^V/Bi^{III} potential appears to be +2.03 V, which suggests that Bi^V is one of the most powerful oxidants in aqueous solution, being comparable to peroxodisulfate ($S_2O_8^{2-}/2SO_4^{2-}$, $E^0 = 2.01$ V) or ozone (O_3, $2H^+/O_2$, H_2O, $E^0 = 2.07$ V). The precise nature of the bismuth (V) species is unknown, but it could be $[Bi(OH)_6]^-$.

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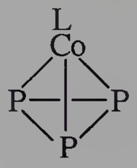
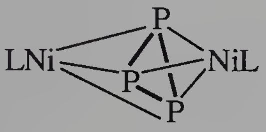
[48] *Financial Times,* 1984, March 21, p. 19.

11-18. Ligands Formed by the Group VA(15) Elements

The Elements and Their Ions. These are a number of ligands that consist exclusively of Group VA(15) atoms.[49] The P_3 unit is often found in complexes that are stabilized by the tripod ligands $MeC(CH_2PPh_2)_3$ or $N(CH_2CH_2PPh_2)_3$, as in (11-XLIII) and (11-XLIV) where L represents a tripod ligand.



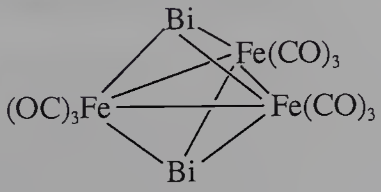
(11-XLIII)



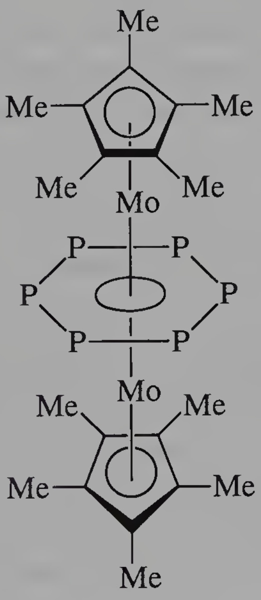
(11-XLIV)

The P_4 molecule itself can serve as an η^1 or an η^2 ligand, for example in $LNi(\eta^1\text{-}P_4)$ and *trans*-$[RhCl(PPh_3)_2\,(\eta^2\text{-}P_4)]$[50a] or as a zigzag chain.[50b]

Single atoms, which can be formally regarded as E^{3-} are known as capping ligands (11-XLV)[51], as centered in planar M_3P groups or encapsulated,[52] as in $[Rh_{10}(CO)_{32}P]^{3-}$ or pyramidal as in $Bi[Mn(CO)_5]_3$.



(11-XLV)



(11-XLVI)

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[49] M. DiVaira and L. Sacconi, *Angew. Chem. Int. Ed. Engl.*, 1982, **21**, 330; A. J. Welch *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 4487; W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 56 (review); P. Stoppioni *et al.*, *Polyhedron*, 1987, **6**, 351 (review).

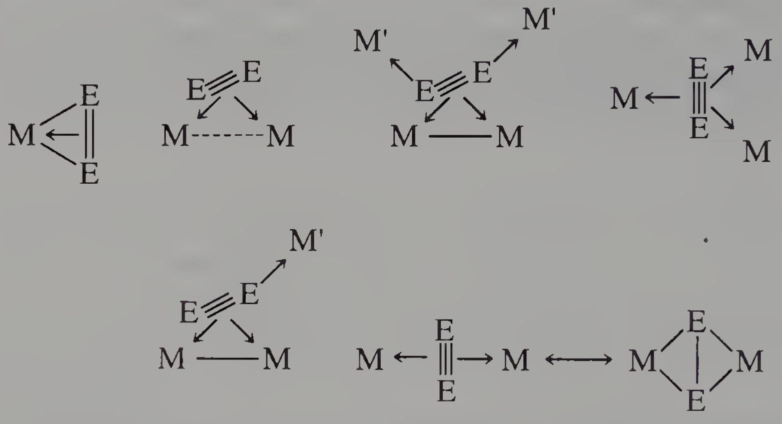
[50a] A. P. Ginsberg *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 403.

[50b] C. A. Ghilardi *et al.*, *Inorg. Chem.*, 1986, **25**, 1776; E. Hey *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987**, 597.

[51] K. H. Whitmore *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987**, 926.

[52] G. Hüttner *et al.*, *J. Organomet. Chem.*, 1985, **282**, 331; A. J. Carty *et al.*, *Inorg. Chem.*, 1983, **22**, 1409.

The P_2 and As_2 molecules can bind in a variety of ways,[53] formally as four-, six-, or eight-electron donors:



There are resemblences in several cases to the binding of acetylene. Examples are $[Cp(CO)_2Mo]_2As_2$, $[(OC)_5W]_3As_2$, and $(diphos)_2NiP_2$.

On refluxing $[Cp^*Mo(CO)_2]_2$ with P_4 in xylene a "hexaphosphabenzene" P_6 ring is formed as shown in (11-XLVI). Similar reactions give Cr and Fe compounds with a P_5 ring.[54a] A similar compound with a *cyclo*-As_5 bridge shows variations in the As—As distances and may be better regarded as having μ,η^2-As_3 and μ,η^2As groups.[54b]

Phosphorus Oxides and Sulfides. Cage molecules such as P_4O_6 and P_4S_3 can employ a lone pair on a phosphorus atom to form complexes such as $Fe(CO)_4(\eta^1\text{-}P_4O_6)$ and $(triphos)Ni(\eta^1\text{-}P_4S_3)$; bridge formation may also occur, as in $[Pt(PPh_3)(\mu\text{-}P_4S_3)]_3$.[55] Removal of P═O from P_4O_{10} to give $P_3O_9^{3-}$ allows binding of three oxygen atoms to a metal.[56]

ER_3 Compounds as Ligands.[57] The bonding of such ligands, for example, PCl_3, PF_3, and PR_3 to transition metals has been discussed in Section 2-10. Analogous compounds for As, Sb, and to a lesser extent Bi have also been studied. Generally, the σ-donor ability decreases $P > As > Sb > Bi$ and BiR_3 compounds are very poor donors. Steric effects due to the donor atom itself will increase in the order $P < As < Sb < Bi$ while steric effects of the substituents on the atom will be in the order $P > As > Sb$. The steric effects on phosphorus may be dominant in determining the stereochemistry and structures as well as the chemistry of PR_3 complexes as discussed earlier (Section 2-10). Tertiary phosphines have been extensively studied in catalytic reactions, where selectivity can be controlled by steric factors and chiral syntheses can be facilitated by use of dissymetric phosphines (Chapter 28).

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[53] H. Schäfer *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 522; G. Hüttner *et al., Organometallics*, 1985, **4**, 326; M. H. Chisholm *et al., Polyhedron*, 1985, **4**, 893.

[54a] M. T. Nguyen and A. F. Hegarty, *J. Chem. Soc. Chem. Commun.*, **1986**, 383. O. Scherer *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 362; 1987, **26**, 59.

[54b] A. L. Rheingold *et al., J. Am. Chem. Soc.*, 1982, **104**, 4727.

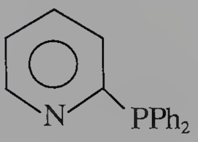
[55] M. DiVaira *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 291.

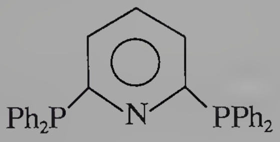
[56] V. W. Day *et al., Organometallics*, 1985, **4**, 564.

[57] C. A. McAuliffe and W. Levason, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Vol. 1, Elsevier, Amsterdam, 1979.

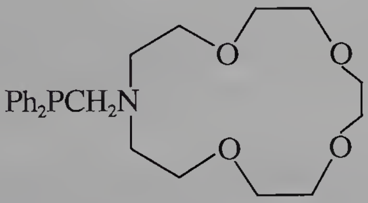
Monophosphines. Probably the most common are triphenylphosphine and trimethylphosphine,[58a] although mixed alkyl/aryl phosphines, for example, PEt_2Ph, have also been much used as their complexes are generally more soluble than those of triaryl phosphines. All manner of phosphines have been made with functional groups[58b] either on aryl rings, as in $[2,4,6\text{-}(MeO)_3C_6H_2]_3P$ (which is as basic as a dialkylamine), or in $P(C_6H_4SO_3^-)_3$, or on alkyls. Examples of the latter type are Ph_2PCH_2CN, $Ph_2PCH_2CO_3Et$, and $Ph_2PCH_2CH_2CO_2^-$.

A useful ligand is 2-diphenylphosphinopyridine (11-XLVII) which can be unidentate, chelating, or bridging[59]; the 2,6-disubstituted pyridine ligand (11-XLVIII) has given only bridged complexes with P,P or P,N,P donation.[60]


(11-XLVII)


(11-XLVIII)

The crown ligand (11-XLIX) has not only P donor capacity but can complex additional alkali metal ions and this dual function allows insertion reactions of CO (Section 27-6) to be facilitated.[61]


(11-XLIX)

Many useful ligands can be derived from $MePCl_2$, which itself can be made commercially by reaction of CH_4 with PCl_3 over a catalyst at 600°C.[62]

Cleavage of P—C bonds in aryl phosphines at elevated temperatures is an important process.[63] It may lead to (*a*) phosphido species with PR_2 or PR groups (to be discussed later), (*b*) aryl group exchange, or (*c*) replacement of aryl groups as in the hydroformylation of propylene (Chapter 28) where

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[58a] H.-F. Klein, *Angew. Chem. Int. Ed. Engl.*, 1980, **19,** 362; M. L. H. Green *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985,** 202.

[58b] See, for example, M. J. Auburn and S. R. Stobart, *Inorg. Chem.*, 1985, **24,** 318; S. E. Bouaoud *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987,** 488.

[59] L. H. Pignolet *et al.*, *Inorg. Chem.*, 1985, **24,** 1935.

[60] A. L. Balch *et al.*, *Inorg. Chem.*, 1984, **23,** 4309.

[61] S. J. McLaine *et al.*, *Inorg. Chem.*, 1986, **25,** 3124.

[62] U.-H. Felcht *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1981, **20,** 223.

[63] P. E. Garrou *et al.*, *Organometallics*, 1985, **4,** 649; *Chem. Rev.*, 1985, **85,** 171 (109 references); A. G. Abatjoglou *et al.*, *Organometallics*, 1985, **4,** 923, 932; F. A. Cotton *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 6049; *Inorg. Chem.*, 1985, **24,** 3584.

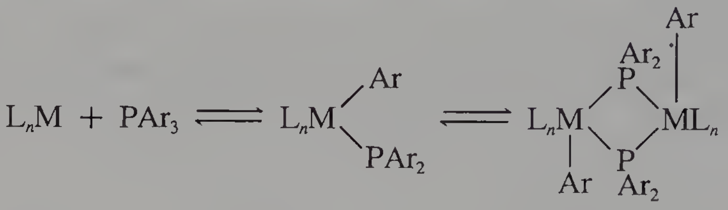
Ph_3P is converted to $Ph_2PCH_2CH_2CH_3$. Two representative reactions are

$$2Pt(PPh_3)_4 \xrightarrow{\Delta} (Ph_3P)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)_2 + Ph{-}Ph$$

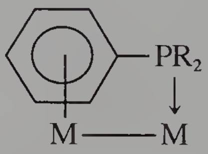
$$2HIr(CO)(PPh_3)_3 \xrightarrow{\Delta} [(Ph_3P)_2(CO)Ir]_2(\mu\text{-}PPh_2)_2 + 2C_6H_6$$

In some cases the aryl group is transferred to the metal atom.

The P—C bond-breaking reactions may proceed by intra- or intermolecular oxidative-addition (Chapter 27) processes, for example,

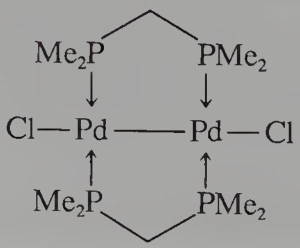


Aryl phosphines may also be bonded to metal atoms as substituted η^6-arenes. The dangling PR_2 may then act as a donor to another metal atom,[64] thus bridging across M—M bonded units:

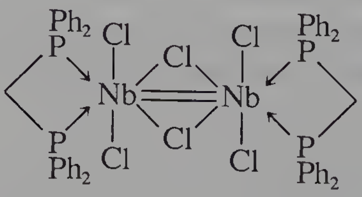


Finally, it may be noted that when thermal or photochemical removal of a PR_3 ligand, in order to open a vacant site on a metal atom, is not feasible, a reagent known as "phosphine sponge" $[9\text{-BBN}]_2$ (Section 6-14) provides an efficient alternative.[65]

Di- and Polyphosphine Ligands.[66] These bi- or polydentate ligands, of which the most widely used are $Me_2PCH_2CH_2PMe_2$ [bis(dimethylphosphinoethane) (dmpe)], $Ph_2PCH_2CH_2PPh_2$ [bis(diphenylphosphinoethane) (dppe)], $Me_2PCH_2PMe_2$ [bis(dimethylphosphinomethane) (dmpm)], and $Ph_2PCH_2PPh_2$ [bis(diphenylphosphinomethane) (dppm)], can form either chelated or bridged complexes, as shown by the examples (11-L) to (11-LIII).



(11-L)



(11-LI)

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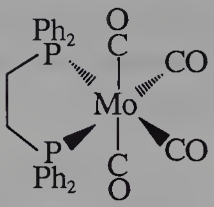
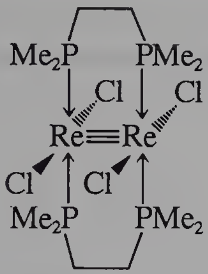
[64] R. H. Morris *et al.*, *Organometallics*, 1984, **3,** 247, 1009; *J. Am. Chem. Soc.*, 1984, **106,** 7978; C. P. Casey and R. M. Bullock, *Organometallics*, 1984, **3,** 1100; H. Werner *et al.*, *J. Organomet. Chem.*, 1984, **276,** 231.

[65] R. Luck and R. H. Morris, *Inorg. Chem.*, 1984, **23,** 1489.

[66] R. J. Puddephat, *Chem. Soc. Rev.*, **1983,** 99; D. M. A. Minahan *et al.*, *Coord. Chem. Rev.*, 1984, **55,** 31; D. R. Powell *et al.*, *Inorg. Chem.*, 1985, **24,** 3589; S. A. Laneman and G. G. Stanley, *Inorg. Chem.*, 1987, **26,** 1177; R. A. Walton and A. C. Price, *Polyhedron*, 1987, **6,** 729.



(11-LII)

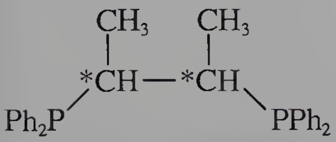


(11-LIII)

There are also cases where the ligand is initially unidentate but can then coordinate to another metal atom so as to produce a binuclear complex.[67]

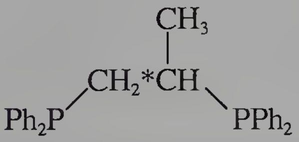
Also, in dmpm or dppm the CH_2 group can be readily deprotonated to give the anionic ligand $[R_2PCHPR_2]^-$, which can act either as a P donor and/or form a metal to carbon bond.[68] An example is $La[(Ph_2P)_2CH]_3$.

There are important optically active diphosphinoethanes, such as (11-LIV)–(11-LVI), which can be used to impose chirality on complexes[69] or on products formed when the chiral complexes serve as catalysts.[70]



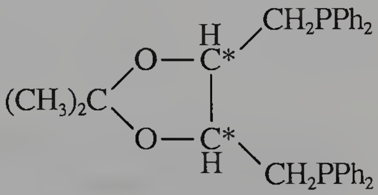
(chiraphos)

(11-LIV)



(prophos)

(11-LV)



(11-LVI)

There is often a considerable difference in the products given by dmpm versus dppm or dmpe versus dppe. Such differences depend in part on the different steric requirements of the Me_2P and Ph_2P groups, but also on their different basicities. For example, dmpe allows the formation of phosphine complexes of metals that otherwise form phosphine complexes only with difficulty, such as U^{IV}, Tc^{IV}, Cr^{II}, and others.[71]

The ligands dppm and dmpm give an important type of complex with d^8 platinum group metal ions that are called A-frame complexes[72] (Section 19-G-1) because of their structure.

Diphosphines with long chains between the P atoms, for example, $t\text{-}Bu_2P(CH_2)_{5-8}Pt\text{-}Bu_2$ can span trans positions in square complexes or give

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[67] B. L. Shaw *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 2131; G. Wilkinson *et al., Polyhedron,* 1985, **4,** 1231.

[68] R. Usón *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 839; H. H. Karsch *et al., Organometallics,* 1987, **6,** 316.

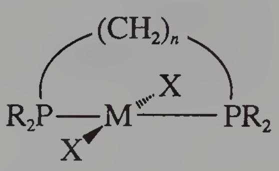
[69] F. A. Cotton *et al., J. Am. Chem. Soc.*, 1984, **106,** 1851.

[70] J. Halpern, *Science,* 1982, **217,** 401.

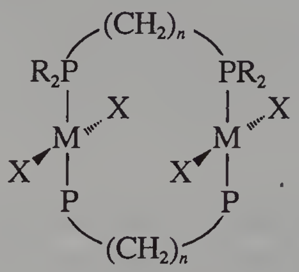
[71] R. A. Andersen *et al., J. Am. Chem. Soc.*, 1982, **104,** 3725; G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 921.

[72] B. Bosnich *et al., Inorg. Chem.*, 1985, **24,** 2334.

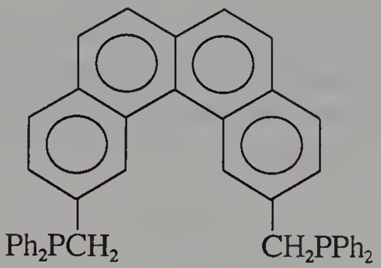
large ring systems (11-LVII) and (11-LVIII), respectively.[73] The reasons for the stabilities of these unusual cyclic systems are complex. That (11-LIX) should span trans positions is less surprising.[74]



(11-LVII)

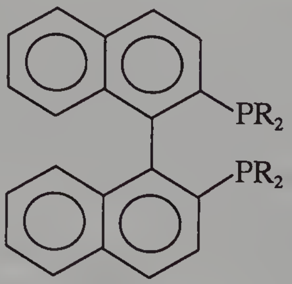


(11-LVIII)

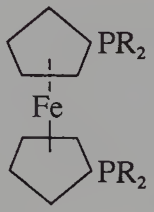


(11-LIX)

Other important biphosphines are the asymmetric binaphthyls[75] (11-LX) and others discussed in Section 28-10 as well as 1,1′-diphosphinoferrocenes (11-LXI) that can act as either chelating or bridging ligands.[76]



(11-LX)



(11-LXI)

Tridentate Phosphines. Perhaps the most important of these are the tripods,[77] such as $HC(CH_2PR_2)_3$, as well as ligands such as $N(CH_2CH_2PPh_2)_3$ or

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[73] B. L. Shaw *et al., J. Chem. Soc. Dalton Trans.,* **1979,** 1972; W. E. Hill *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 2655.

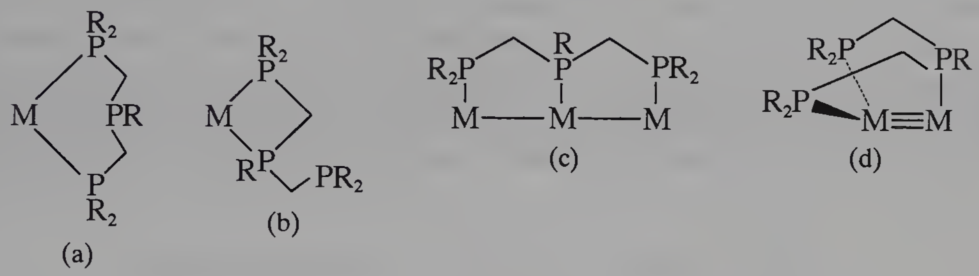
[74] L. M. Venanzi *et al., Helv. Chim. Acta,* 1984, **67,** 65.

[75] J. R. Murdock *et al., J. Am. Chem. Soc.,* 1984, **106,** 4717; H. Takaya *et al., J. Org. Chem.,* 1986, **51,** 629.

[76] W. R. Cullen *et al., Organometallics,* 1985, **4,** 972.

[77] L. Sacconi and F. Mani, in *Transition Metal Chemistry,* G. A. Melson and B. N. Figgis, Eds., Vol. 8, Dekker, New York, 1982.

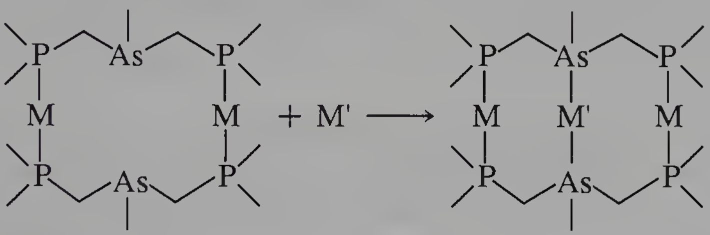
$P(CH_2CH_2PMe_2)_3$, which are potentially tetradentate.[78] Linear tridentate phosphines can behave in a number of ways, as shown in (11-LXIIa) through (11-LXIId).



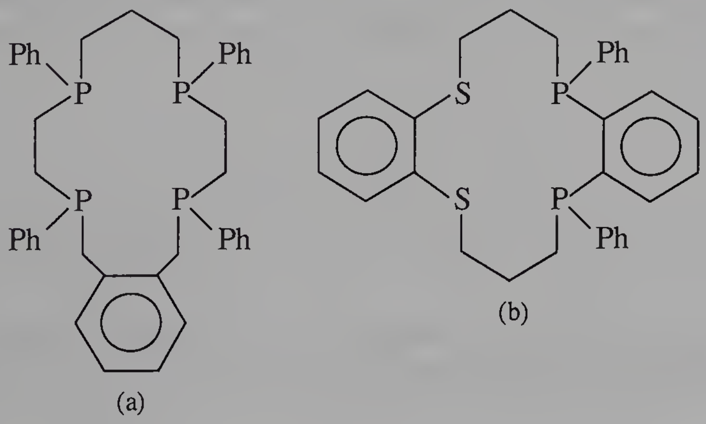
(a) (b) (c) (d)

(11-LXII)

Also, there is the situation where a diphosphinoarsine first forms a binuclear macrocycle, which then adds another metal atom[79]:



Macrocyclic Phosphines.[80] There are a number of macrocycles with phosphorus donors only, or with mixed sets of P and N or P and S donors, for example, (11-LXIIIa and b).



(a) (b)

(11-LXIII)

Phosphite Ligands.[81] There are many ligands similar to the phosphine ligands with OR instead of R groups, such as $P(OMe)_3$ or $(RO)_2POP(OR)_2$.

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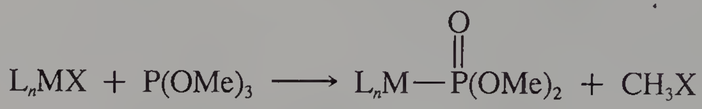
[78] G. A. Ghilardi *et al., Inorg. Chem.*, 1985, **24,** 164; L. Dahlenburg, *Inorg. Chem.*, 1984, **23,** 4170.

[79] A. L. Balch *et al., J. Am. Chem. Soc.*, 1985, **107,** 5273; *Inorg. Chem.*, 1985, **24,** 290.

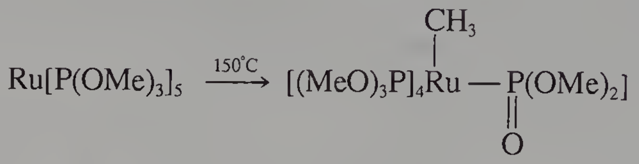
[80] M. Ciampolini *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 479; O. Stelzer *et al., Inorg. Chem.*, 1984, **23,** 3304; E. P. Kyba *et al., Inorg. Chem.*, 1987, **26,** 1647.

[81] T. B. Brill and S. J. Landon, *Chem. Rev.*, **1984,** 577.

There complexes are often similar to those of phosphines but since the phosphites tend to be more basic and less sterically hindered [e.g., $P(OPh)_3$ and, *a fortiori*, $P(OMe)_3$ compared with PPh_3], there are important differences. Thus, there is no phosphine analogue of $Re_2(CO)_{10}$, but $Re_2[P(OMe)_3]_{10}$ can be made.[82] In some cases where a substitution-labile ligand is also present on the metal, the reaction with an alkyl phosphite gives a coordinated phosphonate (a process reminiscent of the Michaelis–Arbusov reaction, Section 11-6).[83] A somewhat comparable methyl migration reaction is the following[84]:



$$L_nMX + P(OMe)_3 \longrightarrow L_nM{-}\overset{\overset{\displaystyle O}{\|}}{P}(OMe)_2 + CH_3X$$

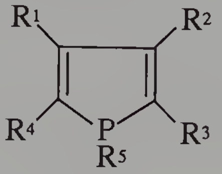


$$Ru[P(OMe)_3]_5 \xrightarrow{150^\circ C} [(MeO)_3P]_4Ru{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle CH_3}{|}}{P}}(OMe)_2]$$

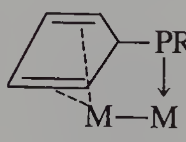
It may be noted that while $(RO)_2POP(OR)_2$ ligands can be unidentate or bridging, because of the wide POP angle, they do not chelate.[85]

Many phosphites and their amido derivatives play a major role in industrial hydrometallurgy as extractants, because of their ability to complex selectively certain metal ions.[86]

Heterocyclic Phosphorus Ligands. The ligand capacity of phosphabenzene has already been noted (Section 11-12). The phospholes[87] (11-LXIV) can also behave simply as η^1 donors, or also engage their π-electron density, whence they generally become bridging ligands, as in (11-LXV).



(11-LXIV)



(11-LXV)

There is also a P,N ligand[88a] analogous to 2,2′-bipyridyl, namely, (11-LXVI). Phosphazenes can also act as ligands.[88b]

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[82] H. W. Choi and E. L. Muetterties, *J. Am. Chem. Soc.*, 1982, **104,** 153.

[83] S. J. Landon and T. B. Brill, *Inorg. Chem.*, 1984, **23,** 1266.

[84] V. W. Day *et al., Inorg. Chem.*, 1982, **21,** 657.

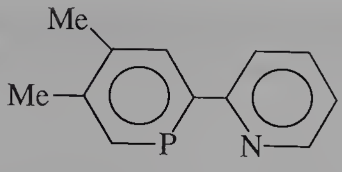
[85] A. L. du Preez *et al., J. Chem. Soc. Dalton Trans.*, **1981,** 1918.

[86] K. Bokolo *et al., Phosphorus Sulfur,* 1983, **18,** 315; M. Burgard and M. Prevost, *ibid.*, 319; C. Yuan, *ibid.*, 323.

[87] F. Mathey *et al., Struct. Bonding, Berlin,* 1983, **55,** 153.

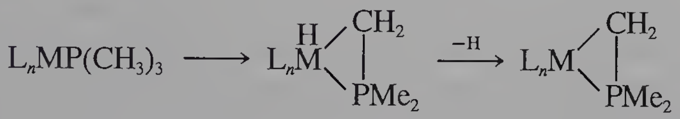
[88a] F. Mathey *et al., Inorg. Chem.*, 1984, **23,** 3463.

[88b] H. R. Alcock *et al., Polyhedron,* 1987, **6,** 119.

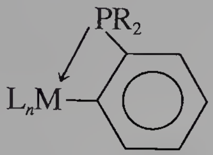


(11-LXVI)

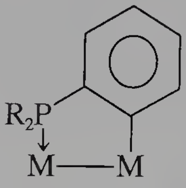
Cyclometallated Phosphine Complexes. Phosphine ligands often engage in H-transfer reactions (Section 27-9) to give M—C bonds. Simple examples are provided by reactions of PMe_3[89]:



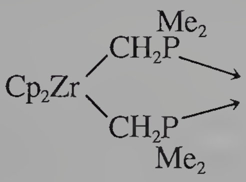
With longer-chain alkyl phosphines, β-, γ-, or δ-hydrogen atoms may be lost leading to 4-, 5-, or 6-membered heterocyclic rings.[90] Hydrogen transfer from phenyl rings has also been observed, to give products with the units (11-LXVII) or (11-LXVIII).[91] It is also possible for CH_2PMe_2 or CH_2PPh_2 groups to be bound only through carbon[92] and for such compounds, the "dangling" phosphorus atom can coordinate further, for example, (11-LXIX).



(11-LXVII)

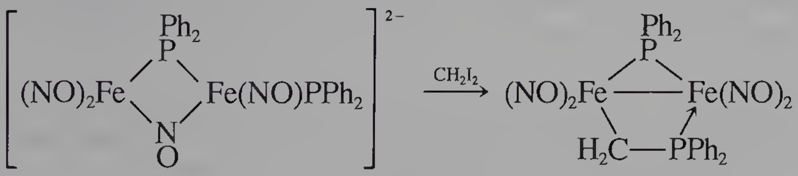


(11-LXVIII)



(11-LXIX)

A bridged species has also been obtained by the following reaction[93]:



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[89] M. H. L. Green *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 202; V. V. Mainz and R. A. Anderson, *Organometallics,* 1984, **3,** 675.

[90] B. L. Shaw *et al., J. Chem. Soc. Dalton Trans.,* **1981,** 1572.

[91] F. A. Cotton *et al., J. Am. Chem. Soc.,* 1984, **106,** 1323.

[92] M. Etienne *et al., Nouv. J. Chim.,* 1984, **8,** 531; N. E. Schore *et al., Organometallics,* 1983, **2,** 1769; H. H. Karsch *et al., J. Organometal. Chem.,* 1984, **273,** 195; F. Senocq *et al., J. Chem. Soc. Chem. Commun.,* **1984,** 1376.

[93] A. Wojcicki *et al., J. Am. Chem. Soc.,* 1984, **106,** 3704.

Dialkylphosphido Ligands.[94] Major methods of preparing complexes of R_2P ligands, which may be either terminal or bridging, are illustrated by the following reactions:

$$Cp_2ZrCl_2 + 2LiPPh_2 \longrightarrow Cp_2Zr(PPh_2)_2 + 2LiCl$$

$$PtCl_2(PPh_2Cl)_2 + 2NaMn(CO)_5 \longrightarrow Cl_2Pt[(\mu\text{-}PPh_2)Mn(CO)_5]_2 + 2NaCl$$

$$L_nMCH_3 + HPPh_2 \longrightarrow L_nMPPh_2 + CH_4$$

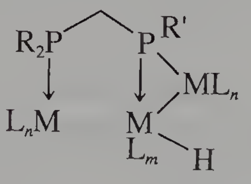
Cleavage of R_2PPR_2 or P—C bonds can also be employed. A variety of R_2As compounds as well as R_2Sb and R_2Bi compounds are also known.[95]

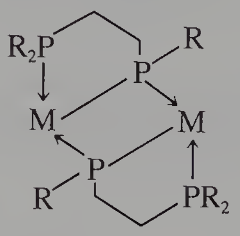
Although bridging R_2P groups are the most common, there are a number of compounds analogous to dialkylamido compounds, such as $Mo[P(c\text{-}C_6H_{11})_2]_4$ and $Zr[P(c\text{-}C_6H_{11})_2]_5^-$.[96] However, homoleptic complexes are relatively rare and usually other ligands such as PR_3 or CO are present.[97a] The nonbridging species can react to form bridges, as in the following example:

$$Cp_2^*Th(PR_2)_2 + Ni(CO)_4 \longrightarrow Cp_2^*Th(\mu\text{-}PR_2)_2Ni(CO)_2 + 2CO$$

A compound[97b] with an M═P double bond is $(C_5H_5)(CO)_2W{=}Pt\text{-}Bu_2$.

Phosphine–phosphido ligands[98] can be made, for example, from $R_2P(CH_2)_nPRH$, and give complexes such as the following:





Phosphinidine Ligands. Compounds with MPR units (cf. MNR) are usually transient intermediates. However, with bulky R groups, compounds such as $Cp_2MoP(C_6H_2t\text{-}Bu\text{-}2,4,6)$ can be isolated[99]; the Mo—P—C angle, 115.8°, is consistent with a Mo—P bond and a lone pair on P. Usually ER(E = P, As, Sb) groups serve as bridges, of μ_2, μ_3, or μ_4 types. For the μ_2 type, the structures may be either open (i.e., no M—M bond) or closed, depending

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[94] See, for example, G. L. Geoffroy *et al., Organometallics,* 1987, **6,** 101; R. A. Jones *et al., Inorg. Chem.,* 1987, **26,** 3943; M. Calligaris *et al., J. Am. Chem. Soc.,* 1987, **109,** 3617.

[95] R. A. Jones and B. R. Whittlesey, *J. Am. Chem. Soc.,* 1985, **107,** 1078.

[96] R. T. Baker *et al., J. Am. Chem. Soc.,* 1983, **105,** 6763.

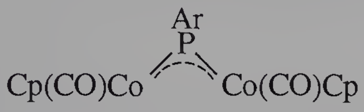
[97a] R. R. Ryan *et al., Organometallics,* 1986, **5,** 90; J. E. Bercaw *et al., J. Am. Chem. Soc.,* 1985, **107,** 4670; J. A. Gladysz *et al., J. Am. Chem. Soc.,* 1985, **107,** 3347; *Inorg. Chem.,* 1985, **24,** 3505; R. T. Baker *et al., Inorg. Chem.,* 1985, **24,** 1379; R. A. Jones *et al., J. Am. Chem. Soc.,* 1985, **107,** 888.

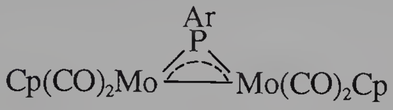
[97b] W. Malisch *et al., Angew. Chem. Int. Ed. Engl.,* 1986, **25,** 92.

[98] O. Stelzer *et al., Angew. Chem. Int. Ed. Engl.,* 1984, **23,** 734; R. Glaser *et al., J. Am. Chem. Soc.,* 1984, **106,** 6324.

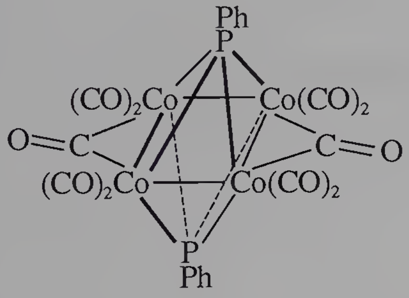
[99] P. B. Hitchcock, *et al., J. Chem. Soc. Chem. Commun.,* **1987,** 1282.

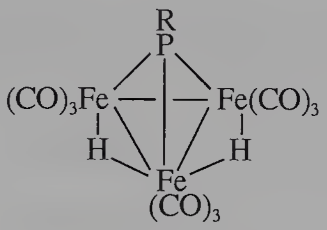
on the overall electronic requirements of the metal atoms,[100] as illustrated by the following examples (where Ar = 2,4,6-t-$Bu_3C_6H_2$):



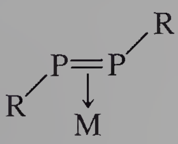


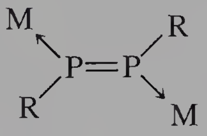
Examples of μ_3- and μ_4-RP complexes[101a] are

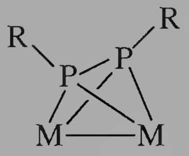




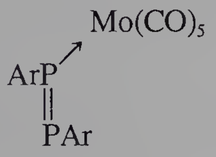
Ligands with P=P, P=C, and P≡C Bonds.[101b] Numerous P and As compounds that contain multiple bonds (Section 11-14) can form a variety of complexes, the following being important types:



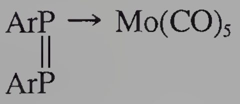




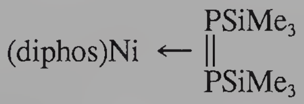
Donation can occur from the multiple bond, from one or both lone pairs, or even all three. Some real examples (Ar = 2,4,6-t-$Bu_3C_6H_2$) are

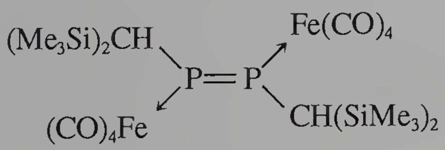


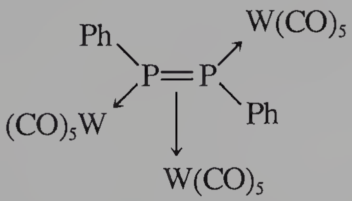
(trans)



(cis)







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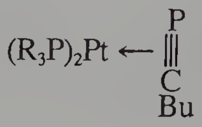
[100] A. H. Cowley *et al.*, *Organometallics*, 1987, **6**, 189; G. Trinquier and G. Bertrand, *Inorg. Chem.*, 1985, **24**, 3842; G. Hüttner and K. Evertz, *Acc. Chem. Res.*, 1986, **19**, 406.

[101a] S. Aime *et al.*, *Organometallics*, 1986, **5**, 245; G. Hüttner *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 1119; 1987, **26**, 743.

[101b] O. J. Sherer, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 924 (a review, covering As, Sb, and Bi ligands as well); A. H. Cowley *et al.*, *Organometallics*, 1984, **3**, 1044; G.Hüttner *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 1069; M. Yoshituji, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 211; H. Schäfer *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 522.

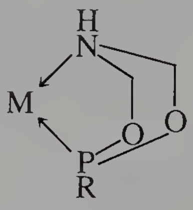
Similarly, phosphaalkenes ($RP{=}CR'_2$) can act as η^1 or η^2 ligands[102] and facile interconversion of isomers is known to occur.

Finally, phosphaalkynes can bind as η^2 ligands,[103] namely,

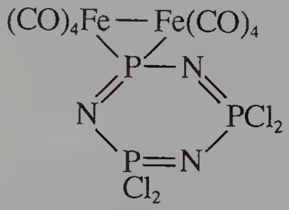


$$(R_3P)_2Pt \leftarrow \begin{array}{c} P \\ ||| \\ C \\ Bu \end{array}$$

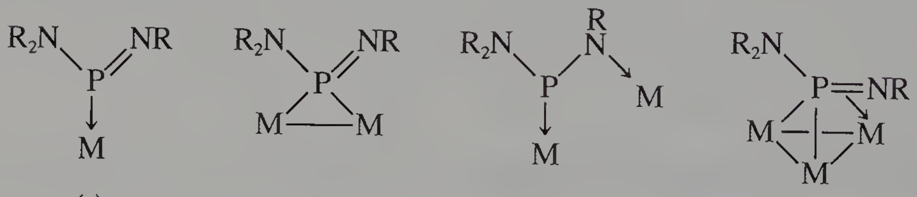
A selection of other examples of phosphorus ligands is represented by (11-LXX),[104] (11-LXXI),[105] (11-LXXII),[106] and (11-LXXIII).[107]



(11-LXX)

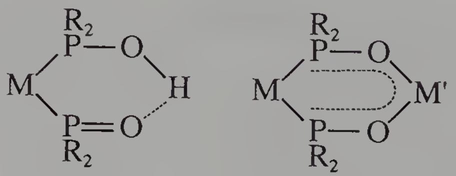


(11-LXXI)



(a) (b) (c) (d)

(11-LXXII)



(a) (b)

(11-LXXIII)

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[102] E. Niecke *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985,** 1687; A. H. Cowley *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 7015; F. Bickelhaupt *et al.*, *Organometallics.*, 1984, **3,** 1803; L. Weber *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 604.

[103] J. F. Nixon *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987,** 658; *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 474.

[104] J. G. Riess *et al.*, *Organometallics.*, 1984, **3,** 714.

[105] H. A. Alcock *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 4966.

[106] O. J. Sherer *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 115.

[107] T. A. Stephenson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984,** 801.

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Sheldrick, W. S., *Topics in Current Chemistry,* Vol. 73, Springer, New York (stereochemistry of five- and six-coordinate phosphorus derivatives).

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Van Wazer, J. R., *Phosphorus and Its Compounds,* Vol. I. Interscience, New York, 1958 (a comprehensive account of all phases of phosphorus chemistry; Vol. II, 1961, technology, biological functions, applications).

Chapter Twelve

Oxygen: Group VIA(16)

GENERAL REMARKS

12-1. Types of Oxides

The oxygen atom has the electronic structure $1s^22s^22p^4$. Oxygen forms compounds with all the elements except He, Ne, and possibly Ar, and it combines directly with all the other elements except the halogens, a few noble metals, and the noble gases, either at room or at elevated temperatures. The earth's crust contains ~50% by weight of oxygen. Most inorganic chemistry is concerned with its compounds, if only in the sense that so much chemistry involves water.

Oxygen follows the octet rule, and the closed-shell configuration can be achieved in ways that are similar to those for nitrogen, namely, by (*a*) electron gain to form O^{2-}, (*b*) formation of two single covalent bonds (e.g., R—O—R) or a double bond (e.g., O═C═O), (*c*) gain of one electron and formation of one single bond (e.g., in OH^-), and (*d*) formation of three or four covalent bonds (e.g., R_2OH^+).

There is a variety of disparate binary oxide compounds. The change of physical properties is attributable to the range of bond types from essentially ionic to essentially covalent.

The formation of the O^{2-} ion from O_2 requires the expenditure of considerable energy, ~1000 kJ mol⁻¹:

$$\tfrac{1}{2}O_2(g) = O(g) \qquad \Delta H = 248 \text{ kJ mol}^{-1}$$

$$O(g) + 2e = O^{2-}(g) \qquad \Delta H = 752 \text{ kJ mol}^{-1}$$

Moreover, in the formation of an ionic oxide, energy must be expended in vaporizing and ionizing the metal atoms. Nevertheless, many essentially ionic oxides exist (e.g., CaO) and are very stable because the energies of lattices containing the relatively small (1.40 Å), O^{2-} ion are quite high. In fact, the lattice energies are often sufficiently high to allow the ionization of metal atoms to unusually high oxidation states. Many metals form oxides in oxidation states not encountered in their other compounds, except perhaps in fluorides or some complexes. Examples of such higher oxides are MnO_2, AgO, and PrO_2, many of which are nonstoichiometric.

In some cases the lattice energy is still insufficient to permit complete ionization, and oxides having substantial covalent character, such as BeO or B_2O_3, are formed. Finally, at the other extreme there are gases or volatile solids or liquids, such as CO_2, the N and P oxides, SO_2, and SO_3, that are essentially covalent molecular compounds. Even in "covalent" oxides, unusually high *formal* oxidation states are often found, as in OsO_4, CrO_3, SO_3, and so on.

In some oxides containing transition metals in very low oxidation states, metal "*d* electrons" enter delocalized conduction bands and the materials have metallic properties. An example is NbO.

In terms of chemical behavior, it is convenient to classify oxides according to their acid or base character in the aqueous system.

Basic Oxides. Although X-ray studies show the existence of discrete oxide ions (O^{2-}) [and also peroxide, (O_2^{2-}), and superoxide (O_2^-) ions, discussed later], these ions cannot exist in any appreciable concentration in aqueous solution owing to the hydrolytic reaction

$$O^{2-} + H_2O = 2OH^- \qquad K > 10^{22}$$

For the per- and superoxide ions we also have:

$$O_2^{2-} + H_2O = HO_2^- + OH^-$$

$$2O_2^- + H_2O = O_2 + HO_2^- + OH^-$$

Thus only those ionic oxides that are insoluble in water are inert to it. Ionic oxides function, therefore, as *basic anhydrides*. When insoluble in water, they usually dissolve in dilute acids, for example,

$$MgO(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O$$

although in some cases, MgO being one, high-temperature ignition produces a very inert material, quite resistant to acid attack.

Acidic Oxides. The covalent oxides of the nonmetals are usually acidic, dissolving in water to produce solutions of acids. They are termed *acid anhydrides*. Insoluble oxides of some less electropositive metals of this class generally dissolve in bases. Thus,

$$N_2O_5(s) + H_2O \longrightarrow 2H^+(aq) + 2NO_3^-(aq)$$

$$Sb_2O_5(s) + 2OH^- + 5H_2O \longrightarrow 2Sb(OH)_6^-$$

Basic and acidic oxides will often combine directly to produce salts, such as:

$$Na_2O + SiO_2 \xrightarrow{\text{fusion}} Na_2SiO_3$$

Amphoteric Oxides. These oxides behave acidically toward strong bases and as bases toward strong acids:

$$ZnO + 2H^+(aq) \longrightarrow Zn^{2+} + H_2O$$

$$ZnO + 2OH^- + H_2O \longrightarrow Zn(OH)_4^{2-}$$

Other Oxides. There are various other oxides, some of which are relatively inert, dissolving in neither acids nor bases, for instance, N_2O, CO, and MnO_2; when MnO_2 (or PbO_2) does react with acids (e.g., concentrated HCl), it is a redox, not an acid–base, reaction.

There are also many oxides that are nonstoichiometric. These commonly consist of arrays of close-packed oxide ions with some of the interstices filled by metal ions. However, if there is variability in the oxidation state of the metal, nonstoichiometric materials result. Thus iron(II) oxide generally has a composition in the range $FeO_{0.90}$ to $FeO_{0.95}$, depending on the manner of preparation. There is an extensive chemistry of mixed metal oxides (Section 1-2).

It may be noted further than when a given element forms several oxides, the oxide with the element in the highest formal oxidation state (usually meaning more covalent) is more acidic. Thus for Cr we have: CrO, basic; Cr_2O_3, amphoteric; and CrO_3, fully acidic.

The Hydroxide Ion.[1] Discrete OH^- ions exist only in the hydroxides of the more electropositive elements such as the alkali metals and alkaline earths. For such an ionic material, dissolution in water results in formation of aquated metal ions and aquated hydroxide ions:

$$M^+OH^-(s) + nH_2O \longrightarrow M^+(aq) + OH^-(aq)$$

and the substance is a strong base. In the limit of an extremely covalent M—O bond, dissociation will occur to varying degrees as follows:

$$MOH + nH_2O \rightleftharpoons MO^-(aq) + H_3O^+(aq)$$

and the substance must be considered an acid. Amphoteric hydroxides are those in which there is the possibility of either kind of dissociation, the one being favored by the presence of a strong acid:

$$M{-}O{-}H + H^+ = M^+ + H_2O$$

the other by strong base:

$$M{-}O{-}H + OH^- = MO^- + H_2O$$

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[1] R. F. W. Bader, in *The Chemistry of the Hydroxyl Group,* S. Patai, Ed., Wiley–Interscience, New York, 1971 (theoretical and physical properties of the hydroxyl ion and group). J. R. Jones, *Chem. Br.*, **1971,** 336 (highly basic media and applications).

because the formation of water is so highly favored, that is,

$$H^+ + OH^- = H_2O \qquad K_{25°C} = 10^{14}$$

Hydrolytic reactions of metal ions can be written

$$M(H_2O)_x^{n+} = [M(H_2O)_{x-1}(OH)]^{(n-1)+} + H^+$$

Thus we may consider that the more covalent the M—O bond tends to be, the more acidic are the hydrogen atoms in the aquated ion, but at present there is no extensive correlation of the acidities of aqua ions with properties of the metal.

The formation of hydroxo bridges occurs at an early stage in the precipitation of hydroxides or, in some cases more accurately, hydrous oxides. In the case of Fe^{3+}, precipitation of $Fe_2O_3{\cdot}xH_2O$ [commonly, but incorrectly, written $Fe(OH)_3$] proceeds through the stages

$$\underset{pH<0}{[Fe(H_2O)_6]^{3+}} \xrightarrow{-H^+} \underset{0<pH<2}{[Fe(H_2O)_5OH]^{2+}} \longrightarrow$$

$$\underset{\sim 2<pH<\sim 3}{[(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+}} \xrightarrow{-xH^+}$$

$$\underset{\sim 3<pH<\sim 5}{\text{colloidal } Fe_2O_3{\cdot}xH_2O} \xrightarrow{-yH^+} \underset{pH \sim 5}{Fe_2O_3{\cdot}zH_2O(ppt)}$$

12-2. Covalent Compounds; Stereochemistry of Oxygen

Two-Coordinate Oxygen. The majority of oxygen compounds contain two-coordinate oxygen, in which the O atom forms two single bonds to other atoms and has two unshared pairs of electrons in its valence shell. Such compounds include water, alcohols, ethers, and a variety of other covalent oxides. In the simple systems without significant π bonding the X—O—X group is bent; typical angles are 104.5° in H_2O and 111° in $(CH_3)_2O$.

In many cases, where the X atoms of the X—O—X group have orbitals (usually *d* orbitals) capable of interacting with the lone-pair orbitals of the O atom, the X—O bonds acquire some π character. Such interaction causes shortening of the X—O bonds and generally widens the X—O—X angle. The former effect is not easy to document, since an unambiguous standard of reference for the pure single bond is generally lacking. However, the increases in the angle are self-evident, for example, $(C_6H_5)_2O$ (124°) and the Si—O—Si angle in quartz (142°). In the case of $H_3Si{-}O{-}SiH_3$ the angle is apparently > 150°.

The limiting case of π interaction in X—O—X systems occurs when the σ bonds are formed by two digonal *sp* hybrid orbitals on oxygen, thus leaving two pairs of π electrons in pure *p* orbitals; these can then interact with empty $d\pi$ orbitals on the X atoms so as to stabilize the linear arrangement (Section

2-11). Many examples of this are known, for example, $[Cl_5Ru—O—RuCl_5]^{4-}$ (Section 12-9).

Three-Coordinate Oxygen. Pyramidal and planar geometries occur, the former being represented by *oxonium ions* (e.g., H_3O^+ and R_3O^+) and by donor–acceptor complexes such as $(C_2H_5)_2OBF_3$. There are examples of both geometric types among trinuclear μ_3-oxo complexes (Section 12-9). The formation of oxonium ions is analogous to the formation of ammonium ions such as NH_4^+, RNH_3^+, . . . , R_4N^+, except that oxygen is less basic and the oxonium ions are therefore less stable. Water, alcohol, and ether molecules serving as ligands to metal ions presumably also have pyramidal structures, at least for the most part. Like NR_3 compounds (Section 10-2), OR_3^+ species undergo rapid inversion.

Four-Coordinate Oxygen. This tetrahedral geometry is found in certain ionic or partly ionic oxides (e.g., PbO), and in polynuclear complexes such as $Mg_4OBr_6{\cdot}4C_4H_{10}O$, $Cu_4OCl_6(Ph_3PO)_4$, and $M_4O(O_2CR)_6$ compounds, where M = Be or Zn.

Unicoordinate, Multiply Bonded Oxygen. There are many examples of XO groups, where the order of the XO bond may vary from essentially unity, as in amine oxides, $\rightarrow\overset{+}{N}:\underset{\cdot\cdot}{\ddot{O}}:^-$, though varying degrees of π bonding up to a total bond order of 2, or a little more. The simplest π-bonding situation occurs in ketones, where one well-defined π bond occurs perpendicular to the molecular plane. In most inorganic situations, such as R_3PO or R_3AsO compounds, tetrahedral ions such as PO_4^{3-}, ClO_4^-, MnO_4^-, OsO_4, or species such as $OsCl_4O_2^{2-}$, the opportunity exists for two π interactions between X and O, in mutually perpendicular planes that intersect along the X—O line. Indeed, the symmetry of the molecule or ion is such that the two π interactions *must* be of equal extent. Thus, in principle the extreme limiting structure (12-Ib) must be considered to be mixed with (12-Ia). In general, available evidence suggests that a partially polar bond of order approaching 2 results; it is important, however, to note the distinction from the situation in a ketone, since a π bond order of 1 in this context does not mean one full π interaction but rather two mutually perpendicular π interactions of order 0.5.

$$\overset{+}{X}\,:\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}: \longleftrightarrow \overset{-}{X}:::\overset{+}{\ddot{O}}:$$

(a) (b)

(12-I)

Catention. As with nitrogen, catenation occurs only to a very limited extent. In peroxides and superoxides there are two consecutive oxygen atoms. Only in O_3, O_3^-, and the few $R_FO_3R_F$ molecules are there well-established chains of three oxygen atoms. There is a four-atom chain in O_4F_2 (Section 12-4).

The weakness of O—O single bonds in H_2O_2 and O_2 and O_2^{2-} is doubtless due to repulsive effects of the electron pairs in these small atoms.

THE ELEMENT

12-3. Occurrence,[2] Properties, and Allotropes

Oxygen occurs in Nature in three isotopic species: ^{16}O (99.759%), ^{17}O (0.0374%), and ^{18}O (0.2039%). The rare isotopes, particularly ^{18}O, can be concentrated by fractional distillation of water, and concentrates containing up to 97 at. % ^{18}O or up to 4 at. % ^{17}O as well as other labeled compounds are commercially available. Oxygen-18 has been widely used as a tracer in studying reaction mechanisms of oxygen compounds. Oxygen-17 has a nuclear spin $\frac{5}{2}$, but because of the low abundance of this isotope and appreciable quadrupole moment, enriched materials and Fourier transform nmr techniques are required; solids can be studied by magic-angle spinning (MAS).[3a]

Dioxygen occurs in two allotropic forms; O_2, and ozone (O_3). The O_2 form is paramagnetic in the gaseous, liquid, and solid states and has the rather high dissociation energy of 496 kJ mol^{-1}. Molecular orbital theory, even in first approximation, correctly accounts for the triplet ground state ($^3\Sigma_g^-$) having a double bond. There are several low-lying singlet states that are important in photochemical oxidations; these are discussed shortly. Like NO, which has one unpaired electron in an antibonding (π^*) MO, oxygen molecules associate only weakly, and true electron pairing to form a symmetrical O_4 species apparently does not occur even in the solid. Both liquid and solid O_2 are pale blue.

Oxygen species $O_2^{n\pm}$ from O_2^+ to O_2^{2-} illustrate the effect of varying the number of antibonding electrons on the length and stretching frequency of the O—O bond (Table 12-1).

Chemical Properties of Dioxygen. Oxygen combines with almost all other elements, usually, however, only on heating. Dioxygen will sometimes react reversibly with certain transition metal complexes (Section 27-3) and the

TABLE 12-1
Various Bond Values for Dioxygen Species[a]

Species	O—O Distance (Å)	Number of π^* electrons	ν_{OO}(cm^{-1})
O_2^+	1.12	1	1905
O_2	1.21	2	1580
O_2^-	1.33	3	1097
O_2^{2-}	1.49	4	802

[a] L. Vaska, *Acc. Chem. Res.*, 1976, **9**, 175.

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[2] J. R. Wiesenfeld, *Acc. Chem. Res.*, 1982, **15**, 110 (atmospheric O_2 and O_3).

[3a] S. Schramm and E. Oldfield, *J. Chem. Soc. Dalton Trans.*, **1984**, 2502.

ligand behavior of O_2 and its ions is discussed in Section 12-10. The potentials in aqueous solution are

$$O_2 + 4H^+ + 4e = 2H_2O \qquad E^0 = +1.229\ \text{V}$$

$$O_2 + 2H_2O + 4e = 4OH^- \qquad E^0 = +0.401\ \text{V}$$

$$O_2 + 4H^+(10^{-7}\ M) + 4e = 2H_2O \qquad E^0 = +0.815\ \text{V}$$

Thus neutral water saturated with O_2 is a fairly good oxidizing agent. For example, although Cr^{2+} is just stable toward oxidation in water, in air-saturated water it is rapidly oxidized; Fe^{2+} is oxidized (only slowly in acid, but rapidly in base) to Fe^{3+} in the presence of air, although in air-free water Fe^{2+} is quite stable ($Fe^{3+} + e = Fe^{2+}$, $E^0 = +0.77$ V).

The rate of oxidation of various substances (e.g., ascorbic acid) may be vastly increased by catalytic amounts of transition metal ions, especially Cu^{2+}, where a Cu^I–Cu^{II} redox cycle is involved.

Oxygen is readily soluble in organic solvents, and merely pouring such liquids in air serves to saturate them with oxygen. This should be kept in mind when determining the reactivity of air-sensitive materials in solution in organic solvents. Note that many organic substances such as ethers readily form peroxides or hydroperoxides in air.

Measurements of the electronic spectra of alcohols, ethers, benzene, and even saturated hydrocarbons show that there is interaction of the charge-transfer type with the oxygen molecule. However, there is no true complex formation, since the heats of formation are negligible and the spectral changes are due to contact between the molecules at van der Waals distances. The classic example is that of *N*,*N*-dimethylaniline, which becomes yellow in air or oxygen but colorless again when the oxygen is removed. Such weak charge-transfer complexes make certain electronic transitions in molecules more intense; they are also a plausible first stage in photooxidations.

Many studies have been made on the precise mechanism[3b] of the reduction of O_2. There is no evidence for four- or two-electron reduction steps, as would be suggested by the overall reactions noted previously, or the following:

$$O_2 + 2H^+ + 2e = H_2O_2 \qquad E^0 = +0.682\ \text{V}$$

$$O_2 + H_2O + 2e = OH^- + HO_2^- \qquad E^0 = -0.076\ \text{V}$$

The first step is a one-electron reduction to the *superoxide radical ion* $O_2^{\dot{-}}$ (Section 12-10). The potential for the reduction

$$O_2 + e = O_2^-$$

ranges from ~ −0.2 to −0.5 V depending on the medium. The O_2^- ion is a moderate reducing agent, comparable to dithionite, and a *very* weak oxidizing

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[3b] J-M. Savéant *et al., J. Am. Chem. Soc.*, 1987, **109**, 3768.

agent. Thus most of the oxidation by O_2 is due to *peroxide* ions HO_2^- and O_2^{2-}, formed by reactions such as

$$H^+ + O_2^- + e = HO_2^-$$

$$2O_2^- + H_2O = O_2 + HO_2^- + OH^-$$

The oxidation of water to O_2 in photosynthetic systems in plants has been greatly studied as have synthetic models such as those of manganese complexes; the oxidation seems most likely to proceed via H_2O_2 rather than OH· radicals and probably two or four manganese centers are involved.[4]

Cleavage of oxygen[5] can occur in certain reactions of transition metal compounds to give M=O bonds, for example,

$$W(CO)_6 + O_2 \xrightarrow[uv]{matrix} [W(\eta^2\text{-}O_2)(CO)_4] \longrightarrow (CO)_3W(O)_2 \longrightarrow \text{and so on}$$

$$(Me_3SiCH_2)_6Ru_2 + O_2 \xrightarrow{-50°C} [(Me_3SiCH_2)_3(O)Ru]_2$$

Singlet Oxygen.[6] The lowest energy electron configuration of O_2, which contains two electrons in π^* orbitals, gives rise to three states, Table 12-2.

The $^1\Delta_g$ state has a much longer lifetime than the $^1\Sigma_g^+$ state. The lifetime is solvent dependent varying by orders of magnitude in organic solvents.[7]

There are three main ways of generating the singlet oxygen molecules: (1) photochemically by irradiation in presence of a sensitizer, (2) chemically, (3) in an electrodeless discharge. The last is inefficient and impractical. The photochemical route proceeds as follows, where "sens" represents the photosensitizer (typically a fluorescein derivative, methylene blue, certain porphyrins, or certain polycyclic aromatic hydrocarbons):

$$^1\text{sens} \xrightarrow{h\nu} {}^1\text{sens}^*$$

$$^1\text{sens}^* \longrightarrow {}^3\text{sens}^*$$

$$^3\text{sens}^* + {}^3O_2 \longrightarrow {}^1\text{sens} + {}^1O_2$$

$$^1O_2 + \text{substrate} \longrightarrow \text{products}$$

Energy transfer from triplet excited ^{3}sens* to $^3O_2$ to give $^1O_2$ is a spin allowed process.

A representative example is the use of $[\text{Ru bipy}_3]^{2+}$ and the *N,N'*-dimethyl-4,4'-bipyridinium(2+) ion with O_2 in aqueous solution.[8] Singlet oxygen can be generated by a variety of chemical reactions including decomposition of

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[4] K. Yamaguchi and D. T. Sawyer, *Inorg. Chem.*, 1985, **24**, 971.

[5] A. J. Downs *et al., Inorg. Chem.*, 1986, **25**, 19; G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 2711. P. Chandrasekar *et al., Inorg. Chim. Acta*, 1987, **129**, 51.

[6] A. A. Frimer, Ed., *Singlet Oxygen*, Vols. I and II, CRC Press, Boca Raton, Florida, 1985; M. Bala, *Chem. Rev.*, 1981, **81**, 91.

[7] P. R. Ogilby and C. S. Foote, *J. Am. Chem. Soc.*, 1983, **105**, 3423; J. R. Hurst and G. B. Schuster, *J. Am. Chem. Soc.*, 1983, **105**, 5756.

[8] A. Haim *et al., Inorg. Chem.*, 1985, **24**, 3978.

TABLE 12-2
States of the O_2 Molecule

State	π_a^*	π_b^*	Energy
$^1\Sigma_g^+$	↑	↓	155 kJ (~13,000 cm^{-1})
$^1\Delta_g$	↑↓	—	92kJ (~8000 cm^{-1})
$^3\Sigma_g^-$	↑	↑	0 (ground state)

H_2O_2 in alkaline solution[9] and thermal decomposition of ozonides (Section 12-3) such as $(PhO)_3PO_3$.[10]

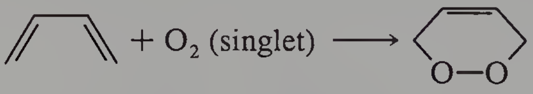
In the reactions

$$H_2O_2 + Cl_2 = 2Cl^- + 2H^+ + O_2$$

$$H_2O_2 + ClO^- = Cl^- + H_2O + O_2$$

the accompanying red chemiluminescent glow is due to the excited oxygen molecules trapped in the bubbles.

The singlet oxygen molecule is ubiquitous, being implicated in biological oxidations, photoconversions of air pollutants, degradation of synthetic polymers, and may well be generated in living cells as side products of enzyme reactions. Large scale photochemical synthesis in the fine chemicals industry is for selective oxidations, since singlet O_2 reacts electrophilically rather than in a free-radical fashion. An example is a Diels–Alder-like 1,4-addition to a 1,3-diene.[11]



Ozone.[12] The diamagnetic triatomic molecule has the structure shown in Fig. 12-1. Since the O—O distance in H_2O_2 is 1.49 Å and in O_2 is 1.21 Å, the bonds in O_3 must have considerable double-bond character.

Ozone is commonly prepared by silent electric discharge in oxygen, which gives up to ~ 10% O_3. The gas is blue. Pure ozone can be obtained by fractional liquefaction of O_2–O_3 mixtures. There is a two-phase liquid system; the one with 25% of O_3 is stable, but a deep purple phase with 70% of O_3 is explosive, as is the deep blue pure liquid (bp −112°C). The solid (mp −193°C) is black violet. Small quantities of O_3 are formed in electrolysis of dilute sulfuric acid, in some chemical reactions producing O_2, and by the action of uv light on O_2.

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[9] D. F. Evans and M. N. Upton, *J. Chem. Soc. Dalton Trans.*, **1985,** 2525; J. M. Aubry, *J. Am. Chem. Soc.*, 1985, **107,** 5844.

[10] P. D. Bartlett and C. M. Lonzetta, *J. Am. Chem. Soc.*, 1983, **105,** 1984.

[11] A. A. Frimer, *Chem. Rev.*, 1979, **79,** 359.

[12] M. Horváth *et al.*, *Ozone*, Elsevier, Amsterdam, 1984.

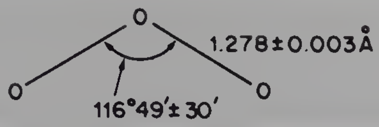

FIG. 12-1. The structure of ozone (O_3).

Ozone is very endothermic

$$O_3 = \tfrac{3}{2}O_2 \qquad \Delta H = -142 \text{ kJ mol}^{-1}$$

but it decomposes only slowly at 250°C in the absence of catalysts and uv light.

Ozone is an important natural constituent of the atmosphere,[13a] being principally concentrated (up to ~27% by weight) between altitudes of 15 and 25 km. It is formed by solar uv radiation in the range 240 to 300 nm via the reactions

$$O_2 \xrightarrow{h\nu} 2O \qquad (12\text{-}1)$$

$$O + O_2 \longrightarrow O_3 \qquad (12\text{-}2)$$

Ozone absorbs uv radiation from 200 to 360 nm. This leads partly to a reversal of reaction 12-2 and thus a steady state concentration is established. The net result of all these processes is absorption and conversion to heat of considerable solar uv radiation that would otherwise strike the earth's surface. Destruction of any significant percentage of this ozone could have serious effects (e.g., increased surface temperature, high incidence of skin cancer), and some human activities are capable of destroying stratospheric ozone. Supersonic aircraft, which fly in the ozone layer, discharge NO and NO_2, and these can catalyze the decomposition of ozone via the following reactions:

$$O_3 + NO \longrightarrow O_2 + NO_2$$

$$NO_2 + O \longrightarrow O_2 + NO$$

$$\text{or} \qquad NO_2 + O_3 \longrightarrow O_2 + NO_3$$

$$NO_3 \xrightarrow{h\nu} O_2 + NO$$

Chlorofluorocarbons such as $CFCl_3$ and CF_2Cl_2, used as foam-blowing agents, aerosol propellants, and refrigerants, are photochemically decomposed to give Cl atoms, and these catalyze ozone decomposition[13b] via the mechanism

$$O_3 + Cl \longrightarrow O_2 + ClO$$

$$ClO + O \longrightarrow O_2 + Cl$$

There has been much study of the very complicated pattern of O_3 decomposition in the upper atmosphere and also of other effects, for example, the

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[13a] A. K. Biswas, Ed., *The Ozone Layer,* Pergamon Press, New York, 1979.

[13b] S. Elliot and F. S. Rowland, *J. Chem. Educ.,* 1987, **64,** 387.

increasing CO_2 concentration. It is not yet known if serious damage has already been done.

Chemical Properties of Ozone. The O_3 molecule is a much more powerful oxidant than is O_2 and reacts with most substances at 25°C. It is often used in organic chemistry.[14] The oxidations doubtless involve free-radical chains as well as peroxo intermediates.

Some compounds form adducts, for example,

$$(PhO)_3P + O_3 \xrightarrow{-78°C} (PhO)_3P(O_3) \xrightarrow{-15°C} (PhO)_3PO + O_2(^1\Delta_g)$$

Complexes are also formed with aromatic compounds and other π systems.

The reaction

$$O_3 + 2KI + H_2O = I_2 + 2KOH + O_2$$

is quantitative and can be used to determine O_3. The overall potentials in aqueous solution are

$$O_3 + 2H^+ + 2e = O_2 + H_2O \qquad E^0 = +2.07\ V$$

$$O_3 + H_2O + 2e = O_2 + 2OH^- \qquad E^0 = +1.24\ V$$

$$O_3 + 2H^+\ (10^{-7}\ M) + 2e = O_2 + H_2O \qquad E^0 = +1.65\ V$$

In acid solution O_3 is exceeded in oxidizing power only by fluorine, the perxenate ion, atomic oxygen, OH radicals, and a few other such species. The rate of decomposition of ozone drops sharply in alkaline solutions,[15] the half-life being ~2 min in 1 *M* NaOH at 25°C, 40 min at 5 *M*, and 83 h at 20 *M*:

$$O_3 + OH^- \longrightarrow HO_2^- + O_2$$

OXYGEN COMPOUNDS

Most oxygen compounds are described in this book during treatment of the chemistry of other elements. Water and the hydroxonium ion have been discussed in Chapter 3.

12-4. Oxygen Fluorides

Since fluorine is more electronegative than oxygen, it is logical to call binary compounds oxygen fluorides rather than fluorine oxides, although the latter names are sometimes seen. Oxygen fluorides have been intensively studied as potential rocket fuel oxidizers.

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[14] S. D. Razumovskii and G. E. Zaikov, *Ozone and its Reactions with Organic Compounds*, Elsevier, Amsterdam, 1984; P. S. Bailey, Ed., *Ozonation in Organic Chemistry*, Vol. 2, Academic Press, New York, 1982.

[15] G. Gordon *et al.*, *Inorg. Chem.*, 1985, **24**, 2962.

Oxygen Difluoride (OF_2).[16a] This is prepared by passing fluorine rapidly through 2% sodium hydroxide solution, by electrolysis of aqueous HF–KF solutions, or by the action of F_2 on moist KF. It is a pale yellow poisonous gas (bp 145°C). It is relatively unreactive and can be mixed with H_2, CH_4, or CO without reaction, although sparking causes violent explosion. Mixtures of OF_2 with Cl_2, Br_2, or I_2 explode at room temperature. It is fairly readily hydrolyzed by base:

$$OF_2 + 2OH^- \longrightarrow O_2 + 2F^- + H_2O$$

It reacts more slowly with water, but explodes with steam:

$$OF_2 + H_2O \longrightarrow O_2 + 2HF$$

and it liberates other halogens from their acids or salts:

$$OF_2 + 4HX(aq) \longrightarrow 2X_2 + 2HF + H_2O$$

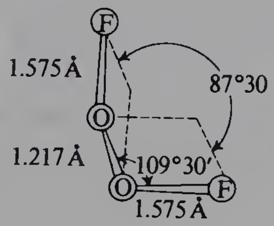
Metals and nonmetals are oxidized and/or fluorinated; in an electric discharge even Xe reacts to give a mixture of fluoride and oxide fluoride.

Dioxygen Difluoride (O_2F_2). This is a yellow-orange solid (mp 109.7 K), obtained by high-voltage electric discharges on mixtures of O_2 and F_2 at 10 to 20-mm pressure and temperatures of 77 to 90 K. It decomposes into O_2 and F_2 in the gas at −50°C with a half-life of ~3 h. It is an extremely potent fluorinating and oxidizing agent, and under controlled conditions OOF groups may be transferred to a substrate. Many substances explode on exposure to O_2F_2 at low temperatures, and even C_2F_4 is converted into COF_2, CF_4, CF_3OOCF_3, and so on. In the presence of F^- acceptors it forms dioxygenyl salts:

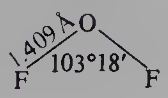
$$O_2F_2 + BF_3 \longrightarrow O_2{}^+BF_4^- + \tfrac{1}{2}F_2$$

Dioxygen difluoride has been used for oxidizing primary aliphatic amines to the corresponding nitroso compounds.

The structure of O_2F_2 (12-II) is notable for the shortness of the O—O bond (1.217 Å, cf. 1.48 Å in H_2O_2 and 1.49 in O_2^{2-}) and the relatively long O—F bonds (1.575 Å) compared with those in OF_2 (12-III) (1.409 Å). The bonding can be rationalized by MO theory.[16b]



(12-II)



(12-III)

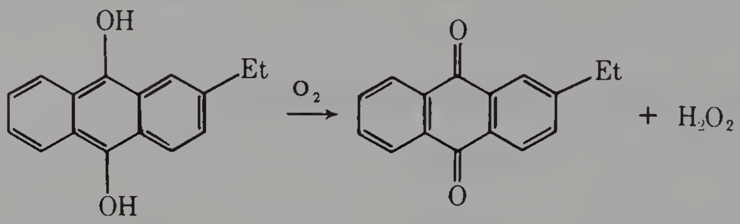
[16a] E. H. Appelman and A. W. Jache, *J. Am. Chem. Soc.*, 1987, **109**, 1754.

[16b] J. K. Burdett *et al.*, *Inorg. Chem.*, 1984, **23**, 2419.

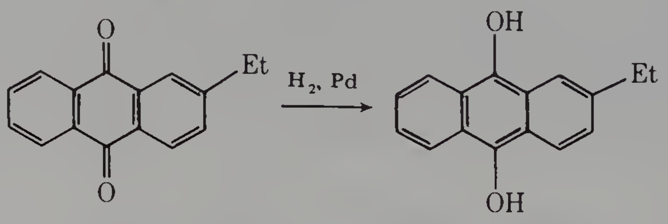
Other, very unstable oxygen fluorides have been reported. The only one known for certain is O_4F_2, which decomposes slowly even at $-183°C$. Some oxygen fluoride chloride compounds are known also.

12-5. Hydrogen Peroxide, Peroxides, and Peroxo Compounds[17]

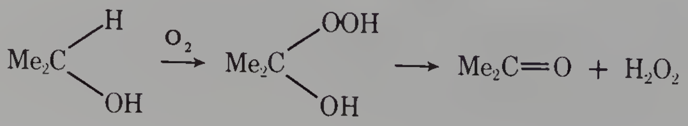
Hydrogen Peroxide.[18] The main process for the synthesis of H_2O_2 is the autooxidation in an organic solvent such as alkylbenzenes of an alkyl anthraquinol



The H_2O_2 is extracted with water and the 20 and 40% solution so obtained purified by solvent extraction. The anthraquinone solution has to be purified by removal of degradation products before reduction back to the quinol on a supported platinum or nickel catalyst:



A second process involves oxidation of isopropanol to acetone and H_2O_2 in either vapor or liquid phases at 15 to 20 atm and ~100°C.



Some secondary reactions also occur giving peroxides of aldehydes and acids. The water–peroxide–acetone–isopropanol mixture is fractionated by distillation.

A new type of electrolytic cell permitting gas–liquid reaction has promise for direct conversion of O_2 into ~2% H_2O_2 in 1 *M* NaOH, a solution used

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[17] S. Patai, Ed., *The Chemistry of Peroxides,* Wiley, New York, 1983 (includes singlet O_2 and ozonides).

[18] K. Pandiarajan, *Synthetic Reagents,* Vol. 6, J. S. Pizey, Ed., Horwood–Wiley, New York, 1985, p. 60.

for bleaching of wood pulp.[19] The cell reactions are

$$\begin{array}{r}
2OH^- = \tfrac{1}{2}O_2 + H_2O + 2e \\
O_2 + H_2O + 2e = HO_2^- + OH^- \\
\hline
OH^- + \tfrac{1}{2}O_2 = HO_2^-
\end{array}$$

Pure H_2O_2, obtained by the concentration of dilute solutions by vacuum distillation, is a colorless liquid (bp 150.2°C, mp −0.43°C) that resembles water in many of its physical properties, although it is denser (1.44 at 25°C). The pure liquid has a dielectric constant at 20°C of 73.2,[20] and a 65% solution in water has a dielectric constant of 120. Thus both the pure liquid and its aqueous solutions are potentially excellent ionizing solvents, but its utility in this respect is limited by its strongly oxidizing nature, and its ready decomposition (eq. 12-3) in the presence of even traces of many heavy metals (see later):

$$2H_2O_2 = 2H_2O + O_2 \qquad \Delta H = -99 \text{ kJ mol}^{-1} \tag{12.3}$$

The structure of the molecule is shown in Fig. 12-2; there is only a low barrier to internal rotation about the O—O bond in the gas phase.

In dilute aqueous solution H_2O_2 is more acidic than water:

$$H_2O_2 = H^+ + HO_2^- \quad K_{20°C} = 1.5 \times 10^{-12}$$

There is ordinarily no exchange of oxygen isotopes between H_2O_2 and H_2O in the liquid phase, even in the presence of strong acids. However, HSO_3F catalyzes the exchange, possibly via the intermediate $H_3O_2^+$.

Hydrogen peroxide has been estimated to be more than 10^6 times less *basic* than H_2O. However, on addition of concentrated H_2O_2 to tetrafluoroboric

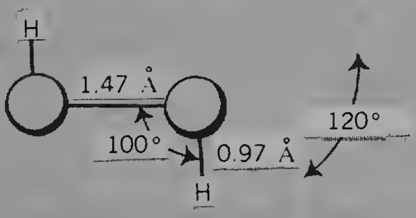

FIG. 12-2. The structure of the free H_2O_2 molecule. In crystalline solids such as H_2O_2(s), $Na_2C_2O_4 \cdot H_2O_2$, $(NH_2)_2 \cdot H_2O_2$, and so on, the parameters may vary. In H_2O_2(s) the O—O distance is 1.453 Å with hydrogen bonding O—H···O, 2.8 Å versus 2.76 Å in ice.

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[19] *Chem. Eng. News,* **1984,** March 12, p. 16.

[20] Compare with value for H_2O, 80.4, P. A. Giguère, *J. Chem. Educ.*, 1983, **60**, 399.

acid in tetrahydrothiophene 1,1-dioxide (sulfolane) the conjugate cation ($H_3O_2^+$) can be obtained. The solutions are very powerful, but unselective, oxidants for benzene, cyclohexane, and other organic materials.

The chemistry in aqueous solution is summarized by the following potentials:

$$H_2O_2 + 2H^+ + 2e = 2H_2O \qquad E^0 = 1.77\ V$$

$$O_2 + 2H^+ + 2e = H_2O_2 \qquad E^0 = 0.68\ V$$

$$HO_2^- + H_2O + 2e = 3OH^- \qquad E^0 = 0.87\ V$$

from which it appears that H_2O_2 is a strong oxidizing agent in either acid or basic solution; only toward very strong oxidizing agents such as MnO_4^- will it behave as a reducing agent.

Dilute or 30% H_2O_2 solutions are widely used as oxidants. In acid solution oxidations with H_2O_2 are most often slow, whereas in basic solution they are usually fast. Decomposition of H_2O_2 according to reaction 12-3, which may be considered a self-oxidation, occurs most rapidly in basic solution; hence an excess of H_2O_2 may best be destroyed by heating in basic solution.

The oxidation of H_2O_2 in aqueous solution by Cl_2, MnO_4^-, Ce^{4+}, and so on, and the catalytic decomposition caused by Fe^{3+}, I_2, MnO_2, and so on, have been studied using labeled H_2O_2. In both cases the oxygen produced is derived entirely from H_2O_2, not from water. This suggests that oxidizing agents do not break the O—O bond but simply remove electrons. In the case of oxidation by Cl_2, a mechanism of the following kind is consistent with the lack of exchange of ^{18}O between H_2O_2 and H_2O

$$Cl_2 + H_2{}^{18}O_2 \longrightarrow H^+ + Cl^- + H^{18}O^{18}OCl$$

$$H^{18}O^{18}OCl \longrightarrow H^+ + Cl^- + {}^{18}O_2$$

As just noted traces of transition metal ions catalyze the decomposition of H_2O_2; the Fe^{2+}–H_2O_2 system, called Fenton's reagent, can oxidize or dehydrogenate organic substances:

$$Fe^{2+}_{aq} + H_2O_2 \longrightarrow Fe^{III}(OH)^{2+}_{aq} + OH^{\cdot}$$

Studies in MeCN suggest that an iron(IV) "ferryl" ion, FeO^{2+}, is initially formed[21]; that is,

$$Fe^{2+} + H_2O_2 \xrightarrow{MeCN} FeO^{2+} + H_2O$$

followed by

$$FeO^{2+} + H_2O_2 = Fe^{2+} + O_2(^1\Delta_g) + H_2O$$

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[21] D. T. Sawyer *et al., Inorg. Chem.*, 1986, **25**, 2089; *J. Am. Chem. Soc.*, 1984, **106**, 4283.

In dry MeCN, Fenton-type reactions, which involve $OH^{\cdot}$ radicals do not occur.

Ionic Peroxides. Peroxides that contain O_2^{2-} ions are known for the alkali metals, Ca, Sr, and Ba. Sodium peroxide is made commercially by air oxidation of Na, first to Na_2O, then to Na_2O_2; it is a yellowish powder, very hygroscopic though thermally stable to 500°C, which also contains, according to esr studies, ~10% NaO_2. Barium peroxide, which was originally used for making dilute solutions of H_2O_2 by treatment with dilute H_2SO_4, is made by the action of air or O_2 on BaO; the reaction is slow below 500°C and BaO_2 decomposes above 600°C.

The ionic peroxides with water or dilute acids give H_2O_2, and all are powerful oxidizing agents. They convert organic materials into carbonate even at moderate temperatures. Sodium peroxide vigorously oxidizes some metals; for example, Fe violently gives FeO_4^{2-}, and Na_2O_2 can be generally employed for oxidizing fusions. The alkali peroxides react with CO_2:

$$2CO_2(g) + 2M_2O_2 \longrightarrow 2M_2CO_3 + O_2$$

Peroxides can also serve as reducing agents for such strongly oxidizing substances as MnO_4^-.

Other electropositive metals such as magnesium, the lanthanides, or uranyl ion also give peroxides that are intermediate in character between the ionic ones and the essentially covalent peroxides of metals such as Zn, Cd, and Hg. The addition of H_2O_2 to solutions of, for example, Zn^{2+} or UO_2^{2+}, gives impure peroxides.

A characteristic feature of the ionic peroxides is the formation of well-crystallized hydrates. Thus $Na_2O_2 \cdot 8H_2O$ can be obtained by adding ethanol to 30% H_2O_2 in concentrated NaOH at 15°C, or by rapid crystallization of Na_2O_2 from ice water. The alkaline earths all form the octahydrates ($M^{II}O_2 \cdot 8H_2O$). They are isostructural, containing discrete O_2^{2-} ions to which the water molecules are hydrogen bonded, giving chains of the type $\text{---}O_2^{2-}\text{---}(H_2O)_8\text{---}O_2^{2-}\text{---}(H_2O)_8\text{---}$. Some salts crystallize with lattice H_2O_2 (cf. H_2O), which is H bonded to the anion.[22] This class of peroxohydrates has to be distinguished from true peroxo compounds. Some examples are $M_2CO_3 \cdot nH_2O_2$, $n = 1$ (NH_4), 1.5 (Na), 3 (K, Rb, Cs) and $KF \cdot H_2O_2$.

Peroxo Compounds. There are numerous species where —O— is replaced by —O—O—. The peroxo carbonate ion O_2COOH^- occurs in $NaHCO_4 \cdot H_2O$ and alkali metal salts of stoichiometry $M_2C_2O_6$ exist in the solid state. In solution in aqueous H_2O_2 there appear to be the reactions[23]:

$$C_2O_6^{2-} + H_2O \xrightarrow{\text{fast}} HCO_4^- + HCO_3^-$$

$$HCO_4^- + H_2O \rightleftharpoons HCO_3^- + H_2O_2$$

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[22] D. P. Jones and W. P. Griffith, *J. Chem. Soc. Dalton Trans.*, **1980**, 2526.

[23] W. P. Griffith *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 20.

Other well-known ions are peroxomono- and disulfate (Section 13-13).[24] A large number of *organic peroxides* and *hydroperoxides* are known. Peroxo carboxylic acids (e.g., peroxoacetic acid, $CH_3CO{\cdot}OOH$) can be obtained by the action of H_2O_2 on acid anhydrides. Peroxoacetic acid is made as 10 to 55% aqueous solutions containing some acetic acid by interaction of 50% H_2O_2 and acetic acid, with H_2SO_4 as catalyst at 45 to 60°C; the dilute acid is distilled under reduced pressure. It is also made by air oxidation of acetaldehyde. The peroxo acids are useful oxidants and sources of free radicals [e.g., by treatment with $Fe^{2+}(aq)$]. Dibenzoyl peroxide, di-*t*-butyl peroxide, and cumyl hydroperoxide are moderately stable and widely used as polymerization initiators and for other purposes where free-radical initiation is required.

Organic peroxo compounds are also obtained by *autooxidation* of ethers, unsaturated hydrocarbons, and other organic materials on exposure to air. A free-radical chain reaction is initiated almost certainly by radicals generated by the interaction of oxygen and traces of metals such as copper, cobalt, or iron. The attack on specific reactive C—H bonds by a radical $X^{\cdot}$ gives first $R^{\cdot}$, then hydroperoxides, which can react further:

$$RH + X^{\cdot} \longrightarrow R^{\cdot} + HX$$

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}$$

$$RO_2^{\cdot} + RH \longrightarrow RO_2H + R^{\cdot}$$

Peroxide formation can lead to explosions if oxidized solvents are distilled. Peroxides are best removed by washing with acidified $FeSO_4$ solution or, for ethers and hydrocarbons, by passage through a column of activated alumina. Peroxides are absent when the $Fe^{2+} + SCN^-$ reagent gives no red color.

There are a number of peroxo compounds that contain fluorine groups, and many of these are reasonably stable. Some examples are

$(FSO_2)OO(SO_2F)$	Peroxodisulfonyldifluoride
SF_5OOSF_5	Bis(pentafluorosulfur)peroxide
CF_3OOCF_3	Bis(perfluoromethyl)peroxide

The compounds are usually prepared by fluorination of oxygen compounds, for example,

$$SO_3 + F_2 \xrightarrow[160°C]{AgF_2} (FSO_2)OO(SO_2F)$$

$$COF_2 + ClF_3 \xrightarrow[250°C]{KF} CF_3OOCF_3$$

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[24] F. Minisci *et al., Acc. Chem. Res.*, 1983, **16**, 27.

12-6. Superoxides, the Superoxide Ion, and Ozonides

The formation of the orange crystalline *superoxides* (MO_2) by the action of O_2 on K, Rb, and Cs has been noted (Section 4-4). Sodium superoxide is obtained only at 500°C and 300 atm while LiO_2 has not been isolated. For Mg, Ca, Sr, and Ba low concentrations exist in the peroxides. The K, Rb, and Cs superoxides have the CaC_2 structure (Section 8-3) while NaO_2 is cubic owing to O_2^- ion disorder. The main source for O_2^- is KO_2, which is normally only ~96% pure having K_2O_2 and KOH impurities. In KO_2, the O—O distance is 1.28 Å. The electronic structure of O_2^- is similar to that of NO and the unpaired electron is in an antibonding (π^*) MO between the two oxygen atoms and consequently its chemical reactions show little radical character.

The superoxides react with water

$$2O_2^- + H_2O = O_2 + HO_2^- + OH^-$$

$$2HO_2^- = 2OH^- + O_2 \qquad \text{(slow)}$$

and with CO_2, a reaction of use in regeneration of oxygen in closed systems:

$$4MO_2(s) + 2CO_2(g) = 2M_2CO_3(s) + 3O_2(g)$$

Although solid superoxides have long been known, the reaction chemistry of the O_2^- ion *in solutions* is relatively recent,[25] being initiated by the discovery of O_2^- from its esr spectrum during an enzyme reaction involving O_2 and that metallaproteins known as superoxide dismutatase (SOD)[26] appear to protect living cells against the toxic effects of O_2^-. The prime action of superoxide dismutase is to catalyze the reaction

$$2O_2^- + 2H^+ = O_2 + H_2O_2$$

which proceeds by two, one-electron transfers[27]:

Solutions of O_2^- can be readily obtained.[28] Thus KO_2 can be solubilized by 18-C-6 in DMSO although it slowly reacts with the solvent. Potassium superoxide can be metathesized with $(Me_4N)_2CO_3$ to $(Me_4N)O_2$, ~93% pure, which is soluble in MeCN and other aprotic solvents.

Transient quantities of O_2^- in aqueous solution can be generated by flash photolysis of H_2O, but photolysis of O_2 in aqueous alcohols using acetone sensitizer can give solutions that have a $t_{1/2}$ ~90 s at pH 11 and 41 m at pH 12.5.[29]

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[25] D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res.*, 1981, **7**, 393.

[26] L. W. Oberley *et al.*, *Superoxide Dismutase,* Vols. I, II, CRC Press, Boca Raton, Florida, 1982.

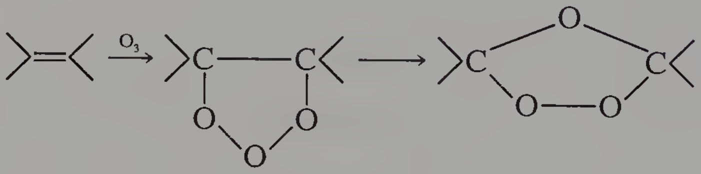
[27] D. T. Sawyer *et al.*, *Inorg. Chem.*, 1986, **25**, 1289; H. Gamp and S. J. Lippard, *Inorg. Chem.*, 1983, **22**, 357.

[28] J. H. Espenson *et al.*, *Inorg. Chem.*, 1983, **22**, 847.

[29] J. A. Fee *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 5290.

In aprotic solvents O_2^- acts as a nucleophile, for example, to alkyl halides, and as a one-electron oxidant for organic compounds and metal ions such as Cu^{2+}. Transition metal complexes are discussed in Section 12-10.

Ozonides. Interaction of K or Rb superoxide with $O_3 + O_2$ followed by extraction and crystallization from liquid ammonia gives the deep red MO_3. Ozonides of other alkali ions and of NH_4^+ are known; all are colored owing to an absorption band in the 400 to 600-nm region. In RbO_3, the C_{2v} ion has an angle of 113.7 with O—O = 1.34 Å, somewhat longer than in O_3 itself (1.278 Å).[30] Thermal stabilities decrease from Cs to Li. The O_3^- ion may be formed in the decomposition of alkaline H_2O_2 and in radiolytic reactions. A number of organic ozonides have been characterized with alkenes; rapid addition of O_3 occurs even at 100°C to give a 1,2,3 trioxide, which isomerizes at higher temperature to a 1,2,4 trioxolane[31]:



Ozonation of saturated compounds appears to proceed by hydride transfer to give the ion pair $[R^+HO_3^-]$, which decomposes by a radical path giving high yields of singlet oxygen; other paths give H_2O_2.

12-7. The Dioxygenyl Cation

The O_2^+ ion was first obtained by the interaction of oxygen with PtF_6, which gives the orange solid O_2PtF_6, isomorphous with $KPtF_6$. Other salts can be made by reactions such as

$$O_2 + BF_3 + \tfrac{1}{2}F_2 \xrightarrow[-78^\circ C]{h\nu} O_2BF_4$$

$$2O_2 + 2GeF_4 + F_2 \xrightarrow{h\nu} 2O_2GeF_5$$

$$O_2 + Pt + 3F_2 \xrightarrow{280^\circ C} O_2PtF_6$$

Clearly, large, inoxidizable anions are required to stabilize O_2^+. Some of the salts are quite volatile (e.g., O_2RhF_6 will sublime at room temperature), but are readily hydrolyzed by water. The O_2^+ ion is paramagnetic and the O—O stretching frequency is 1905 cm^{-1}. Spectroscopic study of gaseous O_2^+ gives an O—O distance of 1.12 Å (cf. 1.09 Å in isoelectronic NO).

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[30] W. Sehnick and M. Jansen, *Z. Anorg. Allg. Chem.*, 1986, **532,** 37.

[31] R. L. Kuczkowski, *Acc. Chem. Res.*, 1983, **12,** 42; A. P. Schapp *et al., J. Am. Chem. Soc.*, 1984, **106,** 6087.

OXYGEN AND OXYGEN COMPOUNDS AS LIGANDS

12-8. Water and Hydroxide Ion

In aqueous solution metal ions are surrounded by water molecules; in some cases, such as the alkali ions, they are weakly bound, whereas in others, such as $[Cr(H_2O)_6]^{3+}$ or $[Rh(H_2O)_6]^{3+}$, they may be firmly bound and exchange with solvent water molecules only very slowly (Chapter 29).

The bound water molecules may be acidic, giving rise to *hydroxo* species and the acidities of aqua ions can vary by orders of magnitude, for example,

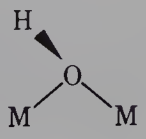
$$[Pt(NH_3)_4(H_2O)_2]^{4+} = [Pt(NH_3)_4(H_2O)(OH)]^{3+} + H^+ \qquad K \approx 10^{-2}$$

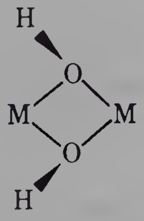
$$[Co(NH_3)_5(H_2O)]^{3+} = [Co(NH_3)_5(OH)]^{2+} + H^+ \qquad K \approx 10^{-5.7}$$

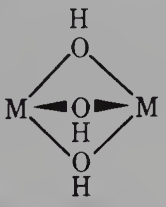
Some molten hydrates (e.g., $ZnCl_2{\cdot}4H_2O$) can act as extremely strong acids, even though the aqua ion $[Zn(H_2O)_4]^{2+}$ in aqueous solution is a very weak acid.

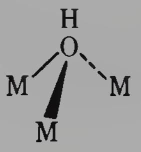
The formation constants and thermodynamic data for hydroxo species of many ions are available.[32] Of particular interest are structural changes, octahedral → tetrahedral, on going from certain aqua ions to higher hydroxo species, for example, $[M(H_2O)_6]^{3+} \rightarrow [M(OH)_4]^{2-}$ for Al^{III} and Co^{II}. For $[Hg(H_2O)_6]^{2+}$ there is a change to linear $(H_2O)Hg(OH)^+_{aq}$ and $(HO)Hg(OH)_{aq}$ species where two Hg—O bonds are shortened and the other four lengthened.

A common feature of hydroxo complexes is the formation of hydroxo bridges of the following types:

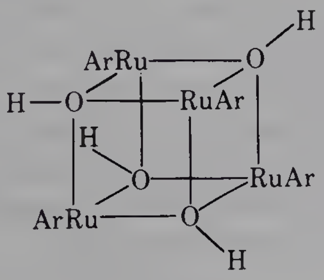








Double bridges are most common. Three μ_2-bridges are found in the π-arene complex $[ArRu(OH)_3RuAr]^+$, whereas a μ_3-hydroxo group occurs in the cubanelike ions $[(ArRuOH)_4]^{4+}$ (12-IV), $[Pt(OH)Me_3]_4$, and some others.



(12-IV)

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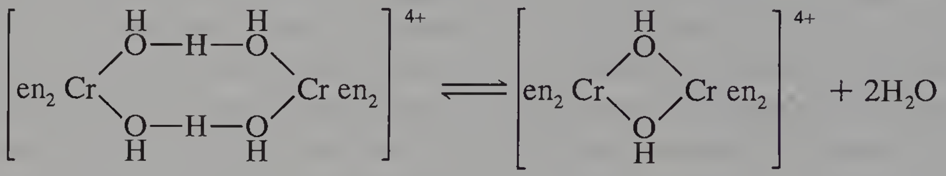
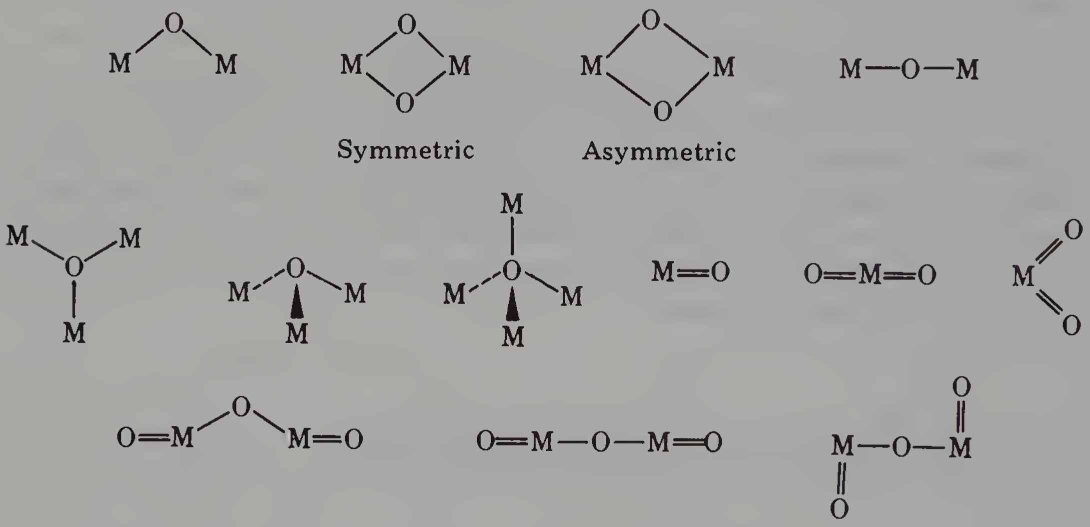
[32] D. W. Barnum, *Inorg. Chem.*, 1983, **21**, 2297.

As discussed in Section 3-6, many hydrated hydroxo complexes have a hydrogen bonded $H_3O_2^-$ ion acting as a bridge and numerous complexes have been established, one example being $\{cis\text{-}[bipy_2Cr^{III}(H_3O_2)]_2\}^{4+}$. The *olation reactions* in either solution or solid states can thus be considered as involving elimination of H_2O from H_3O_2 bridges leading to M(μ-OH)M bridges:



12-9. Oxo Compounds[33]

The loss of a second proton from coordinated water can lead to the formation of *oxo compounds,* which can be of several types, some of which have been noted in Section 12-2.



The multiply bonded oxo group (M═O) is found not only in oxo compounds and oxo anions of non-transition elements such as SO_4^{2-}, $O{=}PCl_3$, and PO_4^{3-}, but also in transition metal compounds such as vanadyl ($O{=}V^{2+}$), uranyl ($O{=}U{=}O^{2+}$), permanganate (MnO_4^-), and osmium tetroxide (OsO_4). In all these cases the bond distances (~1.59–1.66 Å) correspond to a double bond, and the M═O ir stretching frequencies usually lie in the 800 to 1000-cm^{-1} region for transition metal species. In the latter the π component is best regarded as arising from $Op\pi \rightarrow Md\pi$ electron flow. Since this is the opposite of electron flow in π-bonding ligands of the CO type, it is not surprising that the latter are most stable in low oxidation states whereas M═O bonds are most likely in high oxidation states.

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[33] W. A. Herrmann, *Angew, Chem. Int. Ed. Engl.*, 1986, **25,** 56; R. L. Dutta and A. K. Pal, *J. Sci. Ind. Res.*, **1984,** 660 (spectra and bond energies of transition metal M—O bonds); R. Hoppe *et al., Angew. Chem. Int. Ed. Engl.*, 1981, **20,** 63 (oxides and oxometallate anions); K. Saito and Y. Sasaki, in *Advanced Inorganic and Bioinorganic Mechanisms,* Vol. 1, Academic Press, New York, 1982, p. 179 (substitution reactions in M═O complexes).

Correlations between M═O distances, force constants for M═O stretches, and shifts in ^{17}O nmr spectra have been established.[34]

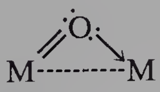
Protonation of M═O to M—OH occurs on interaction with strong acids; in some cases, condensation reactions with amines can give M═NR compounds (Section 10-18):

$$L_nM{=}O + RNH_2 \longrightarrow L_nM{=}NR + H_2O$$

The M═O bonding is commonly affected by the nature of groups trans to oxygen—and oxygen has a strong trans influence. Donors that increase electron density on the metal tend to reduce its acceptor properties, thus *lowering* the M—O multiple bond character, hence the M—O stretching frequency. Because of the strong trans influence, ligands trans to oxygen may be labile.

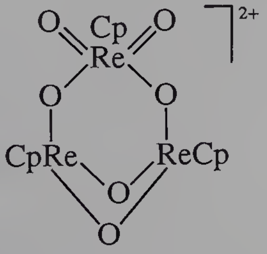
Dioxo compounds may be linear (trans) as in $O{=}U{=}O^{2+}$ or angular (cis) as in some molybdenum complexes and in ReO_2Me_3.

Several cases of bridging groups of the type (12-V) are known.[35] In $(Me_3SiCH_2)_6(O)_2Ru_2$, Ru═O is 1.733 Å and O → Ru is 2.208 Å. In $[OsO_2(\text{cyclohexane-1,2-diolate})\text{quinuclidene}]_2$ there is dimerization *only* via oxygen bridging (1.78, 2.22 Å), but other compounds have metal-metal bonds also.

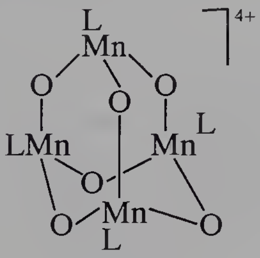


(12-V)

Single MOM bridges may be *bent* or *linear* with the angle varying from ~140 to 180° and being determined to a large extent by the steric requirements of other ligands attached to the metal. Bent bridges are found in many dimeric species such as $Cr_2O_7^{2-}$, $Mo_2O_7^{2-}$, $P_2O_7^{4-}$, $[Fe_2OCl_6]^{2-}$, and in polymeric species such as $Cp_6Ti_6O_8$ and the ions (12-VI)[36a] and (12-VII).[36b]



(12-VI)



(12-VII)

where L = 1,4,7-triazacyclononane.

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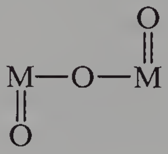
[34] M. Postel *et al., J. Am. Chem. Soc.*, 1983, **105,** 4922.

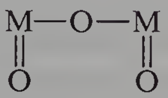
[35] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 2711; M. R. Churchill *et al., Inorg. Chem.*, 1984, **23,** 1017.

[36a] W. A. Herrmann *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 50.

[36b] K. Wieghardt *et al., Angew. Chem. Int. Ed. Engl.*, 1983, **22,** 328.

Linear M—O—M bridges[37a] are found in some complexes and hetero binuclear porphyrin species, porph M^1 (μ-O)M^2porph are also known[37b]; these can be made by reactions of the type porph $M^1{=}O$ + porph $M^2 \rightarrow$ porph $M^1(\mu\text{-}O)M^2$ porph. In the Ru and Os ions, $[M_2OX_{10}]^{4-}$, the M—O—M unit forms an electronically unique independent chromophore. The linearity results from $d\pi$–$p\pi$ bonding through overlap of the p_x and p_y orbitals on O with d_{xz} and d_{yz} orbitals on the metal atoms. Linear M—O—M groups have ir vibrations lower than those in bent bridges. Units of the type $Mo_2O_3^{4+}$ and $Re_2O_3^{6+}$ are common for Mo^V and Re^{VI} complexes; there are linear, O═M—O—M═O and cis or trans types[37c]:

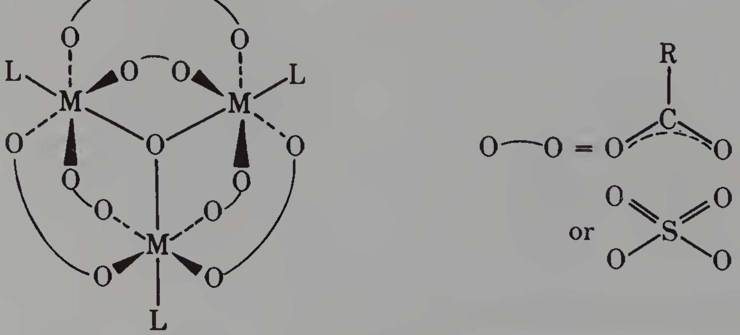




The *pyramidal*(μ_3-O)M_3 unit occurs widely in species such as OHg_3^+, $[Nb_3(\mu_3\text{-}O)_2(O_2CR)_6(THF)_3]^+$, $Os_4O_4(CO)_{12}$, $[Re_3O(H)_3(CO)_9]^{2-}$, $Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5(\mu\text{-}\eta^2 dppm)_2$[38a]; several species have two μ_3-O caps in the (M_3O_2) unit,[38b] and the capping oxygen acts as a 4*e* ligand.

Oxo-centered complexes can have μ_4-tetrahedral oxygen[38c] in the center of a tetrahedron of divalent metal atoms as in $M_4O(O_2CMe)_6$ or in clusters. The best-known complex is $Be_4O(O_2CMe)_4$, but Zn^{II} and Co^{IV} analogues are known. Iron and Mn complexes, for example, $Fe_4^{III}O(O_2CMe)_{10}$, also have μ_4-O, and higher oxo iron polymers may have trigonal bipyramidal coordination, as in $[Fe_5O(O_2CMe)_{12}]^+$. There is one example of μ_5-O.[38d]

Oxygen-centered triangles[39a] are an important unit found widely in so-called *"basic" carboxylates* (and some other bridging anions) of many transition metals, for example, V, Cr, Mn, Fe, Co, Ru, Rh, Ir, and Pt. For the +3 state they have the general formula $[M_3O(O_2CR)_6L_3]^+$ where L is a ligand such as H_2O or pyridine and the structure (12-VIII)



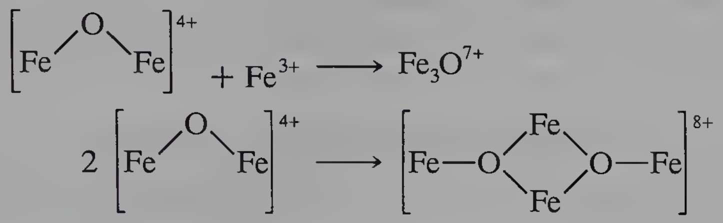
(12-VIII)

[37a] R. Hoffmann *et al., J. Am. Chem. Soc.*, 1986, **108,** 2222.

[37b] C-H. Yang and V. L. Goedken, *Inorg. Chem. Acta.*, 1986, **117,** L19; B. O. West *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 840.

The M_3O group is usually planar on account of π-bonding though in a few cases as in $[Fe_3O(O_2CCMe_3)_6(MeOH)_3]^+$ the O atom may be slightly out of plane.

Although most of the M_3O species have not been made by systematic reactions, some such syntheses have now been achieved,[39b] for example,



Depending on the metal, the $[M_3O(O_2CMe)_6L_3]^+$ ions with the metal being $+3$ can be oxidized or reduced in 1*e* steps. The neutral, mixed valence species,[40] formally $M^{II}M^{III}M^{III}$ have, in some cases been shown to have equivalent metal atoms with a formal oxidation state $2\frac{2}{3}$. Examples are $[Ru_3O(O_2CR)_6py_3]$ and $[Mn_3O(O_2CMe)_6py_3]$. Complexes with different metals in the same or different oxidation states can also be obtained,[41] examples being $[Cr_2MnO(O_2CMe)_6py_3]$ and $[Fe_2CrO(glycine)(H_2O)_3]^{7+}$; others have CrFeMgO, $FeRu_2O$, Cr_2NiO, and so on, cores.

Although the magnetic properties and electronic structures have been studied in some detail, only recently has the ir of the Fe_3O unit been identified at ~600 cm^{-1} in $[Fe_2^{III}Fe^{II}O(O_2CMe)_6py_3]$.[42] Although most planar M_3O species are carboxylates, examples with SO_4^{2-} and NO_2^- bridges are known, for example, $[Pt_3O(NO_2)_6]^{2-}$ and the ion $[Fe_3O(SO_4)_6(H_2O)_3]^{5-}$ that occurs in the mineral metavoltine.[43] The Fe_3O species with amino acid ligands have been considered as a possible model for iron in the protein ferritin (ref. 40 and Chapter 30).

[37c] See G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 2167.

[38a] J-J. Bonnet *et al., Organometallics*, 1986, **5**, 1154.

[38b] Y. Sasaki *et al., J. Am. Chem. Soc.*, 1986, **108**, 6059.

[38c] G. C. Di Donato and K. L. Busch, *Inorg. Chem.*, 1986, **25**, 1551; M. B. Hursthouse *et al., J. Chem. Soc. Chem. Commun.*, **1986**, 1587; C. K. Schauer and D. F. Shriver, *Angew. Chem. Int. Ed. Engl.*, 1987, **26**, 255.

[38d] W. J. Evans and M. S. Sollberger, *J. Am. Chem. Soc.*, 1986, **108**, 6095.

[39a] R. J. Wittebort *et al., J. Am. Chem. Soc.*, 1986, **108**, 2938; C. E. Sumner, Jr., and G. R. Steinmetz, *J. Am. Chem. Soc.*, 1985, **107**, 6124.

[39b] S. J. Lippard, *et al., J. Am. Chem. Soc.*, 1987, **109**, 3337.

[40] D. N. Hendrickson *et al., J. Am. Chem. Soc.*, 1987, **109**, 1063, 1073; F. A. Cotton *et al., Inorg. Chem.*, 1986, **25**, 3505. G. Christou *et al., J. Am. Chem. Soc.*, 1987, **109**, 5703.

[41] B. P. Straughan *et al., Inorg. Chim. Acta.*, 1985, **98**, 7; *J. Chem. Soc. Dalton Trans.*, **1987**, 97; M. Sorai *et al., Inorg. Chem.*, 1987, **26**, 223. A. B. Blake *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 2509.

[42] R. D. Cannon *et al., J. Am. Chem. Soc.*, 1987, **109**, 2009.

[43] H. J. Schugar *et al., Inorg. Chem.*, 1981, **20**, 3314; J. Darriet *et al., New J. Chem.*, 1987, **11**, 21.

12-10. Dioxygen, Superoxo, and Peroxo Ligands[44]

The O_2 molecule and its two reduced species O_2^- and O_2^{2-} can act as ligands to transition metals. Molecular oxygen reacts reversibly with some metal complexes and such reversible reactions are involved in the oxygenation of hemoglobin and myoglobin (Chapter 30).

Generally, electron density is transferred from metal to O_2 with formal oxidation of the metal and reduction of O_2:

$$L_xM^{n+} + O_2 \rightleftharpoons L_xM^{n+1}-O_2^-$$

initially giving a *superoxo* complex. A specific example is

$$Co^{II}(acacen) + O_2 + Me_2NCHO \rightleftharpoons Co^{III}(O_2)(acacen)(Me_2NCHO)$$

However, in certain cases we can have a two-electron transfer giving a peroxo complex as in oxidative-addition reactions (Chapter 27)

$$trans\text{-}Ir^{I}Cl(CO)(PPh_3)_3 + O_2 \rightleftharpoons Ir^{III}(O_2)Cl(CO)(PPh_3)_2$$

The reaction of a superoxo complex with a second metal can lead to a bridging μ-peroxo species

$$L_xM^{n+1}-O_2^- + L_xM^{n+} \rightleftharpoons L_xM^{n+1}-(\mu\text{—}O_2^{2-})-ML_n^{n+1}$$

which in turn can be oxidized to a μ-superoxo species:

$$L_xM^{n+1}-(O_2^{2-})-ML_x^{n+1} \underset{+e}{\overset{-e}{\rightleftharpoons}} L_xM^{n+1}-(\mu-O_2^-)-M^{n+1}L_x$$

Peroxo complexes are often obtainable in aqueous solution from H_2O_2 especially for the early transition metals like Ti, Nb, Cr, or W.[45a] Sometimes the same complex can be obtained from either O_2 or H_2O_2, for example,

$$[Co^{I}(diars)_2]^+ \xrightarrow{O_2} [O_2Co^{III}(diars)_2]^+ \xleftarrow[\substack{-2H_2O\\-2H^+}]{H_2O_2} cis\text{-}[Co^{III}(H_2O)_2(diars)_2]^{3+}$$

but more typically,

$$HCrO_4^- + 2H_2O_2 + H^+ \longrightarrow CrO(O_2)_2(H_2O) + 2H_2O$$

Superoxo complexes can sometimes be made from chlorides by interaction with KO_2 in CH_2Cl_2.[45b]

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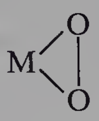
[44] E. C. Niederhoffer, J. H. Timmons, and A. E. Martell, *Chem. Rev.*, 1984, **84,** 137 (oxygen binding in natural and synthetic compounds); F. D. Furia and G. Modena, *Rev. Chem. Intermed.*, 1985, **6,** 51 (peroxo species in iron radical oxidations); R. Boča, *Coord. Chem. Rev.*, 1983, **50,** 1 (X-ray data); T. G. Spiro, Ed., *Metal Ion Activation of Oxygen,* Wiley, New York, 1980; M. H. Gubelmann and A. F. Williams, *Struct. Bonding Berlin,* 1983, **55,** 2 [structure and reactivity of $M(O_2)$]; I. M. Klotz and D. M. Kurtz, Jr., *Acc. Chem. Res.*, 1984, **17,** 16 (binuclear O_2 carriers); S. Fallab and P. R. Mitchell, *Adv. Inorg. Bioinorg. Mech.*, 1984, **3,** 311 (Co—O_2 systems); H. Taube, *Prog. Inorg. Chem.*, 1986, **34,** 607.

[45a] See, for example, W. P. Griffith *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 555.

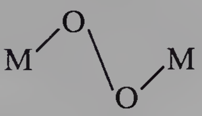
[45b] H. Suzuki *et al., J. Am. Chem. Soc.* 1980, **101,** 1749.

The $M(O_2)$ complexes can broadly be classed in two groups:

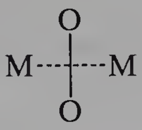
1. Those containing *peroxo groups* (O_2^{2-}) that may be (*a*) part of a three-membered ring, (*b*) bridging staggered, or (*c*) bridging symmetrical



(a)



(b)

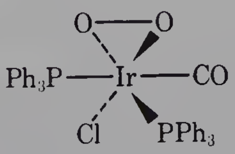


(c)

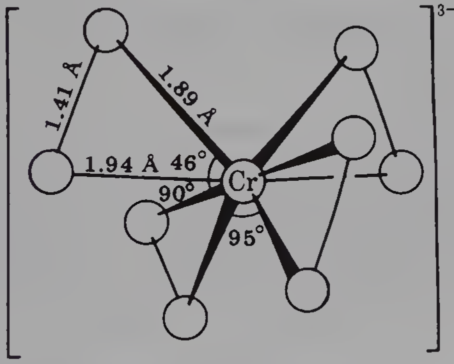
There is only one example of a symmetrical bridge, in the uranyl compound $[Cl_3O_2U\text{-}\mu(O_2)\text{-}UO_2Cl_3]^{4-}$ obtained by action of O_2 on uranyl sulfate (UO_2SO_4) in methanol.

In peroxo compounds the O—O bond distances are *fairly constant* in the range 1.40 to 1.50 Å (O_2^{2-} = 1.49 Å) and *do not depend on the nature of the metal and its ligands.* The O—O stretching frequencies are in the 790 to 930-cm^{-1} region (for Na_2O_2, ν = 738 cm^{-1}). For the triangular η^2-O_2 species these frequencies are around 850 cm^{-1}. It makes no difference whether compounds are made from O_2 or H_2O_2, and there is no correlation between reversible oxidation by O_2 and any bond parameters.

Although the bonding in the three-membered ring is most easily described by localized bonding, it can also be described by an MO treatment similar to that for the bonding of olefins or acetylenes (Section 2-12). Crudely, a σ bond is formed by filled $Op\pi \rightarrow Md\sigma$ bonding and back-bonding is due to $Md\pi \rightarrow O\pi^*$. Representative examples of three-membered ring compounds are oxygen adducts of planar d^8 metal complexes such as *trans*-$IrCl(CO)(PPh_3)_2$ (12-IX) and of Cr, Mo, and W peroxo complexes [46] such as the dodecahedral $[Cr(O_2)_4]^{3-}$ ion (12-X).

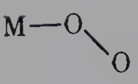


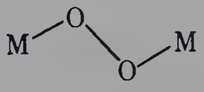
(12-IX)



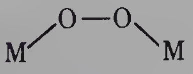
(12-X)

2. The *superoxo* O_2^- *ion* can be bound in the following ways:

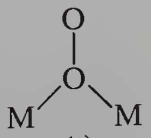




(a)



(b)



(c)

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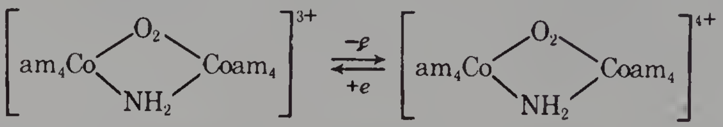
[46] See, for example, J. Weber *et al., Inorg. Chem.*, 1984, **23,** 4571.

Unidentate, end-on and bent superoxo groups occur mainly in complexes of cobalt(III) such as $[Co(O_2)(CN)_5]^{3-}$ and rhodium (III)[47] such as $[Rh(O_2)\ en_2\ (H_2O)]^{2+}$.

The superoxo *bridged species* of types (a) and (b) are again found mostly in Co^{III} and Rh^{III} species by oxidation of peroxo complexes, for example.



The bridged superoxo complexes have O—O distances in the range 1.10 to 1.30 Å, for example, 1.24 Å in $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$, which can be compared to that in O_2^- (1.33 Å). The O—O stretching frequencies lie in the 1075 to 1195 cm^{-1} region (KO_2, 1145 cm^{-1}). The unpaired electron is delocalized over the metal atoms, according to esr studies and lies in an MO of π symmetry relative to the planar MO_2M or MO_2 group.

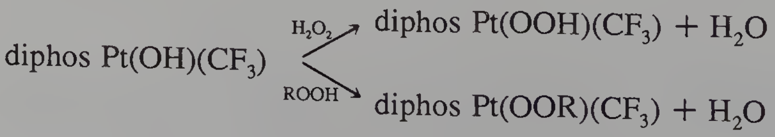
Superoxo bridges of type (c) may be present in certain oxygen carrying proteins (hemerythrins) but so far are known only in a potassium crown ether salt of the ion $[Al_2Me_6(O_2)]^-$ from interaction of KO_2 with Al_2Me_6 where the O—O bond (1.47 Å) is longer than in normal superoxides and the ir stretch is at 851 cm^{-1}.[48]

The oxygen adducts of metal complexes of macrocyclic N ligands have been intensively studied because of the relation to natural oxygen transport molecules containing Fe and Cu. Considerable ingenuity has gone into trying to make truly reversible synthetic models for heme (Chapter 30). The problem is to prevent irreversible oxidation of the iron atom in the macrocycle from Fe^{II} to Fe^{III}.

One approach has been to construct what are termed "picket-fence" or basket handle porphyrins (Section 10-12), whereby the way the oxygen molecule can approach and leave the iron atom axially is sterically restricted by bulky groups.

Although most O_2 "carriers" have organic ligands, a purely inorganic one, $[GeWMnO_{39}]^{6-}$ acts this way at low temperatures.[49]

Hydroperoxo and *alkylperoxo* groups can also act as ligands and MOOH and MOOR species are involved in reactions of MH and MR species with O_2 (Section 28-22). Well-defined stable species have been characterized for Ir, Pt, and other metals,[50] for example, by synthesis of the type:



$$\text{diphos Pt(OH)(CF}_3) \xrightarrow{H_2O_2} \text{diphos Pt(OOH)(CF}_3) + H_2O$$

$$\text{diphos Pt(OH)(CF}_3) \xrightarrow{ROOH} \text{diphos Pt(OOR)(CF}_3) + H_2O$$

$$IrCl(CO)(PR_3)_2 \xrightarrow{t\text{-}BuOOH} cis\text{-}IrCl(O_2t\text{-}Bu)_2(CO)(PR_3)_2$$

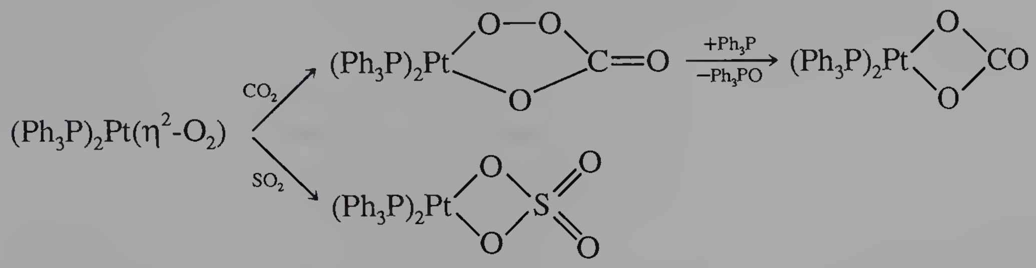
[47] R. D. Gillard and J. D. Pedroso de Jesus, *J. Chem. Soc. Dalton Trans.*, **1984**, 1895.

[48] J. L. Atwood *et al., J. Am. Chem. Soc.*, 1981, **103,** 4277.

[49] D. E. Katsoulis and M. T. Pope, *J. Am. Chem. Soc.*, 1984, **106,** 2737.

[50] P. K. Monaghan *et al., Organometallics*, 1985, **4,** 1669; G. Strukul *et al., Inorg. Chem.*, 1982, **21,** 495; J. E. Bercaw *et al., J. Am. Chem. Soc.*, 1986, **108,** 8291.

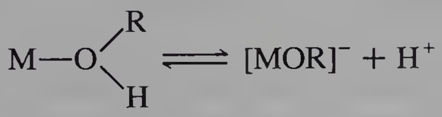
Industrially important oxidations of organic compounds by O_2 and other oxidants are discussed in Chapter 28; many oxidations using O_2 are radical in nature but some do proceed by nonradical paths,[51] for example.



12-11. Alkoxides and Aryloxides[52a]

In solution in alcohols, particularly methanol, metal ions may be solvated just as in water, but the solvent molecules are usually readily displaced by stronger donor ligands such as water itself.

Just as coordinated water can lose a proton to give hydroxo complexes, so can alcohols:



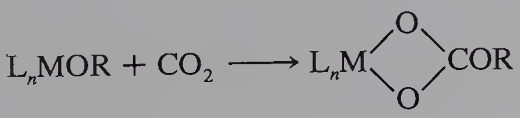
$$M{-}O(R)(H) \rightleftharpoons [MOR]^- + H^+$$

Although M—OR groups are usually bent, in $[ZrCl_4(OMe)(MeOH)]^-$ the ZrOC angle is 171.4° compatible with a triple bond $Zr\overset{\leftarrow}{\underset{\leftarrow}{=}}\ddot{\underset{..}{O}}{-}Me$.[52b] In the deprotonated form RO^-, *all* hydroxo compounds can act as ligands, for example, Schiff bases derived from hydroxo compounds, hydroxo acids, and so on.

Alkoxides (and aryloxides) are usually made by reaction of metal halides and alcohols (or phenols) in the presence of a HX acceptor, for example,

$$TiCl_4 + 4EtOH + 4Et_3N \longrightarrow Ti(OEt)_4 + 4Et_3NH^+Cl$$

or by use of alkali metal or Tl^I alkoxides. They are normally readily hydrolyzed but thermally stable, distillable liquids or volatile solids. They undergo a wide variety of other reactions such as insertions (Chapter 27) with small molecules, for example,



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[51] See A. R. Miksztal and J. S. Valentine, *Inorg. Chem.*, 1984, **23**, 3548; H. Sies, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 1058.

[52a] R. C. Mehrotra, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 269 (alkoxides, 174 references); R. C. Mehrotra *et al.*, *Coord. Chem. Rev.*, 1985, **68**, 101 (Pt metal derivatives); K. C. Malhotra and R. L. Martin, *J. Organomet. Chem.*, 1982, **239**, 159 (aryloxides, 162 references); L. Que, *Coord. Chem. Rev.*, 1983, **50**, 73 (metalloproteins with OAr coordination); D. C. Bradley, R. C. Mehrotra, and D. P. Gaur, *Metal Alkoxides*, Academic Press, New York, 1978.

[52b] R. Karia *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 2493.

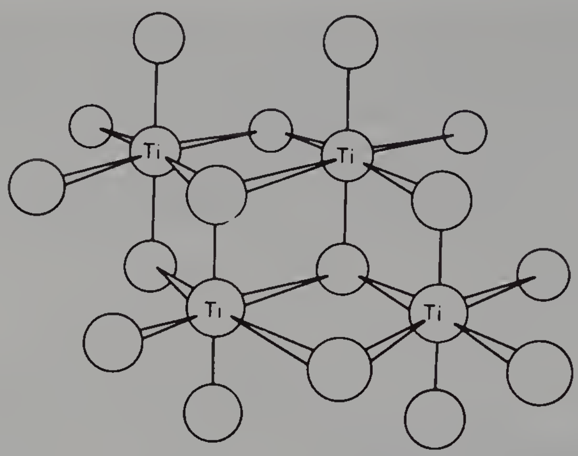
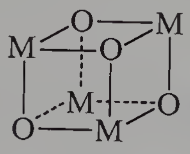


FIG. 12-3. The tetrameric structure of crystalline $[Ti(OC_2H_5)_4]_4$ showing both μ_2 and μ_3 bridges. Only Ti and O atoms are shown. Note that the more bulky trifluoromethyl compound is a monomer.

and hydrogenolysis,[53] for example,

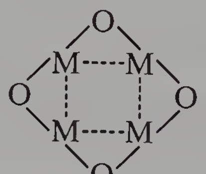
$$(CuO\textit{t}\text{-}Bu)_4 \xrightarrow[PR_3]{H_2} (HCuPR_3)_6 + \textit{t}\text{-}BuOH$$

Most alkoxides with simple groups are polymeric to the extent that maximum coordination of the metal is achieved. Some common types are shown in (12-XI) to (12-XIII) and the structure of another is illustrated in Fig. 12-3.



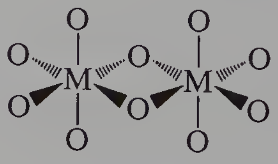
NaO*t*-Bu

(12-XI)



CuO*t*-Bu

(12-XII)



$Nb(OMe)_5$

(12-XIII)

The use of very bulky alkoxide or aryl oxide groups [54] such as $t\text{-}Bu_3CO^-$, $t\text{-}Bu_3SiO^-$, 2,6-di-*t*-butylphenoxide, and adamantoxides, can however, give simple monomeric species with low coordination numbers.

Alkoxo groups not engaged in bridging may, of course act as donors to other metal species.[55] Thus $U(O\textit{i}\text{-}Pr)_6$ gives adducts with Li, Mg, and Al alkyls such as (12-XIV), while in the lithium salt of the $W(OPh)_6^-$ ion, two phenoxides are bound to Li^+(12-XV).

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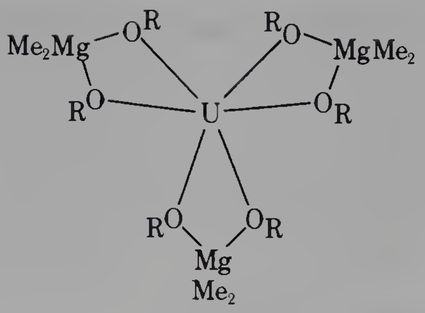
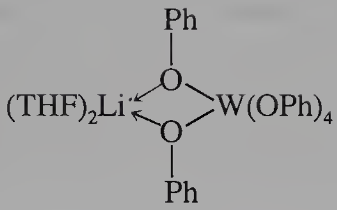
[53] G. V. Goeden and K. G. Caulton, *Inorg. Chem.*, 1981, **20,** 7354.

[54] See, for example, P. T. Wolczanski *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 3535. I. P. Rothwell *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 155; *Organometallics*, 1987, **6,** 73.

[55] G. Wilkinson *et al.*, *Polyhedron*, 1982, **1,** 641; R. C. Mehrotra *et al.*, *Inorg. Chem. Acta*, 1987, **126,** 99; *Polyhedron*, 1987, **6,** 427.

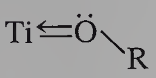


(12-XIV)



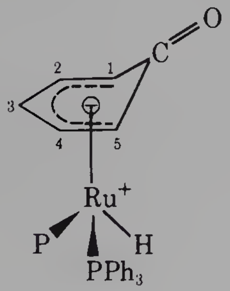
(12-XV)

Although usually considered to be a one-electron ligand there is some evidence that RO can act as a 3*e* donor (cf. NR_2, Section 10-18), (12-XVI), from short M—O distances and the obtuse angles in certain alkoxides such as $Cp_2TiCl(OEt)$[56] and the Zr compound noted on p. 471:



(12-XVI)

Although aryloxides can form unidentate or bridge groups as in $W(OPh)_6$ and $(PhO)Cl_2Ti(\mu\text{-}OPh)_2TiCl_2(OPh)$, respectively, for Ru, Rh, and Ir,[57] the phenoxide ion can be bound as a η-1-5-oxocyclohexadienyl (cf. cyclohexadienyls, Section 26-15) (12-XVII) where the C—O group becomes more keto-like and the bonding is delocalized.



(12-XVII)

An unusual class of aryloxides are the *calixarenes*[58a] (calix, Greek for chalice), which are molecules having a torus shape similar to that of cyclodextrins with potential for enzyme mimicry. The cyclic polymers (12-XVIII) can have a closed or open cavity (12-XIX). They can form complexes with small molecules, behaving as hosts, but can also transport metal ions through hydrophobic liquid membranes, as well as giving phenoxides by loss of protons.

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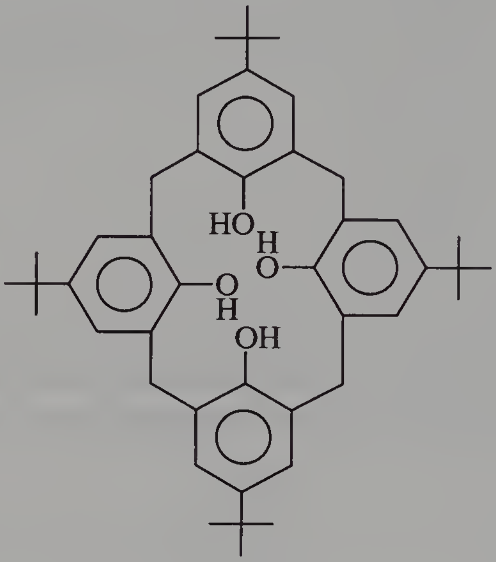
[56] K. G. Caulton *et al., J. Am. Chem. Soc.*, 1980, **101,** 3009.

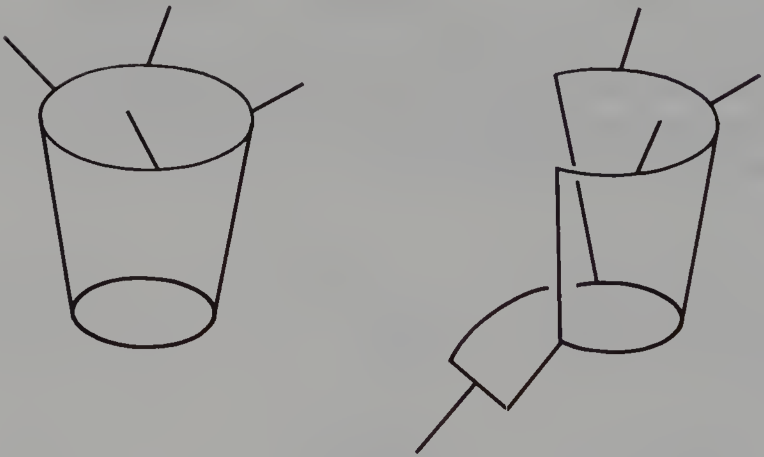
[57] See, for example, L. Dahlenburg and N. Höck, *J. Organomet. Chem.*, 1985, **284,** 129.

[58a] C. D. Gutsche, *Top. Curr. Chem.*, 1984, **123,** 1; S. Shinkai *et al., J. Am. Chem. Soc.*, 1986, **108,** 2409.

Some complexes can be made, for example, by reaction of calixarenes with $M(NMe_2)_n$, M = Ti, Fe, Co, or $TiCl_4$.[58b]



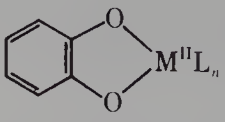
(12-XVIII)



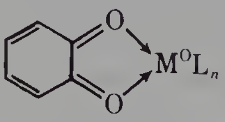
(12-XIX)

12-12. Catecholates and *o*-Quinone Complexes[59]

Phenols with ortho hydroxy groups such as pyrocatechol can give chelates by bonding the 2− anion as in (11-XX) producing complex anions such as $[Cr(O_2C_6H_4)_3]^{3-}$.



(12-XX)



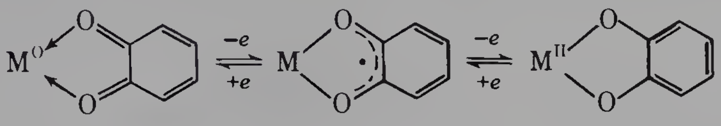
(12-XXI)

[58b] P. P. Power *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 8087; J. L. Atwood *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986,** 610.

[59] C. G. Pierpont, *Coord. Chem. Rev.*, 1983, **38,** 45; W. P. Griffith *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986,** 1125; L. A. de Learie and C. G. Pierpont, *J. Am. Chem. Soc.*, 1986, **108,** 6393.

Formally similar complexes (12-XXI) can be given by *orthoquinones*. Thus interaction of $Cr(CO)_6$ with tetrachlorobenzoquinone (L) gives CrL_3; the oxygen atoms can also bind to separate metals so that a bridged quinone results. The tris species tend to form distorted trigonal prismatic complexes.

The quinone complexes can be considered similar to 1,2-dithiolenes and *o*-quinoneimines and the complexes undergo similar type of oxidation–reduction sequences[60]:



Quinone

Semiquinone

Dihydroxo (pyrocatecholate)

In the paramagnetic semiquinone complex the electron is located on the ligand. The relative importance of the quinone versus dihydroxo species will depend on the basicity of the metal and the oxidizing ability of the quinone.

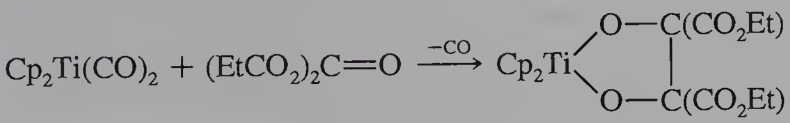
Paraquinones and their mono- and dianions also form complexes: the dianions can form *bridges* between two metals.

The quinone, semiquinone, and catecholate species particularly of iron are important in electron-transfer processes in photosynthesis and respiration.[61]

12-13. Ketones and Esters

Ketones and esters are generally rather weak bases except toward strong Lewis acids such as BF_3. However, most covalent metal halides will form adducts.

Although ketone bonding is normally through oxygen, η^2-complexes with C, O bonding[62a] can be formed (Section 25-2). Coupling of ketones can also occur under some conditions as with diethylketomalonate.[62b]



$$Cp_2Ti(CO)_2 + (EtCO_2)_2C{=}O \xrightarrow{-CO} Cp_2Ti\begin{matrix} O-C(CO_2Et) \\ | \\ O-C(CO_2Et) \end{matrix}$$

12-14. Ethers: Crown Ethers and Cryptates

Metal halides are commonly soluble in, and can form solvates with, THF. Tetrahydrofuran and related ethers, such as dimethoxyethane and ethylene glycol dimethyl ether, are often used as solvents in reactions of transition metal halides with lithium or magnesium alkyls, reductions using sodium, and so on, and the complexing of the alkali metal cation by the ether is of un-

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[60] See, for example, C. G. Pierpont *et al., Inorg. Chem.*, 1983, **21,** 2552.

[61] See J-I. M. Tuchagues and D. N. Hendrickson, *Inorg. Chem.*, 1983, **22,** 2545.

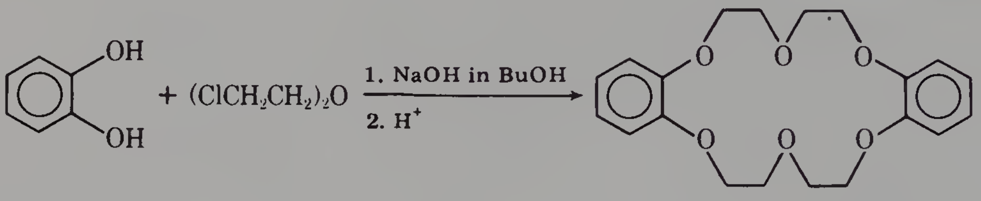
[62a] See, for example, G. Erker *et al., Organometallics*, 1986, **5,** 668 and references quoted.

[62b] C. Floriani *et al., Inorg. Chem.*, 1981, **20,** 349.

doubted importance. Indeed some complexes such as $[K(diglyme)_3]^+$ have been characterized.

Of more importance, however, are the heterocyclic ether ligands we now discuss.

Crown Ethers and Cryptates.[63a,b] The macrocyclic polyethers, termed "crown ethers" from their structural resemblance to crowns, were first synthesized by C. J. Pedersen in 1967 by reactions such as the following:



Dibenzo-18-crown-6

Ethers with from 3 to 20 oxygen atoms have been synthesized. The hydrogenated derivative of dibenzo-18-crown-6 is formally 2,5,8,15,18,21-hexaoxatricyclo$[20.4.0.0^{9,14}]$-hexacosane but usually is called cyclohexyl-18-crown-6. A general abbreviation is *n*-C-*m* where *n* is the ring size and *m* is the number of O atoms, for example, 18-C-6.

Related macropolycycles are the *cryptates* or cryptands, which are N,O compounds such as $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$, the structure of whose complex with Rb^+ is shown in Fig. 4-2.

Crown ethers have particularly large complexity constants for alkali metals—equilibrium constants for cyclohexyl-crown-6, for example, are in the order $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. The cryptates have high complexing ability especially for M^{2+} ions and will render even $BaSO_4$ soluble. They also have good complexing ability for transition metal ions (e.g., for lanthanides).

Crown ethers find many uses. They will render salts such as $KMnO_4$ or KOH soluble in benzene or other aromatic hydrocarbons thus increasing the facility for oxidation or base reactions. Species such as Sn_9^{4+} or Pb_5^{2-} can be isolated as salts of crown-solvated alkali ions. The ethers are widely used as solvents in a variety of organic and organometallic reactions where solvation of alkali ions can effect improvements in rates.

Natural macrocycles concerned with complexing of Na^+ and K^+ and their transport through the hydrophobic lipid bilayer of cell membranes have been noted (see Fig. 4-3).

There are many other heterocycles containing not only oxygen but N and/

[63a] R. M. Izatt *et al., Chem. Rev.,* 1985, **85,** 271 (thermodynamics of complexing); R. M. Izatt and J. J. Christensen, Eds., *Synthetic Multidentate Macrocyclic Compounds.* Academic Press, New York, 1978; D. Parker, *Adv. Inorg. Chem. Radiochem.,* 1983, **27,** 1 (cryptates); F. de Jong and D. N. Reinhoudt, *Stability and Reactions of Crown Ether Complexes,* Academic Press, New York, 1981; G. W. Gokel and S. H. Korzeniowski, *Macrocyclic Polyether Synthesis,* Springer-Verlag, New York, 1982; F. Vögtle and E. Weber, *Top. Curr. Chem.,* 1984; D. J. Cram, *Angew. Chem. Int. Ed. Engl.,* 1986, **25,** 1039.

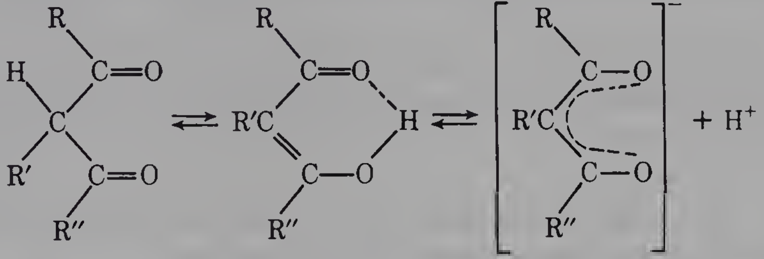
[63b] G. W. Gokel *et al., J. Am. Chem. Soc.,* 1986, **108,** 4078, 4135.

or S. Crown-type groupings can also be attached to other ligand systems to give different types of binding sites, and in "lariat" ethers, which are crowns with side chains.[63b]

An important property of crown ethers (also cyclodextrins) is that they can act as *second coordination sphere ligands.*[63c] (cf., Section 2-7) Thus $[Pt(bipy)(NH_3)_2]^{2+}$ gives crystalline $\{Pt\ (bipy)(NH_3)_2[18\text{-}C\text{-}6]\}^{2+}$, where there is N—H---O) bonding. Ammonium ions can be similarly coordinated. A cheap ether for catalysis of solid-liquid phase reactions is $N(CH_2CH_2OCH_2CH_2OMe]_3$ known as TDA1.[63d]

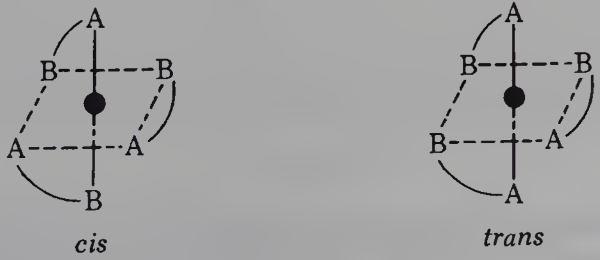
12-15. β-Ketoenolato and Related Ligands[64a]

β-Diketones can form anions as a result of enolization and ionization:



These β-ketoenolate ions form very stable chelate complexes with most metal ions. The commonest ligand is the acetylacetonate ion (acac)$^-$, in which R = R'' = CH_3 and R' = H. A general abbreviation for β-ketoenolate ions in general is dike.

Among the commonest types of diketo complex are those with the stoichiometries $M(dike)_3$ and $M(dike)_2$. The former all have structures based on an octahedral disposition of the six oxygen atoms. The tris(chelate) molecules then actually have D_3 symmetry and exist as enantiomers. When there are unsymmetrical diketo ligands (i.e., those with R ≠ R''), geometrical isomers also exist, as indicated in (12-XXII). Such compounds have been of value in investigations of the mechanism of racemization of tris(chelate) complexes, which are discussed in Section 29-13. Tetradiketo complexes M(β-dike)$_4$ are usually nonrigid.



(12-XXII)

[63c] J. F. Stoddart *et al., Angew. Chem. Int. Ed. Engl.,* 1986, **25**, 487 (100 references);
[63d] L. Echegoyen *et al., J. Am. Chem. Soc.,* 1987, **109**, 3713.
[64a] S. Kawasuchi, *Coord. Chem. Rev.,* 1986, **70**, 51.

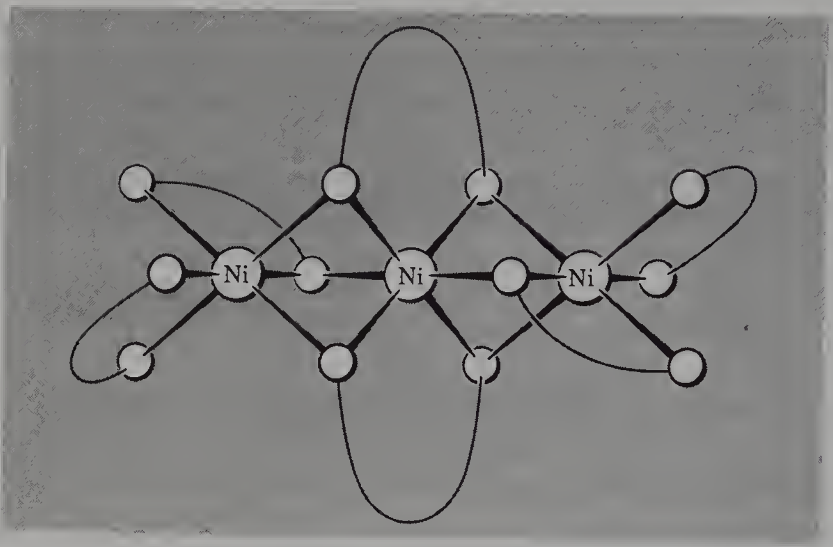
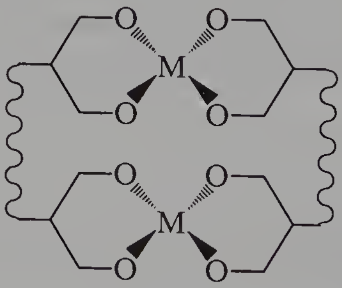


FIG. 12-4. The trimeric structure of nickel(II) acetylacetonate. The unlabeled circles represent O atoms and the curved lines connecting them in pairs represent the remaining portions of the acetylacetonate rings. (Reproduced by permission from J. C. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, 1965, **4**, 456.

Substances of composition M(dike)$_2$ are almost invariably oligomeric, thereby allowing coordinative saturation of the metal.

Thus acetylacetonates of Zn, Ni, and Mn^{II} are trimeric, Fig. 12-4, while Co (acac)$_2$ is tetrameric; all have bridging β-diketonate groups. The presence of bulky substituents on the β-diketones such as Me$_3$C sterically impedes oligomerization and monomers are formed. However, these are commonly solvated by H_2O, ROH, or py to give five- or six-coordinate complexes, *trans*-M(diket)$_2$L$_{1,2}$.

The linking of β-diketonates by bridges allows the formation of "face-to-face" complexes (12-XXIII) similar to those of face-to-face porphyrins (Section 10-12)[64b]; small molecules may occupy the central hole.



(12-XXIII)

For neutral compounds, especially of acetylacetone, the methine CH group of the ring can undergo a wide range of substitution reactions similar to those of aromatic substances, even though the rings have little or no aromatic

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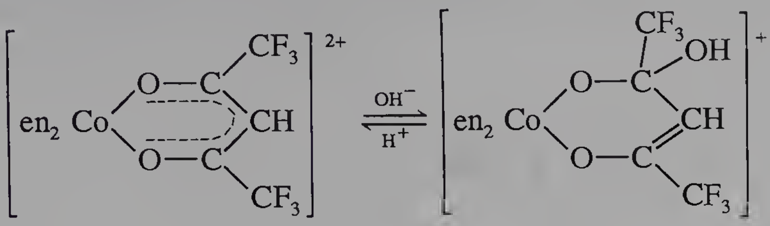
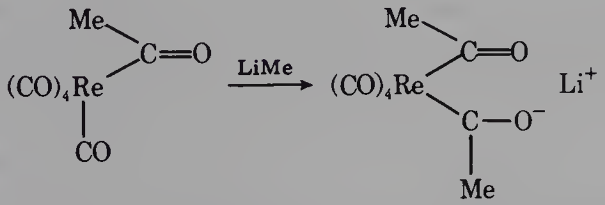
[64b] A. W. Maverick and F. E. Klavetter, *Inorg. Chem.*, 1984, **23**, 4129.

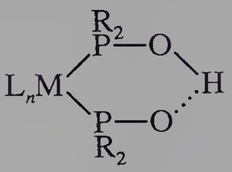
character. However, certain hexafluoroacetylacetonates may be attacked at carbon by nucleophiles[65]:



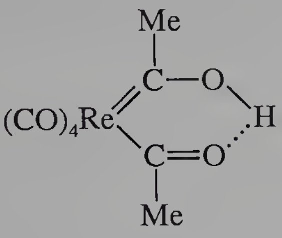
Metalla β-diketonates[66] may be obtained by reactions of the type



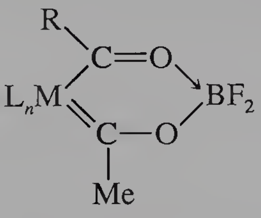
Similar (acac)-like species can also be formed when the metal has R_2PO or R_2POH groups in cis positions (12-XXIV).[67] They all give complexes with other metals.



(12-XXIV)



(12-XXV)



(12-XXVI)

The hydrogen form of the rhenioacac (12-XXV) has a very short symmetrical H-bond, 2.4 Å, with an O—H--O angle of 172°; it is best considered as having a localized π system as shown with an asymmetric H-bond rather than a delocalized one.[68]

By use of 2 mol of MeLi a tridentate ligand can be obtained; this is an analogue of $(MeCO)_3C^-$ and also resembles the tridentate $RBpz_3^-$ ligand (Section 10-14):

$$MeCORe(CO)_5 + 2LiMe \longrightarrow [\textit{fac}\text{-}(CO)_3Re(COMe)_3]^{2-}$$

The keto groups can also undergo base condensations with amines to give ketoimines[69] and be capped by BF_2 groups to give species of type (12-XXVI).[70]

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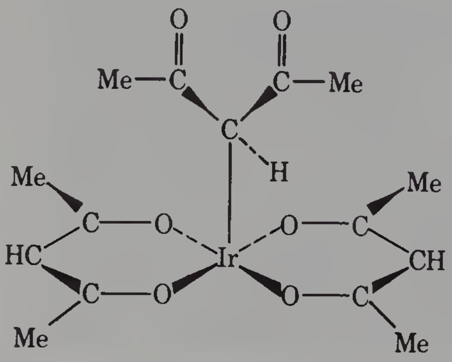
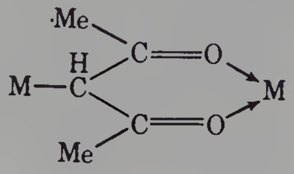
[65] R. van Eldik, *Inorg. Chem.*, 1985, **24,** 423.
[66] C. M. Lukehart, *Adv. Organomet. Chem.*, 1986, **25,** 45.
[67] W. Bushnell *et al., Inorg. Chem.*, 1982, **21,** 957.
[68] A. J. Schultz *et al., J. Am. Chem. Soc.*, 1984, **106,** 999.
[69] C. M. Lukehart *et al., Inorg. Chem.*, 1984, **23,** 438.
[70] C. M. Lukehart *et al., J. Am. Chem. Soc.*, 1984, **106,** 1333.

C-Bonded β-Diketonate Complexes. These have the metal bound to the central carbon atom and are known for a number of metals especially of the Pt group.[71] An example is (12-XXVII), which has both normal and C-bonded groups.



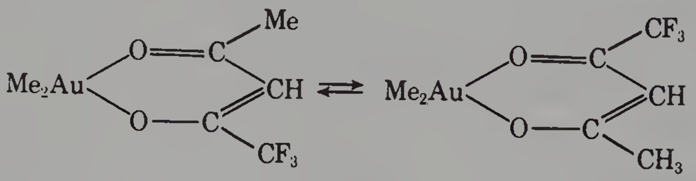
(12-XXVII)



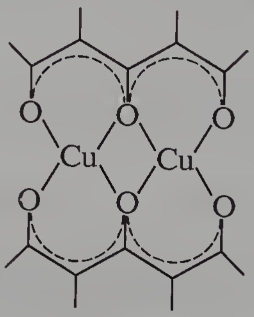
(12-XXVIII)

Note that the C-bonded groups have two free $>$C=O groups that can act as chelate donors to other metals as in (12-XXVIII).

The intermediate formation of a C-bonded species is probably the reason for the existence, even at very low temperatures, of dynamic equilibria such as



1,3,5-Triketonates.[72a] These and similar polyketones can give rise to *compartmental ligands* and link two metal centers (12-XXIX) that can then undergo redox reactions.



(12-XXIX)

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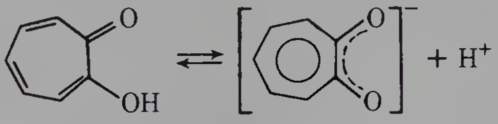
[71] R. K. Mohapatra *et al.*, *Polyhedron,* 1985, **4,** 1297.

[72a] M. J. Hynes and J. Walsh, *J. Chem. Soc. Dalton Trans.*, **1985,** 2565; R. L. Lintvedt and L. S. Kramer, *Inorg. Chem.*, 1983, **21,** 796; L. L. Borer *et al.*, *Inorg. Chem.*, 1986, **25,** 3652.

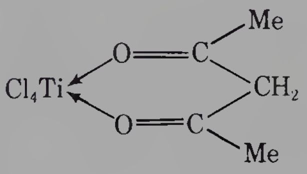
Tropolonates. A system similar to the β-diketonates is provided by *tropolone* and its anion (12-XXX). The tropolonato ion gives many complexes that are broadly similar to analogous β-diketonate complexes, although there are often very significant differences.[72b]



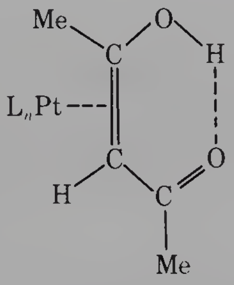
(12-XXX)

It should be noted that the tropolonato ion forms a five-membered chelate ring and that the "bite," that is, the oxygen-to-oxygen distance, is smaller than in the β-diketonato ions. This leads the tristropolonato complexes to considerable distortion from an octahedral set of oxygen atoms. Thus in $Fe(O_2C_7H_5)_3$ the O—Fe—O ring angles are only 78° and the entire configuration is twisted about the threefold axis toward a more prismatic structure. The upper set of Fe—O bonds is twisted only 40° instead of 60° relative to the lower set.

Finally, note that β-diketones can occasionally act as *neutral* ligands, being bound either through oxygen as in (12-XXXI) or for certain metals that can form olefin complexes as shown in (12-XXXII).



(12-XXXI)



(12-XXXII)

12-16. Oxo Anions as Ligands

Essentially all oxo anions, simple like NO_2^- or SO_4^{2-} or substituted like RCO_2^-, act as ligands.

Carbon Oxo Anions. The most important are *carbonate* and *bicarbonate* for which a great variety of bonding modes has been established[73]; these can

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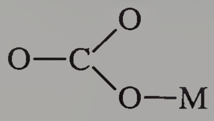
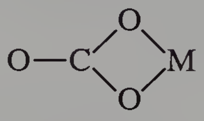
[72b] W. P. Griffith *et al.*, *Polyhedron*, 1987, **6**, 891.

[73] F. W. B. Einstein and A. C. Willis, *Inorg. Chem.*, 1981, **20**, 609; G. Mahal and R. van Eldik, *Inorg. Chem.*, 1985, **24**, 4165; G. Wilkinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 2723; E. Carmona *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 6424; T. C. W. Mak, *J. Chem. Soc. Chem. Commun.*, **1986**, 1597.

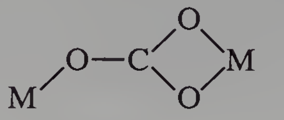
be designated by the link and metal number (L, M):



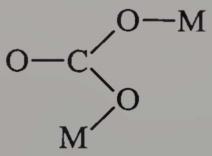
1L1M, η^1



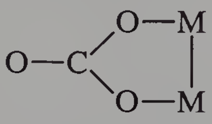
2L1M, η^2



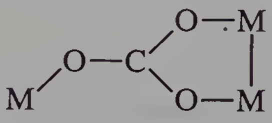
3L2M



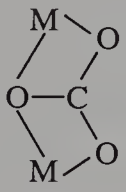
syn, anti; 2L2M



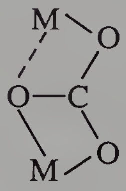
syn, syn; 2L2M



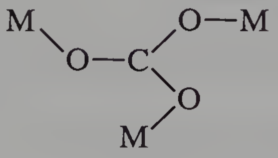
3L3M



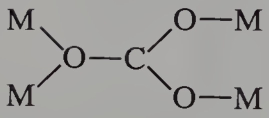
3L2M



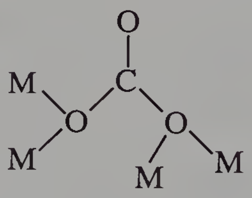
3L2M



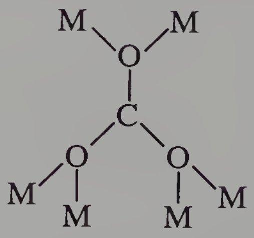
3L3M



3L4M



3L4M

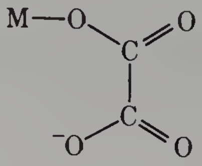


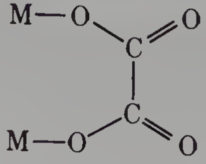
3L6M

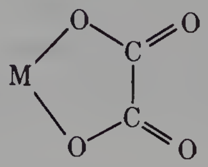
Although carbonate complexes are usually made from CO_3^{2-}, HCO_3^-, or CO_2, they can be formed on oxidation,[74] for example,

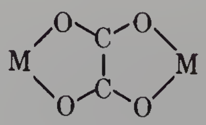
$$[\mathrm{CpMo(CO)_3}]^- \xrightarrow{O_2} \mathrm{CpMo(CO)_2}(\eta^2\text{-}\ \mathrm{O_2CO})$$

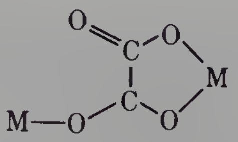
Oxalato complexes[75a] are also common, the main linkage types being











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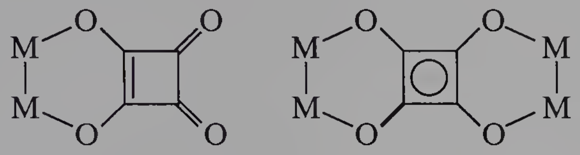
[74] M. D. Curtis and K. R. Han, *Inorg. Chem.*, 1985, **24**, 378.

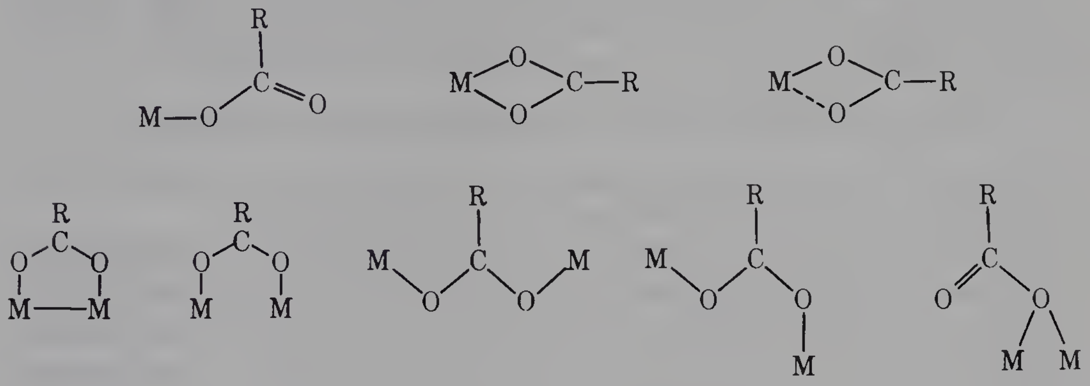
[75a] See, for example, S. Sjöberg and L-O Öhman, *J. Chem. Soc. Dalton Trans.*, **1985**, 2665.

Typical chelate complexes are trisoxalato ions, for example, [Co ox_3]$^{3-}$.

Squarates[75b] may act as chelates or bridges:



Carboxylates.[76] The carboxylates are a very important class of ligands with the following bonding modes.



Syn–syn *Syn–syn* *Anti–anti* *Anti–syn* Monatomic

The most common forms are unidentate, symmetrical chelate, and symmetrical syn–syn bridging. Acetates and trifluoroacetates of weak Lewis acids are usually symmetric, those of very strong Lewis acids are often asymmetric.[77] The other forms are not common, but anti–anti single bridging occurs in $[Mnsal_2enCO_2Me]_n$ and anti–syn in $[(PhCH_2)_3SnO_2CMe]_n$. Trifluoroacetates are known only in unidentate and bridging forms.

The main types of bonding can often be distinguished by ir[78] and nmr spectra. The syn–syn bridging RCO_2^- ligand is extremely common and important in compounds with M—M quadruple bonds.

In "ionic" acetates or in aqueous solution, the "free" $CH_3CO_2^-$ ion has symmetric and antisymmetric C—O stretching modes at ~ 1415 and 1570 cm^{-1}. These frequencies can vary by ±20 cm^{-1}. Since the symmetry of even the free ion is low and it gives two ir-active bands, evidence for the mode of coordination must be derived from the positions rather than the number of bands. When the carboxyl group is unidentate, one of the C—O bonds should have enhanced double-bond character and should give rise to a high-frequency

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[75b] G. Doyle *et al.*, *Organometallics*, 1982, **1**, 1613; O. St. C. Headley and L. A. Hall, *Polyhedron*, 1985, **4**, 1697; A. Weiss *et al.*, *Z. Naturforsch.*, 1986, **41B**, 18.

[76] R. C. Mehrotra and R. Bohra, *Metal Carboxylates*, Academic Press, New York, 1983 (2158 references).

[77] I. D. Brown, *J. Chem. Soc. Dalton Trans.*, **1980,** 1118.

[78] G. B. Deacon *et al.*, *Inorg. Chim. Acta*, 1985, **104**, 41; *Coord. Chem. Rev.*, 1980, **33**, 227.

band. Such bands are observed in the 1590 to 1650-cm^{-1} region and are considered to be diagnostic of unidentate coordination.

Symmetrical bidentate coordination, as in $Zn(CH_3CO_2)_2 \cdot 2H_2O$ and $Na[UO_2(CH_3CO_2)_3]$, and symmetrical bridging, as in the $M_2(O_2CCH_3)_4L_2$ and $M_3O(O_2CCH_3)_6L_3$ types of molecules, leaves the C—O bonds still equivalent, and the effect on the frequencies is not easily predictable. In fact, no criteria for distinguishing these cases have been found. In general, multiple bands appear between 1400 and 1550 cm^{-1}, the multiplicity being attributable to coupling between CH_3CO_2 groups bonded to the same metal atom(s).

While acetates and other lower carboxylate complexes are prepared from the acids or alkali metal salts, for *formates* a different synthesis is the insertion reaction (Chapter 27) of CO_2 into M—H bonds,[79] for example,

$$(Me_3P)_5MoH_2 + CO_2 \longrightarrow (Me_3P)_5MoH(\eta^2\text{-}O_2CH)$$

Probably the only significant reaction of the carboxylate ligand is decarboxylation, which is catalyzed by transition metal species.[80]

Straight-chain alkyl carboxylic acids derived from petroleum that also have a terminal cyclohexyl or cyclopentyl group are known as *naphthenic acids*.[81a] They form complexes, presumably polymeric, with many transition metals, and these compounds are freely soluble in petroleum. Copper naphthenates are used as fungicides, aluminum naphthenate was used as a gelling agent in "napalm," and cobalt naphthenates are used in paints.

There are, of course, more complicated carboxylic acids such as ethylenediaminetetraacetic acid that can function as multidentate ligands with both N and O bound to the metal. Also, *hydroxo carboxylic acids* such as citrate readily form complexes in which both carboxylate and hydroxo groups are involved. Of such acids, probably the best studied are *tartrato complexes*.[81b] A fairly common type of structure is one with bridges linking two metal atoms. A particular example is the antimony complex "tartar emetic" (Fig. 11-15*b*). Because of the chirality and multiplicity of bonding possibilities, many isomers of tartrate complexes are possible, and the relative stabilities of these can be explained in terms of steric constraints of the binuclear structure and conformation of the tartrato groups, and depend strongly on the coordination geometry about the metal.

Carbamates. Complexes of $R_2NCO_2^-$ are not as extensive or as useful as their sulfur analogues the dithiocarbamates (Section 8-8).

Carbamates are often obtained in insertion reactions of CO_2

$$Ti(NMe_2)_4 + 4CO_2 = Ti(O_2CNMe_2)_4$$

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[79] See, for example, G. Wilkinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 695.

[80] E. B. Boyer and S. D. Robinson, *J. Chem. Soc. Dalton Trans.*, **1985**, 2113.

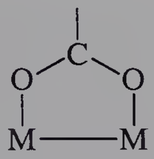
[81a] E. Shower, *Pigm. Resin Technol.*, 1986, **15**, 7.

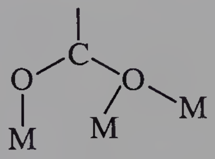
[81b] K. Blomqvist and E. R. Still, *Inorg. Chem.*, 1984, **23**, 3730.

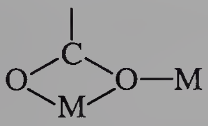
Such insertions may be carried out *in situ* as in reactions of cobalt or lanthanide halides[82] with R_2NH and CO_2 in hexane to give, for example, $Co_6(O_2CNEt_2)_{12}$ or $[Yb(O_2CN\textit{i}\text{-}Pr_2]_4$:

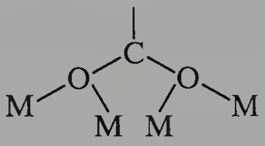
$$MCl_n + 2nNHR_2 + nCO_2 \longrightarrow M(O_2CNR_2)_n + nNH_2R_2Cl$$

Although carbamates are mostly chelate, they can be unidentate and have bridging modes similar to CO_3^{2-} and RCO_2^-

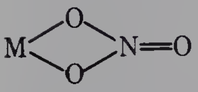


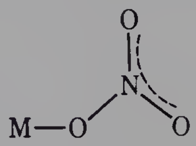


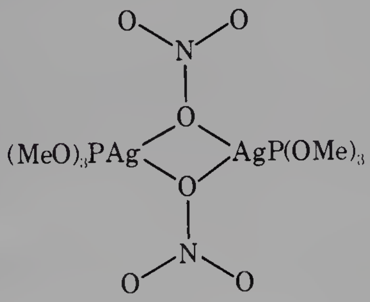


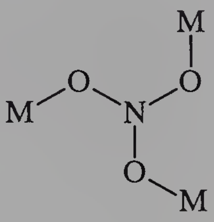


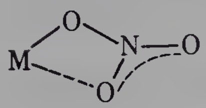
The Nitrate Ion. This ion has several structural roles,[83a] as follows:

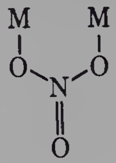










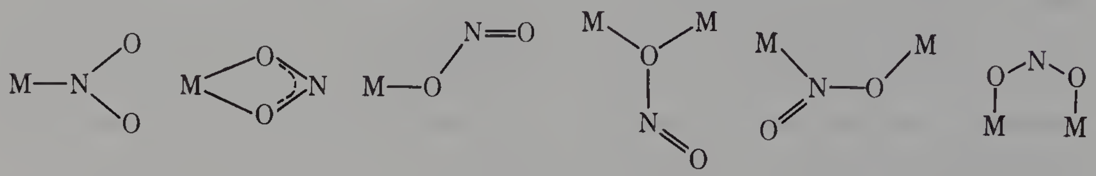


The most common forms of the nitrate ion are symmetrical bidentate followed by η^1. The free NO_3^- ion has relatively high symmetry (D_{3h}); thus its ir spectrum is fairly simple. The totally symmetric N—O stretching mode is not ir active, but the double degenerate N—O stretching mode gives rise to a strong band at ~ 1390 cm^{-1}. There are also two ir-active deformation modes, one of which is doubly degenerate, at 830 and 720 cm^{-1}. When NO_3^- is coordinated, its effective symmetry is reduced, causing the degeneracies to split and all modes (six) to be ir active. Hence, it is possible to distinguish between ionic and coordinated NO_3 groups.

Because the two commonest forms of coordinated NO_3^- have the same effective symmetry, hence the same number of ir-active vibrational modes, criteria for distinguishing between them must be based on the positions of the bands rather than their number. In practice, the situation is quite complex and there are no entirely straightforward criteria. This is because the array of frequencies depends on both the geometry and strength of coordination. A rare case of a planar NO_3^- attached to three metals is found in $[Cu_3(W_9PO_{34})_2(NO_3)]^{13-}$.[83b]

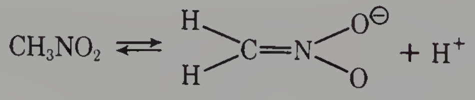
[82] F. Calderazzo *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984,** 647.
[83a] W. L. Driessen *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985,** 2177.
[83b] W. H. Knoth *et al.*, *Inorg. Chem.*, 1986, **25,** 1577.

Nitrite Ion.[84a] The NO_2^- ion can act as an N-ligand to form *nitro* compounds, and as oxygen-bonded *nitrito:*



The NO_2^- ion has low symmetry (C_{2v}) and its three vibrational modes, symmetric N—O stretching, ν_s; antisymmetric N—O stretching, ν_{as}; and bending, δ; are all ir active to begin with. Thus the number of bands cannot change on coordination, and the use of ir spectra to infer structure must depend on interpretation of shifts in the frequencies. The δ vibration is rather insensitive to coordination geometry, but there are characteristic shifts of ν_s and ν_{as} that often can distinguish reliably between the nitro and the nitrito structures. Thus for *nitro* complexes the two frequencies are similar, typical values being 1300 to 1340 cm^{-1} for ν_s and 1360 to 1430 cm^{-1} for ν_{as}. This is in keeping with the equivalence of the N—O bond orders in the nitro case. For *nitrito* bonding, the two N—O bonds have very different strengths and the two N—O stretching frequencies are typically in the ranges 1400 to 1500 cm^{-1} for N═O and 1000 to 1100 cm^{-1} for N—O.

Related to the nitrite ion are the ions derived from the *aci* form of *nitroalkanes,* for example,



Alkane nitronates such as $Zr(O_2N{=}CR_2)_4$ are known.[84b]

In $Ni(O_2N{=}CHPh)_2(tmed)$ the ligand is chelate through both oxygen atoms as it is apparently also in $Ru(O_2N{=}CH_2)H(PPh_3)_3$ and some copper compounds such as $[CuphenO_2N{=}CH_2]^+$. Some tin, lead and mercury compounds have unidentate groups MON(O)CR′R″. However, C bonding, as $M{-}CH_2NO_2$, is also possible, as in the platinum compounds made by the reaction

$$PtCl_2(PEt_3)_2 + CH_3NO_2 \xrightarrow{Ag_2O} cis\text{-}PtCl(CH_2NO_2)(PEt_3)_2$$

This reaction implies initial oxidative addition (Chapter 27) as H and CH_2NO_2, of nitromethane, and indeed such additions are known.

Perchlorate Ion.[85] The ClO_4^- ion is a hard base with low tendency to coordinate, though cases have been established with unidentate, chelating,

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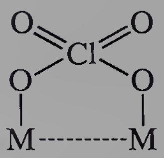
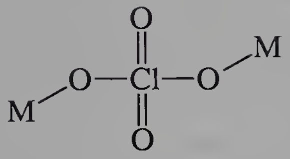
[84a] C. A. Reed *et al., Inorg. Chem.,* 1985, **24,** 2914.

[84b] B. N. Diel and H. Hope, *Inorg. Chem.,* 1986, **25,** 4448; G. Boche *et al., Angew. Chem. Int. Ed. Engl.,* 1987, **26,** 78.

[85] N. M. N. Gowder *et al., Adv. Inorg. Chem. Radiochem.,* 1984, **28,** 255 (162 references); K. R. Grundy and K. N. Robertson, *Inorg. Chem.,* 1985, **24,** 3898.

and the two types of bridges[86]:



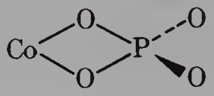


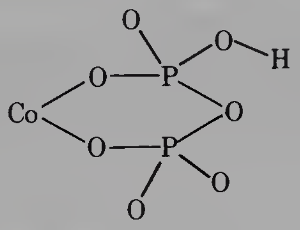
There is evidence for complexing by ClO_4^- in solutions and the reduction of ClO_4^- by metal ions such as Ru^{2+} doubtless involves initial complexing.

Perchlorates should *always* be avoided because of potential explosion hazards and $CF_3SO_3^-$, PF_6^-, and so on, used instead.

Phosphorus Oxo Acids. The many types of phosphorus oxo acids, which may contain either P^{III} or P^V, are discussed in Chapter 11 along with organic-substituted ions such as dialkylphosphinates ($R_2PO_2^-$) and acids such as R_2POH and $(RO)_2POH$.

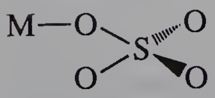
Phosphato complexes may have PO_4^{3-}, HPO_4^{2-}, or $H_2PO_4^-$ coordinated. Few complexes have been studied crystallographically. In Co^{III} $en_2(PO_4)$ there is a bidentate chelate, whereas the pyrophosphate Co^{III} $en_2(HP_2O_7)$ has a six-membered ring:

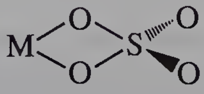


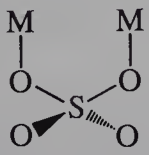


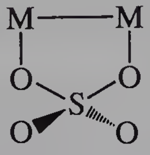
The phosphite ligand $(HO_2P)_2O^{2-}$ is noted in Section 19-H-5. The various polyphosphoric anions such as $[P_3O_{10}]^{5-}$,[87a] and diphosphonates, $[O_3P\text{-}C(R)R'PO_3]^{4-}$,[87b] as well as $[CpCo(R_2P{=}O)_3]^-$,[87c] also give complexes.

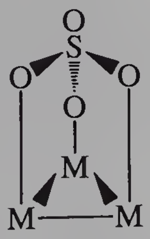
Sulfur Oxo Acids. The sulfate ions HSO_4^- and SO_4^{2-} form numerous complexes. *Sulfate* can have the following bonding modes:











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[86] J. Potier *et al., Inorg. Chem.*, 1985, **24,** 238.

[87a] See, for example, R. D. Cornelius *et al., J. Am. Chem. Soc.*, 1980, **102,** 6151.

[87b] See, for example, E. Deutsch *et al., Inorg. Chem.*, 1983, **22,** 1332.

[87c] W. Klaüi *et al., J. Am. Chem. Soc.*, 1987, **109,** 164.

The μ_3 mode is found only in $H_2Os_3(CO)_9(\mu_3\text{-}O_3SO)$; similar μ_3-modes are known for PO_4^{3-} and AsO_4^{3-}.[88] The free sulfate ion is tetrahedral (T_d), but when it functions as a unidentate ligand, the coordinated oxygen atom is no longer equivalent to the other three and the effective symmetry is lowered to C_{3v}. Since the M—O—S chain is normally bent, the actual symmetry is even lower, but this perturbation of C_{3v} symmetry does not measurably affect the ir spectra. When two oxygen atoms become coordinated, either to the same metal ion or to different ones, the symmetry is lowered still further to C_{2v}.

The distinction between uncoordinated, unidentate, and bidentate SO_4^{2-} by ir spectra is very straightforward. Table 12-3 summarizes the selection rules for the S—O stretching modes in the three cases. It can be seen that uncoordinated SO_4^{2-} should have one, unidentate SO_4^{2-} three, and bidentate SO_4^{2-} four S—O stretching bands in the infrared. Note that the appearance of four bands for the bidentate ion is expected regardless of whether it is chelating or bridging.

Observed spectra are in accord with these predictions, except that ν_1 does appear weakly in the spectrum of the uncoordinated SO_4^{2-} ion. This is due to nonbonded interactions of SO_4^{2-} with its neighbors in the crystal, which perturb the T_d symmetry; the same environmental effects also cause the ν_3 band to be very broad.

Even though bridging and chelating sulfates cannot be distinguished on the basis of the number of bands they give, it appears that the former have bands at different frequencies than the latter, typical values in cm^{-1} being as follows:

Bridging	**Chelating**
1160–1200	1210–1240
~1110	1090–1176
~1130	995–1075
960–1000	930–1000

Sulfites,[89] SO_3^{2-}; *sulfinates,* RSO_2^-; and *sulfenates,* RSO^-, may be bound η^1 through O or through S. In cobalt complexes such as $[(NH_3)_5CoSO_3]^+$, the S-bonded ligand has a high trans effect; S-bonded sulfites are more stable than O-bonded ones. There is some evidence for bridged SO_3^{2-} but chelates are uncertain.

Trifluoromethanesulfonate, $CF_3SO_3^-$, is generally a good leaving group in organic chemistry and in inorganic complexes is readily ionized or displaced, being like ClO_4^- a relatively poor ligand[90]. Uni-, bi- and tridentate and also bridged complexes are known, examples being $(\eta^5\text{-Cp}^*)(CO)_2Fe(OSO_2CF_3)$

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[88] J. R. Shapley *et al., J. Am. Chem. Soc.*, 1986, **108,** 3846.

[89] A. A. El-Awady *et al., Inorg. Chem.*, 1985, **24,** 313.

[90] P. V. Bernhardt and G. A. Lawrence, *Polyhedron*, 1987, **6,** 1875.

TABLE 12-3
Correlation of the Types and Activities of S—O Stretching Modes of SO_4^{2-}

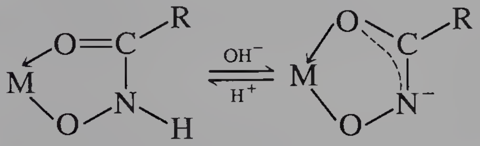
State of SO_4^{2-}	Effective symmetry	Types and activities of modes[a] (R = Raman; I = ir)	
Uncoordinated	T_d	$\nu_1(A_1,R)$	$\nu_3(T_2,I,R)$
Unidentate	C_{3v}	$\nu_1(A_1,I,R)$	$\nu_{3a}(A_1,I,R)$ $\nu_{3b}(E,I,R)$
Bidentate	C_{2v}	$\nu_1(A_1,I,R)$	$\nu_{3a}(A_1,I,R)$ $\nu_{3b}(B_1,I,R)$ $\nu_{3c}(B_2,I,R)$

[a] ν_2 and ν_4 are not listed because they are O—S—O bending modes. Note also that the arrows drawn have only rough qualitative significance, since all modes of the same symmetry will be of mixed parentage in the higher symmetry.

and $TiCl_2(OSO_2CF_3)_2$. Fluorosulfates (FSO_3^-) and other sulfonic acids (RSO_3^-) are similar; an example is $Pt(FSO_3)_4$.[91]

Hydroxamates. Hydroxamates and their monothio and dithio analogs form chelate complexes usually. They have been much studied because hydroxamates are present in siderophores[92], the microbial iron transport systems (Chapter 30) and also because of their use in sequestering agents for actinide ions and in analytical studies[93].

The general system is



where loss of the acidic NH proton gives a complex hydroxamate(2 –) anion.[93]

12-17. Other η^1-O Donors

Dialkyl Sulfoxides.[94] The most common ligand is Me_2SO which, though a relatively poor nucleophile, favors many complexes that can be η^1-O or η^1-S. These types are usually readily distinguished by ir or nmr spectra. Palladium(II) and Pt^{II} are usually S-bonded unless steric factors preclude this.[95]

Pyridine and Dipyridyl *N*-Oxides; Tertiary Phosphine Oxides. These ligands bind only η^1-O.[96] Long chain alkyl phosphine oxides such as *n*-octyl

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[91] M. Brookhart *et al.*, *Inorg. Chem.*, 1983, **22,** 3355; K. C. Lee and F. Aubke, *Inorg. Chem.*, 1984, **23,** 2124.

[92] S. J. Barclay and K. N. Raymond, *Inorg. Chem.*, 1986, **25,** 3561.

[93] See, for example, P. Ghosh and A. Chakravorty, *J. Chem. Soc. Dalton Trans.*, **1985,** 361; L. L. Fish and A. L. Crumbliss, *Inorg. Chem.*, 1985, **24,** 2198; A. R. Martell *et al.*, *Inorg. Chem.*, 1985, **24,** 4343.

[94] J. A. Davies and G. A. Miller, *Thermochim. Acta Rev.*, 1983, **62,** 35; J. A. Davies, *Adv. Inorg. Chem. Radiochem.*, 1981, **24,** 115.

[95] L. Cattalini *et al.*, *Inorg. Chem.*, 1983, **22,** 975.

[96] T. S. Lobana *et al.*, *J. Chem. Soc. Dalton Trans.*, **1983,** 2039 (for RNO˙radicals see T. R. Felthouse *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 8201).

are used for solvent extraction of actinide and lanthanide ions. The ^{31}P chemical shifts for R_3PO provide correlations with the basicity of the corresponding R_3P and other data.[97]

Pentafluorooxoanions of S, Se, and Te. The F_5XO^- ions are both bulky and electronegative.[98] They behave to some extent like pseudohalide anions and give complexes such as $(CO)_5Mn(OTeF_5)$; they can also bridge.

Phenyloxoiodine or iodosylbenzene (PhIO) is much used as an oxygen transfer species but appears to form η^1-O complexes.[99]

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Oxygen and the Conversion of Future Feedstocks, Royal Society of Chemistry Special Publication 48 (3rd Priestly Conference), 1986.

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Wilt, M., *et al., Adv. Inorg. Chem. Radiochem.*, 1986, **30,** 223 (complexes of hexafluoroacetone).

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[97] T. T. Derencsény, *Inorg. Chem.*, 1981, **20,** 665.

[98] K. Seppelt *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2821; S. H. Strauss, *et al., Inorg. Chem.*, 1986, **25,** 3850, 2821; S. H. Strauss *et al., Inorg. Chem.*, 1985, **24,** 4307.

[99] T. Birchall *et al., Inorg. Chem.*, 1984, **23,** 1910.

Chapter Thirteen

The Group VIA(16) Elements: S, Se, Te, Po

GENERAL REMARKS

13-1. Electronic Structures, Valences, and Stereochemistries

Some properties of the elements in Group VIA(16) are given in Table 13-1.

The atoms are two electrons short of the configuration of the next noble gas, and the elements show essentially nonmetallic covalent chemistry except for polonium and to a very slight extent tellurium. They may complete the noble gas configuration by forming (*a*) the *chalconide* ions S^{2-}, Se^{2-}, and Te^{2-}, although these ions exist only in the salts of the most electropositive elements, (*b*) two electron-pair bonds [e.g., $(CH_3)_2S$, H_2S, SCl_2], (*c*) ionic species with one bond and one negative charge (e.g., HS^- and RS^-), or (*d*) three bonds and one positive charge (e.g., R_3S^+).

In addition to such divalent species, the elements form compounds in *formal* oxidation states IV and VI with four, five, or six bonds; tellurium may give an eight-coordinate ion TeF_8^{2-}. Some examples of compounds of Group VIA(16) elements and their stereochemistries are listed in Table 13-2.

13-2. Group Trends

There are great differences between the chemistry of oxygen and that of sulfur, with more gradual variations through the sequence S, Se, Te, and Po. Differences from oxygen are attributable, among other things, to the following:

1. The lower electronegativities of the S—Po elements lessens the ionic character of those of their compounds that are formally analogous to those of oxygen, alters the relative stabilities of various kinds of bonds, and drastically lessens the importance of hydrogen bonding, although weak X—H···S and S—H···X bonds do indeed exist.

2. The maximum coordination number is not limited to 4, nor is the valence limited to 2, as in the case of oxygen, since *d* orbitals may be utilized in

TABLE 13-1
Some Properties of the Group VIA(16) Elements

Element	Electronic structure	Melting point (°C)	Boiling point (°C)	Radius X^{2-} (Å)	Covalent radius —X— (Å)	Electro-negativity
S	$[Ne]3s^23p^4$	119[a]	444.6	1.70	1.03	2.44
Se	$[Ar]3d^{10}4s^24p^4$	221[b]	684.8	1.84	1.17	2.48
Te	$[Kr]4d^{10}5s^25p^4$	450	990	2.07	1.37	2.01
Po	$[Xe]4f^{14}5d^{10}6s^26p^4$	254	962			1.76

[a] For monoclinic S_β see text.
[b] For gray Se.

bonding. Thus sulfur forms several hexacoordinate compounds (e.g., SF_6), and for tellurium 6 is the characteristic coordination number.

3. Sulfur has a strong tendency to catenation, which manifests itself not only in the many forms of the element that all contain S_n rings of various sizes, but in polysulfide ions S_n^{2-}, which may be discrete in highly ionic salts or serve as chelating ligands towards transition metals, sulfanes (XS_nX) (where X may be H, halogen, CN, or NR_2), the polythionic acids ($HO_3SS_nSO_3H$) and their salts, to mention only the longer chains. In addition, the S—S unit

TABLE 13-2
Compounds of Group VIA(16) Elements and Their Stereochemistries

Valence	Number of bonds	Geometry	Examples
II	2	Angular	Me_2S, H_2Te, S_n
	3	Pyramidal	Me_3S^+
	4	Square	$Te[SC(NH_2)_2]_2Cl_2$
IV	2	Angular	SO_2
	3	Pyramidal	SF_3^+, OSF_2, SO_3^{2-}, Me_3TeBPh_4[a]
		Trigonal planar	$(SeO_2)_n$
	4	ψ-Trigonal bipyramidal[b]	SF_4, RSF_3, Me_2TeCl_2
		Tetrahedral	Me_3SO^+
	5	ψ-Octahedral (square pyramidal)	$SeOCl_2py_2$, SF_5^-, TeF_5^-
	6	Octahedral	$SeBr_6^{2-}$, PoI_6^{2-}, $TeBr_6^{2-}$
	7[c]	Distorted pentagonal bipyramidal	$TePh(S_2CNEt_2)_3$
	8[c]	Distorted dodecahedral	$Te(S_2CNEt_2)_4$
VI	3	Trigonal planar	$SO_3(g)$, $S(NCR)_3$[d]
	4	Tetrahedral	SeO_4^{2-}, $SO_3(s)$, SeO_2Cl_2
	5	Trigonal bipyramidal	SOF_4
	6	Octahedral	RSF_5, SeF_6, $Te(OH)_6$
	8(?)	?	TeF_8^{2-} (?)

[a] R. F. Ziolo and J. M. Troup, *Inorg. Chem.*, 1979, **18,** 2271.
[b] Lone pairs are equatorial.
[c] E. Esperas and S. Huseby, *Acta Chem. Scand.*, 1975, **A29,** 185.
[d] O. Glemser *et al., Angew. Chem., Int. Ed. Engl.*, 1977, **16,** 789; has S=N multiple bonds by $p\pi$-$p\pi$ overlap.

occurs in many contexts, especially in organic and biological systems. In the structures of most protein molecules one or more —S—S— bridges are found to play a crucial role. The stereoelectronic behavior of the prototypal molecule HSSH has been extensively studied.[1]

Although selenium and tellurium have a smaller tendency to catenation, they form rings (Se only) and long chains in their elemental forms. None of these chains is branched, because the valence of the element is only 2.

Gradual changes of properties are evident with increasing size, decreasing electronegativity, and so on, such as:

1. Decreasing thermal stability of the H_2X compounds. Thus H_2Te is considerably endothermic.
2. Increasing metallic character of the elements.
3. Increasing tendency to form anionic complexes such as $SeBr_6^{2-}$, $TeBr_6^{2-}$, and PoI_6^{2-}.
4. Decreasing stability of compounds in high formal positive oxidation states.
5. Emergence of cationic properties for Po and, very marginally, for Te. Thus TeO_2 and PoO_2 appear to have ionic lattices and they react with hydrohalic acids to give Te^{IV} and Po^{IV} halides, and PoO_2 forms a hydroxide $Po(OH)_4$. There are also some ill defined "salts" of Te and Po, such as $Po(SO_4)_2$ and $TeO_2{\cdot}SO_3$.

Use of *d* Orbitals.[2,3] The S–Po elements employ *d* orbitals together with their *s* and *p* orbitals to form more than four σ bonds (as in SF_6), and they also make frequent use of $d\pi$ orbitals to form multiple bonds. Thus, for example, in the sulfate ion, where the *s* and *p* orbitals are used in σ bonding, the shortness of the S—O bonds suggests that there must be considerable multiple-bond character. The usual explanation for this is that empty $d\pi$ orbitals of sulfur accept electrons from filled $p\pi$ orbitals of oxygen. Similar $d\pi$–$p\pi$ bonding occurs in some phosphorus compounds, but it seems to be more prominent with sulfur.

Other Remarks. In general, selenium and tellurium compounds are toxic. On the other hand selenium, in *trace* quantities, is biologically essential and may have anticancer properties.

THE ELEMENTS

13-3. Occurrence and Uses

Sulfur occurs widely in Nature as the element, as H_2S and SO_2, in numerous sulfide minerals and in sulfates such as *anhydrite* ($CaSO_4$). It occurs in crude oils and in coal and as H_2S in natural gas, from which it is recovered in large

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[1] D. A. Dixon *et al., J. Phys. Chem.*, 1985, **89**, 5334.

[2] A. Strömberg *et al., Chem. Phys.*, 1984, **89**, 323.

[3] A. R. Reed and F. Weinhold, *J. Am. Chem. Soc.*, 1986, **108**, 3586.

quantities via the reaction

$$2H_2S + SO_2 = 3S + 2H_2O$$

Sulfur is used mainly to manufacture sulfuric acid, but also in vulcanizing rubber and to make CS_2, P_2S_5, and a few other sulfides.

Selenium and tellurium are much less abundant than sulfur and no ores are rich in these elements. They are recovered from the anode slime deposited in the electrolytic purification of copper (having been present as impurities in the copper sulfide ores), as by-products in other sulfide ore processing and in sulfuric acid manufacture.

There is no stable isotope of polonium. The isotope $^{210}Po(\alpha, 138.4d)$ occurs in U and Th minerals as an intermediate in the radioactive decay series, and was discovered by M. S. Curie in 1898. The only practical source of polonium (in gram quantities) is from nuclear reactors by the process

$$^{209}Bi(n,\gamma)^{210}Bi \longrightarrow {}^{210}Po + \beta^-$$

The study of polonium chemistry is difficult owing to the intense α radiation, which causes damage to solutions and solids, evolves much heat, and makes special handling techniques necessary for protection of the chemist.[4]

Selenium and tellurium are mainly used as additives in metallurgy, though selenium is also used in glass and as a photoconductor (especially in Xerox machines). Polonium is used as a heat or power source in satellites.

13-4. Elemental Sulfur

Because of its ability for catenation, sulfur forms open and cyclic S_n species from $n = 2$ to $n = 20$ for cycles and higher for chains. This leads to enormous complexity in the physical and chemical behavior of the element.

Solid Sulfur. Solid forms of sulfur containing S_n rings with $n = 6$–12, 18, and 20 are known.[5] These rings are all similar in their S—S distances (~ 2.05 Å), S—S—S angles (~ 106°), and S—S bond energies (~ 265 kJ mol^{-1}), although the S—S—S—S torsion angles vary considerably. All other rings (and chains) are thermodynamically unstable (at 25°C) relative to the S_8 ring with a crown conformation (Fig. 13-1). Methods of obtaining the

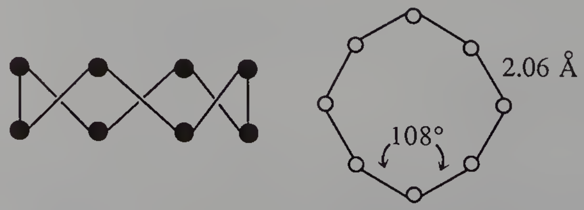

FIG. 13-1. The crown S_8 ring, as found in α sulfur.

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[4] K. W. Bagnall, *Radiochem. Acta*, 1983, **32,** 153.

[5] R. Steudel *et al., Angew. Chem., Int. Ed. Engl.*, 1981, **20,** 394; J. Steidel and R. Steudel, *J. Chem. Soc. Chem. Commun.*, **1982,** 1312.

metastable rings are quite varied, but a reasonably systematic approach is to react linear components with the correct total number of sulfur atoms, for example,

$$H_2S_4 + S_2Cl_2 \longrightarrow \textit{cyclo}\text{-}S_6 + 2HCl$$

$$H_2S_8 + S_4Cl_2 \longrightarrow \textit{cyclo}\text{-}S_{12} + 2HCl$$

$$Cp_2TiS_5 + S_2Cl_2 \longrightarrow \textit{cyclo}\text{-}S_7 + Cp_2TiCl_2$$

The common, stable form of sulfur at 25°C is orthorhombic α sulfur, containing *cyclo*-S_8 molecules. At 368.46 K (95.5°C) S_α transforms to the high-temperature form *monoclinic sulfur* (S_β). The enthalpy of the transition is small (0.4 kJ g-atom^{-1} at 95.5°C) and the process is slow, so that it is possible by rapid heating of S_α to attain the melting point of S_α (112.8°C); S_β melts at 119°C. Monoclinic S_β crystallizes from sulfur melts, and although slow conversion to S_α occurs, the crystals can be preserved for weeks. Its structure contains S_8 rings as in S_α, but differently packed. Another form of sulfur (S_γ, mp 106.8°C) is obtained by decomposition of copper(I) ethyl xanthate in pyridine. It transforms slowly into S_β and/or S_α but is stable in the 95 to 115°C region. It too contains crown S_8 rings.

When α sulfur is dissolved in polar solvents (e.g., MeOH or MeCN) an equilibrium is set up in which ~ 1% of the sulfur is present as S_6 and S_7 rings. Since these rings are more reactive than S_8 rings, they may provide the pathway for reactions of elemental sulfur in polar media.[6a]

Catenasulfur. When molten sulfur is poured into ice water, the so-called plastic sulfur is obtained; although normally this has S_8 inclusions, it can be obtained as long fibers by heating S_α in nitrogen at 300°C for 5 min and quenching a thin stream in ice water. These fibers can be stretched under water and appear to contain helical chains of sulfur atoms with ~3.5 atoms per turn. Unlike the other sulfur allotropes, catenasulfur is insoluble in CS_2; it transforms slowly to S_α.

Liquid Sulfur.[6b] Precisely what happens when S_8 melts is still not fully understood; doubtless much depends on the level of impurities.

On melting, S_8 first gives a yellow, transparent, mobile liquid, which becomes brown and increasingly viscous above ~ 160°C. The viscosity reaches a maximum at ~ 200°C and thereafter falls until at the boiling point (444.60°C) the sulfur is again a rather mobile, dark red liquid. Figure 13-2(a) shows the viscosity and specific heat as a function of temperature. Although S_8 rings persist in the liquid up to ~ 193°C the changes in viscosity are due to ring cleavage and the formation of chains, as well as other sulfur ring species with $n = 6, 7, 12, 18, 20$, and >20 in equilibrium. The average degree of polymerization is shown in Fig. 13-2(b). The sulfur chains must have radical ends;

[6a] F. N. Tebbe *et al., J. Am. Chem. Soc.*, 1982, **104**, 4971.

[6b] R. Steudel, *Z. Anorg. Allg. Chem.*, 1981, **478**, 139.

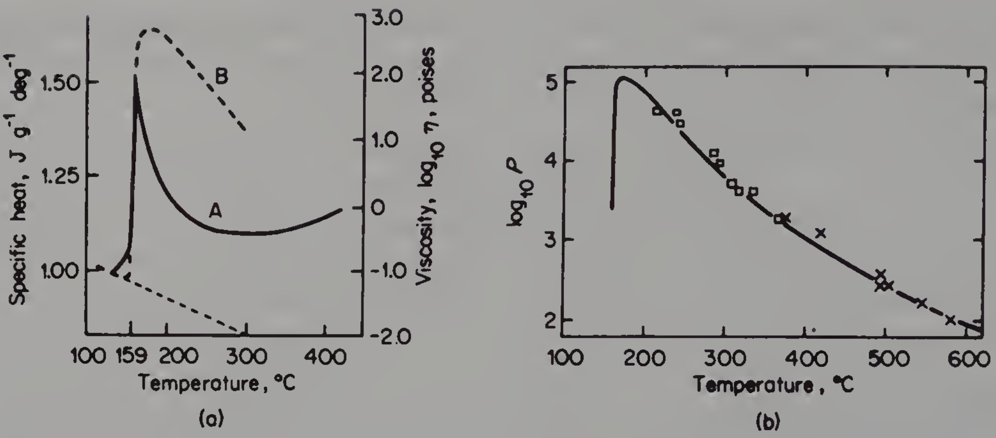

FIG. 13-2. (a) Specific heat (A) and viscosity (B) of liquid sulfur. (b) Chain length (P) as a function of temperature, × from magnetic susceptibility measurements and ☐ from esr measurements. (Reproduced by permission from B. Meyer, Ed., *Elemental Sulfur—Chemistry and Physics,* Interscience, New York, 1965.)

they reach their greatest average length, 5 to 8 × 10^5 atoms, at about 200°C, where the viscosity is highest. The quantitative behavior of the system is sensitive to certain impurities, such as iodine, which can stabilize chain ends by formation of S—I bonds. In the formation of polymers, almost every broken S—S bond of an S_8 ring is replaced by an S—S bond in a linear polymer, and the overall heat of the polymerization is thus expected to be close to zero. An enthalpy of 13.4 kJ mol^{-1} of S_8 converted into polymer has been found at the critical polymerization temperature (159°C).

The color changes on melting are due to an increase in the intensity and a shift of an absorption band to the red. This is associated with the formation above ~ 250°C of the red species S_3 and S_4, which comprise 1 to 3% of sulfur at its boiling point.

Sulfur Vapor. The vapor contains S_n species with *n* from 2 to 10, with S_8 predominating at ~ 600°C while S_2 becomes dominant above ~ 720°C. The color of the vapor changes as its composition changes. Only at very high temperatures (>2200°C) and low pressures ($<10^{-4}$ mm Hg) do sulfur atoms become predominant. The long stability range of S_2 molecules is explained by their strong S═S bond (422 kJ mol^{-1}) based on a triplet ground state analogous to that of O_2.[7] The S═S distance, 1.89 Å, is appreciably shorter than the S—S single bond distance of ~ 2.05 Å.

13-5. Elemental Selenium, Tellurium, and Polonium

Gray selenium (mp 494 K, metallic) is the stable form. It may be obtained crystalline from hot solutions of Se in aniline or from the melt. The structure,

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[7] C. L. Liao and C. Y. Ng, *J. Chem. Phys.*, 1986, **84**, 778.

which has no sulfur analogue, contains infinite, spiral chains of selenium atoms. Although there are fairly strong single bonds between adjacent atoms in each chain, there is evidently weak metallic interaction between the neighboring atoms of different chains. Selenium is not comparable with most true metals in its electrical conductivity in the dark, but it is markedly photoconductive and is widely used in photoelectric devices (e.g., xerography).

In the gas above gray or liquid selenium there is a temperature-dependent mixture of Se_n, $n = 2$ to 10, species, and in solution cyclic Se_6, Se_7, and Se_8 are present. Metastable crystalline solids[8] containing Se_6 and Se_8 (three polymorphs) are known, but any external force (heat, pressure) initiates conversion to grey Se.

The one form of tellurium is silvery-white, semimetallic, and isomorphous with gray Se. Like the latter it is virtually insoluble in all liquids except those with which it reacts.

Whereas sulfur is a true insulator (specific resistivity, in $\mu\Omega$-cm $= 2 \times 10^{23}$), selenium (2×10^{11}) and tellurium (2×10^{5}) are intermediate in their electrical conductivities, and the temperature coefficient of resistivity in all three cases is negative, which is usually considered characteristic of nonmetals.

The trend toward greater metallic character of the elements is complete at polonium, which has two allotropes, both with typically metallic structures: α cubic, converting at 36°C to β rhombohedral (mp 254°C). Each of these has resistivity typical of a true metal with a positive temperature coefficient.

13-6. Reactions of the Elements

The allotropes of S and Se containing cyclo species are soluble in CS_2 and other nonpolar solvents such as benzene and cyclohexane. The solutions are light sensitive, becoming cloudy on exposure, and may also be reactive toward air; unless very special precautions are taken, sulfur contains traces of H_2S and other impurities that can have substantial effects on rates of reactions. The nature of the sulfur produced on photolysis is not well established, but such material reverts to S_8 slowly in the dark or rapidly in the presence of triethylamine. From the solvent CHI_3, sulfur crystallizes as a charge-transfer compound $CHI_3 \cdot 3S_8$, with $I \cdots S$ bonds; isomorphous compounds with PI_3, AsI_3, and SbI_3 are also known. It is probable that similar charge-transfer complexes wherein the S_8 ring is retained are first formed in reactions of sulfur with, for example, bromine. When heated, S, Se, Te, and Po burn in air to give the dioxides MO_2, and the elements react when heated with halogens, most metals, and nonmetals. Sulfur, Se, and Te are not affected by nonoxidizing acids, but the more metallic polonium will dissolve in concentrated HCl as well as in H_2SO_4 and HNO_3, giving solutions of Po^{II} and then Po^{IV}.

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[8] R. Steudel and E.-M. Strauss, *Adv. Inorg. Chem. Radiochem.*, 1984, **28**, 135.

Although Po is distinctly metallic in some ways, [e.g., it forms saltlike Po^{II} and Po^{IV} compounds such as $PoCl_2$, $PoBr_2$, $Po(SO_4)_2$, and $Po(CrO_4)_2$] it also shows nonmetal characteristics by forming numerous polonides (MPo), which are often isostructural with tellurides and appear to be fairly ionic.

Sulfur also dissolves, with reaction, in organic amines such as piperidine, to give colored solutions containing *N,N′*-polythiobisamines in which there are free radicals (~ 1 per 10^4 S atoms):

$$2RR'NH + S_n \longrightarrow (RR'N)_2S_{n-1} + H_2S$$

Many sulfur reactions are catalyzed by amines, and in such S—S bond-breaking reactions free radicals may be involved.

Sulfur and selenium react with many organic molecules. For example, saturated hydrocarbons are dehydrogenated. The reaction of sulfur with alkenes and other unsaturated hydrocarbons is of enormous technical importance: hot sulfurization results in the vulcanization (formation of S bridges between carbon chains) of natural and synthetic rubbers.

It is clear that all reactions of S_8 or other cyclo species require that the initial attack open the ring to give sulfur chains or chain compounds. Many common reactions can be rationalized by considering a nucleophilic attack on S—S bonds. Some typical reactions are

$$S_8 + 8CN^- \longrightarrow 8SCN^-$$
$$S_8 + 8Na_2SO_3 \longrightarrow 8Na_2S_2O_3$$
$$S_8 + 8Ph_3P \longrightarrow 8Ph_3PS$$

Such reactions cannot possibly proceed by what, according to the stoichiometry, would be ninth-order reactions. It appears that the rate-determining step is the initial attack on the S_8 ring and that subsequent steps proceed very rapidly, so that the reactions can be assumed to proceed as follows:

$$S_8 + CN^- \longrightarrow {}^{\cdot}SSSSSSSSCN^-$$
$${}^{\cdot}S_6{-}S{-}SCN^- + CN^- \longrightarrow {}^{\cdot}S_6SCN^- + SCN^- \qquad \text{and so on}$$

Cationic Compounds.[9] It has long been known that sulfur, selenium, and tellurium will dissolve in oleums to give blue, green, and red solutions, respectively, which are unstable and change in color when kept or warmed. The colored species are cyclic polycations in which the element is formally in a fractional oxidation state. Although S_8 can be heated at 75°C in 100% H_2SO_4 without attack, oxidation occurs with time and increasing SO_3 concentration, forming species such as S_4^{2+}, S_8^{2+}, and S_{16}^{2+}, together with SO_2. The oleum solutions of sulfur give esr spectra because of the presence of one or more radicals of the type S_n^+ in low concentration.

It is difficult to isolate solids from oleum solutions, but crystalline salts

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[9] R. J. Gillespie *et al., Inorg. Chem.*, 1987, **26,** 1476.

TABLE 13-3
Polyatomic Cations of Sulfur, Selenium, and Tellurium

Cation type	S	Se	Te	Mixed
E_{19}^{2+}	S_{19}^{2+}			
E_{10}^{2+}		Se_{10}^{2+}		$Te_2S_8^{2+}$
E_8^{2+}	S_8^{2+}	Se_8^{2+}		$Te_2Se_6^{2+}$
E_6^{2+}				$Te_3Se_3^{2+}$ $Te_2Se_4^{2+}$
E_4^{2+}	S_4^{2+}	Se_4^{2+}	Te_4^{2+}	$Te_2Se_2^{2+}$
E_6^{4+}			Te_6^{4+}	

have been obtained by selective oxidations of the elements with SbF_5 or AsF_5 in liquid HF, or with $S_2O_6F_2$ in HSO_3F.

Some representative preparative reactions are given here and the major cations are listed in Table 13-3.

$$S_8 + 3SbF_5 = S_8^{2+} + 2SbF_6^- + SbF_3$$

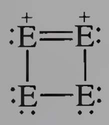
$$4Se + S_2O_6F_2 = Se_4^{2+} + 2SO_3F^-$$

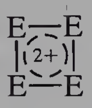
$$Se_8 + 3AsF_5 = Se_8^{2+} + 2AsF_6^- + AsF_3$$

$$7Te + TeCl_4 + 4AlCl_3 = 2Te_4^{2+} + 4AlCl_4^-$$

Many of the structures have been established by X-ray crystallography and by ^{77}Se and ^{125}Te nmr.[10] In the solids, the E_n^{2+} cations are closely surrounded by fluoroanions (e.g., AsF_6^-, $Sb_3F_{14}^-$, and SO_3F^-) and the finer details of the structures are undoubtedly affected by interactions with these anions.

The E_4^{2+} species are thoroughly characterized.[11] They have square structures with bond lengths slightly (~3%) shorter than the conventional E—E single bond lengths. Their electronic structures may be formulated as in (13-I) (with the three analogous structures in resonance with the one shown) or as in (13-II), where a net π bond order of one may be envisioned.


(13-I)


(13-II)

A number of other structures have been established and a few are illustrated schematically in (13-III) through (13-V). These structures are not easy to account for in a fully satisfactory way. The dashed lines in (13-III) and (13-IV) indicate partial bonding, but in none of these three structures is there a clear understanding of how electron density and charge are distributed. The S_{19}^{2+} ion has two S_7 rings linked by an S_5 chain and the Te_6^{4+} ion is a trigonal

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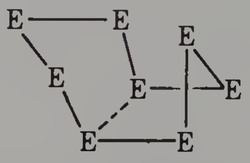
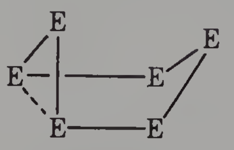
[10] M. J. Collins and R. J. Gillespie, *Inorg. Chem.*, 1984, **23**, 1975.
[11] R. J. Gillespie *et al., Inorg. Chem.*, 1985, **24**, 4302.

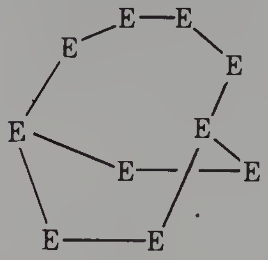
prism with two Te_3 triangles (Te—Te, ~ 2.68 Å) joined by three longer bonds (Te—Te, −3.10 Å).[12]



(13-III)



(13-IV)



(13-V)

BINARY COMPOUNDS

13-7. Hydrides

The dihydrides, H_2S, H_2Se, and H_2Te are extremely poisonous gases with revolting odors; the toxicity of H_2S far exceeds that of HCN. They are readily obtained by the action of acids on metal chalconides. Polonium hydride has been prepared only in trace quantities, by dissolving magnesium foil plated with Po in 0.2 *M* HCl. The thermal stability and bond strengths decrease from H_2S to H_2Po. Although pure H_2Se is thermally stable to 280°C, H_2Te and H_2Po appear to be thermodynamically unstable with respect to their constituent elements. All behave as very weak acids in aqueous solution, and the general reactivity and also the dissociation constants increase with increasing atomic number. *Hydrogen sulfide* dissolves in water to give a solution ~ 0.1 *M* under 1 atm pressure. The dissociation constants are

$$H_2S + H_2O = H_3O^+ + HS^- \qquad pK = 6.88 \pm 0.02$$

$$HS^- + H_2O = H_3O^+ + S^{2-} \qquad pK = 14.15 \pm 0.05$$

In acid solution H_2S is also a mild reducing agent.

Sulfanes. The compounds H_2S_2 through H_2S_8 have been isolated in pure states, whereas higher members are so far known only in mixtures. All are reactive yellow liquids whose viscosities increase with chain length. They may be prepared in large quantities by reactions such as

$$Na_2S_n(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2S_n(l) \qquad (n = 4-6)$$

$$S_nCl_2(l) + 2H_2S(l) \longrightarrow 2HCl(g) + H_2S_{n+2}(l)$$

$$S_nCl_2(l) + 2H_2S_2(l) \longrightarrow 2HCl(g) + H_2S_{n+4}(l)$$

The oils from the first reaction can be cracked and fractionated to give pure H_2S_2 through H_2S_5, whereas the higher sulfanes are obtained from the other

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[12] R. J. Gillespie *et al., Inorg. Chem.,* 1979, **18,** 3086.

reactions. Although the sulfanes are all thermodynamically unstable with respect to the reaction

$$H_2S_n(l) = H_2S(g) + (n-1)S(s)$$

these reactions, which are believed to free radical in nature, are sufficiently slow for the compounds to be stable for considerable periods.

13-8. Metal Chalconides

Most metallic elements react directly with S, Se, Te, and, so far as is known, Po. Often they react very readily, mercury and sulfur, for example, at room temperature. Binary compounds of great variety and complexity of structure can be obtained. The nature of the products usually also depends on the ratios of reactants, the temperature of reaction, and other conditions. Many elements form several compounds and sometimes long series of compounds with a given chalconide. We give here only the briefest account of the more important sulfur compounds. Generally, selenides and tellurides are similar.

Ionic Sulfides; Sulfide Ions. Only the alkalis and alkaline earths form sulfides that appear to be mainly ionic. They are the only sulfides that dissolve in water and they crystallize in simple ionic lattices, for example, an antifluorite lattice for the alkali sulfides and a rock salt lattice for the alkaline earth sulfides. Essentially only SH^- ions are present in aqueous solution, owing to the low second dissociation constant of H_2S. Although S^{2-} is present in concentrated alkali solutions, it cannot be detected below ~ 8 *M* NaOH owing to the reaction

$$S^{2-} + H_2O = SH^- + OH^- \qquad K = \sim 1$$

The alkali and alkaline earth hydrosulfides can be made by the action of H_2S on the metal in liquid ammonia.

When aqueous sulfide solutions are heated with sulfur, solutions containing largely S_4^{2-} and S_3^{2-} are obtained. These polysulfide ions are the only ones stable in solution but a number of crystalline compounds with S_n^{2-} ions from $n = 3$ to $n = 6$ can be prepared, especially by using large cations [e.g., Cs^+, NH_4^-, and enH_2^{2+}.[13] Structures of the S_n^{2-} ions are shown in Fig. 13-3.

High-density power sources can be obtained from lithium and sodium–sulfur batteries. The sulfides present in these systems are M_2S, M_2S_2, M_2S_4, and M_2S_5.

Although polyselenide and polytelluride ions are less common, the Se_3^{2-} and Te_3^{2-} ions are known.[14a]

When alkali polysulfides are dissolved in polar solvents such as acetone,

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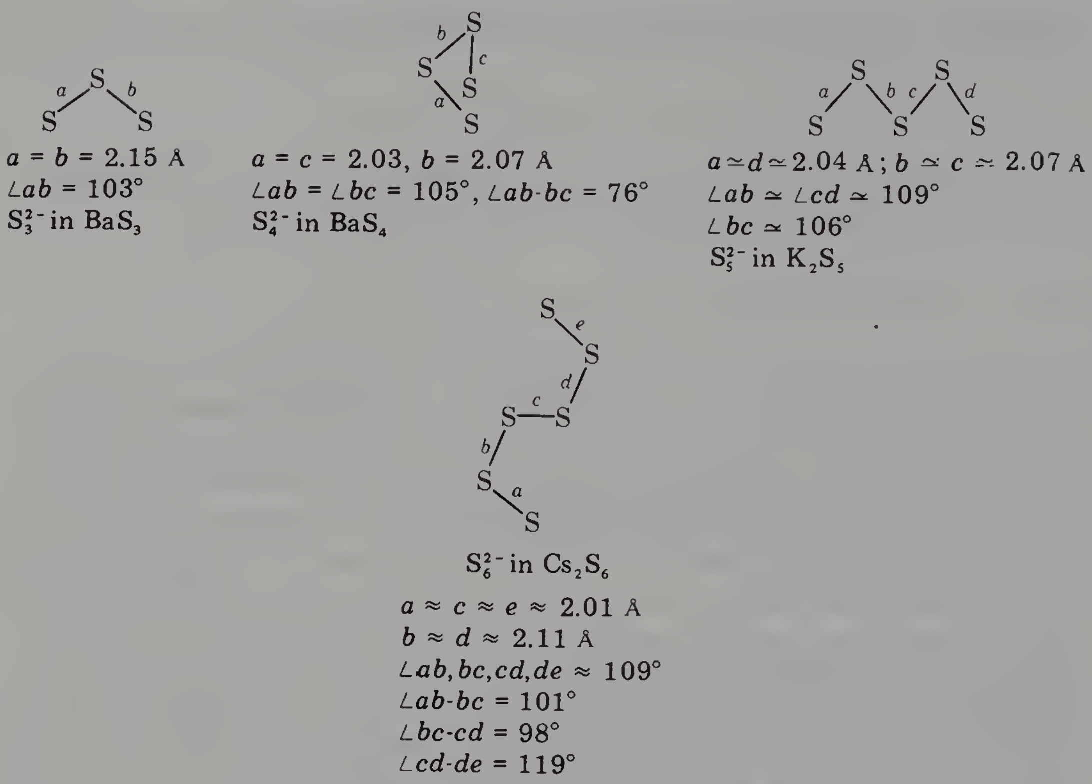
[13] P. Böttcher *et al., Z. Naturforsch.*, 1984, **39B**, 416; P. Böttcher and G. Trampe, *Z. Naturforsch.*, 1985, **40B**, 321; P. Böttcher and W. Flamm, *Z. Naturforsch.*, 1986, **41B**, 405.

[14a] H. Eggert *et al., J. Am. Chem. Soc.*, 1986, **108**, 1725; L. D. Schultz and W. H. Koehler, *Inorg. Chem.*, 1987, **26**, 1989.



$a = b = 2.15$ Å
$\angle ab = 103°$
S_3^{2-} in BaS_3

$a = c = 2.03$, $b = 2.07$ Å
$\angle ab = \angle bc = 105°$, $\angle ab\text{-}bc = 76°$
S_4^{2-} in BaS_4

$a \simeq d \simeq 2.04$ Å; $b \simeq c \simeq 2.07$ Å
$\angle ab \simeq \angle cd \simeq 109°$
$\angle bc \simeq 106°$
S_5^{2-} in K_2S_5

S_6^{2-} in Cs_2S_6
$a \approx c \approx e \approx 2.01$ Å
$b \approx d \approx 2.11$ Å
$\angle ab, bc, cd, de \approx 109°$
$\angle ab\text{-}bc = 101°$
$\angle bc\text{-}cd = 98°$
$\angle cd\text{-}de = 119°$

FIG. 13-3. Structures of representative polysulfide ions.

DMF, or DMSO, deep blue solutions are formed. Certain blue sulfur-containing minerals, notably lapis lazuli and ultramarine, owe their color primarily to the 610-nm absorption associated with the S_3^- radical anion, though in green ultramarine some S_2^- ($\lambda_{max} = 400$ nm) is also present.[14b]

Transition Metal Sulfides.[14c] Metal sulfides frequently have peculiar stoichiometries, are often nonstoichiometric phases rather than compounds in a classical sense, and are often polymorphic, and many of them are alloylike or semimetallic in behavior. Sulfides tend to be much more covalent than the corresponding oxides, with the result that quite often there is only limited and occasionally no stoichiometric analogy between the oxides and the sulfides of a given metal. Very often, indeed possibly in most cases, when there is a sulfide and an oxide of identical empirical formula they have different structures. A few examples are considered.

Several transition metal sulfides (e.g., FeS, CoS, and NiS) adopt a structure called the *nickel arsenide structure,* illustrated in Fig. 13-4. In this structure each metal atom is surrounded octahedrally by six sulfur atoms, but also is approached fairly closely by two other metal atoms. These metal–metal distances are 2.60 to 2.68 Å in FeS, CoS, and NiS, and at such distances there must be a considerable amount of metal–metal bonding, thus accounting for

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[14b] R. J. H. Clark *et al., Inorg. Chem.,* 1983, **22,** 2766.

[14c] J. K. Burdett and E. L. Miller, *J. Am. Chem. Soc.,* 1987, **109,** 4081.

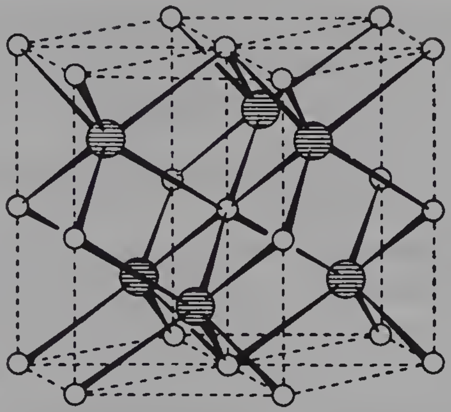


FIG. 13-4. Structure of NiAs (As atoms shaded). The Ni atom in the center of the diagram is surrounded octahedrally by six atoms and has also two near Ni neighbors, which are coplanar with four of the As atoms. [Reproduced by permission from A. F. Wells, *Structural Inorganic Chemistry,* Oxford University Press, Oxford, 1945, p. 387.]

their alloylike or semimetallic character. Note that such a structure is not in the least likely for a predominantly ionic salt, requiring as it would the close approach of dipositive ions.

Another class of sulfides of considerable importance is the *disulfides,* represented by FeS_2, CoS_2, and others. All these contain discrete S_2 units with an S—S distance almost exactly equal to that to be expected for an S—S single bond. These assume one of two closely related structures. First there is the *pyrite structure* named after the polymorph of FeS_2 that exhibits it. This structure may be visualized as a distorted NaCl structure. The Fe atoms occupy Na positions and the S_2 groups are placed with their centers at the Cl positions but turned in such a way that they are not parallel to any of the cube axes. The *marcasite structure* is very similar but somewhat less regular.

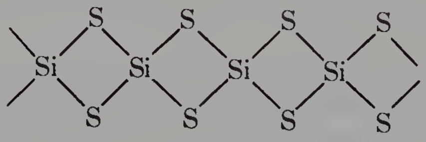
Iron sulfide is a good example of a well-characterized nonstoichiometric sulfide. It has long been known that a sample with an Fe/S ratio precisely unity is rarely encountered, and in the older literature such formulas as Fe_6S_7 and $Fe_{11}S_{12}$ have been assigned to it. The iron–sulfur system assumes the nickel arsenide structure over the composition range 50 to 55.5 at. % of sulfur and, when the S/Fe ratio exceeds unity, some of the iron positions in the lattice are vacant in a random way. Thus the very attempt to assign stoichiometric formulas such as Fe_6S_7 is meaningless. We are dealing not with *one* compound, in the classical sense, but with a *phase* that may be perfect, that is, FeS, or may be deficient in iron. The particular specimen that happens to have the composition Fe_6S_7 is better described as $Fe_{0.858}S$.

An even more extreme example of nonstoichiometry is provided by the Co—Te (and the analogous Ni—Te) system. Here, a phase with the nickel arsenide structure is stable over the entire composition range CoTe to $CoTe_2$. It is possible to pass continuously from the former to the latter by progressive loss of Co atoms from alternate planes (see Fig. 13-4) until, at $CoTe_2$, every other plane of Co atoms present in CoTe has completely vanished.

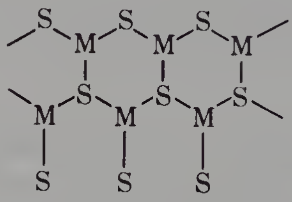
Typical of a system in which many different phases occur (each with a small range of existence so that each may be encountered in nonstoichiometric form) is the Cr—S system, where six phases occur in the composition range $CrS_{0.95}$ to $CrS_{1.5}$.

Although there are differences, the chemistry of selenides and tellurides is generally similar to that of sulfides.

Nonmetallic Binary Sulfides. Most nonmetallic (or metalloid) elements form sulfides that if not molecular, have polymeric structures involving sulfide bridges. Thus silicon disulfide (13-VI) consists of infinite chains of SiS_4 tetrahedra sharing edges, whereas Sb_2S_3 and Bi_2S_3 are isomorphous (13-VII), forming infinite bands that are then held in parallel strips in the crystal by weak secondary bonds.



(13-VI)



(13-VII)

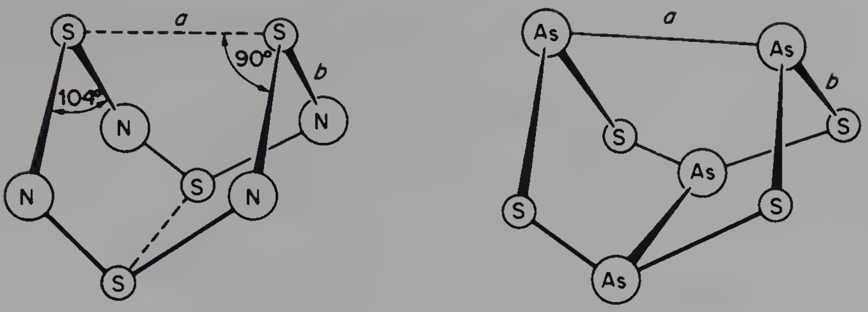
13-9. Sulfur–Nitrogen Compounds

Sulfur and nitrogen have similar electronegativities and strong tendencies to form single and multiple covalent bonds. Hence, it is not surprising that there is a very extensive chemistry of sulfur–nitrogen compounds. Most of them are cyclic (or polymeric) and entail S—N π bonding as well as σ bonding. There is no free NS comparable to NO although NS is known as a ligand; as discussed in Section 13-16 other SN species (e.g., $S_2N_3^{3-}$ and $Sn_2N_2^{2-}$) can serve as ligands.

Binary Neutral S—N Compounds

Tetrasulfur Tetranitride. Aside from its intrinsic interest, S_4N_4 is a source compound for the preparation of other important S—N compounds. It is best made by the action of NH_3 on S_2Cl_2 or SCl_2; the reaction is complex and not well understood, although NSCl and $S_4N_3^+Cl^-$ are probable intermediates. Tetrasulfur tetranitride forms thermochromic crystals (mp 185°C) that are orange yellow at 25°C, red above 100°C, and almost colorless at −190°C. The compound must be handled with care, since grinding, percussion, friction, or rapid heating can cause it to explode.

The structure of S_4N_4 is a cage with a square set of N atoms and a bisphenoid of S atoms (Fig. 13-5), which is in interesting contrast to the structure of As_4S_4 (realgar) also shown in Fig. 13-5. The S···S distance (2.60 Å) is longer than the normal S—S single-bond distance (~2.08 Å) but short enough to indicate significant interaction; even the S-to-S (linked by N) distance (2.71 Å) is indicative of direct S···S interaction. A low-temperature X-ray study indicates electron density along the shorter S···S line. The N—S distances and



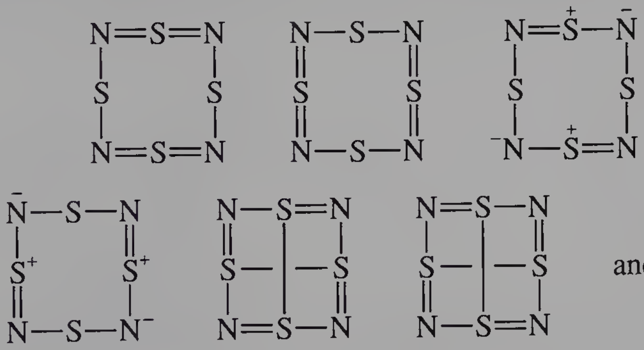
$a = 2.60$ Å
$b = 1.61$ Å

$a = 2.49$ Å
$b = 2.23$ Å

FIG. 13-5. Structures of N_4S_4 and As_4S_4. Both have D_{2d} symmetry.

the angles in N_4S_4 and also the $S_4N_5^-$ below, suggest the presence of lone pairs on the N and S atoms.

Tetrasulfur tetranitride is prototypal for other cyclic S—N compounds in the sense that its electronic structure is not accounted for by any single classical bonding diagram. In terms of a valence bond/resonance approach, the following canonical structures all merit consideration:



and so on

Molecular orbital calculations at various levels have given reasonably satisfactory descriptions of the structure and bonding in S_4N_4 and other related species.[15]

Some reactions of S_4N_4 are given in Fig. 13-6. In addition to its conversion to S_2N_2 and $(SN)_x$, discussed later, it undergoes two main types of reaction: (*a*) reactions in which the S—N ring is preserved as in adducts of BF_3 or $SbCl_5$ or in the reduction to $S_4N_4H_2$; and (*b*) reactions in which ring cleavage occurs with reorganization to form other S—N rings. These products may be cationic as when S_4N_4 reacts with Lewis acids like SbF_5; examples are the ions $S_3N_2^-$ and $S_4N_4^{2+}$. They may also be anionic, as in the reaction of S_4N_4 and N_3^- (see below).

Disulfur Dinitride. Colorless, crystalline S_2N_2 is made by pumping S_4N_4

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[15] R. C. Haddon *et al., J. Am. Chem. Soc.,* 1980, **102,** 6687; R. Gleiter, *Angew. Chem. Int. Ed. Engl.,* 1981, **20,** 444; R. T. Oakley *et al., J. Am. Chem. Soc.,* 1983, **105,** 1186; B. M. Gimarc *et al., Inorg. Chim. Acta,* 1985, **102,** 105.

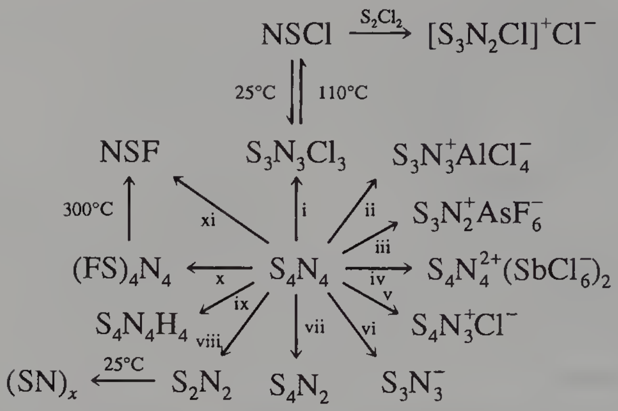
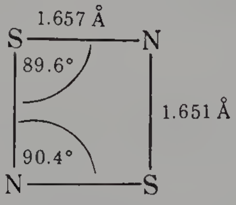


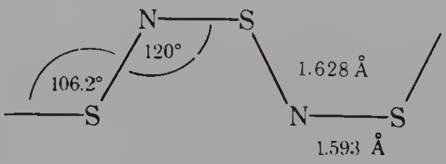
FIG. 13-6. Some reactions of S_4N_4: (i) Cl_2; (ii) $AlCl_3$; (iii) AsF_5; (iv) $SbCl_5$; (v) HCl or S_2Cl_2; (vi) N_3^- or electrolytic reduction; (vii) S_8, 100°C; (viii) Ag, 250°C/1 mm; (ix) $SnCl_2$ in EtOH; (x) AgF in CCl_4; (xi) HgF_2 reflux in CCl_4.

vapor through silver wool or gauze, or in other ways.[16] It has an approximately square structure (13-VIII). Like S_4N_4 it is potentially explosive and can be polymerized to $(SN)_x$, probably by a ring-opening radical mechanism.

Polythiazyl. This polymer, $(SN)_x$, has been known since 1910, but only recently has it been obtained in a pure state and its remarkable properties well studied. It is golden bronze in color and displays metallic type electrical conductance; more remarkable still is the fact that at 0.26 K it becomes a superconductor. In the crystal the kinked, nearly planar, chains (13-IX) lie parallel and conductance takes place along the chains, in which π electrons are extensively delocalized according to molecular quantum mechanical calculations. A partially brominated substance, $(SNBr_{0.4})_n$ is an even better conductor.

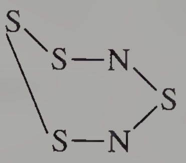


(13-VIII)

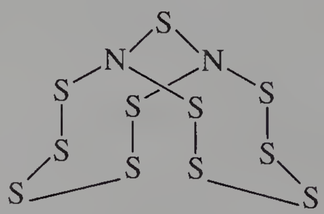


(13-IX)

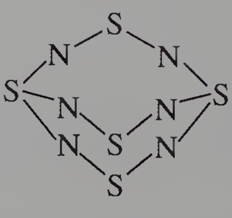
S_xN_y Compounds. A number of such compounds are known, for example, S_4N_2, $S_{11}N_2$, $(S_7N)_2S_x$, and S_5N_6, and have been shown to have cyclic or polycyclic structures, as shown in 13-X to 13-XII:



(13-X)



(13-XI)



(13-XII)

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[16] H. W. Roesky and J. Anhaus, *Chem. Ber.*, 1982, **115**, 3682.

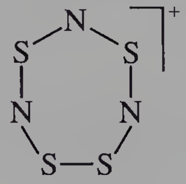
Sulfur–Nitrogen Cations and Anions. The simplest cation, NS_2^+, is the analog of the nitronium (NO_2^+) ion; it is made by the reaction:

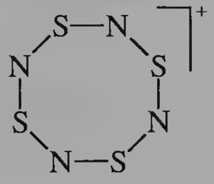
$$S_7NH \xrightarrow[\text{in } SO_2]{SbCl_5} [S_2N^+][SbCl_6^-]$$

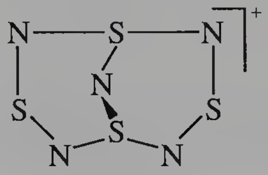
Three other well-established cations are prepared by the following reactions[17]:

$$3S_3N_2Cl_2 + S_2Cl_2 \longrightarrow 2[S_4N_3^+]Cl^- + 3SCl_2$$
$$S_4N_4 + 4SbF_5 \longrightarrow [S_4N_4^{2+}][SbF_6^-][Sb_3F_{14}^-]$$
$$S_3N_3Cl_3 + (Me_3SiN)_2S \longrightarrow [S_4N_5^+]Cl^-$$

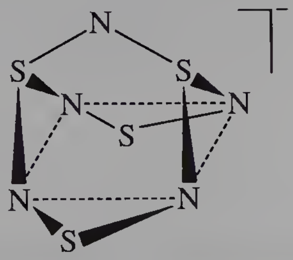
The structures are shown in (13-XIII) to (13-XV).

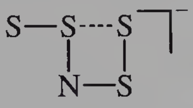

(13-XIII)

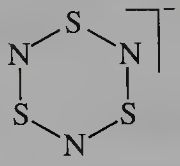

(13-XIV)


(13-XV)

Well-characterized S—N anions include $S_4N_5^-$, S_4N^-, and $S_3N_3^-$, whose structures are shown as (13-XVI) to (13-XVIII).


(13-XVI)


(13-XVII)


(13-XVIII)

The $S_4N_5^-$ ion can be obtained from S_4N_4 in various ways, and its structure (13-XVI) is clearly derived from that of S_4N_4 by addition of a bridging N^- unit.

The $S_3N_3^-$ ion, with its planar, partially π-bonded structure (13-XVIII) is also derived form S_4N_4 by the action of azide ion or metallic potassium. The S_4N^- ion has been obtained by thermal decomposition of $S_4N_5^-$.

Other S–N Compounds. In addition to compounds containing only S and N, there are numerous others in which S—N bonds occur along with other bonds. There is, for example, a series of cyclic $S_x(NH)_y$ compounds with $x + y = 8$. These include S_7NH, $S_6(NH)_2$ (3 isomers), $S_5(NH)_3$ (2 isomers), and $S_4(NH)_4$ (the 1,3,5,7 isomer). These rings contain S—S and S—N bonds but no N—N bonds. There are also many compounds containing rings with additional elements such as C, Si, P, As, Sn, and O.

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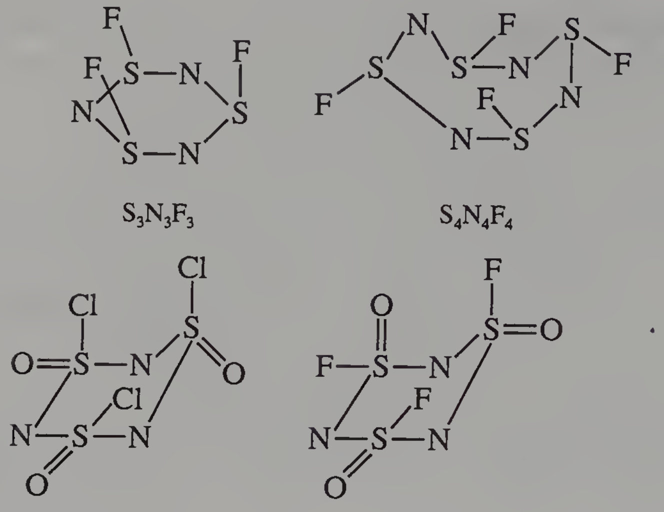
[17] T. Chivers *et al.*, *Inorg. Chem.*, 1979, **18,** 3379; R. J. Gillespie *et al.*, *Inorg. Chem.*, 1981, **20,** 3799; A. J. Banister *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987,** 915.



$S_3N_3F_3$ $S_4N_4F_4$

$S_3N_3O_3Cl_3$(*cis*) $S_3N_3O_3F_3$(*trans*)

FIG. 13-7. Some cyclic S—N compounds with sulfur also bonded to F, Cl, and O.

The S–N compounds containing sulfur in higher oxidation states are also important. Thus, there are cyclic compounds of the types shown in Fig. 13-7. Finally, we should mention the existence of N—S bonds in sulfamic acid ($H_3N^+SO_3^-$), the sulfamate anion ($H_2NSO_3^-$), and sulfamides, $(R_2N)_2SO_2$.

13-10. Halides

Sulfur Fluorides. These are rather different from the other halides and are appropriately dealt with separately.

There are seven sulfur fluorides, six of which are depicted, along with their properties, in Table 13-4. The isomeric *disulfur difluorides* are actually thermodynamically unstable. The compound FSSF, prepared by fluorination of sulfur with AgF, readily isomerizes to SSF_2, which can also be obtained in other ways. However, SSF_2 itself in the presence of acid catalysts (e.g., HF or BF_3) rapidly disproportionates:

$$2SSF_2 \longrightarrow \tfrac{3}{8}S_8 + SF_4$$

Sulfur difluoride is difficult to make and is known only as a dilute gas. It dimerizes to form *disulfur tetrafluoride* (S_2F_4), which has a curious structure (13-XIX) that has only recently been determined by a combination of experimental and theoretical studies.[18] One sulfur atom (S^1) can be considered to occupy an incomplete trigonal bipyramid with two axial F atoms and with a lone pair, an F atom and an S—F group in the equatorial plane. Dissociation

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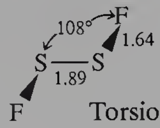
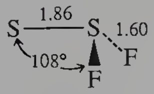
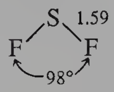
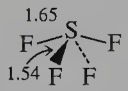
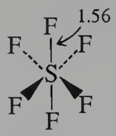
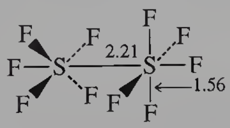
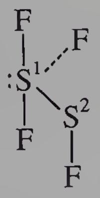
[18] M. V. Carlowitz *et al.*, *J. Mol. Struct.*, 1983, **100**, 161.

TABLE 13-4
Binary Sulfur Fluorides[a]

Compound	(°C)	Structure	Symmetry
FSSF	mp −133 bp +15	 Torsion angle: 88°	C_2
SSF_2	mp −165 bp −10.6		C_s
SF_2	Known only in gas phase		C_{2v}
SF_4	mp −121 bp −38		C_{2v}
SF_6	mp −50.5 subl −63.8		O_h
S_2F_{10}	mp −52.7 bp +30		D_{4d}

[a] Distances in Å; Angles in deg.; mp = melting point and bp = boiling point.

to $2SF_2$ appears to occur unimolecularly by cleavage of the S^1—S^2 and the equatorial S^1—F bonds.



(13-XIX)

Sulfur tetrafluoride (SF_4) is made by reaction of SCl_2 with a 70/30 mixture of HF/pyridine. Sulfur tetrafluoride is an extremely reactive substance (as indicated in Fig. 13-8), instantly hydrolyzed by water to SO_2 and HF, but its fluorinating action is remarkably selective. It will convert C=O and P=O groups smoothly into CF_2 and PF_2, and CO_2H and P(O)OH groups into CF_3 and PF_3 groups, without attack on most other functional or reactive groups that may be present. Compounds of the type $ROSF_3$, which may be intermediates in the reaction with keto groups, have been prepared. Sulfur tetrafluoride is also quite useful for converting metal oxides into fluorides, which are (usually) in the same oxidation state.

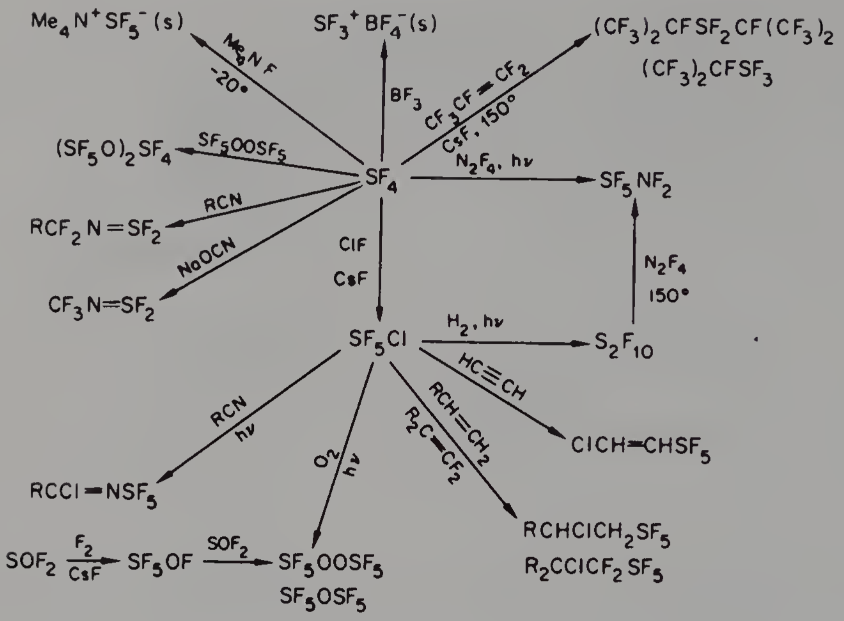


FIG. 13-8. Some reactions of sulfur–fluorine compounds.

Aryl-substituted fluorides can be readily obtained by the reaction

$$(C_6H_5)_2S_2 + 6AgF_2 \longrightarrow 2C_6H_5SF_3 + 6AgF$$

which is carried out in trichloro- or trifluoromethane. The arylsulfur trifluorides are more convenient laboratory fluorinating agents than SF_4 in that they do not require pressure above atmospheric. The structure of SF_4 and of substituted derivatives RSF_3 is that of a trigonal bipyramid with an equatorial position occupied by the lone pair.

Sulfur hexafluoride is chemically very inert, reacting only with such reagents as red hot metals and sodium in liquid ammonia. Molten KOH and steam at 500°C are without effect. Not surprisingly it is nontoxic and finds use as an insulating gas in high voltage electrical equipment. The low reactivity, particularly toward hydrolysis, which contrasts with the very high reactivity of SF_4, is presumably due to a combination of factors including high S—F bond strength and the coordinate saturation and steric hindrance of sulfur, augmented in the case of SF_6 by the lack of polarity of the molecule. The low reactivity is mainly due to *kinetic factors,* not to thermodynamic stability, since the reaction of SF_6 with H_2O to give SO_3 and HF would be decidedly favorable ($\Delta G = -460$ kJ mol^{-1}), and the average bond energy in SF_4 (326 kJ mol^{-1}) is slightly higher than that of SF_6. The possibility of electrophilic attack on SF_6 has been confirmed by its reactions with certain Lewis acids. Thus Al_2Cl_6 at 180 to 200°C gives AlF_3, Cl_2, and sulfur chlorides, whereas the thermodynamically allowed reaction

$$SF_6 + 2SO_3 \longrightarrow 3SO_2F_2$$

proceeds slowly at 250°C. Sulfur hexafluoride also reacts rapidly and quantitatively with sodium in ethylene glycol dimethyl ether containing biphenyl at room temperature:

$$8Na + SF_6 \longrightarrow Na_2S + 6NaF$$

Electron transfer from a biphenyl radical ion to an SF_6 molecule to give an unstable SF_6^- ion is probably involved.

Disulfur decafluoride is best obtained by the photochemical reaction

$$2SF_5Cl + H_2 \xrightleftharpoons{h\nu} S_2F_{10} + 2HCl$$

It is extremely poisonous (the reason for which is not clear), being similar to phosgene in its physiological action. It is not dissolved or hydrolyzed by water or alkalis and is not very reactive. In S_2F_{10} each S atom is octahedral and the S—S bond is unusually long (2.21 Å versus ~2.08 Å expected for a single bond), whereas the S—F bonds are, as in SF_6, ~0.2 Å shorter than expected for an S—F single bond. At room temperature it shows scarcely any chemical reactivity, though it oxidizes the iodide in an acetone solution of KI. At elevated temperatures, however, it is a powerful oxidizing agent, generally causing destructive oxidation and fluorination, presumably owing to initial breakdown to free radicals:

$$S_2F_{10} \longrightarrow 2SF^{\cdot}$$

$$SF_5^{\cdot} \longrightarrow SF_4 + F^{\cdot}$$

Substituted Sulfur Fluorides. There is an extensive chemistry of substituted sulfur fluorides of the types RSF_3 and RSF_5; examples of the former were mentioned previously. The SF_5 derivatives bear considerable resemblance to CF_3 derivatives, with the principal difference that in reactions with organometallic compounds the SF_5 group is fairly readily reduced, whereas the CF_3 group is not.

The mixed halide SF_5Cl is an important intermediate (Fig. 13-8). Although it can be made by interaction of S_2F_{10} with Cl_2 at 200 to 250°C (as can SF_5Br using S_2F_{10} and Br_2) it is best made by the CsF-catalyzed reaction

$$SF_4 + ClF \xrightarrow{25°\text{C, 1 h, CsF}} SF_5Cl$$

A probable intermediate is the salt $CsSF_5$, which dissociates significantly above 150°C:

$$CsF + SF_4 \underset{150°\text{C}}{\overset{100°\text{C}}{\rightleftharpoons}} CsSF_5$$

SF_5Cl is a colorless gas (bp −15.1°C, mp −64°C), which is more reactive than SF_6, being readily attacked by OH^- and other nucleophiles, though it is inert to acids. Its hydrolysis and its powerful oxidizing action toward many organic substances are consistent with the charge distribution $F_5S^{\delta-}—Cl^{\delta+}$. Its radical reactions with olefins and fluoroolefins resemble those of CF_3I. Pentafluorobromosulfur is a pale yellow liquid boiling at 3°C, and also readily hydrolyzed.

The very reactive yellow *pentafluorosulfur hypofluorite* is one of the few known hypofluorites; it is obtained by the catalytic reaction

$$SOF_2 + 2F_2 \xrightarrow{\text{CsF, 25°C}} SF_5OF$$

In the absence of CsF, SOF_4 is obtained and this reacts separately with CsF to give SF_3OF.

The hydroxide SF_5OH and the hydroperoxide, SF_5OOH are also known; the former gives the anion SF_5O^-.

Finally, the carbon compounds F_5SCH_3 and $F_4S{=}CH_2$ can be made by the sequence[19a]

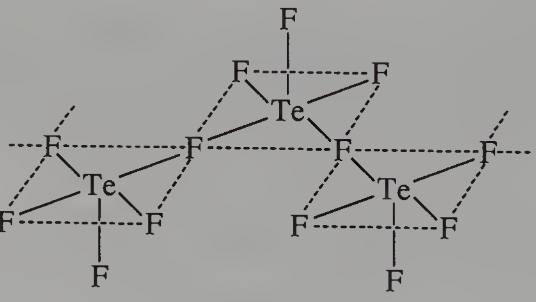
$$\begin{tikzcd}
SF_5Cl \arrow[r, "CH_2=C=O"] & SF_5CH_2COCl \arrow[r, "H_2O"] & SF_5CH_2CO_2H \\
SF_5CH_2CO_2Ag \arrow[r, "Br_2", "-CO_2"'] & SF_5CH_2Br \arrow[r, "Zn/HCl"] \arrow[d, "BuLi"] & SF_5CH_3 \\
 & SF_5CH_2Li \arrow[r, "-70°C", "-LiF"'] & F_4S{=}CH_2
\end{tikzcd}$$

Both are quite stable gases. The compound F_4SCH_2 contains a C═S double bond, 1.554(4)Å.[19b]

Selenium and Tellurium Fluorides.[19c] While SeF_2, FSeSeF, and $SeSeF_2$ have been prepared only in minute amounts and their chemistry is little known, SeF_4 and TeF_4 can be prepared by the reaction

$$EO_2 + 2SF_4 \longrightarrow EF_4 + 2SOF_2$$

The compound SeF_4 (mp ~ −39°C, bp 106°C) resembles SF_4, but being a liquid and somewhat easier to handle, it has some advantages as a fluorinating agent. Tellurium tetrafluoride is a colorless crystalline solid (mp 130°C) with a polymeric structure as shown in (13-XX).



(13-XX)

Selenium hexafluoride and TeF_6 are colorless gases, somewhat more reactive than SF_6. Selenium hexafluoride though unreactive toward water is very toxic, while TeF_6 slowly hydrolyzes through $Te(OH)_nF_{6-n}$ intermediates to $Te(OH)_6$. The compounds Te_2F_{10}, TeF_5Cl, and TeF_5Br are also known.

[19a] G. Kleemann and K. Seppelt, *Chem. Ber.*, 1983, **116,** 645.

[19b] A. Simon *et al., Z. Anorg. Allg. Chem.*, 1980, **468,** 7.

[19c] A. Engelbrecht and F. Sladky, *Adv. Inorg. Chem. Radiochem.*, 1981, **24,** 189.

Other Halides of Group VIA(16). The other halides of S, Se, and Te are listed in Table 13-5.

Sulfur Chlorides. The chlorination of molten sulfur gives S_2Cl_2, an orange liquid of revolting smell. By using an excess of chlorine and traces of $FeCl_3$, $SnCl_4$, I_2, and so on, as catalyst at room temperature, an equilibrium mixture containing ~85% of SCl_2 is obtained. The dichloride readily dissociates within a few hours:

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$$

but it can be obtained pure as a dark red liquid by fractional distillation in the presence of some PCl_5, small amounts of which will stabilize SCl_2 for some weeks.

Sulfur chlorides are used as a solvent for sulfur (giving dichlorosulfanes up to about $S_{100}Cl_2$), in the vulcanization of rubber, as chlorinating agents, and as intermediates. Specific higher chlorosulfanes can be obtained by reactions such as

$$2SCl_2 + H_2S_4 \xrightarrow{-80^\circ C} S_6Cl_2 + 2HCl$$

The sulfur chlorides are readily hydrolyzed by water. In the vapor S_2Cl_2 has a Cl—S—S—Cl chain with C_2 symmetry (S—S = 1.95 Å, S—Cl = 2.05 Å), and a similar structure occurs in the crystal.[20] Sulfur dichloride has a bent structure with S—Cl = 2.014(5)Å and an angle of 102.8(2)°. Both of these chlorides have important industrial uses and are produced in ton quantities. Yellow crystalline SCl_4 (which may be, but there is no firm evidence, $SCl_3^+Cl^-$)

TABLE 13-5
The Group VIA(16) Binary Halides

Chlorides[a]	Bromides[a]	Iodides[a]
	Sulfur	
S_2Cl_2,[b] mp −80, bp 138	S_2Br_2,[b] mp −46, d 90	S_2I_2, dec −30[b]
SCl_2, mp −78, b 59		
SCl_4, dec −31		
	Selenium	
Se_2Cl_2	Se_2Br_2, dec in vapor	
$SeCl_2$, dec in vapor	$SeBr_2$, dec in vapor	
$SeCl_4$, subl 191	$SeBr_4$	
	Tellurium[c]	
Te_4Cl_{16} mp 223, bp 390	Te_4Br_{16}, mp 388, bp 414 dec in vapor	Te_4I_{16}, mp 280 dec 100

[a] mp = melting point; bp = boiling point; dec = decomposes, subl = sublimes; all in °C.
[b] There are also dichloro- and dibromosulfanes, XS_nX with $2 < n < 100$.
[c] Subhalides such as Te_2Br and TeI have also been reported; see R. Kniep and A. Rabenau, *Topics in Current Chemistry*, F. L. Boschke, Ed., Springer-Verlag, New York 1983, p. 145.

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[20] R. Kniep *et al.*, *Z. Naturforsch.*, 1983, **38B**, 1.

is produced by the action of Cl_2 on S_2Cl_2 or SCl_2 at −80°C; it dissociates to $SCl_2 + Cl_2$ above −31°C.

Sulfur Bromide. This compound (S_2Br_2) is isostructural[20] with S_2Cl_2, but the existence of SBr_2 is uncertain.

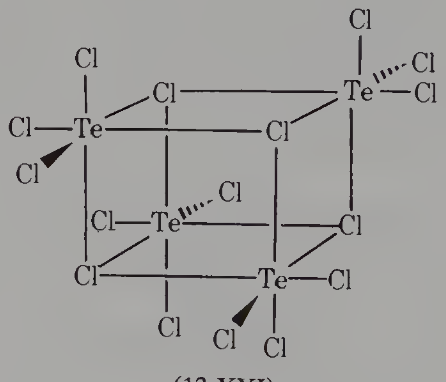
The existence of *sulfur iodides* is controversial, although S_2I_2 may be genuine. The best evidence for S—I bonds is in $[S_7I^+][SbF_6^-]$ and $[(S_7I)_2I^{3+}][SbF_6^-]_3$, prepared from reaction of iodine with sulfur in SbF_5 solution.[21] Comparable Se_6I^+ cations are also known.[22]

Selenium and Tellurium Halides. For selenium, these halides are mostly of marginal stability and the characterization is incomplete; the most stable ones are Se_2Cl_2 and Se_2Br_2, whose structures are known.[20] The two dihalides are known only in the vapor phase; attempts to isolate them as solids (or liquids) result only in disproportionations to yield Se, Se_2X_2, and SeX_4. The SeX_4 molecules themselves tend to decompose under most conditions to, for example, $SeBr_2$, Br_2, and Se_2Br_2. In acetonitrile there are the following equilibria[23]:

$$3SeCl_2 = Se_2Cl_2 + SeCl_4 \qquad K \approx \leqslant 2 \times 10^2$$

$$2SeBr_2 = Se_2Br_2 + Br_2 \qquad K \approx 1 \times 10^{-2}$$

In the vapor state $TeCl_4$ has a ψ-*tbp* structure but forms Te_4Cl_{16} molecules with a cubane-type structure (13-XXI) in the crystal.



(13-XXI)

13-11. Oxides

The principal oxides are listed in Table 13-6. The oxides SO, SeO, and TeO have only transient existences, but PoO is a stable but easily oxidized solid. The oxide S_2O is an unstable colorless gas. The cyclosulfur oxides, S_nO, $n = 5$ to 8, which are formed on treating cyclosulfurs with CF_3CO_3H, have ring structures with one S═O unit.

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[21] J. Passmore *et al., Inorg. Chem.,* 1981, **20,** 3839; 1982, **21,** 2717.
[22] J. Passmore *et al., J. Chem. Soc. Chem. Commun.,* **1983,** 526.
[23] J. Milne, *Polyhedron,* 1985, **4,** 65.

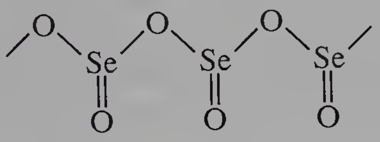
TABLE 13-6
Oxides of S, Se, Te, and Po

$\begin{Bmatrix} S_2O \\ SO \end{Bmatrix}$			PoO
SO_2 bp −10.07°C mp −75.5°C	SeO_2 subl 315°C	TeO_2 mp 733°C	$PoO_2[PoO(OH)_2]$
SO_3 mp 16.8° (γ) bp 44.8°	SeO_3 mp 120°C	TeO_3 dec 400°C Te_2O_5 dec >400°C	
S_nO, $n = 5–8$ S_7O_2			

Dioxides. The dioxides are obtained by burning the elements in air, though small amounts of SO_3 also form in the burning of sulfur. Sulfur dioxide is also produced when many sulfides are roasted in air and when sulfur-containing fuels such as oils and coals are burned. It presents a major pollution and ecological problem. For example, in Norway, the pH of lakes is decreasing because of the sulfuric acid formed from SO_2 pollution originating in the British Isles and Europe. Sulfur dioxide can be removed from flue gases by solid slurries of, say, calcium hydroxide, but there is then still an enormous sludge problem.

Selenium and tellurium dioxides are also obtained by treating the metals with hot nitric acid to form H_2SeO_3 and $2TeO_2{\cdot}HNO_3$, respectively, and then heating these to drive off water or nitric acid.

The dioxides differ considerably in structure. Sulfur dioxide is a gas, SeO_2 is a white volatile solid, while TeO_2 and PoO_2 are nonvolatile solids. The chain polymer structure of SeO_2 is shown in (13-XXII).

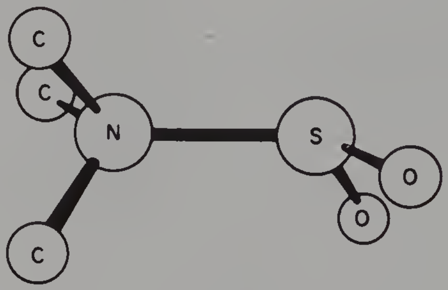


(13-XXII)

Tellurium dioxide has a white (α) and a yellow (β) modification, in both of which Te atoms have a coordination number of 4 and the structure is three dimensional. Polonium dioxide has the fluorite structure.

Sulfur dioxide is by far the most important of the dioxides. It is a weak reductant in aqueous acid but stronger in base where the sulfite ion (Section 13-13) is formed. The pure liquid (bp −10°C) is a useful nonaqueous solvent despite its low dielectric constant (~15), and lack of any self-ionization. It is particularly useful as a solvent for superacid systems (Section 3-10).

Sulfur dioxide has lone pairs and can act as a Lewis base; it can also act as a Lewis acid. With certain amines, crystalline 1:1 charge-transfer complexes are formed in which electrons from nitrogen are presumably transferred to antibonding acceptor orbitals localized on sulfur. One of the most stable is $Me_3N \cdot SO_2$ (13-XXIII) where the dimensions of the SO_2 molecule appear to be unchanged by complex formation.



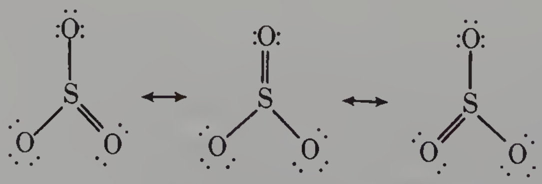
(13-XXIII)

Although crystals are formed with quinol and some other hydrogen-bonding compounds, these are clathrates or, in the case of $SO_2 \cdot 7H_2O$, a clathrate hydrate (Section 3-4).

Sulfur dioxide also forms complexes with a number of transition metal species (Section 13-16).

Trioxides. The only important trioxide in this group, SO_3, is obtained by reaction of sulfur dioxide with molecular oxygen, a reaction that is thermodynamically very favorable but extremely slow in absence of a catalyst. Platinum sponge, V_2O_5, and NO serve as catalysts under various conditions. Sulfur trioxide reacts vigorously with water to form sulfuric acid. Commercially, for practical reasons, SO_3 is absorbed in concentrated sulfuric acid, to give oleum (Section 3-11), which is then diluted. Sulfur trioxide is used as such for preparing sulfonated oils and alkyl arenesulfonate detergents. It is also a powerful but generally indiscriminate oxidizing agent; however, it will selectively oxidize pentachlorotoluene and similar compounds to the alcohol.

The free molecule, in the gas phase, has a planar, triangular structure that may be considered to be a resonance hybrid involving $p\pi$–$p\pi$ S—O bonding, as in (13-XXIV), with additional π bonding via overlap of filled oxygen $p\pi$ orbitals with empty sulfur $d\pi$ orbitals, to account for the very short S—O distance of 1.41 Å.

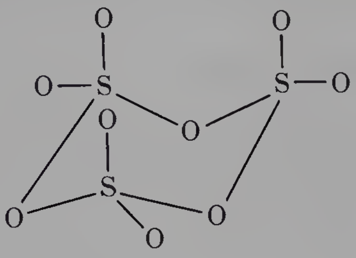


(13-XXIV)

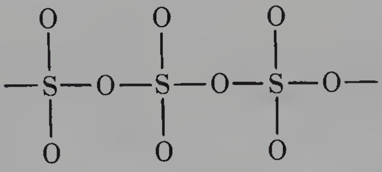
In view of this affinity of S in SO_3 for electrons, it is not surprising that SO_3 functions as a fairly strong Lewis acid toward the bases that it does not preferentially oxidize. Thus the trioxide gives crystalline complexes with pyridine, trimethylamine, or dioxane, which can be used, like SO_3 itself, as sulfonating agents for organic compounds.

The structure of solid SO_3 is complex. At least three well-defined phases are known. There is first γ-SO_3, formed by condensation of vapors at −80°C or below. This icelike solid contains cyclic trimers with structure (13-XXV).

A more stable, asbestos-like phase (β-SO_3) has infinite helical chains of linked SO_4 tetrahedra (13-XXVI), and the most stable form α-SO_3, which also has an asbestoslike appearance, presumably has similar chains crosslinked into layers.



(13-XXV)



(13-XXVI)

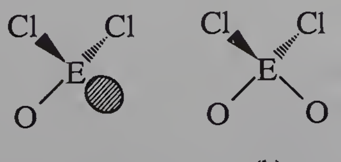
Liquid γ-SO_3, which is a monomer–trimer mixture, can be stabilized by the addition of boric acid. In the pure state it is readily polymerized by traces of water.

Selenium trioxide is made by dehydration of H_2SeO_4 by P_2O_5 at 150 to 160°C; it is a strong oxidant and is rapidly rehydrated by water. Selenium trioxide dissolves in liquid HF to give *fluoroselenic acid* ($FSeO_3H$; cf. FSO_3H), a viscous fuming liquid.

Tellurium trioxide is made by dehydration of $Te(OH)_6$. This orange compound reacts only slowly with water but dissolves rapidly in bases to give tellurates.

13-12. Oxohalides

These are principally formed by sulfur and selenium and the main ones are the EOX_2 and EO_2X_2 molecular compounds, having the structures shown in Fig. 13-9. The E═O bonds are short (~1.45 Å for S═O) and the multiple bond character depends on oxygen to sulfur (or selenium) $p\pi \rightarrow d\pi$ bonding. This is enhanced by the electronegativity of the halogens, and the E═O bond lengths decrease in both series of compounds as the halogens change from Br to Cl to F.



(a) (b)

FIG. 13-9. The structures of $EOCl_2$ and EO_2Cl_2 molecules, C_s and C_{2v} symmetry, respectively.

The *thionyl* and *selenyl halides* are

SOF_4	SOF_2	$SOCl_2$	$SOBr_2$	$SOFCl$
$SeOF_4$	$SeOF_2$	$SeOCl_2$	$SeOBr_2$	

With the exception of SOF_2, which reacts only slowly with water, the compounds are rapidly, sometimes violently hydrolyzed.

The most common compound is *thionyl dichloride,* which is made by the reaction

$$SO_2 + PCl_5 = SOCl_2 + POCl_3$$

It is used to prepare anhydrous metal halides from hydrated chlorides or hydroxides, since the only products of hydrolysis are gases:

$$SOCl_2 + H_2O = 2HCl + SO_2$$

Other representative syntheses are

$$SOCl_2 + 2HF(1) = SOF_2 + 2HCl$$

$$SOCl_2 + 2HBr \overset{0°C}{=} SOBr_2 + 2HCl$$

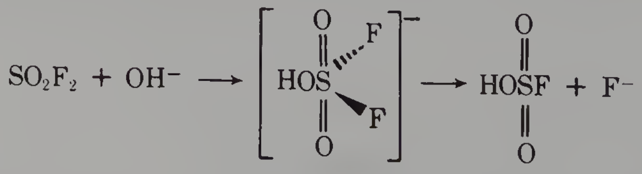
$$SeO_2 + SeCl_4 \xrightarrow{CCl_4} 2SeOCl_2$$

The dihalides are stable at ordinary temperatures but decompose on heating. They can act both as weak Lewis bases using lone pairs on oxygen, and as weak Lewis acids using vacant *d* orbitals. For example, $SeOCl_2(\text{pyrazole})_2$ has a square pyramidal structure with apical O and trans Cl atoms in the base.

Sulfuryl halides are SO_2F_2, SO_2Cl_2, SO_2FCl, and SO_2FBr. *Sulfuryl dichloride* is formed by the action of Cl_2 on SO_2 in the presence of a little $FeCl_3$ catalyst. It is stable to almost 300°C. It fumes in moist air and is hydrolyzed reasonably rapidly with liquid water. It can be used as a chlorinating agent. Sulfuryl difluoride, a rather inert gas, is made by fluorination of SO_2Cl_2 or by heating barium fluorosulfate

$$Ba(SO_3F)_2 \xrightarrow{500°C} SO_2F_2 + BaSO_4$$

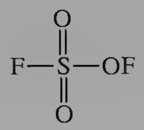
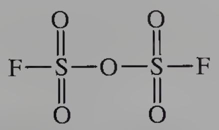
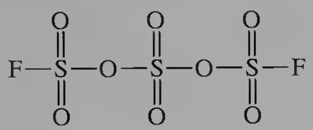
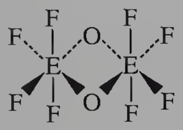
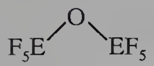
The halide SO_2F_2 is soluble in water without hydrolysis but reacts in base:



It also reacts with other nucleophiles in aqueous solution, probably again by nucleophilic attack on S and displacement of F^-. Thus NH_3 gives $SO_2(NH_2)_2$, and $C_6H_5O^-$ gives $C_6H_5OSO_2F$.

Only SeO_2F_2 is known and for Te there are no $TeOX_2$ or TeO_2X_2 compounds. However, both of these elements, as well as sulfur, form a number

TABLE 13-7
Some Group VIA(16) Oxofluorides

SO_3F_2	 $\mathrm{F{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}OF}$
$S_2O_5F_2$	 $\mathrm{F{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}F}$
$S_3O_8F_2$	 $\mathrm{F{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}F}$
$E_2O_2F_8$ (Se, Te)	
E_2OF_{10} (S, Se)	
$Te_5O_4F_{22}$	$F_2Te(OTeF_5)_4$ (cis and trans isomers)[a]

[a] A number of similar compounds with $OTeF_5$ groups are known e.g., *cis* and *trans*-$F_4Te(OTeF_5)_2$, $FTe(OTeF_5)_5$, and $Te(OTeF_5)_6$. The $OTeF_5$ group forms many other compounds as well (cf. S. H. Strauss *et al., Inorg. Chem.*, 1985, **24,** 4307).

of more complex oxofluorides, a few of which are shown, with their structures, where known, in Table 13-7.

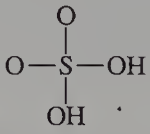
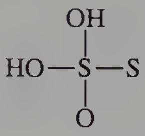
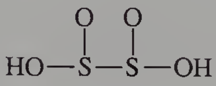
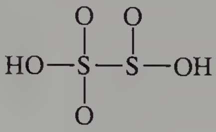
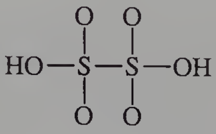
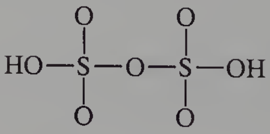
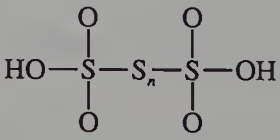
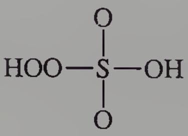
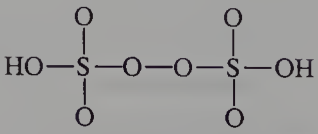
13-13. Oxo Acids of Sulfur

The oxo acids of sulfur are numerous and many are of importance. In some cases the acid is not known as such but the anion and its salts are known. Table 13-8 lists the major types of sulfur oxoacids according to structural type. This classification is to some extent arbitrary, but it corresponds approximately with the order in which we discuss these acids. Sulfuric acid has already been discussed (Section 3-11). None of the oxo acids in which there are S—S bonds has any known Se or Te analogue.

Sulfurous and Disulfurous Acids. Neither of these, H_2SO_3 and $H_2S_2O_5$, respectively, exists as such, but the HSO_3^-, SO_3^{2-}, $HS_2O_5^-$, and $S_2O_5^{2-}$ ions and their salts do.

Sulfur dioxide is quite soluble in water; such solutions, which possess acidic properties, have long been referred to as solutions of sulfurous acid (H_2SO_3). However, H_2SO_3 either is not present or is present only in infinitesimal quantities in such solutions. The so-called hydrate $H_2SO_3{\cdot}{\sim}6H_2O$ is the gas hydrate

TABLE 13-8
Principal Oxo Acids of Sulfur

Name	Formula	Structure[a]
	Acids Containing One Sulfur Atom	
Sulfurous	H_2SO_3[b]	SO_3^{2-} (in sulfites)
Sulfuric	H_2SO_4	 $\mathrm{O{-}\overset{O}{\underset{OH}{S}}{-}OH}$
	Acids Containing Two Sulfur Atoms	
Thiosulfuric	$H_2S_2O_3$	 $\mathrm{HO{-}\overset{OH}{\underset{O}{S}}{-}S}$
Dithionous	$H_2S_2O_4$[b]	 $\mathrm{HO{-}\overset{O}{S}{-}\overset{O}{S}{-}OH}$
Disulfurous	$H_2S_2O_5$[b]	 $\mathrm{HO{-}\overset{O}{\underset{O}{S}}{-}\overset{O}{S}{-}OH}$
Dithionic	$H_2S_2O_6$	 $\mathrm{HO{-}\overset{O}{\underset{O}{S}}{-}\overset{O}{\underset{O}{S}}{-}OH}$
Disulfuric	$H_2S_2O_7$	 $\mathrm{HO{-}\overset{O}{\underset{O}{S}}{-}O{-}\overset{O}{\underset{O}{S}}{-}OH}$
	Acids Containing Three or More Sulfur Atoms	
Polythionic	$H_2S_{n+2}O_6$	 $\mathrm{HO{-}\overset{O}{\underset{O}{S}}{-}S_n{-}\overset{O}{\underset{O}{S}}{-}OH}$
	Peroxo Acids	
Peroxomonosulfuric	H_2SO_5	 $\mathrm{HOO{-}\overset{O}{\underset{O}{S}}{-}OH}$
Peroxodisulfuric	$H_2S_2O_8$	 $\mathrm{HO{-}\overset{O}{\underset{O}{S}}{-}O{-}O{-}\overset{O}{\underset{O}{S}}{-}OH}$

[a] In most cases the structure given is inferred from the structure of anions in salts of the acid.
[b] Free acid unknown.

$SO_2 \cdot {\sim}7H_2O$. The equilibria in aqueous solutions of SO_2 are best represented as

$$SO_2 + xH_2O = SO_2 \cdot xH_2O \qquad \text{(hydrated } SO_2\text{)}$$

$$[SO_2 \cdot xH_2O = H_2SO_3 \qquad K <<< 1]$$

$$SO_2 \cdot xH_2O = HSO_3^- \text{ (aq)} + H_3O^+ + (x-2)H_2O$$

and the first acid dissociation constant for "sulfurous acid" is properly defined as follows:

$$K_1 = \frac{[HSO_3^-][H^+]}{[\text{total dissolved } SO_2] - [HSO_3^-] - [SO_3^{2-}]} = 1.3 \times 10^{-2}$$

The lighter alkali ions give sulfites or disulfites (see later), and it appears that larger ions such as Rb^+, Cs^+, or R_4N^+ are necessary to stabilize HSO_3^-. In the solid state both ions are pyramidal and the H atom in HSO_3^- appears to be on the sulfur atom. In solution ^{17}O nmr shows that the $SO_2(OH)^-$ form also exists and the $[SO_2(OH)^-]/[HSO_3^-]$ ratio is ~5 at 20°C.[24a]

Heating solid bisulfites or passing SO_2 into their aqueous solutions affords *disulfites:*

$$2MHSO_3 \overset{\text{heat}}{\rightleftharpoons} M_2S_2O_5 + H_2O$$

$$HSO_3^- \text{(aq)} + SO_2 = HS_2O_5^- \text{ (aq)}$$

Although condensation processes of this type usually result in an oxobridged diacid or anion, as in disulfuric acid ($H_2S_2O_7$) the $S_2O_5^{2-}$ ion is unsymmetrical and has an S—S bond,[24b] as shown in Table 13-8. Some important reactions of sulfites are shown in Fig. 13-10. The reducing character of SO_2 and sulfites is expressed quantitatively by the following potentials:

$$SO_4^{2-} + 4H^+ + (x-2)H_2O + 2e = SO_2 \cdot xH_2O \qquad E^0 = 0.17 \text{ V}$$

$$SO_4^{2-} + H_2O + 2e = SO_3^{2-} + 2OH^- \quad E^0 = -0.93 \text{ V}$$

The diesters of sulfurous acid exist in tautomeric forms, $(RO)_2SO$ and RSO_2OR.

Thiosulfuric Acid ($H_2S_2O_3$). The thiosulfate ion ($S_2O_3^{2-}$) has a structure[25] comparable to that of the SO_4^{2-} ion with one oxygen atom replaced by a sulfur atom; the S—S and S—O distances [2.013(3) and 1.468(4)Å, respectively] imply that little S—S π bonding and much S—O π bonding are present. Solutions of hydrated sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$ (hypo) are used as a "fixer" in photography because it can dissolve unphotolyzed AgBr from the emulsion by complexing the Ag^+ ion:

$$AgBr(s) + 3S_2O_3^{2-} \text{ (aq)} = Ag(S_2O_3)_3^{5-} + Br^-$$

[24a] D. A. Horner and R. E. Connick, *Inorg. Chem.*, 1986, **25**, 2414.

[24b] I. C. Chen and Y. Wang, *Acta Cryst.*, 1984, **40C**, 1780.

[25] S. T. Teng *et al.*, *Acta Cryst.*, 1984, **40C**, 1785.

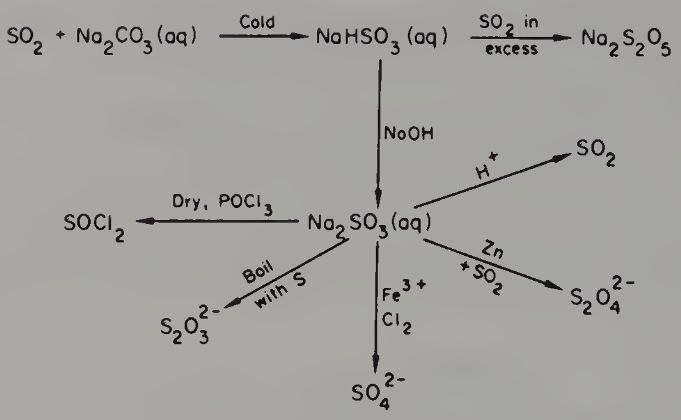


FIG. 13-10. Some reactions of sulfites.

The moderate reducing character of $S_2O_3^{2-}$ provides the basis for analytical determination of iodine:

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

Thiosulfuric acid cannot be generated in aqueous solution by acidifying solutions of thiosulfates because it rapidly decomposes to H_2SO_4 and a mixture of S, H_2S, H_2S_n, and SO_2. It can, however, be prepared by nonaqueous reactions such as:

$$Na_2S_2O_3 + 2HCl \xrightarrow[-78^\circ C]{Et_2O} H_2S_2O_3\cdot 2Et_2O + 2NaCl$$

$$HSO_3Cl + H_2S \xrightarrow[<10^\circ C]{\text{no solvent}} H_2S_2O_3 + HCl$$

Dithionite Ion ($S_2O_4^{2-}$). The reduction of sulfites in aqueous solutions containing an excess of SO_2, usually by zinc dust, or of SO_3 by formate in aqueous methanol, gives the dithionite ion $S_2O_4^{2-}$. Solutions of this ion are not very stable and decompose according to the stoichiometry:

$$2S_2O_4^{2-} + H_2O \longrightarrow S_2O_3^{2-} + 2HSO_3^-$$

In acid solution decomposition is extremely rapid and $H_2S_2O_4$ is unknown under any conditions. The Zn and Na salts are commonly used as powerful and rapid reducing agents in alkaline solution:

$$2SO_3^{2-} + 2H_2O + 2e = 4OH^- + S_2O_4^{2-} \qquad E^0 = -1.12\ \text{V}$$

Because of a reversible dissociation to afford the $SO_2^{\cdot -}$ ion radical,

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^{-\cdot}$$

dithionite solutions show strong esr signals and give kinetic rate laws that are half-order in $S_2O_4^{2-}$. When aqueous $Na_2S_2O_4$ is mixed with 2-anthraquinonesulfonate as a catalyst (Fieser's solution) the solution efficiently removes dioxygen from gases.

The structure of the dithionite ion (Fig. 13-11) has several remarkable

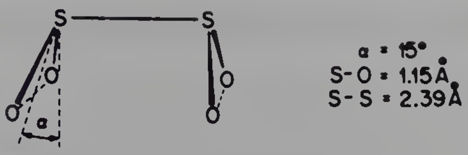


FIG. 13-11. Structure of the dithionite ion ($S_2O_4^{2-}$) in $Na_2S_2O_4$.

features. The oxygen atoms, which must bear considerable negative charge, are closely juxtaposed by the eclipsed (C_{2v}) configuration and by the small value of the angle α, which would be 35° for sp^3 tetrahedral hybridization at the sulfur atom. Second, the S—S distance is much longer than S—S bonds in disulfides, polysulfides, and so on, which are in the range ~2.0 to 2.15 Å. The long bond is believed to be due to weakening by repulsion of lone pairs on sulfur resulting from *dp* hybridized bonding. The weak bonding is consistent with dissociation to SO_2^-.

Dithionic Acid ($H_2S_2O_6$). This cannot be regarded as one of the polythionic acids since it contains no sulfur atom bound only to other sulfur atoms, as in $H_2S_3O_6$ and its $H_2S_nO_6$ homologues. The dithionate ion has a D_{3d} O_3SSO_3 structure with approximately tetrahedral bond angles about each sulfur, and the S—O bond length (1.45 Å; cf. 1.44 Å in SO_4^{2-}) again suggests considerable double-bond character.

Dithionate is usually obtained by oxidation of sulfite or SO_2 solutions with manganese(IV) oxide:

$$MnO_2 + 2SO_3^{2-} + 4H^+ = Mn^{2+} + S_2O_6^{2-} + 2H_2O$$

Other oxo acids of sulfur that are formed as by-products are precipitated with barium hydroxide, and $BaS_2O_6 \cdot 2H_2O$ is then crystallized. Treatment of aqueous solutions of this with sulfuric acid gives solutions of the free acid, which may be used to prepare other salts by neutralization of the appropriate bases. Dithionic acid is a moderately stable strong acid that decomposes slowly in concentrated solutions and when warmed. The ion itself is stable, and solutions of its salts may be boiled without decomposition. Although it contains sulfur in an intermediate oxidation state, it resists most oxidizing and reducing agents, presumably for kinetic reasons.

Polythionates. These anions, $S_nO_6^{2-}$, with n up to 22 or higher, can be separated chromatographically; only lower members are well characterized.[26a] They are normally named according to the total number of sulfur atoms, namely, trithionate, $S_3O_6^{2-}$, and so on. They are occasionally called *sulfanedisulfonates,* for example, disulfanedisulfonate for $S_4O_6^{2-}$. The free acids are unstable as are also the $HS_nO_6^-$ ions.

Polythionates are obtained by reduction of thiosulfate solutions with SO_2 in the presence of As_2O_3 and by the reaction of H_2S with an aqueous solution of SO_2, which produces a solution called Wackenroder's liquid. A general

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[26a] R. Steudel *et al., Angew. Chem. Int. Ed. Engl.,* 1987, **26,** 151.

reaction said to produce polythionates up to very great chain lengths is

$$6S_2O_3^{2-} + (2n-9)H_2S + (n-3)SO_2 \longrightarrow 3S_nO_6^{2-} + (2n-12)H_2O + 6OH^-$$

Many polythionates are best made by selective preparations, for example, the action of H_2O_2 on cold saturated sodium thiosulfate:

$$2S_2O_3^{2-} + 4H_2O_2 \longrightarrow S_3O_6^{2-} + SO_4^{2-} + 4H_2O$$

Tetrathionates are obtained by treatment of thiosulfates with iodine in the reaction used in the volumetric determination of iodine

$$2S_2O_3^{2-} + I_2 \longrightarrow 2I^- + S_4O_6^{2-}$$

Various anions containing Se and Te are also known, such as $Se_nS_2O_6^{2-}(2 \leqslant n \leqslant 6)$, $O_3S_2SeS_2SO_3^{2-}$, and $O_3S_2TeS_2O_3^{2-}$.

There are also some $O_2S(R)S_nS(R)O_2$ and $O_2S(R)Se_nS(R)O_2$ molecules, with n = 1, 2 and R = alkyl or aryl that are structurally related.[26b]

Peroxo Acids. None are known for Se or Te, but those of sulfur, $H_2S_2O_8$, and H_2SO_5, are well known and of commercial importance.

Peroxodisulfuric acid can be obtained from its NH_4^+ or Na^+ salts, which can be crystallized from solutions after electrolysis of the corresponding sulfates at low temperatures and high current densities. The $S_2O_8^{2-}$ ion has the structure $O_3S{-}O{-}O{-}SO_3$, with approximately tetrahedral angles about each S atom.

The peroxodisulfate ion is one of the most powerful and useful of oxidizing agents[26c]:

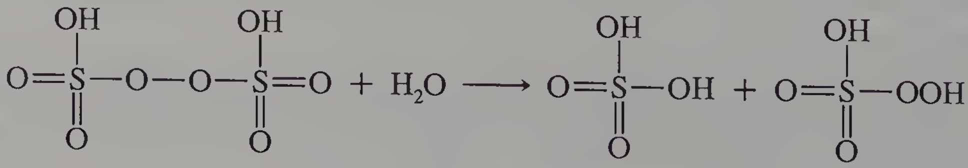
$$S_2O_8^{2-} + 2e = 2SO_4^{2-} \qquad E^0 = 2.01 \text{ V}$$

However, the reactions may be complicated mechanistically and in many of them there is good evidence for the formation of the radical ion SO_4^- by one-electron reduction:

$$S_2O_8^{2-} + e = SO_4^{2-} + SO_4^-$$

The oxidations by $S_2O_8^{2-}$ often proceed slowly but become more rapid in the presence of catalysts, the silver ion being commonly used for this purpose. The precise mechanism is not quite clear, but it appears that a weak 1:1 complex is first formed between Ag^+ and $S_2O_8^{2-}$, the rapidly reacting oxidizing species being Ag^{II}.

Peroxomonosulfuric acid (Caro's acid) is obtained by hydrolysis of peroxodisulfuric acid:



$$O{=}\overset{OH}{\underset{O}{S}}{-}O{-}O{-}\overset{OH}{\underset{O}{S}}{=}O + H_2O \longrightarrow O{=}\overset{OH}{\underset{O}{S}}{-}OH + O{=}\overset{OH}{\underset{O}{S}}{-}OOH$$

[26b] K. Maroy *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985,** 231.

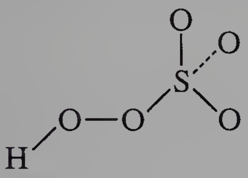
[26c] F. Minisci *et al.*, *Acc. Chem. Res.*, 1983, **16,** 27.

and also by the action of concentrated hydrogen peroxide on sulfuric acid or chlorosulfuric acid:

$$H_2O_2 + H_2SO_4 \longrightarrow HOOSO_2OH + H_2O$$

$$H_2O_2 + HSO_3Cl \longrightarrow HOOSO_2OH + HCl$$

The salts such as $KHSO_5$ and $K_5(HSO_5)_2(HSO_4)(SO_4)$ can be prepared and crystallographic study has shown that the HSO_5^- ion has the structure (13-XXVII), with three S—O distances of ~1.44 Å and one (to O_2H) of 1.63 Å.[27]



(13-XXVII)

Polysulfates. By thermal dehydration of bisulfates it is possible to make compounds containing the disulfate ion ($S_2O_7^{2-}$) in which two tetrahedra share an oxygen atom. Even the long chain $S_3O_{10}^{2-}$, $S_4O_{13}^{2-}$, and $S_5O_{16}^{2-}$ ions are known.

Halooxo Acids. The ones of principal importance are derived from sulfur.

Fluorosulfurous acid exists only as salts, which are formed by the action of SO_2 on alkali fluorides, for example,

$$KF + SO_2 \rightleftharpoons KSO_2F$$

The salts have a measurable dissociation pressure at normal temperatures but are useful and convenient mild fluorinating agents, for example,

$$(PNCl_2)_3 + 6KSO_2F \longrightarrow (PNF_2)_3 + 6KCl + 6SO_2$$

$$C_6H_5COCl + KSO_2F \longrightarrow C_6H_5COF + KCl + SO_2$$

Halogenosulfuric acids (FSO_3H, Section 3-12, $ClSO_3H$, and $BrSO_3H$) can be regarded as derived from SO_2X_2 by replacement of one halogen by OH.

Chlorosulfuric acid, a colorless fuming liquid, explosively hydrolyzed by water, forms no salts. It is made by treating SO_3 with dry HCl. Its main use is for the sulfonation of organic compounds.

Bromosulfuric acid, prepared from HBr and SO_3 in liquid SO_2 at −35°C, decomposes at its melting point (8°C) into Br_2, SO_2, and H_2SO_4.

13-14. Oxo Acids of Selenium and Tellurium

Selenous and Tellurous Acids and Salts. Selenium dioxide dissolves in water to give solutions of selenous acid, $(HO)_2SeO$, while H_2TeO_3 (structure uncertain for both solution and solid) is best obtained by hydrolysis of a

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[27] W. P. Griffith *et al., J. Chem. Soc. Chem. Commun.,* **1984,** 1574; E. O. Schlemper *et al., Acta Cryst.,* 1984, **40C,** 1781.

tetrahalide. Both are weak acids ($K_1 \approx 10^{-3}$ and $K_2 \approx 10^{-8}$). Solid selenous acid has layers of pyramidal SeO_3 groups linked by hydrogen bonds. It is a moderately strong oxidizing agent:

$$H_2SeO_3 + 4H^+ + 4e^- = Se + 3H_2O \qquad E^0 = 0.74\ V$$

Salts of the $HSeO_3^-$, $HTeO_3^-$, SeO_3^{2-}, and TeO_3^{2-} ions can be obtained by neutralization of the acids, but the SeO_3^{2-} and TeO_3^{2-} salts are often prepared by heating a mixture of the metal oxide with SeO_2 or TeO_2.

Selenic Acid (H_2SeO_4). Vigorous oxidation of selenites or fusion of selenium with potassium nitrate gives selenic acid (or its salts). The free acid forms colorless crystals (mp 57°C). It is very similar to sulfuric acid in its formation of hydrates, in acid strength, and in the properties of its salts, most of which are isomorphous with the corresponding sulfates and hydrogen sulfates. It differs mainly in being less stable, and it evolves oxygen when heated above ~200°C. It is a strong, though usually not kinetically fast, oxidizing agent:

$$SeO_4^{2-} + 4H^+ + 2e = H_2SeO_3 + H_2O \qquad E^0 = 1.15\ V$$

Telluric acid is very different from sulfuric and selenic acids and has hydrogen-bonded octahedral molecules $Te(OH)_6$ in both its cubic and monoclinic crystalline forms.[28]

The acid or its salts may be prepared by oxidation of tellurium or TeO_2 by H_2O_2, Na_2O_2, CrO_3, or other powerful oxidizing agents. It is a moderately strong, but, like selenic acid, kinetically slow oxidizing agent ($E^0 = 1.02$ V). It is a very weak dibasic acid with $K_1 \approx 10^{-7}$. Tellurates of various stoichiometries are known and most, if not all, contain TeO_6 octahedra. Examples are $K[TeO(OH)_5]\cdot H_2O$, $Ag_2[TeO_2(OH)_4]$, and Hg_3TeO_6. Tellurates such as $BaTeO_4$ that can be made by heating TeO_2 and metal oxides are *not* isostructural with sulfates. Magnesium tellurate ($MgTeO_4$) is isostructural with $MgWO_4$ and contains again TeO_6 octahedra.

13-15. Other Se and Te Compounds

In keeping with the usual group trend, selenium and even more so tellurium show cationic behavior, which manifests itself in the formation of complexes and organo derivatives. We can deal here only with a few leading examples.

Organotellurium compounds are formed in the II, IV, and VI oxidation states. RX compounds add to TeR_2 to give Te(IV) species, for example,

$$Et_2Te + EtBr \longrightarrow Et_3TeBr$$

These R_3TeX compounds may have either tetrameric or dimeric structures, as shown in Fig. 13-12. The Te···X···Te distances are quite long and are to

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[28] D. F. Mullica *et al., Acta Cryst.*, 1980, **B36**, 2565.

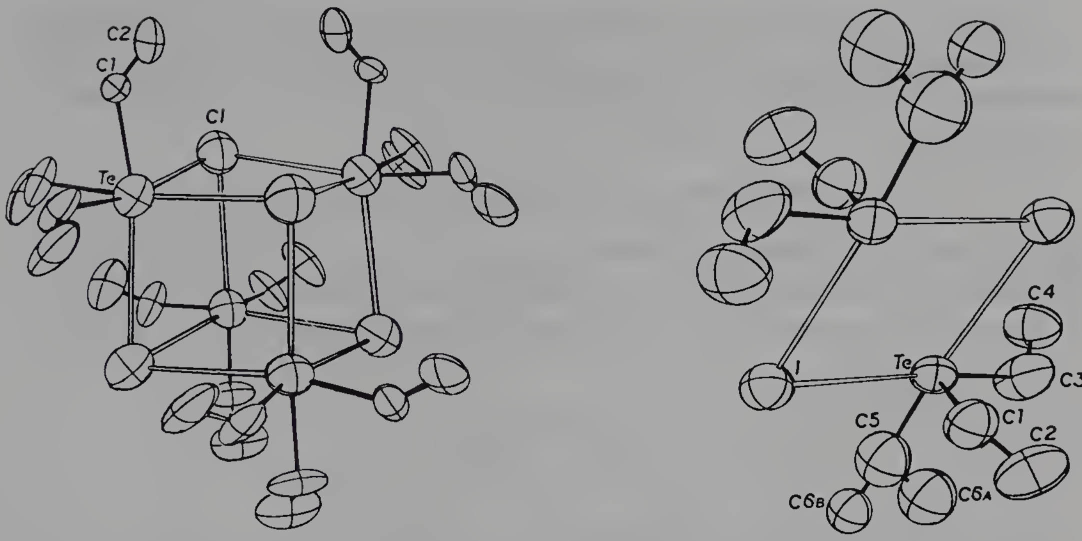

FIG. 13-12. The structures of $[Et_3TeCl]_4$ (left) and $[Et_3TeI]_2$ (right). The solid Te—C bonds are normal covalent bonds while the open bonds represent longer and weaker interactions (taken from R. K. Chadha and J. E. Drake, *J. Organomet. Chem.*, 1986, **299,** 331).

be regarded as secondary, essentially ionic interactions. In compounds like $Me_3Te^+BF_4^-$ the ionic limit is approached even more closely.

Other Te^{IV} organo compounds are of the R_2TeX_2 and $RTeX_3$ types. These also associate through secondary μ-X bonds to dimers.[29] By reaction of Ph_3TeF with XeF_2 it is oxidized to Ph_3TeF_3, which has a meridional octahedral structure.[30]

Sulfur as well as Se and Te form many compounds formally containing EX_3^+ ions, with X = F, Cl, Br, or I. In all of these, however, there are strong secondary interactions between these "cations" and the accompanying anions so that the coordination numbers of the element E, counting both primary and secondary bonds, reaches 7, 8, and even 9.[31]

Octahedral EX_6^{2-} ions of Se^{IV} and Te^{IV} with Cl^- and Br^- have long been known and have been of interest because of their octahedral structures despite the presence of a valence shell electron pair. The stereochemical inactivity of this pair of electrons indicates that they occupy the valence shell *ns* orbital. These EX_6^{2-} complexes are generally obtained by saturating aqueous solutions of EO_2 in KX with HX, and adding appropriate large cations. However, the equilibria in these solutions are very complex[32] and species such as $SeOBr_3^-$ and $TeCl_4(OH)^-$ also form.[33a]

Tellurium forms a number of complex halides in the II as well as the IV

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[29] R. I. Chadha and J. E. Drake, *J. Organomet, Chem.*, 1985, **293,** 37.

[30] A. S. Secco *et al., Inorg. Chem.*, 1986, **25,** 2125.

[31] R. J. Gillespie *et al., Inorg. Chem.*, 1986, **25,** 777.

[32] J. Milne and P. Lahie, *Inorg. Chem.*, 1985, **24,** 840.

[33a] J. Milne *et al., Inorg. Chem.*, 1983, **22,** 268, 2425.

state, some of the best known being those with thiourea (tu) or substituted thioureas as ligands. The red Te^{IV} compounds are made by treating TeO_2 in concentrated hydrochloric acid solution with, for example, tetramethylthiourea (Me_4tu):

$$TeO_2 + 4HCl + 2Me_4tu \longrightarrow trans\text{-}Te(Me_4tu)_2Cl_4 + 2H_2O$$

The structures of these compounds are octahedral with trans sulfur atoms showing no evidence (cf. TeX_6^{2-}) of stereochemical influence of the lone pair.

This ligand can further act as a reducing agent in methanolic 4 *M* HCl.

$$Te(Me_4tu)_2Cl_4 \xrightarrow{\text{heat}} Te^{II}(Me_4tu)Cl_2 + (Me_4tu)^{2+} + 2Cl^-$$

$$\underset{\text{Red}}{Te^{II}(Me_4tu)Cl_2} + Me_4tu \xrightarrow[\text{heat}]{\text{MeOH}} \underset{\text{Yellow}}{Te^{II}(Me_4tu)_2Cl_2}$$

In $TeCl_2(ethylenethiourea)_4{\cdot}2H_2O$ there is a $[TeS_4]^{2+}$ square, but for $TeCl_2(entu)_2$, also square, there can also be cis and trans isomers.

There are also phosphine compounds[33b] such as $TeP(t\text{-}Bu)_3$ and $Te[P(t\text{-}Bu)_2]_2$.

13-16. Sulfur and Sulfur Compounds as Ligands

We deal only with sulfur ligands and it may be assumed that Se or Te compounds behave similarly.

Hydrogen Sulfide. Although action of H_2S on metal species commonly gives insoluble sulfides, some complexes of SH_2 are known, although these may be readily oxidized to sulfur or deprotonated to SH^- complexes.[34]

Thus, in the presence of Eu^{2+}, to keep the system reduced, we have

$$[am_5Ru(OH_2)]^{2+} + H_2S = [am_5Ru(SH_2)]^{2+} \qquad K = 1.5 \times 10^{-3}\ M^{-1}$$

Other examples are $(CO)_5WSH_2$ and $[(CO)_5WSH]^-$, $Mo(SH)(S_2CNEt_2)_3$, and the bridged SH species $(^*Cp_2Mo)_2(\mu\text{-}S)(\mu\text{-}SH)$.

Sulfide (S_n^{2-}) Ions.[35] There are large numbers of compounds with the simple sulfide ion (S^{2-}) as a ligand comparable to O^{2-} that are mononuclear like $S{=}WCl_3$ or bi- or polynuclear with sulfur bridges. These and related species derived from polysulfide ions (S_n^{2-}) have been intensively studied in part because sulfur bridged species occur in Nature in ferredoxins and related compounds (Chapter 30).

Although sulfide species are commonly made from sulfur, alkali sulfides, or polysulfides, a useful procedure for converting oxoanions or alkoxides to

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[33b] C. H. W. Jones and R. D. Sharma, *Organometallics*, 1987, **6**, 1419.

[34] C. J. Casewit and M. R. Du Bois, *J. Am. Chem. Soc.*, 1986, **108**, 5482; J. Jordanov *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 1463; G. J. Kubas and R. R. Ryan, *J. Am. Chem. Soc.*, 1985, **107**, 6138; A. Müller *et al.*, *J. Chem. Soc. Chem. Commun.*, 1987, **35.**

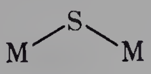
[35] A. Müller *et al.*, *Coord. Chem. Rev.*, 1982, **46**, 245.

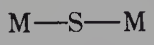
sulfides is by use of trimethylsilyl sulfide,[36] for example,

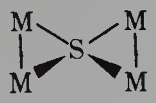
$$\mathrm{Mo_2O_7^{2-}} \xrightarrow{\mathrm{(Me_3Si)_2S}} [\mathrm{MoO_{(3-x)}\,S_x(OSiMe_3)}]^- + [\mathrm{MoS_3(OSiMe_3)}]^-$$

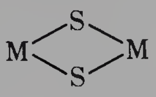
$$\mathrm{Nb(OEt)_5} \xrightarrow{\mathrm{(Me_3Si)_2S}} [\mathrm{Nb_6S_{17}}]^{4-}$$

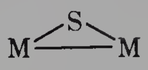
Monosulfide bridges[37] of the following types are known:

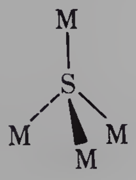


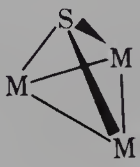


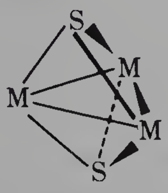


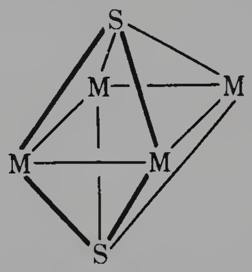






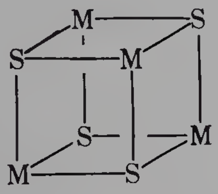






The linear bridges like linear MOM bridges (Section 12-9) have π-bonding interactions between metal $d\pi$ and sulfur $d\pi + p\pi$ orbitals. Planar units of the type M_3O do not appear to exist for sulfur.

Of special importance in ferredoxins and model compounds for ferredoxins are M_4S_4 units, which have a cubane or distorted cubane structure (13-XXVIII).

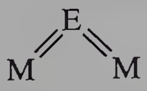


(13-XXVIII)

Examples of such compounds are $[(\eta\text{-Cp})\mathrm{MoS}]_4$ and $[(\mathrm{RS})_4\mathrm{Fe_4S_4}]^{2-}$.

There are also compounds of S, Se, and Te, formally in high oxidation states, that have cumulated multiple bonds.[38]

$M{\equiv}E{\equiv}M$



Examples are $\mathrm{Cp(CO)_2Cr{\equiv}S{\equiv}Cr(CO)_2Cp}$ made by interaction of $[\mathrm{CpCr(CO)_3}]^-$ with $\mathrm{N_3S_3Cl_3}$, and $\mathrm{(triphos)Co{=}S{=}Co(triphos)}$.

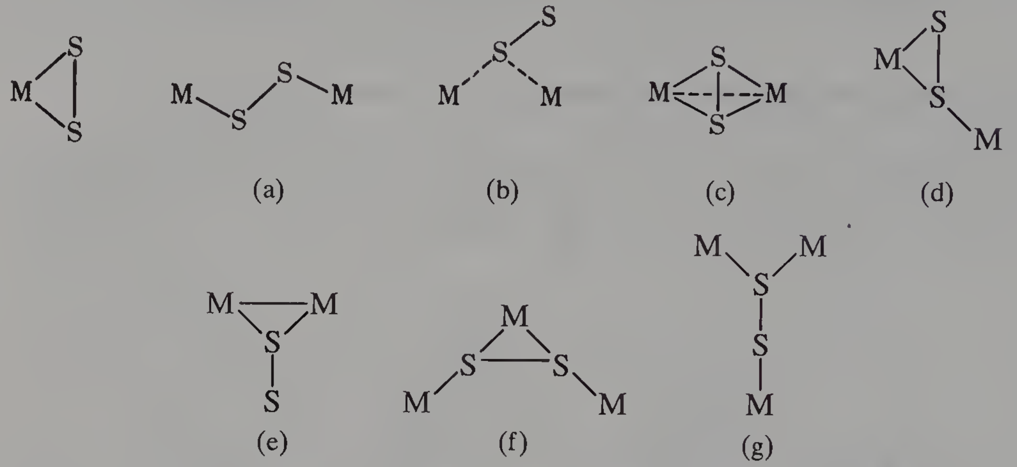
---

[36] R. H. Holm *et al.*, *Inorg. Chem.*, 1985, **24**, 1831, 2827.

[37] R. D. Adams *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 3518.

[38] W. A. Herrmann *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 3134; L. Y. Goh and T. C. W. Mak, *J. Chem. Soc. Chem. Commun.*, **1986**, 1474.

Polysulfide Ions. The disulfide ion (S_2^{2-}) can, like O_2^{2-}, coordinate either side-on[39a] or as a bridge[39b]:



There are relatively few compounds with η^2-S_2^{2-} but examples are $Os(S_2)(CO)_2(PPh_3)_2$ and $[(C_2O_4)(O)Mo(S_2)_2]^{2-}$.

Bridges of type (a) are commonest. The compound $(^*Cp)_2Cr_2S_5$ is remarkable in having three types of bridge: bent μ-S, type (c), and the only example so far of type (e), that is, μ,η^1-S_2. The higher sulfane anions S_n^{2-} commonly give puckered MS_n rings, $n = 4$ to 6 or higher.[40]

Normally made by interaction of ions or halides with alkali polysulfides

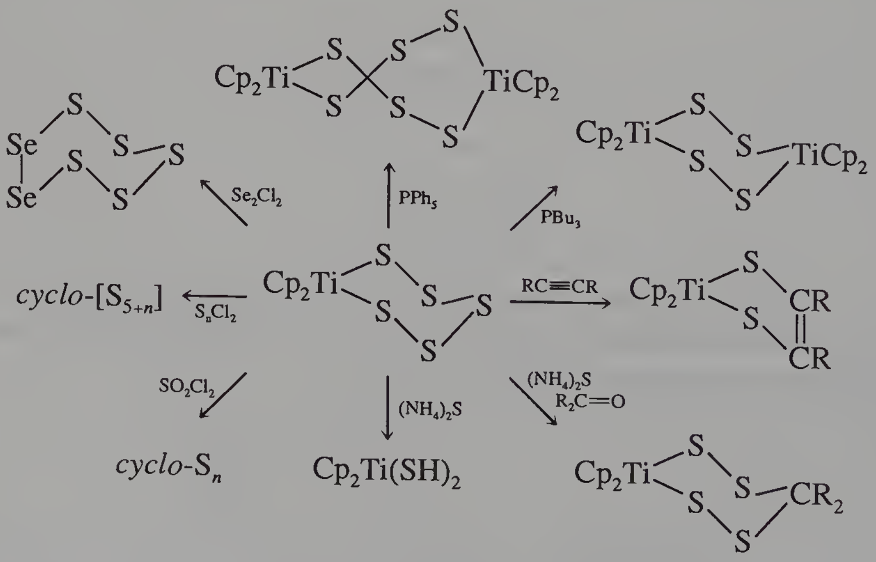


FIG. 13-13. Reactions of the sulfur ring of $(\eta^5$-$C_5H_5)_2TiS_5$ [adapted from M. Draganjac and T. B. Rauchfuss, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 742].

[39a] A. P. Ginsberg *et al., Inorg. Chem.*, 1983, **22,** 254.

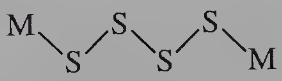
[39b] T. B. Rauchfuss *et al., Inorg. Chem.*, 1986, **25,** 1886.

[40] R. R. Ryan *et al., J. Am. Chem. Soc.*, 1986, **108,** 174; T. B. Rauchfuss *et al., Inorg. Chem.*, 1987, **26,** 2017.

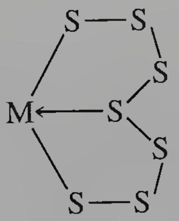
they can be formed from sulfur as in the reaction:

$$Cp_2WH_2 + 5S = Cp_2WS_4 + H_2S$$

Large numbers of *metal complex anions*[41] containing S_2^{2-}, S_3^{2-}, and S_n^{2-} have been characterized. Examples are $[Pt(S_5)_3]^{2-}$, which provides an unusual example of a chiral, purely inorganic, molecule, $[S{=}Mo(S_4)_2]^{2-}$, and $[AuS_9]^-$, which has a unique 10-membered ring. Sulfur moieties such as S_4^{2-} or S_5^{2-} can also bridge two metals[42a] as in (13-XXIX) and can bind in a η^3 mode via donation from a central S atom[42b] (13-XXX). Sulfur ring systems can undergo various reactions as shown in Fig. 13-13.

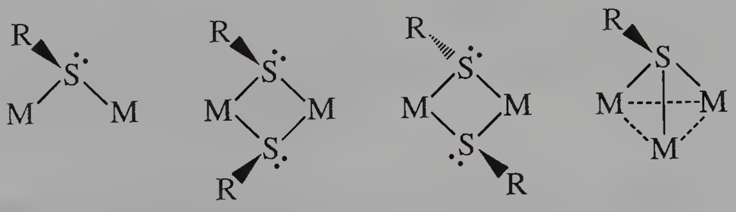


(13-XXIX)



(13-XXX)

Thiolates.[43] Many studies have been made on thiolates (RS⁻) because they have provided models for ferredoxin and related natural sulfur compounds (Chapter 30). Although unidentate groups are well characterized, bridge groups are common and for μ_2 both syn and anti isomers can be obtained; syn–anti isomerization proceeds via a bridge opening mechanism. The main types are



syn *anti*

and μ_2 species with metal–metal bonds are also known. Mononuclear thiolates are formed by ions such as Zn^{II}, Cd^{II}, Mn^{II}, and Fe^{II}, an example being $[Fe(SPh)_4]^{2-}$. Polynuclear compounds commonly have an $M_4(\mu\text{-}SR)_6$ adamantane-like cage structure.

---

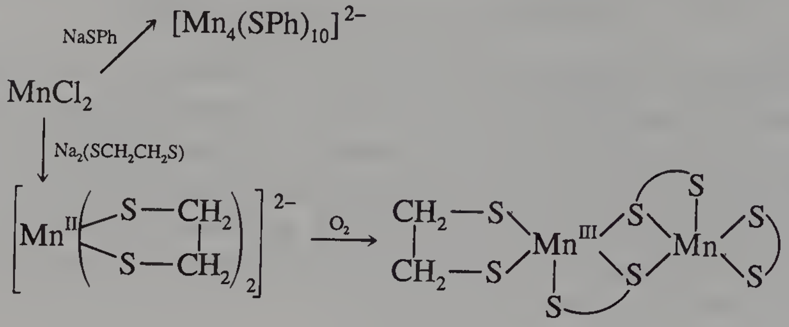
[41] G. Marbach and J. Strähle, *Angew. Chem. Int. Ed. Engl.*, 1984, **23,** 246; A. Müller *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 272.

[42a] M. E. Noble, *Inorg. Chem.*, 1986, **25,** 3311; C. Floriani *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987,** 1367.

[42b] H. Werner *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1984, **23,** 814.

[43] R. H. Holm and E. D. Simhon, *Met. Ions Biol.*, **1985,** 1; I. G. Dance, *Polyhedron*, 1986, **5,** 1037; P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76,** 121.

Thiolates are usually made by direct reactions such as

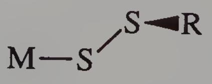


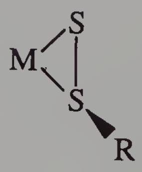
(13-XXXI)

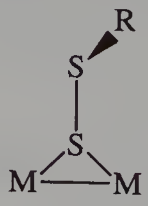
Some species, however, can be made in aqueous solution from Fe^{2+}, $S, ^{-}SCH_2CH_2OH$, and so on, by spontaneous assembly.

The *ethane-1,2-dithiolates*[44] have a variety of structures ranging from chelated octahedra as in $[Ti(S_2C_2H_4)_3]^{2-}$, tetrahedra in $[Co(S_2C_2H_4)_2]^{2-}$, or planar in $[Cr(S_2C_2H_4)_2]^{2-}$, to various types of bridges, one example being the manganese(III) complex (13-XXXI). Thiols such as $HSCH_2CO_2Et$ can give more complicated species such as $Ni_8(SCH_2CO_2Et)_{16}$.[45a] Examples of bulky thiolates are —S*t*-Bu and —$SC(SiMe_3)_3$.[45b] A tripod ligand[45c] is $Me_3C(CH_2S)_3^{3-}$.

Finally, thiolates (RSS—) can give species with the groupings[46]:







Disulfides (RSSR). Disulfides commonly undergo cleavage to give SR compounds, but an intact, bridging, disulfide ligand is found in $(CO)_3Re(\mu\text{-}Br)_2(\mu\text{-}S_2Ph_2)Re(CO)_3$.

Thioethers.[47] Thioethers (R_2S) are relatively weak donors, but stronger binding occurs with chelating or macrocyclic thioethers such as the following or thio analogues of crown ethers such as 24-C-6 or 18-C-6.[48]

[44] R. H. Holm *et al., Inorg. Chem.*, 1986, **25,** 428, 2979.

[45a] I. G. Dance *et al., Inorg. Chem.*, 1985, **24,** 1201.

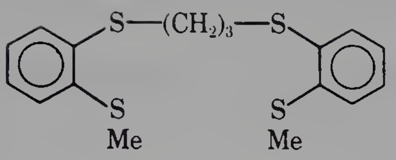
[45b] P. B. Hitchcock *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 1776.

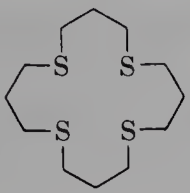
[45c] J. Devilliers *et al., Inorg. Chem.*, 1987, **26,** 1502.

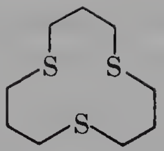
[46] J. E. Hoots and T. B. Rauchfuss, *Inorg. Chem.*, 1983, **22,** 2806.

[47] S. G. Murray and F. R. Hartley, *Chem. Rev.*, **1981,** 365 (R_2S, Se, Te).

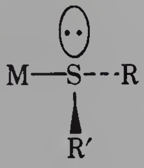
[48] J. H. Enemark *et al., Inorg. Chem.*, 1986, **25,** 3154; M. Schröder *et al., J. Chem. Soc. Chem. Commun.*, **1987,** 118; S. R. Cooper *et al., Inorg. Chem.*, 1987, **26,** 2009; *J. Am. Chem.Soc.*, 1987, **109,** 4328.



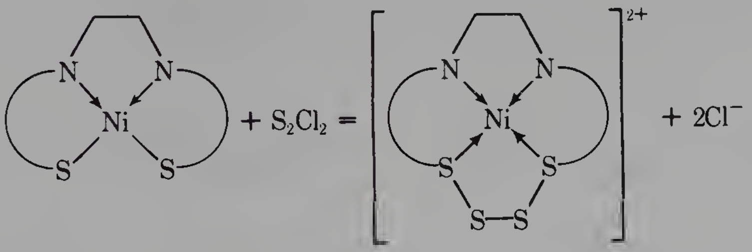




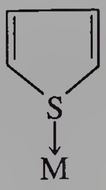
Thioethers have two lone pairs so that when one is involved in metal binding, we have potential for inversion as in NR_3 (Section 10-2) and also chirality:

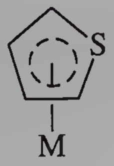


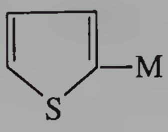
Inversion can be studied by nmr and the barriers determined in compounds such as $Cl_2Pt(SR_2)_2$; for sulfur these are in the range of 51 to 56 kJ mol^{-1} and in the corresponding R_2Se compounds, 60 to 66 kJ mol^{-1}. With chelating and bridging dithioethers, the stereochemical nonrigidity can be quite complicated.[49] A way of making more complex thioether compounds is the following:



Heterocyclics such as thiophen and related compounds[50] can be S-bonded, π-bonded (Chapter 26), or metallated:







Sulfur Oxides[51]

Lower Oxides. Despite the instability of SO, S_2O, and S_2O_2, all can be trapped as ligands. Sulfur monoxide gives bent MSO groups and in addition can have μ_2, μ,η^2, and μ_3 bridging modes.

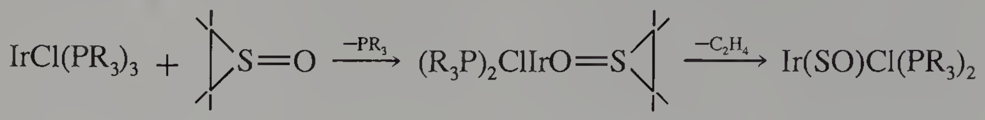
---

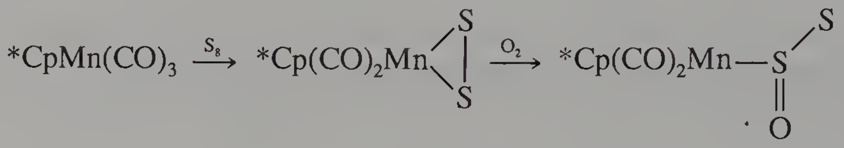
[49] E. W. Abel *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 96; *Progr. Inorg. Chem.*, 1984, **32,** 1.

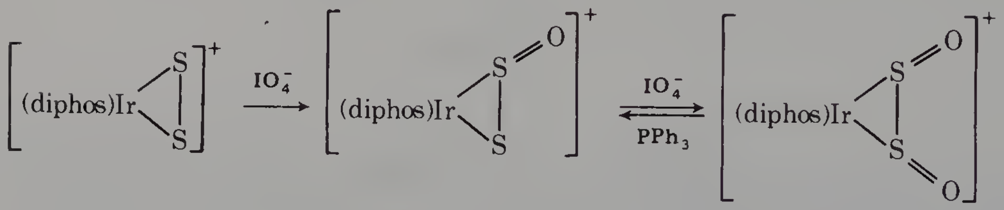
[50] G. J. Kubas *et al., J. Am. Chem. Soc.*, 1986, **108,** 2294; G. H. Spies and R. J. Angelici, *Organometallics*, 1987, **6,** 1897; T. B. Rauchfuss *et al., J. Am. Chem. Soc.*, 1984, **106,** 5379.

[51] W. A. Schenk, *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 98 (review).

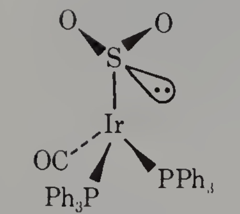
Some synthetic procedures for these complexes are the following:



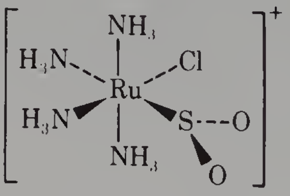




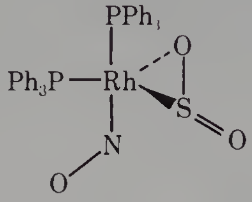
Sulfur Dioxide.[52] The dioxide can be bound in several ways:



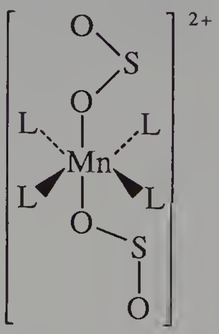
Pyramidal M—SO2



Planar M—SO2

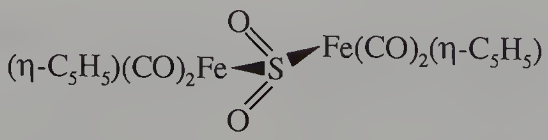


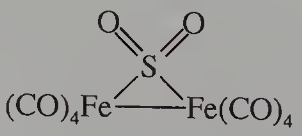
η², Side-bound

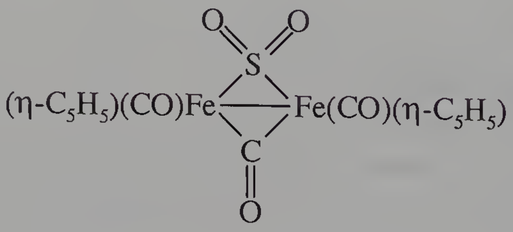


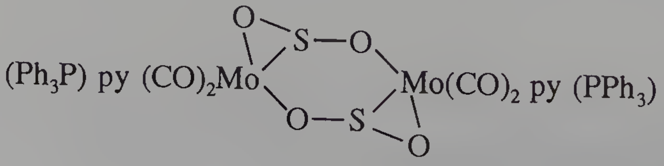
O-bound(L = OPPh3)

Examples of bridged species are









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[52] G. van Koten *et al.*, *Organometallics*, 1986, **5**, 219; D. M. P. Mingos and R. W. M. Wardle, *J. Chem. Soc. Dalton Trans.*, **1986,** 73; G. J. Kubas and R. R. Ryan, *Polyhedron*, 1986, **5,** 473.

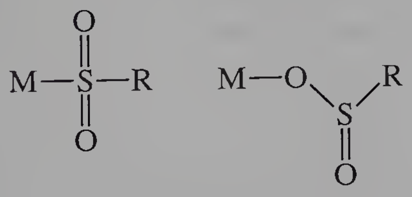
The η^1 pyramidal geometry is found only when the ML_n unit acts as a σ base while η^2 bonding is favored by π donation from ML_n. A unique η^1–η^2 isomerization occurs in $Mo(CO)_2(PPh_3)_2L(SO_2)$ that depends on the nature of ligand L.[53] A rare example of O-bonded SO_2 is *trans*-$[Mn(OPPh_3)_4(SO_2)_2]I_2$ but O-bonded complexes of main group metals like F_5SbOSO are known (see later).

In the compounds such as $[am_4ClRuSO_2]^+$ and $CpRh(C_2H_4)SO_2$ that have planar M—SO_2 groups, there is evidently some M—S π bonding with S acting as σ donor and π acceptor. The bridged molecules with M—M bonds can of course be regarded as derivatives of sulfuryl dichloride (SO_2Cl_2) rather than of SO_2. Similarly, what can be considered to be a bound sulfinate anion is obtained by the action of SO_2 on $CpFe(CO)_2K$ to give the anion $CpFe(CO)_2SO_2^-$.

Finally, cations "solvated" by SO_2 can be obtained for Mn, Fe, Co, Ni, Cu, Zn, and Mg by oxidation of the metal by AsF_5 in liquid SO_2 of the type $[Fe(SO_2)_2(AsF_6)_2]_2$. The magnesium compound has bent *trans*-MgOSO groups with the octahedral coordination completed by F atoms in Mg—F—As bridges.[54]

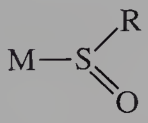
Sulfur Oxoanions. As noted in Section 13-16, *sulfites* can be S or O bonded. Other similar species in which R may be alkyl or aryl are

Sulfinate



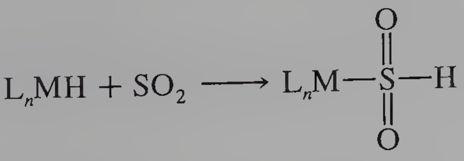
$$\mathrm{M-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-R}$$

Sulfenate



Similar species with alkoxo (RO) groups are known.

The unsubstituted sulfinate (L_nMSO_2H) can be obtained in certain cases:



$$\mathrm{L_nMH + SO_2 \longrightarrow L_nM-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-H}$$

but the reaction can go further to give L_nMS and H_2O. Thus $CpW(CO)_3H$ reacts with excess SO_2 in MeCN to give $[CpW(CO)_3]_2$ and $[CpW(CO)_3]_2S$.[55] However, the corresponding pentamethylcyclopentadienyl gives a unique SO_2

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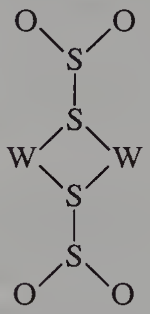
[53] G. J. Kubas *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 1883.

[54] R. Mews *et al.*, *Z. Naturforsch.*, 1982, **37B**, 1116.

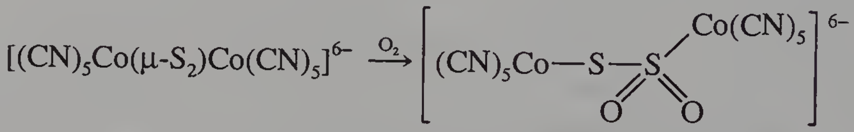
[55] G. J. Kubas *et al.*, *Organometallics* 1985, **4**, 419.

adduct of a bridged sulfide with the group:



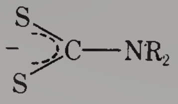
Sulfinates are also made by insertion of SO_2 into M—C bonds (Chapter 27).

Thiosulfate as a bridge has been made by oxidation of a μ-S_2 species[56]:

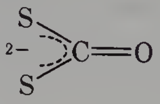


$$[(CN)_5Co(\mu\text{-}S_2)Co(CN)_5]^{6-} \xrightarrow{O_2} \left[(CN)_5Co{-}S{-}S(O_2){-}Co(CN)_5\right]^{6-}$$

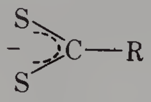
Dithiocarbamates and Related Anions (1,1-Dithiolates).[57] There is a wide variety of compounds of the following anions:



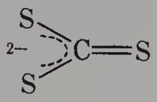
Dithiocarbamate



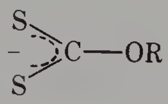
Dithiocarbonate



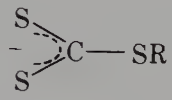
Dithiocarboxylate



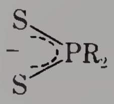
Trithiocarbonate



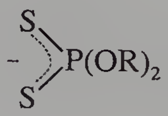
Xanthate



Thioxanthate

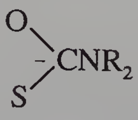


Dithiophosphinate

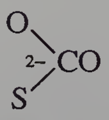


Dialkyldithiophosphate

Each of these ions may have a corresponding monothio analogue that is S,O bound, for example,



Thiocarbamate



Thiocarbonate

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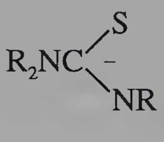
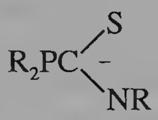
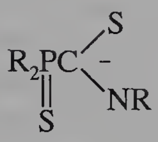
[56] W. P. Schaefer *et al., J. Am. Chem. Soc.*, 1982, **104,** 3382.

[57] A. M. Bond and R. L. Martin, *Coord. Chem. Rev.*, 1984, **54,** 23; B. J. McCormick *et al., Coord. Chem. Rev.*, 1984, **54,** 99; R. C. Mehrotra *et al., Coord. Chem. Rev.*, 1984, **55,** 207; F. P. McCullough *et al., Adv. Inorg. Chem. Radiochem.*, 1980, **23,** 211.

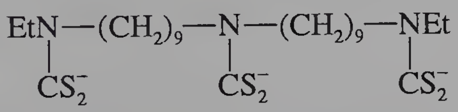
Related species[58] are







where the phosphorus compounds can also donate via the P atom. There are also linear and macrocyclic dithiocarbamates that have high affinity for UO_2^{2+}; one example is

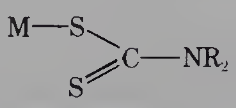


$$\underset{\displaystyle CS_2^-}{EtN}—(CH_2)_9—\underset{\displaystyle CS_2^-}{N}—(CH_2)_9—\underset{\displaystyle CS_2^-}{NEt}$$

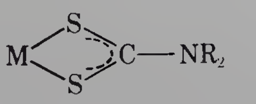
The most important are dithiocarbamate and dithiophosphinate complexes; the former are used as fungicides and for solvent extraction[59] and the latter as high pressure lubricants. Dithiocarbamates stabilize high oxidation states as in $[Fe^{IV}(dtc)_3]^+$ or $[Ni^{IV}(dtc)_3]^+$. Although dithiocarbamates are usually made from sodium salts such as NaS_2CNMe_2 or by oxidations using thiuram disulfides, they can also be made by insertion reactions (Chapter 27) of CS_2 with dialkylamides, for example,

$$Ti(NR_2)_4 + 4CS_2 \longrightarrow Ti(S_2CNR_2)_4$$

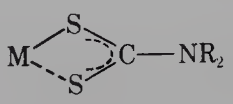
The types of bonding are



Unidentate

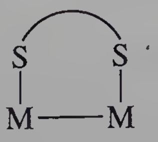


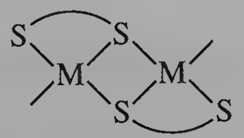
Symmetrical chelate

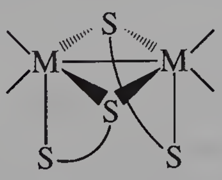


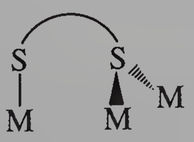
Unsymmetrical chelate

The bridging $^-S_2CNR_2$ groups (shown diagrammatically) can have several forms

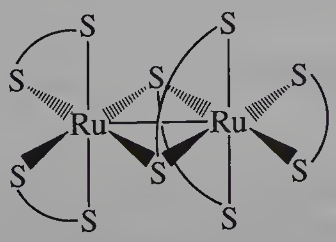




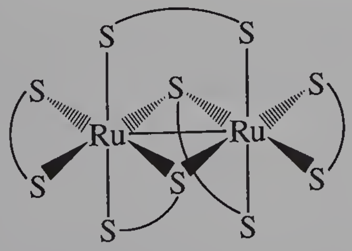




The compound $[Ru_2(S_2CNEt_2)_5]^+$, for example, has two isomers with chelate and different types of bridging dithiocarbamate:



and



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[58] H. P. M. M. Ambrosius *et al.*, *Inorg. Chem.*, 1984, **23**, 2672, 2678.

[59] R. J. Magee, *Rev. Anal. Chem.*, 1985, **8**, 5.

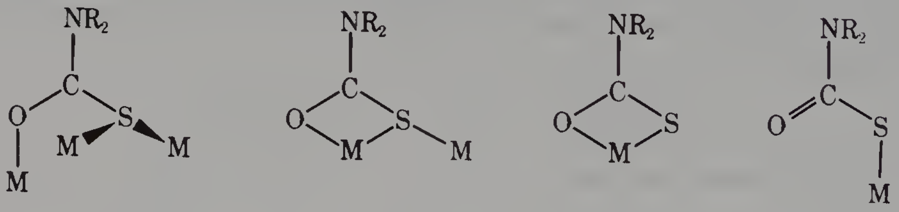
The unidentate and chelate types can be distinguished by ir[60] and nmr spectra.[61a,b] The latter, particularly for chelate ligands, are commonly temperature dependent due to dynamic processes, involving nonequivalence of the R groups resulting from restricted rotation about the C—N bond. The trischelates M dtc$_3$, have intramolecular, metal-centered dynamic processes proceeding via a trigonal twist mechanism.[61a]

The major resonance forms are

and the extent of π bonding in the N—C bond can be correlated with ^{13}C nmr data.[61b]

The unsymmetrical-type dithiocarbamates are found for Sn^{IV} and a number of other metals.[62]

Thiocarbamates are similar, with bonding modes such as:



and chelates have similar nmr behavior to the dithiocarbamates.[63]

The *dithiophosphinate* or diorganophosphinodithioate ligands generally prefer to form four-membered chelate rings as in square $Ni(S_2PMe_2)_4$, but some bridged species, such as $[Zn(S_2PEt_2)_2]_2$ are known.[64]

Another similar type of ligand is *phosphoniodithiocarboxylate,* (R_3P^+-CS_2^-) and complexes may be obtained by insertion reactions (cf. dithiocarbonates)[65]:

$$[Cu(PEt_3)_3]^+ + CS_2 \longrightarrow [(Et_3P)_2CuS_2CPEt_3]^+$$

Trithiocarbonate (CS_3^{2-}) can give η^2 or μ complexes.[66]

Tetrathiometallate and Related Anions.[67] There is an extensive chemistry of complexes of ions such as MoS_4^{2-}, $WO_2S_2^{2-}$, WOS_3^{2-}, ReS_4^{2-}, or CuS_4^{2-}.

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[60] R. Keller *et al., Inorg. Chim. Acta,* 1984, **84,** 233.

[61a] R. C. Fay *et al., Inorg. Chem.,* 1984, **23,** 1079.

[61b] J. G. M. van der Linden *et al., Inorg. Chem.,* 1979, **18,** 3251.

[62] J. J. Zuckerman *et al., Organometallics,* 1985, **4,** 2074.

[63] R. C. Fay *et al., Inorg. Chem.,* 1983, **22,** 3368.

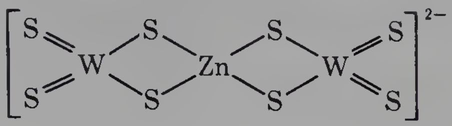
[64] J. M. Burlich *et al., Inorg. Chem.,* 1983, **22,** 1306.

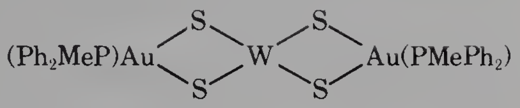
[65] V. Riera *et al., J. Chem. Soc. Chem. Commun.,* **1987,** 472.

[66] C. Bianchini *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 2419.

[67] A. Müller *et al., Chimia,* 1986, **40,** 50; *Z. Anorg. Allg. Chem.,* 1986, **533,** 125; L. D. Rosenhein and J. W. McDonald *Inorg. Chem.,* 1987, **26,** 3414; K. S. Liang *et al., Inorg. Chem.,* 1987, **26,** 1422.

Two typical examples are

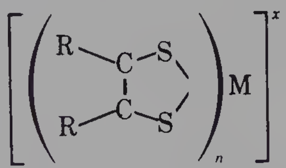




The MoS_4^{2-} ion is of special interest because of the relation to ferredoxin type species (Chapter 30) and ions such as $[Mo_2Fe_6S_6(SEt)_8]^{3-}$ may be models for the Mo—Fe complex in nitrogenase.

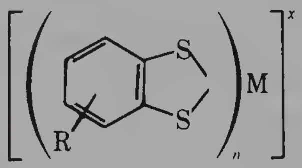
Ions like FeS_2^- in $KFeS_2$ or PdS_2^{2-} in Na_2PdS_2 have chains of tetrahedral or square metal, respectively, with double sulfur bridges.[68]

1,2-Dithiolenes.[69] The 1,2-dithiolenes are a class of ligands that form a wide variety of compounds with metals in apparently many different oxidation states. This is more apparent than real because with ligands having extended π systems, delocalization of electrons onto the ligands occurs. It is very characteristic of dithiolene-type ligands (13-XXXII) and related classes (13-XXXIII), (13-XXXIV), and (13-XXXV)



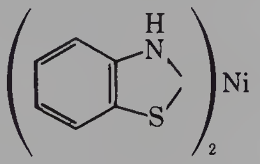
R = H, alkyl, C_6H_5, CF_3, CN
$n = 2; x = 0, -1, -2$
$n = 3; x = 0, -1, -2, -3$

(13-XXXII)

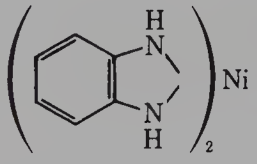


R = alkyl
$n = 2; x = 0, -1, -2$

(13-XXXIII)



(13-XXXIV)



(13-XXXV)

that reversible oxidation–reduction sequences between structurally similar molecules differing only in their electron populations can occur. Examples are

$$\{Ni[S_2C_2(CN)_2]_2\} \underset{-e}{\overset{+e}{\rightleftharpoons}} \{Ni[S_2C_2(CN)_2]_2\}^- \underset{-e}{\overset{+e}{\rightleftharpoons}} \{Ni[S_2C_2(CN)_2]_2\}^{2-}$$

$$[CoL_2]_2^0 \underset{-e}{\overset{+e}{\rightleftharpoons}} [CoL_2]_2^{1-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [CoL_2]_2^{2-} \underset{-2e}{\overset{+2e}{\rightleftharpoons}} 2[CoL_2]^{2-} \qquad [L = S_2C_2(CF_3)_2]$$

$$[CrL_3]^0 \underset{-e}{\overset{+e}{\rightleftharpoons}} [CrL_3]^{1-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [CrL_3]^{2-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [CrL_3]^{3-} \qquad [L = S_2C_2(CN)_2]$$

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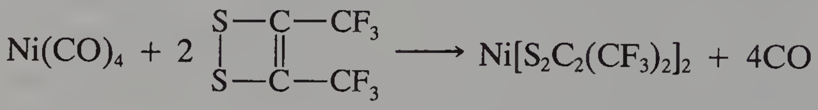
[68] J. Silvestre and R. Hoffmann, *Inorg. Chem.*, 1985, **24,** 4108.

[69] D. T. Sawyer *et al., J. Am. Chem. Soc.*, 1986, **108,** 936; J. Mahadevan, *J. Cryst. Spectr. Res.*, 1986, **16,** 347; S. Alvarez *et al., J. Am. Chem. Soc.*, 1985, **107,** 6253; T. B. Rauchfuss *et al., J. Am. Chem. Soc.*, 1986, **108,** 3114; R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22,** 303.

A few representative syntheses of dithiolene complexes are the following:

$$\mathrm{NiCl_2 + Na_2S_2C_2(CN)_2 \xrightarrow{Et_4N^+} (Et_4N)_2\{Ni[S_2C_2(CN)_2]_2\}}$$

$$\mathrm{Ni(CO)_4 + 2PhC{\equiv}CPh + 4S \longrightarrow Ni(S_2C_2Ph_2)_2 + 4CO}$$



$$\mathrm{Ni(CO)_4 + 2\ S_2C_2(CF_3)_2 \longrightarrow Ni[S_2C_2(CF_3)_2]_2 + 4CO}$$

$$\mathrm{Fe_2S_{12}^{2-} + MeO_2CC{\equiv}CCO_2Me \longrightarrow Fe_2[S_2C_2(CO_2Me)_2]_4^{2-}}$$

For complexes containing only dithiolene ligands, four types of structure have been observed (Fig. 13-14). The planar D_{2h} structure is found for a majority of the structurally characterized bis complexes. The second structure type, observed in the remaining bis complexes, is dimeric, each metal atom being five-coordinate. The metal atoms are significantly displaced from the planes of the dithiolene ligands (by 0.2–0.4 Å), but the bridging linkages are relatively weak. The third type of structure is one having trigonal prismatic D_{3h} coordination geometry. The interligand S---S distances in this structure are rather short (3.0–3.1 Å), indicative of weak interactions directly between the sulfur atoms; this structure is found only in a few of the more highly oxidized or neutral tris complexes, one example being $\mathrm{Mo[Se_2C_2(CF_3)_2]_3}$.

In addition to "pure" dithiolene complexes, compounds are known with additional ligands such as CO, η-C_5H_5, and olefins.

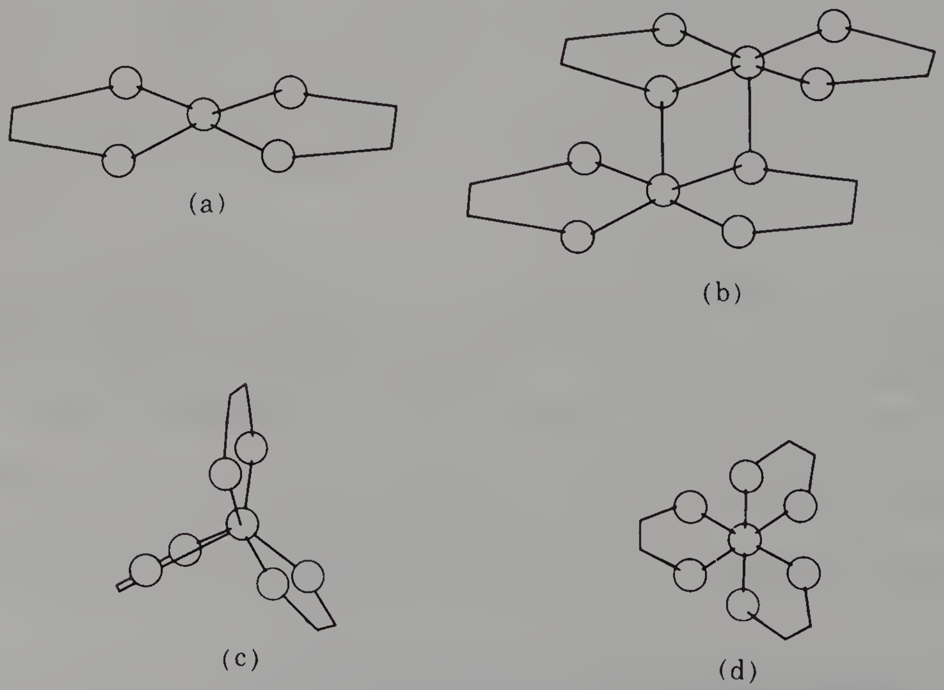
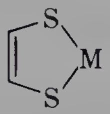
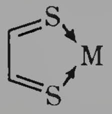


FIG. 13-14. The four basic structure types for "pure" dithiolene complexes: (a) square coordination (D_{2h} molecular symmetry); (b) five-coordinate dimer: (c) trigonal prismatic coordination (D_{3h} symmetry); (d) octahedral coordination (D_3 symmetry).

The electronic structures of the 1,2-dithiolene complexes have provoked a great deal of controversy. The ring system involved can be written in two extreme forms:

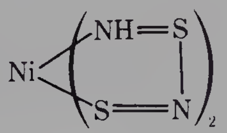


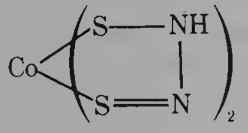


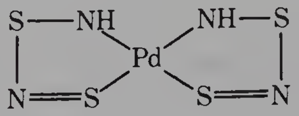
The formal oxidation number of the metal differs by two in these two cases. In molecular orbital terms the problem is one of the extent to which electrons are in metal *d* orbitals or delocalized over the ligand. Undoubtedly, in general, considerable delocalization occurs, which accounts for the ability of these complexes to exist with such a range of electron populations. The exact specification of orbital populations in any given case is a difficult and subtle question that we shall not discuss in detail here. The same problem arises for quinone and diimine complexes.

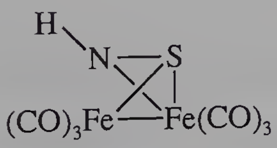
Dithioacetylacetonate(1,3-dithiolate).[70] The sulfur analogue of acetylacetone does not exist in the free state but occurs as the inert dimer tetrathiaadamantane. However, complexes of the anion (sacsac) can be made by template or ligand trapping reactions of diketones and metal ions in the presence of H_2S.[71]

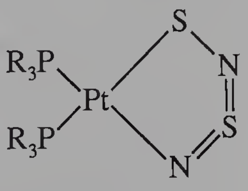
Other Sulfur Ligands. *Sulfur nitrides*[72] give a variety of complexes with NS groups by interaction of N_4S_4, S_7NH, and similar compounds with metal carbonyls or halides. Where hydroxylic solvents are used, hydrogen abstraction occurs to give complexes with N—H bonds. Some examples of the varied types of compounds are the following:











The *thiocyanate* ion is ambidentate but commonly S-bonded with heavier metals. The *sulfides* of P and As such as P_4S_3 and As_2S can act as ligands.[73]

Thiocarboxamido ligands (R_2NCS) can be unidentate through sulfur, η^2-bidentate through carbon and sulfur (cf. CS_2, Section 8-12), or bridging.

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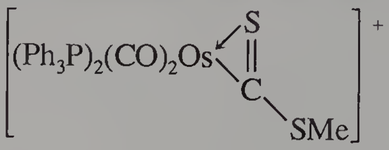
[70] P. D. W. Boy *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 887.

[71] See, for example, G. A. Heath and J. H. Leslie, *J. Chem. Soc. Dalton Trans.,* **1983,** 1587.

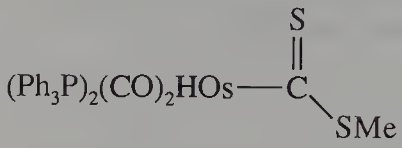
[72] P. F. Kelly and J. D. Woollins, *Polyhedron,* 1986, **5,** 607; T. Chivers and F. Edelmann, *Polyhedron,* 1986, **5,** 1661.

[73] See, for example, M. Di Vaira *et al., Inorg. Chim. Acta,* 1984, **83,** 161.

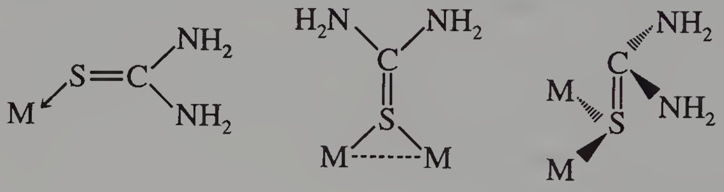
Similar complexes of *dithio esters* can be η^1 or η^2 as in



and



There are numerous compounds with S═C and S═P bonds, as well as others, that bond through sulfur. Most important perhaps are *thiourea* and substituted thioureas. These can be bound as follows:



Tertiary *phosphine sulfides* ($R_3P{=}S$)[74a] can be bound with S unidentate or bridging. *Sulfur ylids,*[74b] sulfines, $R^1R^2C{=}S{=}O$,[75] and *sulfonium ions* (R_3S^+)[76] also act as ligands. *Thiosemicarbazones,* $H_2NHC(S)N(H)N{=}CR_1R_2$, and *thiosemicarbazide,* $H_2NC(S)N(H)NH_2$, usually chelate by both N and S. *Tetrathiosquarate*[77] ($C_4S_4^{2-}$) and tetrathiooxalate[78] also act as ligands.

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[75] M. Herberhold and A. F. Hill, *J. Organomet. Chem.*, 1986, **309,** C29.
[76] R. D. Adams *et al., J. Am. Chem. Soc.*, 1983, **105,** 4319.
[77] W. Beck *et al., Chem. Ber.*, 1986, **119,** 1217.
[78] C. Bianchini *et al., J. Am. Chem. Soc.*, 1987, **109,** 185.

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Chapter Fourteen

The Group VIIA(17) Elements: F, Cl, Br, I, At

GENERAL REMARKS

14-1. Electronic Structures and Valences

Some important properties of the Group VIIA(17) elements (halogens) are given in Table 14-1. Since the atoms are only one electron short of the noble gas configuration, the elements readily form the anion X^- or a single covalent bond. Their chemistries are essentially completely nonmetallic, and in general, the properties of the elements and their compounds change progressively with increasing size. As in other groups there is a much greater change between the first-row element fluorine and the second-row element chlorine than between other pairs, but with the exception of the Li–Cs group there are closer similarities within the group than in any other in the Periodic Table.

The high reactivity of fluorine results from a combination of the low F—F bond energy and the high strength of bonds from fluorine to other atoms. The small size and high electronegativity of the F atom account for many of the other differences between fluorine and the other halogens.

The coordination number of the halogens in the -1 state is normally only 1, but exceptions are found in HXH^+ cations, in polyhalide ions such as $FClF^-$ and I_3^-, and when X^- ions occur as bridging ligands where the coordination number is 2. There are also triply bridging X^- ions in some metal atom cluster compounds (Chapter 23).

Positive *formal* oxidation numbers and higher coordination numbers may be assigned to the central halogen atoms in several classes of compounds such as the halogen fluorides (e.g., ClF_3, ClF_5, BrF_5, and IF_7), oxo compounds (e.g., Cl_2O_7 or I_2O_5), oxofluorides (e.g., F_3BrO, or FIO_3), and a few other cases such as CF_3IF_2. It should be remembered that such formal oxidation numbers, though pragmatically useful in certain ways, bear no relation to actual charges.

For fluorine there is little evidence for positive behavior even in the formal sense. In oxygen fluorides the F atom is probably somewhat negative with

TABLE 14-1
Some Properties of the Halogen Atoms and Molecules

	F	Cl	Br	I	At
At. No.	9	17	35	53	85
At. Wt.	19.00	35.45	79.90	126.90	(210)[a]
Stable isotopes	^{19}F	^{35}Cl,^{37}Cl	^{79}Br,^{81}Br	^{127}I	None
Valence shell	$2s^22p^5$	$3s^23p^5$	$4s^24p^5$	$5s^25p^5$	$6s^26p^5$
mp (°C)	−218.6	−101.0	−7.3	113.6[b]	
bp (°C)	−188.1	−34.9	59.5	185.2[b]	
X—X distance (Å)	1.43	1.99	2.28	2.66	
Covalent radius (Å)	0.64	0.99	1.14	1.33	
van der Waals radius (Å)	1.35	1.80	1.95	2.15	
Radius of X^- (Å)	1.19	1.67	1.82	2.06	
ΔH_{diss} of X_2 (kJ mol^{-1})	158	242	193	151	
Electron attachment enthalpy (kJ mol^{-1})	−328	−349	−325	−295	−270 ± 20
Atomic ionization enthalpy (kJ mol^{-1})	1681	1255	1140	1008	

[a] Longest lived isotope.
[b] Vapor pressure is 90.5 Torr at 113.6°C.

respect to oxygen; whereas in ClF evidence from chlorine nuclear quadrupole coupling shows that the actual charge distribution involves partial positive charge on Cl.

Bond polarities in other halogen compounds indicate the importance of forms such as I^+Cl^- in ICl or I^+CN^- in ICN. In general, when a halogen atom forms a bond to another atom or group more electronegative than itself, the bond will be polar with a partial positive charge on the halogen. Examples are the Cl atoms in SF_5OCl, CF_3OCl, FSO_2OCl, and O_3ClOCl, the bromine atoms in O_3ClOBr and FSO_2OBr, and the iodine atom in $I(NO_3)_3$.

Even for the heaviest member of the group, astatine, there is little evidence for any unambiguously "metallic" behavior.

THE ELEMENTS

Because of their reactivity, none of the halogens occurs in the elemental state in Nature. The elements all consist of nonpolar diatomic molecules between which the forces are of the same character as those between noble gas atoms. The trends in melting and boiling points are therefore qualitatively the same for the two groups of elements. In each case the dominant factor is the increasing magnitude of van der Waals forces as the size and polarizability of the atoms or molecules increase. The colors of both the elements and their compounds increase with increasing atomic number as absorption bands move to longer wavelengths.

14-2. Fluorine

Fluorine is more abundant in the earth's crust (0.065%) than chlorine (0.055%) and forms concentrated deposits in such minerals as fluorite (or fluorspar), CaF_2, cryolite, Na_3AlF_6, and fluorapatite, $3Ca_3(PO_4)_2Ca(F,Cl)_2$.

Only the isotope ^{19}F is found in Nature but ^{18}F with a half-life of 109.7 m is available and can be used, albeit with difficulty, as a tracer.[1]

The estimated standard potential of fluorine ($E^0 = +2.85$ V) clearly indicates why early attempts to prepare the element by electrolytic methods in aqueous solution suitable for chlorine ($E^0 = +1.36$ V) failed. The element was first isolated in 1886 by Moissan, who pioneered the chemistry of fluorine and its compounds. The yellow[2a] gas is obtained by electrolysis of HF. Although anhydrous HF is a poor conductor, the addition of anhydrous KF gives conducting solutions. The most commonly used electrolytes are KF·2–3HF, which is molten at 70 to 100°C, and KF—HF, which is molten at 150 to 270°C. When the melting point begins to be too high because of HF consumption, the electrolyte can be regenerated by resaturation with HF from a storage tank. There have been many designs for fluorine cells; these are constructed of steel, copper, or Monel metal, which become coated with an unreactive layer of fluoride.

Steel or copper cathodes with ungraphitized carbon anodes are used. Although fluorine is often handled in metal apparatus, it can be handled in the laboratory in glass apparatus provided traces of HF, which attack glass rapidly, are removed by passing the gas through sodium or potassium fluoride with which HF forms the bifluorides MHF_2.

Fluorine is the chemically most reactive of all the elements and combines directly at ordinary or elevated temperatures with all the elements other than nitrogen, oxygen, and the lighter noble gases, often with extreme vigor. It also attacks many other compounds, particularly organic compounds, breaking them down to fluorides; organic materials often inflame and burn in the gas.

Purely chemical (as opposed to electrochemical) synthesis of F_2 is extremely difficult because decomposition of fluorine compounds to liberate F_2 is normally very unfavorable thermodynamically. Recently,[2b] the following reaction has been shown to afford the first practicable chemical synthesis:

$$K_2MnF_6 + 2SbF_5 \longrightarrow 2KSbF_6 + MnF_3 + \tfrac{1}{2}F_2$$

The underlying principle is that the stronger Lewis acid (SbF_5) can displace the weaker one (MnF_4) from its salt; the weaker Lewis acid, however, is unstable and decomposes once liberated.

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[1] J. M. Winfield, *J. Fluorine Chem.*, 1980, **16,** 1; G. Schrobilgen *et al., J. Chem. Soc. Chem. Commun.* **1981,** 198.

[2a] A. J. Edwards *et al., J. Fluorine Chem.*, 1987, **34,** 471.

[2b] K. O. Christe, *Inorg. Chem.*, 1986, **25,** 3722; *Chem. Eng. News,* 1987, March 2, p. 5.

The low F—F bond energy, which is so important in the high reactivity of F_2 (in both the kinetic and thermodynamic senses), is best explained by the small size and high nuclear charge of the fluorine atom, which causes decreased overlap of the bonding orbitals and increased repulsion between the nonbonding orbitals on the two fluorine atoms. It should be noted that the O—O bond in peroxides and the N—N bond in hydrazines are also relatively weak for similar reasons. The importance of repulsion between nonbonding electrons on the two F atoms in F_2 is evident when we note (cf. Table 14-1) that for the other halogens the X—X distance in X_2 molecules is essentially twice the covalent radius, whereas for F_2 the internuclear distance 1.43 Å is considerably larger than that (1.28 Å). This is because in, for example, an X_3CF molecule there are no nonbonding electrons on the atom to which F is bonded as compared to the situation in F_2. For the other halogens the X—X distances are large enough that lone-pair to lone-pair repulsions are much less important.

14-3. Chlorine

Chlorine occurs in Nature mainly as sodium chloride in seawater and in various inland salt lakes, and as solid deposits originating presumably from the prehistoric evaporation of salt lakes. Chlorine is prepared industrially mainly by electrolysis of brine:

$$Na^+ + Cl^- + H_2O \longrightarrow Na^+ + OH^- + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2$$

The traditional mercury cells, which pose an environmental hazard because of mercury loss, are being replaced by newer membrane cells.[3] Another process that finds limited use is the Deacon process, based on the reaction:

$$2HCl + \tfrac{1}{2}O_2 = Cl_2 + H_2O$$

Though the equilibrium is unfavorable, it may be shifted by removing the water with H_2SO_4 or the Cl_2 as dichloroethane, which can then be pyrolyzed to vinyl chloride plus recyclable HCl.

Chlorine and hydrogen can also be recovered by electrolysis of warm 22% hydrochloric acid, which is obtained as a by-product in chlorination processes.

Chlorine is a greenish gas. It is moderately soluble in water, with which it reacts (Section 14-13). When chlorine is passed into dilute solutions of $CaCl_2$ at 0°C, feathery crystals of *chlorine hydrate* ($Cl_2 \cdot 7.3H_2O$) are formed. This substance is a clathrate of the gas-hydrate type (Section 3-5), having all medium holes and ~20% of the small holes in the structure filled with chlorine molecules.

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[3] J. Lock, *Chimica,* 1982, **36,** 253; S. Venkatesh and B. V. Tilak, *J. Chem. Educ.,* 1983, **60,** 276; W. N. Brooks, *Chem. Br.,* 1986, **22,** 1095.

14-4. Bromine

Bromine occurs principally as bromide salts of the alkalis and alkaline earths in much smaller amounts than, but along with, chlorides. Bromine is obtained from brines and seawater by chlorination at a pH of ~3.5 and is swept out in a current of air.

Bromine is a dense, mobile, dark red liquid at room temperature. It is moderately soluble in water (33.6 g I^{-1} at 25°C) and miscible with nonpolar solvents such as CS_2 and CCl_4. Like Cl_2 it gives a crystalline hydrate, which appears to have a unique, noncubic structure, with a formula of $\sim Br_2 \leq 7.9H_2O$.[4]

14-5. Iodine

Iodine occurs as iodide in brines and in the form of sodium and calcium iodates. Also, various forms of marine life concentrate iodine. Production of iodine involves either oxidizing I^- or reducing iodates to I^- followed by oxidation to the elemental state. Exact methods vary considerably depending on the raw materials. A commonly used oxidation reaction, and one suited to laboratory use when necessary, is oxidation of I^- in acid solution with MnO_2 (also used for preparation of Cl_2 and Br_2 from X^-).

Iodine is a black solid with a slight metallic luster. At atmospheric pressure it sublimes (violet vapor) without melting. Its solubility in water is slight (0.33 g L^{-1} at 25°C). It is readily soluble in nonpolar solvents such as CS_2 and CCl_4 to give violet solutions; spectroscopic studies indicate that "dimerization" occurs in solutions to some extent:

$$2I_2 \rightleftharpoons I_4$$

Iodine solutions are brown in solvents such as unsaturated hydrocarbons, liquid SO_2, alcohols, and ketones, and pinkish brown in benzene (see Table 14-2).

Iodine forms the well-known blue complex with the amylose form of starch. From resonance Raman and ^{129}I Mossbauer spectroscopy it has been shown that the color is caused by a linear array of I_5^- ($I_2\ I^-\ I_2$) repeating units held inside the amylose helix.[5a]

14-6. Astatine(At), Element 85

Isotopes of element 85 have been identified as short-lived products in the natural decay series of uranium and thorium. The element was first obtained in quantities sufficient to afford a knowledge of some of its properties by the

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[4] G. H. Cady, *J. Phys. Chem.*, 1985, **89,** 3302.

[5a] T. J. Marks *et al., J. Am. Chem. Soc.*, 1980, **102,** 3322.

cyclotron reaction ^{209}Bi(α,2n)^{211}At. The element was named astatine from the Greek for "unstable." About 20 isotopes are known, the longest lived and their half-lives being ^{210}At (8.3h) and ^{211}At (7.2h). Consequently macroscopic quantities cannot be accumulated, although some compounds, HAt, CH_3At, AtI, AtBr, and AtCl, have been detected mass spectroscopically. Our knowledge of the chemistry of At is based mainly on tracer studies, which show that it behaves about as one might expect by extrapolation from the other halogens. The element is rather volatile. It is somewhat soluble in water, from which it may, like iodine, be extracted into benzene or carbon tetrachloride. Unlike iodine, however, it cannot be extracted from basic solutions.

The At^- ion is produced by reduction with SO_2 or zinc and can be carried down in AgI or TlI precipitates. Astatine is also carried by $[Ipy_2]^+$ salts. There is evidence for oxidation to the At^I ion;[5b] powerful oxidants give AtO_3^- (carried by $AgIO_3$), and there is inconclusive evidence for an oxoastatine(VII) species. The aqueous potentials (0.1 M H^+) are estimated to be as follows:

$$At^- \overset{0.3}{\text{---}} At(0) \overset{1.0}{\text{---}} HAtO(?) \overset{1.5}{\text{---}} AtO_3^- \overset{>1.6}{\text{---}} At(VII)$$

Astatine(0) reacts with other halogens or halide ions to give AtX (X = Cl, Br, I) and several polyhalide ions such as AtI_2^-, $AtBr_2^-$, and $AtIBr^-$. There are also a few organic compounds such as PhAt, $PhAtCl_2$, and $PhAtO_2$ known.

14-7. Charge-Transfer Complexes of Halogens

It is well known that iodine dissolves in a variety of organic solvents to give a whole range of colors. The general trend is summarized in Table 14-2. The reason for this is well understood. The iodine molecule has the electronic structure $1\sigma_g^2\ 1\sigma_u^2\ \pi_u^4\ 2\sigma_g^2\ \pi_g^4$ with an empty $2\sigma_u$ orbital, which is antibonding. The normal violet color of gaseous iodine is attributable to absorption caused by an allowed $\pi_g \rightarrow 2\sigma_u$ transition. If the I_2 molecule is dissolved in a solvent, S, that is an electron-pair donor, the situation depicted in Fig. 14-1 will occur. The more strongly the solvent molecule S engages in forming an $S \rightarrow I_2$ donor–acceptor or charge-transfer complex with I_2, the more the energy separation of the π_g and $2\sigma_u$ orbitals will be increased and the higher the energy of the $\pi_g \rightarrow 2\sigma_u$ transition will become. With poor donors such as saturated hydro-

TABLE 14-2
Characteristics of Iodine Solutions

Solvent	Color	Absorption maximum (nm)
C_nH_{2n+2}, CCl_4	Violet	520–540
Aromatic hydrocarbons	Pink-red	490–510
Alcohols, amines	Brown	450–480

[5b] R. Dreyer *et al.*, *Isotopenpraxis*, 1986, **22**, 81.

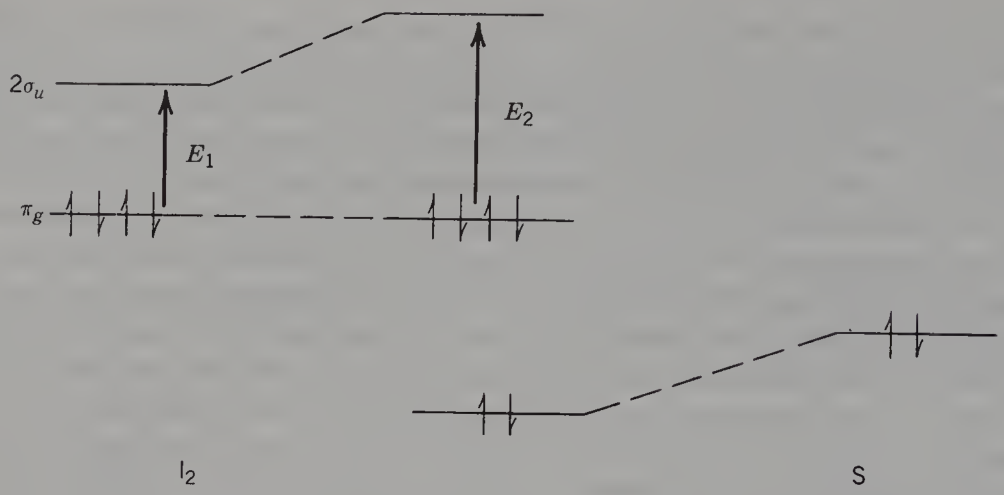

FIG. 14-1. Diagram showing how interaction of I_2 with a donor solvent molecule S causes an increase in the separation of the π_g and $2\sigma_u$ orbitals from E_1 to E_2.

carbons the S → I_2 interaction is extremely weak and hardly perturbs the I_2 molecule.[6] Aromatic solvents donate their π electrons more effectively and regular electron-pair donors ROH, R_2O, RNH_2, and so on, are quite effective donors. Of course with extremely good donors real reactions may occur, such as

$$2I_2 + 2py \longrightarrow 2py I_2 \longrightarrow [I\ py_2^+][I_3^-]$$

Good evidence for the formation of charge-transfer complexes comes from the isolation and structure determination of solids. Before mentioning a few of these it must be noted that the other halogens, Cl_2 and Br_2, as well as the interhalogens IBr and ICl have been found to behave similarly to iodine. Some examples of crystal structures are

1. $Me_3N \rightarrow I_2$, linear, N—I = 2.27 Å, I—I = 2.83 Å. Note that the I—I bond has been weakened, as expected, when there is partial donation to the σ antibonding orbital.

2. Many infinite chain structures such as $Br_2{\cdot}C_6H_6$, $Br_2{\cdot}C_4H_8O_2$, and $Br_2{\cdot}2CH_3OH$ in which each Br_2 molecule is engaged by donors at both ends; the S---Br—Br---S units are essentially linear, as expected for a σ-type acceptor orbital.

A final point concerns the significance of the term "charge-transfer complex." When the S → X_2 complex forms there is actual mixing of the lone-pair orbital on S with the $2\sigma_u$ orbital of X_2; the molecule is polar and in resonance terms can be described as a hybrid $S{-}{-}{-}X_2 \leftrightarrow S^+X_2^-$, with the nonpolar form predominating. In fact, there is another electronic transition, well out into the uv (250–300 nm) in these complexes that can be described as a transition from a ground state where $S{-}{-}{-}X_2$ predominates to an excited state where $S^+X_2^-$ predominates. This is called a *charge-transfer transition*

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[6] B. B. Bhowmik and J. I. Zink, *Spectrochem. Acta,* 1982, **38A**, 877.

and such transitions are, of course, important in many other realms of chemistry as well.

HALIDES

Except for helium, neon, and argon, all the elements in the Periodic Table form halides, often in several oxidation states, and halides generally are among the most important and common compounds. The ionic and covalent radii of the halogens are shown in Table 14-1.

There are almost as many ways of classifying halides as there are types of halide—and this is many. There are not only binary halides that can range from simple molecules with molecular lattices to complicated polymers and ionic arrays, but also oxohalides, hydroxo halides, and other complex halides of various structural types.

14-8. Preparation of Anhydrous Halides

Although preparations of individual halogen compounds are mentioned throughout the text, anhydrous halides are of such great importance in chemistry that a few of the more important general methods of preparation can be noted.

1. *Halogenation of the Elements.* This method is perhaps the most important preparative method for all halides. Higher fluorides, such as AgF_2 or CrF_4, usually require the use of elemental fluorine, with the metal or a lower fluoride or other salt. For chlorides, bromides, and iodides of transition metals, elevated temperatures are usually necessary in dry reactions. Reaction with Cl_2 or Br_2 is often more rapid when THF or some other ether is used as the medium, the halide being obtained as a solvate. Where different oxidation states are possible, F_2 and Cl_2 usually give a higher state than bromine or iodine do. Nonmetals, such as phosphorus, usually react readily without heating, and their reaction with fluorine may be explosive. Elemental Mn, Fe, Co, Ni,Cu, and Zn can be oxidized electrochemically in the presence of Cl_2, Br_2, or I_2 to afford the anhydrous metal(II) halides in a form very useful for synthesis.

2. *Halogen Exchange.* This method is especially important for fluorides, many of which are normally obtained from the chlorides by action of various metal fluorides such as SbF_3, SbF_3Cl_2, and some alkali metal fluorides; this type of replacement is often used for organic fluorine compounds.

Many Cl, Br, and I compounds undergo rapid halogen exchange with either the elements X_2 or the acids HX. An excess of reagent is usually required, since equilibrium mixtures are normally formed.

3. *Halogenation by Halogen Compounds.* This is an important method, particularly for metal fluorides and chlorides. The reactions involve treatment of anhydrous compounds, often oxides, with halogen compounds such as BrF_3,

CCl_4, hexachlorobutadiene, and hexachloropropene at elevated temperatures:

$$NiO + ClF_3 \longrightarrow NiF_2$$

$$UO_3 + CCl_2{=}CCl{-}CCl{=}CCl_2 \xrightarrow{\text{reflux}} UCl_4$$

$$Pr_2O_3 + 6NH_4Cl(s) \xrightarrow{300°C} 2PrCl_3 + 3H_2O + 6NH_3$$

$$Sc_2O_3 + CCl_4 \xrightarrow{600°C} ScCl_3$$

4. *Dehydration of Hydrated Halides.* Hydrated halides are usually obtained easily from aqueous solutions. They can sometimes be dehydrated by heating them in a vacuum, but often this leads to oxo halides or impure products. Various reagents can be used to effect dehydration. For example, $SOCl_2$ is often useful for chlorides. Another fairly general reagent is 2,2-dimethoxypropane.

$$[Cr(H_2O)_6]Cl_3 + 6SOCl_2 \xrightarrow{\text{reflux}} CrCl_3 + 12\,HCl + 6SO_2$$

$$MX_n{\cdot}mH_2O + mCH_3C(OCH_3)_2CH_3 \longrightarrow MX_n + m(CH_3)_2CO + 2mCH_3OH$$

In many cases the acetone and/or methanol becomes coordinated to the metal, but gentle heating or pumping usually gives the solvate-free halide.

5. *Special Methods for Fluorides.* Because the chemical properties of fluorine and its compounds are in many ways not homologous to those of the other halogens, there are some preparative methods for fluorides that are not used for other halides. It is much more difficult to work with F_2 than with the other elemental halogens and thus a number of useful fluorinating agents other than F_2 have been developed for synthetic purposes. These include some of the halogen fluorides, which in increasing order of activity are $IF_5 < BrF_3 < IF_7 < BrF_5 < ClF_3$. Various metal fluorides such as CoF_3, CeF_4, BiF_5, and UF_6 are also used for oxidative fluorinations; XeF_2 also has special applications. Electrolysis in anhydrous or aqueous HF is also widely used and is uniquely satisfactory in certain cases.

14-9. Binary Ionic Halides

Most metal halides are substances of predominantly ionic character, although partial covalence is important in some. Actually, of course, there is a uniform gradation from halides that are for all practical purposes purely ionic, through those of intermediate character, to those that are essentially covalent. As a rough guide, we consider as basically ionic the halides in which the lattice consists of discrete ions rather than definite molecular units, although there may still be considerable covalence in the metal–halogen interaction, and the description "ionic" should never be taken entirely literally. As a borderline case *par excellence*, which clearly indicates the danger of taking such rough classifications as "ionic" and "covalent" or even "ionic" and "molecular" too seriously, we have $AlCl_3$ (Section 7-4); this has an extended structure in which aluminum atoms occupy octahedral interstices in a close-packed array of chlorine atoms; this kind of nonmolecular structure could accommodate an appreciably ionic substance. Yet $AlCl_3$ melts at a low temperature (193°C) to a molecular liquid containing Al_2Cl_6, these molecules being much like the Al_2Br_6 molecules that occur in both solid and liquid states of the bromide. Thus although $AlCl_3$ cannot be called simply a molecular halide, it is an oversimplification to call it an ionic one.

The relatively small radius of F^- (1.19 Å) is almost identical with that of the oxide O^{2-} ion (1.26 Å); consequently many fluorides of monovalent metals and oxides of bivalent metals are ionic with similar formulas and crystal structures—for example, CaO and NaF. The compounds of the other halogens with the same formula usually form quite different lattices due to the change in the anion/cation radius ratios and may even give molecular lattices. Thus chlorides and other halides often resemble sulfides, just as the fluorides often resemble oxides. In several cases the fluorides are completely ionic, whereas the other halides are covalent; for example, CdF_2 and SrF_2 have the CaF_2 lattice (nearly all difluorides have the fluorite or rutile structure), but $CdCl_2$ and $MgCl_2$ have layer lattices with the metal atoms octahedrally surrounded by chlorine atoms.

Many metals show their highest oxidation state in the fluorides. Let us consider the Born–Haber cycle in eq. 14-1:

$$\begin{tikzcd}
M(s) \arrow[r, "S"] & M(g) \arrow[r, "\Delta H_{\text{ion}}^{(4)}"] & M^{4+}(g) \arrow[dr] & \\
 & & & MX_4(s) \\
2X_2(g) \arrow[r, "2D"] & 4X(g) \arrow[r, "4A"] & 4X^-(g) \arrow[ur] &
\end{tikzcd}$$

(14-1)

The value of $(A - D/2)$, the energy change in forming 1 g-ion of X^- from $\frac{1}{2}$ mol of X_2, is ~250 kJ for all the halogens, and S is small compared to $\Delta H_{\text{ion}}^{(4)}$ in all cases. Although the structure of MX_4, hence the lattice energy, may not be known to allow us to say whether $4(A - D/2)$ plus the lattice energy will compensate for $(\Delta H_{\text{ion}}^{(4)} + S)$, we can say that the lattice energy, hence the potential for forming an ionic halide in a high oxidation state, will be greatest for fluoride. Generally, for a given cation size, the greatest lattice energy will be available for the smallest anion, that is, F^-.

However, for very high oxidation states, which are formed notably with transition metals, for example, WF_6 or OsF_6, the energy available is quite insufficient to allow ionic crystals with, say, W^{6+} or Os^{6+} ions; consequently such fluorides are gases, volatile liquids, or solids resembling closely the covalent fluorides of the nonmetals. It cannot be reliably predicted whether a metal fluoride will be ionic or molecular, and the distinction between the types is not always sharp.

In addition to the tendency of high cation charge to militate against ionicity, as just noted, coordination number plays an important role in determining the character of a halide. For a halide of formula MX_n where M is relatively large and has a high coordination number and n is small, the coordination number of M can be satisfied only by having a packing arrangement whereby each X atom is shared so that more than n of them may surround each M atom. Usually such structures are in fact essentially ionic, but the nonmolecular, hence nonvolatile, character of the substance is a consequence of the packing regardless of the degree of ionicity of the bonds. At the other extreme, if n is large and M has a coordination number of n, the halide will be molecular and probably volatile. The sequence KCl, $CaCl_2$, $ScCl_3$, and $TiCl_4$ shows these effects. The first three are nonmolecular solids and are not volatile, whereas $TiCl_4$ is a molecular solid, relatively easy to vaporize. It should not, of course, be thought that there is any sudden discontinuity in the nature of the M—Cl bonds between $ScCl_3$ and $TiCl_4$ even though the physical properties show a qualitative change. Similarly, for a given metal with various oxidation numbers, the lower halide(s) tend to be nonvolatile (and ionic), and the higher one(s) are more covalent and molecular. This is illustrated by $PbCl_2$ versus $PbCl_4$ and UF_4 (a solid of low volatility) versus UF_6, which is a gas at 25°C.

Most ionic halides dissolve in water to give hydrated metal ions and halide ions. However, the lanthanide and actinide elements in the +3 and +4 oxidation states form fluorides insoluble in water. Fluorides of Li, Ca, Sr, and Ba also are sparingly soluble, the lithium compound being precipitated by ammonium fluoride. Lead gives a sparingly soluble salt PbClF, which can be used for gravimetric determination of F^-. The chlorides, bromides, and iodides of Ag^I, Cu^I, Hg^I, and Pb^{II} are also quite insoluble. The solubility through a series of mainly ionic halides of a given element, $MF_n \rightarrow MI_n$, may vary in either order. When all four halides are essentially ionic, the solubility order is iodide > bromide > chloride > fluoride, since the governing factor is the lattice energies, which increase as the ionic radii decrease. This order is found among the alkali, alkaline earth, and lanthanide halides. On the other hand, if covalence is fairly important, it can reverse the trend, making the fluoride most and the iodide least soluble, as in the familiar cases of silver and mercury(I) halides.

14-10. Molecular Halides

Molecular halides are usually volatile, though this will not be so if they are polymeric, as, for example, Teflon $(—CF_2—)_n$. There are also many cases (e.g., $AlCl_3$ and SnF_4) of substances that can exist as molecules in the gas phase, but because of the tendency of the metal atom to have a higher coordination number (4 and 6, respectively, in these cases) the solids have extended array structures. Most of the electronegative elements and the metals in high oxidation states (V, VI) form molecular halides. A unique but very important group of molecular halides are the hydrogen halides (Section 3-12). These form molecular crystals and are volatile, although they readily and extensively dissociate in polar media such as H_2O. The H—X bond energies and the thermal stabilities decrease markedly in the order HF > HCl > HBr > HI, that is, with increasing atomic number of the halogen. The same trend is found, in varying degrees, among the halides of all elements giving a set of molecular halides, such as those of C, B, Si, and P. Interhalogen compounds are discussed in the following sections.

Molecular Fluorides. Many molecular fluorides exist, but it is clear that because of the high electronegativity of fluorine, the bonds in such compounds tend to be very polar. Because of the low dissociation energy of F_2 and the relatively high energy of many bonds to F (e.g., C—F, 486; N—F, 272; P—F, 490 kJ mol^{-1}), molecular fluorides are often formed very exothermically; this is just the opposite of the situation with nitrogen, where the great strength of the bond in N_2 makes nitrogen compounds mostly endothermic. Interestingly, in what might be considered a direct confrontation between these two effects, the tendency of fluorine to form exothermic compounds wins. Thus for NF_3 we have

$$\tfrac{1}{2}N_2(g) = N(g) \qquad \Delta H \approx 475 \text{ kJ mol}^{-1}$$

$$\tfrac{3}{2}F_2(g) = 3F(g) \qquad \Delta H \approx 232 \text{ kJ mol}^{-1}$$

$$N(g) + 3F(g) = NF_3(g) \qquad -3E_{N-F} \approx -3(272) = -816 \text{ kJ mol}^{-1}$$

Therefore

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}F_2(g) = NF_3(g) \qquad \Delta H \approx -109 \text{ kJ mol}^{-1}$$

The high electronegativity of fluorine often has a profound effect on the properties of molecules in which several F atoms occur. Representative are facts such as (*a*) CF_3CO_2H is a strong acid, (*b*) $(CF_3)_3N$ and NF_3 have no basicity, and (*c*) CF_3 derivatives in general are attacked much less readily by electrophilic reagents in anionic substitutions than are CH_3 compounds. The CF_3 group may be considered as a kind of large pseudohalogen with an electronegativity about comparable to that of Cl.

Reactivity. The detailed properties of a given molecular halide depend on the particular elements involved, and these are discussed where appropriate in other chapters. However, a fairly general property of molecular halides is their easy hydrolysis to produce the hydrohalic acid and an acid of the other element. Typical examples are

$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3H^+ + 3Cl^-$$

$$PBr_3 + 3H_2O \longrightarrow HPO(OH)_2 + 3H^+ + 3Br^-$$

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4H^+ + 4Cl^-$$

When the central atom of a molecular halide has its maximum stable coordination number, as in CCl_4 or SF_6, the substance usually is quite unreactive toward water or even OH^-. This does not mean, however, that reaction is thermodynamically unfavorable, but only that it is kinetically inhibited, since there is no room for nucleophilic attack. Thus for CF_4 the equilibrium constant for the reaction

$$CF_4(g) + 2H_2O(l) = CO_2(g) + 4HF(g)$$

is $\sim 10^{23}$. The necessity for a means of attack is well illustrated by the failure of SF_6 to be hydrolyzed, whereas SeF_6 and TeF_6 are hydrolyzed at 25°C through expansion of the coordination sphere, which is possible only for selenium and tellurium.

14-11. Halide Ions and Halogen Compounds as Ligands

All the halide ions have the ability to function as ligands and form, with various metal ions or covalent halides, complexes such as SiF_6^{2-}, $FeCl_4^-$, and HgI_4^{2-}, as well as mixed complexes along with other ligands, for example, $[Co(NH_3)_4Cl_2]^+$. We merely make some general remarks and cite some typical characteristics of such complexes, reserving detailed discussions for other places in connection with the chemistries of the complexed elements.

One of the important general questions that arises concerns the relative affinities of the several halide ions for a given metal ion. There is no simple answer to this, however. For crystalline materials it is obvious that lattice energies play an important role, and there are cases, such as BF_4^-, BCl_4^-, BBr_4^-, in which the last two are known only in the form of crystalline salts with large cations, where lattice energies are governing. In considering the stability of the complex ions in solution, it is important to recognize that (*a*) the stability of a complex involves, not only the absolute stability of the M—X bond, but also its stability relative to the stability of ion-solvent bonds, and (*b*) in general an entire series of complexes will exist, $M^{n+}(aq)$, $MX^{(n-1)+}(aq)$, $MX_2^{(n-2)+}(aq)$,---, $MX_x^{(n-x)+}(aq)$, where x is the maximum coordination number of the metal ion. Of course these two points are of importance in all types of complex in solution.

A survey of all the available data on the stability of halide complexes shows that generally the stability decreases in the series F > Cl > Br > I, but with some metal ions the order is the opposite, namely, F < Cl < Br < I. No rigorous theoretical explanation for either sequence or for the existence of the two classes of acceptors relative to the halide ions has been given. It is likely that charge–radius ratio, polarizability, and the ability to use empty outer *d* orbitals for back-bonding are significant factors. From the available results it appears that for complexes where the replacement stability order is Cl < Br < I, the actual order of M—X bond strength is Cl > Br > I, so that ionic size and polarizability appear to be the critical factors.

The limiting factor in the formation of fluoro complexes for cations of small size and high charge is competitive hydrolysis; even at high concentrations many fluoro complexes are hydrolyzed and particularly so where the oxidation state is high. There is an empirical relation of wide applicability:

$$\log Q = -1.56 + \frac{0.48Z_+^2}{r_+}$$

where Q is the formation constant for the reaction

$$M^{n+} + F^- = MF^{(n-1)+}$$

and Z_+ and r_+ are the charge and radius of the cation. It is to be emphasized that all complex fluoro "acids" such as HBF_4 and H_2SiF_6 are necessarily strong, since the proton can be bound only to a solvent molecule.

There are many references to the effect of steric factors in accounting for such facts as the existence of $FeCl_4^-(aq)$ as the highest Fe^{3+} complex with Cl^-, whereas FeF_6^{3-} is rather stable, and similar cases such as $CoCl_4^{2-}$, SCl_4, and $SiCl_4$ as the highest chloro species compared with the fluoro species CoF_6^{3-}, SF_6, and SiF_6^{2-}. In many such cases thorough steric analysis, considering the probable bond lengths and van der Waals radii of the halide ions, shows that this steric factor alone cannot account for the differences in maximum coordination number, and this point requires further study.

Although iodo complexes are generally the least stable, and are dissociated or unstable in aqueous solution, a large number of complex anions can be made even where the metal M^{n+} is oxidizing toward I^-, provided nonaqueous media (e.g., nitriles, CH_3NO_3, or liquid HI) are used. The latter possibility arises because HCl has a free energy of formation, ~85 kJ mol^{-1} higher than that of HI, so that in the anhydrous reaction

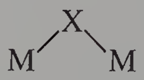
$$MCl_6^{(6-n)-} + 6HI(l) = MI_6^{(6-n)-} + 6HCl$$

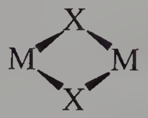
the equilibrium lies to the right and the greater volatility of HCl provides additional driving force.

Finally, it may be mentioned that in effecting the separation of metal ions, one can take advantage of halide complex formation equilibria in conjunction with anion-exchange resins. To take an extreme example, Co^{2+} and Ni^{2+}, which are not easily separated by classical methods, can be efficiently separated by passing a strong hydrochloric acid solution through an anion-exchange column. The ion Co^{2+} forms the anionic complexes $CoCl_3^-$ and $CoCl_4^{2-}$ rather readily, whereas it does not seem that any anionic chloro complex of nickel is formed in aqueous solution even at the highest attainable activities of Cl^-. However, tetrachloronickelates can be obtained in fused salt systems or in nonaqueous media. More commonly, effective separation depends on properly exploiting the difference in complex formation between two cations, both of which have some tendency to form anionic halide complexes.

Halide Bridges. The formation of halide bridges is an important structural feature not only in complex compounds but in many simple molecular compounds. There are the following types:

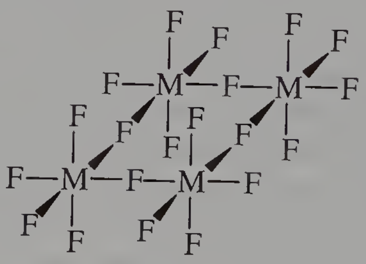
M—X—M





Bridges with two halogen atoms, as in Al_2Cl_6 or edge-sharing bioctahedra, are most common, but systems with three, as in the facesharing bioctahedra of which $[Cl_3Mo(\mu\text{-}Cl)_3MoCl_3]^{3-}$ is representative, are also well known. There are also many extended chain structures, as in $KNiCl_3$ and various $(MX_4)_\infty$, in which M—M bonds may be present.[7,8]

Single fluoride bridges are quite common as in cyclic pentafluoride tetramers (14-I) but both linear and bent single chloride bridges also occur.



(14-I)

A linear bridge is found in $Cu_2Cl_3L_2^+$ compounds,[9] while bent single bridges are known in Pd^{II} and Rh^I compounds and in $[CpFe(CO)_2]_2\mu\text{-}Cl^{+10}$. The tendency of fluorine to form linear bridges may be due in part to the smaller size of the atom, but perhaps also to some π character in the M—F—M bonds. However, bent bridges with angles of ~125° are known.[11a]

A unique example of μ_4-F with two long and two short bonds to Mo occurs in $Mo_4O_{12}F_3^{3-}$.[11b]

The μ_2—X bonding can be interpreted by MO theory. As indicated in Fig. 14-2(a), each metal atom presents an empty σ orbital directed more or less toward the bridging halide X^-; these orbitals are ϕ_1 and ϕ_2. The X^- ion has four filled valence shell orbitals. One of these, ϕ_3 (which may be taken as an *s* orbital, a *p* orbital, or a hybrid) will be directed down, as shown; the other, ϕ_4, is a pure *p* orbital. The metal orbitals may be combined [Fig. 14-2(b)] into a symmetric combination, Φ_1, and an antisymmetric combination, Φ_2, which may interact with ϕ_3 and ϕ_4, respectively, to form bonding and anti-

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[7] P. Sobota *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2077; *Polyhedron,* 1984, **3,** 45.

[8] S. S. Shaik and R. Bau, *Inorg. Chem.*, 1983, **22,** 735.

[9] K. D. Karlin *et al., Transition Met. Chem.*, 1984, **9,** 405.

[10] J. G. Riess *et al., Organometallics,* 1984, **3,** 1034; G. van Koten *et al., J. Am. Chem. Soc.*, 1982, **104,** 828; D. J. Cole-Hamilton *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 1129.

[11a] M. H. Chisholm *et al., Polyhedron,* 1985, **4,** 1203.

[11b] N. Buchholtz and R. Mattes, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 1104.

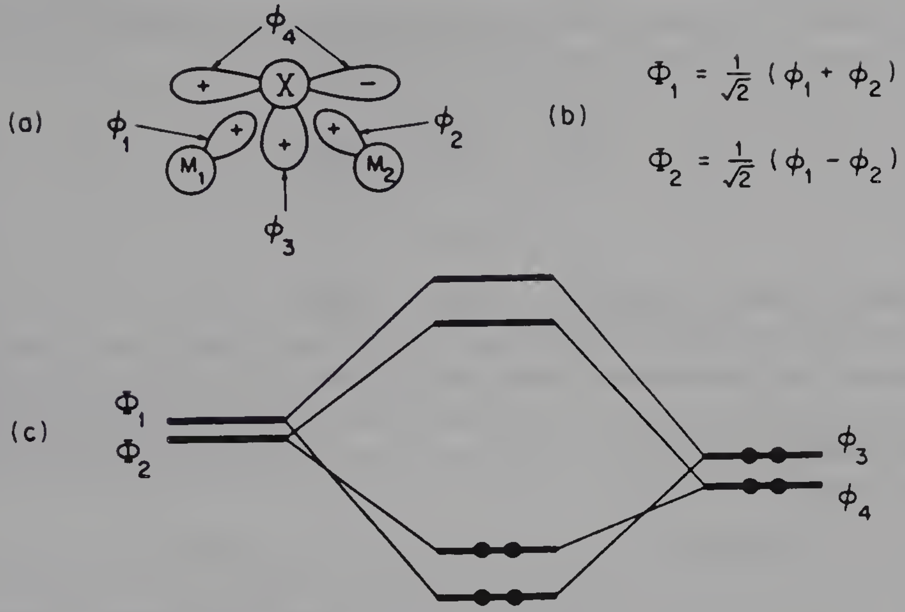
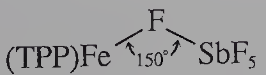


FIG. 14-2. Molecular orbital formation in a bridging halide system MXM.

bonding orbitals, as in Fig. 14-2(c). The four electrons then occupy the two bonding MO's, giving a mean M—X bond order of 1. It is also evident that the M—X—M angle is not sharply limited. In reality, angles varying from 60 to 180° are found, although the majority for Cl and Br are in the range 70 to 100°.

A characteristic and important reaction of halide bridges, especially those of Cl, Br, and I, is that they are cleaved by Lewis bases such as pyridine, other amines, or tertiary phosphines.

Halogen Complex Anions. Although EF_n^{m-} ions (e.g., BF_4^- and PF_6^-) are *relatively* noncomplexing anions, they can exhibit donor properties, forming E—F → M^+ type interactions under various circumstances. In the many compounds containing sulfur or selenium cations (see Section 13-6) where SbF_6^- counterions are present, as well as in salts of various cationic halogens, there are significant partial bonds from fluorine atoms to the cations. A recent example[12] of a bond to a transition metal is (14-II).


$$(TPP)Fe\overset{F}{\underset{150^\circ}{\wedge}}SbF_5$$

(14-II)

The BF_4^- ion can also give complexes such as $(Ph_3P)_2CuFBF_3$ and $[en_2(H_2O)NiFBF_3]^+$, but F^- abstraction often occurs leading to fluoride complexes.[13] Thus the interaction of $MoH_4(PR_3)_4$ with HBF_4 gives $[(R_3P)_2(H)_2Mo(\mu\text{-}F)_3Mo(H)_2(PR_3)_2]^+$.

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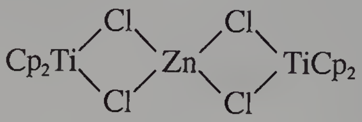
[12] C. A. Reed *et al.*, *Inorg. Chem.*, 1985, **24**, 4325.

[13] R. H. Crabtree *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 7302; G. Wilkinson *et al.*, *Polyhedron*, 1982, **1**, 31; A. Sen *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 4096.

Some weakly associated chloro- or methylchloroaluminate ions are also known,[14] as well as bridge species such as (14-III).

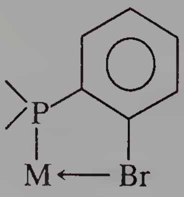


(14-III)

Organic Halides as Ligands. Recently evidence has been found for the ability of halogen atoms in R—X and Ar—X compounds to use a lone pair and form an additional bond, sometimes a rather strong one. It is probable that such complexes (not necessarily strong ones) are intermediates in many reactions such as the oxidative-addition of alkyl halides to transition metal species (Chapter 27), that is,

$$RX + ML_n \longrightarrow [RX \rightarrow ML_n] \longrightarrow L_nMX + R^{\cdot}$$

The most striking examples of strong interactions are to be found in various rhodium and iridium compounds.[15] When phosphines containing *o*-halophenyl groups are present, these give rise to interactions of the type (14-IV), where the metal–bromine distances are nearly as short as expected for an ordinary M—Br bond, namely, Ir—Br of ~2.47 Å.



(14-IV)

OXIDES, OXO ACIDS, AND THEIR ANIONS

14-12. Oxides

Those oxides that are definitely established are listed in Table 14-3. The binary compounds of oxygen and fluorine were discussed earlier as oxygen fluorides, since fluorine is more electronegative than oxygen. The *halogen oxides* to be discussed here are the binary X_nO_m compounds in which X = Cl, Br, or I. A few mixed species, the halogen oxide fluorides, are treated in a later section. It may also be noted that there are a number of more or less evanescent species, mostly radicals, that we shall not discuss in detail. Among these are

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[14] J. M. Mayer and J. C. Calabrese, *Organometallics*, 1984, **3**, 1292; P. R. Sharp, *Organometallics*, 1984, **3**, 1217; E. Samuel *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 7418.

[15] P. Lahuerta *et al.*, *Acta Cryst.*, 1985, **C41**, 841; R. H. Crabtree *et al.*, *Organometallics*, 1987, **6**, 2241; F. A. Cotton *et al.*, *Organometallics*, 1986, **5**, 808.

TABLE 14-3
Oxides of the Halogens

Fluorine[a]	bp (°C)	mp (°C)	Chlorine	bp (°C)	mp (°C)	Bromine[b]	bp (°C)	Iodine[b]
F_2O	−145	−224	Cl_2O	~4	−116	Br_2O	−18	I_2O_4
			Cl_2O_3[c]					
F_2O_2	−57	−163	ClO_2	~10	−5.9			I_4O_9
			Cl_2O_4	44.5	−117			
			Cl_2O_6		3.5	BrO_2		I_2O_5
			Cl_2O_7	82	−91.5			

[a] See Section 12-4.
[b] Decompose on heating.
[c] Explodes below 0°C.

ClO, ClO_2, ClO_4, BrO, IO, IO_2, and IO_3. It is worth pointing out that the ClO radical has been extensively studied because of its key role in reactions, whereby chlorofluorocarbons ($CFCl_3$ and CF_2Cl_2) that reach the stratosphere are oxidized with consequent depletion of the ozone.

While all of the oxides are formally anhydrides or mixed anhydrides of oxo acids, this aspect of their chemistry is of little practical importance. As a class the oxides are uncommon and not useful except for ClO_2 and Cl_2O, which find significant commercial application as bleaching agents (paper pulp and flour, particularly), and I_2O_5.

Chlorine Oxides. All of them are highly endothermic compounds and must be treated with great caution. Because of their endothermicity, none can be obtained by reaction of Cl_2 and O_2. The two best known are Cl_2O and ClO_2.

Dichlorine monoxide (Cl_2O), is a yellow-brown gas at 25°C. It explodes rather easily to Cl_2 and O_2 when heated or sparked, but may be handled safely as an ~1 *M* solution in CCl_4. It is a selective, powerful chlorinating agent for organic compounds.[16] It dissolves readily in water forming an orange solution in which the equilibrium $Cl_2O + H_2O = 2HOCl$ is set up. Commercially it is passed into lime water to form $Ca(OCl)_2$, which is then a safe and effective bleaching agent. The Cl_2O molecule is bent (111°) with $Cl{-}O = 1.71$ Å. The best preparation, both commercially and on a laboratory scale is by reaction of fresh yellow HgO with Cl_2 gas or Cl_2 dissolved in CCl_4

$$2Cl_2 + 2HgO \longrightarrow HgCl_2{\cdot}HgO + Cl_2O$$

Chlorine dioxide is also highly reactive and is liable to explode very violently; apparently mixtures with air containing < ~50-mm partial pressure of ClO_2 are safe. Chlorine dioxide is made on a fairly large scale, but it is always produced where and as required. The best preparation is the reduction of $KClO_3$ by moist oxalic acid at 90°C, since the CO_2 liberated also serves as

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[16] F. D. Marsh *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 4680.

a diluent for the ClO_2. Commercially the gas is made by the exothermic reaction of sodium chlorate in 4 to 4.5 *M* sulfuric acid containing 0.05 to 0.25 *M* chloride ion with sulfur dioxide:

$$2NaClO_3 + SO_2 + H_2SO_4 \longrightarrow 2ClO_2 + 2NaHSO_4$$

Chlorine dioxide is a yellowish gas at room temperature. The molecule is angular (118°) with Cl—O = 1.47 Å. Although ClO_2 is an odd molecule, it has no marked tendency to dimerize, perhaps because the electron is more effectively delocalized than in other odd molecules such as NO_2. It is soluble in water, and solutions with up to 8 g L^{-1} are stable in the dark, but in light decompose slowly to HCl and $HClO_3$. Crystalline clathrate hydrates, $ClO_2 \cdot nH_2O$ ($n \approx 8$) can be separated on cooling. Chlorine dioxide reacts fairly rapidly in alkaline solution to form a mixture of chlorite and chlorate ions:

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

Dichlorine tetraoxide is structurally $ClOClO_3$ and is, accordingly, called chlorine perchlorate; it is unstable at room temperature. It is one of the halogen perchlorates, along with $FOClO_3$ and $BrOClO_3$, to be discussed in Section 14-21.

Dichlorine hexaoxide, made by interaction of ClO_2 and O_3, is an unstable red oil that freezes (3.5°C) to a solid that is yellow at −180°C. X-ray study confirms the ionic $ClO_2^+ClO_4^-$ structure in the solid,[17a] while the structure in the liquid phase is uncertain. Dichlorine hexaoxide reacts with metal(II) chlorides and nitrates to form $ClO_2M(ClO_4)_3$ and $NO_2M(ClO_4)_3$, respectively, both of which can be thermally decomposed to give the anhydrous $M(ClO_4)_2$ compounds.[17b]

Dichlorine heptaoxide is the most stable chlorine oxide. It is a colorless liquid formed by dehydration of perchloric acid with P_2O_5 at −10°C, followed by vacuum distillation with precautions taken against explosion. It reacts with water and OH^- to generate ClO_4^-. Electron diffraction shows the structure $O_3ClOClO_3$, with a ClOCl angle of 118.6°. The reaction of Cl_2O_7 with alcohols yields alkyl perchlorates ($ROClO_3$), which find use as intermediates in synthesis. It reacts similarly with amines to yield R_2NClO_3 or $RHNClO_3$.

Bromine Oxides. None are stable at ordinary temperatures and none are of practical importance. Bromine dioxide is a yellow solid formed by oxidation of Br_2 in CF_3Cl at −78°C with ozone. It is thermally unstable above −40°C and decomposes violently at ~0°C. Dibromine oxide is a brown solid below −17.5°C but appears to be unstable above −60°C. It can be obtained by low-temperature decomposition of BrO_2 in vacuum, or by reaction of Br_2 vapor with Hg_2O. Like Cl_2O it is a bent, symmetrical molecule. Numerous other bromine oxides, for example, Br_2O_3, Br_2O_5, Br_3O_8, and BrO_3 have been reported but all are inadequately characterized and unstable.

[17a] K. M. Tobias and M. Jansen, *Angew Chem. Int. Ed. Engl.*, 1986, **25**, 993.

[17b] J.-L. Pascal *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 297.

Iodine Oxides. Of these, white crystalline iodine pentoxide is the most important and is made by the reaction

$$2HIO_3 \overset{240°C}{\rightleftharpoons} I_2O_5 + H_2O$$

It has IO_3 pyramids sharing one oxygen to give O_2IOIO_2 units, but quite strong intermolecular I---O interactions lead to a three-dimensional network. This compound is stable up to ~300°C, where it melts with decomposition to iodine and oxygen. It is the anhydride of iodic acid and reacts immediately with water. It reacts as an oxidizing agent with various substances such as H_2S, HCl, and CO. One of its important uses is as a reagent for the determination of CO, the iodine that is produced quantitatively being then determined by standard iodometric procedures:

$$5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$$

The other oxides of iodine I_2O_4 and I_4O_9 are of less certain nature. They decompose when heated at ~100°C to I_2O_5 and iodine, or to iodine and oxygen. The yellow solid I_2O_4, which is obtained by partial hydrolysis of $(IO)_2SO_4$ (discussed later), appears to have a network built up of polymeric I—O chains that are cross linked by IO_3 groups. I_4O_9, which can be made by treating I_2 with ozonized oxygen, can be regarded as $I(IO_3)_3$, similarly cross linked.

14-13. Oxo Acids and Anions

The known oxo acids of the halogens are listed in Table 14-4. The chemistry of these acids and their salts is very complicated. Solutions of all the acids and of several of the anions can be obtained by reaction of the free halogens with water or aqueous bases. We discuss these reactions first; the term "halogen" refers to chlorine, bromine, and iodine, only.

Although one often finds hypochlorous and chlorous acids written HClO and $HClO_2$, this is unfortunate and should be discontinued since they are actually HOCl and HOClO. This is not a purely pedantic matter since in studies of gas phase kinetics in the earth's ozone layer, the distinction between the unstable isomer, HClO, and ClOH is significant. Hypochlorous acid is ~280 kJ mol^{-1} more stable than HClO.[18a]

Reaction of Halogens with H_2O and OH^-. A considerable degree of order an be found in this area if full and proper use is made of thermodynamic data in the form of oxidation potentials and equilibrium constants and if the relative rates of competing reactions are also considered. The basic thermodynamic data are given in Table 14-5. From these, all necessary potentials and equilibrium constants can be derived by use of elementary thermodynamic relationships.

The halogens are all to some extent soluble in water. However, in all such

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[18a] A. G. Turner, *Inorg. Chim. Acta*, 1986, **111**, 157.

TABLE 14-4
Oxo Acids of the Halogens

Fluorine	Chlorine	Bromine	Iodine
HOF	HOCl[a]	HOBr[a]	HOI[a]
	HOClO[a]	HOBrO[a]	
	$HOClO_2$[a]	$HOBrO_2$[a]	$HOIO_2$
	$HOClO_3$	$HOBrO_3$[a]	$HOIO_3$, $(HO)_5IO$, $H_4I_2O_9$

[a] Stable only in solution.

solutions there are species other than solvated halogen molecules, since a disproportionation reaction occurs *rapidly*. Two equilibria serve to define the nature of the solution:

$$X_2(g,l,s) = X_2(aq) \qquad K_1$$

$$X_2(aq) = H^+ + X^- + HOX \qquad K_2$$

The values of K_1 for the various halogens are Cl_2, 0.062; Br_2, 0.21; I_2, 0.0013. The values of K_2 can be computed from the potentials in Table 14-4 to be 4.2×10^{-4} for Cl_2, 7.2×10^{-9} for Br_2, and 2.0×10^{-13} for I_2. We can also estimate from

$$\tfrac{1}{2}X_2 + e = X^-$$

and

$$O_2 + 4H^+ + 4e = 2H_2O \qquad E^0 = 1.23 \text{ V}$$

that the potentials for the reactions

$$2H^+ + 2X^- + \tfrac{1}{2}O_2 = X_2 + H_2O$$

are −1.62 V for fluorine, −0.13 V for chlorine, 0.16 V for bromine, and 0.69 V for iodine.

TABLE 14-5
Standard Potentials for Reactions of the Halogens (V)

Reaction	Cl	Br	I
$H^+ + HOX + e = \tfrac{1}{2}X_2(g,l,s) + H_2O$	1.63	1.59	1.45
$3H^+ + HOXO + 3e = \tfrac{1}{2}X_2(g,l,s) + 2H_2O$	1.64		
$6H^+ + XO_3^- + 5e = \tfrac{1}{2}X_2(g,l,s) + 3H_2O$	1.47	1.52	1.20
$8H^+ + XO_4^- + 7e = \tfrac{1}{2}X_2(g,l,s) + 4H_2O$	1.42	1.59[a]	1.34
$\tfrac{1}{2}X_2(g,l,s) + e = X^-$	1.36	1.07	0.54[b]
$XO^- + H_2O + 2e = X^- + 2OH^-$	0.89	0.76	0.49
$XO_2^- + 2H_2O + 4e = X^- + 4OH^-$	0.78		
$XO_3^- + 3H_2O + 6e = X^- + 6OH^-$	0.63	0.61	0.26
$XO_4^- + 4H_2O + 8e = X^- + 8OH^-$	0.56	0.69[a]	0.39

[a] Calculated from data of G. K. Johnson *et al.*, *Inorg. Chem.*, 1970, **9**, 119.
[b] Indicates that I^- can be oxidized by oxygen in aqueous solution.

TABLE 14-6
Equilibrium Concentrations in Aqueous Solutions of the Halogens at 25°C (mol L^{-1})

	Cl_2	Br_2	I_2
Total solubility	0.091	0.21	0.0013
Concentration $X_2(aq)$	0.061	0.21	0.0013
$[H^+] = [X^-] = [HOX]$	0.030	1.15×10^{-3}	6.4×10^{-6}

Thus for saturated solutions of the halogens in water at 25°C we have the results shown in Table 14-6. There is an appreciable concentration of hypochlorous acid in a saturated aqueous solution of chlorine, a smaller concentration of HOBr in a saturated solution of Br_2, but only a negligible concentration of HOI in a saturated solution of iodine.

Hypohalous Acids. The compound HOF, a colorless solid, melts at −117°C to a pale yellow liquid. It is a gas at ambient temperature, highly reactive towards water, and has a half-life for spontaneous decomposition to HF and O_2 of ~30 min at 25°C. It is prepared, with difficulty, by reaction of F_2 with H_2O at low temperature. The molecule has the smallest angle (97°) known at an unconstrained oxygen atom; for HOCl (see later) the angle is 103°. A number of compounds containing covalently bound OF groups, and called hypofluorites, are known, examples being CF_3OF, SF_5OF, O_3ClOF, and FSO_2OF.

The other HOX compounds are also unstable. In water their dissociation constants are HOCl, 3.4×10^{-8}; HOBr, 2×10^{-9}, HOI, 2×10^{-11}. As can be readily seen, reaction of halogens with water does not constitute a suitable method for preparing aqueous solutions of the hypohalous acids owing to the unfavorable equilibria. A useful general method is interaction of the halogen and a well-agitated suspension of mercuric oxide:

$$2X_2 + 2HgO + H_2O \longrightarrow HgO \cdot HgX_2 + 2HOX$$

In the vapor phase, HOCl is formed in the equilibrium[18b]

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$$

The reaction of HgO and I_2 can be used to form organic hypoiodites from alcohols; these can be used as oxidants. The hypohalous acids are good oxidizing agents, especially in acid solution (see Table 14-5) and this accounts for the chief industrial use of hypochlorites, on a tonnage scale, for bleaching and sterilizing. Hypohalites and the acids are also used to halogenate both aromatic and aliphatic organic compounds.

The hypohalite ions can all be produced in principle by dissolving the halogens in cold base according to the general reaction

$$X_2 + 2OH^- \longrightarrow X^- + XO^- + H_2O$$

[18b] C. A. Ennis and J. W. Birks, *J. Phys. Chem.*, 1985, **89**, 186.

and for these reactions the equilibrium constants are all favorable—7.5×10^{15} for Cl_2, 2×10^8 for Br_2, and 30 for I_2—and the reactions are rapid.

The situation, however, is complicated by the tendency of the hypohalite ions to disproportionate further in basic solution to produce the halate ions:

$$3XO^- = 2X^- + XO_3^-$$

For this reaction the equilibrium constant is in each case very favorable, that is, 10^{27} for ClO^-, 10^{15} for BrO^-, and 10^{20} for IO^-. Thus the actual products obtained on dissolving the halogens in base depend on the rates at which the hypohalite ions initially produced undergo disproportionation, and these rates vary from one to the other and with temperature.

The disproportionation of ClO^- is slow at and below room temperature. Thus when chlorine reacts with base "in the cold," reasonably pure solutions of Cl^- and ClO^- are obtained. In hot solutions (~75°C) the rate of disproportionation is fairly rapid and under proper conditions, good yields of ClO_3^- can be secured.

The disproportionation of BrO^- is moderately fast even at room temperature. Consequently solutions of BrO^- can only be made and/or kept at around 0°C. At temperatures of 50 to 80°C quantitative yields of BrO_3^- are obtained:

$$3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O$$

The rate of disproportionation of IO^- is very fast at all temperatures, so that it is unknown in solution. Reaction of iodine with base gives IO_3^- quantitatively according to an equation analogous to that for Br_2.

It remains now to consider the equilibria of the oxo anions not yet mentioned and their kinetic relations to those we have discussed. *Halite ions* and *halous acids* do not arise in the hydrolysis of the halogens. The compound HOIO apparently does not exist, HOBrO is doubtful, and HOClO is not formed by disproportionation of HOCl if for no other reason than that the equilibrium constant is quite unfavorable:

$$2HOCl = Cl^- + H^+ + HOClO \qquad K \sim 10^{-5}$$

The reaction

$$2ClO^- = Cl^- + ClO_2^- \qquad K \sim 10^7$$

is favorable, but the disproportionation of ClO^- to ClO_3^- and Cl^- (cited previously) is so much more favorable that the first reaction is not observed.

Finally, we must consider the possibility of production of *perhalate ions* by disproportionation of the halate ions. Since the acids $HOXO_2$ and $HOXO_3$ are all strong, these equilibria are independent of pH. The reaction

$$4ClO_3^- = Cl^- + 3ClO_4^-$$

has an equilibrium constant of 10^{29}, but it takes place only very slowly in solution even near 100°C; hence perchlorates are not readily produced. Neither perbromate nor periodate can be obtained in comparable disproportionation reactions because the equilibrium constants are 10^{-33} and 10^{-53}, respectively.

The only definitely known halous acid, *chlorous acid,* is obtained in aqueous solution by treating a suspension of barium chlorite with sulfuric acid and filtering off the precipitate of barium sulfate. It is a relatively weak acid ($K_A \approx 10^{-2}$) and cannot be isolated in the free state. *Chlorites* ($MClO_2$) themselves are obtained by reaction of ClO_2 with solutions of bases:

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

Sodium chlorite is manufactured on a ton scale for use as a bleaching agent. In alkaline solution the ion is stable to prolonged boiling and up to a year at 25°C in the absence of light. In acid solutions, however, the decomposition is rapid and is catalyzed by Cl^-:

$$5HOClO \longrightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O$$

but the reaction sequence is complicated.[19]

Halic Acids and Halates. Only iodic acid (HIO_3) is known out of aqueous solution. The white solid consists of pyramidal $IO_2(OH)$ molecules connected by hydrogen bonds. The IO_3^- ion as well as the BrO_3^- and ClO_3^- ions are pyramidal. Iodic acid is easily made by oxidizing I_2 with concentrated nitric acid or other strong oxidizing agents. It can be dehydrated to I_2O_5 and yields salts of the types $M^IH(IO_3)_2$ and $M^IH_2(IO_3)_3$ as well as M^IIO_3. The acids, HXO_3, are all strong.

While all the halates can be obtained by reactions of X_2 with hot aqueous alkali,

$$3X_2 + 6OH^- \longrightarrow XO_3^- + 5X^- + 3H_2O$$

this is unsuitable for the large-scale manufacture of $NaClO_3$ since only $\frac{1}{6}$ of the Cl_2 is converted. Instead an electrolytic oxidation of brine is used, which can give conversions of up to 90% efficiency based on current used.

The halic acids are all good oxidizing agents, but their chemical behavior is extremely complex and varied depending on temperature, acidity, and other factors. We shall mention here only the fact that both iodate and bromate participate in reactions with complex time-dependent behavior. There is the long-known Landolt chemical clock reaction in which HIO_3 and Na_2SO_3 react in acid solution in the presence of starch so as to generate the blue color indicative of free iodine only after predictable time intervals, and when sulfite is in excess in a repetitive, periodic manner. Other periodic reactions include that of HIO_3 with H_2O_2 (Bray reaction), the BrO_3^-/I^- reaction,[20] and finally, the celebrated Belousov–Zhabotinskii oscillating reaction, which occurs in solutions of $KBrO_3$, Ce^{IV}, and malonic acid in stirred sulfuric acid solution.[21]

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[19] G. Schmitz and H. Rooze, *Can. J. Chem.*, 1984, **62,** 2231.
[20] O. Citri and I. R. Epstein, *J. Am. Chem. Soc.*, 1986, **108,** 357.
[21] C. Vidal *et al., J. Am. Chem. Soc.*, 1980, **102,** 1242.

Perchlorates. Although disproportionation of ClO_3^- to ClO_4^- and Cl^- is thermodynamically very favorable, the reaction occurs only very slowly in solution and does not constitute a useful preparative procedure. Perchlorates are commonly prepared by electrolytic oxidation of chlorates. The properties of perchloric acid were discussed in Section 3-11.

Perchlorates of almost all electropositive metals are known. Except for a few with large cations of low charge, such as $CsClO_4$, $RbClO_4$, and $KClO_4$, they are readily soluble in water. Solid perchlorates containing the tetrahedral ClO_4^- ion are often isomorphous with salts of other tetrahedral anions (e.g., MnO_4^-, SO_4^{2-}, and BF_4^-). A particularly important property of the perchlorate ion is its slight tendency to serve as a ligand in complexes. Thus perchlorates are widely used in studies of complex ion formation, the *assumption* being made that no appreciable correction for the concentration of perchlorate complexes need be considered. This may often be true for aqueous solutions, but it is well known that when no other donor is present to compete, perchlorate ion exercises a donor capacity and can be monodentate, bridging bidentate, or chelating bidentate[22] (see also Section 12-16). This is illustrated by structures of compounds such as $(CH_3)_3SnClO_4$, $Co(MeSC_2H_4SMe)_2(ClO_4)_2$, $(Ph_3BiOBiPh_3)(ClO_4)_2$, $Sb_2Cl_6(OH)(O)(ClO_4)$,[23] and $Ti(ClO_4)_4$.[24a]

The use of perchlorate as an ion for the isolation of crystalline salts of organometallic ions such as $(\eta^5\text{-}C_5H_5)_2Fe^+$ is to be avoided, since such salts are often dangerously explosive*. The use of the trifluoromethanesulfonate ion, $CF_3SO_3^-$, PF_6^-, or BF_4^-, which behave very much like ClO_4^-, is preferable, but even these ions may act as ligands. Although ClO_4^- is potentially a good oxidant

$$ClO_4^- + 2H^+ + 2e = ClO_3^- + H_2O \qquad E^0 = 1.23\ V$$

in aqueous solution it is reduced only by Ru^{II} (to ClO_3^-), and by V^{II}, V^{III}, Mo^{III}, Mo_2^{III} and Ti^{III} to Cl^-. Despite the more favorable potential for reduction by Eu^{2+} or Cr^{2+}, no reaction occurs, possibly because intermediates with M═O bonds are required in the reductions.[24b]

Perbromic Acid and Perbromates. Perbromates were prepared only in 1968; previously there were many papers theoretically justifying their nonexistence. This provides an excellent example of the folly of concluding the nonexistence of certain compounds until all conceivable preparative methods have been exhausted.

The potential

$$BrO_4^- + 2H^+ + 2e = BrO_3^- + H_2O \qquad E^0 = +1.76\ V$$

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[22] M. M. Olmstead *et al.*, *Transition Met. Chem.*, 1982, **7**, 140; P. J. Burke *et al.*, *Inorg. Chem.*, 1982, **21**, 1881.

[23] C. H. Belin *et al.*, *Inorg. Chem.*, 1982, **21**, 3557.

[24a] J. Potier *et al.*, *Inorg. Chem.*, 1982, **21**, 3557.

*Even compounds lacking organic components may explode (cf. R. E. Cook and P. J. Robinson, *J. Chem. Res.*, 1982, **S**, 267).

[24b] A.G. Sykes *et al.*, *Inorg. Chem.*, 1986, **25**, 2566.

shows that only the strongest oxidants can form perbromate. Kinetic factors must be responsible for the failure of ozone ($E^0 = +2.07$ V) and $S_2O_8^{2-}$ ($E^0 = +2.01$ V) to cause oxidation.

Small amounts of perbromic acid or perbromates can be obtained by oxidation of BrO_3^- electrolytically or by the action of XeF_2. The best preparation involves oxidation of BrO_3^- by fluorine in 5 *M* NaOH solution; by a rather complicated procedure, pure solutions can be obtained:

$$BrO_3^- + F_2 + 2OH^- \longrightarrow BrO_4^- + 2F^- + H_2O$$

Solutions of $HBrO_4$ can be concentrated up to 6 *M* (55%) without decomposition and are stable indefinitely even at 100°C. More concentrated solutions, up to 83%, can be obtained but these are unstable; the hydrate $HBrO_4 \cdot 2H_2O$ can be crystallized.

Salts such as $KBrO_4$ (dec ~ 275°C) and NH_4BrO_4 are (dec ~ 170°C) are fairly stable thermally and are isomorphous with their perchlorate analogues.[25]

Perbromate is an even stronger oxidant than ClO_4^- (1.23 V) or IO_4^- (1.64 V) but it is very sluggish at 25°C. The dilute acid is only slowly reduced by I^-, Br^- (not at all by Cl^-), and by other reagents.[26] However, the 3 *M* acid readily oxidizes stainless steel and the 12 *M* acid rapidly oxidizes Cl^- and explodes on contact with cellulose.

The high oxidizing power of BrO_4^- can be related to its being thermodynamically less stable than either ClO_4^- or IO_4^-. The ΔG_f^0 values (kJ mol^{-1} at 298°C) for the three potassium salts are as follows: $KClO_4$, −302; $KBrO_4$, −174; KIO_4, −349. This anomaly may be compared with some similar behavior of selenates and arsenates, and is part of the general tendency of these three elements to have properties that cannot be quantitatively interpolated from those of their lighter and heavier congeners.

Periodic Acid and Periodates. This chemistry is more complex than for the other perhalates because there are at least four structural types. In aqueous solution the acid HIO_4, which is strong, and the series based on H_5IO_6 are predominent. The following rapidly established equilibria are of major importance in acid solutions:

$$I(OH)_6^+ = IO(OH)_5 + H^+ \qquad K \approx 6$$

$$IO(OH)_5 = IO_2(OH)_4^- + H^+ \qquad K \approx 5 \times 10^{-4}$$

$$IO_2(OH)_4^- = IO_4^- + 2H_2O \qquad K \approx 29$$

$$IO_2(OH)_4^- = IO_3(OH)_3^{2-} + H^+ \qquad K \approx 5 \times 10^{-9}$$

$$2IO_3(OH)_3^{2-} = (HO)_2I_2O_8^{4-} + 2H_2O \qquad K \approx 820$$

The IO_4^- ion (called periodate or, sometimes, metaperiodate) is tetrahedral while the other species are all based on IO_6 octahedra. The $(HO)_2I_2O_8^{4-}$ ion

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[25] E. Gebert *et al.*, *J. Inorg. Nucl. Chem.*, 1981, **43**, 3085; I. J. Borosova and A. A. Lychev, *Russ. J. Inorg. Chem.*, 1982, **27**, 597.

[26] A. M. Kjaer and J. Ulstrup, *Inorg. Chem.*, 1982, **21**, 3490.

consists of two octahedra sharing a pair of oxygen atoms. The acid H_5IO_6 [≡ $IO(OH)_5$] is called orthoperiodic aid.

Periodates are best obtained by oxidizing iodate (or even I^- or I_2) electrolytically or with Cl_2 in strongly basic solution to give $Na_3H_2IO_6$, or by thermal disproportionation of an iodate:

$$5Ba(IO_3)_2 \longrightarrow Ba_5(IO_6)_2 + 4I_2 + 9O_2$$

The white crystalline acid (H_5IO_6) can then be obtained from strongly acid solutions, and this can be dehydrated at 100°C in vacuum to HIO_4. Under other conditions $H_7I_3O_{14}$ (structure unknown) is obtained. There is also a square pyramidal IO_5^{3-} ion that occurs in K_3IO_5.

The $H_nIO_6^{+n-5}$ ions have an extensive chemistry as ligands. With H^+ in concentrated acid solutions the compounds $[I(OH)_6]HSO_4$ and $[I(OH)_6]_2SO_4$ can be obtained. Colorless $I(OH)_6^+$ is a member of the isostructural series $Sn(OH)_6^{2-}$, $Sb(OH)_6^-$, and $Te(OH)_6$. With many transition metals higher oxidation states such as Mn^{IV}, Ni^{IV}, and Cu^{III} are stabilized in complexes where the IO_6^{5-} ion serves as a bidentate chelating ligand. Examples are $Na_7[H_4Mn(IO_6)_3]\cdot 17H_2O$ with six-coordinate Mn^{IV} and $Na_3K[H_3Cu(IO_6)_2]\cdot 14H_2O$ with square Cu^{III}.

The IO_6^{5-} unit can also participate in the formation of large polyanions similar to those formed by fusing of MoO_6^{6-} and WO_6^{6-} octahedra. For example, the anion $[Co_4I_3O_{24}H_{12}]^{3-}$ has seven octahedra fused together in the way shown in Fig. 19-C-6 for an XM_6O_{24} heteropoly anion of Mo or W.[27]

Finally, an important property of the periodic acids is that they are strong, and usually rapid, oxidizing agents, capable, for example, of oxidizing manganous ion to permanganate rapidly and quantitatively. They also react with many organic molecules in quite specific and hence useful oxidations.

INTERHALOGEN AND POLYHALOGEN COMPOUNDS, CATIONS, AND ANIONS

14-14. General Survey

The halogens form many compounds that are (or contain local units that are) binary or even ternary combinations of halogen atoms. The majority of these (the only important exceptions being BrCl, ICl, ICl_3, and IBr among neutral molecules) contain fluorine. There are four basic types:

1. *Neutral Molecules.* These are all binary compounds such as those just mentioned as well as, for example, BrF_3 and IF_7. They are all of the type XX'_n where n is an odd number. They are all closed shell, diamagnetic species, mostly rather volatile.

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[27] L. C. W. Baker *et al., J. Am. Chem. Soc.*, 1980, **102,** 3274.

2. *Cations.* These are both homonuclear, for example, I_2^+ and Cl_3^+, and heteronuclear, for example, $I_3Cl_2^+$, and may be either paramagnetic (I_2^+) or diamagnetic (ICl_2^+). There is one ternary cation, $IBrCl^+$.

3. *Anions.* A great many of these are known, including the classical I_3^- ion. It is in this group that ternary combinations, such as $IBrCl^-$ and $IBrCl_3^-$ are mostly found. They generally occur in combination with large cations as crystalline solids.

4. *Covalent Organo Derivatives.* These are limited to a relatively few aryl species, mostly of the types $ArXF_n$, where $X = I$ or Br and $n = 2$ or 4, although RXF_2 and Ar_2XF types are also known.[28] A typical preparative route involves low-temperature fluorination of RX or ArX (X = Br and I) compounds,[29] but attack on R or Ar occurs under more strenuous conditions. With C_6F_5Br and C_6F_5I, however, the $C_6F_5XF_4$ as well as the $C_6F_5XF_2$ products are readily accessible.[30] With iodine only it is also possible to obtain compounds such as $ArICl_2$ (see also Section 14-22).

For interhalogen compounds of types (1)–(3) the following sections will provide more detailed information. Chemically, the molecular interhalogens are all rather reactive. They are corrosive oxidizing substances and attack most other elements, producing mixtures of the halides. They are all more or less readily hydrolyzed (some, e.g., BrF_3, being dangerously explosive in this respect), in some cases according to the equation

$$XX' + H_2O = H^+ + X'^- + HOX$$

The diatomic compounds often add to ethylenic double bonds and may react with the heavier alkali and alkaline earth metals to give polyhalide salts.

The *diatomic compounds* are ClF, BrF, BrCl, IBr, and ICl. In their physical properties they are usually intermediate between the constituent halogens.[31a] They are of course polar, whereas the halogen molecules are not. Chlorine monofluoride (ClF) is a colorless gas, whereas BrF, BrCl (bp 20°C), and ICl (mp 27°C, dec 97°C) are red or red brown, and IBr is dark gray (mp 41°C, subl 50°C).

Iodine monofluoride (IF) is unknown except in minute amounts observed spectroscopically: it is apparently too unstable with respect to disproportionation to IF_5 and I_2 to permit its isolation. The other isolable diatomic compounds have varying degrees of stability with respect to disproportionation and fall in the following stability order, where the numbers in parentheses represent the disproportionation constants for the gaseous compounds and the elements in their standard states at 25°C: ClF (2.9×10^{-11}) > ICl (1.8×10^{-3}) > BrF (8×10^{-3}) > IBr (5×10^{-2}) > BrCl (0.34). Bromine

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[28] A. N. Nesmeyanov *et al., Doklady Akad. Nauk.*, 1980, **255**, 1136, 1386.

[29] D. Naumann *et al., J. Fluorine Chem.*, 1980, **15**, 213, 541; I. Ruppert, *J. Fluorine Chem.*, 1980, **15**, 173.

[30] J. A. Obaleye and L. C. Sams, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 343.

[31a] R. E. Willis, Jr., and W. W. Clark, III, *J. Chem. Phys.*, 1980, **72**, 4946.

monofluoride also disproportionates according to

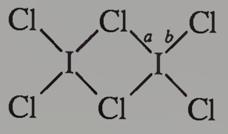
$$3BrF = BrF_3 + Br_2$$

Chlorine monofluoride may be prepared by direct interaction at 220 to 250°C and it is readily freed from ClF_3 by distillation, but it is best prepared by interaction of Cl_2 and ClF_3 at 250 to 350°C. Bromine monofluoride also results on direct reaction of Br_2 with F_2, but it has never been obtained in high purity because of its ready disproportionation. Iodine monochloride[31b] is obtained as brownish-red tablets (β form) by treating liquid chlorine with solid iodine in stoichiometric amount, and cooling to solidify the liquid product. It readily transforms to the α form, ruby-red needles. Bromine monofluoride is prone to dissociation:

$$2BrCl \rightleftharpoons Br_2 + Cl_2 \qquad K = 0.145\ (25°C\ \text{in}\ CCl_4)$$

Iodine monobromide, a solid resulting from direct combination of the elements, is endothermic and extensively dissociated in the vapor. It is used instead of Br_2 in some industrial processes. Despite the general instability of the BrX compounds, the fluorosulfate ($BrOSO_2F$) obtained by treating Br_2 with $S_2O_6F_2$, is stable to 150°C.

Iodine trichloride (ICl_3) is also formed (like ICl) by treatment of liquid chlorine with the stoichiometric quantity of iodine, or with a deficiency of iodine followed by evaporation of the excess of chlorine. It is a fluffy orange powder, unstable much above room temperature, with a planar dimeric structure (14-V).



a = 2.70 Å
b = 2.39 Å

(14-V)

The most imporant class of interhalogen molecules are the fluorides, XF_n (n = 2, 3, 5, and 7), to which we now turn.

14-15. Halogen Fluoride Molecules

These compounds and some of their important physical properties are listed in Table 14-7.

The preparations of ClF and BrF have already been mentioned. Chlorine trifluoride may be prepared by direct combination of the elements at 200 to 300°C and is available commercially. It is purified by converting it into $KClF_4$ by the action of KF and thermally decomposing the salt at 130 to 150°C. Chlorine pentafluoride (ClF_5) can be made efficiently either by interaction

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[31b] C. W. McCleland, *Synthetic Reagents*, Vol. 5, J. S. Pizey, Ed., Horwood-Wiley, Chichester, 1983.

TABLE 14-7
Some Physical Properties of Halogen Fluorides

	mp (°C)	bp (°C)	Specific conductivity[a] at 25°C ($\text{ohm}^{-1}\,\text{cm}^{-1}$)	Structure
ClF	−156.6	−100.1		
ClF_3	−76.3	11.75	3.9×10^{-9}	Planar; distorted T
ClF_5	−103	−14		Square pyramidal
BrF	−33	20		
BrF_3	9	126	$>8.0 \times 10^{-3}$	Planar; distorted T
BrF_5	−60	41	9.1×10^{-8}	Square pyramidal[b]
IF_3				
IF_5	10	101	5.4×10^{-6}	Square pyramidal[b]
IF_7	6.45[c]			Pentagonal bipyramidal[b]

[a] Values in the literature may be very inaccurate in view of the possibility of hydrolysis by traces of water.

[b] Compare R. K. Heenan and A. G. Robiette, *J. Mol. Struct.*, 1979, **54,** 135; *J. Mol. Struct.*, 1979, **55,** 191.

[c] Triple point; sublimes at 4.77°C at 1 atm.

of F_2 with ClF_3[32] or by the reaction:

$$KCl + 3F_2 \xrightarrow[\text{bomb}]{200^\circ\text{C}} KF + ClF_5$$

ClF_5 is a colorless gas; it is less stable thermally but also less reactive than ClF_3, and above 165°C there is the equilibrium

$$ClF_5 \rightleftharpoons ClF_3 + F_2$$

The other halides are best prepared by the reactions

$$Br_2 + 3F_2 \xrightarrow{200^\circ\text{C}} 2BrF_3$$

$$BrF_3 + F_2 \longrightarrow BrF_5$$

$$I_2 + 5F_2 \xrightarrow{25^\circ\text{C}} 2IF_5$$

$$KI + 4F_2 \longrightarrow KF + IF_7$$

Bromine trifluoride and IF_5 are formed by the reaction of X_2 with AgF in HF to give AgX plus XF, followed by disproportionation of XF, but the products are not easily purified. Iodine trifluoride is a yellow powder obtained by fluorination of I_2 in Freon at −78°C; it decomposes to I_2 and IF_5 above −35°C.

The halogen fluorides are very reactive, and with water or organic substances they react vigorously or explosively. They are powerful fluorinating

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[32] A. Smale *et al., J. Fluorine Chem.*, 1981, **17,** 381.

agents for inorganic compounds or, when diluted with nitrogen, for organic compounds. The most useful compounds are ClF, ClF_3, and BrF_3. The order of reactivity is approximately $ClF_3 > BrF_3 > BrF_5 > IF_7 > ClF > IF_5 > BrF$.

Certain compounds, notably ClF, BrF_3, and IF_5, have high entropies of vaporization, and BrF_3 has appreciable electrical conductance. To account for these observations, association by fluorine bridging, in addition to self-dissociation,

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

have been postulated. An analogy with other solvent systems can be made. In liquid BrF_3, for example, the "acid" would be BrF_2^+ and the "base" BrF_4^-. Indeed, suitable compounds such as $BrF_3{\cdot}SbF_5$ (or $BrF_2^+{\cdot}SbF_6^-$) and $KBrF_4$ dissolve in BrF_3 to give highly conducting solutions.

A characteristic property of most halogen fluorides is their amphoteric character; that is, with strong bases, such as alkali metal fluorides, they can form anions, and with strong Lewis acids such as SbF_5 they can form cations:

$$XF_{n+1}^- \xleftarrow{+F^-} XF_n \xrightarrow{-F^-} XF_{n-1}^+$$

Some typical reactions are shown here; the cations and anions will be discussed in detail in later sections.

$$2ClF + AsF_5 \longrightarrow FCl_2^+ AsF_6^-$$
$$ClF + CsF \longrightarrow Cs^+ClF_2^-$$
$$ClF_3 + CsF \longrightarrow Cs^+ClF_4^-$$
$$ClF_5 + SbF_5 \longrightarrow ClF_4^+SbF_6^-$$
$$ClF_3 + AsF_5 \longrightarrow ClF_2^+ AsF_6^-$$
$$IF_5 + CsF \longrightarrow Cs^+IF_6^-$$

14-16. The X_n^+ Ions

The X_2^+ and X_4^{2+} Ions. Iodine has long been known to dissolve in highly acidic, oxidizing media, for example, oleum, to give bright blue paramagnetic solutions; these solutions contain the I_2^+ ion and salts with anions of extremely low basicity can be isolated. The Br_2^+ ion may be similarly generated, but Cl_2^+ is still unknown except in the gas phase. These cations arise by removal of a π^* electron and, accordingly the internuclear distances r decrease and the stretching frequencies ν increase from those in X_2, as shown here:

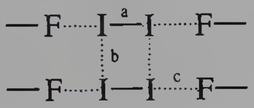
	Br_2	Br_2^+	I_2	I_2^+
r(Å)	2.28	2.13	2.67	2.56
ν(cm^{-1})	319	360	215	238

Salts of the X_2^+ compounds are best prepared[33] by using $S_2O_6F_2$ as an oxidant, followed by addition of SbF_5, namely,

$$X_2 + S_2O_6F_2 \xrightarrow{\text{then } SbF_5} [X_2^+][Sb_3F_{16}^-]$$

Other methods entail direct reaction of I_2 with SbF_5 to give the well known $[I_2^+][Sb_2F_{11}]$ or reactions of X_2 with stoichiometric amounts of XF_n in the presence of SbF_5. These salts are thermodynamically quite stable: bright red $[Br_2^+][Sb_3F_{16}^-]$ melts at 85°C to a red liquid and $[I_2^+][Sb_2F_{11}^-]$ melts sharply at 127°C to a blue liquid.

For the I_2^+ ion, dimerization occurs when solutions are cooled to give a brown I_4^{2+} ion,[34] which is diamagnetic. Two crystalline salts containing this ion, $[I_4^{2+}][AsF_6^-]_2$ and $[I_4^{2+}][Sb_3F_{14}^-][SbF_6^-]$, have been isolated and the cations shown to have structure (14-VI), where the closest approaches of neighboring fluorine atoms are also indicated.[35] This weak dimerization can be attributed to overlap of half-filled π^* orbitals on the two I_2^+ units.



a = 2.58 Å
b = 3.26 Å
c = 2.7−2.9 Å

(14-VI)

Other X_n^+ Ions. The X_3^+ (X = Cl, Br, and I), Br_5^+, and I_5^+ ions are well established, with the I_7^+ ion being possible but uncertain. Salts of these ions can be prepared in a variety of ways, for example,[36]

$$Cl_2 + ClF + AsF_5 \xrightarrow{-78°C} [Cl_3^+][AsF_6^-]$$

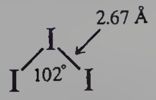
$$Au(S) + 4BrSO_3F \xrightarrow{\text{in } BrSO_3F} [Br_3^+][Au(SO_3F)_4] + \tfrac{1}{2}Br_2$$

$$[Br_3^+][Au(SO_3F)_4] + Br_2 \longrightarrow [Br_5^+][Au(SO_3F)_4]$$

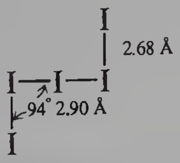
$$3I_2 + 3AsF_5 \xrightarrow{\text{in } SO_2} 2[I_3^+][AsF_6] + AsF_3$$

$$2I_2 + ICl + AlCl_3 \longrightarrow [I_5^+][AlCl_4]$$

The structures of the I_3^+ and I_5^+ ions have been established,[37] and are shown in (14-VII) and (14-VIII).



(14-VII)



(14-VIII)

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[33] W. W. Wilson *et al.*, *Inorg. Chem.*, 1980, **19**, 1489.

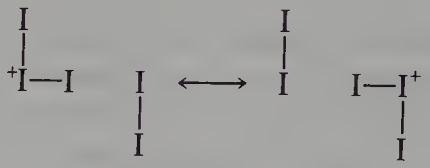
[34] T. Birchall and R. D. Myers, *J. Chem. Soc. Chem. Commun.*, **1982**, 1174.

[35] R. J. Gillespie *et al.*, *J. Chem. Soc. Chem. Commun.*, **1983**, 8.

[36] K. C. Lee and F. Aubke, *Inorg. Chem.*, 1980, **19**, 119.

[37] J. Passmore, *Inorg. Chem.*, 1981, **20**, 2169; *Can. J. Chem.*, 1979, **57**, 968; *Inorg. Chem.*, 1986, **25**, 422.

The structure of I_3^+ is bent as expected (cf. SCl_2) while that of I_5^+ has been explained as a resonance hybrid (14-IX).



(14-IX)

14-17. The Interhalogen Cations

These may be triatomic, pentaatomic, or heptaatomic; the known ones are listed in Table 14-8. The fluorocations are colorless or pale yellow but ICl_2^+, I_2Cl^+, and the others containing heavier halogens are orange, red, or deep purple. Their structures appear to follow the predictions of the VSEPR theory. Thus, several of the triatomics have been shown to be bent, BrF_4^+ has a structure like SF_4, and IF_6^+ is octahedral.

The general method of preparation is to allow a halide ion acceptor to react with an appropriate interhalogen molecule (or its components) as illustrated in the following reactions. Oxidation of the acceptor may also occur:

$$I_2Cl_6 + 2SbCl_5 \longrightarrow 2[ICl_2^+][SbCl_6^-]$$

$$I_2 + 3Cl_2 + 2SbCl_5 \longrightarrow 2[ICl_2^+][SbCl_6^-]$$

$$ClF_3 + AsF_5 \longrightarrow [ClF_2^+][AsF_6^-]$$

$$BrF_5 + 2SbF_5 \longrightarrow [BrF_4^+][Sb_2F_{11}^-]$$

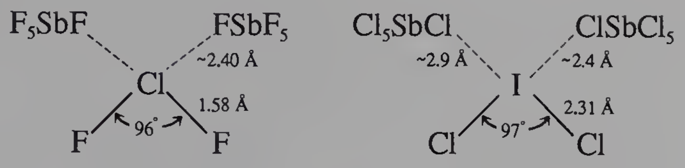
$$IF_7 + BF_3 \longrightarrow [IF_6^+][BF_4^-]$$

$$\tfrac{3}{2}I_2 + SbCl_5 \xrightarrow[-78°C]{\text{in } Cl_2(l)} [I_3Cl_2^+][SbCl_6^-]$$

Since ClF_7 and BrF_7 do not exist the ClF_6^+ and BrF_6^+ cations must be made from ClF_5 and BrF_5 by using strong oxidizing agents that also furnish the

TABLE 14-8
Interhalogen Cations

Triatomic		Pentaatomic	Heptaatomic
ClF_2^+	I_2Cl^+	ClF_4^+	ClF_6^+
Cl_2F^+	IBr_2^+	BrF_4^+	BrF_6^+
BrF_2^+	I_2Br^+	IF_4^+	IF_6^+
IF_2^+	$IBrCl^+$		
ICl_2^+			



$[ClF_2^+][SbF_6^-]$ $[ICl_2^+][SbCl_6^-]$

FIG. 14-3. Two structures showing the close anion–cation interactions typical of polyhalogen cation compounds.

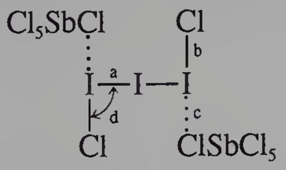
necessary anions:

$$ClF_5 + PtF_6 \longrightarrow [ClF_6^+][PtF_6^-] + [ClF_4^+][PtF_6^-]$$

$$BrF_5 + [KrF^+][AsF_6^-] \longrightarrow [BrF_6^+][AsF_6^-] + Kr$$

It is important to note that in all known structures, the anions make very close contacts, via halogen bridges, with the cations.[38] Two representative structures illustrating this point are shown in Fig. 14-3.

The $I_3Cl_2^+$ cation is rather different from the others (14-X), but structurally rather similar to I_5^+. It is known only in $[I_3Cl_2^+][SbCl_6]$, which is prepared from I_2 and $SbCl_5$ in liquid chlorine.[39]



(14-X)

a = 2.90 Å
b = 2.34 Å
c = 2.95 Å
d = 93°

14-18. Polyiodide Anions

Iodide ions have a pronounced tendency to interact with one or more molecules of I_2 to form polyiodide anions, I_n^{m-}. The earliest to be recognized was I_3^-, which is the only one of importance in aqueous chemistry. In nonaqueous media (e.g., CH_3OH and CH_3CN) stabilities of the others are substantially higher. In water at 25°C we have the equilibrium[40]

$$I^- + I_2 = I_3^- \qquad K \approx 698 \pm 10 \ (25°C)$$

In solution, the I_3^- ion appears to be linear and symmetrical, but in crystalline environments it is often unsymmetrical, though consistently linear or nearly so. In most cases where it does not reside on a crystallographic center of symmetry, the I_3^- ion is distinctly unsymmetrical; the two I—I distances

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[38] T. Birchall and R. D. Meyers, *Inorg. Chem.*, 1981, **20**, 2207.
[39] N. Thorup and J. Shamir, *Inorg. Nucl. Chem. Lett.*, 1981, **17**, 193.
[40] D. A. Palmer *et al.*, *J. Solution Chem.*, 1984, **13**, 673.

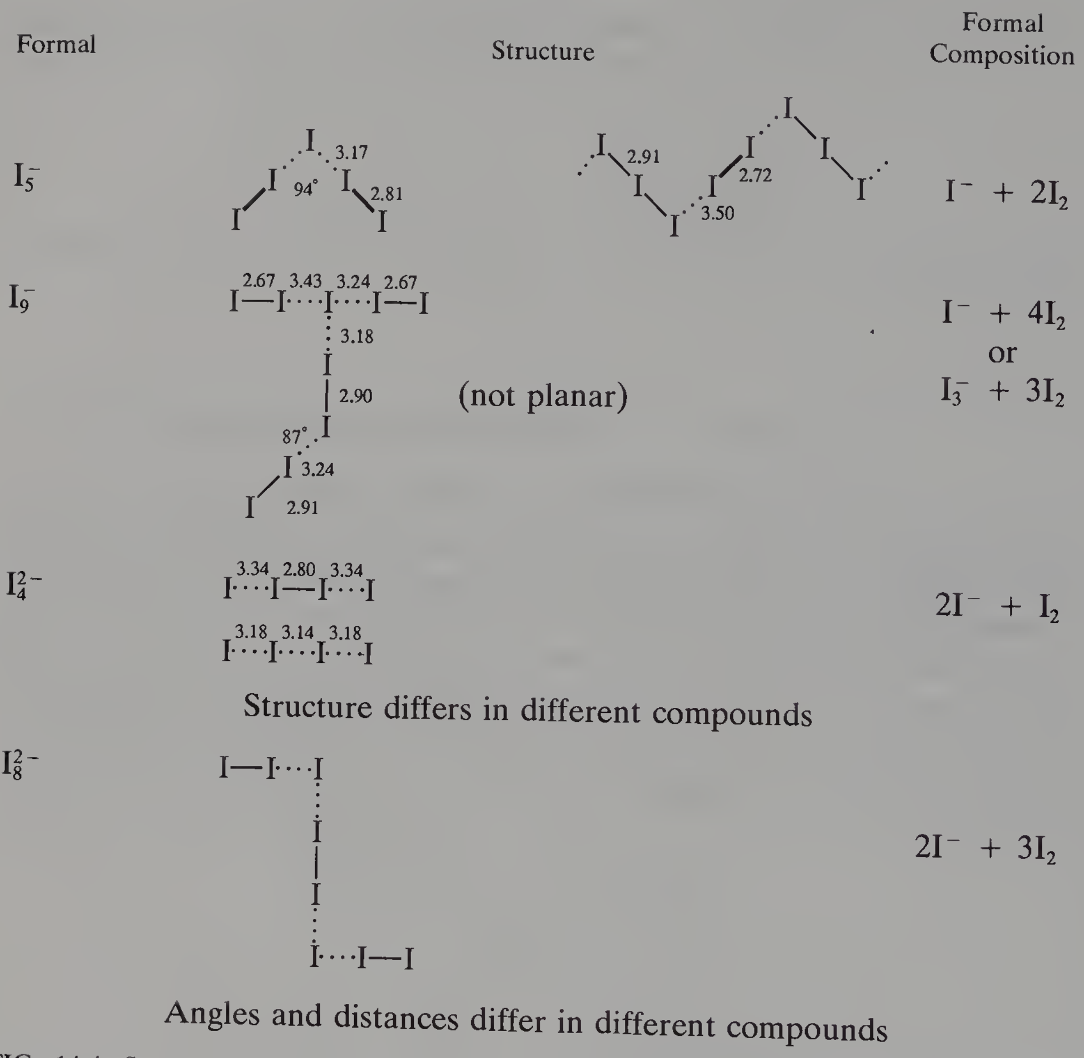

FIG. 14-4. Some higher polyiodide ions (distances in Å). Distances >3.0 and <3.0 Å are indicated by ··· and —, respectively.

may differ by as little as 0.06 Å[41] or by as much as 0.20 to 0.33 Å.[42] On the other hand, there are cases[43] where the ion is essentially symmetrical even though this is not rigorously required by crystallographic symmetry. In the symmetrical I_3^- ions the shortest overall I to I distances are found, ~5.80 Å, and it has been suggested[43] that the more compact I_3^- ions are favored by larger cations and they have the greater tendency to be symmetrical.

Many larger arrays are known[44] (see Fig. 14-4), all of which can be regarded as assemblages of I^- and/or I_3^- ions with I_2 molecules. It should be noted that an I···I van der Waals contact is well over 4 Å (~4.3 Å) so that distances in the range 3.3 to 3.5 Å connote real bond formation although weak as compared to a full single bond in I_2, where the distance is 2.67 Å. Not shown

[41] M. G. Cingi *et al., Inorg. Chem. Acta,* 1981, **52,** 237.

[42] K.-F. Tebbe *et al., Acta Cryst.,* 1985, **C41,** 660.

[43] G. V. Gridunova *et al., J. Organomet. Chem.,* 1982, **238,** 297.

in Fig. 14-4 is the I_{16}^{4-} ion, which can be regarded as a kinked chain of $I_3^- \cdots I_2 \cdots I^- \cdots I_2 \cdots I_2 \cdots I^- \cdots I_2 \cdots I_3^-$, as well as others in which interchain interactions blur the question of how to delimit the anion properly.[44]

Finally, it may be noted that iodine has a tendency to form chain anions, I_3^-, I_5^-, or something more elaborate under a variety of solid state circumstances. The classic starch–iodine complex has already been noted. More recently it has been shown that iodine used as a dopant to enhance the electrical conductivity of polyacetylene is present as I_3^- and I_5^- ions, electrons having been acquired from π orbitals of the polymer.[45]

14-19. Other Polyhalide Anions

The principal anions are listed in Table 14-9. All are of the $X_lY_mZ_n^-$ ($l + m + n$ odd) type. In the hetero species, the central atom is known (or believed) to be always one with the highest atomic number, for example, [Cl—I—Br]$^-$. All the triatomic ions are essentially linear while the pentaatomic ones are based on a square planar motif, with the possible exceptions of the I_4X^- ions. The Br_3^- ion, like the I_3^- ion may be symmetric[46] or unsymmetric[47] depending on its environment. The Cl_3^- ion is so far known only in an unsymmetrical form (distances of 2.31 and 2.23 Å).[48] While the Br_3^- ion does not exist in aqueous solution it has a formation constant[49] (from

TABLE 14-9
Principal Polyhalide Anions (other than polyiodides or fluorospecies)

Trinuclear	Pentanuclear
Cl_3^-	ICl_3F^-
Br_3^-	ICl_4^-
Br_2Cl^-	$IBrCl_3^-$
$BrCl_2^-$	$I_2Cl_3^-$
I_2Cl^-	$I_2BrCl_2^-$
IBr_2^-	$I_2Br_2Cl^-$
ICl_2^-	$I_2Br_3^-$
$IBrCl^-$	I_4Cl^-
$IBrF^-$	I_4Br^-

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[44] P. K. Hon *et al.*, *Inorg. Chem.*, 1979, **18,** 2916; E. Dubler and L. Linowsky, *Helv. Chem. Acta,* 1978, **58,** 2604; F. H. Herbstein and M. Kapon, *J. Chem. Soc. Chem. Commun.*, **1975**, 677; F. H. Herbstein and W. Schwotzer, *Angew. Chem. Int. Ed. Engl.*, 1982, **21,** 219; J. Trotter *et al.*, *Inorg. Chem.*, 1979, **18,** 2916; F. H. Herbstein *et al.*, *J. Inclusion Phenom.*, 1985, **3,** 173.

[45] G. Kaindl *et al.*, *Solid State Commun.*, 1982, **41,** 75.

[46] M. P. Bogaard and A. D. Rae, *Cryst. Struct. Commun.*, 1982, **11,** 175; F. A. Cotton *et al.*, *Inorg. Chem.*, 1986, **25,** 3528.

[47] G. Wolmershäuser *et al.*, *Chem. Ber.*, 1982, **115,** 1126; J. J. Mayerle *et al.*, *Inorg. Chem.*, 1979, **18,** 1161.

[48] M. P. Bogaard *et al.*, *Acta Cryst.*, 1981, **B37,** 1357.

[49] P. Castellonese and P. Villa, *Bull. Soc. Chim. France,* 1982, I-169.

Br_2 and Br^-) in liquid SO_2 of ~100 L mol^{-1}. The mixed ions are formed in quasistatistical equilibria, namely, in methanol[50]:

$$2Cl_2 + 2I_2 + 2Cl^- + 2I^- = Cl_3^- + I_3^- + ICl_2^- + I_2Cl^-$$

OTHER COMPOUNDS

14-20. Oxohalogen Fluorides

This class comprises those compounds containing F, O and X that have fluorine to halogen bonds. They are often called halogen oxofluorides but this term is ambiguous. Compounds containing F—O—X groups are discussed in the next section. The known compounds are listed in Table 14-10. No one halogen has yet been shown to form all six types. The structures of the molecular species, some of which are shown in Fig. 14-5, are all readily predictable from the VSEPR formalism. Thus FXO is bent (two lone pairs), FXO_2 is pyramidal (one lone pair) FXO_3 has C_{3v} symmetry. F_3XO is an incomplete *tbp* with F, O, and a lone pair in the equatorial plane, F_3XO_2 is a complete *tbp* with F, O, O in the equatorial plane, and F_5IO is *octahedral* with C_{4v} symmetry. While most of the molecules are monomers, F_3IO_2 both dimerizes and trimerizes via oxygen bridges. In some cases solid adducts with other molecules are formed. Thus, there is $(F_3IO_2SbF_5)_2$, which is cyclic with alternating SbF_4 and IF_4 units linked by oxygen atoms,[51] and $(F_3IO_2 \cdot F_3IO)_2$, with alternating F_2IO and IF_4 units linked by oxygen atoms.[52]

A variety of cations and anions are derived formally (and as a general rule also in practice) from some of the neutral molecules by removal or addition of F^-. These are of the types shown in Table 14-11. Their structures are again

TABLE 14-10
Oxohalogen Fluorides, F_nXO_m

Formal oxidation No. of X	Chlorine	Bromine	Iodine
III	$FClO$		
V	$FClO_2$	$FBrO_2$	FIO_2
	F_3ClO	F_3BrO	F_3IO
VII	$FClO_3$	$FBrO_3$	FIO_3
	F_3ClO_2		F_3IO_2
			F_5IO

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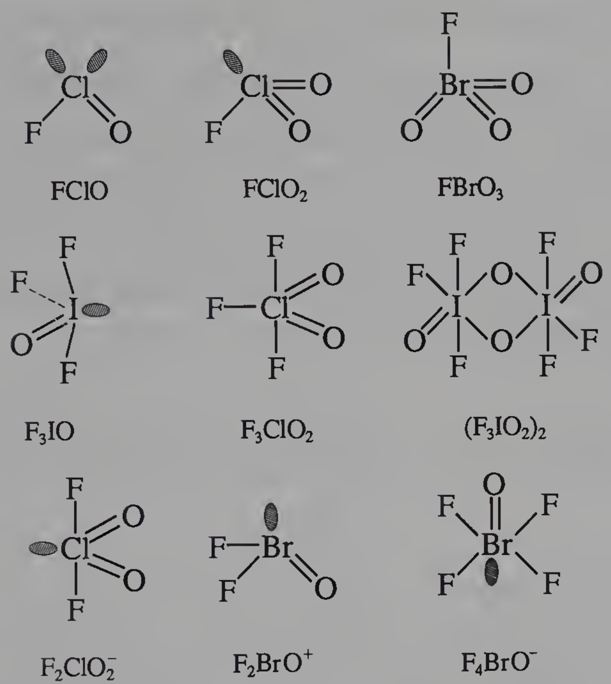
[50] L.-F. Olsson, *Inorg. Chem.*, 1985, **24**, 1398.
[51] A. J. Edwards and A. A. K. Hana, *J. Chem. Soc. Dalton Trans.*, **1980**, 1734.
[52] R. J. Gillespie *et al.*, *J. Chem. Soc. Dalton Trans.*, **1980**, 481.


$FClO$ $FClO_2$ $FBrO_3$

F_3IO F_3ClO_2 $(F_3IO_2)_2$

$F_2ClO_2^-$ F_2BrO^+ F_4BrO^-

FIG. 14-5. Some representative structures of oxohalogen fluoride molecules and ions.

all as expected from the VSEPR formalism. A typical reaction,[53] whereby one of these ions is generated is

$$F_3BrO + BF_3 \longrightarrow [F_2BrO][BF_4]$$

A few representative structures are shown schematically in Fig. 14-5. The methods of preparation of these compounds are enormously diverse. Most of them are highly reactive as oxidizing agents, fluorinating agents, and towards water.

The perhalofluorides (FXO_3), especially $FClO_3$, are probably the most important compounds of this class. Perchloryl fluoride can be prepared by the action of F_2 or FSO_3H on $KClO_4$, but is best made by the solvolytic

TABLE 14-11

Cations and Anions of General Formula $F_nXO_m^{+,-}$

"Parent" molecule	Cations	Anions
FXO_2	ClO_2^+	$F_2ClO_2^-$
	BrO_2^+	$F_2BrO_2^-$
		$F_2IO_2^-$
F_3XO	F_2ClO^+	F_4ClO^-
	F_2BrO^+	F_4BrO^-
F_3XO_2	$F_2ClO_2^+$	

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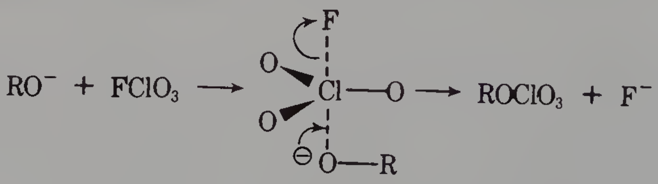
[53] R. J. Gillespie *et al.*, *J. Chem. Soc. Dalton Trans.*, **1979,** 6.

reaction of $KClO_4$ with a superacid (e.g., a mixture of HF and SbF_5):

$$KClO_4 + 2HF + SbF_5 \xrightarrow{40\text{–}50^\circ C} FClO_3 + KSbF_6 + H_2O$$

The toxic gas (mp −147.8°C, bp −46.7°C) is thermally stable to 500°C and resists hydrolysis. At elevated temperatures it is a powerful oxidizing agent and has selective fluorinating properties, especially for replacement of H by F in CH_2 groups. It can also be used to introduce ClO_3 groups into organic compounds (e.g., C_6H_5Li gives $C_6H_5ClO_3$). In these reactions it appears that the nucleophile attacks the chlorine atom, for example,



Perbromyl fluoride (mp −110°C) is made similarly, but it is more reactive than ClO_3F and is hydrolyzed by base:

$$BrO_3F + 2OH^- = BrO_4^- + H_2O + F^-$$

presumably by initial associative attack of OH^- on Br.

14-21. Compounds with —OX Groups

Those that we shall discuss are three classes of halogen derivatives of oxoacids. There are, however, others, such as $CF_3C(O)OF$ and $CF_3C(O)OCl$. The latter, while not very stable can be easily prepared from CF_3CO_2Na and ClF[54] and has some use in synthesis.

Halogen Perchlorates ($XOClO_3$). All four halogen perchlorates appear to exist, but $IOClO_3$ is not well characterized. Bromine perchlorate ($BrOClO_3$) and even $ClOClO_3$ are so unstable and shock sensitive as to be of little importance. Fluorine perchlorate ($FOClO_3$) is a colorless gas (bp 16°C), which can be prepared in extremely pure form by thermal decomposition of NF_4ClO_4 to NF_3 and $FOClO_3$.[55] This very pure material can be handled safely and is very well characterized.[56a] It finds use in the synthesis of anhydrous metal perchlorates and perfluoroalkyl perchlorates, for example,

$$CF_2{=}CF_2 + FOClO_3 \longrightarrow CF_3CF_2OClO_3$$

Halogen Fluorosulfates ($XOSO_2F$). All four halogen fluorosulfates are known, but all are highly reactive and thermally unstable. The fluorine compound $FOSO_2F$ and to a lesser extent $ClOSO_2F$ are most common. The former

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[54] I. Tari and D. D. DesMarteau, *Inorg. Chem.*, 1979, **18,** 3205.
[55] C. J. Schack and K. O. Christe, *Inorg. Chem.*, 1979, **18,** 2619.
[56a] K. O. Christe and E. C. Curtis, *Inorg. Chem.*, 1982, **21,** 2938.

can be made by direct addition of F_2 to SO_3 while the others can be formed by reacting X_2 with $S_2O_6F_2$.

Halogen Nitrates ($XONO_2$). Again, all four halogen nitrates appear to exist but only $FONO_2$, $ClONO_2$ and $BrONO_2$[56b] and its N_2O_5 adduct $NO_2^+[Br(ONO_2)_2]^-$ are well established. They are thermally unstable (potentially explosive) and highly reactive.

14-22. Other Compounds with Formally Positive Halogens

We deal here with some types of compounds formed mainly by iodine although there are a few bromine analogues.

A highly novel I^I compound[57] is obtained by the reaction of I_2 with the [2,2,2]-cryptate (Section 12-14) in $CHCl_3$:

$$I_2 + [2,2,2] \longrightarrow ([2,2,2]I)^+ + I^- \qquad K > 10^7$$

This is reminiscent of the induced ionic disproportionation of Na by similar strong cation encapsulation (Section 4-3).

The formally I^{III} compound iodosylbenzene (PhIO) finds wide use as an oxygen-transfer agent, as, for example, in the conversion of Fe^{III} porphyrins to Fe^VO porphyrins. The solid is polymeric, —I(Ph)—O—I(Ph)—O— and not generally very soluble except in alcohols, especially methanol where $PhI(OMe)_2$ is formed.[58] Many compounds of iodine(III) are known, including some with organic groups. The only bromo analogues are $Br(OSO_2F)_3$ and $K[Br(OSO_2F)_4]$. Among the compounds in which I^{III} is combined with oxo-anions are $I(OSO_2F)_3$, $I(NO_3)_3$, $I(OCOCH_3)_3$, IPO_4, and $I(OClO_3)_3$. These compounds contain essentially covalent I—O bonds. Preparative methods include the following:

$$2I_2 + 3AgClO_4 \xrightarrow{\text{ether}} I(OClO_3)_3 + 3AgI$$

$$I_2 + 6ClOClO_3 \xrightarrow{-85°C} 2I(OClO_3)_3 + 3Cl_2$$

$$CsI + 4ClOClO_3 \longrightarrow Cs[I(OClO_3)_4] + 2Cl_2$$

$$I_2 + HNO_3\ (\text{fuming}) + (CH_3CO)_2O \longrightarrow I(OCOCH_3)_3$$

$$I_2 + HNO_3\ (\text{conc}) + H_3PO_4 \longrightarrow IPO_4$$

The compounds are sensitive to moisture and are not stable much above room temperature. They are hydrolyzed with disproportionation of the I^{III}, as illustrated for IPO_4 thus:

$$5IPO_4 + 9H_2O \longrightarrow I_2 + 3HIO_3 + 5H_3PO_4$$

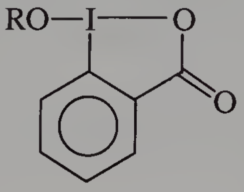
[56b] W. W. Wilson and K. O. Christe, *Inorg. Chem.*, 1987, **26**, 1573.

[57] J.-L. Pierre *et al.*, *J. Am. Chem. Soc.*, 1980, **102**, 6574.

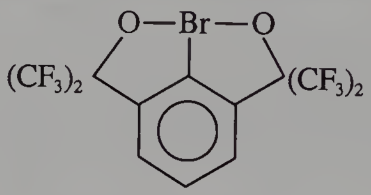
[58] B. C. Schardt and C. L. Hill, *Inorg. Chem.*, 1983, **22**, 1563.

Covalent I^{III} is known also in the compound triphenyliodine $(C_6H_5)_3I$ and a large number of diaryliodonium salts, such as $(C_6H_5)_2I^+X^-$, where X may be one of a number of common anions. Aryl compounds such as $C_6H_5ICl_2$ are also well known and can be made by direct reaction of ArI with Cl_2.

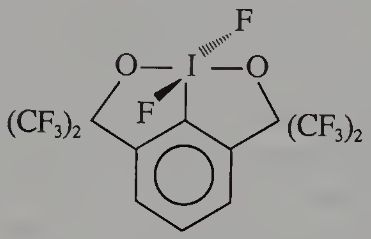
Recently, a number of new I^{III} and I^V compounds with I—aryl bonds have been made by using substituted aryl groups that are especially able to stabilize the higher oxidation states.[59] Representative compounds, including one Br compound, are shown as (14-XI) to (14-XIV).



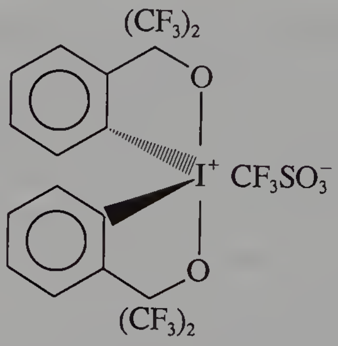
(14-XI)



(14-XII)

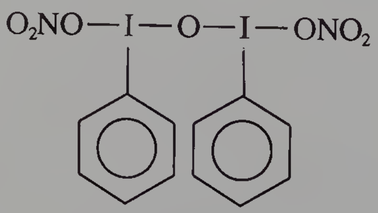


(14-XIII)

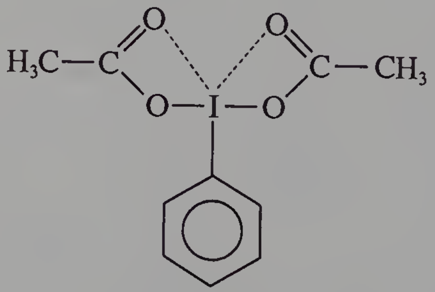


(14-XIV)

The I^V compounds (14-XV) and (14-XVI) are also well characterized, with the expected T geometry at the iodine atom.[60]



(14-XV)



(14-XVI)

Additional I^V compounds are known[61] with the $—OEF_5$ (E = Se and Te) radical, namely, $I(OTeF_5)_5$, $OI(OTeF_5)_3$ and $F_xI(OEF_5)_{5-x}$.

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[59] J. C. Martin *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 902; *J. Organomet. Chem.*, 1979, **44**, 1779; 1982, **47**, 1024.

[60] N. W. Alcock *et al.*, *J. Chem. Soc. Dalton Trans.*, **1979**, 851, 854.

[61] D. Lentz and K. Seppelt, *Z. Anorg. Allg. Chem.*, 1980, **460**, 5.

Finally, it should be noted that there are some I^{III} compounds containing the iodosyl (formally IO^+) group. When I_2 is oxidized with O_3 in strong acids, compounds such as $(IO)_2SO_4$, $(IO)SO_3F$, and $(IO)NO_3$ can be obtained,[62] and another route is the following[63]:

$$CF_3I(O)F_2 \xrightarrow[\text{or } SbF_5]{BF_3, AsF_5,} CF_4 + (IO)MF_n$$

None of these compounds is characterized structurally.

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[62] M. Schmeisser, *Z. Anorg. Allg. Chem.*, 1980, **470,** 84.

[63] D. Naumann and W. Habel, *Z. Anorg. Allg. Chem.*, 1981, **482,** 139.

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Chapter Fifteen

The Group VIIIA(18) Elements: He, Ne, Ar, Kr, Xe

THE ELEMENTS

15-1. Group Trends

The closed-shell electronic structures of the noble gas atoms are extremely stable, as shown by the high ionization enthalpies, especially of the lighter members (Table 15-1). The elements are all low-boiling gases whose physical properties vary systematically with atomic number. The boiling point of helium is the lowest of any known substance. The boiling points and heats of vaporization increase monotonically with increasing atomic number.

The heats of vaporization are measures of the work that must be done to overcome interatomic attractive forces. Since there are no ordinary electron-pair interactions between noble gas atoms, these weak forces (of the van der Waals or London type) are proportional to the polarizability and inversely proportional to the ionization enthalpies of the atoms; they increase therefore as the size and diffuseness of the electron clouds increase.

The ability of the gases to combine with other atoms is very limited. Only Kr, Xe, and Rn have so far been induced to do so. This ability would be expected to increase with decreasing ionization enthalpy and decreasing energy of promotion to states with unpaired electrons. The data in Table 15-1 for ionization enthalpies and for the lowest-energy promotion process show that chemical activity should increase down the group. Apparently the threshold of actual chemical activity is reached only at Kr; that of Xe is markedly greater while that of Rn is presumably still greater, but it is difficult to assess because the half-life of the longest-lived isotope, ^{222}Rn, is only 3.825 days.

15-2. Occurrence, Isolation, and Applications

The noble gases occur as minor constituents of the atmosphere (Table 15-1). Helium is also found as a component (up to ~7%) in certain natural hydro-

TABLE 15-1
Some Properties of the Noble Gases

Element	Outer shell configuration	Atomic number	First ionization enthalpy (kJ mol^{-1})	Normal bp (K)	ΔH_{vap} (kJ mol^{-1})	% by volume in the atmosphere	Promotion energ (kJ mol^{-1}), $ns^2np^6 \rightarrow ns^2np^5(n + 1)s$
He	$1s^2$	2	2372	4.18	0.09	5.24×10^{-4}	
Ne	$2s^22p^6$	10	2080	27.13	1.8	1.82×10^{-3}	1601
Ar	$3s^23p^6$	18	1520	87.29	6.3	0.934	1110
Kr	$4s^24p^6$	36	1351	120.26	9.7	1.14×10^{-3}	955
Xe[a]	$5s^25p^6$	54	1169	166.06	13.7	8.7×10^{-6}	801
Rn	$6s^26p^6$	86	1037	208.16	18.0		656

[a] For nmr of ^{129}Xe and ^{131}Xe, see J. Reisse, *Nouv. J.Chim.*, 1986, **10,** 665 (includes applications).

carbon gases in the United States. This helium undoubtedly originated from decay of radioactive elements in rocks, and certain radioactive minerals contain occluded He that can be released on heating. All isotopes of Rn are radioactive and are occasionally given specific names (e.g., actinon, thoron) derived from their source in the radioactive decay series; ^{222}Rn is normally obtained by pumping off the gas from radium chloride solutions. Neon, Ar, Kr, and Xe are obtainable as products of fractionation of liquid air. The main uses are in providing inert atmospheres, for example, Ar in welding and gas-filled electric light bulbs, Ne in discharge tubes. Liquid He is used extensively in cryoscopy.

The amounts of He and of Ar formed by radioactive decay of U- and K-containing minerals can be used to determine the age of the rock.[1]

Xenon and Kr can be trapped in β-quinol clathrates (Section 3-4).[2]

THE CHEMISTRY OF THE NOBLE GASES

After his observation that O_2 reacts with PtF_6 to give the compound $[O_2^+][PtF_6^-]$ (Section 12-7). N. Bartlett in 1962 recognized that since the ionization enthalpy of Xe is almost identical with that of O_2, an analogous reaction should occur with Xe. He isolated a red crystalline solid, originally believed to be $XePtF_6$ (see later), by direct interaction of Xe with PtF_6.

Some species such as He_2^+ or HeH^+ can be detected by mass spectrometry[3] and the green Xe_2^+ ion has been observed spectroscopically when $XeF^+Sb_2F_{11}^-$ (see later) in SbF_5 is reduced with Xe.

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[1] M. W. Rowe, *J. Chem. Educ.*, 1985, **62,** 580.

[2] D. W. Davidson *et al.*, *J. Incl. Phenom.*, 1984, **2,** 231.

[3] J. H. Beynon *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985,** 210.

15-3. The Chemistry of Xenon

Xenon reacts directly only with F_2, but compounds in oxidation states from II to VIII are known, some of which are exceedingly stable and can be obtained in large quantities. The more important compounds and some of their properties are given in Table 15-2.

Fluorides. The equilibrium constants for the reactions

$$\mathrm{Xe} + \mathrm{F_2} \longrightarrow \mathrm{XeF_2}$$

$$\mathrm{XeF_2} + \mathrm{F_2} \longrightarrow \mathrm{XeF_4}$$

$$\mathrm{XeF_4} + \mathrm{F_2} \longrightarrow \mathrm{XeF_6}$$

for the range 25 to 500°C show unequivocally that only these three binary fluorides exist. The equilibria are established rapidly only above 250°C, which is the lower limit for thermal synthesis. All three fluorides are volatile, readily subliming at room temperature. They can be stored indefinitely in nickel or Monel metal containers, but XeF_4 and XeF_6 are particularly susceptible to hydrolysis and traces of water must be rigorously excluded.

TABLE 15-2
Principal Xenon Compounds

Oxidation state	Compound	Form	mp (°C)	Structure	Remarks
II	XeF_2	Colorless crystals	129	Linear	Hydrolyzed to Xe + O_2: very soluble in HF(l)
IV	XeF_4	Colorless crystals	117	Square	Stable, $\Delta H_f^{298°C} = -284$ kJ mol^{-1}
VI	XeF_6	Colorless crystals	49.6	Complex	Stable, $\Delta H_f^{298°C} = -402$ kJ mol^{-1}
	$CsXeF_7$	Colorless solid		See text	dec > 50°
	Cs_2XeF_8	Yellow solid		Archimedian antiprism[a]	Stable to 400°C
	$XeOF_4$	Colorless liquid	−46	ψ Octahedral[b]	Stable
	XeO_2F_2	Colorless crystals	31	ψ *tbp*[b]	Metastable
	XeO_3	Colorless crystals		ψ Tetrahedral[b]	Explosive, $\Delta H_f^{298°C} = +402$ kJ mol^{-1}; hygroscopic; stable in solution
	$K_n^+[XeO_3F^-]_n$	Colorless crystals		*sp* (F bridges)	Very stable
VIII	XeO_4	Colorless gas	−35.9	Tetrahedral	Highly explosive
	XeO_3F_2	Colorless gas	−54.1		
	XeO_6^{4-}	Colorless salts		Octahedral	Anions $HXeO_6^{3-}$, $H_2XeO_6^{2-}$, $H_3XeO_6^-$ also exist

[a] In the salt $(NO^+)_2[XeF_8]^{2-}$ from XeF_6 and NOF.

[b] Lone pair present.

Xenon Difluoride. This is best obtained by interaction of F_2 and an excess of Xe at high pressure. It is soluble in water, giving solutions 0.15 *M* at 0°C, that evidently contain XeF_2 molecules. The hydrolysis is slow in dilute acid but rapid in basic solution:

$$XeF_2 + 2OH^- \longrightarrow Xe + \tfrac{1}{2}O_2 + 2F^- + H_2O$$

The solutions, which have a pungent odor due to XeF_2, are powerful oxidizing agents (e.g., HCl gives Cl_2, Ce^{III} gives Ce^{IV}), and the estimated potential is

$$XeF_2(aq) + 2H^+ + 2e = Xe + 2HF(aq) \qquad E^0 = +2.64\ V$$

XeF_2 also acts as a mild fluorinating agent for organic compounds;[4] for example, in solution or in the vapor phase benzene is converted into C_6H_5F.

Xenon Tetrafluoride. The easiest tetrafluoride to prepare is XeF_4 and essentially quantitative conversion is obtained when a 1:5 mixture of Xe and F_2 is heated in a nickel vessel at 400°C and ~6-atm pressure for a few hours. Its properties are similar to those of XeF_2 except regarding its hydrolysis, as discussed later. With hydrogen, XeF_4 rapidly gives Xe and HF, and with F_2 under pressure, XeF_6. Xenon tetrafluoride specifically fluorinates the ring in substituted arenes such as toluene.

Xenon Hexafluoride. The synthesis of XeF_6 requires more severe conditions, but at >50 atm and >250°C conversion is quantitative. The solid is colorless but becomes yellow when heated and gives a yellow liquid and vapor. Xenon hexafluoride reacts rapidly with quartz:

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

and is extremely readily hydrolyzed.

The XeF_6 molecule has seven electron pairs in the valence shell of the Xe atom. Experimental and theoretical studies, however, have established a substantially distorted, stereochemically nonrigid (see Section 29-12) structure. The structure of the solid is extremely complex. There are at least four crystalline forms, three of which consist of tetramers and the fourth of both tetramers and hexamers. As shown in Fig. 15-1, these oligomers are built of square pyramidal XeF_5^+ units bridged by F^- ions.

Xenon hexafluoride gives a yellow solution in $(F_5S)_2O$ at 25°C, indicative of XeF_6 molecules; but as the temperature is lowered the solution becomes colorless, and nmr results at −118°C show that tetramers are present.

Fluorocations. One of the characteristic reactions of the binary fluorides is the transfer of F^- to strong fluoride acceptors to form compounds containing cations of the type $Xe_nF_m^+$. These compounds are not fully ionic since the fluoro anions form fluoro bridges to the cations. Compounds in this class formed by XeF_2 are of 2:1, 1:1, and 1:2 stoichiometries, and examples are $2XeF_2 \cdot SbF_5$, $XeF_2 \cdot AsF_5$, and $XeF_2 \cdot 2RuF_5$. Among other fluoride ion acceptors forming such compounds are TaF_5, NbF_5, PtF_5, and OsF_5. Two types of

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[4] B. Zajc and M. Zupan, *J. Chem. Soc. Chem. Commun.*, **1980**, 759.

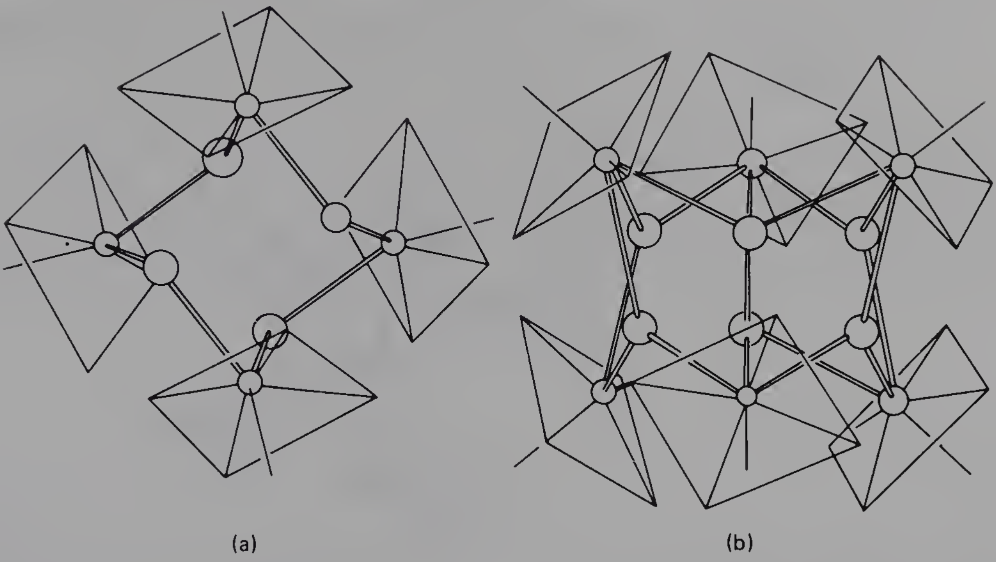
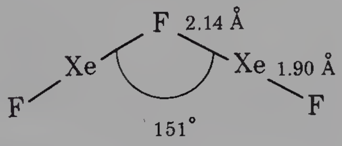


FIG. 15-1. (a) Tetrameric and (b) hexameric units in one of the crystal forms of XeF_6.

cation are formed; XeF^+ and $Xe_2F_3^+$. The way in which XeF^+ typically interacts with an F atom in the accompanying anion is shown for $[XeF^+]$-$[RuF_6^-]$ in Fig. 15-2, and the structure of $Xe_2F_3^+$ appears in (15-I).



(15-I)

Based on the present knowledge of XeF_2 chemistry, it is believed that Bartlett's original reaction is best written

$$\mathrm{Xe} + 2\mathrm{PtF}_6 \xrightarrow{25^\circ\mathrm{C}} [\mathrm{XeF}^+][\mathrm{PtF}_6^-] + \mathrm{PtF}_5 \xrightarrow{60^\circ\mathrm{C}} [\mathrm{XeF}^+][\mathrm{Pt}_2\mathrm{F}_{11}^-]$$

The product obtained at 25°C appears to contain both $[XeF^+][PtF_6^-]$ and $[PtF_5^-]$. $XeF^+Sb_2F_{11}^-$ in SbF_5 reacts[5] with Xe to give the green, paramagnetic, and formally Xe^I ion, Xe_2^+.

The other fluorides have comparable though less extensive cation chemistry. For example, XeF_4 reacts with BiF_5 to give $[XeF_3^+][BiF_6^-]$, and XeF_6 forms the compounds $[XeF_5^+][RuF_6^-]$ and $[XeF_5^+]_2[PdF_6^{2-}]$. The presence of XeF_5^+ cations in such compounds is consistent with their incipient formation in solid XeF_6 (cf. Fig. 15-1). The reaction of XeF_6 with AuF_3 and F_2 gives $[Xe_2F_{11}^+][AuF_6^-]$ in which the cation consists of two XeF_5^+ units bridged by F^- to give the overall composition $Xe_2F_{11}^+$.

When dissolved in PF_5, AsF_5, and SbF_5, the oxofluorides $XeOF_4$ and XeO_2F_2 also form cations believed to be $XeOF_3^+$ and XeO_2F^+.

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[5] L. Stein and W. W. Henderson, *J. Chem. Soc. Dalton Trans.*, **1980**, 2857.

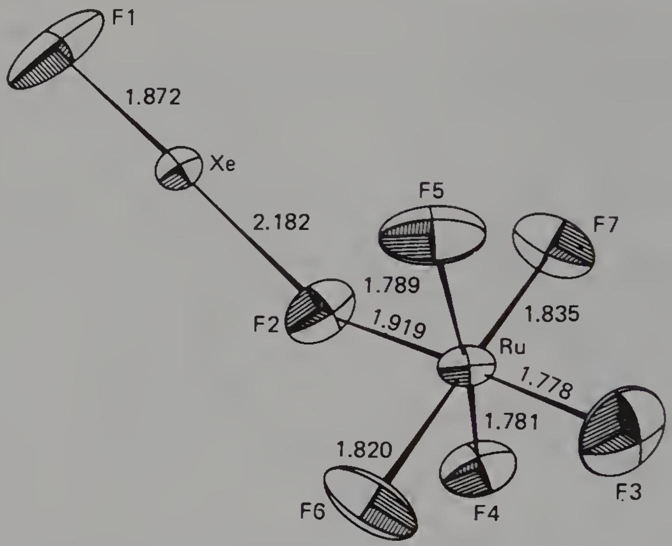

FIG. 15-2. The $[XeF^+][RuF_6^-]$ structural unit [reproduced by permission from N. Bartlett *et al.*, *Inorg. Chem.*, 1973, **12,** 1717].

Fluoroanions. Xenon hexafluoride (XeF_6) acts as a fluoride ion acceptor, reacting with alkali metal fluorides (other than LiF) to give heptafluoro- or octafluoroxenates(VI):

$$XeF_6 + RbF \longrightarrow RbXeF_7$$

The Rb and Cs salts decompose above 20 and 50°C, respectively:

$$2MXeF_7 \longrightarrow XeF_6 + M_2XeF_8$$

The Rb and Cs *octafluoroxenates* are the most stable xenon compounds yet made and decompose only above 400°C; they hydrolyze in the atmosphere to give xenon-containing oxidizing products. The sodium fluoride adduct of XeF_6 decomposes below 100°C and can be used to purify XeF_6.

Compounds with Xe—O Bonds. Both XeF_4 and XeF_6 are violently hydrolyzed by water to give stable aqueous solutions up to 11 *M* of *xenon trioxide* (XeO_3). The oxide is also obtained by interaction of XeF_6 with $HOPOF_2$.[6]

Xenon trioxide is a white deliquescent solid and is dangerously explosive; its formation is why great care must be taken to avoid water in studies of XeF_6. The molecule is pyramidal (C_{3v}). It can be quantitatively reduced by iodide:

$$XeO_3 + 6H^+ + 9I^- \longrightarrow Xe + 3H_2O + 3I_3^-$$

Xenate esters may be formed in violent reactions with alcohols.

In water XeO_3 appears to be present as XeO_3 molecules, but in base solutions we have the main equilibrium

$$XeO_3 + OH^- \rightleftharpoons HXeO_4^- \qquad K = 1.5 \times 10^{-3}$$

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[6] J. Foropoulos, Jr. and D. D. DesMarteau, *Inorg. Chem.*, 1980, **19,** 2503.

where $HXeO_4^-$ slowly disproportionates to produce Xe^{VIII} and Xe:

$$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$$

Aqueous Xe^{VIII} arises also when O_3 is passed through a dilute solution of Xe^{VI} in base. These yellow *perxenate* solutions are powerful and rapid oxidizing agents. The stable salts $Na_4XeO_6\cdot 8H_2O$ and $Na_4XeO_6\cdot 6H_2O$ contain XeO_6^{4-} octahedra. The solutions of sodium perxenate are alkaline owing to hydrolysis, and the following equilibrium constants have been estimated:

$$HXeO_6^{3-} + OH^- = XeO_6^{4-} + H_2O \qquad K < 3$$

$$H_2XeO_6^{2-} + OH^- = HXeO_6^{3-} + H_2O \qquad K \sim 4 \times 10^3$$

so that even at pH 11 to 13 the main species is $HXeO_6^{3-}$. From the equilibria it follows that for H_4XeO_6, pK_3 and pK_4 are $\sim 4 \times 10^{-11}$ and $<10^{-14}$, respectively. Hence, by comparison with H_6TeO_6 and H_5IO_6, H_4XeO_6 appears to be an anomalously weak acid.

Solutions of perxenates are reduced by water at pH 11.5 at a rate of ~1%/h, but in acid solutions almost instantaneously:

$$H_2XeO_6^{2-} + H^+ \longrightarrow HXeO_4^- + \tfrac{1}{2}O_2 + H_2O$$

This reduction appears to proceed almost entirely by a radical process involving hydroxyl radicals and H_2O_2.

Xenon tetroxide is a highly unstable and explosive gas formed by the action of concentrated H_2SO_4 on barium perxenate. It is tetrahedral (Xe—O = 1.736 Å), according to electron diffraction studies.

The aqueous chemistry of xenon is briefly summarized by the potentials

Acid solution	$H_4XeO_6 \overset{2.36\text{ V}}{\text{———}} XeO_3 \overset{2.12\text{ V}}{\text{———}} Xe$ $XeF_2 \overset{2.64\text{ V}}{\text{———}} Xe$
Alkaline solution	$HXeO_6^{3-} \overset{0.94\text{ V}}{\text{———}} HXeO_4^- \overset{1.26\text{ V}}{\text{———}} Xe$

Xenon Oxofluorides. There are several of these but the best characterized are $XeOF_4$ and XeO_2F_2. Some syntheses[7] are

$$XeF_6 + H_2O = XeOF_4 + 2HF$$

$$XeO_3 + XeOF_4 = 2XeO_2F_2$$

$$2XeO_3 + XeF_6 = 3XeO_2F_2$$

$$XeO_3 + 2XeF_6 = 3XeOF_4$$

In the first of these reactions the quantity of H_2O must be limited to the stoichiometric quantity to avoid forming the explosive XeO_3. Xenon oxotetrafluoride ($XeOF_4$) is square pyramidal (C_{4v}), whereas XeO_2F_2 is like SF_4,

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[7] J. L. Huston, *Inorg. Chem.*, 1982, **21**, 685.

with F atoms in axial positions (C_{2v}). Xenon oxodifluoride ($XeOF_2$) and XeO_3F_2 are unstable; XeO_2F_4 has been observed only in the mass spectrometer.

There are also some derivatives[8] of the oxofluorides with the ligand $OTeF_5^-$; these are $XeO(OTeF_5)_4$ and $XeO_2(OTeF_5)_2$. The only compound of Xe^{IV} bound exclusively to oxygen is $Xe(OTeF_5)_4$ made by the reaction

$$3XeF_4 + 4B(OTeF_5)_3 \xrightarrow{0°C} 3Xe(OTeF_5)_4 + 4BF_3$$

Oxofluoroanions can be made from $XeOF_4$ by the reactions[9]

$$XeOF_4(\text{excess}) + CsF \longrightarrow Cs[(XeOF_4)_3F] \xrightarrow{\text{pump, } 25°C} Cs[XeOF_5]$$

The $[XeOF_5]^-$ ion is distorted octahedral with a stereochemically active lone pair. The $[(XeOF_4)_3F]^-$ anion has three $XeOF_4$ molecules linked to a central fluorine with Xe—F bonds in a flattened pyramid.

Stable salts of the $[XeO_3F]^-$ ion are formed when a solution of XeO_3 is treated with KF or CsF while the anion $[XeO_2F_3]^-$ results from disproportionation of $XeOF_2$ in the presence of CsF.

Other species with bonds to oxygen are formed when XeF_2 reacts with strong oxo acids (e.g., HSO_3F) or their anhydrides [e.g., $(F_2OP)_2O$] to give products in which one or both F atoms are replaced. Examples are

$$XeF_2 + HSO_3F \longrightarrow FXeOSO_2F, Xe(OSO_2F)_2$$

$$XeF_2 + P_2O_3F_4 \longrightarrow FXe(OPOF_2), Xe(OPOF_2)_2$$

These products are unstable at about room temperature and several are highly explosive. Xenon tetrafluoride and XeF_6 react with HSO_3F as follows:

$$XeF_4 + HSO_3F \longrightarrow FXe(OSO_2F), Xe(OSO_2F)_2 + S_2O_6F_2$$

$$XeF_6 + HSO_3F \longrightarrow F_5Xe(OSO_2F) + HF$$

$F_5Xe(OSO_2F)$ is a white solid, thermally stable at 22°C but decomposing above 73°C.

Xenon Compounds with Bonds to Other Elements. Xenon difluoride (XeF_2) reacts with $HN(SO_2F)_2$[10] to form HF and $FXe^{II}N(SO_2F)_2$, a white solid decomposing at 70°C and readily hydrolyzed. It reacts with AsF_5 to give $[XeN(SO_2F)_2]^+(AsF_6)^-$ and in CF_2Cl_2 at $\sim -15°C$, it gives a compound with two Xe—N bonds:

$$FXe(NSO_2F)_2 + HN(SO_2F)_2 \rightleftharpoons Xe[N(SO_2F)_2]_2 + HF$$

A similar compound $Xe[N(SO_2CF_3)_2]_2$ is known.

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[8] G. A. Schumaker and G. J. Schrobilgen, *Inorg. Chem.*, 1984, **23**, 2923.

[9] J. H. Holloway *et al.*, *Inorg. Chem.*, 1985, **24**, 678.

[10] G. J. Schrobilgen *et al.*, *Inorg. Chem.*, 1986, **25**, 563.

Xenon dichloride is known only in a xenon matrix when Xe–Cl_2 mixtures are photolyzed. However, XeO_3 reacts with RbCl and CsCl to give compounds with the composition $M_9(XeO_3Cl_2)_4Cl$, which consist of M^+ cations, Cl^- anions, and infinite chain anions —XeO_3Cl—Cl—XeO_3Cl—Cl—, in which each Xe atom is surrounded by a very distorted octahedron of three oxygen atoms (Xe—O ≈ 1.77 Å) and three Cl atoms (Xe—Cl ≈ 2.96 Å). These are the only examples of compounds stable at room temperature that contain Xe—Cl bonds.

A compound $XeCr(CO)_5$ comparable to $(N_2)Cr(CO)_5$ has been characterized in solution at very low temperatures;[11] it has a half-life of ~2 s at −98°C. The only compound with a bond to carbon $Xe(CF_3)_2$ made by the action of CF_3 radicals on XeF_2 has a half-life of ~30 min at room temperature.[12]

15-4. The Chemistry of Krypton and Radon

Krypton difluoride is obtained when an electric discharge is passed through Kr and F_2 at −183°C, or when the gases are irradiated with high-energy electrons or protons. It is a volatile white solid that decomposes slowly at room temperature. It is a highly reactive fluorinating agent.

The linear KrF_2 molecule is thermodynamically unstable, whereas XeF_2 is stable, as the following enthalpies show:

$$KrF_2(g) = Kr(g) + F_2(g) \qquad \Delta H^0 = -63 \text{ kJ mol}^{-1}$$

$$XeF_2(g) = Xe(g) + F_2(g) \qquad \Delta H^0 = 105 \text{ kJ mole}^{-1}$$

These energetic relationships are understandable on the basis of rigorous quantum mechanical calculations, which justify the view that in both difluorides there is considerable ionic character. The bonding can be simply represented by the following resonance

$$F\text{—}Xe^+F^- \longleftrightarrow F^-Xe^+\text{—}F$$

Since the ionization enthalpies (Table 15-1) of Kr and Xe differ by ~182 kJ mol^{-1}, the experimental difference in ΔH_f° values, namely, $105 - (-63) = 168$ kJ mol^{-1} is well explained by this picture.

No other molecular fluoride of Kr has been isolated. The cationic species KrF^+ and $Kr_2F_3^+$ are formed in reactions of KrF_2 with strong fluoride acceptors such as AsF_5 and SbF_5, and compounds have formulas such as $KrF^+Sb_2F_{11}^-$, $KrF^+SbF_6^-$, and $Kr_2F_3^+AsF_6^-$. The KrF^+ salts can be used to fluorinate NF_3 to NF_4^+.[13]

There is some evidence for $KrFe(CO)_5^+$ in γ-irradiated matrices at low temperatures.[14]

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[11] M. B. Simpson *et al., J. Chem. Soc. Chem. Commun.*, **1983,** 1355.

[12] J. K. Hovey and T. B. McMahon, *J. Am. Chem. Soc.*, 1986, **108,** 528.

[13] K. O. Christe *et al., Inorg. Chem.*, 1984, **23,** 2058.

[14] J. R. Morton *et al., Organometallics,* 1984, **3,** 1389.

Since *radon* has only a short half-life, study is difficult but tracer studies allow some properties to be deduced, for example, the formation of RnF_2, $RnF^+TaF_6^-$, and possibly RnO_3. Oxidation of Rn by ClF_3 and study on a fluorinated ion-exchange material (Nafion) suggests that Rn^+ can displace Na^+ or K^+.[15]

ADDITIONAL REFERENCES

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Hopke, P. K., Ed., *Radon and Its Decay Products* (ACS Symposium Ser. No. 331). American Chemical Society, Washington, DC, 1987.

Ozima, M., and Podosek, F. A., *Noble Gas Geochemistry,* Cambridge University Press, Cambridge, 1983.

Selig, H., and Holloway, J. H., *Topics in Current Chemistry,* No. 124, F. L. Boschke, Ed., Springer-Verlag, Berlin, 1984 (cationic and anionic complexes of xenon).

Seppelt, K., and Lentz, D., *Prog. Inorg. Chem.*, 1982, **29,** 168 (an extensive review).

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[15] L. Stein, *J. Chem. Soc. Chem. Commun.*, **1985,** 1631; *Inorg. Chem.*, 1984, **23,** 3670.

Chapter Sixteen

The Group IIB(12) Elements: Zn, Cd, Hg

GENERAL REMARKS

16-1. Position in the Periodic Table: Group Trends

Zinc, cadmium, and mercury follow copper, silver, and gold and have two *s* electrons outside filled *d* shells. Some of their properties are given in Table 16-1. Whereas in Cu, Ag, and Au the filled *d* shells may fairly readily lose one or two *d* electrons to give ions or complexes in the II and III oxidation states, this does not occur for the Group IIB(12) elements.

Divergence from +2 valence occurs in the following cases:

1. The univalent metal–metal bonded ions M_2^{2+}, of which only Hg_2^{2+} is ordinarily stable.

2. Mercury ions in low partial oxidation states, notably $Hg^{0.33+}$.

3. A short-lived (~5 s) Hg^{III} complex. Since the third ionization enthalpies are extremely high, compensating energy from solvation or lattice formation is normally impossible.

Since these elements form no compound in which the *d* shell is other than full, they are regarded as non-transition elements, whereas by the same criterion Cu, Ag, and Au are considered as transition elements. Also, the metals are softer and lower melting, and Zn and Cd are considerably more electropositive than their neighbors in the transition groups. However, there is some resemblance to the *d*-group elements in their ability to form complexes, particularly with ammonia, amines, halide ions, and cyanide. For complexes, even with CN^-, it must be borne in mind that the possibility of $d\pi$ bonding between the metal and the ligand is very much lowered compared to the *d*-transition elements, owing to the electronic structure, and no carbonyl, nitrosyl, olefin complex, and so on, of the type given by transition metals is known.

The chemistries of Zn and Cd are very similar, but that of Hg differs considerably and cannot be regarded as homologous. As examples we quote the following. The hydroxide $Cd(OH)_2$ is more basic than $Zn(OH)_2$, which is amphoteric, but $Hg(OH)_2$ is an extremely weak base. The chlorides of Zn and Cd are essentially ionic, whereas $HgCl_2$ gives a molecular crystal. Zinc

TABLE 16-1
Some Properties of the Group IIB(12) Elements

Property	Zn[a]	Cd	Hg
Outer configuration	$3d^{10}4s^2$	$4d^{10}5s^2$	$5d^{10}6s^2$
Ionization enthalpies (kJ mol^{-1})			
1st	906	867	1006
2nd	1726	1625	1799
3rd	3859	3666	3309
Melting point (°C)	419	321	−38.87
Boiling point (°C)	907	767	357
Heat of vaporization (kJ mol^{-1})	130.8	112	61.3
E^0 for $M^{2+} + 2e = M$ (V)	−0.762	−0.402	0.854
Radii of divalent ions (Å)	0.69	0.92	0.93

[a] For thermodynamic and other data see M. J. S. Dewar and K. M. Mertz, Jr., *Organometallics*, 1986, **5**, 1494.

and Cd are electropositive metals, but Hg has a high positive standard potential; furthermore, the Zn^{2+} and Cd^{2+} ions somewhat resemble Mg^{2+} but Hg^{2+} does not. Though all the M^{2+} ions readily form complexes, those of Hg^{2+} have formation constants greater by orders of magnitude than those for Zn^{2+} or Cd^{2+}.

All three elements form a variety of covalently bound compounds, and the polarizing ability of the M^{2+} ions is larger than would be predicted by comparing the radii with those of the Mg–Ra group, a fact that can be associated with the greater ease of distortion of the filled *d* shell. Compared to the noble-gas-like ions of the latter elements, the promotional energies $ns^2 \rightarrow nsnp$ (433, 408, and 524 kJ mol^{-1} for Zn, Cd, and Hg, respectively) involved in the formation of two covalent bonds are also high, and this has the consequence, particularly for Hg, that further ligands can be added only with difficulty. This is probably the main reason that two-coordination is the commonest for Hg.

16-2. Stereochemistry

The stereochemistry of the elements in the II state is summarized in Table 16-2. Since there is no ligand field stabilization effect in Zn^{2+} and Cd^{2+} ions because of their completed *d* shells, their stereochemistry is determined solely by considerations of size, electrostatic forces, and covalent bonding forces. The effect of size is to make Cd^{2+} more likely than Zn^{2+} to assume a coordination number of 6. For example, ZnO crystallizes in lattices where the Zn^{2+} ion is in tetrahedral holes surrounded by four oxide ions, whereas CdO has the rock salt structure. Similarly $ZnCl_2$ has Zn^{2+} in tetrahedral holes with Cl^- in hexagonally packed layers, whereas Cd^{2+} in $CdCl_2$ is octahedrally coordinated.

In their complexes, Zn, Cd, and Hg commonly have coordination numbers 4, 5, and 6, with 5 especially common for zinc. The coordination number for

TABLE 16-2
Stereochemistry of Divalent Zinc, Cadmium, and Mercury

Coordination number	Geometry	Examples
2	Linear	$Zn(CH_3)_2$, HgO, $Hg(CN)_2$, $Cd[N(SiMe_3)_2]_2$
3	Planar	$[Me_3S]^+HgX_3^-$, $[MeHg\ bipy]^+$, $Hg(SiMe_3)_3^-$, $Zn_2(\mu\text{-}OH)_2[C(SiMe_2Ph)_3]_2$[a]
4	Tetrahedral	$[Zn(CN)_4]^{2-}$, $ZnCl_2(s)$, ZnO, $[Cd(NH_3)_4]^{2+}$, $HgCl_2(OAsPh_3)_2$
	Planar	Bis(glycinyl)Zn
5[b]	*tbp*	Terpy $ZnCl_2$, $[Zn(SCN)\ tren]^+$, $[Co(NH_3)_6][CdCl_5]$
	sp	$Zn(acac)_2 \cdot H_2O$
6	Octahedral	$[Zn(NH_3)_6]^{2+}$ (solid only), CdO, $CdCl_2$, $[Hg(en)_3]^{2+}$, $[Hg(C_5H_4NO)_6]^{2+}$
7	Pentagonal bipyramid	$[Zn(H_2dapp)(H_2O)_2]^{2+}$[c]
	Distorted pentagonal bipyramid	$Cd(quin)(H_2O)(NO_3)_2$
8	Distorted square antiprism	$[Hg(NO_2)_4]^{2-}$
	Dodecahedral[d]	$(Ph_4As)_2Zn(NO_3)_4$

[a] For three-coordinate Zn references see C. Eaborn *et al.*, *J. Chem. Soc. Chem. Commun.* **1986,** 908.

[b] For five-coordinate Zn see T. P. E. Auf der Heyde and L. R. Nassimbeni, *Acta Cryst.*, 1984, **840,** 582.

[c] H_2dapp = 2,6-diacetylpyridine (2′-pyridylhydrazone).

[d] For Cd^{2+} with a complicated ligand see M. A. Romero *et al.*, *Inorg. Chem.*, 1986, **25,** 1498.

all three elements in organo compounds is usually 2, but only Hg commonly forms linear bonds in other cases (e.g., in HgO). Indeed, linear two-coordination is more characteristic for Hg^{II} than for any other metal species.

THE ELEMENTS[1]

16-3. Occurrence, Isolation, and Properties

The elements have relatively low abundance in Nature (of the order of 10^{-6} of the earth's crust for Zn and Cd), but have long been known because they are easily obtained from their ores.

Zinc occurs widely in a number of minerals, but the main source is *sphalerite* [(ZnFe)S], which commonly occurs with galena (PbS); cadmium minerals are scarce, but as a result of its chemical similarity to Zn, Cd occurs by isomor-

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[1] L. G. Hepler and G. Olufsson, *Chem. Rev.*, 1975, **75,** 585 (thermodynamic properties, chemical equilibria, and standard potentials for mercury and its compounds; an authoritative critical compendium); M. J. S. Dewar *et al.*, *Organometallics,* 1985, **4,** 1964, 1967 (thermodynamic data for inorganic and organometallic compounds of mercury).

phous replacement in almost all zinc ores. There are numerous methods of isolation, initially involving flotation and roasting; Zn and Pb are commonly recovered simultaneously by a blast furnace method. Cadmium is invariably a by-product and is usually separated from Zn by distillation or by precipitation from sulfate solutions by zinc dust:

$$\mathrm{Zn} + \mathrm{Cd}^{2+} = \mathrm{Zn}^{2+} + \mathrm{Cd} \qquad E^0 = +0.36\ \mathrm{V}$$

The only important ore of mercury is *cinnabar* (HgS); this is roasted to the oxide, which decomposes at ~500°C, the mercury vaporizing. Much mercury reaches the environment from volcanos.[2a]

Properties. Some properties of the elements are listed in Table 16-1. Zinc and cadmium are white, lustrous, but tarnishable metals. Like Be and Mg, with which they are isostructural, their structures deviate from perfect hexagonal close packing by elongation along the six-fold axis. Mercury is a shiny liquid at ordinary temperatures. All are remarkably volatile for heavy metals, mercury, of course, uniquely so. Mercury gives a monoatomic vapor and has an appreciable vapor pressure (1.3×10^{-3} mm) at 20°C. It is also surprisingly soluble in both polar and nonpolar liquids. The solubility in water[2b] at 298 K is 6.1×10^{-5} g kg^{-1}.

Because of its high volatility and toxicity, mercury should always be kept in stoppered containers and handled in well-ventilated areas. Mercury is readily lost from dilute aqueous solutions and even from solutions of mercuric salts owing to reduction of these by traces of reducing materials and by disproportionation of Hg_2^{2+}.

Both Zn and Cd react readily with nonoxidizing acids, releasing hydrogen and giving the divalent ions, whereas Hg is inert to nonoxidizing acids. Zinc also dissolves in strong bases because of its ability to form zincate ions (see later), commonly written ZnO_2^{2-}:

$$\mathrm{Zn} + 2\mathrm{OH}^- \longrightarrow \mathrm{ZnO}_2^{2-} + \mathrm{H}_2$$

Although cadmiate ions are known, Cd does not dissolve in bases.

Zinc and Cd react readily when heated with oxygen, to give the oxides. Although Hg and O_2 are unstable with respect to HgO at room temperature, their rate of combination is exceedingly slow; the reaction proceeds at a useful rate at 300 to 350°C. But, around 400°C and above, the stability relation reverses and HgO decomposes rapidly into the elements:

$$\mathrm{HgO(s)} = \mathrm{Hg(s)} + \tfrac{1}{2}\mathrm{O}_2 \qquad \Delta H_{\mathrm{diss}} = 160\ \mathrm{kJ\ mol}^{-1}$$

This ability of mercury to absorb oxygen from air and regenerate it again in pure form was of importance in the earliest studies of oxygen by Lavoisier and Priestley.

[2a] S. M. Siegel and B. Z. Siegel, *Nature* (London), 1984, **309**, 146.

[2b] H. L. Clever, *J. Chem. Educ.*, 1985, **62**, 720.

All three elements react directly with halogens and with nonmetals such as S, Se, and Pb.

Zinc and Cd form many alloys, some, such as brass, being of technical importance. Mercury combines with many other metals, sometimes with difficulty but sometimes, as with sodium or potassium, very vigorously, giving *amalgams*. Some amalgams have definite compositions; that is, they are compounds, such as Hg_2Na. Some of the transition metals do not form amalgams, and iron is commonly used for containers of mercury. Sodium amalgams and amalgamated Zn are frequently used as reducing agents for aqueous solutions. Reduction of quaternary ammonium salts at Hg electrodes gives Zintl-type ion salts $[R_4N^+][Hg_4^-]$.[3]

THE UNIVALENT STATE

The univalent state is of importance only for mercury in the Hg_2^{2+} ion.

When Zn is added to molten $ZnCl_2$ at 500 to 700°C, a yellow, diamagnetic glass is obtained on cooling. According to Raman and other spectra, this glass contains Zn_2^{2+}. Reduction of $Cd(AlCl_4)_2$ by Cd also gives yellow solutions from which crystals can be obtained. X-ray studies show that there are Cd_2^{2+} and $AlCl_4^-$ ions, the Cd—Cd bond length being 2.576 Å, which is longer than Hg_2^{2+} bonds, 2.49 to 2.54 Å. Three of the Cl atoms of each $AlCl_4^-$ form weak bridges to Cd so that the coordination of Cd is distorted tetrahedral.[4] Force constant data indicate the bond strength is $Zn_2^{2+} < Cd_2^{2+} < Hg_2^{2+}$.

The greater strength of the Hg—Hg bond compared to the Cd—Cd bond in M_2^{2+} is reflected also on comparison of the bond energies $HgH^+ > CdH^+$ in these spectroscopic ions. Qualitatively the stability of Hg_2^{2+} is probably related to the large electron attachment enthalpy of Hg^+. That of M^+ (equal to the first ionization enthalpy of the metal) is 135 kJ mol^{-1} greater for Hg^+ than for Cd^+ because the 4*f* shell in Hg shields the 6*s* electrons relatively poorly. The high ionization enthalpy of Hg also accounts for the so-called inert pair phenomenon, namely, the noble character of Hg and its low energy of vaporization.

16-4. The Dimercury(I) Ion and its Compounds

The dimercury(I) or mercurous ion $[Hg_2(H_2O)_2]^{2+}$, is readily obtained from mercury(II) salts by reduction in aqueous solution. It is stable in acid solution[5]

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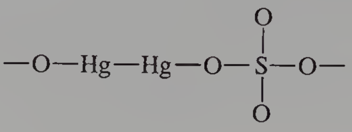
[3] A. J. Bard *et al., J. Am. Chem. Soc.*, 1986, **108,** 6082.

[4] R. Faggiani *et al., J. Chem. Soc. Chem. Commun.* **1986,** 517.

[5] W. R. Mason, *Inorg. Chem.*, 1983, **21,** 147.

TABLE 16-3
Mercury—Mercury Bond Lengths in Dimercury(I) Compounds

Salt	Hg—Hg (Å)	Salt	Hg—Hg (Å)
Hg_2F_2	2.51	$Hg_2(NO_3)_2 \cdot 2H_2O$	2.54
Hg_2Cl_2	2.53	$Hg_2(BrO_3)_2$	2.51
Hg_2Br_2	2.58	Hg_2SO_4[a]	2.50
Hg_2I_2	2.69		

[a] Contains chains,  $—O—Hg—Hg—O—\overset{O}{\underset{O}{S}}—O—$ (E. Dorm, *Acta Chem. Scand.*, 1969, 23, 1607).

and in the absence of coordinating ligands such as OH^-, F^-, and CN^- that promote disproportionation.

The binuclearity has long been established by electrical conductance, Raman spectra and other methods, and abundant X-ray data are available (Table 16-3).

Dimercury(I)–Mercury(II) Equilibria. The important thermodynamic values are the potentials

$$Hg_2^{2+} + 2e = 2Hg(l) \qquad E^0 = 0.7960 \text{ V} \tag{16-1}$$

$$2Hg^{2+} + 2e = Hg_2^{2+} \qquad E^0 = 0.9110 \text{ V} \tag{16-2}$$

$$Hg^{2+} + 2e = Hg(l) \qquad E^0 = 0.8535 \text{ V} \tag{16-3}$$

For the disproportionation reaction, which is rapid and reversible,

$$Hg_2^{2+} = Hg(l) + Hg^{2+} \qquad E^0 = -0.115 \text{ V} \tag{16-4}$$

and we then have

$$K = \frac{[Hg^{2+}]}{[Hg_2^{2+}]} = 1.14 \times 10^{-2}$$

The implication of the potentials is clearly that Hg can be oxidized to Hg_2^{2+} (but not to Hg^{2+}) only by oxidizing agents with potentials in the range -0.79 to -0.85 V. Since no common oxidizing agent meets this requirement, it is found that when mercury is treated with an excess of oxidizing agent it is entirely converted into Hg^{II}. However, when mercury is in at least 50% excess, only Hg^{I} is obtained, since according to eq. 16-4 Hg(l) readily reduces Hg^{2+} to Hg_2^{2+}.

The kinetics of oxidation of Hg_2^{2+} in perchlorate solution by one- and two-electron oxidants suggest that the pathways are different. For one-electron oxidants, breaking of the Hg—Hg bond is involved, namely,

$$(Hg^{I})_2 - e \longrightarrow Hg^{I} + Hg^{II}$$

$$Hg^{I} - e \longrightarrow Hg^{II} \qquad \text{fast}$$

whereas for two-electron oxidants,

$$(\mathrm{Hg}^{\mathrm{I}})_2 \longrightarrow \mathrm{Hg}^0 + \mathrm{Hg}^{\mathrm{II}} \qquad \text{fast}$$

$$\mathrm{Hg}^0 - 2e = \mathrm{Hg}^{\mathrm{II}}$$

The equilibrium constant for reaction 16-4 shows that although Hg_2^{2+} is stable with respect to disproportionation, it is stable only by a small margin. Thus any reagents that reduce the activity (by precipitation or complexation) of Hg^{2+} to a significantly greater extent than they lower the activity of Hg_2^{2+} will cause disproportionation of Hg_2^{2+}. Since there are many such reagents, such as NH_3, amines, OH^-, CN^-, SCN^-, S^{2-}, and acacH, the number of stable Hg^I compounds is rather restricted.

Thus when OH^- is added to a solution of Hg_2^{2+}, a dark precipitate consisting of Hg and HgO is formed; evidently mercury(I) hydroxide, if it could be isolated, would be a stronger base than HgO. Similarly, addition of sulfide ions to a solution of Hg_2^{2+} gives a mixture of Hg and the extremely insoluble HgS. Mercury(I) cyanide does not exist because $Hg(CN)_2$ is so slightly dissociated though soluble. The reactions in these cases are

$$\mathrm{Hg}_2^{2+} + 2\mathrm{OH}^- \longrightarrow \mathrm{Hg(l)} + \mathrm{HgO(s)} + \mathrm{H_2O}$$

$$\mathrm{Hg}_2^{2+} + \mathrm{S}^{2-} \longrightarrow \mathrm{Hg(l)} + \mathrm{HgS}$$

$$\mathrm{Hg}_2^{2+} + 2\mathrm{CN}^- \longrightarrow \mathrm{Hg(l)} + \mathrm{Hg(CN)_2(aq)}$$

The reactions with OH^- and CN^- have been studied kinetically. The rate-determining step appears to be the cleavage of the Hg—Hg bond, namely,

$$\mathrm{Hg}_2^{2+} + \mathrm{OH}^- \rightleftharpoons \mathrm{Hg_2OH}^+ \qquad \text{(rapid equilibrium)}$$

$$\mathrm{Hg_2OH}^+ \longrightarrow \mathrm{Hg} + \mathrm{HgOH}^+$$

$$\mathrm{Hg_2OH}^+ + \mathrm{OH}^- \longrightarrow \mathrm{Hg} + \mathrm{Hg(OH)_2}$$

Dimercury(I) Compounds. The best known are the *halides.* The fluoride is unstable toward water, being hydrolyzed to HF and unisolable mercurous hydroxide (which disproportionates as above). The other halides are highly insoluble, which precludes the possibilities of hydrolysis or disproportionation to give Hg^{II} halide complexes. *Mercurous nitrate* is known only as the dihydrate $Hg_2(NO_3)_2{\cdot}2H_2O$, which contains the ion $[H_2O—Hg—Hg—OH_2]^{2+}$; a *perchlorate* $Hg_2(ClO_4)_2{\cdot}4H_2O$ is also known. Both are very soluble in water, and the halides and other relatively insoluble salts of Hg_2^{2+} may conveniently be prepared by adding the appropriate anions to their solutions. Other known mercurous salts are the sparingly soluble sulfate, chlorate, bromate, iodate, and acetate.

Mercurous ion forms few *complexes;* this may in part be due to a low tendency for Hg_2^{2+} to form coordinate bonds, but it is probably mainly because

Hg^{2+} will form even more stable complexes with most ligands, for example, CN^-, I^-, amines, and alkyl sulfides, so that the Hg_2^{2+} disproportionates. Nitrogen ligands of low basicity tend to favor Hg_2^{2+}, and there are relatively stable complexes with aniline, $[Hg_2(PhNH_2)]^{2+}$, and with 1,10-phenanthroline.

Complexes can readily be obtained in solution with oxygen donor ligands that form essentially ionic metal–ligand bonds, hence no strong complexes with mercury(II). Such ligands are oxalate, succinate, pyrophosphate, and tripolyphosphate. Pyrophosphate gives the species $[Hg_2(P_2O_7)_2]^{6-}$ (pH range 6.5–9) and $[Hg_2(P_2O_7)OH]^{3-}$ for which stability constants have been measured.

Some oxygen donor complexes, for example, $[Hg_2(OPPh_3)_6]^{2+}$, can be isolated.

16-5. Mercury in Oxidation States Below I[6a,b]

Like S, Se, and Te, (Section 13-6) mercury can be oxidized by AsF_5 in liquid SO_2, the nature of the products depending on the mole ratio:

$$2Hg + 3AsF_5 = Hg_2(AsF_6)_2 + AsF_3 \quad \text{colorless solution}$$

$$3Hg + 3AsF_5 = Hg_3(AsF_6)_2 + AsF_3 \quad \text{yellow solution}$$

$$4Hg + 3AsF_5 = Hg_4(AsF_6)_2 + AsF_3 \quad \text{red solution}$$

The various species can be characterized by ^{199}Hg nmr spectra.[6b] The Hg—Hg bond lengths in Hg_2^{2+}, Hg_3^{2+}, and Hg_4^{2+} can be correlated with bond valences. In $Hg_4(AsF_6)_2$ there are almost linear Hg_4^{2+} ions with some interaction between them leading to nonlinear chains.

If smaller amounts of oxidant are used golden metal-like solids $Hg_{3-\delta}MF_6$, $\delta = 0.18$ for M = As and 0.1 for Sb, that have a host lattice of MF_6^- ions with two nonintersecting mutually perpendicular chains of Hg atoms —Hg—Hg—Hg— are obtained. These can be transformed into a silvery Hg_3MF_6 that has hexagonal sheets of close-packed Hg atoms separated by sheets of MF_6^- ions.

Mercury also dissolves in FSO_3H to give a yellow solution of the Hg_3^{2+} ion.

DIVALENT ZINC AND CADMIUM COMPOUNDS

16-6. Oxides and Hydroxides

The *oxides* ZnO and CdO (Table 16-4) are formed on burning the metals in air or by pyrolysis of the carbonates or nitrates; oxide smokes can be obtained by combustion of the alkyls, those of cadmium being exceedingly toxic. *Zinc*

[6a] R. J. Gillespie *et al., Inorg. Chem.*, 1987, **26**, 689.

[6b] G. J. Schrobilgen *et al., Inorg. Chem.*, 1984, **23**, 887.

TABLE 16-4
Structures[a] of Zn and Cd Oxides and Chalconides[b]

Metal	O	S	Se	Te
Zn	W, Z	Z, W	Z	Z, W
Cd	NaCl	W, Z	W, Z	Z

[a] W = wurtzite structure; Z = zinc blende structure; NaCl = rock salt structure.
[b] Where two polymorphs occur, the one stable at lower temperatures is listed first.

oxide[7] is normally white but turns yellow on heating; it is an *n*-type semiconductor because of nonstoichiometry (metal abundance) and impurities. It has many uses including catalysis especially for low pressure methanol synthesis (Chapter 28) where ZnO + CuO is supported on Al_2O_3 or Cr_2O_3. Cadmium oxide varies in color from greenish yellow through brown to nearly black, depending on its thermal history. These colors are the result of various kinds of lattice defect. Both oxides sublime without decomposition at very high temperatures.

The *hydroxides* are precipitated from solutions of salts by addition of bases. The solubility products of $Zn(OH)_2$ and $Cd(OH)_2$ are $\sim 10^{-11}$ and 10^{-14}, respectively, but $Zn(OH)_2$ is more soluble than would be expected from this constant owing to the equilibrium

$$Zn(OH)_2(s) = Zn(OH)_2(aq) \qquad K = 10^{-6}$$

Zinc hydroxide readily dissolves in aqueous NaOH, but $Cd(OH)_2$ dissolves only in concentrated base. From such solutions crystalline zincates or cadmiates, for example, $Na_2[Cd(OH)_4]$, may be obtained. In aqueous solution the principal zincate ion appears to be $[Zn(OH)_3(H_2O)]^-$ according to Raman spectra.

Both Zn and Cd hydroxide readily dissolve in an excess of strong ammonia to form the ammine complexes, for example, $[Zn(NH_3)_4]^{2+}$.

16-7. Sulfides, Selenides, and Tellurides

The sulfides, selenides, and tellurides are all crystalline substances, insoluble in water. Three structures are represented among the eight compounds as shown in Table 16-4. All of these structures have been described in Section 1-2. In the NaCl structure, the cation is octahedrally surrounded by six anions, whereas in the other two the cation is tetrahedrally surrounded by anions. It will be seen from Table 16-4 that zinc and cadmium prefer tetrahedral coordination in their chalconides.

Very pure ZnSe can be made by the reaction[8a]

$$Me_2Zn + H_2Se = ZnSe + 2CH_4$$

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[7] W. H. Hirschwald, *Acc. Chem. Res.*, 1985, **18**, 228.
[8a] G. Fan *et al., J. Chem. Soc. Chem. Commun.*, **1986**, 68.

TABLE 16-5
Some Properties of the Zinc and Cadmium Halides

Halide	Solubility in water (mol L^{-1})	(°C)	mp (°C)	bp (°C)	Structure
ZnF_2	1.57	20	872	1502	Rutile
$ZnCl_2$[a]	31.8	25	275	756	*ccp* anions with Zn in tetrahedral interstices
$ZnBr_2$	20.9	25	394	697	
ZnI_2	13	25	446	(sublimes)	
CdF_2	0.29	25	1110	1747	Fluorite
$CdCl_2$	7.7	20	868	980	Close-packed anions with Cd in octahedral interstices
$CdBr_2$	4.2	20	568	1136	
CdI_2	2.3	20	387	(sublimes)	

[a] Very pure $ZnCl_2$ has but one form; some reported polymorphs contain OH groups.

16-8. Halides

All four halides of both zinc and cadmium are known. Some of their relevant properties are given in Table 16-5.

Both ZnF_2 and CdF_2 show distinct evidence of being considerably more ionic than the other halides of the same element. Thus they have higher melting and boiling points, and they are considerably less soluble in water. The latter property is attributable not only to the high lattice energies of the fluorides, but also to the fact that the formation of halo complexes in solution, which enhances the solubility of the other halides, does not occur for the fluorides (see later).

The structures of the chlorides, bromides, and iodides may be viewed as close-packed arrays of halide ions, but there is a characteristic difference in that zinc ions occupy tetrahedral interstices, whereas cadmium ions occupy octahedral ones.

Zinc chloride is so soluble in water that mole ratios of H_2O to $ZnCl_2$ can easily be $< 2:1$. The hydrates, $ZnCl_2 \cdot nH_2O$, $n = 1\text{–}4$ are liquid at ambient temperature; there is no free Cl^- ion in the liquids and the zinc species have $Zn(\mu\text{-}Cl)_2Zn$ bridges.[8b] Both zinc and cadmium halides are quite soluble in alcohol, acetone, and similar donor solvents, and in some cases adducts can be obtained.

The species in aqueous solutions are discussed next.

16-9. Oxo Salts and Aqua Ions

Salts of oxo acids such as the nitrate, sulfate, sulfite, perchlorate, and acetate are soluble in water. The Zn^{2+} and Cd^{2+} ions are rather similar to Mg^{2+}, and many of their salts are isomorphous with magnesium salts, for example,

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[8b] J. A. Duffy and G. L. Wood, *J. Chem. Soc. Dalton Trans.*, **1987,** 1485.

$Zn(Mg)SO_4{\cdot}7H_2O$. Although the aqua ions are normally $[M(H_2O)_6]^{2+}$, the *tbp* ion $[Zn(H_2O)_5]^{2+}$ has been found in an ionic polymer.[9]

The aqua ions are quite strong acids and salts are hydrolyzed in water. In ClO_4^- solutions the only species for Zn, Cd and Hg below 0.1 *M* are the MOH^+ ions, for example,

$$Cd^{2+}(aq) + H_2O \rightleftharpoons CdOH^+(aq) + H^+ \qquad \log \beta = 6.08$$

For more concentrated cadmium solutions, the principal species is Cd_2OH^{3+}:

$$2Cd^{2+}(aq) + H_2O \rightleftharpoons Cd_2OH^{3+}(aq) + H^+$$

On distillation of the normal acetate in a vacuum, zinc forms a basic acetate $Zn_4O(OCOCH_3)_6$, isomorphous with that of Be. It is a crystalline solid rapidly hydrolyzed by water, unlike the beryllium compound, the difference being due to the possibility of coordination numbers exceeding 4 for zinc.[10] Cadmium gives a tetra-bridged carboxylate, $Cd_2(\mu\text{-}O_2CCF_3)_4(PPh_3)_2$ similar to adducts of other M_2^{II} carboxylates.[11]

16-10. Complexes of Zinc and Cadmium

Halide Complexes. Aqueous solutions[12] of $ZnCl_2$ depending on the concentration of Zn^{2+} and Cl^- ions may have $[Zn(H_2O)_6]^{2+}$, $[ZnCl(H_2O)_5]^+$, $[ZnCl_4]^{2-}$, $[ZnCl_4(H_2O)_2]^{2-}$, and $[ZnCl_2(H_2O)_4]$; in aqueous MeOH or DMF there is also an octahedral–tetrahedral geometry change above a water mole fraction of 0.5.

Aqueous solutions of cadmium halides appear, superficially, to be incompletely dissociated, that is, to be weak electrolytes. Although there are significant amounts of the undissociated halides (CdX_2) and polymeric species present in moderately concentrated solutions, there are other species present (Table 16-6). Thus the solutions are best regarded as systems containing all possible species in equilibrium rather than simply as solutions of a weak electrolyte.

The formation constants for halides and other ligands differ widely and the main feature is that they are many orders of magnitude smaller than those for Hg^{2+} (Table 16-7).

Other points are (*a*) complexing by F^- is very weak; (*b*) for the other halides all species up to MX_4^{2-} are known; the cadmium ones are most stable and the ion $[CdCl_5]^{3-}$ can also be formed; (*c*) Cd^{2+} is bound more strongly to Cl, S, and P ligands, whereas the harder Zn^{2+} ions favors bonds to F and O.

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[9] J. Podlahová *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 2395.

[10] B. P. Straughan *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 1283; M. R. Gordon and H. B. Silver, *Can. J. Chem.*, 1983, **61,** 1218.

[11] A. L. Beauchamp *et al., Inorg. Chem.*, 1984, **23,** 934.

[12] H. B. Silver *et al., Inorg. Chem.*, 1984, **23,** 2844.

TABLE 16-6
Approximate Concentrations of Dissociated and Undissociated Species in 0.5 *M* $CdBr_2$ Solution at 25°C

Species	Concentration (*M*)	Species	Concentration (*M*)
Cd^{2+}	0.013	Br^-	0.200
$CdBr^+$	0.259	$CdBr_2$	0.164
$CdBr_3^-$	0.043	$CdBr_4^{2-}$	0.021

Halide complexes of a different type have been found in reductions of Ti and V chlorides by Zn in THF,[13] namely, $[ZnCl_3THF]^-$ and $[Zn_2(\mu\text{-}Cl)_2Cl_4]^{2-}$.

Sulfur ligands are especially important for Zn and Cd and have been much studied partly because of the biological importance of the elements (Chapter 30) and partly because of the use of zinc dithiocarbamate and related compounds as accelerators in the vulcanization of rubber by sulfur. The simple sulfide anions of Zn, Cd (and also Hg^{II}), $[M(S_6)_2]^{2-}$, can be made by interaction of the acetates with alcoholic polysulfide ions as the NEt_4^+ salts.[14]

Thiolates of many types are known, examples being $Zn(SPh)_2$, $Cd_{10}(SPh)_{20}$, $[Zn(SPh)_4]^{2-}$, $[Cd_4(SPh)_{10}]^{2-}$, $[Cd_{10}S_4(SPh)_{16}]^{4-}$, and $[Zn_4Cl_2(SPh)_8]^{2-}$.[15]

The $[M_4(SPh)_{10}]^{2-}$ and $[Zn_4Cl_2(SPh)_8]^{2-}$ species have an adamantanelike structure with bridges. Other bridged structures occur in cationic complexes[16] such as $[Cd_{10}(SCH_2CH_2OH)_{16}](ClO_4)_4{\cdot}8H_2O$ which contains four octahedral, four *tbp*, and two tetrahedral cadmium atoms.

Dithiocarbamates, $[Zn(S_2CNR_2)_2]$, and *phosphorodithioates* such as $\{Zn[S_2P(OR)_2]_2\}_2$, $[Zn(S_2PR_2)_3]^-$, and $Zn_4O[\mu\text{-}S_2P(OR)_2]_6$ are antioxidants and

TABLE 16-7
Equilibrium Constants for Some Typical Complexes of Zn, Cd, and Hg ($M^{2+} + 4X = [MX_4]$; $K = [MX_4]/[M^{2+}][X]^4$

X	M Ion		
	Zn^{2+}	Cd^{2+}	Hg^{2+}
Cl^-	1	10^3	1.3×10^{15}
Br^-	10^{-1}	10^4	9.2×10^{20}
I^-	10^{-2}	10^6	5.6×10^{29}
NH_3	10^9	10^7	2.0×10^{19}
CN^-	10^{21}	10^{19}	1.9×10^{41}

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[13] K. G. Caulton *et al., Inorg. Chem.*, 1984, **23,** 4589; F. A. Cotton *et al., Inorg. Chem.*, 1985, **24,** 525.

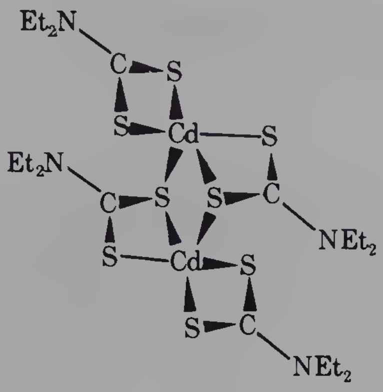
[14] A. Müller *et al., Z. Naturforsch.*, 1985, **40B,** 1277.

[15] I. G. Dance *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 165; *Aust. J. Chem.*, 1986, **39,** 1449; D. G. Tuck *et al., Polyhedron*, 1985, **4,** 1263; P. A. W. Dean *et al., Inorg. Chem.*, 1987, **26,** 1633; C. D. Garner *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 1577.

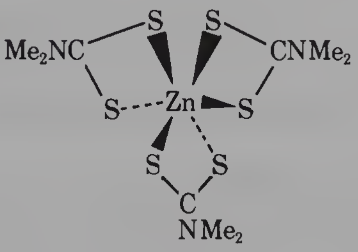
[16] D. M. Kurtz *et al., Inorg. Chem.*, 1984, **23,** 930.

antiwear lubricants as well as vulcanization accelerators.[17] The dimers achieve five-coordination as in (16-I), where one M—S bond is longer than the other. The dimers may be cleaved by amines to give five-coordinate 1:1 adducts.

In the $[\mathrm{Zn\,dtc_3}]^-$ anion (16-II) the Zn is in a distorted tetrahedral environment with one chelate and two formally unidentate S_2CNR_2 groups.



(16-I)



(16-II)

The *dialkylamide,*[18a] $Zn[N(SiMe_3)_2]_2$, in the gas phase has linear N—Zn—N with no dative π contribution (Section 2-11). The bulky *aryloxide,* $[Zn(OAr)_2]_2$, Ar-2,6-di-*t*-butyl, can be made from the dialkylamide.[18b]

Finally, we note that many models for carbonic anhydrase (Chapter 30) such as histadine and imidazole complexes have been studied.

For cadmium, ^{113}Cd nmr has proved useful in biological systems but shifts are very sensitive to concentration and counter ions.[19]

16-11. Compounds with Zn and Cd Bonds to Other Metals

Although less important than for mercury, transition metal carbonyls and organo compounds will form Zn or Cd complexes. Examples[20] are $Zn[Fe(CO)_2Cp]_2$; $[Zn[Fe(CO)_2Cp]_3]^-$, which contains planar three-coordinate zinc; $Zn[Co(CO)_4]_2$; and $\{[CdFe(CO)_4]_4(Me_2CO)_2\}$, which has a Cd_4Fe_4 ring.

The compound $[Cp(CO)_2FeZnOMe]_4$ has a Zn_4O_4 cube similar to that in $[MeZnOMe]_4$.

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[17] P. G. Harrison *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 925, 929; R. L. Blankespoor, *Inorg. Chem.,* 1985, **24,** 1126; M. G. B. Drew *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 1161; R. W. Joyner *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 982.

[18a] K. Hedberg *et al., Inorg. Chem.,* 1984, **23,** 1792.

[18b] K. G. Caulton *et al., Inorg. Chem.,* 1986, **25,** 1803.

[19] M. Munakata *et al., Inorg. Chem.,* 1986, **25,** 964; I. M. Armitage *et al., Inorg. Chem.,* 1985, **24,** 1170; R. S. Honkonen and P. D. Ellis, *J. Am. Chem. Soc.,* 1984, **106,** 5488.

[20] J. M. Burlitch *et al., Inorg. Chem.,* 1983, **22,** 3407; W. Gäde and E. Weiss, *Angew. Chem. Int. Ed. Engl.,* 1981, **20,** 803.

Interaction of Cp_2Zn and $Ni(COD)_2$ gives $Cp_6Ni_2Zn_4$, which has an octahedron of metal atoms with the two Ni atoms apical; $HCo(N_2)_2(PPh_3)_2$ and Cp_2Zn give $CpCo(ZnCp)_2(PPh_3)$ and a similar complex is $Cp_2Ta(ZnCp)_3$.[21]

DIVALENT MERCURY COMPOUNDS

16-12. Mercury(II) Oxide and Sulfide

Red mercuric oxide is formed on gentle pyrolysis of mercurous or mercuric nitrate, by direct interaction of mercury and oxygen at 300 to 350°C, or as red crystals by heating of an alkaline solution of K_2HgI_4. Addition of OH^- to aqueous Hg^{2+} gives a yellow precipitate of HgO; the yellow form differs from the red only in particle size. The usual form of the oxide has a structure with zigzag chains —Hg—O—Hg— (Hg—O = 2.03 Å, $\angle HgOHg = 109°$, $\angle OHgO = 179°$); there is only weak bonding between the chains, the shortest Hg—O distance here being 2.82 Å. In the solid state, mixed oxides such as $Hg_2Nb_2O_7$ are known: all these contain linear O—Hg—O groups.

No hydroxide can be isolated, but the hydrolysis of mercuric ion in perchlorate solutions can be interpreted in terms of the equilibria

$$Hg^{2+} + H_2O = Hg(OH)^+ + H^+ \qquad K = 2.6 \times 10^{-4}$$

$$Hg(OH)^+ + H_2O = Hg(OH)_2 + H^+ \qquad K = 2.6 \times 10^{-3}$$

No polynuclear species appear to be formed.

Mercury(II) sulfide (HgS) is precipitated from aqueous solutions as a black, highly insoluble compound. The solubility product is 10^{-54}, but the sulfide is somewhat more soluble than this figure would imply because of some hydrolysis of Hg^{2+} and S^{2-} ions. The black sulfide is unstable with respect to a red form identical to the mineral cinnabar and changes into it when heated or digested with alkali polysulfides or mercurous chloride. On irradiation in the presence of KI and water cinnabar gives black metacinnabar, a natural mineral with the ZnS structure. Red HgS has a distorted NaCl structure with Hg—S chains.[22]

16-13. Mercury(II) Halides

The *fluoride* of mercury is essentially ionic and crystallizes in the fluorite structure; it is almost completely decomposed, even by cold water, as would

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[21] J. Boersma *et al.*, *Organometallics*, 1985, **4**, 680.

[22] S. R. Davidson and C. J. Wilsher, *J. Chem. Soc. Dalton Trans.*, **1981**, 833.

TABLE 16-8
Hg—X Distances in Mercuric Halides (Å)

	Solid			
Compound	Two at	Two at	Two at	Vapor
HgF_2		Eight at 2.40		
$HgCl_2$	2.25	3.34	3.63	2.28 ± 0.04
$HgBr_2$	2.48	3.23	3.23	2.40 ± 0.04
HgI_2 (red)		Four at 2.78		2.57 ± 0.04

be expected for an ionic compound that is the salt of a weak acid and an extremely weak base. Not only does mercury(II) show no tendency to form covalent Hg—F bonds, but no fluoro complex is known.

In contrast to the fluoride, the other halides show marked covalent character. *Mercuric chloride* crystallizes in an essentially molecular lattice, the two short Hg—Cl distances being about the same length as the Hg—Cl bonds in gaseous $HgCl_2$, whereas the next shortest distances are much longer (see Table 16-8).

In the larger lattice of $HgBr_2$ each Hg atom is surrounded by six Br atoms, but two are so much closer than the other four that it can be considered that perturbed $HgBr_2$ molecules are present. The normal red form of HgI_2 has a layer structure with HgI_4 tetrahedra linked at some of the vertices. However, at 126°C it is converted into a yellow molecular form.

In the vapor all three halides are distinctly molecular, as they are also in solutions. Relative to ionic HgF_2, the other halides have very low melting and boiling points (Table 16-9). They also show marked solubility in many organic solvents. In aqueous solution they exist almost exclusively (~99%) as HgX_2 molecules, but some hydrolysis occurs, the principal equilibrium being, for example,

$$HgCl_2 + H_2O \rightleftharpoons Hg(OH)Cl + H^+ + Cl^-$$

In organic solvents like benzene, there appear to be dimers, probably $XHg(\mu\text{-}X)_2HgX$.

TABLE 16-9
Some Properties of Mercuric Halides

			Solubility (mol/100 mol at 25°C)			
Halide	mp (°C)	bp (°C)	H_2O	C_2H_5OH	$C_2H_5OCOCH_3$	C_6H_6
HgF_2	645 dec		Hydrolyzes	Insoluble	Insoluble	Insoluble
$HgCl_2$	280	303	0.48	8.14	9.42	0.152
$HgBr_2$	238	318	0.031	3.83		
HgI_2	257	351	0.00023	0.396	0.566	0.067

16-14. Mercury(II) Oxo Salts

Among the mercuric salts that are ionic and highly dissociated in aqueous solution, are the nitrate, sulfate, and perchlorate. Because of the great weakness of mercuric hydroxide, aqueous solutions of these salts tend to hydrolyze extensively and must be acidified to be stable. The aqua ion is $[Hg(H_2O)_6]^{2+}$ and on hydrolysis first $HgOH^+_{aq}$, then $Hg(OH)_2(aq)$ in which two Hg—O bonds are shorter than the other four, are formed.[23] Addition of CO_3^{2-} to Hg^{2+} solutions gives $Hg(OH)^+$, $Hg(OH)CO_3^-$, and so on.[24]

In aqueous solutions of $Hg(NO_3)_2$ the main species are $Hg(NO_3)_2$, $HgNO_3^+$, and Hg^{2+}, but at high concentrations of NO_3^- the complex anion $[Hg(NO_3)_4]^{2-}$ is formed.

Mercury(II) carboxylates, especially the acetate and the trifluoroacetate, will attack unsaturated hydrocarbons, as discussed later. They are made by dissolving HgO in the hot acid and crystallizing. The trifluoracetate is also soluble in benzene, acetone, and THF, which increases its utility, while the acetate is soluble in water and alcohols.

Other salts such as the oxalate and phosphates are sparingly soluble in water.

Mercuric ions catalyze a number of reactions of complex compounds such as the aquation of $[Cr(NH_3)_5X]^{2+}$. Bridged transition states, for example,

$$[(H_2O)_5CrCl]^{2+} + Hg^{2+} = [(H_2O)_5Cr—Cl—Hg]^{4+}$$

are believed to be involved.

16-15. Mercury(II) Complexes

A number of the mercury(II) complexes have been mentioned previously. The Hg^{2+} ion has indeed a strong tendency to complex formation, and the characteristic coordination numbers and stereochemical arrangements are two-coordinate, linear and four-coordinate, tetrahedral. Octahedral coordination is less common; a few three- and five-coordinate complexes are also known. There appears to be considerable covalent character in the mercury–ligand bonds, especially in the two-coordinate compounds. The most stable complexes are those with C, N, P, and S as ligand atoms.

Halide and Pseudohalide Complexes. In the halide systems, depending on the concentration of halide ions, there are equilibria such as

$$HgX^+ \rightleftharpoons HgX_2 \rightleftharpoons HgX_3^- \rightleftharpoons HgX_4^{2-}$$

At 1 *M* Cl^- the main species is $[HgCl_4]^{2-}$, but in tributyl phosphate as solvent the most stable ion is $[HgCl_3]^-$; at 10^{-1} *M* Cl^- the concentrations of $HgCl_2$,

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[23] D. W. Barnum, *Inorg. Chem.*, 1983, **22**, 2297.

[24] H. Bilinski *et al.*, *Inorg. Chem.*, 1980, **19**, 3440.

$HgCl_3^-$, and $HgCl_4^{2-}$ are about equal. In $Me_3S^+HgCl_3^-$ the ion is polymeric with mercury *tbp* with equatorial terminal Cl atoms and axial, bridged Cl atoms. In aqueous solutions $HgCl_3^-$ appears to be planar and solvated by axial water molecules in a *tbp* structure, whereas HgI_3^- is solvated by only one H_2O, giving a tetrahedral species.

The $[HgCl_4]^{2-}$ ion in salts is commonly distorted from tetrahedral.[25] The ions $[HgCl_5]^{2-}$ and $[Hg_3Cl_8]^{2-}$ are also known.[26]

Mercuric cyanide $[Hg(CN)_2]$, which contains discrete molecules with linear C—Hg—C bonds, is soluble in CN^- to give $Hg(CN)_3^-$ and $Hg(CN)_4^{2-}$ only. The thiocyanate ion is similar to CN^- in its complexing behavior.

Oxo Ion Complexes. Several of these exist, for example, $[Hg(SO_3)_2]^{2-}$ and $[Hg\ ox_2]^{2-}$. The yellow crystals formed by adding KNO_2 to $Hg(NO_3)_2$ solution contain $K_2[Hg(NO_2)_4]\cdot KNO_3$, where the nitrite ion is bidentate, giving an eight-coordinate, very distorted square antiprism. The acetate and the tropolonate have O—Hg—O bonds but with some much weaker interaction to the other oxygen atom of the ligand.

Sulfur Complexes. The name mercaptan for thiols (RSH) arose from the affinity of mercury for sulfur. Compounds such as $[Hg(SPh)_3]^-$ and $[Hg_2(SMe)_6]^{2-}$ are well established.[27]

The ion $[Hg(S_6)_2]^{2-}$ has seven-membered (HgS_6) rings; it is formed on addition of S_n^{2-} to Hg^{II} acetate in MeOH. Such a sulfido ion could account for the transport of mercury (and similarly of other metals) with excess sulfur under geological conditions.[28]

Mercury(II) dithiocarbamates[29] are also known, examples being $Hg(Et_2dtc)_2$ and a more complicated species, $[Hg_5(Et_2dtc)_8]^{2+}$.

Phosphine Complexes. Most phosphine complexes contain halides or nitrate[30] and have been characterized *inter alia* by ^{31}P and ^{199}Hg nmr spectra. They are of types $HgX_2(PR_3)_{1\text{ or }2}$; the 1:1 species have dimers or polymers with halide bridges.[31]

Amines. Pyridine also forms complexes such as HgI_2py_2, which has discrete molecules and $HgCl_2py_2$ which has chains with octahedral Hg^{II}. However such halides are monomeric in solution.[32] Octahedral Hg^{II} also occurs in $[Hgen_3]^{2+}$.

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[25] I. M. Vezzosi *et al., Inorg. Chim. Acta.,* 1984, **90,** 1.

[26] W. Clegg, *J. Chem. Soc. Dalton Trans.,* **1982,** 593; A. Terzis *et al., Inorg. Chim. Acta,* 1985, **101,** 77.

[27] I. G. Dance *et al., Aust. J. Chem.,* 1984, **37,** 1607; G. Christou *et al., Polyhedron,* 1984, **3,** 1247; G. Henkel *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 1498.

[28] A. Müller, *Angew. Chem. Int. Ed. Engl.,* 1984, **23,** 159.

[29] A. M. Bond *et al., J. Am. Chem. Soc.,* 1987, **109,** 1969.

[30] H. B. Buergi *et al., Inorg. Chem.,* 1980, **19,** 3707; I. W. Nowell *et al., J. Chem. Soc. Dalton Trans.,* **1984,** 1621.

[31] M. Goldstein *et al., Inorg. Chim. Acta,* 1983, **75,** 21.

[32] I. Persson *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 1597; A. J. Carty *et al., J. Chem. Soc. Dalton Trans.,* **1982,** 15.

Ammonia. When NH_3 reacts with $HgCl_2$ it yields dark colored products depending on the conditions, in which Hg is substituted for H.

$$HgCl_2 + 2NH_3 \rightleftharpoons Hg(NH_3)_2Cl_2(s)$$

$$HgCl_2 + 2NH_3 \rightleftharpoons HgNH_2Cl(s) + NH_4^+ + Cl^-$$

$$2HgCl_2 + 4NH_3 + H_2O \rightleftharpoons Hg_2NCl\cdot H_2O + 3NH_4^+ + 3Cl^-$$

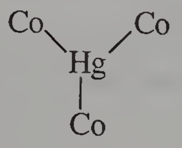
Millon's base ($Hg_2NOH\cdot 2H_2O$) is made by the action of NH_3 on yellow HgO. It has a three-dimensional framework of composition Hg_2N with the OH^- ions and water molecules occupying rather spacious cavities and channels. Many salts of Millon's base are known, for example, $Hg_2NX\cdot nH_2O$ ($X = NO_3^-, ClO_4^-, Cl^-, Br^-$, or I^-; $n = 0$–2). In these the framework appears to remain essentially unaltered; thus it is an ion exchanger similar to a zeolite.

16-16. Compounds with Metal-to-Mercury Bonds

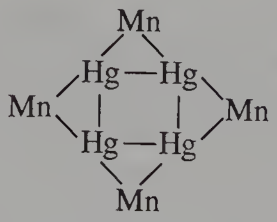
Like Zn and Cd, mercury forms numerous compounds in which there is bonding to other metals.

The bonds are commonly linear, M—Hg—M or M—Hg—X[33a] as in $[en_2RhHgRhen_2]^{2+}$ or $Cp(CO)_3MoHgCl$.

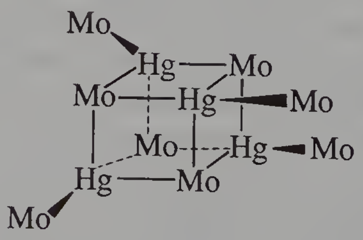
There are, however, complicated compounds[33b] with cores such as the following (16-III – 16-V):



(16-III)



(16-IV)



(16-V)

An even more complex structure is that of $Hg_6Rh_4(PMe_3)_{12}$, which has an octahedron of Hg atoms with $Rh(PMe_3)_2$ groups on the faces, while $Hg_9Co_6(CO)_{18}$ has a trigonal prism[34] with Co atoms at each corner and a Hg atom at the midpoint of each edge.

All the clusters with more than one Hg atom appear to have Hg—M—Hg angles < 90° and Hg—Hg distances similar to that in the metal—hence there need be little actual bonding interaction between the Hg atoms.

[33a] See, for example, O. Rossell *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 119.

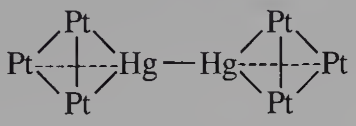
[33b] Y. Yamamoto *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 2329; N. E. Kolobova *et al.*, *Isv. Akad. Nauk SSSR, Ser. Khim.*, **1984**, 920; W. Gäde and E. Weiss, *Angew. Chem. Int. Ed. Engl.*, 1981, **20**, 803; F. Cecconi *et al.*, *J. Chem. Soc. Dalton Trans.*, **1983**, 349; P. Braunstein *et al.*, *Organometallics*, 1986, **5**, 1113.

[34] J. M. Ragosta and J. M. Burlitch, *J. Chem. Soc. Chem. Commun.*, **1985**, 1187.

In compounds with cores of the type (16-VI and 16-VII), for example, $[(triphos)Co]_2Hg_2$ the mercury can be considered as binding as Hg_2^{2+}.

$$\mathrm{Co—Hg—Hg—Co}$$

(16-VI)



(16-VII)

Some of these compounds are made by the action of $HgCl_2$ on hydrido complexes or on carbonylate anions,[35] for example,

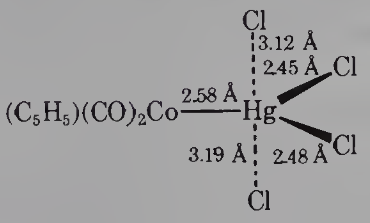
$$2C_5H_5Mo(CO)_3^-Na^+ + HgCl_2 \longrightarrow [C_5H_5Mo(CO)_3]_2Hg + 2NaCl$$

$$(Ph_2MeAs)_3RhHCl_2 + HgCl_2 \longrightarrow (Ph_2MeAs)_3Rh(HgCl)Cl_2 + HCl$$

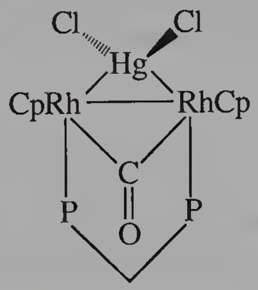
Mercury(II) compounds HgX_2 or RHgX may also undergo the oxidative-addition reaction (Chapter 27) in which metal–mercury bonds are formed, for example,

$$trans\text{-}IrCl(CO)(PPh_3)_2 + HgCl_2 = IrCl_2(HgCl)(CO)(PPh_3)_2$$

The $HgCl_2$ *molecule* may also add as such, for example, to give $Cp(CO)_2Co{\cdot}HgCl_2$ that has the structure (16-VIII) in which axial *tbp* positions are occupied by weakly coordinated Cl atoms of adjacent molecules and across a metal-metal[36] bond in $Rh_2Cp_2(\mu\text{-}CO)\mu\text{-}(dppm)$ (16-IX).



(16-VIII)



(16-IX)

TRIVALENT MERCURY

No compounds of Hg^{III} have yet been isolated, but Born–Haber cycles suggest that Hg^{III} could be accessible, and it would provide a unique case of the removal of a *d* electron from a Group IIB(12) element.

The electrochemical oxidation of acetonitrile solutions at −78°C of the Hg^{II} complex $[Hg\ cyclam](BF_4)_2$ provides evidence for Hg^{III}. Cyclam(1,4,8,11-tetraazacyclotetradecane) is not readily oxidized. A species of half-life ~5 s

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[35] See, for example, E. Rosenberg *et al., Inorg. Chem.*, 1986, **25,** 194.

[36] F. Faraone *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 6.

but characterizable by cyclic voltammetry, epr, and electronic absorption spectroscopy is consistent with a paramagnetic Hg^{III} complex.

The estimated potential is

$$[\text{Hg cyclam}]^{3+} + e = [\text{Hg cyclam}]^{2+} \qquad E^0 = 1.6 \text{ to } 1.8 \text{ v}$$

ORGANOMETALLIC COMPOUNDS[37a]

16-17. Organozinc and Organocadmium Compounds[37a,b]

Organozinc compounds are historically important because they were the first organometallic compounds to be prepared; their discovery by Sir Edward Frankland in 1849 played a decisive part in the development of modern ideas of chemical bonding. The cadmium compounds are also of interest, since their mild reactivities toward certain organic functional groups give them unique synthetic potentialities.

Organozinc compounds of the types R_2Zn and RZnX are known; EtZnI is a polymer with iodide bridges; each iodine atom forms three bonds to zinc, two long and one normal. The chloride and bromide may have cubane-type structures. Except for BuCdCl, only R_2Cd compounds have been isolated.

The constitution of RMX in solution has presented a problem similar to that for Grignard reagents. Monomeric RMX species predominate in ethers, for example,

$$Me_2Cd + CdI_2 \xrightleftharpoons{\text{THF}} 2MeCdI \qquad K \geq 100$$

For the perfluorophenyls, exchange between C_6H_5MX and $(C_6H_5)_2M$ is sufficiently slow that the Schlenk equilibria can be studied by ^{19}F nmr.

There is self-exchange in Me_2Cd and with Zn, Ga, and In alkyls via alkyl-bridged species.

The zinc alkyls can be obtained by thermal decomposition of RZnI, which is prepared by the reaction of alkyl iodides with a zinc–copper couple:

$$C_2H_5I + Zn(Cu) \longrightarrow C_2H_5ZnI \xrightarrow{\text{heat}} \tfrac{1}{2}(C_2H_5)_2Zn + \tfrac{1}{2}ZnI_2$$

The alkyls may also be prepared, and the diaryls most conveniently obtained, by the reaction of zinc metal with an organomercury compound:

$$R_2Hg + Zn \longrightarrow R_2Zn + Hg$$

or by reaction of zinc chloride with organolithium, -aluminum, or -magnesium.

[37a] J. L. Wardell, Ed., *Organometallic Compounds of Zinc, Cadmium and Mercury*, Chapman & Hall, London, 1985.

[37b] J. Boersma, in *Comprehensive Organometallic Chemistry*, Vol. 2, Chapter 16, Pergamon Press, Oxford, 1982; W. Carruthers, in *Comprehensive Organometallic Chemistry*, Vol. 7, Chapter 49 (uses in organic synthesis).

The best preparation of R_2Cd compounds is by treatment of the anhydrous cadmium halide with RLi or RMgX. The reaction of cadmium metal with alkyl iodides in DMF or $(CH_3)_2SO$ gives RCdI in solution.

The perfluoromethyl $(CF_3)_2Cd$[38] can be obtained by the reaction

$$(CF_3)_2Hg + Me_2Cd \xrightarrow{THF} Cd(CF_3)_2THF + Me_2Hg$$

It is more reactive than $(CF_3)_2Hg$ and is useful for synthesis of MCF_3 compounds. The zinc analogue is also known. The $MX(CF_3)$ compounds[38] of both Zn and Cd are also readily made from the metal and CF_2Br_2 via a mechanism[39] involving CF_2:

$$2M + 2CF_2Br_2 \xrightarrow{DMF} CF_3MX + MX_2 + CO + Me_2N{=}CFH^+X^-$$

The R_2Zn and R_2Cd compounds are nonpolar liquids or low-melting solids, soluble in most organic liquids. The lower alkyl zinc compounds are spontaneously flammable, and all react vigorously with oxygen and with water. The cadmium compounds are less sensitive to oxygen but are less stable thermally.

Both zinc and cadmium compounds react readily with compounds containing active hydrogen, such as alcohols:

$$R_2M + R'OH \longrightarrow RMOR' + RH$$

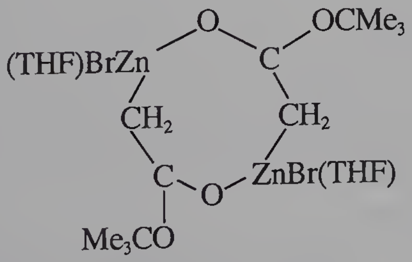
and are generally similar to RLi or RMgX, although their lower reactivity allows selective alkylations not possible with the more standard reagents. An important example is the use of the cadmium compounds in the synthesis of ketones from acyl chlorides:

$$2RCOCl + R'_2Cd \longrightarrow 2RCOR' + CdCl_2$$

In the well-known Reformatsky reaction

$$BrCH_2CO_2R + Zn \xrightarrow[(2)\ H_2O]{(1)\ R'_2CO} R'C(OH)CH_2CO_2R.$$

an organozinc intermediate has an eight-membered[40] ring (16-X).



(16-X)

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[38] L. J. Krause and J. O. Morrison, *J. Chem. Soc. Dalton Trans.*, **1981,** 2995; H. Lange and D. Naumann, *J. Fluorine Chem.*, 1985, **27,** 299, 309; P. L. Heinze and D. J. Burton, *J. Fluorine Chem.*, 1985, **29,** 359.

[39] D. Burton and D. W. Wiemers, *J. Am. Chem. Soc.*, 1985, **107,** 5014.

[40] J. Boersma *et al.*, *Organometallics*, 1984, **3,** 1403.

16-18. Organomercury Compounds[41]

A vast number of organomercury compounds are known, some of which have useful physiological properties. Organomercury compounds are of the types RHgX and R_2Hg. They are commonly made by the interaction of $HgCl_2$ and RMgX, but Hg—C bonds can also be made in other ways discussed later.

The *RHgX compounds* are crystalline solids. When X is an atom or group that can form covalent bonds to mercury (e.g., Cl, Br, I, CN, SCN, or OH), the compound is a nonpolar substance more soluble in organic liquids than in water. When X is SO_4^{2-} or NO_3^-, the substance is saltlike and presumably quite ionic, for instance, $[RHg]^+NO_3^-$. Acetates behave as weak electrolytes. For iodides or thiocyanates, complex anions (e.g., $RHgI_2^-$ and $RHgI_3^{2-}$) may be formed. A particularly important species due to its environmental significance is the ion $CH_3Hg(OH_2)^+$ discussed later.

The *dialkyls and diaryls* are nonpolar, volatile, toxic, colorless liquids or low-melting solids. Unlike the Zn and Cd alkyls they are much less affected by air or water, presumably because of the low polarity of the Hg—C bond and the low affinity of mercury for oxygen. However, they are photochemically and thermally unstable, as would be expected from the low bond strengths, which are of the order 50 to 200 kJ mol^{-1}. In the dark, mercury compounds can be easily kept for months. The decomposition generally proceeds by homolysis of the Hg—C bond and free-radical reactions.

In the linear Me_2Hg, the bonding is usually considered to be *sp* but photoelectron spectra and calculations suggest that there is little *p* character and that the bonding is best described as 3*c*-2*e*.[42]

All RHgX and R_2Hg compounds have linear bonds, but deviation from linearity has been claimed in a few cases, and in solution in particular, solvation effects may contribute to nonlinearity. The cyclopentadienyl [Cp_2Hg, CpHgX] and indenyl [$(C_9H_7)_2Hg$] compounds are fluxional (Section 29-15).

The principal utility of dialkyl- and diarylmercury compounds, and a very valuable one, is in the preparation of other organo compounds by interchange, for example,

$$(n/2)R_2Hg + M \longrightarrow R_nM + (n/2)Hg$$

This reaction proceeds essentially to completion with the Li and Ca groups, and with Zn, Al, Ga, Sn, Pb, Sb, Bi, Se, and Te, but with In, Tl, and Cd reversible equilibria are established. Partial alkylation of reactive halides can be achieved, for example,

$$AsCl_3 + Et_2Hg \longrightarrow EtHgCl + EtAsCl_2$$

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[41] J. L. Wardell, *Comprehensive Organometallic Chemistry*, Vol. 2, Chapter 17, Pergamon Press, Oxford, 1982; W. Carruthers, *Comprehensive Organometallic Chemistry*, Vol. 7, Chapter 49 (uses in organic synthesis).

[42] R. L. De Kock *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 3387.

Perhalogeno alkyls such as $PhHgCX_3$ or $PhHgCX_2Y$ can be used as sources of CX_2 or CX for transfer reactions to organic and inorganic compounds.[43] A convenient preparation of such a compound is

$$PhHgCl + CHX_3 + t\text{-}C_4H_9OK \xrightarrow{\text{benzene}} PhHgCX_3 + KCl + t\text{-}C_4H_9OH$$

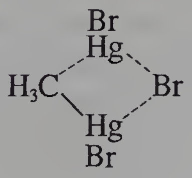
There is much known concerning mechanisms of reaction of organomercury compounds, but only brief mention can be made here. Exchange reactions of the type

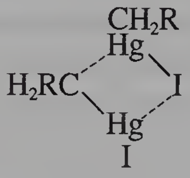
$$RHgBr + {}^*HgBr_2 \rightleftharpoons R^*HgBr + HgBr_2$$

have been studied using tracer mercury. It was shown that the electrophilic substitution, S_E2, proceeds with full retention of configuration when an optically active group, *sec*-butyl, is present. The reaction, which is also catalyzed by anions, is believed to proceed through a cyclic transition state such as (16-XI). Reactions such as

$$R_2Hg + HgX_2 = 2RHgX$$

have equilibrium constants of 10^5 to 10^{11} and proceed at rates that are slow and solvent dependent. Nuclear magnetic resonance studies have also shown that in solutions of RHgI compounds, there is relatively fast exchange of R groups and, again, a mechanism involving a cyclic intermediate or transition state (16-XII) has been postulated.


(16-XI)


(16-XII)

β-Diketonates of Hg^{II} are abnormal in having bonds to carbon like those of Pt^{II}.

Methylmercury Ion. The toxic effects of mercury and mercury compounds in the environment was first noted in Sweden, where the effluent from paper mills contained mercury. Later it was shown that human disasters such as those at Minimata, Japan, and in Iraq, had resulted from mercury poisoning. The effect is ascribed to the methylmercury ion, which induces irreversible complex disturbances of the central nervous system. The mercury released to the environment as metal (e.g., by losses from electrolytic cells used for NaOH and Cl_2 production or in compounds such as mercury seed dressings or fungicides) is converted to CH_3Hg^+ by a biological methylation. Vitamin B_{12} and model compounds such as methylcobaloximes or methylpentacyanocobaltate, which have Co—CH_3 bonds will transfer the CH_3 to Hg^{2+}. Microorganisms probably act similarly.

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[43] See, for example, B. L. Booth *et al.*, *J. Chem. Soc. Dalton Trans.*, **1980**, 403.

In aqueous solutions the CH_3Hg^+ ion is hydrated, and there are pH-dependent reactions giving mercury-substituted oxonium ions:

$$CH_3Hg(OH_2)^+ + OH^- \rightleftharpoons CH_3HgOH + H_2O$$

$$CH_3Hg(OH_2)^+ + CH_3HgOH \rightleftharpoons (CH_3Hg)_2OH^+ + H_2O$$

$$CH_3HgOH + (CH_3Hg)_2OH^+ \rightleftharpoons (CH_3Hg)_3O^+ + H_2O$$

The ion, which can have coordination numbers up to 4, binds to S and Se very strongly. Since such reactions with proteins, peptides, and so on, are presumably involved in toxic behavior (binding to pyrimidines, nucleotides, and nucleosides can also occur), there has been much study of complexes with cysteine, methionine, and other amino acids. The formation constants for CH_3HgSR compounds are $\sim 10^{14}$–10^{18}, some 10^8 times greater than those for the NH_2 group. Despite such favored binding there is high lability and exchange reactions with other thiols are very fast via associative mechanisms, providing pathways for migration.[44] This could explain why CH_3Hg^+ is so toxic at levels well below the thiol levels in cells. The toxic effects differ greatly from those of Hg^{2+} and the types of complex formed by the two ions differ markedly; Hg^{2+} compounds of amino acids containing SH groups are polymeric and polar, whereas the CH_3HgSR species are nonpolar and monomeric; for example, the cysteinate is $CH_3HgSCH_2CH_2CH(\overset{+}{N}H_3)CO_2^-$ with a linear C—Hg—S. The CH_3Hg^+ ion also denatures DNA and causes chromosomal damage.[45]

Other Species. Mercurous perchlorate and nitrate react with acetone to give complex species that have acetone bound to mercury as the enolate ion. However, ethanol reacts in basic solution with HgO to give a polymeric material. This is probably derived by condensation of the unknown molecule $C(HgOH)_4$ to give a polymeric oxonium ion with C—Hg—OH—Hg—C bridges. This is suggested because the polymer dissolves in carboxylic acids to give compounds $C(HgCO_2R)_4$, which have tetrahedral central carbon and linear C—Hg—O bonds. These carboxylates can also be obtained by quite another route:

$$B(OCH_3)_3 + Li + CCl_4 \longrightarrow C[B(OCH_3)_2]_4 \xrightarrow{Hg(O_2CCH_3)_2} C[Hg(CO_2CH_3)]_4$$

Crystalline water-soluble salts of the type $(RHg)_3O^+$ and the compound $C(HgI)_4$ are also known.

Mercuration and Oxomercuration. An important reaction for the formation of Hg—C bonds, and one that can be adapted to the synthesis of a wide variety of organic compounds, is the addition of mercuric salts, notably the acetate, trifluoroacetate, or nitrate to unsaturated compounds.

The simplest reaction, the mercuration reaction of aromatic compounds, is commonly achieved by the action of mercuric acetate in methanol, for example,

$$C_6H_6 + Hg(O_2CMe)_2 \longrightarrow C_6H_5Hg(O_2CMe) + MeCO_2H$$

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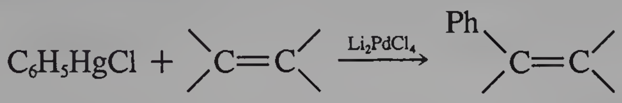
[44] D. L. Rabenstein and R. S. Reid, *Inorg. Chem.*, 1984, **23**, 1246.

[45] R. D. Bach *et al.*, *Organometallics*, 1985, **4**, 846.

Even aromatic organometallic compounds such as tricarbonylcyclobutadienyliron, $C_4H_4Fe(CO)_3$ (Section 26-9) can be mercurated.

By use of aryl compounds prepared in this way, the arylation of alkenes and a variety of other organic unsaturated compounds can be achieved. A palladium compound, usually Li_2PdCl_4, is used as a transfer agent, and organopalladium species are believed to be unstable intermediates; by use of air and a Cu^{II} salt the reaction can be made catalytic, since the Pd metal formed in the reaction is dissolved by Cu^{II} and the Cu^{I} so produced is oxidized by air (cf. the Wacker process, Section 28-20). A typical reaction is



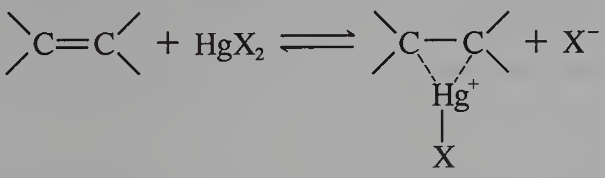
Although Hg–arene complexes have been postulated as intermediates in aromatic mercuration, only recently have such complexes[46] been isolated by reactions such as

$$Hg(SbF_6)_2 + 2C_6H_6 \xrightarrow{SO_2(l)} (C_6H_6)_2 \cdot Hg(SbF_6)_2$$

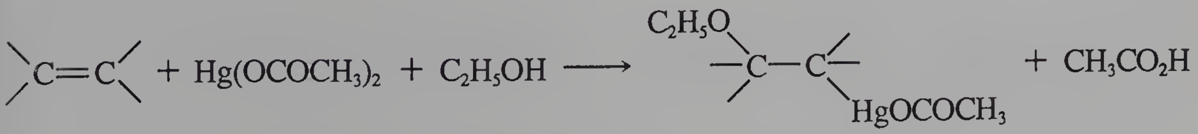
and for benzene, we have the equilibrium

$$Hg^{2+} + C_6H_6 \rightleftharpoons Hg(C_6H_6)^{2+} \qquad K_1 = 0.48 \text{ L mol}^{-1} \text{ (308 K)}$$

The interaction of mercuric salts is not confined to arenes, but with alkenes there appears to be a general reversible reaction involving mercurinium ions:



In most cases, the reactions have to be carried out in an alcohol or other protic medium, so that further reaction with the solvent is normally complete and the reaction is called *oxomercuration*, for example,



The evidence that HgX_2 adds across the bond is usually indirect, often, by observing the products on hydrolysis, for example,

$$CH_2{=}CH_2 + Hg(NO_3)_2 \xrightarrow{OH^-} HOCH_2CH_2Hg^+ + 2NO_3^-$$

or by removal of Hg as $HgCl_2$ by the action of HCl, which reverses the

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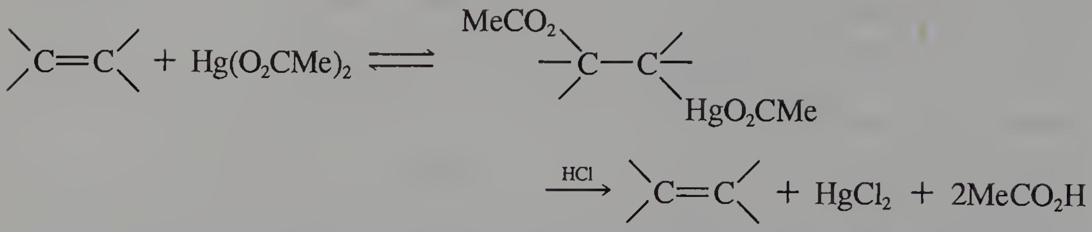
[46] W. Lau and J. K. Kochi, *J. Am. Chem. Soc.*, 1986, **108**, 6720.

addition:



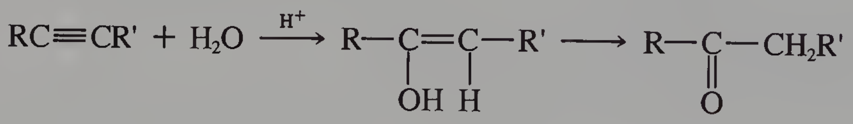
Mercurinium ions are doubtless intermediates and long-lived ions have been shown to exist in $FSO_3H—SbF_5—SO_2$ at −70°C in reactions such as

$$MeOCH_2CH_2HgCl \xrightarrow{H^+} MeOH_2^+ + CH_2CH_2Hg^{2+} + HCl$$

and with cyclohexene

$$C_6H_{10} + Hg(O_2CCF_3)_2 \xrightarrow{H^+} C_6H_{10}Hg^{2+}$$

The catalytic activity of mercuric salts in sulfuric acid solutions for hydration of acetylenes doubtless proceeds by routes similar to these reactions; the overall reaction is



$$RC{\equiv}CR' + H_2O \xrightarrow{H^+} R-\underset{OH}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-R' \longrightarrow R-\underset{O}{\underset{\|}{C}}-CH_2R'$$

Acetylene itself gives acetaldehyde.

Finally, it is of interest that methanolic solutions of Hg^{II} acetate readily absorb carbon monoxide at atmospheric pressure, and the resulting compound can be converted by halide salts into compounds of the type $XHgC(O)OCH_3$. Carbon monoxide is, in effect, inserted between the Hg and O of a solvolyzed mercuric ion, though the mechanism is not established in detail:

$$Hg(OCOCH_3)_2 + CH_3OH \rightleftharpoons CH_3COOHgOCH_3 + CH_3CO_2H$$

$$CH_3COOHg—OCH_3 + CO \rightleftharpoons CH_3COOHgC(O)OCH_3$$

The CO can be regenerated from the compounds by heating or by the action of concentrated hydrochloric acid. Under pressures of 25 atm, reactions such as

$$RHgNO_3 + CO + CH_3OH \longrightarrow RCOOCH_3 + Hg + HNO_3$$

can be carried out.

Additional References

Larock, R. C., *Organomercury Compounds in Organic Synthesis,* Springer-Verlag, Berlin, 1985.
Moore, D. J. and Timbs, A. E., *Chem. Br.*, 1984, 622 (mercury as a health risk).
Nriagu, J. O., *Zinc in the Environment,* Wiley, New York, 1980.

3

THE CHEMISTRY OF THE TRANSITION ELEMENTS

Chapter Seventeen

Survey of the Transition Elements

17-1. Definition and General Characteristics of Transition Elements

The transition elements may be defined strictly as those that *as elements,* have partly filled *d* or *f* shells. Here we shall adopt a slightly broader definition and include also elements that have partly filled *d* or *f* shells in any of their commonly occurring oxidation states. This means that we treat the coinage metals copper, silver, and gold as transition metals, since Cu^{II} has a $3d^9$ configuration, Ag^{II} a $4d^9$ configuration, and Au^{III} a $5d^8$ configuration. From a purely chemical point of view it is also appropriate to consider these elements as transition elements because their chemical behavior is, on the whole, quite similar to that of other transition elements.

With our broad definition in mind, we find that there are now some 56 transition elements, counting the heaviest elements through the one of atomic number 104. Clearly the majority of all known elements are transition elements. All these transition elements have certain general properties in common:

1. They are all metals.
2. They are almost all hard, strong, high-melting, high-boiling metals that conduct heat and electricity well. In short, they are "typical" metals of the sort we meet in ordinary circumstances.
3. They form alloys with one another and with other metallic elements.
4. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are "noble"—that is, they have such positive electrode potentials that they are unaffected by simple acids.
5. With very few exceptions they exhibit variable valence, and their ions and compounds are colored in one if not all oxidation states.
6. Because of partially filled shells, they form at least some paramagnetic compounds.

This large number of transition elements is subdivided into three main groups: (*a*) the main transition elements or *d*-block elements, (*b*) the lanthanide elements, and (*c*) the actinide elements.

The main transition group or *d* block includes the elements that have partially filled *d* shells only. Thus the element scandium, with the outer electron configuration $4s^23d$, is the lightest member. The eight succeeding elements, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu, all have partly filled $3d$ shells either in the ground state of the free atom (all except Cu) or in one or more of their chemically important ions (all except Sc). This group of elements is called the *first transition series.* At zinc the configuration is $3d^{10}4s^2$, and this element forms no compound in which the $3d$ shell is ionized, nor does this ionization occur in any of the next nine elements. It is not until we come to yttrium, with ground state outer electron configuration $5s^24d$, that we meet the next transition element. The following eight elements, Zr, Nb, Mo, Tc, Ru, Rh, Pd, and Ag, all have partially filled $4d$ shells either in the free element (all but Ag) or in one or more of the chemically important ions (all but Y). This group of nine elements constitutes the *second transition series.*

Again there follows a sequence of elements in which there are never *d*-shell vacancies under chemically significant conditions until we reach the element lanthanum, with an outer electron configuration in the ground state of $6s^25d$. Now, if the pattern we have observed twice before were to be repeated, there would follow 8 elements with enlarged but not complete sets of $5d$ electrons. This does not happen, however. The $4f$ shell now becomes slightly more stable than the $5d$ shell, and through the next 14 elements, electrons enter the $4f$ shell until at lutetium it becomes filled. Lutetium thus has the outer electron configuration $4f^{14}5d6s^2$. Since both La and Lu have partially filled *d* shells and no other partially filled shells, it might be argued that both these should be considered as *d*-block elements. However, for chemical reasons, it would be unwise to classify them in this way, since all the 15 elements La ($Z = 57$) through Lu ($Z = 71$) have very similar chemical and physical properties, those of lanthanum being in a sense prototypal; hence these elements are called the *lanthanides,* and their chemistry is considered separately in Chapter 20. Since the properties of Y are extremely similar to, and those of Sc mainly like, those of the lanthanide elements proper, and quite different from those of the regular *d*-block elements, we treat them also in Chapter 20.

For practical purposes, then, the *third transition series* begins with hafnium, having the ground state outer electron configuration $6s^25d^2$, and embraces the elements Ta, W, Re, Os, Ir, Pt, and Au, all of which have partially filled $5d$ shells in one or more chemically important oxidation states as well as (except Au) in the neutral atom.

Continuing on from mercury, which follows gold, we come via the noble gas radon and the radioelements Fr and Ra to actinium, with the outer electron configuration $7s^26d$. Here we might expect, by analogy to what happened at lanthanum, that in the following elements electrons would enter the $5f$ orbitals, producing a lanthanidelike series of 15 elements. What actually occurs is, unfortunately, not so simple. Although immediately following lanthanum the $4f$ orbitals become decisively more favorable than the $5d$ orbitals for the electrons entering in the succeeding elements, there is apparently not so great a difference between the $5f$ and $6d$ orbitals until later. Thus for the elements immediately following Ac, and their ions, there may be electrons in the 5*f* or 6*d* orbitals or both. Since it appears that later on, after four or five more electrons have been added to the Ac configuration, the 5*f* orbitals do become definitely the more stable, and since the elements from about americium on do show moderately homologous chemical behavior, it has become accepted practice to call the 15 elements beginning with Ac the *actinide elements.*

There is an important distinction, based on electronic structures, between the three classes of transition elements. For the *d*-block elements the partially filled shells are *d* shells, 3*d*, 4*d*, or 5*d*. These *d* orbitals project well out to the periphery of the atoms and ions so that the electrons occupying them are strongly influenced by the surroundings of the ion and, in turn, are able to influence the environments very significantly. Thus many of the properties of an ion with a partly filled *d* shell are quite sensitive to the number and arrangement of the *d* electrons present. In marked contrast to this, the 4*f* orbitals in the lanthanide elements are rather deeply buried in the atoms and ions. The electrons that occupy them are largely screened from the surroundings by the overlying shells (5*s*, 5*p*) of electrons; therefore reciprocal interactions of the 4*f* electrons and the surroundings of the atom or the ion are of relatively little chemical significance. This is why the chemistry of all the lanthanides is so homologous, whereas there are seemingly erratic and irregular variations in chemical properties as one passes through a series of *d*-block elements. The behavior of the actinide element lies between those of the two types just described because the 5*f* orbitals are not so well shielded as are the 4*f* orbitals, although not so exposed as are the *d* orbitals in the *d*-block elements.

17-2. Position in the Periodic Table

Figure 17-1 shows in a qualitative way the relative variations in the energies of the atomic orbitals as a function of atomic number in neutral atoms. It is well to realize that in a multielectron atom—one with, say, 20 or more electrons—the energies of all the levels are more or less dependent on the populations of all the other levels. Hence the diagram is rather complicated.

In hydrogen all the subshells of each principal shell are equienergic, but in more complex atoms the *s, p, d, f, g,* and so on subshells split apart and drop to lower energies. This descent in energy occurs because the degree to which an electron in a particular orbital is shielded from the nuclear charge by all the other electrons in the atom is insufficient to prevent a steady increase in the *effective nuclear charge* felt by that electron with increasing atomic number. In other words, each electron is imperfectly shielded from the nuclear charge by the other electrons. The energy of an electron in an atom is given by

$$E = -\frac{2\pi^2\mu e^4(Z^*)^2}{n^2h^2} \qquad (17\text{-}1)$$

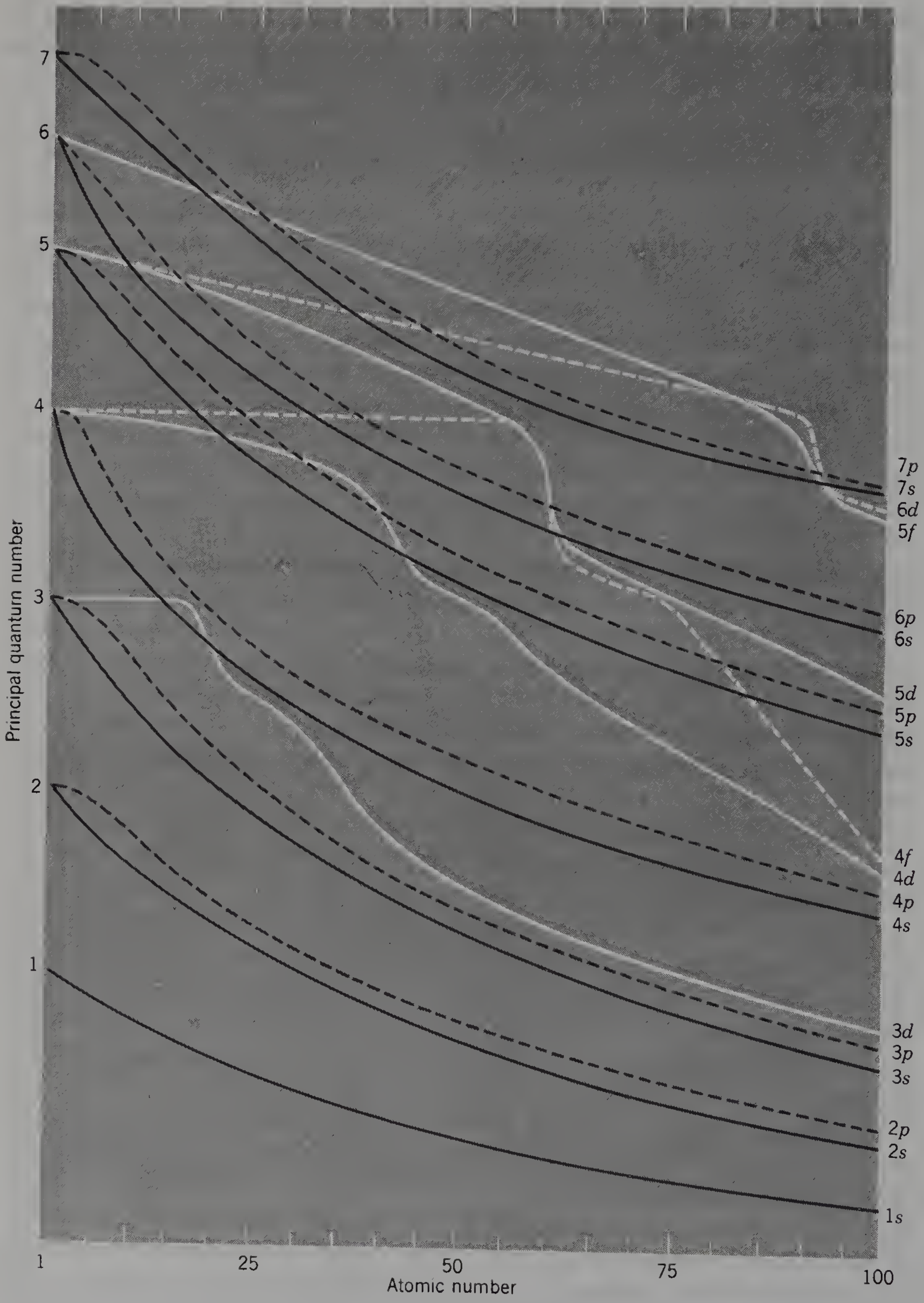


FIG. 17-1. The variation of the energies of atomic orbitals with increasing atomic number in neutral atoms (energies not strictly to scale).

where Z^* is the effective nuclear charge, and the energy of the electron falls as Z^* increases. The diagram is complicated, however, because all subshells do not drop in parallel fashion, since the several subshells of the same principal shell are shielded to different degrees by the core of electrons beneath.

From Fig. 17-1 we see that the $1s$, $2s$, $2p$, $3s$, and $3p$ levels occur in that sequence in all known atoms. Thus through the atoms (H to Ar) in which this sequence of orbitals is being filled, they are filled in that order. While the filling of this set of orbitals is taking place, the energies of the higher and as yet unfilled orbitals are being variously affected by the screening power of these first 18 electrons. In particular, the $3d$ levels, which penetrate the argon core rather little, have scarcely dropped in energy when we reach argon ($Z = 18$), whereas the $4s$ and $4p$ levels, especially the former, which penetrate the argon core quite a bit, have dropped rather steeply. Thus when two more electrons are added to the argon configuration to give the potassium and calcium atoms, they enter the $4s$ orbital, which has fallen below the $3d$ orbitals. As these 2 electrons are added, the nuclear charge is also increased by two units. Since the $3d$ orbitals penetrate the electron density in the $4s$ orbitals very considerably, the net result is that the effective nuclear charge for the $3d$ orbitals increases rather abruptly, and they now drop well below the $4p$ orbitals to about the level of the $4s$ orbital. The next electron therefore enters the $3d$ shell, and scandium has the configuration $[\mathrm{Ar}]4s^23d$. This $3d$ electron screens the $4p$ levels more effectively than it screens the remaining $3d$ orbitals, so the latter remain the lowest available orbitals and the next electron is also added to the $3d$ shell to give Ti, with the configuration $[\mathrm{Ar}]4s^23d^2$. This process continues in a similar way until the entire $3d$ shell is filled. Thus at Zn we have the configuration $[\mathrm{Ar}]4s^23d^{10}$, and the $4p$ orbitals, now the lowest available ones, become filled in the six succeeding elements.

The same sequence of events is repeated again in the elements following krypton, which has the electron configuration $[\mathrm{Ar}]3d^{10}4s^24p^6$. Because of the way in which the shielding varies, the $4d$ levels, which in a one-electron atom would be next in order of stability, are higher in energy than the $5s$ and $5p$ orbitals, so that the next two electrons added go into the $5s$ orbitals, giving the alkali and alkaline earth elements Rb and Sr. But the shielding of the $4d$ orbitals by these $5s$ electrons is very poor, so that the $4d$ orbitals feel strongly the increase of two units of nuclear charge and take a sharp drop, becoming appreciably more stable than the $5p$ orbitals, and the next electron added becomes a $4d$ electron. Thus the next element, Y, is the first member of the second transition series. This series is completed at Ag, configuration $[\mathrm{Kr}]4d^{10}5s^2$; then six $5p$ electrons are added to make Xe, the next noble gas.

At Xe ($Z = 54$) the next available orbitals are the $6s$ and $6p$ orbitals. The $4f$ orbitals are so slightly penetrating with respect to the Xe core that they have scarcely gained any stability, but the more penetrating $6s$ and $6p$ levels have gained a good deal. Hence the next two electrons added are $6s$ electrons, giving again an alkali and an alkaline earth element Cs and Ba, respectively. However, the $6s$ shell scarcely shields the $4f$ orbitals, so the latter abruptly feel an increase in effective nuclear charge and suffer a steep drop in energy. At the same time, however, the energy of the $5d$ levels also drops abruptly, just as did that of $(n - 1)d$ levels previously as electrons are added to the ns level, and the final situation is one in which, at Ba, the $6s$, $5d$, and $4f$ levels are all of about the same energy. The next entering electron, in the element lanthanum, enters a $5d$ orbital, but the following element, cerium, has the configuration $6s^24f^2$. Through the next 12 elements electrons continue to enter the $4f$ orbitals, and it is likely that even at cerium they are intrinsically more stable than the $5d$'s. Certainly they are so by the time we reach ytterbium, with the configuration $6s^44f^{14}$. Now, with the $6s$ and $4f$ shells full, the next lowest levels are unequivocally the $5d$'s, and from lutetium, with the configuration $6s^24f^{14}5d$, through mercury, with the configuration $[Xe]6s^24f^{14}5d^{10}$, the ten $5d$ electrons are added. Chemically, lanthanum and lutetium, each of which has a single $5d$ electron, are very similar to each other, and all the elements in between, with configurations $[Xe]4f^n6s^2$, have chemical properties intermediate between those of lanthanum and lutetium. Consequently these 15 elements are all considered to be members of one class, the lanthanides. Hafnium, $[Xe]4f^{14}5d^26s^2$, through gold are the 8 elements that we regard as the members of the third transition series.

Following mercury there are 6 elements in which electrons enter the $6p$ orbitals until the next noble gas, radon, is reached. Its configuration is $[Xe]4f^{14}5d^{10}6s^26p^6$. Because of their relatively nonpenetrating character, the $5f$ orbitals have dropped so much more slowly than have the $7s$ and $7p$ orbitals that the next two electrons beyond the radon core are added to the $7s$ level, and again an alkali and an alkaline earth element are formed, namely, Fr, $[Rn]7s$, and Ra, $[Rn]7s^2$. But, again in analogy to the situation one row up in the Periodic Table, both the $5f$ and the $6d$ orbitals penetrate the $7s$ orbitals very considerably; they are thus abruptly stabilized relative to the $7p$ orbitals, and the next electrons added enter them. It appears that as we proceed through actinium and the following elements, the energies of the $6d$ and $5f$ orbitals remain for a while so similar that the exact configuration is determined by interelectronic forces. In the case of protactinium it is not certain whether the ground state is $[Rn]7s^26d^3$, $[Rn]7s^26d^25f$, $[Rn]7s^26d5f^2$, or $[Rn]7s^25f^3$. These four configurations doubtless differ very little in energy, and for chemical purposes the question of which is actually the lowest is not of great importance. The next element, uranium, appears definitely to have the configuration $[Rn]7s^25f^36d$, and the elements thereafter are all believed to have the configurations $[Rn]7s^25f^n6d$. The important point is that around actinium, the $6d$ and $5f$ levels are of almost the same energy, with the $5f$'s probably becoming slowly more stable later on.

17-3. Electronic Structure and Bonding

Although the basic principles of chemical bond formation are the same for the transition elements as for all others, practical discussion generally follows a different pattern. This is because d orbitals play the major role in the case of the transition elements, particularly the d-block elements, in contrast to the situation for the main group elements where the s and p orbitals provide all (or practically all) of the bonding.

The repertoire of approximations and formalisms that has been developed for dealing with the electronic structure of transition elements is generally called *Ligand Field Theory* (*LFT*). This rather elastic term includes at one extreme a purely electrostatic model (crystal field theory), at the other, molecular orbital treatments at various levels of sophistication and accuracy, and in between a range of more or less parameterized models such as the angular overlap model or variants thereof.[1] This body of methods is now covered in more elementary textbooks[2] and we shall take it that the user of this book is generally familiar with this material.

The primary "work product" of any form of ligand field theory as applied to a transition metal complex is a description of how the metal atom d orbitals are split (and by how much), and the relative energies of the states that arise when electrons are placed in these orbitals.[3] Once these results are at hand, the spectroscopic and magnetic properties of the complex can be addressed. Again, the basic aspects of these spectroscopic and magnetic properties are assumed to be familiar to the reader from study of more elementary texts.

For complexes of relatively high symmetry and only moderate covalence in the metal to ligand bonds, electronic absorption spectra can usually be interpreted in considerable detail.[4] For those electronic transitions that are "metal centered," where an electron shifts from one orbital of high metal d character to another of high metal d character, ligand field theory, even in its most electrostatic form, affords a generally effective basis for making assignments. When an electron passes from a metal-based orbital to a ligand-based orbital, or vice versa, the transition is called a charge-transfer transition and the applicable type of theory must be more of the MO type.

In this chapter we shall deal with a few topics in the realm of electronic properties that are not covered in more elementary texts.

17-4. Magnetic Properties of Transition Metal Compounds

For the mononuclear complexes of the metal ions of the first transition series, the orbital splitting patterns derived from ligand field theory provide a reliable first-order interpretation (most importantly, in understanding the number of unpaired electrons) of the measured magnetic susceptibilities. Values of the

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[1] M. Gerloch and R. G. Woolley, *Prog. Inorg. Chem.*, 1983, **31,** 371; R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1985, **24,** 1754 and earlier papers cited therein.

[2] See, for example, F. A. Cotton, G. Wilkinson, and P. L. Gaus, *Basic Inorganic Chemistry*, Wiley, 2nd ed., 1987, Chapter 23, and various other texts at a similar level.

[3] E. Koenig and S. Kremer, *Ligand Field Energy Diagrams,* Plenum Press, New York, 1977.

[4] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam, 1984.

magnetic moments based on electron spin require only small corrections for the effects of orbital angular momentum. These matters are covered in contemporary undergraduate texts. We note here, however, that there are two areas in which such a simple approach is inadequate: (1) for even mononuclear complexes of the heavier transition elements, where spin-orbit coupling is larger, and (2) in all bi- and polynuclear complexes where spin-spin coupling takes place, either by direct orbital overlap or mediated by pathways involving bridging ligands, or by magnetic dipole coupling. A third anomalous phenomenon, spin-state crossovers, will be discussed in Section 17-5.

Complexes of the Heavier Elements. One important characteristic of the heavier elements is that they tend to give *low-spin* compounds, which means that in oxidation states characterized by an odd number of *d* electrons there is frequently only one unpaired electron, and ions with an even number of *d* electrons are very often diamagnetic. There are two main reasons for this intrinsically greater tendency to spin pairing. First, the 4*d* and 5*d* orbitals are spatially larger than 3*d* orbitals so that double occupation of an orbital produces significantly less interelectronic repulsion. Second, a given set of ligand atoms produces larger splittings of 5*d* than of 4*d* orbitals and in both cases larger splittings than for 3*d* orbitals.

When there are unpaired electrons, the susceptibility data are often less easily interpreted. For instance, low-spin octahedral Mn^{III} and Cr^{II} complexes have t_{2g}^4 configurations, hence two unpaired electrons. They have magnetic moments in the neighborhood of 3.6 BM that can be correlated with the presence of the two unpaired spins, these alone being responsible for a moment of 2.83 BM, plus a contribution from unquenched orbital angular momentum. Now, Os^{IV} also forms octahedral complexes with t_{2g}^4 configurations, but these commonly have moments of the order of 1.2 BM; such a moment, taken at face value, has little meaning and certainly does not give any simple indication of the presence of two unpaired electrons. Indeed, in older literature it was naïvely taken to imply that there was only one unpaired electron, from which the erroneous conclusion was drawn that the osmium ion was in an odd oxidation state instead of the IV state.

Similar difficulties arise in other cases, and their cause lies in the *high spin-orbit coupling constants* of the heavier ions. Figure 17-2 shows how the effective magnetic moment of a t_{2g}^4 configuration depends on the ratio of the thermal energy kT to the spin-orbit coupling constant λ. For Mn^{III} and Cr^{II}, λ is sufficiently small that at room temperature ($kT \approx 200\ cm^{-1}$) both these ions fall on the plateau of the curve, where their behavior is of the familiar sort. Osmium(IV), however, has a spin-orbit coupling constant that is an order of magnitude higher, and at room temperature kT/λ is still quite small. Thus at ordinary temperatures octahedral Os^{IV} compounds should (and do) have low, strongly temperature-dependent magnetic moments. Obviously, if measurements on Os^{IV} compounds could be made at sufficiently high temperatures—which is usually impossible—they would have "normal" mo-

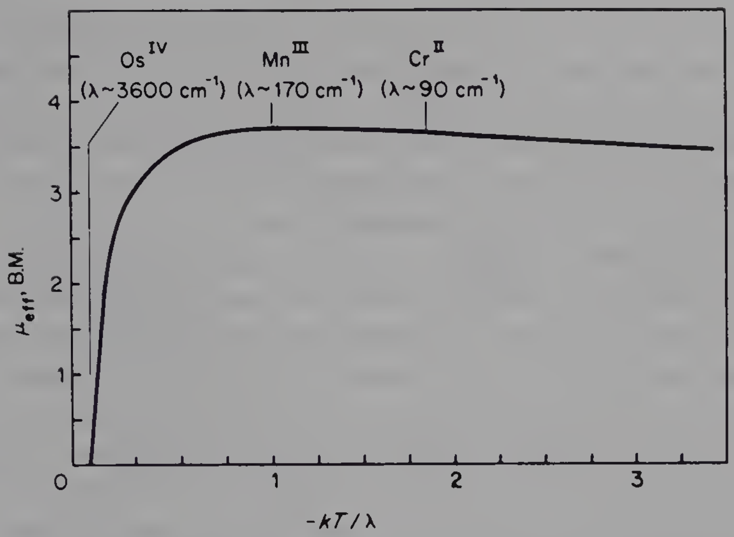


FIG. 17-2. Curve showing the dependence on temperature and on the spin-orbit coupling constant λ of the effective magnetic moment of a d^4 ion in octahedral coordination.

ments, and, conversely, at very low temperatures $\mathrm{Mn^{III}}$ and $\mathrm{Cr^{II}}$ compounds would show "abnormally" low moments.

The curve shown in Fig. 17-2 for the t_{2g}^4 case arises because of the following effects of spin-orbit coupling. First, the spin-orbit coupling splits the lowest triplet state in such a way that in the component of lowest energy the spin and orbital moments cancel one another completely. When λ, hence this splitting, are large compared with the available thermal energy, the Boltzmann distribution of systems among the several spin-orbit split components is such that most of the systems are in the lowest one that makes no contribution at all to the average magnetic moment. At 0 K, of course, all systems would be in this nonmagnetic state and the substance would become entirely diamagnetic. Second, however, the spin-orbit coupling causes an interaction of this lowest nonmagnetic state with certain high-lying excited states so that the lowest level is not actually entirely nonmagnetic at all temperatures, and in the temperature range where kT/λ is much less than unity the effective magnetic moment varies with the square root of the temperature.

Similar difficulties arise for d^1 ions in octahedral fields, when the spin-orbit coupling constant is large. For example, if $\lambda = 500$ (as for $\mathrm{Zr^{III}}$) the nonmagnetic ground state, which splits off from the $^2T_{2g}$ term under the influence of spin-orbit coupling, will be so low that a temperature-independent susceptibility corresponding to an effective moment of only ~0.8 BM at room temperature will be observed. Again, this moment as such has no unique interpretation in terms of the number of unpaired electrons for the ion.

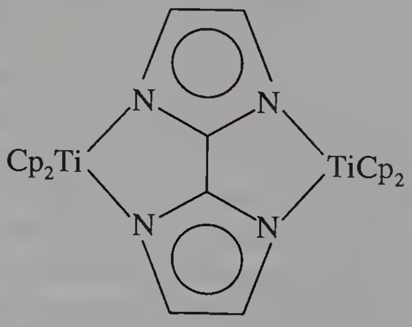
Those systems for which fairly complicated behavior is expected (only octahedral coordination being considered here) are d^1, d^2, d^7, d^8, and d^9. The d^6 systems have no paramagnetism (unless there is some of the temperature-independent type), since they have t_{2g}^6 configurations with no unpaired electrons. The d^3 systems have magnetic moments that are rigorously temperature independent regardless of the magnitude of λ. The d^5 systems have moments that vary with temperature only for very low values of kT/λ, and even then the temperature dependence is not severe; nevertheless, these systems can show complicated behavior because of intermolecular magnetic interactions in compounds that are not magnetically dilute.

Interionic Magnetic Coupling. In cases where direct orbital overlap between metal atoms (or ions) is strong, we are dealing with M—M bonds (single or multiple, as the case may be) and no special problem arises. There are, however, many instances in which the interaction is relatively weak and the energy separation between states with different numbers of unpaired electrons is on the order of a few hundred wave numbers, or less. In such compounds magnetic moments will depend strongly on temperature from 0 K to room temperature or above. The behavior of such systems is generally treated in terms of a model employing the parameter J/kT, where J is a measure of the coupling between spins on adjacent ions (defined by a term $-2JS_1 \cdot S_2$, where S_1 and S_2 are the spin quantum numbers for the two ions). The equations giving molar susceptibility versus T have been derived for a great many bi- and polynuclear systems and are available in the literature.[5]

The Bleaney–Bowers equation, initially derived to deal with the important case of dinuclear Cu^{II} species such as the acetate (see Section 18-H-XIV), is the simplest, but gives an idea of the general form such relations take. With $x = J/kT$, μ_B representing the Bohr magneton, g the gyromagnetic ratio, N Avogadro's number, k the Boltzman constant, and T the Kelvin temperature, the Bleaney–Bowers equation is

$$\chi = \frac{Ng^2\mu_B{}^2}{kT} \cdot \frac{2e^{2x}}{1+3e^{2x}} \tag{17-2}$$

This equation is general for any system with $S_1 = S_2 = \frac{1}{2}$. Figure 17-3 shows the experimental data for an actual system (17-I) and the excellent fit that is obtained using eq. 17-2, with $J = -25.2\ \text{cm}^{-1}$ and $g = 1.984$.[6]



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[5] C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 203, and other literature cited therein.
[6] D. N. Hendrickson *et al.*, *Inorg. Chem.*, 1978, **17**, 2078.

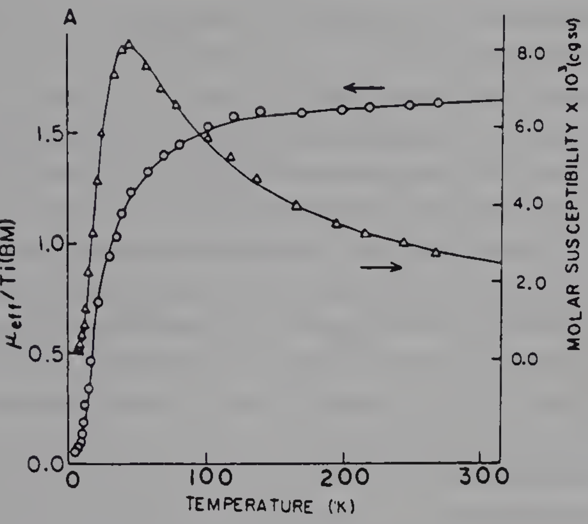

FIG. 17-3. The magnetic susceptibility (Δ) and magnetic moment (○) as a function of temperature for compound (17-I). The solid lines represent the optimal fits to the Bleaney–Bowers expression, eq. 17-1. (Reproduced by permission from ref. 6.)

17-5. Spin-State Crossovers[7]

In the majority of complexes the ligand field is either weak enough to guarantee that a high-spin (HS) ground state prevails at all accessible temperatures, or strong enough to assure that a low-spin (LS) ground state exists at all accessible temperatures. There are, however, cases where a high-spin and a low-spin state are separated by only about the thermal energy prevailing at or below room temperature. The magnetic properties of the complex, therefore, change anomalously (that is, differently from ordinary Curie, or Curie–Weiss behavior) as a function of temperature.

Table 17-1 lists the types of octahedral systems in which spin-state crossovers are commonly observed. There are also important examples in other

TABLE 17-1
Some "Octahedral" Spin Crossover Cases

d^n	Low-spin configuration and state	High-spin configuration and state	Example
d^5	${}^2T_{2g}(t_{2g}^5)$	${}^6A_{1g}(t_{2g}^3e_g^2)$	Fe^{III}
d^6	${}^1A_{1g}(t_{2g}^6)$	${}^3T_{2g}(t_{2g}^4e_g^2)$	Fe^{II}, Co^{III}
d^7	${}^2E_g(t_{2g}^6e)$	${}^4T_{1g}(t_{2g}^5e_g^2)$	Co^{II}

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[7] E. König, *Chem. Rev.*, 1985, **85**, 219. P. Gütlich, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry,* G. J. Long, ed., Plenum Press, New York, 1984; P. Gütlich, in *Mössbauer Spectroscopy and Its Chemical Applications* (Adv. Chem. Ser., Vol. 194), American Chemical Society, Washington, D.C., 1981, p. 404; P. Gütlich, *Struct. Bonding, Berlin,* 1981, **44,** 83.

coordination geometries, especially five-coordinate ones, but we shall not explicitly discuss them here.

The origin of spin-state crossovers can be expressed in terms of ligand field theory by referring to the magnitude of the orbital splitting (Δ_o in an octahedral complex) and the spin-pairing energy P. When P and Δ_o are about equal, the high-spin and low-spin states will have very similar energies.

The experimental methods used to study spin crossovers include measurement of bulk magnetic susceptibility, vibrational spectroscopy (because M—L bond strengths differ appreciably between the HS and LS states), crystallography, and in the case of iron compounds, Mössbauer spectroscopy. It should be noted that because of the change in M—L bond lengths, which decrease in the LS state (by 0.1–0.2 Å) the behavior of the system is strongly dependent on pressure as well as temperature.[8]

The spin crossover behavior of iron(III) d^5 complexes has been extensively studied.[9] In fact, iron(III) d^5 species provided some of the earliest examples (by E. Cambi *et al.*, in the period 1931–1937), and are well represented by a variety of tris(dithiocarbamato) complexes $Fe(S_2CNR_2)_3$, having a trigonally distorted "octahedral" configuration of six sulfur atoms. With most R groups the $^2T_{2g}$ state lies several hundred reciprocal centimeters below the $^6A_{1g}$ state. Thus at low temperatures the effective magnetic moment μ_{eff} tends toward a value of ~2.1 BM, which is characteristic of a t_{2g}^5 configuration. As the temperature increases, molecules begin to populate the HS state and the average effective magnetic moment rises, following a sigmoidal curve that appears to be approaching an asymptotic limit. This limiting value must, of course, be less than the μ_{eff} for a pure high-spin complex, since it will never be possible to excite thermally all the molecules into the HS state. This behavior is shown in Fig. 17-4, for a typical case where ΔE, the energy

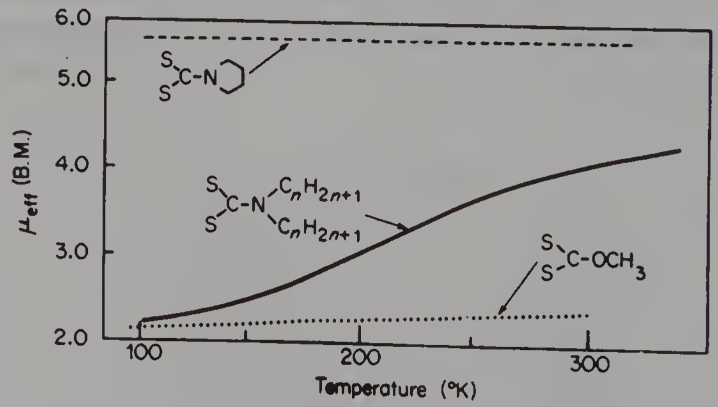

FIG. 17-4. Variation of μ_{eff} with temperature for some FeL_3 complexes, where L is a dithiocarbamate or xanthate.

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[8] C. N. R. Rao *et al.*, *Chem. Phys.*, 1985, **100**, 447.

[9] D. N. Hendrickson *et al.*, *Inorg. Chem.*, 1985, **24**, 3947; 1986, **25**, 160; *J. Am. Chem. Soc.*, 1986, **108**, 395.

difference between the low- and high-spin states is between 50 and 250 cm^{-1}; this is the crucial range, since thermal energies vary from ~70 cm^{-1} at 100 K to ~200 cm^{-1} at room temperature. If ΔE becomes >~29 kJ mol^{-1} (>10 times RT at the highest temperature of measurement) thermal population of the high-spin excited state is negligible—or nearly so—and simple, temperature-independent, low-spin behavior is observed. This is the case when the R,R′ groups are cyclohexyl, or when NRR′ is replaced by OR (to give xanthates instead of dithiocarbamates). Conversely, the replacement of NRR′ by pyrrolidino causes the HS state to become more stable by an energy much in excess of RT and we have simple, temperature-independent high-spin behavior.

It should be noted that although the spin crossover behavior just discussed is relatively simple for solutions (it is formally no different from any ordinary chemical equilibrium, A $\rightleftarrows$ B, between isomers), it becomes much more complex in the solid state. The experimental results can be fitted only approximately by considering a simple Boltzmann distribution of molecules between two states. Because of the redistribution of electrons from nonbonding to antibonding orbitals, the metal-ligand bond lengths and perhaps other structural features change, the packing of the molecules in the crystal may change, vibrational frequencies and energies change, and so forth. Broadly speaking,

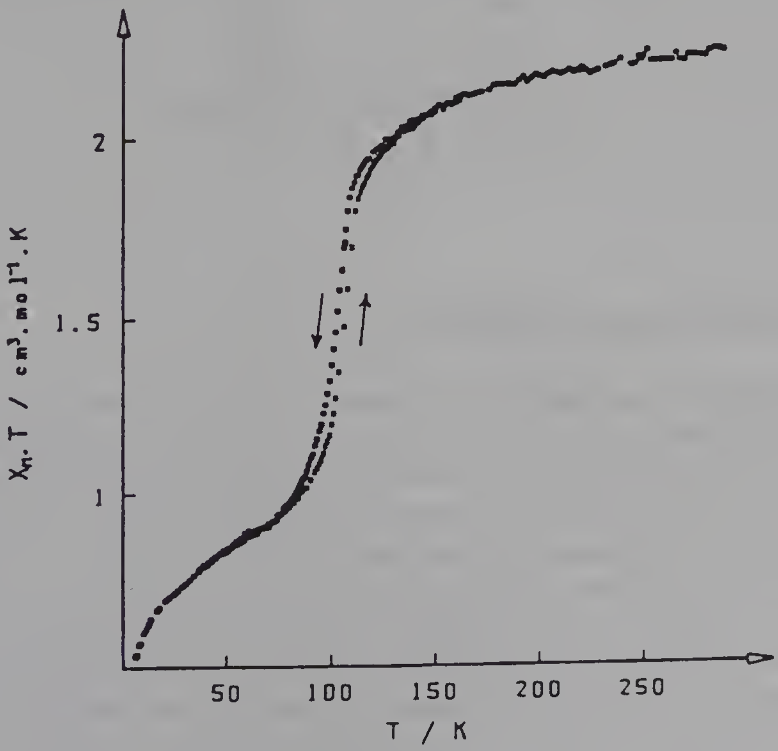
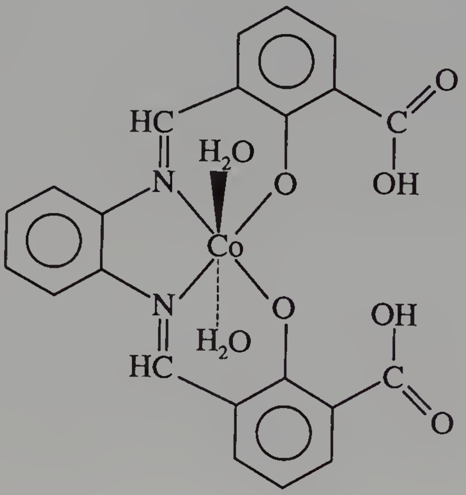


FIG. 17-5. Temperature dependence of the magnetic moment (proportional to χT) of compound (17-II). Falling and rising arrows indicate decreasing and increasing temperatures, respectively. (Reproduced by permission from ref. 11.)

the spin crossover phenomena in solids are of two types:

1. *Continuous:* Occurring smoothly, with little or no hysteresis, over a wide temperature range. This behavior is seen when the HS and LS molecules can form solid solutions within a common packing pattern.
2. *Discontinuous:* Occurring in a narrow range of temperature, often with hysteresis. In these cases there are strong cooperative intermolecular interactions and first-order phase transitions occur.

Needless to say, in the real world there are cases that do not fall neatly into either of the above categories.[10] Reasons for this are not always certain, but one general problem may be development of different domains within the sample, with somewhat different temperature dependencies. An example of nearly discontinuous behavior (called *hindered*) is provided[11] by compound (17-II). This is a d^7 system that crosses between $S = \frac{3}{2}$ and $S = \frac{1}{2}$ states. Its magnetic behavior as a function of temperature is shown in Fig. 17-5.



(17-II)

17-6. Optical Activity in Complexes

Chiral complexes occur mainly when chelate rings are formed, and resolution of enantiomers can be accomplished when the metal ion is one of those (e.g., Co^{III}, Cr^{III}, Rh^{III}, Ir^{III}, and Pt^{IV}) that give kinetically inert complexes. We discuss here some of the fundamentals of optical activity as they pertain to transition metal complexes. Optical activity in a molecule can be expected when and only when the molecule is so structured that it cannot be superposed on its mirror image. Such a molecule is said to be *dissymmetric,* or *chiral.* Chiral, from the Greek word for hand, is useful in emphasizing the left-hand to right-hand type of relationship between nonsuperposable mirror images or

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[10] P. Gütlich *et al., Inorg. Chem.,* 1986, **25,** 1565.

[11] J. Zarembowitch *et al., Nouv. J. Chim.,* 1985, **9,** 467.

enantiomorphs. A dissymmetric or chiral molecule must have either no element of symmetry or, at most, only proper axes of symmetry.

The six-coordinate chelate complexes of the types M(bidentate ligand)$_3$ and *cis*-M(bidentate ligand)$_2$X$_2$, which have symmetries D_3 and C_2, respectively, fulfill this condition and are the commonest cases in which the "center of dissymmetry" is the metal ion itself.

The simplest way in which optical activity may be observed is that the plane of polarization of plane-polarized monochromatic light is rotated on passing through a solution containing one or the other—or an excess of one or the other—of two enantiomorphic molecules.

To appreciate more fully this phenomenon and some others closely related to it, the nature of plane-polarized light must be considered in more detail. When observed along the direction of propagation, a beam of plane-polarized light appears to have its electric vector, which oscillates as a sine wave with the frequency of the light, confined to one plane. There is also an oscillating magnetic vector confined to a perpendicular plane, but we shall not be specifically interested in this.

It is useful to think of a beam of plane-polarized light as the resultant of two coterminous beams of right- and left-circularly polarized light that have equal amplitudes and are in phase. A circularly polarized beam is one in which the electric vector rotates uniformly about the direction of propagation by 2π during each cycle. Figure 17-6 shows how two such beams, circularly

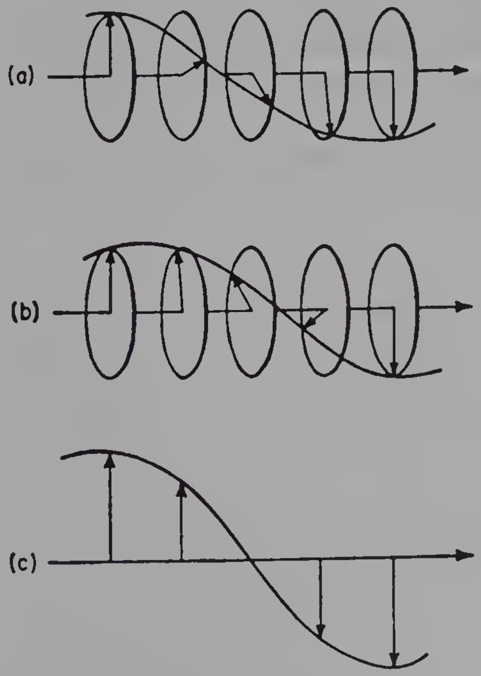

FIG. 17-6. (a) Right-circularly polarized light. (b) Left-circularly polarized light. (c) The plane-polarized resultant of (a) and (b). Horizontal arrow gives direction of propagation, and arrows perpendicular to this direction denote the instantaneous spatial direction of the electric vector. (Reproduced by permission from S. F. Mason, *Chem. Brit.* **1965,** 245.)

polarized in opposite senses, give a plane-polarized resultant. The most important property of the two circularly polarized components to be noted here is that they are enantiomorphous to each other, that is, one is the nonsuperposable mirror image of the other.

Now, just as there are molecules AB consisting of two separately dissymmetric halves, say A(+),A(−), and B(+),B(−), which are different substances [e.g., the diastereoisomers A(+)B(+) and A(−)B(+)] having numerically different physical properties, so the physical interactions of the two circularly polarized beams with a given enantiomorph of a dissymmetric molecule will be quantitatively different. The two important differences are (1) the refractive indices for left- and right-circularly polarized light n_l and n_r, respectively, will be different, and (2) the molar absorbances ϵ_l and ϵ_r, will be different.

If only the refractive index difference existed, the rotation of the plane of polarization would be explained as shown in Fig. 17-7, since the retarding of one circularly polarized component relative to the other can be seen to have this net effect.

Actually, the simultaneous existence of a difference between ϵ_l and ϵ_r means that the rotated "plane" is no longer strictly a plane. This can be seen in Fig. 17-8; since one rotating electric vector is not exactly equal in length to the other after the two components have traversed the optically active medium, their resultant describes an ellipse, whose principal axis defines the "plane" of the rotated beam and whose minor axis is equal to the absolute difference $|\epsilon_l - \epsilon_r|$. This difference is usually very small, so that it is a very good approximation to speak of rotating "the plane"; however, it can be measured and constitutes the *circular dichroism.* It is most important that both the optical rotation and the circular dichroism are dependent on wavelength, especially in the region of an electronic absorption band of the atom or ion lying at the "center of dissymmetry." Moreover, at a given wavelength

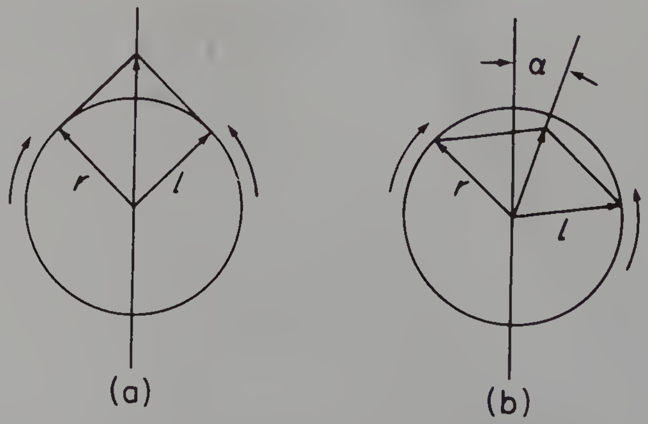

FIG. 17-7. (a) An instantaneous view along the direction of propagation of the two vectors **r** and **l** of the circularly polarized beams and their resultant, which lies in a vertical plane. (b) If $n_l > n_r$, the beam **l** is retarded relative to beam **r**, thus causing the plane of the resultant to be tilted by the angle α.

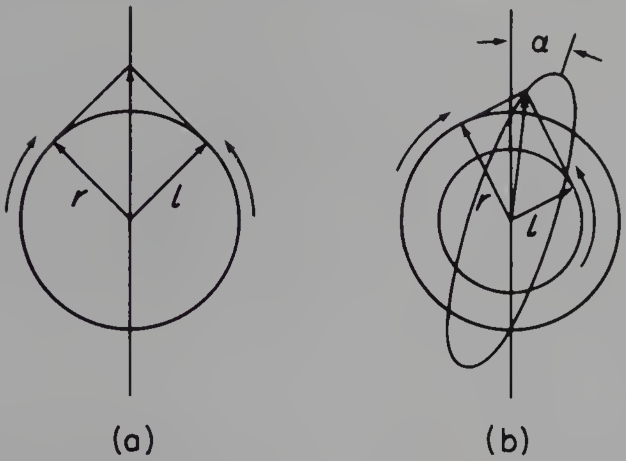

FIG. 17-8. (a) Same as Fig. 17-7(a) and (b). If $n_l > n_r$, and also $\epsilon_l > \epsilon_r$, the vectors **r** and **l** will be affected qualitatively as shown, and they will then give rise to a resultant that traces out the indicated ellipse. To make the diagram clear, the quantity $\epsilon_l - \epsilon_r$ is vastly exaggerated compared to real cases.

the values of $n_l - n_r$ and $\epsilon_l - \epsilon_r$ for one enantiomorph are equal and opposite to those for the other enantiomorph. The variations of $n_l - n_r$ and $\epsilon_l - \epsilon_r$ with wavelength for a pair of enantiomorphs in the region of an absorption band with a maximum at λ_0 are illustrated schematically in Fig. 17-9. The variation of the angle of rotation with wavelength is called *optical rotatory dispersion* (ORD). This, together with the circular dichroism (CD) and the attendant introduction of ellipticity into the rotated beam, are, all together, called the *Cotton effect,* in honor of the French physicist Aimé Cotton, who made pioneering studies of the wavelength-dependent aspects of these phenomena in 1895.

Cotton effects are studied today by inorganic chemists for two principal purposes. First, they can be used in a fairly empirical way to correlate the configurations of related dissymmetric molecules, thus to follow the steric course of certain reactions. Second, both theoretical and experimental work is in progress to establish generally reliable criteria for determining spectroscopically the absolute configurations of molecules.

Before summarizing the results in each of these areas, we mention the types of optically active complex that have been most studied (Fig. 17-10).

The use of ORD and CD data in making empirical correlations of configurations is increasingly important. The basic idea is simply that similar electronic transitions in similar molecules should have the same signs for CD and ORD effects when the molecules have the same absolute chirality. The chief uncertainty in the conclusions arises from failure to satisfy adequately the criteria of "similarity" in the nature of the electronic transitions and in the structures of the molecules themselves. As an illustration, we use a case where the required similarities are obviously present. Figure 17-11 shows the CD curves for (+) $[\mathrm{Co\ en_3}]^{3+}$ and (+)$[\mathrm{Co}(l\text{-pn})_3]^{3+}$, where the (+) signs indicate that these are the enantiomers having positive values of $[\alpha]$ at the sodium D

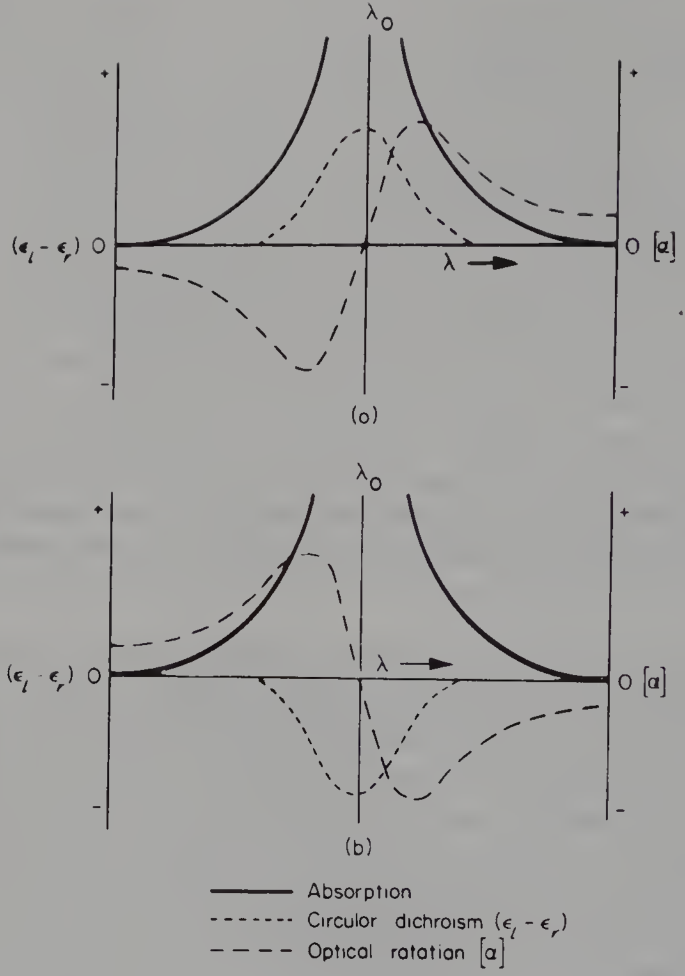

FIG. 17-9. The Cotton effect, as manifested in circular dichroism $\epsilon_l - \epsilon_r$ and optical rotatory dispersion $[\alpha]$, as would be given by a dissymmetric compound with an absorption band centered at λ_0, on the assumption that there are no other absorption bands close by. (a) A positive Cotton effect. (b) A negative Cotton effect.

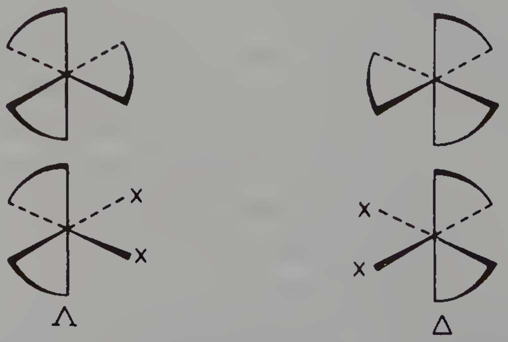

FIG. 17-10. The principal types of optically active chelate molecule and the IUPAC nomenclature. (IUPAC Bulletin No. 33, 1968, p. 68.)

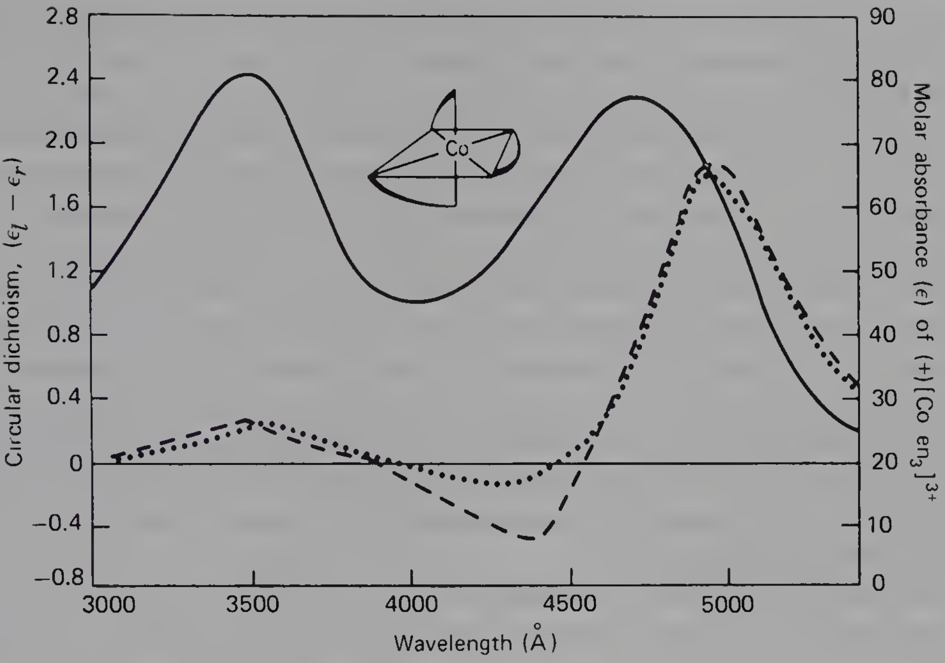

FIG. 17-11. (a) The visible absorption spectrum of (+) [Co en$_3$]$^{3+}$ (solid curve). (b) The circular dichroism of (+)[Co en$_3$)]$^{3+}$ (dotted curve). (c) The circular dichroism of (+)[Co(l-pn)$_3$]$^{3+}$ (dashed curve). The absorption spectrum of (+)[Co(l-pn)$_3$]$^{3+}$ is almost identical with that of (+)[Co en$_3$]$^{3+}$. The small sketch shows the absolute configuration Λ of (+)[Co en$_3$]$^{3+}$ as determined by anomalous scattering of X rays.

line. Clearly these two complex ions must have the same absolute configuration. That of the (+) [Co en$_3$]$^{3+}$ ion has been determined by means of anomalous X-ray scattering as Λ.

It must not be thought that the identical rotational directions at the sodium D line (or at any other single wavelength) could itself have been taken as a criterion of identical absolute configuration. Such relationships fail so frequently as to make the "criterion" useless: for example, (+)[Coen$_2$(NH$_3$)Cl]$^{2+}$ and (−)[Co en$_2$(NCS)Cl]$^{+}$ have the same configuration.

When the ligands themselves have electronic transitions in the uv region that persist in perturbed but identifiable form in the complexes, there is a reliable method of assigning absolute configurations directly from observed ORD or, better, CD data without employing any reference compound of known configuration. This is possible because when two or three such ligands are in close proximity in the complex, their individual electric dipole transition moments can couple to produce exciton splittings. Detailed analysis shows that each component of the split band will have a different sign for its circular dichroism and that this sign may be predicted from the absolute configuration by an argument not dependent on numerical accuracy.

The types of ligand that lend themselves to this treatment are bipyridine and phenanthroline, which have strong near-uv transitions. In the case of

$[Fe(phen)_3]^{2+}$ the correctness of the method has been confirmed by an X-ray crystallographic determination of absolute configuration.

Magnetic Circular Dichroism (MCD). All substances, whether chiral or not, rotate the plane of polarization of light and exhibit ORD and CD effects when placed in a magnetic field that has a component in the direction of propagation of the polarized radiation. Phenomenologically these effects, collectively called the *Faraday effect,* are analogous to ordinary optical activity and the *Cotton effect,* but their interpretation and application to chemical problems are more complicated and have only rather recently received detailed study. Because all substances (including solvents, cell windows, etc.) exhibit the Faraday effect, it is, in general, possible to get interpretable results only by measuring MCD through the electronic absorption bands of the complex of interest. This can be done with apparatus normally used for conventional CD measurements by surrounding the sample cell with a small superconducting solenoid.

The principles of MCD pertinent to metal complexes may be illustrated by considering electronic transitions in an atom. Any orbitally degenerate state (e.g., a *P*, *D*, or *F* state) of an atom consists of components having

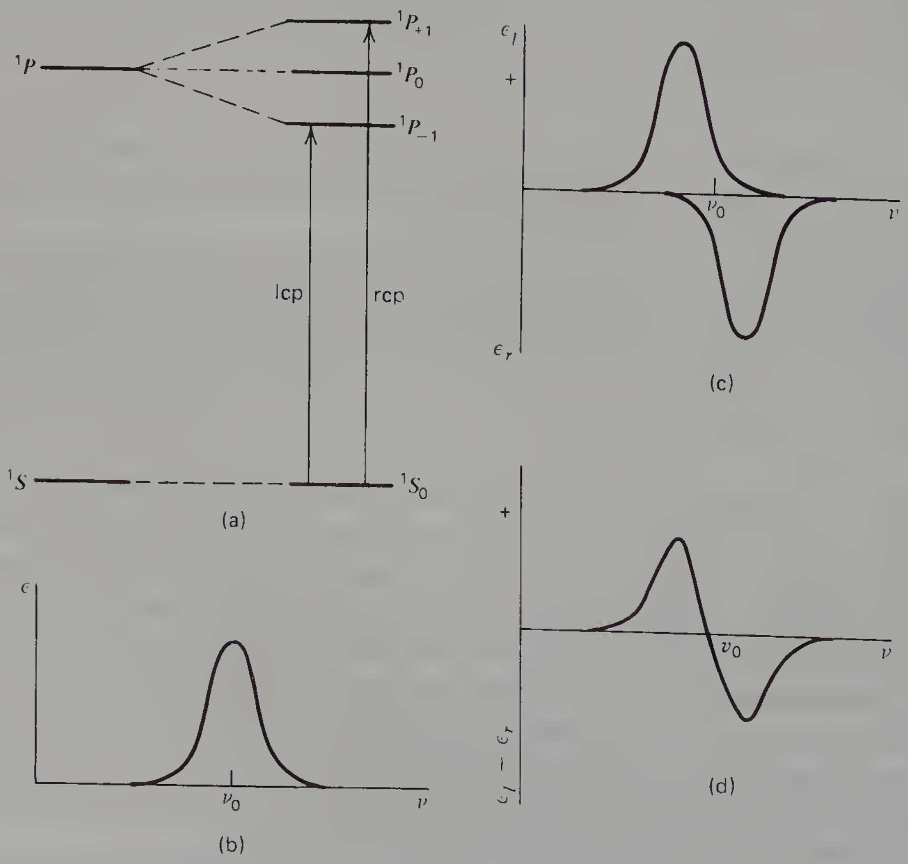

FIG. 17-12. The Faraday effect for an atomic $^1S \rightarrow {}^1P$ transition, showing the origin of a positive Faraday *A* term in the MCD spectrum.

different angular momenta. The energies of these components differ little if at all in the absence of a magnetic field, but when a magnetic field is applied, they diverge in energy (Zeeman splitting) as shown in Fig. 17-12 for a ^1P state. If this ^1P state is an excited state of a system with a ^1S ground state, the transition is split into $^1S \rightarrow {}^1P_{+1}$ and $^1S \rightarrow {}^1P_{-1}$ components; the $^1S \rightarrow {}^1P_0$ component is forbidden. The crucial point is that the two allowed components are sensitive to the polarization of the light, with the former allowed for right-circularly polarized (rcp) light and the latter for left-circularly polarized (lcp) light. This means that for the $^1S \rightarrow {}^1P$ transition in a magnetic field, if we were to measure the absorptions of rcp and lcp light, we would see one absorption for each component, separated by the Zeeman splitting as shown in Fig. 17-12(c). A measurement of the CD spectrum ($\epsilon_l - \epsilon_d$ versus frequency) would then give a curve of the form shown in Fig. 17-12(d). This type of curve is known as a Faraday *A* term and its appearance constitutes proof that the transition has a degenerate upper state. Note that if the nature of the degenerate state is such as to give a Zeeman splitting pattern opposite to that

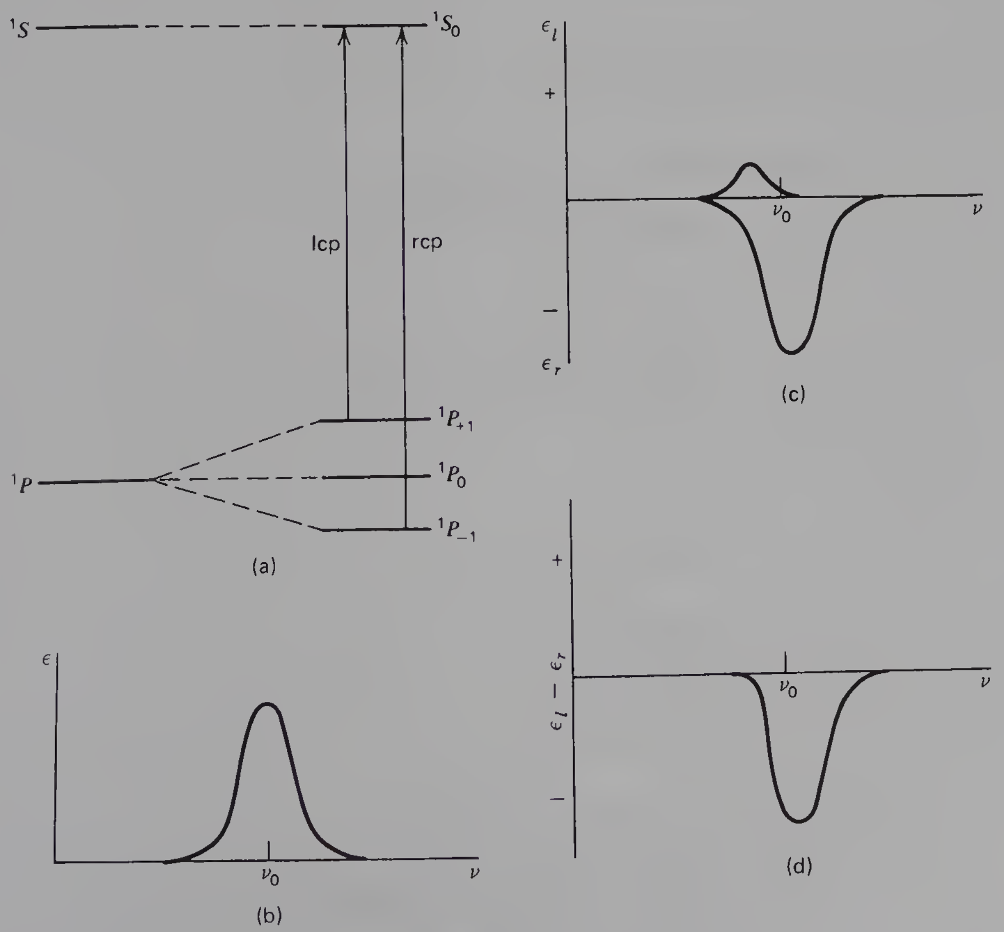

FIG. 17-13. The Faraday effect for atomic $^1P \rightarrow {}^1S$ transition, showing the origin of a Faraday *C* term in the MCD spectrum.

shown, the shape of the CD curve will be reversed; such negative *A* terms have been observed, and the positive or negative character of an *A* term provides further information on the assignment of the band.

In the event that the ground state itself is degenerate, hence undergoes Zeeman splitting, we get the results sketched in Fig. 17-13. The resultant CD spectrum, called a Faraday *C* term, is again a powerful form of evidence in making assignments in appropriate cases. The following example provides an illustration.

For the $Fe(CN)_6^{3-}$ ion there are three charge-transfer bands in the visible and near-uv spectrum as shown in Fig. 17-14. Theory suggested that all must involve transitions from orbitals of t_{1u} and t_{2u} symmetry on the ligands to the vacancy in the metal *d* orbitals of t_{2g} symmetry but could not directly show which transition was which. However, it was possible to show theoretically that a $t_{1u} \rightarrow t_{2g}$ transition should have a positive MCD effect and a $t_{2u} \rightarrow t_{2g}$ transition should have a negative one. From the observed MCD spectrum (Fig. 17-14), it is then clear that the $t_{2u} \rightarrow t_{2g}$ transition lies between the two

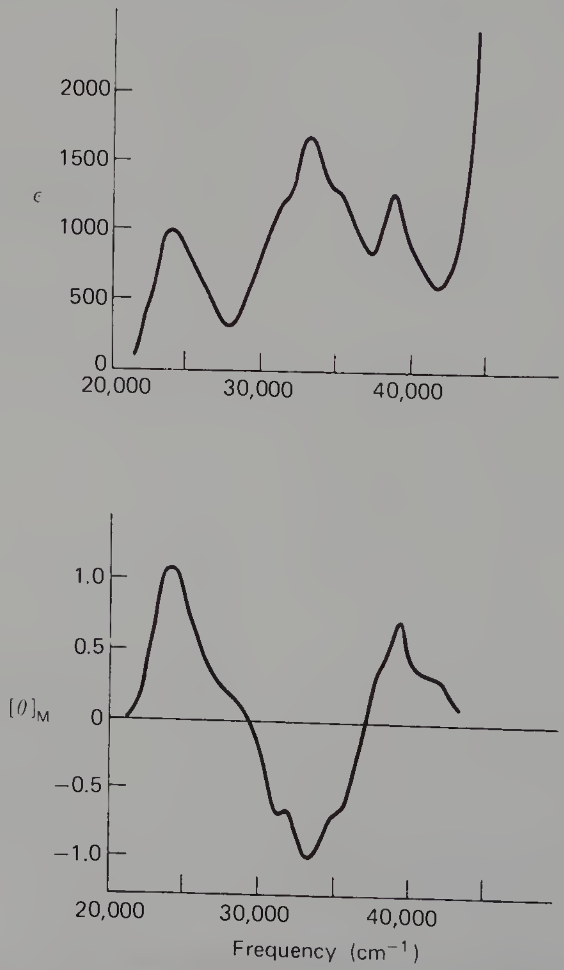

FIG. 17-14. The absorption spectrum (upper) and MCD spectrum (lower) of the $[Fe(CN)_6]^{3-}$ ion showing the three charge-transfer transitions and the signs of their Faraday *C* terms.

$t_{1u} \rightarrow t_{2g}$ transitions. In favorable circumstances the shape and/or magnitude of the MCD effect can show that a transition involves an excited state that is degenerate.

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Chapter Eighteen

The Elements of the First Transition Series

GENERAL REMARKS

We discuss in this chapter the elements of the first transition series, titanium through copper. There are two main reasons for considering these elements apart from their heavier congeners of the second and third transition series: (1) in each group (e.g., V, Nb, and Ta) the first-series element always differs appreciably from the heavier elements, and comparisons are of limited use; and (2) the aqueous chemistry of the first-series elements is much simpler, and the use of ligand field theory in explaining both the spectra and magnetic properties of compounds has been far more extensive.

The separate Sections 18-A through 18-H summarize the oxidation states and stereochemistries for each element. Except in cases of special interest, distortions from perfect geometries that can be expected in octahedral d^1 and d^2 (slight), high-spin octahedral d^4 (two long coaxial bonds), low-spin octahedral d^4 (slight), high-spin octahedral d^6, d^7 (slight), or low-spin octahedral d^7, d^8 molecules (two long coaxial bonds) will not be specified.

The energies of the $3d$ and $4s$ orbitals in the neutral atoms are quite similar so that while most configurations are of the $3d^n4s^2$ type, the exchange-energy stabilization of filled and half-filled shells gives $3d^54s^1$ for Cr and $3d^{10}4s^1$ for Cu. When the atoms are ionized, the $3d$ orbitals become appreciably more stable than the $4s$ orbitals and the ions all have $3d^n$ configurations. The high values of third ionization enthalpies (see Appendix 2) account for the difficulty in obtaining $\mathrm{Ni^{III}}$ and $\mathrm{Cu^{III}}$ compounds, although a few do occur. Copper is the only element in the series to have a $\mathrm{M^I}$ state that exists regularly in the absence of π-acceptor ligands.

It should be recognized that while ionization enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is a very complex one and not amenable to ready generalization. Indeed it is often futile to discuss relative stabilities of oxidation states because some oxidation states may be perfectly stable under certain conditions (e.g., in solid compounds, in fused melts, in the vapor at high temperatures, in absence of air) but nonexistent in aqueous solutions or in air. Thus there is no aqueous chemistry of Ti^{2+}, yet crystalline $TiCl_2$ is stable up to ~400°C in the absence of air; also, in fused potassium chloride, titanium and titanium trichloride give Ti^{II} as the main species and Ti^{IV} is in vanishingly small concentrations; on the other hand, in aqueous solutions in air only Ti^{IV} species are stable.

However, it is sometimes profitable to compare the relative stabilities of ions differing by unit charge when surrounded by similar ligands with similar stereochemistry, as in the case of the Fe^{3+}–Fe^{2+} potentials (Table 18-1), or with different anions. In these cases, as elsewhere, many factors are usually involved; some of these have already been discussed, but they include (*a*) ionization enthalpies of the metal atoms, (*b*) ionic radii of the metal ions, (*c*) electronic structure of the metal ions, (*d*) the nature of the anions or ligands involved with respect to their polarizability, donor $p\pi$- or acceptor $d\pi$-bonding capacities, (*e*) the stereochemistry either in a complex ion or a crystalline lattice, and (*f*) nature of solvents or other media. In spite of the complexities there are a few trends to be found, namely:

1. From Ti to Mn the highest valence, which is usually found only in oxo compounds or fluorides or chlorides, corresponds to the total number of *d* and *s* electrons in the atom. The stability of the highest state decreases from Ti^{IV} to Mn^{VII}. After Mn (i.e., for Fe, Co, and Ni) the higher oxidation states are difficult to obtain.
2. In the characteristic oxo anions of the valence states IV to VII, the metal atom is tetrahedrally surrounded by oxygen atoms, whereas in the oxides of valences up to IV the atoms are usually octahedrally coordinated.
3. The oxides of a given element become more acidic with increasing oxidation state and the halides more covalent and susceptible to hydrolysis by water.
4. In the II and III states, complexes in aqueous solution or in crystals are usually either in four- or six-coordination and, across the first series, generally similar in respect to stoichiometry and chemical properties.
5. The oxidation states <II, except for Cu^{I}, are found only with π-acid-type ligands or in organometallic compounds.

Finally, we reemphasize that the occurrence of a given oxidation state as well as its stereochemistry depend very much on the experimental conditions and that species that cannot have independent existence under ordinary conditions of temperature and pressure in air may be the dominant species under others. In this connection we may note that transition metal ions may be obtained in a particular configuration difficult to produce by other means through incorporation by isomorphous substitution in a crystalline host lattice, for example, tetrahedral Co^{3+} in other oxides, tetrahedral V^{3+} in the $NaAlCl_4$ lattice, as well as by using rigid ligands such as phthalocyanins.

Although some discussion of the relationships between the first, second, and third transition series is useful, we defer this until the next chapter.

In the discussion of individual elements we have kept to the traditional order; that is, elemental chemistries are considered separately, with reference to their oxidation state. However, it is possible to organize the subject matter from the standpoint of the d^n electronic configuration of the metal. This can bring out useful similarities in spectra and magnetic properties in certain cases and has a basis in theory; nevertheless the differences in chemical properties of d^n species due to differences in the nature of the metal, its energy levels, and especially the charge on the ion, often exceed the similarities. Nonetheless, such cross considerations (e.g., in the d^6 series V^{-1}, Cr^0, Mn^I, Fe^{II}, Co^{III}, and Ni^{IV}) can provide a useful exercise for students.

Before we consider the chemistries, a few general remarks on the various oxidation states of the first-row elements are pertinent.

The Lower Oxidation States I, 0, −I. All the elements form some compounds, at least, in these states but only with ligands of the π-acid type. There are few such compounds for Ti, and they are confined to π-acid or π-complexing ligands. An exception, of course, is the Cu^I state for copper, where some insoluble binary Cu^I compounds such as CuCl are known, as well as complex compounds. In the absence of complexing ligands the Cu^+ ion has only a transitory existence in water, although it is quite stable in acetonitrile as $[Cu(MeCN)_4]^+$.

The II State. All the elements Ti to Cu inclusive form well-defined binary compounds in the divalent state, such as oxides and halides, which are essentially ionic. Except for Ti, they form well-defined aqua ions $[M(H_2O)_6]^{2+}$; the potentials are summarized in Table 18-1.

In addition, all the elements form a wide range of complex compounds, which may be cationic, neutral, or anionic depending on the nature of the ligands.

The III State. All the elements form at least some compounds in this state, which is the highest known for copper, and then only in certain complex compounds. The fluorides and oxides are again generally ionic, although the chlorides may have considerable covalent character, as in $FeCl_3$.

The elements Ti to Co form aqua ions, although the Co^{III} and Mn^{III} ones are readily reduced. In aqueous solution certain anions readily form complex species and for Fe^{3+}, for example, one can be sure of obtaining the $Fe(H_2O)_6^{3+}$ ion only at high acidity (to prevent hydrolysis) and when non-

TABLE 18-1

Standard Potentials (strongly acid solution) for the +1, +2, and +3 Oxidation States (V)[a]

Couple	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$M^+ + e = M$								+0.520
$M^{2+} + 2e = M$	[b]	−1.13	−0.90	−1.18	−0.44	−0.277	−0.257	+0.340
$M^{3+} + 3e = M$	−1.21		−0.74		−0.04			
$M^{3+} + e = M^{2+}$	[b]	−0.255	−0.424	+1.54	+0.771	+1.92		

[a] For a general discussion and references see A. J. Bard, R. Parsons, and J. Jordan, *Standard Potentials in Aqueous Solution,* Dekker, New York, 1985.

[b] Values have been reported for these but are dubious because $Ti^{2+}(aq)$ has little (if any) stability.

complexing anions such as ClO_4^- or $CF_3SO_3^-$ are present. There is an especially extensive aqueous complex chemistry of the substitution-inert octahedral complexes of Cr^{III} and Co^{III}.

The trivalent halides, and indeed also the halides of other oxidation states, generally act readily as Lewis acids and form neutral compounds with donor ligands [e.g., $TiCl_3(NMe_3)_2$] and anionic species with corresponding halide ions (e.g., VCl_4^- and FeF_6^{3-}).

The IV State. This is the most important oxidation state of Ti, and the main chemistry is that of TiO_2 and $TiCl_4$ and its derivatives. This is also an important state for vanadium, which forms the vanadyl ion VO^{2+} and many derivatives, cationic, anionic, and neutral, containing the VO group. For the remaining elements Cr to Ni, the IV state is found mainly in fluorides, fluoro complex anions, and cation complexes; however, an important class of compounds are the salts of the oxo ions and other oxo species.

The V, VI, and VII States. These occur only as $Cr^{V,VI}$, $Mn^{V,VI,VII}$, and $Fe^{V,VI}$, and apart from the fluorides CrF_5, CrF_6, and oxofluorides, MnO_3F, the main chemistry is that of the oxo anions $M^nO_4^{(8-n)-}$. All the compounds in these oxidation states are powerful oxidizing agents.

18-A. TITANIUM: GROUP IVB(4)

Titanium has four valence electrons $3d^24s^2$. The most stable and common oxidation state is Ti^{IV}; compounds in lower oxidation states, −I, 0, II, and III, are quite readily oxidized to Ti^{IV} by air, water, or other reagents. The energy for removal of four electrons is high, so that the Ti^{4+} ion may not exist and Ti^{IV} compounds are generally covalent. In this IV state there are some resemblances to the elements Si, Ge, Sn, and Pb, especially Sn. The estimated ionic radii ($Sn^{4+} = 0.71$, $Ti^{4+} = 0.68$ Å) and the octahedral covalent radii ($Sn^{IV} = 1.45$, $Ti^{IV} = 1.36$ Å) are similar; thus TiO_2 (rutile) is isomorphous with SnO_2 (cassiterite) and is similarly yellow when hot. Titanium tetrachloride, like $SnCl_4$, is a distillable liquid readily hydrolyzed by water, behaving as a Lewis acid, and giving adducts with donor molecules; $SiCl_4$ and $GeCl_4$ do not give stable, solid, molecular addition compounds with ethers, although $TiCl_4$ and $SnCl_4$ do so—a difference that may be attributed to the ability of the halogen atoms to fill the coordination sphere of the smaller Si and Ge atoms. There are also similar halogeno anions such as TiF_6^{2-}, GeF_6^{2-}, $TiCl_6^{2-}$, $SnCl_6^{2-}$, and $PbCl_6^{2-}$, some of whose salts are isomorphous; the Sn and Ti nitrates, $M(NO_3)_4$, are also isomorphous. There are other similarities such as the behavior of the tetrachlorides on ammonolysis to give amido species. It is a characteristic of Ti^{IV} compounds that they undergo hydrolysis to species with Ti—O bonds, in many of which there is octahedral coordination by oxygen; compounds with Ti—O—Ti, Ti—O—C, Ti—O—Si, and Ti—O—Sn bonds are known.

The stereochemistry of Ti compounds is summarized in Table 18-A-1.

TABLE 18-A-1
Oxidation States and Stereochemistry of Titanium

Oxidation state	Coordination number	Geometry	Examples
Ti^0, d^4		π-complex	$CpTi(CO)_4^-$
	7		$Ti(CO)_2(PF_3)(dmpe)_2$
Ti^{II}, d^2		π-complex	$Cp_2Ti(CO)_2$, $Ti(\eta^6\text{-}2,6\text{-}Me_2C_5H_3N)_2$[b]
	6	Octahedral	$TiCl_2$
Ti^{III}, d^1	3	Planar	$Ti[N(SiMe_3)_2]_3$
	5	*tbp*	$TiBr_3(NMe_3)_2$
	6[a]	Octahedral	TiF_6^{3-}, $Ti(H_2O)_6^{3+}$, $TiCl_3(THF)_3$
	9	Distorted	$Ti(BH_4)_3$
Ti^{IV}, d^0	4[a]	Tetrahedral	$TiCl_4$
		Distorted tetrahedral	Cp_2TiCl_2
	5	*tbp*	$TiCl_5^-$
		sp	TiO(porphyrin)
	6[a]	Octahedral	TiF_6^{2-}, $Ti(acac)_2Cl_2$
			TiO_2, $[Cl_3POTiCl_4]_2$
	7	ZrF_7^{3-} type	$[Ti(O_2)F_5]^{3-}$
	8	Distorted dodecahedral	$TiCl_4(diars)_2$
		Dodecahedral	$Ti(ClO_4)_4$

[a] Most common state.

[b] E. J. Wucherer and E. L. Muetterties, *Organometallics*, 1987, **6**, 1696.

18-A-1. The Element

Titanium is relatively abundant in the earth's crust (0.6%). The main ores are *ilmenite* ($FeTiO_3$) and *rutile,* one of the several crystalline varieties of TiO_2. It is not possible to obtain the metal by the common method of reduction with carbon because a very stable carbide is produced; moreover, the metal is rather reactive toward oxygen and nitrogen at elevated temperatures. Because the metal has uniquely useful properties, however, expensive methods for its purification are justified. In addition to a proprietary electrolytic method, there is the older Kroll process in which ilmenite or rutile is treated at red heat with carbon and chlorine to give $TiCl_4$, which is fractionated to free it from impurities such as $FeCl_3$. The $TiCl_4$ is then reduced with molten Mg at ~800°C in an atmosphere of argon. This gives Ti metal as a spongy mass from which the excess of Mg and $MgCl_2$ is removed by volatilization at ~1000°C. The sponge may then be fused in an atmosphere of Ar in an electric arc and cast into ingots.

Extremely pure Ti can be made on the laboratory scale by the van Arkel–de Boer method (also used for other metals) in which pure TiI_4 vapor is decomposed on a hot wire at low pressure.

The metal has a hexagonal close-packed lattice and resembles other transition metals such as Fe and Ni in being hard, refractory (mp. 1680 ± 10°C, bp 3260°C), and a good conductor of heat and electricity. It is, however, quite light in comparison to other metals of similar mechanical and thermal properties and unusually resistant to certain kinds of corrosion; therefore, it has come into demand for special applications in turbine engines and industrial chemical, aircraft, and marine equipment.

Although rather unreactive at ordinary temperatures, Ti combines directly with most nonmetals, for example, H_2, the halogens, O_2, N_2, C, B, Si, and S, at elevated temperatures. The nitride (TiN), and borides (TiB and TiB_2) are interstitial compounds that are very stable, hard, and refractory. Thin films of TiC can be made by thermal decomposition of $Ti(CH_2CMe_3)_4$.[1a]

The metal is not attacked by mineral acids at room temperature or even by hot aqueous alkali. It dissolves in hot HCl, giving Ti^{III} species, whereas hot HNO_3 converts it into a hydrous oxide that is rather insoluble in acid or base. The best solvents are HF or acids to which fluoride ions have been added. Such media dissolve Ti and hold it in solution as fluoro complexes.

TITANIUM COMPOUNDS

18-A-2. The Chemistry of Titanium(IV), d^0

Binary Compounds

Halides. The tetrachloride ($TiCl_4$), the usual starting point for the preparation of most other Ti compounds, is a colorless liquid (mp −23°C, bp 136°C) with a pungent odor.

The Ti—Cl bond is short, 2.17 Å, possibly due to π donation $\mathrm{Ti}\overset{\leftarrow}{=}\ddot{\mathrm{C}}\mathrm{l}$.[1b]

Titanium tetrachloride fumes strongly in moist air and is vigorously, though not violently, hydrolyzed by water:

$$TiCl_4 + 2H_2O \longrightarrow TiO_2 + 4HCl$$

With some HCl present or a deficit of H_2O, partial hydrolysis occurs, giving oxo chlorides (see later).

Titanium tetrabromide and a metastable form of TiI_4 are crystalline at room temperature and are isomorphous with SiI_4, GeI_4, and SnI_4, having molecular lattices. The fluoride is obtained as a white powder by the action of F_2 on Ti at 200°C; it sublimes readily and is hygroscopic; its structure is not known. All the halides behave as Lewis acids; with neutral donors such as ethers they give adducts (see later).

Titanium Oxide; Complex Oxides; Sulfide. The naturally occurring dioxide TiO_2 has three crystal modifications, *rutile, anatase,* and *brookite.* In rutile, the commonest, the Ti is octahedral and this structure has been discussed in Section 1-2, since it is a common one for MX_2 compounds. In anatase and brookite there are very distorted octahedra of oxygen atoms about each

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[1a] G. S. Girolami *et al., J. Am. Chem. Soc.,* 1987, **109,** 1579.

[1b] K. G. Caulton *et al., J. Am. Chem. Soc.,* 1980, **102,** 3009.

titanium, two being relatively close. Although rutile has been assumed to be the most stable form because of its common occurrence, anatase is 8 to 12 kJ mol^{-1} more stable than rutile.

The dioxide is used as a white pigment. Naturally occurring forms are usually colored, sometimes even black, owing to the presence of impurities such as iron. Pigment-grade material is generally made by hydrolysis of titanium(IV) sulfate solution or vapor-phase oxidation of $TiCl_4$ with oxygen. The solubility of TiO_2 depends considerably on its chemical and thermal history. Strongly roasted specimens are chemically inert. The dioxide impregnated with platinum metal complexes has been much studied as a catalyst for photodecomposition of water.[2]

Hydrous titanium dioxide made by adding base to Ti^{IV} solutions and by action of acids on alkali titanates is of several types; one with a layer structure acting as an ion exchanger[3] has the composition $H_2Ti_4O_9 \cdot 1.2H_2O$. The hydrous material dissolves in bases and hydrous "titanates" may be obtained.

Many materials called "titanates" are known; nearly all have one of the three major mixed metal oxide structures (Section 1-2). Indeed the names of two of the structures are those of the Ti compounds that were the first found to possess them, namely, *ilmenite* ($FeTiO_3$) and *perovskite* ($CaTiO_3$). Other titanites with the ilmenite structure are $MgTiO_3$, $MnTiO_3$, $CoTiO_3$, and $NiTiO_3$, and others with the perovskite structure are $SrTiO_3$ and $BaTiO_3$. There are also titanates with the spinel structure such as Mg_2TiO_4, Zn_2TiO_4, and Co_2TiO_4.

Barium oxide and TiO_2 react to form an extensive series of phases from simple ones such as $BaTiO_3$ (commonly called barium titanate) and Ba_2TiO_4 to $Ba_4Ti_{13}O_{30}$ and $Ba_6Ti_{17}O_{40}$, the general formula being $Ba_xTi_yO_{x+2y}$. All are of technical interest because of their ferroelectric properties, which may be qualitatively understood as follows. The Ba^{2+} ion is so large relative to the small ion Ti^{4+} that the latter can literally "rattle around" in its octahedral hole. When an electric field is applied to a crystal of this material, it can be highly polarized because each of the Ti^{4+} ions is drawn over to one side of its octahedron thus causing an enormous electrical polarization of the crystal as a whole.

The compound Ba_2TiO_4 has discrete, somewhat distorted TiO_4 tetrahedra and the structure is related to that of β-K_2SO_4 or β-Ca_2SiO_4.

Titanium disulfide, like the disulfides of Zr, Hf, V, Nb, and Ta, has a layer structure; two adjacent close-packed layers of S atoms have Ti atoms in octahedral interstices. These "sandwiches" are then stacked so that there are adjacent layers of S atoms. Lewis bases such as aliphatic amines can be intercalated between these adjacent sulfur layers; similar intercalation compounds can be made with MS_2 and MSe_2 compounds for M = Ti, Zr, Hf, V, Nb, and Ta. Many of these have potentially useful electrical properties, in-

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[2] See, for example, M. Grätzel *et al., Helv. Chim. Acta,* 1984, **67,** 1012.

[3] T. Sasaki *et al., Inorg. Chem.,* 1985, **24,** 2265.

cluding superconductivity, and may be compared with the intercalation compounds of graphite (Section 8-2). There are also alkali metal intercalates M^IMY_2 (where M^I is any alkali metal, M = Ti, Zr, Hf, V, Nb, Ta and Y = S, Se, Te). The lithium intercalates can be made very smoothly by treating MY_2 with butyllithium.

Titanium(IV) Complexes[4]

Aqueous Chemistry: Oxo Salts. No aquated Ti^{4+} salts can be isolated, but Ti^{4+} possibly exists in solution though the main species are hydrolyzed. Many studies in different media show that species such as $Ti(OH)_2^{2+}$, $Ti(OH)Cl^{2+}$, or possibly $Ti_2(OH)_6^{2+}$ may be present.[5] There has been considerable discussion as to whether the ion $Ti{=}O^{2+}$ exists in solutions; as noted later compounds with Ti=O bonds are quite rare. However, Raman and ^{17}O nmr spectra confirm that in strong acid the TiO^{2+} ion is in equilibrium with $Ti(OH)_2$ and $Ti^{4+}_{(aq)}$. At higher pH there are species such as $Ti_3O_4^{4+}$, leading eventually to colloidal or precipitated $TiO_2{\cdot}nH_2O$.[6]

There are a number of basic salts that would appear to have the Ti=O group, for example, $TiOSO_4{\cdot}H_2O$. However, the latter has infinite zigzag Ti—O—Ti—O chains with the octahedral coordination about Ti completed by H_2O and SO_4^{2-}. Similarly $TiO(acac)_2$ is a dimer with a $Ti(\mu\text{-}O)_2Ti$ ring, while $(NH_4)_2TiO(C_2O_4)_2H_2O$ contains cyclic tetrameric anions with a central eight-membered $(\text{—Ti—O—})_4$ ring; the bridging O atoms occupy two cis positions of an octahedron about Ti with the oxalate ions at the other four. Other μ-O species are known, for example, $Ti_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2Cl_4(THF)_2$.[7]

However, there are some rare examples, mostly porphyrins and related complexes that do have Ti=O bonds.[8] The Ti=O bond appears to be short ~1.62 Å while ir bands are in the region 890 to 972 cm^{-1} (Raman, ν 975 in 2 *M* HCl) consistent with a Ti=O double bond.

Anionic Complexes. The solutions obtained by dissolving Ti, TiF_4, or hydrous oxides in aqueous HF contain various fluoro complex ions but predominantly the very stable TiF_6^{2-} ion, which can be isolated as crystalline salts, in which it is distorted octahedral. In moderately polar solvents (e.g., SO_2 and CH_3CN) a variety of mono- and polynuclear fluoro complexes, such as $[TiF_5(solv)]^-$ and $Ti_2F_9^-$ are formed. Various chloro and bromo anions[9a] can be obtained by interaction of TiX_4 with R_4N^+ or other cations in CH_2Cl_2, $SOCl_2$, and so on. Large cations give $[TiX_5]^-$ salts while smaller cations may

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[4] R. C. Fay, *Coord. Chem. Rev.*, 1981, **27**, 9; C. A. McAuliffe, *Comprehensive Coordination Chemistry*, Vol. 3, Chapter 31, Pergamon Press, Oxford, 1987.

[5] L. Ciavatta *et al.*, *Polyhedron*, 1985, **4**, 15.

[6] P. Comba and A. Merbach, *Inorg. Chem.*, 1987, **26**, 1315.

[7] M. G. H. Walbridge *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 614; J. L. Atwood *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 610.

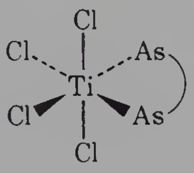
[8] V. L. Goedken *et al.*, *Inorg. Chem.*, 1985, **24**, 99; *Inorg. Chem. Acta*, 1986, **117**, L19; R. Guilard and C. Le Compte, *Coord. Chem. Rev.*, 1985, **65**, 87.

[9a] I. Rytter and S. Kvisle, *Inorg. Chem.*, 1985, **24**, 639; P. Sobota *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 2077.

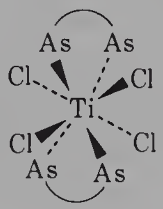
give $[Ti_2Cl_{10}]^{2-}$, $[Ti_2Cl_9]^-$, and $[TiCl_6]^{2-}$. The latter ion is formed[5] in $>12\ M$ HCl solutions probably together with *trans*-$[Ti(OH)_2Cl_4]^{2-}$ and $[Ti(OH)(H_2O)Cl_4]^-$.

Cationic Species. These are rare but an example[9b] is $[TiCl_3(MeCN)_3]SbCl_6$.

Adducts of TiX_4. The halides readily give adducts TiX_4L and TiX_4L_2 with donor molecules; many are crystalline solids soluble in organic solvents. A representative example is $TiCl_4(OMe_2)_2$.[10] Most adducts contain octahedrally coordinated Ti, the monoadducts being dimerized through halogen bridges, for example, $[TiCl_4(OPCl_3)]_2$ and $[TiCl_4(MeCO_2Et)]_2$, whereas the diadducts such as $TiCl_4(OPCl_3)_2$ have cis configurations. With certain chelating ligands such as diars both six-coordinate 18-A-I and eight-coordinate 18-A-II complexes are obtained.



(18-A-I)



(18-A-II)

β-*Diketonate and Other Chelate Complexes.* Titanium tetrachloride reacts with many compounds containing active hydrogen atoms such as those of OH groups, undergoing solvolysis with loss of HCl, but reactions with sodium salts are commonly used. Examples are

$$TiCl_4 + (sal_2en)H_2 \longrightarrow (sal_2en)TiCl_2 + 2HCl$$

$$TiCl_4 + 2Na(acac) \longrightarrow cis\text{-}TiCl_2(acac)_2 + 2NaCl$$

$$TiCl_4 + K[HB(pz)_3] \longrightarrow [HB(pz)_3]TiCl_3 + KCl$$

$$TiCl_4 + nNaS_2CNR_2 \longrightarrow TiCl_{4-n}(S_2CNR_2)_n + nNaCl$$

Hydrous TiO_2 will also dissolve in catechol to give $[Ti(cat)_3]^{2-}$.[11] The β-diketonates may also be of the type $Ti(\beta\text{-dik})X_3$ that are usually halogen-bridged dimers.

The six, seven and eight-coordinate complexes are almost invariably octahedral, pentagonal bipyramidal, and dodecahedral, respectively. Typical examples are $Ti(edta)\cdot H_2O$[12] and $Ti(S_2CNR_2)_4$.

The toluene-3,4-dithiolate complex $[Ti(S_2C_6H_3CH_3)_3]^{2-}$ is octahedral, although many similar dithiolene complexes are trigonal prismatic, which is

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[9b] P. P. Claire *et al., J. Chem. Soc. Chem. Commun.,* **1987,** 1110.

[10] L. K. Tan and S. Brownstein, *Inorg. Chem.,* 1984, **23,** 1353.

[11] K. N. Raymond *et al., Inorg. Chem.,* 1984, **23,** 1009.

[12] J. P. Fackler *et al., Inorg. Chem.,* 1985, **24,** 1857.

consistent with the view that the higher-lying *d* orbitals of Ti do not interact effectively with the lone pairs on the sulfur atoms.

A curiosity is the volatile dodecahedral $Ti(NO_3)_4$, which resembles other anhydrous nitrates of Sn^{IV}, Co^{III}, and Cu^{II}.

The perchlorate, $Ti(ClO_4)_4$, which has η^2-ClO_4 groups is made by interaction of $TiCl_4$ with Cl_2O_6.[13a] A sulfate is made by the reaction

$$TiCl_4 + 6SO_3 \longrightarrow Ti(SO_4)_2 + 2S_2O_5Cl_2$$

while the phosphate[13b] acts as an ion-exchange material.

Alkoxides. These are among the most useful complexes and are made by reactions such as

$$TiCl_4 + 4ROH + 4NH_3 \longrightarrow Ti(OR)_4 + 4NH_4Cl$$

$$TiCl_4 + 3EtOH \longrightarrow 2HCl + TiCl_2(OEt)_2{\cdot}EtOH$$

They are liquids or solids that can be distilled or sublimed and are soluble in organic solvents such as benzene. They are exceedingly readily hydrolyzed by even traces of water, the ease decreasing with increasing chain length of the alkyl group; such reactions give polymeric species with OH or oxygen bridges.

It is characteristic of alkoxides that unless the OR groups are extremely bulky or the compounds are in extremely dilute solutions, they exist as polymers with bridging OR groups and the structure of $[Ti(OEt)_4]_4$ shown in Fig. 12-3, Section 12-11, is representative. In solutions, there may be various degrees and types of polymerization depending on solvent and OR group. In benzene, primary OR groups give trimers, whereas secondary and tertiary OR give only monomers.

Partially substituted compounds like $[TiCl_2(OPh)_2]_2$ have bridging phenoxide groups but with bulky aryloxides a variety of different types may be formed.[14]

Nitrogen Compounds. Titanium tetrachloride interacts with ammonia giving species with $TiNH_2$ bonds and eventually titanium nitride.[15]

Primary and secondary amines react in a similar way to give orange or red solids such as $TiCl_2(NHR)_2$ and $TiCl_3NR_2$, which can be further solvated by the amine.

Dialkylamides. The action of $LiNR_2$ on $TiCl_4$ leads to liquid or solid compounds of the type $Ti(NEt_2)_4$, which, like the alkoxides, are readily hydrolyzed by water with liberation of amine. Similar dialkylamides are also known for both Ti^{III} and Ti^{II}. The compounds, $Ti(NR_2)_4$, undergo insertion reactions; with CS_2, for example, the dithiocarbamates $Ti(S_2CNR_2)_4$ are formed.

In some cases NR_2 groups function as bridges[16] in cyclic oligomers; thus

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[13a] J. Potier *et al.*, *Inorg. Chem.*, 1986, **25,** 1386.

[13b] J. Rodriquez *et al.*, *Inorg. Chem.*, 1987, **26,** 1045.

[14] M. F. Lappert *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986,** 489.

[15] Y. Sacki *et al.*, *Bull. Soc. Chem. Jpn.*, **1982,** 3193; L. Maya, *Inorg. Chem.*, 1986, **25,** 4213.

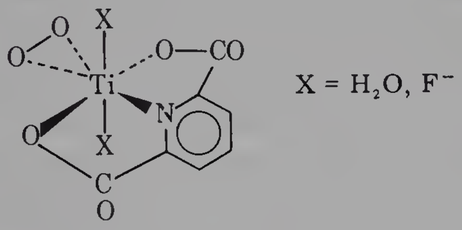
[16] See, for example, P. P. Power *et al.*, *J. Am. Chem. Soc.*, 1983, **105,** 2927.

TiF_4 reacts with $Ti(NMe_2)_4$ to give $[TiF_2(NMe_2)_2]_4$ in which distorted TiF_3N_3 octahedra are linked by μ-F and μ-NMe_2 groups.

Peroxo Complexes. It has long been known that aqueous solutions of Ti^{IV} and its complexes develop an intense orange color with H_2O_2, which can be used for analytical determinations. These colors are due to formation of stable peroxo complexes such as $[Ti(O_2)OH\ aq]^+$, $[Ti(O_2)\ edta]^{2-}$, and so on.[17a]

A number of crystalline salts have been isolated; for example, interaction of TiO_2, 40% HF and 30% H_2O_2 at pH 6 gives $M_3[Ti(O_2)F_5]$ and at pH 9, $M_2[Ti(O_2)_2F_2]$.[17b]

The structure of a typical complex with 2,6-pyridinedicarboxylate as ligand is (18-A-III) where the O—O distance, 1.46 Å, is that of a η^2-peroxo ligand (Section 12-10).



(18-A-III)

Although these peroxo species are not particularly good oxygen transfer agents, the titanium tartrate complexes[17c] of alkyl peroxides are involved in the Sharpless asymmetric epoxidation of allylic alcohols (Section 28-22).

18-A-3. The Chemistry of Titanium(III), d^1

There is an extensive chemistry of solid compounds and Ti^{III} species in solution.

Binary Compounds. The *chloride* $TiCl_3$, has several crystalline forms. It can be made by H_2 reduction of $TiCl_4$ vapor at 500 to 1200°C; this and other high-temperature methods give the violet α form. The reduction of $TiCl_4$ by aluminum alkyls in inert solvents gives a brown β form, which is converted into the α form at 250 to 300°C. Two other forms are known, but these and the α form have layer lattices containing $TiCl_6$ groups, whereas β-$TiCl_3$ is fibrous with single chains of $TiCl_6$ octahedra sharing edges. The latter is of particular importance because the stereospecific polymerization of propene (Section 28-13) depends critically on the structure of the β form.

The trichloride is oxidized by air and reacts with donor molecules to give adducts of the general formula $TiCl_3{\cdot}nL$ (n = 1–6), for example, $TiCl_3$

[17a] M. Tanaka *et al.*, *Inorg. Chem.*, 1985, **24**, 2475; K. Takamura *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 81; E. M. Nour and S. Morsy, *Inorg. Chem. Acta*, 1986, **117**, 45.

[17b] M. K. Chaudhuri and B. Das, *Inorg. Chem.*, 1986, **25**, 168.

[17c] See K. B. Sharpless *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 1279.

$(THF)_3$. When heated above 500°C, $TiCl_3$ disproportionates (see later). The fluoride, bromide, and iodide of Ti^{III} are also known.

The *oxide* Ti_2O_3 (corundum structure) is obtained by reducing TiO_2 at 1000°C in a stream of H_2. It is rather inert and is attacked only by oxidizing acids. The addition of OH^- ions to aqueous Ti^{III} solutions gives a purple precipitate of the hydrous oxide.

Solution Chemistry and Complexes of Titanium(III). Aqueous solutions of the $[Ti(H_2O)_6]^{3+}$ ion can be readily obtained by reducing aqueous Ti^{IV} either electrolytically or with zinc. The violet solutions reduce oxygen and hence must be handled under N_2 or H_2. The potential in the acidity range $0.3\ M \leq [H^+] \leq 12\ M$ can be taken as

$$Ti^{4+} + e = Ti^{3+} \qquad E_0 = 0.2\ V$$

and the following potential has been estimated[5]

$$Ti(OH)_2^{2+} + 2H^+ + e \rightleftharpoons Ti^{3+} + 2H_2O \qquad E_0 = 7.7 \times 10^{-3}\ V$$

The Ti^{3+} ion is extensively used as a reducing agent[18] but though thermodynamically weaker than Cr^{2+} it reacts at a comparable rate in acidic solutions and is generally a kinetically fast reductant; it reduces ClO_4^- to Cl^-.

In all its complexes both neutral and ionic Ti^{III} is normally octahedral. In dilute acids the main species is $[Ti(H_2O)_6]^{3+}$, which hydrolyzes to give $[Ti(OH)(H_2O)_5]^{2+}$. The hexaaqua ion occurs in alums such as $CsTi(SO_4)_2 \cdot 12H_2O$.

In more concentrated HCl or HBr solutions there are species such as $[TiX(H_2O)_5]^{2+}$, $[TiX_5(H_2O)]^{2-}$, and $[TiX_6]^{3-}$. Crystallization of HCl solutions gives *trans*-$[TiCl_2(H_2O)_4]Cl \cdot 2H_2O$ and this ion also occurs in $Cs_2TiCl_5 \cdot 4H_2O$, where Ti^{III} resembles both V^{III} and Cr^{III} in similar salts.[19] A comparable ion is *trans*-$[TiCl_2(THF)_4]^+$ obtained as its $[ZnCl_3THF]^-$ salt by interaction of $ZnCl_2$ and $TiCl_3$ in THF.[20]

There are various adducts of TiX_3 with donors, examples being $TiCl_3(MeCN)_3$, $TiCl_3(NMe_3)_3$, and $[TiCl_4(THF)_2]^-$.

Other complexes include TiCl(sal$_2$en) made by Zn reduction of $TiCl_2$(sal$_2$en),[21] the three-coordinate bulky species $Ti[N(SiMe_3)_2]_3$ and Ti(2,6-di-*t*-$BuC_6H_3O)_3$,[22a] thiocyanate, and carboxylates.[22b] There are also some Ti^{III} and also mixed valence Ti^{III}–Ti^{IV} alkoxides such as $Ti_4O(OPr)_{12}$.[23]

The formally Ti^0 complex $Ti(bipy)_3$ is best formulated as $Ti^{3+}(bipy^-)_3$.[24]

Electronic Structure. The Ti^{III} ion is a d^1 system, and in an octahedral ligand field the configuration must be t_{2g}. One absorption band is expected

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[18] J. Early *et al.*, *Inorg. Chem.*, 1984, **23,** 3418.

[19] P. J. McCarthy and M. F. Richardson, *Inorg. Chem.*, 1983, **22,** 2979.

[20] K. G. Caulton *et al.*, *Inorg. Chem.*, 1984, **23,** 3289.

[21] C. Floriani *et al.*, *J. Chem. Soc. Dalton Trans.*, **1982,** 2197.

[22a] I. P. Rothwell *et al.*, *Inorg. Chem.*, 1985, **24,** 995.

[22b] P. Chauduri and H. Diebler, *J. Chem. Soc. Dalton Trans.*, **1986,** 1693.

[23] D. Gervais *et al.*, *J. Chem. Soc. Dalton Trans.*, **1982,** 2328; E. Albizzati *et al.*, *Inorg. Chim. Acta*, 1986, **120,** 197.

[24] A. Flamini and A. M. Giuliani, *Inorg. Chim. Acta*, 1986, **112,** L7.

($t_{2g} \rightarrow e_g$ transition), and has been observed in several compounds. The $[Ti(H_2O)_6]^{3+}$ ion has a single absorption band ($t_{2g} \rightarrow e_g$) which is placed to permit some blue and most red light to be transmitted.

Although a d^1 ion in an electrostatic field of perfect O_h symmetry should show a highly temperature-dependent magnetic moment as a result of spin-orbit coupling, with μ_{eff} becoming 0 at 0 K, the combined effects of distortion and covalence (which causes delocalization of the electron) cause a leveling out of μ_{eff}, which does in general vary from ~1.5 BM at 80 K to ~1.8 BM at about 300 K. Values of μ_{eff} are generally close to 1.7 BM at 293 K.

18-A-4. The Chemistry of Titanium(II), d^2

Other than those discussed in the next section, compounds of Ti^{II} are few. No aqueous chemistry exists because of oxidation by water, although ice-cold solutions of TiO in dilute HCl are said to contain Ti^{II} ions, which persist for some time. The *halides* are obtained by reduction of the tetrahalides with titanium,

$$TiX_4 + Ti \longrightarrow 2TiX_2$$

or by disproportionation of the trihalides,

$$2TiX_3 \xrightarrow{\Delta} TiX_2 + TiX_4$$

In the presence of $AlCl_3$, Ti^{II} and Ti^{III} become more volatile, presumably because of the formation of species such as $TiAl_2Cl_8$, $TiAlCl_6$, and $TiAl_3Cl_{11}$ (Section 7-7); a halide Ti_7Cl_{16} contains Ti—Ti bonds.

The *oxide*, which is made by heating Ti and TiO_2, has the NaCl structure but is normally nonstoichiometric.

The Ti^{2+} ion isolated in place of Na^+ in an NaCl crystal shows the expected *d–d* transitions, namely, $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g} \rightarrow {}^3T_{1g}(P)$, from which $\Delta_0 = 8520\ cm^{-1}$ and $B = 572\ cm^{-1}$ are calculated.

There are a few complex halides such as $[TiCl_5]^{3-}$ and $[TiCl_4]^{2-}$ and adducts of $TiCl_2$ with MeCN and the complex *trans*-$[TiCl_2\ dmpe_2]$.[25a]

Complexes with bulky aryloxides, *cis*-$Ti(OAr)_2(bipy)_2$ are known.[25b]

18-A-5. Organo Compounds: Titanium(IV), (III), (II), (0), and (-I)[26]

Organotitanium compounds have been intensively studied, initially mainly because of the discovery by Ziegler and Natta that ethylene and propylene can be polymerized by $TiCl_3$–aluminum alkyl mixtures in hydrocarbons at

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[25a] G. Wilkinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 1339.

[25b] I. P. Rothwell *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 4720.

[26] See appropriate chapters in *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, and Gmelin's *Handbook of Inorganic Chemistry;* M. T. Reetz, Organotitanium Compounds in *Organic Synthesis, Topics Curr. Chem.*, Vol. 106, Springer Verlag, Berlin, 1986; D. Cosak, *Coord. Chem. Rev.*, 1986, **74**, 53.

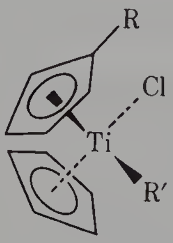
25°C and 1 atm pressure (Section 30-13). More recently, organic compounds have been found to react with N_2 and to act as catalysts in a number of other reactions.

Molecular alkyls of both Ti^{IV} and Ti^{III} can be made using bulky, elimination-stabilized groups (Chapter 25). Examples are $Ti(CH_2Ph)_4$, $Ti(CH_2SiMe_3)_4$, and $Ti[CH(SiMe_3)_2]_3$. Although CH_3TiCl_3 is stable at 25°C, the yellow $TiMe_4$ is unstable above ~ -40°C. However both compounds form thermally stable adducts with donor ligands, for example, Me_4Tibipy, although even these are sensitive to air and water. In the gas phase CH_3TiCl_3 has a symmetrically flattened CH_3 group due to π-donor interactions of the C—H bonds with low lying *d* orbitals.[27]

The compounds (dmpe)$TiCl_3R$, R = CH_3, C_2H_5 both show Ti---H—C "agostic" interactions that are discussed in Section 26-8.

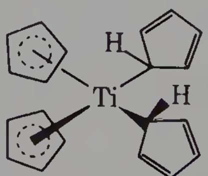
Cyclopentadienyls. The η^5-C_5H_5, η^5-C_5Me_5, and other substituted species are among the most widely studied titanium compounds. The red crystalline Cp_2TiCl_2, which has a quasitetrahedral structure, is the principal starting material for much of the chemistry and some of its reactions are shown in Fig. 18-A-1.

The *alkyl and aryl derivatives* may be quite stable and chiral compounds (18-A-IV) have been resolved. The Cp_4Ti, which has the dialkyl type structure 18-A-V, is nonrigid. As in similar cases (Section 29-15), the σ-bonded rings undergo rapid 1,2 shifts while the two types of rings interchange their roles rapidly so that at 25°C, all 20 ring protons give only a single broad ^1H nmr line.



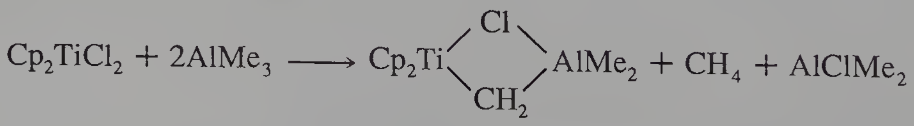
R = CHMePh; R′ = Ph
R = CMe_2Ph; R′ = OPh

(18-A-IV)



(18-A-V)

Interaction of Cp_2TiCl_2 with $AlMe_3$ gives a bridged complex which acts as a CH_2 transfer agent, homologating olefins and converting, for example, R_2CO to $R_2C{=}CH_2$; it has also been used as a model system in alkene metathesis studies (Section 28-16).



$$Cp_2TiCl_2 + 2AlMe_3 \longrightarrow Cp_2Ti\begin{matrix} Cl \\ CH_2 \end{matrix}AlMe_2 + CH_4 + AlClMe_2$$

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[27] A. Berry *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 520.

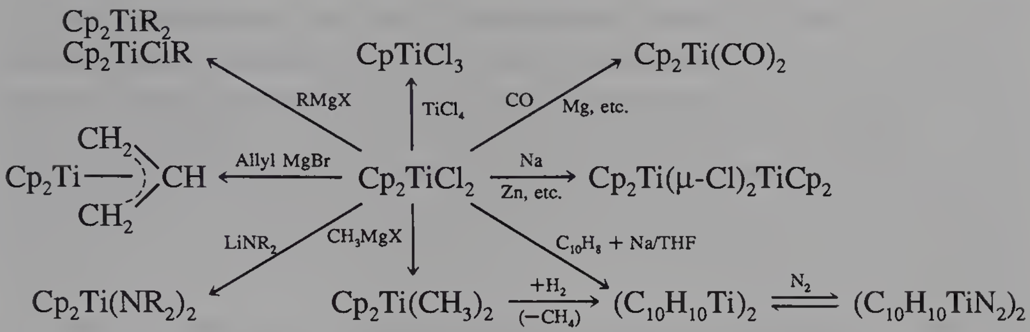


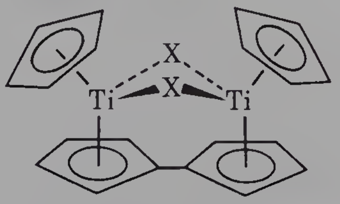
FIG. 18-A-1. Some reactions of dicyclopentadienyl compounds of titanium(II), -III, and -IV. (Cp = η^5-C_5H_5). See, for example, G. P. Pez and J. N. Armour, *Adv. Organomet. Chem.*, 1981, **19,** 2; T. V. Lubben and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1987, **109,** 424 (OC-*t*-Bu_3 derivatives). For CO derivatives see D. J. Sikora *et al., Adv. Organomet. Chem.*, 1986, **25,** 318; F. Basolo *et al., J. Am. Chem. Soc.*, 1986, **108,** 4417. J. Teuben *et al., Organometallics,* 1987, **6,** 1004 (Cp_2TiX). For Ti^{II} pentadienyls, see L. Stahl and R. D. Ernst, *J. Am. Chem. Soc.*, 1987, **109,** 5673.

The dimethyl reacts with silanes, for example,

$$Cp_2TiMe_2 \xrightarrow{R_3SiH} (Cp_2TiH)_2\mu\text{-}H + R_3SiMe + R_6Si_2 + CH_4$$

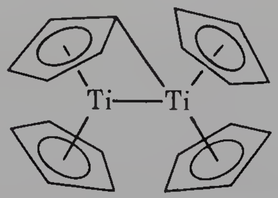
to give a blue hydride.[28]

A green compound produced by interaction of $TiCl_2$ with CpNa, hydrogenolysis of Cp_2TiMe_2, and by reductions of Cp_2TiCl_2 has been much studied and is believed to have the structure 18-A-VI, while a more reactive form obtained by reduction of Cp_2TiCl_2 with potassium naphthalenide has been shown to be 18-A-VII.[29]



X = H or OH

(18-A-VI)



(18-A-VII)

The *pentamethylcyclopentadienyls* often differ from those of the η-C_5H_5 analogs since ring-to-metal hydrogen transfer reactions (as in 18-A-VII) cannot occur. Thus the true monomer $(\eta^5\text{-}C_5Me_5)_2Ti$ can be obtained by dissociation of $[{}^*Cp_2Ti]_2\mu\text{-}N_2$. It has two unpaired electrons and reacts with hydrogen to give $^*Cp_2TiH_2$. In part because of interest in metathesis there has been much study of titanium cyclobutanes and similar compounds, again containing the Cp_2Ti or $^*Cp_2Ti$ unit.[30a] There is also a variety of titanium(III) compounds $^*Cp_2TiX$, where X = H, Cl, BH_4, $OCMe_3$.[30b]

[28] E. Samuel and J. F. Harrod, *J. Am. Chem. Soc.*, 1984, **106,** 1859.

[29] W. A. Herrmann *et al., Organometallics,* 1986, **5,** 2514.

[30a] See, for example, F. Bickelhaupt *et al., Organometallics,* 1985, **4,** 114.

[30b] J. H. Teuben *et al., Organometallics,* 1987, **6,** 1004.

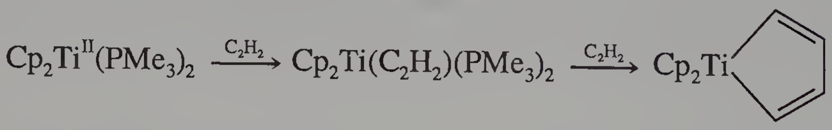
Finally there are a number of oxo species that are obtained by oxidation of $Cp_2M(CO)_2$ (or for other metal species Cp_2M) by N_2O of general formula $Cp_mM_nO_n$, the titanium compound being $Cp_6Ti_6O_8$. These have cage structures with μ_3-O groups[31]; others are $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$. Another oxo species made by interaction of $(Cp_2TiCl)_2$ and N_2O is $(Cp_2TiCl)_2(\mu\text{-}O)$, while $Cp_2Ti(CO)_2$ and RNO gives $[Cp_2TiO]_n$.[32]

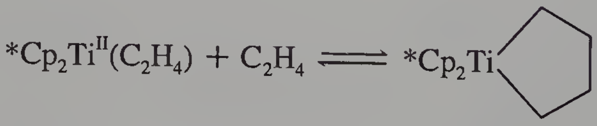
Sulfur species such as $Cp_5Ti_5S_6$ and $^*Cp_2Ti(SH)_2$ have been made from the dicarbonyls and H_2S.[33]

Arenes. These have been made only by metal vapor syntheses from mesitylene, naphthalene, and so on,[34a] while the reduction of TiX_4 and $AlCl_3$ with Al in arenes[34b] gives $[Ti(\eta^6\text{-arene})(\mu\text{-}X)_2AlX_2]_2$. Reduction of the bis arenes gives the only examples of Ti^{-I} compounds in the anions $[TiAr_2]^-$.[35]

Alkene, Alkyne, and Carbonyl Complexes. While titanium alkene complexes are unquestionably involved in polymerizations, relatively few have been isolated. Interactions of $TiCl_4(dmpe)_2$ and butadiene under reducing conditions gives $Ti(\eta\text{-}C_4H_6)_2(dmpe)$, which can be converted by CO and PF_3 to $Ti(CO)_3(dmpe)_2$ and $Ti(CO)_2(PF_3)(dmpe)_2$.[36]

Most of the compounds, however, have Cp or *Cp groups, examples[37] being $Cp_2Ti(CO)_2$, $CpTi(CO)_4^-$, $^*Cp_2Ti(\eta^2\text{-}C_2H_4)$, and $Cp_2Ti(\eta^2\text{-}PhC{\equiv}CPh)PMe_3$. There are similar species like $Cp_2Ti(PMe_3)_2$ or $Cp_2Ti(dmpe)$. These Ti^{II} compounds can often be substituted by other ligands and they also undergo oxidative addition reactions, for example,





and can provide precursors for hydrogenation catalysts.[38]

[31] F. Bottomley and F. Grein, *Inorg. Chem.*, 1982, **21,** 4170; V. W. Day *et al., J. Chem. Soc. Chem. Commun.*, **1987,** 858.

[32] C. Floriani *et al., J. Am. Chem. Soc.*, 1986, **108,** 6823; S. G. Blanco *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 1572.

[33] F. Bottomley *et al., Organometallics,* 1986, **5,** 1620.

[34a] See, for example, P. D. Morand and C. G. Francis, *Inorg. Chem.*, 1985, **24,** 56; M. L. H. Green *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 669.

[34b] P. Biagini *et al., J. Chem. Soc. Chem. Commun.*, **1987,** 1015.

[35] M. L. H. Green *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 729.

[36] S. S. Wreford *et al., Organometallics* 1982, **1,** 935.

[37] B. A. Kelsey and J. E. Ellis, *J. Chem. Soc. Chem. Commun.*, **1986,** 331; *J. Am. Chem. Soc.*, 1986, **108,** 1344; L. B. Kool *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 408; M. D. Rausch *et al., J. Am. Chem. Soc.*, 1983, **105,** 416; *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 394; J. E. Bercaw *et al., J. Am. Chem. Soc.*, 1983, **105,** 1136; B. Demerseman *et al., J. Organometal. Chem.*, 1985, **287,** C35; H. G. Alt *et al., J. Am. Chem. Soc.*, 1985, **107,** 3717; G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2347; J. H. Teuben *et al., Organometallics,* 1987, **6,** 459.

[38] See, for example, D. R. Corbin *et al., Inorg. Chem.*, 1986, **25,** 98.

The compounds are usually made by reducing Cp_2TiCl_2 in the presence of the ligands, for example,

$$Cp_2TiCl_2 + 2PMe_3 + Mg \longrightarrow Cp_2Ti(PMe_3)_2 + MgCl_2$$

Diazabutadienes. The octahedral Ti^0 species, the deep blue $Ti(\sigma,\sigma\text{-}N,N'\text{-}i\text{-}Pr\ dab)_3$, has been made by metal vapor synthesis.[39]

18-B. VANADIUM: GROUP VB(5)

The maximum oxidation state of vanadium is V, but for this there is little similarity, other than in some of the stoichiometry, to the chemistry of elements of the P group. The chemistry of V^{IV} is dominated by the formation of oxo species, and a wide range of compounds with VO^{2+} groups is known. There are four well-defined cationic species, $[V^{II}(H_2O)_6]^{2+}$, $[V^{III}(H_2O)_6]^{3+}$, $V^{IV}O^{2+}(aq)$, and $V^VO_2^+(aq)$, and none of these disproportionates because the ions become better oxidants as the oxidation state increases; both V^{II} and V^{III} ions are oxidized by air. As with Ti, and in common with other transition elements, the vanadium halides and oxohalides behave as Lewis acids, forming adducts with neutral ligands and halogeno complex ions with halide ions.

The oxidation states and stereochemistries for vanadium are summarized in Table 18-B-1. We shall discuss the oxidation states V, IV, III, and II individually, and then turn to compounds with mixed oxidation states, metal–metal bonds, or other unusual features.

18-B-1. The Element

Vanadium has an abundance in Nature of ~0.02%. It is widely spread, but there are a few concentrated deposits. Important minerals are *patronite* (a complex sulfide), *vanadinite* $[Pb_5(VO_4)_3Cl]$, and *carnotite* $[K(UO_2)VO_4\cdot\frac{3}{2}H_2O]$. The last of these is more important as a uranium ore, but the vanadium is usually recovered as well. Vanadium also occurs widely in certain petroleums, notably those from Venezuela, and it can be isolated from them as oxovanadium(IV) porphyrins.[1] Vanadium pentoxide (V_2O_5) is recovered from flue dusts after combustion.

Vanadium is endogenous to some living systems (sea squirts, tunicates, and at least one mushroom[2]) but its role is obscure.[3] There is also uncertainty regarding the nature of the vanadium species[4] and V may be present predominantly in an insoluble matrix rather than as ions such as $[VO(H_2O)_5]^{2+}$

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[39] F. G. N. Cloke *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 1344.

[1] S. A. Miller *et al., Aust. J. Chem.,* 1984, **37,** 761.

[2] H. Kneifel and E. Bayer, *J. Am. Chem. Soc.,* 1986, **108,** 3075; E. Bayer *et al., Angew. Chem. Int. Ed. Engl.,* 1987, **26,** 544.

[3] K. Kustin and I. G. Macara, *Comments Inorg. Chem.,* 1982, **1,** 1.

[4] C. J. Hawkins *et al., Inorg. Chem.,* 1987, **26,** 627.

TABLE 18-B-1
Oxidation States and Stereochemistry of Vanadium

Oxidation state	Coordination number	Geometry	Examples
V^{-1}, d^6	6	Octahedral	$V(CO)_6^-$, $Li[V(bipy)_3]\cdot 4C_4H_8O$
V^0, d^5	6	Octahedral	$V(CO)_6$, $V(bipy)_3$, $V[C_2H_4(PMe_2)_2]_3$
	7	Monocapped octahedral	$[V(CO)_3(PMe_3)_4][V(CO)_6]$[b]
V^I, d^4	6	Octahedral	$[V(bipy)_3]^+$
		Tetragonal pyramidal	η^5-$C_5H_5V(CO)_4$
	7		$V(CO)_2(dmpe)_2Cl$
V^{II}, d^3	6	Octahedral	$[V(H_2O)_6]^{2+}$, $[V(CN)_6]^{4-}$
V^{III}, d^2	3	Planar	$V[N(SiMe_3)_2]_3$, $V[CH(SiMe_3)_2]_3$
	4	Tetrahedral	$[VCl_4]^-$
	5	*tbp*	*trans*-$VCl_3(SMe_2)_2$, $VCl_3(NMe_3)_2$
	6[a]	Octahedral	$[V(NH_3)_6]^{3+}$, $[V(C_2O_4)_3]^{3-}$, VF_3
	7	Pentagonal bipyramidal	$K_4[V(CN)_7]\cdot 2H_2O$
V^{IV}, d^1	4	Tetrahedral	VCl_4, $V(NEt_2)_4$, $V(CH_2SiMe_3)_4$
	5	Tetragonal pyramidal	$VQ(acac)_2$, $PCl_4^+VCl_5^-$
		?	$[VO(SCN)_4]^{2-}$
		tbp	$VOCl_2$ *trans*-$(NMe_3)_2$
	6[a]	Octahedral	VO_2(rutile), K_2VCl_6, $VO(acac)_2(py)$, $V(acac)_2Cl_2$
	8	Dodecahedral	$VCl_4(diars)_2$, $V(S_2CMe)_4$
V^V, d^0	4	Tetrahedral(C_{3v})	$VOCl_3$
	5	*tbp*	$VF_5(g)$
		sp	$CsVOF_4$
	6[a]	Octahedral	$VF_5(s)$, VF_6^-, V_2O_5 (very distorted, almost *tbp* with one distant O); $[VO_2(ox)_2]^{3-}$, V_2S_5
	7	Pentagonal bipyramidal	$VO(NO_3)_3\cdot CH_3CN$, $VO(Et_2NCS_2)_3$

[a] Most important states.
[b] P. J. Charland *et al., Acta Cryst.*, 1987, **C43,** 48.

Very pure vanadium is rare because, like Ti, it is quite reactive toward oxygen, nitrogen, and carbon at the elevated temperatures used in conventional thermometallurgical processes. Since its chief commercial use is in alloy steels and cast iron, to which it lends ductility and shock resistance, commercial production is mainly as an iron alloy, *ferrovanadium*. The very pure metal can be prepared by the de Boer–van Arkel process (Section 18-A-1). It is reported to melt at ~1700°C, but addition of carbon (interstitially) raises the melting point markedly: vanadium containing 10% of carbon melts at ~2700°C. The pure, or nearly pure, metal resembles Ti in being corrosion resistant, hard, and steel gray. In the massive state it is not attacked by air, water, alkalis, or nonoxidizing acids other than HF at room temperature. It dissolves in nitric acid and aqua regia.

At elevated temperatures it combines with most nonmetals. With oxygen it gives V_2O_5 contaminated with lower oxides, and with nitrogen the interstitial nitride VN. Arsenides, silicides, carbides, and other such compounds, many of which are definitely interstitial and nonstoichiometric, are also obtained by direct reaction of the elements.

VANADIUM COMPOUNDS

18-B-2. Vanadium Halides

The halides of vanadium are listed in Table 18-B-2 together with some of their reactions.

The *tetrachloride* is obtained not only from V + Cl_2 but also by the action of CCl_4 on red-hot V_2O_5 and by chlorination of ferrovanadium (followed by distillation to separate VCl_4 from Fe_2Cl_6). It is an oil that is violently hydrolyzed by water to give solutions of oxovanadium(IV) chloride; its magnetic and spectral properties confirm its nonassociated tetrahedral nature. It has a high dissociation pressure and loses chlorine slowly when kept, but rapidly on boiling, leaving VCl_3. The latter may be decomposed to VCl_2, which is then stable (mp 1350°C):

$$2VCl_3(s) \longrightarrow VCl_2(s) + VCl_4(g)$$

$$VCl_3(s) \longrightarrow VCl_2(s) + \tfrac{1}{2}Cl_2(g)$$

The bromide system is similar but there is only indirect evidence for VI_4 in the vapor phase. The trihalides have the BI_3 structure in which each metal atom is at the center of a nearly perfect octahedron of halogen atoms.

The pentafluoride appears to be a trigonal bipyramid in the vapor, but

TABLE 18-B-2
The Halides of Vanadium

VF_5^a	$\xrightarrow{PCl_3}$	VF_4	$\xrightarrow{\sim 150°C^b}$	VF_3	$\xrightarrow[115°C]{H_2+HF}$	VF_2
Colorless, mp, 19.5°C bp. 48°C		Lime green, subl > 150°C		Yellow green		Blue
		25°C $\uparrow$ HF in $CClF_3$		600°C $\uparrow$ HF(g)		600°C $\uparrow$ HF(g)
		VCl_4^a Red brown, bp 154°C	$\underset{Cl_2}{\overset{reflux}{\rightleftarrows}}$	VCl_3 Violet	$\xrightarrow{>450°C^b}$	VCl_2 Pale green
		[VBr_4^c] Magenta	$\underset{Br_2}{\overset{>-23°C}{\rightleftarrows}}$	VBr_3^a Black	$\xrightarrow{>280°C}$	VBr_2 Red brown
		[VI_4(g)]	$\longleftarrow$	VI_3^d Brown	$\xrightarrow{>280°C}$	VI_2 Dark violet

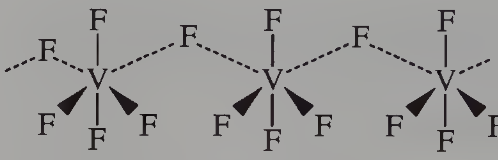
[a] Made by direct interaction at elevated temperatures, F_2, 300°C; Cl_2, 500°C; Br_2, 150°C.

[b] Disproportionation reaction, (e.g., $2VCl_3 = VCl_2 + VCl_4$).

[c] Isolated from vapor at ~550°C by rapid cooling; decomposes above −23°C.

[d] Made in a temperature gradient with V at >400°C, I_2 at 250 to 300°C.

with some unusual vibrational amplitudes or distortion.[5] In the crystal it gives an infinite polymer (18-B-I) fragments of which persist in the liquid, thus explaining the high viscosity.



(18-B-I)

All the halides are Lewis acids and form complexes, which are discussed later under the pertinent oxidation states. The oxohalides are also discussed later.

18-B-3. The Chemistry of Vanadium(V)

Vanadium(V) Oxide. Vanadium(V) oxide is obtained on burning the finely divided metal in an excess of oxygen, although some quantities of lower oxides are also formed. The usual method of preparation is by heating ammonium metavanadate:

$$2NH_4VO_3 \longrightarrow V_2O_5 + 2NH_3 + H_2O$$

It is thus obtained as an orange powder that melts at ~650°C and solidifies on cooling to orange, rhombic needle crystals. Addition of dilute H_2SO_4 to solutions of NH_4VO_3 gives a brick red precipitate of V_2O_5. This has slight solubility in water (~0.007 g L^{-1}) to give pale yellow acidic solutions. Although mainly acidic, hence readily soluble in bases, V_2O_5 also dissolves in acids. That the V^V species so formed are moderately strong oxidizing agents is indicated by the evolution of chlorine when V_2O_5 is dissolved in hydrochloric acid; V^{IV} is produced. This oxide is also reduced by warm sulfuric acid. The following standard potential has been estimated:

$$VO_2^+ + 2H^+ + e = VO^{2+} + H_2O \qquad E^0 = 1.0\ V$$

Vanadates. Vanadium pentoxide dissolves in sodium hydroxide to give colorless solutions and in the highly alkaline region, pH > 13, the main ion is VO_4^{3-}. As the basicity is reduced, a series of complicated reactions occurs. A protonated species is first formed:

$$VO_4^{3-} + H_2O = VO_3(OH)^{2-} + OH^- \qquad pK = 1.0$$

and this then aggregates into binuclear and subsequently more complex species depending on the concentration and pH.

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[5] K. Hedberg *et al., Inorg. Chem.*, 1982, **21,** 2690.

In the pH range 2 to 6 the main species is the orange *decavanadate ion,* which can exist in several protonated forms.

$$V_{10}O_{28}^{6-} + H^+ \rightleftharpoons V_{10}O_{27}(OH)^{5-}$$

$$V_{10}O_{27}(OH)^{5-} + H^+ \rightleftharpoons V_{10}O_{26}(OH)_2^{4-}$$

$$V_{10}O_{26}(OH)_2^{4-} + H^+ \rightleftharpoons V_{10}O_{25}(OH)_3^{3-}$$

$$V_{10}O_{25}(OH)_3^{3-} + H^+ \rightleftharpoons V_{10}O_{25}(OH)_4^{2-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} VO_2^+$$

The $V_{10}O_{25}(OH)_4^{2-}$ ion is very unstable and with further acid rapidly gives the dioxovanadium(V) ion (VO_2^+). In alkaline solution breakup of the $V_{10}O_{28}$ unit is much slower.

Many salts of the decavanadate ion, for example, $Ca_3V_{10}O_{28}\cdot 18H_2O$ and $(EtC_5H_4NH)_4[V_{10}O_{28}H_2]$,[6] can be crystallized and the structure, shown in Fig. 18-B-1(a) is well established. It consists of 10 VO_6 octahedra fused together. Spectroscopic studies (Raman, ^{17}O and ^{51}V nmr) indicate that this structure persists in solution.

Many other vanadates are known. The metavanadates, MVO_3 ($M = NH_4$, K, Rb, and Cs) are isomorphous, and have infinite chains of corner sharing VO_4 tetrahedra[7] [Fig. 18-B-1(b)], while the hydrate $KVO_3\cdot H_2O$ [Fig. 20-B-1(c)] has chains of linked VO_5 polyhedra, and the ion $V_4O_{12}^{4-}$ has a cyclic tetrametaphosphate-like structure. There are also mixed polyvanadates such as $PV_{14}O_{42}^{9-}$, which has a bicapped Keggin structure[8] (see Section 19-C-3), $PV_{12}O_{36}^{7-}$ of which the free hydrated acid can be crystallized,[9] and a series of mixed Mo–V species,[10] for example, $Mo_4V_8O_{36}^{8-}$ and $Mo_8V_5O_{40}^{7-}$.

The tetrathiovanadate (VS_4^{3-}) is also well characterized.[11]

Oxohalides and Their Complexes. The oxohalides are VOX_3 ($X = F$, Cl, and Br), VO_2F, and VO_2Cl. Vanadium oxotrichloride ($VOCl_3$), made by the action of Cl_2 on $V_2O_5 + C$ at ~300°C is the most important. It is a yellow liquid, readily hydrolyzed, and consists of $VOCl_3$ molecules having C_{3v} symmetry. It readily interacts with Cl^- to give $VOCl_4^-$ and with many neutral ligands to give $VOCl_3L$ or $VOCl_3L_2$ adducts.[12] The VO unit in the $VOCl_4^-$ ion [13a] and the $VOCl_3L$ compounds is similar in bond length (~1.55–1.60 Å) and stretching frequency (950–1000 cm^{-1}) to those in VO^{2+} complexes. Mixed

[6] J. M. Amigo *et al., Acta Crystallogr.*, 1982, **B38,** 2465; see also V. W. Day *et al., J. Am. Chem. Soc.*, 1987, **109,** 2991 (for $[V_{10}H_{28}H_3]^{3-}$).

[7] S. Onodera and Y. Ikegami, *Inorg. Chem.*, 1980, **19,** 615.

[8] Y. Sasaki *et al., J. Am. Chem. Soc.*, 1980, **102,** 6571.

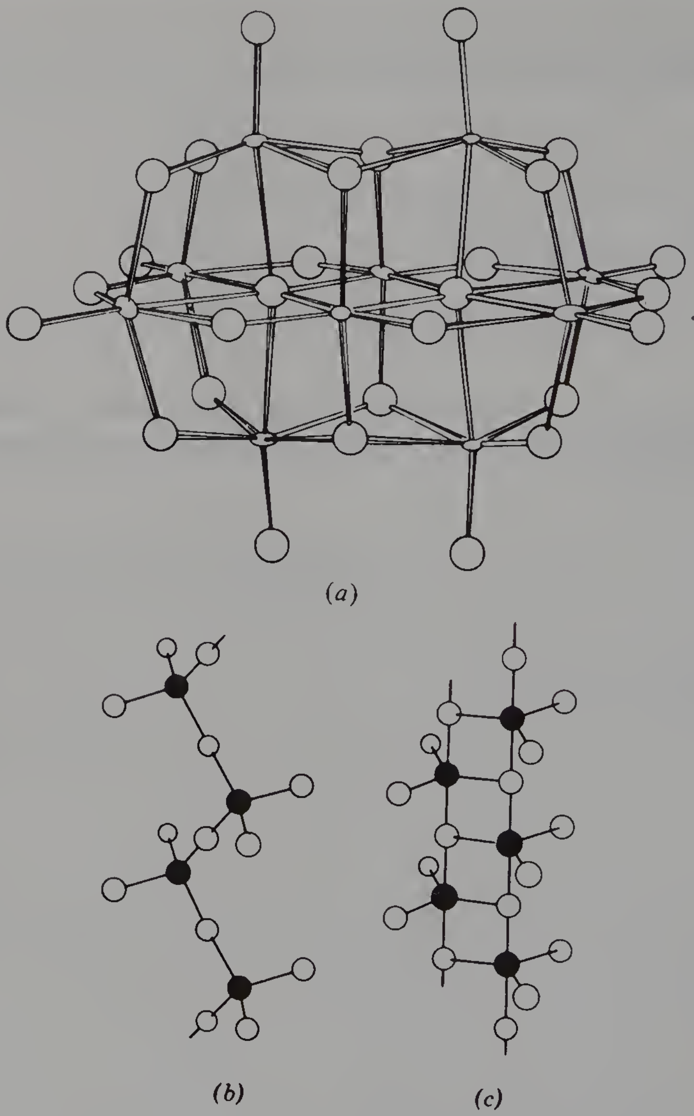
[9] R. Hagenbruch and H. Hahn, *Z. Anorg. Allgem. Chem.*, 1980, **467,** 126.

[10] A. Bjornberg, *Acta Crystallogr.*, 1979, **B35,** 1989; 1980, **B36,** 1530.

[11] R. H. Holm *et al., J. Am. Chem. Soc.*, 1983, **105,** 6731.

[12] Y. Jeannin *et al., Acta Crystallogr.*, 1980, **B36,** 304, 309, 328.

[13a] G. Beindorf *et al., Z. Naturforsch.*, 1980, **35B,** 522.



(a)

(b) (c)

FIG. 18-B-1. The structures in the crystalline state of (a) the decavanadate ion $V_{10}O_{28}^{6-}$, (b) the anion in KVO_3, (c) the anion in $KVO_3{\cdot}H_2O$.

species, $[VOCl_nF_{4-n}]^-$ and $VOClF_2(MeCN)$, and so on, are formed in nonaqueous solvents.[13b]

Other Vanadium(V) Compounds. When vanadates are strongly acidified, the *cis*-$[VO_2(H_2O)_4]^+$ ion is formed, and it can give complexes by displacement of water molecules, for example, $[VO_2Cl_4]^{3-}$, $[VO_2(EDTA)]^{3-}$, and $[VO_2(ox)_2]^{3-}$. The *cis* VO_2 arrangement is favored (as for other d^0 systems) because this allows better $Op\pi \rightarrow Md\pi$ bonding than a linear arrangement would allow. Vanadium(V) complexes with lactate and other anions are known.[14]

[13b] R. C. Hibbert, *J. Chem. Soc. Dalton Trans.*, **1986,** 751.

[14] A. S. Tracey *et al.*, *Inorg. Chem.*, 1987, **26,** 629.

Formally similar to the oxohalides are oxo species in which some or all of the halogens are replaced by OR groups, namely, $VO(OR)_nCl_{3-n}$, and some compounds in which the VO is transformed into V=NR, for example, by the reaction[15]

Other related species are of the type $VO(NR_2)_3$.[16]

The dissolution of V_2O_5 in 30% H_2O, or the addition of H_2O_2 to acidic V^V solutions, gives red peroxo complexes in which oxygen atoms in the vanadate are replaced by one or more O_2^{2-} groups. Several complex peroxovanadates have been isolated and some, like $[VO(O_2)_2NH_3]^-$, and $[V(O)(O_2)_2(ox)]^{3-}$, which have a distorted pentagonal bipyramidal configuration, have been structurally characterized. Peroxo complexes can also be prepared by treating $M^I[VOF_4]$ compounds with a large excess of H_2O_2,[17] and by treating V_2O_5 with H_2O_2 in the presence of KCl or NH_4Cl, salts of the ion $[V(O_2)_3Cl]^{2-}$ may be obtained.[18]

18-B-4. The Chemistry of Vanadium(IV), d^1

The halides (VX_4), have been noted (Section 18-B-2), and there are compounds derived from them such as $V(CH_2SiMe_3)_4$, $V(NR_2)_4$, $[V(OR)_4]_x$, and dithiocarbamates, $V(S_2CNR_2)_4$, but the chemistry of vanadium(IV) is dominated by oxygen compounds.

Vanadium(IV)Oxide and Oxo Anions. The dark blue oxide VO_2 is obtained by mild reduction of V_2O_5, a classic method being by fusion with oxalic acid; it is amphoteric, being about equally readily soluble in both noncomplexing acids, to give the blue ion $[VO(H_2O)_5]^{2+}$, and in base. It has a distorted rutile structure; one bond (the V=O) is much shorter that the others in the VO_6 unit (note that the Ti—O distances in TiO_2 are essentially equal).

When strong base is added to a solution of $[VO(H_2O)_5]^{2+}$, a gray hydrous oxide $VO_2 \cdot nH_2O$, is formed at ~pH 4. This dissolves to give brown solutions from which brown-black salts (e.g., $Na_{12}V_{18}O_{42} \cdot 24H_2O$ can be crystallized. These contain the $V_{18}O_{42}^{12-}$ ion (Fig. 18-B-2), which is somewhat unstable in dilute solution. Vanadium dioxide can be fused with alkaline earth oxides to give incompletely characterized $M^{II}VO_3$ and $M_2^{II}VO_4$ compounds.

The Oxovanadium(IV) Ion(VO^{2+}) and Its Complexes. This ion dominates vanadium(IV) chemistry. It is obtained by mild reduction of the VO_2^+ ion or

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[15] E. A. Maatta, *Inorg. Chem.*, 1984, **23**, 2560.

[16] F. Preuss *et al.*, *Z. Naturforsch.*, 1984, **39B**, 61.

[17] M. K. Chaudhuri and S. K. Ghosh, *J. Chem. Soc. Dalton Trans.*, **1984**, 507; P. Schwendt and D. Joniakova, *Polyhedron*, 1984, **3**, 287.

[18] M. K. Chaudhuri and S. K. Ghosh, *Inorg. Chem.*, 1984, **23**, 534.

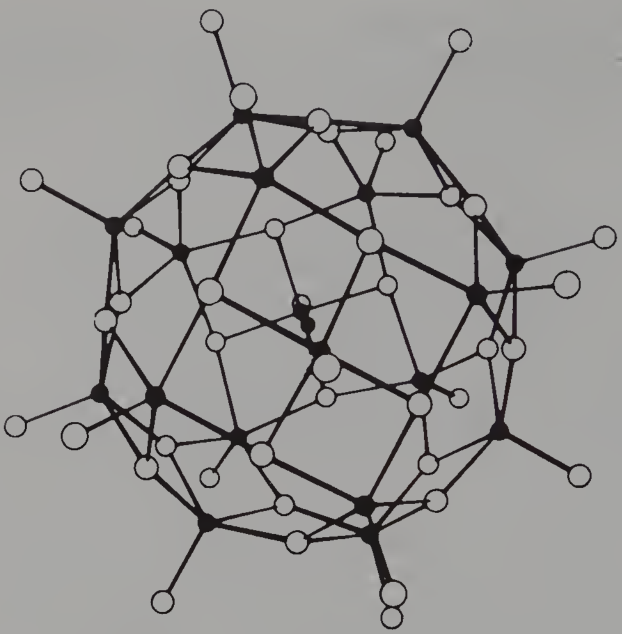

FIG. 18-B-2. The structure of the vanadium(IV) isopolyanion $V_{18}O_{42}^{12-}$.

by oxidation by air of V^{3+} solutions:

$$VO^{2+} + 2H^+ + e = V^{3+} + H_2O \qquad E^0 = +0.34\ V$$

$$VO_2^+ + 2H^+ + e = VO^{2+} + H_2O \qquad E^0 = +1.0\ V$$

The interaction of V_2O_5 with ethanolic HCl gives a solution containing $VOCl_5^{3-}$ that can conveniently be used as a source of V^{IV} oxo complexes. Also, $VOCl_3$ can be reduced by hydrogen to the deliquescent solid $VOCl_2$.

Almost all compounds containing the VO^{2+} unit are blue and display two other characteristic physical properties: (1) an epr spectrum with characteristic g values and ^{51}V hyperfine coupling (8 lines) and (2) a strong V═O stretching band in the ir in the range 950 to 1000 cm^{-1}. Because, as noted later, VO^{2+} complexes may be five- or six-coordinate with the additional ligand (trans to the V═O bond) showing various degrees of interaction, all of the spectral features reflect the exact nature of the ligand set. The V═O bond is very strong, possibly having partial triple-bond character and the V═O distances are thus very short (1.55–1.68 Å) with, again, a dependence on the nature of the ligand set, especially the strength of coordination in the position trans to the V═O bond. In some solid compounds the V═O units are stacked to give V═O···V═O chains.

Representative solid compounds of VO^{2+} include $VOSO_4 \cdot nH_2O$ (n = 5 or 6),[19] which contain discrete $VO(H_2O)_4^{2+}$ and $VO(H_2O)_5^{2+}$ ions, and many compounds with oxo anions in which three-dimensional networks arise by coordination of bridging anions, for example, $VOSO_4 \cdot 3H_2O$, $VOMoO_4$,

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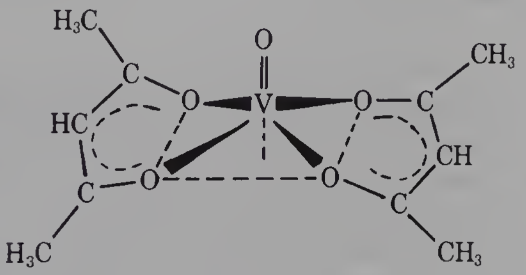
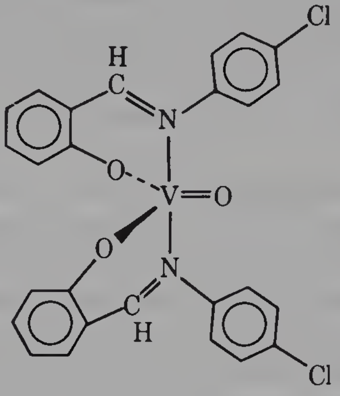
[19] M. Tachez and F. Theobald, *Acta Crystallogr.*, 1980, **B36**, 1757.

$(VO)_2P_2O_7$, $(VO)_2H_4P_2O_9$,[20] and some $VO(RPO_3)$ or $VO(HOPO_3)$ compounds that have layer structures.[21]

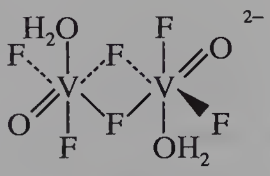
Discrete complexes of VO^{2+} are legion. For the most part they have square pyramidal structures, akin to that shown in (18-B-II) for the acetylacetonate; to these a sixth ligand may be attached trans to V=O. In a few cases, for example, certain Schiff base complexes the structure is distorted trigonal bipyramidal [e.g., (18-B-III)]; these are often not blue, but instead yellow or maroon. In a majority of cases the ligands are bi- or polydentate[22] but simple $[VOX_4]^{2-}$ and $[VOX_5]^{3-}$ species (X = F, Cl, CN, SCN, etc.) have been well characterized.[23,24] There are also bridged binuclear species such as those shown as (18-B-IV),[25] (18-B-V),[26] and (18-B-VI).[27] Finally, we note that complexes of VS^{2+} can be obtained by treating VO^{2+} complexes with B_2S_3.[28]



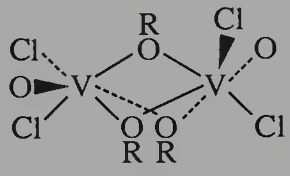
(18-B-II)



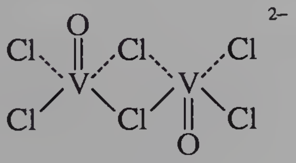
(18-B-III)



(18-B-IV)



(18-B-V)



(18-B-VI)

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[20] C. C. Torardi and J. C. Calabrese, *Inorg., Chem.*, 1984, **23**, 1308.

[21] J. W. Johnson *et al.*, *Inorg. Chem.*, 1984, **23**, 3842.

[22] R. B. Ortega *et al.*, *Acta Crystallogr.*, 1980, **B36**, 1786.

[23] P. Bukovec and L. Golic, *Acta Crystallogr.*, 1980, **B36**, 1925.

[24] C. D. Garner *et al.*, *J. Chem. Soc. Dalton Trans.*, **1980**, 667.

[25] P. Bukovec *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981**, 1802.

[26] F. A. Cotton *et al.*, *Inorg. Chem.*, 1983, **22**, 378.

[27] F. A. Cotton *et al.*, *Inorg. Chem.*, 1986, **25**, 3505.

[28] K. P. Callahan and P. J. Durand, *Inorg. Chem.*, 1980, **19**, 3211.

The occurrence of a VO^{2+} porphyrin complex in petroleum or shale oil has been noted.[1] Many other VO(porph) complexes can be made and have the expected square pyramidal structures.[29]

Other complexes. While the overwhelming majority of V^{IV} complexes contain the VO^{2+} ion, (*vide infra*) there are a few which do not, examples being a tris-catecholate,[30] $[V(cat)_3]^{2-}$, and a series of *cis*- and *trans*-$VX_2(LL)_2$ (X = Cl and Br), in which LL^- is a bidentate ligand employing (O, O), (N, O), or (N, N) donors. These are obtained by deoxygenation of the corresponding $VO(LL)_2$ complexes with $SOCl_2$ or $SOBr_2$.[31] There are also adducts of the halides VX_4 such as $VCl_4(PMe_3)_2$.

18-B-5. The Chemistry of Vanadium(III), d^2

Vanadium(III) Oxide. This black, refractory substance is made by reduction of V_2O_5 with hydrogen or carbon monoxide. It has the corundum structure but is difficult to obtain pure, since it has a marked tendency to become oxygen deficient without change in structure. Compositions as low in oxygen as $VO_{1.35}$ are reported to retain the corundum structure.

Vanadium trioxide is entirely basic and dissolves in acids to give solutions of the V^{III} aqua ion or its complexes. From these solutions addition of OH^- gives the hydrous oxide, which is very easily oxidized in air.

The Aqua Ion and Complexes. The blue aqua ion $[V(H_2O)_6]^{3+}$ can be obtained as above or by electrolytic or chemical reduction of V^{IV} or V^V solutions. Such solutions, and also others, of V^{III} are subject to aerial oxidation in view of the potential

$$VO^{2+} + 2H^+ + e = V^{3+} + H_2O \qquad E^0 = 0.34 \text{ V}$$

The ion hydrolyzes partially to VO^+ and $V(OH)^{2+}$.

When solutions of V^{2+} and VO^{2+} are mixed, V^{3+} is formed, but VOV^{4+}, a brown intermediate species that has an oxo bridge, occurs; structural data for it have been obtained from the crystal structure of $(THF)_3Cl_2VOVCl_2(THF)_3$.[32a]

In the thiolate $[V_2O(SCH_2CH_2NMe_2)_4]$ there is a linear VOV^{4+} unit.[32b]

Vanadium(III) forms a number of complex ions, mostly octahedral, for example, $[V(H_2O)_6]^{3+}$, $[VCl_2(MeOH)_4]^+$, $[V(ox)_3]^{3-}$, $[V(NCS)_6]^{3-}$, and $[VCl_2(THF)_2(H_2O)_2]^+$[33] but a seven-coordinate cyanide complex $K_4[V(CN)_7]\cdot 2H_2O$, can be obtained as red crystals by the action of KCN on VCl_3 in dilute HCl.

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[29] M. G. B. Drew *et al., Inorg. Chim. Acta,* 1984, **82,** 63.

[30] S. J. Cooper *et al., J. Am. Chem. Soc.,* 1982, **104,** 5092.

[31] A. Jezierski and J. B. Raynor, *J. Chem. Soc. Dalton Trans.,* **1981,** 1.

[32a] P. Chandresekhar and P. H. Bird, *Inorg. Chem.,* 1984, **23,** 3677.

[32b] G. Christou *et al., Inorg. Chem.,* 1987, **26,** 944.

[33] K. G. Caulton *et al., Inorg. Chem.,* 1984, **23,** 4589.

The $[V(H_2O)_6]^{3+}$ ion occurs in *alums* $M^IV(SO_4)\cdot 12H_2O$. The ammonium alum is obtained as air-stable, blue-violet crystals by electrolytic reduction of NH_4VO_3 in H_2SO_4. In the compound $[V(H_2O)_6][H_5O_2](CF_3SO_3)_4$ it has been characterized by neutron diffraction.[34] The hydrated halides $VX_3\cdot 6H_2O$, have the structure *trans*-$[VCl_2(H_2O)_4]Cl\cdot 2H_2O$ as found in similar hydrates of Fe^{III} and Cr^{III}. The bromide and some bromo complexes can be made by heating V_2O_5 with ethanolic HBr (as noted previously, HCl gives the VO^{2+} species).

The V^{III} halides form numerous six-coordinate adducts such as *mer*-$VCl_3(THF)_3$[35] and *mer*-$VCl_3(CNCMe_3)_3$[36]; the THF compound is an excellent starting material for synthesis. In addition, with bulkier ligands, five-coordinate, trigonal bipyramidal complexes such as $VCl_3(NMe_3)_2$ and $VCl_3(PR_3)_2$ are formed.[37]

18-B-6. The Chemistry of Vanadium(II)

Binary compounds are few, those of importance being the halides (Section 18-B-2) and the black oxide (VO), which has an NaCl lattice but is prone to nonstoichiometry (obtainable with 45–55 at. % oxygen). It has somewhat metallic physical characteristics. Chemically it is basic, dissolving in mineral acids to give V^{II} solutions.

The ability of several V^{II} containing systems, namely, $V(OH)_2/Mg(OH)_2$ slurry, $V(OH)_2/ZrO_2\cdot H_2O$, and certain catechol complexes of V^{II}, to reduce N_2 to NH_3 and/or N_2H_4 has been demonstrated, but there is disagreement as to the mechanism.[38,39]

The Aqua Ion. Electrolytic or zinc reduction of acidic solutions of V^V, V^{IV}, or V^{III} produces violet air-sensitive solutions containing the $[V(H_2O)_6]^{2+}$ ion. These are strongly reducing (Table 18-1) and are oxidized by water with evolution of hydrogen even though the standard potential V^{3+}/V^{2+} would indicate otherwise. The oxidation of V^{2+} by air is complicated and appears to proceed in part by direct oxidation to VO^{2+} and in part by way of an intermediate species of type VOV^{4+}, noted earlier.

Several crystalline salts contain the $[V(H_2O)_6]^{2+}$ ion, although the hydrate $VCl_2\cdot 4H_2O$ is actually *trans*-$VCl_2(H_2O)_4$. The most important are the sulfate $VSO_4\cdot 6H_2O$,[40] which is formed as violet crystals on addition of ethanol

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[34] F. A. Cotton *et al., J. Am. Chem. Soc.*, 1984, **106,** 5319.

[35] F. A. Cotton *et al., Inorg. Chim. Acta,* 1986, **113,** 81.

[36] S. J. Lippard *et al., Inorg. Chem.*, 1980, **19,** 3379.

[37] K. G. Caulton *et al., Inorg. Chem.*, 1985, **24,** 3003; L. F. Larkworthy *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 2253.

[38] N. P. Luneva *et al., Nouv. J. Chim.*, 1982, **6,** 245.

[39] G. N. Schrauzer *et al., Inorg. Chem.*, 1982, **21,** 2184.

[40] F. A. Cotton *et al., Inorg. Chem.*, 1986, **25,** 3423.

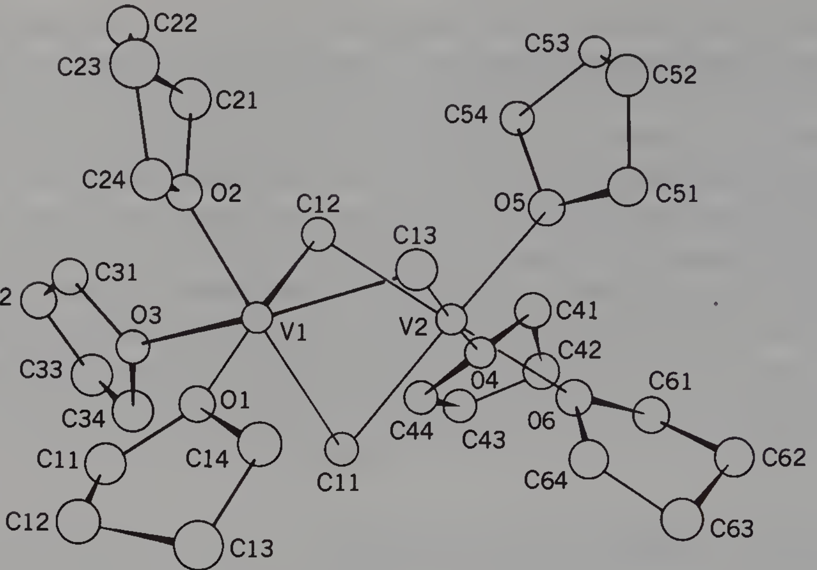


FIG. 18-B-3. The structure of the $[V_2(\mu\text{-Cl})_3(THF)_6]^+$ ion.

to reduced sulfate solutions, and the double sulfates (Tutton salts) $M_2[V(H_2O)_6](SO_4)_2$, where M = NH_4^+, K^+, Rb^+, or Cs^+. The electronic absorption spectra are consistent with octahedral aqua ions both in crystals and in solution, and the energy level diagram is analogous to that for Cr^{III}. The magnetic moments of the sulfates lie close to the spin-only value.

In aqueous solution $[V(H_2O)_6]^{2+}$ is kinetically inert because of its d^3 configuration (cf. Cr^{3+}), and substitution reactions are relatively slow. Although F^- and SCN^- form weak complexes, there is little evidence for complexing with Cl^-, Br^-, I^-, or SO_4^{2-}. Reorganization of the precursor complex is believed to be the rate-determining step in many reductions by V^{2+}, since the rates of redox reactions are similar to those of substitution, for example,

$$V(H_2O)_6^{2+} + SCN^- \longrightarrow (H_2O)_5VNCS^+ + H_2O$$

and reduction reactions appear to proceed by a substitution-controlled inner-sphere mechanism (Section 29-10). However, in the reduction of $IrCl_6^{2-}$ by V^{2+}, the rate constant is higher by ~10^5, so that here an outer-space mechanism is involved.

Complexes. The characteristic coordination is octahedral, and examples are $VCl_2(py)_4$,[41a] *trans*-$[VCl_2(dmpe)_2]$,[41b] $[V(NCS)_6]^{4-}$ salts,[42] and the porphyrin complexes[43] whose preparation and reactivity are as follows:

$$trans\text{-}VCl_2(porph) \xrightarrow[+PR_3]{Zn/Hg} trans\text{-}V(porph)(PR_3)_2 \xrightarrow{O_2} V(O)(porph)$$

[41a] F. A. Cotton and C. A. Murillo, *Ing. Cienc. Quim.*, 1985, **9**, 5.
[41b] G. Wilkinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 1339.
[42] L. F. Larkworthy and B. J. Tucker, *J. Chem, Soc. Dalton Trans.*, **1980**, 2042.
[43] R. Guilard *et al.*, *J. Chem. Soc. Chem. Commun.*, **1982**, 1421.

Previously reported "$VCl_2(THF)_2$" prepared by zinc reduction of VCl_3 in THF by zinc is the salt, $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$,[44] and it has been shown that the same dinuclear cation together with other anions can be obtained in up to 99% yield by reducing VCl_3 in THF with $Et_2Al(OEt)$.[45] The cation, whose structure is shown in Fig. 18-B-3, has V^{II}–V^{II} electronic coupling that makes normally spin-forbidden excitations of the V^{II} ions appear strongly in the spectrum.[44] A similar coupling is detected for V^{II} doped into $CsMgCl_3$.[46] Some or all of the THF ligands in the $[V_2Cl_3(THF)_6]^+$ ion can be replaced by others such as PMe_3 or PPh_3.[47]

18-B-7. Mixed Oxidation States and Other Topics

Vanadates of V^V and V^{IV} have been mentioned. There are also some that contain both V^{IV} and V^V, with the latter predominating, for example, $K_2V_3O_8$ in which V^VO_4 tetrahedra and $V^{IV}O_5$ tetragonal pyramids share vertices to form infinite layers. Others are $(Et_4N)_4[V_{10}O_{26}](H_2O)_2$ in which two $V^{IV}O_5$ square pyramids cap a central ring of V^VO_4 tetrahedra.[48]

The $VO_2^{2+}(aq)$ and $VO^{2+}(aq)$ ions, or some of their complexes if present together in acid solution, associate ($K = 8\ M^{-1}$ in 8.7 M $HClO_4$) to form a $V_2O_3(aq)^{3+}$ ion.[49]

Vanadium forms a series of oxo-centered trinuclear carboxylates,[27] having the general structure shown in (12-VIII). Similar compounds formed by many of the other transition metals will be mentioned later. The vanadium compounds can be prepared from V^{II} or V^{III} starting materials to give compounds with either mixed (formally II, III, III) or entirely trivalent oxidation states. In the former cases electron delocalization appears complete and the three vanadium atoms are indistinguishable.

The compound LiV_2F_6 is also an example of a mixed valence compound in which the vanadium atoms are structurally identical.[50]

V–V Bonding. Since its congeners, Nb and Ta, as well as its neighbor Cr form numerous compounds with strong M—M bonds, similar behavior by vanadium might have been expected. From a theoretical point of view, also, this appears to be a valid expectation,[51] but little success has yet been achieved. A triple bond (V—V = 2.20 Å) occurs in V_2(2,6-dimethoxyphenyl)$_4$, which

[44] F. A. Cotton *et al., Inorg. Chem.*, 1985, **24,** 913.

[45] F. A. Cotton *et al., J. Am. Chem. Soc.*, 1985, **107,** 3850.

[46] H. Riesen and H. U. Güdel, *Inorg. Chem.*, 1984, **23,** 1880.

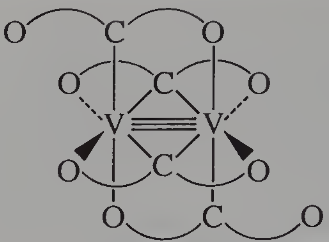
[47] F. A. Cotton *et al., Inorg. Chem.*, 1985, **24,** 525.

[48] A. Bino *et al., Inorg. Chem.*, 1982, **21,** 429.

[49] C. Madic *et al., Inorg. Chem.*, 1982, **21,** 2923.

[50] R. M. Metzger *et al., Inorg. Chem.*, 1983, **22,** 1060.

[51] F. A. Cotton *et al., Inorg. Chem.*, 1985, **24,** 1510.



(18-B-VII)

has an edge-sharing bioctahedral structure shown schematically in (18-B-VII). Two compounds have been reported that appear to contain double bonds; both are rather complicated and it is not clear that either one provides a general approach. Their formulas are $V_2(PMePh_2)_4(H_2ZnH_2BH_2)_2$,[52] and $V_2(salophen)_2Na_2(THF)_6$.[53] No $V_2(O_2CR)_4$ compounds have been reported; all attempts to make them have led to oxo-centered trimers. In the case of $(\eta^5\text{-}C_5H_5)_2V_2(O_2CR)_4$ compounds[54] steric factors appear to prevent close approach of the metal atoms while in $V_2(\mu\text{-Cl})_2(BH_4)_2(dppm)_2$ and its (dmpm) analog[55] it is perhaps the stability of the two t_{2g}^3 configurations that interferes with V—V bond formation. In $(\eta^5\text{-}RC_5H_4)_2V_2S_4$ molecules, however, the V—V distance of 2.610 Å implies the existence of a single bond.[56]

Carbonyl and Organometallic Compounds. In Chapter 22 $V(CO)_6$ will be discussed along with other metal carbonyls. Since it is only a 17-electron species, it has some properties not wholly typical of metal carbonyls. It forms a hydride, $HV(CO)_6$, and an anion, $V(CO)_6^-$. The anion reacts with $[NO][BF_4]$ to form $V(CO)_5(NO)$, an 18-electron system that has an extensive substitution chemistry.[57,58] The hydride also has numerous substituted analogues mostly obtained indirectly by first making substituted anions, for example, $[V(CO)_4(dppe)]^-$ and then protonating these.[59] The compound *trans*-$V(CO)_2(dmpe)_2$ can be oxidized by Ag^+ in MeCN to the 7-coordinate ion $[V(CO)_2(dmpe)_2MeCN]^+$; other species such as $V(CO)_2(dmpe)_2(\eta^1\text{-}O_2CMe)$ can be made.[60]

The chemistry of σ-alkyls and aryls is less well developed than for some other elements, but $V[CH(SiMe_3)_2]_3$, $V(CH_2SiMe_3)_4$, and $VO(CH_2SiMe_3)_3$ are all isolable. Unstable alkyls are present in the solutions of vanadium halides and Al alkyls, which are used in the Ziegler–Natta type of reaction for the copolymerization of styrene, butadiene, and dicyclopentadiene to give

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[52] K. G. Caulton *et al., J. Am. Chem. Soc.*, 1983, **105,** 6163.
[53] C. Floriani *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 1116.
[54] F. A. Cotton *et al., Organometallics,* 1985, **4,** 1174.
[55] F. A. Cotton *et al., Inorg. Chem.*, 1984, **23,** 4113; 1985, **24,** 4389.
[56] T. B. Rauchfuss *et al., J. Am. Chem. Soc.*, 1983, **105,** 6321.
[57] K. L. Fjare and J. E. Ellis, *J. Am. Chem. Soc.*, 1983, **105,** 2308.
[58] W. C. Trogler *et al., J. Am. Chem. Soc.*, 1984, **106,** 71.
[59] G. E. Toogood and M. G. H. Wallbridge, *Adv. Inorg. Chem. Radiochem.*, 1982, **25,** 267.
[60] G. Wilkinson *et al., Polyhedron,* 1987, **6,** 1351.

synthetic rubbers. The dicyclopentadienyl derivatives of V^{II}, V^{III}, and V^{IV} are well established, and unlike the unusual Ti^{II} compound (Section 18-A-5), the V^{II} complex is the simple paramagnetic $(\eta^5\text{-}C_5H_5)_2V$. This undergoes oxidative additions with many compounds to give V^{III} or V^{IV} compounds, for example, Cp_2VCS_2, Cp_2VCl_2. The latter has been found to have significant antitumor activity.[61]

Mixed complexes such as $CpV(CO)_4$, $CpV(CO)_3H^-$,[32] and $CpV(\eta^7\text{-}C_7H_7)$ and the diarenes [e.g., $V(C_6H_6)_2$] are known, as well as some alkene complexes.

General Reference

Rice, D. A., *Coord. Chem. Rev.*, 1981, **37**, 61; 1982, **45**, 67.

18-C. CHROMIUM: GROUP VIB(6)

For chromium, as for Ti and V, the highest oxidation state is that corresponding to the total number of 3*d* and 4*s* electrons. Although Ti^{IV} is the most stable state for titanium and V^V is only mildly oxidizing, chromium(VI), which exists only in the oxo species such as CrO_3, CrO_4^{2-}, and CrO_2F_2, is strongly oxidizing. Apart from stoichiometric similarities, chromium resembles the Group VIA (16) elements of the sulfur group only in the acidity of the trioxide and the covalent nature and ready hydrolysis of CrO_2Cl_2.

The intermediate states Cr^V and Cr^{IV} have somewhat restricted chemistry. The very low formal oxidation states are found largely in carbonyl- and organometallic-type compounds, which are discussed in Chapters 22 and 24–27. With ligands such as aryl isocyanides, bipy, terpy, and phen, which are better donors and somewhat less obligatory back-acceptors than CO, it is possible to generate stable Cr^I compounds. With the isocyanides, electrochemical or Ag^+ oxidation may be used to obtain from $Cr(CNR)_6$ the +1 and +2 ions, with one and two unpaired electrons, respectively. With the amine ligands the entire series of $Cr(LL)_3^n$ with $n = -1, 0, +1, +2$, and $+3$ is obtained and the compounds are electrochemically interconvertible. In the more electron-rich ones electrons enter orbitals with appreciable (for −1, predominant) ligand character. Complexes containing the $[CrNO]^{2+}$ unit,[1a] which contain Cr^I, and the Cr^I species $[Cr(CO)_2(dmpe)_2]^+$ have recently been reported.[1b]

The most stable and generally important states are Cr^{II} and Cr^{III}. This dominance of the II and III states that begins here persists through the following transition elements. We shall discuss these states first.

The oxidation states and stereochemistry are summarized in Table 18-C-1.

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[61] T. J. Marks *et al., J. Am. Chem. Soc.*, 1986, **108**, 7263.

[1a] K. Weighardt *et al., Inorg. Chim. Acta,* 1984, **89,** L43.

[1b] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 1141.

TABLE 18-C-1
Oxidation States and Stereochemistry of Chromium

Oxidation state	Coordination number	Geometry	Examples
Cr^{-II}		?	$Na_2[Cr(CO)_5]$
Cr^{-I}		Octahedral	$Na_2[Cr_2(CO)_{10}]$
Cr^0	6	Octahedral	$Cr(CO)_6$, $[Cr(CO)_5I]^-$, $Cr(bipy)_3$
Cr^I, d^5	6	Octahedral	$[Cr(bipy)_3]^+$, $[Cr(CNR)_6]^+$
Cr^{II}, d^4	3	T shape	$Cr(OCt\text{-}Bu_3)_2LiCl(THF)$
	4	Square	$Cr(O_2CCF_3)_2(Me_2py)_2$
	4	Distorted tetrahedral	$CrCl_2(MeCN)_2$, $CrI_2(OPPh_3)_2$
	5	*tbp*	$[Cr(Me_6tren)Br]^+$
	6	Distorted[a] octahedral	CrF_2, $CrCl_2$, CrS
	5 or 6	Cr—Cr quadruple bond	$Cr_2(O_2CR)_4L_2$, $Cr_2[(CH_2)_2P(CH_3)_2]_4$
	7	?	$[Cr(CO)_2(diars)_2X]X$
Cr^{III}, d^3	3	Planar	$Cr(NPr_2)_3$
	4	Distorted tetrahedral	$[PCl_4]^+[CrCl_4]^-$, $[Cr(CH_2SiMe_3)_4]^-$
	5	*tbp*	$CrCl_3(NMe_3)_2$
	6[b]	Octahedral	$[Cr(NH_3)_6]^{3+}$, $Cr(acac)_3$, $K_3[Cr(CN)_6]$
Cr^{IV}, d^2	4	Tetrahedral	$Cr(OC_4H_9)_4$, Ba_2CrO_4, $Cr(CH_2SiMe_3)_4$
	6	Octahedral	K_2CrF_6, $[Cr(O_2)_2(en)]\cdot H_2O$, *trans*-$[Cr(NCHMe)_2(dmpe)_2]^{2+}$
	8	Dodecahedral	$CrH_4(dmpe)_2$
Cr^V, d^1	4	Tetrahedral	CrO_4^{3-}
	5	Distorted *tbp*	$CrF_5(g)$
	5	*sp*	$CrOCl_4^-$
	6	Octahedral	$K_2[CrOCl_5]$, $(CrF_5)_n$
	8	Quasi-dodecahedral	$K_3Cr(O_2)_4$
Cr^{VI}, d^0	4	Tetrahedral	CrO_4^{2-}, CrO_2Cl_2, CrO_3
	6	Octahedral	CrF_6(matrix)

[a] Four short and two long bonds.
[b] Most stable state.

18-C-1. The Element

The chief ore is *chromite* ($FeCr_2O_4$), which is a spinel with Cr^{III} on octahedral sites and Fe^{II} on the tetrahedral ones. If pure chromium is not required—as for use in ferrous alloys—the chromite is reduced with carbon in a furnace, affording the carbon-containing alloy ferrochromium:

$$FeCr_2O_4 + 4C \longrightarrow Fe + 2Cr + 4CO$$

When pure chromium is required, the chromite is first treated with molten alkali and oxygen to convert the Cr^{III} to chromate(VI), which is dissolved in water and eventually precipitated as sodium dichromate. This is then reduced with carbon to Cr^{III} oxide:

$$Na_2Cr_2O_7 + 2C \longrightarrow Cr_2O_3 + Na_2CO_3 + CO$$

This oxide is then reduced with aluminum:

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$

Chromium is a white, hard, lustrous, and brittle metal (mp 1903 ± 10°C). It is extremely resistant to ordinary corrosive agents, which accounts for its extensive use as an electroplated protective coating. The metal dissolves fairly readily in nonoxidizing mineral acids, for example, hydrochloric and sulfuric acids, but not in cold aqua regia or nitric acid, either concentrated or dilute. The last two reagents passivate the metal in a manner that is not well understood. The electrode potentials of the metal are

$$Cr^{2+} + 2e = Cr \qquad E^0 = -0.91\ V$$

$$Cr^{3+} + 3e = Cr \qquad E^0 = -0.74\ V$$

Thus it is rather active when not passivated, and it readily displaces copper, tin, and nickel from aqueous solutions of their salts.

At elevated temperatures chromium unites directly with the halogens, sulfur, silicon, boron, nitrogen, carbon, and oxygen.

CHROMIUM COMPOUNDS

18-C-2. Binary Compounds

Halides. These are listed in Table 18-C-2. The anhydrous Cr^{II} halides are obtained by action of HF, HCl, HBr, or I_2 on the metal at 600 to 700°C or by reduction of the trihalides with H_2 at 500 to 600°C. Chromium dichloride

TABLE 18-C-2
Halides of Chromium

Halogen	Cr^{II}	Cr^{III}	Higher and mixed oxidation states		
F	CrF_2	CrF_3[a] Green, mp 1404°C	CrF_4[b] Green, subl 100°C Cr_2F_5[d]	CrF_5 Red, mp 30°C	CrF_6[c] Yellow
Cl	$CrCl_2$	$CrCl_3$ Violet, mp 1150°C	$CrCl_4$[e]		
Br	$CrBr_2$	$CrBr_3$ Black, subl	$CrBr_4$[e]		
I	CrI_2	CrI_3 Black, dec			

[a] Melts only in a closed system; in an open system disproportionates above 600°C to give CrF_5.

[b] Becomes brown on slightest contact with moisture.

[c] Sublimes at room temperature.

[d] Often nonstoichiometric; contains regular $Cr^{III}F_6$ and highly distorted $Cr^{II}F_6$ octahedra sharing corners and edges.

[e] Not known as solids; appear to exist in vapors formed when the trihalides are heated in an excess of the halogen. The tetrachloride is tetrahedral and $CrCl_3$ planar in the vapor (J. S. Ogden and R. S. Wyatt, *J. Chem. Soc. Dalton Trans.*, **1987,** 859).

is the most common and most important of these halides, dissolving in water to give a blue solution of Cr^{2+} ion.

Of the Cr^{III} halides the red-violet chloride, which can be prepared in a variety of ways (e.g., by the action of $SOCl_2$ on the hydrated chloride) is singularly important. It can be sublimed in a stream of chlorine at ~600°C, but if heated to such a temperature in the absence of chlorine it decomposes to Cr^{II} chloride and chlorine. The flaky or leaflet form of $CrCl_3$ is a consequence of its crystal structure, which is of an unusual type. It consists of a cubic close-packed array of chlorine atoms in which two thirds of the octahedral holes between *every other* pair of Cl planes are occupied by metal atoms. The alternate layers of chlorine atoms with no metal atoms between them are held together only by van der Waals' forces; thus the crystal has pronounced cleavage parallel to the layers. Chromium trichloride is the only substance known to have this exact structure, but $CrBr_3$, as well as $FeCl_3$ and triiodides of As, Sb, and Bi, have a structure that differs only in that the halogen atoms are in hexagonal rather than cubic close packing.

Chromium(III) chloride does not dissolve at a significant rate in pure water, but it dissolves readily in the presence of Cr^{II} ion or reducing agents such as $SnCl_2$ that can generate some Cr^{II} from the $CrCl_3$. This is because the process of solution can then take place by electron transfer from Cr^{II} in solution via a Cl bridge to the Cr^{III} in the crystal. This Cr^{II} can then leave the crystal and act on a Cr^{III} ion elsewhere on the crystal surface, or perhaps it can act without moving. At any rate, the "solubilizing" effect of reducing agents must be related in this or some similar way to the mechanism by which chromium(II) ions cause decomposition of otherwise inert Cr^{III} complexes in solution (Section 29-10).

Chromium(III) chloride forms adducts with a variety of donor ligands. The tetrahydrofuranate ($CrCl_3 \cdot 3THF$), which is obtained as violet crystals by action of a little zinc on $CrCl_3$ in THF, is a particularly useful material for the preparation of other chromium compounds such as carbonyls or organo compounds, as it is soluble in organic solvents.

Chromium (IV) fluoride is made by fluorination of the metal at 350°C. Both CrF_5 and CrF_6 may be obtained by fluorination of CrO_3 under relatively mild conditions[2] or by more vigorous fluorination of the metal. Both are powerful fluorinating agents. The CrF_6 is volatile; at 25°C it slowly decomposes to CrF_5; $(CrF_5)_n$ is polymeric with *cis*-F bridges.

Oxides. Only Cr_2O_3, CrO_2, and CrO_3 are of importance. The green oxide α-Cr_2O_3, which has the corundum structure (Section 1-2), is formed on burning the metal in oxygen, on thermal decomposition of Cr^{VI} oxide or ammonium dichromate, or on roasting the hydrous oxide $Cr_2O_3 \cdot nH_2O$. The latter, normally obtained by adding hydroxide to aqueous Cr^{III} at room temperature, has variable water content. It is often called chromic hydroxide, but there is in fact a true, crystalline hydroxide, $Cr(OH)_3(H_2O)_3$ that can be prepared by

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[2] W. Levason *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 1443.

slow addition of base to a cold solution of $[Cr(H_2O)_6]^{3+}$. The crystalline material quickly becomes amorphous at higher temperatures.

If ignited too strongly Cr_2O_3 becomes inert toward both acid and base, but otherwise it and its hydrous form are amphoteric, dissolving readily in acid to give aqua ions $[Cr(H_2O)_6]^{3+}$, and in concentrated alkali to form "chromites."

Chromium oxide and chromium supported on other oxides such as Al_2O_3 are important catalysts for a wide variety of reactions.

Chromium(IV) oxide (CrO_2) is normally synthesized by hydrothermal reduction of CrO_3. It has an undistorted rutile structure (i.e., no M—M bonds as in MoO_2). It is ferromagnetic and has metallic conductance, presumably because of delocalization of electrons into energy bands formed by overlap of metal d and oxygen $p\pi$ orbitals.

Chromium(VI) oxide (CrO_3) can be obtained as an orange-red precipitate on adding sulfuric acid to solutions of Na or K dichromate. The red solid, which consists of infinite chains of CrO_4 tetrahedra sharing vertices, is unstable above its melting point 197°C, losing oxygen to give Cr_2O_3 after various intermediate stages. It is readily soluble in water and is highly poisonous.

Interaction of CrO_3 and organic substances is vigorous and may be explosive. However, CrO_3 is widely used in organic chemistry as an oxidant, commonly in acetic acid as solvent. The mechanism has been greatly studied and is believed to proceed initially by the formation of chromate esters (when pure, they are highly explosive) that undergo C—H bond cleavage as the rate-determining step to give Cr^{IV} as the first product; the general scheme appears to be

$$H_2A + Cr^{VI} \rightleftharpoons Cr^{IV} + A \qquad \text{(slow)}$$

$$Cr^{IV} + Cr^{VI} \rightleftharpoons 2Cr^{V}$$

$$Cr^{V} + H_2A \rightleftharpoons Cr^{III} + A$$

The oxides give rise to various mixed metal oxides; those containing the higher oxidation states are discussed later. Chromium(III) oxide can be fused with a number of M^{II} oxides to give crystalline $M^{II}O \cdot Cr_2O_3$ compounds having the spinel structure (Section 1-2) with Cr^{III} ions in the octahedral holes. Sodium metal reacts with each of the oxides Cr_2O_3, CrO_2, CrO_3, as well as with Na_2CrO_4, to give the "chromite" $NaCrO_2$, in which both cations have octahedral coordination.

Other Binary Compounds. The chromium sulfide system is very complex, with two forms of Cr_2S_3 and several intermediate phases between these and CrS. Rhombohedral Cr_2S_3 has complex electrical and magnetic properties.

18-C-3. The Chemistry of Chromium(II)

Mononuclear Compounds; The Aqua Ion. This ion is bright blue and is best obtained in solution by dissolving the very pure metal in deoxygenated, dilute mineral acids or by reducing Cr^{III} solutions electrolytically or with Zn/Hg. The ion is readily oxidized:

$$Cr^{3+} + e = Cr^{2+} \qquad E^0 = -0.41 \text{ V}$$

and the solutions must be protected from air—even then, they decompose at rates varying with acidity and the anions present, by reducing water with liberation of hydrogen.

The Cr^{2+} aqua ion undergoes hydrolysis[3]

$$Cr^{2+}(aq) = CrOH^{+}(aq) + H^{+}(aq) \qquad pK = -5.30$$

and is not strongly complexed in aqueous solution.

The aqua ion has been extensively used as a reductant in mechanistic studies, since the resulting Cr^{III} species are substitution inert and can provide evidence as to the participation of bridging groups in the electron transfer step. This aspect is treated in detail in Section 29-10. It has been proposed that oxidation of the aqua ion by O_2 gives first the CrO_2Cr group, which undergoes protonation to $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{2+}$; this in turn splits to give $[Cr(H_2O)_6]^{3+}$, which according to labeling studies, contains all atoms originally in the O_2.

The $Cr^{2+}(aq)$ ion reacts readily with alkyl halides, apparently by a radical mechanism, to generate $[RCr(H_2O)_5]^{2+}$ ions; these in turn can be cleaved by H_3O^+. On the basis of these fundamental processes, $Cr^{2+}(aq)$ finds important use as a reductant for organic compounds, especially in aqueous DMF as solvent, with ethylenediamine present to complex the Cr^{III} produced.

Mononuclear Complexes. Chromium(II) forms three major types of discrete complexes: (1) High-spin ($S = 2$) "octahedral" complexes, which show marked tetragonal distortion owing to the Jahn–Teller effect; (2) low-spin ($S = 1$) octahedral complexes; (3) square complexes. The low-spin octahedral complexes, which require strong-field ligands, are represented by $[Cr(CN)_6]^{4-}$, $[Cr(bipy)_3]^{2+}$, $[Cr(phen)_3]^{2+}$, $[Cr(phen)_2(NCS)_2]$, and $[Cr(diars)X_2]$ (X = Cl, Br, and I). The high-spin "octahedral" complexes are relatively unstable towards hydrolysis.

The square complexes, which may be thought of as the asymptotic limit of tetragonal Jahn–Teller distortion of high-spin six-coordinate species, are numerous and stable. Representative complexes are $Cr(acac)_2$, the $Cr(R_2Bpz_2)_2$ compounds with R = H or Et,[4] a series of Schiff base complexes[5] such as (18-C-I) and (18-C-II), and the tetraphenylporphyrin complex, which takes up to two pyridine ligands to become low-spin $[Cr(porph)py_2]$. A *trans*-$CrBr_2(H_2O)_2$ unit is found in the compound $CrBr_2(H_2O)_2{\cdot}(pyH)Br$.[6]

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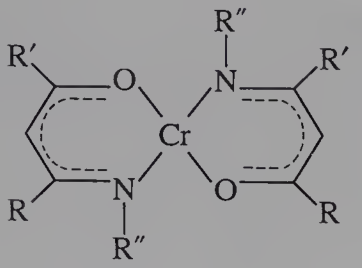
[3] I. Nagypal *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 1335.

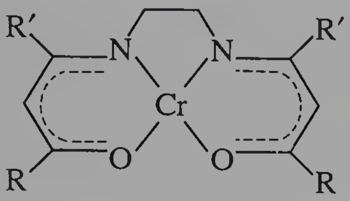
[4] F. A. Cotton and G. N. Mott, *Inorg. Chem.,* 1983, **22,** 1136.

[5] L. F. Larkworthy *et al., Inorg. Chim Acta,* 1984, **83,** L29.

[6] L. F. Larkworthy *et al., J. Chem. Soc. Dalton Trans.,* **1984,** 2351.



(18-C-I)



(18-C-II)

With tripod ligands, five-coordinate *tbp* complexes are formed, for example, $[Cr(Me_6tren)Br]^+$ and $[Cr(pn_3)I]^+$, and with the very bulky Me_3CO^- an unusual T-shaped three-coordinate species is formed in $Cr(OCMe_3)_2 \cdot LiCl(THF)_2$.[7] There is also a series of thiourea complexes, all high spin, but not structurally characterized.[8]

Finally, we should mention that there are numerous compounds of the types $M^I_2CrX_4$ and M^ICrX_3 that contain infinite polymer anions. Many of the former have the K_2NiF_4 structure or a similar one and they display complex and unusual magnetic properties (e.g., ferromagnetism) at very low temperatures.[9] The M^ICrCl_3 compounds have high-spin Cr^{II} ions in distorted octahedra and show antiferromagnetism.

Binuclear Compounds: Quadruple Bonds.[10] One of the earliest Cr^{II} compounds discovered (1844) was the acetate hydrate $Cr_2(O_2CCH_3)_4(H_2O)_2$. It was long recognized as anomalous because it is red and diamagnetic, whereas the mononuclear Cr^{II} compounds are blue or violet and strongly paramagnetic. This compound, as well as numerous others of the general formula

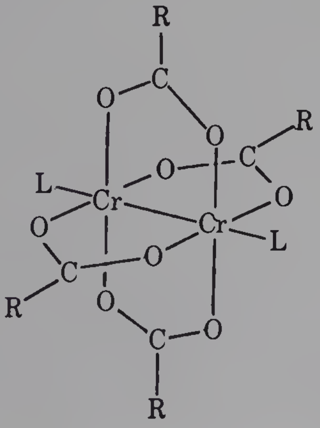


FIG. 18-C-1. The general structure of Cr^{II} carboxylate compounds.

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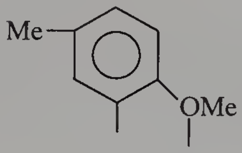
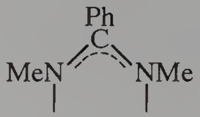
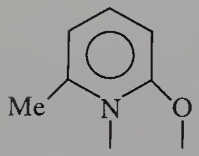
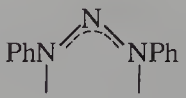
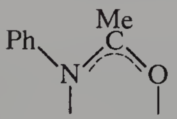
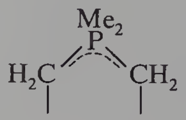
[7] P. P. Power *et al., J. Chem. Soc. Chem. Commun.,* **1983,** 1438.

[8] L. F. Larkworthy and M. H. O. Nelson-Richardson, *Inorg. Chim Acta,* 1980, **40,** 217.

[9] P. Day *et al., Inorg. Chem.,* 1985, **24,** 558.

[10] F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms,* Chapter 4, Wiley, New York, 1982.

TABLE 18-C-3
Some Bridging Ligands That Occur in Cr^{II} Compounds with Strong Quadruple Bonds

Ligand	$d_{Cr—Cr}$(Å)	Ligand	$d_{Cr—Cr}$(Å)
	1.828(2)		1.843(2)
	1.889(1)		1.858(1)
	1.873(4)		1.895(3)

$Cr_2(O_2CR)_4L_2$, have the type of structure[11] shown in Fig. 18-C-1. The chromium atoms are united by a quadruple bond (Section 23-14) but the strength of this interaction is a sensitive inverse function of the strength of the axial ligand bonding, and also (to a much lesser extent) sensitive to the basicity of the RCO_2^- groups. The Cr—Cr distances vary from 2.28 to ~2.54 Å. In the $Cr_2(O_2CCH_3)_4$ molecule itself, which was studied in the gas phase by electron diffraction[12] because axial interactions of some kind always occur in condensed phases, the Cr—Cr distance is 1.96 Å, which is similar to those in numerous other Cr_2^{4+} compounds where there are no axial ligands and hence very strong Cr—Cr quadruple bonds. These other compounds are nearly all of the type in which the $[Cr \equiv Cr]^{4+}$ unit is bridged by a ligand with two donor atoms separated by one other atom, and some representative ones, together with the Cr—Cr distance they span are listed in Table 18-C-3. The shortest Cr—Cr quadruple bond known has a length of only 1.828 (2) Å.

The relationship between reactivity and the strength of the Cr—Cr bond is not a direct one. Thus, while the second compound in Table 18-C-3 is one of the most generally stable compounds of Cr^{II} known, so also are the glycine complexes, $[Cr_2(O_2CCH_2NH_3)_4X_2]X_2$ (X = Cl and Br) which are permanently stable in air, even though their Cr—Cr distances are ~2.51 Å.[13]

18-C-4. The Chemistry of Chromium(III), d^3

Chromium(III) Complexes. There are literally thousands of chromium (III) complexes that with a few exceptions, are all hexacoordinate. The prin-

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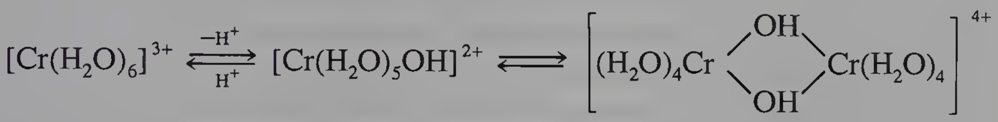
[11] F. A. Cotton and W. Wang, *Nouv. J. Chim.*, 1984, **8,** 331.
[12] S. N. Ketkar and M. Fink, *J. Am. Chem. Soc.*, 1985, **107,** 338.
[13] A. Bino *et al.*, *Inorg. Chem.*, 1984, **23,** 3450.

cipal characteristic of these complexes in aqueous solutions is their relative kinetic inertness.

Ligand displacement reactions of Cr^{III} complexes are only ~10 times faster than those of Co^{III}, with half-times in the range of several hours. It is largely because of this kinetic inertness that so many complex species can be isolated as solids and that they persist for relatively long periods of time in solution, even under conditions of marked thermodynamic instability.

The hexaaqua ion $[Cr(H_2O)_6]^{3+}$, which is regular octahedral, occurs in aqueous solution and in numerous salts such as the violet hydrate $[Cr(H_2O)_6]Cl_3$ and in an extensive series of alums $M^ICr(SO_4)_2 \cdot 12H_2O$. The chloride has three isomers, the others being the dark green *trans*-$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$, which is the normal commercially available salt, and pale green $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$. The aqua ion is acidic (pK = 4), and the hydroxo ion condenses to give a dimeric hydroxo bridged species:

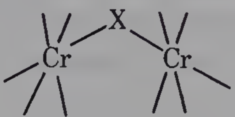


$$[Cr(H_2O)_6]^{3+} \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} [Cr(H_2O)_5OH]^{2+} \rightleftharpoons \left[(H_2O)_4Cr\begin{matrix}OH\\ \\ OH\end{matrix}Cr(H_2O)_4\right]^{4+}$$

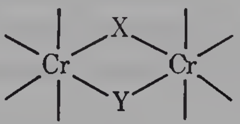
On addition of further base, a precipitate that consists of H-bonded layers of $Cr(OH)_3(H_2O)_3$, and readily redissolves in acid, is formed. Within a minute or less, however, this precipitate begins "aging" to an oligomeric or polymeric structure that is much less soluble.[14]

The ammonia and amine complexes are the most numerous chromium derivatives and the most extensively studied. They include the pure ammines $[CrAm_6]^{3+}$, the mixed ammine–aqua types, that is, $[CrAm_{6-n}(H_2O)_n]^{3+}$ (n = 0–4, 6), the mixed ammine–acido types, that is, $[CrAm_{6-n}R_n]^{(3-n)+}$ (n = 1–4, 6), and mixed ammine–aqua–acido types, for example, $[CrAm_{6-n-m}(H_2O)_nR_m]^{(3-m)+}$. In these general formulas Am represents the monodentate ligand NH_3 or half of a polydentate amine such as ethylenediamine, and R represents an acido ligand such as halide, nitro, or sulfate ion. These complexes provide examples of virtually all the kinds of isomerism possible in octahedral complexes.

The preparation of polyammine complexes sometimes presents difficulties, partly because in neutral or basic solution hydroxo or oxobridged polynuclear complexes are often formed. Such polyammines are often conveniently prepared from the Cr^{IV} peroxo species, noted below; thus the action of HCl on $[Cr^{IV}en(H_2O)(O_2)_2] \cdot H_2O$ forms the blue salt $[Cr^{III}en(H_2O)_2Cl_2]Cl$.



(18-C-III)



(18-C-IV)

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[14] L. Spiccia *et al., Inorg. Chem.*, 1987, **26**, 474; see also D. Rai *et al., Inorg. Chem.*, 1987, **26**, 345.

The majority of polynuclear complexes are of one of the types (18-C-III) or (18-C-IV). In the former there is a single bridging group, which is usually O or OH. Some representative reactions involving such compounds are shown below.

$$\begin{tikzcd}
{[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}} \arrow[r, shift left, "OH^-"] \arrow[d, "\begin{array}{l}H_2O\\ \text{1 day}\\ 100^\circ C\end{array}"] & {[(NH_3)_5CrOCr(NH_3)_5]^{4+}} \arrow[l, shift left, "H^+"] \arrow[d, "\begin{array}{l}OH^-\\ \text{several days}\\ 25^\circ C\end{array}"] \\
{[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}} & {[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]^{4+}} \arrow[l, "H^+"']
\end{tikzcd}$$

The oxo-bridged complex has a linear Cr—O—Cr group, indicating $d\pi$–$p\pi$ bonding as in other cases of M—O—M groups. Even in the "acid rhodo" complex $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ the bridge is nearly linear ($\angle$Cr—O—Cr = 166°), and there is considerable magnetic coupling. A large number of the (18-C-IV) type of complex are known, especially with X = Y = OH. Many have been carefully studied both structurally and magnetically.[15] All show a repulsion between the Cr^{III} atoms (distances >3.0 Å) and weak but significant magnetic interactions that are nearly always antiferromagnetic. Other bridged dichromium(III) complexes have also been studied; Cr^{III}–Cr^{III} systems are almost as popular as the Cu^{II}–Cu^{II} complexes for studies of such magnetic interactions.

Anionic complexes are also common and are of the type $[CrX_6]^{3-}$, where X may be F^-, Cl^-, NCS^-, or CN^-, but they may also have lower charges if neutral ligands are present as in the ion $[Cr(NCS)_4(NH_3)_2]^-$. Complexes of bi- or polydentate anions are also known, one example being $[Cr\ ox_3]^{3-}$.

A different type of anionic complex is represented by the $Cr_2X_9^{3-}$ ions, which have a confacial bioctahedron structure similar to $W_2Cl_9^{3-}$ (Section 23-13) except that the Cr^{3+} ions repel each other from the centers of their octahedra and the magnetic moments are normal, indicating that there is no Cr—Cr bond.

As expected, Cr^{III} can also form complexes of other types, including neutral complexes with β-diketonates and similar ligands [e.g., $Cracac_3$ and $Cr(OCOCF_3)_3$]. It also forms oxo-centered trinuclear carboxylates (Section 12-9) such as $[Cr_3O(O_2CMe)_6(H_2O)_3]^+$, which has the structure (12-VIII).

Distorted tetrahedral coordination, presumably due to extreme steric factors, is found in the compound $LiCr[OCH(CMe_3)_2]_4\cdot THF$.[16]

The coordination number 3 occurs in dialkylamides [e.g., $Cr(N\text{-}i\text{-}Pr_2)_3$]. A combination of steric factors and multiple bonding has been proposed to explain the stability of such monomers. Another of the rare nonoctahedral Cr^{III} complexes is that shown in (18-C-V), where there is distorted pentagonal bipyramid.[17]

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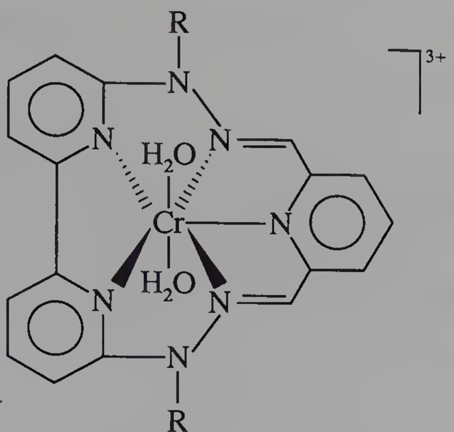
[15] D. J. Hodgson *et al., Inorg. Chem.*, 1983, **22,** 637; 1984, **23,** 4755.

[16] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1980,** 1863.

[17] J. Lewis *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 1425.



(18-C-V)

Compounds of formula M^ICrX_4 such as $KCrF_4$ and $[PCl_4][CrCl_4]$, contain CrX_6 octahedra with some sharing of the X atoms.

Finally, as noted previously, $CrCl_3$ forms numerous adducts with ethers, nitriles, amines, and phosphines, which have formulas $CrCl_3{\cdot}2L$ or $CrCl_3{\cdot}3L$. The adduct $CrCl_3{\cdot}2NMe_3$ provides another of the very few examples of an authenticated nonoctahedral Cr^{III} complex; here X-ray studies confirm the trigonal bipyramidal structure with axial amine groups. Halide-bridged complexes such as $[CrCl_3(PR_3)_2]_2$ have been prepared by direct interaction.

Electronic Structures of Chromium(III) Complexes. The magnetic properties of the octahedral Cr^{III} complexes are uncomplicated. All such complexes must have three unpaired electrons irrespective of the strength of the ligand field, and this has been confirmed for all known mononuclear complexes. More sophisticated theory further predicts that the magnetic moments should be very close to, but slightly below, the spin-only value of 3.88 BM; this, too, is observed experimentally.

The spectra of Cr^{III} complexes are also well understood in their main features. A partial energy level diagram (Fig. 18-C-2) indicates that three spin-allowed transitions are expected, and these have been observed in a considerable number of complexes. Indeed, the spectrochemical series was originally established by Tsuchida using data for Cr^{III} and Co^{III} complexes. In the aqua ion the bands are found at 17,400, 24,700, and 37,000 cm^{-1}.

Ruby, natural or synthetic, is α-Al_2O_3 containing occasional Cr^{III} ions in place of Al^{III} ions. The environment of the Cr^{III} in ruby is thus a slightly distorted (D_{3d}) octahedron of oxide ions. The frequencies of the spin-allowed bands of Cr^{III} in ruby indicate that the Cr^{III} ions are under considerable compression, since the value of Δ_0 calculated is significantly higher than in the $[Cr(H_2O)_6]^{3+}$ ion or in other oxide lattices and glasses. Also, in ruby, spin-forbidden transitions from the $^4A_2$ ground state to the doublet states arising from the ^2G state of the free ion are observed. The transitions to the ^2E and $^2T_1$ states give rise to extremely sharp lines because the slopes of the

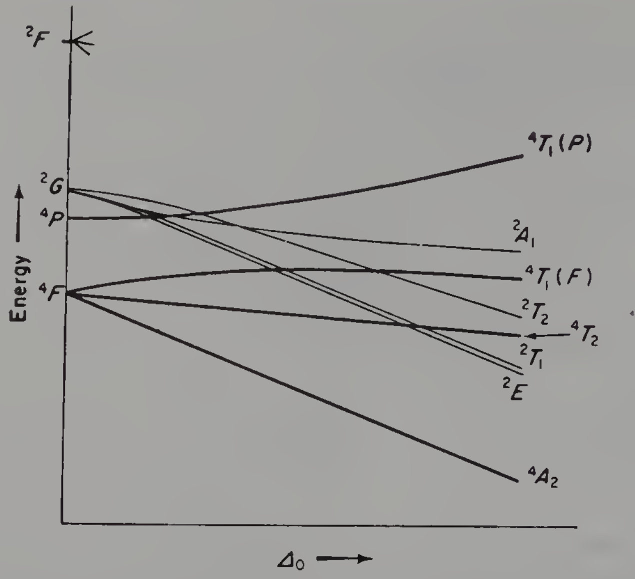


FIG. 18-C-2. Partial energy level diagram for a d^3 ion in an octahedral field (also for a d^7 ion in a tetrahedral field). The quartet states are drawn with heavier lines.

energy lines for these states are the same as that for the ground state (except in extremely weak fields).

The same doublet states play a key role in the operation of the ruby laser. In this device a large single crystal of ruby is irradiated with light of the proper frequency to cause excitation to the $^4T_2(F)$ state. The exact magnitudes of certain energy differences and relaxation times are such, in the ruby, that the system rapidly makes a radiationless transition (i.e., by loss of energy to the crystal lattice in the form of vibrations) to the ^2E and $^2T_1$ states, instead of decaying directly back to the ground state. The systems then return from these doublet states to the ground state by stimulated emission of very sharp lines that are in phase with the stimulating radiation. Thus bursts of extremely intense, monochromatic, and coherent (all emitters in phase) radiation are obtained, which are of use in communication and as sources of energy.

Organochromium(III) Complexes. Mention has already been made of the reactions of Cr^{2+} with alkyl halides to generate RCr^{2+} species, which can be complexed by additional ligands. The hydrolysis of the Cr—C bonds occurs slowly by a homolytic pathway.[18] In addition, there are a number of other alkyls and aryls of formula CrR_3L_n, where L is usually an ether molecule such as THF. These are obtained by the action of lithium alkyls or Grignard reagents on $CrCl_3 \cdot 3THF$. The alkyls are rather unstable and their modes of decomposition have been greatly studied, but the aryls such as $Cr(C_6H_5)_3 \cdot 3THF$ are considerably more stable. Some anionic methyl complex anions, for example, $Li_3[Cr(CH_3)_6]$, are also reasonably stable, as is the six-coordinate chelate complex $[Cr\{(CH_2)_2PMe_2\}_3]$ (see Chapter 25).

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[18] J. H. Espenson, in *Advances in Inorganic and Bioinorganic Mechanisms*, Vol. 1, A. G. Sykes, Ed., Academic Press, New York, 1982; K. Crouse and L. Goh, *Inorg. Chem.*, 1986, **25**, 478.

18-C-5. The Chemistry of Chromium(IV), d^2

Chromium(IV) chemistry is limited, but growing.[19] The classical compounds are oxides and fluorides. The oxide CrO_2 is well defined, and there are some mixed oxides such as the deep green Na_4CrO_4 and the blue black $M_2^{II}CrO_4$ (M^{II} = Sr and Ba). The latter are stable in air and contain discrete CrO_4^{4-} groups with magnetic moments of ~2.8 BM. Preparative reactions are

$$NaCrO_2 + 2Na_2O \xrightarrow{1000°C} Na_4CrO_4 + Na\uparrow$$

$$SrCrO_4 + Cr_2O_3 + 5Sr(OH)_2 \xrightarrow{1000°C} 3Sr_2CrO_4 + 5H_2O\uparrow$$

The compounds $M_3^{II}CrO_5$ and $M_4^{II}CrO_6$ have also been reported. There are also some peroxo species, mentioned in Section 18-C-8.

There are no Cr^{IV} halides or halo complexes that are stable except the fluoro species CrF_4, $CrOF_2$, $M_2^{I}CrF_6$, and $M^{II}CrF_6$, the latter arising by fluorination of stoichiometric mixtures of $CrCl_3$ and $M^{I}Cl$ or $M^{II}Cl_2$.

There is an interesting series of relatively stable, volatile, monomeric species, all of which are paramagnetic, and green or blue in color: CrX_4 compounds with X = $c\text{-}C_6H_{11}$,[20] $Me_2C{=}CPh$—,[21] Me_3SiCH_2—, Et_2N—, Me_3CO—, and $(Me_3C)_2HCO$—.[16] The alkyls are obtained by reactions of RMgX or RLi with $CrCl_3(THF)_3$ followed by oxidation and the Et_2N— compound by disproportionation of $(Et_2N)_3Cr$. The alkoxides can be made by reaction of the amide with the alcohols. All of these compounds consist of tetrahedral molecules.

There is a relatively stable (tetraphenylporphyrin)CrO complex,[22a] dodecahedral hydride, $CrH_4(dmpe)_2$, and some octahedral species such as $\{Cr[NC(H)Me]_2(dmpe)_2\}^{2+}$.[22b]

18-C-6. The Chemistry of Chromium(V), d^1

This is a small but growing area.[19,23] In addition to the stable compounds to be mentioned later, there are many observations of transient Cr^V species by esr spectroscopy[24] as well as similar evidence for Cr^V in certain oxide lattices and catalysts. Electron spin resonance detection of this d^1 ion, usually in an

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[19] N. Nag and S. N. Bose, *Struct. Bonding, Berlin,* 1985, **63**, 153.

[20] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1987**, 557.

[21] C. J. Cardin *et al., J. Chem. Soc. Dalton Trans.,* **1983**, 671.

[22a] S. E. Creager and R. W. Murray, *Inorg. Chem.,* 1985, **24,** 3824; D. J. Liston and B. O. West, *Inorg. Chem.,* 1985, **24,** 1568.

[22b] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 685; **1987,** 2947.

[23] M. Mitewa and P. R. Bontchev, *Coord. Chem. Rev.,* 1985, **61,** 241.

[24] J. T. Groves and R. C. Haushalter, *J. Chem. Soc. Chem. Commun.,* **1981,** 1165; M. Mitewa *et al., Inorg. Chim. Acta,* 1983, **70,** 179; D. M. L. Goodgame *et al., Inorg. Chim. Acta,* 1984, **91,** 113; F. Freeman *et al., J. Chem. Soc. Chem. Commun.,* **1980,** 65; P. O'Brien *et al., Inorg. Chim Acta,* 1985, **108,** L19; D. M. L. Goodgame and A. M. Joy, *Inorg. Chim. Acta,* 1987, **135,** 115.

axially symmetric environment is relatively easy. The reduction of Cr^{VI} by oxalic acid, citric acid, isopropanol, and various other organic reductants gives esr-detectable Cr^{V} intermediates of varying lifetimes, and on dissolving chromates(VI) in 65% oleum, blue solutions containing Cr^{V} species are formed.

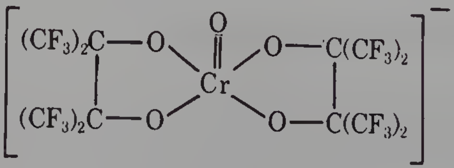
The stable compounds of Cr^{V} nearly all involve oxygen and/or the halogens. Dark green, hygroscopic chromates(V) such as Li_3CrO_4, Na_3CrO_4, and $Ca_3[CrO_4]_2$ contain discrete tetrahedral CrO_4^{3-} ions, and one-electron reduction of $HCrO_4^-$ in acid solution apparently gives H_3CrO_4. It should be noted that the series of $M^{I}Cr_3O_8$ compounds do *not* contain Cr^{V}, but rather are built of $Cr^{VI}O_4$ tetrahedra and $Cr^{III}O_6$ octahedra.

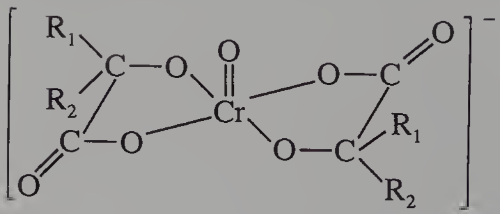
The pentafluoride has been mentioned (Section 18-C-2). The oxofluoride can be prepared in several ways[25] (e.g., by action of ClF_3 or BrF_3 on CrO_3) but the pure crystalline, solid is obtained by the reaction:

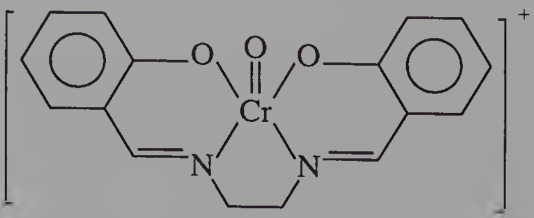
$$XeF_2 + 2CrO_2F_2 \longrightarrow 2CrOF_3 + Xe + O_2$$

The crystal structure consists of an infinite three-dimensional array of corner-shared $CrOF_5$ octahedra.[26] Chromium oxotrichloride ($CrOCl_3$), which can be made by reaction of $SOCl_2$ with CrO_3 or BCl_3 with CrO_2Cl_2, is volatile, although its crystal structure is unknown. It has been thoroughly studied in Kr and Ar matrices where it has C_{3v} molecular symmetry.[27]

Among the most stable Cr^{V} compounds are complexes of the CrO^{3+} ion. Many compounds containing the $[CrOX_4]^-$ (X = F, Cl, and Br) ions have been prepared and well characterized. These species are square pyramidal, with very short Cr—O distances (~1.52 Å), magnetic moments of ~1.7 BM, and ν_{Cr-O} values of ~1000 cm^{-1}. There are also a number of CrO^{3+} complexes in which the four basal positions of the square pyramid are occupied by O


(18-C-VI)


(18-C-VII)


(18-C-VIII)

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[25] W. Levason *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 2445.
[26] G. L. Gard *et al.*, *Inorg. Chem.*, 1986, **25,** 426.
[27] J. S. Ogden *et al.*, *J. Chem. Soc. Dalton Trans.*, **1980**, 419.

or N atoms[28] as in (18-C-VI) and (18-C-VII). The Schiff base type 18-C-VIII can be very conveniently prepared by treating the Cr^{III} complex, for example, $Cr(sal_2en)^+$ with PhIO.[29]

18-C-7. The Chemistry of Chromium(VI), d^0

Chromate and Dichromate Ions. In basic solutions above pH 6, CrO_3 forms the tetrahedral yellow *chromate* ion CrO_4^{2-}; between pH 2 and 6, $HCrO_4^-$ and the orange-red *dichromate* ion $Cr_2O_7^{2-}$ are in equilibrium; and at pH values <1 the main species is H_2CrO_4. The equilibria are the following:

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad K = 10^{-5.9}$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad K = 4.1$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \qquad K = 10^{-2.2}$$

In addition there are the base-hydrolysis equilibria:

$$Cr_2O_7^{2-} + OH^- \rightleftharpoons HCrO_4^- + CrO_4^{2-}$$

$$HCrO_4^- + OH^- \rightleftharpoons CrO_4^{2-} + H_2O$$

which have been studied kinetically for a variety of bases.

The pH-dependent equilibria are quite labile, and on addition of cations that form insoluble chromates (e.g., Ba^{2+}, Pb^{2+}, and Ag^+) the chromates and not the dichromates are precipitated. Furthermore, the species present depend on the acid used, and only for HNO_3 and $HClO_4$ are the equilibria as given. When hydrochloric acid is used, there is essentially quantitative conversion into the chlorochromate ion; with sulfuric acid a sulfato complex results:

$$CrO_3(OH)^- + H^+ + Cl^- \longrightarrow CrO_3Cl^- + H_2O$$

$$CrO_3(OH)^- + HSO_4^- \longrightarrow CrO_3(OSO_3)^{2-} + H_2O$$

Orange potassium chlorochromate can be prepared simply by dissolving $K_2Cr_2O_7$ in hot 6*M* HCl and crystallizing. It can be recrystallized from HCl but is hydrolyzed by water:

$$CrO_3Cl^- + H_2O \longrightarrow CrO_3(OH)^- + H^+ + Cl^-$$

The potassium salts of CrO_3F^-, CrO_3Br^-, and CrO_3I^- are obtained similarly. They owe their existence to the fact that dichromate, though a powerful oxidizing agent, is kinetically slow in its oxidizing action toward halide ions. The pyridinium salt of CrO_3F^- finds use as an oxidant in organic chemistry.[30]

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[28] R. N. Bose *et al.*, *Inorg. Chem.*, 1986, **25**, 165; E. S. Gould *et al.*, *Inorg. Chem.*, 1987, **26**, 899; P. A. Lay *et al.*, *Inorg. Chim.*, 1987, **26**, 2189.

[29] K. Srinivasan and J. K. Kochi, *Inorg. Chem.*, 1985, **24** 4671.

[30] M. N. Bhattacharjee *et al.*, *Synthesis*, **1982,** 588; T. Nonaka *et al.*, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2019.

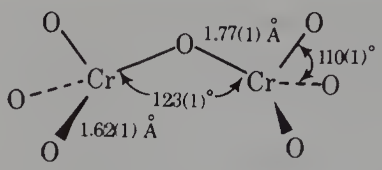

FIG. 18-C-3. The structure of the dichromate ion as found in $Rb_2Cr_2O_7$ (P. Löfgren and K. Waltersson, *Acta Chem. Scand.*, 1971, **25**, 35).

Acid solutions of dichromate are strong oxidants:

$$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O \qquad E^0 = 1.33 \text{ V}$$

The mechanism of oxidation of Fe^{2+} and other common ions by Cr^{VI} has been studied in detail; with one- and two-electron reductants, respectively, Cr^{V} and Cr^{IV} are initially formed. The reaction with H_2O_2 in acid solution has a very complex and imperfectly understood mechanism.

The chromate ion in basic solution, however, is much less oxidizing:

$$CrO_4^{2-} + 4H_2O + 3e = Cr(OH)_3(s) + 5OH^- \qquad E^0 = -0.13 \text{ V}$$

Chromium(VI) does not give rise to the extensive and complex series of polyacids and polyanions characteristic of the somewhat less acidic oxides of V^V, Mo^{VI}, and W^{VI}. The reason for this is perhaps the greater extent of multiple bonding (Cr=O) for the smaller chromium ion. However, compounds containing the $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ ions are known; the structures continue the pattern set by the $Cr_2O_7^{2-}$ ion (Fig. 18-C-3) in having chains of CrO_4 tetrahedra sharing corners. In the limit of course we have CrO_3, which consists of infinite chains of corner-sharing tetrahedra —O—CrO_2—O—.

Oxohalides. Five of these are known. The only oxohalide with the $CrOX_4$ stoichiometry, $CrOF_4$ (mp 55°C, bp 95°C), can be obtained by fluorination of CrO_3[31] or by reaction of CrO_2F_2 with KrF_2 in liquid HF.[32] In the gaseous state as well as in various solutions and inert gas matrices it consists of square pyramidal molecules; the solid has a fluorine-bridged polymeric structure. It shows little activity as either a Lewis acid or base, but does form some salts, for example, $NO^+CrOF_5^-$ and $Cs[CrOF_5]$.

The most important oxohalide is chromyl chloride, CrO_2Cl_2 (bp 117°C). There are analogous CrO_2F_2, CrO_2Br_2,[33a] and CrO_2ClBr[33a] molecules, although the last is incompletely characterized. The related molecules $CrO_2(O_2CCF_3)_2$ and $CrO_2(ONO_2)_2$ and alkoxides,[33b] $CrO_2(OR)_2$, are known. The compound CrO_2Cl_2 is formed by the action of HCl on chromium(VI) oxide:

$$CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O$$

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[31] W. Levason *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 529.
[32] K. O. Christe *et al., Inorg. Chem.*, 1986, **25**, 2163.
[33a] W. Levason, *J. Chem. Soc. Dalton Trans.*, **1986**, 1587.
[33b] S. L. Chadha *et al., J. Chem. Soc. Dalton Trans.*, **1987**, 1253.

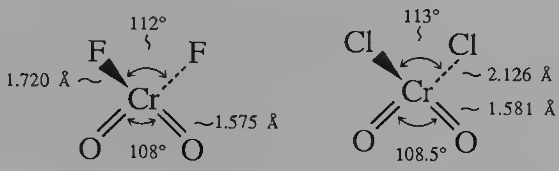

FIG. 18-C-4. The molecular structures (from ref. 35) of CrO_2F_2 and CrO_2Cl_2.

by warming dichromate with an alkali metal chloride in concentrated sulfuric acid:

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 3K_2SO_4 + 3H_2O$$

and in other ways. It is photosensitive but otherwise rather stable, although it vigorously oxidizes organic matter, sometimes selectively. It is hydrolyzed by water to the chromate ion and hydrochloric acid.

The vibrational spectra[33a,34] and structures[35] of the CrO_2X_2 molecules have been carefully studied. The structural results for the fluoride and chloride are shown in Fig. 18-C-4. The C_{2v} symmetry and bond lengths are as expected, but it is to be noted that these molecules have angles that are not in accord with the VSEPR theory (thus differing from SO_2F_2 and SO_2Cl_2, which are in accord) in that the angle between the doubly bonded ligands is smaller rather than larger than that between the singly bonded ligands. No straightforward explanation for this has yet been suggested.

18-C-8. Peroxo Complexes of Chromium(IV), (V), and (VI)

Like other transition metals, notably Ti, V, Nb, Ta, Mo, and W, chromium forms peroxo compounds in the higher oxidation states. They are all more or less unstable, and in the solid state some of them are dangerously explosive or flammable in air.

When acid dichromate solutions are treated with hydrogen peroxide, a deep blue color rapidly appears but does not persist long. The overall reaction is

$$2HCrO_4^- + 3H_2O_2 + 8H^+ \longrightarrow 2Cr^{3+} + 3O_2 + 8H_2O$$

but depending on the conditions, the intermediate species may be characterized. At temperatures below 0°C, green cationic species are formed:

$$2HCrO_4^- + 4H_2O_2 + 6H^+ \longrightarrow Cr_2(O_2)^{4+} + 3O_2 + 8H_2O$$

$$6HCrO_4^- + 13H_2O_2 + 16H^+ \longrightarrow 2[Cr_3(O_2)_2]^{5+} + 9O_2 + 24H_2O$$

The blue species, which is one of the products at room temperature,

$$HCrO_4^- + 2H_2O_2 + H^+ \longrightarrow CrO(O_2)_2 + 3H_2O$$

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[34] I. R. Beattie *et al.*, *J. Chem. Soc. Dalton Trans.*, **1980**, 535.

[35] K. Hedberg *et al.*, *Inorg. Chem.*, 1982, **21**, 1115; 1983, **22**, 892.

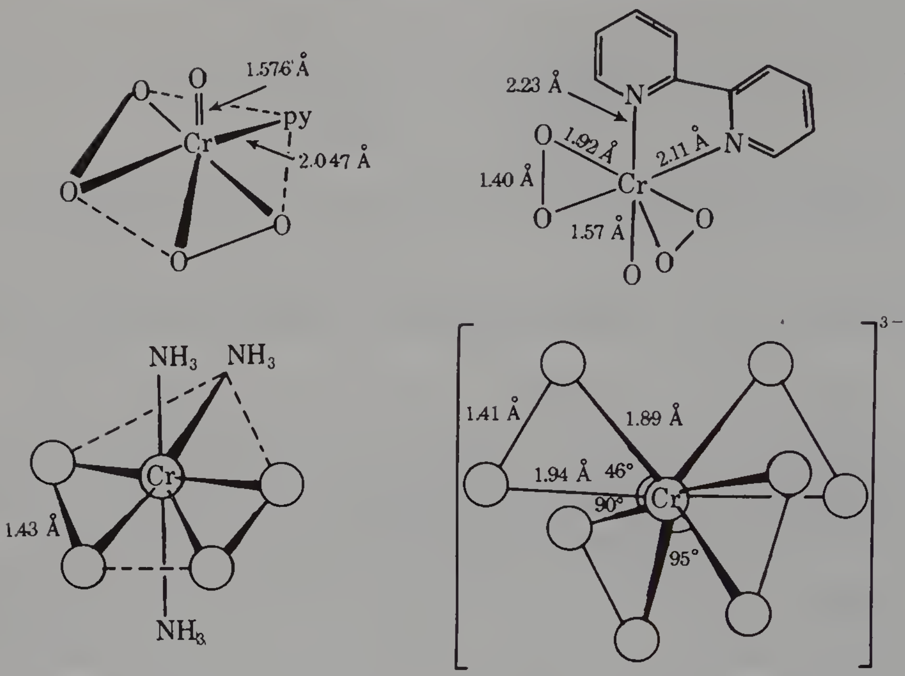

FIG. 18-C-5. The structures of some peroxo chromium species mentioned in the text.

decomposes fairly readily, giving Cr^{3+}, but it may be extracted into ether where it is more stable and, on addition of pyridine to the ether solution, the compound $pyCrO_5$, a monomer in benzene and essentially diamagnetic, is obtained. The structures of two typical adducts, $pyCrO_5$ and $bipyCrO_5$ are shown in Fig. 18-C-5. These compounds can be used to hydroxylate hydrocarbons.[36]

The action of H_2O_2 on neutral or slightly acidic solutions of K, NH_4, or Tl dichromate leads to diamagnetic, blue-violet, violently explosive salts, believed to contain the ion $[Cr^{VI}O(O_2)_2OH]^-$.

On treatment of alkaline chromate solutions with 30% hydrogen peroxide—and after further manipulations—the red-brown peroxochromates $M^I_3CrO_8$, can be isolated. They are paramagnetic with one unpaired electron per formula unit, and K_3CrO_8 forms mixed crystals with K_3NbO_8 and K_3TaO_8; the heavy metals are pentavalent in both. The $[Cr(O_2)_4]^{3-}$ ion has the dodecahedral structure shown in Fig. 18-C-5. This ion can be converted to the previously mentioned $[Cr(O_2)_2O(OH)]^-$ ion, and there is evidence that the following equilibrium is attained:

$$\underset{\text{Red brown}}{[Cr(O_2)_4]^{3-}} + 2H^+ + H_2O = \underset{\text{Violet}}{[Cr(O_2)_2(O)(OH)]^-} + \tfrac{3}{2}H_2O_2$$

When the reaction mixture used in preparing $(NH_4)_4CrO_8$ is heated to 50°C and then cooled to 0°C, brown crystals of $(NH_3)_3CrO_4$ are obtained. The structure of this molecule is also shown in Fig. 18-C-5.

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[36] H. Mimoun *et al.*, *Nouv. J. Chim.*, 1984, **8**, 271.

The action of H_2O_2 on aqueous solutions of CrO_3 containing ethylenediamine or other amines gives chromium(IV) complexes such as the olive green $[Cren(H_2O)(O_2)_2]\cdot H_2O$. As noted previously, these are useful sources for the preparation of Cr^{III} ammine complexes.

General References

Colton, R., *Coord. Chem. Rev.*, 1984, **58,** 245; 1985, **62,** 85.
Larkworthy, L. F., *Coord. Chem. Rev.*, 1981, **37,** 91; 1982, **45,** 105.

18-D. MANGANESE: GROUP VIIB(7)

As with Ti, V, and Cr, the highest oxidation state of Mn corresponds to the total number of 3*d* and 4*s* electrons. This VII state occurs only in the oxo compounds MnO_4^-, Mn_2O_7, and MnO_3F, and these compounds show some similarity to corresponding compounds of the halogens, for example, in the instability of the oxide. Manganese(VII) is powerfully oxidizing, usually being reduced to Mn^{II}. The intermediate oxidation states are known, but only a few compounds of Mn^V have been characterized; nevertheless, Mn^V species are frequently postulated as intermediates in the reduction of permanganates. Although Mn^{II} is the most stable state, it is quite readily oxidized in alkaline solution.

The oxidation states and stereochemistry are summarized in Table 18-D-1.

18-D-1. The Element

Manganese is relatively abundant, constituting about 0.085% of the earth's crust. Among the heavy metals, only Fe is more abundant. Although widely distributed, it occurs in a number of substantial deposits, mainly oxides, hydrous oxides, or carbonate. It also occurs in nodules on the Pacific seabed together with Ni, Cu, and Co.

The metal is obtained from the oxides by reduction with Al. A large use of Mn is in ferromanganese for steels.

Manganese is roughly similar to Fe in its physical and chemical properties, the chief difference being that it is harder and more brittle but less refractory (mp 1247°C). It is quite electropositive and readily dissolves in dilute, nonoxidizing acids. It is not particularly reactive toward nonmetals at room temperatures, but at elevated temperatures it reacts vigorously with many. Thus it burns in Cl_2 to give $MnCl_2$, reacts with F_2 to give MnF_2 and MnF_3, burns in N_2 above 1200°C to give Mn_3N_2, and combines with O_2, giving Mn_3O_4, at high temperatures.

TABLE 18-D-1
Oxidation States and Stereochemistry of Manganese

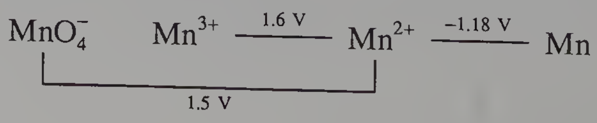
Oxidation state	Coordination number	Geometry	Examples
Mn^{-III}	4	Tetrahedral	$Mn(NO)_3CO$
Mn^{-II}	4 or 6	Square	$[Mn(phthalocyanine)]^{2-}$
Mn^{-I}	5	*tbp*	$Mn(CO)_5^-$, $[Mn(CO)_4PR_3]^-$
	4 or 6	Square	$[Mn(phthalocyanine)]^-$
Mn^0	6	Octahedral	$Mn_2(CO)_{10}$
Mn^I, d^6	6	Octahedral	$Mn(CO)_5Cl$, $K_5[Mn(CN)_6]$, $[Mn(CNR)_6]^+$
Mn^{II}, d^5	2	Linear	$Mn[C(SiMe_3)_2]_2$[a]
	4	Tetrahedral	$MnCl_4^{2-}$, $MnBr_2(OPR_3)_2$, $[Mn(CH_2SiMe_3)_2]_n$
	4	Square	$[Mn(H_2O)_4]SO_4 \cdot H_2O$, $Mn(S_2CNEt_2)_2$
	5	Distorted *tbp*	$MnBr_2[(MeHN)_2CO]_3$[c]
		tbp	$[Mn(trenMe_6)Br]Br$
	6[b]	Octahedral	$[Mn(H_2O)_6]^{2+}$, $[Mn(NCS)_6]^{4-}$
	7	NbF_7^{2-} structure	$[Mn(EDTA)H_2O]^{2-}$[d]
		Pentagonal bipyramidal	$MnX_2(N_5$ macrocycle$)$[d]
	8	Dodecahedral	$(Ph_4As)_2Mn(NO_3)_4$
Mn^{III}, d^4	4	Square	$[Mn(S_2C_6H_3Me)_2]^-$[e]
	5	*sp*	MnX sal_2en, $[bipyH_2]MnCl_5$
	5	*tbp*	$MnI_3(PMe_3)_2$[f]
	6[b]	Octahedral	$Mn(acac)_3$, $[Mn(ox)_3]^{3-}$, MnF_3(distorted), $Mn(S_2CNR_2)_3$
	7		$[Mn(EDTA)H_2O]^-$, $MnH_3(dmpe)_2$
Mn^{IV}, d^3	4	Tetrahedral	$Mn(1\text{-norbornyl})_4$
	6	Octahedral	MnO_2, $MnMe_4(dmpe)$, $MnCl_6^{2-}$, $Mn(S_2CNR_2)_3^+$
Mn^V, d^2	4	Tetrahedral	MnO_4^{3-}
Mn^{VI}, d^1	4	Tetrahedral	MnO_4^{2-}
Mn^{VII}, d^0	3	Planar	MnO_3^+
	4[b]	Tetrahedral	MnO_4^-, MnO_3F

[a] C. Eaborn *et al., J. Chem. Soc. Chem. Commun.*, **1985**, 1380.
[b] Most common states.
[c] J. Delaunay and R. P. Hugel, *Inorg. Chem.*, 1986, **25**, 3957.
[d] G. Pelizzi *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 215.
[e] H. Henkel *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 117.
[f] B. Beagley *et al., J. Chem. Soc. Chem. Commun.*, **1984**, 658.

MANGANESE COMPOUNDS

18-D-2. The Chemistry of Divalent Manganese, d^5

The divalent state is the common and most stable oxidation state. In neutral or acid aqueous solution there is the very pale pink hexaaqua ion $[Mn(H_2O)_6]^{2+}$, which is resistant to oxidation as shown by the potentials



$$MnO_4^- \qquad Mn^{3+} \xrightarrow{1.6\ V} \underbrace{Mn^{2+}}_{1.5\ V\ (from\ MnO_4^-)} \xrightarrow{-1.18\ V} Mn$$

In basic media the hydroxide $Mn(OH)_2$ is formed; this is very easily oxidized by air, as shown by the potentials:

$$MnO_2{\cdot}yH_2O \xrightarrow{-0.1\ V} Mn_2O_3{\cdot}xH_2O \xrightarrow{-0.2\ V} Mn(OH)_2$$

Binary Compounds. Manganese(II) oxide is a gray-green to dark green powder made by roasting the carbonate in H_2 or N_2 or by the action of steam on $MnCl_2$ at 600°C. It has the rock salt structure and is insoluble in water. Manganese(II) hydroxide is precipitated from Mn^{2+} solutions by alkali metal hydroxides as a gelatinous white solid that rapidly darkens because of oxidation by atmospheric O_2. The $Mn(OH)_2$ has the same crystal structure as $Mg(OH)_2$. It is only very slightly amphoteric:

$$Mn(OH)_2 + OH^- = Mn(OH)_3^- \qquad K \approx 10^{-5}$$

Hydrous manganese(II) sulfide is a salmon-colored substance precipitated by alkaline sulfide solutions. It has a relatively high K_{sp} (10^{-14}) and redissolves easily in dilute acids. It becomes brown when left in air owing to oxidation; if air is excluded, the material changes on long storage, or more rapidly on boiling, into green, crystalline, anhydrous MnS.

Manganese sulfide, MnSe, and MnTe have the NaCl structure. They are all strongly antiferromagnetic, as are also the anhydrous halides. A superexchange mechanism is believed responsible for their antiferromagnetism.

Manganese(II) Salts. Manganese(II) forms an extensive series of salts with all common anions. Most are soluble in water, although the phosphate and carbonate are only slightly so. Most of the salts crystallize from water as hydrates; those with weakly coordinating anions, such as $Mn(ClO_4)_2{\cdot}6H_2O$ and $MnSO_4{\cdot}7H_2O$, contain $[Mn(H_2O)_6]^{2+}$. However, $MnCl_2{\cdot}4H_2O$ contains *cis*-$MnCl_2(H_2O)_4$ units, and $MnCl_2{\cdot}2H_2O$ has polymeric chains with *trans*-$Mn(H_2O)_2Cl_4$ octahedra sharing edges. The sulfate, $MnSO_4$, obtained on fuming down H_2SO_4 solutions, is quite stable and may be used for Mn analysis, provided no other cations giving nonvolatile sulfates are present.

Manganese(II) Complexes. The equilibrium constants for complex formation in aqueous solution are not high compared to those for Fe^{2+}–Cu^{2+} because the Mn^{II} ion is the largest of these and it has no ligand field stabilization energy in its complexes (except in the few of low spin).

Halide Ligands. The formation constants in aqueous solution are very low, for example,

$$Mn^{2+}_{aq} + Cl^- \rightleftharpoons MnCl^+_{aq} \qquad K \approx 3.85$$

but when ethanol or acetic acid is used as solvent, salts of complex anions of varying types[1] may be isolated, such as:

MnX_3^-	Octahedral with perovskite structure
MnX_4^{2-}	Tetrahedral (green yellow) or polymeric octahedral with halide bridges (pink)

---

[1] U. Kambli and H. U. Güdel, *Inorg. Chem.*, 1984, **23**, 3479.

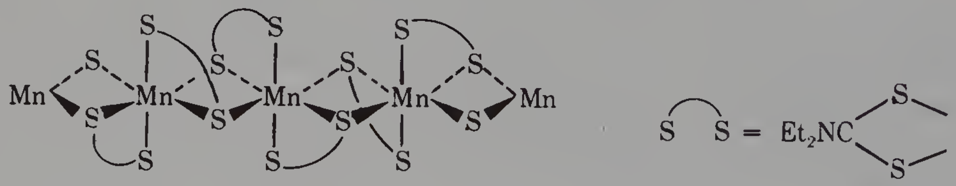
$MnCl_6^{4-}$	Only Na and K salts known; octahedral
$Mn_2Cl_7^{3-}$	With Me_3NH^+, linear chain of face-sharing $MnCl_6$ octahedra; also discrete $MnCl_4^{2-}$, tetrahedral

The precise nature of the product obtained depends on the cation used and also on the halide and the solvent, but MnI_2 gives only MnI_4^{2-}. By contrast, the thiocyanates $M_4^I[Mn(NCS)_6]$ can be crystallized as hydrates from aqueous solution. Salts of ions such as *trans*-$[MnCl_4(H_2O)_2]^{2-}$ and *trans*-$[Mn_2Cl_6(H_2O)_4]^{2-}$ are also known.

Oxygen Ligands. The *acetylacetonate,* like other divalent acetylacetonates polymerizes to increase the coordination number and $[Mn(acac)_2]_3$ is trimeric [cf. $Ni(acac)_2$, Fig. 12-4] but unlike the Ni^{II} complex where all metal atoms are octahedral, the two end Mn atoms are trigonal prismatic.[2]

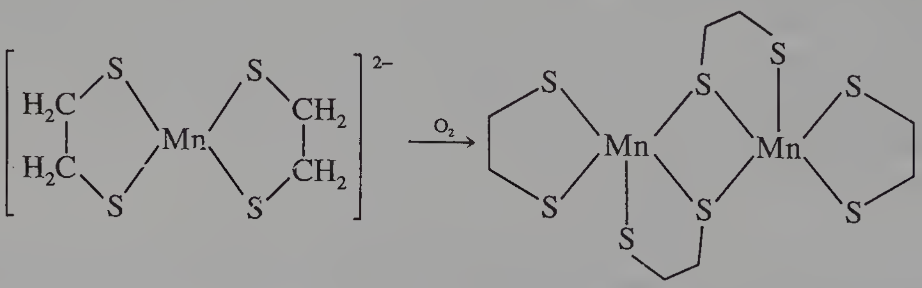
Alkoxides[3] are similarly polymeric and for the same reason; thus $[Mn(OCHt\text{-}Bu_2)_2]_3$ is a trimer with a $OMn(\mu\text{-}O)_2Mn(\mu\text{-}O)_2MnO$ core. There are also the oxalate $[Mn\ ox_3]^{4-}$ and catecholate $[Mn\ cat_3]^{4-}$ ions; like other Mn^{II} species these may be oxidized to Mn^{III}.[4]

Sulfur Ligands. The dithiocarbamate (18-D-I) in contrast to the acetylacetonate, dialkylamides, and alkoxides is an infinite polymer.



(18-D-I)

The thiolates have been studied in detail. Examples are the toluene-3,4-dithiolate $[MnL_2]^{2-}$, which has a distorted MnS_4 core and $[Mn_4(SPh)_{10}]^{2-}$ which, like many other thiolates, has an adamantane-type $Mn_4(\mu\text{-}S)_6$ cage. The tetrahedral anion (18-D-II) is oxidized by air to a Mn^{III} dimer that has *tbp* Mn^{III} with a structure reminiscent of that of the Mn^{II} dithiocarbamate (18-



(18-D-II)

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[2] S. Shibata *et al., Inorg. Chem.*, 1985, **24,** 1723.

[3] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1980,** 1863; P. P. Power *et al., J. Am. Chem. Soc.*, 1985, **107,** 169.

[4] D. T. Sawyer *et al., Inorg. Chem.*, 1980, **19,** 492.

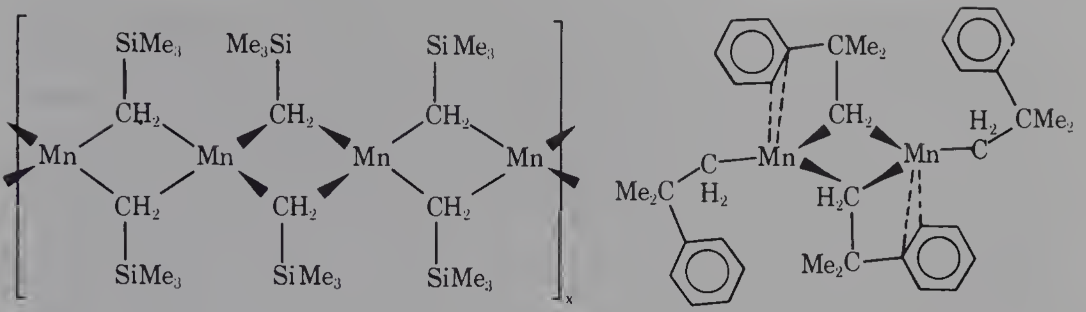

FIG. 18-D-1. The structures of bis(trimethylsilylmethyl) manganese and dineophylmanganese. (Reproduced by permission from G. Wilkinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1976**, 2204.)

D-I). All the thiolates are generally made by the action of NaSR on $MnCl_2$ in methanol.[5]

Nitrogen Ligands. Some adducts of manganese salts contain the $[Mn(NH_3)_6]^{2+}$ ion and other ions such as $[Mn\ en_3]^{2+}$ are formed in aqueous solution but certain tridentate amines can give five-coordinate species.

The *dialkylamides* dimerize as in $Mn_2[N(SiMe_3)_2]_4$, which has an $NMn(\mu\text{-}N)_2MnN$ core.[6]

Porphyrin and phthalocyanin complexes have been studied primarily because of their oxidation to higher valent species, discussed later. There are also Schiff base complexes.[7]

Phosphine Ligands. Although complexes of stoichiometry $MnX_2(PR_3)$ are polymeric with halide bridges, there are octahedral chelates such as *trans*-$MnX_2(dmpe)_2$ and a distorted tetrahedral monomer $MnI_2(PEt_3)_2$.[8]

The unidentate phosphine complexes $MnX_2(PR_3)$ in THF at low temperatures react with a number of small molecules, O_2, CO, SO_2, and C_2H_4, evidently reversibly.[9] The O_2 species are deep blue or purple and probably peroxo ones; irreversible oxidation of R_3P to R_3PO also occurs slowly.

Carbon Ligands. Like the alkoxides and dialkylamides the thermally stable *alkyls* and *aryls* may be polymeric or dimeric (Fig. 18-D-1), trimeric in the mesityl[10] with a $CMn(\mu\text{-}C)_2Mn(\mu\text{-}C)_2MnC$ skeleton, or, with a very bulky alkyl, linear in $Mn[C(SiMe_3)_2]_2$[11a]; the neopentyl is also monomeric in the gas phase.[11b]

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[5] R. H. Holm *et al.*, *Inorg. Chem.*, 1983, **22**, 4091; G. Henkel *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 117.

[6] B. D. Murray and P. P. Power, *Inorg. Chem.*, 1984, **23**, 4584.

[7] J-P. Tuchagues *et al.*, *Inorg. Chem.*, 1986, **25**, 1420.

[8] D. A. Wickens and G. Abrams, *J. Chem. Soc. Dalton Trans.*, **1985**, 2203; G. Wilkinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 921; F. H. Köhler *et al.*, *Inorg. Chem.*, 1984, **23**, 3043; C. A. McAuliffe *et al.*, *J. Chem. Soc. Chem. Commun.*, **1984**, 305.

[9] C. A. McAuliffe *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 1415, 1785; S. D. Worley *et al.*, *Inorg. Chem.*, 1984, **23**, 3911; W. E. Hill *et al.*, *Inorg. Chem.*, 1985, **24**, 4429; D. A. Wickens and G. Abram, *J. Chem. Soc. Dalton Trans.*, **1987**, 1581.

[10] C. Floriani *et al.*, *J. Chem. Soc. Chem. Commun.*, **1983**, 1128.

[11a] C. Eaborn *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985**, 1380.

[11b] R. A. Andersen *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985**, 1807.

The alkyls act as Lewis acids and (*a*) react with lithium alkyls to give alkylate anions such as $[Li\ tmed]_2[MnR_4]$ and (*b*) are cleaved by tertiary phosphines to give monomeric or dimeric alkyl bridged species with tetrahedral Mn^{II}, generally, $MnR_2(PR'_3)_2$ and $Mn_2R_2(\mu\text{-}R)_2(PR'_3)_2$. These phosphine species[12] are more easily made directly from $MnCl_2$, PR_3, and an alkylating agent. The octahedral dimethyl *trans*-$MnMe_2(dmpe)_2$ is also known.

There are also the important *cyclopentadienyls* $(\eta\text{-}C_5H_5)_2Mn$ and $(\eta\text{-}C_5Me_5)_2Mn$. The former is brown and antiferromagnetic below 180°C; between this temperature and its mp (193°C) it is pink and has high spin. The brown form is polymeric with zigzag chains and C_5H_5 bridges as shown in Fig. 2-18, which evidently allow antiferromagnetic interaction between the Mn^{2+} ions. The bonding is essentially ionic. The pink form appears to have the ferrocene structure, which is found in the gas phase. Chemically, $(\eta\text{-}C_5H_5)_2Mn$ behaves as an ionic cyclopentadienide. $(MeC_5H_4)_2Mn$ shows low-spin high-spin crossover behavior.[13] By contrast $^*Cp_2Mn$ has a normal sandwich structure and an exclusively low-spin ground state. Adducts of Cp_2Mn with PMe_3 and dmpe have nonplanar tilted rings[14] while the tmed adduct[15] has both η^5 and η^1 C_5H_5 rings.

Electronic Spectra of Manganese(II) Compounds. The high-spin d^5 configuration has certain unique properties and manganese(II) is the most prominent example of this configuration. The majority of Mn^{II} complexes are high spin. In *octahedral fields* this configuration gives spin-forbidden as well as parity-forbidden transitions, thus accounting for the extremely pale color of such compounds. In *tetrahedral environments,* the transitions are still spin forbidden but no longer parity forbidden; these transitions are therefore ~100 times stronger and the compounds have a noticeable pale yellow-green color. Tetrahedral Mn^{2+} can also show intense yellow-green fluorescence and commercial phosphors are Mn^{II} activated Zn^{II} compounds like Zn_2SiO_4. The high-spin d^5 configuration gives an essentially spin-only, temperature-independent magnetic moment of ~5.9 BM.

At sufficiently high values of Δ_0, a t_{2g}^5 configuration gives rise to a doublet ground state; for Mn^{II} the pairing energy is high and only a few of the strongest ligand sets, for example, those in $[Mn(CN)_6]^{4-}$, $[Mn(CN)_5NO]^{3-}$, and $[Mn(CNR)_6]^{2+}$, can accomplish this.

In the square environment provided by phthalocyanine, Mn^{II} has a $^4A_{1g}$ ground state.

18-D-3. The Chemistry of Manganese(III), d^4

Binary Compounds. The oxides are the most important. The final product of oxidation of Mn or MnO at 470 to 600°C is Mn_2O_3. At 1000°C this de-

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[12] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1985**, 921 and references therein.
[13] D. Cozak *et al., Can. J. Chem.,* 1986, **64,** 71; *Organometallics,* 1987, **6,** 1912.
[14] G. Wilkinson *et al., J. Am. Chem. Soc.,* 1984, **106,** 2033.
[15] F. H. Köhler *et al., Angew. Chem. Int. Ed. Engl.,* 1984, **23,** 720.

composes giving black Mn_3O_4 (*hausmannite*), which is a spinel, $Mn^{II}Mn_2^{III}O_4$. The higher or lower oxides can be interconverted by proper choice of temperature and oxygen partial pressure. A brown hydrous oxide of stoichiometry MnO(OH) is formed when $Mn(OH)_2$ is oxidized by air. Although the mineral *manganite* [γ-MnO(OH)] formally contains Mn^{III}, magnetic measurements suggest that it contains both Mn^{II} and Mn^{IV}. Manganese(III) occurs in other mixed oxide systems including the alkali $LiMnO_2$, Na_5MnO_4,[16] and $K_6Mn_2O_6$ oxides, the latter containing discrete $Mn_2O_6^{6-}$ ions with the Al_2Cl_6 type structure.

Manganese(III) fluoride is obtained on fluorination of $MnCl_2$ or other compounds and is a red-purple solid instantaneously hydrolyzed by water. It has been used as a fluorinating agent. The black trichloride can be made by the action of HCl on Mn^{III} acetate or by chlorination of MnO(OH) in CCl_4 at low temperatures. Although it decomposes $\sim -40°C$, its purple solutions in diethyl ether are reasonably stable at $-10°C$ and can be used to make compounds such as $(R_4N)_2MnCl_5$ or $MnCl_3(PR_3)_3$.

The Manganese(III) Ion. The aqua ion[17] can be obtained by electrolytic or peroxosulfate oxidation of Mn^{2+} solutions, or by reduction of MnO_4^-. The ion plays a central role in the complex redox reactions of the higher oxidation states of manganese in aqueous solutions.

It is most stable in acid solutions, since it is very readily hydrolyzed:

$$Mn^{3+} + H_2O = Mn(OH)^{2+} + H^+ \qquad K = 0.93$$

the initial monomer slowly polymerizing.[18]

Under suitable conditions the Mn^{3+}–Mn^{2+} couple is reversible ($E^0 = 1.559$ V in 3 *M* $LiClO_4$). The Mn^{3+} ion is slowly reduced by water:

$$3Mn^{3+} + H_2O = 2Mn^{2+} + 2H^+ + \tfrac{1}{2}O_2$$

Manganese(III) Complexes.[19] The Mn^{III} state can be stabilized in aqueous solution by complexing anions such as $C_2O_4^{2-}$,[20] SO_4^{2-}, and $EDTA^{4-}$, but even the most stable species $[MnEDTA(H_2O)]^-$ undergoes decomposition because of slow oxidation of the ligand.

Halogeno Complexes. Dissolution of MnO(OH) in HF followed by addition of CsF gives $Cs[MnF_4(OH_2)_2]$, which is octahedral with *trans*-H_2O molecules. Anhydrous salts of MnF_4^-, MnF_5^{2-}, and MnF_6^{3-} are also known, as are chloro anions such as $MnCl_5^{2-}$ and neutral complexes like $MnCl_3(dioxan)_2$.

Oxygen Ligands. The trisacetylacetonate is readily obtained[21] by interaction of acacH with concentrated $KMnO_4$ as dark brown crystals. It can be

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[16] R. Hoppe *et al., Z. Anorg. Allg. Chem.*, 1984, **515**, 101.

[17] D. H. Macartney and N. Sutin, *Inorg. Chem.*, 1985, **24**, 3403.

[18] R. E. Huie *et al., Inorg. Chem.*, 1984, **23**, 1134.

[19] K. S. Yamaguchi and D. T. Sawyer, *Isr. J. Chem.*, **1985**, 164.

[20] M. K. Chaudhuri *et al., Inorg. Chem.*, 1985, **24**, 447.

[21] M. K. Chaudhuri *et al., J. Chem. Soc. Dalton Trans.*, **1982**, 669.

oxidized[22] to $[Mn^{IV}(acac)_3]^+$ that rapidly oxidizes H_2O_2 and OH^- while $Mn(acac)_3$ also acts as an oxidant for organic compounds.

The so-called "manganic acetate" is actually an oxo-centered species (Section 12-9), $[Mn_3O(O_2CMe)_6]CO_2Me$. Other species with Mn_3^{III} or $Mn^{II}Mn_2^{III}$ of the type $[Mn_3O(O_2CR)_6L_3]^{+,0}$, L = pyridines, can be made by interaction of Bu_4NMnO_4 and Mn^{II} carboxylate in the pyridine.[23a] Interaction of the "acetate" with bipy in MeCN gives $Mn_4O_2(O_2CMe)_7\,bipy_2$, which may be a model for the Mn complex involved in photosynthesis.[23b]

The acetate or its adducts will oxidize many organic compounds by free-radical processes.[24]

Nitrogen Ligands. Schiff base complexes of various types are known, a typical one being $MnX_2(sal_2en)$, where X can be halide, Me, or Ph.

The porphyrin complexes[25] XMnporph have been intensively studied in part because in the presence of PhIO, H_2O_2, or O_2 they can act as oxygen-transfer agents oxidizing various organic substrates including alkenes and alkanes and they serve as a model for P_{450} enzymes (Chapter 30). The oxidized products, for example, $[tpp\,XMn(OIPh)]_2(\mu\text{-}O)$ are Mn^{IV} species.

Oxo-bridged species of other types[26] are known, for example, $[N_3Mn(\mu\text{-}O)(\mu\text{-}O_2CMe)_2MnN_3]^+$, N_3 = 1,4,7-triazacyclononane, which can be oxidized in a 1*e* step to a Mn^{III}–Mn^{IV} mixed valence dication; there are similar derivatives with bipy and phen ligands, as also noted later under Mn^{IV}.

Other Complexes. A unique dark green complex $MnI_3(PMe_3)_2$, which has axial PMe_3 groups, is formed on an oxidation of MnI_2 in excess PMe_3.[27]

Interaction of KCN with aqueous $KMnO_4$ gives the anion $[(CN)_5MnOMn(CN)_5]^{6-}$. There is also a seven-coordinate trihydride $MnH_3(dmpe)_2$.[28]

Electronic Structure of Mn^{III} Compounds. The $^5E_g(t_{2g}^3e_g)$ state for octahedral Mn^{III} is subject to a Jahn–Teller distortion. Because of the odd number of e_g electrons, this distortion should be appreciable and resemble the distortion in Cr^{II} and Cu^{II} compounds. Indeed, a considerable elongation of two trans bonds with little difference in the lengths of the other four has been observed in many Mn^{III} compounds. For example, MnF_3 has the same basic structure as VF_3 where each V^{3+} ion is surrounded by a regular octahedron of F^- ions, except that two Mn—F distances are 1.79 Å, two more are 1.91 Å,

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[22] K. Yamaguchi and D. T. Sawyer, *Inorg. Chem.*, 1985, **24,** 971.

[23a] G. Christou *et al., J. Am. Chem. Soc.*, 1987, **109,** 5703.

[23b] G. Christou *et al., J. Chem. Soc. Chem. Commun.*, **1987,** 236, 1303; *Inorg. Chim. Acta,* 1987, **136**(b19)L41; *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 915.

[24] See, for example, B. B. Snider *et al., J. Org. Chem.*, 1985, **50,** 3659.

[25] C. L. Hill and M. M. Williamson, *Inorg. Chem.*, 1985, **24,** 2836; J-P. Renaud *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 888; L. O. Spreer *et al., J. Am. Chem. Soc.*, 1986, **108,** 1949.

[26] See K. Wieghardt *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 1030; H-B. Bürgi *et al., Inorg. Chem.*, 1986, **25,** 4743; M. Kaneko *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 825; S. J. Lippard *et al., J. Am. Chem. Soc.*, 1987, **109,** 1435.

[27] C. A. McAuliffe *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 1999.

[28] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 921.

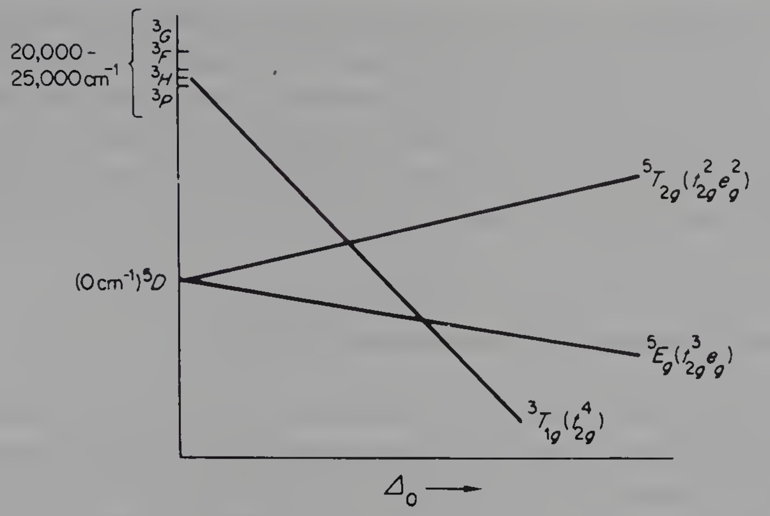

FIG. 18-D-2. Simplified energy level diagram for the d^4 system Mn^{III} in octahedral surroundings.

and the remaining two are 2.09 Å. There is also distortion of the spinel structure of Mn_3O_4 where Mn^{2+} ions are in tetrahedral interstices and Mn^{3+} in octahedral interstices: Each of the latter tends to distort its own octahedron, and the cumulative effect is that the entire lattice is distorted from cubic to elongated tetragonal.

The complex Mn(acac)$_3$ has two forms, one of which shows a substantial tetragonal elongation (two Mn—O = 2.12 Å; four Mn—O = 1.93 Å) as do other high-spin complexes such as porphyrin adducts; the other form shows a moderate tetragonal compression (two Mn—O = 1.95 Å; four Mn—O = 2.00 Å).

In $[Mn(urea)_6]^{3+}$ all six Mn—O distances are equal (1.986 Å) but analysis of displacements of the O atoms and electronic spectra are in agreement with a dynamic Jahn–Teller effect.[29]

The very strong acidity of the aqua ion has been attributed to a strong ligand field stabilizing a distorted ion, possibly $[Mn(OH)(H_2O)_5]^{2+}$.

A simplified energy level diagram for d^4 systems is shown in Fig. 18-D-2. It is consistent with the existence of both high-spin and low-spin octahedral complexes. Because the next quintet state (^5F, derived from the d^3s configuration) lying ~110,000 cm^{-1} above the ^5D ground state of the free ion is of such high energy, only one spin-allowed absorption band ($^5E_g \rightarrow {}^5T_{2g}$) is to be expected in the visible region. For $[Mn(H_2O)_6]^{3+}$ and tris(oxalato)- and tris(acetylacetonato)manganese(III) a rather broad band appears around 20,000 cm^{-1} and the red or red-brown colors of high-spin Mn^{III} compounds may be attributed to such absorption bands. However, the spectra of some six-coordinate Mn^{III} complexes are not so simple, and they are difficult to interpret in all their details, presumably because both static and dynamic Jahn–Teller effects perturb the simple picture based on O_h symmetry.

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[29] R. C. Stouter *et al., Inorg. Chem.*, 1982, **21**, 3902.

Low-spin manganese(III) compounds are the diamagnetic $MnH_3(dmpe)_2$ and salts of the $[Mn(CN)_6]^{3-}$ ion. Manganese(II) in the presence of an excess of CN^- is readily oxidized, even by a current of air, with the production of this ion that is first isolated from the solution as the Mn^{II} salt $Mn_3^{II}[Mn(CN)_6]_2$, from which other salts are obtained. For $[Mn(CN)_6]^{3-}$ there appears to be no transition likely below a frequency where it would be obscured by strong uv bands, and none has been observed.

18-D-4. The Chemistry of Manganese(IV)[19], d^3

Binary Compounds. *Manganese dioxide,* a gray to black solid, occurs in ores such as *pyrolusite,* where it is usually nonstoichiometric. When made by the action of O_2 on Mn at a high temperature, it has the rutile structure found for many other oxides MO_2 (e.g., those of Ru, Mo, W, Re, Os, Ir, and Rh). However, as normally made by heating $Mn(NO_3)_2{\cdot}6H_2O$ in air (~530°C), it is nonstoichiometric. A hydrated form is obtained by reduction of aqueous $KMnO_4$ in basic solution. Manganese(IV) occurs in a number of mixed oxides.

Manganese dioxide is inert to most acids except when heated, but it does not dissolve to give Mn^{IV} in solution; instead it functions as an oxidizing agent, the exact manner of this depending on the acid. With HCl, chlorine is evolved:

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

and this reaction is often used for small-scale generation of Cl_2 in the laboratory. With H_2SO_4 at 110°C, O_2 is evolved and an Mn^{III} acid sulfate is formed. Hydrated MnO_2 is used in organic chemistry for the oxidation of alcohols and other compounds.

The *tetrafluoride* MnF_4, obtained by direct interaction, is an unstable blue solid decomposing slowly to MnF_3 and F_2.

Complexes. Non-oxo cationic species are the dithiocarbamates $[Mn(S_2CNR_2)_3]^+$, obtained as the dark purple BF_4^- salts by air oxidation of the Mn^{III} dithiocarbamates in CH_2Cl_2 in the presence of BF_3 (cf. Fe^{IV} and Co^{IV} analogues), or by electrochemical oxidation. The salt K_2MnF_6, obtained by reaction of $KMnO_4$ in 40% HF, is stable, but the $[MnCl_6]^{2-}$ ion is not, although it can be studied in a K_2SnCl_6 matrix where it is obtained by reduction of $KMnO_4$ by strong HCl in the presence of K_2SnCl_6. There are 2,2′-bipyridyl and 1,10-phenanthroline complexes that have a $(\mu\text{-}O)_2$ bridge. They can be reduced stepwise to III–IV and III–III complexes, for example,

$$\begin{aligned}[\text{phen}_2\,Mn^{IV}(\mu\text{-}O)_2Mn^{IV}\,\text{phen}_2]^{4+} &\underset{-e}{\overset{+e}{\rightleftharpoons}} [\text{phen}_2\,MnO_2Mn\,\text{phen}_2]^{3+}\\ &\underset{-e}{\overset{+e}{\rightleftharpoons}} [\text{phen}_2\,Mn^{III}O_2Mn^{III}\,\text{phen}_2]^{2+}\end{aligned}$$

The Mn^{IV} complex can be used for one-electron oxidations in aqueous media.

There are also a number of similar complexes of Schiff bases, polyhydroxo, and macrocyclic ligands that contain Mn^{IV}. One example is $[Mn^{IV}(sal_2en)O]_n$, which is a polymer with Mn—O—Mn bridges. Another example, formed by a tetradentate Schiff base, L, is $LMn^{IV}(\mu\text{-}O)_2Mn^{IV}L$.

In addition to the μ-O porphyrin complex noted previously there are numerous compounds of the type *trans*-X_2Mn(porph) where X can be OMe, N_3, NCO, and so on. Like the Mn^{III} species these also act as oxidants in the presence of O_2, PhIO, and so on, and the actual oxidizing species are probably the same,[30] possibly a peroxo species[31a] or $[\text{porph } Mn^{V}{=}O]^+$.[31b] Other Mn^{IV} species[32] include a sorbitolate, $[Mn(C_6H_{12}O_6)_3]^{2-}$, catecholates, $[Mn(O_2C_6H_4)_3]^{2-}$, dithiocarbamates, thiohydroxamates, and $Mn(bipy)(salicylate)_2$, all of which are octahedral or close to it.

Oxidation of $MnCl_2$ by O_2 in aqueous alkaline solution in the presence of 1,4,7-triazacyclononane (L) gives a Mn^{IV} tetranuclear species $[Mn_4O_6L_4]^{4+}$ that has an adamantane skeleton with a Mn_4 tetrahedron and a μ_3-O centered on each face.[33a] Manganese tetramers have been proposed in photosynthetic systems.[33b]

There is a remarkably stable though photosensitive green alkyl, Mn(1-norbornyl)$_4$, and other less stable green tetraalkyls can be made from $Mn(acac)_3$ by an alkylation involving disproportionation

$$2Mn^{III} \longrightarrow Mn^{IV}R_4 + Mn^{II}R_2$$

The reaction in the presence of PMe_3 or dmpe leads to thermally stable octahedral methyls, for example, $Me_4Mn(dmpe)$.[34]

18-D-5. The Chemistry of Manganese(V), d^2

There are few authenticated examples of compounds in the Mn^{V} state. The *oxohalide* $MnOCl_3$, which decomposes above 0°C to give $MnCl_3$ and is readily hydrolyzed, is formed by reducing $KMnO_4$ dissolved in HSO_3Cl with sucrose.

The oxo anion MnO_4^{3-} and Mn^{V} esters have often been invoked as intermediates in the reduction of MnO_4^- but with little substantiating evidence. However, unstable manganate(V) and -(VI) intermediates have been detected in the reduction of MnO_4^- by SO_3^{2-} where the overall reaction[35] is

$$2MnO_4^- + 3SO_3^{2-} + H_2O = 2MnO_2 + 3SO_4^{2-} + 2OH^-$$

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[30] C. L. Hill *et al., Inorg. Chem.*, 1983, **22,** 3776; *J. Am. Chem. Soc.*, 1983, **105,** 2920.

[31a] See J. E. Newton and M. B. Hall, *Inorg. Chem.*, 1985, **24,** 2573.

[31b] O. Bortolini and B. Meuniev, *J. Chem. Soc. Chem. Commun.*, **1983,** 1364.

[32] G. Christou *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 43; S. R. Cooper *et al., Inorg. Chem.*, 1984, **23,** 1386; A. Chakravorty *et al., Inorg. Chem.*, 1985, **24,** 3704.

[33a] K. Wieghardt *et al., Angew. Chem. Int. Ed. Engl.*, 1983, **22,** 328.

[33b] W. Beck *et al., J. Am. Chem. Soc.*, 1986, **108,** 4002, 4018; G. W. Brudvig *et al., New J. Chem.*, 1987, **11,** 103.

[34] G. Wilkinson *et al., J. Chem. Soc. Chem. Commun.*, **1983,** 1163.

[35] L. I. Simándi *et al., J. Am. Chem. Soc.*, 1984, **106,** 6866.

The oxoporphyrin noted previously has a nitrido analogue (porph)Mn≡N that is made by photolysis of (porph)$Mn^{III}N_3$ with loss of N_2.[36]

18-D-6. The Chemistry of Manganese(VI), d^1, and -(VII), d^0

Manganese(VI). This is known in only one environment, namely, as the deep green *manganate* ion MnO_4^{2-}.[37] It is formed on oxidizing MnO_2 in fused KOH with potassium nitrate, air, or other oxidizing agent, or by evaporating $KMnO_4$ and KOH solutions. Only two salts, K_2MnO_4, and several hydrated forms of Na_2MnO_4, have been isolated pure. Both are very dark green.

The manganate ion is stable only in very basic solutions. In acid, neutral, or only slightly basic solutions it readily disproportionates in a kinetically complex way, according to the equation:

$$3MnO_4^{2-} + 4H^+ = 2MnO_4^- + MnO_2(s) + 2H_2O \qquad K \sim 10^{58}$$

Manganese(VII). The best known compounds are salts of the *permanganate* ion MnO_4^-. Sodium and potassium permanganates are made on a large scale by electrolytic oxidation of basic solutions of MnO_4^{2-}.

Potassium permanganate solubilized by crown ethers or cryptands in benzene is a useful oxidant.[38] The tetraalkylammonium or phosphonium salts are also soluble in organic solvents[39] and useful sources for synthesis of other Mn compounds. Zinc and Mg salts are very reactive but can be used as oxidants on a silica support.[40a] The photochemical decomposition in aqueous solution may proceed via a Mn^V peroxo intermediate.[40b]

The MnO_4^- ion has no unpaired electron, but it does have a small temperature-independent paramagnetism. A fully satisfactory theoretical treatment of the electronic structures and spectra of the MnO_4^{n-} ions has proved difficult to obtain.

Manganese(VII) Oxide and Oxo Halides. The addition of small amounts of $KMnO_4$ to concentrated H_2SO_4 gives a clear green solution where the ionization

$$KMnO_4 + 3H_2SO_4 \rightleftharpoons K^+ + MnO_3^+ + H_3O^+ + 3HSO_4^-$$

appears to occur. The electronic absorption spectra are consistent with a planar trigonal ion MnO_3^+.

With larger amounts of $KMnO_4$, the explosive oil Mn_2O_7 separates. This

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[36] J. T. Groves and T. Takahashi, *J. Am. Chem. Soc.*, 1983, **103**, 2073; J. W. Buchler *et al.*, *Chem. Ber.*, 1984, **117**, 2261.

[37] R. J. H. Clark *et al.*, *Inorg. Chem.*, 1985, **24**, 2088.

[38] H. Bock and D. Jaculi, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 305; F. Freeman and J. C. Kappos, *J. Am. Chem. Soc.*, 1985, **107**, 6628.

[39] H. Karaman *et al.*, *J. Org. Chem.*, 1984, **49**, 4509; G. Christou *et al.*, *Inorg. Chem.*, 1986, **25**, 996.

[40a] S. Wolfe and C. F. Ingold, *J. Am. Chem. Soc.*, 1983, **105**, 7755.

[40b] D. G. Lee *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 3003.

can be extracted into CCl_4 or chlorofluorocarbons in which it is reasonably stable and safe. It solidifies at 5 to 9°C to red crystals. The structure[41] is $O_3Mn—O—MnO_3$ with a MnOMn angle of 120.7°.

By interaction of Mn_2O_7 and $ClSO_3H$, the green, volatile, explosive liquids MnO_3Cl and $MnOCl_3$ and the highly unstable brown MnO_2Cl_2 can be obtained. Interaction of $KMnO_4$ and FSO_3H gives the green liquid MnO_3F, which also explodes at room temperature.

18-D-7. The Chemistry of Managanese(I), (0), and (-I)

Compounds in these states are mainly with π-bonding or π-complexing ligands. One of the most important is $Mn_2(CO)_{10}$, which has an extensive chemistry. One recent example is the reaction

$$Mn_2(CO)_{10} + 3PhS^- \xrightarrow[-CO]{MeCN} [(CO)_3Mn(\mu\text{-}SPh)_3Mn(CO)_3]^-$$

where the bridged species can exist in $(Mn^I–Mn^I)^-$, $(Mn^I–Mn^{II})^0$, and $3(Mn^{II}–Mn^{II})^+$ states.[42] Other Mn^I derivatives include isocyanides,[43] $[Mn(CNR)_6]^+$ which can be oxidized to the 2+ ion, the cyanide $[Mn(CN)_6]^{5-}$, the ion $[Mn(dmpe)_3]^+$, which is a unique homoleptic phosphine complex of Mn,[44] and mixed species[45] like $[Mn(CO)_3(CNR)bipy]^+$.

Alkene complexes such as $Mn(\eta^4\text{-}C_4H_6)_2PR_3$[46] and *trans*-$MnH(C_2H_4)(dmpe)_2$[28] are quite rare.

The cyclopentadienyl, $\eta\text{-}C_5H_5Mn(CO)_3$, or cymantrene, undergoes an extensive ring substitution chemistry like ferrocene. It is also a source of $(\eta\text{-}C_5H_5)Mn(CO)_2THF$ and many other derivatives.[47a]

Arene complexes, for example, $\eta^6\text{-}C_6H_6Mn(CO)_3^+$ have an extensive chemistry. Manganese(II) species $(CpMnXL)_2$ are also known.[47b]

Cyclopentadienyl and arene complexes are discussed in Chapter 26.

18-E. IRON: GROUP VIII(8)

With iron the trends already noted in the relative stabilities of oxidation states continue, except that there is now no compound or chemically important circumstance in which the oxidation state is equal to the total number of valence shell electrons, which in this case is eight. The highest oxidation state

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[41] A. Simon *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1987, **26**, 139.

[42] J. W. McDonald, *Inorg. Chem.*, 1985, **24**, 1734.

[43] R. M. Nielsen and S. Wherland, *Inorg. Chem.*, 1986, **25**, 2437.

[44] J. R. Bleeke and J. J. Kotyk, *Organometallics*, 1985, **4**, 194.

[45] F. Garcia-Alfonso *et al.*, *Transition Met. Chem.*, 1985, 19.

[46] S. S. Wreford *et al.*, *Organometallics*, 1982, **1**, 1506.

[47a] See, for example, G. Huttner *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 975.

[47b] F. H. Köhler *et al.*, *Organometallics*, 1987, **6**, 115.

TABLE 18-E-1
Oxidation States and Stereochemistry of Iron

Oxidation state	Coordination number	Geometry	Examples
Fe^{-II}	4	Tetrahedral	$Fe(CO)_4^{2-}$, $Fe(CO)_2(NO)_2$
Fe^0	5	*tbp*	$Fe(CO)_5$, $(Ph_3P)_2Fe(CO)_3$, $Fe(PF_3)_5$
	6	Octahedral(?)	$Fe(CO)_5H^+$, $Fe(CO)_4PPh_3H^+$
Fe^I, d^7	6	Octahedral	$[Fe(H_2O)_5NO]^{2+}$
Fe^{II}, d^6	4	Tetrahedral	$FeCl_4^{2-}$, $FeCl_2(PPh_3)_2$
	4	Square	Fe(tpp)
	5	*tbp*	$[FeBr(Me_6tren)]Br$, $FeCl_2(bipy)$[a]
	5	*sp*	$[Fe(ClO_4)(OAsMe_3)_4]ClO_4$
	6[b]	Octahedral	$[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{4-}$
	8	Dodecahedral (D_{2h})	$[Fe(1,8\text{-naphthyridine})_4](ClO_4)_2$
Fe^{III}, d^5	3	Trigonal	$Fe[N(SiMe_3)_2]_3$
	4	Tetrahedral	$FeCl_4^-$, Fe^{III} in Fe_3O_4
	5	*sp*	$FeCl(dtc)_2$, $Fe(acac)_2Cl$
	5	*tbp*	$Fe(N_3)_5^{2-}$, $FeCl_5^{2-}$
	6[b]	Octahedral	Fe_2O_3, $[Fe(C_2O_4)_3]^{3-}$, $Fe(acac)_3$, $FeCl_6^{3-}$
	7	Approx. pentagonal bipyramidal	$[FeEDTA(H_2O)]^-$
	8	Dodecahedral	$[Fe(NO_3)_4]^-$
Fe^{IV}, d^4	4	Tetrahedral	$Fe(I\text{-norbornyl})_4$
	6	Octahedral	$[Fe(diars)_2Cl_2]^{2+}$
Fe^{VI}, d^2	4	Tetrahedral	FeO_4^{2-}

[a] F. F. Chavron, Jr., and W. M. Ruff, *Inorg. Chem.*, 1986, **25**, 2786; probably has single μ-Cl.
[b] Most common states.

known is VI, and it is rare. The only oxidation states of importance in the ordinary aqueous and related chemistry of iron are II and III.

The oxidation states and stereochemistries are given in Table 18-E-1.

18-E-1. The Element

Iron is the second most abundant metal after Al and the fourth most abundant element in the earth's crust. The earth's core is believed to consist mainly of iron and nickel, and the occurrence of iron meteorites suggests that it is abundant throughout the solar system. The major iron ores are *hematite* (Fe_2O_3), *magnetite* (Fe_3O_4), *limonite* [FeO(OH)], and *siderite* ($FeCO_3$).

Because of its high abundance, iron is often found as an impurity in other materials. For example, corundum (γ-Al_2O_3) of gem quality is sapphire, and its colors are caused by small amounts of Fe^{IV}.

Chemically pure Fe can be prepared by reduction of pure iron oxide (which is obtained by thermal decomposition of iron(II) oxalate, carbonate, or nitrate) with H_2, by electrodeposition from aqueous solutions of Fe salts, or by thermal decomposition of $Fe(CO)_5$.

Iron is a white, lustrous metal (mp 1528°C). It is not particularly hard, and it is quite reactive. In moist air it is rather rapidly oxidized to give a hydrous oxide that affords no protection because it flakes off, exposing fresh metal surfaces. Finely divided Fe is pyrophoric. Iron combines vigorously with Cl_2 on mild heating and also with a variety of other nonmetals including the other halogens, S, P, B, C, and Si. The carbide and silicide phases play a major role in the technical metallurgy of iron.

The metal dissolves readily in dilute mineral acids, in the absence of air and with nonoxidizing acids to give Fe^{II}. With air present or when warm dilute HNO_3 is used, some of the iron goes to Fe^{III}. Very strongly oxidizing media such as concentrated HNO_3 or acids containing $Cr_2O_7^{2-}$ passivate iron. Air-free water and dilute air-free hydroxides have little effect on the metal, but hot concentrated NaOH attacks it. In the presence of air and water iron rusts to give a hydrated Fe^{III} oxide.

IRON COMPOUNDS

The compounds of iron in low oxidation states, notably the iron carbonyls and their derivatives, are considered in Chapter 22, and organo compounds are considered in Chapters 25 and 26.

18-E-2. The Hydroxides and Oxides of Iron[1]

Because of the interrelationships between them it is convenient to discuss the hydroxides and oxides together.

Iron(II) Oxides.[2] Thermal decomposition of iron(II) oxalate in a vacuum gives a pyrophoric black powder that becomes less reactive if heated to higher temperatures. The crystalline substance can be obtained only by establishing equilibrium conditions at high temperature, then rapidly quenching the system, since at lower temperatures FeO is unstable with respect to Fe and Fe_3O_4; slow cooling allows disproportionation. Iron oxide has the rock salt structure. The FeO referred to thus far is iron defective (see later), having a typical composition of $Fe_{0.95}O$. Essentially stoichiometric FeO has been prepared from $Fe_{0.95}O$ and Fe at 1050 K and 50 katm; it is ~0.4% less dense.

The white hydroxide $Fe(OH)_2$ is precipitated from Fe^{2+} solutions by base; it can be obtained crystalline with the $Mg(OH)_2$ structure. The hydroxide is rapidly oxidized in air turning red brown and eventually giving $Fe_2O_3 \cdot nH_2O$. It is soluble in acids and in strong base; on boiling Fe powder with 50% KOH blue-green crystals of $K_4[Fe(OH)_6]$ can be obtained. Interaction of FeO and Na_2O give Na_4FeO_3, which has a planar FeO_3^{4-} ion.

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[1] C. M. Flynn, Jr., *Chem. Rev.*, 1984, **84**, 31; S. Mann, *Chem. Brit.*, **1987**, 137.

[2] A. K. Cheetham *et al., Inorg. Chem.*, 1984, **23**, 3136, 3141; D. J. C. Yates and J. A. McHenry, *Inorg. Chem.*, 1987, **26**, 3193.

Iron(III) Oxides.[3] Hydrous iron(III) oxides,[4] FeO(OH), have different types (α, β, γ) of chain structures with FeO_6 octahedra sharing edges and they resemble those of AlO(OH). They are generally red-brown gels and are a major constituent of soils. Oxidation of Fe^{2+} in basic solution [or $Fe(OH)_2$] by air is complicated but can lead to γ-FeO(OH) and also Fe_3O_4. Cobalt catalyzed oxidation of $FeSO_4$ with H_2O_2 in acid solution gives crystals of what appears to be $Fe(OH)_3$.[5]

The hydrous oxide is soluble in acids and to some extent in bases. On boiling $[Fe(H_2O)_6]^{3+}$ with $Ba(OH)_2$, crystalline $Ba_3[Fe(OH)_6]_2$ can be obtained and moderate concentrations of $[Fe(OH)_6]^{3-}$ can be maintained in strong base solution.

The oxide obtained on heating the hydrous oxide at 200°C is α-Fe_2O_3, which occurs as the mineral hematite. This has the corundum structure where the oxide ions form a *hexagonally* close-packed array with Fe^{III} ions occupying octahedral interstices. By careful oxidation of Fe_3O_4 or by heating one of the modifications of FeO(OH) (lepidocrocite) one obtains γ-Fe_2O_3, which may be regarded as a *cubic* close-packed array of oxide ions with the Fe^{III} ions distributed randomly over both the octahedral and the tetrahedral interstices. There is also a rare form designated β-Fe_2O_3.

The oxide Fe_3O_4 occurs as the mineral magnetite. It is a Fe^{II}–Fe^{III} mixed oxide with the inverse spinel structure (Section 1-2) with Fe^{II} in octahedral interstices and Fe^{III} ions half in tetrahedral and half in octahedral interstices of a cubic close-packed array of oxide ions. The electrical conductivity ($\sim 10^6$ that of Fe_2O_3) is probably due to rapid valence oscillation between the Fe sites. It can be made by oxidation of Fe^{2+} with alkaline KNO_3 in the presence of phosphite.[6]

Ferrites.[7] These are important mixed oxide materials with octahedral Fe^{3+} ions used in magnetic tapes. Examples are the spinels $M^{II}Fe_2O_4$, $BaFe_{12}O_{19}$, and $Ba_2Mn_2^{II}Fe_{12}O_{22}$. However, some discrete ions[8] are known.

Ferrites can be made by fusing Fe_2O_3 with carbonates or by various hydrothermal methods from $Fe(OH)_2$ or FeO(OH) suspensions in the presence of metal ions.[9a]

Perovskite-type oxides[9b] with Fe^{IV}, for example, $SrFeO_3$, can be made

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[3] T. Birchall, *Inorg. Chem.*, 1984, **23,** 1513; J. W. Geus, *Appl. Catal.*, 1986, **25,** 313 (also catalytic properties).

[4] T. Kanzaki and T. Katsura, *J. Chem. Soc. Dalton Trans.*, **1986,** 1243; P. S. Braterman *et al.*, *J. Chem. Soc. Dalton Trans.* **1984,** 1441; J. Subrt, *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986,** 1713; R. M. Cornell and R. Giovanoli; *J. Chem. Soc. Chem. Commun.*, **1987,** 413.

[5] S. C. F. An-Yeung *et al.*, *Can. J. Chem.*, 1985, **63,** 3378.

[6] S. B. Couliny and S. Mann, *J. Chem. Soc. Chem. Commun.*, **1985,** 713.

[7] H. Hibst, *Angew. Chem. Int. Ed. Engl.*, 1982, **21,** 270.

[8] See, for example, R. Luge and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1985, **520,** 39.

[9a] Y. Tamaura, *Inorg. Chem.*, 1985, **24,** 4363.

[9b] M. Takano and Y. Takeda, *Bull. Inst. Chem. Res. Kyoto Univ.*, 1983, **61,** No. 5–6; T. C. Gibb, *J. Chem. Soc. Dalton Trans.*, **1986,** 1447.

under high O_2 pressures and spinels such as Ba_2FeO_4 can be made by the reaction

$$M_3^{II}[Fe(OH)_6]_2 + M^{II}(OH)_2 + \tfrac{1}{2}O_2 \xrightarrow{800\text{–}900^\circ C} 2M_2^{II}FeO_4 + 7H_2O$$

18-E-3. Halides and Sulfides

Iron(II) fluoride, chloride, and bromide are made by interaction of Fe with HX; FeI_2 can be made using the halogen, which does not oxidize Fe^{II} to Fe^{III}. Iron dichloride ($FeCl_2$) is best made by reduction of $FeCl_3$ with Fe in THF.

Iron(III) halides are obtained by direct halogenation of Fe; FeI_3 does not exist pure.

The fluoride is white, having only spin-forbidden electronic transitions in the visible spectrum (cf. Mn^{II}); it has no low-energy charge-transfer band and has FeF_6 octahedra.[10] Iron trichloride and $FeBr_3$ are red brown because of charge-transfer transitions and have nonmolecular crystal structures with Fe^{III} ions occupying two thirds of the octahedral holes in alternate layers. The molecules are dimers in the gas phase and Fe_2Cl_6 has a puckered four-membered Fe_2Cl_2 ring.[11]

Interaction of $FeCl_3$ and Fe_2O_3 at high temperatures gives FeOCl; this has a layer lattice into which small molecules can be intercalated.[12]

Iron forms many binary compounds with the Group VA(15) and Group VIA(16) elements. Many are nonstoichiometric and/or interstitial. The sulfides are the most common. Iron(II) sulfide (FeS) and FeS_2 have been discussed (Section 13-8). Iron(III) sulfide is unstable and can be prepared and stored only with difficulty. By quantitative treatment of aqueous Fe^{III} with Na_2S at 0°C or below it is obtained as a black air-sensitive solid.

18-E-4. Aqueous and Coordination Chemistry of Iron(II), d^6

Aqueous solutions of Fe^{II} in the absence of complexing anions contain the pale blue-green ion $[Fe(H_2O)_6]^{2+}$, which is oxidized in acid solution:

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ = 2Fe^{3+} + H_2O \qquad E_0 = 0.46\ V$$

As noted earlier, oxidation is easier in basic solution but neutral and acid solutions of Fe^{2+} oxidize *less* rapidly with increasing acidity (even though the potential of the oxidation reaction becomes more positive). This is because Fe^{III} is actually present in the form of hydroxo complexes, except in extremely acid solutions, and there may also be kinetic reasons.

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[10] M. Leblanc *et al., Rev. Chim. Miner.*, 1985, **22,** 107.

[11] I. Hargittai *et al., J. Chem. Soc. Dalton Trans.*, **1980,** 87.

[12] B. K. Teo *et al., Inorg. Chem.*, 1986, **25,** 1209; B. A. Averill *et al., J. Am. Chem. Soc.*, 1987, **109,** 4561; *J. Chem. Soc. Chem. Commun.*, **1987,** 399; T. J. Marks *et al., J. Am. Chem. Soc.*, 1987, **109,** 3797.

The oxidation of Fe^{II} to Fe^{III} in neutral solutions by molecular oxygen may involve a reaction between $FeOH^+$ and O_2H^- but details are uncertain.

The Fe^{2+} ion is also oxidized by other common oxidants. The action of NO_3^- or NO_2^- involves the transient formation of a brown nitrosyl $[FeNO(H_2O)_5]^{2+}$ in the overall reaction[13]

$$3Fe^{2+} + 4H^+ + NO_3^- = 3Fe^{3+} + 2H_2O + NO$$

At pH 5, NO_2^- is reduced to NO and N_2O possibly via HNO and above pH 4 an $Fe(NO)_2^{2+}$ species may be involved as well as $FeNO^+$,[14] which is stable to reduction below ~ pH 4. This nitrosyl chemistry may have relevance to the reduction of NO_2^- and NO_3^- by microorganisms in soils.

The mixture of Fe^{2+} and H_2O_2 or $S_2O_8^{2-}$ is called Fenton's reagent; it oxidizes due to the presence of $OH\cdot$ and $SO_4^{-\cdot}$ radicals although Fe^{IV} oxo species may be present in the complicated solutions.[15a] Iron(II) forms salts with virtually every stable anion, generally as green, hydrated, crystalline substances isolated by evaporation of aqueous solutions. The sulfate and perchlorate contain octahedral $[Fe(H_2O)_6]^{2+}$ ions. Mohr's salt $(NH_4)_2SO_4\cdot FeSO_4\cdot 6H_2O$, is fairly stable toward both air oxidation and loss of water. It is commonly used in volumetric analysis to prepare standard solutions of Fe^{II} and as a calibration substance in magnetic measurements. The hydrated halides (F, Cl, and Br) can be made by dissolving Fe in the aqueous acids and crystallizing. The compound $FeCl_2\cdot 6H_2O$ contains *trans*-$[FeCl_2(H_2O)_4]$; all the species from $[Fe(H_2O)_6]^{2+}$ to $[FeCl_4]^{2-}$ are known in solution.[15b]

Complexes. Most Fe^{II} complexes are octahedral. There are few *tetrahedral* complexes but these include the $[FeCl_4]^{2-}$ ion in salts with large cations, $[Fe(OPPh_3)_4]^{2+}$, and a few others. *Pentacoordinate* species, usually distorted *tbp*, include those of tripod ligands such as $[Fe(np_3)X]^+$. *Dodecahedral* complexes include $[Fe(napthyridine)_4]^{2+}$ and the crown ether complex noted below.

The aqueous system provides a good example of the effect of complexing ligands on the redox potentials

$$[Fe(CN)_6]^{3-} + e = [Fe(CN)_6]^{4-} \qquad E^0 = 0.36\ V$$

$$[Fe(H_2O)_6]^{3+} + e = [Fe(H_2O)_6]^{2+} \qquad E^0 = 0.77\ V$$

$$[Fe(phen)_3]^{3+} + e = [Fe(phen)_3]^{2+} \qquad E^0 = 1.12\ v$$

Nitrogen Ligands. Iron(II) halides and other salts absorb NH_3 in excess giving the $[Fe(NH_3)_6]^{2+}$, but ammonia complexes are stable only in saturated excess ammonia. Stable complexes with chelating amines are formed, for

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[13] I. R. Epstein *et al., J. Am. Chem. Soc.*, 1980, **102,** 3751.

[14] F. T. Bonner and K. A. Pearsall, *Inorg. Chem.*, 1982, **21,** 1978.

[15a] K. Sasaki *et al., J. Am. Chem. Soc.*, 1986, **108,** 6012.

[15b] L. V. Koplitz *et al., Inorg. Chem.*, 1987, **26,** 308.

example, for ethylenediamine:

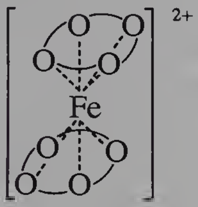
$$[Fe(H_2O)_6]^{2+} + en = [Fe(en)(H_2O)_4]^{2+} + 2H_2O \qquad K = 10^{4.3}$$
$$[Fe(en)(H_2O)_4]^{2+} + en = [Fe(en)_2(H_2O)_2]^{2+} + 2H_2O \qquad K = 10^{3.3}$$
$$[Fe(en)_2(H_2O)_2]^{2+} + en = [Fe(en)_3]^{2+} + 2H_2O \qquad K = 10^{2}$$

Ligands like phen, dipy, and others supplying imine nitrogen donor atoms give stable low-spin (i.e., diamagnetic), octahedral, or distorted octahedral complexes.

The most important ligands, however, are porphyrins (Section 10-2) as many enzyme systems are iron porphyrins (Chapter 30).

Oxygen Ligands. The β-diketonates like those of other M^{II} ions are polymeric and $[Fe(acac)_2]_4$ is a tetramer in the solid with six-coordinate Fe^{II} as a result of both oxygen bridges and weak Fe—C bonds.

A remarkable crown (12-C-4) ether complex (18-E-I),

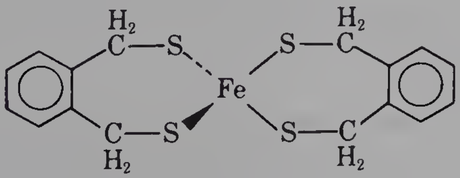


(18-E-I)

which has a "sandwich" structure, can be made by irradiation of a $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_5Me)]^+$ sandwich cation in CH_2Cl_2 in the presence of ethylene oxide. The Fe^{2+} is eight-coordinate in a slightly twisted cube.[16]

There are also oxalates, catecholates, and phosphates. Open framework "zeolite-like" materials with $[Fe_5P_4O_{20}H_4]^{6-}$ ions are obtained from the reaction of $Fe(CO)_5$, H_3PO_4, and Bu_4NOH at 150°C in aqueous acetone.[17]

Sulfur Ligands. Many studies have been made on thiolates[18] because of their relevance to natural Fe—S proteins (Chapter 30). Some are monomeric and tetrahedral like $[Fe(SPh)_4]^{2-}$, but others can form adamantanelike cages, $[Fe_4(SPh)_{10}]^{2-}$, or six-membered rings, for example, $[FeCl_2SR]_3^{3-}$. Tetrahedral compounds such as (18-E-II) provide models for Fe in rubredoxin (Chapter 30). Other Fe—S species are noted later.



(18-E-II)

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[16] K. Meir and G. Rihs, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 858.

[17] D. R. Corbin *et al., Inorg. Chem.*, 1986, **25,** 2279.

[18] R. H. Holm *et al., J. Am. Chem. Soc.*, 1986, **108,** 5607.

Phosphorus Ligands. These ligands give a variety of complexes such as *cis*- and *trans*-$FeX_2(diphos)_2$ where X can be halogen, H, Me, and so on.

Carbon Ligands. Probably the most important compound *ferrocene,* $(\eta^5\text{-}C_5H_5)_2Fe$, and related compounds are discussed in Chapter 26.

The hexacyanoferrate(II) ion, commonly called ferrocyanide, is very stable. The free acid $H_4[Fe(CN)_6]$ can be precipitated as an ether addition compound (probably containing oxonium ions R_2OH^+) by adding ether to a solution of the ion in strongly acidic solution; the ether can then be removed to leave the acid as a white powder. It is a strong tetrabasic acid when dissolved in water; in the solid the protons are bound to the nitrogen atoms of the CN groups and intermolecular hydrogen bonding. Hexacyanoferrate dissolves without decomposition in liquid HF and is protonated to give $[Fe(CNH)_6]^{2+}$.

Electronic Structures of Iron(II) Complexes. The ground state ^5D of a d^6 configuration is split by octahedral and tetrahedral ligand fields into $^5T_2$ and ^5E states; there are no other quintet states; hence only one spin-allowed *d–d* transition occurs if one of these is the ground state. All tetrahedral complexes are high spin, and the $^5E \rightarrow {}^5T_2$ band typically occurs at ~4000 cm^{-1}. The magnetic moments are normally 5.0 to 5.2 BM, owing to the spins of the four unpaired electrons and a small, second-order orbital contribution. For high-spin octahedral complexes, for example, $Fe(H_2O)_6^{2+}$, the $^5T_{2g} \rightarrow {}^5E_g$ transition occurs in the visible or near-ir region (~10,000 cm^{-1} for the aqua ion) and is broad or even resolvably split owing to a Jahn–Teller effect in the excited state, which derives from a $t_{2g}^3e_g^3$ configuration. Magnetic moments are ~5.2 BM in magnetically dilute compounds.

For Fe^{II} quite strong ligand fields are required to cause spin pairing, but a number of low-spin complexes, such as $[Fe(CN)_6]^{4-}$, $[Fe(CNR)_6]^{2+}$, and $[Fe(phen)_3]^{2+}$ are known. The best characterized exceptions are those with 2-chloro-phen and 2-methyl-phen as ligands. The former has four unpaired electrons at all temperatures from 4 to 300 K; the latter is a temperature-dependent mixture of quintet and singlet states. Comparison with the known structure of $Fe(phen)_3^{3+}$, even allowing for some difference between the Fe^{II} and Fe^{III} radii, makes it clear that ligands with Cl or CH_3 at the 2-position will be unable to approach the iron atom as closely as phen itself. $Fe(phen)_2(CN)_2$ is also diamagnetic, though most $Fe(phen)_2X_2$ complexes are high spin. When X = SCN or SeCN a spin state crossover situation (Section 17-5) occurs, and the magnetic moment is temperature dependent, ranging from ~5.1 BM at 300 K to ~1.5 BM at ≤150 K. Numerous other crossover cases have been studied.[19]

Although for strict octahedral symmetry no d^6 ion can have a ground state with two unpaired electrons (only 4 or 0), this might be possible in six-coordinate complexes in which there are significant departures from O_h symmetry in the ligand field. Perhaps the best documented examples are com-

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[19] See E. König *et al., Chem. Rev.,* 1985, **85,** 219; M. Bacci, *Inorg. Chem.,* 1986, **25,** 2322; P. Gutlich, *et al., Inorg. Chem.* 1986, **25,** 1565.

plexes of the type $[Fe(LL)_2ox]$ and $[Fe(LL)_2mal]$, where LL represents a bidentate diamine ligand such as *o*-phen or bipy, and ox and mal represent oxalato and maleato ions. These complexes have magnetic susceptibilities that follow the Curie–Weiss law over a broad temperature range, with $\mu \approx 3.90$ BM (part of which is due to a temperature-independent paramagnetism).

For a strictly square, four-coordinate complex such as phthalocyanin iron(II), the extreme tetragonality of the ligand field apparently places one *d* orbital ($d_{x^2-y^2}$,) at high energy, and the six electrons adopt a high-spin distribution among the remaining four, thus giving a triplet ground state, independent of temperature.

18-E-5. Aqueous and Coordination Chemistry of Iron(III), d^5

Iron(III) occurs in salts with most anions, except those with reducing capacity. Examples obtained as pale pink to nearly white hydrates from aqueous solutions are $Fe(ClO_4)_3 \cdot 10H_2O$, $Fe(NO_3)_3 \cdot 9$(or 6)H_2O, and $Fe_2(SO_4)_3 \cdot 10H_2O$.

Aqueous Chemistry. One of the most conspicuous features of iron(III) in aqueous solution is its tendency to hydrolyze and/or to form complexes.

The hydrolysis of the pale purple ion $[Fe(H_2O)_6]^{3+}$ in noncomplexing media is complicated and condition dependent.[1,20a]

At pH < 1 the sole species is the aqua ion but above pH 1 stepwise hydrolysis occurs. At the lower concentrations the main equilibrium is

$$[Fe(H_2O)_6]^{3+} = [Fe(OH)(H_2O)_5]^{2+} + H^+ \qquad K = 1.84 \times 10^{-3}$$

A small amount of $Fe(OH)_2^+$ may be formed but the second main species is the diamagnetic μ-oxo dimer:

$$2[Fe(OH)(H_2O)_5]^{2+} \rightleftharpoons [(H_2O)_5FeOFe(H_2O)_5]^{4+} + H_2O$$

In the 1 to 2 mol ratio range other types of oxo species may be formed.

At pH >2 more condensed species and colloidal gels are formed leading to precipitation of the red brown gelatinous hydrous oxide.

The hydroxo species are yellow because of charge-transfer bands in the uv region that have tails in the visible.

In the presence of complexing anions such as Cl^-, the hydrolysis of Fe^{3+} or of $FeCl_3$ is more complicated giving chloro, aqua, and hydroxy species as well as $[FeCl_4]^-$ at high Cl^- concentration.[20b]

Iron(III) has a high affinity for F^- as shown by the constants:

$$Fe^{3+} + F^- = FeF^{2+} \qquad K_1 \approx 10^5$$

$$FeF^{2+} + F^- = FeF_2^+ \qquad K_2 \approx 10^5$$

$$FeF_2^+ + F^- = FeF_3 \qquad K_3 \approx 10^3$$

[20a] G. H. Khoe *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986,** 1901.

[20b] R. Schlögel and W. Jones, *J. Chem. Soc. Dalton Trans.*, **1984,** 1283; M. Magini *et al.*, *Inorg. Chem.*, 1983, **22,** 1001.

which are ~10^4 greater than those for Cl^-. Thiocyanate forms intense red complexes and $[Fe(NCS)_4]^-$ can be extracted into ether as its $(H_3O)^+$ salt.

Complex Compounds

Halides. The halogen complex anions have just been noted and crystalline salts such as K_3FeF_6[20c] and $CsFeF_4$, which has octahedral FeF_6 sharing F ions, and those of $FeCl_4^-$, $FeCl_5^{2-}$, $FeCl_6^{3-}$, and $Fe_2Cl_9^{3-}$ can be obtained, usually with large cations.

Iron(III) chloride forms adducts with donors, for example, $FeCl_3(THF)_3$.

Nitrogen Ligands. The affinity of Fe^{III} for amines is very low. No simple ammine complex exists in aqueous solution; addition of aqueous ammonia only precipitates the hydrous oxide. Chelating amines, for example, EDTA, form complexes, among which is the seven-coordinate $[Fe(EDTA)H_2O]^-$ ion. Also, ligands such as bipy and phen that produce ligand fields strong enough to cause spin pairing form fairly stable complexes, isolable in crystalline form with large anions.

Oxygen Ligands. These have high affinity for Fe^{III} and complexes are formed by phosphate and oxalate ions, glycerol, sugars, and so on, while β-diketones give octahedral neutral $Fe(dike)_3$.

Largely because of interest in iron transport and storage molecules (siderophores and ferritin) in living systems (Chapter 30) there has been much study of model compounds especially with hydroxamate, hydroxypyridinone, catecholate, catecholamide, and related ligands.[21a] There are relatively simple compounds like the alkoxides, $[Fe(OR)_4]^-$ and $Fe_2(\mu\text{-}OSiMe_3)_2(OSiMe_3)_4$.[21b]

A characteristic feature is the formation of *oxo* and/or *hydroxo bridges*.[22a] Binuclear systems may be (*a*) doubly bridged and (*b*) singly bridged with a linear or bent FeOFe. The bent ones have angles 140 to 180° and are known with four-, five-, and six-coordinate iron(III). An example is $[(sal_2en)Fe]_2(\mu\text{-}O)$. Porphyrin and phthalocyanine complexes are linear bridged species of the type $(porph\ Fe)_2\mu\text{-}X$ where X = O, N, and C.[22b]

Like OH, OR can also bridge and the alkoxide $[(acac)_2Fe(\mu\text{-}OEt)]_2$ has a planar Fe_2O_4 ring.[23]

Oxo bridges can also be formed from OH groups on multidentate ligands as in (18-E-III).

[20c] M. K. Chaudhuri and N. S. Islam, *Inorg. Chem.*, 1986, **25,** 3749.

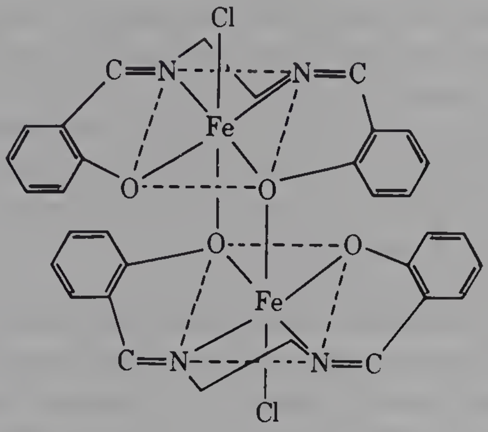
[21a] See, for example, L. Que, Jr., *et al., J. Am. Chem. Soc.*, 1985, **107**, 6528; K. N. Raymond *et al., J. Am. Chem. Soc.* 1985, **107,** 6540.

[21b] R. H. Holm, *et al., Inorg. Chem.*, 1983, **22,** 3809; S. A. Koch and M. Miller, *J. Am. Chem. Soc.*, 1982, **104,** 5255.

[22a] Y. Nisida *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 2375; T. G. Spiro *et al., Inorg. Chem.*, 1987, **26,** 2063.

[22b] L. A. Bottomley *et al., Inorg. Chem.*, 1986, **25,** 2338.

[23] O. Piovesana *et al., Inorg. Chem.*, 1984, **23,** 3398.



(18-E-III)

The simple ion[24] $[Fe_2(\mu\text{-}O)Cl_6]^{2-}$ is bent in most salts but linear with a very large cation; in solution it forms $[(H_2O)_4ClFe]_2(\mu\text{-}O)^{24}$. An unsymmetrical bridge system[25] occurs in a complex with a pentadentate N_5 ligand, L, $[LFeOFeCl_3]^+$.

It may be noted that there is only one example of a sulfur bridge, in $[Fe(sal_2en)]_2S$ which has an angle much smaller (121.8°) than in $[Fe(sal_2en)]_2O$ (145°) from which it is made by interaction with $(Me_3Si)_2S$.[26]

In complexes with linear FeOFe links there is π bonding across the bridge and even bent species have large bond angles; this can lead to antiferromagnetic coupling of the electron spins on each Fe^{III}.

Iron(III) forms extensive series of *basic carboxylates* of the type $[Fe_3O(O_2CR)_6L_3]^+$, discussed in Section 12-9. For some, reduction gives mixed valence species; thus $Fe_3O(O_2CMe)_6(py)_3$ has a localized Fe_2^{III}, Fe^{II} electronic structure in the solid at 100 K according to Mössbauer spectra.[27a] Many more complicated polymeric oxo species are also known,[27b] for example $Fe_{11}O_6(PhCO_2)_{15}(OH)_6$; such species may provide models for the core of ferritin.

Cyanide. In contrast to $[Fe(CN)_6]^{4-}$, the $[Fe(CN)_6]^{3-}$ ion is quite poisonous; for kinetic reasons the latter dissociates and reacts rapidly, whereas the former is not labile. There is a variety of substituted ions $[Fe(CN)_5X]$ ($X = H_2O$, NO_2, etc.), of which the best known is the nitroprusside ion $[Fe(CN)_5NO]^{2-}$; this is attacked by OH^- to give $[Fe(CN)_5NO_2]^{2-}$ (Section 10-6).

[24] G. J. Bullen *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986,** 1937; J. A. Taies and J. Silver, *Inorg. Chim. Acta,* 1986, **125,** 67; W. H. Armstrong and S. J. Lippard, *Inorg. Chem.*, 1985, **24,** 981; U. Thewalt *et al.*, *J. Crystallogr. Spectros. Res.*, 1986, **16,** 483.

[25] G. B. Jameson *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 851.

[26] R. H. Holm *et al.*, *Inorg. Chem.*, 1984, **23,** 4407.

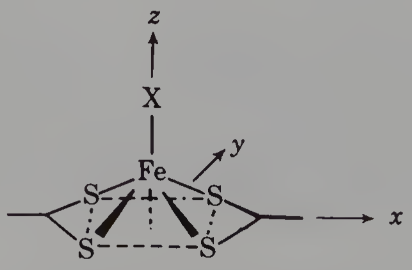
[27a] D. N. Hendricksen *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 8009; M. Sorai *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 702.

[27b] S. J. Lippard *et al.*, *J. Am. Chem. Soc.*, 1987, **109,** 3337, 4244.

Electronic Structures of Iron(III) Compounds. Iron(III) is isoelectronic with Mn^{II}, but less is known of the details of Fe^{III} spectra because of the much greater tendency of the trivalent ion to have charge-transfer bands in the near-uv region with strong low-energy wings in the visible that obscure the very weak, spin-forbidden *d–d* bands. Insofar as they are known, however, the spectral features of Fe^{III} ions in octahedral surroundings are in accord with theoretical expectations.

Iron(III), like manganese(II), is high spin in nearly all its complexes, except those with the strongest ligands, exemplified by $[Fe(CN)_6]^{3-}$; $[Fe(bipy)_3]^{3+}$, $[Fe(phen)_3]^{3+}$, and other tris complexes with imine nitrogen atoms as donors. In the high-spin complexes the magnetic moments are always very close to the spin-only value of 5.9 BM because the ground state (derived from the ^5S state of the free ion) has no orbital angular momentum and there is no effective mechanism for introducing any by coupling with excited states. The low-spin complexes, with t_{2g}^5 configurations, usually have considerable orbital contributions to their moments at about room temperature, values of ~2.3 BM being obtained. The moments are, however, intrinsically temperature dependent, and at liquid nitrogen temperature (77 K) they decrease to ~1.9 BM. There is evidence of very high covalence and electron delocalization in low-spin complexes such as $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$.

Five-coordinate complexes may be high- or low-spin depending on the ligands; some of the important high-spin complexes have already been encountered in oxo-bridged dinuclear complexes. The $Fe(S_2CNR_2)_2X$ (X = Cl, Br, and I) complexes that form readily on treating $Fe(S_2CNR_2)_3$ with halogens have three unpaired electrons. These molecules have a very distorted *sp* configuration with X axial (actual symmetry C_{2v}), and with coordinate axes as defined in (18-E-IV) the electron configuration is $d_{x^2-y^2}^2$, d_{xz}^1, d_{yz}^1, $d_{z^2}^1$, d_{xy}^0, according to magnetic anisotropy measurements.



(18-E-IV)

Dithiocarbamates and Schiff base complexes provide many good examples of spin crossovers[28] and low-spin–high-spin equilibria.

[28] D. N. Hendrickson *et al., Inorg. Chem.*, 1986, **25**, 160; 1985, **24**, 3497; N. Matsumoto *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 2575.

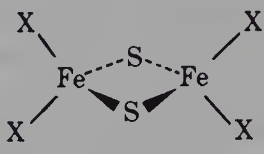
18-E-6. Mixed Valence Compounds of Iron

Prussian Blues.[29] The blue precipitates obtained on mixing Fe^{3+} with [Fe^{II}(CN)$_6$]$^{4-}$ or Fe^{2+} and [Fe^{III}(CN)$_6$]$^{3-}$ have long been known; both products are Fe$_4^{III}$[Fe^{II}(CN)$_6$]$_3$·xH$_2$O.

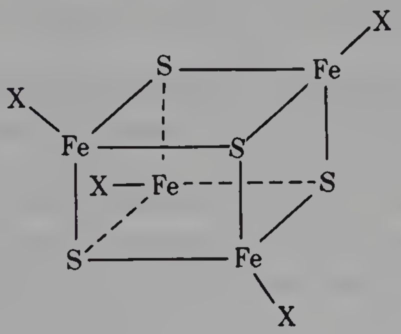
The structure of Prussian blue, which has been used as a pigment, and other similar materials such as Cu$_2^{II}$[Fe^{II}(CN)$_6$](aq) or M$_3^{II}$[Co^{III}(CN)$_6$]$_2$(aq) are based on a three-dimensional cubic framework[30] with M^A and M^B atoms at the corners of a cube and with M^A—N—C—M^B links. There can be empty metal and CN sites depending on the stoichiometry, that is, on the valence of M^A and M^B. Water molecules can also be bound to Fe^{III} in Prussian blue as well as being interstitial as in zeolites. Reduction of Prussian blue gives Everitt's salt K$_2$[Fe^{II}Fe^{II}(CN)$_6$].

Iron–Sulfur Complexes. Iron–sulfur systems have been intensively studied because of their relationship to nonheme iron–sulfur proteins (Chapter 30).

The compounds, many of which have thiolato groups, can have iron in II, III, and mixed oxidation states; they are of types such as [Fe(SR)$_4$]$^{1-,2-}$, [Fe$_2$(μ-S)$_2$(SR)$_4$]$^{2-}$, [Fe$_4$(μ_3-S)$_4$(SR)$_4$]$^{2-,3-}$, and [Fe$_3$S$_4$(SR)$_4$]$^{3-}$ where there are Fe(μ-S)$_2$Fe(μ-S)$_2$Fe groups,[31] and [Fe$_6$S$_9$(SR)$_2$]$^{4-}$, which has both μ-S and μ_3-S groups. Two simpler cases, where charges are omitted, are shown in (18-E-V) and (18-E-VI).



(18-E-V)



(18-E-VI)

In most cases the group X is an RS— or half of an —S—S— ligand, but compounds in which X = Cl, Br, I, or OR[32] are known.

A prime feature of many of these systems and others with both Fe and Mo, are reversible electron transfer redox reactions and these give a clue to the importance of such polynuclear species in Nature. The compounds are

[29] D. B. Brown *Ed., Mixed Valence Compounds,* Reidel, Dordrecht, 1980; K. Ogura and K. Takamagari, *J. Chem. Soc. Dalton Trans.,* **1986,** 1519.

[30] A. Ludi *et al., Inorg. Chem.,* 1980, **19,** 956.

[31] D. Coucouvanis *et al., Inorg. Chem.,* 1986, **25,** 2460.

[32] W. E. Cleland, Jr., and B. A. Averill, *Inorg. Chem.,* 1984, **23,** 4192.

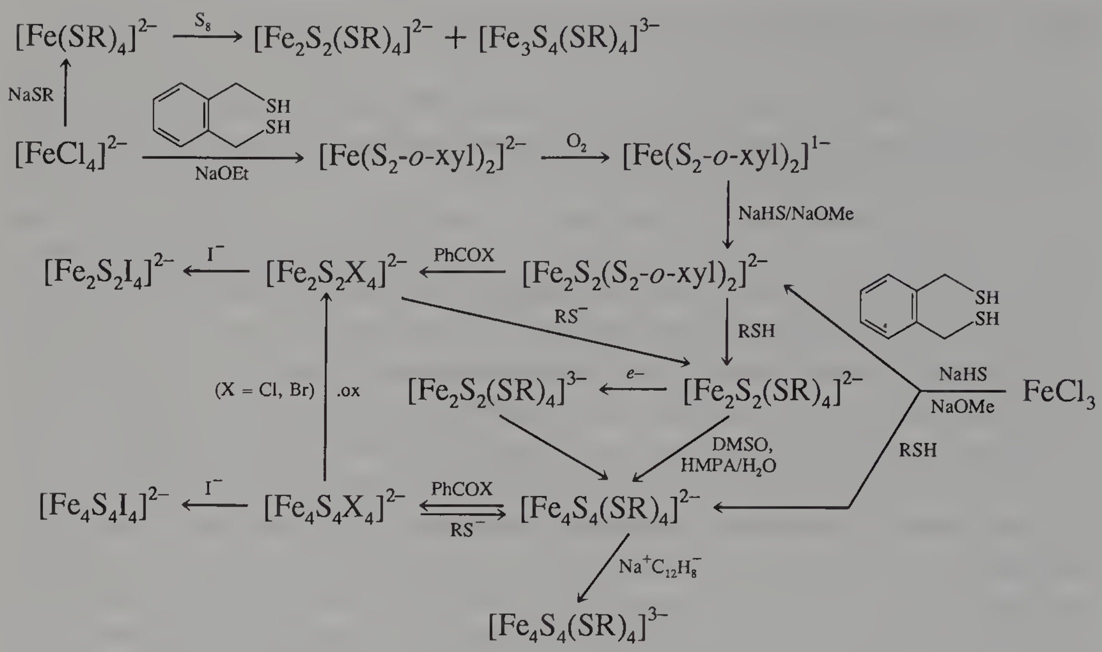


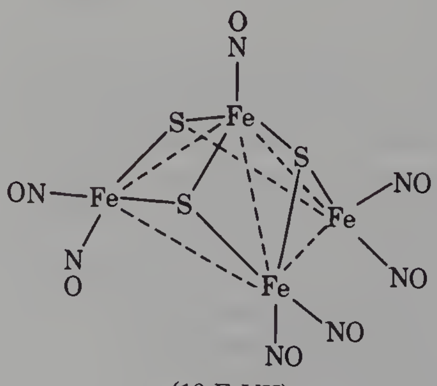
FIG. 18-E-1. Some important reactions of iron–sulfur clusters.

made quite readily from $FeCl_2$, $FeCl_3$, $[FeCl_4]^{1-,2-}$, or $[Fe(SR)_4]^{1-,2-}$ (Fig. 18-E-1); an important role is played by mono–bi and bi–tetra nuclear interconversion. Other preparations include[33]

$$[Fe(H_2O)_6]^{3+} + PEt_3 + NaBPh_4 + H_2S \longrightarrow [Fe_3(\mu\text{-}S)_8(PEt_3)_6]^{2+}$$

Some complexes can also be spontaneously assembled from the components, for example, $FeCl_3$, S_8, and RSH or $Fe + S_8 + I_2 + 2I^-$, which gives $[Fe_6S_6I_6]^{2-}$.[34]

Another class of polynuclear iron–sulfur compounds, some of which have been known for a very long time, are those containing NO. These include the red Roussin ester $(NO)_2Fe(\mu\text{-}SEt)_2Fe(NO)_2$, the black Roussin salts (18-E-VII), and the cubane-like $Fe_4(\mu_3\text{-}S)_4(NO)_4$.



(18-E-VII)

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[33] M. Bacci *et al., Inorg. Chem.*, 1985, **24,** 689.

[34] S. Pohl *et al., Angew. Chem. Int. Ed. Engl.*, 1984, **23,** 150.

18-E-7. Porphyrins[35]

Complexes of conjugated macrocycles (Section 10-12) are of prime importance in living systems and for similar reasons other N_4 macrocyclic complexes have been intensively studied.[36]

The square Fe^{II} porphyrins initially add O_2 reversibly but, unlike heme and ligand protected systems, undergo autoxidation even at low temperatures to give μ-peroxo species, $[\text{porph}Fe^{III}]_2\mu\text{-}(O_2)$, which can react with bases to give $(\text{base})(\text{porph})Fe^{IV}{=}O$.

The Fe^{IV} species[37] are unstable decomposing to $(\text{porph}Fe^{III})_2\mu\text{-}O$. The oxygenated species can oxidize organic substrates.

There are also other porphyrin compounds such as (porph)FePh,[38] bridged species $(\text{porph}Fe)_2X$, X = O, N, or C[22b] and carbenes,[39] $(\text{porph})Fe{=}CCl_2$, that are of the type implicated in CCl_4 and DDT toxicity. There are also other Fe^{IV} species[40a] such as (porph)Fe(X)Ph, (porph)Fe=NR, and so on. Reduced $Fe(\text{oep})^{n-}$ species with Fe^0 and Fe^I are also known.[40b]

18-E-8. The Higher Oxidation States

Iron(IV). Although relatively few iron(IV) compounds have been characterized, transient FeO^{IV} species appear to be involved in many natural oxidation systems (Chapter 30) especially in porphyrin and related complexes (see last section); mixed oxides containing Fe^{IV} have been noted (Section 18-E-2).

Various cationic complexes[41] can be made by chemical or electrochemical oxidation of Fe^{III} analogues; examples are $[Fe(S_2CNR_2)_3]^+$ and $[Fe(\text{bipy})_3]^{4+}$ that are octahedral with two unpaired electrons; phosphine complexes of the type *trans*-$[\text{diphos}_2FeCl_2]^{2+}$ have a t_{2g}^4 configuration.

The stability of the tetrahedral purple alkyl Fe(1-norbornyl)$_4$ is doubtless due to the steric bulk of the ligand. The $(Me_5C_5)_2Fe^{2+}$ ion is also reasonably stable in $AlCl_3$-1-butylpyridinium chloride melts.

Iron(VI). Alkali metal salts can be obtained by hypochlorite oxidation of iron(III) nitrate in strong alkali solution.[42a] The blue K_2FeO_4 is isomorphous

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[35] A. P. B. Lever and H. B. Gray, Eds., *Iron Porphyrins,* Vols, 1, 2, Addison-Wesley, Reading, Massachusetts 1983.

[36] See papers by D. H. Busch, mainly in *Inorganic Chemistry.*

[37] K. Shin and H. M. Goff, *J. Am. Chem. Soc.,* 1987, **109,** 3140.

[38] R. Guilard, *Inorg. Chem.,* 1985, **24,** 2509.

[39] T. C. Bruice *et al., J. Am. Chem. Soc.,* 1981, **103,** 4578.

[40a] D. Mansuy *et al., J. Am. Chem. Soc.,* 1986, **108,** 1079; A. L. Balch *et al., J. Am. Chem. Soc.* 1986, **108,** 2603.

[40b] T. Kitagawa *et al., J. Am. Chem. Soc.,* 1987, **109,** 180.

[41] W. Levason *et al., J. Am. Chem. Soc.,* 1986, **108,** 1789, 526; E. F. Trogu *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 365.

[42a] R. J. Audette and J. W. Quail, *Inorg. Chem.,* 1972, **11,** 1904.

with K_2CrO_4 and K_2MnO_4[42b] having the discrete FeO_4^{2-} ion. It is a stronger oxidant than MnO_4^-.

Iron(V) may be present in some mixed oxide systems.[9]

Additional References

Herber, R. H., Ed., *Chemical Mössbauer Spectroscopy,* Plenum, New York, 1985 (includes Fe compounds).

Long, G. J., *Mössbauer Spectra Applied to Inorganic Chemistry,* Vol. 1, Plenum, New York, 1984.

18-F. COBALT: GROUP VIII(9)

The trends toward decreased stability of the very high oxidation states and the increased stability of the II state relative to the III state, which have been noted through the series Ti, V, Cr, Mn, and Fe, persist with cobalt. Indeed, the first trend culminates in the complete absence of oxidation states higher than IV under chemically significant conditions. The oxidation state IV is represented by only a few compounds. The III state is relatively unstable in simple compounds, but the low-spin complexes are exceedingly numerous and stable, especially where the donor atoms (usually N) make strong contributions to the ligand field. There are also some important complexes of Co^I; this oxidation state is better known for cobalt than for any other element of the first transition series except copper.

The oxidation states and stereochemistry are summarized in Table 18-F-1.

18-F-1. The Element

Cobalt always occurs in Nature in association with Ni and usually also with arsenic. The most important Co minerals are *smaltite* ($CoAs_2$) and *cobaltite* (CoAsS), but the chief technical sources of Co are residues called "speisses," which are obtained in the smelting of arsenical ores of Ni, Cu, and Pb.

Cobalt is a hard, bluish-white metal (mp 1493°C, bp 3100°C). It is ferromagnetic with a Curie temperature of 1121°C. It dissolves slowly in dilute mineral acids, the Co^{2+}/Co potential being -0.277 V, but it is relatively unreactive. It does not combine directly with H_2 or N_2; in fact, no hydride or nitride appears to exist. The metal will combine with C, P, and S on heating. It also is attacked by atmospheric O_2 and by water vapor at elevated temperatures, giving CoO. Very reactive metal can be made by reduction of $CoCl_2$ with Li naphthalenide in glyme.[1]

[42b] M. L. Hoppe *et al., Acta Crystallogr.*, 1982, **B38**, 2237.

[1] G. L. Rochefort and R. D. Riecke, *Inorg. Chem.*, 1986, **25**, 348.

TABLE 18-F-1
Oxidation States and Stereochemistry of Cobalt

Oxidation state	Coordination number	Geometry	Examples
Co^{-I}, d^{10}	4	Tetrahedral	$Co(CO)_4^-$, $Co(CO)_3NO$
Co^0, d^9	4	Tetrahedral	$K_4[Co(CN)_4]$, $Co(PMe_3)_4$
Co^I, d^8	3	Planar	(tempo)$Co(CO)_2$[a]
	4	Tetrahedral	$CoBr(PR_3)_3$
	5[b]	*tbp*	$[Co(CO)_3(PR_3)_2]^+$, $HCo(PR_3)_4$, $[Co(NCMe)_5]^+$
	5	*sp*	$[Co(NCPh)_5]ClO_4$
	6	Octahedral	$[Co(bipy)_3]^+$
Co^{II}, d^7	3	Trigonal[c]	$\{Co(OCBu_3)_2[N(SiMe_3)_2]\}^-$, $Co_2(NPh_2)_4$
	4[b]	Tetrahedral	$[CoCl_4]^{2-}$, $CoBr_2(PR_3)_2$, Co^{II} in Co_3O_4
	4	Square	$[(Ph_3P)_2N]_2[Co(CN)_4]$[d]
	5	*tbp*	$[Co(Me_6tren)Br]^+$, $CoH(BH_4)(PCy_3)_2$
	5	*sp*	$[Co(ClO_4)(MePh_2AsO)_4]^+$, $[Co(CN)_5]^{3-}$, $[Co(CNPh)_5]^{2+}$
	6[b]	Octahedral	$CoCl_2$, $[Co(NH_3)_6]^{2+}$
	8	Dodecahedral	$(Ph_4As)_2[Co(NO_3)_4]$
Co^{III}, d^6	4	Tetrahedral	In a 12-heteropolytungstate; in garnets
	4	Square[e]	$[Co(SR)_4]^-$
	5	*sp*	RCo(saloph)[f]
	6[b]	Octahedral	$[Co(en)_2Cl_2]^+$, $[Cr(CN)_6]^{3-}$, $ZnCo_2O_4$, CoF_3, $[CoF_6]^{3-}$
Co^{IV}, d^5	4	Tetrahedral	Co(1-norbornyl)$_4$[g]
	6	Octahedral	$[CoF_6]^{2-}$, *trans*-Co(CHBADCB)(*t*-Bupy)$_2$[h]
Co^V, d^4	4	Tetrahedral	[Co(1-norbornyl)$_4$]$^+$

[a] From $Co_2(CO)_8$ and 2,2,6,6-tetramethylpiperidine-1-oxyl(tempo). P. Jartner *et al.*, *J. Organomet. Chem.*, 1986, **311,** 379.

[b] Most common states.

[c] P. P. Power *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 712; *Inorg. Chem.*, 1986, **25,** 1027.

[d] L. S. Stuhl *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 4265.

[e] For references see T. J. Collins *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 2088.

[f] L. G. Marzilli *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 6880.

[g] K. H. Theopold *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986,** 1491.

[h] T. J. Collins, *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 5037 (CHBADCB = chlorinated Schiff base).

COBALT COMPOUNDS

18-F-2. Binary Cobalt Compounds: Simple Salts

Oxides. On heating Co^{II} carbonate, nitrate, and so on, olive-green cobalt(II) oxide is obtained. It normally has a slight excess of oxygen and is a *p*-type semiconductor. It has the NaCl structure.

At 400 to 500°C in air the oxide Co_3O_4 is obtained.[2] This is a normal spinel with Co^{2+} ions in tetrahedral interstices and Co^{3+} ions in octahedral interstices. Other oxides Co_2O_3 and CoO_2 and a red oxocobaltate(II) $Na_{10}[Co_4O_9]$, are known.

The hydrous oxide CoO(OH) occurs as the mineral *heterogenite*. It has a layer lattice with $Co^{III}O_6$ octahedra and gives Co_3O_4 on heating.[3]

Halides. The anhydrous halides CoX_2 may be made by dehydration of hydrated halides and for CoF_2 by action of HF on $CoCl_2$. The chloride is bright blue.

The action of fluorine or other fluorinating agents on cobalt halides at 300 to 400°C gives dark brown CoF_3 commonly used as a fluorinating agent. It is reduced by water.

Sulfide. From Co^{2+} solutions, a black solid CoS is precipitated by the action of H_2S.

Salts. *Cobalt(II)* forms an extensive group of simple and hydrated salts. The latter are red or pink and contain the $[Co(H_2O)_6]^{2+}$ ion or other octahedrally coordinated ions. Addition of OH^- to Co^{2+} solutions gives $Co(OH)_2$, which may be pink or blue depending on the conditions; only the pink form is stable. It is amphoteric, dissolving in concentrated hydroxide to give a deep blue solution containing $[Co(OH)_4]^{2-}$ ions, from which crystalline salts can be obtained.

Cobalt(III) forms few simple salts, but the green hydrated fluoride $CoF_3 \cdot 3.5H_2O$ and the blue hydrated sulfate $Co_2(SO_4)_3 \cdot 18H_2O$ separate on electrolytic oxidation of Co^{2+} in 40% HF and 8 *M* H_2SO_4, respectively. Alums, $M^ICo(SO_4)_2 \cdot 12H_2O$, are dark blue; they are reduced by water.

18-F-3. Complexes of Cobalt(II), d^7

In aqueous solutions containing no complexing agents, oxidation of $[Co(H_2O)_6]^{2+}$ to Co^{III} is very unfavorable:

$$[Co(H_2O)_6]^{3+} + e = [Co(H_2O)_6]^{2+} \qquad E^0 = 1.84\ V$$

However, electrolytic or O_3 oxidation of cold acidic perchlorate solutions of Co^{2+} gives $[Co(H_2O)_6]^{3+}$, which is in equilibrium with $[Co(OH)(H_2O)_5]^{2+}$. At 0°C, the half-life of these diamagnetic ions is about a month. In the presence of complexing agents such as NH_3, which form stable complexes with Co^{III}, the stability of Co^{III} is greatly improved,

$$[Co(NH_3)_6]^{3+} + e = [Co(NH_3)_6]^{2+} \qquad E^0 = 0.1\ V$$

and in basic media,

$$CoO(OH)(s) + H_2O + e = Co(OH)_2(s) + OH^- \qquad E^0 = 0.17\ V$$

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[2] L. Hernan *et al.*, *J. Solid State Chem.*, 1985, **59**, 388.

[3] P. O'Brian and U. Patel, *J. Chem. Soc. Dalton Trans.*, **1982,** 1407.

Water rapidly reduces uncomplexed Co^{3+} at room temperature and this relative instability is evidenced by the rarity of simple salts and binary compounds, whereas Co^{II} forms such compounds in abundance.

Cobalt(II) forms numerous complexes, mostly either octahedral or tetrahedral but five-coordinate and square species are also known.

There are more *tetrahedral complexes* of Co^{II} than for other transition metal ions. This is in accord with the fact that for a d^7 ion, ligand field stabilization energies disfavor the tetrahedral configuration relative to the octahedral one to a smaller extent than for any other d^n ($1 \le n \le 9$) configuration, although it should be noted that this argument is valid only in comparing the behavior of one metal ion to another, not for assessing the absolute stabilities of the configurations for any particular ion. The only d^7 ion of common occurrence is Co^{2+}.

Because of the small stability difference between octahedral and tetrahedral Co^{II} complexes, there are several cases in which the two types with the same ligand are both known and may be in equilibrium. An example is that of the thiocyanates in methanol.[4] There is always some $[Co(H_2O)_4]^{2+}$ in equilibrium with $[Co(H_2O)_6]^{2+}$ in aqueous solution.

Tetrahedral complexes, $[CoX_4]^{2-}$, are generally formed with monodentate anionic ligands such as Cl^-, Br^-, I^-, SCN^-, N_3^-, and OH^-; with a combination of two such ligands and two neutral ones, tetrahedral complexes of the type CoL_2X_2 are formed. With ligands that are bidentate monoanions, tetrahedral complexes are formed in some cases (e.g., with *N*-alkylsalicylaldiminato and bulky β-diketonate anions). With the less hindered ligands of this type, association to give a higher coordination number often occurs. Thus in bis(*N*-methylsalicylaldiminato)cobalt(II) a dimer with five-coordinate Co atoms is formed [Fig. 18-F-1(a)], whereas $Co(acac)_2$ is a tetramer in which each Co atom is six-coordinate [Fig. 18-F-1(b)].

Planar complexes are formed with several bidentate monoanions such as dimethylglyoximate, *o*-aminophenoxide, dithioacetylacetonate, and dithiolate-type ligands. Several neutral bidentate ligands also give planar complexes, although it is either known or reasonable to presume that the accompanying anions are coordinated *to some degree,* so that these complexes could also be considered as very distorted octahedral ones. Examples are $[Coen_2](AgI_2)_2$ and $[Co(CH_3SC_2H_4SCH_3)_2](ClO_4)_2$. With tetradentate ligands such as sal_2en and porphyrins, planar complexes are also obtained.

The addition of KCN to aqueous Co^{2+} gives a green solution and a purple solid. The anion in the purple salt $Ba_3[Co_2(CN)_{10}]\cdot 13H_2O$ has the $Mn_2(CO)_{10}$ type structure (Chapter 22) with a Co—Co bond. In solution the primary species is probably $[Co(CN)_5(H_2O)]^{3-}$, but there are also species with less CN^-, and the solution is unstable, reacting with water to give $[Co(CN)_5H]^{3-}$,

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[4] H. B. Silver and M. A. Murguia, *Inorg. Chem.*, 1985, **24**, 3794.

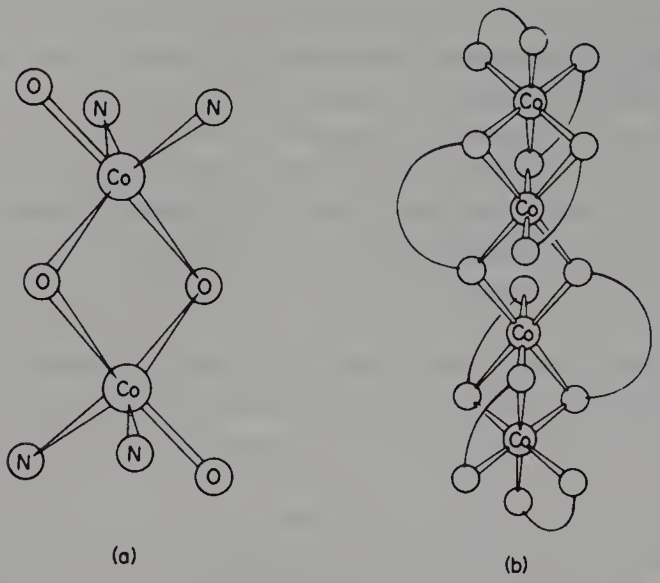


FIG. 18-F-1. Schematic representations of the structures of (a) the dimer of bis(*N*-methylsalicylaldiminato)cobalt(II) and (b) the tetramer of bis(acetylacetonato)cobalt(II).

$[Co(CN)_5OH]^{3-}$, and other species. In solvents like MeCN or DMF salts such as $Li_3[Co(CN)_5]\cdot 3DMF$ or $(PPN)_2[Co(CN)_4]\cdot 4DMF$ can be obtained.[5a]

The green aqueous solution reacts with hydrogen

$$2[Co(CN)_5]^{3-} + H_2 = 2\,[Co^{III}(CN)_5H]^{3-}$$

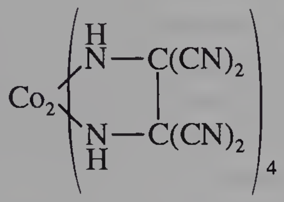
and is a catalyst for homogeneous hydrogenation of conjugated alkenes, especially under phase transfer conditions. The ion also reacts with C_2F_4, C_2H_2, SO_2, or $SnCl_2$ to give cobalt(III) complexes in which the small molecule is "inserted" between two cobalt atoms as in $[(NC)_5Co{-}CF_2CF_2{-}Co(CN)_5]^{6-}$ and $K_6[(CN)_5CoCH{=}CHCo(CN)_5]$, where the configuration is trans about the double bond. The red-brown $[Co(CN)_5O_2]^{3-}$ is best regarded as a superoxo complex of Co^{III} (see later).

Five coordinate species that are *tbp* or *sp* are phosphine adducts such as $CoBr_2(PMe_3)_3$ or $Co(CN)_2(PMe_2Ph)_3$[5b] that bind O_2. Other types are mainly with polydentate ligands. The geometry varies, some approaching the *tbp* and others the *sp* limiting cases and many have an intermediate (C_{2v}) arrangement. Interest in these complexes has centered mainly on correlating their electronic structures with molecular symmetry and the atoms constituting the ligand set; these points are mentioned later in connection with electronic structures.

The benzoate $Co_2(CO_2Ph)_4L_2$ (L = quinoline) has a typical tetra bridged structure but the Co—Co distance is very long and there is no metal-metal bond. There are other similar carboxylates.[6a]

[5a] L. S. Stuhl *et al., Inorg. Chem.*, 1986, **25**, 2888.
[5b] R. S. Drago *et al., J. Am. Chem. Soc.*, 1980, **102**, 1884.
[6a] B. P. Straughan and P. Thornton, *J. Chem. Soc. Dalton Trans.*, **1986**, 2211.

Dialkylamides, $Co_2(NR_2)_4$, have two μ-NR_2 groups and trigonal planar Co atoms with a Co—Co bond of ~2.6 Å. The magnetic moments vary considerably: for R = $SiMe_3$, μ_B = 4.83 but for R = Ph, μ_B = 1.72.[6b] In a similar complex (18-F-1) there is a Co—Co bond only, with no bridge.[7] There are also thiolates such as $[Co(SPh)_4]^{2-}$ and $[Co_4(SPh)_{10}]^{2-}$,[8a] and alkoxides[8b] such as $[Co(OSiPh_3)_2THF]_2$.



(18-F-I)

Electronic Structures of Cobalt(II) Compounds. As already noted, cobalt(II) occurs in a great variety of structural environments; because of this the electronic structures, hence the spectral and magnetic properties of the ion, are extremely varied.

High-Spin Octahedral and Tetrahedral Complexes. For qualitative purposes the partial energy level diagram in Fig. 18-F-2 is useful. In each case there is a quartet ground state and three spin-allowed electronic transitions to the excited quartet states. Quantitatively the two cases differ considerably,

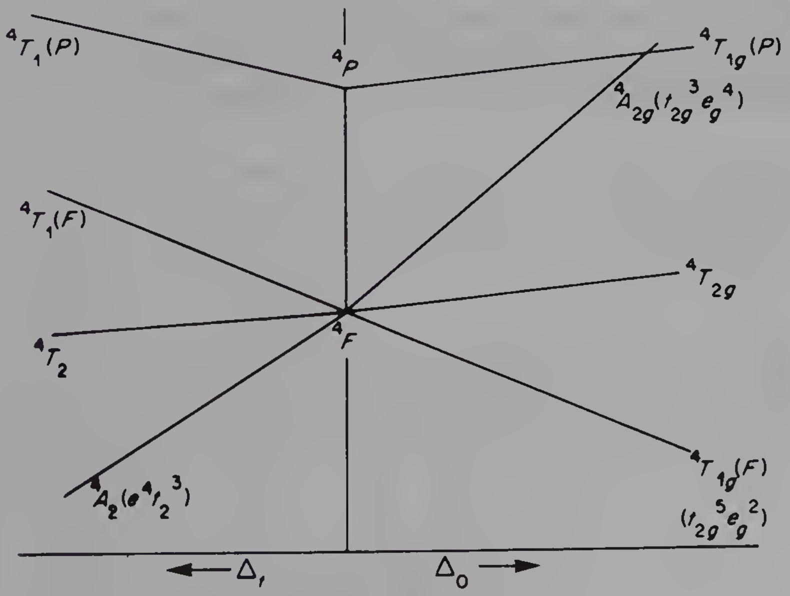


FIG. 18-F-2. Schematic energy level diagram for quartet states of a d^7 ion in tetrahedral and octahedral ligand fields.

[6b] P. P. Power *et al., J. Am. Chem. Soc.*, 1985, **107,** 712.

[7] S-M. Peng *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 210.

[8a] S. A. Koch *et al., Inorg. Chem.*, 1987, **26,** 3079; *J. Chem. Soc. Chem. Commun.*, **1987,** 966.

[8b] P. P. Power *et al., Inorg. Chem.*, 1987, **26,** 1773.

as might be inferred from the simple observation that octahedral complexes are typically pale red or purple, whereas many common tetrahedral ones are an intense blue. In each case the visible spectrum is dominated by the highest energy transition, ${}^4A_2 \rightarrow {}^4T_1(P)$ for tetrahedral and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ for octahedral complexes; but in the octahedral systems the ${}^4A_{2g}$ level is usually close to the ${}^4T_{1g}(P)$ level and the transitions to these two levels are close together. Since the ${}^4A_{2g}$ state is derived from a $t_{2g}^3e^4$ electron configuration, and the ${}^4T_{1g}(F)$ ground state is derived mainly from a $t_{2g}^5e_g^2$ configuration, the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition is essentially a two-electron process; thus it is weaker by about a factor of 10^{-2} than the other transitions. In the tetrahedral systems, as illustrated in Fig. 18-F-3, the visible transition is generally about an order of magnitude more intense and displaced to lower energies, in accord with the observed colors mentioned previously. For octahedral complexes, there is one more spin-allowed transition (${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$) which generally occurs in the near-ir region. For tetrahedral complexes there is also a transition in the near-ir region [${}^4A_2 \rightarrow {}^4T_1(F)$], as well as one of quite low energy (${}^4A_2 \rightarrow {}^4T_2$), which is seldom observed because it is in an inconvenient region of the spectrum (1000–2000 nm) and it is orbitally forbidden. The visible transitions in both cases, but particularly in the tetrahedral case, generally have complex envelopes because a number of transitions to doublet excited states occur in the same region, and these acquire some intensity by means of spin-orbit coupling.

The octahedral and tetrahedral complexes also differ in their magnetic properties. Because of the intrinsic orbital angular momentum in the octahedral ground state, there is consistently a considerable orbital contribution, and effective magnetic moments for such compounds around room temper-

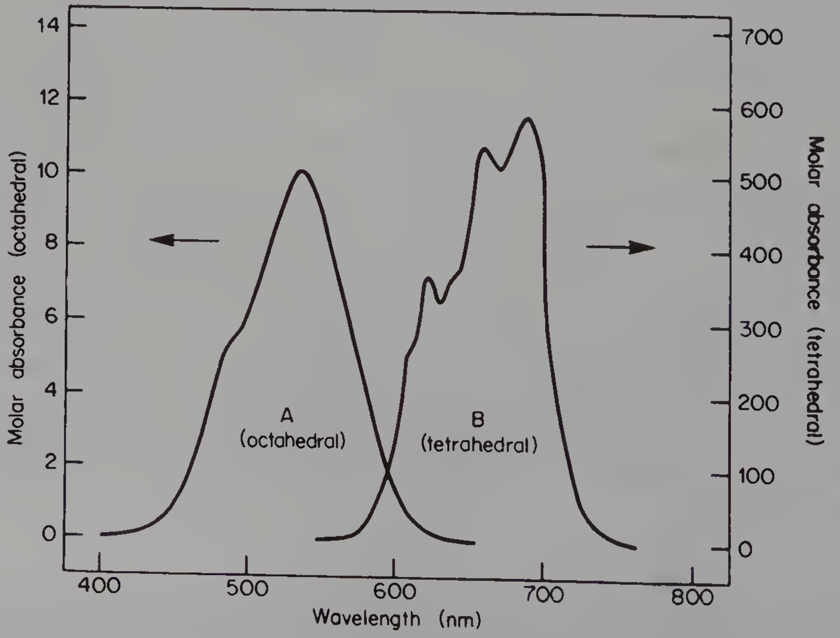


FIG. 18-F-3. The visible spectra of $[Co(H_2O)_6]^{2+}$ (curve A) and $[CoCl_4]^{2-}$ (curve B).

ature are between 4.7 and 5.2 BM. For tetrahedral complexes the ground state acquires orbital angular momentum only indirectly through mixing in the $^4T_2$ state by a spin-orbit coupling perturbation. First-order perturbation theory leads to the expression

$$\mu = 3.89 - \frac{15.59\lambda'}{\Delta_t}$$

where 3.89 is the spin-only moment for three unpaired electrons and λ' is the effective value of the spin-orbit coupling constant (which is inherently negative). Since λ' varies little from one complex to another, orbital contributions vary inversely with the strength of the ligand field. For example, among the tetrahalo complexes we have: $CoCl_4^{2-}$, 4.59 BM; $CoBr_4^{2-}$, 4.69 BM; CoI_4^{2-}, 4.77 BM.

Low-Spin Octahedral Complexes. A sufficiently strong ligand field ($\Delta_O \gtrsim$ 15,000 cm^{-1}) can cause a ^2E state originating in the ^2G state of the free ion to become the ground state. The electron configuration here is mainly $t_{2g}^6e_g$; thus a Jahn–Teller distortion would be expected. Consequently perfectly octahedral low-spin Co^{II} complexes are rare, tending to lose ligands and form low spin four- or five-coordinate species. An authentic example, however, is a complex of an S_6 crown, [Co hexathio-18-C-6]$^{2+}$, but unlike a comparable Ni^{II} complex there is a tetragonal distortion (equatorial Co—S 2.25 to 2.29 Å, axial Co—S 2.48 Å) and there is a strong resemblance to Jahn–Teller distorted Cu^{2+} complexes structurally and also magnetically.[9]

As noted previously, the $[Co(CNC_6H_5)_6]^{2+}$ ion in solution is axially distorted. It appears that ligands tending to give a strong enough field to cause spin pairing give five- rather than six-coordinate complexes, or dinuclear ones such as $[Co_2(CNCH_3)_{10}]^{4+}$.

Square Complexes. All these are low spin with magnetic moments of 2.2 to 2.7 BM at 300 K. Their spectra are complex, and neither magnetic nor spectral properties of such compounds have been treated in detail. There are some data to suggest that the unpaired electron occupies the d_{z^2} orbital, as might be expected.

Five-Coordinate Complexes. Both high-spin (three unpaired electrons) and low-spin (one unpaired electron) configurations are found for both trigonal bipyramidal and square pyramidal as well as for intermediate configurations. The following configurations are for the four spin-structure combinations:

Spin	D_{3h}	C_{4v}
High	$(e'')^4(e')^2(a_1')$	$b_2^2e^3a_1b_1$
Low	$(e'')^4(e')^3$	$b_2^2e^4a_1$

It appears that the relationships between spin state, geometry, and nature of the ligand atoms are closely interlocked, so that no simple relationship be-

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[9] S. R. Cooper *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 386.

tween any two of these factors has been found. However, it does appear that spin state and the nature of the donor atom set are roughly correlated independently of geometry in such a way that the more heavy atom (e.g., P, As, Br, or S) donors (as compared with O and N) are present, the greater is the tendency to spin pairing; this is hardly surprising. For high-spin complexes with fairly regular geometry, for example, $[Co(Me_6tren)Br]^+$ (C_{3v}) and $[Co(Ph_2MeAsO)_4(ClO_4)]^+$ (C_{4v}), detailed and reasonably convincing spectral assignments have been made. For irregular geometries and for low-spin complexes there are more uncertainties.

18-F-4. Complexes of Cobalt(III), d^6

The complexes of Co^{III} are exceedingly numerous.[10] Because they generally undergo ligand-exchange reactions relatively slowly, they have, from the days of Werner and Jørgensen, been extensively studied and a large fraction of our knowledge of the isomerism, modes of reaction, and general properties of octahedral complexes as a class is based on studies of Co^{III} complexes. Almost all discrete Co^{III} complexes are octahedral, though a few cases of tetrahedral, planar, and square antiprismatic complexes are known.

Cobalt(III) shows a particular affinity for nitrogen donors, and the majority of its complexes contain NH_3, ethylenediamine, NO_2 groups, or N-bonded SCN groups, as well as halide ions and water molecules. In general, these complexes are synthesized in several steps beginning with one in which the aqua Co^{II} ion is oxidized in solution, typically by O_2 (see later discussion) or H_2O_2 and often a surface-active catalyst such as activated charcoal, in the presence of the ligands. For example, when a vigorous stream of air is drawn for several hours through a solution of a Co^{II} salt, CoX_2 (X = Cl, Br, or NO_3), containing NH_3, the corresponding ammonium salt and some activated charcoal, good yields of hexammine salts are obtained:

$$4CoX_2 + 4NH_4X + 20NH_3 + O_2 \longrightarrow 4[Co(NH_3)_6]X_3 + 2H_2O$$

In the absence of charcoal, replacement usually occurs to give, for example, $[Coam_5Cl]^{2+}$ and $[Coam_4(CO_3)]^+$. There is a similar oxidation:

$$4CoCl_2 + 8en + 4en{\cdot}HCl + O_2 = 4[Co(en)_3]Cl_3 + 2H_2O$$

However, a similar reaction in acid solution with the hydrochloride gives the green *trans*-$[CoCl_2(en)_2]^+$ ion as the salt *trans*-$[Co(en)_2Cl_2][H_5O_2]Cl_2$, which loses HCl on heating. This trans isomer may be isomerized to the red racemic cis isomer on evaporation of a neutral aqueous solution at 90 to 100°C. Both

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[10] W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.*, 1974, **12**, 151 (Co^{III}, Co^{IV}, and Co^V compounds).

the cis and the trans isomers are aquated when heated in water:

$$[Co(en)_2Cl_2]^+ + H_2O \longrightarrow [Co(en)_2Cl(H_2O)]^{2+} + Cl^-$$

$$[Co(en)_2Cl(H_2O)]^{2+} + H_2O \longrightarrow [Co(en)_2(H_2O)_2]^{3+} + Cl^-$$

and on treatment with solutions of other anions are converted into other $[Co(en)_2X_2]^+$ species, for example,

$$[Co(en)_2Cl_2]^+ + 2NCS^- \longrightarrow [Co(en)_2(NCS)_2]^+ + 2Cl^-$$

These few reactions are illustrative of the very extensive chemistry of Co^{III} complexes with nitrogen-coordinating ligands.

In addition to the numerous mononuclear ammine complexes of Co^{III}, there are a number of polynuclear complexes in which hydroxo (OH^-), peroxo (O_2^{2-}), amido (NH_2^-), and imido (NH^{2-}) groups function as bridges. Some typical complexes of this class are

$$[(am)_5Co—O—O—Co(am)_5]^{4+} \qquad [(am)_3Co(OH)_3Co(OH)_3Co(am)_3]^{3+},$$

and $[(am)_4Co(OH)(NH_2)Co(am)_4]^{4+}$

Some other Co^{III} complexes of significance are the hexacyano complex $[Co(CN)_6]^{3-}$, the oxygen-coordinated complexes such as carbonates, for example, the green ion $[Co(CO_3)_3]^{3-}$ and *cis*-$[Co(CO_3)_2(py)_2]^-$, $Co(acac)_3$, and salts of the trisoxalatocobalt(III) anion.

There is a thiolate $[Co(SR)_4]^-$, where R = 2,4,6-triisopropylbenzenethiolate; the square structure appears not to be due to steric factors since the Fe^{III} analogue is tetrahedral.[11a] A tetraanionic Schiff-type N_2O_2 ligand (cf. 10-XXXII) also gives a paramagnetic square complex $[CoL]^-$.[11b]

Ozonation of Co^{II} acetate in acetic acid gives a green substance, usually as an oil. There has been considerable discussion on the nature of this and other Co^{III} carboxylates. The first fully characterized species is an oxo-centered (Section 12-9) carboxylate, $[Co_3O(O_2CMe)_5(OH)(py)_3]^+$.[12] The Co^{III} carboxylates can oxidize, sometimes catalytically, with O_2, aromatic and other organic compounds by a radical pathway.

Electronic Structures of Cobalt(III) Complexes. The free Co^{III} ion d^6 has qualitatively the same energy level diagram as does Fe^{II}. However, with Co^{III} the ${}^1A_{1g}$ state originating in one of the high-energy singlet states of the free ion drops very rapidly and crosses the ${}^5T_{2g}$ state at a very low value of Δ. Thus all known octahedral Co^{III} complexes, including even $[Co(H_2O)_6]^{3+}$ and $[Co(NH_3)_6]^{3+}$, have diamagnetic ground states, except for $[Co(H_2O)_3F_3]$ and $[CoF_6]^{3-}$, which are paramagnetic with four unpaired electrons.

[11a] S. A. Koch *et al.*, *Inorg. Chem.*, 1985, **24**, 3312.

[11b] T. J. Collins *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 2088.

[12] C. E. Summer, Jr., and G. R. Steinmetz, *J. Am. Chem. Soc.*, 1985, **107**, 6124.

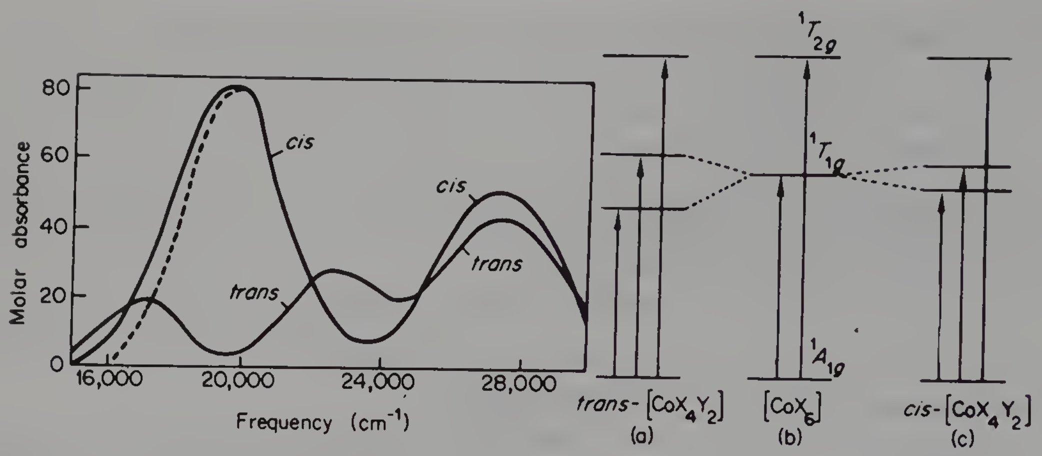

FIG. 18-F-4. *Left:* The visible spectra of *cis*- and *trans*-$[Co(en)_2F_2]^+$. The broken line shows where the low-frequency side of the $A_{1g} \rightarrow T_{1g}$ band of the cis isomer would be if the band were completely symmetrical. The asymmetry is caused by slight splitting of the $^1T_{1g}$ state. *Right:* diagrammatic representation (not to scale) of the energy levels involved in the transitions responsible for the observed bands of octahedral Co^{III} complexes: (b) the levels for a regular octahedral complex $[CoX_6]$; (a) and (c) the splittings caused by the replacement of two ligands X by two ligands Y.

The visible absorption spectra of Co^{III} complexes thus may be expected to consist of transitions from the $^1A_{1g}$ ground state to other singlet states. The two absorption bands found in the visible spectra of regular octahedral Co^{III} complexes represent transitions to the upper states $^1T_{1g}$ and $^1T_{2g}$. In complexes of the type CoA_4B_2, which can exist in both cis and trans configurations, certain spectral features are diagnostic of the cis or trans configuration (Fig. 18-F-4).

The origin of these features lies in the splitting of the $^1T_{1g}$ state by the environments of lower than O_h symmetry, as also shown diagrammatically in Fig. 18-F-4. Theory shows that splitting of the $^1T_{2g}$ state will always be slight, whereas the $^1T_{1g}$ state will be split markedly in the trans isomer whenever there is a substantial difference in the positions of the ligands, A and B, in the spectrochemical series. Moreover, because the cis isomer lacks a center of symmetry it may be expected to have a somewhat more intense spectrum than the trans isomer. These predictions are nicely borne out by the spectra of *cis*- and *trans*-$[Co(en)_2F_2]^+$.

Cobaloximes and Related Compounds.[13] Since the recognition of Vitamin B_{12} and the existence in Nature of Co—C bonds (Chapter 30), there has been much study of "model" systems. These have been mainly complexes of dimethyl and other glyoximes (the so-called cobaloximes), and Schiff base and macrocyclic ligand complexes. The main interest has centered on the reduction

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[13] L. Randaccio *et al., Inorg. Chem.*, 1986, **25**, 3489, 1303; E. G. Samsel and J. K. Kochi, *Inorg. Chem.*, 1986, **25**, 2450; N. Bresciani-Pahor *et al., Coord. Chem. Rev.*, 1985, **63**, 1 (263 references); L. G. Marzilli *et al., J. Am. Chem. Soc.*, 1987, **109**, 6045.

to Co^I species (see later) and to the formation of Co—C bonds and their reactions.

Reduction of cobaloximes, like the reduction of B_{12}, gives blue or green Co^I species that are very powerful reducing agents and nucleophiles. Thus they may react with water to give the hydridocobalt(III) species, especially if tertiary phosphine ligands are also present.

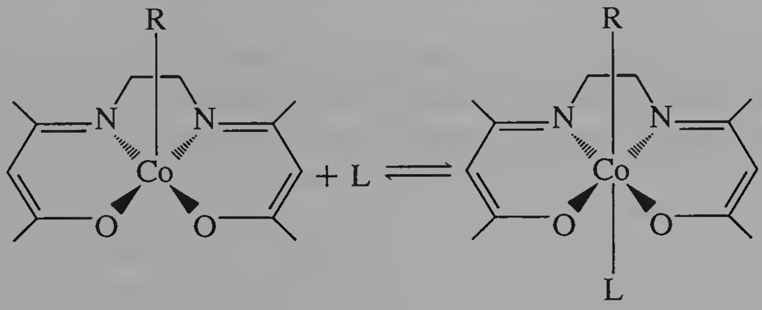
Reduced Vitamin B_{12} itself will reduce ClO_3^- to Cl^- [14] and at pH 1.5 to 2.5 NO_3^- to NH_4^+. The latter is an overall 8*e* reduction and probably initially proceeds by a hydride transfer

$$Co^I—H + NO_3^- \longrightarrow NO_2^- + Co^{III} + OH^-$$

and overall

$$8Co^I + NO_3^- + 10H^+ = 8Co^{II} + NH_4^+ + 3H_2O$$

In the Schiff base complexes such as (18-F-II) the strength of the bonding of the trans ligand is determined mainly by the inductive effects of the R group, although there is some evidence that the nature of the cis ligand atoms is important. The reactivity of the Co—C bond and its ease of photolysis also are powerfully affected by the nature of the trans ligand.



(18-F-II)

Alkylcobalt(III) species can also undergo a one-electron oxidation to give organocobalt(IV) radical ions, stable at low temperatures (< −50°C). The C atom bound to the metal is very susceptible to nucleophilic attack.

18-F-5. The Oxidation of Cobalt(II) Complexes by Molecular Oxygen; Peroxo and Superoxo Species; Oxygen Carriers[15]

The interaction of Co^{II} complexes in solution with O_2 has been the subject of intensive study. Under certain conditions oxidation ultimately to Co^{III} complexes occurs. However, in the absence of charcoal or other catalysts, or by

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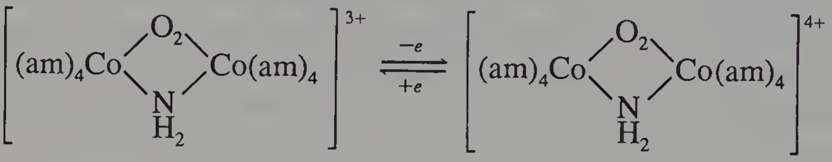
[14] P. N. Balasubramian and E. S. Gould, *Inorg. Chem.*, 1984, **23**, 3689.

[15] L. Casella and M. Gulloti, *Inorg. Chem.*, 1986, **25**, 1293; Y. Sasaki *et al.*, *Inorg. Chem.*, 1985, **24**, 4096; D. C. Chen and A. E. Martell, *Inorg. Chem.*, 1987, **26**, 1026; H. Taube, *Prog. Inorg. Chem.*, 1986, **34**, 607.

the choice of suitable ligands, the intermediate peroxo and superoxo species can be isolated. Some of these complexes behave as reversible carriers of O_2 and have been studied intensively because of their potential utility and as models for natural oxygen transport systems (Chapter 30).

We first consider the situation for ligands like NH_3 or CN^-. The first in the sequence of steps may involve oxidative-addition of O_2 to give a transient Co^{IV} species, which then reacts with another Co^{II} species to give a binuclear peroxo-bridged species such as $[(am)_5Co(\mu\text{-}O_2)Co(am)_5]^{4+}$ or $[(NC)_5Co(\mu\text{-}O_2)Co(CN)_5]^{6-}$. These species are isolable as moderately stable solid salts but decompose fairly easily in water or acids. The open-chain species $[(am)_5Co(\mu\text{-}O_2)Co(am)_5]^{4+}$ can be cyclized in the presence of base to give (18-F-III). It seems safe to assume that all such species, open-chain or cyclic, contain low-spin Co^{III} and bridging peroxide (O_2^{2-}) ions; in $[(am)_5Co(\mu\text{-}O_2)Co(am)_5]^{4+}$ the O—O distance (1.47 Å) is the same as in H_2O_2.


(18-F-III) (18-F-IV)

These μ-O_2 complexes can often be oxidized in a one-electron step to species such as $[(am)_5CoO_2Co(am)_5]^{5+}$ and 18-F-IV. These ions were first prepared by Werner, who formulated them as peroxo-bridged complexes of Co^{III} and Co^{IV}. The esr data show that the single unpaired electron is distributed equally over both cobalt ions, thus ruling out that description. The problem of formulation has been settled by X-ray structural determination as in Fig. 18-F-5. The O—O distances may be compared with that (1.28 Å) characteristic of the superoxide ion, (O_2^-). The unpaired electron formally belonging to O_2^- resides in a molecular orbital of π symmetry relative to the planar $Co(\mu\text{-}O_2)Co$ groupings and is delocalized over these four atoms. The cobalt atoms are formally described as Co^{III} ions.

In the case of cyanide we have the system

$$\begin{tikzcd}
2[Co(CN)_5]^{3-} \arrow[r, "O_2"] & \{[(CN)_5Co^{III}]_2\mu\text{-}O_2\}^{6-} \\
& \text{Peroxo, diamagnetic} \arrow[d, "-e"] \\
\{[(am)_5Co]_2\mu\text{-}O_2\}^{5+} \arrow[r, "CN^-"] & \{[(CN)_5Co]_2\mu\text{-}O_2\}^{5-} \\
\text{Superoxo} & \text{Superoxo}
\end{tikzcd}$$

With polyfunctional ligands different behavior may be obtained, and we have (*a*) oxidation of Co^{II} to Co^{III} as before, (*b*) formation of mononuclear oxygen adducts in addition to the possibility of bridged species as just noted, or (*c*) oxidation of the ligand such as conversion of $>CH_2$ to $>CO$.

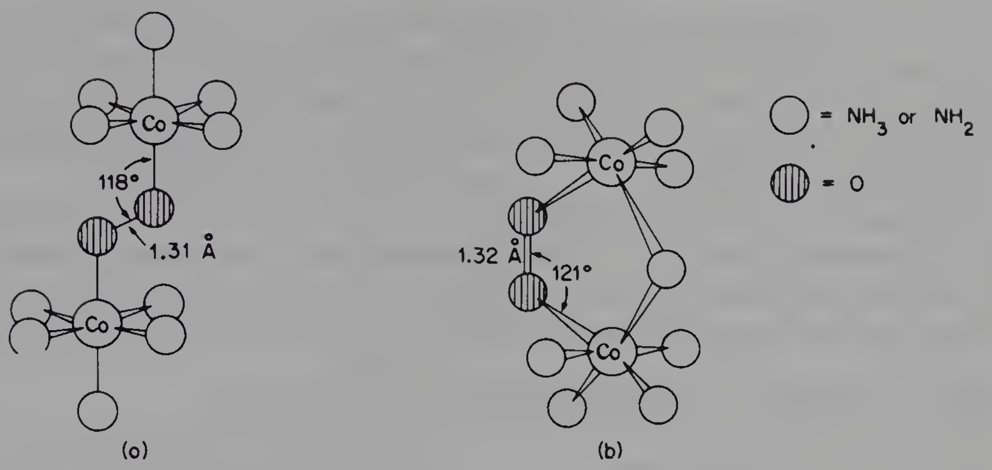
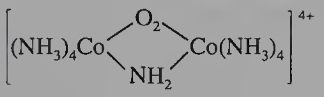


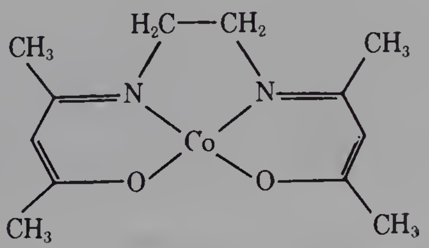
FIG. 18-F-5. The structures of (a) $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{5+}$ and (b)



$$\left[(NH_3)_4Co\begin{matrix}O_2\\NH_2\end{matrix}Co(NH_3)_4\right]^{4+}$$

showing the octahedral coordination about each cobalt ion and the angles and distances at the bridging superoxo groups. The five-membered ring in (b) is essentially planar. Both peroxo and superoxo complexes have these two types of bridged structure.

The best studied are Schiff base complexes such as Co^{II}(acacen) (18-F-V), which in solution in pyridine, DMF, or similar solvents will pick up O_2. Oxygenation of other complexes such as those of amino acids has been studied.

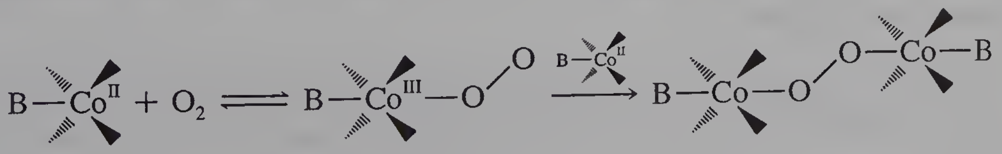


$$+ \text{DMF} + O_2 \longrightarrow \text{Co(acacen)(DMF)}O_2$$

K = 21 at −10°

(18-F-V)

The oxygenation reactions are usually reversible only at low temperatures, since the complex is either irreversibly oxidized or bridged peroxo or superoxo species are formed:



Dimerization can be avoided at low temperatures in dilute solutions or by choice of appropriate ligands and axial bases B, and some monomeric species stable at room temperature are known. X-ray structures confirm that O_2 is best regarded as bound to Co^{III}, bent, as the superoxide ion O_2^-.

The O—O distances so far determined seem to indicate that they are dependent on all electronic factors present in the complexes. Some are shorter than the O—O distance in O_2^- (1.28 Å) and some longer. The esr spectra show that in the O_2 adducts the unpaired electron is largely located on the oxygen atoms.

Although the oxidation of substrates by O_2 in the presence of metal complexes generally appears to be a free radical process, it has been claimed that the catalytic oxidation of Bu_3P to Bu_3PO by $Co(acac)_2$ proceeds by a non-radical path involving intermediates with $Co(\mu\text{-}O_2)Co$ and $\dot{C}o$—O bonds.

18-F-6. Cobalt(IV), d^5 and Cobalt(V), d^4 Compounds[10]

Fusing NaO_2 and Co_3O_4 gives Na_4CoO_4, which has tetrahedral $Co^{IV}O_4$ anions with Na^+ coordinated to the oxygen atoms.

The action of oxidizing agents (e.g., Cl_2, O_2, or O_3) on strongly alkaline Co^{II} solutions produces a black material believed to be hydrous CoO_2, at least in part, but it is ill characterized. The compound Ba_2CoO_4, a red-brown substance obtained by oxidation of $2Ba(OH)_2$ and $2Co(OH)_2$ at 1050°C, and a heteropolymolybdate of Co^{IV}, namely, $3K_2O{\cdot}CoO_2{\cdot}9MoO_3{\cdot}6H_2O$, have been reported.

Fluorination of Cs_2CoCl_4 gives Cs_2CoF_6, isomorphous with Cs_2SiF_6 and with a magnetic moment rising from 2.46 BM at 90 K to 2.97 BM at 294 K. The reflectance spectrum has been assigned to an octahedrally coordinated t_{2g}^5 ion. The high magnetic moments could be due to a large orbital contribution in the ${}^2T_{2g}$ ground state or to partial population of a ${}^6A_{1g}(t_{2g}^3e_g^2)$ state.

A well-characterized Co^{IV} compound is the remarkable alkyl tetra(1-norbornyl)cobalt, which is made from $CoCl_2$ and Li norbornyl (nor) probably via oxidation of $Li_2[Co\ nor_4]$. The brown compound is paramagnetic low spin and reasonably stable to air and heat. On oxidation with $AgBF_4$ it yields the diamagnetic $[Co\ nor_4]^+$ ion.[16] Some organocobalt(IV) compounds with Schiff bases are known.[17a]

Oxidation of Co^{III} dithiocarbamates gives $[Codtc_3]^+$ compounds, which are d^5 low spin with magnetic moments between 2.2 and 2.7.[17b] Similar Ce^{4+} oxidation of $[Co\ py_2L]^-$, L = the tetradentate anion of the oxidation resistant ligand (10-XXXII), which gives the dark green octahedral *trans*-$[Co\ py_2L]$.[17c]

18-F-7. Complexes of Cobalt(-I), (I), (II), and (III) with Phosphorus and Some Other Ligands

There is an extensive chemistry of cobalt in which phosphines or phosphites are coordinated alone or with other ligands. Examples are given in Table 18-F-2.

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[16] E. K. Byrne and K. H. Theopald, *J. Am. Chem. Soc.*, 1987, **109**, 1282.
[17a] M. E. Vol'pin *et al.*, *J. Organomet. Chem.*, 1985, **279**, 263.
[17b] J-P. Barbier *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 597.
[17c] T. J. Collins *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 5037.

TABLE 18-F-2
Phosphine or Phosphite Complexes of Cobalt

Co^{-I}	Co^{0}	Co^{I}	Co^{II}	Co^{III}
$K(N_2)Co(PMe_3)_3$[a]	$Co(PMe_3)_4$	$CoCl(PR_3)_3$	$CoCl_2(PR_3)_3$	$CoH_3(PPh_3)_3$
	$Co_2[P(OMe)_3]_8$	$CoCl(CO)_2(PR_3)_2$	$CoH[P(OPh)_3]_4^+$	$CoMe_3(PMe_3)_3$
		$CoH(N_2)(PPh_3)_3$		$CoH_2[P(OR)_3]_4^+$
		$CoH(PMe_3)_3$		
		$CoH(CO)(PPh_3)_3$		
		$Co(CO)_2(PR_3)_3^+$		
		$Co[P(OEt)_3]_5^+$		
		$Co(C_2H_4)(MeCN)(PMe_3)_2^+$		

[a] H-F. Klein *et al.*, *Organometallics,* 1987, **6,** 1341.

The Co^I compounds[18a] are typically made by reductions such as

$$CoCl_2 + 4PMe_3 \xrightarrow{Na/Hg} Co(PMe_3)_4 + 2NaCl$$

$$CoCl_2 + 3PR_3 \xrightarrow{Zn/MeCN} CoCl(PR_3)_3 + ZnCl_2$$

$$Co(acac)_3 + N_2 + PR_3 \xrightarrow{AlEt_3} CoH(N_2)(PR_3)_3$$

Finally, note that disproportionation[18b] of $Co^{II} \rightarrow Co^I + Co^{III}$ is possible with certain ligands, mostly phosphites, for example,

$$2Co^{2+} + 11PR_3 \longrightarrow Co(PR_3)_5^+ + Co(PR_3)_6^{3+}$$

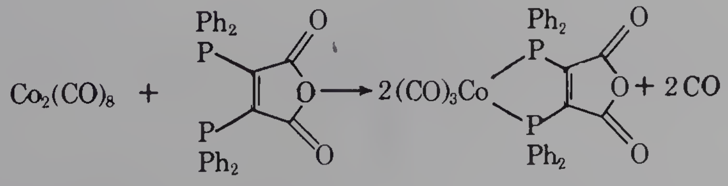
The hydrido species such as $HCo[P(OPh)_3]_3(MeCN)$ may be catalysts for homogeneous hydrogenation of unsaturated substances.

Phosphine derivatives obtained from $Co_2(CO)_8$ (Chapter 22) invariably have CO groups present also, but these are either dimeric Co^0 species, or Co^I and Co^{-I} species formed by disproportionation:

$$Co_2(CO)_8 + 2PPh_3 \xrightarrow{0°,\ benzene} Co_2(CO)_6(PPh_3)_2$$

$$Co_2(CO)_8 + 2PR_3 \xrightleftharpoons{polar\ solvent} [Co(CO)_3(PR_3)_2][Co(CO)_4] + CO$$

However, in one case a dark green, air-stable paramagnetic species is formed:



[18a] See, for example, M. Dartiguenave *et al., Inorg. Chem.,* 1986, **25,** 2205; H-F. Klein *et al., Z. Naturforsch.,* 1985, **40B,** 1377.

[18b] S. M. Socol and J. G. Verkade, *Inorg. Chem.,* 1986, **25,** 2658.

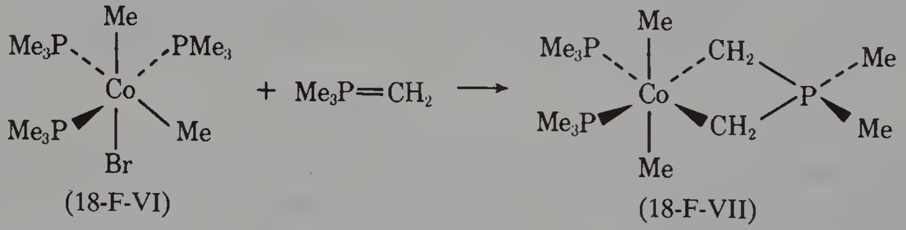
Examples of other paramagnetic Co^0 species are the maleic anhydride (L) complex $CoL[P(OMe)_3]_3$,[19] $[(triphos)Co]_2(\mu\text{-}N_2)$,[20] and $[(Me_3P)_3Co]_2(\eta\text{-}C_7H_8)$, where both double bonds of norbornadiene are coordinated and there is strong antiferromagnetic coupling of the d^9 centers,[21] and $Co[P(Oi\text{-}Pr)_3]_4$. For the phosphites $P(OMe)_3$ and $P(OEt)_3$ there are both paramagnetic monomers and diamagnetic dimers, presumably because steric hindrance is less than for the isopropyl.[22] The isopropyl also gives the compound $Na\{Co[P(Oi\text{-}Pr)_3]_5\}$, which has strong ion pairs with Na^+ bound to the O of the phosphite, since the compound is very soluble in pentane.

Several Co^{III} complexes are known with H and CH_3 ligands. The former can be made by oxidative-addition reactions:

$$CoH(N_2)(PPh_3)_3 + H_2 = CoH_3(PPh_3)_3 + N_2$$

$$CoH[P(OR)_3]_4 + HX = CoH_2[P(OR)_3]_4^+ + X^-$$

The *cis*-dimethyl-*mer*-trimethylphosphine Co^{III} complex (18-F-VI) reacts with $Me_3P{=}CH_2$ to give the metallacyclic alkyl (18-F-VII).

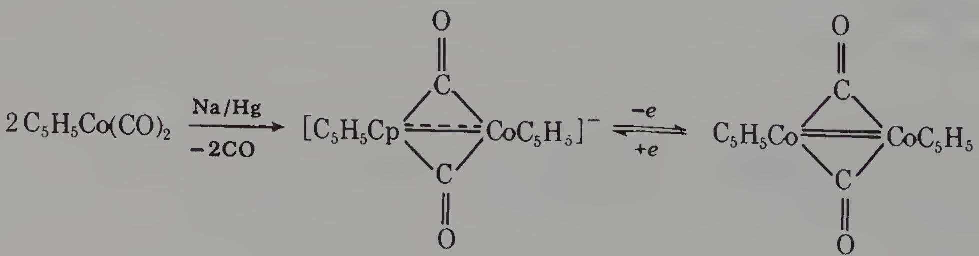


Isocyanides may be formed either by reduction of $CoCl_2(CNR)_4$ with an active metal, N_2H_4, $S_2O_4^{2-}$, and so on, or by interaction of RNC with $Co_2(CO)_8$, which leads to disproportionation:

$$Co_2(CO)_8 + 5RNC = [Co(CNR)_5]^+[Co(CO)_4]^- + 4CO$$

In $[Co(NCMe)_5]ClO_4$ the cation has *tbp* geometry, but in $[Co(NCPh)_5]ClO_4$ it is *sp*.

There is an extensive Co^I chemistry of *monocyclopentadienyl* compounds, of which $(\eta\text{-}C_5H_5)Co(CO)_2$ is one example. The CO may be replaced by phosphines, alkenes, isocyanides, and so on. The dicarbonyl itself can be reduced to a radical ion that contains formally cobalt (0.5), or Co^0 + Co^I, and can be isolated as its $(Ph_3P)_2N^+$ salt:



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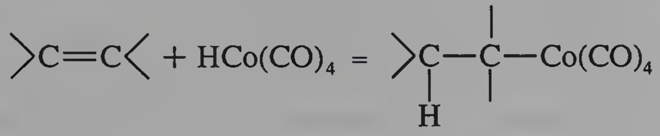
[19] J. C. J. Bart *et al.*, *Organometallics*, 1983, **2,** 627.
[20] F. Cecconi *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985,** 731.
[21] H-F. Klein *et al.*, *Inorg. Chem.*, 1985, **24,** 683.
[22] E. L. Muetterties *et al.*, *J. Am. Chem. Soc.*, 1982, **104,** 2940.

Alkyl cobalt(I) carbonyls,[23] generally made by the reactions

$$\mathrm{NaCo(CO)_4 + RI = RCo(CO)_4 + NaI}$$



$$\mathrm{>C{=}C< + HCo(CO)_4 = >\underset{\underset{\textstyle H}{|}}{C}-\overset{|}{\underset{|}{C}}-Co(CO)_4}$$

are important intermediates in catalytic reactions, Chapter 28.

The hydride $\mathrm{HCo(CO)_4}$ (Section 24-6) is similarly involved in numerous reactions of $\mathrm{Co_2(CO)_8}$.

18-G. NICKEL: GROUP VIII(10)

The trend toward decreased stability of higher oxidation states continues with nickel, so that only $\mathrm{Ni^{II}}$ occurs in the ordinary chemistry of the element. However, there is a complex array of stereochemistries associated with this species. The oxidation numbers 0 and +1 are found largely under conditions where such numbers have little physical meaning. The higher oxidation states, $\mathrm{Ni^{III}}$ and $\mathrm{Ni^{IV}}$ occur in very few compounds, and in many of these it is not clear whether it is really the metal atom rather than the ligand that is oxidized.

Nickel has an enormous, and important, organometallic chemistry, and some of these aspects are noted in Chapters 25 and 26.

The oxidation states and stereochemistry of nickel are summarized in Table 18-G-1.

18-G-1. The Element

Nickel occurs in Nature mainly in combination with arsenic, antimony, and sulfur, for example, as *millerite* (NiS), as a red nickel ore that is mainly NiAs, and in deposits consisting chiefly of NiSb, $\mathrm{NiAs_2}$, NiAsS, or NiSbS. The most important deposits commercially are *garnierite,* a magnesium–nickel silicate of variable composition, and certain varieties of the iron mineral *pyrrhotite* ($\mathrm{Fe}_n\mathrm{S}_{n+1}$), which contain 3 to 5% Ni. Elemental nickel is also found alloyed with iron in many meteors, and the central regions of the earth are believed to contain considerable quantities. The metallurgy of nickel is complicated in its details, many of which vary a good deal with the particular ore being processed. In general, the ore is transformed to $\mathrm{Ni_2S_3}$, which is roasted in air to give NiO, and this is reduced with carbon to give the metal. Some high-purity nickel is made by the *carbonyl process:* carbon monoxide reacts with impure nickel at 50°C and ordinary pressure or with nickel–copper matte

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[23] G. Palyi *et al., Coord. Chem. Rev.,* 1984, **59,** 203.

TABLE 18-G-1
Oxidation States and Stereochemistry of Nickel

Oxidation state	Coordination number	Geometry	Examples
Ni^{-1}	4?	?	$[Ni_2(CO)_6]^{2-}$
Ni^0	3	?	$Ni[P(OC_6H_4\text{-}o\text{-}Me)_3]_3$
	4	Tetrahedral	$Ni(PF_3)_4$, $[Ni(CN)_4]^{4-}$, $Ni(CO)_4$
	5	?	$NiH[P(OEt)_3]_4^+$
Ni^I, d^9	4	Tetrahedral	$Ni(PPh_3)_3Br$
Ni^{II}, d^8	3	Trigonal planar	$[Ni(NPh_2)_3]^-$, $Ni_2(NR_2)_4$[a]
	4[b]	Square	$NiBr_2(PEt_3)_2$, $[Ni(CN)_4]^{2-}$, $Ni(DMGH)_2$
	4[b]	Tetrahedral	$[NiCl_4]^{2-}$, $NiCl_2(PPh_3)_2$
	5	*sp*	$[Ni(CN)_5]^{3-}$, BaNiS, $[Ni_2Cl_8]^{4-}$
	5	*tbp*	$[NiX(trident)]^+$[c], $[Ni(CN)_5]^{3-}$, $Ni(SiCl_3)_2(CO)_3$[d]
	6[b]	Octahedral	NiO, $[Ni(NCS)_6]^{4-}$, $KNiF_3$, $[Ni(NH_3)_6]^{2+}$, $[Ni(bipy)_3]^{2+}$
	6	Trigonal prism	NiAs
Ni^{III}, d^7	5	*tbp*	$NiBr_3(PR_3)_2$
	6	Octahedral (distorted)	$[Ni(diars)_2Cl_2]^+$, $[NiF_6]^{3-}$
Ni^{IV}, d^6	6	Octahedral (distorted)	K_2NiF_6, $\{Ni[Bu_2(dtc)]_3\}^+$, $\{Ni[Se_2C_2(CN)_2]_3\}^{2-}$

[a] P. P. Power *et al., J. Am. Chem. Soc.*, 1985, **107,** 712.
[b] Most common states.
[c] See, for example, E. Grimley and D. W. Meek, *Inorg. Chem.*, 1986, **25,** 2049.
[d] L. J. Radonovich *et al., Organometallics,* 1985, **4,** 396.

under more strenuous conditions, giving volatile $Ni(CO)_4$, from which metal of 99.90 to 99.99% purity is obtained on thermal decomposition at 200°C.

Nickel is silver-white, with high electrical and thermal conductivities (both ~15% of those of silver) and mp 1452°C, and it can be drawn, rolled, forged, and polished. It is quite resistant to attack by air or water at ordinary temperatures when compact and is therefore often electroplated as a protective coating. Because nickel reacts but slowly with fluorine, the metal and certain alloys (Monel) are used to handle F_2 and other corrosive fluorides. It is also ferromagnetic, but not as much as iron. The finely divided metal is reactive to air, and it may be pyrophoric under some conditions.

The metal is moderately electropositive:

$$Ni^{2+} + 2e = Ni \qquad E^0 = -0.24\ V$$

and dissolves readily in dilute mineral acids. Like iron, it does not dissolve in concentrated nitric acid because it is rendered passive by this reagent.

NICKEL COMPOUNDS[1]

18-G-2. The Chemistry of Nickel(II), d^8

Binary Compounds. *Nickel(II) oxide,* a green solid with the rock salt structure, is formed when the hydroxide, carbonate, oxalate, or nitrate of nickel(II) is heated. It is insoluble in water but dissolves readily in acids.

The *hydroxide* $Ni(OH)_2$ may be precipitated from aqueous solutions of Ni^{II} salts on addition of alkali metal hydroxides, forming a voluminous green gel that crystallizes [$Mg(OH)_2$ structure] on prolonged storage. It is readily soluble in acid and also in aqueous ammonia owing to the formation of ammine complexes. When a concentrated solution of NaOH is added to a considerable molar excess of dilute $Ni(ClO_4)_2$ solution, a soluble hydroxo species is formed that is believed, on the basis of equilibrium and kinetic studies, to be $[Ni(OH)]_4^{4+}$ with a cubic structure consisting of interpenetrating Ni_4 and $(OH)_4$ tetrahedra. However, $Ni(OH)_2$ is not amphoteric.

Addition of sulfide ions to aqueous solutions of Ni^{2+} precipitates black NiS. This is initially freely soluble in acid, but like CoS, on exposure to air it soon becomes insoluble owing to conversion to Ni(OH)S. Fusion of Ni, S, and BaS gives $BaNiS_2$, which forms black plates; this product is metallic and has Ni in square pyramidal coordination.

All four nickel *halides* are known in the anhydrous state. Except for the fluoride, which is best made indirectly, they can be prepared by direct reaction of the elements. All the halides are soluble in water (the fluoride only moderately so), and from aqueous solutions they can be crystallized as the hexahydrates, except for the fluoride, which gives $NiF_2 \cdot 3H_2O$. Lower hydrates are obtained from these on storage or heating.

On addition of CN^- ions to aqueous Ni^{II} the *cyanide* is precipitated in a green hydrated form. When heated at 180 to 200°C the hydrate is converted into the yellow-brown, anhydrous $Ni(CN)_2$. The green precipitate readily redissolves in an excess of cyanide to form the yellow $[Ni(CN)_4]^{2-}$ ion, which is both thermodynamically very stable ($\log \beta_4 \approx 30.5$) and kinetically slow to release CN^- ion. Many hydrated salts of this ion, for example, $Na_2[Ni(CN)_4] \cdot 3H_2O$, may be crystallized from such solutions. In strong cyanide solutions a further CN^- is taken up to give the red $[Ni(CN)_5]^{3-}$ ion, the structure of which is discussed later. Nickel(II) thiocyanate is also known, as a yellow-brown hydrated solid that reacts with an excess of SCN^- to form the complex ions $[Ni(NCS)_4]^{2-}$ and $[Ni(NCS)_6]^{4-}$.

Other binary nickel compounds, probably all containing Ni^{II} but not all stoichiometric, may be obtained by the direct reaction of nickel with various nonmetals such as P, As, Sb, S, Se, Te, C, and B. Nickel appears to form a nitride Ni_3N. The existence of a hydride is doubtful, although the finely divided metal absorbs hydrogen in considerable amounts.

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[1] K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, 1980, **33,** 87 ($Ni^{I,III,IV}$).

Salts of Oxo Acids. A large number of these are known. They occur most commonly as hydrates, for example, $Ni(NO_3)_2 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$, and most of them are soluble in water. Exceptions are the carbonate $NiCO_3 \cdot 6H_2O$, which is precipitated on addition of alkali hydrogen carbonates to solutions of Ni^{II}, and the phosphate $Ni_3(PO_4)_2 \cdot nH_2O$.

Aqueous solutions of Ni^{II} not containing strong complexing agents contain the green hexaaquanickel(II) ion, $[Ni(H_2O)_6]^{2+}$, which also occurs in a number of hydrated nickel(II) salts [e.g., $Ni(NO_3)_2 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$, and $Ni(ClO_4)_2 \cdot 6H_2O$].

18-G-3. Stereochemistry and Electronic Structures of Nickel(II) Complexes

Nickel(II) forms a large number of complexes with coordination numbers 3 to 6 (Table 18-G-1).

A particular characteristic is the existence of complicated equilibria, commonly temperature and concentration dependent, involving different structural types.

Octahedral Complexes. The maximum coordination number of nickel(II) is 6. A considerable number of neutral ligands, especially amines, displace some or all of the water molecules in the octahedral $[Ni(H_2O)_6]^{2+}$ ion to form complexes such as *trans*-$[Ni(H_2O)_2(NH_3)_4](NO_3)_2$, $[Ni(NH_3)_6](ClO_4)_2$, and $[Ni(en)_3]SO_4$. These complexes are characteristically blue or purple in contrast to the bright green of the hexaaquanickel ion. This is because of shifts in the absorption bands when H_2O ligands are replaced by others lying toward the stronger end of the spectrochemical series. This can be seen in Fig. 18-G-1, where the spectra of $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ are shown. Three spin-allowed transitions are expected from the energy level diagram for d^8 ions and the three observed bands in each spectrum may thus be assigned as shown in Table 18-G-2. It is a characteristic feature of the spectra of octahedral

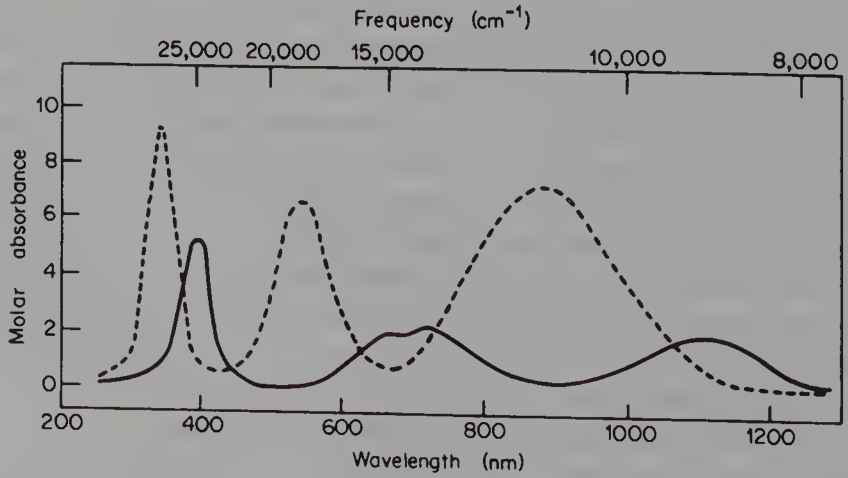


FIG. 18-G-1. Absorption spectra of $[Ni(H_2O)_6]^{2+}$ (solid curve) and $[Ni(en)_3]^{2+}$ (dashed curve).

TABLE 18-G-2
Spectra of Octahedral Nickel(II) Complexes

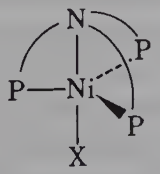
Transition	Approximate band positions (cm^{-1}) $[Ni(H_2O)_6]^{2+}$	$[Ni(en)_3]^{2+}$
$^3A_{2g} \rightarrow {}^3T_{2g}$	9,000	11,000
$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	14,000	18,500
$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	25,000	30,000

nickel(II) complexes, exemplified by those of $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$, that molar absorbances of the bands are at the low end of the range (1–100) for octahedral complexes of the first transition series in general, namely, between 1 and 10. The splitting of the middle band in the $[Ni(H_2O)_6]^{2+}$ spectrum is due to spin-orbit coupling that mixes the $^3T_{1g}(F)$ and ^1E_g states, which are very close in energy at the Δ_0 value given by $6H_2O$, whereas in the stronger field of the 3en they are so far apart that no significant mixing occurs. An analysis of the spectrum at the level of the previous discussion is adequate for almost all chemical purposes, but it is worth noting that at higher resolution the spectra show much greater complexity and require much more sophisticated analysis.

Magnetically, octahedral nickel(II) complexes have relatively simple behavior. From both *d*-orbital splitting and energy level diagrams it follows that they all should have two unpaired electrons, and this is found always to be the case, the magnetic moments ranging from 2.9 to 3.4 BM, depending on the magnitude of the orbital contribution.

The type of structure found in $CsNiCl_3$ is often considered to be the generic structure for a large number of $M^IM^{II}X_3$ compounds, where M^I is a large univalent cation and M^{II} is a transition metal ion. In this structure there are infinite parallel chains of NiX_6 octahedra sharing opposite faces, and the M^I ions lie between these chains in an ordered pattern. The M^{II} ions generally show significant antiferromagnetic coupling that is believed to occur by a superexchange mechanism via the bridging X ions.

Five-Coordinate Nickel(II) Complexes.[2] A considerable number of both trigonal bipyramidal and square pyramidal complexes occur and high- (S = 1) and low-spin (S = 0) examples of each geometry are known. Many of the trigonal bipyramidal complexes contain one of the tripod ligands such as pp_3 and np_3 and have the type structure shown in (18-G-I).



(18-G-I)

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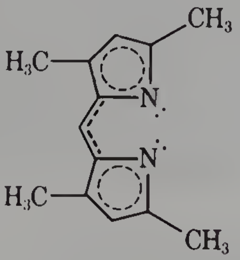
[2] T. P. E. Auf der Heyde and L. R. Nassimbeni, *Inorg. Chem.*, 1984, **23**, 4525 (data and reaction pathways for $Ni^{I,II,III}$ compounds).

The fifth ligand is typically a halide ion, though H, SR, RSO_3, and R also occur; thus the complex is a +1 cation. The symmetry cannot, of course, ever be the full D_{3h} symmetry of a true *tbp,* but such cases are usually called *tbp* complexes for simplicity. With few exceptions they are low spin (i.e., diamagnetic). $[Ni(Me_6tren)Br]^+$ is high spin, but replacement of ligand N atoms by P, As, S, Se, and so on, causes larger ligand field splittings and stabilizes the low-spin configuration. There are other low-spin, five-coordinate Ni^{II} complexes with $[NiL_5]^{2+}$ and $[NiL_3X_2]$ compositions, as well as $[NiL_4X]^+$ types, and in many cases the ligands L are unidentate, as in $[Ni(SbMe_3)_5]^{2+}$, $[Ni(PMe_3)_4Br]^+$, $NiX_2(SbMe_3)_3$ and $MeNi(PMe_3)_4^+$.

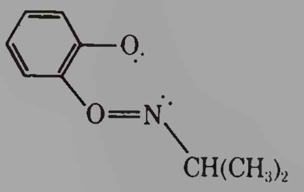
The $[Ni(CN)_5]^{3-}$ ion is usually found with *sp* geometry, but in $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ there are two crystallographically independent $[Ni(CN)_5]^{3-}$ ions, one with *sp* and the other with *tbp* geometry. However, when this compound is dehydrated or subjected to pressure the crystal structure changes and the *tbp* one becomes *sp*.

There are relatively few *sp* complexes, most of which, like $[Ni(Ph_2MeAsO)_4(ClO_4)]^+$ and $[Ni(Me_3AsO)_5](ClO_4)_2$, are high spin. The complexes $[Ni(p_3)SO_4]$ and $[Ni(p_3)SeO_4]$, where $p_3 = CH_3C(CH_2PPh_2)_3$ and the oxo anions are bidentate, are *sp* and paramagnetic in the crystal but become mainly diamagnetic in solution.

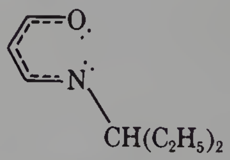
Tetrahedral Complexes. These are mainly of the following stoichiometric types: NiX_4^{2-}, NiX_3L^-, NiL_2X_2, and $Ni(L—L)_2$, where X represents a halogen or SPh, L a neutral ligand such as phosphine, phosphine oxide, or arsine, and L—L is one of several types of bidentate ligand [e.g., (18-G-II) to (18-G-IV)]. These three bidentate ligands all contain sufficiently bulky substituents on, or adjacent to, the nitrogen atoms to render planarity of the $Ni(L—L)_2$ molecule sterically impossible. When small substituents are present, planar, or nearly planar complexes are formed. It must be stressed that except for the NiX_4^{2-} species, a rigorously tetrahedral configuration cannot be expected. However, in some cases there are marked distortions even from the highest symmetry possible, given the inherent shapes of the ligands. Thus in $Ni(L—L)_2$ molecules the most symmetrical configuration possible would have the planes of the two L—L ligands perpendicular. Most often, however, this dihedral angle differs considerably from 90°; for example, when L—L is (18-G-III) the angle is 82°, and when L—L is (18-G-II) it is only 76°. Thus



(18-G-II)



(18-G-III)



(18-G-IV)

the term "tetrahedral" is sometimes used very loosely (i.e., does not imply a regular tetrahedron); since all the so-called tetrahedral species are paramagnetic with two unpaired electrons, it would perhaps be better to simply call them paramagnetic rather than tetrahedral. Indeed, the most meaningful way to distinguish between tetrahedral and "planar" four-coordinate nickel(II) complexes is to consider that for a given ligand set ABCD, there is a critical value of the dihedral angle beween two planes, such as A—Ni—B and C—Ni—D. When the angle exceeds this value the molecule will be paramagnetic; it may be called tetrahedral even though the dihedral angle is appreciably <90°. Conversely, when the angle is below the critical value the complex will be diamagnetic; it may be called planar even if the limit of strict planarity is not actually attained.

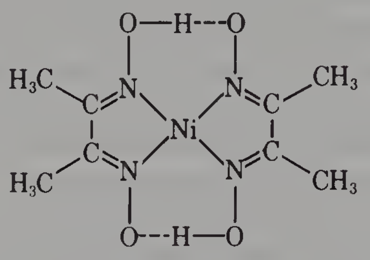
For regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties. Naturally the more irregular the geometry of a paramagnetic nickel(II) complex the less likely it is to conform to these specifications. In T_d symmetry the d^8 configuration gives rise to a ${}^3T_1(F)$ ground state. The transition from this to the ${}^3T_1(P)$ state occurs in the visible region (~15,000 cm^{-1}) and is relatively strong ($\epsilon \approx 10^2$) compared to the corresponding ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transition in octahedral complexes. Thus tetrahedral complexes are generally strongly colored and tend to be blue or green unless the ligands also have absorption bands in the visible region. Because the ground state ${}^3T_1(F)$ has much inherent orbital angular momentum, the magnetic moment of truly tetrahedral Ni$^{\text{II}}$ should be ~4.2 BM at room temperature. However, even slight distortions reduce this markedly (by splitting the orbital degeneracy). Thus fairly regular tetrahedral complexes have moments of 3.5 to 4.0 BM; for the more distorted ones the moments are 3.0 to 3.5 BM (i.e., in the same range as for six-coordinate complexes).

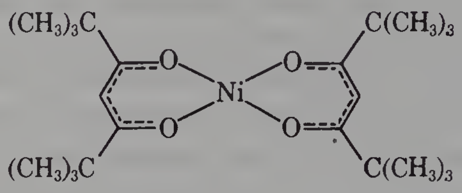
The $NiCl_4^{2-}$ ion, a representative tetrahedral complex, has been studied in great detail spectroscopically at 2.2 K. The observations can all be accounted for by a parameterized crystal field model, with $\Delta_t \approx 3500$ cm^{-1}.

Planar Complexes. For the vast majority of four coordinate nickel(II) complexes, planar geometry is preferred. This is a natural consequence of the d^8 configuration, since the planar ligand set causes one of the d orbitals ($d_{x^2-y^2}$) to be uniquely high in energy and the eight electrons can occupy the other four d orbitals but leave this strongly antibonding one vacant. In tetrahedral coordination, on the other hand, occupation of antibonding orbitals is unavoidable. With the congeneric d^8 systems Pd$^{\text{II}}$ and Pt$^{\text{II}}$ this factor becomes so important that no tetrahedral complex is formed.

Planar complexes of Ni$^{\text{II}}$ are thus invariably diamagnetic. They are frequently red, yellow, or brown owing to the presence of an absorption band of medium intensity ($\epsilon \approx 60$) in the range 450 to 600 nm, but other colors do occur when additional absorption bands are present.

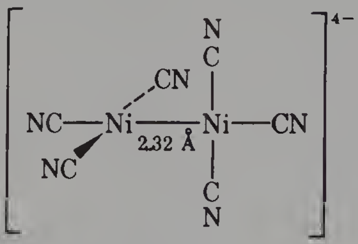
As important examples of square complexes, we may mention yellow $Ni(CN)_4^{2-}$, red bis(dimethylglyoximato)nickel(II) (18-G-V), which gives a stacked polymer, the red β-keto-enolate complex (18-G-VI), the yellow to brown $Ni(PR_3)_2X_2$ compounds in which R is alkyl, and complexes containing homologues of the ligands (18-G-III) and (18-G-IV) in which the substituents on nitrogen are small.

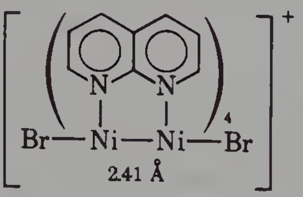

(18-G-V)

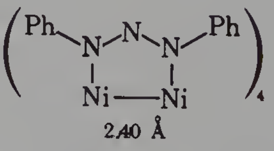

(18-G-VI)

Trigonal Complexes. These are so far known only for dialkylamides, $[Ni(NPh_2)_3]^-$ and $Ni_2(NR_2)_4$; the latter have two μ-NR_2 groups and a Ni—Ni bond.[3]

Ni—Ni Bonded Binuclear Compounds. Nickel forms a moderately large and very heterogeneous group of compounds in oxidation states of 2, 1.5, and 1, in which there are Ni—Ni bonds varying in length from 2.32 to 2.79 Å. Unlike the M—M bonds formed by some of the early transition elements such as Cr, Mo, W, Re, and Ru, many of these Ni—Ni bonds have received little theoretical discussion and are not well understood. A few examples are shown in (18-G-VII) to (18-G-IX).


(18-G-VII)


(18-G-VIII)


(18-G-IX)

18-G-4. "Anomalous" Properties of Nickel(II) Complexes; Conformational Changes

A considerable number of nickel(II) complexes do not behave consistently in accord with expectations for any discrete structural types, and they have in the past been termed "anomalous". All the anomalies can be satisfactorily explained in terms of several types of conformational or other structural change and, ironically, so many examples are now known that the term anomalous is no longer appropriate. The three main structure and confor-

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[3] P. P. Power *et al., J. Am. Chem. Soc.*, 1985, **107**, 712.

mational changes that nickel(II) complexes undergo are described and illustrated next.

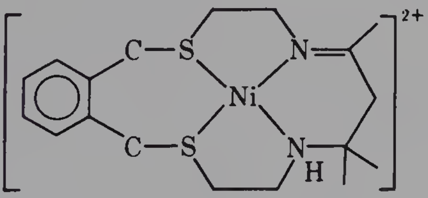
1. *Formation of Five- and Six-Coordinate Complexes by Addition of Ligands to Square Complexes.* For any square complex NiL_4, the following equilibria with additional ligands L′ must in principle exist:

$$ML_4 + L' = ML_4L'$$

$$ML_4 + 2L' = ML_4L_2'$$

In the case where L = L′ = CN, only the five-coordinate species is formed, but in most cases equilibria strongly favor the six-coordinate species that have trans structures and two unpaired electrons. The complex (18-G-VI), for example, is normally prepared in water or alcohol and first isolated as a green, paramagnetic dihydrate or dialcoholate. Heating then drives off the H_2O or C_2H_5OH to leave the red, diamagnetic square complex.

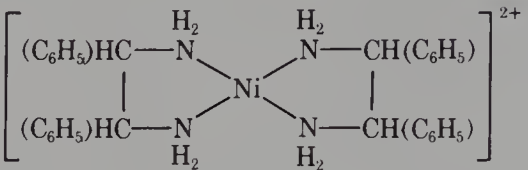
An interesting series of compounds is provided by the series based on $[NiL]^{2+}$, shown as (18-G-X). In the perchlorate $[NiL](ClO_4)_2$ the nickel atom is four-coordinate and the compound is red and diamagnetic. The compounds [NiLX]X (X = Cl, Br, and I) are blue or green and have two unpaired electrons; the cationic complex is five-coordinate *sp*. The complex $[NiL(NCS)_2]$ is octahedral, violet, and has two unpaired electrons.



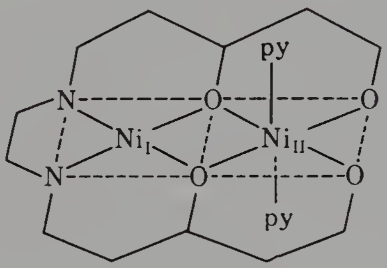
(18-G-X)

Well-known examples of the square–octahedral ambivalence are the Lifschitz salts, complexes of nickel(II) with substituted ethylenediamines, especially the stilbenediamines, one of which is illustrated in (18-G-XI). Many years ago Lifschitz and others observed that such complexes were sometimes blue and paramagnetic and other times yellow and diamagnetic, depending on many factors such as temperature, identity of the anions present, the solvent in which they are dissolved or from which they were crystallized, exposure to atmospheric water vapor, and the particular diamine involved. The bare experimental facts bewildered chemists for several decades, and many hypotheses were promulgated in an effort to explain some or all of them. It is now recognized that the yellow species are square complexes, as typified by (18-G-XI), and the blue ones are octahedral complexes, derived from the square complexes by coordination of two additional ligands—solvent molecules, water molecules, or anions—above and below the plane of the square complex.

The complex (18-G-XII) is interesting in that it contains, side by side, low-spin, square-coordinated and high-spin, octahedrally coordinated nickel atoms.



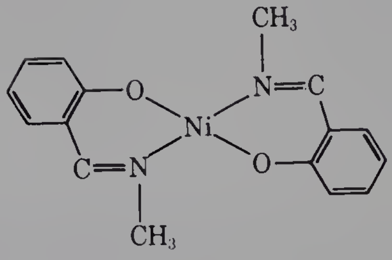
(18-G-XI)



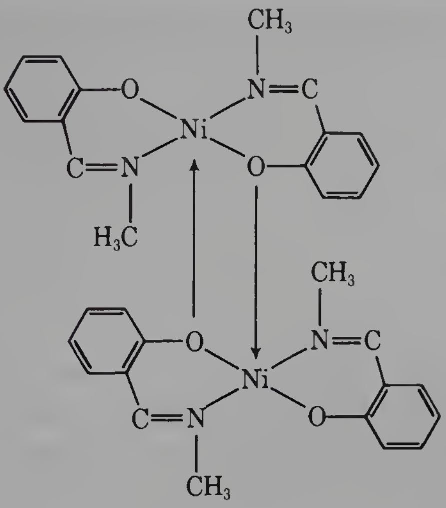
(18-G-XII)

2. *Monomer–Polymer Equilibria.* In many cases four-coordinate complexes associate or polymerize, to give species in which the nickel ions become five- or six-coordinate. In some cases the association is very strong and the four-coordinate monomers are observed only at high temperatures; in others the position of the equilibrium is such that both red, diamagnetic monomers and green or blue, paramagnetic polymers are present in a temperature- and concentration-dependent equilibrium around room temperature. A clear example of this situation is provided by various β-ketoenolate complexes. The acetylacetonate has the trimeric structure shown in Fig. 12-4, where each nickel atom achieves octahedral coordination. This trimer is very stable and only at temperatures around 200°C (in a noncoordinating solvent) do detectable quantities of monomer appear. It is, however, readily cleaved by donors such as H_2O or pyridine, to give six-coordinate monomers. When the methyl groups of the acetylacetonate ligand are replaced by the very bulky $C(CH_3)_3$ group, trimerization is completely prevented and the planar monomer results. When groups sterically intermediate between CH_3 and $C(CH_3)_3$ are used, temperature- and concentration-dependent purple monomer–green trimer equilibria are observed in noncoordinating solvents.

Partial dimerization, presumably to give five-coordinate, high-spin nickel(II), is known to be the cause of anomalous behavior in some instances. Thus although *N*-(*n*-alkyl)salicylaldiminato complexes or Ni^{II} are, in general, planar, diamagnetic monomers in chloroform or benzene, when the alkyl group is CH_3 there is an equilibria between the diamagnetic monomer and a paramagnetic dimer, presumably as shown in (18-G-XIII) and (18-G-XIV).



(18-G-XIII)



(18-G-XIV)

Polymeric Ni^{II} thiolates with cage structures, such as $Ni_4(SR)_8$, $Ni_6(SR)_{12}$, and $Ni_8(SR)_{16}$, do not dissociate and resemble the cage structures given by other metals.[4]

Alkoxides that are polymeric, such as $[Ni_4(OMe)_4(O_2CMe)_2L_4]^{2+}$, L = a diisocyanide, are known[5]; this one has a cubane $Ni_4O_4^{4+}$ core.

3. *Square–Tetrahedral Equilibria and Isomerism.* We have already indicated that nickel(II) complexes of certain stoichiometric types, namely, the bishalobisphosphino and bis(salicylaldiminato) types may have either square or tetrahedral structures, depending on the identity of the ligands. For example, in the NiL_2X_2 cases, when L is triphenylphosphine, tetrahedral structures are found, whereas the complexes with trialkylphosphines generally give square complexes. Perhaps it is then not very surprising that a number of NiL_2X_2 complexes in which L represents a mixed alkylarylphosphine exist in solution in an equilibrium distribution between the tetrahedral and square forms. The influence of the varying R groups in the phosphines is almost entirely electronic rather than steric. For example, in CH_2Cl_2 solution, for PPh_2Bu and $P(cyclohexyl)_3$, which do not differ greatly in size, the mole fractions of the tetrahedral form are 1.00 and 0.00, respectively. At 25°C the rate constants for conversion of tetrahedral into planar isomers are in the range of 10^5 to 10^6 s^{-1} with enthalpies of activation of around 45 kJ mol^{-1}.

In some cases it is possible to isolate two crystalline forms of the compound, one yellow to red and diamagnetic, the other green or blue with two unpaired electrons. There is even $Ni[(C_6H_5CH_2)(C_6H_5)_2P]_2Br_2$, in which both tetrahedral and square complexes are found together in the same crystalline substance.

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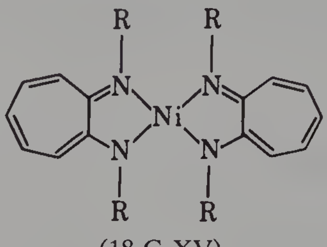
[4] I. G. Dance *et al., Inorg. Chem.*, 1985, **24,** 1201. For other thiolates see P. K. Mascharak *et al., Inorg. Chem.*, 1986, **25,** 3014.

[5] H. B. Gray *et al., Inorg. Chem.*, 1981, **20,** 2390.

Planar–tetrahedral equilibria in compounds of the type (18-G-XV) have been well studied by nmr. In the tetrahedral forms unpaired electron spin density from the nickel atoms is introduced into the ligand π system, which results in large shifts in the positions of the various proton nuclear magnetic resonances. To a certain extent the position of the equilibrium is a function of steric factors, that is, of the repulsion between the R groups on the nitrogen atoms of one ligand and various parts of the other ligand, the greater degree of repulsion encountered in the square configuration tending to shift the equilibrium to the tetrahedral side. However, some ring substituents affect the equilibrium by means of electronic effects as well.



(18-G-XV)

Thermochromism. This phenomenon is frequently encountered among Ni^{II} complexes. It comes in general from temperature-dependent variability of structure, which causes variation in the *d–d* absorption bands. Specific mechanisms differ from case to case. In some cases it appears that there are only relatively small relocations of ligands within a qualitatively fixed type of symmetry, whereas in others gross changes in coordination geometry occur. In $(NR_xH_{4-x})_2NiCl_4$ compounds ($x = 1$, 2, and 3), reversible thermochromism, from yellow brown or green at low temperature to blue at high temperature, appears to be due to changes from octahedral (with bridging Cl atoms) to tetrahedral coordination.

18-G-5. The Chemistry of Nickel(III), d^7, Compounds[1,2,6]

Binary Compounds. Nickel(III) fluoride has been prepared as an impure black, noncrystalline solid, marginally stable at 25°C. There is no good evidence for Ni_2O_3, but there are two proved crystalline forms of black NiO(OH). The more common β-NiO(OH) is obtained by the oxidation of nickel(II) nitrate solutions with bromine in aqueous potassium hydroxide below 25°C. It is readily soluble in acids; on aging, or by oxidation in hot solutions, a Ni^{II}—Ni^{III} hydroxide of stoichiometry $Ni_3O_2(OH)_4$ is obtained. The oxidation of alkaline nickel sulfate solutions by NaOCl gives a black "peroxide" $NiO_2 \cdot nH_2O$. This is unstable, being readily reduced by water, but it is a useful oxidizing agent for organic compounds.

The compound $NaNiO_2$ and several related ones also seem to be genuine.

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[6] R. L. Haines and A. McAuley, *Coord. Chem. Rev.*, 1981, **39,** 77; A. Chakvavorty *et al.*, *Inorg. Chem.*, 1986, **25,** 3448.

They can be made by bubbling oxygen through molten alkali metal hydroxides contained in nickel vessels at about 800°C. Other oxides and oxide phases can be made by heating NiO with alkali or alkaline earth oxides in oxygen. These mixed oxides evolve oxygen on treatment with water or acid.

The Edison or nickel–iron battery, which uses KOH as the electrolyte, is based on the reaction

$$\mathrm{Fe} + 2\mathrm{NiO(OH)} + 2\mathrm{H_2O} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{Fe(OH)_2} + 2\mathrm{Ni(OH)_2} \qquad (\sim 1.3\ \mathrm{V})$$

but the mechanism and the true nature of the oxidized nickel species are not fully understood.

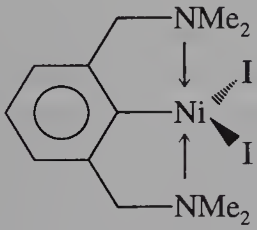
Complexes. There are a number of $\mathrm{Ni^{III}}$ complexes, mostly with macrocyclic nitrogen ligands and peptides. For the macrocycles which are made by one electron oxidation of the $\mathrm{Ni^{II}}$ species, the ring size and size of cavity in the macrocycles has an influence on the $\mathrm{Ni^{II}/Ni^{III}}$ redox potential.[7] Some $\mathrm{Ni^{III}}$ macrocycles can also be oxidized to $\mathrm{Ni^{IV}}$.

The open chain ligands such as $\mathrm{EDTA^{4-}}$ and deprotonated peptides give stable complexes in aqueous solution.[8] The ion $[\mathrm{Nibipy_3}]^{3+}$ is octahedral[9] with a tetragonal distortion having short axial bonds as in $\mathrm{K_3NiF_6}$ due to the Jahn–Teller effect in the $t_{2g}^6e_g^1$ configuration.

Examples of neutral complexes are $\mathrm{NiX_2}$(dioximate)[10] and $\mathrm{NiBr_3}$ dppe· toluene, which is *sp* with an apical Br.[11]

Tertiary phosphine complexes of this type were the first $\mathrm{Ni^{III}}$ species to be made—by halogen oxidation of $\mathrm{NiX_2(PR_3)_2}$.

An organometallic derivative (18-G-XVI) is similar.[12]



(18-G-XVI)

18-G-6. The Chemistry of Nickel(IV), d^6 Compounds[1]

The alkali salts $\mathrm{M_2^INiF_6}$ made by fluorination are red or purple[13] and oxo species like $\mathrm{BaNiO_3}$ and $[\mathrm{NiNb_{12}O_{38}}]^{12-}$ have $\mathrm{Ni^{IV}}$.

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[7] K. Wieghardt *et al., Inorg. Chem.*, 1986, **25,** 1650; L. Fabbrizzi *et al., Inorg. Chem.*, 1986, **25,** 4256.

[8] See, for example, D. W. Margerum *et al., Inorg. Chem.*, 1985, **24,** 4356.

[9] N. Sutin *et al., Inorg. Chem.*, 1984, **23,** 3473.

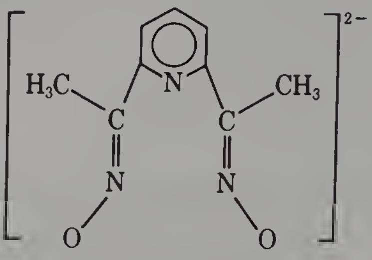
[10] A. von Zelewsky *et al., Inorg. Chem.*, 1983, **22,** 3576.

[11] W. Levason *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 459.

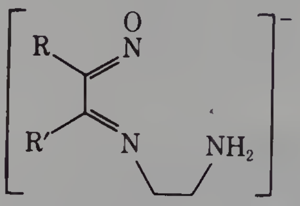
[12] G. van Koten *et al., J. Am. Chem. Soc.*, 1983, **105,** 1379.

[13] W. W. Wilson and K. O. Christe, *Inorg. Chem.*, 1984, **23,** 3261.

There are other well-established octahedral complexes (*a*) with phosphine or arsine ligands,[14] for example, $[\text{diphos}_2\text{NiCl}_2]^{2+}$ (*b*) with dimethylglyoximate $[\text{Ni dmg}_3]^{2-}$ and other oximes such as (18-G-XVII) and (18-G-XVIII), that can be made usually by oxidation of Ni^{II} complexes.[15]



(18-G-XVII)



(18-G-XVIII)

Note, however, that some formally Ni^{IV} compounds, particularly ones of sulfur ligands such as 1,2-dithiolates, contain the oxidized form of the ligand and are properly considered as Ni^{II} species. An example of this situation[16] is the olive green "$[\text{Ni}^{\text{IV}}\text{S}(\text{S}_2\text{CPh}_2)_2]_2$", which is actually $[\text{Ni}^{\text{II}}(\text{S}_2\text{CPh}_2)_3]^-$.

There are also some mixed valence chain compounds similar to those of $\text{Pt}^{\text{II}}\text{—Pt}^{\text{IV}}$ (Section 19-H-4) that contain square Ni^{II} and octahedral Ni^{IV} units linked by $\text{Ni}^{\text{II}}\text{—X—Ni}^{\text{IV}}$ halogen bonds.[17]

18-G-7. Lower Oxidation States (−1), (0), (+1)[1,2]

Compounds of Ni^{-1}, which are few, and those of Ni^0 are formed mainly with π-bonding ligands.

The majority of *nickel(I) complexes*[1] contain phosphine ligands, or closely related ones, and have tetrahedral or *tbp* structures. They are paramagnetic as expected for d^9 configurations. The tetrahedral compounds $\text{Ni}(\text{PPh}_3)_3\text{X}$ (X = Cl, Br, and I) were among the first of this sort to be isolated; they decompose only slowly in air and are stable for long periods of time in nitrogen. Electrolytic reductions of Ni^{2+} in MeCN in the presence of PR_3 can stabilize Ni^{I} but phosphites stabilize Ni^0 or Ni^{II}, although due to kinetic effects $\{\text{Ni}[\text{P(OEt)}_3]_4\}^+$ can be isolated.[18]

With the tripod ligand np_3 an entire series of compounds with *tbp* structures, $\text{Ni}(np_3)\text{X}$ (X = Cl, Br, I, CN, CO, and H) can be prepared by reaction of nickel halides with the np_3 ligand in the presence of borohydride, followed, if necessary, by metathesis with other X groups.

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[14] W. Levason *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 317.

[15] R. K. Panda *et al., Inorg. Chem.*, 1984, **23**, 4393; D. H. Macartney and A. McAuley, *J. Chem. Soc. Dalton Trans.*, **1984**, 105; A. G. Lappin *et al., J. Chem. Soc. Dalton Trans.*, **1984**, 1371.

[16] J. P. Fackler *et al., J. Am. Chem. Soc.*, 1984, **106**, 7883.

[17] M. Yamashita and T. Ito, *Inorg. Chim. Acta*, 1984, **87**, L5.

[18] G. Bontempelli *et al., Inorg. Chem.*, 1981, **20**, 2579.

Nickel(II) complexes of certain N_4 macrocycles can be reduced by solvated electrons (from pulse radiolysis of water) to radical species $Ni^{II}L^{\cdot}$ and on treatment with CO the electron on the ligand moves to the metal giving $Ni^{I}(CO)N_4$.[19] The isocyanide $[Ni_2(MeNC)_8]^{2+}$ that has a Ni—Ni bond is made by interaction of $Ni(MeNC)_4^{2+}$ with $Ni(MeNC)_4$.[20]

Nickel(0) also forms isocyanide complexes such as $Ni_4(CNR)_6$[21]; $Ni(bipy)_2$ made by metal vapor synthesis shows formal oxidation states in MeCN as solvent from -2 to $+3$.[22]

Most Ni^0 complexes have CO and/or PR_3 ligands; cyanide species such as $[Ni(CN)_4]^{4-}$ and $[Ni(CN)_2(CO)_2]^{2-}$ are also well characterized.[23]

18-H. COPPER: GROUP IB(11)

Copper has a single *s* electron outside the filled 3*d* shell but essentially nothing in common with the alkalis except formal stoichiometries in the +1 oxidation state. The filled *d* shell is much less effective than is a noble gas shell in shielding the *s* electron from the nuclear charge, so that the first ionization enthalpy of Cu is higher than those of the alkalis. Since the electrons of the *d* shell are also involved in metallic bonding, the heat of sublimation and the melting point of Cu are also much higher than those of the alkalis. These factors are responsible for the more noble character of copper, and the effect is to make the compounds more covalent and to give them higher lattice energies, which are not offset by the somewhat smaller radius of the unipositive ion compared to the alkali ions in the same period—Cu^+, 0.93; Na^+, 0.95; and K^+, 1.33 Å.

The second and third ionization enthalpies of Cu are very much lower than those of the alkalis and account in part for the transition metal character shown by the existence of colored paramagnetic ions and complexes in the II, III, and IV oxidation states. Even in the I oxidation state numerous transition-metal-like complexes are formed (e.g., those with olefins).

There is only moderate similarity between Cu and the heavier elements Ag and Au, but some points are noted in the later discussions of these elements (Chapter 19).

The oxidation states and stereochemistry of Cu are summarized in Table 18-H-1. Stable copper(0) compounds are not confirmed, but reactive intermediates appear to occur in some reactions.

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[19] R. R. Gagné and D. M. Ingle, *Inorg. Chem.*, 1981, **20,** 420; J. Lewis and M. Schröder, *J. Chem. Soc. Dalton Trans.*, **1982,** 1085.

[20] C. P. Kubiak *et al.*, *Organometallics*, 1985, **4,** 954.

[21] E. L. Muetterties *et al.*, *Inorg. Chem.*, 1980, **19,** 1552.

[22] B. J. Henne and D. E. Bartak, *Inorg. Chem.*, 1984, **23,** 369.

[23] R. del Rosario and L. S. Stuhl, *Organometallics*, 1986, **5,** 1260.

TABLE 18-H-1
Oxidation States and Stereochemistry of Copper

Oxidation state	Coordination number	Geometry	Examples
Cu^I, d^{10}	2	Linear	Cu_2O, KCuO, $CuCl_2^-$
	3	Planar	$K[Cu(CN)_2]$, $[Cu(SPMe_3)_3]ClO_4$
	4[a]	Tetrahedral	CuI, $[Cu(CN)_4]^{3-}$, $[Cu(MeCN)_4]^+$
	4	Distorted planar	CuL[c]
	5	*sp*	[CuLCO][c]
	6	Octahedral	$\{(Ph_2MeP)_3ReH_5\}_2Cu^+$[d]
Cu^{II}, d^9	3	Trigonal planar	$Cu_2(\mu\text{-}Br)_2Br_2$
	4[a,b]	Tetrahedral (distorted)	(*N*-Isopropylsalicylaldiminato)$_2$Cu $Cs_2[CuCl_4]$
	4[a,b]	Square	CuO, $[Cu(py)_4]^{2+}$, $(NH_4)_2[CuCl_4]$
	6[a,b]	Distorted octahedral	K_2CuF_4, $K_2[CuEDTA]$, $CuCl_2$
	5	*tbp*	$[Cu(bipy)_2I]^+$, $[CuCl_5]^{2-}$, $[Cu_2Cl_8]^{4-}$
	5	*sp*	$[Cu(DMGH)_2]_2(s)$, $[Cu(NH_3)_5]^{2+}$[e]
	6	Octahedral	$K_2Pb[Cu(NO_2)_6]$
	7	Pentagonal bipyramidal	$[Cu(H_2O)_2(dps)]^{2+}$[f]
	8	Distorted dodecahedron	$Ca[Cu(CO_2Me)_4]\cdot 6H_2O$
Cu^{III}, d^8	4	Square	$KCuO_2$, $CuBr_2(S_2CNBu_2)$
	6	Octahedral	K_3CuF_6
Cu^{IV}, d^7	6	?	Cs_2CuF_6

[a] Most common states.

[b] These three cases are often not sharply distinguished; see text.

[c] L = a macrocyclic N_4 anionic ligand (R. R. Gagne *et al.*, *Inorg. Chem.*, 1978, **17**, 3563).

[d] Copper coordinated to six H atoms in $Re(\mu\text{-}H)_3Cu$ system (K. G. Caulton *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 5137).

[e] In $K[Cu(NH_3)_5](PF_6)_3$ (M. Sano *et al.*, *Inorg. Chem.*, 1984, **23**, 4466).

[f] dps = 2,6-diacetylpyridine bis(semicarbazone).

Note: A species formally with Cu^0 has been made by reduction of the Cu^I complex of an N_4 macrocycle; A. M. Bond and M. A. Khalifa, *Inorg. Chem.*, 1987, **26**, 413.

18-H-1. The Element

Copper is widely distributed in Nature as metal, in sulfides, arsenides, chlorides, carbonates, and so on. It is extracted from ores, usually by wet processes, for example, by leaching with dilute sulfuric acid, or by solvent extraction[1] using salicylaldoximes and similar ligands. Copper is refined by electrolysis.

Copper is a tough, soft, and ductile reddish metal, second only to Ag in its high thermal and electrical conductivities. It is used in alloys such as brasses and is completely miscible with Au. It is only superficially oxidized in air, sometimes acquiring a green coating of hydroxo carbonate and hydroxo sulfate.

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[1] See H. Freiser, *Acc. Chem. Res.*, 1984, **17**, 126.

Copper reacts at red heat with O_2 to give CuO and, at higher temperatures, Cu_2O; with sulfur it gives Cu_2S or a nonstoichiometric form of this compound. It is attacked by halogens but is unaffected by nonoxidizing or noncomplexing dilute acids in absence of air. Copper readily dissolves in HNO_3 and H_2SO_4 in the presence of O_2. It is soluble in NH_4OH, ammonium carbonate, or KCN solutions in the presence of O_2, as indicated by the potentials

$$\mathrm{Cu + 2NH_3 \xrightarrow{-0.12\,V} [Cu(NH_3)_2]^+ \xrightarrow{-0.01\,V} [Cu(NH_3)_4]^{2+}}$$

It is also soluble in acid solutions containing thiourea, which stabilizes Cu^I as a complex; acid thiourea solutions are also used to dissolve copper deposits in boilers.

COPPER COMPOUNDS[2]

18-H-2. The Chemistry of Copper(I), d^{10}

Copper(I) compounds are diamagnetic and, except where color results from the anion or charge-transfer bands, colorless.

The relative stabilities of the Cu^I and Cu^{II} states are indicated by the following potential data:

$$\mathrm{Cu^+} + e = \mathrm{Cu} \qquad E^0 = 0.52\ \mathrm{V}$$

$$\mathrm{Cu^{2+}} + e = \mathrm{Cu^+} \qquad E^0 = 0.153\ \mathrm{V}$$

whence

$$\mathrm{Cu + Cu^{2+} = 2Cu^+} \qquad E^0 = -0.37\ \mathrm{V} \qquad K = [\mathrm{Cu^{2+}}]/[\mathrm{Cu^+}]^2 = \sim 10^6$$

The relative stabilities of Cu^I and Cu^{II} in aqueous solution depend very strongly on the nature of anions or other ligands present and vary considerably with solvent or the nature of neighboring atoms in a crystal.

In aqueous solution only low equilibrium concentrations of Cu^+ ($<10^{-2}$ M) can exist (see later) and the only simple compounds that are stable to water are the highly insoluble ones such as CuCl or CuCN. This instability toward water is due partly to the greater lattice and solvation energies and higher formation constants for complexes of the Cu^{II} ion, so that ionic Cu^I derivatives are unstable. Of course numerous Cu^I cationic or anionic complexes are stable in aqueous solution.

The equilibrium $2Cu^I \rightleftharpoons Cu + Cu^{II}$ can readily be displaced in either direction. Thus with CN^-, I^-, and Me_2S, Cu^{II} reacts to give the Cu^I compound; with anions that cannot give covalent bonds or bridging groups (e.g., ClO_4^- and SO_4^{2-}) or with complexing agents that have their greater affinity for Cu^{II},

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[2] K. D. Karlin and J. Zubieta, Eds., *Copper Coordination Chemistry, Biochemical and Inorganic Perspectives,* Adenine Press, Guilderland, New York, 1983, 1986; J. O. Nriagu, *Copper in the Environment,* Wiley, New York, 1980.

the Cu^{II} state is favored—thus ethylenediamine reacts with CuCl in aqueous potassium chloride solution:

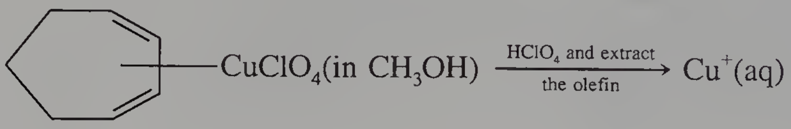
$$2CuCl + 2en = [Cu\,en_2]^{2+} + 2Cl^- + Cu^0$$

That the latter reaction also depends on the geometry of the ligand, that is, on its chelate nature, is shown by differences in the $[Cu^{2+}]/[Cu^+]^2$ equilibrium with chelating and nonchelating amines. Thus for ethylenediamine, K is $\sim 10^5$, for pentamethylenediamine (which does not chelate) 3×10^{-2}, and for ammonia 2×10^{-2}. Hence in the last case the reaction is

$$[Cu(NH_3)_4]^{2+} + Cu^0 = 2[Cu(NH_3)_2]^+$$

In ClO_4^- solution from 6.4 to 14.2 M in NH_3 only $[Cu(NH_3)_2]^+$ and $[Cu(NH_3)_3]^+$ occur.[3] For a macrocyclic N_4 complex a reversible Cu^I/Cu^{II} redox is observed.[4]

The lifetime of the Cu^+ aqua ion in water depends strongly on conditions. Usually disproportionation is very fast (<1 s), but ~0.01 M solutions prepared in 0.1 M $HClO_4$ at 0°C by the reaction



or by reduction of Cu^{2+} with V^{2+} or Cr^{2+}, may last for several hours if air is excluded.

An excellent illustration of how the stability of Cu^I relative to Cu^{II} may be affected by solvent is acetonitrile. The Cu^+ ion is very effectively solvated by MeCN, and the copper(I) halides have relatively high solubilities (e.g., CuI, 35 g/kg MeCN), versus negligible solubilities in H_2O. Copper(I) is more stable than Cu^{II} in MeCN and the latter is, in fact, a comparatively powerful oxidizing agent. The tetrahedral ion $[Cu(MeCN)_4]^+$ can be isolated in salts with large anions (e.g., ClO_4^- and PF_6^-).

Copper(I) Binary Compounds. The *oxide* and the *sulfide* are more stable than the corresponding Cu^{II} compounds at high temperatures. Copper(I) oxide (Cu_2O) is made as a yellow powder by controlled reduction of an alkaline solution of a Cu^{2+} salt with hydrazine or, as red crystals, by thermal decomposition of CuO. A yellow "hydroxide" is precipitated from the metastable Cu^+ solution mentioned previously. Copper(I) sulfide (Cu_2S) is a black crystalline solid prepared by heating copper and sulfur in the absence of air.

Alkali metal oxocuprates[5] are made by heating Cu_2O with Na_2O, K_2O, and so on. The compounds $M^I_4Cu_4O_4$ have $[Cu_4O_4]^{4-}$ rings with the Cu atoms planar. There are similar Ag and Au compounds.

Copper(I) chloride and bromide are made by boiling an acidic solution of

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[3] K. L. Stevenson *et al., Inorg. Chem.*, 1984, **23,** 4072.

[4] D. Meyerstein *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 1683.

[5] W. Losert and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1985, **524,** 7.

the Cu^{II} salt with an excess of Cu; on dilution, white CuCl or pale yellow CuBr is precipitated. Addition of I^- to a solution of Cu^{2+} forms a precipitate that rapidly and quantitatively decomposes to CuI and iodine. Copper(I) fluoride is unknown. The halides have the zinc blende structure (tetrahedrally coordinated Cu^+). Copper(I) chloride and CuBr are polymeric in the vapor state, and for CuCl the principal species appears to be a six ring of alternating Cu and Cl atoms with Cu—Cl, ~2.16 Å. White CuCl becomes deep blue at 178°C and melts to a deep green liquid. The halides are very insoluble in water but are solubilized by complex formation[6]

$$CuX(s) + nX^- \rightleftharpoons CuX_{n+1}^{n-} \qquad n = 2\text{–}4$$

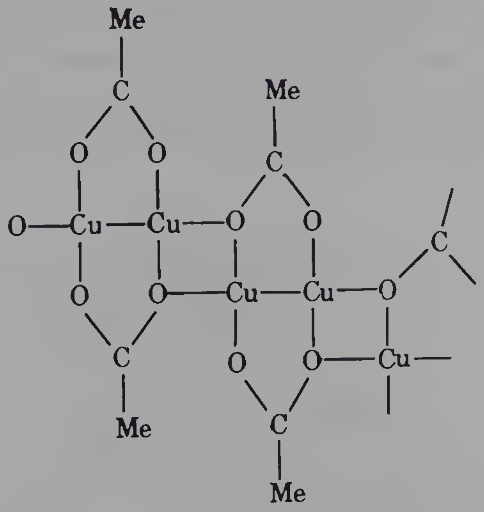
and also by complexing with CN^- or NH_3.

Other relatively common Cu^I compounds are the *cyanide,* conveniently prepared by the reaction

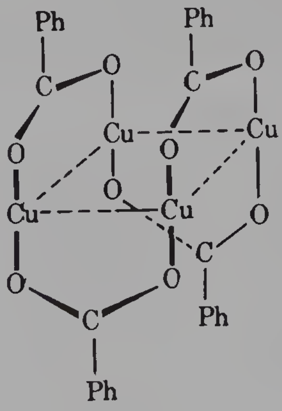
$$2Cu^{2+}(aq) + 4CN^-(aq) \longrightarrow 2CuCN(s) + C_2N_2$$

and soluble in an excess of cyanide to give the ions $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$. Although compounds such as $KCu(CN)_2$ and $NaCu(CN)_2{\cdot}2H_2O$ are known, they do not contain a simple ion analogous to $[Ag(CN)_2]^-$, but instead have infinite chains. However, in $Na_2[Cu(CN)_3]{\cdot}3H_2O$ there is a discrete three-coordinate ion.

Copper(I) Carboxylates, Triflate, Alkoxides, and Dialkylamides. The carboxylates[7a] have different structures. The acetate that is obtained as white air-sensitive crystals by reduction of Cu^{II} acetate by Cu in pyridine or MeCN has a planar chain structure (18-H-I). By contrast the trifluoroacetate $[CuO_2CCF_3]_4{\cdot}2C_6H_6$, and benzoate $[CuO_2CPh]_4$ complexes are tetramers with bridging carboxylates as in (18-H-II). This is only one type of Cu_4 polynuclear



(18-H-I)



(18-H-II)

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[6] See M. Munaka and J. F. Endicott, *Inorg. Chem.,* 1984, **23,** 3693.

[7a] T. P. Lockhart and D. A. Haitko, *Polyhedron,* 1985, **4,** 1745; S. Shibata *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 2555; C. Floriani *et al., Inorg. Chem.,* 1987, **26,** 236.

structure (see later). There are also bridged pyrazole and pyrazolylborate compounds.[7b]

Copper(I)trifluoromethanesulfonate (triflate) can be isolated as a white crystalline, but air-sensitive complex $[Cu(O_3SCF_3)]_2 \cdot C_6H_6$ by interaction of Cu_2O and trifluoromethanesulfonic anhydride in benzene. The benzene is readily displaced by a variety of olefins to give cationic olefin complexes (see later). The complex also catalyzes the cyclopropanation of olefins by use of diazoalkanes $RCHN_2$.

Copper(I) alkoxides (CuOR) are yellow substances that can be made, for example, by the reactions:

$$CuCl + LiOR = LiCl + CuOR$$

$$(CuMe)_n + nC_6H_5OH = nCuOC_6H_5 + nCH_4$$

The methoxide is insoluble, but other alkoxides can be sublimed and are soluble in ethers. The *t*-butoxide is a tetramer $[CuOCMe_3]_4$, with alkoxo bridges [see (12-XII)]. There are also aryloxides such as $[Cu(OAr)_2]^-$ and $(RNC)_2Cu(OAr)$.[8]

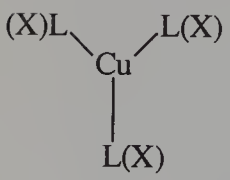
Alkoxides react with organic halides R′I to give ethers ROR′. The butoxide will metallate acidic hydrocarbons such as C_5H_6 or $PhC \equiv CH$ and reacts with CO_2 and NHR_2 to give the carbamate.

Copper(I)dialkylamides. Only a few are known so far[9]; colorless $[Cu(NEt_2)]_4$ is a tetramer.

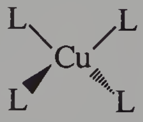
Copper(I) Complexes. Copper(I) halide and other complexes are usually obtained by (*a*) direct interaction of ligands with copper(I) halides or the triflate, (*b*) reduction of corresponding copper(II) compounds, or (*c*) reduction of Cu^{2+} in the presence of, or by, the ligand.

The stoichiometries of the compounds give little clue to their structures, which can be very complicated, being mononuclear, binuclear with halide bridges, polynuclear and the copper atom two-, three-, or four-coordinate, or infinite chains.

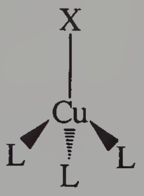
Mononuclear species can be of the structural types,[10] L = neutral ligands:



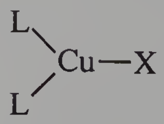
CuL_3^+
CuX_3^{2-}



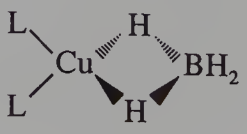
CuL_4^+



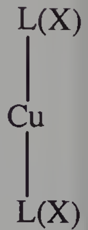
$CuXL_3$



$CuXL_2$



$CuXL_2$



CuL_2^+
CuX_2^-
CuXL

[7b] T. N. Sorrele and A. S. Brook, *J. Am. Chem. Soc.*, 1987, **109**, 4255.

[8] C. Floriani *et al.*, *J. Chem. Soc. Chem. Commun.*, **1984**, 888.

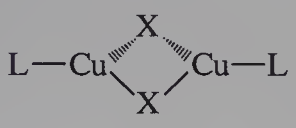
[9] C. Floriani *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 1883.

[10] E. C. Alyea *et al.*, *Inorg. Chem.*, 1985, **24**, 3719; N. P. Rath and E. M. Holt, *J. Chem. Soc. Chem. Commun.*, **1986**, 311; A. H. White *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 125; *Inorg.*

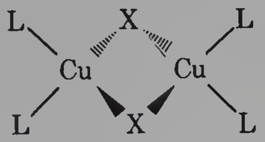
Compounds of a particular stoichiometry, for example, CuXL or $CuXL_2$ may have more than one structure depending on the nature of L.

Many discrete halogeno ions are known, examples being $CuCl_2^-$, $CuBr_3^{2-}$, and CuL_2^+.

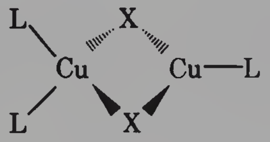
Binuclear Species. These are of formulas Cu_2X_2L, $Cu_2X_2L_4$, and $Cu_2X_2L_3$ and structures (18-H-III) to (18-H-V). An example of the latter, which has both three- and four-coordinate copper(I), is $Cu_2Cl_2(PPh_3)_3$.



(18-H-III)



(18-H-IV)



(18-H-V)

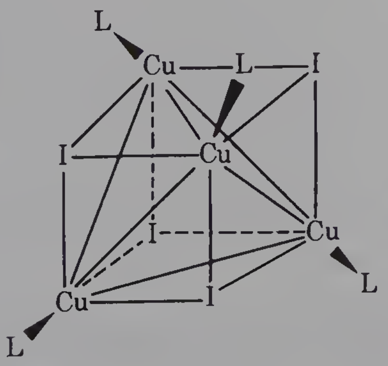
Chain Structures. Halide anions can have the following types:

1. Infinite chains of $CuCl_4$ tetrahedral units sharing edges, e.g., $[Cu(NH_3)_4]Cu_2Cl_4$.
2. Infinite chains of $CuCl_4$ tetrahedral units sharing corners, e.g., K_2CuCl_3.
3. Infinite double chains of $CuCl_4$ tetrahedra sharing corners, e.g., $CsCu_2Cl_3$.

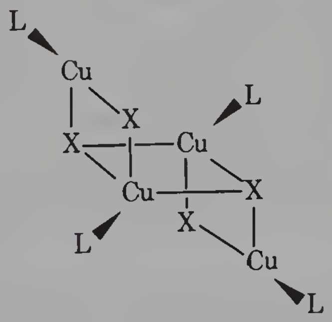
Spiral chains with almost planar trigonal Cu^I are formed in $[Cu(CN)_2]^-$ ions, —Cu(CN)(μ-CN)Cu(CN)(μ-CN)Cu(CN)—.

Tetrameric Structures. Copper benzoate and other compounds discussed previously have four Cu atoms that although part of a ring, in themselves form a parallelogram. Tetrameric Cu_4^I complexes may have the structures in which the four Cu atoms are in (*a*) a parallelogram, rectangle, or a square; (*b*) most commonly, at the vertices of a tetrahedron, regular or slightly distorted, and (*c*) in a halogen-bridged step structure.

Another class[11] are those with monatomic ligands $(CuXL)_4$ where L is usually R_3P but can be py and X is usually halogen but can be SR. These have two main limiting structures each of which may be distorted. The first is the *cubane structure* (18-H-VI) in which there is a Cu_4 tetrahedron with a triply bridging halide and a ligand on each Cu atom, which is four-coordinate.



(18-H-VI)



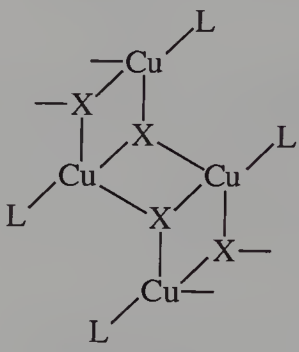
(18-H-VII)

Chem., 1985, **23,** 1957; S. Kitagawa and M. Munakata, *Inorg. Chem.*, 1984, **23,** 4388; G. A. Bowmaker *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984,** 37.

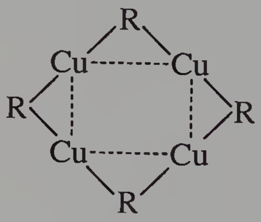
[11] See A. H. White *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985,** 2541 and earlier papers; I. G. Dance *et al.*, *Inorg. Chem.*, 1985, **24,** 2547.

The second has the *step form* (18-H-VII) with double and triple halide bridges and 2 four-coordinate, tetrahedral and 2 three-coordinate, trigonal copper atoms.

The silver analogues (Section 19-I-2) are similar. Which structure a complex has depends on the sizes of the metal and halide atoms and on the steric bulk of the ligand and the solvent from which it crystallized. Some, for example, $[Ph_3PCuX]_4$, X = Br and I can have both forms. Certain other compounds may have the cubane form but are linked by corner Cu—X bonds into a polymer, for example, $[Cu_4I_4(NEt_3)_3]_\infty$, while the step form can also give a stair structure (18-H-VIII). Compounds with *planar* cores $(CuR)_4$ have squares with two-coordinate copper and bridge groups giving eight-membered rings (18-H-IX). For R = CH_2SiMe_3 and O*t*-Bu the ring is almost planar but for NEt_2 the N atoms are alternately above and below the Cu_4 square.



(18-H-VIII)



(18-H-IX)

Pentanuclear Complexes. In $[Cu_5(\mu\text{-S}t\text{-Bu})_6]^-$ there is *tbp* Cu^I with μ-SR and this structure is also found in the aryl species (see later), Cu_4MgPh_6, Cu_4LiPh_6, $[Cu_5Ph_6]^-$, and $[Cu_3Li_2Ph_6]^-$. The phenyl groups bridge metal atoms that may be Cu only, Cu + Li, or Cu + Mg.[12]

Hexanuclear Complexes. The hydrides, $[HCuPR_3]_6$, can be obtained by hydrogenolysis of $(CuOt\text{-Bu})_4$ in the presence of phosphine or by borohydride reduction of $[CuClPR_3]_n$.[13a] There is an octahedron of copper atoms each with a phosphine; the H atoms probably bridge.

Other Polynuclear Complexes. $H_8Cu_8(dppp)_4$dppp = $Ph_2P(CH_2)_3PPh_2$, has a distorted dodecahedron of Cu atoms.[13a] Other complexes mainly have sulfur

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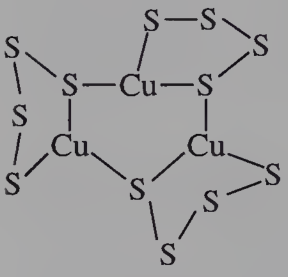
[12] R. Bau *et al., J. Am. Chem. Soc.,* 1982, **104,** 2072; 1985, **107,** 1682; P. P. Power *et al., J. Am. Chem. Soc.,* 1984, **106,** 1149.

[13a] K. G. Caulton *et al., J. Am. Chem. Soc.,* 1985, **107,** 7774.

ligands with Cu_8S_{12} and $Cu_{10}S_6$ cores or, for $[CuSR]_8$ a 16-membered ring with alternate Cu and S atoms.[13b] Various iodide anions including $Cu_8I_{13}^{5-}$ are known and an even more complicated ion is $Cu_{36}I_{56}^{20-}$.[14]

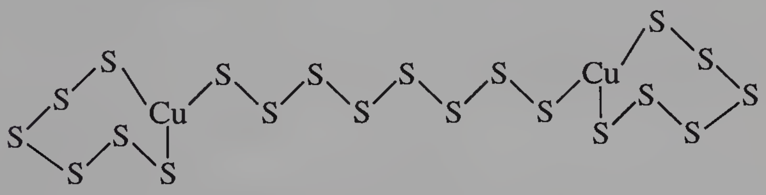
Cu–Cu Interaction in Cu^I Polynuclear Compounds. In many of these structures there are relatively short Cu—Cu distances 2.38 to 3.2 Å (Cu—Cu in metal 2.40 Å). However, there are always bridges present and since Cu^I is d^{10} metal–metal bonding would appear to be weak if existing at all. The compounds are hence best referred to as aggregates or cages[15] and *not* clusters whose defining property is the existence of M—M bonds (Chapter 23).

Copper(I) Sulfido Anions. There is a remarkable array of polynuclear anions containing sulfur rings or chains that can be isolated as salts of large cations. They are formed by dissolution of copper sulfides in polysulfide solutions or by the action of sulfur and H_2S on ethanolic solutions of Cu^{II} acetate, and so on.[16] Examples are ions such as $[Cu_2S_{20}]^{4-}$, $[Cu_3S_{12}]^{3-}$, and $[Cu_4S_{12}]^{4-}$. Many of the structures are quite complex, for example, (18-H-X) and (18-H-XI).



$[Cu_3(S_4)_3]^{3-}$

(18-H-X)



$[S_6Cu(\mu\text{-}S_8)CuS_6]^{4-}$

(18-H-XI)

Copper(I) Organo Compounds.[17] Copper(I), but not copper(II), forms a variety of compounds with Cu—C bonds.

The *alkyls* and *aryls* may be obtained by interaction of copper(I) halides with lithium or Grignard results. The *alkyls* usually decompose readily but methyl copper, a bright yellow polymer insoluble in organic solvents, is reasonably stable; it can be used in certain organic syntheses, but the use of lithium alkyl cuprates (see later) is more common. Alkyls can be stabilized by phosphine ligands as in, for example, $n\text{-}Bu_3PCu(CH_2)_3CH_3$.

Like the $[CuCH_2SiMe_3]_4$ noted earlier the *aryls* are aggregates of Cu_4, Cu_5, Cu_6, or Cu_8 with organic groups acting as bridges, for example, the mesityl $(Cumes)_5$ is a puckered 10-membered ring, which surprisingly undergoes ring

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[13b] Q. Yang *et al., J. Am. Soc. Chem. Commun.*, **1987**, 1076.

[14] H. Hartl and J. Fuchs, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 569.

[15] See I. G. Dance, *Comprehensive Coordination Chemsitry*, Vol. 1, Chapter 4, Pergamon Press, Oxford, 1987.

[16] A. Müller *et al., Z. Anorg. Allg. Chem.*, 1985, **521**, 89; *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 632; G. Henkel *et al., Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 311.

[17] J. G. Noltes and G. van Koten, *Comprehensive Organometallic Chemistry*, Vol. 2, Chapter 14, Pergamon Press, Oxford, 1982.

contraction on treatment with thiophen to give Cu_4 $mes_4(SC_4H_8)_2$ that now has a $Cu_4C_4S_4$ ring.[18]

The fluoroaryls, for example, $[CuC_6F_5]_4$, and perfluoroalkyls are more stable than hydrocarbon analogues; the aryl group $C_6H_4(2\text{-}NMe_2)$ has been much used, since the N atom can also occupy a coordination site and stabilize the molecules.

Mixed aryl (R) compounds such as $R_6Cu_6(C{\equiv}CR')_2$ and $R_4Cu_4Ag_2(CF_3SO_3)_2$ are also known.

The decarboxylation of copper perfluorobenzoate in quinoline gives $(CuC_6F_5)_n$. The catalytic action of copper or copper salts on decarboxylation reactions of carboxylic acids presumably involves organo intermediates.

Lithium Alkyl Cuprates. These important species are made by interaction of CuI or MeCu with LiR. They are commonly used *in situ* in ether or similar solvent for a wide variety of organic syntheses. They are especially useful for C—C bond formation by interaction with organic halides;

$$LiCuR_2 + R'X \longrightarrow R{-}R' + LiX + CuR$$

The species in solution[19a] depend on the solvent and the ratio of Cu to LiR; in THF there is an equilibrium

$$Me_2CuLi + MeLi \rightleftharpoons Me_3Cu_2Li$$

In the presence of lithium salts there are different species which can also give different reactions depending on the Cu to LiR ratio.

The structures of several of the isolated compounds have been determined.[12,19b] Those based on an M_5 unit have been noted earlier. Simpler species are the linear ions $[Cu\,mes_2]^-$ and $\{Cu[C(SiMe_3)_3]_2\}^-$ and the neutral complex $Cu_2Li_2(C_6H_4CH_2NMe_2)_2$.[19b]

Alkene Complexes. Of all the metals involved in biological systems only Cu reacts with ethylene, and a Cu^I complex is involved in binding C_2H_4, which acts as a hormone in plants.[20] Formation constants can be determined in solutions[21a] and several complexes[21b] have been isolated, for example, $Cu(C_2H_4)(bipy)^+$. The reaction

$$Cu + Cu^{2+} + 2C_2H_4 \xrightleftharpoons{H_2O} 2[Cu(C_2H_4)(H_2O)_2]^+$$

gives the perchlorate. Other alkene complexes can be made by direct interaction of CuCl or $CuCF_3SO_3$ with olefins or by reduction of Cu^{II} salts by trialkylphosphites in ethanol in the presence of alkene. The crystalline compounds obtained when using chelating alkenes such as norbornadiene or cyclic

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[18] C. Floriani *et al., J. Chem. Soc. Chem. Commun.*, **1983,** 1156.

[19a] B. H. Lipshutz *et al., J. Am. Chem. Soc.*, 1985, **107,** 3197.

[19b] G. van Koten *et al., J. Am. Chem. Soc.*, 1985, **107,** 697.

[20] J. S. Thompson *et al., Inorg. Chem.*, 1984, **23,** 2813.

[21a] I. Renken and S. W. Orchard, *Inorg. Chem.*, 1986, **25,** 1972.

[21b] J. S. Thompson and R. M. Swiatek, *J. Am. Chem. Soc.*, 1985, **107,** 110; M. Munakata and J. F. Endicott, *Inorg. Chem.*, 1984, **23,** 3693.

polyenes usually have polymeric structures. Usually only one double bond is coordinated, and dissociation is relatively easy.

Cationic complexes are readily obtained by displacement of benzene from $(CuSO_3CF_3)_2 \cdot C_6H_6$. These are thermally stable and often soluble in organic solvents. They are of the types LCu^+ and L_2Cu^+, where L is a chelating diolefin such as cycloocta-1,5-diene. Cationic complexes, not only of alkenes, with diethylenetriamine can be made by the general reaction

$$CuI + dien + L \xrightarrow{MeOH} [Cu\,dien\,L]^+ + I^-$$

Carbonyls. In concentrated H_2SO_4 under pressure, the species $[Cu(CO)_3]^+$ and $[Cu(CO)_4]^+$ can be obtained but at atmospheric pressure complexes can be made by a reaction similar to that using C_2H_4, that is,

$$Cu + Cu^{2+} + 2CO \xrightleftharpoons{H_2O} 2[Cu(CO)(H_2O)_2]^+$$

and salts of $[Cu(CO)\,bipy)^+$ can be isolated.

Other ligand stabilized carbonyls, many of which are quite stable are η^5-$C_5H_5Cu(CO)$, $Cu(CO)[HB(pz)_3]$, and $[Cu(CO)dien]^+$. Interaction of $[CuO\textit{t}\text{-}Bu]_4$ with CO gives a cage carbonyl $[Cu(CO)O\textit{t}\text{-}Bu]_4$.[22] There are also Schiff base compounds[23] and mixed carbonyls made by interaction of CuCl with sodium carbonylate ions. In some cases like $[CuCo(CO)_4]_n$ there is no Cu—CO bond but only $(CO)_4Co—Cu—Co(CO)_4$ polymeric chains[24] and in $(Ph_3P)_3CuV(CO)_6$ there are $[(Ph_3P)_3Cu]^+$ and $[V(CO)_6]^-$ ions. However, other compounds do have bridging or semibridging CO groups[25] as in $(tmed)Cu(\mu\text{-}CO)_2Mo(CO)(\eta^5\text{-}C_5H_5)$ and $tmed\,Cu(\mu\text{-}CO)Co(CO)_3$, which has a long Cu—C and short C—Co distance.

Acetylene Compounds. Copper(I) chloride in concentrated hydrochloric acid absorbs acetylene to give colorless species such as $CuCl(C_2H_2)$ and $[CuCl_2(C_2H_2)]^-$. These halide solutions can also catalyze the conversion of acetylene into vinylacetylene (in concentrated alkali chloride solution) or to vinyl chloride (at high HCl concentration), and the reaction of acetylene with hydrogen cyanide to give acrylonitrile is also catalyzed.

Copper(I) ammine solutions react with acetylenes containing the $HC\equiv C$ group to give yellow or red precipitates, which are believed to have the $RC\equiv C—Cu$ unit π bonded to another Cu atom. The trimer $[Et_3PCuC\equiv CMe]_3$ is of this type.

Copper(I) acetylides provide a useful route to the synthesis of a variety of organic acetylenic compounds and heterocycles, by reaction with aryl and other halides. A particularly important indirect use, where acetylides are probable intermediates, is the oxidative dimerization of acetylenes. A common procedure is to use the *N,N,N′,N′*-tetramethylethylenediamine complex

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[22] K. G. Caulton *et al., J. Am. Chem. Soc.,* 1983, **105,** 3503.

[23] C. Floriani *et al., Inorg. Chem.,* 1985, **24,** 648.

[24] P. Klüfers, *Angew. Chem. Int. Ed. Engl.,* 1985, **24,** 70.

[25] G. Doyle *et al., Organometallics,* 1985, **4,** 877, 220.

of CuCl in a solvent, or CuCl in pyridine–methanol, and oxygen as a reoxidant for Cu^+.

$$2RC{\equiv}CH + 2Cu^{2+} + 2py \longrightarrow RC{\equiv}C{-}C{\equiv}CR + 2Cu^+ + 2pyH^+$$

Finally, an unusual cluster compound $Cu_4Ir_2(PPh_3)_2(C_2Ph)_8$ formally containing Cu^0 and Ir^{IV} has been made by the reaction of *trans*-$IrCl(CO)(PPh_3)_2$ and $(PhC{\equiv}CCu)_n$. It has an octahedron of metal atoms with *trans*-Ir atoms. Each Ir is bound to one PPh_3 and four acetylide groups.

Hydrides. The phosphine hydrides have been noted earlier. Others are those such as $Li_2Cu_3H_5$ and Li_5CuH_6 obtained by interaction of lithium methyl cuprates with $LiAlH_4$ in ether, for example,

$$LiCuMe_2 + LiAlH_4 \longrightarrow LiCuH_2 + LiAlH_2Me_2$$

A bridge hydride $Cu_2(\mu\text{-}H)_2(\text{triphos})_2$ has been made by hydrogenolysis of $(CuO\textit{t}\text{-}Bu)_4$ in the presence of the tripod phosphine.[26]

18-H-3. The Chemistry of Copper(II),[27] d^9

Most Cu^I compounds are fairly readily oxidized to Cu^{II} compounds, but further oxidation to Cu^{III} is more difficult. There is a well-defined aqueous chemistry of Cu^{2+}, and a large number of salts of various anions, many of which are water soluble, exist in addition to a wealth of complexes. The aqua ion $[Cu(H_2O)_6]^{2+}$ is distorted both in crystals and in solution.[28]

Stereochemistry. The d^9 configuration makes Cu^{II} subject to Jahn–Teller distortion if placed in an environment of cubic (i.e., regular octahedral or tetrahedral) symmetry, and this has a profound effect on all its stereochemistry. With only one possible exception, mentioned below, it is never observed in these regular environments. When six-coordinate, the "octahedron" is severely distorted, as indicated by the data in Table 18-H-2. The typical

TABLE 18-H-2
Interatomic Distances in Some Copper(II) Coordination Polyhedra

Compound	Distances (Å)
$CuCl_2$	4 Cl at 2.30, 2 Cl at 2.95
$CsCuCl_3$	4 Cl at 2.30, 2 Cl at 2.65
$CuCl_2{\cdot}2H_2O$	2 O at 2.01, 2 Cl at 2.31, 2 Cl at 2.98
$CuBr_2$	4 Br at 2.40, 2 Br at 3.18
CuF_2	4 F at 1.93, 2 F at 2.27
$[Cu(H_2O)_2(NH_3)_4]$ in $CuSO_4{\cdot}4NH_3{\cdot}H_2O$	4 N at 2.05, 1 O at 2.59, 1 O at 3.37
K_2CuF_4	2 F at 1.95, 4 F at 2.08

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[26] K. G. Caulton *et al., Inorg. Chem.*, 1986, **25,** 2484.

[27] O. Kahn, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 834 (binuclear bridged complexes); M. Melnik, *Coord. Chem. Rev.*, 1982, **47,** 239 (structure and isomerism); B. J. Hathaway, *Struct. Bonding Berlin,* 1984, **57,** 55 (stereochemistry and electronic structures).

[28] M. Magini *et al., Inorg. Chem.*, 1984, **23,** 1184.

distortion is an elongation along one fourfold axis, so that there is a planar array of four short Cu—L bonds and two trans long ones. In the limit, of course, the elongation leads to a situation indistinguishable from square coordination as found in CuO and many discrete complexes of Cu^{II}. Thus the cases of tetragonally distorted octahedral coordination and square coordination cannot be sharply differentiated.

Chloro Complexes. Chloro complexes are formed in aqueous solutions[29] and many salts have been isolated.[30] Salts of stoichiometry M^ICuCl_3 usually contain $[Cu_2Cl_6]^{2-}$ ions and large cations (e.g., Ph_4P^+) to keep the anions well separated; the $[Cu_2Cl_6]^{2-}$ ions are formed by two tetrahedra sharing an edge. For smaller cations, the dimers become linked by long Cu—Cl bonds giving infinite chains with five- or six-coordinate Cu^{II}. The chloro complex $CsCuCl_3$ is unique in forming infinite chains of distorted octahedra sharing opposite triangular faces.

For $[CuCl_4]^{2-}$, theory predicts the flattened tetrahedral (D_{2d}) geometry in $M^I_2[CuCl_4]$ when the cation is very large, thus isolating the anions (Fig. 18-H-1).[31] With smaller cations, linking of $CuCl_4$ units occurs as for $[Cu_2Cl_6]^{2-}$ units just mentioned and a linked two-dimensional layer structure results in which Cu^{II} is in a tetragonally elongated octahedron. The compound $(NH_4)_2CuCl_4$ contains square $[CuCl_4]^{2-}$ ions.

Some compounds with formulas corresponding to $[CuCl_5]^{3-}$ do, in fact, contain such discrete *tbp* anions if the cations are large and tripositive, for example, $[M(NH_3)_6]^{3+}$. However, with smaller cations (e.g., $M^I_3CuCl_5$ of the alkalis) there are discrete $[CuCl_4]^{2-}$ ions of D_{2d} structure together with isolated Cl^- ions.

Other Complexes. In $K_2Pb[Cu(NO_2)_6]$ there is a *regular* octahedron of nitrogen atoms about the Cu^{2+} ion in the room-temperature cubic form.

Distorted tetrahedral species occur and $[Cu(C_6H_{11}NH_2)_4](NO_3)_2$ is actually intermediate between tetrahedral and square.[32] Distorted tetrahedral struc-

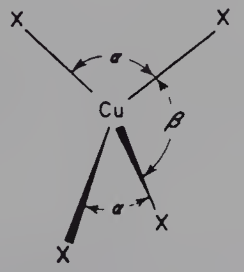

FIG. 18-H-1. Squashed tetrahedral structures of $[CuX_4]^{2-}$ ions in Cs_2CuX_4 salts; $\alpha > \beta$.

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[29] R. W. Ramette, *Inorg. Chem.*, 1986, **25,** 2481.

[30] R. D. Willett *et al., J. Am. Chem. Soc.*, 1986, **108,** 1173; *Inorg. Chem.*, 1987, **26,** 1716, 2235. O. Piovesana *et al., Inorg. Chem.*, 1986, **25,** 2408; E. I. Solomon *et al., Inorg. Chem.*, 1987, **26,** 288.

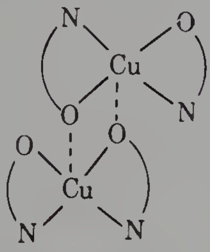
[31] See H. J. Schugar *et al., Inorg. Chem.*, 1987, **26,** 1133.

[32] Y. Jeannin *et al., Inorg. Chem.*, 1984, **23,** 3387.

tures with imidazole, cysteine, methionine, and similar ligands have been greatly studied as models for Cu^{II} in azurin and plastacyanin (Chapter 30).

Similar distorted Cu^{II} is found in some Schiff base complexes with bulky substituents on N and in some dipyrromethane species. With these few exceptions neutral four-coordinate Cu^{II} complexes with chelate ligands have planar coordination.

Variants on this include some cases where additional ligands complete a very elongated octahedron and many where there is dimerization of the type shown schematically in (18-H-XII) for the β form of bis(8-quinolinolato)copper(II), in which each metal atom becomes five-coordinate.



(18-H-XII)

Trigonal bipyramidal coordination[33] is found in other cases, mostly with distortion. Examples are $Cu(terpy)Cl_2$, $[Cu(bipy)_2I]^+$, and $[Cu(phen)_2(H_2O)]^{2+}$.

Spectral and Magnetic Properties. Because of the relatively low symmetry (i.e., less than cubic) of the environments in which the Cu^{2+} ion is characteristically found, detailed interpretations of the spectra and magnetic properties are somewhat complicated, even though one is dealing with the equivalent of a one-electron case. Virtually all complexes and compounds are blue or green. Exceptions are generally caused by strong uv bands—charge-transfer bands—tailing off into the blue end of the visible spectrum, thus causing the substances to appear red or brown. The blue or green colors are due to the presence of an absorption band in the 600 to 900-nm region of the spectrum. The envelopes of these bands are generally unsymmetrical, seeming to encompass several overlapping transitions, but definitive resolution into the proper number of subbands with correct locations is difficult. Only when polarized spectra of single crystals have been measured had this resolution been achieved unambiguously.

The magnetic moments of simple Cu^{II} complexes (those lacking Cu—Cu interactions, described later) are generally in the range 1.75 to 2.20 BM, regardless of stereochemistry and independently of temperature except at extremely low temperatures (<5 K).

Binary Copper(II) Compounds. Black crystalline CuO is obtained by pyrolysis of the nitrate or other oxo salts; above 800°C it decomposes to Cu_2O. The hydroxide is obtained as a blue bulky precipitate on addition of

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[33] R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1984, **23**, 3853.

alkali hydroxide to cupric solutions; warming an aqueous slurry dehydrates this to the oxide. The hydroxide is readily soluble in strong acids and also in concentrated alkali hydroxides, to give deep blue anions, for example, $[Cu(OH)_4]^{2-}$ + $[Cu(OH)_6]^{4-}$.[34a] In aqueous ammonia deep blue $[Cu(NH_3)_{4,5}]^{2+}$ is formed.

Copper(II), and also copper(III), form oxometallate ions of various structural types, but mainly containing linked CuO_4 planar units. Examples are Ba_2CuO_3, Sr_2CuO_3, and $BaCuO_2$. Mixed oxides of stoichiometries of the type $La_{2-x}M^{II}_xCuO_{4-y}$ $x \leq 0.2$, $y \simeq 0$ are now under intense study as high temperature superconducting materials.[34b]

The *halides* are the colorless CuF_2, with a distorted rutile structure, the yellow chloride and the almost black bromide, the last two having structures with infinite parallel bands of square CuX_4 units sharing edges. The bands are arranged so that a tetragonally elongated octahedron is completed about each copper atom by bromine atoms of neighboring chains. Copper dichloride and $CuBr_2$ are readily soluble in water, from which hydrates may be crystallized, and also in donor solvents such as acetone, alcohol, and pyridine.

Salts of Oxo Acids. The most familiar compound is the blue hydrated sulfate $CuSO_4 \cdot 5H_2O$, which contains four water molecules in the plane with O atoms of SO_4 groups occupying the axial positions, and the fifth water molecule hydrogen bonded in the lattice. It may be dehydrated to the virtually white anhydrous substance. The hydrated nitrate cannot be fully dehydrated without decomposition. The anhydrous nitrate is prepared by dissolving the metal in a solution of N_2O_4 in ethyl acetate and crystallizing the salt $Cu(NO_3)_2 \cdot N_2O_4$, which probably has the constitution $[NO^+][Cu(NO_3)_3^-]$. When heated at 90°C this solvate gives the blue $Cu(NO_3)_2$, which can be sublimed without decomposition in a vacuum at 150 to 200°C. There are two forms of the solid, both possessing complex structures in which Cu^{II} ions are linked together by nitrate ions in an infinite array. The vapor has planar molecules with chelated NO_3.

The triflate, $Cu(CF_3SO_3)_2$, is soluble in MeOH, MeCN, and DMF.[35]

Aqueous Chemistry and Complexes of Copper(II). Most Cu^{II} salts dissolve readily in water and give the aqua ion. Addition of ligands to such aqueous solutions leads to the formation of complexes by successive displacement of water molecules. With NH_3, for example, the species $[Cu(NH_3)(H_2O)_5]^{2-}$, . . . , $[Cu(NH_3)_4(H_2O)_2]^{2+}$ are formed in the normal way. Addition of the fifth NH_3 can occur in aqueous solution,[36] but the sixth occurs only in liquid ammonia. The reason for this unusual behavior is connected with the Jahn–Teller effect. Because of it, the Cu^{II} ion does not bind the fifth and sixth ligands strongly (even the H_2O). When this intrinsic weak

[34a] B. N. Ivanov-Emin *et al., Zh. Neorg. Khim.*, 1984, **29**, 1497.

[34b] See J. M. Williams *et al., Inorg. Chem.*, 1987, **26**, 1829.

[35] T. Takei, *Surf. Technol.*, 1984, **22**, 343.

[36] M. Sano *et al., Inorg. Chem.*, 1984, **23**, 4466.

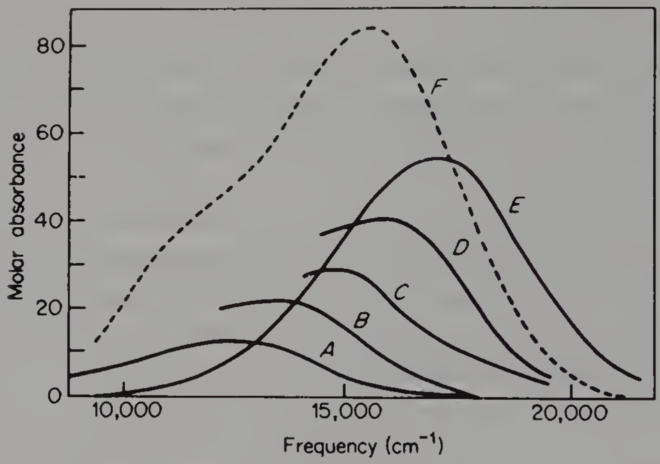
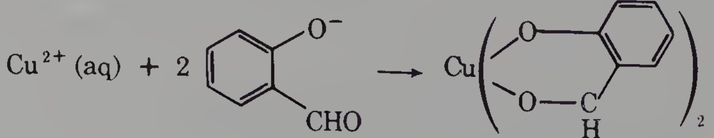


FIG. 18-H-2. Absorption spectra of (*A*) $[Cu(H_2O)_6]^{2+}$ and of the ammines in 2 *M* ammonium nitrate of 25°C: (*B*) $[Cu(NH_3)(H_2O)_5]^{2+}$; (*C*) $[Cu(NH_3)_2(H_2O)_4]^{2+}$; (*D*) $[Cu(NH_3)_3(H_2O)_3]^{2+}$; (*E*) $[Cu(NH_3)_4(H_2O)_2]^{2+}$; and (*F*) $[Cu(NH_3)_5H_2O]^{2+}$.

binding of the fifth and sixth ligands is added to the normally expected decrease in the stepwise formation constants (Section 2-3), the formation constants K_5 and K_6 are very small indeed. Similarly, it is found with ethylenediamine that $[Cuen(H_2O)_4]^{2+}$ and $[Cuen_2(H_2O)_2]^{2+}$ form readily, but $[Cuen_3]^{2+}$ is formed only at extremely high concentrations of en. Many other amine complexes of Cu^{II} are known, and all are much more intensely blue than the aqua ion. This is because the amines produce a stronger ligand field, which causes the absorption band to move from the far red to the middle of the red region of the spectrum. For example, in the aqua ion the absorption maximum is at ~800 nm, whereas in $[Cu(NH_3)_4(H_2O)_2]^{2+}$ it is at ~600 nm, as shown in Fig. 18-H-2. The reversal of the shifts with increasing takeup of ammonia for the fifth ammonia is to be noted, indicating again the weaker bonding of the fifth ammonia molecule.

In halide solutions the equilibrium concentrations of the various possible species depend on the conditions; although $CuCl_5^{3-}$ has only a low formation constant, it is precipitated from solutions by large cations of similar charge (see above).

Many other Cu^{II} complexes may be isolated by treating aqueous solutions with ligands. When the ligands are such as to form neutral, water-insoluble complexes, as in the following equation, the complexes are precipitated and can be purified by recrystallization from organic solvents. The bis(acetylacetonato)copper(II) complex is another example of this type.



Although as noted previously, addition of CN^- normally leads to reduction to CuCN, in the presence of nitrogen donors like 1,10-phenanthroline reduction is inhibited and five-coordinate complexes like $[\mathrm{Cuphen_2(CN)}]^+$ and $[\mathrm{Cuphen_2(CN)_2}]$ are obtained.

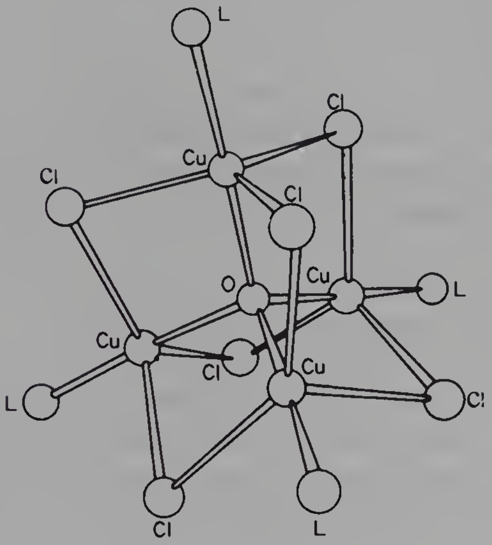
Multidentate ligands that coordinate through oxygen or nitrogen, such as amino acids, form $\mathrm{Cu^{II}}$ complexes, often of considerable complexity.

The well-known blue solutions formed by addition of tartrate to $\mathrm{Cu^{2+}}$ solutions (known as Fehling's solution when basic and when *meso*-tartrate is used) may contain monomeric, dimeric, or polymeric species at different pH values. One of the dimers, $\mathrm{Na_2[Cu\{(\pm)C_4O_6H_2\}]\cdot 5H_2O}$, has square coordinate $\mathrm{Cu^{II}}$, two tartrate bridges, and a Cu—Cu distance of 2.99 Å.

Halide complexes have been noted earlier. The main characteristic is the large number of salts of differing stoichiometries and cation-dependent structures that may be crystallized from solutions.

Cage Polynuclear Copper(II) Complexes. These are less common than for $\mathrm{Cu^I}$. Oxidation of $\mathrm{(CuClPEt_3)_4}$ and similar complexes by oxygen leads to $\mathrm{Cu^{II}}$ complexes of the type $\mathrm{Cu_4OX_6L_4}$, L = $\mathrm{OPEt_3}$, py, $\mathrm{NH_3}$, or $[\mathrm{Cu_4OCl_{10}}]^{4-}$ in chloride media.[37]

The structure (18-H-XIII) has a μ_4-oxygen atom at the center of a $\mathrm{Cu_4}$ tetrahedron; each Cu is bound to a ligand L, and three Cl atoms act as bridges, so that $\mathrm{Cu^{II}}$ is approximately *tbp*. The magnetic properties show strong to weak antiferromagnetism.[38]



(18-H-XIII)

A different type of compound, $\mathrm{Cu_4Cl_4(OR)_4}$, where the alkoxide is 2-diethylaminoethanolate, has a cubane-type structure with a $\mathrm{Cu_4O_4}$ cube and tetrahedral $\mathrm{Cu^{II}}$.

Dimeric or polymeric compounds are also known for alkoxides or aryl

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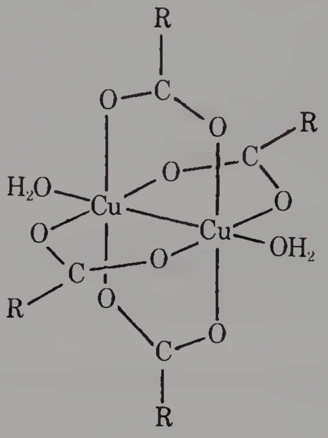
[37] See, for example, G. Davies *et al., Inorg. Chem.*, 1986, **25,** 4479; M. A. El-Sayed *et al., Inorg. Chem.*, 1985, **24,** 3387.

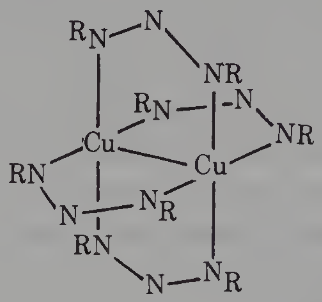
[38] E. Sinn *et al., J. Chem. Soc. Dalton Trans.*, **1980,** 786.

oxides, for example, $[Cu(OPh)_2en]_2{\cdot}2PhOH$, which has distorted *sp* copper.[39]

Copper(II) Carboxylates. These are readily made by interaction of the acid with $CuCO_3$. They are binuclear with four carboxylate bridges and may have end groups as in (18-H-XIV).[40] The 1,3-triazenate (18-H-XV) is similar. In these compounds the Cu—Cu distance varies from ~2.67 to 2.81 Å.[41] There is weak coupling of the unpaired electrons, one on each Cu^{II} ion, giving rise to a singlet ground state with a triplet state lying only a few kilojoules per mole above it; the latter state is thus appreciably populated at normal temperatures and the compounds are paramagnetic. At 25°C μ_{eff} is typically ~1.4 BM/Cu atom and the temperature dependence is very pronounced.



(18-H-XIV)



(18-H-XV)

Binding of a nitroxide radical in $Cu_2(O_2CCCl_3)_4(RNO)_2{\cdot}H_2O$ gives a diamagnetic species with five-coordinate Cu^{II}; only two of the carboxylates are now bridging but a third bridge is provided by OH_2.[42]

Phenomenologically the interaction in the dinuclear acetate and many other compounds with similar temperature dependences of the magnetic moment can be described as antiferromagnetic couplings of the unpaired spins on the adjacent Cu^{II} atoms, without invoking any Cu—Cu bonding.

Attempts to specify this interaction in detail have been plagued by controversy, and there are still differences of opinion. The interaction appears basically to be one between orbitals of δ symmetry, but whether this is primarily a direct interaction between $d_{x^2-y^2}$ orbitals of the two metal atoms or one that is substantially transmitted through the π orbitals of the bridging RCO_2^- groups is not clear.

Mixed Valence Complexes. A number of compounds containing both Cu^I and Cu^{II} are well established. The sulfides, for example, $K_3Cu_8S_6$ made by

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[39] F. Calderazzo *et al., J. Chem. Soc. Dalton Trans.*, **1980**, 1419; R. P. Willet and G. L. Breneman, *Inorg. Chem.*, 1983, **22**, 326.

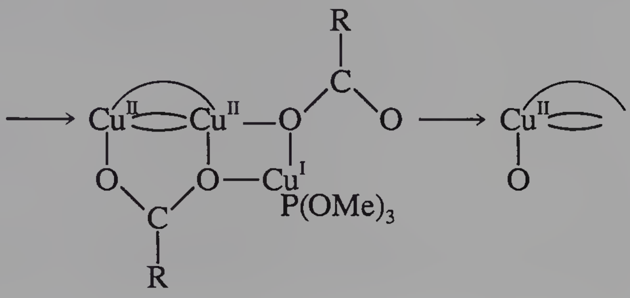
[40] L. P. Battaglia *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 1653; R. D. Harcourt *et al., J. Am. Chem. Soc.*, 1986, **108**, 5403.

[41] H. Manohar *et al., J. Chem. Soc. Dalton Trans.*, **1983**, 2167.

[42] L. C. Porter and R. J. Doedens, *Inorg. Chem.*, 1985, **24**, 1006.

heating K_2CO_3, Cu, and S, may have metal-like electrical conductivities and magnetic properties.[43]

Polymeric species have been formed by interaction of tetrahydrothiophen (L) and $CuCl_2$, which gives $[Cu^{I}_{3}Cu^{II}LCl_5]_n$, while the action of $P(OMe)_3$ on copper carboxylates gives[44a] $Cu_3(CO_2R)_5[P(OMe)_3]_2$ that may have units linked as (18-H-XVI). A similar complex is $Cu_4(\mu\text{-}CO_2Me)_6(PPh_3)_4$.[44b]



(18-H-XVI)

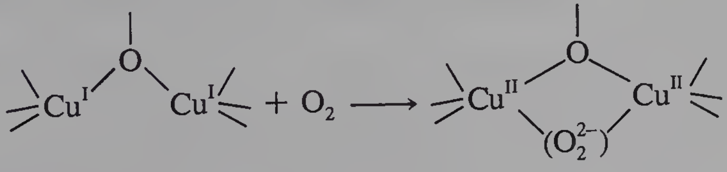
A purple complex of D-penicillamine, $\{Cu^{I}_{8}Cu^{II}_{6}[SCMe_2CH(NH_2)CO_2]_{12}Cl\}^{5-}$ has resemblance to the Cu^{I} thiolates discussed earlier and may be related to copper enzymes (Chapter 30); it has a Cl atom at the center of the Cu^{I}_{8} cage. A similar species is the L-cysteine thiolate Cu^{I}_{2}, $Cu^{II}_{3}[(SCH_2CHCO_2MeNHCH_2)_2]^{2+}_{3}$.[44c]

Copper Catalyzed Oxidations; Peroxo Species. Copper ions and compounds catalyze a varied array of oxidation reactions involving O_2 and copper in hemocyanin (Chapter 30) has an important biological role in binding and transporting O_2.

In some oxidations it seems likely that the actual oxidant is Cu^{II} or possibly the Cu^{III} species and that the function of O_2 is to reoxidize the Cu^{I} so produced.[45a] This is probably the case in the Pd—Cu chloride system for oxidation of ethylene to acetaldehyde (Section 28-20).

However, hydroperoxo peroxo and superoxo complexes can be formed.

1. A Cu^{I} dimer with a binucleating bridging ligand gives a violet Cu^{II} species with O_2 that appears to have an unsymmetrical peroxo bridge[45b]:



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[43] E. Kwiatkowski *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 2319.

[44a] J. A. Connor *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981**, 2119.

[44b] G. Ondrejovič *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 2339.

[44c] D. N. Hendrickson *et al.*, *Inorg. Chem.*, 1986, **25**, 4541.

[45a] G. Davies *et al.*, *Inorg. Chem.*, 1987, **26**, 3266.

[45b] N. J. Blackburn *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 1235; K. D. Karlin *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 2668; *J. Chem. Soc. Chem. Commun.*, **1987**, 599.

Similar oxidation of a Cu^I ethylene tetraethylethylenediamine(teen) complex also gives a blue peroxo species and in this case the reaction is reversible in $MeOH/H_2O$:

$$2[Cu(teen)(C_2H_4)]^+ \underset{C_2H_4}{\overset{O_2}{\rightleftharpoons}} \{[Cu^{II}(teen)(H_2O)]_2\mu\text{-}O_2\}^{2+}$$

Peroxo species with other and more complicated ligands have been observed.[46]

2. Interaction of O_2 with $Cu(C_2H_4)[HB(3,5\text{-}Me_2pz)_3]$ gives a tetrahedral Cu^{II} superoxo complex $Cu(O_2)[HB(3,5\text{-}Me_2pz)_3]$.

Since copper enzymes oxidize phenols and cleave C—C bonds, some simpler systems that do these reactions catalytically in the presence of O_2 have been much studied, for example, CuCl in pyridine–methanol.[47] Oxidized complexes such as $Cu_2Cl_2py_2(OMe)_2$ and $Cu_4OCl_6py_4$ have been isolated.

Oxidation can occur in the absence of O_2, however, in some cases where Cu^{II} is the oxidant.

18-H-4. The Chemistry of Copper(III), d^8 and Copper(IV), d^7

Oxides. Some alkali and alkaline earth compounds (e.g., $NaCuO_2$) obtained by heating the oxides in oxygen contain Cu^{III} and $BaCuO_{2.63}$ and may also contain Cu^{IV}.

Complexes.[48] Until recently only a few Cu^{III} complexes were known, but it now appears that Cu^{III} has an important biological role (Chapter 30), and a number of Cu^{III} complexes of deprotonated peptides and other ligands have been made.

With the exception of K_3CuF_6 all are diamagnetic with square- or five-coordination of Cu^{III}. There are some relatively simple Cu^{III} compounds:

1. Fluorination of KCl + CuCl yields K_3CuF_6 as a pale green solid. This is the only high-spin octahedral Cu^{III} complex.

2. Oxidation of $Cu(S_2CN\mathit{t}\text{-}Bu_2)$ by Br_2 in CS_2 gives violet needles $CuBr_2(S_2CN\mathit{t}\text{-}Bu_2)$.

3. Peroxosulfate oxidation in alkaline solution of the biuret complex of Cu^{II}, K_2Cubi_2 ($biH_2 = H_2NCONHCONH_2$), gives $KCubi_2$ in which Cu^{III} has square coordination.

4. Oxidation by alkaline ClO^- of Cu^{2+} in the presence of iodate and tellurate gives $[Cu(IO_4OH)_2]^{5-}$ and $\{Cu[TeO_4(OH)_2]_2\}^{5-}$.

5. Oxidation of Cu^{2+} in the presence of oxalodihydrazide and acetaldehyde gives a very stable violet anion that has five-coordinate Cu^{III} (18-H-XVII).

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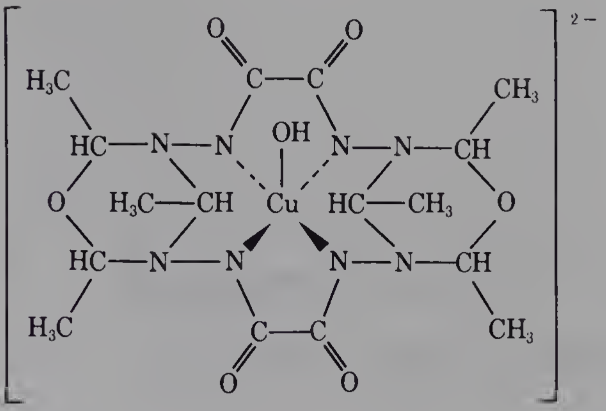
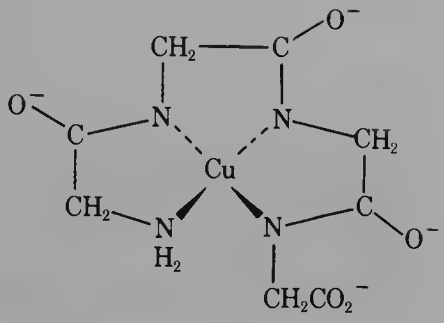
[46] K. D. Karlin *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 6194; S. Bhaduri *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 197.

[47] R. D. Willett and G. L. Breneman, *Inorg. Chem.*, 1983, **22**, 326; G. Speier and Z. Tyeklár, *J. Chem. Soc. Dalton Trans.*, **1983**, 1995.

[48] W. Levason and M. D. Spicer, *Coord. Chem. Rev.*, 1987, **76**, 45.



(18-H-XVII)



(18-H-XVIII)

A variety of deprotonated peptide complexes of Cu^{III} are reasonably stable in alkaline solution. The Cu^{III}–Cu^{II} potentials are very sensitive to the nature of the ligand and vary from 0.45 to 1.02 V; for example, for the tetraglycine (GH_4) complex (18-H-XVIII).

$$[Cu^{III}H_{-3}G]^{-} + e = [Cu^{II}H_{-3}G]^{2-} \qquad E^0 = +0.631 \text{ V}$$

A cationic Cu^{III} complex that is stable in acid solution has been made by electrolysis; it has a deprotonated diglycylethylenediamine-($NH_2CH_2CONHCH_2CH_2NHCOCH_2NH_2$,) as ligand.

Copper(III) also occurs in N_4-macrocyclic complexes where the Cu^{II}/Cu^{III} potential depends on the ring size, and also in tetradentate Schiff base complexes.[49]

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[49] L. Fabbrizzi *et al.*, *Inorg. Chem.*, 1984, **23,** 2917; C. A. McAuliffe *et al.*, *Inorg. Chim. Acta,* 1985, **99,** 103.

Chapter Nineteen

The Elements of the Second and Third Transition Series

GENERAL COMPARISONS WITH THE FIRST TRANSITION SERIES

In general, the second and the third transition series elements of a given group have similar chemical properties but both show pronounced differences from their light congeners. A few examples will illustrate this generalization. Although Co^{II} forms a considerable number of tetrahedral and octahedral complexes and is the characteristic state in ordinary aqueous chemistry, Rh^{II} occurs only in a few complexes and Ir^{II} is virtually unknown. Similarly, the Mn^{2+} ion is very stable, but for Tc and Re the II oxidation state is known only in a few complexes. Chromium III forms an enormous number of cationic amine complexes, whereas Mo^{III} and W^{III} form only a few such complexes, none of which is especially stable. Again, Cr^{VI} species are powerful oxidizing agents, whereas Mo^{VI} and W^{VI} are quite stable and give rise to an extensive series of polynuclear oxo anions.

This is not to say that there is no valid analogy between the chemistry of the three series of transition elements. For example, the chemistry of Rh^{III} complexes is in general similar to that of Co^{III} complexes, and here, as elsewhere, the ligand field bands in the spectra of complexes in corresponding oxidation states are similar. On the whole, however, there are certain consistent differences of which the above-mentioned comparisons are only a few among many obvious manifestations.

Some important features of the elements and comparison of these with the corresponding features of the first series are the following:

1. *Radii.* The filling of the 4*f* orbitals through the lanthanide elements causes a steady contraction, called the *lanthanide contraction* (Section 20-1), in atomic and ionic sizes. Thus the expected size increases of elements of the third transition series relative to those of the second transition series, due to an increased number of electrons and the higher principal quantum numbers of the outer ones, are almost exactly offset, and there is in general much less difference in atomic and ionic sizes between the two heavy atoms of a group, whereas the corresponding atom and ions of the first transition series are significantly smaller. Recent studies have shown that relativistic effects in the

third transition series also have a significant effect on radii, ionization energies, and other properties.[1]

2. *Oxidation States.* For the heavier transition elements, higher oxidation states are in general much more stable than for the elements of the first series. Thus the elements Mo, W, Tc, and Re form oxo anions in high valence states which are not especially easily reduced, whereas the analogous compounds of the first transition series elements, when they exist, are strong oxidizing agents. Indeed, the heavier elements form many compounds such as RuO_4, WCl_6, and PtF_6 that have no analogues among the lighter ones. At the same time, the chemistry of complexes and aquo ions of the lower valence states, especially II and III, which plays such a large part for the lighter elements, is of relatively little importance for most of the heavier ones.

3. *Aqueous Chemistry.* Aqua ions of low and medium valence states are not in general well defined or important for any of the heavier transition elements, and some, such as Zr, Hf, and Re, do not seem to form any simple cationic complexes. For most of them anionic oxo and halo complexes play a major role in their aqueous chemistry although some, such as Ru, Rh, Pd, and Pt, do form important cationic complexes as well.

4. *Metal–Metal Bonding.* In general, although not invariably, the heavier transition elements are more prone to form strong M—M bonds than are their congeners in the first transition series. The main exceptions to this are the polynuclear metal carbonyl compounds and some related ones, where analogous or similar structures are found for all three elements of a given family. Aside from these, however, it is common to find that the first series metal will form few or no M—M bonded species, whereas the heavier congeners form an extensive series. Examples are the $M_6X_{12}^{n+}$ species formed by Nb and Ta, with no V analogues at all, the Mo_3^{IV} and W_3^{IV} oxo clusters for which no chromium analogues exist, and the $Te_2Cl_8^{3-}$ and $Re_2Cl_8^{2-}$ ions, which have no manganese analogues.

5. *Magnetic Properties.* In general, the heavier elements have magnetic properties that are less useful to the chemist than was the case in the first transition series. For one thing there is a much greater tendency to form low-spin complexes, which means that those with an even number of electrons are usually diamagnetic and therefore lack informative magnetic characteristics. The paramagnetic complexes usually have complicated behavior in which magnetic moments differ considerably from spin-only values and often vary markedly with temperature (Section 17-4).

19-A. ZIRCONIUM AND HAFNIUM: GROUP IVB(4)

The chemistries of zirconium and hafnium are more nearly identical than for any other two congeneric elements. This is due in considerable measure to the effect of the lanthanide contraction having made both the atomic and

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[1] D. R. McKelvey, *J. Chem. Educ.*, 1983, **60**, 112.

TABLE 19-A-1
Oxidation States and Stereochemistry of Zirconium and Hafnium

Oxidation state	Coordination number	Geometry	Examples
Zr^0, Hf^0	6	Octahedral	$[Zr(bipy)_3]$, $Zr(C_4H_6)_2$dmpe, $(arene)_2HfPMe_3$
Zr^I, Hf^I, d^3 Zr^{II}, d^2		Complex sheet and cluster structures; see text	
Zr^{II}, Hf^{II}	8		$*Cp_2M(CO)_2$, $CpZrCl(dmpe)_2$
Zr^{III}, Hf^{III}, d^1	6	Octahedral	$ZrCl_3$, $ZrBr_3$, ZrI_3, HfI_3
Zr^{IV}, Hf^{IV}, d^0	4	Tetrahedral	$ZrCl_4(g)$, $Zr(CH_2C_6H_5)_4$
	6	Octahedral	Li_2ZrF_6, $Zr(acac)_2Cl_2$, $ZrCl_6^{2-}$, $ZrCl_4(s)$
	7	Pentagonal bipyramidal	Na_3ZrF_7, Na_3HfF_7, $K_2CuZr_2F_{12}\cdot 6H_2O$
		Capped trigonal prism	$(NH_4)_3ZrF_7$
		See text, (Fig. 19-A-2)	ZrO_2, HfO_2(monoclinic)
	8	Square antiprism	$Zr(acac)_4$, $Zr(SO_4)_2\cdot 4H_2O$
		Dodecahedral	$[Zr(C_2O_4)_4]^{4-}$, $[ZrX_4(diars)_2]$, $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$

ionic radii (1.45 and 0.86 Å for Zr and Zr^{4+}; 1.44 and 0.85 Å for Hf and Hf^{4+}) essentially identical.

The oxidation states and stereochemistries are summarized in Table 19-A-1.

These elements, because of the larger atoms and ions, differ from Ti in having more basic oxides, having somewhat more extensive aqueous chemistry, and more commonly attaining higher coordination numbers, 7 and 8. They have a more limited chemistry of the III oxidation state.

19-A-1. The Elements

Zirconium occurs widely over the earth's crust but not in very concentrated deposits. The major minerals are *baddeleyite,* a form of ZrO_2, and *zircon* ($ZrSiO_4$). The chemical similarity of Zr and Hf is well exemplified in their geochemistry, for Hf is found in Nature in all zirconium minerals in the range of fractions of a percentage of the Zr content. Separation of the two elements is extremely difficult, even more so than for adjacent lanthanides, but it can now be accomplished satisfactorily by ion-exchange, solvent-extraction, or electrochemical[1] methods.

Zirconium metal (mp 1855°C ± 15°C), like titanium, is hard and corrosion resistant, resembling stainless steel in appearance. It is made by the Kroll process (Section 18-A-1). Hafnium metal (mp 2222°C ± 30°C) is similar. Like titanium, these metals are fairly resistant to acids, and they are best dissolved

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[1] G. Mamantov *et al., Inorg. Chem.,* 1982, **21,** 3569.

in HF where the formation of anionic fluoro complexes is important in the stabilization of the solutions. Zirconium will burn in air at high temperatures, reacting more rapidly with nitrogen than with oxygen, to give a mixture of nitride, oxide, and oxide nitride (Zr_2ON_2).

19-A-2. Compounds of Zirconium(IV) and Hafnium(IV)

Halides. The tetrahalides MCl_4, MBr_4, and MI_4 are all tetrahedral monomers in the gas phase, but the solids are polymers with halide bridging. Zirconium tetrachloride, a white solid subliming at 331°C, has the structure shown in Fig. 19-A-1 with zigzag chains of $ZrCl_6$ octahedra; $ZrBr_4$, $HfCl_4$, and $HfBr_4$ are known to be isotypic. Zirconium tetrachloride resembles $TiCl_4$ in its chemical properties. It may be prepared by chlorination of heated zirconium, zirconium carbide, or a mixture of ZrO_2 and charcoal; it fumes in moist air, and it is hydrolyzed vigorously by water. Hydrolysis proceeds only part way at room temperature, affording the stable oxide chloride

$$ZrCl_4 + 9H_2O \longrightarrow ZrOCl_2{\cdot}8H_2O + 2HCl$$

Zirconium tetrabromide and ZrI_4 are similar to $ZrCl_4$. Zirconium tetrafluoride is a white crystalline solid subliming at 903°C; unlike the other halides, it is insoluble in donor solvents; it has an eight-coordinate structure with square antiprisms joined by sharing fluorines. Hydrated fluorides $ZrF_4{\cdot}1$ or $3H_2O$, can be crystallized from $HF–HNO_3$ solutions. The trihydrate has an eight-coordinate structure with two bridging fluorides, $(H_2O)_3F_3ZrF_2ZrF_3(H_2O)_3$. The hafnium hydrate has the same stoichiometry but a different structure with chains of $HfF_4(H_2O)$ units linked through four bridging fluorine atoms.

Hexahalozirconates(IV) and hafnates(IV) are known for F^-, Cl^-, Br^-, and, recently, also for I^-.[2] None of these MX_6^{2-} ions are very resistent to hydrolysis and the iodide species are best obtained by reaction of CsI and MI_4 in a sealed tube.

Zirconium tetrachloride, $HfCl_4$, and some of the other halides also combine with neutral donors to form adducts of varied stereochemistry. In many cases the structures appear to be, or are known to be, octahedral,[3] typically *trans*-MX_4L_2 or *cis*-$MX_4(LL)$. However, $ZrCl_4$ also combines with 2 mol of certain

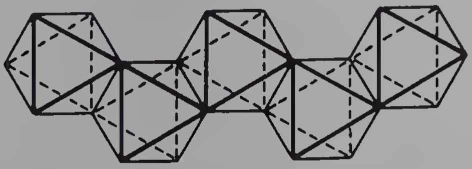

FIG. 19-A-1. The zigzag $ZrCl_6$ chains in $ZrCl_4$.

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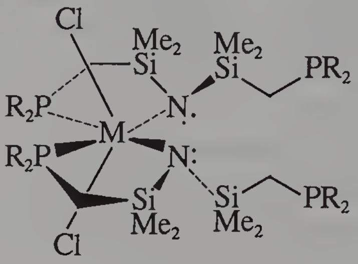
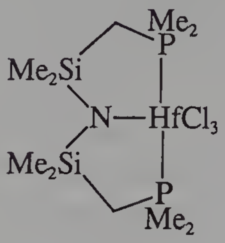
[2] D. Sinram *et al.*, *Inorg. Chim. Acta,* 1982, **64,** L131.

[3] D. Gordon and M. G. H. Wallbridge, *Inorg. Chim. Acta,* 1986, **111,** 77.

chelating bidentate ligands to form $ZrCl_4(LL)_2$ complexes that are usually of dodecahedral structure [e.g., for LL = diars or $MeSCH_2CH_2SMe$] but which can be strongly distorted toward square antiprismatic with ligands that are not compatible with the dodecahedral arrangement.[4] The halides also react with anionic polydentate ligands to give products in which there is partial or even complete replacement of halide ions. For example, the ligands $[N(SiMe_2CH_2PR_2)_2]^-$ react with $ZrCl_4$ or $HfCl_4$ to give, depending on preparative procedures, complexes of the types (19-A-I) or (19-A-II).[5] The ligand $\{NCC[C(O)CH_3]_2\}^-$ replaces two, three, or all Cl atoms of $ZrCl_4$ to give complexes of uncertain structure but probably with coordination numbers exceeding six.[6]


(19-A-I)


(19-A-II)

Zirconium Oxide and Mixed Oxides. Addition of hydroxide to zirconium(IV) solutions causes the precipitation of white gelatinous $ZrO_2 \cdot nH_2O$, where the water content is variable; no true hydroxide exists. On strong heating, this hydrous oxide gives hard, white, insoluble ZrO_2. This has an extremely high melting point (2700°C), exceptional resistance to attack by both acids and alkalis, and good mechanical properties; it is used for crucibles and furnace cores. Zirconium dioxide in its monoclinic (baddeleyite) form and one form of HfO_2 are isomorphous and have a structure in which the metal atoms are seven-coordinate, as shown in Fig. 19-A-2. Three other forms of ZrO_2 have been described, but none has the rutile structure so often found among MO_2 compounds.

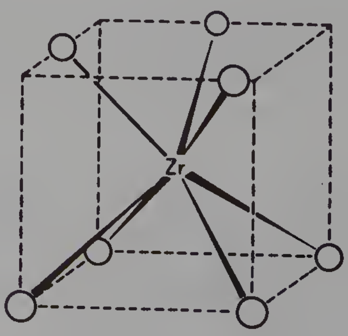


FIG. 19-A-2. Coordination geometry in the baddeleyite form of ZrO_2.

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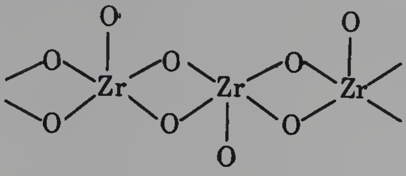
[4] R. B. von Dreele *et al.*, *Inorg. Chem.*, 1984, **23,** 4302.

[5] M. D. Fryzuk *et al.*, *Inorg. Chem.*, 1983, **22,** 863; 1985, **24,** 642.

[6] G. A. Lock and D. W. Thompson, *J. Chem. Soc. Dalton Trans.*, **1980,** 1265.

A number of compounds called "zirconates" may be made by combining oxides, hydroxides, nitrates, and so on, of other metals with similar zirconium compounds and firing the mixtures at 1000 to 2500°C. These, like their titanium analogue, are mixed metal oxides; there are no discrete zirconate ions known. The zirconate $CaZrO_3$ is isomorphous with perovskite. By dissolving ZrO_2 in molten KOH and evaporating off the excess of solvent at 1050°C, the crystalline compounds $K_2Zr_2O_5$ and K_2ZrO_3 may be obtained. The former contains ZrO_6 octahedra sharing faces to form chains that in turn, share edges and corners with other chains. The latter contains infinite chains of ZrO_5 square pyramids (19-A-III).



(19-A-III)

The other chalcogenides, ZrY_2 and HfY_2 (Y = S, Se, and Te) have layered structures and are intrinsic semiconductors. They can also form intercalation compounds, generally similar to those formed by other such layered chalcogenides.

Aqueous Chemistry. This is not very extensive because even a large +4 ion tends strongly to be hydrolyzed. At very low concentration ($\sim 10^{-4}$ *M*) and high acidity ($[H^+]$ of 1–2 *M*) the $Zr^{4+}(aq)$ ion appears to exist. No ZrO^{2+} ion has been detected convincingly. Instead, there seems to be a more or less direct conversion of $Zr^{4+}(aq)$ to the tetranuclear $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ ion as Zr(IV) concentration increases and/or $[H^+]$ decreases; the kinetics of the reverse process have been studied.[7] From dilute HX solutions compounds of composition $ZrOX_2 \cdot 8H_2O$ for X = Cl, Br, and I can be crystallized and they contain the tetranuclear ion, whose structure is shown in Fig. 19-A-3. A tetranuclear peroxo complex of Zr^{IV} has been shown to exist to which the formula $[Zr_4(O_2)_2(OH)_4]^{8+}$ has been tentatively assigned.[8] ZrO_2 is more basic than TiO_2 and is virtually insoluble in excess base.

Both zirconium and hafnium form many other basic salts, such as sulfates

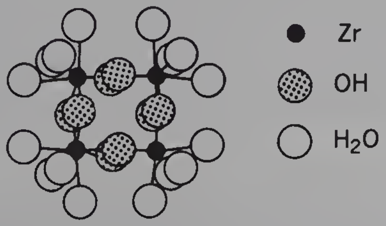


FIG. 19-A-3. The structure (schematic) of the $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ ion.

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[7] D. H. Devia and A. G. Sykes, *Inorg. Chem.*, 1981, **20**, 910.

[8] R. C. Thompson, *Inorg. Chem.*, 1985, **25**, 3542.

and chromates, in which there are infinite chains of composition $[M(\mu\text{-}OH)_2]_n^{2n+}$. In addition to the bridging OH groups, the metal ions are coordinated by oxygen atoms of the anions and achieve coordination numbers of 7 or 8, with geometries of pentagonal bipyramid and square antiprism, respectively.

Other Complexes and Compounds. The Zr^{4+} ion is relatively large, highly charged, and spherical, with no partly filled shell to give it stereochemical preferences. Thus it is not surprising that zirconium(IV) compounds exhibit high coordination numbers and a great variety of coordination polyhedra. This is well illustrated by the fluoro complexes. Compounds containing (*a*) octahedral ZrF_6^{2-} ions, (*b*) ZrF_7^{3-} ions with both pentagonal bipyramidal and capped trigonal prismatic structures, (*c*) $Zr_2F_{12}^{4-}$ ions formed by edge-sharing pentagonal bipyramids, (*d*) square antiprismatic ZrF_8^{4-} ions, (*e*) $Zr_2F_{14}^{6-}$ ions formed by edge-sharing square antiprisms, and (*f*) still other structures, are known.

While the coordination chemistry is not highly developed it shows considerable variety. There are acetylacetonates of the six-coordinate $M(acac)_2X_2$ and seven-coordinate $M(acac)_3X$ types, as well as eight-coordinate $M(dik)_4$ and $M(sacsac)_4$.[9] Six-coordinate pyrazolylborate complexes, $RB(pz)_3ZrCl_3$ are also known,[10] and an anionic, six-coordinate complex, $[Zr(LL)_3]^-$, $LL = Ph_2Si(O)OSi(O)Ph_2^-$ has been structurally characterized.[11]

Some seemingly simple zirconium salts are best regarded as essentially covalent molecules or as complexes; examples are the carboxylates $Zr(OCOR)_4$, the tetrakis(acetylacetonate), the oxalate, and the nitrate. Like its Ti analogue, the last of these is made by heating the initial solid adduct of N_2O_5 and N_2O_4 obtained in the reaction

$$ZrCl_4 + (4+x+y)N_2O_5 \xrightarrow{30°C} Zr(NO_3)_4 \cdot xN_2O_5 \cdot yN_2O_4 + 4NO_2Cl$$

It forms colorless sublimable crystals, and ir and Raman spectra suggest that the molecule is isostructural with $Ti(NO_3)_4$ and $Sn(NO_3)_4$. It is soluble in water but insoluble in toluene, whose ring it nitrates. Hafnium gives only $Hf(NO_3)_4 \cdot N_2O_5$. Nitrato complexes $M(NO_3)_6^{2-}$ are also known but not structurally characterized.

Some other complexes include the tetrahedral $Zr(H_3BH)_4$ and $Zr(H_3BMe)_4$ molecular species in which 12 hydrogen atoms are in contact with the metal atom,[12] mono- and dithiocarbamate complexes, $Zr(OSCNR_2)_4$ and $Zr(S_2CNR_2)_4$, which have dodecahedral structures, tetrahedral $MCl[N(SiMe_3)_2]_3$ compounds,[13] a porphyrin complex, $Zr(TPP)Cl_2$,[14] and some alkoxo molecules,[15]

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[9] R. C. Fay *et al.*, *Inorg. Chem.*, 1982, **21**, 3765.

[10] D. L. Reger and M. E. Tarquini, *Inorg. Chem.*, 1982, **21**, 840.

[11] M. A. Hossain and M. B. Hursthouse, *Inorg. Chim. Acta*, 1980, **44**, L259.

[12] N. M. Edelstein *et al.*, *Inorg. Chem.*, 1983, **22**, 2351.

[13] D. C. Bradley *et al.*, *J. Chem. Soc. Dalton Trans.*, **1980**, 2010.

[14] B. D. Berezin and T. N. Lomova, *Russ. J. Inorg. Chem.*, 1981, **26**, 203.

[15] I. P. Rothwell *et al.*, *Inorg. Chem.*, 1985, **24**, 995, 4569.

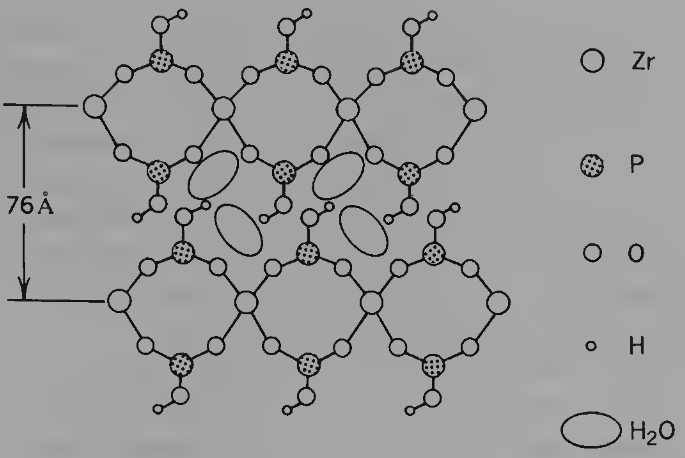

FIG. 19-A-4. A schematic representation of the layer structure of α-$Zr(HPO_4)_2{\cdot}H_2O$.

$Zr(OR)_4$ and $ZrCl(OR)_3$, which remain monomeric because of the steric bulk of R, which is a 2,6-disubstituted phenyl group.

α-Zirconium phosphate, $Zr(HPO_4)_2{\cdot}H_2O$, has a layer structure,[16] shown in Fig. 19-A-4. The spaces between the sheets, where the H_2O molecules and P—OH groups are, allow for ion-exchange activity, whereby some or all of the hydrogen ions as well as the H_2O molecules can be displaced by metal cations.[17] β-Zirconium phosphate, $Zr(HPO_4)_2{\cdot}2H_2O$, has a similar structure and similar properties. When certain transition metal cations have been introduced catalytic properties are developed.[18] It is also possible to modify these zirconium phosphates by replacing some HPO_4^{2-} groups by $ROPO_3^{2-}$ or $HAsO_4^{2-}$ ions.[19]

19-A-3. Oxidation State III

There is no aqueous or other conventional solution chemistry known. The best known compounds are the trihalides $ZrCl_3$, $ZrBr_3$, and ZrI_3, which have a structure consisting of close-packed halide layers between which equally spaced zirconium (or hafnium) atoms occupy one-third of the octahedral interstices, to form infinite linear chains of metal atoms, perpendicular to the layers. In terms of coordination polyhedra the structure may be described as infinite parallel chains of MX_6 octahedra sharing opposite faces. There are various synthetic methods, such as reduction of ZrX_4 with Al or Zr in molten AlX_3. In this process the HfX_4 compounds are reduced more slowly (10 times for the chloride), thus allowing separation of Zr from contaminating Hf.[1]

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[16] P. R. Rudolf and A. Clearfield, *Inorg. Chem.*, 1985, **24**, 3714.

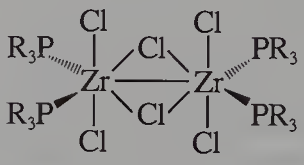
[17] A. A. G. Tomlinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981**, 2376; J. W. Johnson, *J. Chem. Soc. Chem. Commun.*, **1980**, 263; J. P. Gupta and D. V. Nowell, *J. Chem. Soc. Dalton Trans.*, **1981**, 385.

[18] A. Clearfield *et al.*, *Appl. Catal.*, 1986, **26**, 1, 91; M. Iwamoto *et al.*, *J. Catal.*, 1981, **69**, 234.

[19] S. Yamanaka and M. Hattori, *Inorg. Chem.*, 1981, **20**, 1929; A. La Ginestera *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 1737.

The trihalides can also be synthesized by reactions of ZrX_4 with ZrX in sealed systems at temperatures of 435 to 600°C. It is found that they are nonstoichiometric phases rather than distinct compounds. Their ranges of phase stability (i.e., values of x in ZrX_x) are for Cl, 2.94 to 3.03; for Br, 2.87 to 3.23; for I, 2.83 to 3.43. The color of each phase varies markedly over its composition range (e.g., from olive green to bluish black for $ZrBr_x$). For the HfI_3 phase a composition as high as $HfI_{3.5}$ can be obtained. Whether these "off-stoichiometric" compositions involve replacements of the type $4M^{III} \rightarrow 3M^{IV} + [\ \ ]$ or some other variation is not known.

The coordination chemistry is very limited. There are a few poorly characterized amine complexes. The only well-characterized compound is $Zr_2Cl_6(PBu_3)_4$ (which has PEt_3 and PPr_3 homologues); it has the structure (19-A-IV) and since it is diamagnetic with a Zr—Zr distance of 3.182 Å, the existence of a Zr—Zr single bond may be assumed.[20]



(19-A-IV)

Perhaps related to the tendency of the trihalides to be nonstoichiometric is the existence of a novel solid that is formed by a $ZrCl_4/Zr/AlCl_3$ mixture of ~200°C. It consists of "chicken wire" layers of $Zr_xCl_{3x}^{n+}$ where $0 < n < 1$. In other words the mean oxidation state of Zr is between III and IV. Rather large holes in this layer structure are occupied by Al and Cl atoms giving a composition approximating to $Zr_{12}Al_4Cl_5$, but these "interstitial" atoms of Al and Cl were not clearly defined in the structure.[21]

19-A-4. Oxidation States Below III

Our detailed knowledge of this chemistry is almost entirely due to the work of J. D. Corbett and his co-workers.[22]

Zirconium(I). The compounds ZrCl and ZrBr (which have hafnium analogues) are obtained by reactions of MX_4 with M at 800 to 850°C. The structures consist of stacked, hexagonally packed layers of either all metal atoms or all X atoms, with a stacking sequence ---XMMX---XMMX---. There are two slightly different stacking patterns. The X---X interlayer distances (e.g., ~3.60 Å for chlorides) are normal van der Waals contacts, and the M—X distances (e.g., 2.63 Å in ZrCl) are appropriate for single bonds. Within the adjacent metal atom layers there are two sets of distances. Within one layer Zr—Zr distances are 3.42 Å, and between layers they are 3.09 Å;

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[20] R. R. Schrock *et al.*, *Inorg. Chem.*, 1981, **20**, 1844.
[21] E. M. Larsen *et al.*, *Inorg. Chem.*, 1980, **19**, 3172.
[22] J. D. Corbett, *Acc. Chem. Res.*, 1981, **14**, 239.

these may be compared to an average distance of 3.20 Å in α-Zr. The monohalides have great thermal stability (mp > 1100°C) and metallic character; they cleave like graphite. A compound of composition Hf_2S also appears to have a structure with double layers of metal atoms.

Both ZrCl and ZrBr react with hydrogen,[23] oxygen, or zirconium dioxide[24] to form phases in which H or O atoms have been introduced within the double layer of metal atoms. With hydrogen compositions of $ZrXH_{0.5}$ and ZrXH are well defined, while with oxygen there is a greater tendency to nonstoichiometry, $ZrXO_{0.43}$ and $ZrBrO_{0.23}$ being typical compositions that have been studied. It may be noted that nonstoichiometric ZrH_x ($x < 2$) and ZrO_y ($y < 1$) are also known.

Zirconium(II) Halides. Three of these, $ZrCl_2$, $ZrBr_2$, and ZrI_2, are known and well characterized.[25] They can be made by the reactions of ZrX_4 with Zr at high temperatures in sealed tantalum containers. The chloride and bromide can also be obtained by disproportionation of the ZrXH phases to ZrX_2 + ZrH_2, at ~700°C.[26] Zirconium diiodide has three polymorphs, in two of which (α and β) there are infinite, planar, zigzag chains of Zr atoms (Zr—Zr = 3.185 Å) lying between sheets of iodine atoms. In γ-ZrI_2, as well as $ZrCl_2$ and $ZrBr_2$, there is a layer structure, similar to that in the molybdenite variety of MoS_2, with the Zr atoms grouped to form trigonal antiprisms (only slightly distorted from being octahedra), very similar to the M_6X_{12} units formed by niobium and tantalum (Section 19-B-8). The Zr—Zr distances in these clusters are ~3.20 Å and each edge is bridged by a halogen atom. There are 12 electrons available for bonding within the cluster, making the formal Zr—Zr bond order 0.5.

By carrying out preparations in the presence of alkali metal halides, structurally related compounds such as $Zr_6Cl_{12}\cdot K_2ZrCl_6$ and $CsZr_6I_{14}$ can be obtained, in which the Zr_6X_{12} units are interspersed with additional cations and anions. Another interesting development is the preparation of Zr_6X_{12} (X = Cl, Br, and I) compounds in which Be, B, Al, C, Si, or N atoms lie within the Zr_6 cluster and supply additional electrons which strengthen the bonding.[27,28] An example, the $(Zr_6I_{12}Si)I_6$ unit in the compound $Cs_{0.3}Zr_6I_{14}Si$ is shown in Fig. 19-A-5.

Apart from organometallic compounds there are a few compounds of zerovalent zirconium. The reduction of $ZrCl_4$ with lithium in the presence of bipyridine in THF gives the violet $Zr(dipy)_4$ where, doubtless there is considerable delocalization of electrons over the ligands. The reaction of KCN or RbCN with $ZrCl_3$ in liquid ammonia is reported to give $M^I_5Zr(CN)_5$.

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[23] J. D. Corbett and H. S. Marek, *Inorg. Chem.*, 1983, **22,** 3194.

[24] L. M. Seaverson and J. D. Corbett, *Inorg. Chem.*, 1983, **22,** 3202.

[25] J. D. Corbett and D. H. Guthrie, *Inorg. Chem.*, 1982, **21,** 1747, 3290; J. D. Corbett *et al.*, *Inorg. Chem.*, 1979, **18,** 836.

[26] J. D. Corbett *et al.*, *Inorg. Chem.*, 1981, **20,** 145.

[27] R. P. Ziebarth and J. D. Corbett, *J. Am. Chem. Soc.*, 1985, **107,** 4571.

[28] J. D. Smith and J. E. Corbett, *J. Am. Chem. Soc.*, 1986, **108,** 1927.

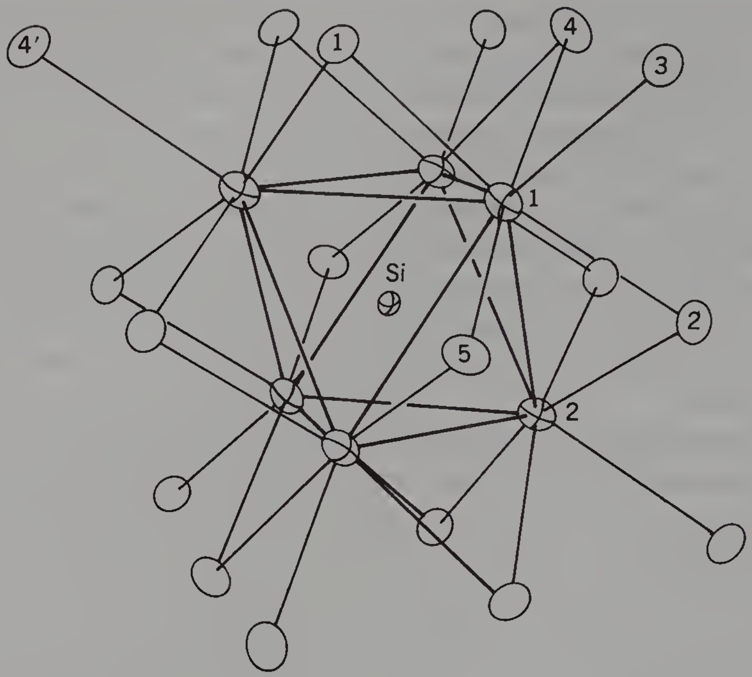

FIG. 19-A-5. The $(Zr_6I_{12}Si)I_6$ cluster in $Cs_{0.3}Zr_6I_{14}Si$. Crossed ellipsoids interconnected by heavy lines represent zirconium while open figures are iodine. (Reproduced by permission from ref. 28.)

19-A-5. Organometallic Compounds

Organozirconium and organohafnium chemistry resemble organotitanium chemistry (Section 18-A-5). There are some stable MR_4 compounds with β-elimination stabilized alkyls such as $PhCH_2$, but the most extensive and important chemistry in both the IV and II states involves $(C_5H_5)_2M$ and $(Me_5C_5)_2M$ groups. The M^{IV} compounds[29a] are of the Cp_2MXY type, where X and Y may be R, Ar, Cl, Br, H, and others such as Cp_2ZrMe^+. There are relatively few $CpMX_3$ compounds[29b] or Cp_3MX compounds; the Cp_4M molecules are also known, in which one (or two) of the Cp rings are monohapto. In all cases the four ligands provide an approximately tetrahedral array about the metal atom. Examples of M^{II} compounds[30] are $CpZrCl(dmpe)_2$, $Cp_2Zr(alkyne)$ and $Li_2[Zr(CH_2Ph)_4]$.

In the reactions of CO with Zr and Hf compounds[31] the oxophilicity of these elements is important, because it leads to the formation of a variety of compounds that have M—O bonds.

[29a] see A. Antiñolo *et al., J. Chem. Soc. Dalton Trans.*, **1987**, 1463; R. F. Jordan *et al., J. Am. Chem. Soc.*, 1987, **109**, 4111.

[29b] G. Erker *et al., Inorg. Chem.*, 1982, **21**, 1277.

[30] S. Gambarolta and M. Y. Chiang, *J. Chem. Soc. Chem. Commun.*, **1987**, 698; S. L. Buchwald *et al., J. Am. Chem. Soc.*, 1987, **109**, 2544; A. Kruger and K. H. Thiele, *Z. Anorg. Allg. Chem.*, 1986, **532**, 53.

[31] G. Erker, *Acc. Chem. Res.*, 1984, **17**, 103.

An important use of Cp_2ZrHCl is in the so-called hydrozirconation reaction with alkenes which generates a Zr-alkyl group which can then be converted to alcohols or other products.[32]

General References

Cardin, D. J., M. F. Lappert, and C. L. Raston, *Chemistry of Organo-Zirconium and -Hafnium Compounds,* Horwood, Chichester, 1986.

Fay, R. C., *Coord. Chem. Rev.,* 1981, **37,** 41; 1982, **45,** 41; 1983, **52,** 285.

19-B. NIOBIUM AND TANTALUM: GROUP VB(5)

These two elements have very similar chemistries, though not so nearly identical as in the case of zirconium and hafnium. They have very little cationic behavior, but they form many complexes in oxidation states II, III, IV, and V. In oxidation states II and III M—M bonds are fairly common and in addition there are numerous compounds in lower oxidation states where metal atom clusters exist. An overview of oxidation states and stereochemistry (excluding the cluster compounds) is presented in Table 19-B-1. In discussing these elements it will be convenient to discuss some aspects (e.g., oxygen compounds, halides, and clusters) as classes without regard to oxidation state, while the complexes are more conveniently treated according to oxidation state.

The elements themselves require little comment. Niobium is 10 to 12 times more abundant in the earth's crust than tantalum. The main commercial sources of both are the *columbite–tantalite* series of minerals, which have the general composition $(Fe/Mn)(Nb/Ta)_2O_6$, with the ratios Fe/Mn and Nb/Ta continuously variable. Niobium is also obtained from *pyrochlore,* a mixed calcium–sodium niobate. Separation and production of the metals is complex. Both metals are bright, high melting (Nb, 2468°C; Ta, 2996°C), and very resistant to acids. They can be dissolved with vigor in an HNO_3–HF mixture, and very slowly in fused alkalis.

19-B-1. Oxygen Compounds

The oxides are numerous and structurally elaborate. Both Nb_2O_5 and Ta_2O_5 are relatively inert white solids. Concentrated HF is the only acid that attacks them, but they can be dissolved by fusion with an alkali hydrogen sulfate, carbonate, or hydroxide. They are obtained by roasting the hydrous oxides (so-called niobic and tantalic acids) or other compounds in excess oxygen. The hydrous oxides themselves are gelatinous white precipitates of variable water content obtained on neutralizing acid solutions of Nb^V and Ta^V halides.

Both of the pentoxides, but especially Nb_2O_5, have complex structural

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[32] T. Gibson, *Organometallics,* 1987, **6,** 918.

TABLE 19-B-1
Oxidation States and Stereochemistries of Niobium and Tantalum

Oxidation state	Coordination number	Geometry	Examples
$\mathrm{Nb^{-3}}$, $\mathrm{Ta^{-3}}$	5	*tbp*	$\mathrm{M(CO)_5^{3-}}$
$\mathrm{Nb^{-1}}$, $\mathrm{Ta^{-1}}$	6	Octahedral	$\mathrm{[M(CO_6]^-}$
$\mathrm{Nb^{I}}$, $\mathrm{Ta^{I}}$, d^4	7	π Complex	$\mathrm{(C_5H_5)M(CO)_4}$
	7	Distorted capped octahedron (nonrigid)	$\mathrm{TaH(CO)_2(diphos)_2}$
$\mathrm{Nb^{II}}$, $\mathrm{Ta^{II}}$, d^3		See text	NbO
	6	Octahedral	$\mathrm{TaCl_2(dmpe)_2}$
$\mathrm{Nb^{III}}$, $\mathrm{Ta^{III}}$, d^2	6	Trigonal prism	$\mathrm{LiNbO_2}$
		Octahedral	$\mathrm{Nb_2Cl_9^{3-}}$, $\mathrm{M_2Cl_6(SMe_2)_3}$
	7	Complex	$\mathrm{TaCl_3(CO)(PMe_2Ph)_3{\cdot}EtOH}$
	8	Dodecahedral	$\mathrm{K_5[Nb(CN)_8]}$
$\mathrm{Nb^{iV}}$, $\mathrm{Ta^{IV}}$, d^1	6	Octahedral	$\mathrm{(NbCl_4)}$, $\mathrm{TaCl_4py_2}$, $\mathrm{MCl_6^{2-}}$
	7	Distorted pentagonal bipyramidal	$\mathrm{K_3NbF_7}$
	7	Capped octahedron	$\mathrm{MCl_4(PMe_3)_3}$
	8	Nonrigid in solution	$\mathrm{TaH_4(diphos)_2}$
		Square antiprism	$\mathrm{Nb(\beta\text{-}dike)_4}$, $\mathrm{M_2Cl_8(PMe_3)_4}$, $\mathrm{Nb(SCN)_4(dipy)_2}$,
		Dodecahedral	$\mathrm{K_4Nb(CN)_8{\cdot}2H_2O}$
		π Complex	$\mathrm{(\eta\text{-}C_5H_5)_2NbMe_2}$
$\mathrm{Nb^{V}}$, $\mathrm{Ta^{V}}$, d^0	4	Tetrahedral	$\mathrm{ScNbO_4}$
	5	*tbp*	$\mathrm{MCl_5(vapor)}$, $\mathrm{TaMe_5}$, $\mathrm{Nb(NR_2)_5}$
		Distorted tetragonal pyramid	$\mathrm{Nb(NMe_2)_5}$
	6	Octahedral	$\mathrm{NaMO_3}$ (perovskite), $\mathrm{NbCl_5{\cdot}OPCl_3}$, $\mathrm{TaCl_5{\cdot}S(CH_3)_2}$, $\mathrm{TaF_6^-}$, $\mathrm{NbOCl_3}$, $\mathrm{M_2Cl_{10}}$, $\mathrm{MCl_6^-}$
	6	Trigonal prism	$\mathrm{[M(S_2C_6H_4)_3]^-}$
	7	Distorted pentagonal bipyramidal	$\mathrm{NbO(S_2CNEt_2)_3}$
		Pentagonal bipyramidal, fluxional	$\mathrm{S{=}Ta(S_2CNEt_2)_3}$, $\mathrm{Ta(NMe_2)\,(S_2CNMe_2)_3}$, $\mathrm{(S_2CNR_2)_2TaMe_3}$
	8	Bicapped trigonal prism	$\mathrm{[Nb(trop)_4]^+}$
		Square antiprism	$\mathrm{Na_3TaF_8}$
		Dodecahedral	$\mathrm{Ta(S_2CNMe_2)_4^+}$
	9	π Complex	$\mathrm{(\eta^5\text{-}C_5H_5)_2TaH_3}$

relationships. They are built of $\mathrm{MO_6}$ octahedra sharing edges and corners, but this can be (and is) done in an almost unlimited number of ways. By partial oxygen loss various $\mathrm{Nb^V/Nb^{IV}}$ phases, for example, $\mathrm{Nb_{12}O_{29}}$ and $\mathrm{Nb_{22}O_{54}}$ can form, and the $\mathrm{Ta_2O_5}$ phase exists with an excess of Ta atoms from $\mathrm{TaO_{2.5}}$ to nearly $\mathrm{TaO_2}$.

Tantalum dioxide has the rutile structure; so also does $\mathrm{NbO_2}$ at higher temperatures, but either of two similar phases with alternating short (2.71 Å) and long (3.30 Å) Nb—Nb bond distances may be obtained at low temperatures.[1]

Niobium oxide has a unique structure, shown in Fig. 19-B-1(a), which gives each metal atom square coordination. It is what remains of the NaCl structure if all the atoms at the center and vertices of the unit cells are removed, and it has provoked much discussion.[2] Tantalum oxide has the regular NaCl structure. There is also a distinct Ta_4O phase.

Niobate and tantalate isopolyanions can be obtained by fusing the oxides in an excess of alkali hydroxide or carbonate and dissolving the melts in water. The solutions are stable only at higher pH: precipitation occurs below pH ~7 for niobates and ~10 for tantalates. The only species that appear to be present in solution are the $[H_xM_6O_{19}]^{(8-x)-}$ ions (x = 0, 1, or 2), despite frequent claims for others. The structure of the $M_6O_{19}^{8-}$ ions, found in crystals and believed to persist in solutions, is shown in Fig. 19-B-1(b).

Heteropolyniobates and -tantalates are not well known, but a few of the former have been prepared and characterized.

With the exception of a few insoluble lanthanide niobates and tantalates (e.g., $ScNbO_4$) that contain discrete, tetrahedral MO_4^{3-} ions, the coordination number of Nb^V and Ta^V with oxygen is essentially always 6. The various "niobates" and "tantalates" are really mixed metal oxides. Thus, for example, the M^IXO_3 compounds are perovskites.

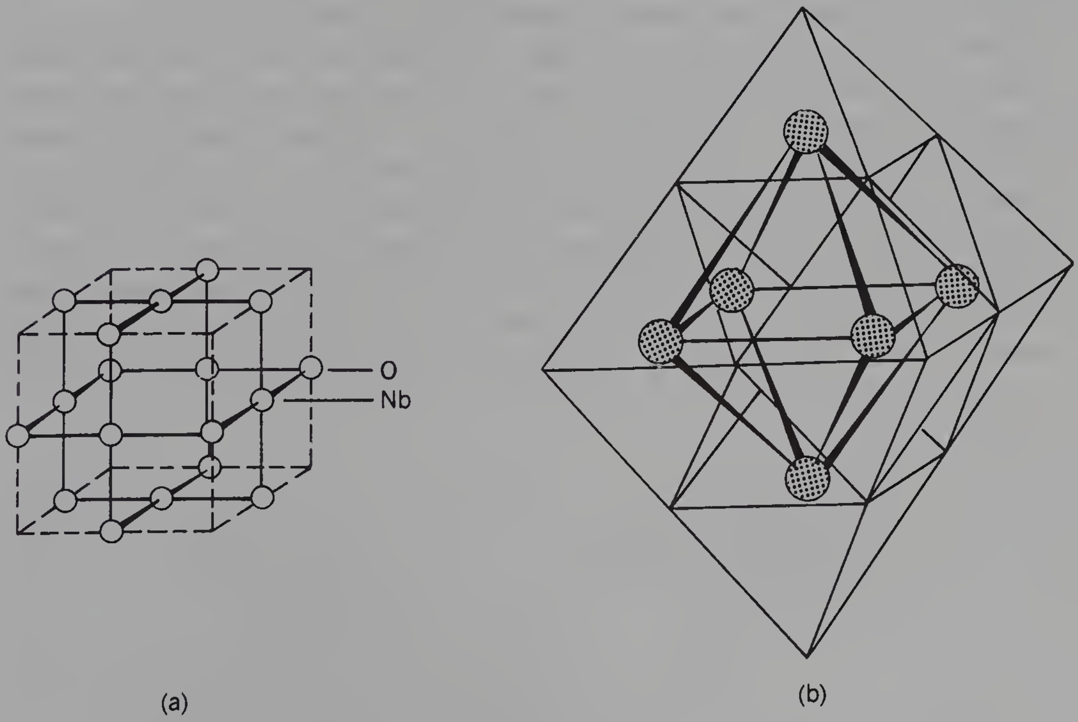

FIG. 19-B-1. (a) The NbO structure. (b) The structure of the $M_6O_{19}^{8-}$ ions (M = Nb or Ta). The central oxygen atom is shared by all six octahedra.

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[1] H. J. Schweizer and R. Gruehn, *Z. Naturforsch.*, 1982, **37b**, 1361.

[2] J. K. Burdett and T. Hughbanks, *J. Am. Chem. Soc.*, 1984, **106**, 3101.

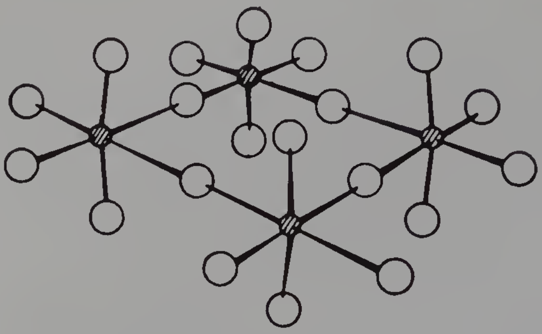


FIG. 19-B-2. The tetrameric structures of NbF_5 and TaF_5 (also MoF_5 and, with slight distortion, RuF_5 and OsF_5) Nb—F bond lengths: 2.06 Å (bridging), 1.77 Å (nonbridging). (Adapted by permission from A. J. Edwards, *J. Chem. Soc.*, **1964**, 3714.)

19-B-2. Halides and Oxohalides

Simple binary halides are known for oxidation states IV and V, those in lower states being cluster compounds (see Section 19-B-8).

Fluorides. The pentafluorides are made by direct fluorination of the metals or the pentachlorides. Both are volatile white solids (Nb: mp 80°C, bp 235°C; Ta: mp 95°C, bp 229°C), giving colorless liquids and vapors. They have the tetrameric structures shown in Fig. 19-B-2. Niobium(IV) fluoride is a black, nonvolatile, paramagnetic solid; TaF_4 is unknown.

Other Halides of Niobium(V) and Tantalum(V). These are yellow to brown or purple-red solids best prepared by direct reaction of the metals with excess of the halogen. The halides are soluble in various organic liquids such as ethers and CCl_4. They are quickly hydrolyzed by water to the hydrous pentoxides and the hydrohalic acid. The chlorides give clear solutions in concentrated hydrochloric acid, forming oxochloro complexes. All the pentahalides, which melt and boil between 200 and 300°C, can be sublimed without decomposition in an atmosphere of the appropriate halogen; in the vapor they are monomeric and probably trigonal bipyramidal. Crystalline

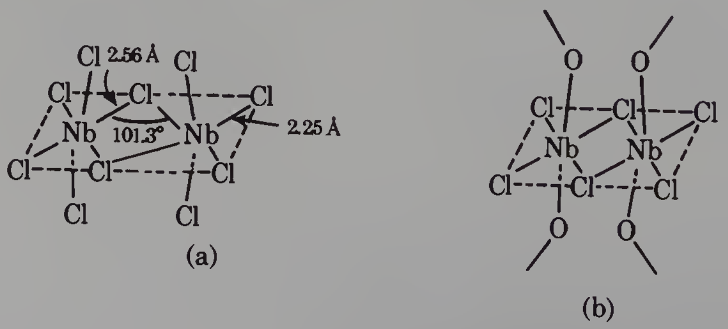
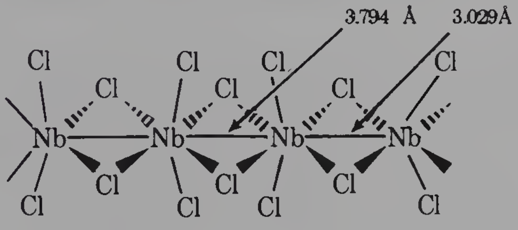


FIG. 19-B-3. (a) The dinuclear structure of $NbCl_5$ in the solid; the octahedra are distorted as shown. The Nb—Nb distance, 3.951 Å indicates no metal–metal bonding. (b) The structure of $NbOCl_3$ in the crystal. The oxygen atoms form bridges between infinite chains of the planar Nb_2Cl_6 groups.

$NbCl_5$ has the dimeric structure shown in Fig. 19-B-3(a); $NbBr_5$, $TaCl_5$, and $TaBr_5$ are isostructural. In CCl_4 and $MeNO_2$, both $NbCl_5$ and $TaCl_5$ are dimeric but in coordinating solvents adducts are formed. It appears probable that NbI_5 has a hexagonal close-packed array of iodine atoms with niobium atoms in octahedral interstices; TaI_5 is not isomorphous, and its structure is unknown.

Other Halides of Niobium(IV) and Tantalum(IV). All six are known and resemble one another in their structures and in being diamagnetic.

The *tetrachlorides* and *tetrabromides* are all brown-black or black isomorphous solids, obtained by reduction of the pentahalides with H_2, Al, Nb, or Ta at elevated temperatures. Crystalline $NbCl_4$ has linear chains with chlorine bridges (19-B-I) and alternating Nb—Nb bonds.



(19-B-I)

Niobium(IV) iodide is obtained on heating NbI_5 to 300°C. It is diamagnetic and trimorphic. One form contains infinite chains of octahedra with the Nb atoms off center so as to form pairs with Nb—Nb distances of 3.31 Å. Tantalum tetraiodide appears to be similar. The latter can be made most easily by allowing TaI_5 to react with an excess of pyridine to give $TaI_4(py)_2$ which, on heating, loses pyridine to give TaI_4.

Oxohalides. A large number are known,[3] although only a few are of common occurrence. They are of three main types. For the $M^{V}OX_3$ and $M^{V}O_2X$ compounds all possible types (16 in all) are known. For the $M^{IV}OX_2$ type, the six with M = Nb or Ta and X = Cl, Br, and I are known. The M_3O_7Cl and $Nb_5O_{11}Cl_3$ compounds have also been reported.

The MOX_3 compounds with X = Cl, Br, and I can generally be obtained by controlled reactions between MX_5 and O_2, and in some special ways, for example, by pyrolysis of $TaCl_5OEt_2$ for $TaOCl_3$. All are readily hydrolyzed, but from solutions in concentrated HX larger cations will precipitate salts of ions such as $[NbOCl_5]^{2-}$, $[NbOF_5]^{2-}$, or $[NbOCl_4]^{-}$. Neutral adducts such as $NbOCl_3(MeCN)_2$ can also be formed. The white chlorides and yellow bromides are volatile, giving monomeric vapors although the solids have polymeric structures, as shown in Fig. 19-B-3(b) for $NbOCl_3$.

There are thio analogues (MX_3S) that are less well known. Like the MOX_3 compounds, they form five- and six-coordinate adducts with neutral donors.[4]

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[3] H. Schäfer *et al.*, *Z. Anorg. Allg. Chem.*, 1986, **534**, 209.

[4] M. G. B. Drew and R. J. Hobson, *Inorg. Chim. Acta*, 1983, **72**, 233.

19-B-3. Oxidation State V

Fluoride Complexes. The metals and the pentoxides dissolve in aqueous HF to give fluoro complexes, whose composition depends markedly on the conditions. Addition of CsF to niobium in 50% HF precipitates $CsNbF_6$, while in weakly acidic solutions hydrolyzed species $[NbO_xF_y{\cdot}3H_2O]^{5-2x-y}$ occur, and components such as $K_2NbOF_5{\cdot}H_2O$ may be isolated. Raman and ^{19}F nmr spectra show that $[NbOF_5]^{2-}$ is present in aqueous solution up to ~35% in HF, and $[NbF_6]^-$ becomes detectable beginning at ~25% HF. The ion $[NbF_6]^-$ is normally the highest fluoro complex of Nb^V formed in solution, although in 95 to 100% HF, NbF_7^{2-} may possibly be present. Salts containing the NbF_7^{2-} ion can be crystallized from solutions with very high F^- concentrations. From solutions of low acidity and high F^- concentration, salts of the $[NbOF_6]^{3-}$ ion can be isolated.

There are crystalline tantalum fluoro compounds such as $KTaF_6$, K_2TaF_7, and K_3TaF_8. The TaF_8^{3-} ion, like NbF_7^{2-}, may be stabilized by crystal forces, since in aqueous HF or NH_4F solutions Raman spectra show the presence of TaF_6^- and TaF_7^{2-} ions only. In anhydrous HF solutions of $KTaF_6$ and K_2TaF_7 the only species identified by ^{19}F nmr spectra is TaF_6^-. In HF solutions tantalum can be separated from niobium by selective extraction into isobutyl methyl ketone.

The hexafluoro anions can also be made by the dry reaction:

$$M_2O_5 + 2KCl \xrightarrow{BrF_3} 2KMF_6$$

and the $[MOF_6]^{3-}$ salts can be prepared by bromination of the metals in methanol followed by addition of NH_4F or KF.

The ions $M_2F_{11}^-$, obtained by the reaction

$$MF_5 + n\text{-}Bu_4NBF_4 \xrightarrow{CH_2Cl_2} (n\text{-}Bu_4N)[MF_6]$$

$$(n\text{-}Bu_4N)[MF_6] + MF_5 \longrightarrow (n\text{-}Bu_4N)[M_2F_{11}]$$

have two octahedra linked by an M—F—M bridge. When H_2O_2 is added to solutions of the pentoxides in HF, mixed fluoro–peroxo complexes, $[MF_4(O_2)_2]^{3-}$, can be precipitated.[5]

Pentahalides as Lewis Acids. All of the pentahalides can combine with halide ions to form MX_6^- ions or with neutral Lewis bases (N, O, P, or S donors, commonly) to form MX_5L species. With amines, $NbCl_5$ often undergoes reduction leading to Nb^{IV} complexes such as $NbCl_4py_2$.

Because of their Lewis acidity, the MX_5 species, usually the fluorides or the chlorides, can act as catalysts in cyclotrimerizing or linearly polymerizing[6] acetylenes (although in the latter case metal alkylidene intermediates may be important) and in Friedel–Crafts and related alkylation reactions.[7]

[5] Z. Ruzic-Toros *et al., Inorg. Chim. Acta,* 1984, **86,** 205.

[6] T. Masuda *et al., J. Chem. Soc. Chem. Commun.,* **1982,** 1297.

[7] J. Sommer *et al., Nouv. J. Chim.,* 1982, **6,** 3.

The chlorides and bromides can also abstract oxygen from certain donor solvents (cf. VCl_4 and $MoCl_5$) to give the oxohalides:

$$NbCl_5 + 3Me_2SO \longrightarrow NbOCl_3{\cdot}2Me_2SO + Me_2SCl_2$$

$$Me_2SCl_2 \longrightarrow ClCH_2SMe + HCl$$

Other Complexes and Compounds. In addition to the anionic or neutral complexes formed by Lewis acid behavior of MX_5 (or MOX_3), there is an extensive chemistry of compounds in which halogen is replaced by alkoxide (OR), dialkylamide (NR_2), and alkyl (CR_3) groups. These compounds may be coordinately unsaturated, and they form anionic complexes like $[Ta(C_6H_5)_6]^-$ or neutral adducts.

Some reactions of $TaCl_5$ that are also, in general, typical for $NbCl_5$ are given in Fig. 19-B-4.

Oxygen Ligands. The dimeric *alkoxides,* $M_2(OR)_{10}$, obtained by the action of alcohols and an amine on the pentachlorides, have two alkoxo bridges. These may be cleaved by donors to give monomeric compounds like $Nb(OMe)_5py$. Partially substituted compounds can be made with alcohols like 2-methoxyethanol, which gives the six-coordinate $MCl_3(OCH_2CH_2OMe)_2$. With extremely bulky OR groups (e.g., R = 1- or 2-adamantyl) monomeric $M(OR)_5$ species can be isolated.[8]

Cationic eight-coordinate complexes with tropolonato and β-diketonato anions, for example, $[M[\beta\text{-dike})_4]^+$ are also well known.

Nitrogen Ligands. While they form few complexes with simple amines, the pentavalent metals form important $M(NR_2)_xX_{5-x}$ compounds. The $M(NMe_2)_5$ compounds, obtained by reaction of MCl_5 with $LiNMe_2$, have been greatly studied[9a] and used for synthesis of other compounds.[9b] They are monomeric with apparently identical structures in the gas phase but in the solid $Ta(NMe_2)_5$ is *tbp* while $Nb(NMe_2)_5$ approaches an *sp* structure. Mixed amidochloro species can be obtained by reactions such as:

$$Ta(NMe_2)_5 + 2Me_3SiCl \longrightarrow TaCl_2(NMe_2)_3 + 2Me_3SiNMe_2$$

$$TaCl_5 + 5HNMe_2 \longrightarrow TaCl_3(NMe_2)_2(HNMe_2) + 2Me_2NH_2Cl$$

It should also be noted that there are a number of compounds containing M=NR units, especially with tantalum, examples being $Ta(NMe_2)_3(Nt\text{-}Bu)$, $TaCl_3(THF)_2(NR)$ and $Ta(S_2CNMe_2)_3(NSiMe_3)$,[10a] and $TaCl_3(PEt_3)(THF)({=}NPh)$.[10b] A particularly interesting compound of this type is the binuclear dinitrogen complex, which could be formulated as consisting of an N_2 molecule donating to two Ta^{III} atoms, but, on the basis of the observed N—N

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[8] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1980,** 901.

[9a] M. H. Chisholm *et al., J. Am. Chem. Soc.,* 1980, **102,** 46.

[9b] M. H. Chisholm *et al., Inorg. Chem.* 1981, **20,** 1859.

[10a] D. C. Bradley *et al., J. Chem. Soc. Dalton Trans.,* **1984,** 1069.

[10b] M. R. Churchill and H. J. Wasserman, *Inorg. Chem.,* 1982, **21,** 223.

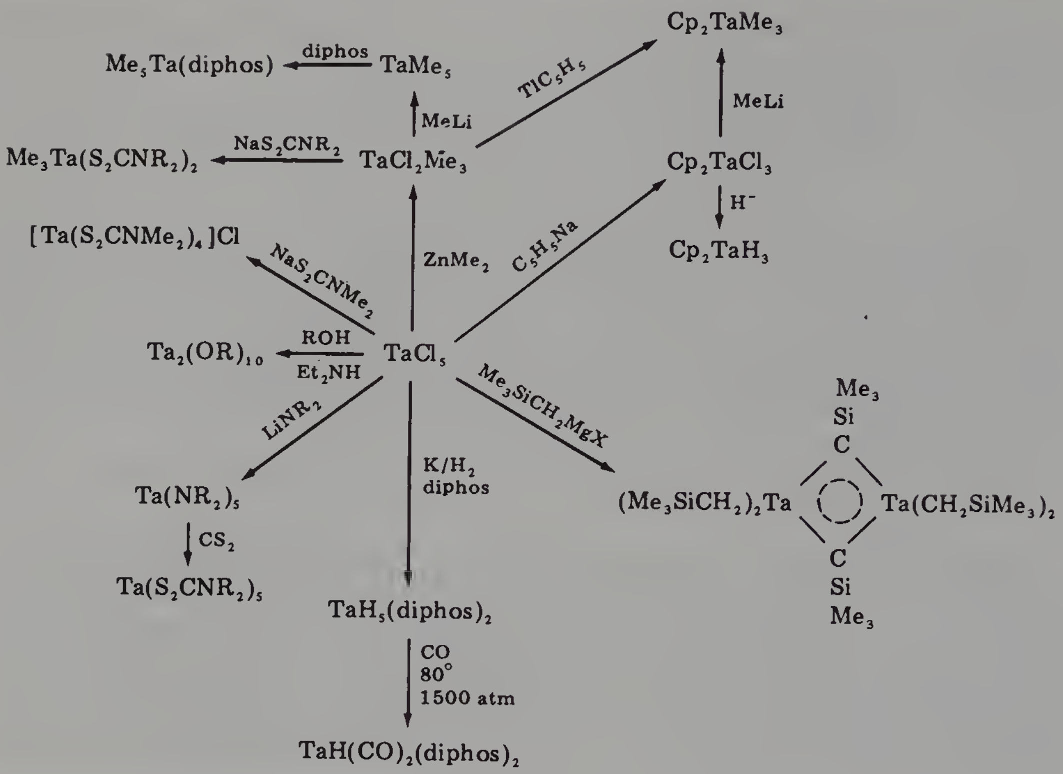

FIG. 19-B-4. Some reactions of tantalum pentachloride.

(1.28 Å) and N—Ta (1.80 Å) distances[10c] is probably better represented as a diimine complex involving two Ta^V atoms, namely,

$$(\text{benzyl})_3P(THF)Cl_3Ta{=}N{-}N{=}TaCl_3(THF)P(\text{benzyl})_3$$

Reactions of $M(NR_2)_5$ compounds with alcohols provide an excellent route to the alkoxides. Moreover, the $M(NR_2)_5$ compounds undergo insertion reactions with CS_2 and CO_2

$$Nb(NMe_2)_5 + 5CO_2 \longrightarrow Nb(O_2CNMe_2)_5$$

$$Ta(NMe_2)_5 + 5CS_2 \longrightarrow Ta(S_2CNMe_2)_5$$

The metal atoms in the resulting carbamates and dithiocarbamates are eight-coordinate, with two monodentate and three bidentate ligands. The CO_2 insertion is partially reversible so that the carbamates can exchange with labeled CO_2

$$\begin{tikzcd}
Nb(O_2CNMe_2)_5 \arrow[r, rightharpoonup, shift left] & Nb(O_2CNMe_2)_4(NMe_2) + CO_2 \arrow[l, leftharpoondown, shift left] \arrow[d, "{}^*CO_2"] \\
 & Nb(O_2CNMe)_4(O_2{}^*CNMe_2)
\end{tikzcd}$$

[10c] M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, 1982, **21**, 218.

Some niobium porphyrin (por) complexes in which the Nb atom lies well out of the porphyrin plane and is bonded to three oxygen atoms are known, namely, (por)Nb(μ-O)$_3$Nb(por) and (por)Nb(O)(O_2CMe).[11]

Sulfur Ligands. Besides the $M(S_2CNMe_2)_5$ compounds just mentioned many other dithiocarbamates are known, of which the cationic species, $[M(S_2CNR_2)_4]^+$ are most important. They have generally dodecahedral structures in which the S_2CNR_2 ligands span the four *m* edges (see Fig. 1-9) of the dodecahedron[12] but many are fluxional. Compounds of this type can be made by the reaction:

$$TaCl_5 + 4NaS_2CNR_2 \xrightarrow[\text{reflux}]{CH_2Cl_2} [Ta(S_2CNR_2)_4]Cl$$

There are some trigonal prismatically coordinated complexes formed by reaction of $M(NR_2)_5$ with dithiolate dianions, for example, $[M(1,2\text{-}S_2C_6H_4)_3]^-$.

Other Compounds. These include nitrides, sulfides, silicides, selenides, and phosphides, as well as many alloys. Definate hydride phases also appear to exist.

There are no simple salts such as sulfates and nitrates. Sulfates such as $Nb_2O_2(SO_4)_3$ probably have oxo bridges and coordinated sulfato groups. In HNO_3, H_2SO_4, or HCl solutions, Nb^V can exist as cationic, neutral, and anionic species, hydrolyzed, polymeric, and colloidal forms in equilibrium, depending on the conditions.

Organometallic Chemistry of Nb^V and Ta^V. There is an extensive chemistry of these elements with M—C σ bonds, η-C_5H_5 and cyclooctatetraene groups.

Niobium and tantalum methyls, Me_3MCl_2, were among the first known stable transition metal methyls. Other partially substituted alkyls, as well as the pentamethyl, are now known. These compounds are made by the reactions:

$$2TaCl_5 + 3ZnMe_2 \xrightarrow{\text{ether}} 2TaCl_2Me_3 + 3ZnCl_2$$

$$TaCl_2Me_3 + 2LiMe \xrightarrow{\text{ether}} TaMe_5 + 2LiCl$$

The niobium compounds are less stable than the tantalum ones. The formation of adducts such as $TaMe_5$(diphos) increases the stability, however. All these compounds (*a*) act as Lewis bases, adding neutral ligands or forming anions, and (*b*) can undergo insertion reactions into the M—CH_3 group (e.g., with NO or CS_2). Furthermore, the halide atoms can be replaced by other groups such as acac, Schiff bases, NR_2, or OR, to give compounds such as $R_3Ta(OR')_2$, which are monomeric if R and R′ are very bulky.[13]

Other important types of compounds are the Ta=CH_2, Ta=CR_2, and Ta≡CR types to be discussed in Chapter 25 and a variety of Cp_2MX_3 compounds, of which the hydrides are particularly interesting.

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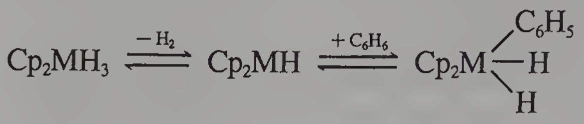
[11] R. Guilard *et al., J. Chem. Soc. Chem. Commun.*, **1980,** 516.

[12] M. G. B. Drew *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 1821.

[13] P. T. Wolczanski *et al., Organometallics,* 1985, **4,** 1810.

The compounds Cp_2MH_3 also catalyze the exchange of D_2 with aromatic compounds at 1 to 2 atm and 80 to 100°C. The pentahydride $TaH_5(diphos)_2$, will also do this. The mechanism involves dissociation to form the monohydrido species and oxidative addition of benzene, namely,



$$Cp_2MH_3 \xrightleftharpoons{-H_2} Cp_2MH \xrightleftharpoons{+C_6H_6} Cp_2M(C_6H_5)(H)(H)$$

The cyclooctatetraene complexes, for example, $[Nb(C_8H_8)_3]^-$ and $CH_3Ta(C_8H_8)_2$, have η^4, butadienelike, and η^3-allyllike bonding of the rings to the metal; they are nonrigid.

19-B-4. Oxidation State IV

The oxides, halides, and oxohalides have been mentioned. The disulfides (MS_2) have layer structures with adjacent layers of sulfur atoms. Intercalation compounds can be formed by insertion between these sheets. Both simple (e.g., $NbS_2 \cdot \frac{1}{2}py$) and ionic [e.g., $TaS_2^{x-}(NH_4^+)_x(NH_3)_{1-x}$] compounds can be formed.

There are several Nb^{IV} alkoxides such as $Nb(OEt)_4$, $[NbCl(OEt)_3py]_2$, $NbCl_3(OR)bipy$, and salts of the ion $[NbCl_5OEt]^{2-}$. There are also cyclopentadienyl compounds of stoichiometry Cp_2NbX_2 (X = CH_3, C_6H_5, H, Cl, Br, and I).

The paramagnetic hydride and also the tetrahydride $TaH_4(diphos)_2$ are obtained from the M^V hydrides by H-abstraction using di-*tert*-butylperoxide, namely

$$\left.\begin{array}{l} Cp_2NbH_3 \\ (diphos)_2TaH_5 \end{array}\right\} \xrightarrow{(t\text{-BuO})_2} \left\{\begin{array}{l} Cp_2NbH_2 \\ (diphos)_2TaH_4 \end{array}\right.$$

Halide and Pseudohalide Complexes. They are usually prepared by reacting the ligand with the tetrahalide or by reduction of the pentahalides, either electrolytically or with metals like Na, Zn, Al, Mg, and Nb. Substitution of weakly coordinating THF in $NbCl_4(THF)_2$ is also a convenient route to $NbCl_4$ adducts. Typical homoleptic complexes are the octahedral $[MX_6]^{2-}$ ions (X = Cl, Br, and SCN), pentagonal bipyramidal $[NbF_7]^{3-}$, and dodecahedral $[Nb(CN)_8]^{4-}$.

Adducts of the types MX_4L_n (n = 1–4) are numerous, with the octahedral (MX_4L_2) complexes being most common. Some are cis [e.g., $NbX_4(MeCN)_2$[14] and $TaCl_4(PMe_2Ph)_2$[15]] and others are trans [e.g., $MCl_4(PEt_3)_2$[15]]. It is possible that the red and green forms of $NbBr_4py_2$ may be cis and trans isomers. All mononuclear species display paramagnetism corresponding to one d electron and many give sharp esr signals.

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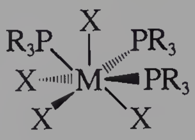
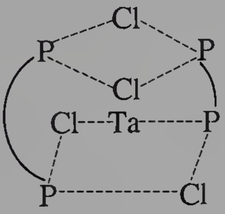
[14] M. G. B. Drew *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981**, 1304.

For the smallest phosphines, PMe_3 and PMe_2Ph, higher coordination numbers are found.[15–17] Thus, there are $MX_4(PR_3)_3$ species, which have capped octahedral structures (19-B-II) and there are several examples of diamagnetic $M_2X_8(PR_3)_4$ complexes[16,18] having the type of structure shown in Fig. 19-B-5, with an M—M single bond. The compound $NbCl_4(PMe_3)_4$ was identified in solution by esr but could not be isolated.[16] Other isolable eight-coordinate species, $MX_4(LL)_2$, are obtained with diphosphines, diarsines, and bipyridyl. For $TaCl_4(dmpe)_2$ the structure is approximately square antiprismatic (19-B-III), which contrasts with the dodecahedral structure of the corresponding $[TaCl_4(dmpe)_2]^+$ ion.[19]



(19-B-II)



(19-B-III)

Other Complexes. There are numerous mixed ligand complexes, such as $NbCl_2(\beta\text{-dike})_2$ compounds,[20] $[NbCl_5(OR)]^{2-}$, $[NbCl_3(OR)bipy]$, $NbCl_2$(phthalocyanine), and so on. Frequently, Ta^{IV} reacts by abstracting oxygen

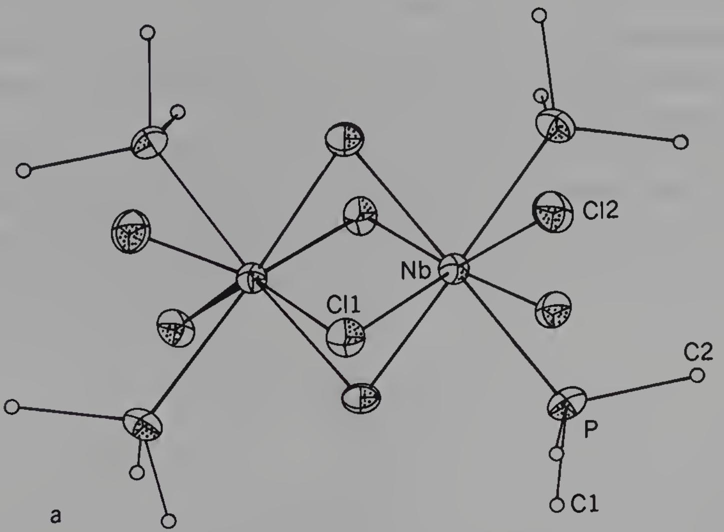


FIG. 19-B-5. The structure of $Nb_2Cl_8(PMe_3)_4$, consisting of two square antiprisms sharing a Cl_4 face (from ref. 15).

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[15] F. A. Cotton *et al., Inorg. Chem.*, 1984, **23**, 3592; 4046.
[16] F. A. Cotton *et al., Polyhedron,* 1985, **4,** 1103.
[17] F. A. Cotton *et al., Inorg. Chim. Acta,* 1985, **105,** 41.
[18] A. J. Nielson *et al., J. Chem. Soc. Chem. Commun.,* **1984**, 1086.
[19] F. A. Cotton *et al., Inorg. Chem.*, 1983, **22,** 770.
[20] F. A. Cotton *et al., Polyhedron,* 1985, **4,** 1485.

and thus some Ta analogues of Nb complexes with oxygen-containing ligands have not been isolated.

There are various dinuclear compounds having the structure of an edge-sharing bioctahedron, in which there is a metal–metal bond of order 1. This results in diamagnetism and M—M distances of 2.80 to 2.90 Å. Some examples are $[(THT)_2Cl_2Nb]_2(\mu\text{-}S)_2$,[21] $[(MeCN)_2Cl_2Nb]_2(\mu\text{-}S)_2$,[14] $[(MeOH)(MeO)Cl_2Nb]_2(\mu\text{-}OMe)_2$ and a related oxo-bridged tetramer,[22] and $[(Me_2S)Cl_3Ta]_2(\mu\text{-}SPh)_2$.[23] There is also a similar compound with one S^{2-} and one S_2^{2-} bridge, namely, $[(THT)_2Br_2Nb]_2(\mu\text{-}S)(\mu\text{-}S_2)$.[24]

Several different hydrido compounds of Nb^{IV} and Ta^{IV} have been obtained from low valent phosphine complexes. The reaction of M^{II} adducts with H_2 gives stable paramagnetic $MH_2Cl_2L_4$,[25] where $L = PMe_3$ or $\frac{1}{2}$ dmpe. Dinuclear species of the general formula $[TaCl_3(PMe_3)]_2(\mu\text{-}Cl)_n(\mu\text{-}H)_{4-n}$ where $n = 0$, 1, and 2 are formed upon reacting $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_2$ with H_2, HCl, and Cl_2, respectively.[26]

There are also cyclopentadienyl complexes of stoichiometry Cp_2MX_2 where X is a monovalent group like H^-, BH_4^-, halide, pseudohalide, alkyl, aryl, alkoxide, carboxylate, or thiolate.

19-B-5. Oxidation State III

This oxidation state is readily accessible via reduction of pentahalides with two equivalents of sodium amalgam in the presence of neutral ligands like SC_4H_8 (tetrahydrothiophene, THT), SMe_2, or PMe_3. The sulfur donors afford confacial bioctahedral $M_2Cl_6L_3$ complexes,[27] while with PMe_3 the edge-sharing bioctahedral molecule, $M_2Cl_6(PMe_3)_4$ is obtained.[28]

The THT and SMe_2 adducts have structures of the type (19-B-IV). Their chemistry has been extensively studied[29a–g] and it is summarized in Fig. 19-B-6. The diverse, and in some cases unique, reactivity of these compounds includes: substitution with preservation of the geometry or with conversion to $(MX_4)_2(\mu\text{-}X)_2$ species, oxidative-addition, cluster formation, and above all

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[21] M. G. B. Drew *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 417.
[22] F. A. Cotton *et al.*, *Inorg. Chem.*, 1985, **24**, 3509.
[23] F. A. Cotton *et al.*, *Inorg. Chem.*, 1986, **25**, 287.
[24] M. G. B. Drew *et al.*, *Inorg. Chim. Acta*, 1980, **44**, L217.
[25] A. P. Sattelberger *et al.*, *Inorg. Chem.*, 1984, **23**, 1718.
[26] A. P. Sattelberger *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 858.
[27] F. A. Cotton and R. C. Najjar, *Inorg. Chem.*, 1981, **20**, 2716.
[28] A. P. Sattelberger *et al.*, *Inorg. Chem.*, 1982, **21**, 2392.
[29a] F. A. Cotton and W. T. Hall, *Inorg. Chem.*, 1981, **20**, 1285.
[29b] F. A. Cotton *et al.*, *Macromolecules*, 1981, **14**, 233.
[29c] H. E. Clay and T. M. Brown, *Inorg. Chim. Acta*, 1982, **58**, 1; 1983, **72**, 75.
[29d] F. A. Cotton *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 4749, 6987.
[29e] F. A. Cotton *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 1276.
[29f] F. A. Cotton and W. J. Roth, *Inorg. Chem.*, 1983, **22**, 3654.
[29g] F. A. Cotton *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 971.

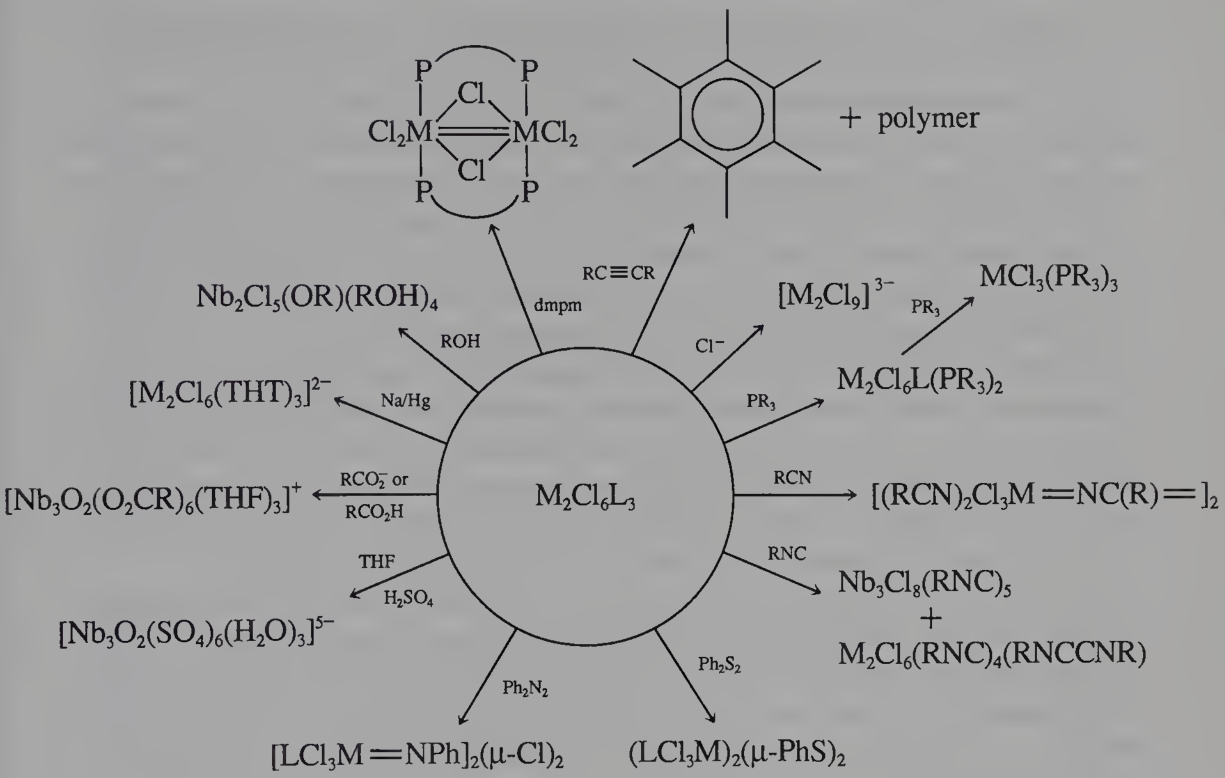
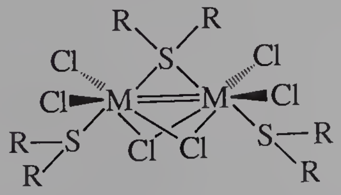


FIG. 19-B-6. Some reactions of the $M_2Cl_6L_3$ species (M = Nb and Ta; L = Me_2S, and THT) (see ref. 29).

coupling of the molecules with triply bonded carbon atoms. They trimerize and polymerize catalytically terminal acetylenes[29b], and dimerize nitriles[29a] and isonitriles[29d] to $=NC(R)=C(R)N=$ and $R-N=C=C=N-R$, respectively, with incorporation of the new ligand into the complex. Another remarkable reaction of $M_2Cl_6L_3$ is the metathesis of M=M and N=N bonds into two M=N bonds upon reaction with azobenzene.[29d]



(19-B-IV)

The reactivity of $Ta_2Cl_6(PMe_3)_4$ is also extraordinary. It provided the first example of oxidative-addition of molecular hydrogen to a multiple M—M bond, by forming $[Ta_2Cl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2(\mu\text{-}H)_2$.[30] The latter, a Ta^{IV} complex, can be reduced to a Ta^{III} dimer, $Ta_2Cl_4(PMe_3)_4H_2$,[26] which contains bridging hydrides and the TaX_4 squares are eclipsed. The Ta—Ta bond distance in this compound, namely, 2.545 Å, is the shortest metal–metal bond found for

[30] A. P. Sattelberger *et al., Inorg. Chem.*, 1982, **21,** 4179.

either element. The compound $Ta_2Cl_6(PMe_3)_4$ also reacts with ethylene yielding a monomeric adduct of composition $TaCl_3(PMe_3)_2(C_2H_4)$.

In general this oxidation state is dominated by highly reactive dinuclear complexes, usually possessing an M—M double bond with a typical length around 2.7 Å, although M—M distances >2.8 Å are also encountered. Due to this tendency to form dimers with a strong interaction between metal atoms the stabilization of monomeric compounds requires the presence of excess ligand or coordinative saturation. The latter is exemplified by $Nb(CN)_8^{5-}$,[31] $NbBr_3(PMe_2Ph)_3$,[17] $MH_2X(PMe_3)_4$,[32] $CpNb(t\text{-}BuNC)_4Cl^+$.[33]

The three different Ta^{III} species obtained by reduction of $TaCl_5$ in the presence of PMe_3 provide an excellent illustration of this point. In toluene either $Ta_2Cl_6(PMe_3)_4$ or $TaCl_3(PMe_3)_3$ is obtained.[34] The preparation of the latter requires excess ligand, and the monomer dimerizes with a loss of one PMe_3 upon dissolution. A reduction in neat phosphine leads to deprotonation of methyl groups producing $Ta(PMe_3)_3(\eta^2\text{-}CHPMe_2)(\eta^2\text{-}CH_2PMe_2)$.[35]

A number of M^{III} compounds containing one or two cyclopentadienyl anions is known. The former are of stoichiometry $CpMX_5$ with X_5 being an appropriate combination of monovalent (halide, H) and neutral ligands (CO, phosphine), for example, $CpMCl_2(CO)_3$, $CpMX_2(CO)(diphos)$, and $[CpMH(CO)_2(diphos)]^+$. Bis(cyclopentadienyl) derivatives are usually of composition $Cp_2MX(L)$, with the most common X and L being an alkyl and CO, respectively.

19-B-6. Oxidation State II

There are three types of compounds; mononuclear, binuclear, and organometallic, and relatively few of each type. Paramagnetic, octahedral MX_2L_4 species[25,36] with either metal and X = Cl, L = PMe_3, or ½dmpe, and with M = Nb, X = OAr, and L = ½dmpe, can be prepared by reduction of higher-valent chlorides or aryl oxides with Na/Hg. The $MCl_2(PMe_3)_4$ compounds undergo phosphine exchange with dmpe and all the chloro complexes react with H_2 to give M^{IV} hydrides of composition $MH_2Cl_2L_4$.

The first dinuclear M^{II} complex in which there is an M—M triple bond is $[Cl_3Ta(\mu\text{-}THT)_3TaCl_3]^{2-}$ (Ta—Ta = 2.626 Å).[37] This bright red species is obtained by reduction of $Ta_2Cl_6(THT)_3$ with Na/Hg; it is stable towards water and, in general, chemically inert.

Dinuclear M^{II} complexes with η^5-Cp or substituted Cp ligands possess

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[31] W. P. Griffith *et al., J. Chem. Soc. Chem. Commun.*, **1980**, 1167.

[32] A. P. Sattelberger *et al., J. Am. Chem. Soc.*, 1987, **26**, 2430.

[33] S. J. Lippard *et al., Inorg. Chem.*, 1984, **23**, 1782.

[34] R. R. Schrock *et al., Organometallics*, 1982, **1**, 703.

[35] M. L. H. Green *et al., J. Chem. Soc. Chem. Commun.*, **1983**, 1101.

[36] I. P. Rothwell *et al., J. Chem. Soc. Chem. Commun.*, **1985**, 1519.

[37] F. A. Cotton *et al., J. Am. Chem. Soc.*, 1987, **109**, 5506.

only single M—M bonds of length around 3 Å. They are of composition $(CpNbL_2)_2(\mu\text{-}Cl)_2$,[38] where L = CO or $\frac{1}{2}$PhCCPh, and are obtained by a sodium amalgam reduction of Nb^{III} complexes of general formula $(CpNbCl_2L_2)_n$, with the carbonyl species being dinuclear while the acetylene one is mononuclear. The profound structural difference between the Nb^{II}-carbonyl and Nb^{II}-acetylene compounds, namely butterfly versus planar Nb_2Cl_2 moiety, and much shorter Nb—Cl(terminal) distances in the latter, introduces ambiguity as to the oxidation state assignment. The usually observed strong interaction within the MC_2 unit may require its formal treatment as $M^{2+}—C_2^{2-}$, rather than as a π complex. In the above case this would account for the difference between seemingly analogous compounds with the acetylene derivative being formally a Nb^{IV} complex.

19-B-7. Compounds with Very Low Formal Oxidation States

The majority of these contain CO ligands. The neutral carbonyls have not been isolated but anionic $M(CO)_6^-$ as well as highly reduced $M(CO)_5^{3-}$ are known. The original synthesis of the −1 species required elevated temperatures and high pressure but recently two simple, atmospheric pressure methods have been developed. They involve reduction of pentahalides in pyridine with Zn/Mg[39] or in dimethoxyethane with sodium naphthalenide[40] under an atmosphere of CO. These yellow salts contain discrete $M(CO)_6^-$, octahedral anions. The facile syntheses of the hexacarbonyl anions allowed systematic exploration of the previously difficult to access area of low valent complexes of Nb and Ta. Since $M(CO)_6^-$ are rather inert towards displacement of CO the substitution products of general formula $M(CO)_{6-n}L_n$ have to be obtained by other routes, for example, by reduction of $MX(CO)_{6-n}L_n$ compounds. The monosubstituted derivatives are conveniently prepared via the following method:[41]

$$M(CO)_6^- \xrightarrow[-78°C]{Na,NH_3(l)} M(CO)_5^{3-} \xrightarrow{NH_4^+} M(CO)_5NH_3^- \xrightarrow{L} M(CO)_5L^-$$

The highly reduced $M(CO)_5^{3-}$ is stable only at low temperature and explodes upon warming especially when dry.

Oxidation of $M(CO)_6^-$ with halogens affords $M_2(CO)_8X_3^-$ anions[42] but in the presence of PMe_3 neutral monomers, $MX(CO)_3(PMe_3)_3$ are formed.[43] The former contain three bridging halide atoms, which can be substituted by MeO^- or $CH_3CO_2^-$ by reaction with methanol or acetic acid. The metal–metal distance of over 3.5 Å precludes direct interaction. The dimeric chloro anions

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[38] M. D. Curtis and J. Real, *Organometallics*, 1985, **4**, 940.

[39] F. Calderazzo *et al.*, *Inorg. Chem.*, 1983, **22**, 1865.

[40] J. E. Ellis *et al.*, *Organometallics*, 1983, **2**, 388.

[41] J. E. Ellis *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 672.

[42] F. Calderazzo *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985**, 1989.

[43] A. P. Sattelberger *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985**, 552.

are converted to $CpM(CO)_4$ by reaction with LiCp and to (η^6-arene)$M(CO)_4^+$ in the presence of arene and $AlBr_3$.

There are also seven-coordinate M^I complexes of stoichiometry $MX(CO)_2(diphos)_2$ for X = H, Cl, and CH_3. In one such compound, $TaCl(CO)(dmpe)_2$, there is, under appropriate conditions, reductive coupling of the two ligating carbonyls as shown by the isolation of $Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl$.[44]

Finally, we note that by metal vapor synthesis zerovalent Nb and Ta compounds, such as $M(arene)_2$[45] and $M(dmpe)_3$[46] can be prepared in substantial quantities.

19-B-8. Niobium and Tantalum Cluster Complexes

Both of these elements show a marked tendency to form metal atom cluster compounds in their lower oxidation states. The best known cluster complexes, obtained by reduction of the pentahalides by the metal alone, or in the presence of sodium chloride, contain as their key structural unit an $[M_6X_{12}]^{n+}$ group, shown in Fig. 19-B-7. A typical reaction is

$$14NbCl_5 + 16Nb + 20NaCl \xrightarrow{12h, 850°C} 5Na_4Nb_6Cl_{18}$$

The extraction of the melt with very dilute HCl gives a green solution from which, by addition of concentrated HCl, the black solid $Nb_6Cl_{14}\cdot 8H_2O$ is

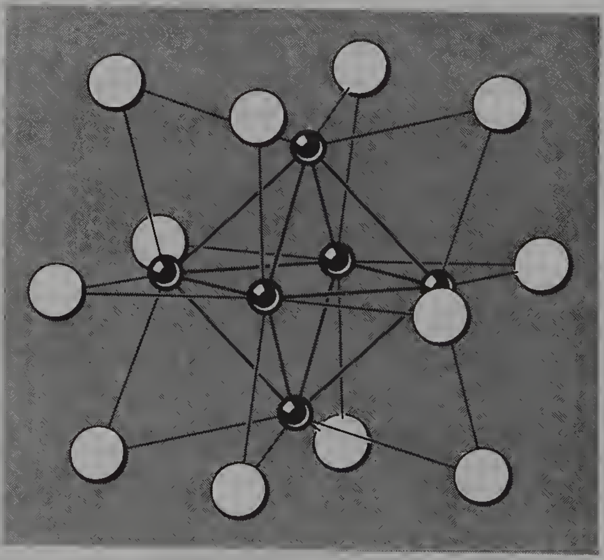

FIG. 19-B-7. The structure of the $[M_6X_{12}]^{n+}$ unit found in many halogen compounds of lower-valent niobium and tantalum. (Reproduced by permission from L. Pauling, *The Nature of the Chemical Bond,* 3rd ed., Cornell University Press, Ithaca, New York, 1960.)

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[44] S. J. Lippard *et al., J. Am. Chem. Soc.* 1986, **108,** 311.

[45] F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc. Dalton Trans.,* **1981,** 1938.

[46] F. G. N. Cloke *et al., J. Organomet. Chem.,* 1984, **277,** 61.

obtained. Corresponding tantalum compounds are obtained similarly, and mixed metal species, for example, $[(Ta_5MoCl_{12})Cl_6]^{2-}$, can be obtained by the reduction of $TaCl_5$ + $MoCl_5$ in $NaAlCl_4$—$AlCl_3$ melts by Al.

The M_6X_{12} units are usually found with a charge of 2+ and one additional ligand (X^-, H_2O, etc.) is coordinated to the external site on each metal atom.[47] Within the M_6 octahedron there are M—M bonds of fractional order; in $[Nb_6Cl_{12}]^{2+}$, for example, there are 16 electrons so that a bond order of $\frac{16}{24} = \frac{2}{3}$ can be assigned, consistent with the Nb—Nb bond distances of ~2.80 Å.

More recently it has been found that the compounds Nb_6I_{11}, $CsNb_6I_{11}$, $Nb_6I_{11}H$, and $CsNb_6I_{11}H$ can be made.[48,49] These also contain octahedral Nb_6 clusters, but of a different type in which there are eight face-bridging (i.e., μ_3) iodine atoms (see section 19-C-10 for similar Mo and W clusters). In the hydrido species the hydrogen atom is inside the Nb_6 octahedron.

Similar octahedral clustering of niobium atoms has also been found in $Mg_3Nb_6O_{11}$ (Nb—Nb = 2.81 Å).[50]

There are also many compounds in which triangular Nb_3 clusters (few if any tantalum analogues have yet been reported) are found. Among the earliest examples were the halides Nb_3X_8 in which Nb atoms occupy octahedral interstices in a close-packed array of halide ions so as to form Nb_3 clusters. In Nb_3Cl_8, for example, the Nb—Nb bond distances are ~2.80 Å. There are also $M^INb_4X_{11}$ compounds that contain an Nb_4 cluster, which is effectively two triangular clusters fused together, as shown in Fig. 19-B-8.

Another example, long known (1912) but only recently structurally defined,[51] is the red-brown compound obtained by electrochemical reduction of Nb_2O_5 in H_2SO_4. It contains a trinuclear, bioxocapped anion of composition $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$. It was the first example of such a trimer outside the Group VI(B) transition elements. A more convenient method for its preparation involves reaction of $Nb_2Cl_6(THT)_3$ in THF with H_2SO_4.[29c] Carboxylato analogues of the sulfate can also be obtained from the Nb^{III} dimer.[29c] All of them contain an equilateral triangle of Nb atoms <2.9 Å apart. The reaction between $Nb_2Cl_6(THT)_3$ and concentrated HCl affords an as yet unidentified green aquo complex, which, upon reaction with SCN^-, gives another type of a trinuclear d^4 cluster containing a capping sulfur atom and three bridging oxygen atoms, namely, $Nb_3SO_3(NCS)_9^{6-}$.[29c]

Two trinuclear carbonyl[52] and isonitrile[53] compounds, $Cp_3Nb_3(CO)_7$ and $Nb_3Cl_8(t\text{-}BuNC)_5$ contain CO and *t*-BuNC acting as six-electron donors due to formation of a two center cap over the isosceles triangles of metal atoms.

[47] F. Ueno and A. Simon, *Acta Crystallogr.*, 1985, **C41**, 308.

[48] H. Imoto and J. D. Corbett, *J. Am. Chem. Soc.*, 1980, **19**, 1241.

[49] H. Imoto and A. Simon, *Inorg. Chem.*, 1982, **21**, 308.

[50] B.-O. Marinder, *Chem. Scripta*, 1977, **11**, 97.

[51] A. Bino, *Inorg. Chem.*, 1982, **21**, 1917.

[52] W. A. Herrmann *et al.*, *J. Am. Chem. Soc.*, 1981, **103**, 1692.

[53] F. A. Cotton and W. J. Roth, *J. Am. Chem. Soc.*, 1983, **105**, 3734.

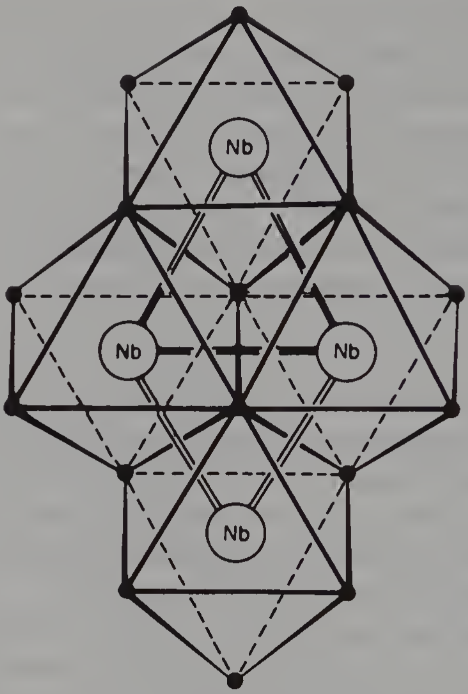

FIG. 19-B-8. The key structural unit in $M^1Nb_4X_{11}$ compounds. Small solid circles are halogen atoms and double lines represent M—M bonds. Many of the peripheral halogen atoms are shared with other units.

General References

Holloway, C. E. and Melnik, M., *Rev. Inorg. Chem.*, 1985, **7,** 1 and 161; *J. Organomet. Chem.*, 1986, **303,** 1 and 39 (structures of Nb and Ta Compounds).

Rice, D. A., *Coord. Chem. Rev.*, 1981, **37,** 77; 1982, **45,** 87.

19-C. MOLYBDENUM[1] AND TUNGSTEN[2]: GROUP VIB(6)

Molybdenum and tungsten are similar chemically, although there are differences between them in various types of compounds that are not easy to explain. Thus some compounds of the same type differ noticeably in their reactivities toward various reagents: for example, $Mo(CO)_6$ but not $W(CO)_6$ reacts with acetic acid to give the quadruply bonded dimetal tetraacetate.

Except for compounds with π-acid ligands, there is not a great deal of similarity to chromium. The divalent state, well defined for Cr, is not well known for Mo and W except in strongly M—M bonded compounds; and the high stability of Cr^{III} in its complexes has no counterpart in Mo or W chemistry. For the heavier elements, the higher oxidation states are more common and more stable against reduction.

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[1] E. I. Stiefel, *Prog. Inorg. Chem.*, 1977, **22,** 1; Proceedings of the Fifth International Conference on Chemistry and Uses of Molybdenum, *Polyhedron*, 1986, **5,** 3–606.

[2] Z. Dori, *Prog. Inorg. Chem.*, 1981, **28,** 239.

Both Mo and W have a wide variety of stereochemistries in addition to the variety of oxidation states, and their chemistry is among the most complex of the transition elements. Uranium has sometimes been classed with Mo and W in Group VIB(6), and indeed there are some valid, though often rather superficial, similarities; the three elements form volatile hexafluorides, oxide halides, and oxo anions that are similar in certain respects. There is little resemblance to the sulfur group except in regard to stoichiometric similarities (e.g., SeF_6, WF_6, SO_4^{2-}, and MoO_4^{2-}), and such comparisions are not profitable.

The oxidation states and stereochemistry are summarized in Table 19-C-1.

Molybdenum is one of the biologically active transition elements.[3] It is intimately involved in the functioning of enzymes called nitrogenases, which cause atmospheric N_2 to be reduced to NH_3 or its derivatives, in enzymes concerned with reduction of nitrate, and in still other biological processes. Several aspects of molybdenum chemistry have been vigorously studied in the past decade, principally because of their possible relation to the biological processes. We refer to this point at appropriate places in this chapter, but the main discussion of molybdenum biochemistry and related matters appears in Chapter 30.

19-C-1. The Elements

In respect to occurrence (abundance $\sim 10^{-4}\%$), metallurgy, and properties of the metals, molybdenum and tungsten are remarkably similar.

Molybdenum occurs chiefly as *molybdenite* (MoS_2) but also as molybdates such as $PbMoO_4$ (*wulfenite*) and $MgMoO_4$. Tungsten is found almost exclusively in the form of tungstates, the chief ones being *wolframite* (a solid solution and/or mixture of the isomorphous substances $FeWO_4$ and $MnWO_4$), *scheelite* ($CaWO_4$), and *stolzite* ($PbWO_4$).

The small amounts of MoS_2 in ores are concentrated by the foam flotation process; the concentrate is then converted into MoO_3 which, after purification, is reduced with hydrogen to the metal. Reduction with carbon must be avoided because this yields carbides rather than the metal.

Tungsten ores are concentrated by mechanical and magnetic processes and the concentrates attacked by fusion with NaOH. The cooled melts are leached with water, giving solutions of sodium tungstate from which hydrous WO_3 is precipitated on acidification. The hydrous oxide is dried and reduced to metal by hydrogen.

In the powder form in which they are first obtained both metals are dull

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[3] M. Coughlan, Ed., *Molybdenum and Molybdenum-Containing Enzymes;* Pergamon Press, New York, 1980; W. E. Newton and W. Otsuka, Eds., *Molybdenum Chemistry of Biological Significance;* Plenum Press, New York, 1980; T. G. Spiro, Ed., *Molybdenum Enzymes,* Interscience-Wiley, New York, 1985.

TABLE 19-C-1
Oxidation States and Stereochemistry of Molybdenum and Tungsten

Oxidation state	Coordination number	Geometry	Examples
Mo^{-II}, W^{-II}	5	?	$[Mo(CO)_5]^{2-}$
Mo^0, W^0, d^6	6	Octahedral	$W(CO)_6$,$(py)_3Mo(CO)_3$, $[Mo(CO)_5I]^-$, $[Mo(CN)_5NO]^{4-}$, $Mo(N_2)_2(diphos)_2$
Mo^I, W^I, d^5	6[a]	π Complex	$(C_6H_6)_2Mo^+$, η^5-$C_5H_5MoC_6H_6$,
	7[a]		$[\eta^5$-$C_5H_5Mo(CO)_3]_2$
	6	?	$MoCl(N_2)(diphos)_2$
Mo^{II}, W^{II}, d^4		π Complex	η^5-$C_5H_5W(CO)_3Cl$
	5	M—M quadruple bond	$Mo_2(O_2CR)_4$, $[Mo_2Cl_8]^{4-}$, $W_2Cl_4(dppe)_2$
	6	Octahedral	$Mo(diars)_2X_2$, *trans*-$Me_2W(PMe_3)_4$
	7	Capped trigonal prism	$[Mo(CNR)_7]^{2+}$
		Pentagonal bipyramidal	$[Mo(CN)_7]^{5-}$
	9	Cluster compounds	Mo_6Cl_{12}, W_6Cl_{12}
Mo^{III}, W^{III}, d^3	4	M—M triple bond	$Mo_2(OR)_6$, $W_2(NR_2)_6$
	6	Octahedral	$[Mo(NCS)_6]^{3-}$, $[MoCl_6]^{3-}$, $[W_2Cl_9]^{3-}$
	7	?	$[W(diars)(CO)_3Br_2]^+$
	8	Dodecahedral (?)	$[Mo(CN)_7(H_2O)]^{4-}$
Mo^{IV}, W^{IV}, d^2	8[a]	π Complex	$(\eta^5$-$C_5H_5)_2WH_2$,$(\eta^5$-$C_5H_5)_2MoCl_2$
	9[a]	π Complex	$(\eta^5$-$C_5H_5)_2WH_3^+$
	4	Tetrahedral	$Mo(NMe_2)_4$, Mo(S*t*-Bu)$_4$
	6	Octahedral	$[Mo(NCS)_6]^{2-}$, $[Mo(diars)_2Br_2]^{2+}$, $WBr_4(MeCN)_2$, $MoOCl_2(PR_3)_3$
	6	Trigonal prism	MoS_2
	8	Dodecahedral or square antiprism	$[Mo(CN)_8]^{4-}$, $[W(CN)_8]^{4-}$, $Mo(S_2CNMe_2)_4$, M(picolinate)$_4$
Mo^V, W^V, d^1	5	*tbp*	$MoCl_5(g)$
	6	Octahedral	$Mo_2Cl_{10}(s)$, $[MoOCl_5]^{2-}$, WF_6^-
	8	Dodecahedral or square antiprism	$[Mo(CN)_8]^{3-}$, $[W(CN)_8]^{3-}$
Mo^{VI}, W^{VI}, d^0	4	Tetrahedral	MoO_4^{2-}, MoO_2Cl_2, WO_4^{2-}, WO_2Cl_2
	5?	?	$WOCl_4$, $MoOF_4$
	6	Octahedral	MoO_6, WO_6 in polyacids, WCl_6, $Mo(OMe)_6$, $WOCl_4(s)$, MoF_6, $[MoO_2F_4]^{2-}$, MoO_3(distorted), WO_3(distorted)
	7	Distorted pentagonal bipyramid	$WOCl_4(diars)$, $K_2[MoO(O_2)_2(ox)]$
	8	?	MoF_8^{2-}, WF_8^{2-}, $[WMe_8]^{2-}$
	9	?	$WH_6(Me_2PhP)_3$

[a] Assuming η^6-C_6H_6 or η^5-C_5H_5 occupy three coordination sites.

gray, but when converted into the massive state by fusion are lustrous, silver-white substances of typically metallic appearance and properties. They have electrical conductances ~30% that of silver. They are extremely refractory; Mo melts at 2610°C and W at 3410°C.

Neither metal is readily attacked by acids. Concentrated nitric acid initially attacks molybdenum, but the metal surface is soon passivated. Both metals can be dissolved—tungsten only slowly, however—by a mixture of concentrated nitric and hydrofluoric acids. Oxidizing alkaline melts such as fused KNO_3–NaOH or Na_2O_2 attack them rapidly, but aqueous alkalis are without effect.

Both metals are inert to oxygen at ordinary temperatures, but at red heat they combine with it readily to give the trioxides. They both combine with chlorine when heated, but they are attacked by fluorine, yielding the hexafluorides, at room temperature. The metals also react on heating with B, C, N, and Si. Molybdenum disilicide ($MoSi_2$) is used in resistance heating elements, and WC is used to tip cutting tools.

Molybdenum is used in a variety of catalysts, especially combined with cobalt in desulfurization of petroleum. Another major use for both metals is in alloy steels to which they impart hardness and strength. Tungsten is also used in lamp filaments.

19-C-2. Oxides, Sulfides, Simple Oxo, and Sulfido Anions

Oxides. Many molybdenum and tungsten oxides are known. The simple ones are MoO_3, WO_3, MoO_2, and WO_2. Other, nonstoichiometric oxides have been characterized and have complicated structures.

The ultimate products of heating the metals or other compounds such as the sulfides in oxygen are the *trioxides*. They are not attacked by acids but dissolve in bases to form molybdate and tungstate solutions, which are discussed later.

Molybdenum trioxide is a white solid at room temperature but becomes yellow when hot and melts at 795°C to a deep yellow liquid. It is the anhydride of molybdic acid, but it does not form hydrates directly, although these are known (see later). Molybdenum trioxide has two polymorphs,[4] the stable α-form has a rare type of layer structure in which each molybdenum atom is surrounded by a distorted octahedron of oxygen atoms.

Tungsten trioxide is a lemon yellow solid (mp 1200°C); it has a slightly distorted form of the cubic rhenium trioxide structure (Fig. 19-D-1).

Molybdenum(IV) oxide (MoO_2), is obtained by reducing MoO_3 with hydrogen or NH_3 below 470°C (above this temperature reduction proceeds to the metal) and by reaction of molybdenum with steam at 800°C. It is a brown-violet solid with a coppery luster, insoluble in nonoxidizing mineral acids but soluble in concentrated nitric acid with oxidation of the molybdenum to Mo^{VI}.

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[4] E. M. Carron III *et al., Inorg. Chem.*, 1987, **26,** 370.

The structure is similar to that of rutile but so distorted that strong Mo—Mo bonds are formed. Tungsten dioxide is similar. Mo—Mo and W—W distances are 2.51 and 2.49 Å.

Although older literature describes simple oxides in intermediate oxidation states [e.g., Mo_2O_5 and $MoO(OH)_3$], these are apparently not genuine. There is, however, a large number of oxides of composition MO_x $(2 < x < 3)$ obtainable by simply heating MoO_3 with Mo at 700°C or WO_3 with W at 1000°C or by heating the trioxides in a vacuum. The structures of these intensely blue or purple solids are varied. One important structural class are the *shear structures,* an example of which is shown in Fig. 19-C-1. The principle on which these are built is that beginning with a structure of composition MoO_3 in which every MoO_6 octahedron shares every corner (but no edges) with neighboring octahedra, edge sharing is systematically introduced. In this way phases of compositions M_nO_{3n-1} (e.g., M_8O_{23} in the example shown), M_nO_{3n-2} (e.g., $W_{20}O_{58}$), and so on, are obtained.

There are also lower oxides in which some Mo atoms are in pentagonal bipyramidal coordination (e.g., Mo_5O_{14} and $W_{18}O_{49}$) or tetrahedral coordination (e.g., Mo_4O_{11}).

Mixed oxide–hydroxide materials, called *blue oxides,* are obtained by reduction of acidified solutions of molybdates or tungstates (or suspensions of MO_3) with Sn^{II}, SO_2, and so on. Because they are noncrystalline, the structures are not known and the cause of the color is uncertain. They may resemble the heteropoly blues to be discussed later.

On fusion of MoO_3 or WO_3 with alkali or alkaline earth oxides, mixed oxide systems are obtained. These consist so far as is known, of infinite chains or rings of MO_6 octahedra, and are unrelated to the aqueous molybdates and tungstates.

Tungsten Bronzes. The reduction of sodium tungstate with hydrogen at red heat gives a chemically inert substance with a bronzelike appearance.

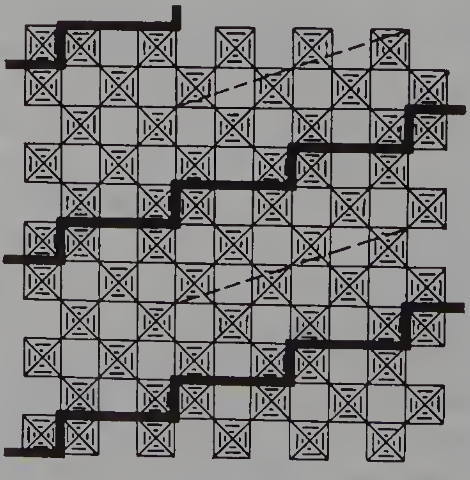

FIG. 19-C-1. One plane of the idealized Mo_8O_{23} structure. The shear planes that disturb the otherwise perfect checkerboard arrangement of MoO_6 octahedra sharing only corners are shown by heavy lines. The dashed lines outline the true unit cell.

Similar materials are obtained by vapor phase reduction of WO_3 with alkali metals.

The tungsten bronzes are nonstoichiometric substances of general formula $M^I_nWO_3$ ($0 < n \leqslant 1$). The colors vary greatly with composition from golden yellow for $n \approx 0.9$ to blue violet for $n \approx 0.3$. Tungsten bronzes with $n > 0.3$ are extremely inert and have semimetallic properties, especially metallic luster, and good electrical conductivity in which the charge carriers are electrons. Those with $n < 0.3$ are semiconductors. They are insoluble in water and resistant to all acids except hydrofluoric, and they can be oxidized by oxygen in the presence of base to give tungstates(VI):

$$4NaWO_3 + 4NaOH + O_2 \longrightarrow 4Na_2WO_4 + 2H_2O$$

Structurally the sodium tungsten bronzes may be regarded as defective M^IWO_3 phases having the perovskite structure. In the defective phase $M^I_nWO_3$ there are $(1 - n)$ W^{VI} atoms, and $(1 - n)$ of the Na sites of the pure $NaWO_3$ phase are unoccupied. It appears that completely pure $NaWO_3$ has not been prepared, although phases with sodium enrichment up to perhaps $n \sim 0.95$ are known. The cubic structure collapses to rhombic and then triclinic for $n < \sim 0.3$. In the limit of $n = 0$ we have, of course, WO_3, which is known to have a triclinically distorted ReO_3 structure (Fig. 19-D-1). The cubic ReO_3 structure is the same as the perovskite structure with all the large cations removed. Thus the actual range of composition of the tungsten bronzes is approximately $Na_{0.3}WO_3$–$Na_{0.95}WO_3$.

The semimetallic properties of the tungsten bronzes are associated with the fact that no distinction can be made between W^V and W^{VI} atoms in the lattice, all W atoms appearing equivalent. Thus the n "extra" electrons per mole (over the number for WO_3) are distributed throughout the lattice, delocalized in energy bands somewhat similar to those of metals.

Sulfides. The MS_2 and MS_3 compounds are those of importance, although others, such as hydrated Mo_2S_5 (precipitated from Mo^V solutions), anhydrous Mo_2S_5 and a few others (Mo_2S_3, MoS_4) are known.

Molybdenum disulfide (MoS_2) occurs in nature as molybdenite, the most important ore of molybdenum. It can be prepared by direct combination of the elements, by heating molybdenum(VI) oxide in hydrogen sulfide, or by fusing molybdenum(VI) oxide with a mixture of sulfur and potassium carbonate. It is the most stable sulfide at higher temperatures, and the others that are richer in sulfur revert to it when heated in a vacuum. It dissolves only in strongly oxidizing acids such as aqua regia and boiling concentrated sulfuric acid. Chlorine and oxygen attack it at elevated temperatures giving $MoCl_5$ and MoO_3, respectively.

Molybdenum disulfide has a structure built of close-packed layers of sulfur atoms stacked to create trigonal prismatic interstices that are occupied by Mo atoms. The stacking is such as to permit easy slippage of alternate layers; thus MoS_2 has mechanical properties (lubricity) similar to those of graphite. Tungsten disulfide is similar.

Brown hydrous MoS_3, obtained on passing H_2S into slightly acidified solutions of molybdates, dissolves on digestion with alkali sulfide solution to give brown-red thiomolybdates (see later).

Finally note that the sulfides, MoO_3, and compounds such as $WO(P_2O_7)$ that have layer structures can, on reduction, intercalate cations or solvent molecules.[5a]

Simple Molybdates[5b] and Tungstates. Defined as those containing only the simple MO_4^{2-} ions, they can be obtained from solutions of MO_3 in aqueous alkali. The MO_4^{2-} ions persists as such in basic solution. Although both molybdates and tungstates can be reduced in solution (see later), they lack the powerful oxidizing property so characteristic of chromates(VI). The normal tungstates and molybdates of many other metals can be prepared by metathetical reactions. The alkali metal, ammonium, magnesium, and thallous salts are soluble in water, whereas those of other metals are nearly all insoluble.

When solutions of molybdates and tungstates are made weakly acidic, polymeric anions are formed, but from more strongly acid solutions substances often called molybdic or tungstic acid are obtained. At room temperature the yellow $MoO_3 \cdot 2H_2O$ and the isomorphous $WO_3 \cdot 2H_2O$ crystallize, the former very slowly. From hot solutions, monohydrates are obtained rapidly. These compounds are oxide hydrates. $MoO_3 \cdot 2H_2O$ contains sheets of MoO_6 octahedra sharing corners and is best formulated as $[MoO_{4/2}O(H_2O]\cdot H_2O$ with one H_2O bound to Mo, the other hydrogen bonded in the lattice.

The discrete $[Mo_2O_7]^{2-}$, analogous to the dichromate ion, has been obtained by addition of $[n\text{-}Bu_4N]OH$ to a solution of $[n\text{-}Bu_4N]_4Mo_8O_{26}$ in CH_3CN. It retains its structure in organic solvents, but on addition of small cations it is converted to $[Mo_7O_{24}]^{6-}$. Other compounds with the composition $M_2^IMo_2O_7$ contain polymeric anions. An example is the commercially important $(NH_4)_2Mo_2O_7$, which has an infinite polymer of linked MoO_6 octahedra and MoO_4 tetrahedra, as shown in Fig. 19-C-2.

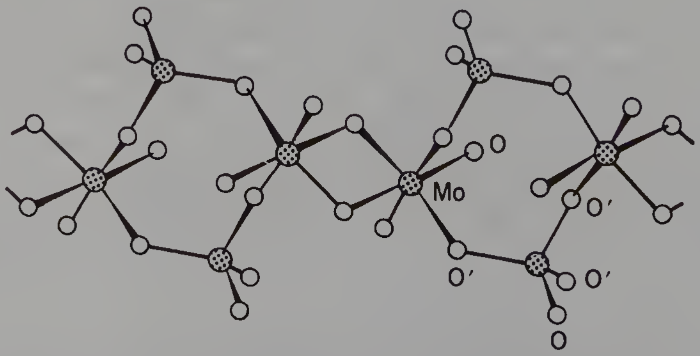

FIG. 19-C-2. The polymeric anion present in $(NH_4)_2Mo_2O_7$.

[5a] See N. Kinomura *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 609; R. Schöllhorn *et al.*, *Inorg. Chem.*, 1987, **26**, 1805.

[5b] G. A. Tsigdinos and F. W. Moore, Bulletin of the Climax Molybdenum Co., January 1981.

Thiomolybdates and Thiotungstates. The perthio ions (MS_4^{2-}) have been long known and well characterized. They show marked ability to serve as ligands, most commonly bidentate (Section 13-16), and are important starting materials for preparation of many of the more elaborate thio complexes to be discussed later. In addition, the mixed thio/oxo ions MOS_3^{2-} and $MO_2S_2^{2-}$ are known for both metals as well as the MoO_3S^{2-} ion. The MSe_4^{2-} ions are also known.

19-C-3. Isopoly and Heteropoly Acids and Salts[6]

A prominent feature of the chemistry of molybdenum and tungsten is the formation of numerous polymolybdate(VI) and polytungstate(VI) acids and their salts. Vanadium(V), Nb^V, Ta^V, and U^{VI} show comparable behavior, but to a more limited extent.

The poly acids of molybdenum and tungsten are of two types: (*a*) the *isopoly acids* and their related anions, which contain only molybdenum or tungsten along with oxygen and hydrogen, and (*b*) the *heteropoly acids* and anions, which contain one or two atoms of another element in addition to molybdenum or tungsten, oxygen, and hydrogen.

During the past decade there has been a resurgence of interest in this area for three reasons: (1) X-ray crystallography can now cope with such large structures efficiently; (2) the use of ^{17}O nmr provides direct information on solution structures[7]; and (3) the relationship of these species to metal oxide-type catalysts, and even the actual use of some polyoxoanions as catalysts, broadens the base of interest in them.

It is to be noted that while many structures that have been determined crystallographically apparently persist in solution, this is not likely to always be true and it can never be taken for granted. There are also many problems concerning the formation and relative stabilities of these substances. The polyanions are built primarily of MO_6 octahedra, but they are prepared by starting with the tetrahedral MO_4^{2-} ions. Moreover, only certain metals (e.g., Mo and W particularly, but not Cr) form polyanions. Some information bearing on these points is available. Let us consider the initial steps leading to isopolymolybdates.

In strongly basic solution Mo^{VI} is present only as MoO_4^{2-}. On addition of acid, the following protonation equilibria are established:

	K	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	
$MoO_4^{2-} + H^+ \overset{K_1}{\rightleftharpoons} HMoO_4^-$	$10^{3.7}$	20	140	(19-C-1)
$HMoO_4^- + H^+ + 2H_2O \overset{K_2}{\rightleftharpoons} Mo(OH)_6$	$10^{3.7}$	-49	-92	(19-C-2)

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[6] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, 1983; V. W. Day and W. G. Klemperer, *Science*, 1985, **228**, 533.

[7] W. G. Klemperer *et al.*, *Inorg. Chem.*, 1985, **24**, 1027.

It might be considered surprising that K_2 is as large as K_1, especially since the incorporation of two water molecules should cause a very unfavorable entropy change, as indeed it does. The ΔH and ΔS values for the first protonation are perfectly normal for a reaction of its type. The high value of K_2 is due to the large negative enthalpy change, and this may be attributed to the formation of two new Mo—O bonds while the number of O—H bonds is maintained (remember that H^+ belongs to H_3O^+). From these data we can see why the reaction

$$2HMoO_4^- = Mo_2O_7^{2-} + H_2O \tag{19-C-3}$$

is not observed, even though the analogous reaction is very important for Cr^{VI}.

It is also remarkable that no polynuclear Mo^{VI} species containing fewer than seven molybdenum atoms is observed in solution. In other words, in addition to these two equilibria, the system is described by

$$7MoO_4^{2-} + 8H^+ = Mo_7O_{24}^{6-} + 4H_2O \tag{19-C-4}$$

together with, at more acid pH's,

$$Mo_7O_{24}^{6-} + 3H^+ + HMoO_4^- = Mo_8O_{26}^{4-} + 2H_2O \tag{19-C-5}$$

The absence of any detectable amounts of polynuclear species between the mononuclear ones and $Mo_7O_{24}^{6-}$ may be understood as follows. In view of the large value for K_2, $Mo(OH)_6$ is present in concentrations less than that of $HMoO_4^-$ by only a factor of $K_2[H^+]$. Thus reactions 19-C-6

$$\begin{gathered}
Mo(OH)_6 + HMoO_4^- = (HO)_5MoOMoO_3^- + H_2O \\
(HO)_5MoOMoO_3^- + HMoO_4^- = (HO)_4Mo(OMoO_3)_2^{2-} + H_2O \\
\vdots \\
(HO)Mo(OMoO_3)_5^{5-} + HMoO_4^- = Mo(OMoO_3)_6^{6-} + H_2O \\
Mo(OMoO_3)_6^{6-} = Mo_7O_{24}^{6-}
\end{gathered} \tag{19-C-6}$$

can compete effectively with reaction 19-C-3. The species $Mo(OMoO_3)_6^{6-}$, with six MoO_4 tetrahedra, each attached through an oxygen atom to the central Mo atom, can rearrange internally to afford the final $Mo_7O_{24}^{6-}$ structure, which consists entirely of octahedra. Of course such a rearrangement may take place partially at earlier stages, and the extent of protonation of any species can vary, so the foregoing should not be taken literally. For tungsten[8a] in the pH range 5 to 7.8, the equilibria involve WO_4^{2-}, $W_6O_{20}(OH)_2^{6-}$, $W_7O_{24}^{6-}$, $HW_7O_{24}^{5-}$ and $H_2W_{12}O_{42}^{10-}$.

In addition to the species consisting of only molybdenum or only tungsten,

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[8a] J. J. Cruywagen and I. F. J. van der Merwe, *J. Chem. Soc. Dalton Trans.*, **1987,** 1701.

there are mixed anions, of both iso- and heteropoly types in which another metal, most commonly vanadium, is present in place of one or several of the Group VIB(6) metal atoms.[8b]

Isopolymolybdates and -Tungstates. These are broadly similar in modes of preparation, general properties, and in being built up almost entirely by the condensation of MO_6 octahedra through sharing of vertices or edges, but not faces. However, they differ as far as detailed compositions and structures go. Only one imporant species, $[M_6O_{19}]^{2-}$, is common to both series, although $[Mo_6O_{19}]^{2-}$ appears to exist only in solids but not in solution. Figure 19-C-3 shows some important structures in a conventional, stylized way. It should be noted that the octahedra are actually not at all regular. For oxygen atoms bonded to only one metal atom the M—O bond lengths are ~1.70 Å, while the M—O—M bond lengths are ~1.90 Å and any deeply buried oxygen atoms, such as the central one in $[M_6O_{19}]^{2-}$, form very long bonds, ~2.30 Å.

An important structure that does not consist entirely of MO_6 octahedra is the α-$[Mo_6O_{26}]^{4-}$ structure shown in Fig. 19-C-4. This structure can be regarded as consisting of a central ring, or crown, of six edge-sharing distorted octahedra capped by two tetrahedral MoO_4 units. The α and β structures (Figs. 19-C-3 and 19-C-4) can coexist in solution, where the equilibrium distribution and the products precipitated depend strongly on the accompanying cations. Crystalline compounds[9] containing pure α or pure β isomers can be obtained, although in solution they interconvert rapidly by an intramolecular pathway. The dynamic properties of the α-$[Mo_8O_{26}]^{4-}$ structure have been partly elucidated by ^{17}O nmr studies[10] of the Mo_8 ion itself and derivatives thereof in which one or both of the capping MoO_4^{2-} tetrahedra are replaced by isostructural units such as $PhAsO_3^-$, as indicated in Fig. 19-C-4(b).

The sort of mixed species just discussed is but one type in this relatively new branch of polyoxoanion chemistry. This new area is of interest because of its potential relationship to catalysis by metal oxide surfaces. Besides the derivatives of the α-$[Mo_8O_{26}]^{4-}$ ion just mentioned, there are others such as $[(Me_2As)Mo_4O_{14}OH]^{2-}$, easily prepared by acidification of a mixture of MoO_4^{2-} and $Me_2AsO_2^-$ ions, and $[MePMo_5O_{21}]^{4-}$. The structures of these two are shown in Fig. 19-C-5. The different products formed with MeP and PhAs may have a steric basis. Apparently the smaller, buckled Mo_5O_{21} ring, formed by a combination of both edge and corner sharing, gives smaller sets of three O atoms, better suited to the formation of the RPO_3 group, whereas the Mo_6O_{24} unit provides larger triangles of oxygen atoms that better fit the larger As atom.

More complex systems can be made by reaction of organometal and organometalloidal halides such as $RSnCl_3$ or $RAsCl_2$, with fragments of the Keggin ion (see Fig. 19-C-6), the latter being, for example, $[PW_{11}O_{39}]^{7-}$ or

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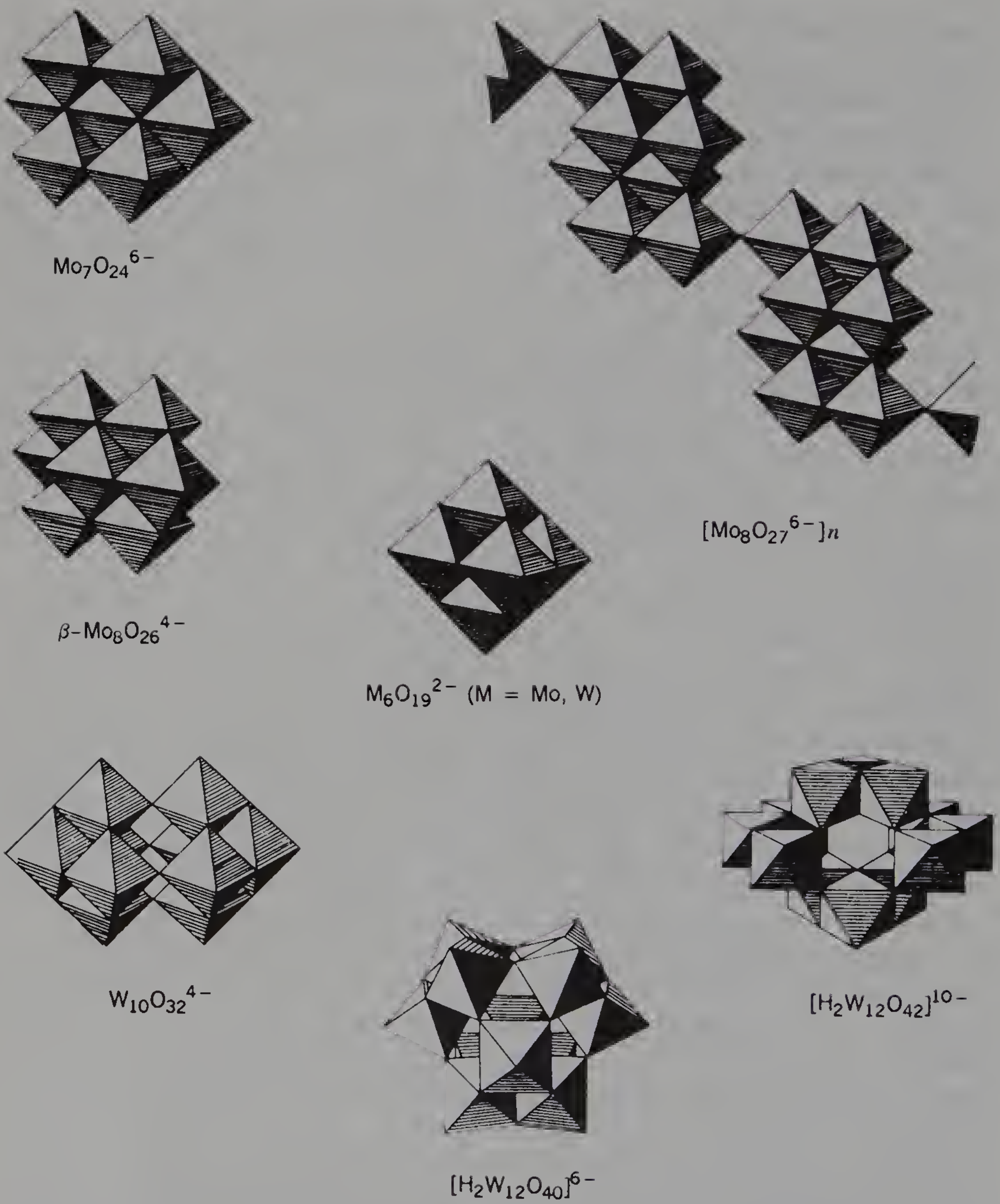
[8b] R. G. Finke *et al., J. Am. Chem. Soc.*, 1986, **108,** 2947.

[9] A. J. Wilson *et al., Acta Crystallogr.*, 1984, **C40,** 2027.

[10] W. G. Klemperer *et al., J. Am. Chem. Soc.*, 1985, **107,** 6941.



$Mo_7O_{24}^{6-}$

$[Mo_8O_{27}^{6-}]n$

β-$Mo_8O_{26}^{4-}$

$M_6O_{19}^{2-}$ (M = Mo, W)

$W_{10}O_{32}^{4-}$

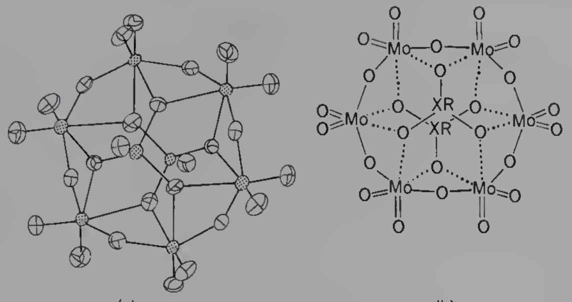
$[H_2W_{12}O_{42}]^{10-}$

$[H_2W_{12}O_{40}]^{6-}$

FIG. 19-C-3. Some of the important isopoly anion structures. Structures known only for molybdates or tungstates are shown at top and bottom. The $[M_6O_{19}]^{2-}$ structure known for both is in the center.

$[SiMo_{11}O_{39}]^{8-}$. The entering RSn or RAs unit binds to three oxygen atoms replacing the missing MoO or WO groups. If an (η-C_5H_5)$TiCl_3$ group is used the (η-C_5H_5)Ti unit is introduced. Finally, some formylated species with Mo—O—CHO and Mo—OCH_2O— groups have been made.

Although the preparative procedures for isopoly anions have traditionally been based exclusively on condensations occurring upon acidification of aqueous



(a) (b)

FIG. 19-C-4. Two representations of the α-$[Mo_8O_{26}]^{4-}$ structure. (a) The crystallographically determined stucture. (b) A schematic drawing emphasizing the variable nature of the capping XR groups.

MO_4^{2-} solutions, it has recently been found that the β-$[Mo_8O_{26}]^{4-}$ and $[Mo_6O_{19}]^{2-}$ ions can be obtained from dioxomolybdenum(VI) starting materials in completely anhydrous conditions. Treatment of compounds such as $(Et_2NCS_2)_2MoO_2$ with $Ph_3P{=}CHR$ compounds induces oxygen atom transfers to form MoO_3 units that condense to the polyanions.[11]

Heteropoly Anions. These can be formed either by acidification of solutions containing the requisite simple anions, or by introduction of the heteroelement after first acidifying the molybdate or tungstate:

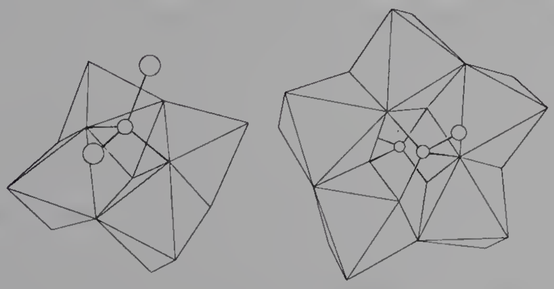
$$HPO_4^{2-} + MoO_4^{2-} \xrightarrow{H^+,\ 25°C} [PMo_{12}O_{40}]^{3-}$$

$$WO_4^{2-} \xrightarrow{H^+ \text{ to pH } = 6} \xrightarrow{Co^{2+},\ 100°C} [Co_2W_{11}O_{40}H_2]^{8-}$$

Interconversions are also possible, namely,

$$[P_2W_{18}O_{62}]^{6-} \xrightarrow{HCO_3^-,\ 25°C} [P_2W_{17}O_{61}]^{10-}$$

Many of the heteropoly anions are quite robust toward excess acid and may be protonated to give the *heteropoly acids* both in solution and as crystalline hydrates.



(a) (b)

FIG. 19-C-5. The structures of the (a) $[Me_2AsMo_4O_{14}OH]^{2-}$ and (b) $[MePMo_5O_{21}]^{4-}$ ions.

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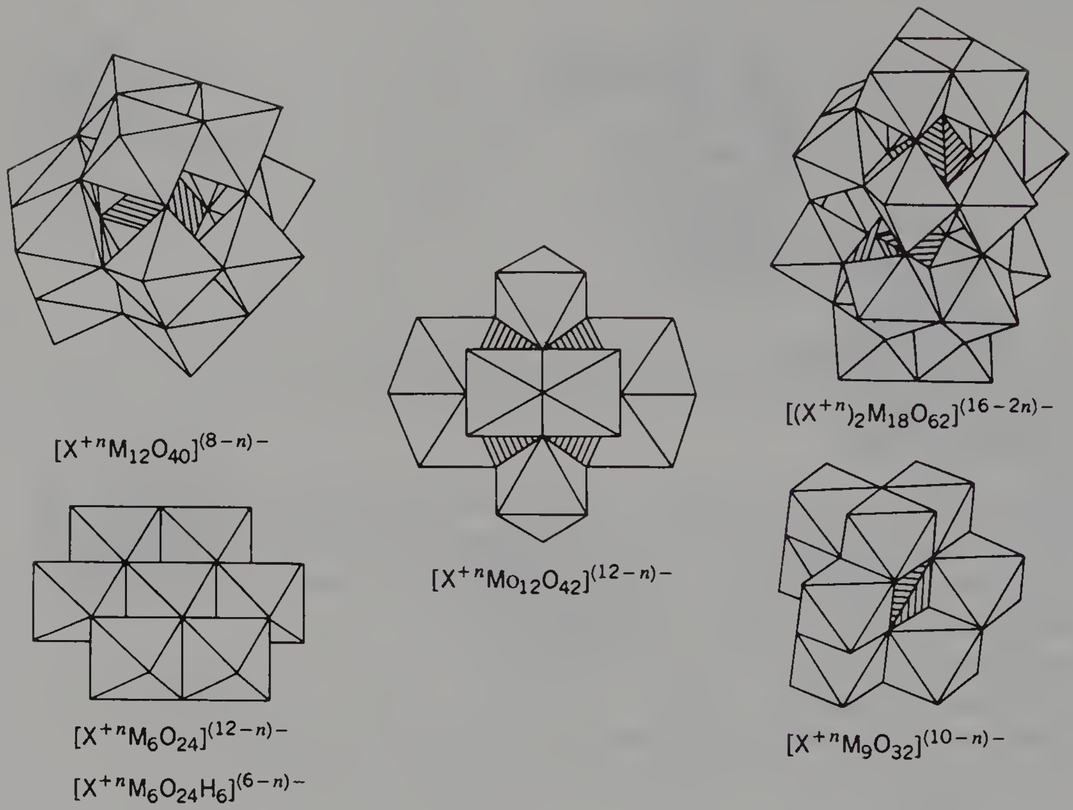
[11] H. Arzoumanian *et al.*, *J. Organomet. Chem.*, 1985, **295,** 343.



$[X^{+n}M_{12}O_{40}]^{(8-n)-}$

$[X^{+n}Mo_{12}O_{42}]^{(12-n)-}$

$[(X^{+n})_2M_{18}O_{62}]^{(16-2n)-}$

$[X^{+n}M_6O_{24}]^{(12-n)-}$

$[X^{+n}M_6O_{24}H_6]^{(6-n)-}$

$[X^{+n}M_9O_{32}]^{(10-n)-}$

FIG. 19-C-6. Structures of important types of heteropolymolybdate and -tungstate ions with "enshrouded" heteroatoms. The general formula of each is shown below it.

This is a truly enormous class of compounds, and we note here only the main types. The largest and best known group is composed of those with the hetero atom(s) enshrouded by a cage of MO_6 octahedra. Table 19-C-2 lists most of those that have known structures. Six of the important structures that predominate in this group are shown schematically in Fig. 19-C-6.

The $[X^{+n}M_{12}O_{40}]^{(8-n)-}$ structure is often called the *Keggin structure* after its discoverer. It has full tetrahedral (T_d) symmetry and although very compact, it accommodates a variety of heterocations that differ considerably in size, as Table 19-C-2 shows. There are many heteropolyanions with structures that can be regarded as modifications of the Keggin structure. One such modification is obtained by twisting one of the four sets of three octahedra in the Keggin structure by 60° and reattaching all the same corners. This spoils the T_d symmetry, leaving only one threefold axis, that around which the 60° rotation was made. This "isomeric" Keggin structure differs little in stability from the true Keggin structure, and the anions $[XW_{12}O_{40}]^{4-}$ with X = Si and Ge, for example, can be isolated in either form by varying the conditions of acidification in the preparation.

The structure of the $[(X^{+n})_2M_{18}O_{62}]^{(16-2n)-}$ ion (sometimes called the Daw-

TABLE 19-C-2
Some Heteropoly Anions with Buried Heteroatoms

Formula type	Central group	M = Mo	M = W
$X^{+n}M_{12}O_{40}^{(8-n)-}$	XO_4	Si^{IV}, Ge^{IV}, P^V, As^V, Ti^{IV}, Zr^{IV}	B^{III}, Si^{IV}, Ge^{IV}, P^V, As^V, Al^{III}, Fe^{III}, Co^{II}, Co^{III}, Cu^I, Cu^{II}, Zn^{II}, Cr^{III}, Mn^{IV}, Te^{IV}[a], Ga^{III}[b]
$X_2^{+n}M_{18}O_{62}^{(16-2n)-}$	XO_4	P^V, As^V	P^V, As^V
$X_2^{+n}Z_4^{+m}M_{18}O_{70}H_4^{(28-2n-4m)-}$	XO_4		X = P^V, As^V Z = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}
$X^{+n}M_9O_{32}^{(10-n)-}$	XO_6	Mn^{IV}, Ni^{IV}	
$X^{+n}M_6O_{24}^{(12-n)-}$	XO_6	Te^{VI}, I^{VII}	Ni^{IV}, Te^{VI}, I^{VII}
$X^{+n}M_6O_{24}H_6^{(6-n)-}$	XO_6	Al^{III}, Cr^{III}, Co^{III}, Fe^{III}, Ga^{III}, Rh^{III}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}	Ni^{II}
$X_2^{+n}M_{10}O_{38}H_4^{(12-2n)-}$	XO_6	Co^{III}	
$X^{+n}M_{12}O_{42}^{(12-n)-}$	XO_{12}	Ce^{IV}, Th^{IV}, U^{IV}	

[a] Existence of anion, or membership of series, requires confirmation.
[b] Closely related 11-tungstate.

son structure) is closely related to that of the Keggin ion. If three adjacent corner-linked MO_6 octahedra are removed from the Keggin structure, to leave a fragment with a set of three octahedra over a ring of six, we have one-half of this M_{18} anion. These two halves are then linked by corner sharing as shown in Fig. 19-C-6. Actually there are two such ways to link the halves. The way shown gives a structure of D_{3h} symmetry, but by rotating one half 60° relative to the other an isomer with D_{3d} symmetry is obtained; both occur.

The $[X^{+n}M_6O_{24}]^{(12-n)-}$ ion, its protonated form $[X^{+n}M_6O_{24}H_6]^{(6-n)-}$, and the $[X^{+n}M_9O_{32}]^{(10-n)-}$ ion are among those in which the heteroatom finds itself in an octahedron of oxygen atoms. The latter is known for only two cases, namely, those in which $X^{+n} = Mn^{+4}$ or Ni^{+4} and M = Mo, but these are of interest because the hetero ions are examples of unusual oxidation states stabilized by the unusual "ligand."

The $[X^{+n}M_{12}O_{42}]^{(12-n)-}$ ion provides an icosahedral set of 12 oxygen ligands for the hetero cation. In addition to Ce^{4+}, Th^{4+}, and U^{4+}, which have already been found in such a structure, a number of other M^{4+} ions from the lanthanides and actinides can probably be expected to form such anions.

Just as the heteropoly (and isopoly) ions are built up by acidification of solutions of the mononuclear oxo ions, the action of strong base on the heteropoly ions (and on the isopoly ions) will eventually degrade them entirely to mononuclear anions. There are well-defined steps in both processes, and intermediates can be observed and even isolated in crystalline compounds. Examples of spcies that have been well established are fragments of Keggin anions, especially those in which formal loss of "MO" has occurred, for example, $[PW_{11}O_{39}]^{7-}$ or $[SiMo_{11}O_{39}]^{8-}$. There are also the "enneatungsto" compounds, such as $Na_{10}SiW_9O_{34}\cdot 18H_2O$, that are thought to contain half-Dawson structures, but this lacks proof. The $[P_2Mo_5O_{23}]^{6-}$ ion is an example of one of the intermediates that has been characterized structurally. It consists of a cyclic assemblage of MoO_6 octahedra with four edge junctions and one corner junction, and there is a PO_4 tetrahedron fused over the hole on each side. Another example of this type of heteropoly anion in which the heteroatoms are exposed rather than buried is the $[As_2Mo_6O_{26}]^{6-}$ ion, whose structure has been determined by ^{17}O nmr. This structure is much like the $[X^{+n}M_6O_{24}]^{(12-n)-}$ structure except that the central, octahedrally coordinated X^{+n} ion is replaced by two AsO^{+3} groups, one above and the other below the central cavity in the six-membered ring of MoO_6 octahedra.

Heteropoly Blues. Anions of the Keggin and Dawson types can undergo reduction to blue mixed-valence species without loss of structure. These reduction products are formed rapidly and reversibly at least to the brown-violet stage of six-electron reduction, but further reduction may involve isomerizations that are irreversible. The question of whether the added electrons enter delocalized orbitals or tend to be localized on individual Mo or W atoms has received considerable attention. The role of the heteroatoms is in general insignificant. Even when these are transition metal ions, as in $[Co^{II}W_{12}O_{40}]^{6-}$ and $[Fe^{III}W_{12}O_{40}]^{5-}$, the epr spectra of doubly reduced blues obtained from them continue to show the signals characteristic of the Co^{II} and Fe^{III} species present prior to reduction.

The present consensus seems to be that in the singly reduced species the electron is weakly trapped at Mo^{5+} or W^{5+} centers but thermally mobile, whereas greater delocalization seems to occur in the more highly reduced species.[12] There is, however, one marked exception to this, namely, the $[H_2W_{12}O_{40}]^{12-}$ ion, which is obtained by six-electron reduction of the metatungstate ion (Fig. 19-C-3), $[H_2W_{12}O_{40}]^{6-}$. It appears that all six electrons enter one W_3O_{13} subunit converting it to a metal atom cluster like that in the $[W_3O_4]^{4+}$(aq) ion (see Section 19-C-6). The Keggin structure remains otherwise intact.[13]

Other Polyoxo Ions. In addition to the traditional iso- and heteropoly anions just discussed, recent work has revealed that others, many of them very large, with crown-type structures can be obtained. Examples of these are the $[NaP_5W_{30}O_{110}]^{14-}$ ion, which has a double crown structure with fivefold

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[12] R. I. Buckley and R. J. H. Clark, *Coord. Chem. Rev.* 1985, **65,** 167; G. B. Jameson *et al., J. Am. Chem. Soc.,* 1985, **107,** 1771.

[13] J. P. Launay *et al., Inorg. Chem.,* 1980, **19,** 2933.

symmetry,[14] $[H_7P_8W_{48}O_{184}]^{33-}$, which has a double crown structure with fourfold symmetry,[15] and two structurally similar crown species of molybdenum, $[Mo_{36}O_{112}]$,[8-16] and $Mo_{36}O_{110}(NO)_4(H_2O)_{14}$.[17] The last one is the only confirmed example of a nitrosyl polyacid or polyanion species.

19-C-4. Halides

The halides are listed in Table 19-C-3. Those containing metal atom clusters or presumed to contain Mo—Mo quadruple bonds are discussed in Sections 19-C-9 and 19-C-7, respectively. Those with metal oxidation states III to VI, are discussed here.

TABLE 19-C-3
Halides of Molybdenum and Tungsten[a]

III	IV	V	VI[b]
MoF_3 Yellow brown, nonvolatile	MoF_4 Lt. green nonvolatile	$(MoF_5)_4$ Yellow, mp 67°C, bp 213°C	MoF_6 Colorless, mp 17.5°C, bp 35.0°C
	WF_4 Red brown, nonvolatile	$(WF_5)_4$ Yellow, disprop. 25°C	WF_6 Colorless, mp 2.3°C, bp 17.0°C
$MoCl_3$ Dark red	$MoCl_4$[c] Dark red	$(MoCl_5)_2$ Black, mp 194°C, bp 268°C	
WCl_3 Red	WCl_4 Black	$(WCl_5)_2$ Green black, mp 242°C, bp 286°C	WCl_6 Blue black, mp 275°C, bp 346°C
$MoBr_3$ Green mp 977°C	$MoBr_4$ Black		
WBr_3 Black	WBr_4 Black	WBr_5 Black	
MoI_3 Black mp 927°C			

[a] For halides of Mo^{II} and W^{II} see Sections 19-C-8 and 19-C-10.

[b] Mixed halides, for example, WF_5Cl, WCl_5F, and WCl_4F_2 are also known.

[c] $MoCl_4$ exists in three forms.

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[14] Y. Jeannin *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 2662.

[15] R. Contant and A. Teze, *Inorg. Chem.*, 1985, **24**, 4610.

[16] B. Krebs and I. Paulat-Böschen, *Acta Crystallogr.*; 1982, **B38**, 1710.

[17] S. Zhang *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 835.

Hexahalides. The MF_6 compounds are volatile, colorless liquids, readily hydrolyzed. Molybdenum hexafluoride is more reactive, less stable, and a considerably stronger oxidizing agent. The existence of $MoCl_6$ is very doubtful, but WCl_6 and WBr_6 are both obtained by direct halogenation of the metal. Tungsten hexachloride can be volatilized to a monomeric vapor and is soluble in liquids such as CS_2, CCl_4, EtOH, and Et_2O, whereas WBr_6, a dark blue solid, gives WBr_5 on moderate heating. Both are hydrolyzed to tungstic acid.

Pentahalides. Treatment of molybdenum carbonyl with fluorine diluted in nitrogen at −75°C gives a product of composition Mo_2F_9. The nature of this substance has not been investigated, but when it is heated to 150°C it yields the nonvolatile MoF_4 as a residue and the volatile MoF_5 condenses in cooler regions of the apparatus. Molybdenum pentafluoride is also obtained by the reactions:

$$5MoF_6 + Mo(CO)_6 \xrightarrow{25^\circ C} 6MoF_5 + 6CO$$

$$Mo + 5MoF_6 \longrightarrow 6MoF_5$$

$$Mo + F_2(\text{dilute}) \xrightarrow{400^\circ C} MoF_5$$

WF_5 is obtained by quenching the products of reaction of W with WF_6 at 800 to 1000 K. It disproportionates above 320 K into WF_4 and WF_6. Crystalline MoF_5 and WF_5 (and WOF_4, p. 822) have the tetrameric structure common to many pentafluorides (p. 558).

Molybdenum(V) and W^V chlorides are obtained by direct chlorination of the metals under proper conditions, and the solids consist of edge-sharing bioctahedra (M_2Cl_{10}) in which there are no M—M bonds (Mo—Mo = 3.84 Å; W—W = 3.81 Å); they are paramagnetic. Little is known about W^V bromide. In the vapor state Mo_2Cl_{10} is entirely or at least mainly monomeric but the structure or structures are uncertain.[18] It is soluble, and monomeric, in many organic media. It is very reactive, being hydrolyzed by water, reduced by amines to give amido complexes, and abstracting oxygen from some oxygenated solvents to give Mo═O species. Further reactions are shown in Figs. 19-C-7 and 19-C-8.

Tetrahalides. These include MoF_4 and WF_4, the former arising on disproportionation of Mo_2F_9 as noted previously, and both by reduction of the hexahalides with hydrocarbons (e.g., benzene at ~110°C). Both are nonvolatile. Molybdenum tetrachloride, which is very sensitive to oxidation and hydrolysis, exists in three forms. By the reaction

$$MoCl_5 + C_2Cl_4 \longrightarrow \alpha\text{-}MoCl_4$$

a form isomorphous with $NbCl_4$ (p. 791) is obtained. The same form, contaminated with carbon, is also obtained when $MoCl_5$ is reduced with hydrocarbons. On being heated to 250°C in the presence of $MoCl_5$, the α form changes into the high temperature β form. The α-$MoCl_4$ has partial spin

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[18] J. Brunvoll *et al., Acta Chem. Scand.,* 1984, **A38,** 115.

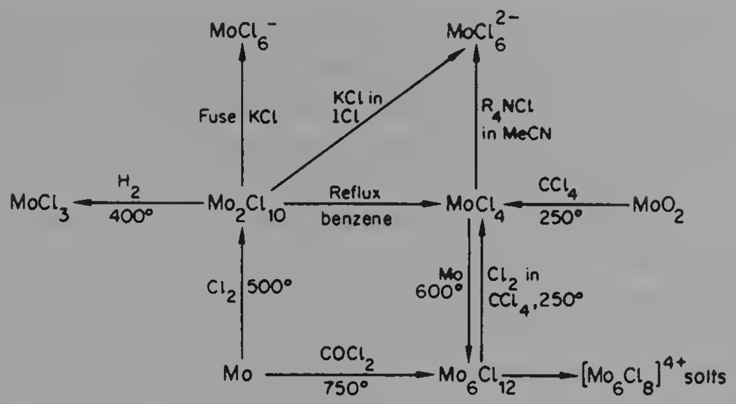

FIG. 19-C-7. Preparation of molybdenum chlorides and chloro complexes.

pairing through Mo–Mo interactions, whereas the β form has molybdenum atoms occupying selected octahedral interstices in an *hcp* array of Cl atoms, giving hexagonal arrays but with no Mo—Mo bonding (Mo—Mo = 3.67 Å)[19] The third form, obtained by treatment of MoO_2 with carbon in an N_2-borne stream of CCl_4 vapor, has a magnetic moment of ~1.9 BM and its structure is unknown.

Tungsten tetrachloride is a very useful starting material for preparing many lower-valent tungsten compounds. The best methods of preparation are

$$2WCl_6 + W(CO)_6 \xrightarrow[\text{reflux}]{C_6H_5Cl} 3WCl_4$$

$$3WCl_6 + \tfrac{1}{2}P_4 \xrightarrow[\text{tube}]{\text{sealed}} 3WCl_4 + 2PCl_3$$

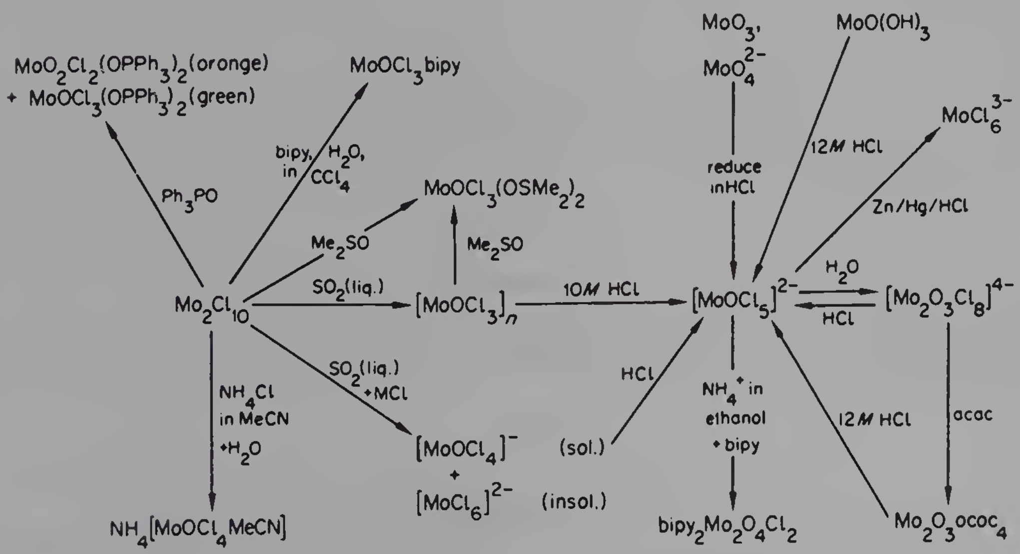

FIG. 19-C-8. Some preparations and reactions of molybdenum pentachloride and of oxomolybdenum compounds.

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[19] U. Müller, *Angew. Chem. Int. Ed. Engl.*, 1981, **20**, 692.

The method employing P_4 has the advantage of eliminating all contamination by oxohalides of tungsten, since $POCl_3$ forms preferentially with any oxygen present. Tungsten tetrachloride disproportionates at 500°C to $WCl_2 + 2WCl_5$. The tetrahalides $MoBr_4$ and WBr_4 are not well characterized.

Trihalides. These include MoF_3, $MoCl_3$, $MoBr_3$, MoI_3, WCl_3, WBr_3, and WI_3. Molybdenum trifluoride, a nonvolatile brown solid in which Mo atoms are found in octahedra of F atoms, is obtained by reaction of Mo with MoF_6 at ~400°C. Molybdenum trichloride has two polymorphs, with *hcp* and *ccp* arrays of Cl atoms and, in each case, Mo atoms in pairs of adjacent octahedral holes at a distance of 2.76 Å across a common edge. The magnetic properties confirm the expected M—M interaction. WCl_3 has an especially interesting cluster structure (Section 19-C-10).

19-C-5. Oxide Halides

These are formed by both metals in oxidation states V and VI. Some of them are notorious as unwanted by-products in the preparation of anhydrous binary halides, since the formation of M═O bonds from any O_2, H_2O, or other sources of oxygen is strongly favored thermodynamically. The established oxide halides are listed in Table 19-C-4.

Methods of preparation are varied.[20] Some of the important preparative reactions are as follows (where M represents both Mo and W):

$$\left.\begin{array}{l} M + O_2 + F_2 \\ MO_3 + F_2 \\ MOCl_4 + HF \end{array}\right\} \longrightarrow MOF_4$$

$$MoO_3 + SO_2Cl_2 \longrightarrow MoOCl_5$$

$$\begin{aligned} WO_3{\cdot}xH_2O + SO_2Cl_2 &\longrightarrow WOCl_5 \\ MoO_2 + Cl_2 &\longrightarrow MoO_2Cl_2 \\ WOX_4 + \tfrac{1}{3}Al &\longrightarrow WOX_3 + \tfrac{1}{3}AlX_3 \\ MoOCl_4 + C_6Cl_6 &\longrightarrow MoOCl_3 \\ W + O_2 + \tfrac{1}{2}xI_2 &\longrightarrow WO_2I_x \qquad (x = 1 \text{ and } 2) \end{aligned}$$

TABLE 19-C-4
Oxide Halides of Molybdenum and Tungsten[a]

V	VI	VI
	$MoOF_4$, colorless mp 97°C, bp 180°C WOF_4, colorless mp 105°C, bp 186°C	MoO_2F_2, colorless subl 270°C WO_2F_2 ?
$MoOCl_3$, green subl 100°C $WOCl_3$	$MoOCl_4$, green mp 102°C $WOCl_4$, red mp 208°C	MoO_2Cl_2, yellow volatile WO_2Cl_2
$MoOBr_3$ $WOBr_3$	$WOBr_4$, purple black	MoO_2Br_2, orange WO_2Br_2
WO_2I, blue black		WO_2I_2, dk. green

[a] Also $WOCl_3Br$ and $WOCl_2Br_2$.

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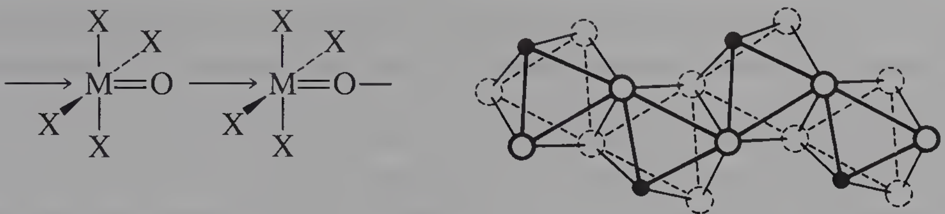
[20] See, e.g., R. H. Crabtree and G. G. Hlatky, *Polyhedron*, 1985, **4**, 521 ($WOCl_5$).



(a) (b)

FIG. 19-C-9. (a) The mode of association of MOX_4 molecules in the solid state. (b) The infinite chain structure of $MoOCl_3$, consisting of $MoOCl_5$ octahedra sharing cis pairs of Cl atoms.

The oxide halides are all rather reactive, though less so than the binary halides. Thio analogues are known for many of them. The MOX_4 species readily form adducts with neutral donors, for example, $MoOCl_5(MeCN)$. In the vapor phase the MOX_4 molecules are tetragonal pyramids, but they associate into infinite chains, Fig. 19-C-9(a), in the crystal, which lengthens the M=O bonds by ~0.08 Å.[21] All of the MOX_3 compound are crystallographically isotypic with $NbOCl_3$, but $MoOCl_3$ has a second form, shown in Fig. 19-C-9(b).

19-C-6. Halogen Containing Complexes

Homoleptic Complexes. Tungsten(V) gives the octahedral WX_6^- (X = F, Cl, and Br) species and also WF_8^{3-}; the only molybdenum(V) analogues are the fluoro complexes MoF_6^- and MoF_8^{3-}. Molybdenum(V) is prone to form oxo complexes (Section 19-C-7). The MX_6^{2-} complexes of M^{IV} are known but, again, of little importance.

For oxidation state III, molybdenum forms MoX_6^{3-} ions for X = F, Cl, and Br, but no such complex has been obtained for tungsten. Instead, there are the face-sharing bioctahedral species $W_2Cl_9^{3-}$ and $W_2Br_9^{3-}$ in which strong W≡W triple bonds are formed. The $Mo_2X_9^{3-}$ analogues exist, but they have relatively long Mo—Mo distances with only partial bonding and are paramagnetic. The $W_2X_9^{3-}$ species can be oxidized to $W_2X_9^{2-}$, which have one unpaired electron.

Mixed Ligand Complexes. Complexes of the type $[MX_nL_{6-n}]$ are fairly numerous. The pentahalides can form adducts (MX_5L) with many donors, although with amines or RCN they more commonly react to give M^{IV} complexes:

$$MCl_{5\,or\,6} + \left\{ \begin{matrix} py \\ bipy \\ RCN \end{matrix} \right\} \longrightarrow \left\{ \begin{matrix} MCl_4py_2 \\ MCl_4bipy \\ MCl_4(RCN)_2 \end{matrix} \right\}$$

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[21] U. Müller, *Acta Crystallogr.*, 1984, **C40**, 951.

From these many other MX_4L_2 complexes may be obtained by ligand replacement reactions. In some cases coordination number 7 is reached, as in $MoCl_4(PMe_2Ph)_3$.

The pentachlorides react with ROH and RO^- to yield various types of alkoxo complex. Tungsten forms an extensive series of complexes that includes the paramagnetic $[M(OR)Cl_5]^-$ and $[M(OR)_2Cl_4]^-$ ions as well as the diamagnetic $W_2Cl_2(OR)_8$ and $W_2Cl_4(OR)_6$ molecules, which presumably contain octahedrally coordinated metal atoms, bridging Cl atoms, and W—W bonds. Molybdenum pentachloride reacts with alcohols and amines to give products of the types $MoCl_3(OR)_2$ and $MoCl_3(NRR')_2$, which appear generally to be dinuclear with bridging chlorine atoms. The chief products of the reaction with phenols are of the type $[MoCl_2(OAr)_3]_3$. Reactions of halides with $LiNR_2$ are mentioned later in connection with M—M triple bonds.

For molybdenum(III), the $MoCl_3L_3$ complexes with L = THF or RCN are useful reactants, as is also $MoI_3(THF)_3$.[22] These molecules have meridional structures and readily undergo ligand replacement reactions with phosphines.

Another route to some MX_nL_{6-n} complexes is by oxidation of *cis*-$M(CO)_4L_2$ with Cl_2 or Br_2, for example,

$$cis\text{-}W(CO)_4(PMe_2Ph)_2 + 2Br_2 \longrightarrow WBr_4(PMe_2Ph)_2 + 4CO$$

There are also some monomeric Mo^{II} complexes, such as $MoCl_2(dmpe)_2$[23a] which can be both oxidized and reduced:

$$[MoCl_2(dmpe)_2]PF_6 \xleftarrow{AgPF_6} MoCl_2(dmpe)_2 \xrightarrow[N_2]{Na/Hg} Mo(dmpe)_2(N_2)_2$$

and $MoH(SR)(dppe)_2$,[23b] as well tungsten(II) phosphine complexes such as $WCl_2(PR_3)_4$.[23c]

19-C-7. Aqua and Oxo Complexes

Aqua Ions.[24a] Genuine aqua ions (containing only Mo and H_2O) are known only for oxidation states II and III. For Mo^{II} the aqua ion is $Mo_2^{4+}(aq)$, formed when a solution of $K_4[Mo_2(SO_4)_4]$ is treated with $Ba(CF_3SO_3)_2$ in dilute CF_3SO_3H solution. This quadruply bonded species is a powerful reducing agent but thermally stable at 25°C. The yellow $[Mo(H_2O)_6]^{3+}$ ion can be obtained by dissolving an $[MoCl_6]^{3-}$ or $[MoCl_5(H_2O)]^{2-}$ salt in aqueous CF_3SO_3H and separating the $Mo^{3+}(aq)$ ion from Cl^- ions on a cation-exchange column.

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[22] S. Y. Roh and J. W. Bruno, *Inorg. Chem.*, 1986, **25,** 3105; J. R. Dilworth and J. A. Zubieta, *J. Chem. Soc. Dalton Trans.*, **1983,** 397; F. A. Cotton and R. Poli, *Inorg. Chem.*, 1987, **26,** 1514.

[23a] N. J. Cooper *et al.*, *Inorg. Chem.*, 1986, **25,** 1880.

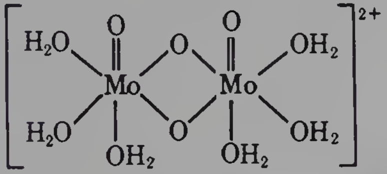
[23b] R. L. Richards *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987,** 1115.

[23c] J. M. Mayer *et al.*, *J. Am. Chem. Soc.*, 1987, **109,** 2826; G. Williamson *et al.*, *Polyhedron*, 1983, **2,** 803.

[24a] D. T. Richens and A. G. Sykes, *Comments Inorg. Chem.*, 1981, **1,** 141.

Its formulation as $[Mo(H_2O)_6]^{3+}$ is supported by its spectrum and magnetic moment (3.69 BM). The ion has been characterized by X-ray study of an alum.[24b] No tungsten analogues for these are known.

The "aqua" ions for oxidation states IV and V are actually di- or trinuclear oxo species, and Mo^{III} also forms a binculear ion that is either $[(H_2O)_4Mo(OH)_2Mo(H_2O)_4]^{4+}$ or possibly $[(H_2O)_5MoOMo(H_2O)_5]^{4+}$. The Mo^{IV} aqua ion has now been well established[25] to be $[Mo_3O_4(H_2O)_9]^{4+}$, from which (*vide infra*) numerous $Mo_3O_4^{4+}$ complexes can be derived. A similar $W_3O_4^{4+}(aq)$ ion has also been described.[26a] The Mo^V aqua ion ($Mo_2O_4^{2+}$) is diamagnetic and probably has the structure (19-C-I) in which an Mo—Mo single bond exists. Numerous complexes containing this $Mo_2O_4^{2+}$ core, and the related trans one are known and will be discussed later. The $W_2O_4^{2+}(aq)$ ion is known[26b]. There have been a number of kinetic and mechanistic studies of the reactivity and redox behavior of the $Mo_3O_4^{4+}$ ion and its complexes.[27]



(19-C-I)

Trinuclear M^{IV} Oxo Complexes. We have already mentioned the $Mo_3O_4^{4+}(aq)$ ion. The essential structure of this, shown in Fig. 19-C-10(a), can be described in three complementary ways: (1) As an M_3 triangle capped on one side, with three edge bridges on the other side and three more nonbridging ligands on each metal atom. (2) As three MO_6 octahedra sharing a common vertex and also having one edge common to each pair. (3) As two adjacent close-packed layers of ligand atoms with metal atoms occupying octahedral interstices—but moved off the centers of these interstices toward each other. Description (2) emphasizes the relationship of these M—M bonded species to the M_3O_{13} subunits in various iso- and heteropoly anion structures, such as the Keggin structure (Fig. 19-C-3), while description (3) relates this unit to the structures of mixed oxide systems such as $Zn_2Mo_3O_8$ (see Section 23-11).

From the $Mo_3O_4^{4+}$ aqua ion many complexes can be obtained by replacing some, or all of the nine outer water molecules by other ligands. Examples

[24b] M. Brorson and M. Gajhede, *Inorg. Chem.*, 1987, **26,** 2109.

[25] A. Bino *et al., Inorg. Chim. Acta,* 1985, **99,** 137 and prior references therein.

[26a] M. Segawa and Y. Sasaki, *J. Am. Chem. Soc.*, 1985, **107,** 5565.

[26b] A. G. Sykes *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 2293.

[27] A. G. Sykes *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 1397; *Inorg. Chem.*, 1986, **25,** 2566; C. Millan and H. Diebler, *Inorg. Chem.*, 1985, **24,** 3729; A. G. Sykes *et al., Inorg. Chem.*, 1985, **24,** 2950; G. P. Haight *et al., Isr. J. Chem.*, 1985, **25,** 177; R. K. Murmann *et al., Inorg. Chem.*, 1985, **24,** 1313; D. T. Richens and A. G. Sykes, *Inorg. Chem.*, 1982, **21,** 418; A. G. Sykes *et al., Inorg. Chem.*, 1981, **20,** 4.55; M. T. Paffett and F. C. Anson, *Inorg. Chem.*, 1983, **22,** 1347.

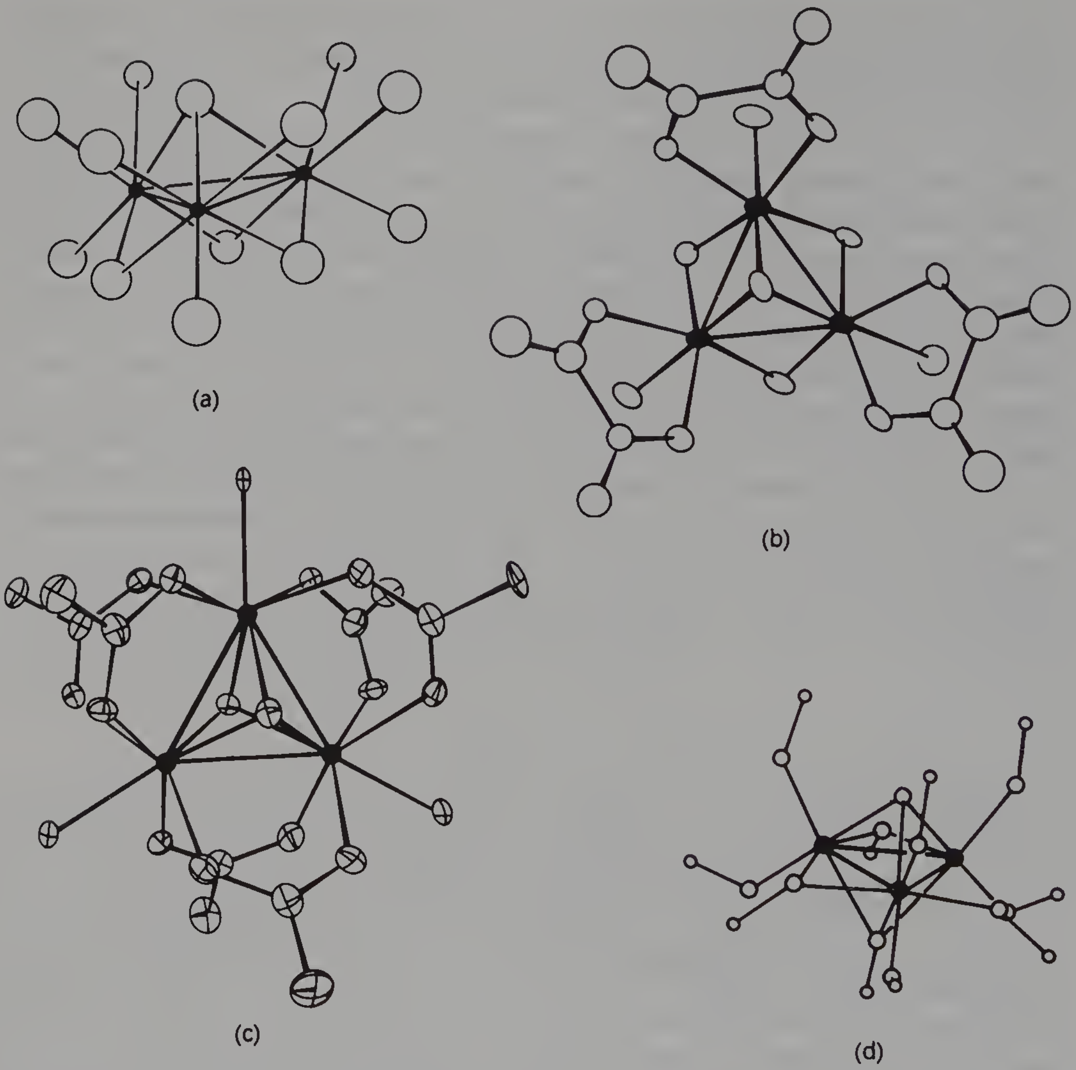


FIG. 19-C-10. Important trinuclear oxo species of Mo^{IV} and W^{IV}. (a) The basic M_3O_{13} unit. (b) The $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ ion. (c) The $[M_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ (M = Mo or W) structure. (d) The $W_3O(OR)_{10}$ type structure.

are the $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ ion, Fig. 19-C-10(b),[28] $[Mo_3O_4F_9]^{5-}$,[29] and $\{Mo_3O_4[(O_2CCH_2)_2NCH_3]_3\}^{2-}$.[30] There are some analogous tungsten complexes, for example, $[W_3O_4F_9]^{5-}$ and $[W_3O_4L_3]^{4+}$ where L = 1,4,7-triazacyclononane.[31]

A second major type of oxo trinuclear cluster is the type with two μ_3-O caps; molybdenum and tungsten form them with equal frequency.[32] They are obtained by treating $M(CO)_6$ with a mixture of a carboxylic acid and its anhydride, $RCO_2H/(RCO)_2O$, pouring the reaction mixture on a cation-exchange column and eluting with an acid such as CF_3SO_3H or HBF_4.

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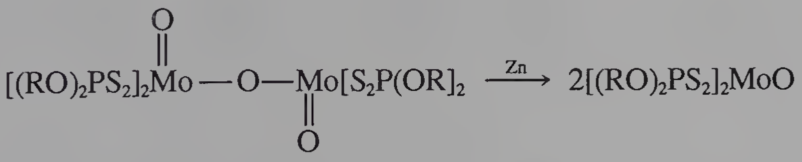
[28] A. Bino *et al., Inorg. Chim. Acta,* 1985, **99,** 137.
[29] A. Müller *et al., Angew. Chem. Int. Ed. Engl.,* 1981, **20,** 483.
[30] M. J. O'Connor *et al., J. Am. Chem. Soc.,* 1983, **105,** 1527.
[31] K. Wieghardt *et al., Z. Anorg. Allg. Chem.,* 1985, **521,** 23.
[32] F. A. Cotton *et al., Inorg. Chem.,* 1983, **22,** 3104; 1984, **23,** 4738.

The products contain trinuclear cations of the general type $[M_3O_2(RCO_2)_6(H_2O)_3]^{2+}$, one of which is illustrated in Fig. 19-C-10(c). There are some remarkable variations on the basic M_3O_2 structural theme. It is possible to obtain an essentially identical type of complex except that one capping oxygen atom is absent.[33] Even more remarkable is that under certain preparative conditions products are obtained in which one or both μ_3-O ligands are replaced by μ_3-CR (alkylidyne) caps.[34] The stability of these systems in acid, aqueous media, and in the presence of oxygen is surprising. The reason for it is in part kinetic inertness of all species with this type of bicapped structure. Counting the M—M bonds, each metal atom is nine-coordinate and employs all nine valence orbitals in bonding, thus, making associative reaction pathways inaccessible. The general kinetic inertness of all bicapped species is further shown by the fact that the $[M_3O_2(O_2CC_6H_5)_6(H_2O)_3]^{2+}$ ions can be fully nitrated in all 12 meta positions, employing a mixture of concentrated sulfuric and nitric acids at 40°C, without detectable core degradation.[35]

One more important type of trinuclear oxo structure is that adopted by $Mo_3O(OR)_{10}$ compounds[36] and shown in Fig. 19-C-10(d). This has two capping groups (μ_3-O and μ_3-OR), three bridging OR groups, and six terminal ones.

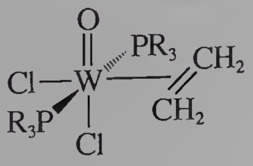
Mononuclear Mo^{IV} Oxo Complexes.[37] These contain the $[Mo{=}O]^{2+}$ unit and have quasi-octahedral structures with a very weak bond (or sometimes no bond) trans to the oxygen atom. They can be prepared by reduction of oxo complexes of Mo^{V} or Mo^{VI}, for example,



$$[(RO)_2PS_2]_2\overset{\overset{O}{\|}}{Mo}{-}O{-}\underset{\underset{O}{\|}}{Mo}[S_2P(OR]_2 \xrightarrow{Zn} 2[(RO)_2PS_2]_2MoO$$

$$(R_2NCS_2)_2MoO_2 + Ph_3P \longrightarrow (R_2NCS_2)_2MoO + Ph_3PO$$

There are rather few W^{V} analogues, mostly of the type WOX_2L_3. An unusual one is the ethylene complex,[38] $WOCl_2(PMePh_2)_2(CH_2{=}CH_2)$ (19-C-II).



(19-C-II)

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[33] M. Ardon *et al., J. Am. Chem. Soc.*, 1982, **104,** 5394.

[34] A. Bino *et al., J. Am. Chem. Soc.*, 1981, **103,** 5779; F. A. Cotton *et al., Inorg. Chem.*, 1981, **20,** 4083; F. A. Cotton *et al., Inorg. Chem.*, 1982, **21,** 3750.

[35] F. A. Cotton *et al., Inorg. Chem.*, 1984, **23,** 4033.

[36] M. H. Chisholm *et al., Inorg. Chem.*, 1984, **23,** 749.

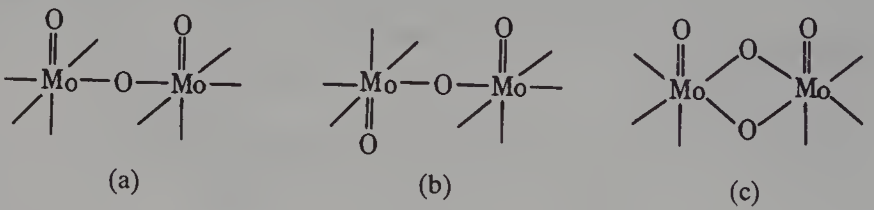
[37] C. G. Young and J. H. Enemark, *Inorg. Chem.*, 1985, **24,** 4416 (38 representative complexes and their ^{95}Mo nmr spectra); J. H. Enemark *et al., Inorg. Chem.*, 1987, **26,** 1017.

[38] J. M. Mayer *et al., J. Am. Chem. Soc.*, 1986, **108,** 3545; 1987, **109,** 2826.

M^V Oxo Species. An extensive range of Mo^V compounds can be obtained by reduction of molybdates or MoO_3 in acid solution either chemically (e.g., by shaking with mercury) or electrolytically. The nature of the resultant species depends critically on the anions present and on conditions of pH and concentration. Probably the most important species, and one that is often used as a source material for preparation of other Mo^V compounds, is the emerald green ion $[MoOCl_5]^{2-}$ or the closely related $[MoOCl_4]^-$ and $[MoOCl_4(H_2O)]^-$ ions, all of which are readily interconverted by varying (or removing) the ligand trans to the Mo=O bond. There are also bromo and iodo analogues. These ions can be obtained by reduction of Mo^{VI} in aqueous HX, by oxidation of $Mo_2(O_2CCH_3)_4$ in aqueous HX, or by dissolving $MoCl_5$ in aqueous acid. Molybdenum pentachloride will also react with many organic compounds or solvents (e.g., Me_2SO or Ph_3PO) to abstract oxygen and form oxo-molybdenum(V) complexes such as $MoOCl_3(OSMe_2)_2$.

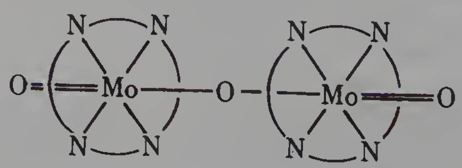
When WO_4^{2-} is reduced in 12 *M* HCl, the blue $[WOCl_5]^{2-}$ ion is obtained. There are also various neutral complexes of the types $WOCl_3L_2$ and $WOCl_3(LL)$.

Although the mononuclear complexes just mentioned are important, the oxo chemistry of Mo^V is dominated by dinuclear complexes. Curiously, similar dinuclear oxo complexes of W^V are not in general known. These dinuclear oxo complexes of Mo^V are of two main types; singly bridged ones that exist in cis and trans rotamers (19-C-IIIa) and (19-C-IIIb), and doubly bridged ones (19-C-IIIc), which are cis. In most cases some or all of the ligands (not shown in these sketches) are chelating. Examples of type (19-C-IIIa) are $Mo_2O_3(S_2COEt)_4$ and $Mo_2O_3(S_2CNPr_2)_4$; complexes of the type (19-C-IIIb) are $Mo_2O_3[S_2P(OEt)_2]_4$ and $Mo_2O_3(LL)_4$ in which LL represents *o*-thiopyridine. The doubly bridged structure (19-C-IIIc) is found in $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$, for example, where the water molecules are only weakly bound trans to the Mo=O bonds. In all mono- and dinuclear oxo complexes of Mo^V, ligands trans to Mo=O bonds are rather weakly bonded and are often entirely absent.


(a) (b) (c)

(19-C-III)

The tetraphenylporphyrin complex (19-C-IV), with its trans, trans set of Mo—O bonds, is structurally atypical; this linear arrangement is due to the planar nature of the porphyrin ligand.



(19-C-IV)

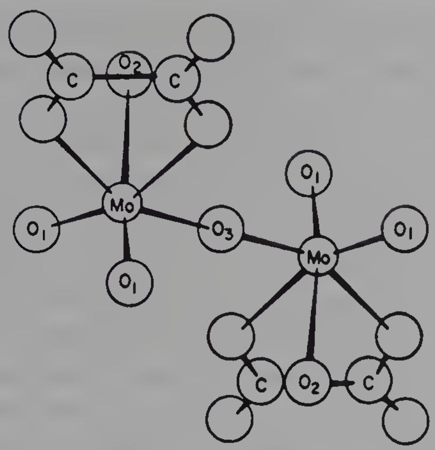


FIG. 19-C-11. The structure of the anion in $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$.

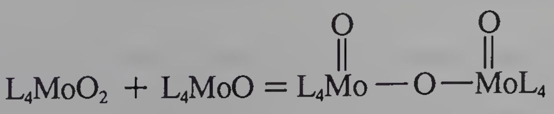
M^{VI} Oxo Species. Tungsten(VI) forms only a few of these, most of which resemble their molybdenum analogues, but those of molybdenum are numerous and important. With but few exceptions such as (triamine)MoO_3 compounds,[39a] the mononuclear ones are MoO_2^{2+} complexes, all of which have distorted octahedral structures with *cis* oxygen atoms, Mo—O distances of 1.70 ± 0.02 Å and O—Mo—O angles of 106 ± 3°.[39b] They are off-white to orange in color and have strong Mo—O stretching bands in the ir at ~880 and 920 cm^{-1}. Examples are the $[MoO_2Cl_4]^{2-}$ and $[MoO_2Cl_2(H_2O)_2]$ complexes obtained by dissolving MoO_3 in aqueous HCl, the former predominating in 12 *M* and the latter in 6 *M* acid. Adducts such as $MoO_2Cl_2(OPPh_3)_2$ and species with chelating ligands, for example, $[MoO_2(acac)_2]$ and $[MoO_2(S_2CNEt_2)_2]$, are also well known. Tungsten(VI) forms a few oxo complexes such as WOF_5^-, $WO_2F_4^{2-}$, $WO_2Cl_4^{2-}$, and $WO_3F_3^{3-}$.

With Mo^{VI} there are also a few binuclear species having both Mo═O and Mo—O—Mo groups. The anion in $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ has the centrosymmetric structure in Fig. 19-C-11; the bridge Mo—O—Mo group is linear and symmetrical.

Dioxomolybdenum(VI) species can serve as oxygen atom transfer agents,[40] eq. 19-C-7. The acceptor may be a thiol, a tertiary phosphine, or any one

$$L_4MoO_2 + X \longrightarrow L_4MoO + OX \qquad (19\text{-C-}7)$$

of various organic molecules. There is, however, a secondary reaction, eq. 19-C-8, that often makes this chemistry more complicated. The presence of



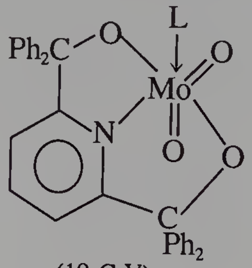
$$L_4MoO_2 + L_4MoO = L_4\overset{\overset{\displaystyle O}{\|}}{Mo}—O—\overset{\overset{\displaystyle O}{\|}}{Mo}L_4 \qquad (19\text{-C-}8)$$

[39a] P. S. Roy and K. Wieghardt, *Inorg. Chem.*, 1987, **26,** 1885.

[39b] E. I. Stiefel *et al., Inorg. Chim. Acta*, 1984, **90,** 25, 35, 41.

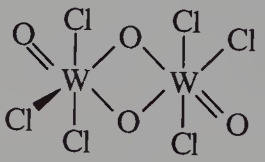
[40] J. Topich and J. L. Lyon, III, *Inorg. Chem.*, 1984, **23,** 3202 (gives many leading references).

unreacted dioxomolybdenum(VI) complex together with the five-coordinated oxomolybdenum(IV) product can give rise to the oxo-bridged dimolybdenum(V) compound. This is an equilibrium reaction, and the position of the equilibrium is strongly dependent on the nature of the ligands (L) especially their steric properties. With sufficiently bulky polydentate ligands reaction 19-C-8 can be blocked.[41] In cases where it cannot be entirely suppressed it is necessary to include it in carrying out a correct kinetic analysis of the coupled reactions.[42] There are two reasons for being interested in the nature of reaction 19-C-7 uncomplicated by reaction 19-C-8. If the L_4MoO_2 is to be used fully and efficiently as an oxidant, one does not wish to tie up half of it in the dimolybdenum(V) species. In addition, there is much evidence that a number of molybdenum containing enzymes (cf. Section 30-11) actually employ a reaction like eq. 19-C-7, but in the enzymes massive steric hindrance entirely suppresses the dimerization; good models for the enzymic activity must therefore also be designed to prevent reaction 19-C-8. Considerable success in designing good enzyme models has been reported[43] in which appropriately bulky tridentate ligands, as shown in (19-C-V), are present.

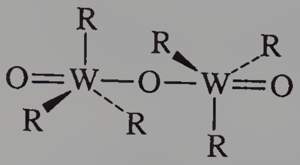


(19-C-V)

Some unusual oxo tungsten(VI) species have been reported, such as $[W_2Cl_6O_4]^{2-}$ with the structure[44] shown as (19-C-VI) and $W_2O_3(CH_2CMe_3)_6$, the only organo oxo W^{VI} species,[45] (19-C-VII).



(19-C-VI)



(19-C-VII)

Both molybdenum and tungsten form peroxo complexes, some of which are specific stoichiometric reagents for epoxidation of olefins. Structures of

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[41] J. M. Berg and R. H. Holm, *Inorg. Chem.*, 1983, **22**, 1768; *J. Am. Chem. Soc.*, 1984, **106**, 3035.

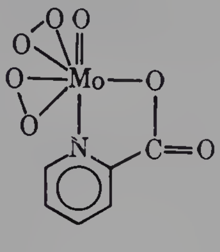
[42] M. S. Reynolds, J. M. Berg, and R. H. Holm, *Inorg. Chem.*, 1984, **23**, 3057.

[43] J. M. Berg and R. H. Holm, *J. Am. Chem. Soc.*, 1985, **107**, 917, 925; R. H. Holm and J. M. Berg, *Acc. Chem. Res.*, 1986, **19**, 363.

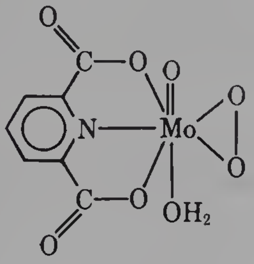
[44] K. Dehnicke *et al.*, *Z. Anorg. Allg. Chem.*, 1986, **532**, 137.

[45] S. J. Lippard *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 6305.

two Mo complexes of this type, containing Mo^{VI}, are (19-C-VIII) and (19-C-IX). Both have pentagonal bipyramidal coordination. The O—O distances in the peroxo ligands are 1.45 to 1.47 Å.



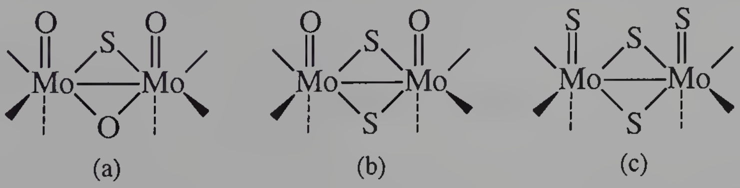
(19-C-VIII)



(19-C-IX)

Thio Analogues.[46] Just as there are analogues of simple MO_4^{2-} ions in which one to four of the oxygen atoms have been replaced by sulfur atoms, there are thio analogues of many of the more complex oxo species we have just discussed. We shall also mention some thio species that have no oxo analogues.

There are many thio analogues to the complexes of $Mo_2O_4^{2+}$. Sulfur prefers the bridging positions; hence the available thio species are those in (19-C-X). Species with μ-O and terminal S atoms have not, and perhaps cannot, be prepared.



(a) (b) (c)

(19-C-X)

There are per-thio analogues of both of the $M_3O_4^{4+}$(aq) ions,[47] obtainable by several synthetic methods and isolable in the form of various complexes:

$$Mo_3S_{13}^{2-} + \text{excess } CN^- \longrightarrow [Mo_3S_4(CN)_9]^{5-} + nSCN^-$$

$$[Mo_4S_4(NCS)_{12}]^{6-} \xrightarrow{C_6H_{12}N_3} [Mo_3S_4(C_6H_{12}N_3)_3]^{4+}$$

$$3WS_4^{2-} \xrightarrow{BH_4^-} \xrightarrow{SCN^-} [W_3S_4(NCS)_9]^{5-}$$

All of the possible mixed oxo/thio species of molybdenum, namely, the six shown in (19-C-XI) have been made. There are alternative routes to some

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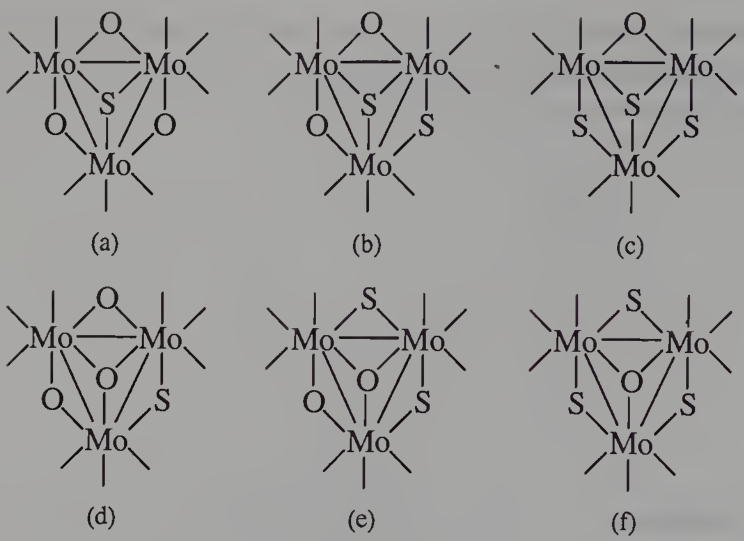
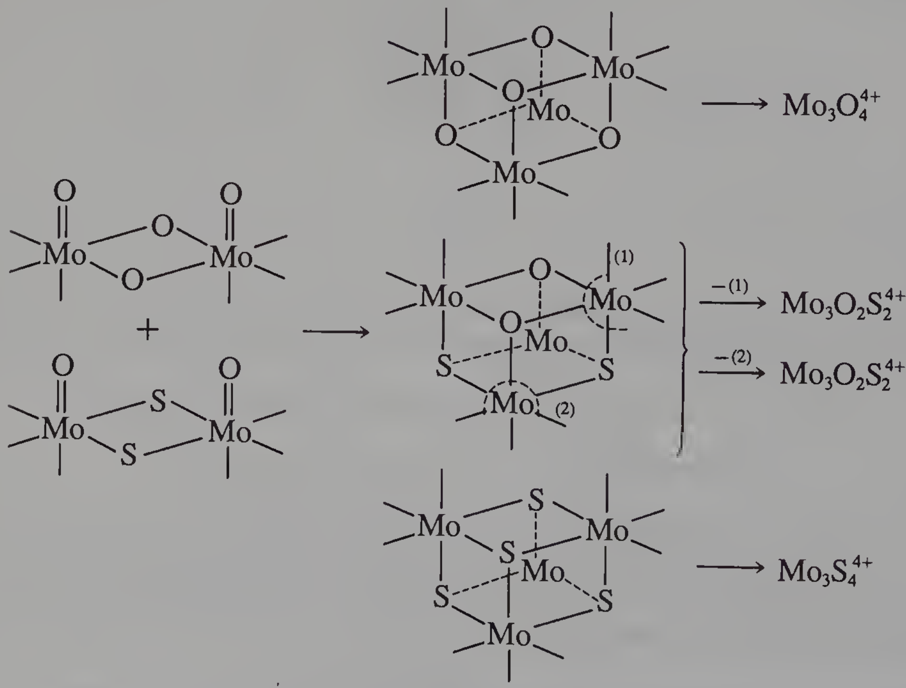
[46] A. Müller *et al., Inorg. Chem.*, 1985, **24,** 2872; A. G. Sykes *et al., J. Am. Chem. Soc.*, 1987, **109,** 4615.

[47] A. Müller and U. Reinsch, *Angew. Chem. Int. Ed. Engl.*, 1980, **19,** 72; F. A. Cotton *et al., Inorg. Chem.*, 1986, **25,** 3654; E. I. Stiefel *et al., J. Am. Chem. Soc.*, 1984, **106,** 1849; T. Shibahara *et al., J. Am. Chem. Soc.*, 1986, **108,** 2757.



(19-C-XI)

of them,[48] but the most interesting synthetic approach which is general and can be controlled to obtain each of these products (as well as $Mo_3O_4^{4+}$ and $Mo_3S_4^{4+}$) employs the coupling of $Mo_2O_nS_{4-n}^{2+}$ species.[49] The initial products are cuboidal species, as indicated in the representative reactions (19-C-9), and these are then degraded to the trinuclear species. A tungsten analogue



(19-C-9)

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[48] T. Shibahara *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 2710; *Inorg. Chim. Acta*, 1986, **113**, L19; *Chem. Lett.*, **1986**, 139.

[49] A. G. Sykes *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985**, 1437.

$[Mo_3S(S_2)_6]^{2-}$ $[Mo_2S_4(S_2)_2]^{2-}$

$[Mo_2(S_2)_6]^{2-}$ $[Mo_2S_4(S_4)_2]^{2-}$

FIG. 19-C-12. The structures of four representative Mo_2 or Mo_3 anions containing S^{2-}, S_2^{2-}, or S_4^{2-} ions.

$[W_3(\mu\text{-}O)_3(\mu_3\text{-}S)(NCS)_9]^{5-}$ has also been reported[50] and doubtless other $[W_3O_nS_{4-n}]^{4+}$ species can be made.

The $[Mo_3S_{13}]^{2-}$ ion, from which the $Mo_3S_4^{4+}$ unit may be obtained in a number of desulfurization reactions, has the structure shown in Fig. 19-C-12. There are both bridging and terminal S_2^{2-} ions present. There are numerous other species that contain S_2^{2-} and other S_n^{2-} units as ligands,[51] three of which are also shown in Fig. 19-C-12.

The existence of cuboidal $M_4S_4^{n+}$ units, which can be isolated as anionic complexes[52] such as $[Mo_4S_4(NCS)_{12}]^{6-}$ and $[Mo_4S_4(EDTA)_2]^{3-}$, has already been referred to. These tend to extrude one Mo atom rather easily to leave the pyramidal $Mo_3S_4^{4+}$ units.

The catenation of MS_4 tetrahedra or a combination of tetrahedra with MS_5 tetragonal pyramids leads to the formation of the anions shown in Fig. 19-

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[50] Z. Dori *et al.*, *Polyhedron*, 1986, **5,** 907.

[51] A. Müller, *Polyhedron,* 1986, **5,** 323; D. Coucouvanis *et al., Polyhedron,* 1986, **5,** 349; *Inorg. Chem.*, 1987, **26,** 2400.

[52] F. A. Cotton *et al., J. Am. Chem. Soc.*, 1985, **107,** 6735; A. Müller *et al., Angew. Chem. Int. Ed. Engl.*, 1982, **21,** 795; T. Shibahara *et al., Inorg. Chim. Acta*, 1986, **116,** L25.

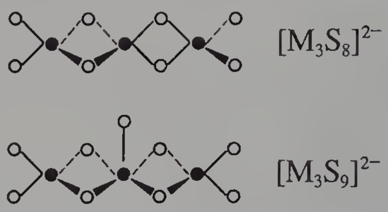

FIG. 19-C-13. The structures of two types of trinuclear thio anions containing MS_4^{2-} subunits.

C-13. These can be regarded as having MS_4^{2-} ions acting as ligands toward the central M^{II} or M^{IV} atoms.[53]

19-C-8. Other Complexes

These elements form an enormous variety of complexes besides the halide, oxide, and sulfide complexes already considered. Some of these others will now be mentioned. Those with metal-to-metal bonds are covered in subsequent sections.

Complexes of CO, NO, and N_2. Such complexes are discussed generically in Chapters 22 (CO) and 10 (NO, N_2). The hexacarbonyls are the source of many of the mixed ligand complexes that contain CO. It should also be noted that coordination number 7 is not uncommon. Either $Mo(CO)_6$ itself or substitution products thereof, such as $Mo(CO)_4$diars, react with the halogens to produce Mo^{II} complexes such as $[Mo(CO)_4X_2]_2$ or, in the presence of other ligands, L, $Mo(CO)_3X_2L_2$, or Mo^{III} complexes such as $[MoX_3(CO)_3PR_3]$.[54] The $[Mo(CO)_4X_2]_2$ compounds and their tungsten analogues, are dimerized through X bridges, as shown in Fig. 19-C-14 for $W_2Br_4(CO)_8$.[55] They are generally good starting materials for the synthesis of many other complexes, as illustrated in the following reactions[56–58]:

$$[WBr_2(CO)_4]_2 \xrightarrow{PPh_3} WBr_2(CO)_3(PPh_3)_2 \xrightarrow{\Delta} WBr_2(CO)_3(PPh_3).$$

$$[MoI_2(CO)_4]_2 \xrightarrow{PMe_3} Mo_2I_4(PMe_3)_4 + 8CO$$

$$[MoI_2(CO)_4]_2 \xrightarrow{dmpm} 2MoI_2(CO)(dmpm)_2$$

The *nitrosyl* chlorides, $M(NO)_2Cl_2$, are polymeric solids that react with a variety of Lewis bases to give $M(NO)_2Cl_2L_2$ adducts that have *cis*-L_2 for small (e.g., CH_3CN) and *trans*-L_2 for large L (e.g., R_3P).[59a] The reaction of Mo_2Cl_{10} with NO, followed by the addition of other ligands gives rise to mononitrosyl

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[53] J. Bernholc and E. I. Stiefel, *Inorg. Chem.*, 1985, **24**, 1323; S. Bhaduri and J. A. Ibers, *Inorg. Chem.*, 1986, **25**, 4.

[54] P. K. Baker and S. G. Fraser, *Inorg. Chim. Acta*, 1986, **116**, L1, L3.

[55] F. A. Cotton *et al.*, *Inorg. Chem.*, 1985, **24**, 514.

[56] F. A. Cotton and J. H. Meadows, *Inorg. Chem.*, 1984, **23**, 4688.

[57] F. A. Cotton and R. Poli, *J. Am. Chem. Soc.*, 1986, **108**, 5628.

[58] F. A. Cotton and R. Poli, *Inorg. Chem.*, 1986, **25**, 3703.

[59a] A. D. Hunter and P. Legzdins, *Inorg. Chem.*, 1984, **23**, 4198.

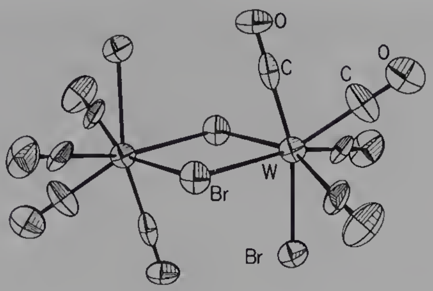
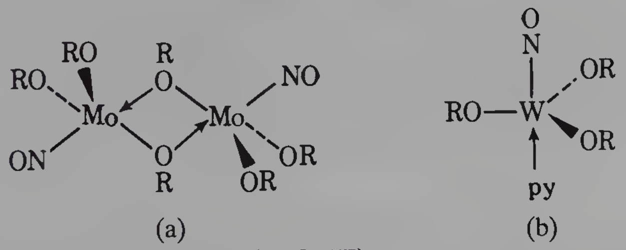


FIG. 19-C-14. The centrosymmetric $W_2Br_4(CO)_8$ molecule.

complexes of the types $[MoCl_4(NO)L]^-$, $MoCl_3(NO)L_2$, $[MoCl_3(NO)L_2]^-$, and $MoCl(NO)L_4$. Other derivatives[59b] include $WH(CO)_2(NO)(PPh_3)_2$, $W(CO)_3NO(PR_3)_2^+$, and several pyrazolylborate species.[59c]

Reactions of $M_2(OR)_6$ compounds also give nitrosyl complexes such as (19-C-XII). These are unusual among nitrosyl complexes in having only 14-electron configurations, very short M—N distances, and very low (1560–1640 cm^{-1}) N—O stretching frequencies.



(a) (b)

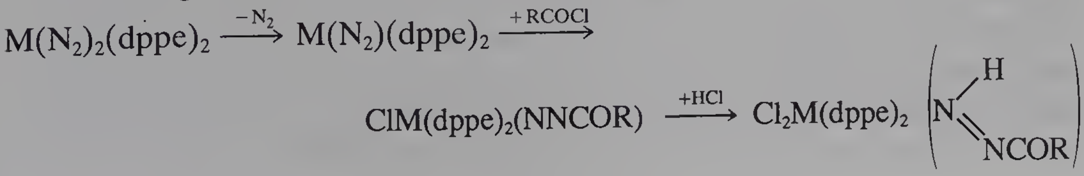
(19-C-XII)

Dinitrogen complexes have been studied extensively with a view to understanding natural nitrogen-fixing systems.[60] The bis(dinitrogen) complexes are generally prepared by reactions of higher-valent halo complexes already containing the phosphine ligands with strong reducing agents (e.g., Na/Hg) in the presence of N_2 gas.[61] For example,

$$WCl_4(PMe_2Ph)_2 + N_2 \xrightarrow[\text{Na/Hg}]{\text{excess } PMe_2Ph} W(N_2)_2(PMe_2Ph)_4$$

$$MoCl_5 + 4R_3P + N_2 \xrightarrow[\text{Na/Hg}]{\text{THF}} trans\text{-}Mo(N_2)_2(R_3P)_4$$

Acylation occurs thermally and alkylation photochemically according to the following scheme, where M represents Mo or W:



$$M(N_2)_2(dppe)_2 \xrightarrow{-N_2} M(N_2)(dppe)_2 \xrightarrow{+RCOCl} ClM(dppe)_2(NNCOR) \xrightarrow{+HCl} Cl_2M(dppe)_2\left(N\begin{matrix}H\\ \\ NCOR\end{matrix}\right)$$

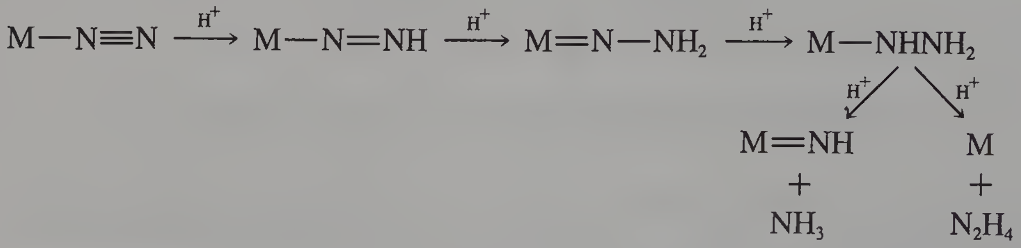
[59b] G. L. Hillhouse and B. L. Haymore, *Inorg. Chem.*, 1987, **26,** 1876.

[59c] C. J. Jones *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 1733.

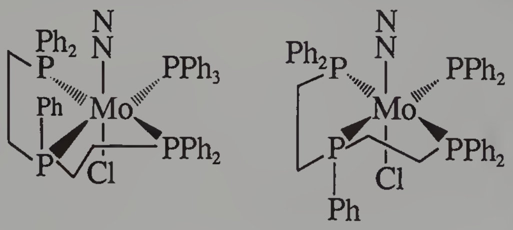
[60] R. A. Henderson *et al., Adv. Inorg. Chem. Radiochem.*, 1983, **27,** 197.

[61] E. Carmona *et al., Inorg. Chem.*, 1985, **24,** 4033.

On treatment with anhydrous HCl or HBr in organic solvents the N_2 complexes afford both hydrazine and ammonia in varying yields.[62] The pathways to both N_2H_4 and NH_3 are believed to involve successive protonation of the N_2 ligand, with subtle electronic and/or steric factors controlling the product distribution (see also p. 335):



An interesting example of emerging insight into these details is the discovery that $[Mo(Ph_3P)[(Ph_2PC_2H_4)_2PPh]Cl(N_2)]^+$ exists as two isomers, (19-C-XIII), which display significant reactivity differences.[63]



(a) (b)

(19-C-XIII)

We may also mention that there are numerous *isocyanide complexes.* Isoleptic species are obtained smoothly by the reaction of RNC with $Mo_2(O_2CCH_3)_4$ and isolated as $[Mo(RNC)_7](PF_6)_2$, and in other ways, some of which allow preparation of analogous W^{II} complexes. Substitution of RCN ligands by phosphines, phen, bipy, and so on, lead to many other complexes[64a] particularly the types $[M(RCN)_nL_{7-n}]^{2+}$. The $[MoX_2(CO)_4]_2$ compounds react with RNC to give $Mo(RNC)_5X_2$. The $[Mo(CNR)_6I]^+$ and $[Mo(CNR)_7]^{2+}$ ions can be made reaction of $Mo(CO)_6$ with RNC and I_2 or by alkylation and reduction of $[Mo(CN)_8]^{4-}$. Both types have capped trigonal prismatic geometry.

Cyano Complexes. The best known and most thoroughly studied cyano complexes are the octacyano ions $M(CN)_8^{3-}$ and $M(CN)_8^{4-}$ (M = Mo or W). The interest here has centered on their structures, which appear to vary with environment. The similar energies of dodecahedral (D_{2d}) and square antiprismatic (D_{4d}) structures, and the attendant fluxional character for the former, have been mentioned (p. 16). In solid compounds the structures found

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[62] T. A. George *et al., Inorg. Chem.,* 1985, **24,** 3568; M. Hidai in *Molybdenum Enzymes,* T. G. Spiro, Ed., Interscience-Wiley, New York, 1985, p. 285.

[63] J. Zubieta *et al., Inorg. Chem.,* 1986, **25,** 405.

[64a] S. J. Lippard *et al., Organometallics,* 1983, **2,** 1562.

for the $M(CN)_8^{n-}$ ions are as follows (where M indicates that both the Mo and W compounds have the stated structure):

$Na_3M(CN)_8{\cdot}4H_2O$	D_{4d}	M^V species
$[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$	D_{2d}	
$K_4M(CN)_8{\cdot}2H_2O$	D_{2d}	M^{IV} species
$K_4M(CN)_8{\cdot}6H_2O$	D_{4d}	

Thus the surroundings play a decisive role in stabilizing one or the other geometry. Most Raman and ir studies of solutions have been inconclusive, though Raman and ^{99}Mo nmr[64b] spectra unequivocally favor the D_{2d} structure for $Mo(CN)_8^{4-}$ in aqueous solution. The esr studies were at first believed to favor D_{4d} symmetry or a fluxional D_{2d} structure rearranging through a D_{4d} intermediate.

The $M(CN)_8^{4-}$ ions in aqueous solution are photochemically converted, through several intermediates, into isolable species long believed to be $[M(CN)_4(OH)_4]^{4-}$ but more recently shown to be six-coordinate, *trans*-dioxo complexes $[MO_2(CN)_4]^{4-}$.

A cyano complex reported for Mo^{III} is $K_4Mo(CN)_7{\cdot}2H_2O$, which readily oxidizes to $K_4Mo(CN)_8{\cdot}2H_2O$. It has $\mu_{eff} = 1.75$ BM at room temperature. The apparent presence of only one unpaired electron has been attributed to *d*-orbital splitting in the necessarily low symmetry of either an $[Mo(CN)_7]^{4-}$ or an $[Mo(CN)_7(H_2O)]^{4-}$ ion. The molybdenum(II) ion, $Mo(CN)_7^{5-}$ has a pentagonal bipyramidal structure.

Thiocyanate complexes are formed by molybdenum in the III, IV, and V oxidation states, the last being of the oxo type, for example, $[MoO(NCS)_5]^{2-}$. The $[Mo(NCS)_6]^{3-}$ ion has been shown conclusively to have *N*-bonded thiocyanate ions, and this appears likely to be the case also in all other molybdenum thiocyanato species.

Hydrido and η^2-H_2 Complexes. Both metals form a series of mixed hydrido phosphine complexes[65] (Chapter 24), typical examples being $M(PR_3)_5H_2$, $M(PR_3)_4H_4$, and $\{Li[WH_5(PMe_3)_2]\}_4$. They are obtained by reducing $MCl_4(PR_3)_3$ complexes with Na in the presence of H_2 or with hydridic reducing agents such as $Li[BEt_3H]$, or by treating $W(CH_3)_6$ with H_2 in the presence of PR_3. It is notable that the first η^2-H_2 complexes (Section 24-7) to be isolated and characterized were of the type $M(CO)_3(PR_3)_2(H_2)$, where R is cyclohexyl or isopropyl.[66]

Nitrido Complexes. These are known with both terminal and bridging nitrogen atoms. Among the former are species such as $[MNCl_4]^{n-}$, which are complexes of M^V ($n = 2$) or M^{VI} ($n = 1$) with very short (~1.70 Å) $M{\equiv}N$ bonds.[67] There are also $(RO)_3MN$ species, which will be discussed in Section

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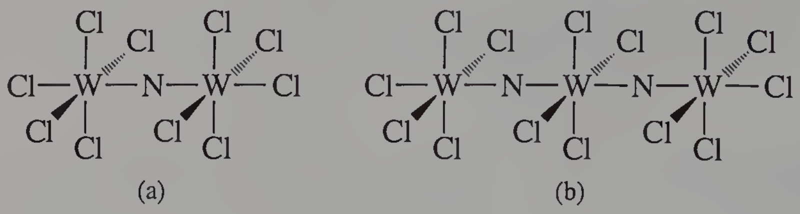
[64b] R. T. C. Brownlee *et al.*, *Inorg. Chem.*, 1987, **26,** 2022.

[65] R. H. Crabtree and G. G. Hlatky, *Inorg. Chem.*, 1984, **23,** 2388; V. C. Gibson *et al.*, *J. Chem. Soc., Dalton Trans.*, **1985,** 2025; G. Wilkinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987,** 837.

[66] G. J. Kubas *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 451.

[67] K. Dehnicke *et al.*, *Z. Anorg. Allg. Chem.*, 1982, **495,** 148.

19-C-9. Species with nitrido bridges include $[W_2NCl_{10}]^-$, $[W_2NCl_{10}]^{2-}$, and $[W_3N_2Cl_{14}]^{2-}$, which have the structures[68] shown in (19-C-XIV).


(a) (b)

(19-C-XIV)

Unusual M^{IV} Compounds. The tetravalent metals form compounds that are surprisingly varied in stereochemistry. In addition to the octahedral halo complexes, $[MX_6]^{2-}$, or mixed halo complexes, MX_4L_2, already mentioned, there are eight-coordinate species such as the $[M(CN)_8]^{4-}$ ions and the $M(pic)_4$ molecules, where pic represents the anion of 2-carboxylato pyridine (picolinic acid). There are also some four-coordinate compounds that may have either planar or tetrahedral structures. There are homologous $M(SCMe_3)_4$ molecules that are tetrahedral,[69a] like $Mo(NMe_2)_4$, whereas the $W(OR)_4$ molecules, with R being 2,6-dimethylphenyl or 2,6-diisopropylphenyl, are essentially planar.[68] The relative importance of steric and electronic factors in determining these stereochemistries is uncertain. Finally there are alkyne complexes such as $MoCl_4$(alkyne) and $Mo(OR)_4$(alkyne).[69b]

Tungsten Alkylidyne Complexes. Alkylidyne complexes are discussed generically in Chapter 25. We note here that tungsten is one of the principal formers of such complexes and does so in some unique ways. The complexes are of particular interest because of their promise as catalysts, for example, in alkene metathesis[70] (Section 28-16). The most remarkable aspect of this chemistry, although there are many others[71] that we cannot cover here, is the unique series of reactions between $(Me_3CO)_3W{\equiv}W(OCMe_3)_3$ and nearly all $RC{\equiv}CR$ molecules, whereby alkylidyne complexes are smoothly formed:

$$W_2(Me_3CO)_6 + RCCR \longrightarrow 2(Me_3CO)_3W{\equiv}CR$$

This particular $M_2(OR)_6$ compound is the only one of its kind that reacts in this way. It will also react with nitriles in a similar way,[72] giving rise to the nitrido product mentioned earlier:

$$W_2(Me_3CO)_6 + RCN \longrightarrow (Me_3CO)_3W{\equiv}CR + (Me_3CO)_3W{\equiv}N$$

There are, of course, other ways to prepare both tungsten and molybdenum alkylidyne and nitrido species.

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[68] K. Dehnicke *et al.*, *Z. Naturforsch.*, 1985, **40B**, 999, 1005.

[69a] R. R. Schrock *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 7207.

[69b] R. R. Schrock *et al.*, *Inorg. Chem.*, 1987, **26**, 1615.

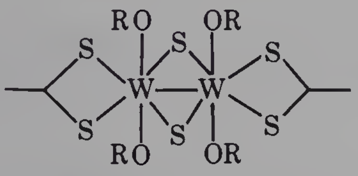
[70] R. R. Schrock, *Science*, 1983, **219**, 13; *J. Organomet. Chem.*, 1986, **300**, 249; *Acc. Chem. Res.*, 1986, **19**, 342.

[71] R. R. Schrock *et al.*, *Organometallics*, 1985, **4**, 1937; *J. Am. Chem. Soc.*, 1985, **107**, 5987, 5999.

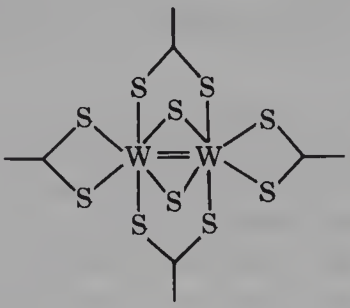
[72] D. M. Chan *et al.*, *Inorg. Chem.*, 1986, **25**, 4170.

Miscellaneous Complexes. There are many other kinds of ligands besides those specifically mentioned already, and molybdenum and tungsten form complexes with most of them.[1,2] A few more complexes of importance may be mentioned. The purple-brown, air-sensitive solid, $Mo(acac)_3$, is obtained by heating $Mo(CO)_6$ or K_3MoCl_6 with Hacac. Pyrazolylborate complexes, $(HBpz_3)MCl_3$, can be obtained,[73] and for the molybdenum compounds, oxidation to a variety of mixed oxo-chloro species can be carried out.[74]

Thio ligands of various kinds readily complex both Mo and W. Dithiocarbamates are among the most important of these.[75] There are two interesting binuclear tungsten complexes (19-C-XV) and (19-C-XVI) that both contain the same planar $Et_2NCS_2W(\mu\text{-}S)_2W(S_2CNEt_2)$ group but differ in the other four ligands. In (19-C-XV) the W^V atoms are separated by 2.79 Å and a W—W single bond is assigned, whereas in (19-C-XVI) the W^{IV} atoms are separated by only 2.53 Å and are united by a double bond.



(19-C-XV)



(19-C-XVI)

19-C-9. Triple and Quadruple M—M Bonds[76]

Molybdenum is the most prolific former of such bonds among all metals. Tungsten forms many analogous compounds[77] but they are often more reactive, and/or less easily prepared. Table 19-C-5 lists representative examples. It will be noted that the Mo—Mo distances are 0.10 ± 0.04 Å shorter than corresponding W—W distances. This reflects the fact that at the sorts of distances involved the much denser cores of tungsten atoms create a significantly greater core–core repulsion than occurs for a pair of molybdenum atoms. This, in turn, leads to a weakening of the δ component of the W—W quadruple bond. This is the principal reason why many quadruply bonded W_2 species are less easy to prepare and more reactive than their molybdenum analogues.[78] The effect of the greater W—W distance for the triple bonds is

[73] M. Millar *et al., J. Am. Chem. Soc.,* 1982, **104,** 288.

[74] S. Lincoln and S. A. Koch, *Inorg. Chem.,* 1986, **25,** 1594.

[75] J. L. Templeton *et al., J. Am. Chem. Soc.,* 1985, **107,** 6956.

[76] F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms,* Chapter 3, Wiley, New York.

[77] F. A. Cotton and R. A. Walton, *Struct. Bonding,* (*Berlin*), 1985, **62,** 1.

[78] F. A. Cotton *et al., J. Am. Chem. Soc.,* 1982, **104,** 679; F. A. Cotton and G. N. Mott, *J. Am. Chem. Soc.,* 1982, **104,** 5978.

TABLE 19-C-5

Representative Triple and Quadruple Mo—Mo and W—W Bonds and Their Lengths (Å)

	Quadruple Bonds		
$Mo_2(O_2CCH_3)_4$	2.09	$W_2(O_2CC_2H_5)_4$	2.19[a]
$[Mo_2Cl_8]^{4-}$	2.14	$[W_2Cl_8]^{4-}$	2.25[b]
$Mo_2Cl_4(PMe_3)_4$	2.13[c]	$W_2Cl_4(PMe_3)_4$	2.26[c]
$Mo_2(mph)_4$[d]	2.07	$W_2(mph)_4$[d]	2.16
	Triple Bonds		
$Mo_2(CH_2SiMe_3)_6$	2.17	$W_2(CH_2SiMe_3)_6$	2.26
$Mo_2(NMe_2)_6$	2.21	$W_2(NMe_2)_6$	2.29
$Mo_2Cl_2(NMe_2)_4$	2.20	$W_2Cl_2(NMe_2)_4$	2.29
$Mo_2(OCH_2CMe_3)_6$	2.22		
$[Mo_2(HPO_4)_4]^{2-}$	2.23		
		$W_2(O_2CNMe_2)_6$	2.28

[a] M. H. Chisholm *et al.*, *Polyhedron,* 1984, **3,** 759.

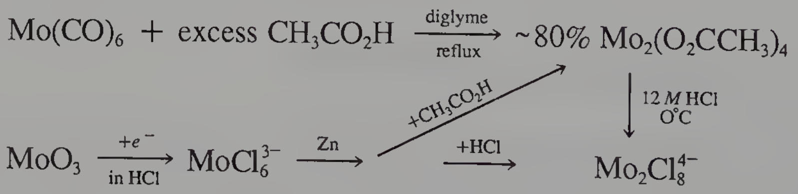
[b] R. R. Schrock *et al.*, *Inorg. Chem.*, 1983, **22,** 2801.

[c] F. A. Cotton *et al.*, *J. Am. Chem. Soc.*, 1981, **103,** 4040.

[d] mph = anion of 2-hydroxo-6-methylpyridine.

negligible and there is great similarity between the two sets of triply bonded compounds. The general discussion of M—M multiple bonds in Chapter 23 should be consulted in this connection.

Quadruple Bonds. Molybdenum forms hundreds of compounds containing Mo—Mo quadruple bonds. The most generally useful entries to this chemistry are shown in the following equations[79]:



Yellow $Mo_2(O_2CCH_3)_4$ (19-C-XVII) is thermally stable but slowly decomposes in air. The red $[Mo_2Cl_8]^{4-}$ ion (19-C-XIII) can be isolated in a variety of air-stable salts. Some important reactions of these key complexes are shown in Fig. 19-C-15.

Among the reactions of $Mo_2(O_2CCH_3)_4$ and $[Mo_2Cl_8]^{4-}$ are many simple (i.e., nonredox) ligand-exhange reactions in which the quadruply bonded Mo_2^{4+} unit remains intact. There are also reactions in which the products are mononuclear, such as $[Mo(CNR)_7]^{2+}$ where there is no oxidation, and $[MoOX_4(H_2O)]^-$ where oxidation occurs. The reaction of $[Mo_2Cl_8]^{4-}$ with sulfuric acid in presence of O_2 gives $[Mo_2(SO_4)_4]^{3-}$ in which the loss of one electron reduces the Mo—Mo bond order to 3.5, and reaction with phosphoric acid in O_2 gives $[Mo_2(HPO_4)_4]^{2-}$, which contains only a triple bond. The decrease in bond order from 4.0 to 3.5 to 3.0 in the series $[Mo_2(SO_4)_4]^{4-}$,

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[79] A. Bino and D. Gibson, *J. Am. Chem. Soc.*, 1980, **102,** 4277.

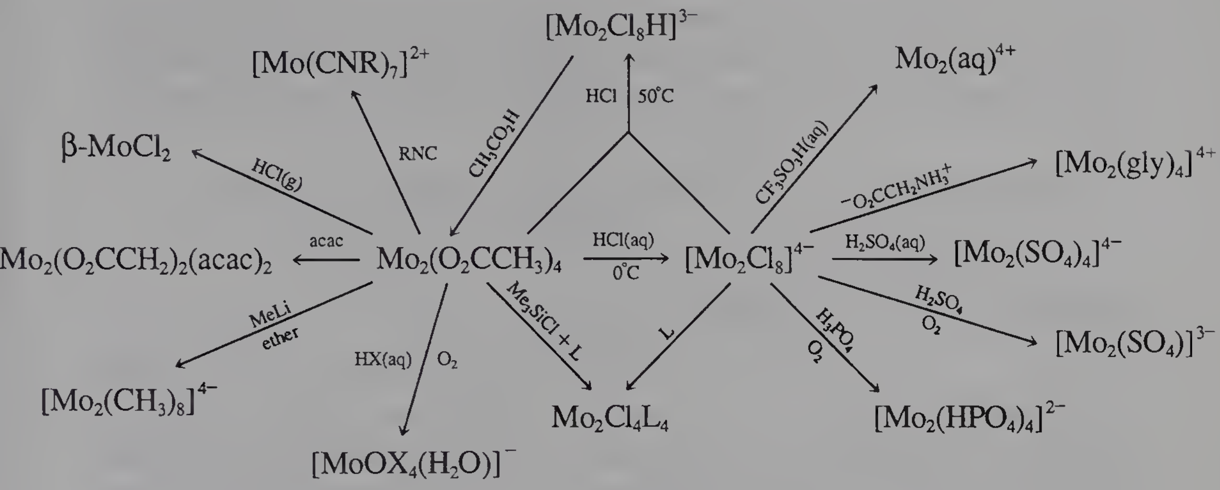
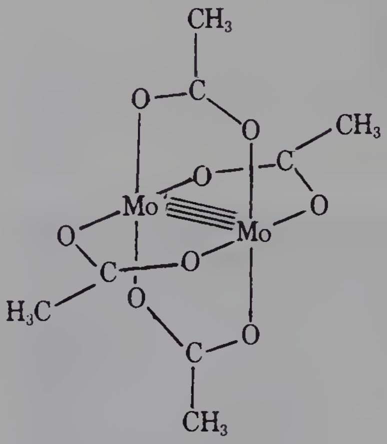
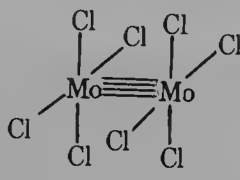


FIG. 19-C-15. Some important reactions of species with Mo—Mo quadruple bonds.

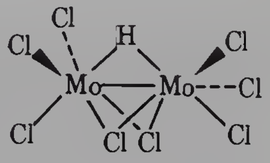
$[Mo_2(SO_4)_4]^{3-}$, $[Mo_2(HPO_4)_4]^{2-}$ is accompanied by a steady increase in bond lengths (2.11, 2.16, and 2.23 Å, respectively).



(19-C-XVII)



(19-C-XVIII)



(19-C-XIX)

The reaction of $Mo_2(O_2CCH_3)_4$ with gaseous HCl, HBr, or HI at ~300°C gives dihalides, β-MoX_2, which are different from the long known "$MoCl_2$," which (see Section 19-C-10) is a Mo_6 cluster compound. Though these powders have not been characterized by crystallography, their chemistry indicates that the quadruply bonded Mo_2 unit is present. The reaction of $Mo_2(O_2CCH_3)_4$ or $Mo_2Cl_8^{4-}$ with aqueous HX at 50°C gives the hydrido bridged $[Mo_2X_8H]^{3-}$ ions,[80] (19-C-XIX), which retain a strong Mo—Mo bond,[81] and can be reconverted to $Mo_2(O_2CCH_3)_4$ by CH_3CO_2H. These reactions are examples of oxidative-addition and reductive-elimination reactions involving dinuclear rather than the usual mononuclear complexes.

Treatment of M—M quadruply bonded (and also triply bonded) compounds with strongly π-accepting ligands (e.g., CO, RNC, and NO) causes

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[80] F. A. Cotton *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 117.
[81] F. A. Cotton *et al.*, *Inorg. Chem.*, 1982, **21**, 3755.

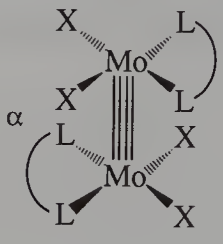
fission of the M—M bond and affords mononuclear products.[82] Such reactions may often constitute a good way (sometimes the best way, and even the only way) to prepare such products. Examples are provided by the following reactions:

$$Mo_2(O_2CCH_3)_4 + 14CH_3NC \longrightarrow 2[Mo(CNCH_3)_7](CH_3CO_2)_2$$

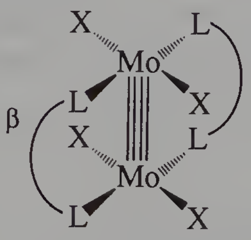
$$Mo_2(OR)_6 + 2NO + 2py \longrightarrow 2(RO)_3Mo(NO)py$$

$$W_2Cl_4(PEt_3)_4 + CO \longrightarrow W(CO)_3(PEt_3)_2Cl_2 + W(CO)_4(PEt_3)_2 + W(CO)_5(PEt_3)$$

It is possible to prepare compounds of the type $Mo_2X_4(LL)_2$, where LL represents a diphosphine such as dppm or dppe by several routes, and depending on preparative details either or both of two isomers (19-C-XX) and (19-C-XXI), α and β, respectively, may be obtained. In the β(bridged) isomers with dmpe or dppe, the steric requirements of the bridging diphosphines result in the rotational conformations about the Mo—Mo bonds being twisted to varying degrees away from the eclipsed conformation that prevails in species such as $Mo_2(O_2CR)_4$, $[Mo_2Cl_8]^{4-}$, and $Mo_2Cl_4(PR_3)_4$. Thus the purely schematic representation shown in (19-C-XXI) should not be taken literally. Figure 19-C-16 shows a real example of the twisted conformation of such a molecule. By studying the dependence of the Mo—Mo distance[83] and the position of the δ → δ* absorption band in the visible spectrum[84] on the magnitude of the twist angle, considerable insight into the properties of the quadruple bond has been obtained. It is also notable that such a twisted molecule is chiral and displays pronounced ORD and CD spectra. It is indicative of how well we understand the nature of quadruple bonds (or at least the δ components thereof) that we can predict correctly from first principles how the sign of the δ → δ* CD band correlates with the absolute rotational conformation of the molecule.[85] The compound shown in Fig. 19-C-16 is one in which only one helical isomer is locked in by use of a chiral ligand.



(19-C-XX)



(19-C-XXI)

A final, interesting point concerning these $Mo_2Cl_4(LL)_2$ molecules is that

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[82] R. A. Walton, in *Reactivity of Metal–Metal Bonds*, M. H. Chisholm, Ed., (ACS Symposium Series, No. 155), American Chemical Society, Washington, DC, 1981, p. 207.

[83] F. A. Cotton *et al., Inorg. Chem.*, 1985, **24,** 4384.

[84] F. A. Cotton *et al., Inorg. Chem.*, 1985, **24,** 177.

[85] F. A. Cotton *et al., J. Am. Chem. Soc.*, 1984, **106,** 1851.

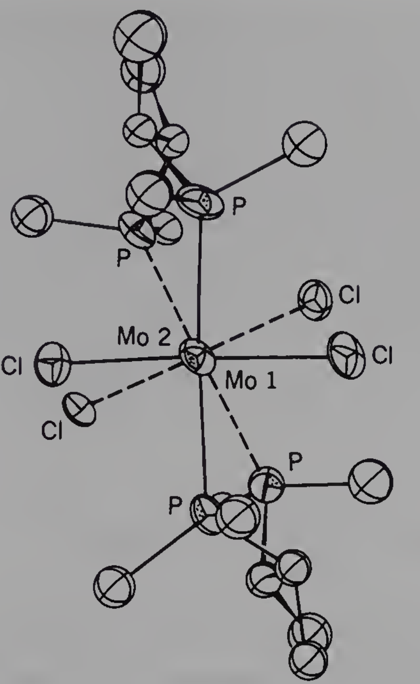
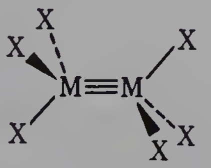


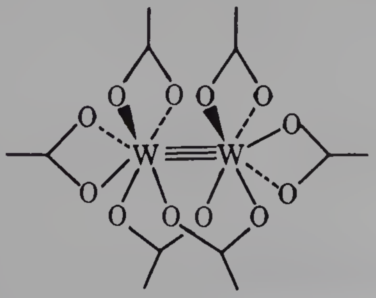
FIG. 19-C-16. A view of the β-$Mo_2Cl_4[Ph_2PCH(CH_3)CH(CH_3)PPh_2]_2$ molecule down the Mo(L)–Mo(2) axis, showing the internal rotation. The ligand has the S configuration at each asymmetric carbon atom thus giving rise to only one of the two helical conformations about the Mo—Mo bond.

in general the β isomers appear to be more stable thermodynamically than the α isomers and on heating the α isomers, either in the solid state or in solutions they are transformed to the β isomers. It is believed that these isomerizations take place by a simple flip of the Mo_2 unit within the cage formed by the ligands.[86]

Triple Bonds. These are found mainly in compounds of stoichiometry M_2X_6 with staggered (D_{3d}) conformations (19-C-XXII) where X represents one of the univalent groups R, OR, NR_2, or a mixture thereof. A few representative examples are mentioned, with their M—M bond lengths, in Table 19-C-5.



(19-C-XXII)



(19-C-XXIII)

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[86] F. A. Cotton *et al., Inorg. Chem.,* 1985, **24,** 2786; P. A. Agaskar and F. A. Cotton, *Inorg. Chem.,* 1986, **25,** 15.

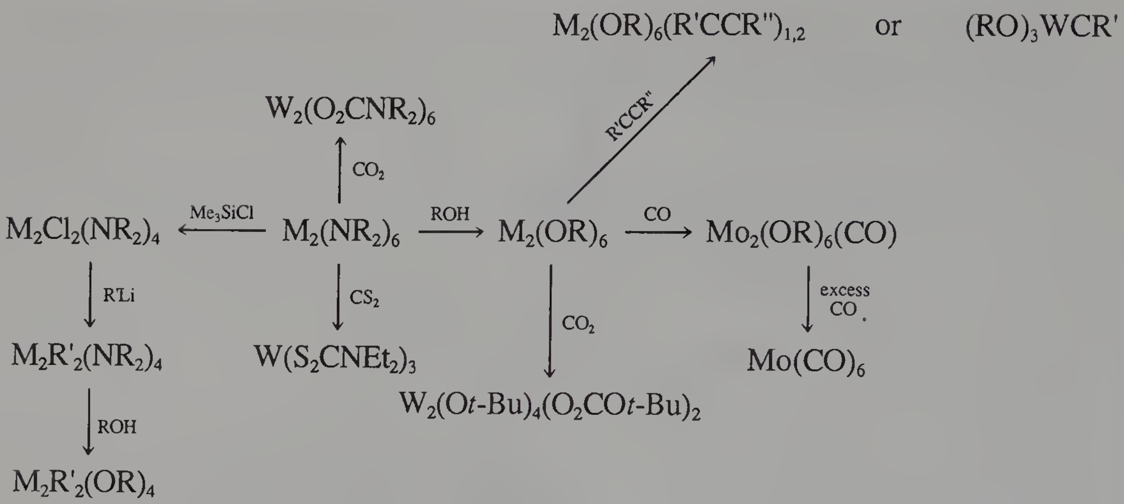


FIG. 19-C-17. Some reactions of Mo and W compounds with metal-to-metal triple bonds.

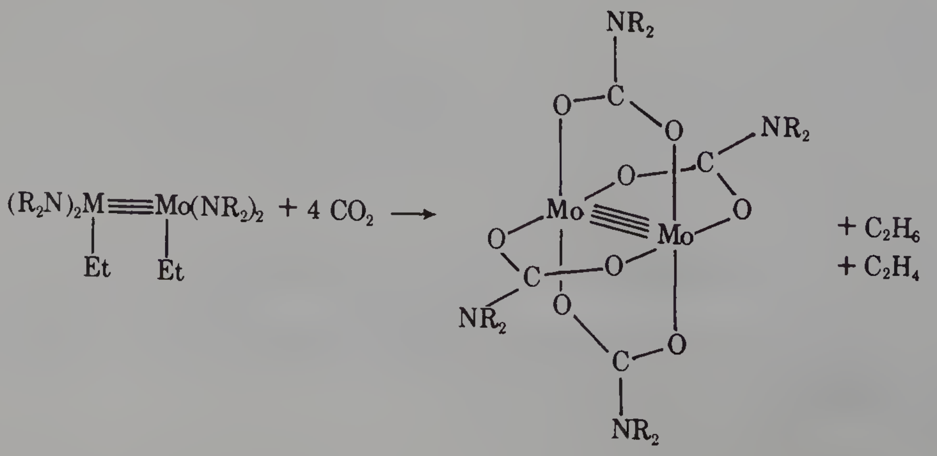
The classical, and still most important, synthetic entry to this class of compounds is via the $M_2(NR_2)_6$ species. They are obtained by reactions of $MoCl_5$, WCl_4, or WCl_6 with $LiNR_2$ reagents. The use of $LiNMe_2$ and WCl_6 gives a mixture of $W(NMe_2)_6$ and $W_2(NMe_2)_6$, which cocrystallize and are difficult to separate; but using an alcohol with a very bulky R group, the following process effects a separation of the mono- and dinuclear species.

$$W(NMe_2)_6\cdot W_2(NMe_2)_6 \xrightarrow{6t\text{-BuOH}} W_2(Ot\text{-Bu})_6 + 6HNMe_2 + W(NMe_2)_6$$

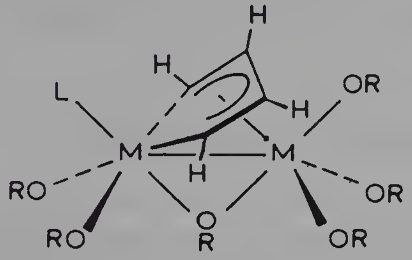
A schematic overview of the chemistry of M_2X_6 compounds is given in Fig. 19-C-17. The $M_2Cl_2(NR_2)_4$ compounds are important because they give access to many other mixed ligand species.

The carboxylation reactions proceed differently with the Mo and W compounds, only the $W_2(NR_2)_6$ giving complete carboxylation. The product $W_2(O_2CNR_2)_6$ has a very complex structure in which the triple bond is retained, but each W atom is bonded to six oxygen atoms, as shown in (19-C-XXIII).

A combined carboxylation and thermolysis reaction, shown below, leads to smooth conversion of a triple bond to a quadruple bond:

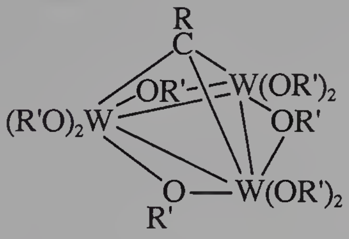


Particularly important advances have been made recently in the chemistry of $M_2(OR)_6$ compounds.[87] Many examples of simple crosswise addition of a $R'C{\equiv}CR''$ molecule to $M_2(OR)_6$, in the presence of pyridine, have been observed. The products differ in the details of structure and composition depending on the nature of R, R′, and R″, and on whether M is Mo or W, but in each case there is a quasitetrahedral M_2C_2 cluster in which an M═M bond (2.55 to 2.66 Å in length) is present. These simple adducts will react further with alkynes to give products in which two or more alkyne molecules have been coupled,[88] as in (19-C-XXIV). Further reaction affords alkyne cyclotrimerization products (substituted benzenes).



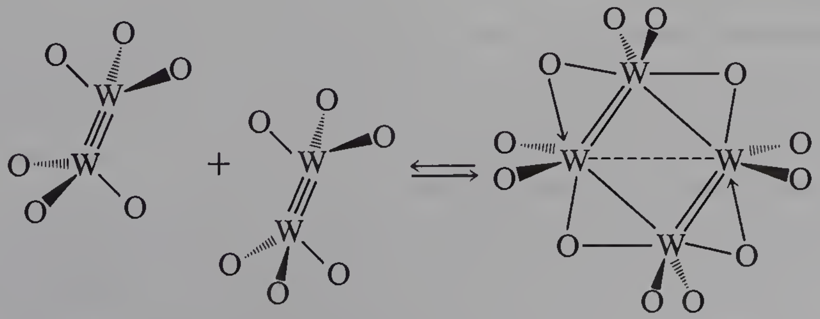
(19-C-XXIV)

We have already mentioned that in the specific case of $W_2(OCMe_3)_6$, acetylenes react to give alkylidyne compounds, $(Me_3CO)_3W{\equiv}CR$. These alkylidyne species can react with $W_2(OR')_6(py)_2$ molecules to give CR capped



(19-C-XXV)

trinuclear species of type (19-C-XXV).[89] The $W_2(Oi\text{-}Pr)_6$ molecule undergoes reversible dimerization to give a metallocyclobutadiene,[90] as shown in the following reaction:



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[87] See numerous papers by M. H. Chisholm *et al.*, for example, *J. Am. Chem. Soc.*, 1987, **109,** 2514, 4552; *Organometallics*, 1987, **6,** 1532; *Inorg. Chem.*, 1987, **26,** 1920.

[88] M. H. Chisholm *et al., J. Am. Chem. Soc.*, 1984, **106,** 6806.

[89] M. H. Chisholm *et al., J. Am. Chem. Soc.*, 1985, **107,** 1234.

[90] M. H. Chisholm *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 1014.

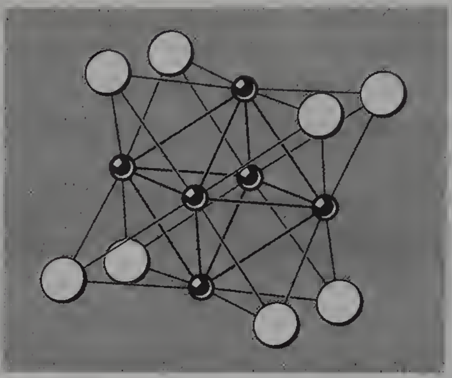

FIG. 19-C-18. The key structural unit $M_6X_8^{4+}$ found in metal atom cluster compounds of Mo^{II} and W^{II}.

19-C-10. Metal Atom Cluster Compounds

The existence of Mo^{II} and W^{II} halides has been known for more than 130 years, but only in the last 40 years have their structures and properties been fully appreciated. The key structural unit is an octahedron of metal atoms surrounded by a cubic array of halogen atoms, as shown in Fig. 19-C-18. In addition, each metal atom can coordinate another ligand along a four-fold axis of the octahedron and, so far as is known, they always do so. In the "dihalides" themselves the M_6X_8 units are linked together by four additional X atoms that are shared between two units and there are also two unshared X atoms per cluster, thus satisfying the net composition $M_6X_{12} \equiv MX_2$. Numerous compounds can be isolated in which there is a complete set of six external X atoms, thereby giving $[M_6X_{14}]^{2-}$ ions, which form nicely crystalline salts with a variety of large cations. Examples of structurally characterized compounds are the $[(C_4H_9)_4N]_2[W_6X_{14}]$ (X = Cl, Br, and I series.[91] Numerous other related compounds of both Mo and W are well characterized structurally. The outer six ligands are kinetically labile and it is possible to obtain a wide variety of complexes such as $[(Mo_6Cl_8)Cl_nL_{6-n}]^{(4-n)+}$. In aqueous solution the $[M_6X_8]^{4+}$ units are unstable toward strongly nucleophilic groups such as OH^-, SH^-, and CN^-.

Replacement reactions for the μ_3-X atoms forming the X_8 cube are very slow, but some mixed species have been obtained, examples being $Mo_6S_6X_2$ (X = Br and I). The Mo_6S_8 and Mo_6Se_8 type clusters are those that make up the Chevrel phases and are discussed in Section 23-10, where further information on all Mo and W cluster species will be found.

The usual synthetic routes to these cluster compounds begin with preparation of the anhydrous halides. The preparation of Mo_6Cl_{12}, a yellow, nonvolatile solid is shown in Fig. 19-C-7. The tungsten halides W_6X_{12}(X = Cl or Br) are obtained on disproportionation of WX_4 at 450 to 500°C or by reduction of WCl_5 or WBr_5 with aluminum in an appropriate temperature gradient. The

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[91] H. B. Gray *et al., Inorg. Chem.*, 1986, **25**, 2195.

compound W_6I_{12} is obtained by fusing W_6Cl_{12} with a 10-fold excess of a KI–LiI mixture at 540°C.

The molybdenum species show little tendency to act as reducing agents, despite the low formal oxidation number, but the tungsten compounds are fairly reactive reductants in aqueous media. It may be recalled that the $(Nb_6X_{12})^{2+}$ and $(Ta_6X_{12})^{2+}$ species (Section 19-B-8) can sustain reversible oxidation to the 3+ and 4+ species. There is little evidence that oxidation (or reduction) is possible for the $(Mo_6X_8)^{4+}$ species, but W_6Cl_{12} and W_6Br_{12} are oxidized by free halogen at elevated temperatures. In the case of W_6Br_{12} the products are W_6Br_{14}, W_6Br_{16}, and W_6Br_{18} if the temperature is kept below 150°C (above which WBr_6 is obtained). In all these there has been a two-electron oxidation of the W_6Br_8 group. The compound W_6Br_{14} may be formulated as $(W_6Br_8)Br_6$; the others contain bridging Br_4^{2-} units and are formulated as $(W_6Br_8)Br_4(Br_4)_{2/2}$ and $(W_6Br_8)Br_2(Br_4)_{4/2}$. A clean one-electron oxidation of $[W_6Br_{14}]^{2-}$ to $[W_6Br_{14}]^-$ can be achieved by use of $NOPF_6$.[92]

The reaction of Cl_2 with W_6Cl_{12} at 100°C results in an intriguing structural change. The product is of stoichiometry WCl_3 and has been shown to contain the $(W_6Cl_{12})^{6+}$ unit, isostructural with the $(M_6X_{12})^{n+}$ units found characteristically in the cluster compounds of Nb and Ta (Section 19-B-8); the complete formulation of WCl_3 is $(W_6Cl_{12})Cl_6$.

The photochemical and photophysical properties of the $[M_6X_{14}]^{2-}$ ions have been extensively studied[93] because they provide a new class of photoreceptors for light-induced chemical reactions that are chemically very stable and undergo facile electron-transfer reactions in their ground and excited states.

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Comprehensive Coordination Chemistry, Pergamon Press, Oxford, 1987. Vol. 3, Mo: E. I. Stiefel, C. D. Garner, G. Pimblett, A. E. Sykes, R. L. Richards and G. J. Leigh. W: Z. Dori. Iso and heteropolyands: M. T. Pope.

Garner, C. D. and S. Bristow in *Molybdenum Enzymes,* T. G. Spiro, Ed., Interscience-Wiley, New York, 1985. Oxomolybdenum complexes.

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Mabbs, F. E., *Coord. Chem. Rev.,* 1981, **37,** 157.

19-D. TECHNETIUM AND RHENIUM:[1] GROUP VII B(7)

These elements differ markedly from manganese but show considerable similarity to each other. Similarities to Mn in the stoichiometries of a few com-

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[92] H. B. Gray *et al., Inorg. Chem.,* 1986, **25,** 2198.

[93] H. B. Gray *et al., J. Am. Chem. Soc.,* 1983, **105,** 1878.

[1] K. A. Connor and R. A. Walton, *Comprehensive Coordination Chemistry,* Vol. 4, Chapter 43, Pergamon Press, Oxford 1987 (Re).

TABLE 19-D-1
Oxidation States and Stereochemistry of Technetium[a] and Rhenium[b,c]

Oxidation state	Coordination number	Geometry	Examples
Te^{-1}, Re^{-1}, d^8	5	?	$[M(CO)_5]^-$
Te^0, Re^0, d^7	6	Octahedral	$M_2(CO)_{10}$
Te^I, Re^I, d^6	5	*tbp*	$ReCl(dppe)_2$, $ReCl(CO)_2(PPh_3)_2$
		π Complex	$\eta^5\text{-}C_5H_5Re(CO)_2C_5H_8$, $\eta^5\text{-}C_5H_5Re(CO)_3$
	6	Octahedral	$Re(CO)_5Cl$, $K_5[Re(CN)_6]$, $Re(CO)_3(py)_2Cl$, $[(CH_3C_6H_4NC)_6Re]^+$ $ReCl(N_2)(PR_3)_4$
Te^{II}, Re^{II}, d^5	6	Octahedral	$ReCl(N_2)(PR_3)_3^+$, $ReH_2(NO)(PPh_3)_3$, $ReCl_2(NO)(PPh_3)_2L$ $M(diars)_2Cl_2$, $[Re(bipy)_3]^{2+}$
Te^{III}, Re^{III}, d^4	4	Distorted tetrahedral	$Re[P(C_6H_{11})_2]_4^-$
		Dinuclear (3° bond)	$Re_2Cl_4(RP_3)_4$
		π Complex	$(\eta^5\text{-}C_5H_5)_2ReH$, $(\eta^5\text{-}C_5H_5)_2ReH_2^+$
	5	*tbp*	$Ph_3Re(PPhEt_2)_2$
	6	Octahedral	$[Tc(diars)_2Cl_2]^+$, $ReCl_2(acac)(PPh_3)_2$, *trans*-$TcCl(acac)_2PPh_3$, *mer*-$MCl_3(PR_3)_3$
		Trigonal prism	$Re(S_2C_2Ph_2)_3$
	7	Pentagonal bipyramidal	$ReH_3(diphos)_2$, $K_4[M(CN)_7]\cdot 2H_2O$, $Te(CO)(Etdtc)_3$
		Dinuclear (4° bond)	$M_2X_8^{2-}$
		Metal atom cluster	$Re_3X_9L_3$, $Re_3Cl_3(CH_2SiMe_3)_6$, Re_3Me_9
Te^{IV}, Re^{IV}, d^3	4	Tetrahedral	$Re(o\text{-}MeC_6H_4)_4$
	5	?	$(Me_3SiCH_2)_4Re(N_2)Re(CH_2SiMe_4)_4$
	6[d]	Octahedral	MX_6^{2-}, $ReI_4(py)_2$, MCl_4, $Tc(C_2O_4)_3^{2-}$ $[Re_2OCl_{10}]^{4-}$, $ReCl_4(diars)$, MO_2
	8	?	$Tc(S_2CNC_4H_8O)_4$
	7	?	$[ReCO(diars)_2I_2](ClO_4)_2$
		Metal atom cluster	$Re_3(CH_2SiMe_3)_{12}$
Te^V, Re^V, d^2	5	*tbp* or distorted *tbp*	$ReCl_5(g)$, ReF_5, $NReCl_2(PPh_3)_2$, $ReIO_2(PPh_3)_2$
		sp	$[MOX_4]^-$
	6[d]	Octahedral	$ReOCl_3(PPh_3)_2$, $[MOCl_5]^{2-}$, Re_2Cl_{10}, $Tc(NCS)_6^-$
	7	?	$ReOCl_3TAS$
	8	Dodecahedral(?)	$[M(diars)_2Cl_4]^+$
		Distorted (C_s)	$ReH_5(PEtPh_2)_3$
Te^{VI}, Re^{VI}, d^1	4	Distorted tetrahedral	$Re(O)_2(mesityl)_2$, ReO_4^{2-}
	5	*sp*	$ReOMe_4$, $ReOCl_4$
	6	Octahedral	MF_6, $ReMe_6$, $Re(OMe)_6$[e]
	7	?	$ReOCl_6^{2-}$
	8	Square antiprism	ReF_8^{2-}
		Dodecahedral	$[ReMe_8]^{2-}$
Te^{VII}, Re^{VII}, d^0	4	Tetrahedral	MO_4^-, MO_3Cl, $Me_3SiOReO_3$
	5	*tbp*	*cis*-ReO_2Me_3, $ReCl_3(N\textit{t}\text{-}Bu)_2$
	6	Octahedral	$ReO_3Cl_3^{2-}$
	7	Pentagonal bipyramidal	ReF_7
	9	Tricapped trigonal prism	ReH_9^{2-}

[a] G. Bandoli *et al.*, *Coord. Chem. Rev.*, 1982, **44**, 191.

[b] Some compounds in nonintegral oxidation states are also known (see text).

[c] Use of M implies that both the Tc and the Re species are well known.

[d] Most common states.

[e] E. Jacob, *Angew. Chem. Int. Ed. Engl.*, 1982, **21**, 142.

pounds [e.g., $M_2(CO)_{10}$, MO_4^-] are superficial since the reactivities of these compounds tend to differ. The most stable and characteristic oxidation state for manganese is the II state, for which the chemistry is mainly that of the high-spin Mn^{2+} cation. Technetium and rhenium have little cationic chemistry, form few compounds in the II oxidation state, and have extensive chemistry in the IV and, especially, the V states. The TcO_4^- and ReO_4^- ions are much less oxidizing than MnO_4^-. A characteristic feature of Re^{III} in its halides is the formation of metal–metal bonds. Technetium also does this to some extent, whereas manganese forms no such compounds at all. Indeed rhenium shows a marked tendency to form M—M bonds in oxidation states up to at least IV. The ion $Re_2X_9^-$ has Re—Re = 2.71 Å, and in $La_4Re_6O_{19}$ where the mean oxidation number is +4.33 there are $Re(O)_2Re$ groups with the Re—Re distance 2.42 Å.

The oxidation states and stereochemistries of compounds of the elements are summarized in Table 19-D-1.

Technetium in Nuclear Medicine.[2] The term nuclear medicine implies, *inter alia,* the use of radioisotopes to make possible noninvasive examination of internal organs by staining them with a γ-ray emitter. Technetium has been extensively used for this purpose and because of research done to develop improved reagents, probably more has been learned about Tc chemistry in the last 5 to 10 years than in all the prior years since it was discovered in 1937. Two of the major applications of Tc reagents are as imaging agents for bones and the heart. The principles on which these applications are based are, briefly: (1) Neutron irradiation of ^{98}Mo, namely, $^{98}Mo(n,\beta)\ ^{99m}Tc$. The ^{99m}Tc is a metastable isotope that decays ($t_{1/2}$ = 6 h) by gamma emission. (2) The ^{99m}Tc is complexed to produce species with affinity for a particular organ or tissue type. (3) The ^{99m}Tc complex is introduced into the body and an image of the organ is made with a γ-ray scanning device. Because of research directed towards better imaging reagents certain types of complexes [e.g., $(LL)_2MO$] are better characterized for Tc than for Re.

19-D-1. The Elements

Although its existence was predicted much earlier from the Periodic Table, rhenium was first detected, by its X-ray spectrum, only in 1925; later Noddack, Berg, and Tacke isolated about a gram of rhenium from molybdenite. Rhenium is now recovered on a fairly substantial scale from the flue dusts in the roasting of molybdenum sulfide ores and from residues in the smelting of some copper ores. The element is usually left in oxidizing solution as per-

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[2] E. Deutch and K. Libson, *Comments Inorg. Chem.*, 1984, **3,** 83; R. E. Boyd, *Int. J. Appl. Radiat. Isot.*, 1982, **33,** 801; W. C. Eckelman and W. A. Volkert, *Int. J. Appl. Radiat. Isot.*, 1982, **33,** 945; A. Davison and A. G. Jones, *Int. J. Appl. Radiat. Isot.*, 1982, **33,** 867, 875.

rhenate ion, ReO_4^-. After concentration, the perrhenate is precipitated by addition of potassium chloride as the sparingly soluble salt $KReO_4$.

All isotopes of technetium are unstable toward β decay or electron capture, and traces exist in Nature only as fragments from the spontaneous fission of uranium. The element was named technetium by the discoverers of the first radioisotope—Perrier and Segré. Three isotopes have half-lives $>10^5$ years, but the only one that has been obtained on a macro scale is ^{99}Tc (β^-, 2.12×10^5 yr). The nmr spectra of this spin $\frac{9}{2}$ nucleus can be recorded.[3a] Technetium is recovered from waste fission product solutions after removal of plutonium and uranium. It is an interesting irony that the supply of technetium, which does not exist in Nature, might easily be made to exceed that of Re, which does, because of the increasing number of reactors and the very low ($\sim 10^{-9}\%$) abundance of Re in the earth's crust.

The metals resemble platinum in appearance but are usually obtained as gray powders; Re has a higher melting point (3180°C) than any metal except W (3400°C). Rhenium and Tc are both obtained by thermal decomposition of NH_4MO_4 or $(NH_4)_2MCl_6$ in H_2. Technetium can also be made by electrolysis of NH_4TcO_4 in 2 *M* H_2SO_4, with continuous addition of H_2O_2 to reoxidize a brown solid also produced. Rhenium can be electrodeposited from H_2SO_4 solutions, although special conditions are required to obtain coherent deposits. Both metals crystallize in an *hcp* arrangement. They burn in oxygen above 400°C to give the oxides M_2O_7 that sublime; in moist air the metals are slowly oxidized to the oxo acids. The latter are also obtained by dissolution of the metals in concentrated nitric acid or hot concentrated sulfuric acid. The metals are insoluble in hydrofluoric or hydrochloric acid but are conveniently dissolved by warm bromine water. Rhenium, but not technetium, is soluble in hydrogen peroxide.

Technetium is used for organ imaging as already noted but has few if any other uses. Rhenium is used in several bimetallic heterogeneous catalysts, for example, alloyed with Pt as a petroleum reforming catalyst.[3b]

TECHNETIUM AND RHENIUM COMPOUNDS

19-D-2. Oxides and Sulfides

The known *oxides* of Re and Tc are shown in Table 19-D-2. The *heptaoxides*, obtained by burning the metals, are volatile. If acid solutions containing TcO_4^- are evaporated, the oxide is driven off, a fact that can be utilized to isolate and separate technetium; rhenium is not lost from acid solutions on evaporation (i.e., at 100°C), but can be distilled from hot concentrated H_2SO_4.

[3a] G. J. Schrobilgen *et al., J. Am. Chem. Soc.*, 1982, **104,** 5303.

[3b] See J. H. Sinfelt, *Bimetallic Catalysts,* Wiley, New York, 1983, and references therein.

TABLE 19-D-2
Oxides of Rhenium and Technetium[a]

Rhenium		Technetium	
Oxide	Color	Oxide	Color
$Re_2O_3 \cdot xH_2O$	Black		
ReO_2	Brown	TcO_2	Black
ReO_3	Red	TcO_3(?)	
Re_2O_5	Blue		
Re_2O_7	Yellow (mp 220°C)	Tc_2O_7	Yellow (mp 119.5°C)

[a] Lower hydrated oxides formulated as $ReO \cdot H_2O$ and $Re_2O \cdot 2H_2O$, are obtained by Zn reduction of weakly acid ReO_4^- solutions; they are not fully investigated.

The heptaoxides readily dissolve in water, giving acidic solutions, and Re_2O_7 is deliquescent. The oxides differ structurally and in various physical properties. The structure of Re_2O_7 consists of an infinite array of alternating ReO_4 tetrahedra and ReO_6 octahedra sharing corners, whereas Tc_2O_7 consists of molecules in which TcO_4 tetrahedra share an oxygen atom and the Tc—O—Tc chain is linear. On evaporation of aqueous solutions of Re_2O_7 over P_2O_5 slightly yellow crystals of so-called perrhenic acid are obtained. These are actually $Re_2O_7(H_2O)_2$, which is binuclear with both tetrahedral and octahedral rhenium atoms, as in Re_2O_7 itself [i.e., $O_3Re—O—ReO_3(H_2O)_2$]. The Re—O—Re bond is essentially linear.

The only definite lower oxide of Tc is TcO_2. This and ReO_2 have distorted rutile structures with M—M bonds, like MoO_2 and WO_2. The hydrous oxide, $TcO_2 \cdot xH_2O$ ($x \approx 2$), a convenient starting material for preparing many Tc compounds, is obtained by reduction of TcO_4^- in aqueous solution or by hydrolysis of $[TcCl_6]^{2-}$ with aqueous ammonia.

Rhenium forms the important oxide ReO_3 whose structure (Fig. 19-D-1) is also that of CrO_3, WO_3, and so on. It is usually termed the ReO_3 structure and is closely related to the perovskite structure (Section 1-2). Some other lower oxides of rhenium and some Re bonzes[4] are known. Rhenium oxides

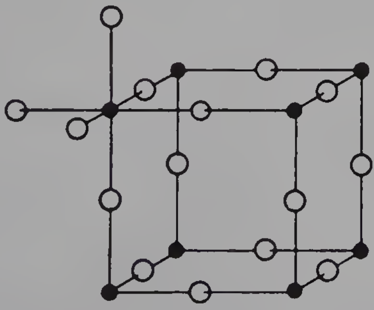

FIG. 19-D-1. The ReO_3 structure. Each metal atom lies at the center of an octahedron of oxygen atoms. This structure is closely related to the perovskite structure, since the latter is obtained from this one by insertion of a large cation into the center of the cube.

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[4] P. G. Dickens and M. T. Waller, *J. Solid State Chem.*, 1983, **48**, 407.

on supports are catalysts for metathesis of functionalized alkenes (Section 28-16).

The pairs of *sulfides* TcS_2, ReS_2, and Tc_2S_7, Re_2S_7 are isomorphous. The black heptasulfides are obtained by saturation of 2 to 6 *M* hydrochloric acid solutions of TcO_4^- or ReO_4^- with hydrogen sulfide. The precipitation is sensitive to conditions and is often incomplete. Treatment of neutral solutions of the oxo anions with thioacetamide or sodium thiosulfate followed by acidification gives a better yield. An excess of sulfur in the precipitates may be extracted with CS_2. By reducing Re_2S_7 with hydrogen ReS_3 is obtained.

The disulfides are obtained by heating the heptasulfides with sulfur in a vacuum; they are commonly nonstoichiometric.

Rhenium sulfides are effective catalysts for hydrogenation of organic substances and they have the advantage over heterogeneous platinum metal catalysts in that they are not poisoned by sulfur compounds. An inorganic reduction that they catalyze is that of NO to N_2O at 100°C.

There are also well-characterized MSe_2 and MTe_2 compounds; all of the compounds, including the disulfides, but excepting $ReTe_2$, have layer structures in which there is considerable M—M bonding.[5]

19-D-3. Halides of Technetium and Rhenium

The halides of Tc and Re are listed in Table 19-D-3.

Technetium. Fluorination of Tc at 400°C gives TcF_6 that is readily hydrolyzed to a black hydrous oxide.

The tetrachloride is obtained as paramagnetic red crystals by the action of carbon tetrachloride on Tc_2O_7 in a bomb, and is the major product on direct chlorination of the metal. The structure of $TcCl_4$ is very similar to that of

TABLE 19-D-3
The Halides of Technetium and Rhenium

		$TcCl_4$ Red brown, subl >300°C		$TcCl_6$ mp 25°C	
		ReF_4 Blue subl >300°C	ReF_5 Greenish yellow, mp 48°C	TcF_6 Golden yellow, mp 37°C	ReF_7 Pale yellow, mp 48°C
	Re_3Cl_9 Dark red	$ReCl_4$ Black	$ReCl_5$ Dark red-brown, mp 261°C	ReF_6 Pale yellow, mp 18.7°C	
	Re_3Br_9 Red-brown	$ReBr_4$ Dark red	$ReBr_5$ Dark brown	$ReCl_6$ Red-green, mp 29°C	
ReI_2 Black	Re_3I_9 Black	ReI_4 Black			

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[5] J. C. Wildervank and F. Jellinek, *J. Less-Common Met.* 1971, **24,** 73.

$ZrCl_4$ (Fig. 19-A-1) in which there are linked $TcCl_6$ octahedra. Neither the magnetic behavior nor its structure indicate metal–metal bonding, in marked contrast to $ReCl_4$ (see later); the Tc—Tc distance is 3.62 Å.

Rhenium. The heptafluoride resembles the only other heptahalide IF_7; it is obtained by fluorination of Re at 400°C under pressure. At 120°C and 1 atm, ReF_6 is obtained. This is octahedral, and strong spin-orbit coupling of the unpaired electron is reflected in a very low magnetic moment and in the electronic spectrum. On partial hydrolysis it gives blue $ReOF_4$ and on complete hydrolysis, hydrated ReO_2, $HReO_4$, and HF. Interaction of ReF_6 with H_2 in liquid HF at 25°C gives ReF_5; reduction with Re at 500°C gives ReF_4.

The most important halide and a common starting material in rhenium syntheses is *rhenium pentachloride* (Re_2Cl_{10}), which is obtained on chlorination of Re at ~600°C as a dark red-brown vapor that condenses to a dark red solid. It is rapidly hydrolyzed by water or base:

$$3ReCl_5 + 16OH^- = 2ReO_2{\cdot}2H_2O + ReO_4^- + 15\,Cl^- + 4H_2O$$

Re_2Cl_{10} is reduced by many ligands and solvents such as Et_2O and MeCN, often to Re^{IV} complexes (see later). Some of its reactions are given in Fig. 19-D-2. In the crystal, $ReCl_6$ octahedra share an edge; the magnetic properties imply substantial exchange even though the distance (3.74 Å) is too large for Re—Re bonding. Rhenium pentachloride thermally decomposes to Re_3Cl_9.

Rhenium tetrachloride can be prepared in several ways, for example,

$$2ReCl_5 + SbCl_3 \longrightarrow 2ReCl_4 + SbCl_5$$

$$3ReCl_5 + Re_3Cl_9 \longrightarrow 6ReCl_4$$

$$2ReCl_5 + CCl_2{=}CCl_2 \longrightarrow 2ReCl_4 + C_2Cl_6$$

Rhenium(IV) chloride has a unique structure consisting of zigzag chains of Re_2Cl_9 confacial bioctahedra where an end Cl atom is shared between two bioctahedra. The Re—Re distance (2.73 Å) indicates bonding. Although in both $ReCl_4$ and $TcCl_4$ there are distorted MCl_6 octahedra, as noted above, there is no metal–metal bonding in the latter.

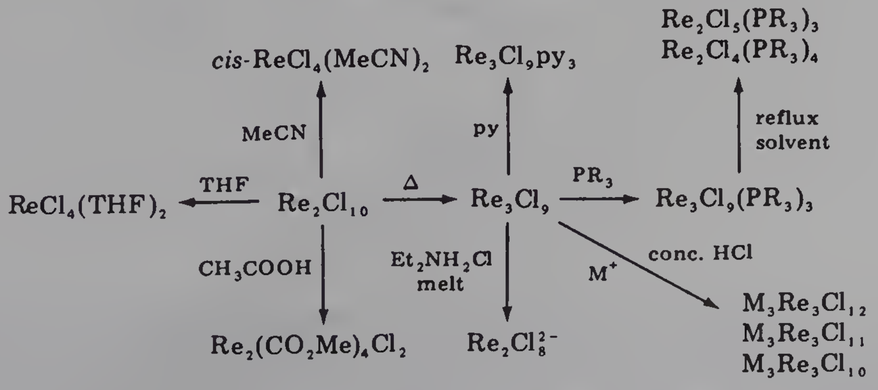

FIG. 19-D-2. Some reactions of Re_2Cl_{10} and Re_3Cl_9. Note that Re_3Cl_9 obtained from Re_2Cl_{10} is usually unreactive and is activated by exposure to air, giving $Re_3Cl_9(H_2O)_n$ or conversion to $Re_3Cl_9(THF)_3$ or $Re_3Cl_9(PPh_3)_3$.

Bromination of rhenium at 600°C gives the pentabromide, which decomposes readily to Re_3Br_9 when heated. The *tetrabromide* and *tetraiodide* can be made by careful evaporation of solutions of $HReO_4$ in an excess of HBr or HI. The tetraiodide is unstable and when heated at 350°C in a sealed tube gives ReI_3. At 110°C in nitrogen, ReI_2 is obtained; this is diamagnetic and is believed to be polymeric with Re—Re bonds.

The rhenium trihalides (for which Tc analogues are not known) have a type of structure unique among M^{III} halides. They consist of M_3X_9 molecules linked together by bridging. Figure 19-D-3 shows the structure of the M_3X_9 unit and the mode of linkage in Re_3Cl_9; the Re_3Br_9 and Re_3I_9 structures are similar but differ in detail. The most common of the Re^{III} halides (Re_3Cl_9) is best obtained by thermal decomposition of Re^V chloride as nonvolatile, dark purple crystals.

The Re_3X_9 units, in which there are Re=Re double bonds, are very stable and form complexes in which addition ligands [L in Fig. 19-D-3(a)] occupy

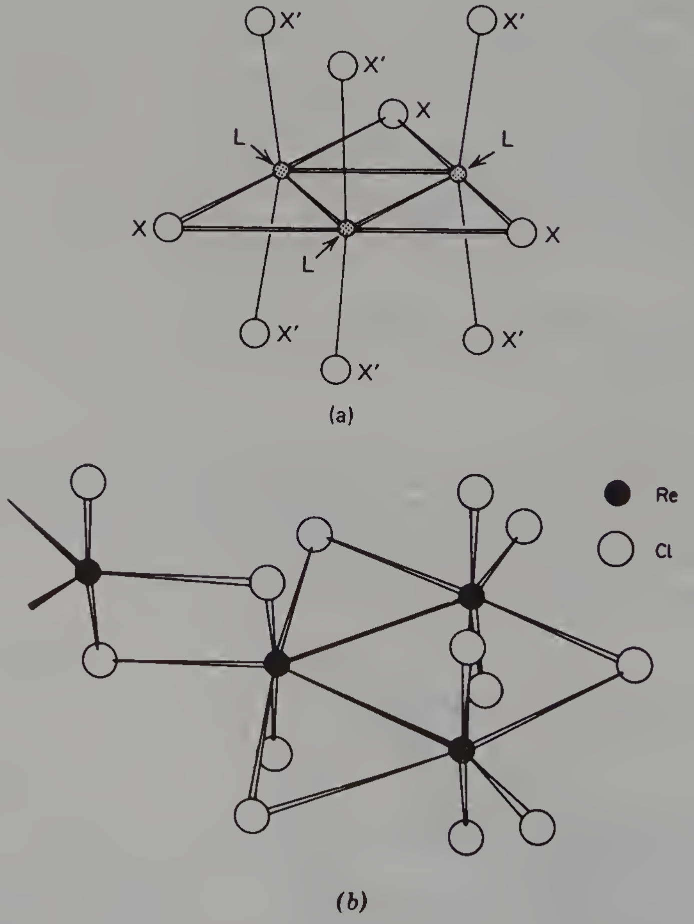

FIG. 19-D-3. (a) Sketch of the isolated Re_3X_9 unit, which has D_{3h} symmetry. The bridging halogens of the planar Re_3X_3 unit are marked X, the terminal halogen atoms X'. The positions on each Re where addition ligands may be coordinated are marked by ←L. When L is a halide ion, we obtain the anions $[(Re_3X_3)X'_{6+n}]^{n-}$ ($n = 1, 2,$ or 3 depending on the nature of the cation). (b) The structure of Re_3Cl_9 showing the linking of Re_3 units by chloride bridges.

the outer positions. Reactions of Re_3Cl_9 leading to such complexes, as well as other reactions, are summarized in Fig. 19-D-2. In addition, two other sorts of reaction should be mentioned.

1. Replacement of terminal Re—X. The bridging halides of the Re_3X_9 unit are much less reactive than the terminal X atoms, and these in turn are less labile than halogen atoms added in the L positions of Fig. 19-D-3(a). Accordingly it is possible to obtain via exchange reactions species such as $Cs[Re_3Cl_3Br_7(H_2O)_2]$ with the planar Re_3Cl_3 core, Br atoms in X′ and one L position, with two H_2O molecules in L positions.
2. With certain ligands, notably tertiary phosphines, under more forcing conditions, reduction may occur to give reduced trimeric clusters or more commonly, cleavage reactions, whereby rhenium dimeric species are formed. These dimer species, which can be in III, II, or mixed valence states, are an important feature of rhenium and technetium chemistry; we consider them separately.

19-D-4. Multiply-Bonded Dirhenium and Ditechnetium Compounds[6]

The dinuclear anion, $[Re_2Cl_8]^{2-}$, which has the structure shown in Fig. 19-D-4, was the first stable chemical species shown to possess a quadruple bond. Further discussion of this point will be found in Section 23-13. While the $[Re_2Cl_8]^{2-}$ ion can be prepared from Re_3Cl_9 or by reduction of ReO_4^- in aqueous HCl with H_2 or H_3PO_2, the best method is by treatment of $(Bu_4N)ReO_4$ with refluxing PhCOCl. Like Re_2Cl_{10} and Re_3Cl_9 it holds a key position in rhenium chemistry (Fig. 19-D-5). The $[Re_2X_8]^{2-}$ analogues with X = F, Br, I and NCS^- are known.

There are three principal classes of reactions for $[Re_2Cl_8]^{2-}$: (1) simple ligand replacements; (2) redox reactions (sometimes together with ligand

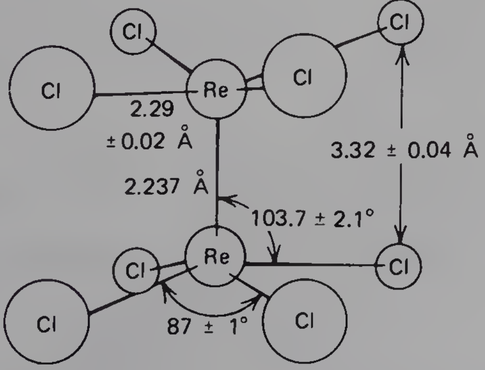

FIG. 19-D-4. The structure of the $Re_2Cl_8^{2-}$ ion in $Cs_2Re_2Cl_8 \cdot H_2O$.

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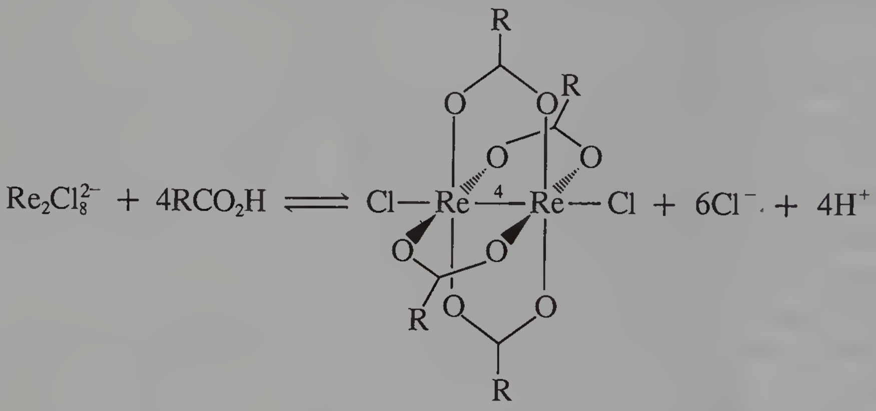
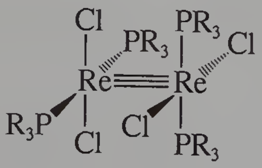
[6] F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms,* Wiley, 1982, Chapter 2; F. A. Cotton and R. A. Walton, *Struct. Bonding, (Berlin),* 1985, **62,** 1.

replacements); (3) Re—Re bond splitting reactions. The reversible reactions with carboxylic acids are perhaps the most important examples of class (1):



Redox reactions can be carried out as indicated in Fig. 19-D-5 electrochemically, but more important are reactions which lead to species such as $Re_2Cl_4(PR_3)_4$ (19-D-I) in which two electrons are added to a δ* orbital thus



(19-D-1)

reducing the Re—Re bond order to 3. These phosphine species can then be oxidized in two steps, namely,

$$Re_2^{II}X_4(PR_3)_4 \underset{}{\overset{-e}{\rightleftharpoons}} [Re_2X_4(PR_3)_4]^+ \overset{-e}{\rightleftharpoons} [Re_2^{III}X_4(PR_3)_4]^{2+}$$

When $NaBH_4$ together with PR_3 react with $[Re_2Cl_8]^{2-}$ the rhenium(IV) hydrido compound $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ is obtained.

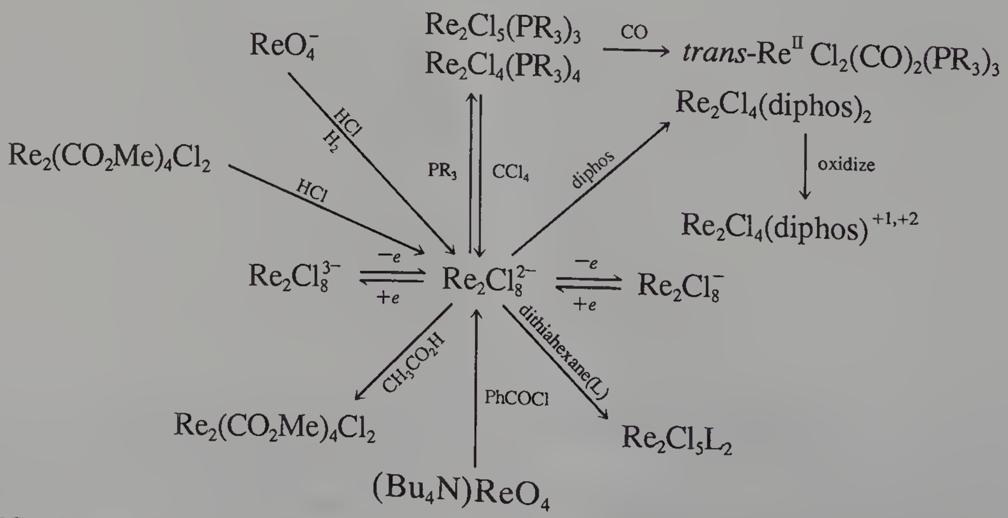


FIG. 19-D-5. Some reactions of dirhenium species in II, III, and mixed oxidation states.

With strongly π-accepting ligands, the $[Re_2Cl_8]^{2-}$ ion (as well as other Re_2^{6+} and Re_2^{4+} species) react to give mononuclear products, for example,

$$Re_2(O_2CR)_4Cl_2 + R'NC \longrightarrow [Re(CNR')_6]^+$$

$$[Re_2Cl_8]^{2-} + RNC \longrightarrow [Re(CNR)_5Cl_2]^+$$

$$Re_2Cl_4(PR_3)_4 + 4CO \longrightarrow 2Re(CO)_2Cl_2(PR_3)_2$$

The chemistry of ditechnetium species is less extensive and qualitatively different. While the $Tc_2Cl_8^{2-}$ ion can be obtained it is much less stable than the $Tc_2Cl_8^{3-}$ ion, and in general species based on the Tc_2^{5+} core (bond order 3.5) are more stable than those based on the Tc_2^{6+} core (bond order 4.0).

OXO COMPOUNDS AND COMPLEXES

For rhenium particularly, oxo compounds are predominant and of key importance in the higher oxidation states, especially V and VII. It is convenient to discuss all the oxo compounds and complexes together rather than under the separate oxidation numbers.

19-D-5. The MO_4^{n-} Species

The pertechnetates and perrhenates (MO_4^-) are among the most important compounds formed by these elements. The aqueous acids or their salts are formed on oxidation of all technetium or rhenium compounds by nitric acid, hydrogen peroxides, or other strong oxidizing agents. Pure perrhenic acid has not been isolated, but a red crystalline product, claimed to be $HTcO_4$, has been obtained; both acids are strong acids in aqueous solution. The solubilities of alkali perrhenates generally resemble those of the perchlorates, but pertechnetates are more soluble in water than either (cf. $KReO_4$ 9.8 gL^{-1}, $KTcO_4$ 126 gL^{-1} at 20°C). Highly insoluble precipitates, suitable for gravimetric determination, are given by tetraphenylarsonium chloride and nitron with both anions.

The tetrahedral TcO_4^- and ReO_4^- ions are quite stable in alkaline solution, unlike MnO_4^-. They are also much weaker oxidizing agents than MnO_4^-, but they are reduced by HCl, HBr, or HI. In acid solutions the ions can be extracted into various organic solvents such as tributyl phosphate, and cyclic amines extract them from basic solution. Such extraction methods of purification suffer from difficulties because of reduction of the ions by organic material. The anions can be readily absorbed by anion-exchange resins, from which they can be eluted by perchloric acid. The ReO_4^- ion can function as a ligand that coordinates more strongly than ClO_4^- or BF_4^- but less strongly than Cl^- or Br^-.

Cathodic reduction of the $(Me_4N)MO_4$ compounds in acetonitrile gives the paramagnetic (d^1) salts of violet TcO_4^{2-} and olive ReO_4^{2-}, both of which are extremely air sensitive.

There is a well-established ReS_4^- ion, whose chemistry is not yet extensive,[7] as well as ReO_3S^-.

When $Ba(ReO_4)_2$ and $BaCO_3$ are heated in stoichiometric proportions and for optimal temperatures and times, $Ba_3(ReO_5)_2$ and $Ba_5(ReO_6)_2$, the so-called meso- and orthoperrhenates, respectively, are obtained. Their structures are uncertain though spectroscopic data suggest discrete ReO_6^{5-} octahedra in the latter.

Mixed oxides such as $MgReO_4$ and Cr_2ReO_6 can be obtained at high temperature and pressure.

19-D-6. Oxohalides and Their Complexes

Oxohalides. These are listed in Table 19-D-4. The MOF_4 compounds form stable solid phases with infinite chains of octahedra bridged by *cis*-fluorine atoms and also metastable solids containing $[OF_3M(\mu\text{-}F)]_3$ rings. They vaporize to MOF_4 molecules which have C_{4v} structures with apical oxygen atoms. The important compound, $ReOCl_4$, can be made by the action of SO_2Cl_2 on Re at 350°C or by reaction of O_2 with $ReCl_5$ at 300°C. It is essentially molecular with long intermolecular Cl---Re bonds.

TABLE 19-D-4

Oxohalides of Technetium and Rhenium[a,b,c]

V	VI	VII	
	$(TcOF_4)_n$ Blue	TcO_3F Yellow, mp 18.3°C	
$TcOCl_3$ Brown, subl ~500°C	$TcOCl_4$ Purple, mp ~35°C	TcO_3Cl Colorless liquid, bp ~25°C	
$TcOBr_3$ Brown			
$ReOF_3$ Black, nonvolatile	$(ReOF_4)_n$ Blue, mp 107.8°C	ReO_3F Yellow, mp 147°C	$ReOF_5$ Cream, mp 34.5°C
$ReOCl_3$(?)	$ReOCl_4$, Green-brown, mp 30°C	ReO_3Cl Colorless liquid, bp 131°C	ReO_2F_3 Pale yellow, mp 90°C
$ReOBr_3$(?)	$ReOBr_4$ Blue, dec > 80°C	ReO_3Br Colorless, mp 39.5°C	

[a] Other, more complex compounds are known, for example, $Re_2O_4Cl_5$, an adduct of ReO_3Cl and $ReOCl_4$, with one oxygen of the former giving an Re—O—Re bridge.

[b] Some thiofluorides ($ReSF_3$, $ReSF_4$, and $ReSF_5$) are known (cf. J. H. Holloway *et al.*, *Inorg. Chim. Acta*, 1982, **64,** L209).

[c] ReO_2F and $ReOF_2$ have been reported: Yu. A. Politov *et al.*, *Zh. Neorg. Khim.*, 1987, **32,** 520.

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[7] R. H. Holm *et al.*, *Inorg. Chem.*, 1985, **24,** 4635.

The MO_3F compounds result from the reaction of MO_4^- salts with liquid HF, while ReO_3Cl is best made by the reaction

$$ReCl_5 + 3Cl_2O \xrightarrow[250°C]{CCl_4} ReO_3Cl + 5Cl_2$$

Oxohalogeno Anions. The most common ones are MOX_4^- and MOX_5^{2-}, but the MOX_5^- and *fac*-$ReO_3Cl_3^{2-}$ ions[8a] are also known. Salts of $ReOCl_5^{2-}$ are obtained on addition of large cations to a solution of $ReCl_5$ in concentrated HCl; in solution $[ReOCl_4(H_2O)]^-$ probably predominates. The $[TcOCl_5]^-$ ion is rather unstable.[8b]

Rhenium also forms the $[Cl_5Re—O—ReCl_5]^{4-}$ ion, which is diamagnetic because of π interactions through the oxygen atom of the linear Re—O—Re group.

Oxohalide Complexes. The oxohalides may form adducts with various ligands directly (e.g., $ReOCl_4OPCl_3$), but the most important class of compounds are those of oxorhenium(V) with phosphine ligands of the type $ReOX_3(PR_3)_2$. These compounds are readily obtained by interaction of ReO_4^- with PR_3 in ethanolic HCl. There is a striking difference between technetium and rhenium, since under similar conditions, the complexes *trans*-

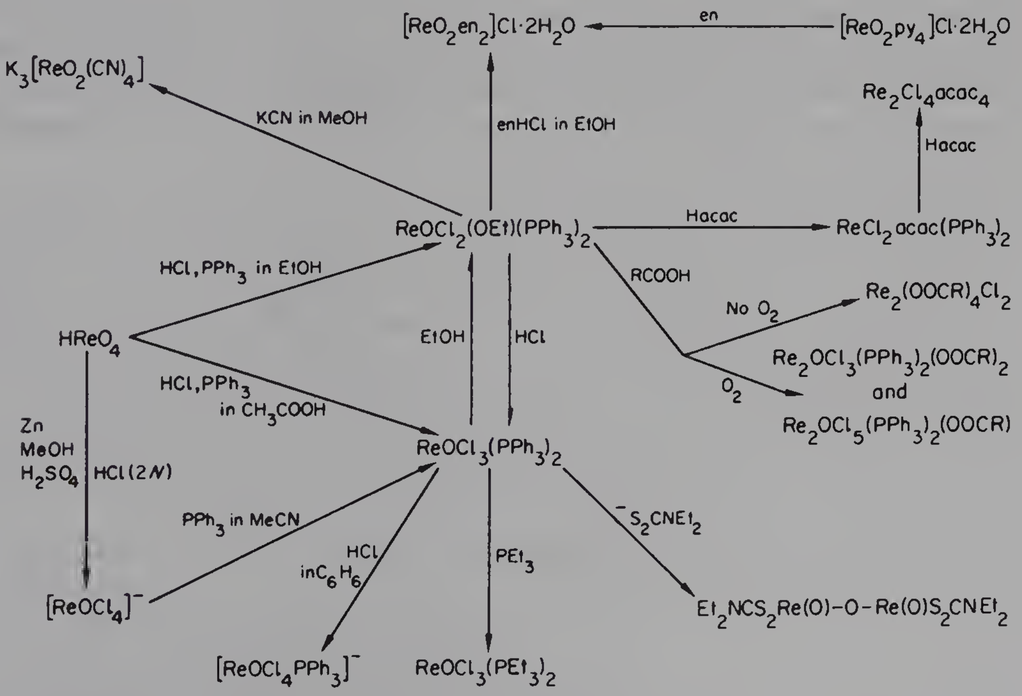


FIG. 19-D-6. Some reactions of $ReOCl_3(PPh_3)_2$. Related compounds (i.e., with various PR_3, AsR_3, or SbR_3 groups in place of PPh_3) are known and have similar though not always identical reactions. For recent reactions see J. M. Mayer *et al.*, *Inorg. Chem.*, 1987, **26,** 2283.

[8a] T. Lis, *Acta Crystallogr.*, 1983, **C39,** 961.

[8b] R. Kirmse *et al.*, *Inorg. Chem.*, 1985, **24,** 2196.

$TcCl_4(PR_3)_2$ and *mer*-$TcCl_3(PR_3)_3$ are obtained from TcO_4^-, whereas a very long reaction time is required to convert $ReOCl_3(PPh_3)_2$ to $ReCl_3(PPh_3)_3$.

Some of the more important reactions of $ReOCl_3(PPh_3)_2$ are shown in Fig. 19-D-6. The halide ion (or other ligand) opposite to the Re=O bond is labile; in ethanol, for example, it is rapidly replaced, giving the compound $ReOX_2(OEt)(PR_3)_2$. Two of the three possible isomers of $ReOX_3(PR_3)_2$ are known, the trans phosphine isomer being green, the fac one blue.

Complexes with ReO_2 and Re_2O_3 Groups. Rhenium forms numerous complexes that have a *trans*-dioxo unit. Some of the syntheses are shown in Fig. 19-D-6. The compounds $ReO(OEt)I_2L_2$ (L = py or PPh_3) can also be converted to dioxo species by the reactions

$$ReO(OEt)I_2L_2 \xrightarrow{H_2O} ReO_2I_2L_2 \xrightarrow{CNS^-} ReO_2(SCN)_2L_2$$

and with moist pyridine, $ReOCl_3(PPh_3)_2$, $ReO(OEt)Cl_2(PPh_3)_2$, or $ReOCl_4^-$ react to give the orange salt *trans*-$[ReO_2py_4]Cl\cdot 2H_2O$, probably via the sequence shown in Fig. 19-D-7, where the intermediate dimer has been isolated.

The O=Re—O—Re=O complexes may be *linear* as in $Re_2O_3(S_2NCEt_2)_4$ or *bent* with either *cis*- or *trans*-Re=O groups as in $Re_2O_3(CH_2SiMe_3)_6$; the criteria for the formation of linear versus bent bridges are not established.

Other Oxo Complexes. There are now a great many well-characterized compounds containing oxo-technetium(V), most of which have been prepared in the course of searching for new imaging agents. Many of them have square pyramidal structures with an apical oxygen atom and bi- or tetradentate ligands in the basal positions (19-D-II) and (19-D-III). These include examples

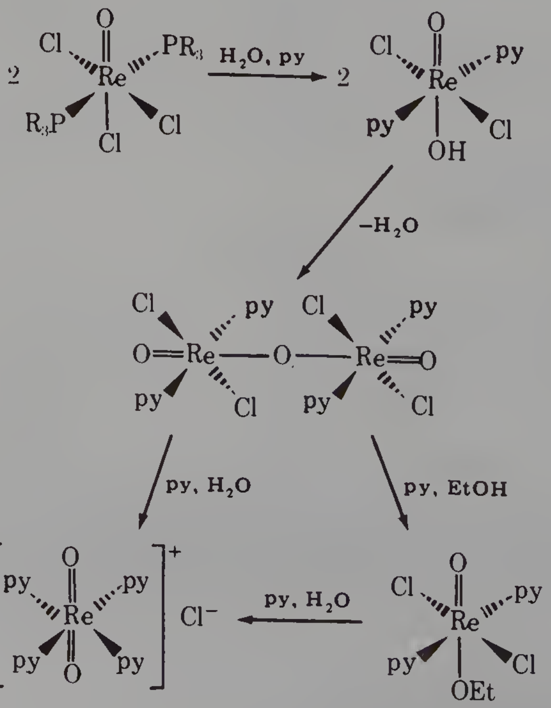
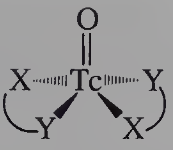
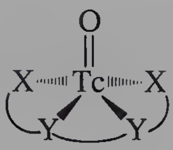


FIG. 19-D-7. Reactions of $ReOCl_3(PPh_3)_2$ with pyridine.

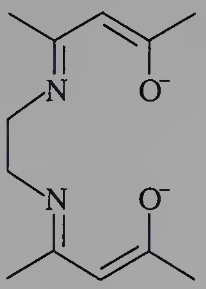


(19-D-II)

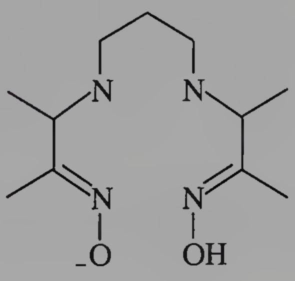


(19-D-III)

with X—Y being the anion of dimercaptosuccinic acid or its esters,[9] $[RO_2CCH(S)—CH(S)CO_2R]^{2-}$, or the tetradentate X—Y—Y—X ligand being $[SCH_2CONCH_2CONCH_2CH_2S]^{2-}$,[10] one of several double Schiff base ligands [e.g., (19-D-IV)],[11] or an amine oxime [e.g., (19-D-V)].[12] A related five-coordinate complex is TcOCl(LL), where LL is an $O—N—O^-$ tridentate ligand.[13] Many of these have been structurally characterized by X-ray crystallography and the Tc═O bond lengths are in the range 1.60 to 1.70 Å, indicative of strong double bonds. Characteristic strong Tc═O stretching bands are found at about 920 cm^{-1} in the ir spectra.



(19-D-IV)



(19-D-V)

A variety of other oxo-technetium complexes are known, including six-coordinate $TcOCl(LL)_2$ [LL = $PhNCH_2(o\text{-}C_6H_4O)^-$],[14] several *trans*-dioxo species[15] such as (19-D-VI), and some oxo-bridged species[16] such as (19-D-VII). The Tc^{VII} complexes $TcO_3X(LL)$ (X = Cl, Br and LL = bipy or *o*-phen) can be prepared and reduced to the Tc^{V} complexes $TcOX_3(LL)$.[17]

There are also oxo-rhenium(V) complexes, namely, $ReOI_2(OR)(Ph_3P)_2$ (R = Me and Et) and their hydrolysis product, the five-coordinate (*tbp*) complex $ReO_2I(Ph_3P)_2$,[18] and the $[ReO(SCH_2CH_2S)_2]^-$ ion, which has been shown to have a thio analogue, $[ReS(SCH_2CH_2S)_2]^-$.[19a]

[9] G. Bandolini *et al., Transition Met. Chem.*, 1984, **9,** 127; H. Spies and D. Scheller, *Inorg. Chim. Acta,* 1986, **116,** 1.

[10] A. Davison *et al., Inorg. Chem.*, 1984, **23,** 3793.

[11] E. Deutch *et al., Inorg. Chem.,* 1984, **23,** 227.

[12] S. Jurisson *et al., Inorg. Chem.,* 1986, **25,** 543.

[13] G. Bandolini *et al., Inorg. Chim. Acta,* 1984, **95,** 217.

[14] G. Bandolini *et al., J. Chem. Soc. Dalton Trans.,* **1982,** 2455.

[15] M. J. Clarke *et al., Inorg. Chem.,* 1982, **21,** 2037; *Inorg. Chim. Acta,* 1985, **109,** 39.

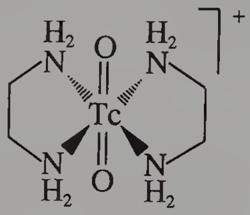
[16] M. J. Clarke *et al., Inorg. Chim. Acta,* 1986, **114,** L11; H. B. Burgi *et al., Inorg. Chem.,* 1981, **20,** 3829.

[17] A. Davison *et al., Inorg. Chem.,* 1981, **20,** 4300.

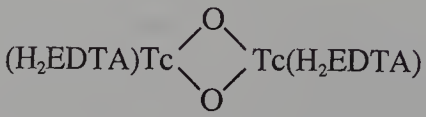
[18] G. Ciani *et al., Inorg. Chim. Acta,* 1983, **72,** 29.

[19a] J. R. Dilworth *et al., Inorg. Chim. Acta,* 1982, **65,** L225.

Finally, trioxorhenium(VII) species, $LReO_3^+$, L = 1,4,7-triazacyclononane are similar[19b] to the corresponding neutral compounds of Mo^{VI} and W^{VI}.



(19-D-VI)



(19-D-VII)

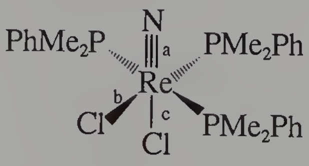
OTHER COMPLEXES

19-D-7. Complexes of Nitrogen Ligands

The main types are those with Re=NR, Re≡N, and Tc≡N bonds, but there are also some $Re(N_2)$, Re(NO), and Tc(NO) compounds.

The Nitrido (M≡N) Compounds. Nitrido compounds are known for both metals in oxidation states V and VI. Representative compounds are the following:

Rhenium(V): $(R_3P)_nX_2ReN$, with $n = 2$ or 3, depending on the steric requirement of R_3P. With Ph_3P we have $n = 2$, while with $PhMe_2P$, $n = 3$. The structure of the $PhMe_2P$ complex,[20] (19-D-VIII) is representative. The



$a = 1.660$ Å
$b = 2.442$ Å
$c = 2.633$ Å

(19-D-VIII)

strong structural trans effect of the nitride ligand is notable. Other Re^V nitrido complexes can be derived from these by ligand exchange reactions.[21]

Rhenium(VI): The $[Cl_4ReN]^-$ ion is representative. It has a square pyramidal structure with an apical Re≡N bond of length 1.619 Å.[22]

Technetium(V): The first Tc≡N bond was reported only in 1981 in the compound $(Et_2NCS_2)_2TcN$.[23] The square pyramidal coordination has four basal sulfur atoms and an apical Tc≡N bond of length 1.604 Å. Other Tc^V≡N compounds containing a great variety of ligands are now known.[24]

Technetium(VI): Compounds containing the $[X_4TcN]^-$ ions, X = Cl and

[19b] P. S. Roy and K. Wieghardt, *Inorg. Chem.*, 1987, **26**, 1855.

[20] E. Forsellini *et al.*, *Acta Crystallogr.*, 1982, **38B**, 3081.

[21] P. J. Blower and J. R. Dilworth, *J. Chem. Soc. Dalton Trans.*, **1985**, 2305.

[22] K. Dehnicke *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981**, 1061.

[23] J. Baldas *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981**, 1798.

[24] U. Abram *et al.*, *Inorg. Chim. Acta*, 1985, **109**, L9; J. Baldas *et al.*, *Inorg. Chem.*, 1986, **25**, 150.

Br, can be obtained by the reaction of TcO_4^- in aqueous HX with N_3^-, whereby the nitride ligand and N_2 are formed. The structure of $[Cl_4TcN]^-$ is very similar to that of its Re analogue with the Tc≡N bond a bit shorter at 1.581 Å.[25]

In general these M≡N bonds, like those of other metals (cf. Mo, W, Ru, and Os) exhibit donor properties like those of a nitrile and form adducts with BX_3 or other acceptors [e.g., $(PhMe_2P)_3Cl_2ReNBCl_3$, with a linear Re—N—B chain[26]]. The M≡N bonds generally persist while other ligand exchanges occur, for example,

$$(Ph_3P)_2Br_2ReN \xrightarrow{\text{excess KCN(aq)}} K_2[ReN(CN)_4]\cdot H_2O$$

The M≡N bonds can be identified in ir spectra by their strong absorptions in the 1000 to 1100-cm^{-1} range.

A Re^{VII} nitrido compound (F_4ReN) is also known and it reacts with ClF_3 to give a mixture of $F_5Re{=}NCl$ and $F_5Re{=}NF$.[27]

The Imino or Nitrene (M=NR) Compounds. The reaction of $ReOCl_3(PPh_3)_2$ with $PhNH_2$ gives $Re(NPh)Cl_3(Ph_3P)_2 + H_2O$. Other routes to Re=NR bonds are

$$ReOCl_4 + PhNCO \longrightarrow Cl_4ReNPh + CO_2$$

$$ReOCl_3(PPh_3)_2 + RNH{-}NHR\cdot 2HCl \xrightarrow{PPh_3} Re(NR)Cl_3(PPh_3)_2 + RNH_3Cl + PPh_3O + HCl$$

The alkylimino complexes react with Cl_2 according to the equation

$$Re(NR)Cl_3(PPh_3)_2 \xrightarrow[CCl_4]{Cl_2 \text{ in}} ReCl_4(PPh_3)_2$$

Ligand replacement reactions in which the Re=NR moiety is conserved can also be carried out, as, for example[21,28]:

$$Re(NPh)Cl_3(PMe_3)_2 \xrightarrow{Me_2Mg} Re(NPh)Me_3(PMe_3)_2$$

Dinitrogen Complexes. Rhenium forms a number of N_2 complexes, of which the Re^I species, such as $Re(N_2)X(PR_3)_4$, $Re(N_2)X(CO)_2(PR_3)_2$, and $Re(N_2)X(diphos)_2$ are best known.[29] They undergo oxidation and reduction reactions either electrochemically or with reagents such as Cl_2.

The dinitrogen ligand can act also as a donor to give bridged species, $(PhMe_2P)_4ClReNNCrCl_3(THF)_2$ and $[(PhMe_2P)_4ClReNN]_2MoCl_4$, the latter having linear Re—N—N—Mo groups.

Nitrosyl (NO) Complexes. Only a few of these have been characterized but more presumably can exist. Those first made were $[Tc(NH_3)_4(NO)(H_2O)]Cl_2$, $[Tc(NO)Br_4]^-$, $[Tc(NO)(NCS)_5]^{2-}$, $[Tc(NO)(NCS)_5]^{3-}$, and $Re(NO)Cl_2$-

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[25] J. Baldas *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 2395.

[26] R. Dantona *et al.*, *Z. Naturforsch.*, 1984, **39B**, 733.

[27] J. Fawcett *et al.*, *J. Chem. Soc. Chem. Commun.* **1982**, 958.

[28] G. Wilkinson *et al.*, *Polyhedron*, 1982, **1**, 31, 37.

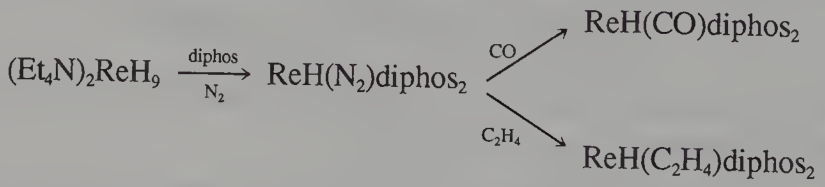
[29] G. J. Leigh *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981**, 800.

(OMe)(PPh_3)$_2$. More recent examples are $TcCl_3(NO)(PMe_2Ph)_2$[30] and $Re(NO)Cl_3(Ph_3PN)(Ph_3PO)$,[31] and species such as $Re(NO)(SAr)_4$ or $(ArS)_2(NO)Re(\mu\text{-}SAr)_3Re(NO)(SAr)_2$, where Ar is a highly hindered thiophenol.[32]

19-D-8. Hydrido Complexes

For rhenium especially there is an extensive chemistry of complexes with M—H bonds (Chapter 24) of the following types.

1. Polyhydrides with three to eight hydrogen atoms such as $ReH_5(PPh_3)_3$ and $ReH_7(PPh_3)_2$. These may be protonated[33a] to give species like $[ReH_6(PR_3)_3]^+$.
2. Carbonyl hydrides that may be monomeric like $HRe(CO)_5$, or clusters like $Re_3H_3(CO)_{12}$ or $[Re_3H_2(CO)_{12}]^-$.
3. The dimeric hydrides $Re_2H_8(PR_3)_4$, which have four bridge hydrogen atoms, can be prepared best by reaction of BH_4^- with $Re_2Cl_8^{2-}$ in presence of PR_3.[33b]
4. The hydride $(\eta\text{-}C_5H_5)_2ReH$, which is a base, giving $(\eta\text{-}C_5H_5)_2ReH_2^+$.
5. Alkene complexes[33c] like $Re(\eta^4\text{-}C_5H_6)H_3(PR_3)_2$.
6. The unique anions MH_9^{2-}. The ReH_9^{2-} ion is made by reduction of ReO_4^- with an excess of sodium in ethanol. The structure (Fig. 24-4) has two kinds of H atoms, but shows only one ^1H nmr signal because of fluxionality. The ReH_9^{2-} ion is a source of other hydrido species, for example



19-D-9. Other Complexes in Oxidation States II to V

The elements Tc and Re form a large number of rather conventional complexes in these middle oxidation states; most of them involve octahedral six-coordination.

Although $ReCl_6^-$ is formed as $[PCl_4][ReCl_6]$ when rhenium metal reacts with PCl_5 at 500°C, the most important of all the halogeno ions are the yellow *hexachlororhenate(IV)* and yellow-green *hexachlorotechnetate* ions (MCl_6^{2-}). These are obtained by reduction of the oxo ions, MO_4^- in hydrochloric acid solution by KI. The salts have solubilities similar to those of K_2PtCl_6, those

[30] R. Kirmse *et al.*, *Polyhedron*, 1983, **2,** 935.

[31] K. Dehnicke *et al.*, *Z. Anorg. Allg. Chem.* 1983, **502,** 35.

[32] P. J. Blower *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985,** 1533.

[33a] G. A. Moehring and R. A. Walton, *J. Chem. Soc. Dalton Trans.*, **1987,** 715.

[33b] F. A. Cotton *et al.*, *Inorg. Chem.*, 1984, **23,** 159.

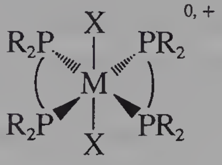
[33c] W. D. Jones and J. A. Maguire, *Organometallics,* 1987, **6,** 1301.

with large cations being insoluble. The complex K_2ReCl_6 hydrolyzes in water to hydrous ReO_2 but it is stable in HCl solution.

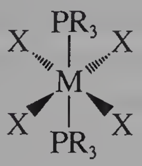
By reaction of the MCl_6^{2-} ions, or MO_4^- in the presence of a reducing agent, tris-β-diketonate complexes, for example, $Tc[Me_3CC(O)CHC(O)CCMe_3]_3$, can be prepared; these may then be oxidized to the $[Tc(dik)_3]^+$ ions.[34]

Other homoleptic octahedral complexes include the triscatecholates,[35] the thiocyanates,[36a] $[M(NCS)_6]^{2-}$ and $[M(NCS)_6]^{3-}$, and various $\{Tc[S{=}C(NR_2)_2]_6\}^{3+}$ complexes.[36b] A polymeric octahedral complex of Tc^{IV} in which there are bridging $O_3PCH_2PO_3^{4+}$ and OH^- ligands is structurally characterized.[37]

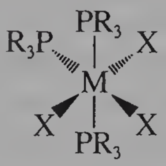
Octahedral complexes with mixed ligand sets are numerous. A large and important group are the mixed halogeno–phosphine complexes, which are mainly of the types (19-D-IX) to (19-D-XI). The pairs of Tc compounds of type (19-D-IX) with X = Cl, Br, and NCS, can be reversibly interconverted by cyclic voltammetry.[38] Some other complexes in this category are $[Tc(PR_3)_2L]^{0,+,2+}$, where L is a tetradentate Schiff base,[39] and the bipy complexes $[TcCl_2(bipy)_2]^{2+}$ and $[TcCl_4(bipy)]$.



(19-D-IX)



(19-D-X)



(19-D-IX)

Higher coordination numbers are also found. The isomorphous $K_4[M(CN)_7]$ compounds contain pentagonal bipyramidal anions.[40] The $[Tc(CN)_7]^{4-}$ ion readily undergoes oxidation to $[TcO(CN)_5]^{2-}$ which hydrolyzes to the $[TcO_2(CN)_4]^{3-}$ ion.[41] A number of eight-coordinate complexes are known for the M^{IV} ions. Reaction of $TcOCl_4^-$ with the dithiocarbamate ion derived from morpholine gives $Tc(S_2CNC_4H_8O)_4$,[42] and octahedral $[TcCl_2(diars)_2]^+$ is oxidized by Cl_2 to give $[TcCl_4(diars)_2]^+$, which is isostructural with many other dodecahedral $[MX_4(diars)_2]$ species.[43a] There are a few divalent halide complexes with phosphine or arsine ligands,[43b] and the complex[43c] $[Re(bipy)_3](ReO_4)_2$.

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[34] G. S. Patterson *et al.*, *Inorg. Chim Acta,* 1986, **114,** 141.

[35] C. G. Pierpont *et al.*, *Inorg. Chem.*, 1987, **26,** 87.

[36a] A. Davison *et al.*, *Inorg. Chem.*, 1980, **19,** 1105.

[36b] A. Davison *et al.*, *Inorg. Chim. Acta,* 1983, **77,** L127.

[37] E. Deutch *et al.*, *J. Am. Chem. Soc.*, 1980, **102,** 2476.

[38] E. Deutch *et al.*, *Inorg. Chem.*, 1983, **22,** 1696.

[39] W. R. Heineman *et al.*, *Inorg. Chem.*, 1985, **24,** 2134.

[40] J.-M. Manoli *et al.*, *J. Chem. Soc. Dalton Trans.*, **1980,** 192.

[41] A. Davison *et al.*, *Inorg. Chem.*, 1980, **19,** 1993.

[42] T. I. A. Gerber *et al.*, *Inorg. Chim. Acta,* 1985, **109,** L17.

[43a] E. Deutch *et al.*, *J. Am. Chem. Soc.*, 1980, **102,** 2103.

[43b] R. A. Walton *et al.*, *Polyhedron,* 1987, **6,** 907.

[43c] H.-B. Bürgi *et al.*, *Inorg. Chem.*, 1987, **26,** 1449.

Sulfur Complexes. The compound $Re(S_2C_2Ph_2)_3$ has a trigonal prismatic structure. Interaction of K_2ReCl_6 with KSCN gives the aggregate $[Re_4S_4(CN)_{12}]^{4-}$, which has a typical M_4S_4 core. Another unusual species is $Na_4Re_6^{III}S_{10}(S_2)$, which has a regular octahedron of Re atoms inside a cube of S atoms with μ-S and μ-S_2 bridges between the octahedra.

19-D-10. Carbonyl, Isocyanide, and Organo Compounds

Carbonyls. In addition to the binary carbonyls, $M_2(CO)_{10}$, and some metal cluster carbonyls, there are numerous mixed ligand carbonyl species, $M(CO)_xX_yL_z$, which are all six-coordinate. Although some additional carbonyl chemistry of Tc has been developed,[44] for example, $[Tc(CO)_2(PR_3)_4]^+$, $Tc(CO)_2Cl(PR_3)_3$, $Tc(CO)_3Cl(PR_3)_2$, and derivatives thereof, the carbonyl chemistry of Re is more extensive. The compound $Re_2(CO)_{10}$ is conveniently obtained by the reaction of CO with NH_4ReO_4,[45] and many derivatives then made on reaction with halogens, phosphines, and so on. Another route to such compounds is by the action of CO on $Re_2X_4(PR_3)_4$ compounds.[46,47]

There are many *isocyanide complexes* of M^I and M^{II}. The stable d^6 com-

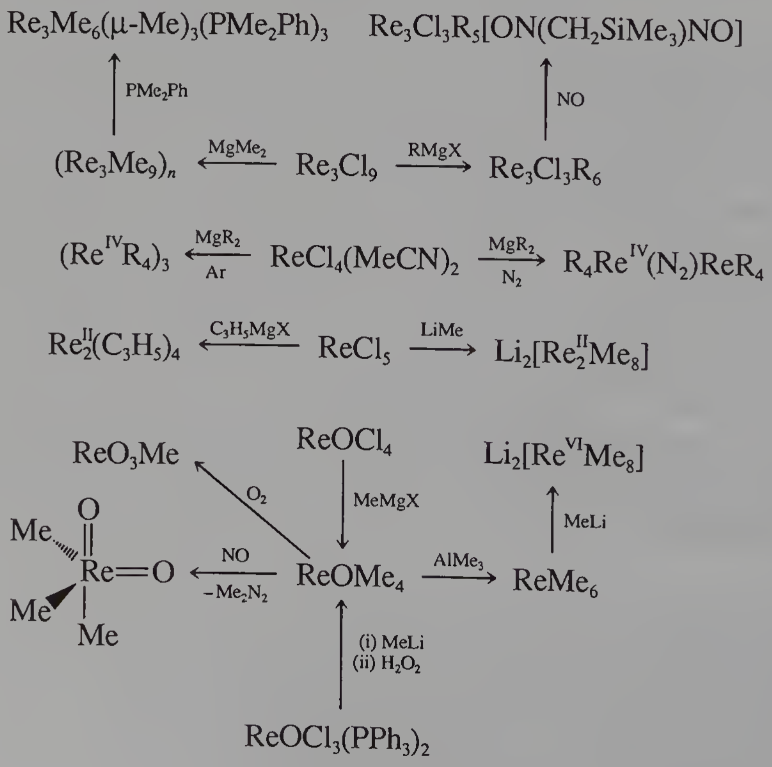


FIG. 19-D-8. Synthesis of some rhenium alkyls ($R = CH_2SiMe_3$).

[44] L. Magon *et al.*, *Inorg. Chem.*, 1985, **24**, 4744.

[45] F. Calderazzo and R. Poli, *Gazz. Chim. Ital.*, 1985, **115**, 573.

[46] K. R. Dunbar and R. A. Walton, *Inorg. Chim. Acta*, 1984, **87**, 185.

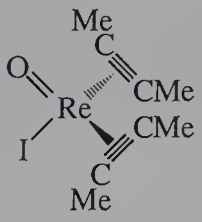
[47] F. A. Cotton *et al.*, *Inorg. Chem.*, 1986, **25**, 1021.

pounds, $[Tc(CNR)_6]PF_6$, are obtained by reduction of pertechnetate[48] and these, on treatment with Cl_2 or Br_2 yield $[Tc(CNR)_6X]^{2+}$ cations.[49] Rhenium isocyanides[50] can be readily derived from $[Re_2Cl_8]^{2-}$ or $Re_2(O_2CCH_3)_4Cl_2$, or by treating $ReH_n(PR_3)_m$ or $ReH_n(PR_3)_m(RCN)_r$ complexes with isocyanides. These reactions afford species such as $Re(PPh_3)_2(CH_3CN)_2(Me_3CNC)_2$.

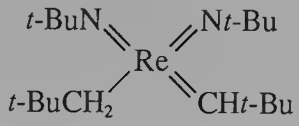
Rhenium forms a number of *σ-bonded alkyls and aryls,* in all oxidation states from I to VII. Some of the chemistry is shown in Fig. 19-D-8. The structures of several of these species have been determined, including trirhenium(III) cluster alkyls and species such as $(Me_4ReO)_2Mg(THF)_4$, where the oxygen atom on Re is bound to the Mg ion, $ReO(o\text{-tol})_4$, $ReO_2(\text{mesityl})_2$, and $Re(o\text{-tol})_4$.[51]

The arene complex, $[Re(\eta\text{-}C_6H_6)(PMe_3)_2]_2$ with an Re—Re bond can be made by metal atom synthesis; the Re—Re bond may then be cleaved by I_2 and a variety of $Re(\eta\text{-}C_6H_6)(PMe_3)_2X$ derivatives isolated.[52]

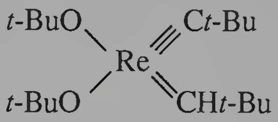
A variety of oxorhenium organo compounds can be made, for example $(C_5Me_5)ReO_3$[53] and the 2-butyne complex (19-D-XII),[54] and oxoalkyls and -aryls noted previously. Like other early transition metals (Nb, Ta, Mo, and W), rhenium in its highest oxidation state(VII) forms alkylidene and alkylidyne compounds,[55] such as (19-D-XIII) and (19-D-XIV).



(19-D-XII)



(19-D-XIII)



(19-D-XIV)

General References

Melnik, M., and J. E. Van Lier, *Coord. Chem. Rev.*, 1987, **77**, 275 (X-ray structures of Tc compounds).

Seddon, K. R., *Coord. Chem. Rev.*, 1981, **37**, 199.

Turp, J. E., *Coord. Chem. Rev.*, 1982, **45**, 281; 1983, **52**, 245, 249.

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[48] A. Davison *et al., Inorg. Chem.*, 1983, **22,** 2798.

[49] A. Davison *et al., Organometallics,* 1985, **4,** 139.

[50] R. A. Walton *et al., Organometallics,* 1984, **3,** 240; P. E. Fanwick *et al., Organometallics,* 1984, **3,** 1515.

[51] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 169; *Polyhedron,* 1987, **6,** 1081.

[52] M. L. H. Green *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 233.

[53] W. A. Herrmann *et al., Polyhedron,* 1987, **6,** 1165; *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 787.

[54] J. M. Mayer *et al., J. Am. Chem. Soc.*, 1985, **107,** 7454.

[55] D. S. Edwards and R. R. Schrock, *J. Am. Chem. Soc.*, 1982, **104,** 6806.

19-E. THE PLATINUM GROUP METALS

19-E-1. Occurrence

Ruthenium, osmium, rhodium, iridium, palladium, and platinum are the six heaviest members of Group VIII (8–10). They are rare elements; Pt is the most common with an abundance of $\sim 10^{-6}\%$, whereas the others have abundances $\sim 10^{-7}\%$ of the earth's crust. They occur as metals, often as alloys such as "osmiridium," and in sulfide, arsenide, and other ores. They are commonly associated with Cu, Ag, and Au. Abnormally high Ir in rocks has been taken to come from a meteorite 65 M years ago.[1] The main sources of the metals are South Africa, the USSR, and Canada; in all ores the "values" of the platinum metals are in grams per ton, and concentration by gravitation and flotation is required. Extraction methods depend on the ore, but the concentrate is smelted with coke, lime, and sand and bessemerized in a converter. The resulting Ni—Cu sulfide "matte" is cast into anodes. On electrolysis in sulfuric acid solution, Cu is deposited at the cathode, and Ni remains in solution, from which it is subsequently recovered by electrodeposition, and the platinum metals, Ag, and Au collect in the anode slimes. The subsequent procedures for separation of the elements are very complicated. Although most of the separations used to involve classical precipitation, fractional crystallization of salts, and so on, current procedures involve ion exchange and particularly solvent extraction, for example, by 2-nonylpyridine-1-oxide.[2a] Ruthenium and Os are recovered first, however, as MO_4 from oxidizing solutions.

19-E-2. The Metals

Some properties of the platinum metals are collected in Table 19-E-1.

The metals are obtained initially as sponge or powder by ignition of ammonium salts of the hexachloro anions. Almost all complex and binary compounds of the elements give the metal when heated above 200°C in air or oxygen; Os is oxidized to the volatile OsO_4, and at dull red heat Ru gives RuO_2, so that reduction in hydrogen is necessary. The finely divided metals are also obtained by reduction of acidic solutions of salts or complexes by Mg, Zn, H_2, or other reducing agents, such as, citrate,[2b] oxalic or formic acid, or by electrolysis under proper conditions.

The metals, as gauze or foil, and especially on supports such as charcoal or alumina on to which the metal salts are absorbed and reduced *in situ* under specified conditions, are widely used as catalysts for an extremely large range of reactions in the gas phase or in solution. One of the larger uses of Pt is for the reforming of hydrocarbons. Commercial uses in homogeneous reac-

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[1] A. W. Alvarez, *Proc. Natl. Acad. Sci.*, 1983, **80,** 627.

[2a] M. J. Hudson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985,** 771.

[2b] J. Turkevitch *et al.*, *J. Phys. Chem.*, 1986, **90,** 4745.

TABLE 19-E-1
Some Properties of the Platinum Metals

Element	mp (°C)	Form	Best solvent
Ru	2546	Gray-white, brittle, fairly hard	Alkaline oxidizing fusion
Os	~3050	Gray-white, brittle, fairly hard	Alkaline oxidizing fusion
Rh	1960	Silver-white, soft, ductile	Hot conc. H_2SO_4; conc. HCl + $NaClO_3$ at 125–150°C
Ir	2443	Silver-white, hard, brittle	Conc. HCl + $NaClO_3$ at 125–150°C
Pd	1552	Gray-white, lustrous, malleable, ductile	Conc. HNO_3, HCl + Cl_2
Pt	1769	Gray-white, lustrous, malleable, ductile	Aqua regia

tions are fewer, but palladium is used in the Smidt process and Rh in hydroformylation and in acetic acid synthesis (Sections 28-4 and 6). Industrially as well as in the laboratory, catalytic reductions are especially important.

Platinum or its alloys are used for electrical contacts, for printed circuitry, for plating and on a large scale, together with Rh, automobile exhaust convertors.

Ruthenium and Os are unaffected by mineral acids below ~100°C and are best dissolved by alkaline oxidizing fusion (e.g., NaOH + Na_2O_2, $KClO_3$). Rhodium and Ir are extremely resistant to attack by acids, neither metal dissolving even in aqua regia when in the massive state. Finely divided Rh can be dissolved in aqua regia or hot concentrated H_2SO_4. Both metals also dissolve in concentrated HCl under pressure of oxygen or in presence of sodium chlorate in a sealed tube at 125 to 150°C. At red heat Cl_2 leads to the trichlorides.

Palladium and Pt are more reactive than the other metals. Palladium is dissolved by nitric acid, giving $Pd^{IV}(NO_3)_2(OH)_2$; in the massive state the attack is slow, but it is accelerated by oxygen and oxides of nitrogen. As a sponge, Pd also dissolves slowly in HCl in the presence of chlorine or oxygen. Platinum is considerably more resistant to acids and is not attacked by any single mineral acid, although it readily dissolves in aqua regia and even slowly in HCl in the presence of air since

$$PtCl_4^{2-} + 2e = Pt + 4Cl^- \qquad E^0 = 0.75 \text{ V}$$

$$PtCl_6^{2-} + 2e = PtCl_4^{2-} + 2Cl^- \qquad E^0 = 0.77 \text{ V}$$

Platinum is not the inert material that it is often considered to be. There are at least 70 oxidation-reduction and decomposition reactions in solution that are catalyzed by metallic platinum. Examples are the Ce^{IV}–Br^- reaction and the decomposition of N_2H_4 to N_2 and NH_3. It is possible to predict whether catalysis can occur from a knowledge of the electrochemical properties of the reacting couples.

Both Pd and Pt are rapidly attacked by fused alkali oxides, and especially by their peroxides, and by F_2 and Cl_2 at red heat. It is of importance in the use of Pt for laboratory equipment that on heating it combines with, for example, elemental P, Si, Pb, As, Sb, S, and Se, so that the metal is attacked when compounds of these elements are heated in contact with Pt under reducing conditions.

Both Pd and Pt are capable of absorbing large volumes of molecular hydrogen, and Pd is used for the purification of H_2 by diffusion.

19-E-3. General Remarks on the Chemistry of the Platinum Metals

The chemistries of these elements have some common features, but there are nevertheless wide variations depending on differing stabilities of oxidation states, stereochemistries, and so on. The principal areas of general similarity are as follows:

1. *Binary Compounds.* There are a large number of oxides, sulfides, phosphides, and so on, but the most important are the halides.

2. *Aqueous Chemistry.* This chemistry is almost exclusively that of complex compounds. Aqua ions of Ru^{II}, Ru^{III}, Rh^{III}, Ir^{III}, Pd^{II}, and Pt^{II} exist, but complex ions are formed in the presence of anions other than ClO_4^-, BF_4^-, or *p*-toluenesulfonate. The precise nature of many supposedly simple solutions (e.g., of rhodium sulfate) is complicated and often unknown.

A vast array of complex ions, predominantly with halide or nitrogen donor ligands, are water soluble. Exchange and kinetic studies have been made with many of these because of interest in (*a*) trans effects, especially with square Pt^{II}, (*b*) differences in substitution mechanisms between the ions of the three transition metal series, and (*c*) the unusually rapid electron transfer process with heavy metal complex ions.

Although the species involved may often not be fully identified, much potential information has been collected from polarographic and other studies.[3]

3. *Compounds with π-Acid Ligands.*

(*a*) Binary carbonyls are formed by all but Pd and Pt, the majority of them polynuclear. Substituted polynuclear carbonyls are known for Pd and Pt, and all six elements give carbonyl halides and a wide variety of carbonyl complexes containing other ligands and carbonyl anions.

(*b*) Nitric oxide complexes are a feature of the chemistry of Ru.

(*c*) An especially widely studied area is the formation of complexes with trialkyl- and triarylphosphines and related phosphites, and to a lesser extent with R_3As and R_2S. The most important are those with triphenylphosphine and methyl-substituted phosphines (e.g., $PPhMe_2$). The latter are more

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[3] R. N. Goldberg and L. G. Hepler, *Chem. Rev.*, 1968, **68**, 229 (an authoritative collection of thermodynamic data on compounds of the Pt metals and their oxidation–reduction potentials; also contains much descriptive chemistry).

soluble in organic solvents than PPh_3 complexes, and have proved particularly useful for the determination of configuration by nmr.

Mixed complexes of PR_3 with CO, alkenes, halides, and hydride ligands in at least one oxidation state are common for all of the elements.

(*d*) All these elements have a strong tendency to form bonds to carbon, especially with alkenes and alkynes; Pt^{II}, Pt^{IV}, and to a lesser extent Pd^{II} have a strong tendency to form σ bonds, and Pd^{II} very readily forms π-allyl species.

(*e*) A highly characteristic feature is the formation of hydrido complexes, and M—H bonds may be formed when the metal halides in higher oxidation states are reduced, especially in the presence of tertiary phosphines or other ligands. Hydrogen abstraction from reaction media such as alcohols or DMF is common.

(*f*) For the d^8 ions Rh^I, Ir^I, Pd^{II}, and Pt^{II}, the normal coordination is square (though five-coordinate species are fairly common) and oxidative-addition reactions are of great importance.

Platinum group metal chemistry is an exceedingly active area of research, and even omitting patents, which are very numerous, the research papers number in the many hundreds per year.

BINARY COMPOUNDS

19-E-4. Oxides, Sulfides, Phosphides, and Similar Compounds.

Oxides. The best known anhydrous oxides are listed in Table 19-E-2; the tetraoxides of Ru and Os are discussed later (Section 19-F-1). The oxides are generally rather inert to aqueous acids, are reduced to the metal by hydrogen, and dissociate on heating. There are mixed metal oxides[4] (e.g., $BaRuO_3$, $CaIrO_3$, and $Tl_2Pt_2O_7$) and platinum and palladium "bronzes" of formula $M^I_xPt_3O_4$ (x = 0–1). Some oxides like $M^{II}Pt_3O_6$ have Pt—Pt bonds. Mixed oxides are used for electrodes in H_2—O_2 fuel cells and in the chloralkali process.

Hydrous oxides are commonly precipitated when NaOH is added to aqueous metal solutions, but they are difficult to free from alkali ions and sometimes readily become colloidal. When freshly precipitated, they may be soluble in acids, but only with great difficulty or not at all after aging.

The black precipitate, probably $Ru_2O_3\cdot nH_2O$, from Ru^{III} chloride solutions is readily oxidized by air, probably to the black $RuO_{2+x}\cdot yH_2O$, which is formed on reduction of RuO_4 or RuO_4^{2-} solutions by alcohol, hydrogen, and so on. Reduction of OsO_4 or addition of OH^- to $OsCl_6^{2-}$ solutions gives $OsO_2\cdot nH_2O$.

The hydrous oxide, $Rh_2O_3\cdot nH_2O$, is formed as a yellow precipitate from

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[4] P. Kroeschell and R. Hoppe, *Naturwiss.*, 1985, **72,** 442; R. D. Shannon *et al., Inorg. Chem.*, 1982, **21,** 3372.

TABLE 19-E-2
Anhydrous Oxides of Platinum Metals[a]

Oxide	Color/form	Structure	Comment
RuO_2	Blue-black	Rutile	From O_2 on Ru at 1250°C or $RuCl_3$ at 500–700°C; usually O-defective
RuO_4	Orange-yellow crystals, mp 25°C, bp 129.6°C[b]	Tetrahedral molecules	See Section 19-F-1
OsO_2	Coppery	Rutile	Heat Os in NO or OsO_4 or dry $OsO_2{\cdot}n H_2O$
OsO_4	Colorless crystals, mp 40°C, bp 129.7°C[b]	Tetrahedral molecules	Normal product of heating Os in air; see Section 19-F-1
Rh_2O_3	Brown	Corundum	Heat Rh^{III} nitrate or $Rh_2O_3(aq)$
RhO_2	Black	Rutile	Heat $Rh_2O_3(aq)$ at 700–800°C in high-pressure O_2
Ir_2O_3	Brown		Impure by heating $K_2IrCl_6 + Na_2CO_3$
IrO_2	Black	Rutile	Normal product of $Ir + O_2$; dissociates > 1100°C
PdO	Black		From $Pd + O_2$; dissociates 875°C; insoluble in all acids
PtO_2	Brown		Dehydrate $PtO_2(aq)$; dec 650°C

[a] In oxygen at 800–1500°C, gaseous oxides exist: RuO_3, OsO_3, RhO_2, IrO_3, and PtO_2. A number of other solids of uncertain nature exist: RuO_3, OsO_3, Ru_2O_5, Rh_2O_5, Os_2O_3, and Ru_2O_3. Two forms of PtO_2, and Pt_3O_4 are also known.

[b] Y. Koda, *J. Chem. Soc. Chem. Commun.*, **1986,** 1347.

Rh^{III} solutions. In base solution, powerful oxidants convert it into $RhO_2{\cdot}n H_2O$; the latter loses oxygen on dehydration. The hydrous oxide, $Ir_2O_3{\cdot}n H_2O$, can be obtained only in moist atmospheres; it is at least partially oxidized by air to $IrO_2{\cdot}n H_2O$, which is formed either by the action of mild oxidants on $Ir_2O_3{\cdot}n H_2O$ or by addition of OH^- to $IrCl_6^{2-}$ in the presence of H_2O_2. The precipitation of the oxides of Rh and Ir from buffered $NaHCO_3$ solutions by the action of ClO_2^- or BrO_3^- provides a rather selective separation of these elements.

The hydrous oxide, $PdO{\cdot}n H_2O$, is a yellow gelatinous precipitate that dries in air to a brown, less hydrated form and at 100°C loses more water, eventually becoming black; it cannot be dehydrated completely without loss of oxygen.

When $PtCl_6^{2-}$ is boiled with Na_2CO_3, red-brown $PtO_2{\cdot}n H_2O$ is obtained. It dissolves in acids and also in strong alkalis to give what can be regarded as solutions of hexahydroxoplatinate, $[Pt(OH)_6]^{2-}$. The hydrous oxide becomes insoluble on heating to ~200°C. The brown material formed by fusion of $NaNO_3$ and chloroplatinic acid at ~550°C followed by extraction of soluble salts with water is known as Adams's catalyst and is widely used in organic chemistry for catalytic reductions.

A very unstable Pt^{II} hydrous oxide is obtained by addition of OH^- to $PtCl_4^{2-}$; after drying in CO_2 at 120 to 150°C it approximates to $Pt(OH)_2$, but at higher temperatures gives PtO_2 and Pt.

Sulfides, Phosphides, and Similar Compounds. Direct interaction of the metal and other elements such as S, Se, Te, P, As, Bi, Sn, or Pb under selected conditions produces dark, often semimetallic solids that are resistant to acids other than nitric. These products may be stoichiometric compounds and/or nonstoichiometric phases depending on the conditions of preparation.

The chalcogenides and phosphides are generally rather similar to those of other transition metals; indeed many of the phosphides, for example, are isostructural with those of the iron group, namely, Ru_2P with Co_2P; RuP with FeP and CoP; RhP_3, PdP_3 with CoP_3 and NiP_3.

Sulfides can also be obtained by passing H_2S into platinum metal salt solutions. Thus from $PtCl_4^{2-}$ and $PtCl_6^{2-}$ are obtained PtS and PtS_2, respectively; from Pd^{II} solutions PdS, which when heated with S gives PdS_2; the Rh^{III} and Ir^{III} sulfides are assumed to be $M_2S_2 \cdot nH_2O$, but exact compositions are uncertain.

The disulfides have pyrite (Ru and Os), distorted pyrite (Pd) and CdI_2 (Pt) structures; all are diamagnetic.[5a]

There are various mixed sulfides such as Ta_2PdS_6.[5b]

19-E-5. Halides of the Platinum Metals

We discuss here primarily the binary halides. All the platinum metals form halogeno complexes in one or more oxidation states and these, as well as the hydrated halides, which are closely related to them, are discussed under the respective elements.

Fluorides. These are listed in Table 19-E-3. The most interesting are the *hexafluorides*. They are prepared by fluorination under pressure (4–6 atm) of the metal at elevated temperatures and are purified by vacuum distillation. Platinum wire ignited electrically in fluorine continues to react exothermally to give red vapors of PtF_6.

The hexafluorides decrease in stability in the order $W > Re > Os > Ir > Pt$, and $Ru > Rh$, dissociating into F_2 and lower fluorides. Platinum hexafluoride is one of the most powerful oxidizing agents known; it reacts with oxygen and xenon to give $O_2^+PtF_6^-$ and $Xe(PtF_6)_n$. The volatility of the compounds also decreases with increasing mass.

The hexafluorides are extraordinarily reactive and corrosive substances and normally must be handled in Ni or Monel apparatus, although quartz can be used. Only PtF_6 and RhF_6 actually react with glass (even when rigorously dry) at room temperature. In addition to thermal dissociation, uv radiation causes decomposition to lower fluorides, even OsF_6 giving OsF_5. The vapors hydrolyze with water vapor, and liquid water reacts violently; for example, IrF_6 gives HF, O_2, O_3, and IrO_2(aq); OsF_6 gives OsO_4, HF, and OsF_6^-. The hexafluorides are octahedral, and their magnetic and spectral properties have been studied in detail.

The *pentafluorides* can be obtained by controlled fluorination of the metal.

[5a] A. Wold *et al., Inorg. Chem.,* 1981, **20,** 501.

[5b] J. A. Ibers *et al., Inorg. Chem.,* 1985, **24,** 3063.

TABLE 19-E-3
Fluorides of the Platinum Metals

II	III	IV	V	VI
	RuF_3 Brown	RuF_4 Sandy yellow	RuF_5 Dark green[a] mp 86.5°C; bp 227°C	RuF_6 Dark brown, mp 54°C
		OsF_4 Yellow-brown	OsF_5 Blue, mp 70°C; bp 225.9°C	OsF_6[b] Pale yellow,[a] mp 33.2°C; bp 47°C
	RhF_3 Red	RhF_4 Purple-red	RhF_5 Dark red	RhF_6 Black
	IrF_3 Black	IrF_4 Red-brown	IrF_5 Yellow-green, mp 104°C	IrF_6 Yellow, mp 44.8°C; bp 53.6°C
PdF_2 Violet	[c]	PdF_4 Brick-red		[d]
		PtF_4 Yellow brown	PtF_5 Deep red, mp 80°C	PtF_6 Dark red, mp 61.3°C; bp 69.1°C

[a] Colorless vapor.

[b] OsF_7, made under drastic conditions (500°C, 400 atm, F_2), dissociates above -100°C and is stable only under high-pressure F_2 (O. Glemser *et al.*, *Chem. Ber.*, 1966, **99**, 2652); there is some evidence for OsF_8.

[c] PdF_3 is $Pd^{2+}PdF_6^{2-}$.

[d] Unstable even at 273 K to $PdF_4 + F_2$ (A. Timakov *et al.*, *Zh. Neorg. Khim.*, 1982, **27**, 3007).

Thus action of F_2 (7 atm) at 370°C on Ru gives RuF_5, and fluorination of Rh at 400°C gives RhF_5, Ir at ~360°C gives IrF_5, and $PtCl_2$ at 350°C gives PtF_5.

However, OsF_5 and IrF_5 are best made by reduction of the hexafluoride with Si or H_2 in liquid HF, or for OsF_5, by $W(CO)_6$. The pentafluorides are very reactive, hydrolyzable substances. In the condensed phases these fluorides may be tetramers or chain polymers. The structure of $(RhF_5)_4$ is shown in Fig. 19-E-1; the Rh—F—Rh bridges are bent, unlike the linear ones in, for example, $(NbF_5)_4$ (Section 19-B-2). The polymers appear to have *cis*-F_2 bridges. In the gas phase, oligomers are also present, but depolymerization occurs to give *tbp* monomers that may be accompanied by color changes; thus blue $(OsF_5)_n$ gives a colorless vapor.

The *tetrafluorides* may be obtained by reactions such as

$$10RuF_5 + I_2 = 10RuF_4 + 2IF_5$$

$$2IrF_5 + H_2 = 2IrF_4 + 2HF$$

$$RhCl_3 \xrightarrow{BrF_3(l)} RhF_4{\cdot}2BrF_3 \xrightarrow{heat} RhF_4$$

$$Pt \xrightarrow{BrF_3(l)} PtF_4{\cdot}2BrF_3 \xrightarrow{heat} PtF_4 \xleftarrow{F_2} PtBr_4$$

$$PdBr_2 \xrightarrow{BrF_3(l)} Pd^{II}Pd^{IV}F_6 \xrightarrow{F_2,\ 100\ psi,\ 150°C} PdF_4$$

The formation of BrF_3 adducts in these reactions is a fairly common feature in the preparation of heavy metal fluorides; such adducts may be ionic, that

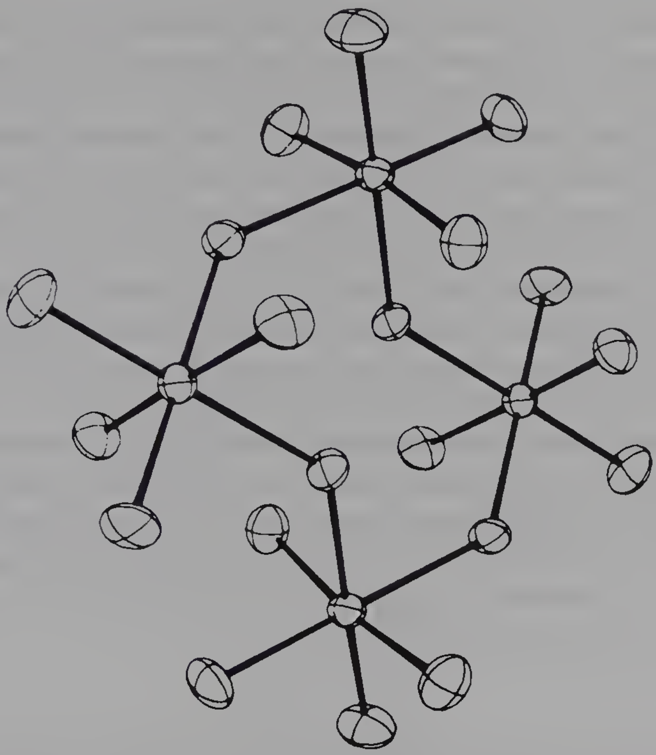
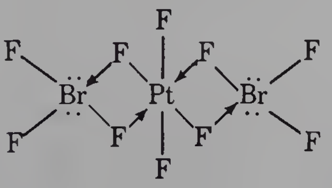


FIG. 19-E-1. Structure of rhodium pentafluoride. [Reproduced by permission from N. Bartlett, *et al., Inorg. Chem.,* 1973, **12,** 2640].

is, $[BrF_2^+]_2\cdot MF_6^{2-}$, but it is more likely that they are fluoride-bridged species of the type (19-E-I) or singly bridged polymers.



(19-E-I)

Like the other fluorides, the tetrafluorides are violently hydrolyzed by water. The structure of diamagnetic PdF_4 indicates approximately octahedral coordination of the metal with two *cis*-Pd—F and four bridging Pd—F—Pd groups. The other tetrafluorides are probably similar; IrF_4 and RhF_4 are paramagnetic.

Trifluorides. Ruthenium(III) fluoride is best obtained by reduction:

$$5RuF_5 + 2Ir \xrightarrow{250°C} 5RuF_3 + 2IrF_5$$

Fluorination of $RhCl_3$ at 500°C gives RhF_3. The solid is unaffected by water or bases. Iridium trifluoride, which can be obtained only indirectly by reduction of IrF_6 (e.g., by Ir at 50°C), is also relatively inert to water. The Rh and Ir trifluorides have a slightly distorted ReO_3 structure.

Difluorides. Palladium(II) fluoride can be obtained by the reaction

$$Pd^{II}Pd^{IV}F_6 + SeF_4 \xrightarrow{\text{reflux}} 2PdF_2 + SeF_6$$

It is the only simple compound of Pd^{II} that is paramagnetic, and the moment is consistent with the observed octahedral coordination. The Pd^{2+} ion also occurs in $Pd^{II}Pd^{IV}F_6$, $Pd^{II}Sn^{IV}F_6$, and $Pd^{II}Ge^{IV}F_6$, which can be obtained by addition of BrF_3 to mixtures of $PdBr_2$ and, for example, $SnBr_4$.

Chlorides, Bromides, and Iodides. The anhydrous halides (other than fluorides—see Table 19-E-3) are listed in Table 19-E-4; they are normally obtained by direct interaction under selected conditions.

Except for those of Pd and Pt, the halides are generally insoluble in water, rather inert, and of little utility for the preparation of complex compounds. Hydrated halides, discussed later, are normally used for this purpose. We discuss only some of the more important chlorides.

Ruthenium trichloride has two forms. Interactions of the metal with Cl_2 + CO at 370°C gives the β form, which is converted into black leaflets of the α form at 450°C in Cl_2. The latter has a layer lattice and is antiferromagnetic. The so-called *iodide,* which is precipitated from aqueous ruthenium chloride solutions by KI, invariably contains strong OH bands in its ir spectrum and probably has OH bridges in the lattice.

TABLE 19-E-4
Anhydrous Chlorides, Bromides, and Iodides of Platinum Metals[a]

Oxidation state	Ru	Os	Rh	Ir	Pd	Pt
II					$PdCl_2$[b] Red	$PtCl_2$[b] Black-red
					$PdBr_2$ Red black	$PtBr_2$ Brown
		[c]			PdI_2 Black	PtI_2[d] Black
III	$RuCl_3$[e]	$OsCl_3$ Dark gray	$RhCl_3$ Red	$IrCl_3$ Brown-red		$PtCl_3$; Green-black
	$RuBr_3$ Dark brown	$OsBr_3$ Black	$RhBr_3$ Dark red	$IrBr_3$ Yellow		$PtBr_3$ Green-black
	RuI_3 Black	OsI_3 Black	RhI_3(?) Black	IrI_3 Black		PtI_3(?) Black
IV	[f]	$OsCl_4$ Black		$IrCl_4$(?)		$PtCl_4$ Red-brown
		$OsBr_4$[g] Black		$IrBr_4$(?)		$PtBr_4$ Dark red
V		$(OsCl_5)_2$ Black		IrI_4(?)		PtI_4[d] Brown-black

[a] There is some evidence for gray metallic OsI, and lower halides of Rh and Ir.

[b] Two or more polymorphs; $PtCl_2$ yellowish brown when powdered.

[c] Alleged lower iodides are mixtures of OsI_3 and oxides (H. Schäfer *et al., Z. Anorg. Allg. Chem.*, 1971, **383,** 49).

[d] G. Thiele *et al., Z. Anorg. Allg. Chem.*, 1986, **539,** 141.

[e] Two forms: α-$RuCl_3$ (black) or β-$RuCl_3$ (brown).

[f] Some evidence for existence of $RuCl_4$ in vapor.

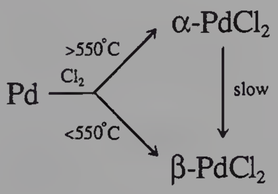
[g] G. Thiele *et al., Z. Anorg. Allg. Chem.*, 1985, **530,** 178.

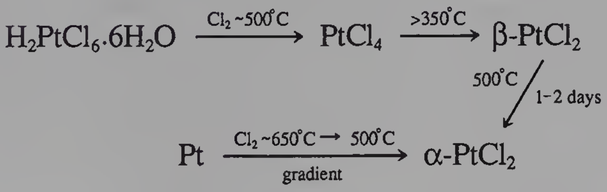
Osmium tetrachloride[6a] is formed when an excess of Cl_2 is used at temperatures above 650°C; otherwise a mixture with the *trichloride* is formed. The latter is obtained when $OsCl_4$ is decomposed at 470°C in a flow system with a low pressure of chlorine. Osmium tetrachloride in its orthorhombic high-temperature form has infinite chains of octahedra sharing opposite edges with no structural indication of metal-metal bonding.

The *pentachloride,* made by interaction of OsO_4 and SCl_2,[6b] is isomorphous with Re_2Cl_{10}, but the Os—Os distance is too long for metal bonding and the antiferromagnetic coupling is through the two μ-Cl atoms.

Rhodium trichloride has a layer lattice isostructural with $AlCl_3$ and is exceedingly inert. However, when $RhCl_3·3H_2O$ (see following reactions) is dehydrated in dry HCl at 180°C, the red product is much more reactive and dissolves in water or THF; this property is lost on heating at 300°C.

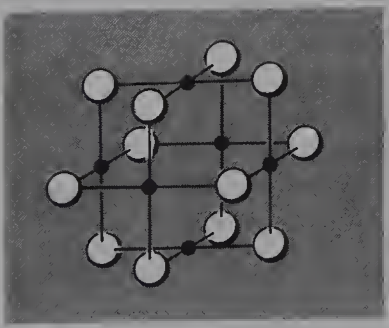
Palladium and platinum(II) chlorides exist in two forms, which may be obtained in the following ways:

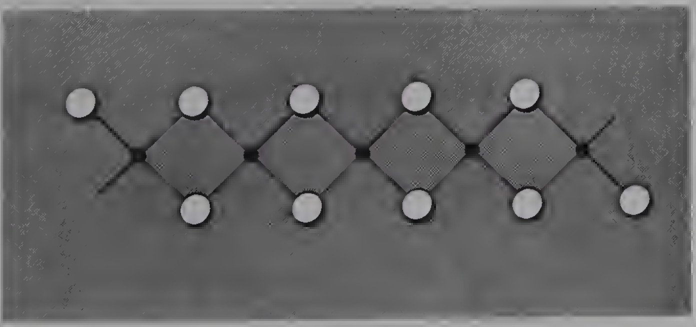




Unlike the Ni halides or PdF_2, which are ionic and paramagnetic, these chlorides are molecular or polymeric and diamagnetic, and Born–Haber calculations indicate that ionic lattices would be endothermic.

The β-forms are isomorphous and have the molecular structure (19-E-II) with M_6Cl_{12} units; the structures appear to be stabilized mainly by the halogen bridges rather than by metal–metal bonds. The adducts of Pt_6Cl_{12} with ben-


(19-E-II)


(19-E-III)

[6a] K. H. Hunecke and H. Schaefer, *Z. Anorg. Allg. Chem.*, 1986, **534,** 216.
[6b] K. Dehnicke *et al.*, *Inorg. Chem.*, 1984, **23,** 2563.

zene, CS_2, $CHCl_3$, and Br_2, are clathrates. On heating with $AlCl_3$, Pt_6Cl_{12} gives a purple vapor of an aluminum chloride complex similar to those noted in Section 7-7.

Interaction of $Pd_3(O_2CMe)_6$ with HCl in acetic acid gives Pd_6Cl_{12}, which is soluble in aromatic solvents.[7]

The structure of α-$PdCl_2$ is that of a flat chain (19-E-III), but that of α-$PtCl_2$ is uncertain.

Palladium(II) chloride is soluble in hydrochloric acid, forming the ion $[PdCl_4]^{2-}$; it also reacts with many ligands (L), such as amines, benzonitrile, and phosphines, to give complexes of the types L_2PdCl_2 and $[LPdCl_2]_2$. Platinum dichloride is similar.

The greenish-black "*trichloride*" $PtCl_3$ contains both Pt^{II} and Pt^{IV} with units of $[Pt_6Cl_{12}]$ and an infinite chain, $(1/\infty)[PtCl_2^aCl_{4/2}^b]$ containing distorted $PtCl_6$ octahedra linked by common edges, similar to the chain of PtI_4. The chloride and the similar $PtBr_3$ and PtI_3 are made by thermal gradient reactions of Pt and halogen.

Platinum(IV) chloride is commonly made by heating $(H_3O)_2PtCl_6$ to 300°C in Cl_2, but is best made by interaction of Pt and SO_2Cl_2. The reddish-brown crystals are readily soluble in water, presumably giving ions such as $[PtCl_4(OH)_2]^{2-}$, and in polar solvents. The structure is not yet known but PtI_4 has PtI_6 octahedra linked by iodide bridges with two *cis*-nonbridging I atoms.

Oxo Halides. The fluorides, $RuOF_4$, OsO_3F_2, $OsOF_5$, and PtO_xF_{3-x}(?) are of little importance. The interaction of OsO_4 and BCl_3 gives $OsOCl_4$[6a,8], red brown mp 32°C; $OsOCl_2$[6a] and Os_2OCl_6[9] are known. Interaction of RuS_2 and S_2Cl_2 gives $RuSCl_4$.[10] The oxochloride Pd_2OCl_2 is also known.[11]

19-F. RUTHENIUM AND OSMIUM: GROUP VIII(8)

The chemistry of Ru and Os[1] bears little resemblance to that of Fe except in some solids such as sulfides or phosphides and in complexes with π-bonding ligands like CO, PR_3, or η^5-C_5H_5. The higher oxidation states are much more

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[7] A. Yatsimirski and R. Ugo, *Inorg. Chem.*, 1983, **22,** 1395.

[8] D. A. Rice *et al., Inorg. Chem.*, 1986, **25,** 3659.

[9] W. Levason *et al., J. Chem. Soc. Dalton Trans.*, **1982,** 1877; see H. Schaefer *et al., Z. Anorg. Allg. Chem.*, 1986, **535,** 219 for Os_2OBr_6.

[10] K. Dehnicke *et al., Chem. Ztg.*, 1981, **105,** 377.

[11] B. Dannecker and G. Thiele, *Z. Naturforschg.*, 1986, **41B,** 1363.

[1] E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984 (exhaustive reference text); W. P. Griffith, *The Chemistry of the Rarer Platinum Metals: Os, Ru, Ir, Rh,* Wiley–Interscience, New York, 1967; D. J. Gulliver and L. Levason, *Coord. Chem. Rev.*, 1982, **46,** 1 (Os^{IV}); J. A. Rard, *Chem. Rev.*, 1985, **85,** 1 (critical review of inorganic aspects of Ru chemistry, thermodynamic properties, and aqueous chemistry); M. I. Bruce, M. A. Bennett, and T. W. Matheson, Vol. 4, Chapters 32.1–32.9 (Ruthenium), R. D. Adams and J. P. Selegue, Vol. 4, Chapter 33 (Osmium), *Comprehensive Organometallic Chemistry,* Pergamon Press, Oxford, 1982; T. A. Stephenson and M. Schröder, Vol. 4, Chapter 45, (Ruthenium); W. P. Griffith, Vol. 4, Chapter 46, (Osmium), *Comprehensive Coordination Chemistry,* Pergamon Press, Oxford, 1987.

readily obtained than for Fe and there is an extensive and important chemistry of oxo species.

Because of the complexities we here treat classes of compounds rather than considering the separate oxidation states.

The oxidation states and stereochemistries are summarized in Table 19-F-1.

TABLE 19-F-1

Oxidation States and Stereochemistry of Ruthenium and Osmium

Oxidation state	Coordination number	Geometry	Examples
Ru^{-II}	4	Tetrahedral(?)	$Ru(CO)_4^{2-}$(?), $[Ru(diphos)_2]^{2-}$
Ru^0, Os^0	5	*tbp*	$Ru(CO)_5$, $Os(CO)_5$, $Ru(CO)_3(PPh_3)_2$
Ru^I, Os^I, d^7	6^a		$[\eta^5\text{-}C_5H_5Ru(CO)_2]_2$, $[Os(CO)_4X]_2$
Ru^{II}, Os^{II}, d^6	5	See text	$RuCl(PPh_3)_3$
	5	*tbp*	$RuHCl(PPh_3)_3$
	5	Distorted *sp*	$OsCl_2(PPh_3)_3$
	6^b	Octahedral	$[RuNOCl_5]^{2-}$, $[Ru(bipy)_3]^{2+}$, $[Ru(NH_3)_6]^{2+}$, $[Os(CN)_6]^{4-}$, $RuCl_2CO(PEtPh_2)_3$, $OsHCl(diphos)_2$
Ru^{III}, Os^{III}, d^5	4	Distorted tetrahedral	$Ru_2(CH_2SiMe_3)_6^c$
	$6^{b,d}$	Octahedral	$[Ru(NH_3)_5Cl]^{2+}$, $[RuCl_5H_2O]^{2-}$, $[Os(dipy)_3]^{3+}$, K_3RuF_6, $[OsCl_6]^{3-}$
Ru^{IV}, Os^{IV}, d^4	4	Tetrahedral	$Ru(c\text{-}C_6H_{11})_4$, $OsPh_4$
	5	*tbp*	$Ru(SR)_4(MeCN)$
	$6^{b,d}$	Octahedral	K_2OsCl_6, K_2RuCl_6, $[Os(diars)_2X_2]^{2+}$, RuO_2^c
	7	Distorted	$OsH_4(PMe_2Ph)_3$,^{e} $OsH_3(PPh_3)_4^+$
		Pentagonal bipyramidal	$[RuCl(S_2CNMe_2)_3]$
Ru^V, Os^V, d^3	5		$Ru_2(O)_2(CH_2SiMe_3)_6^c$
	6	Octahedral	$KRuF_6$, $NaOsF_6$, $(RuF_5)_4$
Ru^{VI}, Os^{VI}, d^2	4	Tetrahedral	RuO_4^{2-}, $OsO_2(mesityl)_2$
	5	*sp*	$Os(NMe)(CH_2SiMe_3)_4$, $OsOCl_4$
		tbp	$[RuO_3(OH)_2]^{2-}$
	6^d	Octahedral	RuF_6, OsF_6, $[OsO_2Cl_4]^{2-}$, $[OsO_2(OH)_4]^{2-}$, $[OsNCl_5]^{2-}$
	8	Dodecahedral	$OsH_6[PPh(i\text{-}Pr_2)]_2^g$
Ru^{VII}, Os^{VII}, d^1	4	Tetrahedral	RuO_4^-, OsO_4^-
	6	Octahedral	$OsOF_5$
Ru^{VIII}, Os^{VIII}, d^0	4	Tetrahedral	RuO_4, OsO_4, $[OsO_3N]^-$
	5	Distorted *tbp*	$[(OsO_4)_2(\mu\text{-}OH)]^-$
		tbp	OsO_4py^f
	6	Octahedral	$[OsO_3F_3]^-$, $[OsO_4(OH)_2]^{2-}$

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[a] If $\eta^5\text{-}C_5H_5$ is assumed to occupy three coordination sites.

[b] Most common states for Ru.

[c] Metal–metal bond present.

[d] Most common states for Os.

[e] $RuH_4(PPh_3)_3$ is $Ru(H_2)(H)_2(PPh_3)_3$ (see Chapter 24).

[f] S. F. Kobs and E. J. Behrman, *Inorg. Chim. Acta,* 1987, **128,** 21.

[g] J. A. K. Howard *et al., Inorg. Chem.,* 1987, **26,** 2930.

19-F-1. Oxo Compounds of Ruthenium and Osmium

There is an exceedingly rich chemistry of compounds that have bonds to oxygen in oxidation states IV to VIII. The species can have M═O, *cis* or *trans* M(═O)$_2$, linear or bent MOM bridges, or O═MOM═O groups; oxo-centered species for ruthenium with $Ru_3^{III}O$ cores are also known.

The Tetraoxides RuO_4 and OsO_4. These volatile, toxic, low melting crystalline solids have characteristic, penetrating, ozonelike odors. Osmium tetraoxide is a particular hazard to the eyes because of its ready reduction by organic matter to a black oxide, a property utilized in its employment in dilute aqueous solution as a biological fixative.

Ruthenium tetraoxide, mp 25.5°C, is obtained when acid ruthenium solutions are treated with oxidizing agents such as MnO_4^-, $AuCl_4^-$, BrO_3^-, or Cl_2; the oxide can be swept out by a gas stream or extracted into CCl_4; it may also be obtained by distillation from concentrated perchloric acid solutions or by passing Cl_2 into a melt of ruthenate in NaOH. The tetroxides are powerful oxidants. Above ~180°C RuO_4 can explode giving RuO_2 and O_2 and it is decomposed by light. Osmium tetraoxide is more stable in both respects.

Osmium tetraoxide can be obtained as a yellow solid, mp 40°C by burning osmium or by oxidation of osmium solutions with nitric acid, peroxodisulfate in sulfuric acid, or NaOCl. Osmium tetraoxide forms very stable five-coordinate *tbp* adducts with quinuclidine, hexamethylene tetramine and, other N donors.

Both compounds have a tetrahedral structure. They are extremely soluble in CCl_4. Ruthenium tetraoxide is quite soluble in dilute sulfuric acid giving golden yellow solutions. Osmium tetraoxide is moderately soluble in water but the absorption spectrum is the same as in hexane so that it is probably unsolvated.

Osmium tetraoxide is used commercially in the important cis- hydroxylation of alkenes.[2] Interaction initially gives 1,2-diolato complexes. These include the mononuclear complexes such as (19-F-Ia) and (19-F-Ib), as well as binuclear complexes, that exist in syn and anti forms, (19-F-IIa and b); all of these can be reduced by Na_2SO_3 to give *cis*-diols. The oxide can also be used catalytically for the same conversion in presence of H_2O_2 or ClO_3^-.

(a) (b)

(19-F-I)

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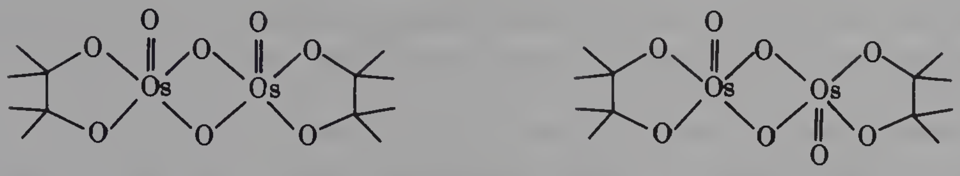
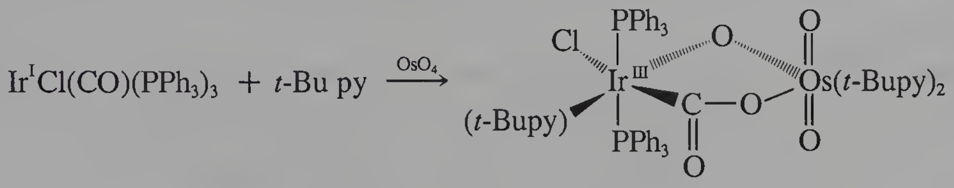
[2] K. A. Jørgensen and R. Hoffmann, *J. Am. Chem. Soc.*, 1986, **108**, 1867; M. R. Barbachyn, *J. Am. Chem. Soc.*, 1984, **106**, 2459; K. Tomioka *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 6213.



(a) (b)

(19-F-II)

Osmium tetraoxide oxidizes and complexes with $IrCl(CO)(PPh_3)_3$ giving a new type of bridging CO_2 complex[3]:



Ruthenium tetraoxide is a much more vigorous oxidant for organic substances and is best used in basic oxidizing solution where ruthenate anions are the oxidizing species.[4a,b] However, $[(i\text{-Pr})_4N]RuO_4$ is a milder oxidant and in the presence of *N*-methylmorpholine-*n*-oxide is catalytic for some oxidations.[4a]

Both tetraoxides are soluble in alkali hydroxide solutions, but the behaviors are quite different. Ruthenium tetraoxide is reduced by OH^- first to perruthenate(VII), which in turn is further reduced to ruthenate(VI):

$$4RuO_4 + 4OH^- \longrightarrow 4RuO_4^- + 2H_2O + O_2$$

$$4RuO_4^- + 4OH^- \longrightarrow 4RuO_4^{2-} + 2H_2O + O_2$$

On the other hand, OsO_4 gives hydroxo species, discussed later. This difference between Ru and Os appears to be due to the ability of the 5*d* metal oxo anion to increase the coordination shell. Similar behavior occurs for ReO_4^-, which in concentrated alkali gives yellow *meso*-perrhenate:

$$ReO_4^- + 2OH^- = [ReO_4(OH)_2]^{3-} = ReO_5^{3-} + H_2O$$

Ruthenates(VII) and –(VI). The simplest preparation of the tetrahedral green perruthenate ion, RuO_4^-, is the oxidation of aqueous $RuCl_3$ by KIO_4. The RuO_4 is swept into a molar solution of tetraisopropylammonium hydroxide, when the organic solvent soluble $(i\text{-Pr})_4N^+$ salt precipitates.[4a] As noted above, it is a mild oxidant.

The RuO_4^- ion can be reduced to the orange ruthenate(VI) ion, which is relatively stable in basic solution, but ruthenates are best prepared by peroxodisulfate oxidation of $RuCl_3$ in KOH.[5] Although the ion is normally tetrahedral, the red barium salt precipitated from RuO_4^{2-} solution is

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[3] T. J. Collins *et al., J. Am. Chem. Soc.*, 1982, **104,** 7352.
[4a] W. P. Griffith *et al., J. Chem. Soc. Chem. Commun.*, **1987,** 1625.
[4b] S. Torii *et al., J. Org. Chem.*, 1985, **50,** 4980.
[5] W. P. Griffith *et al., J. Chem. Soc. Perkin Trans.* I, **1984,** 681.

$Ba[RuO_3(OH)_2]$; this ion has axial OH groups. Most Ru species in alkaline solution are oxidized to RuO_4^{2-} by $KMnO_4$; OCl^- gives RuO_4^- plus RuO_4^{2-} while Br_2 gives only RuO_4^-.

Kinetic studies of the reduction of green RuO_4^- solutions by OH^- suggest that unstable intermediates with coordinated OH^- are involved—this contrasts with the case of 3*d* metal oxo anions, where there is no evidence for addition of OH^-. Since H_2O_2 is also formed in the reduction and RuO_4^- is incompletely reduced to RuO_4^{2-} by H_2O_2, a step such as

$$[RuO_4(OH)_2]^{2-} \longrightarrow RuO_4^{2-} + H_2O_2$$

is plausible.

Interaction of RuO_4 with $HCl_{(g)}$ and Cl_2 gives hygroscopic crystals of $(H_3O)_2[RuO_2Cl_4]$; the ion hydrolyzes:

$$2[RuO_2Cl_4]^{2-} + 2H_2O \longrightarrow RuO_4 + RuO_2 + 4Cl^- + 4HCl$$

The reduction by aqueous HCl is discussed later.

Some hydroxoruthenates $[RuO_2(OH)_2(H_2O)_2]^{2-}$ have been claimed.[6]

Osmates. Although osmates are normally octahedral as discussed later, OsO_4 in CH_2Cl_2 is reducd by $[Ph_4As]I$, KI, and so on, to salts of the $[Os^{VII}O_4]^-$ ion analogous to the long known $[RuO_4]^-$; it has a distorted tetrahedral structure.[7]

Interaction of OsO_4 with $[Ph_4P]Cl$ gives the salt of the *tbp* ion $[OsO_4Cl]^-$ that has axial chlorine.[8] Interaction of OsO_4 with alkali hydroxides in various ratios gives $[OsO_4(OH)]^-$, $[O_4Os(\mu\text{-}OH)OsO_4]^-$ and *trans*-$[OsO_4(OH)_2]^{2-}$ but KOH and NaOH give only the latter while Rb and CsOH give all three.[9] Another nucleophilic attack, by F^-, gives $[OsO_4F_2]^{2-}$.[10]

Ethanol reduction of $[OsO_4(OH)_2]^{2-}$ gives the dark purple dioxoosmate (VI), $[OsO_2(OH)_4]^{2-}$, which, unlike $[Ru^{VI}O_4]^{2-}$ is diamagnetic. The diamagnetism of the ion, its substituted derivatives such as $[OsO_2Cl_4]^{2-}$ and of $[RuO_2Cl_4]^{2-}$, all of which have *trans*-dioxo groups, can be explained in terms of ligand field theory. If the z axis passes through the two oxide ligands and the x and y axes through OH, there will be a tetragonal splitting of the e_g level into two singlets $d_{x^2-y^2}$ and d_{z^2}, whereas the t_{2g} level gives a singlet d_{xy} and a doublet $d_{xz}d_{yz}$. The oxide ligands will form Os=O bonds by π overlap mainly with d_{xz} and d_{yz}, thus destabilizing those orbitals, leaving a low-lying d_{xy} orbital that will be occupied by the two electrons, leading to diamagnetism.

The osmate ion $[OsO_2(OH)_4]^{2-}$ can undergo substitution reactions with various ions such as Cl^-, Br^-, CN^-, $C_2O_4^{2-}$, and NO_2^-, to give orange or red

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[6] T. L. Popov *et al., Zh. Neorg. Khim.*, 1985, **30,** 407.

[7] W. Levason *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 1735; E. Bilger *et al., Z. Naturforsch.* **1984B,** 259.

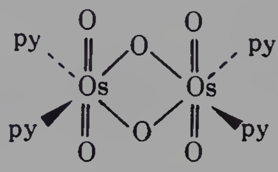
[8] K. Dehnicke *et al., Z. Anorg. Allg. Chem.*, 1984, **516,** 214.

[9] W. Levason *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 199; R. N. Mehrotra, *J. Chem. Soc. Dalton Trans.*, **1984,** 999.

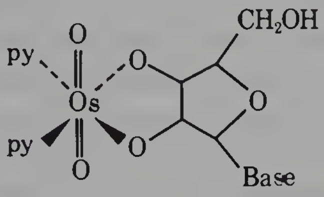
[10] P. J. Jones *et al., J. Fluorine Chem.*, 1984, **25,** 195.

crystalline salts, sometimes referred to as osmyl derivatives. They can also be obtained directly from OsO_4 with which, for example, aqueous KCN gives the salt $K_2[OsO_2(CN)_4]$. The osmate ion and acetic acid gives[11] *cis*- $[OsO_2(\eta^1\text{-}O_2CMe)_2(\eta^2\text{-}O_2CMe)]^-$ and with ethylenediamine *trans*-$[OsO_2en_2]^{2+}$. From this ion other complexes may be made. Reduction with Zn/Hg affords $[OsH_2en_2]^{2+}$ from which aqueous HX produces the $[Os\ en_2X_2]^{2+}$ ions.

When OsO_4 is reduced by EtOH in the presence of pyridine, the binuclear complex (19-F-III) is obtained. This compound reacts with nucleosides via the 2′ and 3′ hydroxyl groups of the sugar ring to give complexes like (19-F-IV).



(19-F-III)



(19-F-IV)

With tRNA a similar reaction occurs and has provided a way to introduce heavy atoms for structure determination.

Reduction by R_2S in EtOH–HCl can give, for example, $OsO_2Cl_2(Me_2S)_2$[12] while R_3P gives $OsO_2Cl_2(PR_3)_2$; these complexes have *trans* O=Os=O groups. Further reductions of $OsO_2Cl_2(PR_3)_2$ give $OsX_3(PR_3)_3$ and $OsX_4(PR_3)$ while carboxylic acids give $Os_2^{IV}(\mu\text{-}O)(\mu\text{-}O_2CR)_2Cl_4(PR_3)_2$.[13] Only few cases of bridging oxo osmium compounds are known, another example being $[Os_2(\mu\text{-}O)Cl_{10}]^{4-}$. Use of the oxidation-resistant N_2O_2 ligand (L) (Section 10-13) allows the following reductions[14] giving osmium species in oxidation states from +2 to +6:

$$\begin{tikzcd}
 & & Os\ py_2L_2 \arrow[d, shift left, "+e"] \\
{[Os^{VI}O_2(OH)_4]^{2-}} \arrow[r, "L"] & {[\textit{trans}\text{-}OsO_2L_2]^{2-}} \arrow[r, "Ph_3P/py"] & {[Os^{V}py_2L_2]^{-}} \arrow[u, shift left, "-e"] \arrow[d, shift left, "+e"] \\
 & & {[Os\ py_2L_2]^{2-}} \arrow[u, shift left, "-e"]
\end{tikzcd}$$

Other Oxo Species. *Trans* O=Ru=O groups[15] exist in $(porph)Ru^{VI}(O)_2$ and $[N_4]$-macrocyclic complexes, $[Ru(O)_2(N_4)]^{2+,1+}$ of Ru^{VI} or Ru^{V}, and in

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[11] G. Wilkinson *et al., Polyhedron,* 1982, **1,** 840.

[12] S. K. Harbron and W. Levason, *J. Chem. Soc. Dalton Trans.,* **1985,** 205.

[13] R. A. Walton *et al., Inorg. Chem.,* 1983, **22,** 1301.

[14] T. J. Collins *et al., Inorg. Chem.,* 1987, **26,** 1157, 1161, and references listed.

[15] See, for example, C-M. Che *et al., J. Am. Chem. Soc.,* 1986, **108,** 4644; *Inorg. Chem.,* 1987, **26,** 2289; T. C. Lau and J. K. Kochi, *J. Chem. Soc. Chem. Commun.,* **1987,** 798.

trans-$[Ru(O)_2bipy_2]^{2+}$. Also *cis*- as well as *trans*-dioxo groups are known as in, for example, *cis*-$[M(O)_2bipy_2]^{2+}$ for Ru and Os.[16]

Other complexes with Ru=O and $Os(=O)_2$ are involved in redox reactions[17] of hydroxo and aqua species with $[N_4]$-macrocycles, bipy, terpy, and py, for example, at pH 7,

$$[\text{py bipy}_2\text{Ru}^{IV}\text{O}]^{2+} \longleftrightarrow [\text{py bipy}_2\text{Ru}^{III}(\text{OH})]^{2+} \longleftrightarrow [\text{py bipy}_2\text{Ru}^{II}(\text{H}_2\text{O})]^{2+}$$

Other Ru^{IV} complexes include $[bipy_2Ru{=}O]^{2+}$. In CF_3SO_3H, oxidation of $RuBr_6^{2-}$ by BrO_3^-[18a] gives what may be $Ru_4O_6^{4+}(aq)$.[18b] Some of the oxoruthenium complexes will oxidize alkenes, alcohols, and other organic substrates. Interaction[18c] of OsO_4, KCl, and chelating phosphines (PP) in EtOH gives complexes of the type *trans*-$Os(O)_2Cl_2(PP)$.

Bridged Oxo Complexes. Reduction of RuO_4 by HCl gives the ion $[Ru_2OCl_{10}]^{4-}$; the reported bromide analogue is erroneous, being actually $Ru_2Br_9^{3-}$.[19] The Ru—O—Ru group is linear due to π-bonding, which leads also to diamagnetism of the ion.

Other examples with linear Ru—O—Ru units are the porphyrins $[X(porph)Ru^{IV}]_2(\mu\text{-}O)$, X = OH, OR, or halogens.[20] There are, however, nonlinear μ-oxo groups[21] in $[bipy_2(H_2O)Ru^{III}](\mu\text{-}O)$ where the Ru—O—Ru angle is 165°.

Osmium compounds with Os—O—Os groups are similar structurally and electronically. Ruthenium "reds" that have oxo bridges and Ru_3O species are discussed later.

Oxo imido osmium compounds $RNOsO_3$ and $(RN)_2OsO_2$, which has one linear and one bent OsNR group, and $(RN)_4Os$ can be obtained by interaction of OsO_4 with certain amines such as 1-adamantamine.[22] The imido groups can be added to alkenes (cf. additions of Os=O cited previously). The *nitrido complex* known as the osmiamate ion, $[N{\equiv}OsO_3]^-$, is obtained when OsO_4 in KOH solution is treated with ammonia; orange crystals of $K[NOsO_3]$ are obtained. Other nitrido species are discussed in Section 19-F-5.

19-F-2. Ruthenium(II) and (III) Aqua Ions[23]

The reduction by Pb of RuO_4 in H_2SiF_6 solutions followed by precipitation of Pb^{2+} by SO_4^{2-} and ion-exchange separation gives the Ru^{III} aqua ion that

[16] T. J. Meyer *et al., Inorg. Chem.*, 1986, **25,** 2357.

[17] See, for example, T. J. Meyer *et al., J. Am. Chem. Soc.*, 1987, **109,** 746; *Inorg. Chem.*, 1987, **26,** 1126. K-Y. Wong *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 546.

[18a] M. E. Marmion and K. J. Takeuchi, *J. Am. Chem. Soc.*, 1986, **108,** 510.

[18b] J. P. Deloume *et al., Polyhedron*, 1985, **4,** 875.

[18c] S. K. Harbron and W. Levason, *J. Chem. Soc. Dalton Trans.*, **1987,** 633.

[19] K. R. Seddon *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 483.

[20] J. P. Collman *et al., J. Am. Chem. Soc.*, 1984, **106,** 5151.

[21] T. J. Meyer, *et al., J. Am. Chem. Soc.*, 1985, **107,** 3855; *Inorg. Chem.*, 1987, **26,** 2027.

[22] W. A. Nugent *et al., J. Am. Chem. Soc.*, 1979, **101,** 7265.

[23] A. Ludi *et al., J. Am. Chem. Soc.*, 1985, **107,** 312; *Organometallics*, 1986, **5,** 298; *Inorg. Chem.*, 1985, **24,** 2582.

can be reduced to Ru^{II}:

$$[Ru(H_2O)_6]^{3+} + e = [Ru(H_2O)_6]^{2+} \qquad E_0 = +0.23 \text{ V}$$

The Ru^{II} ion is readily oxidized by air, ClO_4^-, and so on. The hydrated toluene sulfonate and the alum $Cs_2Ru^{III}(SO_4)_2 \cdot 12H_2O$ can be crystallized. The Ru^{2+}_{aq} ion is a useful starting material for synthesis of organo complexes such as $[Ru(\eta^5\text{-dienyl})(\eta^6\text{-arene})]^+$ and hydrides like *cis*-RuH_2dppe_2.

19-F-3. Ruthenium Chloro Complexes

The oxo species $[Ru_2OCl_{10}]^{4-}$ has been noted previously. Further reduction gives the yellow and rather unstable *hexachlororuthenate(IV)* ion,[24a] $[RuCl_6]^{2-}$, whose brown or purple salts are isomorphous with $[MCl_6]^{2-}$ salts of Os, Ir, Pd, and Pt; they are best made by oxidation of Ru^{III} chloro species by Cl_2.

Ruthenium(III) Complexes.[24b] When RuO_4 solutions in concentrated HCl are evaporated a dark red deliquescent material, $RuCl_3 \cdot 3H_2O$, is obtained. This is the commonest starting material for ruthenium chemistry; it is a mixture mainly of Ru^{IV} complexes probably with some $RuCl_3(H_2O)_3$. It is readily soluble in H_2O, EtOH, and Me_2CO, so that reactions with organic soluble compounds such as phosphines and alkenes are feasible. There is the full range of chloro complexes from $[Ru(H_2O)_5Cl]^{2+}$ to $[RuCl_6]^{3-}$ of which the *cis*- and *trans*-$[RuCl_2(H_2O)_4]$ are most stable; $[RuCl_6]^{3-}$ is formed in high Cl^- ion concentrations. The rate of replacement of Cl^- by H_2O increases with the number of Cl^- ions present: the aquation of $[RuCl_6]^{3-}$ to $[RuCl_5H_2O]^{2-}$ is of the order of seconds in water, but the half-reaction time for conversion of $[RuCl(H_2O)_5]^{2+}$ into $[Ru(H_2O)_6]^{3+}$ is about a year. The yellow *trans*-$[RuCl_2(H_2O)_4]^+$ and green *trans*-$[RuCl_4(H_2O)_2]^-$ can be obtained by oxidation of the deep blue complexes to be discussed next.

Ruthenium(III) chloro species catalyze the reduction of Fe^{3+} by H_2O_2 and also the hydration of acetylenes.

Ruthenium(II) Chloro Complexes. Deep inky-blue solutions are obtained when solutions of Ru^{III} chloro complexes in HCl solution are reduced electrolytically or chemically, for example, by Ti^{3+}, or by H_2 (2 atm) in the presence of platinum black. Blue solutions are also obtained on treating the acetate $Ru_2(O_2CMe)_4$ with HCl. The constitution of the blue species is not settled, and there may be more than one but they are probably dimers with mixed valence Ru^{II} and Ru^{III}. A green salt[25] obtained from a blue solution of $Ru_2^{II,III}(O_2CMe)_4Cl$ in 12 *M* HCl is probably an oxidation product and has the structure $[Cl_3Ru^{III}(\mu\text{-}Cl)_3Ru^{II}(\mu\text{-}Cl)_3Ru^{III}Cl_3]^{4-}$ (see Section 19-F-5 for blue ammine of Ru^{II}/Ru^{III}).

The blue solutions are air sensitive and form *trans*-$[RuCl_4(H_2O)_2]^-$; in the absence of air, oxidation by water gives hydrogen and yellow

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[24a] W. P. Griffith *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 1673.

[24b] M. M. Taqui Khan *et al., Inorg. Chem.*, 1986, **25,** 665.

[25] A. Bino and F. A. Cotton, *J. Am. Chem. Soc.*, 1980, **102,** 608.

trans-$[RuCl_2(H_2O)_4]^+$. The blue solutions prepared by reduction of $RuCl_3{\cdot}3H_2O$ in methanol provide a useful source for the preparation of other Ru^{II} and Ru^{III} complexes.

Other Species. The fluoroanions $[RuF_6]^{n-}$, $n = 1, 2$, and 3 are well known as are bromo analogues of most of the chloro complexes. Dimeric halide bridged species, for example, $[Ru_2^{III}Br_9]^{3-}$ can be oxidized to $Ru_2^{III,IV}$ and Ru_2^{IV} species.[26]

19-F-4. Osmium Halide Complexes

Starting from $[OsO_2(OH)_4]^{2-}$ in HCl solution there are complex transformations giving species in oxidation states III to VI, some oxo and highly acidic hydroxo complexes.[27] One sequence is

$$\begin{tikzcd}
{[Os^{VI}O_2Cl_3H_2O]^-} \arrow[r, shift left, "Cl^-"] & {[OsO_2Cl_4]^{2-}} \arrow[l, shift left, "H_2O"] \arrow[r, "3e"] & {[OsCl_4(H_2O)_2]^-} \arrow[d, shift right, "Cl^-"'] \\
{[OsCl_6]^{2-}} \arrow[r, shift right, "+e"'] & {[OsCl_6]^{3-}} \arrow[l, shift right, "-e"'] \arrow[r, shift right, "H_2O"'] & {[OsCl_5(H_2O)]^{2-}} \arrow[l, shift right, "Cl^-"'] \arrow[u, shift right, "H_2O"']
\end{tikzcd}$$

The most common and useful salts for synthesis are those of the *hexachloroosmate(IV) ion,* $[OsCl_6]^{2-}$, which is readily obtained by reducing HCl solution of OsO_4 by Fe^{2+}; the salts are brown or orange.[24a] The ion can be further reduced only to $[OsCl_6]^{3-}$. The Os^V ion, $[OsCl_6]^-$, is obtained by the reaction

$$OsO_4 + SCl_2 + Cl_2 \xrightarrow{25^\circ C} [SCl_3]^+[OsCl_6]^- \xrightarrow{70^\circ C} Os_2Cl_{10} + SCl_2 + Cl_2$$

or by PbO_2 oxidation of $[OsCl_6]^{2-}$.

The OsX_6^{n-} ions are all octahedral[24a,28]; there are also, like Ru, various halide bridged species,[29] for example, $[Os_2(\mu\text{-}Br)_2Br_8]^{2-}$ and the ion $[Os_2^{III}Cl_8]^{2-}$ that has an Os≡Os bond.[30]

19-F-5. Complexes of Nitrogen Donor Ligands

Some oxo species with *N*-donor ligands have been noted previously, but the main chemistry, especially for ruthenium, involves the II and III states.[31]

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[26] G. A. Heath *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 2307.

[27] C. Brennard and B. Monchel, *Inorg. Chem.,* 1982, **21,** 1810.

[28] K. Dehnicke *et al., Inorg. Chem.,* 1984, **23,** 2563; R. H. Magnusen *et al., Inorg. Chem.,* 1984, **23,** 387, 393.

[29] F. A. Cotton *et al., Inorg. Chem.,* 1984, **23,** 3080.

[30] R. A. Walton *et al., Inorg. Chem.,* 1986, **25,** 4546; F. A. Cotton *et al., J. Am. Chem. Soc.,* 1986, **108,** 4850.

[31] J. T. Hupp and M. J. Weaver, *Inorg. Chem.,* 1984, **23,** 3639 (redox couples); C. Creutz, *Inorg. Chem.,* 1981, **20,** 1522 (Ru—N bond distances).

Ammonia Complexes.[32] Some important reactions of Ru^{II} and Ru^{III} ammines are given in Fig. 19-F-1.

The orange hexammine, $[Ru(NH_3)_6]Cl_2$, is obtained by Zn dust reduction of a strongly ammoniacal solution of $RuCl_3 \cdot 3H_2O$ containing excess NH_4Cl. As obtained by this method it is often contaminated by the nitrogen complex $[Ru(NH_3)_5N_2]Cl_2$ (see below). The hexammine is a reductant,

$$[Ru(NH_3)_6]^{3+} + e = [Ru(NH_3)_6]^{2+} \qquad E^0 = 0.24 \text{ V}$$

but it is sufficiently substitution inert for the electron transfer to proceed by an outer-sphere mechanism.[33a] Oxidation by O_2 proceeds via outer-sphere formation of a superoxo species, which then gives Ru^{III} and H_2O_2[33b]:

$$2Ru^{II} + 2H^+ + O_2 = 2Ru^{III} + H_2O_2$$

The aquation of $[Ru(NH_3)_6]^{2+}$ depends on pH, but gives $[Ru(NH_3)_5H_2O]^{2+}$ in which the H_2O molecule can be substituted by an extremely wide range of

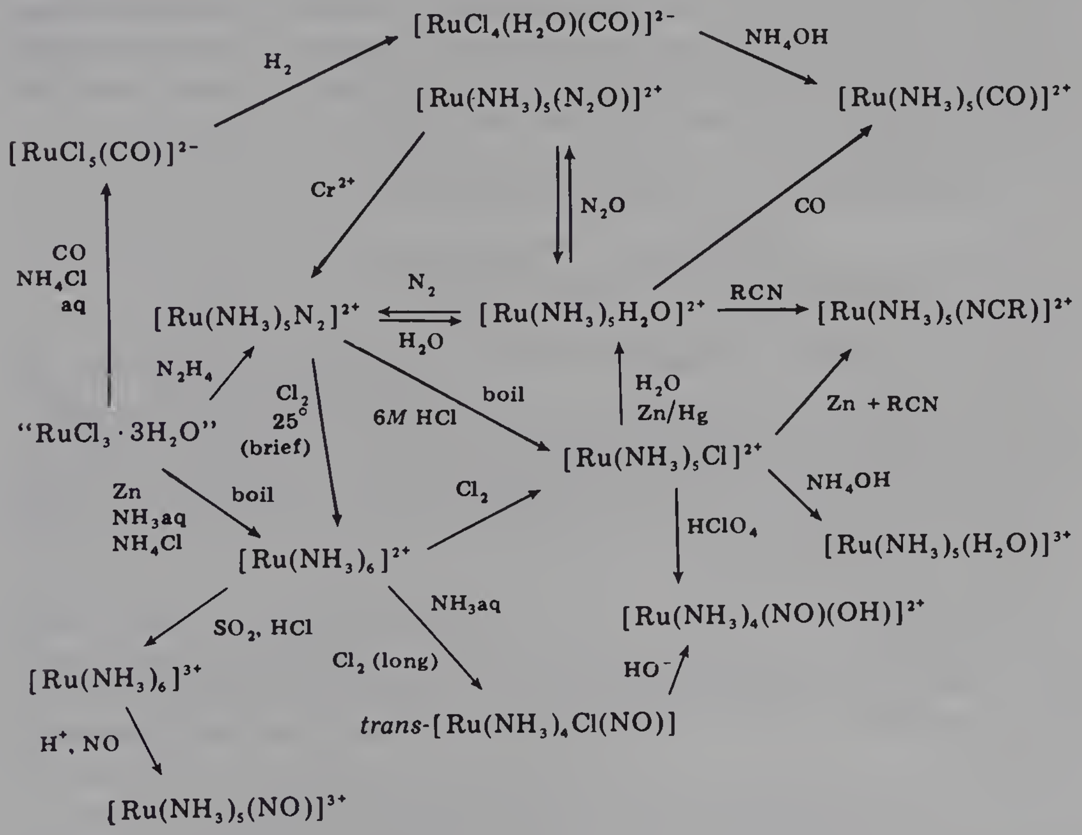

FIG. 19-F-1. Some reactions of ruthenium ammines in aqueous solutions.

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[32] H. Taube *et al.*, *Inorg. Chem.*, 1986, **25,** 3318; R. E. Shepherd *et al.*, *Organometallics*, 1986, **5,** 506; Y. Ilan and M. Kapon, *Inorg. Chem.*, 1986, **25,** 2350; J. R. Winkler *et al.*, *J. Am. Chem. Soc.*, 1987, **109,** 2381; U. Fürholz and A. Haim, *Inorg. Chem.*, 1987, **26,** 3243.

[33a] P. J. Smolenaers and J. K. Beattie, *Inorg. Chem.*, 1986, **25,** 2259.

[33b] H. Taube *et al.*, *Inorg. Chem.*, 1980, **19,** 518.

neutral or anionic ligands, including CO, N_2, N_2O, alkenes, and alkynes. It also reacts with a variety of compounds containing sulfur to give the $[Ru(NH_3)_5SSRu(NH_3)_5]^{4+}$ ion, in which there is a trans, planar Ru—S—S—Ru bridge. This cation is best regarded as a Ru^{II}/Ru^{III} complex bridged by S_2^- with the odd electron delocalized.

It is also possible to prepare more highly substituted complexes from the aqua pentammine ion. For example, a series of *trans*-$[Ru(NH_3)_4(H_2O)L]^{2+}$ ions has been used to establish a trans-labilizing order for ligands (L) in octahedral complexes.

The Ru^{II} ion is low spin (t_{2g}^6) in all its ammine complexes and $Ru(NH_3)_5^{2+}$ is a remarkably good π donor. This is shown not only by the formation of N_2, CO, and similar complexes, but also by the fact that in nitrile complexes $[Ru(NH_3)_5NCR]^{2+}$, the CN stretching frequency is substantially lower than in the free nitrile, whereas in other metal nitrile complexes, even in $[Ru^{III}(NH_3)_5NCR]^{3+}$, the frequency is invariably higher.

Doubtless the most celebrated ammine complex of Ru^{II} is the nitrogen complex $[Ru(NH_3)_5N_2]^{2+}$, which was the first N_2 complex recognized to exist and triggered the rapid development of the chemistry of such complexes (Section 10-9). This particular complex can be prepared in many ways. With the $[Ru(NH_3)_5H_2O]^{2+}$ ion there are the following two reactions:

$$Ru(NH_3)_5(H_2O)^{2+} + N_2 \rightleftharpoons Ru(NH_3)_5N_2^{2+} \qquad K \sim 3 \times 10^4$$

$$Ru(NH_3)_5N_2^{2+} + Ru(NH_3)_5H_2O^{2+} \rightleftharpoons$$
$$[(NH_3)_5Ru{-}N{-}N{-}Ru(NH_3)_5]^{4+} \qquad K \sim 7 \times 10^3$$

The second reaction, forming the bridged ion, exemplifies the donor properties of coordinated N_2. The Ru—N—N—Ru group is nearly linear and the N—N distance (1.124 Å) is only slightly longer than in N_2 itself (1.0976 Å). The bonding can be described by MO theory similar to that for Ru—O—Ru.

The N_2O complex is very rapidly reduced by Cr^{2+} to form the N_2 complex, the overall reaction being

$$[Ru(NH_3)_5N_2O]^{2+} + 2Cr^{2+} + 2H^+ \longrightarrow [Ru(NH_3)_5N_2]^{2+} + 2Cr^{3+} + H_2O$$

It is evident that coordination of N_2O lowers the N—O bond strength, but the precise course of the reduction is still uncertain. Azido Ru^{III} ammines are unstable:

$$[Ru(NH_3)_5N_3]^{2+} \longrightarrow [Ru(NH_3)_5N_2]^{2+} + \tfrac{1}{2}N_2$$

but in the presence of acid, bridged dimers are also formed, and a nitrene complex Ru=NH may be involved.

Still another reaction leading to $[Ru(NH_3)_5N_2]^{2+}$ is the following:

$$[Ru(NH_3)_6]^{3+} + NO + OH^- \longrightarrow [Ru(NH_3)_5N_2]^{2+} + 2H_2O$$

It is interesting that in acid solution one gets only the simple replacement of NH_3 by NO

$$[Ru(NH_3)_6]^{3+} + NO + H^+ \longrightarrow [Ru(NH_3)_5NO]^{3+} + NH_4^+$$

Action of concentrated HCl on $[Ru(NH_3)_6]^{2+}$ gives blue solutions (cf. blue chlorides just cited) and the product is the mixed valence (II, III) ion[34] $[(NH_3)_3Ru(\mu\text{-}Cl)_3Ru(NH_3)_3]^{2+}$ (cf., also Creutz–Taube complexes in a later section).

Ruthenium(III), with a t_{2g}^5 configuration, is, in contrast to Ru^{II}, a very good π acceptor. This is dramatically demonstrated by the rates of base hydrolysis of free and coordinated nitriles:

$$[Ru(NH_3)_5NCR]^{3+} + H_2O \longrightarrow [Ru(NH_3)_5NH_2C(O)R]^{3+}$$

$$NCR + H_2O \longrightarrow H_2NC(O)R$$

The reaction of the coordinated RCN is 10^8 to 10^9 times faster because the π-acceptor character of the $Ru(NH_3)_5^{3+}$ moiety stabilizes the transition state or intermediate resulting from attack of OH^- on the carbon atom by taking electron density from the C≡N bond.

The reduction of ammines of the type $[Ru(NH_3)_5L]^{3+}$ with Cr^{2+} and other reducing agents has been studied in detail. The reactions are similar to those of Co^{III} complexes except that the electron enters the t_{2g} rather than the e_g level and the resulting Ru^{II} complexes are diamagnetic. Bridged species are probably intermediates.

In some reactions the rate-determining step appears to be attack on the *d*-electron density of the metal atom. Thus the hexaammine $[Ru(NH_3)_6]^{3+}$ undergoes aquation only very slowly at room temperature but reacts rapidly with NO, as noted previously.

"Ruthenium Red". A characteristic of ruthenium complex ammine chemistry is the formation of highly colored red or brown species usually referred to as ruthenium reds. Thus if $RuCl_3(aq)$ is treated with NH_4OH in air for several days, a red solution is obtained. Alternatively, if Ru^{III} chloro complexes are reduced by refluxing ethanol and the resulting solution is treated with ammonia and exposed to air at 90°C with addition of more ammonia at intervals, again a red solution is obtained. Crystallization of the solutions gives ruthenium red, $[Ru_3O_2(NH_3)_{14}]Cl_6 \cdot 4H_2O$. This contains an essentially linear trinuclear ion with Ru—O = 1.85 Å and Ru—N = 2.13 Å, $[am_5Ru^{III}—O—Ru^{IV}am_4—O—Ru^{III}am_5]^{6+}$.

The ethylenediamine ion $[am_5RuORu(en)_2ORu\ am_5]^{6+}$ is similar. Since the average oxidation state of Ru is $3\frac{1}{3}$, the metal atoms must be in different formal oxidation states. The diamagnetism can be ascribed to Ru—O—Ru π bonding as in the $[M_2OX_{10}]^{4-}$ ions. The red ion can be oxidized in acid solution by air, Fe^{3+}, or Ce^{4+} to a brown paramagnetic ion of the same

[34] M. N. Hughes *et al., Polyhedron,* 1987, **6,** 1711.

constitution but with charge +7. It is likely that there are corresponding trinuclear chloro complexes, such as $[Ru_3O_2Cl_6(H_2O)_6]$, in the violet aqueous solutions of $RuCl_3{\cdot}3H_2O$.

Osmium ammines. These are less intensively studied but complexes in oxidation states IV–II exist and Os^{II} and Os^{III} are even better π bonders than the Ru^{II} ammines.[35] Examples are $[Osam_4X_2]^{2+}$, *mer*-$Osam_3X_3$, $[Os(N_2)am_5]^{2+}$, and $[Os(CO)am_5]^{2+}$. The triflate, $[Osam_5(CF_3SO_3)]^{2+}(CF_3SO_3^-)_2$ is a useful source for other Os^{III} complexes. There are also the bridged complexes $\{[am_5Os]_2\mu\text{-}N_2\}^{4,5,6+}$ of which the Os^{II} species is most stable.

Although no direct analogues of Ru reds are known there are complexes formed by air oxidation of NH_4OH solutions of $[OsCl_6]^{2-}$ but these have nitrido groups as in $[(H_2O)am_4Os(\mu\text{-}N)Os(H_2O)_4(\mu\text{-}N)Osam_4(H_2O)]^{6+}$ and $[Os_3(N)_2(CN)_{10}(H_2O)_4]^{4-}$.[36]

Aromatic Amine Complexes. Complexes with aromatic amine ligands, which have π systems, have distinctly different features from the ammine complexes. The most important species are those containing 2,2′-bipyridyl (bipy), or 1,10-phenanthrolene (phen), and mixed terpyridyl (terpy) species. Some are tris chelates,[37] others[38] typically, *cis*-Os $bipy_2Cl_2$, $[Os\ bipy(PPh_3)_2(CO)H]^+$, $[Ru\ bipy_2pyX]^+$, $[Ru\ terpy(bipy)NH_3]^{2+}$, $[Ru\ bipy_2(CO)H]^+$, $[Ru\ bipy_2(MeCN)_2]^{2+}$, and oxo species noted Section 19-F-1. The latter have been much studied mainly by T. J. Meyer *et al.*[17,39] There is also an analogue of ruthenium red, $[bipy_2(H_2O)Ru^{III}ORu^{IV}bipy_2ORu^{III}(H_2O)bipy_2]^{6+}$.

$[Ru(bipy)_3]^{2+}$ is extensively used as a sensitizer in photodriven chemical and physical processes such as photolysis of water. The electronic structure of the excited ion $^*[Ru(bipy)_3]^{2+}$ appears to result from transfer of an electron from a metal t_{2g} orbital to a ligand π^* orbital. This excited state can be described as Ru^{III}—L^-, and it reverts to the ground state by photoemission without chemical reaction unless suitable reactants called quenchers are present, as discussed shortly. This is in distinct contrast to the photochemical behavior of the simple ammines, which respond to photoexcitation by promptly aquating or oxidizing:

$$[Ru(NH_3)_5L]^{2+} + H_2O \xrightarrow{h\nu} [Ru(NH_3)_5H_2O]^{2+} \quad \text{or} \quad [Ru(NH_3)_4L(H_2O)]^{2+}$$

$$[Ru(NH_3)_5L]^{2+} + H^+ \xrightarrow{h\nu} [Ru(NH_3)_5L]^{3+} + \tfrac{1}{2}H_2$$

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[35] H. Taube *et al., J. Am. Chem. Soc.*, 1982, **104,** 7658.

[36] J. P. Hall and W. P. Griffith, *J. Chem. Soc. Dalton Trans.*, **1980,** 2410.

[37] M. N. Ackermann and L. V. Interrante, *Inorg. Chem.*, 1984, **23,** 3904; E. M. Kober and T. J. Meyer, *Inorg. Chem.*, 1984, **23,** 3877; R. H. Schmehl, *et al., Inorg. Chem.*, 1985, **24,** 1758; T. C. Strekas *et al., J. Am. Chem. Soc.*, 1987, **109,** 2691.

[38] See, for example, D. J. Hodgson *et al., Inorg. Chem.*, 1985, **24,** 4573; J. M. Kelly *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 253; T. J. Meyer *et al., Inorg. Chem.*, 1985, **24,** 3640; B. Durham *et al., Inorg. Chem.*, 1987, **26,** 53; B. P. Sullivan *et al., Inorg. Chem.*, 1987, **26,** 1247.

[39] T. J. Meyer *et al., J. Am. Chem. Soc.*, 1987, **109,** 3287; 1986, **108,** 1493; *Inorg. Chem.*, 1986, **25,** 2015, 1513, 1041.

The quenching of the emission from the $^*[\mathrm{Ru(bipy)_3}]^{2+}$, $^*[\mathrm{Ru(phen)_3}]^{2+}$, and related ions has been extensively studied. There are three important quenching processes as summarized by the following general equation:

$$^*[\mathrm{RuL_3}]^{2+} + \begin{cases} Q_1 \longrightarrow [\mathrm{RuL_3}]^{+} + Q_1^{+} \\ Q_2 \longrightarrow [\mathrm{RuL_3}]^{3+} + Q_2^{-} \\ Q_3 \longrightarrow [\mathrm{RuL_3}]^{2+} + Q_3^{*} \end{cases}$$

Q_1, Q_2, and Q_3 represent quenching agents that work by reduction, oxidation, or energy transfer, respectively. Reductive quenchers include Eu^{2+}, a series of pentacyanoferrate(II) complexes, and others. Oxidative quenching is given by $[\mathrm{Co(NH_3)_5py}]^{3+}$ and energy transfer by $[\mathrm{Ni(CN)_4}]^{2-}$. The $^*[\mathrm{RuL_3}]^{2+}$ complexes are much stronger oxidizing agents (by ~2 V) than the ground state species, and reductive quenching is perhaps the most common process.

Comparable osmium species are less studied, but $[\mathrm{Os(bipy)_3}]^{2+}$ and $[\mathrm{Os(terpy)_2}]\mathrm{Cl_2}$ are more photolabile and reactive than their Ru analogues.[40]

Finally, there are pyridine complexes such as $[\mathrm{Rupy_6}]^{2+}$ and *trans*-$\mathrm{RuCl_2py_4}$.[41]

Macrocyclic ligands with $[\mathrm{N_4}]$, $[\mathrm{S_3}]$, $[\mathrm{S_4}]$, and mixed donor atoms are known for both Ru and Os and can be made, for example, by interaction of the macrocycle with $[\mathrm{Ru\ ox_3}]^{3-}$. Typical are *cis*- and *trans*-$\{\mathrm{M[N_4]Cl_2}\}^{+}$, $\{\mathrm{Os[S_3]_2}\}^{2+}$, $\{\mathrm{Ru[N_4]ClCO}\}^{+}$, and $\{\mathrm{Ru[N_4](MeCN)_2}\}^{2+}$.[42] There are also many porphyrin compounds[43] such as *trans*-$\mathrm{(CO)_2Ru(porph)}$; $\mathrm{py_2Ru(porph)}$ on heating gives the dimer $[\mathrm{Ru(porph)}]_2$ that has Ru=Ru bonds. The dimer undergoes cleavage on reduction by K in THF to give formally $[\mathrm{Ru^0(porph)}]^{2-}$. The dimer also cleaves with $\mathrm{CH_2N_2}$, $\mathrm{C_2H_4}$ and other reagents. Oxo porphyrin species were noted (Section 19-F-1). There are also the species $\mathrm{Ru^{IV}(oep)X_2}$, X = alkyl or halogen.

The Creutz–Taube Complex[44a,b] and Related Complexes. There is a series of complexes whose common feature is the presence of two (or more) Ru atoms bridged by bidentate ligands through which some, potentially adjustable, degree of electron transfer can take place. Such complexes have been extensively studied in recent years because of the information they may give about the processes of electron exchange in bimolecular redox reactions (cf. Chapter 29), and about the general character of electron transmission through chemical systems, including the spectroscopic phenomena associated with such processes.

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[40] J. N. Demas *et al.*, *Inorg. Chem.*, 1984, **23,** 875.

[41] See, for example, F. Bottomley and M. Mukaida, *J. Chem. Soc. Dalton Trans.*, **1982,** 1933.

[42] M. Schröder *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986,** 471, 334; *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 250; C. Marzin *et al.*, *Inorg. Chem.*, 1986, **25,** 1775, 1778; C-M. Che *et al.*, *Inorg. Chem.*, 1986, **25,** 1809.

[43] J. P. Collman *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 2916; *Inorg. Chem.*, 1987, **26,** 1152; B. R. James *et al.*, *Inorg. Chem.*, 1987, **26,** 1181.

[44a] C. Creutz, *Prog. Inorg. Chem.*, 1983, **30,** 1.

[44b] M. J. Ondrechan *et al.*, *J. Am. Chem. Soc.*, 1987, **109,** 1666, 1672.

A point of focus for much of this work has been the complex (19-F-V),

(19-F-V)

often called the Creutz–Taube complex, after its discoverers. As depicted in (19-F-V) it is formally a mixed-valence (Ru^{II}–Ru^{III}) species; the +4 (Ru^{II}–Ru^{II}) and +6 (Ru^{III}–Ru^{III}) ions are also known and can be isolated as salts of various large anions such as tosylate, perchlorate, or dithionate.

The question at issue in the Creutz–Taube ion, and similar ions, is whether the Ru valences of II and III are localized (trapped), one at each end, thus making the ends nonequivalent, or whether there is delocalization through the bridging ligand to make the whole ion symmetrical. Present conclusions[44b] are that there is delocalization with strong metal-to-bridge coupling.

Crystal structure data on +4, +5, and +6 salts are most consistent with symmetrical ions[45]; even with trapped valences only small bond length differences for $Ru^{II}N$ and $Ru^{III}N$ would be expected and disordering of slightly unsymmetrical ions is possible. However, X-ray photoelectron spectra show two Ru core peaks with binding energies close to $Ru^{II,II}$ and $Ru^{III,III}$ systems consistent with a trapped valence dimer, but a distinction from a delocalized mixed valence dimer cannot be made.[46] Mössbauer (^{99}Ru) spectra of the +5 species suggest this is not an average of +4 and +6 and the odd electron in the *d* orbitals is capable of delocalization into the pyrazine π^* orbitals, indicating strong interaction between the metal centers and between Ru and pyrazine.[47] The epr spectra of the +5 ion also indicate delocalization.[48]

Though the nature of the Creutz–Taube ion itself has been controversial, the related ion (19-F-VI) is clearly a trapped-valence case.

(19-F-VI)

(19-F-VII)

In the necessarily unsymmetrical ion (19-F-VII), the Ru^{III} is definitely localized at the pentammine end. This ion provides a good model for study of the intervalence transfer absorption bands characteristic of trapped-valence species.

The intervalence transfer absorption band corresponds to the energy required for the process

$$[Ru^{II}\text{-}Ru^{III}]^{3+} \xrightarrow{h\nu} {}^*[Ru^{III}\text{-}Ru^{II}]^{3+}$$

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[45] H. B. Bürgi *et al., Inorg. Chem.*, 1985, **24**, 943, 949.

[46] P. H. Citrin and A. P. Ginsberg, *J. Am. Chem. Soc.*, 1981, **103**, 3673.

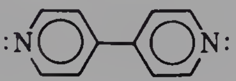
[47] A. Ludi *et al., J. Am. Chem. Soc.*, 1984, **106**, 121.

[48] A. Stebler *et al., Inorg. Chem.*, 1984, **23**, 2764.

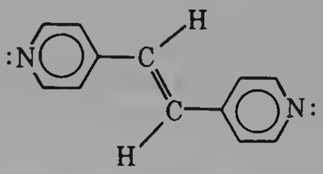
This process absorbs energy even when both metal atoms have the same ligand set because the product contains its Ru^{II} in a ligand arrangement (bond lengths and angles) characteristic of Ru^{III} and its Ru^{III} in an environment suited to Ru^{II}. According to the Franck–Condon principle, the electron "jumps" instantaneously, and only later can vibrational relaxation allow the environmental relaxation process to catch up. Actually, the differences in environments, mainly Ru—N distances, are probably quite small, and that is why only the low energy (~100 kJ] mol^{-1}) of ir radiation suffices to cause the jump.

Some ions similar to (19-F-VI) but with different bridging ligands, such as (19-F-VIII) through (19-F-X), have also been shown to have trapped valences.

(19-F-VIII)

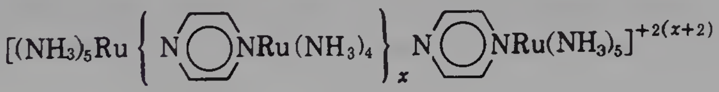


(19-F-IX)



(19-F-X)

A series of extended species of the type (19-F-XI) has been reported, with $x = 1$ to 4. As these are oxidized, the terminal Ru atoms are oxidized to Ru^{III} first and, except for the trinuclear species, the site of oxidation is well localized, with no detectable end-to-end electron transfer.



(19-F-XI)

Bridging by μ-Cl atoms does not appear to be effective compared to that by pyrazine or related aromatic diamines. Thus when $[(bipy)_2Ru(\mu\text{-}Cl)_2Ru(bipy)_2]^{2+}$ is oxidized it gives a transient 3+ ion that cleaves spontaneously to give $[Ru(bipy)_2Cl_2]^+$ and $[Ru(bipy)_2L_2]^{2+}$, where L is a solvent molecule. Evidently there is only weak interaction between discrete Ru^{II} and Ru^{III} sites in the 3+ dimer.

19-F-6. Nitric Oxide Complexes of Ruthenium and Osmium

The formation of nitric oxide complexes is a marked feature of ruthenium chemistry; those of Os have been less well studied, but where known they are even more stable than the Ru analogues.

The group RuNO can occur in both anionic and cationic octahedral complexes in which it is remarkably stable, being able to persist through a variety of substitution and oxidation–reduction reactions. Ruthenium solutions or compounds that have at any time been treated with nitric acid can be suspected of containing NO. Such species have been troublesome in reprocessing of nuclear fuels since the Ru fission products occur as nitrosyl complexes; the neutral complex. $Ru(NO)(NO_3)_3(H_2O)_2$ is extractable by Bu_3PO from the high nitrate concentrations used in reprocessing.[49]

Almost any ligand can be present with the RuNO unit, examples[50] being $[Ru(NO)(CN)_5]^{2-}$ and $Ru(NO)(S_2CNMe_2)_3$, which has two bi- and one unidentate dithiocarbamate. The source of NO can be NO_3^-, NO_2^-, or NO.

The NO group is electrophilic[51] and susceptible to nucleophilic attack (Section 10-10) by OH^-, SH^-, N_3^-, RNH_2, and so on, for example,

$$[RuX\ bipy_2NO]^{2+} + 2OH^- \longrightarrow [RuX\ bipy_2NO_2] + H_2O$$

$RuNO^{3+}$ can also be electrolytically reduced to $RuNH_3^{2+}$.

The vast majority of RuNO complexes are of the general type $Ru(NO)L_5$, in which the metal atom is *formally* in the divalent state and may be designated $\{RuNO\}^6$ complexes. There is a significant number of $\{RuNO\}^8$ and $\{RuNO\}^{10}$ complexes, but these all contain π-acid ligands such as phosphines. In all $\{RuNO\}^6$ complexes the Ru—N—O chains are essentially linear.

19-F-7. Tertiary Phosphine and Related Complexes of Ru and Os

In common with other platinum metals, an intensively studied area is the chemistry involving trialkyl- and triarylphosphines, the corresponding phosphites and, to a lesser extent, the arsines.[52] An extremely wide range of complexes is known, mainly of the II state, although compounds in the 0, III, and less commonly, IV state are known; other ligands commonly associated with the PR_3 group are halogens, alkyl and aryl groups, CO, NO, and alkenes.

The main preparative routes are as follows:

1. Interaction of $RuCl_3 \cdot 3H_2O$, K_2OsCl_6, or other halide species with PR_3 in an alcohol or other solvent. In many of these reactions, either hydride or CO may be abstracted from the solvent molecule, leading to hydrido or carbonyl species. Sodium borohydride is also used as reducing agent.
2. Complexes in the 0 oxidation state may be obtained either by reduction of halides such as $RuCl_2(PPh_3)_3$ with Na or Zn in presence of CO or other ligands such as RNC, or by reaction of metal carbonyls with phosphines. Reactions of polynuclear carbonyls such as $Ru_3(CO)_{12}$ with phosphines tend to preserve the cluster structure.
3. For the M^0 and M^{II} species, oxidative-addition reactions with halogens or other molecules give oxidized species.

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[49] P. Turq *et al., J. Phys. Chem.*, 1984, **88**, 5265; E. Blasius *et al., Fresenius Z. Anal. Chem.*, 1984, **319**, 38.

[50] J. A. Olabe *et al., Inorg. Chem.*, 1984, **23**, 4297.

[51] F. Bottomley *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 2427.

[52] See, for example, M. M. Taqui Khan *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 2603; J. A. Marsella *et al., Inorg. Chem.*, 1986, **25**, 4136; F. H. Jardine, *Prog. Inorg. Chem.*, 1984, **31**, 265 [$RuCl_2(PPh_3)_3$].

4. Carbonyl-containing complex ions such as $M(CO)Cl_5^{3-}$, *cis*-$M(CO)_2Cl_4^{2-}$, and $M(CO)_3Cl_3^-$ are formed by the action of CO or formic acid on Ru and Os chloro complexes, and addition of phosphines to such solutions gives replacement products.

Some typical reactions for ruthenium, which are generally representative also for osmium, are given in Fig. 19-F-2. Phosphines with differing steric and basic properties often give different types of product. The reaction conditions are also critical: for example, for trialkylphosphines and $RuCl_3$ in ethanol, short reaction times give $RuCl_3(PR_3)_3$, whereas prolonged reactions give $[Ru_2Cl_3(PR_3)_6]Cl$.

Some examples are the following. The red-brown $RuCl_2(PPh_3)_3$ has an *sp* structure in which the sixth octahedral position is blocked by an ortho hydrogen atom of one phenyl ring. On treatment with H_2 in base it is converted to $RuHCl(PPh_3)_3$, which has a *tbp* structure and is one of the most active catalysts known for homogeneous hydrogenation of alkenes, with remarkable specificity towards 1-alkenes (Section 28-10).

The dihydrides $RuH_2(PPh_3)_n$ ($n = 3$ or 4) may be obtained by borohydride reduction. They undergo reversible additions of H_2, CO, N_2, and so on, and will act as hydrogenation catalysts for olefins, although orthometallated species (Section 27-9) such as $HRu(C_2H_4)(C_6H_4PPh_2)(PPh_3)_2$ produced by inter-

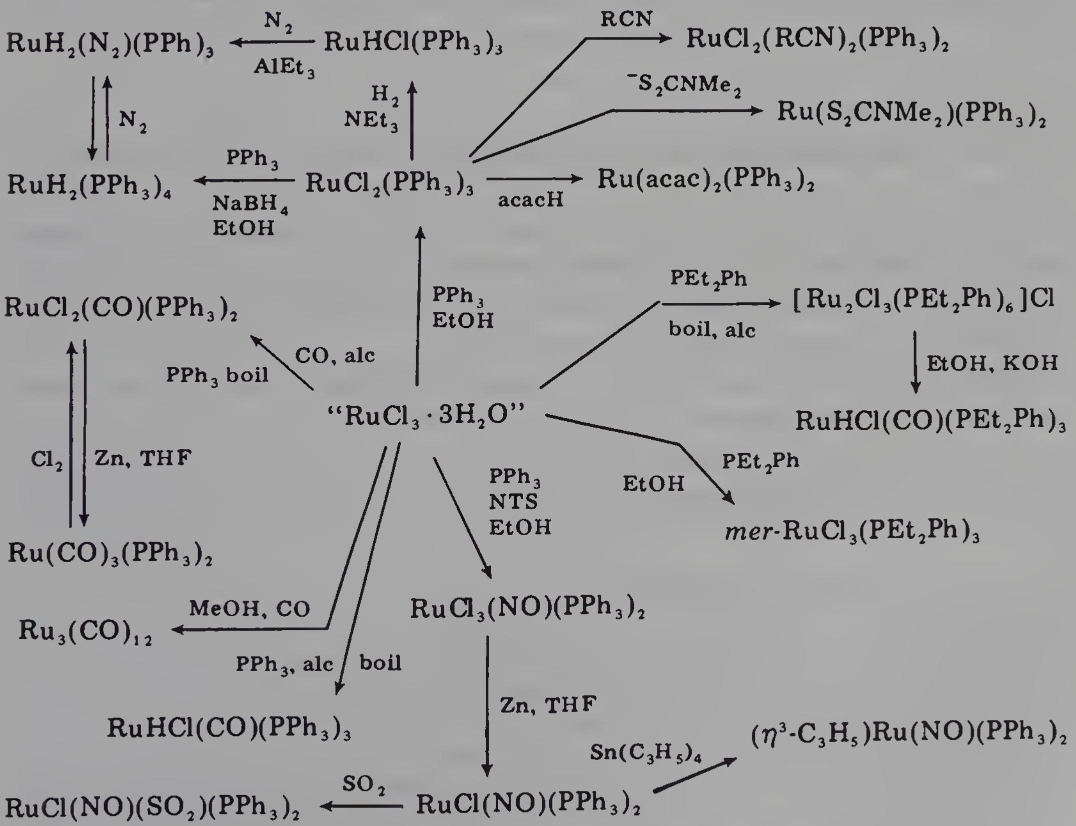

FIG. 19-F-2. Some reactions of tertiary phosphine complexes of ruthenium (alc = 2-methoxyethanol).

action of the hydrides with alkenes are doubtless involved. Some of the compounds, for example, $H_2Ru[P(OMe)_3]_4$, are nonrigid.

Other hydrido species are $RuH_4(PR_3)_3$ and $RuH_6(PR_3)_2$[53] that probably have η^2-(H_2) (see Chapter 24), HRu(η^2-BH_4)triphos,[54a] $[(Me_3P)_3HRu]_2\mu$-AlH_5,[54b] $Ru_2^{III}H_4Cl_2(PR_3)_4$,[55a] and $OsH_3(PPh_3)_4^+$.[55b] Osmium gives $OsH_2(PMe_3)_4$,[56] $OsH_4(PMe_2Ph)_3$, and $OsH_6(PPh\textit{i}\text{-}Pr_2)_2$.[57a] An unusual anionic species is $K[(Ph_3P)_2Ru[C_6H_4PPh_2]H_2]$.[57b]

Both Ru^{II} and Os^{II} form a series of complexes containing PR_3 and CO, H^-, X^-, RCO_2^-, acac$^-$, and so on. Some, for example, Ru(CO)-$(O_2CCF_3)_2(PR_3)_2$, function as dehydrogenation catalysts, converting alcohols to aldehydes or ketones; the catalytic cycle includes the intermediate $RuH(CO)(O_2CCF_3)(PR_3)_2$, from which CF_3CO_2H regenerates the dicarboxylato complex with evolution of hydrogen. The hydrido intermediate can be isolated as a yellow, air-sensitive material.

Osmium(III) forms a variety of OsX_3L_3 type complexes with X = Cl, Br, and I, and L = PR_3 and AsR_3. These undergo ligand replacement reactions, for example, with isocyanides, to give $OsCl_3(AsR_3)(CNR')_2$. The compound $OsCl_3(PEt_3)_3$ can be reduced to $[Os^{II}Cl_3(PEt_3)_2]^-$ with Zn but in THF under N_2, $OsCl_2(N_2)(PEt_3)_2$ is formed.

Chelating phosphines give complexes such as *trans*-$[MH(N_2)diphos_2]^+$, *trans*-$MCl_2diphos_2$, and so on.

Many Ru^{III} species have halide bridges, for example, $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]^+$.

19-F-8. Other Complexes of Ruthenium and Osmium (II), (III), and (IV)

There are many complexes of *oxygen ligands* such as $[Ru(ox)_3]^{3-}$, $Ru(acac)_3$, and $[RuEDTA(H_2O)]^{2-}$. The DMSO complexes, *cis* or *trans*-$RuX_2(Me_2SO)_4$, may have S or S and O bonds to Me_2SO[58]; they catalyze oxidation of R_2S to R_2SO by O_2.

Many studies have been made on the *carboxylates*, and they are useful sources of other complexes, particularly of Ru.

The oxo-centered acetate, $[Ru_3O(O_2CMe)_6L_3]^+$, obtained on refluxing $RuCl_3$(aq), with sodium acetate in acetic acid undergoes complex redox

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[53] B. Chaudret *et al., J. Chem. Soc. Chem. Commun.*, **1983,** 641.

[54a] D. W. Meek *et al., J. Am. Chem. Soc.*, 1982, **104,** 3898.

[54b] A. R. Barron and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, **1986,** 287.

[55a] B. R. James *et al., Inorg. Chim. Acta*, 1985, **100,** 49.

[55b] A. R. Siedle *et al., Inorg. Chem.*, 1986, **25,** 3412.

[56] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 877.

[57a] P. W. Frost *et al., Acta Cryst.*, 1984, **C40,** 946; N. G. Connelly *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2003.

[57b] J. Halpern *et al., J. Organomet. Chem.*, 1985, **296,** 115.

[58] D. P. Riley and J. D. Oliver, *Inorg. Chem.*, 1986, **25,** 1814.

reactions[59] especially when Ru_3O units are linked together by pyrazine. The carboxylates can act as a hydrogenation catalyst in DMF and in the presence of phosphines.

The interaction of the blue Ru^{II} chloride solution in MeOH with sodium acetate gives $Ru_2^{II}(O_2CMe)_4(MeOH)_2$, which has the classical tetra bridged structure for many other divalent carboxylates, for example, of Rh and Mo, and a metal–metal bond with end-coordinated ligands.[60a] The similar mixed valence carboxylates[60b] $[Ru_2^{II,III}(O_2CR)_4]Cl$ were known much earlier. In these the two Ru atoms are identical and the mean oxidation state is 2.5; the Cl acts as a bridge between $Ru_2(O_2CR)_4$ units in a chain structure.

Similar tetra-bridged carboxylates for osmium with Os_2^{III} and $Os_2^{II,III}$ are known. For example, $Os_2Cl_2(\mu\text{-}O_2CMe)_4$ is made by interaction of $(H_3O^+)_2^+[OsCl_6]^{2-}$ with sodium acetate.[61]

For both Os and Ru other 3*e* donor ligands such as acetamidate, or oxopyridinate can give similar species,[62] while action of aqueous Na_2CO_3 on $Ru_2(O_2CMe)_4$ gives the compound[63] $\{Na_3Ru_2(\mu\text{-}O_2CO)_4\cdot 6H_2O\}_n$. Some carbonyl carboxylates can also be obtained by interaction of acid with $M_3(CO)_{12}$.[64]

Sulfur ligands also give a variety of complexes such as $M(S_2CNR_2)_3$, *trans*-$[Ru\ bipy_2(SMe_2)_2]^{2+}$, and *cis*-$bipy_2Ru(SC_6F_5)_2$.[65]

There are tetrathiolates[66] of Ru and Os^{IV}, $M(SR)_4L$ where L = MeCN or CO. These have *tbp* structures and in the carbonyl the CO is axial, which may be attributed to electron donation from S to the metal, which increases the electron density so as to allow π bonding of CO.

Nitrido complexes are quite important. The oxo anion $[OsO_3N]^-$ (Section 19-F-1) is reduced by HCl or HBr and from the resulting red solution salts of the ions $[OsNX_4]^-$, $[OsNX_4(H_2O)]^-$, and $[OsNX_5]^{2-}$ can be obtained.[67a] All have C_{4v} symmetry and very short $Os\equiv N$ bonds. Further reduction with $SnCl_2/HCl$ gives $[Os(NH_3)Cl_5]^{2-}$ while nucleophilic attack on the N atom of $MNCl_3(AsPh_3)_2$ gives Ru or Os imidato complexes having an $MNPR_3$ group. Conversion of $[NMCl_4]^-$ (M = Ru and Os) to $[NM(OSiMe_3)_4]^-$ and alkylation of the latter gives the square pyramidal nitrido alkyls, for example, $[RuNMe_4]^-$ and $[NOs(CH_2SiMe_3)_4]^-$; the latter with $Me_3O^+BF_4^-$ gives $(MeN)Os(CH_2SiMe_3)_4$.[67b]

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[59] T. J. Meyer *et al., Inorg. Chem.*, 1980, **19,** 2145; 1979, **18,** 2472.

[60a] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 2321; **1987,** 2723.

[60b] V. M. Miskowski *et al., Inorg. Chem.*, 1987, **26,** 1098.

[61] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 305; T. A. Stephenson *et al., Inorg. Chem.*, 1984, **23,** 4567.

[62] See, for example, F. A. Cotton *et al., Inorg. Chem.*, 1986, **25,** 1585.

[63] G. Wilkinson *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 433.

[64] Y. Shuo *et al., Organometallics,* 1984, **3,** 1758; A. J. Deeming *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 2473.

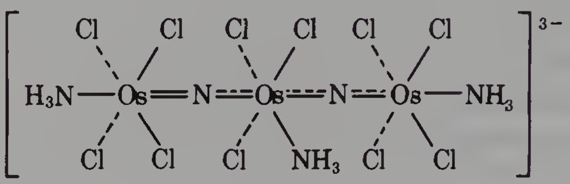
[65] See E. Deutsch *et al., Inorg. Chem.*, 1985, **24,** 2731.

[66] M. M. Millar *et al., J. Am. Chem. Soc.*, 1985, **107,** 3714.

[67a] M. D. Hopkins *et al., J. Am. Chem. Soc.*, 1986, **108,** 6908.

[67b] P. A. Shapley *et al., Organometallics,* 1986, **5,** 1269, 1515.

Nitrido-bridged complexes of both Os and Ru are also known, examples being $K_3[(H_2O)Cl_4RuNRuCl_4(H_2O)]$ obtained by reduction of $K_2[RuCl_5(NO)]$ with HCl and $SnCl_2$ and $[Cl(NH_3)_4RuNRu(NH_3)_4Cl]^{3+}$ obtained by treating the chloro anion with NH_3. Structure and π bonding in these species are analogous to those in the $[Ru_2OCl_{10}]^{4-}$ ion. There are also some larger complexes containing two nitrido bridges, such as (19-F-XII), which is a mixed-valence (V-IV-V) species.

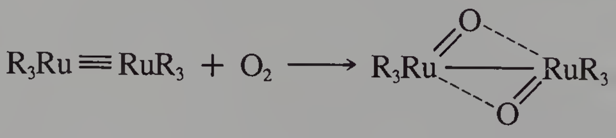


(19-F-XII)

Carbon ligands are also common in ruthenium chemistry. There are various cyanide complexes and isocyanides[68] give ions $[M(CNR)_6]^{2+}$.

Although $(\eta^5\text{-}C_5H_5)_2Ru$ was the first purely organometallic compound of the platinum metals, only recently have pure alkyls and aryls been made.[69]

Interaction of $Ru_2(O_2CMe)_4Cl$ with alkylating agents gives, depending on the alkyl group and solvent, the purple-red dimeric alkyls $Ru_2^{III}R_6$ (R = CH_2SiMe_3 or CH_2CMe_3) that have a multiple bond and are isostructural with Mo_2R_6. The Ru_2R_6 species react with O_2 to give a remarkable Ru^V alkyl:



where there is some weak interaction between the oxygen and the other Ru atom.

For osmium, alkylation of $Os_2Cl_2(\mu\text{-}O_2CMe)_4$ gives $R_2Os(\mu\text{-}O_2CMe)_2OsR_2$ and the bridged acetates can be removed only by use of Li allyl to give, for example, $[(Me_3SiCH_2)_2(\eta^3\text{-}C_3H_5)Os]_2$.

Alkylation or arylation of $[RuCl_5MeCN]^-$ or OsO_4 by Grignard reagents or Al alkyls gives compounds such as $Ru^{IV}(o\text{-}MeC_6H_4)_4$, $Os^{IV}Ph_4$, $Os^{VI}OMe_4$, and $Os^{VI}O_2mes_2$.[69]

19-F-9. Non-oxo Complexes in Higher Oxidation States

Apart from the oxo species that have been mentioned earlier, there are very few compounds other than fluorides. The octahedral hexafluoro complexes

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[68] D. R. McMillin *et al., Inorg. Chem.*, 1987, **26,** 966.

[69] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 271, **1987,** 169, **1987,** 557.

can be prepared by various nonaqueous reactions, for example,

$$RuCl_3 + M^ICl + F_2 \xrightarrow{300°C} M^I[RuF_6]$$

$$Ru + M^{II}Cl_2 + BrF_3 \longrightarrow M^{II}[RuF_6]_2$$

$$OsCl_4 + M^ICl + BrF_3 \longrightarrow M^I[OsF_6]$$

The fluororuthenates(V) dissolve in water with evolution of oxygen, undergoing reductions to $[RuF_6]^{2-}$ and also producing traces of RuO_4. The osmium salts dissolve in water without reaction, but when base is added oxygen is evolved and $[OsF_6]^{2-}$ is formed.

The $[MF_6]^-$ ions have t_{2g}^3 configurations with three unpaired electrons. Their magnetic moments are independent of temperature, averaging ~3.7 BM for the $[RuF_6]^-$ salts and ~3.2 BM for the $[OsF_6]^-$ salts. The differences from the spin-only moment (3.87 BM) may be due in part to certain second-order spin-orbit coupling effects, but since observed moments are perhaps lower than can be explained by this process alone, probably antiferromagnetic interactions also contribute.

There is also the complex of Os^{VII}, F_5OsNCl.[70]

19-F-10. Lower Oxidation States: Organometallic Compounds

The principal chemistry in oxidation states below II is that of the Ru and Os polynuclear carbonyls and their cluster derivatives[71a] that are noted in Chapters 22 and 23. There are also numerous carbonyl, isocyanide, and tertiary phosphine complexes such as $dmpe_2Ru(PMe_3)$, $Ru(CO)_3(PPh_3)_2$, $[Ru(CO)_2(CO_2Me)]_n$, $[Os(CO)_3(O_2CR)]_2$, and $[Ru_2^I(CNR)_{10}]^{2+}$.[71b] It may be noted that carbonyls in high oxidation states are possible, for example, $[Os^{IV}Cl_5(CO)]^-$.[72] In addition to the alkyls and aryls noted previously there is an extensive chemistry of cyclopentadienyl and arene complexes of both Ru and Os, mainly in the II oxidation states, although the metal–metal bonded $(Cp_2Os^{IV})_2^{2+}$ ion has been made by Ce^{IV} oxidation of Cp_2Os.[73a] These include aqueous complexes[73b] such as $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ and $[(\eta^6\text{-}C_6H_6)Os\ am_3]^{2+}$ and neutral compounds[74] such as $(\eta^6\text{-arene})OsMe_2(PR_3)$ and $(\eta^5\text{-}C_5H_5)RuH_3(PPh_3)$.[75] Alkene, diene, alkyne, and allyl complexes include

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[70] R. W. Coleman and R. D. Peacock, *J. Fluorine Chem.*, 1986, **30,** 469.

[71a] N. C. Thomas, *Coord. Chem. Rev.*, 1986, **70,** 121 (Ru carbonyl halides); M. I. Bruce, *Coord. Chem. Rev.*, 1987, **76,** 1 (Ru cluster carbonyls).

[71b] E. Singleton *et al., Organometallics,* 1986, **5,** 1262; W. D. Jones and E. Libertini, *Inorg. Chem.*, 1986, **25,** 1794.

[72] M. Brins and W. Preetz, *Z. Naturforsch.*, 1986, **41B,** 25.

[73a] H. Taube *et al., Inorg. Chem.*, 1987, **26,** 1309, 3316.

[73b] M. Stebler-Röthlisberger and A. Ludi, *Polyhedron,* 1986, **5,** 1217.

[74] J. A. Cabeza and P. M. Maitlis, *J. Chem. Soc. Dalton Trans.*, **1985,** 573; H. Suzuki *et al., Inorg. Chem.* 1986, **25,** 3407; F. B. McCormick *et al., Inorg. Chem.*, 1986, **25,** 3501; J. A. Bandy *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 2477.

[75] S. G. Davies *et al., J. Chem. Soc. Chem. Commun.*, **1983,** 1278.

$Ru(styrene)_2(PPh_3)_2$, (1-4η-COT)($η^6$-C_6Me_6)Ru^0, and ($η^6$-COT)Ru($η^4$-COD) the latter made by reduction of aqueous $RuCl_3$ by Zn in the presence of cycloocta-1,5-diene.[76] There are also ethylene complexes[77] like *cis*-$RuH(C_2H_4)(PMe_3)_4$, $(C_2H_4)Ru(PMe_3)_4$, and $Os(CO)_2(C_2H_4)_3$. Finally, some alkylidene and alkylidyne complexes[78] (see Chapter 25) such as $(R_3P)_2(CO)Cl_2Os{=}CCl_2$ and $(Me_3P)_3Ru(\mu\text{-}CH_2)_3Ru(PMe_3)_3$ are known.

19-G. RHODIUM AND IRIDIUM[1]: GROUP VIII(9)

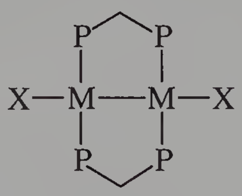
19-G-1. General Remarks: Stereochemistry

The chemistry of Rh and Ir centers around the oxidation states I, II, and III for Rh and I to IV for Ir. The 0 and −I oxidation states are mainly found in carbonyls, especially metal clusters.

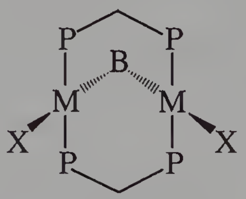
In the II oxidation state there is no evidence for the existence of complexes comparable to those of Co^{II} and the best characterized are those with metal-metal bonds as exemplified by $Rh_2(O_2CMe)_4$.

The oxidation states and stereochemistries are summarized in Table 19-G-1.

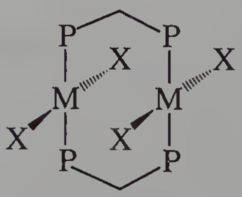
Since their chemistry is very important for the d^8 species Rh^I, Ir^I, Pd^{II}, and Pt^{II} it is convenient to discuss here three classes of binuclear compounds. (19-G-I), (19-G-II), and (19-G-III), that are formed mainly by bifunctional phosphines such as $Ph_2PCH_2PPh_2$ or Ph_2P(1-pyridyl).[2]



Side by-side
(19-G-I)



A frame
(19-G-II)



Face to face
(19-G-III)

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[76] M. A. Bennett *et al., Inorg. Chem.*, 1980, **19,** 1014; G. Vitalli *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2255.

[77] G. Wilkinson *et al., Polyhedron,* 1984, **3,** 1255; J. Takats *et al., J. Am. Chem. Soc.*, 1987, **109,** 2227.

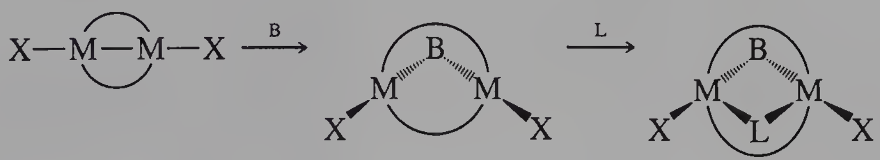
[78] M. A. Gallop and W. R. Roper, *Adv. Organomet. Chem.*, 1986, **25,** 121.

[1] W. P. Griffith, *The Chemistry of the Rarer Platinum Metals,* Wiley–Interscience, New York, 1967. H. Sheridan and F. H. Jardine, *Comprehensive Coordination Chemistry,* Vol. 4, Chapter 48, Pergamon Press, Oxford, 1987 (Rh); N. Serpone and K. Jamieson, *Comprehensive Coordination Chemistry,* Vol. 4, Chapter 49, Pergamon Press, Oxford, 1987 (Ir).

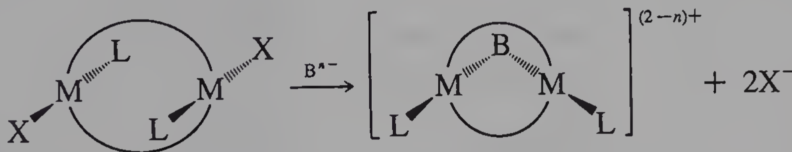
[2] A. L. Balch *et al.*, numerous papers in *Inorganic Chemistry;* J. H. Espenson *et al., Inorg. Chem.*, 1986, **25,** 2557; M. Cowie and S. J. Loeb, *Organometallics,* 1985, **4,** 852; R. J. Puddephat, *Chem. Soc. Rev.*, 1983, **12,** 99; D. M. Hoffman and R. Hoffmann, *Inorg. Chem.*, 1981, **20,** 3543; C. Woodcock and R. Eisenberg, *Inorg. Chem.*, 1985, **24,** 1285; P. R. Sharp, *Inorg. Chem.*, 1986, **25,** 4185; C. P. Kubiak *et al., Inorg. Chem.*, 1987, **26,** 247; N. G. Connelly *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 1403; M. Cowie *et al., Inorg. Chem.*, 1987, **26,** 3333.

These complexes show unique reactions due to the proximity of the metals including (*a*) oxidation of one or both metal atoms with formation of M—M bond. (*b*) addition of neutral molecules with formation of M—M bonds, (*c*) formation of bridge groups such as μ-CO, μ-CH_2, and η^2-CO or η^2-RNC.

The *A frames* are especially important having square M^I, a nonphosphine bridge (μ-B) that may be neutral or anionic, and a vacant site to which small molecules or ions (L) can be bound. Thus we have reactions such as 19-G-1 and 19-G-2 (⌒ = phosphine bridge) where B can be neutral, anionic, or cationic:

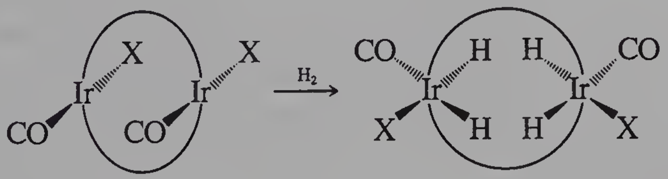


(19-G-1)



(19-G-2)

In some cases, the A-frame structure is not obtained and oxidation giving octahedral metal occurs, for example, 19-G-3



(19-G-3)

Some representative A frames are $[Rh_2(\mu\text{-}Cl)(CO)_2dppm_2]^+$, $[Rh_2(\mu\text{-}\sigma, \pi, C{\equiv}CBu)(CO)_2dppe_2]^+$, $Rh_2(\mu\text{-}S)(CO)_2dppm_2$, and $[Ir_2(\mu\text{-}CO)(CO)_2(dppm)_2]^+$.

19-G-2. Complexes of Rhodium(I) and Iridium(I), d^8

The chemistry is exclusively one involving π and or π-complexing ligands such as CO, PR_3, alkenes, and arenes, and is extremely extensive.

Square, tetrahedral and five-coordinate species are formed. The latter are commonly produced by addition of neutral ligands to the former, for example,

$$trans\text{-}IrCl(CO)(PPh_3)_2 + CO \rightleftharpoons IrCl(CO)_2(PPh_3)_2$$

The criteria for relative stability of five- and four-coordinate species are by no means fully established. Substitution reactions of square species, which are often rapid, proceed by an associative pathway involving five-coordinate intermediates, for example,

$$RhCl(C_8H_{12})SbR_3 + \text{amine} \rightleftharpoons RhCl(C_8H_{12})\text{amine} + SbR_3$$

TABLE 19-G-1
Oxidation States and Stereochemistry of Rhodium and Iridium

Oxidation state	Coordination number	Geometry	Examples
Rh^{-I}, Ir^{-I}, d^{10}	4	Tetrahedral	$Rh(CO)_4^-$, $Ir(CO)_3PPh_3^-$
Rh^0, Ir^0, d^9	4	Tetragonal distorted tetrahedral	$Rh[P(Oi\text{-}Pr)_3]_4$
Rh^I, Ir^I, d^8	3	Planar	$RhCl(PCy_3)_2$, $Rh[N(SiMe_3)_2](PPh_3)_2$, $Rh(PPh_3)_3^+ClO_4^-$
	$4^{a,b}$	Planar	$PhCl(PMe_3)_3$, $[RhCl(CO)_2]_2$, $IrCl(CO)(PR_3)_2$
		Tetrahedral	$[Rh(PMe_3)_4]^+$
	5	*tbp*	$HRh(diphos)_2$, $HIrCO(PPh_3)_3$, $HRh(PF_3)_4$, $(C_8H_{10})_2RhSnCl_3$
Rh^{II}, Ir^{II}, d^7	?	?	$[Rh_2I_2(CNPh)_8]^{2+}$
	4	Square	$[Rh\{S_2C_2(CN)_2\}_2]^{2-}$, $RhCl_2[P(o\text{-}MeC_6H_4)_3]_2$
	5	?	$[Rh(bipy)_2Cl]^+$
	5	Cu^{II} acetate structure	$[Rh(OCOR)_2]_2$
	6	Cu^{II} acetate structure	$[Ph_3PRh(OCOCH_3)_2]_2$
Rh^{III}, Ir^{III}, d^6	5	*tbp*	$IrH_3(PR_3)_2$
	5	*sp*	$RhI_2(CH_3)(PPh_3)_2$
	$6^{a,b}$	Octahedral	$[Rh(H_2O)_6]^{3+}$, $RhCl_6^{3-}$, $IrH_3(PPh_3)_3$, $RhCl_3(PEt_3)_3$, $IrCl_6^{3-}$, $[Rh(diars)_2Cl_2]^+$, RhF_3, IrF_3(ReO_3 type)
Rh^{IV}, Ir^{IV}, d^5	6^b	Octahedral	K_2RhF_6, $[Ir(C_2O_4)_3]^{2-}$, $IrCl_6^{2-}$, IrO_2 (rutile type)
Rh^V, Ir^V, d^4	6	Octahedral	$CsIrF_6$
	7	Pentagonal bipyramidal	$H_5Ir(Pi\text{-}Pr_3)_2$[c]
Rh^{VI}, Ir^{VI}, d^3	6	Octahedral	RhF_6, IrF_6

[a] Most common states for Rh.

[b] Most common states for Ir.

[c] This is a classical pentahydride and not a compound with η^2-H_2. See Chapter 24 and R. H. Crabtree *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 4032.

The Rh^I and Ir^I complexes are invariably prepared by some form of reduction, either of similar M^{III} complexes or of halide complexes such as $RhCl_3 \cdot 3H_2O$ or K_2IrCl_6 in the presence of the complexing ligand. As noted under Ru, alcohols, aldehydes, or formic acid may furnish CO and/or H under certain circumstances; the ligand itself may also act as a reducing agent.

Most of the square Rh^I and Ir^I complexes undergo oxidative-addition reactions (Chapter 27), and this constitutes a way of making M^{III} complexes with π-bonding ligands.

Rhodium. Some preparations and reactions of Rh^I complexes are shown in Figs. 19-G-1 and 19-G-4 (p. 910). We can discuss only a few of the more important compounds.

Tetracarbonyldichlorodirhodium. This is most easily obtained by passing CO saturated with ethanol over $RhCl_3 \cdot 3H_2O$ at ~100°C, when it sublimes as red needles. It has the structure shown in Fig. 19-G-2, where the coordination

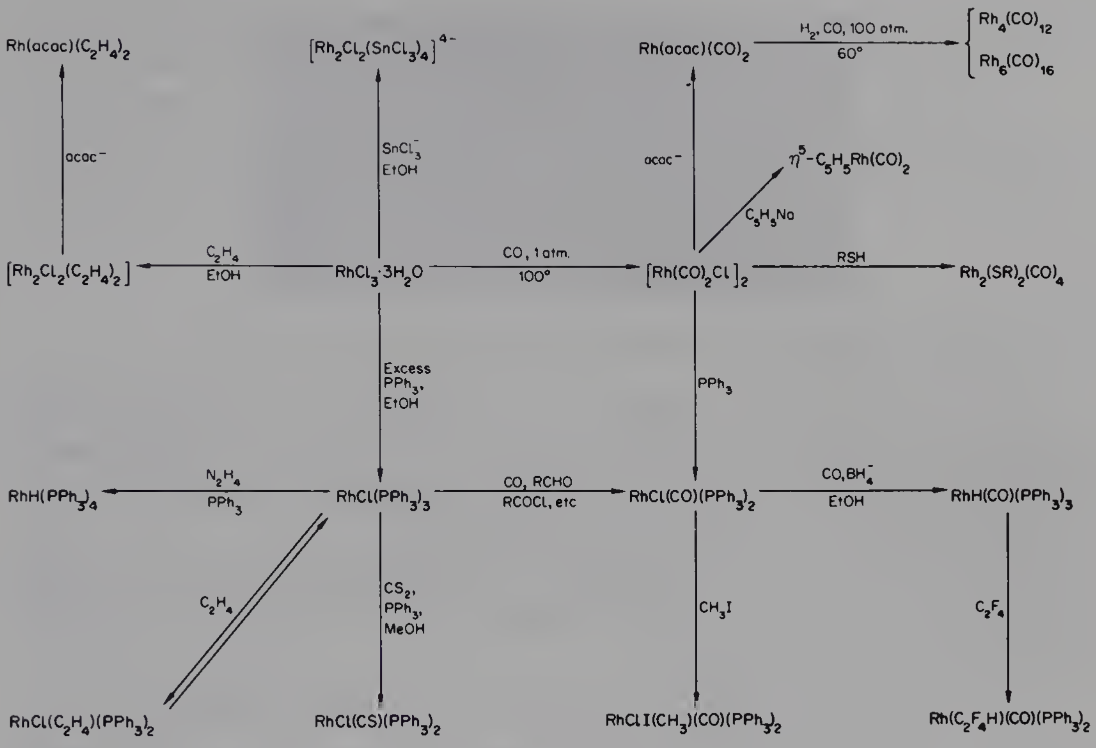


FIG. 19-G-1. Some preparations and reactions of rhodium(I).

around each Rh atom is planar, and there are bridging chlorides with a marked dihedral angle, along the Cl—Cl line.

Electronic factors within the molecule result in the pronounced bending in the dimer; there seems to be only a very weak metal–metal interaction[3] [3.12 Å, cf. 2.73 Å in $Rh_4(CO)_{12}$] and even weaker interaction between adjacent molecules in the lattice (3.31 Å). The carbonyl chloride is an excellent source of other rhodium(I) species, and the halogen bridges are readily cleaved by a wide variety of donor ligands to give *cis*-dicarbonyl complexes, for example,

$$[Rh(CO)_2Cl]_2 + 2L \longrightarrow 2RhCl(CO)_2L$$

$$[Rh(CO)_2Cl]_2 + 2\,Cl^- \longrightarrow 2[Rh(CO)_2Cl_2]^-$$

$$[Rh(CO)_2Cl]_2 + 2(acac)^- \longrightarrow 2Rh(CO)_2(acac) + 2Cl^-$$

Some of the complexes produced thus may be made directly from rhodium trichloride, however.

trans-Chlorocarbonylbis(*triphenylphosphine*)*rhodium.* Although not as widely studied as its iridium analogue, this is an important compound and is an intermediate in the preparation of $RhH(CO)(PPh_3)_3$ discussed later.

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[3] Weak Rh—Rh bond formation also accounts for the oligomerization of $[Rh(RNC)_4]^+$ species. Other Rh^I species also have stacks with Rh—Rh interactions.

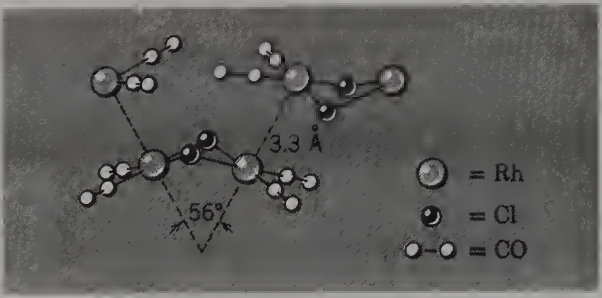

FIG. 19-G-2. The structure of crystalline $[Rh(CO)_2Cl]_2$.

The yellow crystalline complex is best obtained by the reduction of $RhCl_3 \cdot 3H_2O$ in ethanol, with formaldehyde as both a source of CO and as reductant. It is also formed by PPh_3 bridge cleavage from $[Rh(CO)_2Cl]_2$, and by the action of CO on $RhCl(PPh_3)_3$ (see later).

Although it is readily oxidized by Cl_2 to $RhCl_2(CO)(PPh_3)_2$ it is less basic than its Ir^I analogue[4] and the Rh^{III} products of oxidative-addition are also less stable in that equilibria such as

$$trans\text{-}RhCl(CO)(PPh_3)_2 + HCl \rightleftharpoons RhHCl_2(CO)(PPh_3)_2$$

generally lie well to the left-hand side. Flash photolysis of $RhCl(CO)(PPh_3)_3$ leads to transient species that readily react with small molecules.[5]

Other Rhodium Carbonyl Species. In addition to $Rh(CO)_2Cl_2^-$ noted previously, other carbonyl anions are known and are best made by the action of CO or formic acid on $RhCl_3$ solutions. In the CO reduction there is an intermediate Rh^{III} complex $[RhCl_5CO]^{2-}$, and reduction probably occurs by transfer of H_2O to CO, giving a formato intermediate that then loses CO_2. The overall reaction is hence

$$Rh^{III} + H_2O + 3CO \longrightarrow Rh^I(CO)_2 + CO_2 + 2H^+$$

The final product, $Rh(CO)_2Cl_2^-$, can be reoxidized in HCl solution by O_2, so that there is a catalytic cycle for oxidation of CO to CO_2

$$[Rh(CO)_2Cl_2]^- + O_2 + 2H^+ + 3Cl^- \longrightarrow [Rh(CO)Cl_5]^{2-} + CO_2 + H_2O$$

In rhodium (and iridium) β-diketonates there is distinct Rh–Rh interaction in the lattice (see later).

Hydridocarbonyltris(triphenylphosphine)rhodium.[6] This yellow crystalline solid has a *tbp* structure with equatorial phosphine groups. It is best prepared from $RhCl(CO)(PPh_3)_2$ by the reaction

$$trans\text{-}RhCl(CO)(PPh_3)_2 + PPh_3 \xrightarrow[EtOH]{NaBH_4} RhH(CO)(PPh_3)_3$$

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[4] R. G. Pearson and C. T. Kresge, *Inorg. Chem.*, 1981, **20**, 1878.
[5] D. Wink and P. C. Ford, *J. Am. Chem. Soc.*, 1985, **107**, 1794.
[6] F. H. Jardine, *Polyhedron*, 1982, **1**, 569 (231 references).

but it is also formed by the action of CO + H_2 under pressure with virtually any rhodium compound in the presence of an excess of PPh_3. It is important as the catalyst precursor for alkene hydroformylation (Section 28-4).

Related complexes include $RhH(CO)(PCy_3)_2$[7a] and *phosphites,*[7b] for example, $RhH(CO)[P(OiPr)_3]_4$, which differ from phosphine complexes in that CO rather than PR_3 tends to dissociate in solution, that is,

$$RhH(CO)[P(OR)_3]_4 \overset{-CO}{\rightleftharpoons} RhH[P(OR)_3]_4$$

Chlorotris(triphenylphosphine)rhodium.[8a] This remarkable complex is formed by reduction of ethanolic solutions of $RhCl_3 \cdot 3H_2O$ with an excess of triphenylphosphine; triphenylphosphine oxide is a by-product.

$RhCl(PPh_3)_3$ exists in two forms, the normal red-violet and orange. Both have structures that are square with a distortion to tetrahedral and in both there are close contacts with *ortho* hydrogen atoms on a phenyl ring. The complex was the first compound to be discovered that allowed the catalytic hydrogenation (Chapter 28) of alkenes and other unsaturated substances in homogeneous solutions at room temperature and pressure, and its discovery stimulated an enormous development in synthesis of related complexes of rhodium (and other metals) with tertiary phosphine ligands. Not only monophosphine but chelating phosphine complexes behave similarly.

Although the catalytic cycle for hydrogenation requires a three-coordinate species, $RhCl(PPh_3)_2$ only a few complexes of this type, all with bulky ligands[8b] have been isolated, for example, $RhCl(PCy_3)_2$, and $RhH(Pt\text{-}Bu_3)_2$. Removal of chloride leads to the $[Rh(PPh_3)_3]^+$ ion[9a] in which one of the phosphines shows some interaction between the metal and an *ortho* C atom or, in MeCN, to $[Rh(MeCN)(PPh_3)_3]^+$.[9b]

Tris(triphenylphosphine)chlororhodium undergoes a wide variety of oxidative-addition and other reactions (Fig. 19-G-1).

It also readily abstracts CO from other molecules stoichiometrically, for example, where R = adamantyl:

$$CpFe(CO)_2(COR) + RhCl(PPh_3)_3 \longrightarrow CpFe(CO)(PPh_3)(R) + RhCl(CO)(PPh_3)_2 + CO$$

In all such cases *trans*-$RhCl(CO)(PPh_3)_2$ is formed. Catalytic decarbonylation of aldehydes and acyl halides where $RhCl(PPh_3)_3$ is used as starting material doubtless involve the carbonyl complex first formed (Chapter 28).

Both $RhCl(PPh_3)_3$ and $Rh_2Cl_2(PPh_3)_4$ react with and can act as oxidation catalysts for cyclohexene and other molecules, probably via a free-radical

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[7a] M. A. Freeman and D. A. Young, *Inorg. Chem.*, 1986, **25,** 1556.

[7b] E. L. Muetterties *et al., J. Am. Chem. Soc.*, 1981, **103,** 5517; *Inorg. Chem.*, 1987, **26,** 1296.

[8a] F. H. Jardine *Prog. Inorg. Chem.*, 1981, **28,** 63 (650 references).

[8b] For references see P. P. Power *et al., Organometallics,* 1984, **3,** 657.

[9a] A. R. Siedle *et al., Organometallics,* 1984, **3,** 855.

[9b] C. D. Garner *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 1977.

reaction (Chapter 28), also giving Ph_3PO. The compounds $RhCl(\eta^2\text{-}O_2)(PPh_3)_2$ and $RhCl(\eta^2\text{-}O_2)(PPh_3)_2 \cdot 2CH_2Cl_2$, which contains H-bonded dichloromethane, have been structurally characterized.

Hydrides, $HRh(PR_3)_{3,4}$, can be made by reduction of $RhCl_3$ and PR_3 under H_2 by Na/Hg[10a] while under N_2 rather unstable species $RhH(N_2)(PR_3)_2$ can be obtained.

Other Complexes. There are numerous complexes with chelating phosphines and with dppe the species can be obtained in three oxidation states,[10b] namely, $[Rh\ dppe_2]^{+,0,-}$.

Iridium. The most important of Ir^I complexes are *trans*-$IrCl(CO)(PPh_3)_2$ (*Vaska's compound*) and its analogues with other phosphines.[11] Many studies have been carried out on these compounds because they provide some of the clearest examples of oxidative-addition reactions, since the equilibria

$$trans\text{-}IrX(CO)(PR_3)_2 + AB \rightleftharpoons Ir^{III}XAB(CO)(PR_3)_2$$

lie well to the oxidized side and the oxidized compounds are usually stable octahedral species, unlike many of their rhodium analogues.

It is of interest to note that the complex from *o*-tolylphosphine, unlike the PPh_3 and *m*- or *p*-tolylphosphine complexes, is inert to H_2, O_2, SO_2, and $(CN)_2C{=}C(CN)_2$. This is attributed to the steric effect of the *o*-methyl group that blocks the apical sites, thus preventing reaction.

The complexes are usually made by refluxing Na_2IrCl_6 and phosphine in 2-methoxyethanol or diethylene glycol under an atmosphere of CO.

The carbonyl is readily converted into the five-coordinate hydride:

$$trans\text{-}IrCl(CO)(PPh_3)_2 \overset{CO}{\rightleftharpoons} IrCl(CO)_2(PPh_3)_2 \xrightarrow[EtOH]{NaBH_4} IrH(CO)_2(PPh_3)_2$$

and this is of interest in that it is much more stable than its Rh analogue, hence allows many prototypes for intermediates in the hydroformylation sequence to be isolated.

Like rhodium, Ir forms alkene complexes. Examples are the cyclooctene or 1,5-cyclooctadiene (COD) compounds, for example, $[IrCl(COD)_2]_2$, formed by boiling $(NH_4)_2IrCl_6$ with the olefin in alcohols; this product can be converted into $IrCH_3(COD)(PMe_2Ph)_2$, which shows unusual fluxional behavior. Ethylene forms the usual five-coordinate $IrCl(C_2H_4)_4$. Finally $IrCl(PPh_3)_3$ can be obtained by the action of PPh_3 on $[IrCl(COD)]_2$. This product differs from $RhCl(PPh_3)_3$ in reacting irreversibly with H_2 to give $IrClH_2(PPh_3)_3$. Since this octahedral species does not dissociate in solution, it does not act as a hydrogenation catalyst for olefins at 25°C, although it will do so under uv irradiation. By contrast, the bis species $IrCl(PPh_3)_2$, which is made *in situ* by the action

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[10a] T. P. Hanusa and W. J. Evans, *J. Coord. Chem.*, 1986, **14**, 223.
[10b] R. Eisenberg *et al.*, *Inorg. Chem.*, 1985, **24**, 1852.
[11] M. J. Burk and R. H. Crabtree, *Inorg. Chem.*, 1986, **25**, 931.

of PPh_3 on the cyclooctene complex $[IrCl(C_8H_{14})_2]_2$, is an active catalyst. These observations clearly show the necessity for having a vacant site for coordination of olefin on the hydrido complex.

Cationic and Anionic Complexes. For both metals a variety of related cationic and some anionic species (which may be either four- or five-coordinate) are known, for example,

$$\textit{trans}\text{-}IrCl(CO)(PR_3)_2 + CO - \begin{cases} \xrightarrow{Na/Hg} Na[Ir(CO)_3(PR_3)] \\ \xrightarrow{NaClO_4} [Ir(CO)_3(PR_3)_2]ClO_4 \end{cases}$$

$$\textit{trans}\text{-}IrCl(CO)(PR_3)_2 \xrightarrow{(diphos)} [Ir(diphos)_2]Cl$$

$$Rh(diene)acac \xrightarrow{HClO_4,\ PPh_3} [Rh(diene)(PPh_3)_2]ClO_4 + acacH$$

The cationic phosphine species[12] have been intensively studied because of their reactions with hydrogen and with alkanes (Chapter 24). They are generally of the form $[M^I(diphos)_2]^+$, $[Ir(CO)(dppe)_2]^+$, $[\eta^6\text{-(arene)}Ir(COD)]^+$ and the M^{III} species, $[MH_2(PR_3)_2S_2]^+$, S-solvent, and $[IrH(dppe)_2]^{2+}$.

Mixed Ir^{III}–Rh^I complexes[13] can be made by the reactions:

$$RhCl(PEt_3)_2 + IrH_5(PEt_3)_2 \longrightarrow (Et_3P)_2Rh(\mu\text{-H})(\mu\text{-Cl})IrH_2(PEt_3)_2$$

$$[Rh(diphos)(Me_2CO)_2]^+ + IrHCl_2(PR_3)_2 \longrightarrow [(diphos)Rh(\mu\text{-H})(\mu\text{-Cl})IrCl(PR_3)_2]^+$$

Solvated species are commonly made by hydrogenation of a cyclooctadiene complex:

$$[Ir(COD)(PR_3)_2]^+ + H_2 + solvent(s) \longrightarrow [IrH_2(PR_3)_2S_2]^+$$

where the ease of solvation is $H_2O < THF < BuOH < Me_2CO < MeOH < MeCN$.

Isocyanides can give cationic species:

$$RhCl(CO)(PPh_3)_3 \xrightarrow{RNC} Rh(CNR)_4Cl + CO + 2PPh_3$$

In polar solvents such as MeCN the solutions may be yellow when dilute, blue when concentrated. This is attributable to polymerization:

$$n[Rh(CNR)_4]^+ \rightleftharpoons [Rh(CNR)_4]_2^{2+},\quad [Rh(CNR)_4]_3^{3+},\quad \text{etc.}$$

For the dimer, there are two planar face to face $Rh(CNR)_4$ units with a weak Rh—Rh bond.[14]

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[12] For examples, see M. A. Lilga and J. A. Ibers, *Inorg. Chem.*, 1984, **23,** 3538; R. H. Crabtree *et al., J. Am. Chem. Soc.*, 1982, **104,** 6994.

[13] L. M. Venanzi *et al., Inorg. Chem.*, 1985, **24,** 4821.

[14] Y. Yamamoto *et al., Organometallics,* 1983, **2,** 1604; I. S. Sigal and H. B. Gray, *J. Am. Chem. Soc.*, 1981, **103,** 2220.

Bipyridyls[15] give quite complicated air-sensitive systems whose nature, for Rh, depends on pH and concentration. Like the isocyanides there are mono- and dimeric species, for example, $[Rh(bipy)_2]^+$, $[Rh(bipy)_2]_2^{2+}$, as well as oxidized species formed on acidification, for example, $[Rh(bipy)_2H(H_2O)]^{2+}$. Some of these may be involved in photochemical reaction leading to water cleavage and other reactions such as the water gas shift reaction.

Some carbonyl *anionic complexes* have been studied because like other square compounds, they are stacked so that linear chains of metal–metal bonded atoms are formed (Section 19-H-4), and such compounds are potential one-dimensional electrical conductors. Holes in the *d* bands that allow conduction, arising from metal–metal interaction, may be formed by partial oxidation.

Typical complexes such as $K_{0.98}[Ir(CO)_2Cl_{2.42}]\cdot 0.2MeCOMe$ and $K_{0.6}[Ir(CO)_2Cl_2]\cdot 0.5H_2O$, which form conducting bronzelike needles, can be obtained by carbonylation of K_2IrCl_6.

19-G-3. Complexes of Rhodium(III) and Iridium(III), d^6

Both Rh and Ir form many octahedral complexes, cationic, neutral, and anionic; in contrast to Co^{III} complexes, reduction of Rh^{III} or Ir^{III} does not give rise to divalent complexes (except in a few special cases). Thus depending on the nature of the ligands and on the conditions, reduction may lead to the metal — usually with halogens, water, or amine ligands present — or to hydridic species of M^{III} or to M^I when π-bonding ligands are involved.

Though similar to Co^{III} in giving complex anions with CN^- and NO_2^-, Rh and Ir differ in readily giving octahedral complexes with halides, for example, $[RhCl_5H_2O]^{2-}$ and $[IrCl_6]^{3-}$, and with oxygen ligands such as oxalate and EDTA.

The cationic and neutral complexes of all three elements are generally kinetically inert, but the anionic complexes of Rh^{III} are usually labile. By contrast, anionic Ir^{III} complexes are inert, and the preparation of such complexes is significantly harder than for the corresponding Rh species.

Rhodium complex cations have proved particularly suitable for studying trans effects in octahedral complexes.

In their magnetic and spectral properties the Rh^{III} complexes are fairly simple. All the complexes, and indeed all compounds of rhodium(III), are diamagnetic. This includes even the $[RhF_6]^{3-}$ ion, of which the cobalt analogue constitutes the only example of a high-spin Co^{III}, Rh^{III}, or Ir^{III} ion in octahedral coordination. Thus the inherent tendency of the octahedral d^6 configuration to adopt the low-spin t_{2g}^6 arrangement, together with the relatively high ligand field strengths prevailing in these complexes of tripositive higher transition series ions, as well as the fact that all $4d^n$ and $5d^n$ configurations are more

[15] H. A. Schwartz and C. Creutz, *Inorg. Chem.*, 1983, **22**, 707.

prone to spin pairing than their $3d^n$ analogues, provide a combination of factors that evidently leaves no possibility of there being any high-spin octahedral complex of Rh^{III} or Ir^{III}.

The visible spectra of Rh^{III} complexes have the same explanation as do those of Co^{III} complexes. As illustrated in Fig. 19-G-3 for the $[Rh(NH_3)_6]^{3+}$ and $[RhCl_6]^{3-}$ ions, there are in general two bands toward the blue end of the visible region, which together with any additional absorption in the blue due to charge-transfer transitions, are responsible for the characteristic orange, red, yellow, or brown colors of rhodium(III) compounds. These bands are assigned as transitions from the ${}^1A_{1g}$ ground state to the ${}^1T_{1g}$ and ${}^1T_{2g}$ upper states just as in the energy level diagram for Fe^{II} and Co^{III}. The spectra of Ir^{III} complexes have a similar interpretation.

The Rhodium and Iridium Aqua Ions. Unlike cobalt, rhodium gives a stable yellow aqua ion $[Rh(H_2O)_6]^{3+}$. It is obtained by dissolution of $Rh_2O_3(aq)$ in cold mineral acids, or, as the perchlorate by repeated evaporation of $HClO_4$ solutions of $RhCl_3(aq)$. Exchange studies with $H_2{}^{18}O$ confirm the hydration number as 5.9 ± 0.4. The ion is acidic, $pK_A \sim 3.3$, giving $[Rh(H_2O)_5OH]^{2+}$ in solutions $< \sim 0.1\ M$ in acid. The crystalline deliquescent perchlorate is isomorphous with other salts containing octahedral cations, for example, $[Co(NH_3)_6](ClO_4)_3$. The aqua ion also occurs in the yellow sulfate $Rh_2(SO_4)_3 \cdot 12H_2O$, obtained by vacuum evaporation at 0°C of solutions of $Rh_2O_3(aq)$ in H_2SO_4. A red sulfate $Rh_2(SO_4)_3 \cdot 6H_2O$, obtained by evaporation of the yellow solutions at 100°C gives no precipitate with Ba^{2+} ion and is presumably a sulfato complex.

The $[Ir(H_2O)_6]^{3+}$ ion can be made by dissolution of hydrous oxide in $HClO_4$ and isolated as the perchlorate. It has $pK_A = 4.37$ and is readily oxidized to hydroxo aqua ions of Ir^{IV} and Ir^{V} that are probably binuclear but is extremely

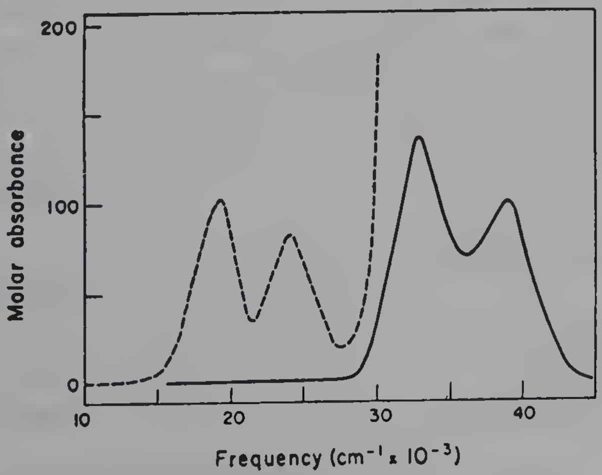

FIG. 19-G-3. The visible spectra of the $[RhCl_6]^{3-}$ (dashed curve) and the $[Rh(NH_3)_6]^{3+}$ (solid curve) ions.

inert to substitution.[16a] The alums, $CsM(SO_4)_2 \cdot 12H_2O$ have the $[M(H_2O)_6]^{3+}$ ions.[16b]

Rhodium(III) and Iridium(III) Chloride Complexes. One of the most important of Rh^{III} compounds and the usual starting material for the preparation of rhodium complexes (see Figs. 19-G-1 and 19-G-4) is the dark red, crystalline, deliquescent trichloride, $RhCl_3 \cdot nH_2O$; n is usually 3 or 4. This is obtained by dissolving hydrous Rh_2O_3 in aqueous hydrochloric acid and evaporating the hot solutions. It is very soluble in water and alcohols, giving red-brown solutions.

On boiling the aqueous solutions $[Rh(H_2O)_6]^{3+}$ is formed, and on heating with excess HCl, the rose-pink hexachlororhodate ion $[RhCl_6]^{3-}$. The complexes intermediate between these two extremes, including the various isomers, have been isolated and their interconversions studied. The steric course of the reactions is governed by the trans effect of chloride. For example, on aquation $[RhCl_6]^{3-}$ produces only cis compounds ending with the very stable neutral *fac*-$RhCl_3(H_2O)_3$:

$$[RhCl_6]^{3-} \underset{}{\overset{H_2O}{\rightleftharpoons}} [RhCl_5(H_2O)]^{2-} \overset{H_2O}{\rightleftharpoons} cis\text{-}[RhCl_4(H_2O)_2]^- \overset{H_2O}{\rightleftharpoons} fac\text{-}RhCl_3(H_2O)_3$$

Hexahalogenorhodates may be obtained also by heating Rh metal and alkali metal halide in Cl_2 (plus a little carbon), extracting the melt, and crystallizing.

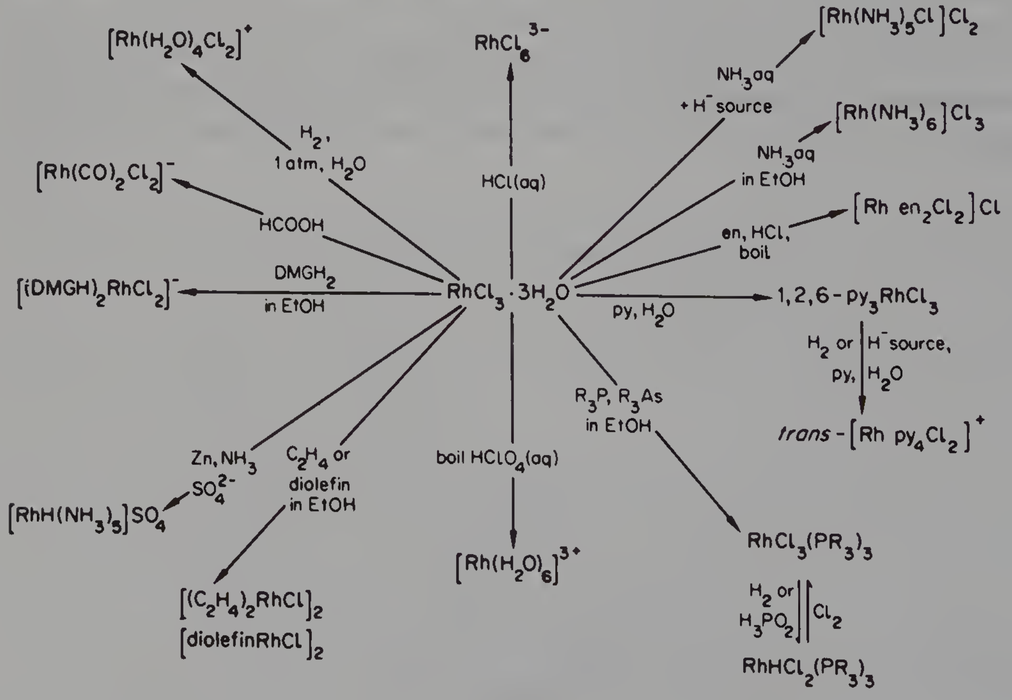

FIG. 19-G-4. Some reactions of rhodium trichloride.

[16a] R. S. Armstrong *et al., J. Chem. Soc. Dalton Trans.*, **1983,** 1973.
[16b] A. G. Sykes *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 1120; *Polyhedron,* 1987, **6,** 101.

With very large cations halogen-bridged species like $Rh_2Cl_9^{3-}$ can be obtained and there are similar $Ir_2X_9^{3-}$ species.[17]

Several dark green, hydrated Ir^{III} halides are obtained by dissolution of $Ir_2O_3(aq)$ in the appropriate acid; species formed by aquation of $[IrCl_6]^{3-}$, for example, $[Ir(H_2O)Cl_5]^{2-}$, $[Ir(H_2O)_2Cl_4]^-$, and $[Ir(H_2O)_3Cl_3]$ have been studied in great detail.

Cationic Complexes. Both Rh and Ir give cobalt-like ammines of the types $[ML_6]^{3+}$, $[ML_5X]^{2+}$, and $[ML_4X_2]^+$, of which $[Rh\ am_5Cl]Cl_2$ is a typical example. The salts are made in various ways, but usually by the interaction of aqueous solutions of $RhCl_3(aq)$ with the ligand.

The formation of complex ions from $RhCl_3(aq)$, $[Rh(H_2O)Cl_5]^{2-}$, or $[RhCl_6]^{3-}$ is often catalyzed by the addition of reducing agents that can furnish hydride ions; ligands such as ethylenediamine may also themselves act in this way. The effect of ethanol was discovered by Delépine long before the general nature of such catalysis was recognized. It now appears that many rhodium complexes have been made only because ethanol was used as a solvent. One example of the catalysis is the action of pyridine, which with $RhCl_3(aq)$ gives mainly $Rh\ py_3Cl_3$ and with aqueous $[Rh(H_2O)Cl_5]^{2-}$ gives $[Rh\ py_2Cl_4]^-$. On addition of alcohol, hydrazine, BH_4^-, or other reducing substances—even molecular hydrogen at 25°C and ≤1 atm—conversion into *trans*-$[Rh\ py_4Cl_2]^+$ rapidly occurs. Kinetic studies of this reaction suggest that Rh^I complexes, rather than hydridic ones, are involved in the catalysis, since $[Rh(CO)_2Cl]_2$ and $Rh(acac)(CO)_2$ are more effective than hydride-producing substances. Further evidence comes from the reaction of $[Rh(H_2O)_6]^{3+}$ in ethanolic ClO_4^- solution with 2,2′-bipyridine, when an air-sensitive brown complex $[Rh^Ibipy_2]ClO_4{\cdot}3H_2O$ can be isolated (cf. above).

The reduction of $[Rh\ en_2Cl_2]^+$ at a mercury electrode does not give a Rh^{II} species as first thought, but a mercury complex $\{[en_2Rh]_2Hg\}^+$; the formation of bonds to mercury is a common phenomenon for Rh, Ru, and some other elements, and the formation of mercury complexes can always be suspected whenever mercury or its compounds are used.

The formation of *iridium* complexes is normally very slow but, as for rhodium, can be catalyzed. Thus to convert $Na_2Ir^{IV}Cl_6$ into py_3IrCl_3 and *trans*-$[Ir\ py_4Cl_2]Cl$, a bomb reaction was formerly used. Quite rapid conversions are obtained as follows:

$$Na_2IrCl_6 \xrightarrow[\text{boil 30 min}]{NaH_2PO_2(aq)\ +\ py} cis\text{-}py_3IrCl_3 \xrightarrow[6\ h]{} [Ir\ py_4Cl_2]Cl$$

$$H_2IrCl_6 \xrightarrow[\substack{\text{2-methoxyethanol,}\\ \text{boil 10 min}}]{\text{HCl in}} IrCl_6^{3-} \xrightarrow[1\ h]{+py,\ boil} mer\text{-}py_3IrCl_3$$

trans-$[Ir\ en_2Cl_2]^+$ can be similarly obtained by using hypophosphorous acid as catalyst.

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[17] H. J. Steinebach and W. Preetz, *Z. Anorg. Allg. Chem.*, 1985, **530**, 155.

The complex *cis*-$[Ir\ bipy_2(OSO_2CF_3)_2]^+$ made from *cis*-$[Ir\ bipy_2Cl_2]Cl$ is a useful precursor[18] for other bipyridyls such as *cis*-$[IrH_2bipy_2]^+$.

Hydrido Complexes. With NH_3 or amines, quite stable octahedral hydrido complexes can be obtained for rhodium. Thus the reduction of $RhCl_3 \cdot 3H_2O$ in NH_4OH by Zn in presence of SO_4^{2-} leads to the white, air-stable, crystalline salt $[RhH\ am_5]SO_4$. In aqueous solution the ion dissociates:

$$[RhH\ am_5]^{2+} + H_2O = [RhH\ am_4H_2O]^{2+} + NH_3 \qquad K \sim 2 \times 10^{-4}$$

Various substitution reactions with other amines can be carried out, and with alkenes remarkably stable alkyl derivatives, for example, $[RhC_2H_5am_5]SO_4$, can be obtained. The structure of $[RhH\ am_5](ClO_4)_2$ shows a distinct hydridic trans weakening effect (0.165 Å) on the trans Rh—N bond. The cyanide $[RhH(CN)_5]^{3-}$ is also known.

For complexes with tertiary phosphines, carbon monoxide, and similar ligands, innumerable hydrido complexes of Rh and Ir are known, not only in the I state but in the III state, an example being *fac*-$RhH_3(PMe_3)_3$[19a]; those for Ir^{III} are particularly stable.[19b] Most are obtained by oxidative-addition of HX or H_2 to the corresponding M^I species. One example is *mer*-$IrH_3(PPh_3)_3$, which though thermally stable, loses hydrogen on irradiation to give the orthometallated product:

$$IrH_3(PPh_3)_3 \xrightarrow{h\nu} 2H_2 + Ir^I(o\text{-}C_6H_4PPh_2)(PPh_3)_2$$

The *mer* and *fac* isomers of $IrH_3(CO)(PPh_3)_2$ interconvert via dissociation of H_2 and a $IrH(CO)(PPh_3)_2$ intermediate.[19c]

Neutral Complexes. Interaction of acetylacetone and hydrous Rh_2O_3 gives the trisacetylacetonate, which has been resolved into enantiomeric forms. It undergoes a variety of electrophilic substitution reactions of the coordinated ligand, such as chlorination. The stereochemistry and racemization of the cis and trans isomers of the unsymmetrical trifluoroacetylacetonate have been studied by nmr spectroscopy; the compound is extremely stable to isomerization.

Neutral complexes with CO, PR_3, pyridines, and so on as ligands may be made directly from $RhCl_3 \cdot 3H_2O$ or Na_3IrCl_6, but as noted before, they are also commonly and often readily obtained by oxidative-addition to the M^I complexes. Typical formulas are MCl_3L_3, $MHCl_2I_3$, and $MCl_3(CO)L_2$.

19-G-4. Complexes of Rhodium(II)[20] and Iridium(II), d^7

Short lived Rh^{II} species can be made by flash photolysis of Rh^{III} complexes and some paramagnetic square complexes of bulky phosphines such as

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[18] B. P. Sullivan *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 403.

[19a] V. V. Mainz and R. A. Andersen, *Organometallics,* 1984, **3,** 675.

[19b] P. A. Harding and S. D. Robinson, *J. Chem. Soc. Dalton Trans.*, **1987,** 947.

[19c] J. F. Harrod and W. J. Yorke, *Inorg. Chem.*, 1981, **20,** 1156.

[20] T. R. Felthouse, *Prog. Inorg. Chem.*, 1982, **29,** 73 (exhaustive review including catalytic and biochemical aspects); E. B. Boyer and S. D. Robinson, *Coord. Chem. Rev.*, 1983, **50,** 109.

$RhCl_2(PCy_3)_2$ are known. However, the main classes of complex are binuclear and diamagnetic with Rh—Rh bonds.

Carboxylates and Related Complexes. These are of the type $Rh_2(\mu\text{-}O_2CR)_4$ or have other bridge groups, such as acetamidate or pyrazolate.[21] They have been intensively studied in part because some have anti-tumor properties and catalyze reactions such as hydrogenation or cyclopropanation of alkenes, as well as for their spectroscopic properties.

The most accessible complex is the *acetate* $Rh_2(\mu\text{-}O_2CMe)_4$, obtained on heating sodium acetate with $RhCl_3{\cdot}3H_2O$ in methanol. For this and similar carboxylates the end positions are always occupied by donor ligands; with adducts of oxygen donors they are green or blue, but with π acids such as PPh_3 they are red.[22]

The adducts of the carboxylates and other species may undergo reversible redox reactions[23]:

$$Rh_2^{I,II} \underset{+e}{\overset{-e}{\rightleftharpoons}} Rh_2^{II,II} \underset{+e}{\overset{-e}{\rightleftharpoons}} Rh_2^{II,III}$$

The acetate $[Rh_2^{II,III}(O_2CMe)_4(H_2O)_2]^+$ like $Rh_2(O_2CMe)_4$ itself has a short Rh—Rh bond of order 1.5.

The *green* Rh_2^{4+} aqua ion can be obtained by reduction[24] of $[Rh(H_2O)_6]^{3+}$ by Cr^{2+} and from this ion other bridged species such as $[Rh_2(\mu\text{-}SO_4)_4]^{4-}$ and $[Rh_2(\mu\text{-}CO_3)_4]^{4-}$ can be synthesized.

The dimethylglyoximate[25] $Rh_2(dmgH)_4(PPh_3)_2{\cdot}(H_2O){\cdot}C_3H_7OH$ and the porphyrin complexes $Rh_2(porph)_2$,[26a] have unsupported Rh—Rh bonds. The latter can react with O_2 to give superoxo and μ-peroxo Rh^{III} complexes. Porphyrin dimers have been converted to hydrides, for example, RhH(oep), and formyls, and they slowly catalyze the reaction $H_2 + CO \rightarrow HCHO + MeOH$ (Chapter 28).

Metal–metal bonded *isocyanides*[26b] may be obtained by the reaction

$$Rh^I(CNR)_4^+ + Rh^{III}X_2(CNR)_4 \rightleftharpoons Rh^{II}X_2(CNR)_8^{2+}$$

Using 1,3,diisocyanopropane(L), a linear chain complex $Rh_4L_8^{6+}$ is obtained.[26b]

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[21] C. D. Garner *et al., Inorg. Chem.*, 1984, **23**, 1500; I. Bernal *et al., Inorg. Chem.*, 1986, **25**, 260; G. Wilkinson *et al., Polyhedron*, 1985, **4**, 1103; K. M. Kadish *et al., Inorg. Chem.*, 1987, **26**, 830. P. Piraino *et al., Inorg. Chem.*, 1987, **26**, 2705.

[22] See, for example, R. S. Drago *et al., Inorg. Chem.*, 1986, **25**, 2989; 1985, **24**, 4268; J. L. Bear *et al.*, 1986, **25**, 3218; R. J. H. Clark *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 1775; P. Piraino *et al., Inorg. Chem.*, 1987, **26**, 91.

[23] J. L. Bear *et al., Inorg. Chem.*, 1987, **26**, 2927; J. W. Herbert and D. H. Macartney, *J. Chem. Soc. Dalton Trans.*, **1986**, 1931.

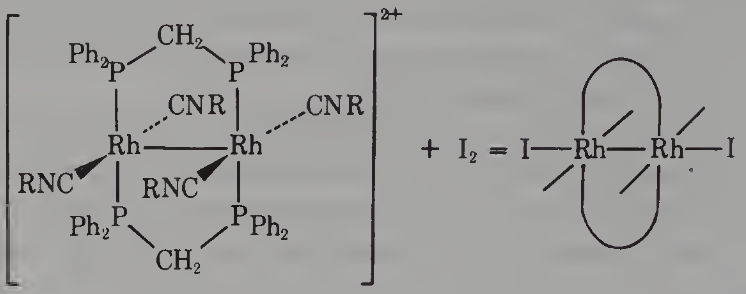
[24] A. G. Sykes *et al., Inorg. Chem.*, 1986, **25**, 339.

[25] T. Ramasami and J. H. Espenson, *Inorg. Chem.*, 1980, **19**, 1846.

[26a] K. M. Kadish *et al., Organometallics*, 1987, **6**, 706; J. Halpern *et al., J. Am. Chem. Soc.*, 1985, **107**, 4333; B. B. Wayland *et al., Inorg. Chem.*, 1986, **25**, 4039; *Organometallics*, 1987, **6**, 204; *J. Chem. Soc. Chem. Commun.*, **1986**, 900.

[26b] V. Miskowski and H. B. Gray, *Inorg. Chem.*, 1987, **26**, 1108.

With diphosphines that can bridge two metal atoms, rhodium(II) complexes have been obtained by oxidation of the corresponding rhodium(I) complexes, eq. (19-G-4).



(19-G-4)

Except for the porphyrin complex $Ir_2^{II}(oep)_2$,[27a] which is similar in its reactions to its rhodium analogue, only one Ir_2^{II} complex with four bridging ligands has so far been made,[27b] viz., $Ir_2(tolNCHNtol)_4$. Others have phosphine or other π-bonding ligands present. Oxidation of $Ir_2^{I}(OMe)_2(COD)_2$ with iodine gives $Ir_2^{II}(\mu\text{-}I)_2I_2(COD)_2$,[28a] while similar oxidation of a chelating diisocyanide complex (L) gives $[Ir_2^{II}L_4I_2]^{2+}$.[28b] Bridged pyrazoyl complexes, for example, $(CO)_2(I)Ir(\mu\text{-}(py)_2)_2Ir(CH_2I)(CO)_2$ have also been made[29a] and some alkyl cations $Ir^{II}R(CO)(PR_3)_3^+$.[29b]

19-G-5. Complexes of Rhodium(IV) and Iridium(IV), d^5

Rhodium. Oxidation of Rh^{III} sulfate solutions with O_3 or with sodium bismuthate gives red solutions that may contain Rh^{IV} sulfate complexes. Higher states, even V and VI, have been postulated in reactions of Rh^{III} with hypobromite, but these are not established—a possibility is $[RhO_3OH]^{2-}$.[30a]

The only well-defined species are the halides RhF_6^{2-} and $RhCl_6^{2-}$. The yellow, readily hydrolyzed salts of the former are obtained when $RhCl_3$ and an alkali chloride are treated with F_2 or BrF_3. The magnetic moments of ~1.8 BM are consistent with a t_{2g}^5 configuration.

The dark green Cs_2RhCl_6 is made by oxidation of ice-cold solutions of $RhCl_6^{3-}$ by Cl_2 in the presence of CsCl. It is isomorphous with Cs_2PtCl_6. The salt decomposes in water.

There are also unusual organometallic compounds such as $(Me_5C_5)MeRh(\mu\text{-}$

[27a] J. P. Collman and K. Kim, *J. Am. Chem. Soc.*, 1986, **108,** 7847; K. J. Del Rossi and B. B. Wayland, *J. Chem. Soc. Chem. Commun.*, **1986,** 1653.

[27b] F. A. Cotton and R. Poli, *Polyhedron*, 1987, **6,** 1625; *Organometallics*, 1987, **6,** 1743.

[28a] F. A. Cotton *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 8284; L. A. Oro *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 444.

[28b] H. B. Gray *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 7925.

[29a] D. G. Harrison and S. R. Stobart, *J. Chem. Soc. Chem. Commun.*, **1986,** 285.

[29b] S. Zecchin *et al.*, *J. Organomet. Chem.*, 1985, **294,** 379.

[30a] S. Sarangiapari and J. E. Early, *J. Inorg. Nucl. Chem.*, 1981, **43,** 2991.

$CH_2)_2RhMe(Me_5C_5)$ that have cis and trans isomers[30b] and some labile Schiff base species.[30c]

Iridium. By contrast, Ir^{IV} is comparatively stable. Crystalline ions IrX_6^{2-} (X = F, Cl, and Br), as well as a variety of aquated complex ions such as $[IrCl_3(H_2O)_3]^+$, $[IrCl_5(H_2O)]^-$, and $[IrCl_4(H_2O)_2]$ have been characterized. Some highly colored, probably hydroxo aqua species have been detected in solution.[16b] The *N*- and *O*-centered triangular species (Sections 10-18 and 12-9) can have Ir in fractional oxidation states such $3\frac{1}{3}$ or III, III, IV.

Hexachloroiridates(*IV*) can be made by chlorinating a mixture of iridium powder and an alkali metal chloride, or, in solution, by adding the alkali metal chloride to a suspension of hydrous IrO_2 in aqueous HCl. The black crystalline sodium salt Na_2IrCl_6, which is very soluble in water, is the usual starting material for the preparation of other Ir^{IV} complexes.

Action of aqua regia on the ammonium salt gives "chloroiridic acid," which is soluble in ether and hydroxylated solvents and is probably $(H_3O)_2IrCl_6{\cdot}4H_2O$.

In basic solution the dark red-brown $IrCl_6^{2-}$ is rather unstable, undergoing spontaneous reduction within minutes to pale yellow-green $IrCl_6^{3-}$:

$$2IrCl_6^{2-} + 2OH^- \rightleftharpoons 2IrCl_6^{3-} + \tfrac{1}{2}O_2 + H_2O$$

From known potentials the *acid* reaction can be written:

$$2IrCl_6^{2-} + H_2O = 2IrCl_6^{3-} + \tfrac{1}{2}O_2 + 2H^+$$

$$K = 7 \times 10^{-8}\ \text{atm}^{1/2}\ \text{mol}^2\ \text{l}^{-2}\ (25°\text{C})$$

Thus in strong acid, say 12 *M* HCl, $IrCl_6^{3-}$ is partially oxidized to $IrCl_6^{2-}$ in the cold and completely on heating, whereas in strong base ($\text{pH} > 11$) $IrCl_6^{2-}$ is rapidly and quantitatively reduced to $IrCl_6^{3-}$.

The ion $IrCl_6^{2-}$ is readily and quantitatively reduced to $IrCl_6^{3-}$ by KI or sodium oxalate and photochemically[31] (254 nm) to $[IrCl_5(H_2O)]^{2-}$. In neutral solution, $IrCl_6^{2-}$ undergoes slow spontaneous reduction. Salts of $IrCl_6^{2-}$ have often been studied as convenient one-electron reducing agents for both organic and inorganic substrates.

Interaction of $IrBr_6^{2-}$ and N_2O_5 gives the ion $[Ir(NO_3)_6]^{2-}$ while 100% HNO_3 gives the purple ion $[Ir_3(\mu\text{-}O)(NO_3)_9]^+$.[32] There are some phosphine complexes, for example, $IrCl_4(PMe_2Ph)_2$ that are soluble in organic solvents[33] and the hydride $Ir(H)_2(Cl)_2(P\textit{i}\text{-}Pr_3)_2$ is unusual for a hydride in being paramagnetic.[34]

Octahedral Ir^{IV}, t_{2g}^5, has one unpaired electron.[35] For pure $IrCl_6^{2-}$ salts the

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[30b] P. M. Maitlis *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984,** 1215.

[30c] M. E. Vol'pin *et al.*, *J. Organomet. Chem.*, 1985, **279,** 263.

[31] S. Fukuzumi and J. K. Kochi, *Inorg. Chem.*, 1980, **19,** 3022.

[32] N. Logan *et al.*, *J. Chem. Soc. Dalton Trans.*, **1980,** 2382.

[33] W. Levason *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987,** 1901.

[34] P. Mura, *J. Am. Chem. Soc.*, 1986, **108,** 351.

[35] A. Goursot *et al.*, *Inorg. Chem.*, 1984, **23,** 305.

μ_{eff} values are low (1.6–1.7 BM) owing to antiferromagnetic interactions; on dilution with isomorphous $\mathrm{PtCl_6^{2-}}$ salts, normal values are found.

19-G-6. Complexes of Rhodium(V) and Iridium(V), d^4

Salts of the hexafluoro ions $\mathrm{MF_6^-}$ of $\mathrm{Rh^V}$ and $\mathrm{Ir^V}$ are made by reactions such as

$$\mathrm{RhF_5 + CsF \xrightarrow{IF_5} CsRhF_6}$$

$$\mathrm{IrBr_3 + CsCl \xrightarrow{BrF_3} CsIrF_6}$$

The red-brown Rh salt is isomorphous with $\mathrm{CsPtF_6}$. The iridium salts are pink, with magnetic moments ~1.25 BM at 273°C; they are temperature dependent, suggesting strong spin-orbit coupling and possibly antiferromagnetic interaction. They dissolve in water, evolving $\mathrm{O_2}$ and being reduced to $\mathrm{IrF_6^{2-}}$. Oxidation of $\mathrm{[Ir(H_2O)_6]^{3+}}$ gives colored complexes, not yet isolated, in aqueous solution.[16b]

The most unusual chemistry of the V state is in polyhydrides and organo compounds.

There are *hydrides* of the type $\mathrm{IrH_5(PR_3)_2}$[36] made by reduction of the chloride complexes with $\mathrm{LiAlH_4}$ followed by hydrolysis, and compounds such as $^*\mathrm{CpIrH_4}$ and $^*\mathrm{CpIrH_3(PMe_3)^+}$.[37]

The organometallic compounds are again mostly derivatives of $(\eta^5\text{-}\mathrm{Me_5C_5})$[38] but $\mathrm{Ir^V}$ can also be present in metalloborane clusters.[39]

Examples of syntheses are:

$$(^*\mathrm{CpIr})_2\mathrm{Cl_4} \xrightarrow{\mathrm{Al_2Me_6}} [^*\mathrm{CpIrMe_3}]_2\mathrm{AlMe} \xrightarrow{\mathrm{O_2}} {}^*\mathrm{CpIrMe_4} + [^*\mathrm{CpIrMe_3OAlO}]_n$$

$$(^*\mathrm{CpRh})_2\mathrm{Cl_4} \underset{\mathrm{HCl}}{\overset{\mathrm{Et_3SiH}}{\rightleftharpoons}} {}^*\mathrm{CpRh(H)_2(SiEt_3)_2} \xrightarrow{\mathrm{HBF_4}} [(^*\mathrm{CpRhH})_4]^{2+}$$

19-G-7. Carbonyls and Organometallic Compounds[40]

There is an extensive chemistry of carbonyls, some of which has been noted previously. However, there is a wide range of cluster carbonyls and anionic species that are discussed in Chapters 22 and 23.

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[36] R. Bau *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 7212.

[37] R. G. Bergman *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 3502, 3508.

[38] P. M. Maitlis *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 5458; *J. Chem. Soc. Dalton Trans.*, **1987**, 1963; *J. Organomet. Chem.*, 1986, **229**, 383.

[39] N. N. Greenwood *et al.*, *J. Chem. Soc. Chem. Commun.*, **1982**, 465.

[40] R. P. Hughes, *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Vol. 5, Chapter 35 (Rh); G. J. Leigh and R. L. Richards, *Comprehensive Organometallic Chemistry*, Chapter 36 (Ir), Pergamon Press, Oxford, 1982; R. S. Dickson, *Organometallic Chemistry of Rhodium and Iridium*, Academic Press, New York, 1983; R. S. Dickson, *Hydrogen and Carbon Compounds of Rhodium and Iridium*, D. Reidel, Amsterdam, 1985.

The hydride $HRh(CO)_4$ is very much less stable than $HCo(CO)_4$ and has been made only under ~1400 atm pressure since it readily loses hydrogen to give clusters.[41]

Typical clusters are $M_6(CO)_{16}$[42] but there is also an unusual phosphine cluster $Rh_{55}Cl_{20}(Pt\text{-}Bu_3)_{12}$,[43] which is made by interaction of $(Bu_3P)_2RhH_2Cl$ and $(Bu_3P)_2Rh(CO)Cl$ with diborane in benzene at 50 to 60°C.

Many studies have been made on the rhodium carbonyl cluster system because it appears to be the "dead end" for active species in direct synthesis of glycol from CO and H_2 at high temperature and pressure. The anion $[Rh(CO)_4]^-$ in the presence of R_3NH^+ salts gives the equilibrium

$$R_3NH^+Rh(CO)_4^- \underset{+CO}{\overset{-CO}{\rightleftharpoons}} HRh(CO)_3NR_3$$

which catalyzes glycol formation.[44]

There is a particularly extensive chemistry of η^5-C_5H_5 compounds of the type $CpRhL_n$.[45]

A formally zerovalent dimer [cf. $Co_2(CO)_8$], $Rh_2[P(OMe)_3]_8$, has been shown to be $Rh^I(OP(OMe)_2[P(OMe)_3]_4$.[46]

19-H. PALLADIUM AND PLATINUM[1]: GROUP VIII(10)

19-H-1. General Remarks; Stereochemistry

The principal oxidation states of Pd and Pt are II and IV, but there is extensive chemistry in the I and III states where M—M bonds are involved, and in the 0 state, where PR_3, CO, or other π-acid ligands are present and Pt_3 and Pt_4 clusters are also found. Formal negative oxidation states occur in certain carbonyl anions of general formula $[Pt_3(CO)_3(\mu\text{-}CO)_3]_n^{2-}$. The higher states V and VI occur only in a few fluoro compounds (Section 19-E-5).

There are also compounds with mixed oxidation states, usually II and IV but some with III.

The II State, d^8. The Pd^{2+} ion occurs in PdF_2 (Section 19-E-5) and is paramagnetic. In aqueous solution, however, the $[Pd(H_2O)_4]^{2+}$ ion is dia-

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[41] J. L. Vidal and W. E. Walker, *Inorg. Chem.*, 1981, **20**, 249.

[42] L. Garlaschelli *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 6664.

[43] G. Schmidt *et al.*, *Inorg. Chim. Acta*, 1984, **85**, 97.

[44] K. Wada *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 227.

[45] H. Werner, *J. Organomet. Chem.*, 1985, **281**, 317.

[46] S. I. Klein and J. F. Nixon, *J. Organomet. Chem.*, 1986, **302**, 87.

[1] F. R. Hartley, *The Chemistry of Platinum and Palladium*, Applied Science Publishers London, 1973; M. J. Russell, C. F. J. Barnard and A. T. Hutton (Pd) and D. M. Roundhill (Pt), *Comprehensive Coordination Chemistry*, Pergamon Press, Oxford, 1987, Vol. 5, Chapters 51 and 52; R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, New York, 1985; A. L. Balch, *Comments Inorg. Chem.*, 1984, **3**, 51 (odd oxidation states); R. J. Cross, *Chem. Soc. Rev.*, 1985, **14**, 197 (reactions of Square Pt^{II} complexes).

magnetic and is presumably square. In general, however, Pd^{II} and Pt^{II} complexes are square or five-coordinate and are diamagnetic. They can be of all possible types, for example, ML_4^{2+}, ML_3X^+, *cis-* and *trans*-ML_2X_2, MLX_3^-, and MX_4^-. Similar types with chelate acido or other chelate ligands are common.

Palladium and platinum(II) generally show low affinity for F^- and O ligands and a preference for halogens, and ligands that can π bond such as R_3P, R_2S, CN^-, NO_2^-, alkenes, and alkynes.

The formation of cationic species even with non-π-bonding ligands and anionic species with halide ions contrasts with the chemistry of the isoelectronic Rh^I and Ir^I where most of the complexes involve π bonding. The difference is presumably a reflection of the higher charge. Furthermore, although Pd^{II} and Pt^{II} species add neutral molecules to give five- and six-coordinate species, they do so with much less ease; also the oxidative-addition reactions characteristic of square d^8 complexes tend to be reversible except with strong oxidants, presumably owing to the greater promotional energy for M^{II}—M^{IV} than for M^I—M^{III}.

Palladium(II) complexes are somewhat less stable in both the thermodynamic and the kinetic sense than their Pt^{II} analogues, but otherwise the complexes are usually similar. The kinetic inertness of the Pt^{II} (and also Pt^{IV})

TABLE 19-H-1
Oxidation States and Stereochemistry of Palladium and Platinum

Oxidation state	Coordination number	Geometry	Examples
Pd^0, Pt^0, d^{10}	3	Planar	$Pd(PPh_3)_3$, $Pt(SO_2)(PCy_3)_2$, $Pt[Sn(NR_2)_2]_3$[1]
	4	Distorted	$Pt(CO)(PPh_3)_3$
	4	Tetrahedral	$Pt(Ph_2PCH_2CH_2PPh_2)_2$, $Pd(PF_3)_4$
Pd^I, d^9	4	Square	$[Pd(N_4macrocycle)]^+$
Pd^{II}, Pt^{II}, d^8	4[a,b]	Planar	$[PdCl_2]_n$, $[Pd(NH_3)_4]Cl_2$, PdO, PtO, $PtCl_4^{2-}$, $PtHBr(PEt_3)_2$, $[Pd(CN)_4]^{2-}$, PtS, $[Pd\,py_2Cl]_2$, PdS, $Pt(PEt_3)_2(C_6F_3)_2$
	5	*tbp*	$[Pd(diars)_2Cl]^+$, $[Pt(SnCl_3)_5]^{3-}$,
		sp	$[PtI(PMe_3)_4]^+$
	6	Octahedral	PdF_2(rutile type), $[Pt(NO)Cl_5]^{2-}$, $Pd(diars)_2I_2$, $Pd(dmgH)_2$[c]
Pd^{III}, Pt^{III}, d^7	4	Square	$[Pt(C_6Cl_5)_4]^-$
		Octahedral	$[Pt_2(\mu\text{-}SO_4)_4(H_2O)_2]^{2-}$
Pd^{IV}, Pt^{IV}, d^6	6[b]	Octahedral	$[Pt(en)_2Cl_2]^{2+}$, $PdCl_6^{2-}$, $[Pt(NH_3)_6]^{4+}$, $[Me_3PtCl]_4$, *fac*-$Me_3PtIbipy$[2]
Pt^V, d^5	6	Octahedral	$[PtF_5]_4$, PtF_6^-
Pt^{VI}, d^4	6	Octahedral	PtF_6

[a] Most common states for Pd.

[b] Most common states for Pt.

[c] Has planar set of N atoms with weak Pd—Pd bonds completing a distorted octahedron.

[1] M. F. Lappert *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 863.

[2] P. K. Byers *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 1722.

complexes has allowed them to play an important role in the development of coordination chemistry such as studies of geometrical isomerism and reaction mechanisms.

The IV State, d^6. Although Pd^{IV} compounds exist, they are generally less stable than those of Pt^{IV}. The coordination number is invariably 6. The substitution reactions of Pt^{IV} complexes are greatly accelerated by the presence of Pt^{II} species. Solutions also readily undergo photochemical reactions in light.

The oxidation states and stereochemistries are summarized in Table 19-H-1.

19-H-2. Complexes of Palladium(II) and Platinum(II), d^8

Aqua Ions and Simple Cations. The $[Pd(H_2O)_4]^{2+}$ ion[2] is obtained on dissolution of PdO in $HClO_4$ and in ~4 *M* $HClO_4$ the Pd/Pd^{2+} potential is 0.98 V.

The acetonitrile complex $[Pd(MeCN)_4]^{2+}$ polymerizes alkenes and alkynes.[3]

The $[Pt(H_2O)_4]^{2+}$ ion is obtained by interaction of K_2PtCl_4 and $AgClO_4$. An nmr study using ^{195}Pt shows that it reacts with various anions to give substituted species.[4] Thus OH^- gives $[Pt(OH)_4]^{2-}$ although in concentrated solution disproportionation to Pt + $[Pt(OH)_6]^{2-}$ occurs. The $[Pt(H_2O)_4]^{2+}$ ion also reacts ~10^{-6} times as rapidly in water exchange as does $[Pd(H_2O)_4]^{2+}$.[5]

Of interest, in view of the antitumor properties of *cis*-$PtCl_2(NH_3)_2$ (see next section) are the cations such as *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$. Exposure of solutions containing phosphate to air gives blue species that may be related to the platinum blues discussed later. There are also well-established amine complexes such as $[\mathrm{Mam}_4]^{2+}$ and $[\mathrm{Men}_2]^{2+}$.

Halogen and Other Anions. Salts of the ions $[MCl_4]^{2-}$ are common source materials for the preparation of other complexes in the II and the 0 oxidation states. The yellowish $[PdCl_4]^{2-}$ ion is formed when $PdCl_2$ is dissolved in aqueous HCl or when $[PdCl_6]^{2-}$ is reduced with Pd sponge. The red $[PtCl_4]^{2-}$ ion is normally made by reduction of $[PtCl_6]^{2-}$ with a stoichiometric amount of N_2H_4—HCl, oxalic acid, or other reducing agent. The sodium salt cannot be obtained pure. In water solvolysis of $[PtCl_4]^{2-}$ is extensive at 25°C but the rate is slow:

$$[PtCl_4]^{2-} + H_2O = [PtCl_3(H_2O)]^- + Cl^- \qquad K = 1.34 \times 10^{-2}\ M$$

$$[PtCl_3(H_2O)]^- + H_2O = PtCl_2(H_2O)_2 + Cl^- \qquad K = 1.1 \times 10^{-3}\ M$$

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[2] A. E. Merbach, *Helv. Chim. Acta,* 1984, **67,** 1453.

[3] A. Sen and T-W. Lai, *Organometallics,* 1982, **1,** 415.

[4] J. R. Hall *et al., Inorg. Chem.,* 1984, **23,** 3521.

[5] L. I. Elding *et al., Inorg. Chem.,* 1985, **24,** 1719.

so that a 10^{-3} *M* solution of K_2PtCl_4 at equilibrium contains only 5% of $[PtCl_4]^{2-}$ with 53% of mono- and 42% of bisaqua species.

For both metals, bromo and iodo complex anions occur, and if large cations such as Et_4N^+ are used, salts of halogen-bridged ions $[M_2X_6]^{2-}$ may be obtained. Both $[MX_4]^{2-}$ and $[M_2X_6]^{2-}$ are square, but in crystals the ions in K_2MCl_4 are stacked one above the other. However, unlike other stacks containing $[MCl_4]^{2-}$ ions discussed later, the M—M distances (Pd, 4.10 Å; Pt, 4.13 Å) are too large for any chemical bonding; similarly in the dimeric ions there is no evidence for metal–metal interaction.

The $[PdCl_4]^{2-}$ and $[Pd\ phen_2]^{2+}$ ions associate with Cl^- in solution to give five-coordinate species but the Pt analogues appear not to do so.

An important feature of chloro species of both Pd and Pt is the reaction with $SnCl_2$ and $SnCl_3^-$ (or $GeCl_3^-$), whereby $SnCl_3^-$ (or $GeCl_3^-$) complexes are obtained.[6] The nature of the species depends on the conditions but those like *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ and $[Pt(SnCl_3)_5]^{3-}$, which can be obtained in crystalline salts, are well characterized. The platinum species catalyze the homogeneous hydrogenation of alkenes. Neutral phosphine or phosphite complexes such as *trans*-$Pt(SnCl_3)_2[P(OR)_3]_2$ can be obtained also and these can be used in hydroformylation of alkenes. The ready dissociation of $SnCl_3^-$ due to its high trans effect helps leave vacant sites for coordination of small molecules.

Nitrato anions $[Pt(NO_3)_4]^{2-}$ can be obtained by treating $[Pt(H_2O)_4]^{2+}$ with KNO_3 and K_2CO_3.[7a]

The *cyano* anions $[M(CN)_4]^{2-}$ of both Pd and Pt[7b] are extremely stable with high formation constants. Other square anions are the σ alkyls and aryls, of which the perhalogenated anions such as $[Pd(C_6F_5)_4]^{2-}$ and $[Pt(C_6Cl_5)_4]^{2-}$ are most stable.[8] The neutral aryls *cis*-$Pt(C_6X_5)_2L_2$ $L = CO$ or THF also exist.

Neutral Complexes. There are many Pd and Pt complexes of the general formula $MXYL_1L_2$ where X and Y are anionic, and L_1 and L_2 are neutral donors. X and Y can be halides, oxalate, SO_4^{2-}, H, alkyl, or aryl while L can be NR_3, PR_3, CO, and so on.

The complexes are almost invariably planar but with bulky ligands some distortion can occur as with substituents ortho to the nitrogen atom in $bipy_2PdCl_2$.[9]

The square compounds show cis–trans isomerism as, for example, in *cis*- and *trans*-$PtCl_2(Me_2SO)_2$.[10]

The carbonyls *cis*-$M(CO)_2(C_6F_5)_2$ have very high CO stretches ~2186 cm^{-1}, suggesting negligible π bonding of CO.[11]

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[6] P. S. Pregosin *et al.*, *Inorg. Chem.*, 1985, **24,** 4430 and references therein; A. Albinato *et al.*, *J. Organomet. Chem.*, 1985, **295,** 239.

[7a] L. I. Elding and Å. Oskarsson, *Inorg. Chim. Acta*, 1985, **103,** 127.

[7b] G. Glieman and H. Yersin, *Struct. Bonding*, 1985, **62,** 87.

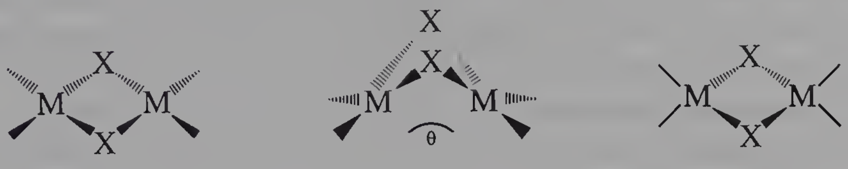
[8] R. Usón *et al.*, *Organometallics*, 1986, **5,** 1576, 1581.

[9] G. R. Newcome *et al.*, *J. Am. Chem. Soc.*, 1982, **104,** 1782.

[10] L. Cattalini *et al.*, *Inorg. Chem.*, 1985, **24,** 797.

[11] R. Usón *et al.*, *Organometallics*, 1985, **4,** 1912; see also F. Calderazzo and D. B. Dell'Amico, *Pure Appl. Chem.*, 1986, **58,** 561.

Bridged Complexes. There are three types of bridged complexes,[12] (19-H-Ia, b, and c). The structure of types (a) and (b) are commonly found when

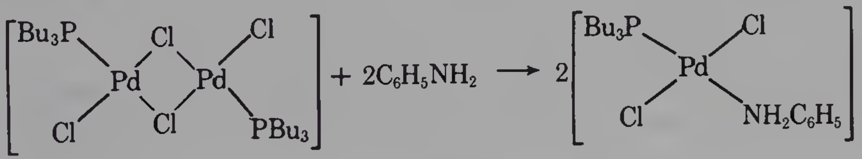


(a) Flat Square (b) Hinged Square $\theta = 120–140°$ (c) Tetrahedral

(19-H-I)

μ-X = halogen, S^{2-}, and SR, whereas type (c) is confined to PR_2 and where the M—M distance is shorter than in (a) and (b). Subtle electronic and packing effects in crystals can influence the distance while the adoption of a particular geometry is related to the π-donor capability of the *bridge* ligand. Representative examples of type (a) are $[Pt_2Br_6]^{2-}$ and of type (b) $Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4$, where $\theta = 121°$. Note that other d^8 metal complexes can adopt similar structures, for example, $Rh_2Cl_2(CO)_4$ is (a) type (Fig. 19-G-2) and $Ir_2(\mu\text{-}PPh_2)_2(CO)_2(PMe_3)_2$ is (c) type.

Bridges like SCN may form *linkage isomers*. For Pt^{II} the bridge tendencies are in the order $SnCl_3^- < RSO_2^- < Cl^- < Br^- < I^- < R_2PO^- < SR^- < PR_2^-$. Bridged species are generally subject to cleavage[13a] by donors giving mononuclear species, for example,



When the bridges are Cl^- or Br^-, the equilibria generally lie toward the mononuclear complexes. It might be supposed that such bridge-splitting reactions should give trans products, and these are probably the initial products of most cleavage reactions. However, the relative stabilities of the cis and trans isomers of L_2PdX_2 and L_2PtX_2 complexes vary greatly, depending on the identities of L and X. A major difference between square complexes of the two metals is that for $PtX_2(PR_3)_2$ complexes cis–trans isomerization normally proceeds extremely slowly unless catalyzed by excess PR_3, whereas the analogous isomerization of Pd^{II} complexes proceeds rapidly to give equilibrium mixtures. Many substitution and isomerization reactions of square complexes normally proceed by association involving distorted five-coordinate intermediates, and there is evidence for solvation, for example, of $PtCl_2(n\text{-}Bu_3P)_2$ by MeCN. The cis–trans isomerization of $PtCl_2(n\text{-}Bu_3P)_2$ and similar Pd complexes, where the isomerization is immeasurably slow in the absence

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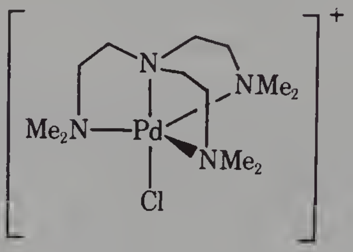
[12] D. M. P. Mingos *et al., J. Chem. Soc. Dalton Trans.*, **1984**, 2645.

[13a] See, for example, H. C. Clark *et al., Inorg. Chem.*, 1985, **24,** 1477.

of an excess of phosphine, is very fast when phosphine is present. The isomerization doubtless proceeds by pseudorotation of the five-coordinate state. In this case an ionic mechanism is unlikely, since polar solvents actually slow the reaction. Photochemical isomerizations, on the other hand, appear to proceed through tetrahedral intermediates.

Pentacoordinate Complexes.[13b] Typical examples are $PtI_2(PMe_3)_3$, R_4N^+ salts of $[Pt(SnCl_3)_5]^{3-}$, and tripod species like (19-H-II). Substitution and isomerization reactions of square complexes normally proceed via five-coordinate intermediates.



(19-H-II)

The "vacant" positions on square species may of course be occupied by weakly bound solvent molecules in solution. Also interaction between the metal and suitably placed atoms on the ligand may lead to blocking of one or both positions. Thus in the complex ion $[Pt(Et_4dien)Cl]^+$ the ethyl groups block the axial positions so that in substitution reactions the ion behaves kinetically as an octahedral rather than a square complex.

Tertiary Phosphine Complexes of Palladium(II) and Platinum(II). Some of these have just been mentioned but they are of such importance in the chemistry not only of the II state but also of the 0 and I states that further description is necessary. They are among the most intensively studied complexes both chemically and spectroscopically, especially for the more stable Pt ones.

Hydrides. These may be of the types $MXH(PR_3)_2$ and $MH_2(PR_3)_2$ with both cis and trans isomers; diphosphines necessarily give only the cis species. The X can be a halide, alkyl, aryl, and so on. The stable dihydrides[14] are usually trans but for PMe_3 and PEt_3 the isomers are in equilibrium with the ratio depending on the solvent. Pure *trans*-$PtH_2(PEt_3)_2$ is obtained on cooling hexane solutions. Addition of excess PEt_3 gives $H_2Pt(PEt_3)_3$, which is *tbp* with axial hydrogen atoms.

Phosphines, phosphites, and arsines give similar complexes. They are obtained from the dihalides (the cis isomer is usually most reactive) by the action of hydride transfer agents such as KOH in ethanol, 90% N_2H_4, Na naphthal-

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[13b] A. Viragliano *et al., Organometallics,* 1987, **6,** 517.

[14] C. E. Strouse *et al., Inorg. Chem.,* 1985, **24,** 3578.

enide under H_2, etc., for example[15a]:

$$PtCl_2[P(OMe)_3]_2 \xrightarrow[MeCN]{NaBH_4} PtHCl[P(OMe)_3]_2$$

Examples of cationic species are $[PtCl(PR_3)(P\frown P)]^+$ and $[Pt(PR_3)_2(P\frown P)]^{2+}$ where $P\frown P$ is a chelating phosphine.[15b]

The hydride compounds are usually colorless crystalline solids soluble in organic solvents. They can undergo oxidative-addition reactions but the octahedral Pt^{IV} species usually readily lose the added molecules.

The nmr and ir spectra have been studied in detail because of information that can be obtained concerning trans effects. Thus there is a dependence of Pt—H stretching frequencies, ^1H chemical shifts, and ^{195}Pt—H and ^{31}P—H coupling constants depending on the ligand trans to H. For example the Pt—H stretches and σ values increase for the trans ligand in the order $Cl < Br < I < NCS < SnCl_3 < CN$. Studies on *trans*-$PtHR(PR'_3)_2$ where R = Me or Ph have also allowed correlations of Taft parameters for substituents on phosphorus against Pt—H stretching frequencies, ^{195}Pt—H J, and ^1H δ values.[16]

Cationic hydrido complexes can be made by reactions such as

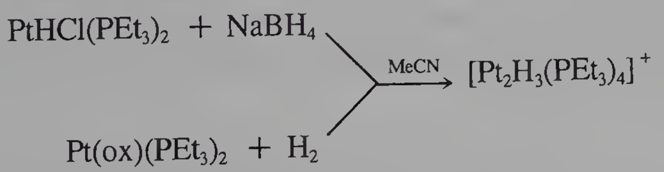
$$trans\text{-}PtHCl(AsPh_3)_2 + NaClO_4 + CO \longrightarrow [PtH(CO)(AsPh_3)_2]ClO_4 + NaCl$$

Binuclear hydrides with a $[Pt_2H_3(PR_3)_2]^+$ unit comprise a general category of 30-electron dimers with H and PR_3 ligands and similar complexes are known[17] for Ni, Fe, and Re, for example, $[Fe_2(\mu\text{-}H)_3(triphos)_2]^+$. The Pt species have both terminal and μ-H that undergo exchange.

Although usually symmetrical, that is, $[L_2HPt(\mu\text{-}H)PtHL_2]^+$ there are unsymmetrical ones that have both square and *tbp* Pt^{II}, for example, [diphos $Pt(\mu\text{-}H)_2PtH$ diphos$]^+$. They are commonly made by the general reaction

$$PtH_2L_2 + PtHXL_2 \longrightarrow [Pt_2H_3L_4]X$$

but also by reactions such as



$$PtHCl(PEt_3)_2 + NaBH_4 \text{ or } Pt(ox)(PEt_3)_2 + H_2 \xrightarrow{MeCN} [Pt_2H_3(PEt_3)_4]^+$$

Alkyls and Aryls. $MXR(PR'_3)_2$ and $MR_2(PR'_3)_2$ have also been intensively studied in the past because of interest in decomposition pathways such as reductive-elimination and β-hydride transfers (see Chapter 25).

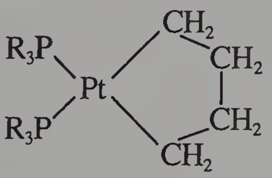
[15a] W. R. Meyer and L. M. Venanzi, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 529.

[15b] G. K. Anderson and G. J. Lumetta, *Inorg. Chem.*, 1987, **26**, 1518.

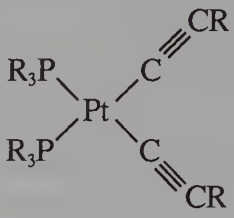
[16] D. P. Arnold and M. A. Bennett, *Inorg. Chem.*, 1984, **23**, 2110, 2117.

[17] For examples, see L. M. Venanzi *et al.*, *Inorg. Chem.*, 1983, **22**, 1031; C. B. Knobler *et al.*, *Inorg. Chem.*, 1983, **22**, 2324; G. Minghetti *et al.*, *Inorg. Chem.*, 1983, **22**, 2332.

There has, for similar reasons, also been much study on metallacycles such as (19-H-III).



(19-H-III)



(19-H-IV)

The Pd alkyls are less stable than those of Pt.[18] There are also acetylides such as (19-H-IV).[19]

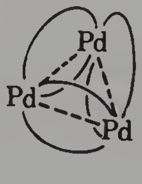
The important A frame and other bridged phosphine species are discussed later in connection with M^I chemistry.

Oxygen and Sulfur Ligands. Although Pd^{II} and Pt^{II} are generally viewed as having low affinity for oxygen donors, in the latter case there are some notable exceptions. There are various μ-OH dimers and trimers that have outstanding stability. There are also sulfoxide complexes in which, depending on the particular sulfoxide used, there may be *S*-bonded, *O*-bonded, or a mixture of *S*- and *O*-bonded ligands.

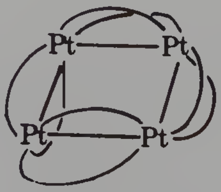
Palladium(II) acetate, one of the most important palladium compounds, is used as a source for other Pd compounds and has been greatly studied in a wide variety of Pd catalyzed reactions of organic compounds. It is readily obtained by dissolving Pd in acetic acid containing some concentrated HNO_3 and forms brown crystals. It acts somewhat like $Hg(O_2CMe)_2$ and $Pb(O_2CMe)_4$ in attacking aromatic hydrocarbons electrophilically in acidic media although in acetic acid it will attack the CH_3 group of toluene.

The acetate readily undergoes cleavage with donors to give yellow trans compounds, $Pd(O_2CMe)_2L_2$.

In the crystal the acetate is trimeric (19-H-V) but dissociates in hot benzene.[20a] Platinum(II) acetate, which is much more difficult to make, has a quite different structure with Pt—Pt single bonds (19-H-VI).[20b] The only compound with a tetra bridged structure is Pd_2 (μ-form)$_4$, where form is *N,N,*di-*p*-tolylformamidate.[21]



(19-H-V)



(19-H-VI)

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[18] See for example, G. Wilkinson *et al., Polyhedron,* 1984, **3,** 436.

[19] A. Furlani *et al., J. Chem. Soc. Dalton Trans.,* **1984,** 2197.

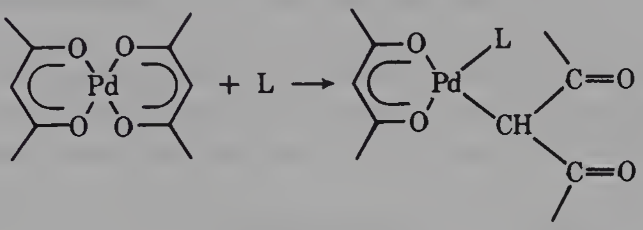
[20a] F. A. Cotton and S. Han, *Rev. Chim. Minerale,* 1983, **20,** 496.

[20b] M. A. A. de Carrondo and A. C. Skapski, *Acta Crystallogr.,* 1978, **B34,** 1857.

[21] F. A. Cotton *et al., Inorg. Chem.,* 1987, **26,** 1472.

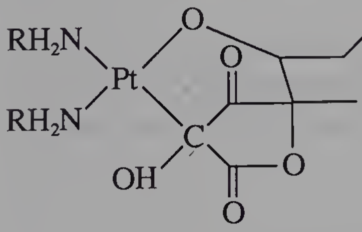
Other carboxylates of Pd are similar, but the 6-methyl-2-oxopyridinate made from the acetate has the common tetra-bridged structure found in many divalent carboxylate and related species but without a Pd—Pd bond. The difference from the acetate is probably due to steric factors.[22]

β-*Diketonates* form conventional square compounds with O,O′ binding[23] but *C*-bonded complexes can be obtained as in the reaction:

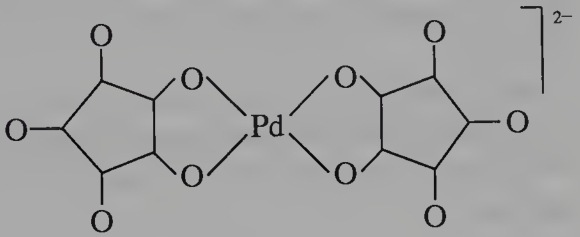


L = PR_3, py, Et_2HN, and so on

The hexafluoroacetylacetonates[24] are strong Lewis acids and give five-coordinate adducts usually of a distorted structure. Other *C*-bonded Pt complexes include the ascorbate (19-H-VII).[25] There is also a croconate (19-H-VIII).



(19-H-VII)



(19-H-VIII)

Dithiocarbamates and related sulfur ligands form stable complexes with both Pd and Pt. The dithioacetates $M_2(\mu\text{-}S_2CMe)_4$ have the tetra bridged dimer structure (cited previously)[26a] and the dimers are stacked in columns.

The 2-aminoethane thiolate[26b] has an unusual hexanuclear structure, $[Pt_6(SCH_2CH_2NH_2)_8]^{4+}$ with the six Pt atoms joined by doubly bridging S into three fused rings, a central Pt_4S_4 eight membered ring, and two outer Pt_3S_3 six membered rings.

Finally, the sulfide anion $[Pd_2(\mu\text{-}S_7)_4]^{2-}$ has been characterized.[27]

Ammine, Nucleotide, and Related Compounds. Although the simple ammonia complexes *cis*- and *trans*-$PtCl_2(NH_3)_2$ are among the oldest known platinum(II) complexes, the discovery, *ca.* 1968, by B. Rosenberg that the

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[22] W. Clegg *et al., Inorg. Chem.*, 1982, **21**, 1897.

[23] See, for example, A. R. Siedle *et al., Inorg. Chem.*, 1983, **22**, 2281; S. Okeya *et al., Bull. Chem. Soc. Jpn.*, 1984, **57**, 375.

[24] A. R. Siedle and L. H. Pignolet, *Inorg. Chem.*, 1982, **21**, 3090.

[25] L. S. Hollis *et al., J. Am. Chem. Soc.*, 1985, **107**, 275.

[26a] C. Bellito *et al., Inorg. Chem.*, 1983, **22**, 444; *J. Chem. Soc. Dalton Trans.*, **1987**, 35.

[26b] D. Gibson and S. J. Lippard, *Inorg. Chem.*, 1986, **25**, 219.

[27] A. Müller *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 453.

cis isomer has anti-tumor activity stimulated the synthesis and screening of over 2000 different types of complexes with different amines and anionic ligands.[28a]

There has also been intense study of the way in which the platinum attacks DNA; it appears that coordination of the N(7) atoms of two guanines makes these rings tilt from their normal stacked positions leading to disruption of the helix and interference with replication.[28b] The trans-isomer also reacts but in a different way that can be repaired.

One of the problems of *cis*-$PtCl_2(NH_3)_2$ is toxicity, which can be overcome by substituting the chlorides by cyclobutanedicarboxylate. The toxicity probably arises in part by the quite rapid aquation in aqueous solution

$$cis\text{-}PtCl_2(NH_3)_2 \overset{H_2O}{\rightleftharpoons} cis\text{-}[Pt(H_2O)Cl(NH_3)_2]^+ \rightleftharpoons \text{and so on}$$

to which the carboxylate is not susceptible.

There are also $(NH_3)_2Pt$ complexes with adenines, cytosines, and so on, as models for DNA interaction[29] and similar complexes of Pd^{II}.[30]

Phosphate Complexes. These have also been studied in part because of their relevance in biological systems[31] and the structure of $Pt_2(NH_3)_4(\mu\text{-}P_2O_7)$ is known.

Phosphite bridged species are noted later in connection with Pt^{III} chemistry, but an important Pt^{II} species is $K_4[Pt_2^{II}(POP)_4]\cdot 2H_2O$ where POP is $P_2O_5H_2^{2-}$[32]; this is made by interaction of solutions of K_2PtCl_4 with H_3PO_3 on heating to dryness.

19-H-3. Complexes of Palladium(IV) and Platinum(IV), d^6

Palladium. Apart from $Pd(NO_3)_2(OH)_2$ formed on dissolution of Pd in concentrated nitric acid, the complexes are mainly the octahedral halide anions. The fluoro complexes of Ni, Pd, and Pt are all very similar and are rapidly hydrolyzed by water. The chloro and bromo ions are stable to hydrolysis but are decomposed by hot water to give the Pd^{II} complex and hal-

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[28a] J. C. Dabrowiak *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 5643; N. P. Johnson *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 6376; S. K. Millar and L. G. Marzilli, *Inorg. Chem.*, 1985, **24,** 2421; S. J. Lippard *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 4079; C. F. J. Barnard *et al.*, *Chem. Br.*, **1986,** 1001; M. Kraus *et al.*, *Inorg. Chem.*, 1986, **25,** 684. A. Pasini and F. Zunino, *Angew Chem. Int. Ed. Engl.*, 1987, **26,** 615.

[28b] See S. J. Lippard *et al.*, *Inorg. Chem.*, 1987, **26,** 1524; J. Reedijk *et al.*, *Inorg. Chem.*, 1987, **26,** 1536.

[29] B. Lippert *et al.*, *Inorg. Chem.*, 1985, **24,** 4001.

[30] L. D. Pettit and M. Bezar, *Coord. Chem. Rev.*, 1985, **61,** 97.

[31] R. N. Bose *et al.*, *Inorg. Chem.*, 1985, **24,** 3989.

[32] D. M. Roundhill *et al.*, *J. Am. Chem. Soc.*, 1987, **109,** 6076; A. Vlček and H. B. Gray, *Inorg. Chem.*, 1987, **26,** 1997.

ogen. The red $PdCl_6^{2-}$ ion is formed when Pd is dissolved in aqua regia or when $PdCl_4^{2-}$ solutions are treated with chlorine.

Oxidation of K_2PdCl_4 by persulfate in the presence of KCN gives the yellow salt $K_2[Pd(CN)_6]$.

Pyridine and bipyridine complexes such as $[PdpyX_5]^-$ and *cis*-[bipyPdCl$_4$] and similar complexes with PR_3 and AsR_3 donors can be obtained by halogen oxidation of the Pd^{II} complex.[33] Other stable complexes include Pd am$_2$(NO$_2$)$_2$Cl$_2$, $[Pd(S_2CNR_2)_3]^+$, and $Pd(S_2CNR_2)_2X_2$.

Platinum. In marked contrast to Pd^{IV}, Pt^{IV} forms many thermally stable and kinetically inert complexes that are invariably octahedral. Platinum(IV) has such a pronounced tendency to be six-coordinate that in some of its compounds quite unusual structures are adopted (see later). An apparent exception to the rule is $(\eta^5\text{-}C_5H_5)Pt(CH_3)_3$, but as with other $(\eta^5\text{-}C_5H_5)$ complexes, the ring can be considered as occupying three positions of an octahedron.

Apart from $PtCl_4$ and other halides (Section 19-E-5) the only simple compound[34] is $Pt(SO_3F)_4$ made by interaction of Pt with $S_2O_6F_2$—HSO_3F at 120°C as orange crystals. Since spectra show both uni- and bidentate (μ) SO_3F groups, a polymeric structure is most likely. The anion $[Pt(SO_3F)_6]^{2-}$ can also be obtained.

The most important Pt^{IV} compounds are salts of the red *hexachloroplatinate* ion $PtCl_6^{2-}$. The "acid," commonly referred to as chloroplatinic acid, has the composition $H_2[PtCl_6]\cdot nH_2O$ (n = 2, 4, and 6) and contains H_3O^+, $H_5O_2^+$, and $H_7O_3^+$ ions. On thermal decomposition it eventually gives mainly the metal, but Pt_6Cl_{12} is one of the intermediates. The acid or its Na or K salts are the normal starting materials for the preparation of many Pt compounds. The ion is formed on dissolving Pt in aqua regia or HCl saturated with Cl_2. In aqueous alcohol solution the ion is reduced to $PtCl_4^{2-}$ and eventually to Pt in the presence of visible light.[35a]

Other simple anionic species are the azide[35b] $[Pt(N_3)_6]^{2-}$ and the sulfide[36] $[Pt(S_5)_3]^{2-}$ that has PtS_5 rings; the anion can be resolved into *d* and *l* isomers, and is one of the few completely inorganic compounds that can be resolved. The anion $[PtMe_6]^{2-}$ exists but only in solution.

Amine Ligands. The ammonia complexes span the entire range from [Pt am$_6$]X$_4$, including all intermediates such as [Pt am$_4$X$_2$]X$_2$ and M^I[Pt am X$_5$], to $M_2^I[PtX_6]$. Some are notable as examples of the classical evidence that led Werner to assign the coordination number 6 to Pt^{IV}. The amine ligands include ammonia, ethylenediamine, hydrazine, and hydroxylamine and the acido groups include halogen, SCN$^-$, NO$_2^-$, and so on. Although not all these

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[33] W. Levason *et al., J. Chem. Soc. Dalton Trans.*, **1983**, 133.

[34] K. C. Lee and F. Aubke, *Inorg. Chem.*, 1984, **23**, 2124.

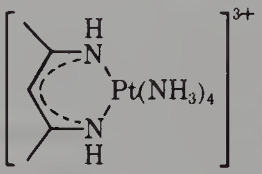
[35a] R. E. Cameron and A. B. Bocarsly, *Inorg. Chem.*, 1986, **25**, 2910.

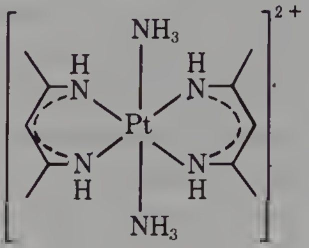
[35b] A. Vogeler and J. Hlavatsch, *Angew. Chem. Int. Ed. Engl.*, 1983, **22**, 154.

[36] R. D. Gillard *et al., Nouv. J. Chim.*, 1986, **10**, 783.

groups are known to occur in all possible combinations in all types of compounds, it can be said that with a few exceptions, they are generally interchangeable.

Interaction of $[Pt(NH_3)_6]Cl_4$ with β-diketones in basic solution gives iminato complexes such as (19-H-IX) and (19-H-X).

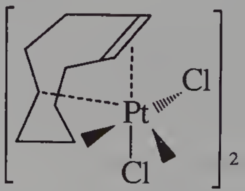

(19-H-IX)


(19-H-X)

Hydrido complexes such as $PtH_2Cl_2(PR_3)_2$ are usually made by oxidative-addition to the Pt^{II} complexes. They tend rather easily to eliminate and re-form Pt^{II}.

Platinum–Carbon Bonds. The first isolable organometallic compound of a transition metal was $(Me_3PtI)_4$ made in 1907 by Pope and Peachy. There is an extensive range of stable compounds having the Me_3Pt grouping all of which have octahedral Pt^{IV}. The iodide has a cubane structure with Pt and I atoms at the corners, the I atoms being triply bridging. In aqueous solutions the stable ion $[Me_3Pt(H_2O)_3]^+$ is formed with noncoordinating anions such as BF_4^- or ClO_4^-. Tetramethylplatinum does not exist, and what was thought to be this compound is actually $[Me_3Pt(OH)]_4$; however, there is an extensive chemistry of tetramethyl complexes such as $PtMe_4$bipy.[37a] The only Pd^{IV} compound is *fac*-$[PdMe_3L]I$ where L is tris(pyrazolyl) methane.

A unique compound that is the only example of a Pt^{IV} alkene complex[38] is (19-H-XI).


(19-H-XI)

19-H-4. Mixed Valence (II, IV) Linear Chain Compounds[39]

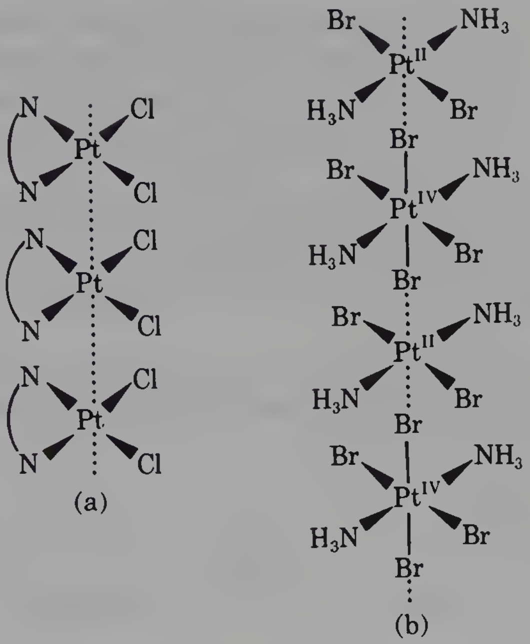
Many square complexes of Pd^{II} or Pt^{II} are packed in crystals to form infinite chains of metal atoms (Fig. 19-H-1a) close enough to interact electronically

[37a] J. E. Hux and R. J. Puddephat, *Inorg. Chim. Acta,* 1985, **100**, 1.

[37b] A. J. Canty *et al., J. Chem. Soc. Chem. Commun.,* **1987**, 1093.

[38] P. W. Jennings *et al., J. Am. Chem. Soc.,* 1985, **107**, 1793.

[39] J. M. Williams, *Adv. Inorg. Chem. Radiochem.,* 1983, **26**, 235; M. L. Rogers and D. S. Martin, *Polyhedron,* 1987, **6**, 225.



$Pt^{II} \cdots Br$ (chain) = 3.1 Å

FIG. 19-H-1. (a) Linear stacks of planar $Pt(en)Cl_2$ molecules, (b) Chains of alternating Pt^{II} and Pt^{IV} atoms with bridging bromide ions in $Pt(NH_3)_2Br_3$.

with one another, giving rise to marked spectral dichroism and electrical conductivity. These substances are discussed further in Section 23-17.

A related class of compound with chainlike structures contains both M^{II} and M^{IV} but differs from the above in that the metal units are linked by halide bridges. Both show high electrical conductivity along the direction of the $—Cl—M^{II}—Cl—M^{IV}$ chains, for example, in $[Pd^{II}(NH_3)_2Cl_2][Pd^{IV}(NH_3)_2Cl_4]$. One of the best known, *Wolfram's red salt,* has octahedral $[Pt(EtNH_2)_4Cl_2]^{2+}$ and planar $[Pt(EtNH_2)_4]^{2+}$ ions linked in chains, the other four Cl^- ions being within the lattice. The structure in Fig. 19-H-1b is typical.

Other examples[40] are the 1,2-diaminopropane complex $[Pt^{II}pn_2][Pt\,pn_2X_2]^{4+}$ and $[Pt(NH_3)_4][Pt(NH_3)_4Br_2]^{4+}$. These compounds commonly show dichroic behavior, intense absorption polarized parallel to the chain, exceptionally strong resonance Raman spectra and electrical conductance. All these can be associated with intervalence electron transfer. Other important mixed valence chain species are those, such as $Rb_2[Pt(CN)_4Cl_{0.3}]3H_2O$, obtained by partial oxidation of $[Pt(CN)_4]^{2-}$ salts; these are essentially electrically conducting one-dimensional metals.[41] Finally, as well as Pt^{II} and Pt^{IV} it is possible to have Pt_2^{III} anions as in the copper colored needles,[42] $\{[Pt^{II}en_2][Pt^{IV}en_2X_2]\}^{4+}$ $[Pt_2^{III}(H_2P_2O_5)_4X_2]^{4-}$. Platinum(III) species are discussed later.

Platinum Blues. Although not directly related to the previously men-

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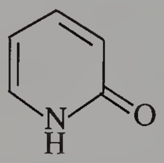
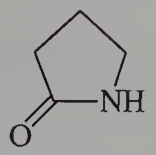
[40] R. J. H. Clark *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 273, 403.
[41] G. S. V. Coles *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 141; G. Gliemann and Y. Yersin, *Struct. Bonding* (Berlin), Vol. 62, Springer, Berlin, 1986.
[42] R. J. H. Clark and M. Kurmoo, *J. Chem. Soc. Dalton Trans.,* **1985,** 579.

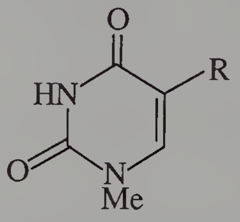
tioned chain species, a remarkable class of compounds generally called platinum blues contain limited chains with Pt–Pt interaction and variable oxidation states, $Pt^{II,III,IV}$.[43a] They have long been known from hydrolysis of *cis*-$PtCl_2(MeCN)_2$ in the presence of Ag^+ salts, but such materials could never be crystallized.

Blue compounds are formed generally when *cis*-$Pt(NH_3)_2Cl_2$ is treated in aqueous solution with uracils[43b] and uridines, and with thymine and other related pyrimidines. The pyrimidine blues like *cis*-$PtCl_2(NH_3)_2$ have antitumor activity.

Much progress[44] has been made by studying the products of oxidation of Pt^{II} ammines in the presence of potentially bridging ligands such as:


α-Pyridone


α-Pyrrolidone


Pyrimidine

The structures of two blue species are shown in Fig. 19-H-2.

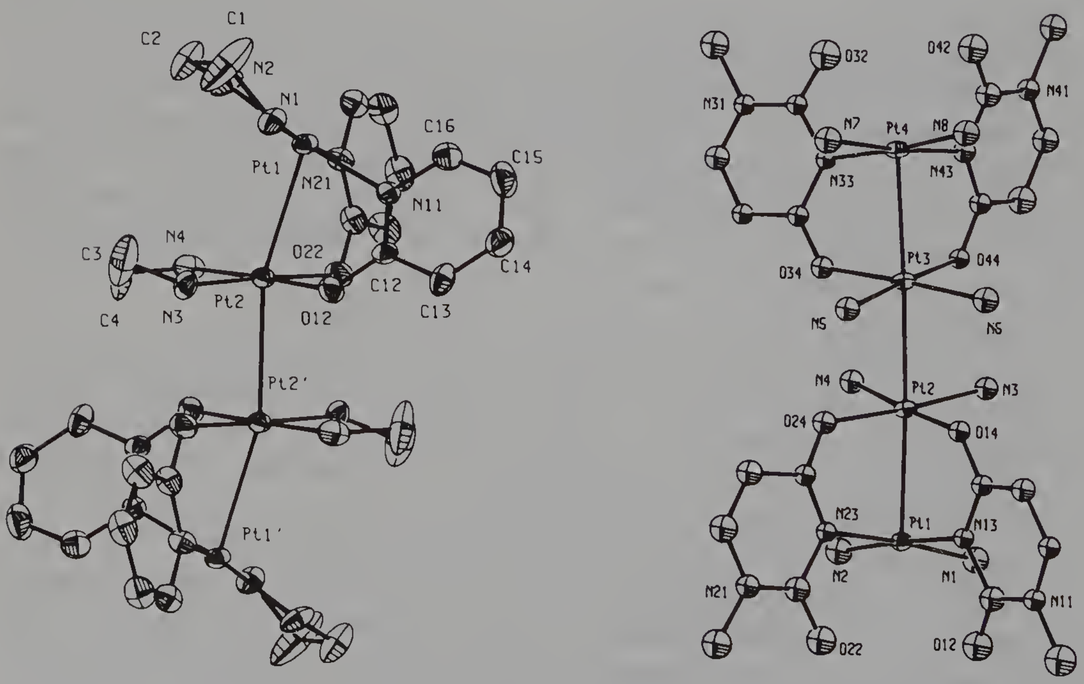


FIG. 19-H-2. The structures of (a) $[Pt_4en_4(\alpha\text{-pyridone})_4]^{5+}$ and (b) $[Pt_4(NH_3)_8(1\text{-methyluracil})_4]^{5+}$. [Reprinted with permission from S. J. Lippard *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 6427, 6428. Copyright (1984) American Chemical Society.]

[43a] P. Arrizabalaga *et al.*, *Inorg. Chem.*, 1985, **24**, 3656 and references quoted.

[43b] B. Lippert *et al.*, *Inorg. Chem.*, 1987, **26**, 1736; *J. Chem. Soc. Chem. Commun.*, **1987**, 76.

[44] S. J. Lippard *et al.*, *Inorg. Chem.*, 1987, **26**, 1261.

Materials similar to the original Pt blue can be made by treating aqueous acidic K_2PtCl_4 with amides.[45]

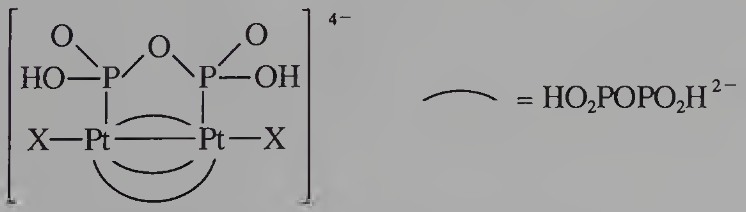
Other partially oxidized, nonstoichiometric complexes can be green, blue, or tan, depending on the oxidation state and without a change in the basic structure of the Pt_4 chain; examples are the green α-pyrrolidone complex $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5.48+}\cdot 3H_2O$ and the yellow $[Pt_4^{III}(NH_3)_8(C_4H_6NO)_4]^{6+}$.[46]

19-H-5. Complexes[47] of Palladium(III) and Platinum(III), d^5

We have just noted that Pt^{III} may be present in chain compounds with non-integral mean oxidation states. There are numerous other complexes, mostly binuclear with metal–metal bonds, that can *formally* be described as having Pt^{III}. Some compounds have a mean oxidation number of III while others contain Pt^{II} and Pt^{IV} and it is often difficult to decide whether there is Pt^{II}—Pt^{IV} or Pt^{III}—Pt^{III}. In other cases, the unpaired electrons may reside on the ligand rather than on the metal as in the well-known bipyridyl and dithiolene complexes.

Mononuclear compounds are so far rare. A blue aryl anion $[Pt^{III}(C_6Cl_5)_4]^-$ is obtained[8] by Cl_2 oxidation of yellow $[Pt(C_6Cl_5)_4]^{2-}$; it is paramagnetic (μ_{eff} = 2.4–2.5 BM) and square. Certain sulfur macrocycles such as 1,4,7-trithiacyclononane (L) can also stabilize Pd^{III} and Pt^{III} as shown by oxidation, for example, of $[PtL_2]^{2+}$, which is square pyramidal with a non-bonded S atom, to a paramagnetic species with a characteristic esr spectrum.[48]

Although one of the simplest *binuclear compounds*[49a] is $[Pt_2(\mu\text{-}SO_4)_4(H_2O)_2]^{2-}$ the most extensively studied compounds are those of the phosphite $(HO_2P)_2O^{2-}$ abbreviated POP.[49b] The Pt_2^{III} species are made by oxidation of $K_4[Pt_2^{II}(POP)_4]$ with halogens or CH_3I and have the tetra-bridged type structure (19-H-XII).



(19-H-XII)

There are also the intermediate (II)–(III) mixed oxidation state species such as $[Pt_2(POP)_4Br]^{4-}$, which has infinite chains with Pt—Pt—Br—Pt—Pt—Br linkages [cf. $Ru_2^{II,III}(O_2CMe)_4Cl$].

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[45] P. Castan *et al., J. Am. Chem. Soc.*, 1984, **106,** 4814.

[46] K. Matsumoto and T. Watanabe, *J. Am. Chem. Soc.*, 1986, **108,** 1308.

[47] D. J. Woollins and P. T. Kelly, *Coord. Chem. Rev.*, 1985, **65,** 115.

[48] M. Schröder *et al., J. Chem. Soc. Chem. Commun.*, **1987,** 118; *J. Organomet. Chem.*, 1987, **323,** 261.

[49a] J. R. Hall *et al., Inorg. Chim. Acta,* 1985, **104,** 19.

[49b] R. J. H. Clark *et al., Inorg. Chem.*, 1986, **25,** 409; 1985, **24,** 4220; D. M. Roundhill *et al., Inorg. Chem.*, 1986, **25,** 1155, 3714; C-M. Che *et al., J. Am. Chem. Soc.*, 1986, **108,** 4446, 7840; *Inorg. Chem.*, 1986, **25,** 4906; H. B. Gray *et al., J. Am. Chem. Soc.*, 1987, **109,** 286.

Similar species include phosphates,[50] $[Pt_2^{III}(\mu\text{-}PO_4H)_4(H_2O)_2]^{2-}$ and pyrophosphite, $[Pt_2^{III}(P_2O_5H_2)_4(NO_2)_2]^{4-}$.

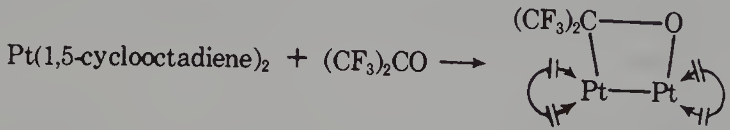
Finally, there are some tetra bridged methyl uracil[51a] and dithioacetate[51b] compounds, for example, $Pt_2^{III}(\mu\text{-}S_2CMe)_4I_2$, and the methyl, $Pt_2Me_4(MeCO_2)_2py_2$.[52]

Few Pd^{III} complexes are confirmed; one is $[PdL_2]^{3+}$, L = 1,4,7-trithiacyclononane formed[53a] on oxidation of $[PdL_2]^{2+}$.

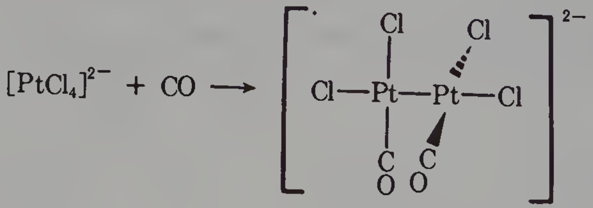
19-H-6. Complexes of Palladium and Platinum in Low Oxidation States

There is a variety of compounds that have oxidation states formally <II. They are mostly tertiary phosphine or carbonyl species and although some monomeric M^0 compounds are well established, others are binuclear or polynuclear with metal–metal bonds. However, a Pd^{II} complex of an N_4-macrocycle can be reduced[53b] to a square, very reactive species $\{Pd[N_4]\}^+$.

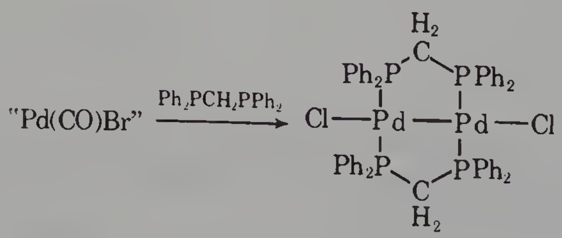
Binuclear compounds commonly have formal oxidation state 1 with M—M bonds in the region 2.53 to 2.70 Å. Some representative compounds and methods used to prepare them are the following:



2.58 Å



2.58 Å



2.70 Å

[50] D. M. Roundhill *et al., J. Am. Chem. Soc.*, 1985, **107**, 6282; *Inorg. Chem.*, 1985, **24**, 3146.

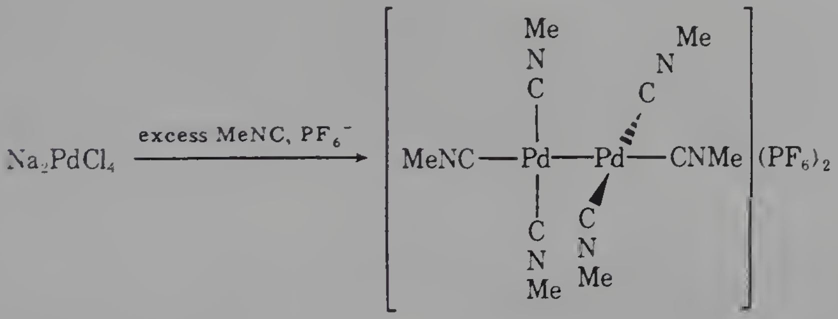
[51a] B. Lippert *et al., Inorg. Chem.*, 1986, **25**, 3384; *J. Am. Chem. Soc.*, 1986, **108**, 525; *J. Chem. Soc. Chem. Commun.*, **1986**, 258.

[51b] C. Bellito *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 595.

[52] F. A. Cotton *et al., Inorg. Chem.*, 1986, **25**, 763.

[53a] M. Schröder *et al., J. Chem. Soc. Chem. Commun.*, **1987**, 987.

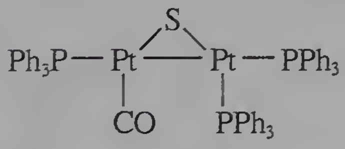
[53b] M. Schröder *et al., J. Chem. Soc. Chem. Commun.*, **1987**, 431.



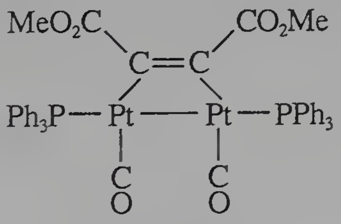
2.53 Å

Other *nonbridged* species include isocyanides,[54a] for example, $Pd_2I_2(MeNC)_4$. The ion $[Pd_2(MeNC)_6]^{2+}$ has the two $Pd(MeNC)_3$ planes at 90° in crystalline salts but in solution the ion is nonrigid; the Pt_2 analogue, however, *is* rigid.[54b]

Bridged species with nonphosphine groups such as (19-H-XIII) and (19-H-XIV) can force planarity, whereas in the phosphine species, the dihedral angle can vary, for example, for dppm between 4 to 48°.

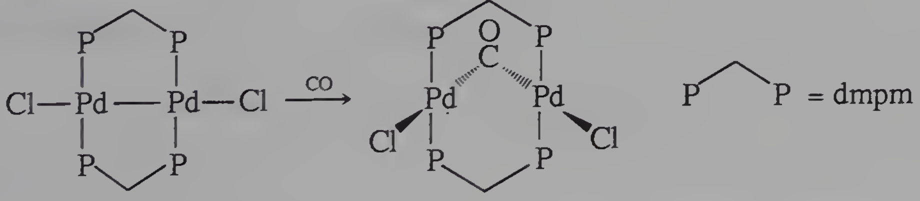


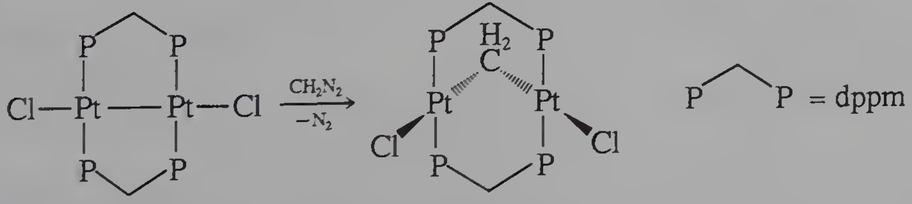
(19-H-XIII)



(19-H-XIV)

The bridged phosphine compounds[55] can react with CO, SO_2, CH_2N_2, S_8, and HCl, to give A-frame compounds that have M^I or, on oxidation M^{II}. Examples are

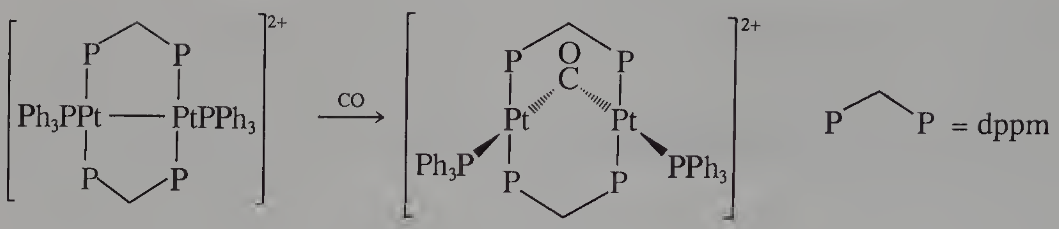




[54a] A. L. Balch *et al., Inorg. Chem.*, 1984, **23**, 2833; C. P. Kubiak *et al., J. Am. Chem. Soc.*, 1985, **107**, 3517.

[54b] P. A. Metcalf and C. P. Kubiak, *J. Am. Chem. Soc.*, 1986, **108**, 4682.

[55] See, for example, M. L. Kullberg and C. P. Kubiak, *Inorg. Chem.*, 1986, **25**, 26; R. J. Puddephat *et al., Organometallics*, 1987, **6**, 424; J. H. Espenson *et al., Inorg. Chem.*, 1986, **25**, 757, 878; *J. Am. Chem. Soc.*, 1986, **108**, 1962; Y. Yamamoto *et al., J. Am. Chem. Soc.*, 1986, **108**, 2458; R. Usón *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 1849.



Note that species without M—M bonds are obtained.

Monomeric Phosphine Complexes. There are many compounds such as $Pd(P^{t}\text{-}Bu_3)_2$, $Pd(CO)(PPh_3)_3$, $Pt(PPh_3)_3$, and $Pt[P(OR)_3]_4$.[56] Although analogues of $Ni(CO)_4$ do not exist, $Pt(PF_3)_4$ and $Pt[PF(CF_3)_2]_4$ are stable although $Pd(PF_3)_4$ decomposes above −20°C. The complexes can be made by a variety of reactions including reductions or eliminations,[57] for example,

$$K_2MCl_4 + 4PPh_3 \xrightarrow{N_2H_4,\ EtOH} M(PPh_3)_4$$

$$(C_2H_5)_2Pt(PEt_3)_2 \xrightarrow{\Delta} Pt(C_2H_4)(PEt_3)_2 + C_2H_6$$

The tendency of $M(PR_3)_4$ molecules to dissociate giving three-coordinate $M(PR_3)_3$ and two-coordinate[58a] $M(PR_3)_2$ in solution depends mainly on the

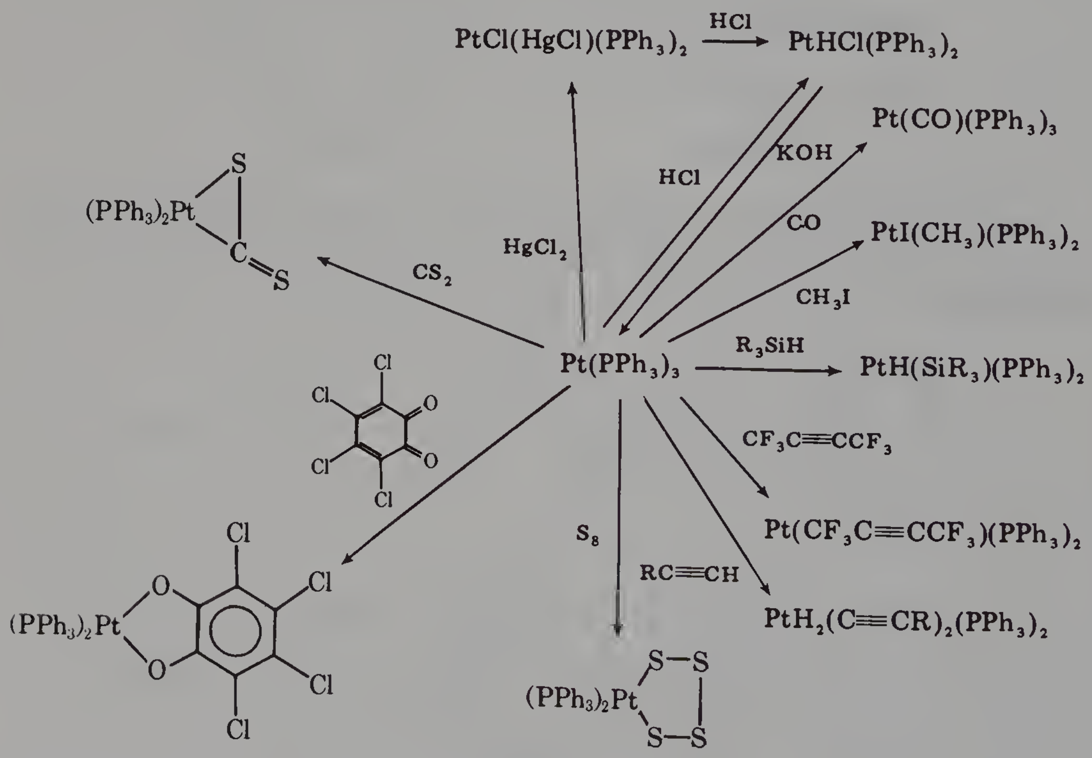


FIG. 19-H-3. Oxidative-addition and related reactions of $Pt(PPh_3)_3$. Reactions of $Pt(PPh_3)_4$ and corresponding palladium compounds are similar.

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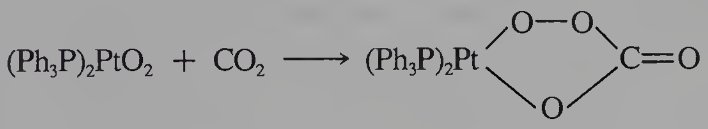
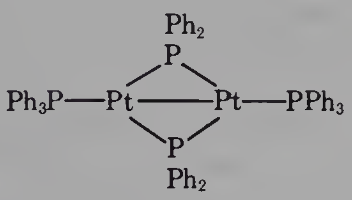
[56] See, for example, F. R. Hartley *et al.*, *Inorg. Chem.*, 1985, **24**, 2849.
[57] See, for example, W. C. Trogler *et al.*, *Organometallics*, 1985, **4**, 647.
[58a] J. A. Davies *et al.*, *Organometallics*, 1986, **5**, 1264.

cone angle of the phosphine and on electronic factors.[58b] For triaryl and alkyl diaryl phosphines dissociation is extensive, whereas for trialkyl or dialkylaryl phosphines it is not; PMe_3 gives only $Pt(PMe_3)_4$, $Pt(PEt_3)_4$ on heating will give $Pt(PEt_3)_2$, while with very bulky phosphines such as $P(c\text{-}C_6H_{11})_3$ only $Pt(PR_3)_2$ can be isolated.[59]

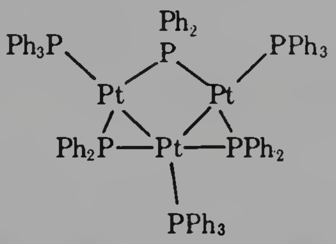
The complexes undergo displacement reactions with CO, C_2H_4, dienes, and other donors to give complexes such as $(Ph_3P)_2Pt(RC{\equiv}CR)$ or $(Ph_3P)_2Pt[Sn(acac)_2]_2$ but the important chemistry is of oxidative-addition reactions to the M^0 species (Fig. 19-H-3). The oxygen adducts[60] formally having Pt^{II}, $Pt(\eta^2\text{-}O_2)(PR_3)_2$, have an extensive chemistry and will react with CO_2, SO_2, and organic molecules initially to give peroxo compounds, for example,



Thermolysis of $Pt(PPh_3)_3$ or $Pt(PPh_3)_2(C_2H_4)$ in benzene gives deep red solutions from which the diphenylphosphido species are obtained evidently via cleavage of P—C bonds (19-H-XV) and (19-H-XVI)



(19-H-XV)



(19-H-XVI)

Interaction of $Pt(PPh_3)_4$ with $Ph_2PCH_2PPh_2$ gives $Pt_2(\mu\text{-dppm})_3$.[61]

Carbonyl Compounds. Carbonyl halides of Pt were the first CO compounds ever to be made, by the French chemist P. Schutzenberger in 1868–1870, considerably preceding Mond's discovery of $Ni(CO)_4$. Schutzenberger also made the first PX_3 compounds using PCl_3. The compounds were obtained by action of $PtCl_2$ and CO (or PCl_3) and had stoichiometries $PtCl_2CO$, $PtCl_2(CO)_2$, and $2PtCl_2{\cdot}3CO$.

The structures of the carbonyl halides[62] are now well established. For Pt we have the sequence

$$Pt_2(CO)_2Cl_2(\mu\text{-}Cl)_2 \overset{CO}{\rightleftharpoons} trans\text{-}PtCl_2(CO)_2 \longrightarrow cis\text{-}PtCl_2(CO)_2$$

[58b] A. Sen and J. Halpern, *Inorg. Chem.*, 1980, **19**, 1073; B. E. Mann and A. Musco, *J. Chem. Soc. Dalton Trans.*, **1980**, 776.

[59] E. Negishi *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 1338.

[60] R. D. W. Kemmitt *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 1993; M. Kubota *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 4558.

[61] L. Manojlovic-Muir *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 1955; S. S. M. Ling *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985**, 566.

[62] F. Calderazzo *et al.*, *Inorg. Chem.*, 1984, **23**, 137, 3030.

The palladium compounds can be obtained, for example, by the reaction

$$2PdCl_2 + 2CO \xrightarrow{SOCl_2} Pd_2(CO)_2Cl_2(\mu\text{-}Cl)_2$$

but the Pd—CO bond is inherently weaker than either NiCO or PtCO due to lack of efficient π bonding.[11]

A Pt^{IV} carbonyl $[Pt(CO)Cl_5]^-$ can be made by oxidation of $Pt(CO)Cl_3^-$ by Cl_2 in $SOCl_2$.[63]

Since the M—CO bonding in all these compounds is substantially a σ donation to metal, the MCO bond is especially prone to nucleophilic attack by H_2O or amines (Section 22-8).

There is a wide variety of neutral clusters for both Pd and Pt usually containing PR_3 ligands. Examples[64] are $Pd_4(CO)_5(PR_3)_4$, $Pt_3(CO)_3(PR_3)_3$, $Pt_4(\mu\text{-}SO_2)_3(PMe_2Ph)_3$, $Pd_{10}(CO)_{12}(PR_3)_6$, and $Pd_{23}(CO)_{22}(PEt_3)_{10}$.

Polynuclear carbonyl anions[65] of the general formula $[Pt_3(CO)_6]_n^{2-}$ where n depends on the alkali metal to Pt ratio, are obtained on reduction of $Na_2PtCl_6\cdot 6H_2O$ or $PtCl_2(CO)_2$ under CO (1 atm, 25°C). They are usually crystallized with large cations such as $(C_4H_9)_4N^+$ or Ph_4P^+. The structures (see Section 23-9) of three representative ions are shown in Fig. 23-13 and indicate $Pt_3(CO)_3(\mu\text{-}CO)_3$ units arranged to form skewed and twisted stacks. The chemistry is very complicated and isolation of the anions requires great skill. Ions of other stoichiometries, for example, with Pt_{19} (Fig. 23-14) and Pt_{38} can also be obtained.

All the species $[Pt_3(CO)_6]_n^{2-}$ are quite reactive, the specific character of their reactivity depending on n, since the greater the value of n, the less "reduced" is the metal. The larger the value of n, the greater is the reactivity toward nucleophilic and reducing agents; with small n it is greatest toward electrophiles and oxidizing agents. Thus the lower members react very avidly:

$$(n + 1)[Pt_3(CO)_6]_n^{2-} + \tfrac{1}{2}O_2 + H_2O \longrightarrow n[Pt_3(CO)_6]_{n+1}^{2-} + 2OH^-$$

$$3[Pt_{12}(CO)_{24}]^{2-} + H_2O = 4[Pt_9(CO)_{18}]^{2-} + 2H^+ + \tfrac{1}{2}O_2$$

The base so formed favors reductive carbonylation, tending to reverse this change from n to $n + 1$ if CO is present. Moreover, the various species tend to react with each other, namely,

$$[Pt_3(CO)_6]_2^{2-} + [Pt_3(CO)_6]_4^{2-} = 2[Pt_3(CO)_6]_3^{2-}$$

Relatively little chemistry has been done on these cluster anions but $[Pt_{15}(CO)_{30}]^{2-}$ catalyzes hydrogenation of MeCN, PhCHO, and other organic substances.[66]

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[63] F. Calderazzo *et al., J. Chem. Soc. Dalton Trans.*, **1982,** 2257.

[64] R. D. Feltham *et al., Inorg. Chem.*, 1985, **24,** 1503; Yu T. Struchkov *et al., J. Organomet. Chem.*, 1986, **301,** C35; D. M. P. Mingos *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 1535.

[65] B. K. Teo *et al., Inorg. Chem.*, 1986, **25,** 2262.

[66] S. Bhaduri and K. R. Sharma, *J. Chem. Soc. Dalton Trans.*, **1982,** 927.

Other Cluster Compounds. There is a very extensive chemistry particularly of triangular M_3 compounds.[67] Examples are $Pt_3(\mu\text{-CNR})_3(CNR)_3$, $[Pd_3(\mu_3\text{-CO})(\mu\text{-dppe})_3]^+$, and mixed metal species like $[PtPd_2Cl(PPh_2)_2(PPh_3)_3]^+$.

There are also much bigger clusters, such as $Pd_{38}(\mu_3\text{-CO})_4(\mu_2\text{-CO})_{24}(PEt_3)_{12}[Pt_6Ni_{38}(CO)_{48}H_{6-n}]^{n-}$, $n = 4, 5$,[68] as well as smaller ones such as $[Pt_2Ag_2Cl_4(C_6F_5)_4]^{2-}$.[69]

Reduction of, for example, $PtCl_2(RNC)_2$ leads to isocyanide polynuclear species such as $Pt_3(RNC)_6$ or $Pt_7(RNC)_{12}$. The Pt_3 and Pd_3 compounds have three terminal and three μ-RNC groups, but the oxidized $[Pd_2(MeNC)_8]^{2+}$ is linear without bridges.[70]

Other Complexes. The 16*e* complex $Pt(C_2H_4)_3$,[71] which has the Pt and six carbon atoms coplanar is made by the reactions:

$$PtCl_2(COD) \xrightarrow{\text{LiCOT}} Pt(COD)_2 \xrightarrow{C_2H_4} Pt(C_2H_4)_3$$

It is a useful starting material for other syntheses.

There are also the three-coordinate species $M[Sn(NR_2)_2]_3$, which are also made from $Pt(COD)_2$ and have planar M, Sn, and N.[72]

Additional References

Maitlis, P. M., M. J. H. Russell, and P. Espinet, Vol. 6, Chapters 38.1–38.9 (Palladium), F. R. Hartley, Vol. 6, Chapter 39 (Platinum), *Comprehensive Organometallic Chemistry,* Pergamon Press, Oxford, 1982.

19-I. SILVER AND GOLD: GROUP IB(11)

Like copper, silver and gold have a single *s* electron outside a completed *d* shell, but in spite of the similarity in electronic structures and ionization potentials there are few resemblances between Ag, Au, and Cu. There are no simple explanations for many of the differences although some of the differences between Ag and Au may be traced to relativistic effects on the 6*s* electrons of the latter.

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[67] R. Hoffmann *et al., J. Am. Chem. Soc.,* 1985, **107,** 5968; K. R. Dixon *et al., Inorg. Chem.,* 1985, **24,** 2625; D. P. Mingos *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 1693; D. H. Farrer *et al., Organometallics,* 1985, **4,** 1750; L. Manojlovič-Muir *et al., Inorg. Chem.,* 1987, **26,** 231.

[68] G. Longoni *et al., Angew. Chem. Int. Ed. Engl.,* 1985, **24,** 697; J. L. Spencer *et al., J. Chem. Soc. Dalton Trans.,* **1987,** 259; Y. L. Slovokhotov *et al., J. Chem. Soc. Chem. Commun.,* **1987,** 218.

[69] R. Usón *et al., Inorg. Chem.,* 1985, **24,** 4651.

[70] C. G. Francis *et al., Inorg. Chem.,* 1984, **23,** 3680; Y. Yamamoto *et al., Organometallics,* 1983, **2,** 1377.

[71] F. G. A. Stone, *Acc. Chem. Res.,* 1981, **14,** 318.

[72] P. B. Hitchcock *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 863; T. A. K. Al-Allaf *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 548.

Apart from obviously similar stoichiometries of compounds in the same oxidation state (which do not always have the same structure), there are some similarities within the group—or at least between two of the three elements:

1. The metals all crystallize with the same face centered cubic (*ccp*) lattice.
2. Cu_2O and Ag_2O have the same body centered cubic structure where the metal atom has two close oxygen neighbors and every oxygen is tetrahedrally surrounded by four metal atoms.
3. Although the stability constant sequence for halide complexes of many metals is F > Cl > Br > I, Cu^I and Ag^I belong to the group of ions of the more noble metals, for which it is the reverse.
4. Cu^I and Ag^I (and to a lesser extent Au^I) form very much the same types of ion and compound, such as $[MCl_2]^-$, $[Et_3AsMI]_4$, and K_2MCl_3.
5. Certain complexes of Cu^{II} and Ag^{II} are isomorphous, and Ag^{III}, Au^{III}, and Cu^{III} also give similar complexes.

The only aqua ions are $Ag^+(aq)$ and $Ag^{2+}(aq)$. However, the former binds H_2O molecules only weakly,[1] and the crystalline salts of the Ag^+ ion are rarely, if ever, hydrated. By contrast the Au^+ ion is exceedingly unstable with respect to the disproportionation

$$3Au^+(aq) = Au^{3+}(aq) + 2Au(s) \qquad K \approx 10^{10}$$

Gold(III) is invariably complexed in all solutions, usually as anionic species such as $[AuCl_3OH]^-$. The other oxidation states, Ag^{II}, Ag^{III}, and Au^I, are either unstable to water or exist only in insoluble compounds or complexed species. Intercomparisons of the standard potentials are of limited utility, particularly since these strongly depend on the nature of the anion; some useful ones are

$$Ag^{2+} \xrightarrow{1.98} Ag^+ \xrightarrow{0.799} Ag$$

$$Ag(CN)_2^- \xrightarrow{-0.31} Ag + 2CN^-$$

$$AuCl_4^- \xrightarrow{1.00} Au + 4Cl^-$$

$$Au(CN)_2^- \xrightarrow{-0.6} Au + 2CN^-$$

Gold(II) occurs *formally* in dithiolene compounds (Section 13-16) and in the dicarbollyl $[Au(B_9C_2H_{11})_2]^{2-}$ but otherwise possibly exists only as a transient intermediate in reactions.

The chemistry of gold is more diversified than that of silver. Six oxidation states, from −I to III and V, occur in its chemistry. Gold(−I) and Au^V have no counterparts in the chemistry of silver. Solvated electrons in liquid ammonia can reduce gold to give the Au^- ion, which is stable in liquid ammonia (E^0 = −2.15 V). In the series of MAu alloys (M = Na, K, Rb, and Cs) metallic character decreases from NaAu to CsAu and the latter is best regarded as an ionic compound Cs^+Au^-. The CsAu molecule is also

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[1] T. Yamaguchi *et al., Acta Chem. Scand.*, 1984, **A38,** 437.

known. The electron attachment enthalpy for the Au atom is relatively high (-223 kJ mol^{-1} vs. -295 kJ mol^{-1} for I). Oxidation state IV may exist under chemically significant conditions, but the evidence is not entirely convincing. There are no properly characterized compounds. Gold(V) is known as AuF_5 and $[AuF_6]^-$, in which it has a low-spin $[Xe]4f^{14}5d^6$ configuration. Gold also differs from silver in forming numerous Au_n cluster compounds and in forming many bonds to other metals.[2]

The oxidation states and stereochemistry are summarized in Table 19-I-1.

19-I-1. The Elements

Silver and gold are widely distributed in Nature. They occur as metals and also as numerous sulfide ores, usually accompanied by sulfides of Fe, Cu, Ni, and so on. The main sources are South Africa and the USSR. Silver also occurs as *horn silver* (AgCl).

After flotation or other concentration processes, the crucial chemical steps are cyanide leaching and zinc precipitation, for example,

$$4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH$$

$$2KAu(CN)_2 + Zn \longrightarrow K_2Zn(CN)_4 + 2Au$$

Silver and gold are normally purified by electrolysis.

Silver is a white, lustrous, soft, and malleable metal (mp 961°C) with the highest known electrical and thermal conductivities. It is chemically less reactive than copper, except toward sulfur and hydrogen sulfide, which rapidly blacken silver surfaces. The metal dissolves in oxidizing acids and in cyanide solutions in presence of oxygen or peroxide.

Gold is a soft, yellow metal (mp 1063°C) with the highest ductility and malleability of any element. It is chemically unreactive and is not attacked by oxygen or sulfur, but reacts readily with halogens or with solutions containing or generating chlorine such as aqua regia; and it dissolves in cyanide solutions in presence of air or hydrogen peroxide to form $[Au(CN)_2]^-$. The reduction of solutions of $AuCl_4^-$ by various reducing agents may, under suitable conditions, give highly colored solutions containing colloidal gold. The "purple of Cassius" obtained using Sn^{II} is used for coloring ceramics. Silver atoms that do not aggregate but are trapped in a macrocyclic poly-nitrogen ligand are obtained by photochemical or electrochemical reductions of the Ag^+ complex; the Ag^0 complex can be reoxidized.

19-I-2. Compounds of Silver(I)

This is the common oxidation state. The salts $AgNO_3$, $AgClO_3$, and $AgClO_4$ are water soluble, but Ag_2SO_4 and $AgOOCCH_3$ are sparingly so. The salts

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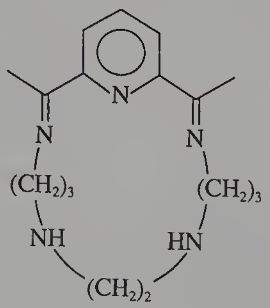
[2] J. W. Lauher and K. Wald, *J. Am. Chem. Soc.*, 1981, **103,** 7648; J. Lewis *et al., J. Chem. Soc. Dalton Trans.*, **1983,** 2447.

TABLE 19-I-1
Oxidation States and Streochemistry of Silver and Gold

Oxidation state	Coordination number	Geometry	Examples
Ag^{I}, d^{10}	2[a]	Linear	$[Ag(CN)_2]^-$, $[Ag(NH_3)_2]^+$, $AgSCN$
	3	Trigonal	$(Me_2NC_6H_4PEt_2)_2AgI$
	4[a]	Tetrahedral	$[Ag(SCN)_4]^{3-}$, $[AgIPR_3]_4$, $[Ag(py)_4]ClO_4$ $[Ag(PPh_3)_4]ClO_4$
	5	Distorted pentagonal plane	$[Ag(L)]^{+2}$[b]
	5	Pentagonal pyramidal	$[Ag(L)]_2^{2+}$[b]
	6	Octahedral	AgF, AgCl, AgBr(NaCl structure)
Ag^{II}, d^9	4	Planar	$[Ag(py)_4]^{2+}$
	6	Distorted octahedral	Ag(2,6-pyridinedicarboxylate)$_2\cdot H_2O$
Ag^{III}, d^8	4	Planar	AgF_4^-, half Ag atoms in AgO, $[Ag(ebg)_2]^{3+}$[c]
	6	Octahedral	$[Ag(IO_6)_2]^{7-}$, Cs_2KAgF_6
Au^{I}, d^{10}	2[a]	Linear	$[Au(CN)_2]^-$, $Et_3P\cdot AuC{\equiv}C\cdot C_6H_5$; $(AuI)_n$
	3	Trigonal	$AuCl(PPh_3)_2$
	4	Tetrahedral	$[Au(diars)_2]^+$
Au^{II}, d^9	4	Square	$[Au(mnt)_2]^{2-}$
Au^{III}, d^8	4[a]	Planar	$AuBr_4^-$, Au_2Cl_6, $[(C_2H_5)_2AuBr]_2$, R_3PAuX_3, $[AuPh_4]^-$[d]
	5	*tbp*	$[Au(diars)_2I]^{2+}$
		sp	$AuCl_3$(2,9-Me$_2$-1,10-phen), AuCl(TPP)
	6	Octahedral	$AuBr_6^{3-}$, *trans*-$[Au(diars)_2I_2]^+$
Au^{V}, d^6	6	Octahedral	$(Xe_2F_{11})^+(AuF_6)^-$
	?	?	AuF_5
Au^{VII}, d^4	?	?	AuF_7[e]

[a] Most common states

[b] L is an N_5 macrocycle:



[c] ebg = ethylenedibiguanide.

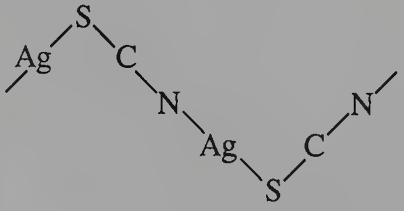
[d] A. J. Markwell, *J. Organomet. Chem.*, 1985, **293,** 257.

[e] From AuF_5 and atomic fluorine; said to be stable with high vapor pressure. A. A. Timakov *et al., Dokl. Akad. Nauk. S.S.R.*, 1986, **291,** 125.

of oxo anions are primarily ionic, but although the water-insoluble halides AgCl and AgBr have the NaCl structure, there appears to be appreciable covalent character in the Ag---X interactions, whereas in compounds such as AgCN and AgSCN, which have chain structures (19-I-I) and (19-I-II), the bonds are considered to be predominantly covalent.

—Ag—C—N—Ag—C—N—

(19-I-I)



(19-I-II)

As illustrated in Table 19-I-1, Ag^I and Au^I show a pronounced tendency to exhibit linear twofold coordination.

There is a relatively small energy difference between the filled *d* orbitals and the unfilled valence shell *s* orbital,[3] which permits extensive hybridization of the d_{z^2} and *s* orbitals, as shown in Fig. 19-I-1. The electron pair initially in the d_{z^2} orbital occupies ψ_1, giving a circular region of relatively high electron density from which ligands are somewhat repelled, and regions above and below this ring in which the electron density is relatively low. Ligands are attracted to the latter regions. By further mixing of ψ_2 with the p_z orbital, two hybrid orbitals suitable for forming a pair of linear covalent bonds can be formed.

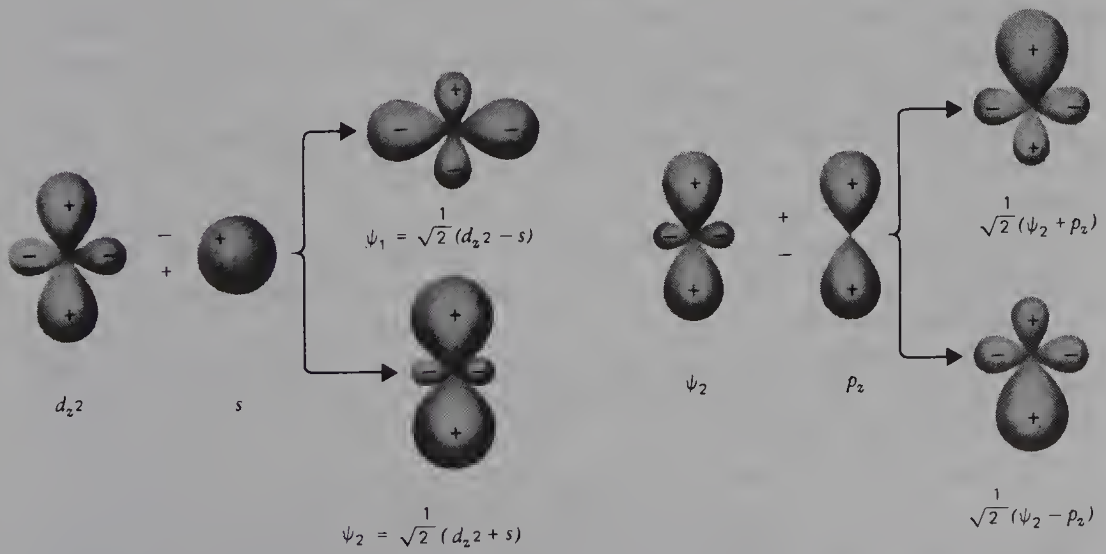


FIG. 19-I-1. The hybrid orbitals formed from a d_{z^2} and an *s* orbital ψ_1 and ψ_2, and the hybrids that can be formed from ψ_2 and a p_z orbital. In each sketch the *z* axis is vertical and the actual orbital is the figure generated by rotating the sketch about the *z* axis.

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[3] G. M. Bancroft *et al., Inorg. Chem.*, 1982, **21**, 2946; S. K. Chastain and W. Roy Mason, *Inorg. Chem.*, 1982, **21**, 3717.

Binary Compounds

Silver(I) Oxide. The addition of alkali hydroxide to Ag^+ solutions produces a dark brown precipitate that is difficult to free from alkali ions. It is strongly basic, and its aqueous suspensions are alkaline:

$$\tfrac{1}{2}Ag_2O(s) + \tfrac{1}{2}H_2O = Ag^+ + OH^- \qquad \log K = -7.42 \text{ (25°C, 3 } M \text{ NaClO}_4)$$

$$\tfrac{1}{2}Ag_2O(s) + \tfrac{1}{2}H_2O = AgOH \qquad \log K = -5.75$$

they absorb carbon dioxide from the air to give Ag_2CO_3. The oxide decomposes above ~160°C and is readily reduced to the metal by hydrogen. Silver oxide is more soluble in strongly alkaline solution than in water, and AgOH and $Ag(OH)_2^-$ are formed. The treatment of water-soluble halides with a suspension of silver oxide is a useful way of preparing hydroxides, since the silver halides are insoluble. Analogously to copper and gold, alkali metal silver oxides contain $Ag_4O_4^{4-}$ units.

Silver(I) Sulfide. The action of hydrogen sulfide on argentous solution gives black Ag_2S, which is the least soluble in water of all silver compounds ($\log K_{sp} \approx 50$). The black coating often found on silver articles is the sulfide; this can be readily reduced by contact with aluminum in dilute sodium carbonate solution.

Silver(I) Halides. The *fluoride* is unique in forming hydrates such as $AgF{\cdot}4H_2O$, which are obtained by crystallizing solutions of Ag_2O in aqueous HF. The other well-known halides are precipitated by the addition of X^- to Ag^+ solutions; the color and insolubility in water increase $Cl < Br < I$.

Silver chloride can be obtained as rather tough sheets that are transparent over much of the ir region and have been used for cell materials. Silver chloride and bromide are light sensitive and have been intensively studied because of their importance in photography.

Both AgCl and AgBr have a rock salt structure, though they are covalent insulators. AgI has both zinc blende and wurtzite structures with tetrahedral coordination about Ag.

Several combinations of silver salts (e.g., $AgNO_3$—AgBr) exist that give low melting eutectics that are useful as reaction media and catalysts.

Complexes of Ag^I

Nitrogen Ligands. Many of these form readily in aqueous solution, NH_3 being the most important of the nitrogen ligands. In general, large formation constants are seen only for the AgL^+ and AgL_2^+ complexes[4,5] and this is due to the preference for linear coordination; the linear $[H_3N{-}Ag{-}NH_3]^+$ ion has been observed crystallographically in several compounds.[6] With polyamine ligands more complex behavior can occur and AgL(OH) complexes may also form.[7] Aqueous pyridine and substituted pyridines also form $Ag(py)^+$

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[4] M. Maeda *et al., J. Phys. Chem.*, 1983, **87,** 121.

[5] R. D. Hancock *et al., Inorg. Chem.*, 1983, **22,** 2531.

[6] T. Yamaguchi and O. Lindquist, *Acta Chem. Scand.*, 1983, **A37,** 685.

[7] J. Yperman *et al., Inorg. Chem.*, 1983, **22,** 1361.

and $Ag(py)_2^+$ ions[8] but when nonaqueous conditions are employed (e.g., $CHCl_3$/py mixtures) solids containing other complexes can be obtained. For example, $[Ag(py)_4]ClO_4$ contains an essentially tetrahedral cation.[9]

The tetrahedral $[Ag(MeCN)_4]^+$ ion[10] is quite stable and the linear $[OCN—Ag—NCO]^-$ ion is also known. There are also Ag^I complexes of pyrazolylborate ligands, but these are generally of the mixed ligand type, $Ag[R_nB(pz)_{4-n}]L$, where L is, for example, a phosphine. The structure of one shows a curious coordination sphere in which there is one normal Ag—P and one normal Ag—N bond together with a very long (2.41 Å) Ag—N bond.[11]

Halogeno Complexes. The halides, AgX, form complex ions of the types AgX_2^- and AgX_3^{2-} with relative stabilities $I^- > Br^- > Cl^-$. The constants for formation of the AgX_2^- ions vary considerably with solvent and they are relatively low in water. Nonetheless, AgCl is ~100 times more soluble in 1 *M* HCl than in pure water. The linear $[X—Ag—X]^-$ ions have been observed in crystals, but the compounds of composition $M_2^IAgX_3$ have infinite chain anions consisting of AgX_4 tetrahedra sharing corners.

Cationic species such as Ag_2X^+ and Ag_3X^{2+} are formed when the silver halides are dissolved in aqueous solutions of $AgNO_3$ or $AgClO_4$.

Other Ligands. Silver(I) has a relatively low affinity for oxygen donors, although compounds and complexes containing carboxylate ions, DMSO, DMF, and crown ethers[12] are known. However, it forms numerous complexes with the donor atoms S, Se, P, and As. With sulfur the thiosulfate complexes, $[Ag(S_2O_3)]^-$ and $[Ag(S_2O_3)_2]^{3-}$ are quite stable and silver chloride and bromide will dissolve in aqueous thiosulfate, thus providing a means of "fixing" photographic images. Other important sulfur ligands for Ag^I are thiolate anions,[13a] which give oligomers, $(AgSR)_n$, dithiocarbamate ions, SCN^-,[13b] thioureas, and thioethers. Silver(I) binds to peptides and proteins with a preference for the thioether sulfur atoms and imidazole nitrogen atoms.[14]

With certain sulfur ligands Ag^I forms some interesting cluster species. With $Pr_2NCS_2^-$ a hexamer is formed in which the silver atoms define an elongated trigonal antiprism. The six shorter Ag—Ag distances are comparable to that in metallic Ag. The species $[(Et_2NCS_2)Ag]_6$ gives a similar molecule, but also an isomeric form with a more irregular structure.[15] By reaction of $AgNO_3$ in CH_3CN with a tetraalkylammonium salt of the $(NC)_2C{=}CS_2^{2-}$

[8] D. K. Lavallee and J. D. Doi, *Inorg. Chem.*, 1981, **20,** 3345.

[9] K. Nilsson and A. Oskarsson, *Acta Chem. Scand.*, 1982, **A36,** 605.

[10] K. Nilsson and A. Oskarsson, *Acta Chem. Scand.*, 1984, **A38,** 79.

[11] M. I. Bruce *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981,** 956.

[12] Y. Takeda *et al.*, *Bull. Soc. Chem. Jpn.*, 1982, **55,** 3438.

[13a] E. Block *et al.*, *Inorg. Chem.*, 1987, **26,** 1488.

[13b] P. Gans *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981,** 1708.

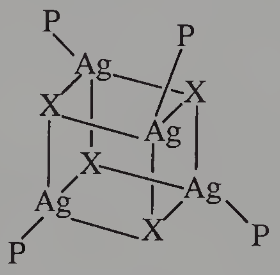
[14] Y. Kojima *et al.*, *Bull. Soc. Chem. Jpn.*, 1983, **56,** 3841.

[15] H. Anacker-Eickhoff *et al.*, *Acta Chem. Scand.* 1982, **A36,** 251.

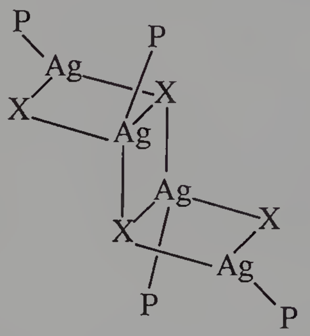
ion, two products may be obtained depending on the ratio of reactants: $[Ag_6(S_2C{=}C(CN)_2)_6]^{6-}$ and $[Ag_8(S_2C{=}C(CN)_2)_6]^{4-}$. The former[16] contains a distorted octahedral cluster similar to that mentioned previously for the $Ag_6(S_2CNR_2)_6$ molecules, while the latter[17] contains a distorted Ag_8 cube with a ligand across each face; the Ag—Ag distances are 2.96 to 3.09 Å.

A number of Ag^I thiolates have been found to be oligomeric or polymeric, with Ag atoms connected by μ-RS^- groups.[18]

Numerous phosphine complexes (and some arsine and stibine analogues) are known. With monophosphines these are mainly of the type $(R_3P)_nAgX$, with n = 1–4. The 1:1 complexes are tetrameric, with either cubane (19-I-III) or chair (19-I-IV) structures depending on the steric requirements of both X and R_3P.



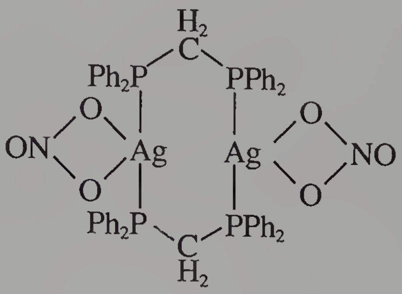
(19-I-III)



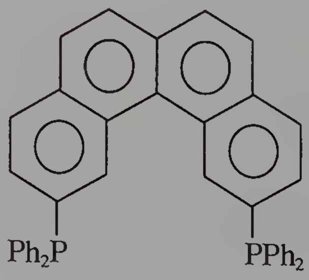
(19-I-IV)

The $(R_3P)_2AgX$ complexes are generally dimeric with bridging X, but for very bulky phosphines such as $(\text{tert-Bu})_3P$ or $(\text{mesityl})_3P$[19] linear cations, $[R_3P{-}Ag{-}PR_3]^+$, occur.

Complexes with bridging bidentate phosphines[20a] tend to be dimers or tetramers with bridging phosphines, as in (19-I-V), but with the unusual diphosphine (19-I-VI), monomers with the diphosphine chelating are formed.[20b]



(19-I-V)



(19-I-VI)

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[16] H. Dietrich *et al., J. Chem. Soc. Chem. Commun.* **1982,** 1036.

[17] P. J. M. W. L. Birker and G. C. Verschoor, *J. Chem. Soc. Chem. Commun.*, **1981,** 322.

[18] I. G. Dance *et al., Inorg. Chem.*, 1981, **20,** 1487; 1983, **22,** 3785.

[19] G. Ferguson *et al., Inorg. Chem.*, 1982, **21,** 1369.

[20a] Y. Inogushi *et al., Chem. Ber.*, 1983, **116,** 1487; D. M. Ho and R. Bau, *Inorg. Chem.*, 1983, **22,** 4073.

[20b] L. Venanzi *et al., Inorg. Chem.*, 1983, **22,** 2356.

Organosilver Compounds. Virtually all alkenes and many aromatic compounds form complexes when the hydrocarbon is shaken with aqueous solutions of soluble silver salts. Equilibrium constants for the formation of the complexes with alkenes and other compounds with double bonds have been measured. Similar complexes are formed between $AgBF_4$ and aliphatic or aromatic ketones in CH_2Cl_2. In all these cases, the order of stability is generally $AgBF_4 > AgClO_4 > AgNO_3$.

Di- or polyalkenes commonly give crystalline complexes that may have Ag^+ bound to one, two, or three double bonds. The structures of many such compounds are known. Because of differing stabilities, the formation of crystalline complexes can be useful for the purification of particular alkenes, or for separation of mixtures (e.g., 1,3-,1,4-, and 1,5-cyclooctadienes) or of the optical isomers of α- and β-pinene. Silver nitrate/ethane-1,3-diol columns have also been used for gas–liquid chromatographic separations of alkenes.

Substituted acetylenes give white solids that are insoluble and polymeric, probably owing to π bonding between Ag and the triple bond, as in the copper compounds.

The silver(I) alkyls and aryls are less stable than those of copper, but comparatively stable fluoroalkyls can be obtained by reactions such as

$$AgF + CF_3CF{=}CF_2 \xrightarrow{MeCN} Ag\{CF(CF_3)_2\}(MeCN)$$

These compounds are polymeric when nonsolvated.

Like copper, silver also forms compounds with acetylenes that have σ bonds to the metal. Thus the action of acetylene on Ag^+ solutions gives a yellow precipitate:

$$C_2H_2 + 2Ag^+ = AgC{\equiv}CAg + 2H^+$$

19-I-3. Compounds of Silver(II),[21a] d^9

There are but few binary compounds. The black oxide AgO, obtained by ozonation of Ag_2O in water[21b] or by electrolysis of 2 *M* $AgNO_3$ solutions, is actually $Ag^IAg^{III}O_2$.

Silver(II) fluoride is obtained as a dark brown solid by fluorination of AgF or other Ag compounds at elevated temperatures. It is evidently an Ag^{II} compound, although it is antiferromagnetic, with a magnetic moment well below that expected for one unpaired electron. It is a useful fluorinating agent. It is hydrolyzed rapidly by water.

Silver(II) fluorosulfate is made by heating Ag with $S_2O_6F_2$ at 70°C and is stable to 210°C.

The aqua ion, $[Ag(H_2O)_4]^{2+}$, which is paramagnetic with one unpaired

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[21a] W. Levason and M. D. Spicer, *Coord. Chem. Rev.*, 1987, **76**, 45.

[21b] T. Tissot, *Polyhedron,* 1987, **6**, 1309.

electron, is obtained in $HClO_4$ or HNO_3 solution by oxidation of Ag^+ with ozone or by dissolution of AgO in acid.

The potentials for the Ag^{2+}/Ag^+ couple, +2.00 V in 4 M $HClO_4$ and +1.93 V in 4 M HNO_3, show that Ag^{2+} is a powerful oxidizing agent. There is evidence for complexing by NO_3^-, SO_4^{2-}, and ClO_4^- in solution, and the electronic spectra in $HClO_4$ solutions are dependent on acid concentration. The ion is reduced by water, even in strongly acid solution, but the mechanism is complicated.

Although the disproportionations

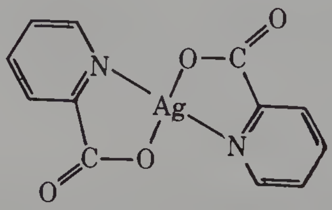
$$2Cu^+ = Cu + Cu^{2+} \qquad \text{and} \qquad 3Au^+ = 2Au + Au^{3+}$$

have been long known, only recently has a ligand-induced disproportionation of Ag^+ been discovered. The low heat of hydration of Ag^{2+} makes the equilibrium unfavorable in water:

$$2Ag^+ = Ag + Ag^{2+} \qquad K \approx 10^{-20}$$

However, using a tetraazamacrocyclic ligand (L) this has been achieved in both H_2O and molar CN^- solutions, and a paramagnetic complex AgL^{2+}, has been isolated. Normally, however, Ag^{II} species can be obtained only by oxidation.

Many oxidations (e.g., of oxalate) by the peroxodisulfate ion are catalyzed by Ag^+ ion, and the kinetics are best interpreted by assuming initial oxidation to Ag^{2+}, which is then reduced by the substrate. Decarboxylation of carboxylic acids is also promoted by Ag^{II} complexes, such as (19-I-VII), and others.[22]



(19-I-VII)

Numerous complexes of Ag^{II} are known, and they are normally prepared by peroxosulfate oxidation of Ag^+ solutions containing the complexing ligand. With neutral ligands cationic species such as $[Ag(py)_4]^{2+}$, $[Ag(bipy)_2]^{2+}$, and $[Ag(phen)_2]^{2+}$ form crystalline salts, whereas with uninegative chelating ligands such as 2-pyridinecarboxylate, neutral species such as (19-I-VII) are obtained. Neutral porphyrin complexes are also known; they dimerize in solution, as evidenced by epr but the structures of the dimers are unknown.[23] In acid solution the $[Ag(bipy)_2]^{2+}$ ion is in equilibrium with the $[Ag(bipy)]^{2+}$ ion[24] and it is the latter that oxidizes H_2O_2 in acid solution.[25]

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[22] W. E. Fristad and J. A. Klang, *Tetrahedron Lett.* 1983, **24,** 2219.
[23] S. Konishi *et al., J. Phys. Chem.,* 1983, **86,** 4888.
[24] M. P. Heyward and C. F. Wells, *J. Chem. Soc. Dalton Trans.,* **1981,** 431.
[25] M. P. Heyward and C. F. Wells, *J. Chem. Soc. Dalton Trans.,*,.**1981,** 1863.

The Ag^{II} complexes have $\mu_{eff} = 1.75$ to 2.2 BM, consistent with the d^9 configuration, and their electronic spectra accord with square coordination. The salt $[Ag(py)_4]S_2O_8$ and the bispicolinate (19-I-VII) are isomorphous with the planar copper(II) analogues.

19-I-4. Compounds of Silver(III), d^8

Few simple compounds are known. Anodic oxidation of Ag^I in alkaline solution yields Ag_2O_3 in impure form. As mentioned previously, Ag^{III} is present in AgO, where it has square coordination while the Ag^I coordination is linear. When AgO is dissolved in acid a comproportionation occurs:

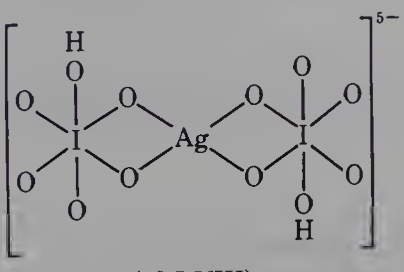
$$AgO^+ + Ag^+ + 2H^+ \longrightarrow 2Ag^{2+} + H_2O$$

but, in the presence of complexing agents in alkaline solution, Ag^{III} complexes are obtained (see later). The separation of Ag^I and Ag^{III} can be made by the reaction

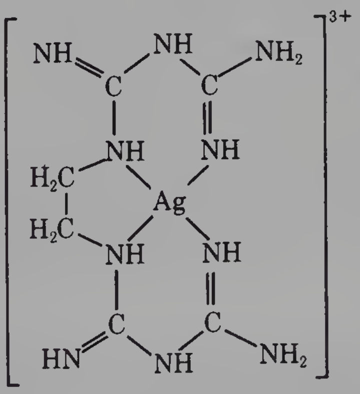
$$4AgO + 6KOH + 4KIO_4 \longrightarrow 2K_5H_2[Ag^{III}(IO_6)_2] + Ag_2O + H_2O$$

Unusual salts of stoichiometry $Ag_7O_8^+\ HF_2^-$, which are obtained as black needles by electrolysis of aqueous solutions of AgF, contain a polyhedral ion, $Ag_6O_8^+$, that acts as a clathrate to enclose Ag^+ and HF_2^-. The salts thus contain Ag^I and Ag^{III} with an average oxidation state of $2\frac{3}{7}$.

Complexes of Silver(III). The anodic oxidation of silver metal in strong KOH solution gives the yellow tetrahydroxoargentate(III) ion $[Ag(OH)_4]^-$, which has a half-life of ~100 min in 1.2 *M* NaOH, (<30 min in 0.1 *M* NaOH), decomposing to AgO and O_2. The anion reacts rapidly with tellurate or periodate to give very stable complexes, which are usually obtained by direct oxidation of Ag^+ in alkaline solutions by $K_2S_2O_8$ in the presence of periodate or tellurate ions. Representative are the ions $\{Ag[TeO_4(OH)_2]_2\}^{5-}$ and $\{Ag[IO_5(OH)]_2\}^{5-}$; copper(III) complexes (Section 18-H-4) are analogous, and all the ions appear to have Te—OH or I—OH groups as in (19-I-VIII).



(19-I-VIII)



(19-I-IX)

In acid solution, the AgO^+ ion is extensively hydrolyzed even in 1.5 to 6 *M* acid. An Ag^{III} complex of remarkable stability is the one with ethylenedibiguanide (19-I-IX), which is obtained as the red sulfate when Ag_2SO_4 is treated with aqueous potassium peroxodisulfate in the presence of ethylenedibiguanidinium sulfate. The hydroxide, nitrate, and perchlorate have been prepared metathetically. These salts are diamagnetic and oxidize two equivalents of iodide ion per gram-atom of silver. Silver(III) porphyrin complexes are also stable.

Less accessible are the yellow fluoro complexes, (e.g., $KAgF_4$ or Cs_2KAgF_6), obtained by action of F_2 at 300°C on a stoichiometric mixture of the alkali chlorides and silver nitrate. The AgF_6^{3-} ion appears to be octahedral according to its magnetism and electronic absorption spectrum.

19-I-5. Compounds of Gold (I)

Simple Compounds. No Au^I oxide is known although AuO contains Au^I along with Au^{III}. The gold sulfide (Au_2S) is a very insoluble, luminescent solid. The three gold(I) halides, AuCl, AuBr, and AuI, are all well characterized. They form chain structures with linear X—Au—X groups linked by angular (72–90°) Au—X—Au bridges.

Complexes. The $[AuX_2]^-$ ions are all known as linear, symmetrical species in crystalline solids. They also exist in aqueous solution where $[AuI_2]^-$ is stable but $[AuCl_2]^-$ and $[AuBr_2]^-$ disproportionate according to eq. 19-I-1 unless excess halide is present. Similar $[Au(N_3)_2]^-$ and $[Au(SCN)_2]^-$ ions are known also.

$$3[AuX_2]^- = [AuX_4]^- + 2Au + 2Cl^- \qquad (19\text{-I-}1)$$

The majority of other Au^I complexes are also linear and tend to be of the LAuX type where L is a neutral donor such as R_3P or R_2S and X is a halogen, pseudohalogen or RS. The phosphine complexes are particularly stable and easy to prepare. Those with thioether ligands, for example, $(R_2S)AuCl$, are useful preparative intermediates since R_2S is easily displaced by other good ligands for gold(I).[26] With higher concentrations of R_3P ligands higher coordination numbers are achieved, as in $(Ph_3P)_3AuCl$, $(Ph_3P)_3AuSCN$, and $[Au(PMePh_2)_4][PF_6]$, where tetrahedral coordination is found.[27]

Gold(I) thiolates, $[AuSR]_n$, have been extensively studied in relation to chemotherapy for arthritis. They exist as linear and cyclic oligomeric or polymeric species.[28a] Other gold compounds such as $[Au\ mesityl]_5$ and $[Au(3,5\text{-diphenylpyrazolate})]_6$ are also oligomers.[28b]

Chemotherapeutic applications of gold compounds and complexes, principally to treating rheumatoid arthritis, have been extensively studied recently

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[26] R. Usón *et al., Inorg. Chim. Acta,* 1983, **73,** 63.

[27] P. T. Beurskens *et al., Cryst. Struct. Commun.,* 1982, **11,** 1039; P. G. Jones, *Acta Crystallogr.* 1980, **B36,** 3105; P. G. Jones, *Z. Naturforsch.,* 1982, **B37,** 937.

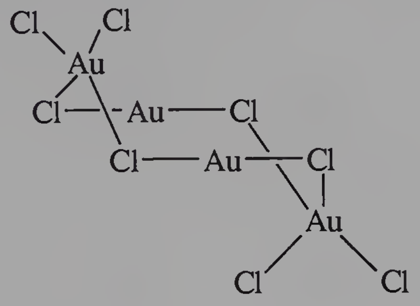
[28a] A. A. Islab and P. J. Sadler, *J. Chem. Soc. Dalton Trans.,* **1981,** 1657; **1982,** 135; C. F. Shaw *et al., J. Inorg. Biochem.,* 1981, **14,** 267.

[28b] J. P. Fackler *et al., J. Chem. Soc. Chem. Commun.,* **1987,** 737.

and this has spawned an enormous literature.[29] The mechanism of action is not clear but interaction of gold(I) centers with thiol groups of proteins and enzymes is believed to be critical.

19-I-6. Compounds of Gold(II)

Atomic ionization potentials show that it is more difficult to obtain Au^{2+} than either Cu^{2+} or Ag^{2+}, but easier to obtain Au^{3+} than either of the other two +3 ions. It is thus not surprising that genuine gold(II) compounds are rare, unless special factors come into play. Thus $Au_2(SO_4)_2$ contains Au^I and Au^{III} as does Au_4Cl_8, which has the structure (19-I-X).[30]



(19-I-X)

Both are diamagnetic. In a few cases Au^{II} is stabilized by extensive delocalization into ligand orbitals so that the oxidation state assignment is blurred. Examples as $Au(mnt)_2^{2-}$ and Au(phthalocyanine).

The only extensive series of genuine Au^{II} compounds are the dinuclear ones with Au—Au bonds. These are obtained by oxidative-additions to dinuclear Au^I phosphine ylide complexes,[31] as shown in Fig. 19-I-2. Even these compounds have somewhat limited stability. In several cases the oxidative-addition reaction is reversible and in others, the Au^{II}—Au^{II} unit is transformed by ligand transfers to an Au^I, Au^{III} pair. Furthermore, oxidative-addition to the Au^{II}—Au^{II} species often proceeds readily to give a Au^{III}, Au^{III} compound. All of these processes are shown schematically in Fig. 19-I-2.

In addition to the $Au_2(CH_2PR_2CH_2)_2$ based chemistry shown in Fig. 19-I-2, there are related bridged dinuclear Au^I complexes that can similarly be oxidized to give Au^{II}—Au^{II} bonds, namely, $Au_2(S_2CNR_2)_2$, $Au_2(CH_2PPh_2S)_2$, and $Au_2Cl_2(Ph_2PCR_2PPh_2)_2$.[32]

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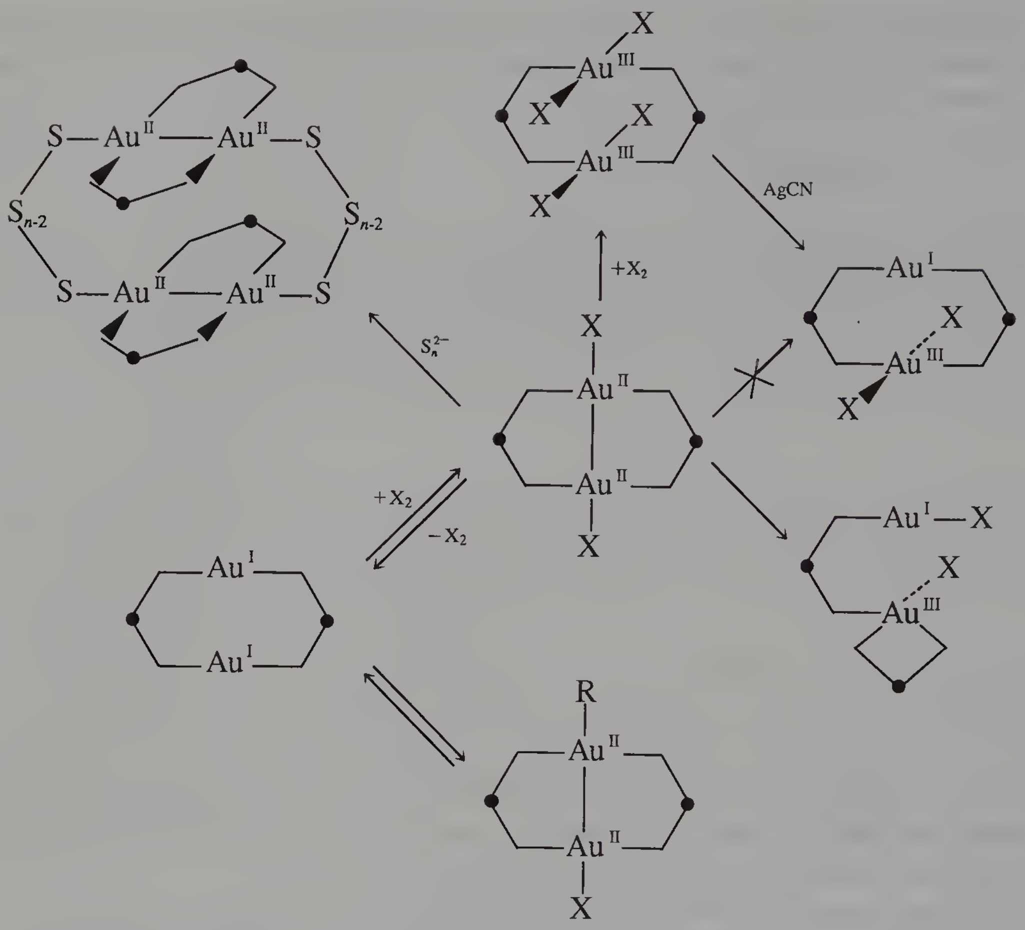
[29] S. J. Lippard, Ed., *Platinum, Gold and Other Metal Chemotherapeutic Agents: Chemistry and Biochemistry* (ACS Symposium Series, No. 209), American Chemical Society, Washington, DC, 1983; A. J. Lewis and D. T. Walz, *Prog. Med. Chem.*, 1982, **19**, 1; D. H. Brown and W. E. Smith, *Chem. Soc. Rev.*, 1980, **9**, 217; S. J. Berners-Price and P. J. Sadler, *Chem. Br.*, **1987**, 541.

[30] F. Calderazzo *et al.*, *J. Chem. Soc. Dalton Trans.*, **1982**, 2257.

[31] J. P. Fackler, Jr., *et al.*, *Organometallics*, 1985, **4**, 1891; *J. Am. Chem. Soc.*, 1985, **107**, 6908; *J. Chem. Soc. Chem. Commun.*, **1986**, 321; *J. Am. Chem. Soc.*, 1986, **108**, 2750; *Inorg. Chim. Acta*, 1986, **114**, 171; M. A. Bennett *et al.*, *Angew Chem. Int. Ed. Engl.*, 1987, **26**, 258, 259.

[32] H. Schmidbauer *et al.*, *Z. Naturforsch.*, 1983, **B38**, 62; J. L. Burmeister *et al.*, *Inorg. Chem.*, 1981, **20**, 4311; J. P. Fackler, Jr., *et al.*, *Inorg. Chem.*, 1987, **26**, 357.



R = Me, CCl_3; X = Cl, Br, I; $\wedge$ = $H_2CPR_2CH_2$(R = Me, Ph)

FIG. 19-I-2. Some reactions involving ylide bridged Au^{II}—Au^{II} compounds.

19-I-7. Compounds of Gold(III)

Simple Compounds. These, except the halides, play a minor role in gold(III) chemistry. Gold trioxide (Au_2O_3) is obtained in hydrated form as an amorphous brown precipitate on addition of base to $AuCl_4^-$ solutions. It decomposes on heating to Au, O_2, and H_2O. It is weakly acidic and dissolves in excess strong base, probably as $Au(OH)_4^-$. Crystalline Au_2O_3, made by hydrothermal methods, contains square AuO_4 groups sharing O atoms. Au_2E_3 (E = S, Se, and Te) exist but their structures are unknown.

Halides. *Gold*(III) *fluoride* is best made by fluorination of Au_2Cl_6 at 300°C and forms orange crystals, which decompose to the metal at 500°C. It has a unique structure with square AuF_4 units linked into a chain by cis fluoride bridges; the F atoms of adjacent chains interact weakly with the axial sites.

The *chloride* and *bromide*, which form red crystals, are made by direct interaction, but Au_2Cl_6 is best made by the reaction

$$2H_3O^+AuCl_4^- + 2SOCl_2 = 2SO_2 + 6HCl + Au_2Cl_6$$

Both are dimers in the solid and in the vapor. They dissolve in water, undergoing hydrolysis, but in HX the ions AuX_4^- are formed. Gold(III)chloride (or $AuCl_4$) is a powerful oxidant, being reduced to Au; it will, for example, oxidize ruthenium complexes in aqueous solution to RuO_4.

Complexes. Gold(III) like Pt^{II} displays predominantly square coordination. Although there is little evidence for any persisting five-coordinate complexes, there is no doubt that, as with Pt^{II} species, substitution reactions proceed via five-coordinate intermediates. There is no evidence for a simple aqua ion, $[Au(H_2O)_4]^{3+}$ but mixed chloro-aqua and chloro-hydroxo complexes are formed by hydrolysis of $[AuCl_4]^-$. Distorted octahedral coordination occurs rarely, $[Au(en)_2Cl_2]^+$ being an example.[33]

Complexes of the type $[AuX_4]^-$ where X is a halogen or pseudohalogen are well characterized. By action of BrF_3 on a mixture of gold and an alkali metal chloride the M^IAuF_4 compounds may be obtained.

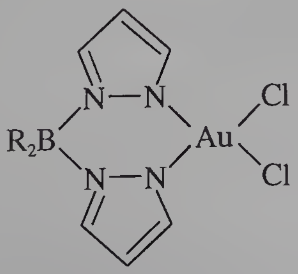
When gold is dissolved in aqua regia or Au_2Cl_6 is dissolved in HCl and the solution of $AuCl_4^-$ is evaporated, *chloroauric acid* can be obtained as yellow crystals $[H_3O]^+[AuCl_4]^-\cdot 3H_2O$. Other water-soluble salts such as $KAuCl_4$ and $NaAuCl_4\cdot 2H_2O$ are readily obtained. In water, hydrolysis to $AuCl_3OH^-$ occurs. From the dilute hydrochloric acid solutions the gold can be solvent extracted with a very high partition coefficient into ethyl acetate or diethyl ether; the species in the organic solvent appears to be $[AuCl_3OH]^-$, which is presumably associated in an ion pair with an oxonium ion. Gold is readily recovered from such solutions (e.g., by precipitation with SO_2).

The $[AuBr_4]^-$ ion is similar to $[AuCl_4]^-$ but $[AuI_4]^-$, obtainable in solid compounds, is subject to the decomposition in solution:

$$[AuI_4]^- = [AuI_2]^- + I_2 \qquad K \approx 0.005$$

Other $[AuX_4]^-$ complexes are those with $X^- = SCN^-$ (*S*-bonded), N_3^-,[34] and CN^-. The reactions of $AuCl_3$ with ECl_4 (E = S, Se, and Te) gives compounds that contain distorted $[AuCl_4]^-$ ions with one Cl bridging to the ECl_3^+ ion.[35]

Many neutral complexes can be obtained as simple adducts of R_3E (E = P, As, and Sb) with AuX_3, for example, $(Et_3P)AuCl_3$ and $(Et_3P)Au(CN)_3$.[36] With bidentate chelating anionic ligands, species such as (19-I-XI) can be obtained.



(19-I-IX)

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[33] L. K. Minacheva *et al.*, *Koord. Khim.*, 1983, **9**, 566.

[34] W. Beck and H. Nöth, *Chem. Ber.*, 1984, **117**, 419.

[35] P. N. Gates, *et al.*, *J. Chem. Soc. Dalton Trans.*, **1983**, 1837.

[36] C. F. Shaw *et al.*, *Inorg. Chem.*, 1986, **25**, 3953.

The cationic complex $[Au(NH_3)_4]^{3+}$ is well characterized and numerous others exist, for example, $[Au\ py_2Cl_2]^+$ and $[Au\ dien\ Cl]^{2+}$.

19-I-8. Metal Atom Cluster Species[37]

The gold compounds used for decorating china and glass articles and known as "liquid golds" are made by interaction of gold(III) chloro complexes with sulfurized terpenes or resins and are very soluble in organic solvents. Doubtless they were the first known, though unrecognized, thiolate gold aggregates.

Modern work on gold cluster complexes (for which there are, incidently, no known silver analogues) centers on the reduction, usually by $NaBH_4$, of R_3PAuX compounds ($X = Cl^-, Br^-, NO_3^-$, etc.). In one case B_2H_6 has been used to reduce Ph_3PAuCl, resulting in the formation of $Au_{55}(PPh_3)_{12}Cl_6$. This is the largest metal atom cluster compound presently known, and is thought to contain a cubo-octahedral fragment of close-packed metal atoms.[38] With $NaBH_4$, however, the products are Au_9 or Au_{11} species. There are also Au_n cluster compounds with $n = 4, 5, 6, 8$, and 13.

The structures of the gold cluster species are partly known. For some of them it is clear that the potential energy surface interconnecting alternative polyhedral geometries is relatively flat allowing skeletal isomers to exist and to interconvert easily. To some extent, the structures can be rationalized on the motif of a centered icosahedron. Such a structure is found for an Au_{13} cluster, Fig. 19-I-3(a), and those of Au_{11} and Au_9 species can be viewed as

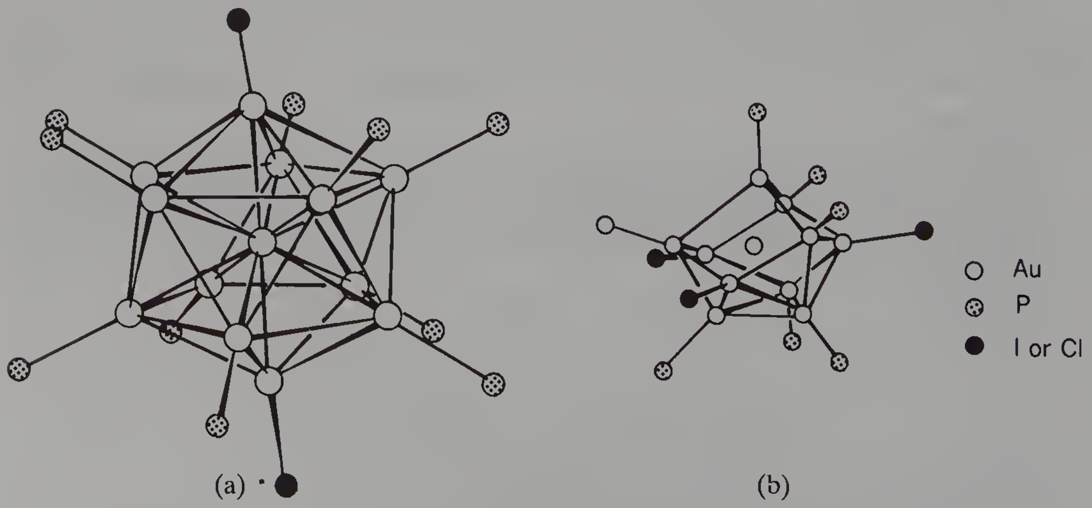

FIG. 19-I-3. (a) The centered icosahedral structure found in $[Au_{13}Cl_2(PMe_2Ph)_{10}](PF_6)_3$ and (b) the distorted icosahedral fragment found in $Au_{11}I_3[P(tol)_3]_7$.

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[37] D. M. P. Mingos *et al., Prog. Inorg. Chem.*, 1984, **32,** 237; *Polyhedron,* 1984, **3,** 1289.
[38] G. Schmid *et al., Chem. Ber.*, 1981, **114,** 3634.

fragments thereof, in which the central Au atom remains, while two or four peripheral ones are lost, followed by some distortion to maximize Au—Au bonding. This can be seen in Fig. 19-I-3(b). Smaller clusters, such as the two Au_4 types[39] cannot, obviously, be understood in this way, nor can the $[Au_7(PPh_3)_7]^+$ cluster, which has a pentagonal bipyramidal structure.[40]

19-I-9. Organogold Compounds.[41]

Alkyl derivatives of gold were among the first organometallic compounds of transition metals to be prepared. Both gold(I) and gold(III) compounds with σ bonds to carbon, as well as olefin complexes, are known.

Gold(I) complexes are mainly of the type RAuL, where L is a stabilizing ligand such as R_2S,R_3P, or RNC. They are made from the corresponding halides by action of LiR or RMgX. Acetylides such as $(R_3PAuC{\equiv}CR')_n$ are also known.

Gold (III) compounds are mainly complexes of the types R_3AuL,[42] $[R_2AuL_2]^+$,[43] or R_2AuXL. Aryl gold(III) compounds are also well known; those containing the $C_6F_5^-$ group, e.g., $[Au(C_6F_5)_4]^-$, are particularly numerous and stable.[32b,44] Another notable group of Au^{III} organometallic compounds are those containing ylides, for example $(CH_3)_3AuCH_2S(O)(CH_3)_2$ and $(CH_3)_3AuCH_2PPh_3$.[45] We have already mentioned (see Section 19-I-6) the dinuclear gold ylides that give a variety of gold oxidation states.

Although the formation of Au^{III} from Au^I compounds could be anticipated, oxidative-addition reactions such as

$$MeAu^IPR_3 + CH_3I = (Me)_2Au^{III}IPR_3$$

are slow and are complicated mechanistically. Additions to anionic Au^I species proceed more rapidly, for example,

$$RAuPEt_3 + R'Li = Li[AuRR'PEt_3] \xrightarrow{R''X} RR'R''AuPEt_3 + LiX$$

Interaction of the triphenylphosphine complexes of gold(I) and gold(III), $MeAuPPh_3$, and Me_3AuPPh_3, respectively, with methyllithium in ether gives the methylate ions $[AuMe_2]^-$ and $[AuMe_4]^-$, which can be isolated as lithium amine salts and are the most stable organogold compounds.

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[39] M. Manassero *et al., J. Chem. Soc. Chem. Commun.,* **1981,** 222; J. W. A. van der Velden *et al., Inorg. Chem.,* 1983, **22,** 3112.

[40] J. W. A. van der Velden *et al., Inorg. Chem.,* 1984, **23,** 146; D. G. Evans and M. P. Mingos, *J. Organometal. Chem.,* 1985, **295,** 389.

[41] G. K. Anderson, *Adv. Organomet. Chem.,* 1982, **20,** 39.

[42] G. M. Bancroft *et al., Inorg. Chem.,* 1983, **22,** 2133.

[43] A. J. Canty *et al., J. Chem. Soc. Dalton Trans.,* **1982,** 1795.

[44] R. Usón and A. Laguna, *Coord. Chem. Rev.,* 1986, **70,** 1; J. P. Fackler Jr. *et al., Inorg. Chem.,* 1987, **26,** 357.

[45] J. P. Fackler, Jr., *et al., J. Am. Chem. Soc.,* 1981, **103,** 2192.

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Gold Bulletin, a periodical publication frequently containing technical reviews. See, in particular, reviews of structures by P. G. Jones, in 1981, **14,** 102, 159; 1983, **16,** 114; 1986, **19,** 46.

Melnik, M., and R. V. Parrish, *Coord. Chem. Rev.,* 1986, **70,** 157 (review of X-ray and Mössbauer data and coordination numbers of gold compounds).

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Puddephat, R. J., *The Chemistry of Gold,* Elsevier, Amsterdam, 1978.

Smith, W. E., *Coord. Chem. Rev.,* 1982, **45,** 307, 319.

Chapter Twenty

The Lanthanides; Also Scandium IIIB(3) and Yttrium IIIB(3)

GENERAL

20-1. Lanthanides and the Lanthanide Contraction

The term lanthanides strictly defined refers to the 14 elements following lanthanum in the periodic table, but as normally used also includes lanthanum itself. From lanthanum ($Z = 57$) to lutetium ($Z = 71$) we go from a $[Xe]4f^0$ to a $[Xe]4f^{14}$ configuration. Since the $4f$ electrons are *relatively* uninvolved in bonding, these highly electropositive elements have as their prime oxidation number +3 and, overall, closely resemble one another chemically and physically. They generally occur together in Nature. Table 20-1 gives a complete list of the lanthanide elements and some of their properties.

The element *yttrium,* Y, ($Z = 39$), which lies above La, and has a similar +3 ion with a noble gas core, [Ar], has atomic and ionic radii close to those for terbium and dysprosium. It therefore resembles them closely in its chemistry and is generally found in Nature with the lanthanides. The lanthanides plus yttrium are commonly called the *rare earths,* although many of them are relatively abundant. Lanthanum, Ce, and Nd are all more abundant than lead.

The element above yttrium is scandium, Sc. The radii of scandium are appreciably smaller than those for any of the rare earth elements and its chemical behavior is intermediate between that of aluminum and that of lanthanides. It is not, therefore, truly a rare earth, but it is convenient to discuss its chemistry in this chapter.

An important feature of the lanthanide elements is the occurrence of the *lanthanide contraction,* a steady decrease in atomic and ionic size with increasing atomic number. The lanthanium +3 ion has a radius ~0.13 Å larger than that of Y^{3+} and if the next 14 elements did not intervene (if, in other words, La with its $[Xe]5d6s^2$ configuration were followed by an element with

TABLE 20-1
Some Properties of Lanthanide Atoms and Ions[a]

Atomic number	Name	Symbol	Electronic configuration[b] Atom	Electronic configuration[b] M^{3+}	E^0(V)[c]	Radius[d] M^{3+} (Å)
57	Lanthanum	La	$5d6s^2$	[Xe]	−2.37	1.17
58	Cerium	Ce	$4f^15d^16s^2$	$4f^1$	−2.34	1.15
59	Praseodymium	Pr	$4f^36s^2$	$4f^2$	−2.35	1.13
60	Neodymium	Nd	$4f^46s^2$	$4f^3$	−2.32	1.12
61	Promethium	Pm	$4f^56s^2$	$4f^4$	−2.29	1.11
62	Samarium	Sm	$4f^66s^2$	$4f^5$	−2.30	1.10
63	Europium	Eu	$4f^76s^2$	$4f^6$	−1.99	1.09
64	Gadolinium	Gd	$4f^75d6s^2$	$4f^7$	−2.29	1.08
65	Terbium	Tb	$4f^96s^2$	$4f^8$	−2.30	1.06
66	Dysprosium	Dy	$4f^{10}6s^2$	$4f^9$	−2.29	1.05
67	Holmium	Ho	$4f^{11}6s^2$	$4f^{10}$	−2.33	1.04
68	Erbium	Er	$4f^{12}6s^2$	$4f^{11}$	−2.31	1.03
69	Thulium	Tm	$4f^{13}6s^2$	$4f^{12}$	−2.31	1.02
70	Ytterbium	Yb	$4f^{14}6s^2$	$4f^{13}$	−2.22	1.01
71	Lutetium	Lu	$4f^{14}5d6s^2$	$4f^{14}$	−2.30	1.00

[a] See also L. R. Morss, *Chem. Rev.* 1976, **76,** 827 and W. C. Martin *et al.*, *J. Phys. Chem. Ref. Data*, 1974, 3, 771.

[b] Only the valence shell electrons, that is, those outside the [Xe] shell, are given.

[c] For $M^{3+} + 3e = M$, D. A. Johnson, *J. Chem. Soc. Dalton Trans.* **1974,** 1671; L. J. Nugent, *J. Inorg. Nucl. Chem.*, 1975, **37,** 1767 (other values: Sc = −1.88 V, Y = −2.37 V).

[d] Values are from R. D. Shannon, *Acta Crystallogr.*, 1976, **A32,** 751 (for CN = 6, Sc^{+3} = 0.89, Y^{+3} = 1.04, Å).

a $[Xe]5d^26s^2$ configuration) we should expect that element, standing where hafnium does, to have radii ~0.13 Å larger than those of zirconium. Instead, there is a steady shrinkage whose cumulative effect is to make the hafnium atom almost exactly the same size as the zirconium atom.

A major cause of the lanthanide contraction is the electrostatic effect of increasing nuclear charge very imperfectly screened by the 4*f* electrons. In this sense it is comparable to the smaller contractions observed through each of the *d*-block transition series. Since the 4*f* electrons screen the outer electrons even more poorly than do the *nd* electrons, and because there are 14 lanthanides, the cumulative effect is greater. The chemistry of the Ln^{3+} ions (Ln being a generic symbol for these elements) thus changes gradually across the series in the ways that would be expected for increasing charge to radius ratio, but the trend is not completely smooth.

It has been concluded in recent years that the lanthanide contraction is also partly due to relativistic effects which influence the shielding characteristics of inner shell electrons.[1a]

[1a] K. S. Pitzer, *Acc. Chem. Res.*, 1979, **12,** 271.

20-2. Oxidation States

The sum of the first three ionization enthalpies is comparatively low, so that the elements are highly electropositive. They readily form +3 ions in solids like oxides and in aqua ions, $[M(H_2O)_n]^{3+}$, and complexes. However, cerium can give Ce^{4+} and Sm, Eu, and Yb, the M^{2+} ions, in aqueous solutions and in solids. Other elements can give the +4 state in solids, whereas the reduction of MX_3 with M can give not only MX_2 but in certain cases other more complicated reduced species that may have metal-metal bonds.

Formerly the existence of +2 and +4 oxidation states was simply ascribed to the extra stability associated with the formation of stable empty $4f^0$ (Ce^{4+}), half-filled $4f^7$ (Eu^{2+}, Tb^{4+}), and filled $4f^{14}$ (Yb^{2+}) subshells. This argument is unconvincing when we note that Sm and Tm give M^{2+} species having f^6 and f^{13} configurations but no M^+ ion, whereas Pr and Nd give M^{4+} ions with configurations f^1 and f^2 but no penta- or hexavalent species. The idea that stability is already favored by the mere *approach* to an f^0, f^7, or f^{14} configuration, even though such a configuration is not actually attained, is of dubious validity. The existence of the various oxidation states is best interpreted by consideration of the ionization enthalpies, enthalpies of sublimation of the metals, lattice energies, and so on, in Born–Haber cycles.[1b] For the +2 state, as we shall see later, there is a good correlation with the enthalpies of sublimation of the metals.

20-3. Magnetism and Spectra

In their magnetic and spectroscopic properties the lanthanides show important differences from the *d*-block elements. This happens because the 4*f* electrons are pretty well (although not totally) shielded from external fields by the overlying $5s^2$ and $5p^6$ shells. The states arising from the various $4f^n$ configurations therefore tend to remain nearly invariant for a given ion.

The states of the $4f^n$ configurations are all given, to a useful approximation, by the Russell–Saunders coupling scheme. In addition, the spin-orbit coupling constants are quite large (order of 1000 cm^{-1}). The result of all this is that with only a few exceptions, the lanthanide ions have ground states with a single well-defined value of the total angular momentum J, with the next lowest J state at energies many times kT (at ordinary temperatures equal to ~200 cm^{-1}) above, hence virtually unpopulated.

Thus the susceptibilities and magnetic moments should be given straightforwardly by formulas considering only this one well-defined J state, and indeed such calculations give results that are, with only two exceptions, in excellent agreement with experimental values (Fig. 20-1). For Sm^{3+} and

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[1b] D. A. Johnson, *Thermodynamic Aspects of Inorganic Chemistry* 2nd ed., Cambridge University Press, 1982.

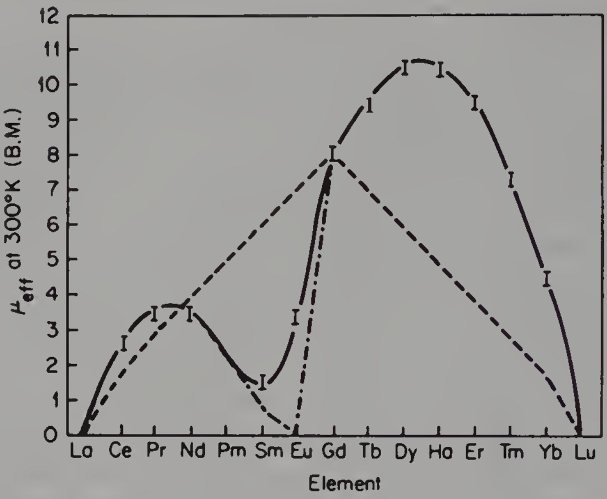

FIG. 20-1. Measured and calculated effective magnetic moments of lanthanide M^{3+} ions at 300 K: I's are ranges of experimental values; solid curve gives values calculated for appropriate *J* ground states with allowance for the Sm and Eu anomalies; dash–dot curve gives values calculated without allowance for the Sm and Eu anomalies; dashed curve gives calculated spin-only values.

Eu^{3+}, it turns out that the first excited *J* state is sufficiently close to the ground state for this state (and in the case of Eu^{3+} even the second and third excited states) to be appreciably populated at ordinary temperatures. Since these excited states have higher *J* values than the ground state, the actual magnetic moments are higher than those calculated by considering the ground states only. Calculations taking into account the population of excited states afford results in excellent agreement with experiment (Fig. 20-1).

It should be emphasized that magnetic behavior depending on *J* values is qualitatively different from that depending on *S* values—that is, the "spin-only" behavior—which gives a fair approximation for many of the *d*-block transition elements. Only for the f^0, f^7, and f^{14} cases, where there is no orbital angular momentum ($J = S$), do the two treatments give the same answer. For the lanthanides the external fields do not either appreciably split the free-ion terms or quench the orbital angular momentum.

Because the *f* orbitals are so well shielded from the surroundings of the ions, the various states arising from the f^n configurations are split by external fields only to the extent of ~100 cm^{-1}. Thus when electronic transitions, called *f–f* transitions, occur from one *J* state of an f^n configuration to another *J* state of this configuration, the absorption bands are *extremely sharp*. They are similar to those for free atoms and are quite unlike the broad bands observed for the *d–d* transitions. Virtually all the absorption bands found in the visible and near-uv spectra of the lanthanide +3 ions have this linelike character. The intensities of the *f–f* bands show measurable sensitivity to the nature of the coordination sphere but the relationship is complex and not quantitatively understood.[2]

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[2] F. S. Richardson *et al., Inorg. Chem.,* 1984, **23,** 4607, 4611.

TABLE 20-2
Colors and Electronic Ground States of the M^{3+} Ions

Ion	Ground state	Color	Ion	Ground state
La	$^1S_0$	Colorless	Lu	$^1S_0$
Ce	$^2F_{5/2}$	Colorless	Yb	$^2F_{7/2}$
Pr	$^3H_4$	Green	Tm	$^3H_6$
Nd	$^4I_{9/2}$	Lilac	Er	$^4I_{15/2}$
Pm	$^5I_4$	Pink; yellow	Ho	$^5I_8$
Sm	$^6H_{5/2}$	Yellow	Dy	$^6H_{15/2}$
Eu	$^7F_0$	Pale pink	Tb	$^7F_6$
Gd	$^8S_{7/2}$	Colorless	Gd	$^8S_{7/2}$

The colors and electronic ground states of the M^{3+} ions are given in Table 20-2; the color sequence in the La to Gd series is accidentally repeated in the series Lu to Gd. As implied by the earlier discussion, insofar as the colors are due to the *f–f* transitions, they are virtually independent of the environment of the ions.

An important feature in the spectroscopic behavior is that of fluorescence or luminescence of certain lanthanide ions, notably Tb, Ho, and Eu. They are used commercially in oxide phosphors for television tubes and related devices. The luminescence of the Eu^{3+} ion can be used as a probe of its environment, giving information on ligand charges, binding constants, site symmetry, number of OH or NH bonds in the first coordination sphere and ligand exchange rates.[3]

Finally, it may be noted that several of the paramagnetic lanthanide ions, especially Pr^{3+}, Eu^{3+}, and Yb^{3+} are useful as nmr shift reagents. When an organic molecule with a complex nmr spectrum is coordinated to one of these ions, the large magnetic moment of the ion causes displacements and a spreading out of the spectrum and this often helps in assigning and interpreting the peaks.[4]

20-4. Coordination Numbers and Stereochemistry

Examples of the various coordination numbers and stereochemistries are presented in Table 20-3. The most common coordination numbers are 8 and 9. Many previously accepted examples of coordination number 6 are actually invalid because coordinated solvent molecules are present and raise the true coordination number to 7, 8, or 9.

The considerable change in size of the Ln^{3+} ions from La^{3+} (1.17 Å) to Lu^{3+} (1.00 Å) means that homologous compounds of lanthanides with appreciably different radii may differ in structure. For example, the

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[3] W. D. Horrocks, Jr., *et al., Inorg. Chem.*, 1985, **24,** 895, 4591.

[4] R. E. Sievers, Ed., *Nuclear Magnetic Resonance Shift Reagents,* Academic Press, New York, 1973.

TABLE 20-3
Oxidation States, Coordination Numbers, and Stereochemistry of Lanthanide Ions

Oxidation state	Coordination number	Geometry	Examples
+2	6	NaCl type	EuTe, SmO, YbSe
	6	CdI_2 type	YbI_2
	8	CaF_2 type	SmF_2
+3	3	Pyramidal	$M[N(SiMe_3)_2]_3$
	4	Distorted tetrahedral	$La[N(SiMe_3)_2]_3OPPh_3$
		Tetrahedral	$[Lu(mesityl)_4]^-$, $[Y(CH_2SiMe_3)_4]^-$
	6	Octahedral	$[Er(NCS)_6]^{3-}$, $[Sc(NCS)_2(bipy)_2]^+$, MX_6^{3-}
	6	$AlCl_3$ type	MCl_3(Tb–Lu)
	6	Distorted trigonal prism	$Pr[S_2P(C_6H_{11})_2]_3$
	7	Monocapped trigonal prism	Gd_2S_3, $Y(acac)_3 \cdot H_2O$
	7	ZrO_2 type	ScOF
	8	Distorted square antiprism	$Y(acac)_3 \cdot 3H_2O$; $La(acac)_3(H_2O)_2$
	8	Dodecahedral	$Cs[Y(CF_3COCHCOCF_3)_4]$
	8	Distorted dodecahedral	$Na[Lu(S_2CNEt_2)_4]$
	8	Cubic	$La[(bipyO_2)_4]^+$
	8	Bicapped trigonal prism	Gd_2S_3; MX_3($PuBr_3$ type)
	9	Tricapped distorted trigonal prism	$[Nd(H_2O)_9]^{3+}$, $Y(OH)_3$, $K[La(EDTA)] \cdot 8H_2O$, $La_2(SO_4)_3 \cdot 9H_2O$
	9	Complex	LaF_3, MCl_3(La–Gd), $[Sc(NO_3)_5]^{2-}$
	10	Complex	$La_2(CO_3)_3 \cdot 8H_2O$
	10	Bicapped dodecahedron	$Ce(NO_3)_5^{2-}$; $La(NO_3)_2(DMSO)_4$
	11	Complex	$La(NO_3)_3(H_2O)_5 \cdot H_2O$
	12	Distorted icosahedron	$Ce(NO_3)_6^{3-}$, $[Pr(1,8\text{-naphthyridine}]_6^{3+}$
+4	6	Octahedral	Cs_2CeCl_6
	8	Square antiprism	$Ce(acac)_4$
	8	Distorted square antiprism (chains)	$(NH_4)_2CeF_6$
	8	CaF_2 type	CeO_2
	10	Complex	$Ce(NO_3)_4(OPPh_3)_2$
	12	Distorted icosahedron	$(NH_4)_2[Ce(NO_3)_6]$

$Ln(CF_3CO_2)_3(C_4H_8SO)_2$ compounds with Ln = La and Nd have different structures; the La compound has dodecahedral coordination while the Nd compound has square antiprismatic coordination.[5]

Aqua ions found in crystalline compounds are generally nine-coordinate with the tri-capped trigonal prism being the favored structure.[6] The

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[5] E. E. Castellano *et al.*, *Inorg. Chim. Acta,* 1985, **110,** 77.

[6] J. C. Gallucci *et al.*, *Cryst. Struct. Commun.*, 1982, **11,** 1141; C. O. Paiva Santos *et al.*, *Inorg. Chim. Acta,* 1985, **110,** 83; J. C. Barnes and G. Y. R. Nicoll, *Inorg. Chim. Acta,* 1985, **110,** 47; A. White, *Aust. J. Chem.*, 1983, **36,** 483.

$[Ln(H_2O)_n]^{3+}$ ions in aqueous solution are either eight- or nine-coordinate and this may vary with ionic strength.[7]

20-5. Variations Through the Lanthanide Series

Despite the general similarities to be expected from the electronic structures and sizes of the elements and their ions, there are, nevertheless, some important variations in going from La to Lu.

1. *The +3 Ions.* As a result of the lanthanide contraction, changes in coordination through the series La to Lu are to be expected.

In the *solid state* there may be a pronounced change in structural type at one or more points in the series; at such changeover points a compound may have two or more crystal forms. Examples are the following:

(*a*) The anhydrous halides MCl_3 of La to Gd are all nine-coordinate with a UCl_3 type lattice; $TbCl_3$ and one form of $DyCl_3$ are of the $PuBr_3$ type, and the Tb–Lu chlorides have the octahedral $AlCl_3$ type structure.

(*b*) In the M_2S_3 series there are three main structure types: La to Dy (orthorhombic, eight- or seven-coordinate); Dy to Tm (monoclinic, seven- or six-coordinate; Ho_2S_3 actually has half its atoms six- and half seven-coordinate); Yb and Lu (corundum type, six-coordinate).

(*c*) The enthalpies of sublimation of certain volatile chelates show irregular decreases from Pr to Lu, but with a plateau at Gd.

(*d*) Because ligand field stabilization energies are very small for the lanthanide ions, the thermodynamic properties of their compounds as well as their electrode potentials can be fairly accurately correlated by equations based on the electrostatic consequences of charge and size.[8]

2. *The Metals.* The chemical properties of the metals are noted later, but here we point out that some physical properties, most importantly the enthalpy of sublimation (Fig. 20-2) show considerable differences, especially for the elements that have the greatest tendency to exist in the divalent state.

Unlike the other lanthanide metals, where the 6*s* and 5*d* electrons populate the conduction bonds, and the 4*f* electrons remain bound to the M^{3+} ions, for Eu and Yb only two electrons enter the conduction bands, thus leaving larger cores and affording lower binding forces. Note that the metallic radius of Eu (12-coordination) of 2.041 Å can be compared with those of Ca (1.976 Å), Ba (2.236 Å), and the next lanthanide Gd (1.802 Å). It may be noted also that corresponding to the variation in enthalpies of sublimation from 176 to 431 kJ mol^{-1} there is a 10^9 range in the actual vapor pressures of the metals at a given temperature.

3. *Compounds.* The variation in sublimation energies of the metals is paralleled by dissociation energies of certain refractory compounds such as the

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[7] H. Kanno and J. Hiraishi, *J. Phys. Chem.*, 1982, **86**, 1488; G. Johnson and H. Wakita, *Inorg. Chem.*, 1985, **24**, 3047.

[8] S. G. Bratsch and J. J. Lagowski, *J. Phys. Chem.*, 1985, **89**, 3310, 3317.

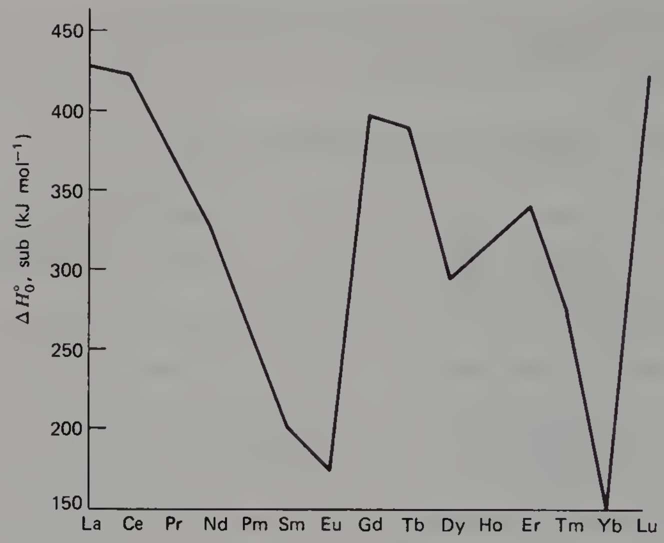

FIG. 20-2. Enthalpies of sublimation of the lanthanide metals (data from E. D. Cater, *J. Chem. Educ.*, 1978, **55**, 697.

monoxides, monosulfides, and dicarbides. These periodic variations are a result of the differing relative energies required to promote a 4*f* electron to the 5*d* level in successive lanthanide atoms.

By contrast, heats of reaction of solid compounds where lanthanide atoms are in combined states in *both* reactants and products show fluctuations of only ~40 kJ mol^{-1}.

20-6. Occurrence, Isolation, and Uses[9]

The lanthanide elements were originally called the "rare earths" because of their occurrence in oxide (or, in old usage, earth) mixtures. The abbreviation RE is often used to represent them generically. They are not, in fact, particularly rare in the earth's crust. Even the scarcest, thulium, is as common as bismuth ($\sim 2 \times 10^{-5}$ wt %) and more common than As, Cd, Hg, or Se, none of which are normally considered rare. The largest deposits are found in Scandinavia, Brazil, Australia, India, the Soviet Union, and the United States. Commercial production employs three ores: *monazite* and *xenotime,* which are rare earth orthophosphates that also contain appreciable thorium, and *bastnasite,* a rare earth fluoride-carbonate (approximately $LnFCO_3$). The approximate compositions of these ores are shown in Table 20-4. The relative amounts of the RE's in monazite and bastnasite are about the same as those in Nature generally (i.e., the early ones predominate) while xenotime is valuable as a source of the heavier RE's. Bastnasite is mined mainly in California and provides most of the 35 to 40×10^3 tons of RE oxides used annually.

Missing from Table 20-4 is the element *promethium,* which occurs in Nature

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[9] H. E. Kremers, *J. Chem. Educ.*, 1985, **62,** 665.

TABLE 20-4
Approximate Composition of Beneficiated Commercial Rare Earth Ores[a]

Oxide		Percentage		
		Bastnasite	Monazite	Xenotime
ThO_2		<0.05	3–9	4–6
Total rare earth oxides		60–70	~60	~60
La_2O_3		32	22	0.5
CeO_2		49	45	5
Pr_6O_{11}		4.4	5	0.7
Nd_2O_3		13.5	17	2.2
Sm_2O_3		0.5	4	1.9
Eu_2O_3		0.1	0.1	0.2
Gd_2O_3	Basis total rare earth oxides = 100%[b]	0.3	2	4
Tb_4O_7			0.2	1
Dy_2O_3			1	8.6
Ho_2O_3			0.1	2
Er_2O_3		0.1	0.4	5.4
Tm_2O_3			trace	0.9
Yb_2O_3			0.2	6.2
Lu_2O_3			trace	0.4
Y_2O_3		0.1	3	61

[a] Taken from ref. 9.

[b] Oxides are shown in the form in which they exist in as-ignited mixed oxides as weighed for gravimetric analysis.The data for bastnasite and monazite reflect the relative abundances of the rare earths in nature.

only in traces of uranium ores, where it forms by spontaneous fission of ^{238}U. Milligram quantities of pink $^{147}Pm^{3+}$ salts can be isolated by ion exchange methods from the fission products of nuclear reactors. The isotope ^{147}Pm decays by β emission with $t_{1/2}$ = 2.64 yr.

The methods by which the lanthanide elements are extracted from their ores and processed depend on the intended end uses. About two thirds of the commercial production and use entails no separation at all and nearly all the rest involves only partial separations. For example, ~15% of commercial rare earth (RE) production is as "Misch metal" an alloy of lighter RE's, in just the proportions in which they occur in the ore. An alloy of Misch metal and iron is used in steel making and also as "flints" in cigarette lighters.

It is essentially only for purely scientific purposes that separated RE elements (>98%) are required. The first general separation procedures, introduced in the 1950s, were based on complexation-enhanced ion exchange processes. A cation exchange resin alone can provide separations since the affinities of the lanthanide ions for the resin vary inversely with their hydrated radii and these in turn vary inversely with the crystallographic radii. Thus, the order of elution is Lu···La. For a practical, large-scale process, this trend is enhanced by the use of complexing agents at the appropriate pH. The complexing agents prefer the smaller ions (in the crystallographic sense) and thus enhance the tendency of the ions to elute in the order Lu···La. Among the useful ligands are α-hydroxyisobutyric acid, EDTA, and 2-hydroxy

EDTA. The eluates are then treated with oxalate ion and the precipitated RE oxalates ignited to the oxides.

In the mid-1960s liquid–liquid extraction processes were introduced and today all large-scale commercial production is done in this way. An aqueous solution of the Ln^{3+} ions is extracted in a continuous countercurrent process into a nonpolar organic liquid containing tri-*n*-butylphosphine oxide or bis(2-ethylhexyl)phosphinic acid (DEHPA). Typical separation factors for adjacent rare earths using DEHPA are 2.5 per extraction step so that under automatic multistep or countercurrent conditions purities of 99 to 99.9% are routinely achieved.

In general, lanthanides can be separated from mixtures with other elements by precipitation as oxalates or fluorides. Cerium and europium can conveniently be removed from the others, the former by oxidation to Ce^{IV} and precipitation as the iodate, and the latter by reduction to Eu^{2+}, which can be precipitated as $EuSO_4$.

20-7. The Metals

The lighter metals (La–Gd) are obtained by reduction of the trichlorides with Ca at 1000°C or more, whereas for others (Tb, Dy, Ho, Er, Tm, and also Y) the trifluorides are used because the chlorides are too volatile. Promethium metal is made by reduction of PmF_3 with Li. Trichlorides of Eu, Sm, and Yb are reduced only to the dihalides by Ca, but the metals can be prepared by reduction of the oxides M_2O_3 with La at high temperatures.

The metals are silvery-white and very reactive. They all react directly with water, slowly in the cold, rapidly on heating, to liberate hydrogen. Their high potentials (Table 20-1) show their electropositive character. They tarnish readily in air and all burn easily to give the sesquioxides, except cerium, which gives CeO_2. Yttrium is remarkably resistant to air even up to 1000°C owing to formation of a protective oxide coating. The metals react exothermically with hydrogen, though heating to 300 to 400°C is often required to initiate the reaction. The resulting phases MH_2 and MH_3, which are usually in a defect state, have remarkable thermal stability, in some cases up to 900°C. The metals also react readily with C, N_2, Si, P, S, halogens, and other nonmetals at elevated temperatures.

Metallic Eu and Yb dissolve in liquid ammonia at -78°C to give blue solutions, golden when concentrated. The spectra of the blue solutions, which decolorize slowly, are those expected for M^{2+} and solvated electrons.

THE TRIVALENT STATE

20-8. Simple Binary and Ternary Compounds

The trivalent state is the characteristic one for all the lanthanides. They form *oxides* M_2O_3, which resemble the Ca to Ba group oxides and absorb carbon dioxide and water from the air to form carbonates and hydroxides, respectively. The *hydroxides* $M(OH)_3$ are definite compounds, not merely hydrous oxides, and may be obtained crystalline by aging M_2O_3 in strong alkali at high temperature and pressure. They have hexagonal structures with nine-coordinate tricapped trigonal prismatic coordination. The basicities of the hydroxides decrease with increasing atomic number, as would be expected from the decrease in ionic radius. They hydroxides are precipitated from aqueous solutions by ammonia or dilute alkalis as gelatinous precipitates. They are not amphoteric.

A range of mixed oxides, many with commercial uses, are known. Perhaps the most interesting are those containing La, Ba or Sr, and Cu, such as $La_{2-x}Sr_xCuO_4$, which are superconducting above liquid nitrogen temperature.[10]

Among the *halides,*[11a] the fluorides are of particular importance because of their insolubility. Addition of hydrofluoric acid or fluoride ions precipitates the fluorides from Ln^{3+} solutions even 3 *M* in nitric acid and is a characteristic test for lanthanide ions. The fluorides, particularly of the heavier lanthanides, are slightly soluble in an excess of HF owing to complex formation. They may be redissolved in 3 *M* nitric acid saturated with boric acid, which removes F^- as BF_4^-. The chlorides are soluble in water, from which they crystallize as hydrates, the La to Nd group often with $7H_2O$, and the Nd to Lu group (including Y) with $6H_2O$; other hydrates may also be obtained.

The anhydrous *chlorides* cannot easily be obtained from the hydrates because when heated these lose hydrochloric acid (to give the oxochlorides, MOCl) more readily than they lose water. (However scandium and cerium give Sc_2O_3 and CeO_2, respectively). The chlorides are made by heating oxides with an excess[11b] of ammonium chloride:

$$Ln_2O_3 + 6NH_4Cl \xrightarrow{\sim 300^\circ C} 2LnCl_3 + 3H_2O + 6NH_3$$

or as methanolates $LnCl_3 \cdot 4CH_3OH$, by treating the hydrates with 2,2-dimethoxypropane (Section 14-8). The halides can also be prepared from the metals by action of HCl(g), Br_2, or I_2. At high temperatures they react with glass:

$$2LnX_3 + SiO_2 = 2LnOX + SiX_4$$

The oxohalides (LnOX) form readily when the halides are heated in the presence of water vapor. There are several structural types depending on mode of preparation and the Ln element.[12]

Numerous other binary compounds are obtained by direct interaction at elevated temperatures; examples are the semiconducting sulfides Ln_2S_3, which can also be made by reaction of $LnCl_3$ with H_2S at 1100°C, Group VA com-

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[10] E. M. Engler *et al., J. Am. Chem. Soc.,* 1987, **109,** 2848; J. M. Williams *et al., Inorg. Chem.,* 1987, **26,** 1474, 1829.

[11a] J. Burgess and J. Kijowski, *Adv. Inorg. Chem. Radiochem.,* 1981, **24,** 57.

[11b] G. Meyer and P. Ax, *Mater. Res. Bull.,* 1982, **17,** 1447.

[12] J. D. Corbett *et al., Inorg. Chem.,* 1985, **24,** 494.

pounds LnX (X = N, P, As, Sb, or Bi) that have the NaCl structure, a variety of borides,[13] carbides (LnC_2) and (Ln_2C_3), and hydrides that tend strongly to be nonstoichiometric, $LnH_{1.8}$–$LnH_{3.0}$.

20-9. Oxo Salts

Hydrated salts of common acids, which contain the ions $[Ln(H_2O)_n]^{3+}$, are readily obtained by dissolving the oxide in acid and crystallizing.

Double salts are very common, the most important being the double nitrates and double sulfates such as $2Ln(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$, $Ln(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$, and $Ln_2(SO_4)_3 \cdot 3Na_2SO_4 \cdot 12H_2O$. The solubilities of double sulfates of this type fall roughly into two classes: the cerium group La to Eu, and the yttrium group Gd to Lu and Y. Those of the Ce group are only sparingly soluble in sodium sulfate, whereas those of the Y group are appreciably soluble. Thus a fairly rapid separation of the entire group of lanthanides into two subgroups is possible. Various of the double nitrates were used in the past for further separations by fractional crystallization procedures.

The precipitation of the *oxalates* from dilute nitric acid solution is a quantitative and fairly specific separation procedure for the lanthanides, which can be determined gravimetrically in this way, with subsequent ignition to the oxides. The actual nature of the oxalate precipitate depends on conditions. In nitric acid solutions, where the main ion is Hox^-, ammonium ion gives double salts $NH_4Ln(ox)_2 \cdot yH_2O$ ($y = 1$ or 3). In neutral solution, ammonium oxalate gives the normal oxalate with lighter, but mixtures with heavier, lanthanides. Washing the double salts with 0.01 *M* HNO_3 gives, with some ions, the normal oxalates. The phosphates are sparingly soluble in dilute acid solution. Although carbonates exist, many are basic; the normal carbonates are best made by hydrolysis of the chloroacetates:

$$2Ln(C_2Cl_3O_2)_3 + (x+3)H_2O \longrightarrow Ln_2(CO_3)_3 \cdot xH_2O + 3CO_2 + 6CHCl_3$$

$La_2(CO_3)_3 \cdot 8H_2O$ has a complex structure with 10-coordinate La, and both uni- and bidentate carbonate ions.

20-10. Other Compounds and Complexes

The aqua ions hydrolyze, increasingly so from La[14a] to Lu as they become smaller.

$$[Ln(H_2O)_n]^{3+} + H_2O = [Ln(H_2O)_{n-1}(OH)]^{2+} + H_3O^+$$

Polymeric species such as $Ln_2(OH)_3^{3+}$ and $Ln_3(OH)_3^{6+}$ may also be present for La.

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[13] J. Etourneau, *J. Less-Common Met.*, 1985, **110**, 267.

[14a] L. Ciavatta *et al.*, *Polyhedron*, 1987, **6**, 1283.

Halide complexes are of relatively little importance in aqueous media, but several types can be isolated in the solid state, for example, $(NH_4)_3LnCl_6$, Ph_4PLnBr_4, and so on.[14b]

Oxygen Ligands. By far the most stable and common of lanthanide complexes are those with chelating oxygen ligands. The use of EDTA-type anions and hydroxo acids such as tartaric or citric, for the formation of water-soluble complexes is of great importance in ion-exchange separations, as noted previously. All of these can be assumed to have coordination numbers exceeding 6, as in $[La(OH_2)_4EDTAH]\cdot 3H_2O$.

The β-*diketonates*[15] have been extensively studied, particularly since some of the fluorinated derivatives give complexes that are volatile and suitable for gas-chromatographic separation. The preparation of β-diketonates by conventional methods *invariably* gives hydrated or solvated species such as $[Ln(acac)_3]\cdot C_2H_5OH\cdot 3H_2O$. Anhydrous species obtained by vacuum dehydration appear to be polymeric, not octahedral. The β-diketonates can complex further to give anionic species such as the eight-coordinate thenoyltrifluoroacetate $[Nd(TTA)_4]^-$. The alkali metal salts of $[Ln(\beta\text{-dike})_4]^-$ are sometimes appreciably volatile and can be sublimed. The nmr shift reagents mentioned earlier are usually β-diketonate complexes, and other lanthanide β-diketonate complexes have been found to possess antiknock activity.

Under highly basic conditions anionic catecholate complexes, for example, $[Gd(cat)_4]^{5-}$ and $[Gd_2(cat)_6]^{6-}$ in which the coordination numbers are 8 and 7, respectively, can be obtained as crystalline salts.[16]

In aqueous solution many other types of polyoxo ligands effectively complex the Ln^{3+} ions, including polyphosphates,[17] mixed phosphoryl–carbonyl species,[18] and crown ethers.[19,20]

Complexes of monodentate oxygen ligands are less stable than those of chelates and tend to dissociate in aqueous solution, but many crystalline compounds or salts have been obtained from the lanthanide salts in ethanolic solutions with hexamethylphosphoramide, which gives six-coordinate species, for example, $Pr(HMPA)_3Cl_3$ and $[Ln(HMPA)_6](ClO_4)_3$, with triphenylphosphine oxide or triphenyl arsine oxide, and pyridine-*N*-oxides, for example, $Ln(NO_3)_3(OAsPh_3)_4$, and $[Ln(pyO)_8](ClO_4)_3$, and with DMSO, for example, $(DMSO)_nM(NO_3)_3$.

Nitrogen Ligands. Lanthanide compounds with La—N bonds to the bulky dialkylamido group $(Me_3Si)_2N$— are well characterized[21] and include py-

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[14b] W. Urland, *Z. Naturforsch.*, 1985, **40B,** 496.

[15] T. J. Wenzel *et al., Polyhedron,* 1985, **4,** 369.

[16] G. E. Freeman and K. N. Raymond, *Inorg. Chem.*, 1985, **24,** 1410.

[17] M. S. Nieuwenhuizen *et al., J. Am. Chem. Soc.*, 1985, **107,** 12.

[18] R. T. Paine *et al., Inorg. Chem.*, 1985, **24,** 4626.

[19] J. G. Bünzli *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 885; W. R. Moomaw *et al., J. Phys. Chem.*, 1985, **89,** 5659.

[20] R. D. Rogers and L. K. Kurihana, *Inorg. Chem.*, 1987, **26,** 1498.

[21] J. M. Boncella and R. A. Andersen, *Organometallics,* 1985, **4,** 205.

ramidal $Ln[N(SiMe_3)_2]_3$ (Ln = Sc, Nd, Eu, and Gd), the bridged dimer $Yb_2[N(SiMe_3)_2]_4$, and $Yb[N(SiMe_3)_2]_2(AlMe_3)_2$.

More conventional complexes of *amines* such as en, dien, and dipy are known, together with *N*-bonded *thiocyanato* complexes. With few exceptions they have high coordination numbers. Some examples of such complexes are Ln en_3Cl_3, $[La\ en_4CF_3SO_3]^{2+}$, $[LaL(CF_3SO_3)_2]^+$, and $[YbL(CF_3SO_3)]^{2+}$ (where L represents a macrocyclic octaamine), in which coordination numbers of 9, 9, 10, and 9, respectively, are displayed.[22] In aqueous solution thiocyanato complexes have appreciable formation constants, and SCN^- can be used as elutant for ion-exchange separations. The $[Ln(NCS)_6]^{3-}$ ions are octahedral.

Porphyrin complexes can be made by reaction of $Ln(acac)_3(H_2O)_x$ with H_2porphyrin in 1,2,4-trichlorobenzene.

Sulfur Ligands. There are relatively few Ln^{3+} complexes of sulfur ligands. The best known ones contain dithiocarbamates and dithiophosphinates and are prepared by reaction of $LnCl_3$ with $Na[S_2CNR_2]$ or $Na[S_2PR_2]$ in ethanol. Examples include eight-coordinate $[Ln(S_2CNR_2)_4]^-$ and $[Ln(S_2PMe_2)_4]^-$ ions and six-coordinate trigonal prismatic $Pr[S_2P(C_6H_{11})_2]_3$. Mixed sulfur/nitrogen compounds, $\{Ln[N(SiMe_3)_2][\mu\text{-S}t\text{-Bu}]\}_2$, Ln = Eu, Gd, and Y have recently been reported.[23]

20-11. Organometallic Compounds[24a-24e]

The organometallic chemistry of the lanthanides is predominantly, though not exclusively, that of cyclopentadienyl and substituted cyclopentadienyl compounds. The properties of these cyclopentadienyl compounds are influenced markedly by the relationship between the size of the lanthanide atom and the steric demand of the cyclopentadienyl group. The former varies from La to Lu according to the lanthanide contraction, while the latter varies from C_5H_5 (Cp), which makes the least steric demand, to heavily substituted cyclopentadienyl rings, such as C_5Me_5, which is appreciably larger. The organometallic chemistry of Sc[25] and Y[26] is very similar to that of the lanthanides with proper allowance for the relative sizes of these atoms.

It should be noted that all organolanthanide compounds are markedly sensitive to oxygen and moisture.

Cyclopentadienyl Compounds. The simple Cp_3Ln compounds, Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, and Yb, prepared by the reaction

$$LnCl_3 + 3NaCp \longrightarrow Cp_3Ln + 3NaCl$$

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[22] P. H. Smith and K. N. Raymond, *Inorg. Chem.*, 1985, **24,** 3469.

[23] D. C. Bradley and M. B. Hursthouse *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 1585.

[24a] T. J. Marks and R. D. Ernst, in *Comprehensive Organometallic Chemistry*, Vol. 3, G. Wilkinson, F. G. A. Stone, and E. W. Abel, Eds., Pergamon Press, New York, 1982, pp. 180–210.

[24b] W. J. Evans, *Polyhedron,* 1987, **6,** 803; *Adv. Organomet. Chem.*, 1985, **24,** 131.

[24c] J. R. Long, *Aldrichimica Acta,* 1985, **18,** 87 (lanthanides in organic synthesis).

[24d] P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, 1985, **18,** 51 (organoianthanides in catalysis).

[24e] W. J. Evans, *J. Organomet. Chem.*, 1983, **250,** 217.

[25] M. J. McGlinchey *et al., Inorg. Chem.*, 1985, **24,** 93.

[26] W. J. Evans *et al., Organometallics,* 1985, **4,** 324.

were the first authentic organolanthanides to be prepared and characterized (Birmingham and Wilkinson, 1956). These compounds are associated in the solid state[27] but react with neutral ligands, for example, R_3P, RNC, and THF, to give discrete Cp_3LnL molecules, which have three η^5-C_5H_5 rings and L arranged in a quasitetrahedral fashion.[28]

A very useful group of compounds are the Cp_2LnCl[29a] species and their derivatives, including those with partially substituted rings such as $CH_3C_5H_4$, $Me_3SiC_5H_4$, and others. These can be obtained in a variety of ways, for example,

$$LnCl_3 + 2MCp \longrightarrow Cp_2LnCl + 2MCl$$

$$2Cp_3Ln + LnCl_3 \longrightarrow 3Cp_2LnCl$$

$$Cp_3Ln + \left\{\begin{matrix} NH_4Cl \\ HCl \end{matrix}\right\} \longrightarrow Cp_2LnCl + \left\{\begin{matrix} C_5H_6 + NH_3 \\ C_5H_6 \end{matrix}\right\}$$

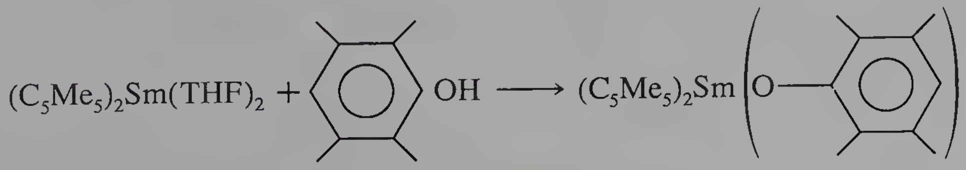
From these the Cp_2LnR compounds can easily be obtained[29b] and these in turn react readily with H_2 to produce hydrides.

The $CpLnCl_2$ type compounds, usually in the form $CpLnCl_2(THF)_2$, are known but less important.[30] In addition, there are Ln^{II} compounds, namely, the Cp_2Ln compounds of Eu and Sm and $(MeC_5H_4)_2Yb(THF)$, as well as the Ce(IV) compounds Cp_4Ce, Cp_3CeCl, and others.

The Cp_2Ln compounds are often useful as starting materials for preparing a range of Cp_2LnX compounds, as illustrated by the use of $Cp_2Yb(MeOC_2H_4OMe)$ to prepare Cp_2YbX compounds with X = RCO_2, Cl, Br, I, C_6F_5, and so on.[31] In a very similar way the $(C_5Me_5)_2Ln$ or $(C_5Me_4Et)_2Ln$ compounds are also good starting materials, as illustrated by the following reactions of $(C_5Me_5)_2Sm(THF)_2$[32]

$$(C_5Me_5)_2Sm(THF)_2 + \tfrac{1}{2}Hg(C_6H_5)_2 \longrightarrow (C_5H_5)_2Sm(C_6H_5)(THF) + Hg$$

$$(C_5Me_5)_2Sm(THF)_2 + (NO, N_2O, C_5H_5NO, etc.) \longrightarrow [(C_5Me_5)_2Sm]_2O$$



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[27] R. D. Fischer *et al., Organometallics,* 1986, **5,** 383.

[28] C. Ni *et al., Inorg. Chim. Acta,* 1985, **110,** L7.

[29a] W. J. Evans *et al., J. Am. Chem. Soc.,* 1987, **109,** 3929 (includes X-ray data for Cp_2M and $*Cp_2M$ compounds).

[29b] W. J. Evans *et al., Organometallics,* 1986, **5,** 263.

[30] G. B. Deacon *et al., J. Organomet. Chem.,* 1985, **293,** 45.

[31] G. B. Deacon *et al., J. Organomet. Chem.,* 1984, **277,** C21.

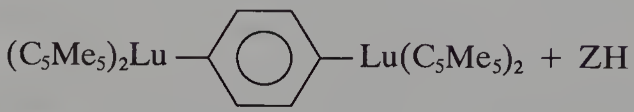
[32] W. J. Evans *et al., J. Am. Chem. Soc.,* 1985, **107,** 405, 941; *J. Am. Chem. Soc.,* 1987, **109,** 4292; *Organometallics,* 1985, **4,** 112; *Inorg. Chim. Acta,* 1985, **110,** 191. See also R. G. Fink *et al., Organometallics,* 1987, **6,** 1356 ($*Cp_2SmOEt_2$).

Pentamethylcyclopentadienyl Compounds. The increased bulk of the C_5Me_5 ligand causes major changes in the structural[29a] and chemical properties of the organolanthanide compounds. A very large fraction of recent organolanthanide work has focused on exploiting these effects. In the following summary we shall specifically cite C_5Me_5 compounds, but some of the reactions have analogs among C_5H_5 or RC_5H_4 compounds.[33] However, it should be recognized that the combination of bulky C_5Me_5 groups with a small Ln atom, such as Lu, will have unique potentialities. The $(C_5Me_5)_2LuZ$ ($Z = CH_3$ and H) well illustrate this,[24d] as the following reactions show:

$$(C_5Me_5)_2LuZ + SiMe_4 \longrightarrow (C_5Me_5)_2LuCH_2SiMe_3 + ZH$$

$$(C_5Me_5)_2LuZ + C_6H_6 \longrightarrow (C_5Me_5)_2LuC_6H_5 + ZH$$

$$(C_5Me_5)_2LuC_6H_5 + (C_5Me_5)_2LuZ \longrightarrow$$

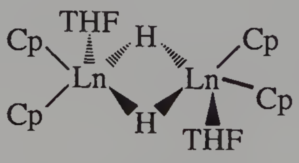


$$(C_5Me_5)_2LuH + D_2 \longrightarrow (C_5Me_5)_2LuD + HD$$

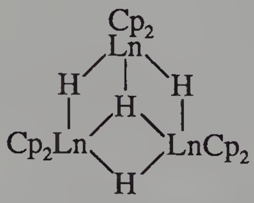
$$(C_5Me_5)_2LuZ + {}^*CH_4 \longrightarrow (C_5Me_5)_2Lu{}^*CH_3 + ZH$$

The last reaction was the first unequivocal example of the reaction of methane homogeneously to form an M—C bond, and it proceeds under relatively mild conditions (see Section 27-9).

There are many structurally and chemically interesting hydrido derivatives of the C_5H_5 and C_5Me_5 lanthanide compounds. In many of these there are double hydrido bridges[34–36] (20-I) but a number of more complex structures (e.g., 20-II) are also known. The hydrido compounds are generally quite reactive and often show activity as hydrogenation catalysts. They are most commonly obtained by hydrogenolysis of Cp_2LnR compounds. Since the Ln atoms cannot change oxidation numbers by ±2, it is unlikely that these reactions proceed, as is often the case with *d*-block elements, via oxidative-addition of H_2 to Ln. Instead, a four-center transition state, possibly preceded



(20-I)



(20-II)

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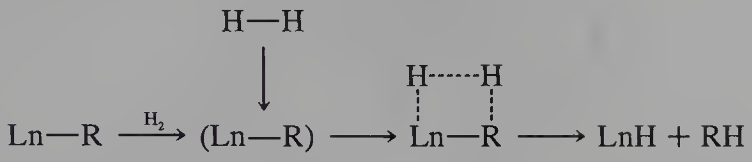
[33] H. Schumann *et al., Organometallics,* 1985, **4,** 321.

[34] H. Schumann *et al., J. Organomet. Chem.,* 1986, **299,** 67.

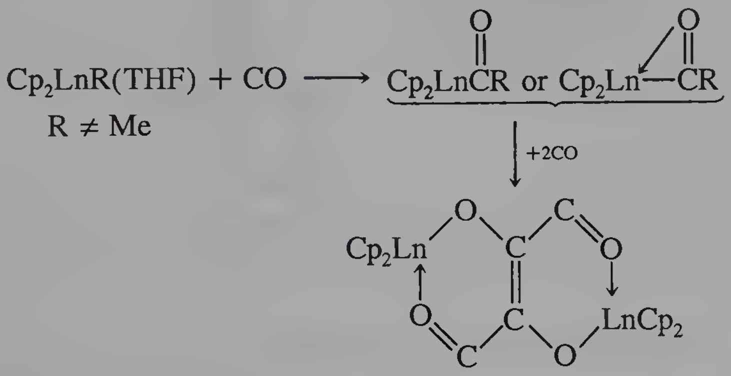
[35] T. J. Marks *et al., Organometallics,* 1985, **4,** 200.

[36] W. J. Evans *et al., J. Am. Chem. Soc.,* 1985, **107,** 1671.

by a true H_2 complex, may be employed:



In addition to hydrogenolysis, the Ln—R bonds undergo many other reactions, of which those with CO are often especially interesting, for example,



Cyclooctatetraene Compounds. The majority of these contain Ln^{III} atoms, but a few are known that contain Ln^{II} atoms, such as $Yb(C_8H_8)$ which is probably polymeric, $C_8H_8Ybpy_3 \cdot 0.5\ py$[37a] and $[K_2(C_4H_{10}O_2)_2][Yb(C_8H_8)_2]$ which contains discrete sandwich anions,[37b] as well as $Ce(C_8H_8)_2$ which contains Ce^{IV} sandwiched symmetrically between the two rings.[38] The Ln^{III} compounds include those containing $[Ln(C_8H_8)_2]^-$ anions (with a staggered sandwich structure) and several $[Ln(C_8H_8)Cl(THF)_2]_2$ compounds which have the type of structure shown in Fig. 20-3. With the very small Lu atom, $Lu(C_8H_8)Cl(THF)$, is obtained. This compound reacts with Li[*o*-$C_6H_4CH_2NMe_2$] to give $Lu(C_8H_8)$(*o*-$C_6H_4CH_2NMe_2$)(THF) which contains a five-membered Lu—C—C—C—N ring.[39a]

There are $Ln_2(C_8H_8)_3$ compounds that have not been structurally characterized, but their THF solvates are known and the structure of the neodymium compound is shown in Fig. 20-4. There are also mixed cyclopentadienyl/cyclooctatetraene species known, $Ln(C_5H_5)(C_8H_8)$, which, with the possible exception of the scandium compound, are believed to have polymeric rather than simple sandwich structures.

In all these cyclooctatetraene compounds the C_8H_8 rings can best be regarded as essentially $C_8H_8^{2-}$ anions. The preparative methods are consistent with this since the commonest routes employ $LnCl_3$ and $K_2C_8H_8$ as reactants,

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[37a] A. L. Wayda *et al., Organometallics,* 1987, **6,** 1328.

[37b] A. Streitwieser, Jr., *et al., Organometallics,* 1985, **4,** 52.

[38] A. Streitwieser, Jr., *et al., J. Am. Chem. Soc.,* 1985, **107,** 7786.

[39a] A. L. Wayda and R. D. Rogers, *Organometallics,* 1985, **4,** 1440.

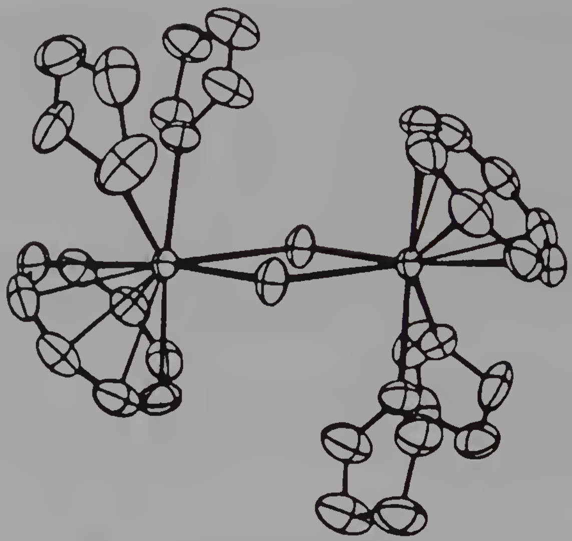

FIG. 20-3. The molecular structure of $\{(\eta^8\text{-}C_8H_8)Ln(THF)_2\}(\mu\text{-}Cl)_2$ compounds.

although the $Ln_2(C_8H_8)_3$ compounds are made by atom vapor reactions, that is, cocondensation of Ln atoms with C_8H_8 on a cold surface.

Other Organometallic Compounds. The lanthanides are known to form η^3-allyl compounds of two sorts: $LnCp_2(C_3H_5)$ and $LiLn(C_3H_5)_4$.[39b]

Because of the tendency of the lanthanides to form highly ionic compounds, the majority of their organometallic compounds are those we have already mentioned, in which the organic residues (or at least some of them) are those that can be formally regarded as anions,[40] namely, $C_5H_5^-$, $RC_5H_4^-$, $C_5Me_5^-$, $C_8H_8^{2-}$, and $C_3H_5^-$. However, it has recently been shown that a neutral arene ligand which is a good π donor can be bonded to a lanthanide. The compound[41] is $(\eta^6\text{-}C_6Me_6)Sm(\eta^2\text{-}AlCl_4)_3$, whose structure is shown in Fig. 20-5.

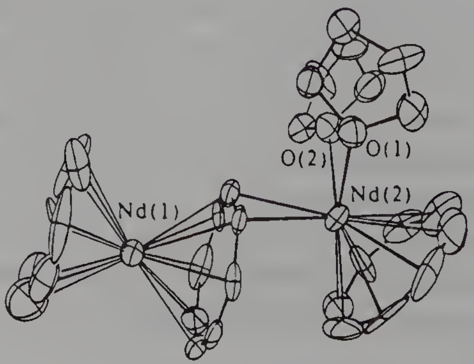

FIG. 20-4. The molecular structure of $Nd_2(C_8H_8)_3(THF)_2$.

[39b] T. Cohen *et al., J. Am. Chem. Soc.,* 1987, **109,** 4710.

[40] R. A. Andersen *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 405.

[41] F. A. Cotton and W. Schwotzer, *Organometallics,* 1987, **6,** 1275.

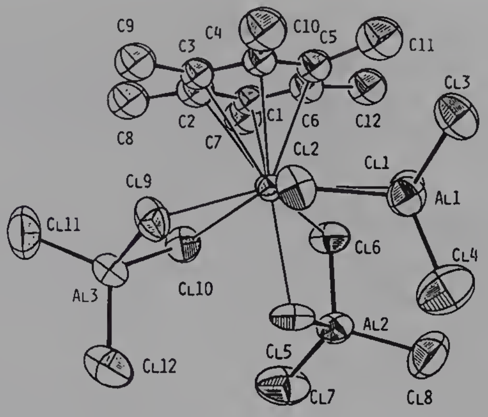

FIG. 20-5. The structure of $(C_6Me_6)Sm(AlCl_4)_3$.

A number of compounds are known in which the only Ln—C bonds are σ bonds. These include anionic, homoleptic species such as $[LnPh_4]^-$ and $[LnMe_6]^{3-}$, the ylide complexes $Ln[(CH_2)_2PMe_2]_3$, as well as other neutral molecules in which there are additional neutral ligands, such as $Ln(CH_2SiMe_3)_3(THF)_3$ and $Ln(o\text{-}C_6H_4CH_2NME_2)_3$, where the formation of chelate rings enhances stability.[42a]

The metals Eu, Sm, and Yb react directly at −20°C with alkyl and aryl iodides in THF to afford Grignard-like compounds, RLnI and ArLnI; the metals not having a stable oxidation state II react to form more complex products. All of these compounds have Grignard-like reactivity, as well as other interesting behavior.[42b]

Finally, some carbonyls of the type $Ln[M(CO)_n]_3$ are known.[43]

20-12. Scandium

Scandium is perhaps as similar to aluminum as to yttrium and the lanthanides because of its small ionic radius (0.68 Å). Thus, Sc is characteristically six-coordinate and higher coordination numbers occur only rarely, as in $Na_5[Sc(CO_3)_4]\cdot 6H_2O$ and the tropolonate $[ScT_4]^-$, where the coordination number is eight. Scandium is also, in many respects, a typical first transition series metal rather than a lanthanide.[44] The aqua ion, $[Sc(H_2O)_6]^{3+}$, undergoes significant hydrolysis, giving rise to OH-bridged dimers and trimers.[45]

Although relatively abundant (comparable to As), scandium has been uncommon owing to the lack of rich sources and to difficulties in separating it.

Binary Compounds. The oxide (Sc_2O_3) is more similar to Al_2O_3 than to the Ln_2O_3 oxides. From solutions of Sc^{3+} bases precipitate a hydrous oxide

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[42a] A. L. Wayda *et al., Organometallics,* 1984, **3,** 939.

[42b] Y. Fujiwara *et al., J. Organomet. Chem.,* 1985, **279,** C19.

[43] I. P. Beletskaya *et al., J. Organomet. Chem.,* 1986, **299,** 239.

[44] H. B. Silber and T. Mioduski, *Inorg. Chem.,* 1984, **23,** 1577.

[45] R. N. Sylva *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 35.

($Sc_2O_3 \cdot nH_2O$) but a hydroxide isostructural with AlO(OH) is also known. "Scandates" such as $LiScO_2$ can be made by fusing alkali metal oxides and Sc_2O_3. The hydrous oxide will dissolve in concentrated NaOH and the compound $Na_3[Sc(OH)_6] \cdot 2H_2O$ can be crystallized from solutions >8*M* in hydroxide ion.

The fluoride is insoluble in water but dissolves readily in an excess of HF or in NH_4F to give fluoro complexes such as ScF_6^{3-}, and the similarity to Al is confirmed by the existence of a cryolite phase Na_3ScF_6, as well as $NaScF_4$ in the NaF–ScF_3 system. The chloride $ScCl_3$, and $ScBr_3$, can be obtained by P_2O_5 dehydration of hydrated halides; the anhydrous chloride sublimes at a much lower temperature than the lanthanide halides, and this can be associated with the different structure of the solid, which is isomorphous with $FeCl_3$. Unlike $AlCl_3$ it does not act as a Friedel–Crafts catalyst.

Oxo Salts and Complexes. Simple hydrated oxo salts are known, as well as some double salts such as $K_2SO_4 \cdot Sc_2(SO_4)_3 \cdot nH_2O$, which is very insoluble in K_2SO_4 solution. Ammonium double salts such as the tartrate, phosphate, and oxalate are also insoluble in water.

The β-diketonates resemble those of Al rather than of the lanthanides. Thus the acetylacetonate is normally anhydrous and may be sublimed around 200°C; it has a distorted octahedral structure.

The TTA complex can be extracted from aqueous solutions at pH 1.5 to 2 by benzene, and the 8-quinolinolate (cf. Al) can be quantitatively extracted by $CHCl_3$; Sc^{3+} can also be extracted from aqueous sulfate solutions by a quaternary ammonium salt.

Lower Oxidation States. Although there are some Sc^{II} compounds of the type M^IScX_3 as well as a series of nonstoichiometric $M^ISc_xCl_3$ phases,[46] and a few Sc(II) species have been obtained and studied in argon at 14 K,[47] the most important compounds are those highly air-sensitive substances obtained by prolonged reaction of Sc and ScX_3 at high temperatures.[48] In addition to the monochloride, which is similar to the LnCl compounds, scandium forms Sc_5Cl_8, Sc_7Cl_{10}, and Sc_7Cl_{12}. All of these have in common the presence of Sc_6 octahedra.

In Sc_5Cl_8 there are chains of these sharing opposite edges (Fig. 20-6) linked together by Sc^{3+} ions that form chains of edge-sharing $ScCl_6$ octahedra. In Sc_7Cl_{10}, which has been shown to have metallic conduction and puzzling magnetic properties[49] there are double Sc_6 octahedra sharing edges to form infinite chains and, again, Sc^{3+} ions tying these chains together. In Sc_7Cl_{12} there are discrete $[Sc_6Cl_{12}]^{3-}$ groups (with Sc—Sc distances of 3.20–3.23 Å) similar to

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[46] G. Meyer and J. D. Corbett, *Inorg. Chem.*, 1981, **20**, 2627.

[47] L. B. Knight, Jr., *et al., Inorg. Chem.*, 1981, **20**, 2623.

[48] J. D. Corbett, in *Solid State Chemistry: A Contemporary Overview* (*Adv. Chem. Ser.* Vol. 186) American Chemical Society, Washington, DC, 1980, p. 329.

[49] F. J. DiSalvo *et al., Inorg. Chem.*, 1985, **24**, 4624.

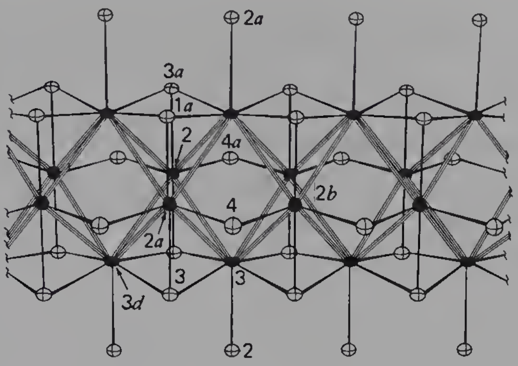

FIG. 20-6. The anionic chain of Sc_6 octahedra, $(Sc_4Cl_8)_\infty$, in Sc_5Cl_8. These are tied together by Sc^{3+} ions.

the M_6Cl_{12} clusters formed by Nb and Ta, packed with Sc^{3+} ions that tie them together.[50]

20-13. The Oxidation State IV

This oxidation state is very important for cerium and of minor, though not negligible, importance for praseodymium and terbium. With the possible exception of a few fluorides, for example, Cs_3LnF_7 for Nd and Dy, no other Ln^{IV} compounds are known.[51]

Cerium(IV) The terms cerous and ceric are commonly used for Ce^{III} and Ce^{IV}. Solid ceric compounds include CeO_2, the hydrous oxide $CeO_2 \cdot nH_2O$ and CeF_4. The dioxide CeO_2, white when pure, is obtained by heating cerium metal, $Ce(OH)_3$, or any of several Ce^{III} salts of oxo acids such as the oxalate, carbonate, or nitrate, in air or oxygen; it is a rather inert substance, not attacked by either strong acids or alkalis; it can, however, be dissolved by acids in the presence of reducing agents (H_2O_2, Sn^{II}, etc.), giving Ce^{III} solutions. Hydrous ceric oxide $CeO_2 \cdot nH_2O$ is a yellow, gelatinous precipitate obtained on treating Ce^{IV} solutions with bases; it redissolves fairly easily in acids. CeF_4 is prepared by treating anhydrous $CeCl_3$ or CeF_3 with fluorine at room temperature; it is relatively inert to cold water and is reduced to CeF_3 by hydrogen at 200 to 300°C.

Cerium (IV) in solution is obtained by treatment of Ce^{III} solutions with very powerful oxidizing agents, for example, peroxodisulfate or bismuthate in nitric acid. The aqueous chemistry of Ce^{IV} is similar to that of Zr, Hf, and, particularly, tetravalent actinides. Thus Ce^{IV} gives phosphates insoluble in $4\ M$ HNO_3 and iodates insoluble in $6\ M$ HNO_3, as well as an insoluble oxalate. The phosphate and iodate precipitations can be used to separate Ce^{IV} from the trivalent lanthanides. Ce^{IV} is also much more readily extracted into

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[50] J. D. Corbett *et al., Z. Anorg. Allg. Chem.*, 1982, **491,** 51.

[51] R. Hoppe, *J. Solid State Chem.*, 1979, **27,** 99.

organic solvents by tributyl phosphate and similar extractants than are the M^{III} lanthanide ions.

The hydrated ion $[Ce(H_2O)_n]^{4+}$ is a fairly strong acid, and except at very low pH, hydrolysis and polymerization occur. It is probable that the $[Ce(H_2O)_n]^{4+}$ ion exists only in concentrated perchloric acid solution. In other acid media there is coordination of anions, which accounts for the dependence of the potential of the Ce^{IV}/Ce^{III} couple on the nature of the acid medium:

$$Ce^{IV} + e = Ce^{III} \qquad E^0 = +1.44 \text{ V } (1\ M\ H_2SO_4),\ +1.61 \text{ V } (1\ M\ HNO_3),\ +1.70 \text{ V } (1\ M\ HClO_4)$$

Comparison of the potential in sulfuric acid, where at high SO_4^{2-} concentrations the major species is $[Ce(SO_4)_3]^{2-}$, with that for the oxidation of water:

$$O_2 + 4H^+ + 4e = 2H_2O \qquad E^0 = +1.229 \text{ V}$$

shows that the acid Ce^{IV} solutions commonly used in analysis are metastable. The oxidation of water is kinetically controlled but can be temporarily catalyzed by fresh glass surfaces.

Cerium(IV) is used as an oxidant both in analysis and in preparative chemistry. Dissolved in acetic acid it oxidizes aldehydes and ketones at the α-carbon atom; a solution of ammonium hexanitratocerate(IV) will oxidize toluene to benzaldehyde. Aqueous Ce^{IV} oxidizes concentrated HCl to Cl_2.

Many complex ions are formed, such as the $[Ce(NO_3)_6]^{2-}$ ion, where bidentate NO_3^- ions afford 12-coordination. Fluoro complexes have been isolated as $(NH_4)_4[CeF_8]$, which on heating gives $(NH_4)_2[CeF_6]$, and $(NH_4)_3CeF_7 \cdot H_2O$, which comes out of 28% NH_4F solution. Reaction of CeO_2 with HCl in dioxane gives orange needles of the oxonium salt of $[CeCl_6]^{2-}$, and various other salts such as the pyridinium salt can be made.

Ceric alkoxides can be prepared by the reaction:

$$(C_5H_5NH)_2CeCl_6 + 4ROH + 6NH_3 \longrightarrow Ce(OR)_4 + 2C_5H_5N + 6NH_4Cl$$

The isopropoxide is crystalline, subliming in a vacuum at 170°C, but other alcoxides, prepared from the isopropyl compound by alcohol exchange, are nonvolatile and presumably polymerized by Ce—O(R)—Ce bridges.

Praseodymium(IV). Only a few solid compounds are known, the commonest being the black nonstoichiometric oxide formed on heating Pr^{III} salts or Pr_2O_3 in air. The oxide system, which is often formulated as Pr_6O_{11} is actually very complicated.[52] Pr_6O_{11} dissolves in acids to give aqueous Pr^{III} and liberate oxygen, chlorine, and so on, depending on the acid used.

When alkali fluorides mixed in the correct stoichiometric ratio with Pr salts are heated in F_2 at 300 to 500°C, compounds such as $NaPrF_5$ or Na_2PrF_6 are obtained. The action of dry HF on the latter gives PrF_4, although this cannot

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[52] K. Otsuka *et al.*, *Inorg. Chim. Acta*, 1986, **115**, L31.

be obtained by direct fluorination of PrF_3. There is some evidence that $Pr(NO_3)_4$ is partially formed by action of N_2O_5 and O_3 on PrO_2.

Praseodymium(IV) is a very powerful oxidizing agent, the Pr^{IV}/Pr^{III} couple being estimated as +2.9 V. This potential is such that Pr^{IV} would oxidize water itself, so that its nonexistence in solution is not surprising.

Terbium(IV). The chemistry resembles that of Pr^{IV}. The Tb—O system is complex and nonstoichiometric, and when oxo salts are ignited under ordinary conditions, an oxide of approximately the composition Tb_4O_7 is obtained. This formula $TbO_{1.75}$ is the nearest approach, using small whole numbers, to the true formula of the stable phase obtained, which varies from $TbO_{1.71}$ to $TbO_{1.81}$, depending on the preparative details. For the average formula Tb_4O_7, Tb^{III}, and Tb^{IV} are present in equal amounts. Terbium dioxide, with a fluorite structure, can be obtained by oxidation of Tb_2O_3 with atomic oxygen at 450°C. Colorless TbF_4, isostructural with CeF_4 and ThF_4, is obtained by treating TbF_3 with gaseous fluorine at 300 to 400°C, and compounds of the type M_nTbF_{n+4}(M = K, Rb, or Cs; $n \geqslant 2$) are known.

No numerical estimate has been given for the Tb^{IV}/Tb^{III} potential, but it must certainly be more positive than +1.23 V, since dissolution of any oxide containing Tb^{IV} gives only Tb^{III} in solution and oxygen is evolved.

20-14. Oxidation State II

All of the lanthanides can give Ln^{2+} ions under unusual conditions, for example, trapped in place of Ca^{2+} in CaF_2, or by reduction of $NdCl_3$, $DyCl_3$, or $TmCl_3$ by Na naphthalide in THF.[53a] The colors and reduction potentials for these ions (in THF) are reported to be Tm^{2+} (emerald, −2.3 V), Dy^{2+} (brown, −2.5 V), and Nd^{2+} (cherry, −2.6 V). However, it is only the elements Eu, Yb, and Sm that have significant "normal" chemistry in this oxidation state. We have already mentioned organometallic compounds of these Ln^{II} species in Section 20-11. Properties of the Eu^{2+}, Yb^{2+}, and Sm^{2+} ions are given in Table 20-5.

The stabilities of the Eu^{2+}, Yb^{2+}, and Sm^{2+} ions correlate with the third

TABLE 20-5
Properties of the Lanthanide M^{2+} Ions

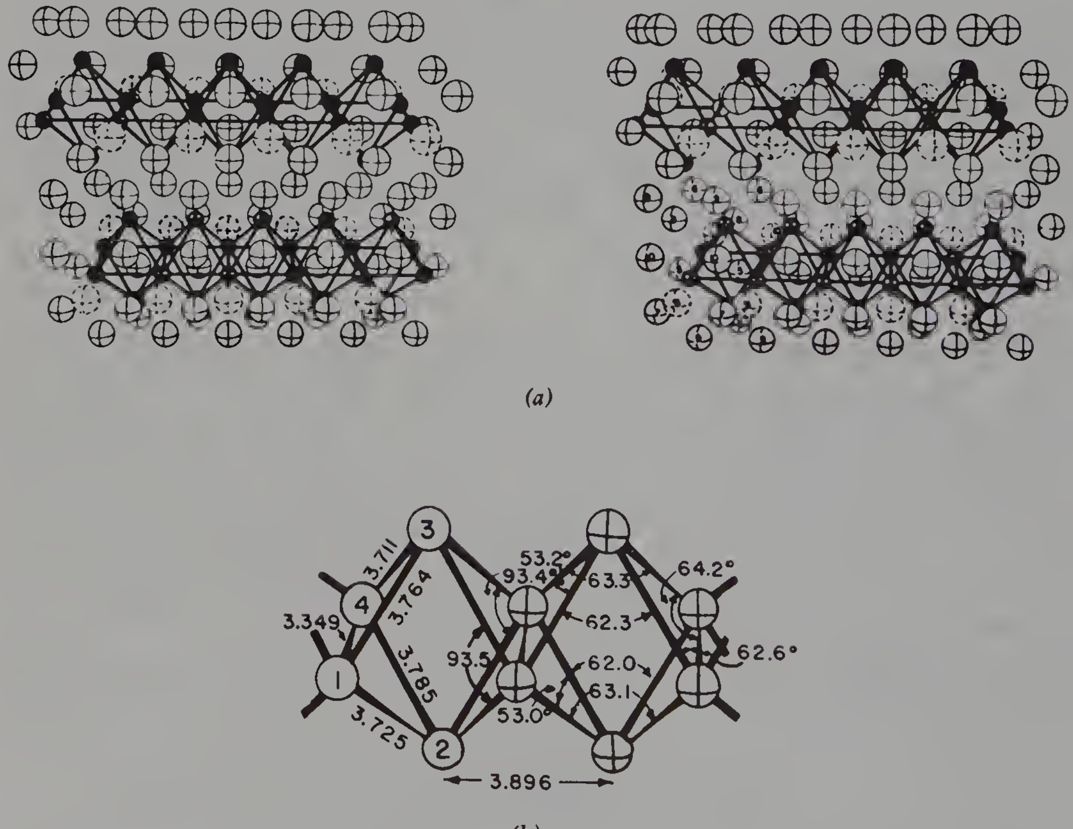
Ion	Color	$E^0(V)^a$	Crystal Radius (Å)
Sm^{2+}	Blood red	−1.40	1.36
Eu^{2+}	Colorless	−0.34	1.31
Yb^{2+}	Yellow	−1.04	1.16

[a] $Ln^{3+} + e^- = Ln^{2+}$.

[53a] A. N. Kamenskaya *et al., Dokl. Akad. Nauk. SSR,* 1982, **266,** 393.

ionization enthalpies of the atoms and the sublimation enthalpies of the metals. The Eu^{2+}(aq) ion is readily obtained by reducing Eu^{3+}(aq) with Zn or Mg, while preparation of the others requires use of Na/Hg or electrolysis. The aqueous Eu^{2+} solutions are easily handled, but those of Sm^{2+} and Yb^{2+} are rapidly oxidized by air and by water itself. The Ln^{2+} ions show many resemblences to Ba^{2+}, giving insoluble sulfates, for example, but soluble hydroxides. Europium can be easily separated from other lanthanides by Zn reduction followed by precipitation of the other hydroxides.

Many solid Ln^{II} compounds are known and those of Eu^{II} are especially well characterized.[53b] The $LnCl_2$ and $LnBr_2$ compounds have eight-coordinated Ln^{2+} ions while seven coordination is found in EuI_2. The LnX_2 compounds react with donor solvents to give solvates, for example, $LnX_2(THF)_x$,


(a)

(b)

FIG. 20-7. (a) Stereoscopic view of the structure of Gd_2Cl_3 with gadolinium atoms represented by small solid circles and chlorine atoms by larger open circles. The *b* axis is horizontal in the plane of the paper to the right; *a* is approximately toward the viewer. "Bridging" atoms Cl(5) and Cl(10) from a neighboring sheet are shown dashed. (b) Portion of the metal chain, with distances in angstroms and angles in degrees. The pairs of gadolinium atoms 1 4 and 2 3 lie on mirror planes perpendicular to the chain. (Reproduced by permission from D. A. Lokken and J. D. Corbett, *Inorg. Chem.*, 1973, **12**, 556.)

[53b] J. P. Sanchez *et al., Inorg. Chem.*, 1985, **24,** 408; J. A. Rard, *Chem. Rev.*, 1985, **85,** 555 (europium chemistry).

that are useful in synthesis. Samarium diiodide has been shown to form an eight-coordinate solvate, $SmI_2[O(CH_2CH_2OMe)_2]_2$ with triglyme and a polymeric (I-bridged) six-coordinate solvate, $SmI_2(Me_3CCN)_2$.[54] In addition to the halides, the oxides (LnO), sulfides (LnS), carbonates, sulfates, and many other compounds are known.

20-15. Other Lower Oxidation State Compounds

For lanthanide metals other than Eu, Sm, and Yb, compounds in lower oxidation states generally involve metal–metal bonding rather than discrete Ln^{2+} ions. In general they are formed by heating LnX_3 with Ln in tantalum containers. In addition to the lower halides there are golden-yellow sulfides (LnS), which have NaCl-type structures and exhibit metallic conductance. The lower halides are air- and moisture-sensitive; many of them have unusual compositions that have not yet been structurally elucidated.

Sesquichlorides of unique type are formed by Gd and Tb. In Gd_2Cl_3 or $[Gd_4^{6+}(Cl^-)_6]_n$ there are infinite chains of metal atoms in octahedra sharing opposite edges (Fig. 20-7); chlorine atoms are located over triangles formed by three Gd atoms. These halides can be further reduced at 800°C to GdCl and TbCl. The latter materials are graphitelike platelets. They have a layer structure like ZrCl and ScCl where close-packed double layers of metal atoms alternate with double layers of halide atoms (XMMX···XMMX) and are related to the CdI_2 type (XMX···XMX) (Section 16-8).

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[54] A. Sen *et al., Inorg. Chem.,* 1985, **24,** 3082.

Chapter Twenty One

Actinium, Thorium, Protactinium, and The Actinide Elements

21-1. Occurrence and General Properties

The actinide elements (which are all radioactive) are listed in Table 21-1 along with some of their properties. The principal isotopes that can be obtained in macroscopic amounts are listed in Table 21-2. The significance of the term "actinide" series is justified by the overall agreement of the chemistry of these elements with that concept, although it is not as clearly justified as is the lanthanide concept. Note in Table 21-1 that some irregular variation in the $5f/6d$ electron distribution does occur.

Only thorium, protactinium, and uranium[1] occur in Nature in amounts sufficient for practical extraction. Thorium and uranium occur in enriched deposits, workable by normal mining procedures and are available in ton quantities from deposits in Canada, USA, South Africa, Australia and Namibia.

Actinium and protactinium are present in uranium minerals but recovery is not generally practiced. Neptunium (^{237}Np and ^{239}Np) and plutonium (^{239}Pu) are present in minute amounts in uranium ores because they result from reaction of neutrons with uranium isotopes, not due to survival from primordial formation. All other actinides are entirely synthetic. Methods of preparation for those up to Cf are given in Table 21-2. Other preparations are discussed individually.

All of the actinide elements are toxic to humans and these biochemical effects have been studied extensively.[2]

The atomic spectra of the heavy elements are very complex, and it is difficult to identify levels in terms of quantum numbers and configurations.

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[1] *Uranium Geochemistry, Mineralogy, Geology, Exploration and Resources,* B. DeVito, F. Ippolito, G. Capoldi, and P. R. Simpson, Eds., Institution of Mining and Metallurgy (London), 1984.

[2] R. A. Bulman, *Coord. Chem. Rev.,* 1980, **31,** 221.

TABLE 21-1

The Actinide Elements and Some of Their Properties

				Metal		$-E°$ (V)		Ionic radius (Å)	
Z	Symbol	Name	Electronic structure	mp (°C)	Radius (Å)	0–III	0–II	M^{3+}	M^{4+}
89	Ac	Actinium	$6d7s^2$	1100	1.898	2.13		1.26	
90	Th	Thorium	$6d^27s^2$	~1750	1.798	1.17			1.08
91	Pa	Protactinium	$5f^26d7s^2$ or $5f^16d^27s^2$	1572	1.642	1.49		1.18	1.04
92	U	Uranium	$5f^36d7s^2$	1132	1.542	1.66		1.17	1.03
93	Np	Neptunium	$5f^57s^2$	639	1.503	1.79		1.14	1.00
94	Pu	Plutonium	$5f^67s^2$	640	1.523	2.00		1.15	1.01
95	Am	Americium	$5f^77s^2$	1173	1.730	2.07	2.0	1.12	0.99
96	Cm	Curium	$5f^76d7s^2$	1350	1.743	2.06	0.9	1.11	0.99
97	Bk	Berkelium	$5f^97s^2$	986	1.704	1.97	1.6	1.10	0.97
98	Cf	Californium	$5f^{10}7s^2$	900	1.694	2.01	2.2	1.09	0.96
99	Es	Einsteinium	$5f^{11}7s^2$		(1.69)	1.98	2.3		
100	Fm	Fermium	$5f^{12}7s^2$		(1.94)	1.95	2.5		
101	Md	Mendelevium	$5f^{13}7s^2$		(1.94)	1.66			
102	No	Nobelium	$5f^{14}7s^2$		(1.94)	1.78	1.6		
103	Lr	Lawrencium	$5f^{14}6d7s^2$		(1.71)	2.06			
104	Rf	Rutherfordium (eka-hafnium)							
105	Ha	Hahnium (eka-tantalum)							
106		eka-tungsten							

TABLE 21-2
Principal Actinide Isotopes Available in Macroscopic Amounts[a]

Isotope	Half-life	Source
^{227}Ac	21.7 yr	Natural $^{226}\text{Ra}(n\gamma)^{227}\text{Ra} \xrightarrow[41.2\ \text{min}]{\beta^-} {}^{227}\text{Ac}$
^{232}Th	1.39×10^{10} yr	Natural; 100% abundance
^{231}Pa	3.28×10^{5} yr	Natural; 0.34 ppm of U in uranium ores
^{235}U	7.13×10^{8} yr	Natural 0.7204% abundance
^{238}U	4.50×10^{9} yr	Natural 99.2739% abundance
^{237}Np	2.20×10^{6} yr	$^{235}\text{U}(n\gamma)^{236}\text{U}(n\gamma)^{237}\text{U} \xrightarrow[6.75\ \text{days}]{\beta^-} {}^{237}\text{Np}[\text{and } {}^{238}\text{U}(n, 2n)^{237}U]$
^{238}Pu	86.4 yr	$^{237}\text{Np}(n\gamma)^{238}\text{Np} \xrightarrow{\beta^-} {}^{238}\text{Pu}$
^{239}Pu	24,360 yr	$^{238}\text{U}(n\gamma)^{239}\text{U} \xrightarrow[23.5\ \text{min}]{\beta^-} {}^{239}\text{Np} \xrightarrow[2.35\ \text{days}]{\beta^-} {}^{239}\text{Pu}$
^{242}Pu	3.79×10^{5} yr	Successive $n\gamma$ in ^{239}Pu
^{244}Pu	8.28×10^{7} yr	Successive $n\gamma$ in ^{239}Pu
^{241}Am	433 yr	$^{239}\text{Pu}(n\gamma)^{240}\text{Pu}(n\gamma)^{241}\text{Pu} \xrightarrow[13.2\ \text{yr}]{\beta^-} {}^{241}\text{Am}$
^{243}Am	7650 yr	Successive $n\gamma$ on ^{230}Pu
^{242}Cm	162.5 days	$^{241}\text{Am}(n\gamma)^{242m}\text{Am} \xrightarrow[16.0\ \text{h}]{\beta^-} {}^{242}\text{Cm}$
^{244}Cm	18.12 yr	$^{239}\text{Pu}(4n\gamma)^{243}\text{Pu} \xrightarrow[5.0\ \text{h}]{\beta^-} {}^{243}\text{Am}(n\gamma)^{244}\text{Am} \xrightarrow[26\ \text{min}]{\beta^-} {}^{244}\text{Cm}$
^{249}Bk	325 days	Successive $n\gamma$ on ^{239}Pu; $^{248}\text{Cm}(n\gamma) \xrightarrow{\beta^-} {}^{247}\text{Bk}$
^{252}Cf	2.57 yr	Successive $n\gamma$ on ^{242}Pu

[a] ^{237}Np and ^{239}Pu are available in multikilogram quantities; ^{238}Pu, ^{242}Pu, ^{241}Am, ^{243}Am, and ^{244}Cm in amounts of 100 g or above; ^{244}Pu, ^{252}Cf, ^{249}Bk, ^{248}Cm (4.7×10^{5} yr), ^{253}Es (20 days). ^{254}Es (1.52 years for α) in milligram and ^{257}Fm (94 days) in microgram quantities. Other long-lived isotopes are known but can be obtained only in traces by use of accelerators [e.g., ^{247}Bk ($\sim 10^{4}$ yr). ^{252}Es, 471.7 days].

For chemical behavior the lowest configuration is of greatest importance and the competition between $5f^n7s^2$ and $5f^{n-1}6d7s^2$ is of interest.

For the elements in the first half of the f shell it appears that less energy is required for the promotion of $5f \rightarrow 6d$ than for the $4f \rightarrow 5d$ promotion in the lanthanides; there is thus a greater tendency to supply more bonding electrons with the corollary of higher valences in the actinides. The second half of the actinides resembles the lanthanides more closely.

Another difference is that the $5f$ orbitals have a greater spatial extension relative to the $7s$ and $7p$ orbitals than the $4f$ orbitals have relative to the $6s$ and $6p$ orbitals. The greater spatial extension of the $5f$ orbitals has been shown experimentally; the esr spectrum of UF_3 in a CaF_2 lattice shows structure attributable to the interaction of fluorine nuclei and the electron spin of the U^{3+} ion. This implies a small overlap of $5f$ orbitals with fluorine and constitutes an f covalent contribution to the ionic bonding. With the neodymium ion a similar effect is *not* observed. Because they occupy inner orbitals, the $4f$ electrons in the lanthanides are not accessible for bonding purposes; and virtually no compound in which $4f$ orbitals are used can be said to exist.

In the actinide series, therefore, the energies of the 5*f*, 6*d*, 7*s*, and 7*p* orbitals are about comparable over a range of atomic numbers (especially U to Am), and since the orbitals also overlap spatially, bonding can involve any or all of them. In the chemistries this situation is indicated by the fact that the actinides are much more prone to complex formation than are the lanthanides, where the bonding is almost exclusively ionic. Indeed the actinides can even form complexes with certain π-bonding ligands as well as forming complexes with halide, sulfate, and other ions. The difference from lanthanide chemistry is usually attributed to the contribution of covalent hybrid bonding involving 5*f* electrons.

A further point is that since the energies of the 5*f*, 6*d*, 7*s*, and 7*p* levels are comparable, the energies involved in an electron shifting from one to another, say 5*f* to 6*d*, may lie *within* the range of chemical binding energies. Thus the electronic structure of the element in a given oxidation state may vary between compounds and in solution be dependent on the nature of the ligands. It is accordingly also often impossible to say *which* orbitals are being utilized in bonding or to decide meaningfully whether the bonding is covalent or ionic.

The ionic radii for the commonest oxidation states (Table 21-1) are compared with those of the lanthanides in Fig. 21-1. There is clearly an "actinide" contraction, and the similarities in radii of both series correspond to similarities in their chemical behavior for properties that depend on the ionic radius, such as thermodynamic results for hydrolysis of halides. It is also generally the case that similar compounds in the same oxidation state have similar crystal structures that differ only in the parameters.

The electronic absorption spectra of the actinide ions, like those of the lanthanides, are due to transitions within the $5f^n$ levels and consist of narrow

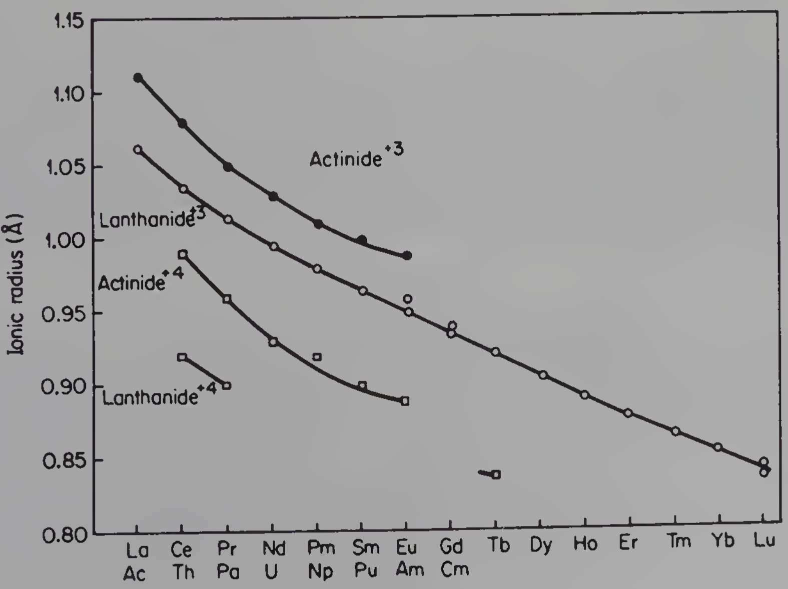

FIG. 21-1. Radii of actinide and lanthanide ions. (Reproduced by permission from D. Brown, *Halides of the Lanthanides and Actinides*, Wiley-Interscience, New York, 1968.)

bands, relatively uninfluenced by ligand fields; the intensities are generally ~10 times those of the lanthanide bands.

Spectra involving only one *f* electron are simple, consisting of only a single transition $^2F_{5/2}$–$^2F_{7/2}$. For the f^7 configuration (Cm^{3+}; cf. Gd^{3+}) the lowest excited state lies about 4 eV above the ground level, so that these ions show only charge-transfer absorption in the ultraviolet. Most actinide species have complicated spectra.

The magnetic properties of the actinide ions are considerably harder to interpret than those of the lanthanide ions, although there are similarities.[3] The experimental magnetic moments are usually lower than the values calculated by using Russell–Saunders coupling, and this appears to be due both to ligand field effects similar to those operating in the *d* transition series and to inadequacy of this coupling scheme. Since 5*f* orbitals can participate to some extent in covalent bonding, ligand effects are to be expected.

For the ions Pu^{3+} and Am^{3+}, the phenomenon noted for Sm^{3+} and Eu^{3+} is found; since the multiplet levels are comparable to kT, anomalous temperature dependence of the susceptibilities occurs.

GENERAL CHEMISTRY OF THE ACTINIDES

Given the close similarities in preparations and properties of actinide compounds in a given oxidation state, it is convenient to discuss some general features and to follow this by additional descriptions for the separate elements. Methods of chemical separations of the elements are also discussed. Just as Ln is often used as a generic symbol for lanthanide elements, An is so used for the actinides.

21-2. The Metals

A general method for preparation of all An metals, on almost any scale, is by reduction of AnF_3 or AnF_4 with vapors of Li, Mg, Ca, or Ba at 1100 to 1400°C. The chlorides or oxides are sometimes used. There are some special methods such as the preparation of Th or Pa from their tetraiodides by the van Arkel-de Boer process,[4] or the following reaction for the relatively volatile americium:

$$2La + Am_2O_3 \xrightarrow{1200°C} 2Am\uparrow + La_2O_3$$

Uranium is one of the densest metals (19.07 g cm^{-3} at 25°C) and has three crystalline modifications. It forms a wide range of intermetallic compounds (U_6Mn, U_6Ni, USn_3, etc.), but owing to its unique crystal structures, it cannot form extensive ranges of solid solutions. Uranium is chemically reactive and combines directly with most elements. In air the surface is rapidly converted into a yellow and subsequently a black nonprotective film. Powdered uranium

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[3] P. G. Huray, *J. Less-Common Met.*, 1983, **93**, 293.

[4] J. C. Spirlet, *J. Less-Common Met.*, 1983, **92**, L27.

is frequently pyrophoric. The reaction with water is complex; boiling water forms UO_2 and hydrogen, the latter reacting with the metal to form a hydride, which causes disintegration. Uranium dissolves rapidly in hydrochloric acid (a black residue often remains) and in nitric acid, but slowly in sulfuric, phosphoric, or hydrofluoric acid. It is unaffected by alkalis. An important reaction of uranium is that with hydrogen, forming the hydride (Section 3-14), which is a useful starting material for the synthesis of uranium compounds.

Thorium. This metal is white but tarnishes in air. It can be readily machined and forged. It is highly electropositive, resembling the lanthanide metals, and is pyrophoric when finely divided. It is attacked by boiling water, by oxygen at 250°C, and by N_2 at 800°C. Dilute HF, HNO_3, and H_2SO_4, and concentrated HCl or H_3PO_4, attack thorium only slowly, and concentrated nitric acid makes it passive. The attack of hot 12 *M* hydrochloric acid on thorium gives a black residue that appears to be a complex hydride approximating to $ThH(O)(Cl)(H_2O)$ that is very pyrophoric and appears to give ThO on heating in vacuum.

Plutonium. This metal is similar to U chemically; it is pyrophoric and must be handled with extreme care owing to the health hazard. Also, above a certain critical size the pure metal can initiate a nuclear explosion. The metal is unique in having at least six allotropic forms below its melting point, each with a different density, coefficient of expansion, and resistivity; curiously, if the phase expands on heating, the resistance decreases. Plutonium forms numerous alloys.

Protactinium is silvery and relatively unreactive, but *actinium* and *curium* are so radioactive that they glow. *Neptunium* is similar to uranium and plutonium in appearance. *Americium* is similar to the actinides and is very electropositive, dissolving readily in acids to give the Am^{3+} ion.

21-3. Survey of Oxidation States

The known oxidation states of the actinides are given in Table 21-3. With the exception of Th and Pa, the common oxidation state, and for trans-americium elements the dominant oxidation state, is +3, and the behavior is similar to the +3 lanthanides. Thorium and the other elements in the +4 state show

TABLE 21-3
Oxidation States of the Actinide Elements[a]

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
						2			2	2	2	2	2
3		3	3	3	3	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
	4	**4**	**4**	4	**4**	**4**	4	4	4				
		5	5	**5**	5	5							
			6	6	6	6							
				7	7								

[a] Bold number signifies most stable state.

resemblances to Hf or Ce^{IV}, whereas Pa and the elements in the +5 state show some resemblances to Ta^{V}. Exceptions to the latter statement are the +5 state of U, Np, Pu, and Am in the *dioxo ions* MO_2^+; these ions and the MO_2^{2+} ions of the +6 states show unusual and exceptional behavior, as discussed below.

Oxidation State +2. As Table 21-3 shows, this is somewhat unusual. The pertinent standard solution potentials are given in Table 21-4. The Md^{2+} ion is even more stable than Eu^{2+} or Yb^{2+}. It, and the other An^{2+} ions, have properties similar to the Ln^{2+} and Ba^{2+} ions.

Oxidation State +3. This is the most common oxidation state although for Th, Pa, and U it is of secondary importance. The general chemistry closely resembles that of the lanthanides. The halides MX_3 may be readily prepared and are easily hydrolyzed to MOX. The oxides M_2O_3 are known only for Ac, Pu, and heavier elements. In aqueous solution there are M^{3+} ions, and insoluble hydrated fluorides and oxalates can be precipitated. Isomorphism of crystalline solids is common. Since Ln^{3+} and An^{3+} ions are similar in size the formation of complex ions and their stability constants are similar. Thus it is difficult to separate actinide from lanthanide elements, though it can be done by ion-exchange or solvent-extraction procedures.

Oxidation State +4. This is the principal one for Th and has considerable importance for Pa, U, and Pu. For Am, Cm, Bk, and Cf it is much more easily reduced and stable only under special conditions of complexing. Points of importance concerning the +4 state are (*a*) the dioxides MO_2 from Th to Cf all have the fluorite lattice, (*b*) the tetrafluorides MF_4 are isostructural with lanthanide tetrafluorides, (*c*) the chlorides and bromides are known only for Th, Pa, U, and Np, presumably owing to the inability of the halogen to oxidize the heavier metals, and for iodides only those of Th, Pa, and U exist, (*d*) oxohalides MOX_2 can be made for Th–Np, for example, by the reaction

$$3MX_4 + Sb_2O_3 \xrightarrow{\text{heat}} 3MOX_2 + 2SbX_3\uparrow \quad 450^\circ C$$

(*e*) hydrolysis, complexation, and disproportionation are important in aqueous solution, as discussed later.

Oxidation State +5. This is the principal state for Pa, whose chemistry resembles that of Nb^{V} and Ta^{V}. For the other +5 elements, U^{V}, Np^{V}, Pu^{V}, and Am^{V}, however, there is no particular resemblence to Nb^{V} and Ta^{V} because

TABLE 21-4
Actinide Potentials, $M^{3+} + e = M^{2+}$

Element	$E^0(V)^a$	Element	$E^0(V)^a$
Am	−2.3	Es	−1.3
Cm	−4.4	Fm	1.0
Bk	−2.8	Md	−0.15
Cf	−1.6	No	1.45

[a] I., J. Nugent, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1767.

of the importance of the AnO_2^+ ions. Comparatively few solid An^V compounds, other than those of Pa^V are known; the most notable are the U^V halides, the pentafluorides PaF_5, NbF_5, and UF_5,[5] fluoro anions, namely, AnF_6^-, AnF_7^{2-}, and AnF_8^{3-} for Pa—Pu and the oxochlorides $PaOCl_3$ and $UOCl_3$.

Oxidation State +6. The most important examples are the AnO_2^{2+} ions of U, Np, Pu, and Am (to be discussed later). Otherwise, there are only a few compounds such as the hexafluorides of U, Np, and Pu, as well as UCl_6, various oxohalides and oxohalide complexes (UOF_4, UOF_5^-, and $UOCl_5^-$) and the uranium alkoxides, $U(OR)_6$.

Oxidation State +7. There are only a few marginally stable Np^{VII} and Pu^{VII} compounds, which formally contain oxo anions such as $[Np_2O_8(OH)_2]^{4-}$ and PuO_6^{5-}.

21-4. The Dioxo Ions, AnO_2^+ and AnO_2^{2+}

The dioxo ions are remarkably stable with respect to the strength of the M—O bond. Unlike some other oxo ions they can persist through a variety of chemical changes, and they behave like cations whose properties are intermediate between those of M^+ or M^{2+} ions of similar size but greater charge. The MO_2 group even appears more or less as an "yl" group in certain oxide and oxo ion structures; furthermore, whereas MoO_2F_2 or WO_2F_2 are molecular halides, in UO_2F_2 there is a linear O—U—O group with F bridges. The stability of UO_2^{2+} and PuO_2^{2+} ions in aqueous solution is shown by the very long half-life for exchange with $H_2{}^{18}O$ ($>10^4$ h).

So far as is known the AnO_2^{n+} ions are all linear.[6] The ThO_2 molecule (matrix isolated) is, however, bent; this has been explained, as well as the linearity of the ions, by good calculations in which allowance is made for relativistic effects.[7] The An—O distances vary somewhat from compound to compound in the solid state and for UO_2^{2+} the frequency of the antisymmetric stretching mode (ν, in cm^{-1}) seen easily in the ir and the U—O distance (D in Å) are related by the equation

$$D = 81.2\nu^{-2/3} + 0.85$$

The order of stability of the dioxo ions is implied by their symmetric stretching frequencies measured by Raman spectroscopy on aqueous solutions.[8] This order, with the frequencies (in cm^{-1}) is $UO_2^{2+}(856) \sim NpO_2^{2+}(854) > PuO_2^{2+}(833) > NbO_2^{+}(767) > PuO_2^{+}(748) > AmO_2^{+}(730)$. The An—O bonding can be formulated with a scheme in which appropriate *d* and *f* orbitals can be combined into molecular orbitals to give one σ plus two π bonds. The MOs are filled at UO_2^{2+}, and succeeding electrons are fed into

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[5] D. Brown *et al.*, *J. Less-Common Met.*, 1982, **86**, 75.

[6] R. Fischer *et al.*, *J. Less-Common Met.*, 1981, **80**, 121.

[7] W. R. Wadt, *J. Am. Chem. Soc.*, 1981, **103**, 6053.

[8] G. M. Begun *et al.*, *Inorg. Chem.*, 1984, **23**, 1914.

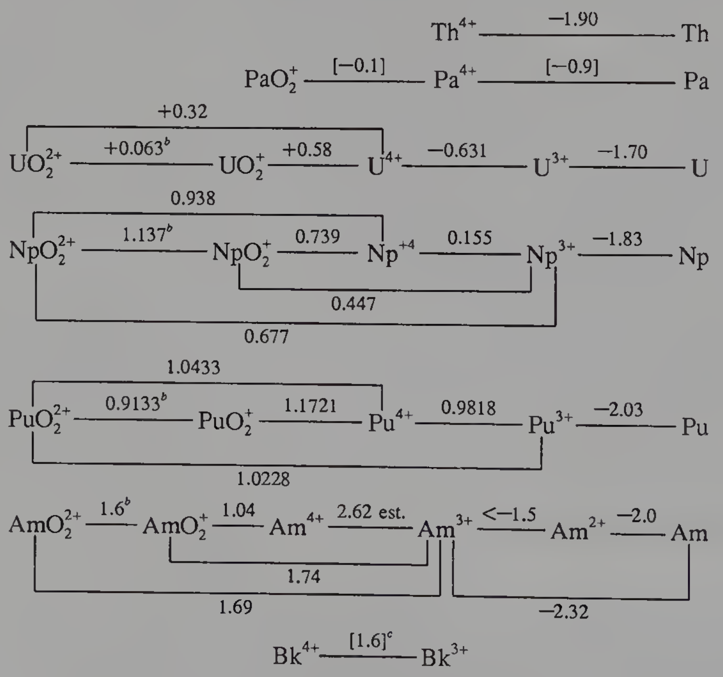
non-bonding orbitals. The MO scheme allows detailed interpretation of spectroscopic and magnetic data for the oxo ions. It also provides an explanation of the U—Am stability sequence and the nonexistence of PaO_2^{2+}. The latter is connected with the fact that for Pa the 6*d* is higher than the 5*f* level, whereas for U($5f^36d^17s^2$) it is the reverse, so that for Pa, the 5*f*σ–2*p*σ metal–oxygen overlap is poor. The instability of UO_2^+ is probably also connected with the sensitivity of the energy of the 5*f* electrons to total charge, thus critically affecting the U—O overlap. The UO_2^+ ion disproportionates according to the following equation:

$$2UO_2^+ + 4H^+ = U^{4+} + UO_2^{2+} + 2H_2O \qquad K = 1.7 \times 10^6$$

The PuO_2^+ ion is also somewhat unstable although the exact nature of the Pu^{IV} species is not certain.

TABLE 21-5[a]

Formal Reduction Potentials (V) of the Actinides for 1 *M* Perchloric Acid Solutions at 25°C (brackets indicate estimate)



Notes:

1. $PaO_2^+ + 4H^+ + 5e = Pa + 2H_2O$, $E = [-1.0]$.

2. Couples involving oxygen transfer, for example, $UO_2^{2+} + 4H^+ + 2e = U^{4+} + 2H_2O$ are *irreversible* and are of course hydrogen ion dependent. Couples such as PuO_2^{2+}/PuO_2^+ *are* reversible.

[a] See also Table 21-1.

[b] The true E^0 values for U, Np, Pu, and Am are 0.163, 1.236, 1.013, and 1.7 V, respectively (J. R. Brand and J. W. Cobble, *Inorg. Chem.* 1970, **9**, 912).

[c] By direct measurement in 0.1 *M* H_2SO_4, E = 1.43 V (R. C. Propst and M. L. Hyder, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2205).

21-5. Actinide Ions in Aqueous Solution[9]

The formal reduction potentials of actinide ions in aqueous solution are given in Tables 21-2 and 21-5, from which it is clear that the electropositive character of the metals increases with increasing Z and that the stability of the higher oxidation states decreases. A comparison of various actinide ions is given in Table 21-6. It must be noted also that for comparatively short-lived isotopes decaying by α emission or spontaneous fission, heating, and chemical effects

TABLE 21-6
The Principal Actinide Ions[a] in Aqueous Solution

Ion	Color[a]	Preparation	Stability
U^{3+}	Red brown	Na or Zn/Hg on UO_2^{2+}	Slowly oxidized by H_2O, rapidly by air to U^{4+}
Np^{3+}	Purplish	H_2(Pt) or electrolytic	Stable in water; oxidized by air to Np^{4+}
Pu^{3+}	Blue violet	SO_2, NH_2OH on higher states	Stable to water and air; easily oxidized to Pu^{4+}
Am^{3+}	Pink	I^-, SO_2, etc., on higher states	Stable; difficult to oxidize
Cm^{3+}	Pale yellow		Stable; not oxidized chemically
U^{4+}	Green	Air or O_2 on U^{3+}	Stable; slowly oxidized by air to UO_2^{2+}
Np^{4+}	Yellow green	SO_2 on NpO_2^+ in H_2SO_4	Stable; slowly oxidized by air to NpO_2^{2+}
Pu^{4+}	Tan	SO_2 or NO_2^- on PuO_2^{2+}	Stable in 6 M acid; disproportionates in low acid → $Pu^{3+} + PuO_2^{2+}$
Am^{4+}	Pink red	$Am(OH)_4$ in 15 M NH_4F	Stable in 15 M NH_4F; reduced by I^-
Cm^{4+}	Pale yellow	CmF_4 in 15 M CsF	Stable only 1 h at 25°C
UO_2^+	?	Transient species	Stability greatest pH 2–4; disproportionates to U^{4+} and UO_2
NpO_2^+	Green	Np^{4+} and hot HNO_3	Stable; disproportionates only in strong acid
PuO_2^+	?	Hydroxylamine on PuO_2^{2+}	Always disproportionates; most stable at low acidity
AmO_2^+	Pale yellow	Am^{3+} with OCl^-, cold $S_2O_8^{2-}$	Disproportionates in strong acid; reduced (2%/hr) by-products of own α radiation
UO_2^{2+}	Yellow	Oxidize U^{4+} with HNO_3, etc.	Very stable; difficult to reduce
NpO_2^{2+}	Pink	Oxidize lower states with Ce^{4+}, MnO_4^-, O_3, BrO_3^-, etc.	Stable; easily reduced
PuO_2^{2+}	Yellow pink		Stable; fairly easy to reduce
AmO_2^{2+}	Rum		Reduced (4%/hr) by-products from own α radiation

[a] Ac^{3+}, Th^{4+}, Cm^{3+}, and ions of Pa are colorless.

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[9] G. R. Choppin, *Radiochem. Acta*, 1983, **32,** 43; *J. Less-Common Met.*, 1983, **93,** 323.

due to the high level of radioactivity occur in both solids and aqueous solutions (e.g., for ^{238}Pu, ^{241}Am, and ^{242}Cm the heat output is calculated as 0.5, 0.1, and 122 $W\,g^{-1}$, respectively). Radiation-induced decomposition of water leads to H and OH radicals, H_2O_2 production, and so on, and in solution higher oxidation states such as Pu^{V}, Pu^{VI}, and $Am^{IV,VI}$ are reduced. Chemical reactions observable with a short-lived isotope, for example, ^{242}Cm (163 days), may differ when a longer-lived isotope is used; thus Cm^{IV} can be observed only when ^{244}Cm (17.6 years) is employed.

The possibility of several cationic species introduces complexity into the aqueous chemistries, particularly of U, Np, Pu, and Am. Thus all four oxidation states of Pu can coexist in appreciable concentrations in a solution. The solution chemistries and the oxidation–reduction potentials are further complicated by the formation in the presence of ions other than perchlorate, of cationic, neutral or anionic species. Furthermore, even in solutions of low pH, hydrolysis and the formation of polymeric ions occurs. Third, there is the additional complication of disproportionation of certain ions, which is particularly dependent on the pH.

Since extrapolation to infinite dilution is impossible for most of the actinide ions, owing to hydrolysis—for example, Pu^{4+} cannot exist in solution below 0.05 *M* in acid—sometimes only approximate oxidation potentials can be given. The potentials are sensitive to the anions and other conditions.

21-6. Complexes and Stereochemistry

The actinides have a far greater tendency to form complexes than do the lanthanides. There are extensive series of complexes with oxo anions of all types (RCO_2^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, $H_nPO_4^{-3+n}$, $C_2O_4^{2-}$), halide ions, BH_4^-, and other ligands, especially chelating ones.

A vast amount of data exists on complex ion formation in solution, since this has been of primary importance in connection with solvent extraction, ion-exchange behavior, and precipitation reactions involved in the technology of actinide elements. The general tendency to complex ion formation decreases in the direction controlled by factors such as ionic size and charge, so that the order is generally $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$. For anions the order of complexing ability is generally: uninegative ions, $F^- > NO_3^- > Cl^- > ClO_4^-$; binegative ions, $CO_3^{2-} > ox^{2-} > SO_4^{2-}$.

There are a great many actinide nitrato complexes, many of which are important in separation procedures whereby the elements are extracted from aqueous nitric acid into nonpolar solvents.[10] Of these, the UO_2^{2+} complexes are best characterized; they are typically eight-coordinate with two bidentate NO_3^- ions and two neutral ligands (H_2O, THF, DMSO, and R_3PO) forming a distorted equatorial hexagon.

Because of the enormous variety of ligands that form actinide complexes

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[10] U. Casellato *et al.*, *Coord. Chem. Rev.*, 1981, **36**, 183.

and the number of oxidation states, the stereochemistry found in complexes and compounds of the actinides is extraordinary. An overview is presented in Table 21-7. The relatively large sizes of the actinide ions coupled with the high electrostatic attraction due to formal charges of +3 to +6, along with the fact that a large number of valence shell orbitals are potentially available for bonding, all lead to the result that higher coordination numbers, especially 8 and 9, are very common.

For the +3 oxidation state, where there is much resemblence to the lanthanides, octahedral coordination is often found, but so also is coordination number 9. Eight-coordination is very common for the +4 oxidation state. In the +5 oxidation state the AnF_8^{3-} ions afford rare examples of discrete cubic coordination. In oxidation state +6, the hexafluorides are strictly octahedral,

TABLE 21-7
Stereochemistry of Actinides

Oxidation state	Coordination number	Geometry[a]	Examples
+3	5	*tbp*	AcF_3, $BaUF_6$(LaF_3 type)
	6	Octahedral	An(acac)$_3$, $[An(H_2O)_6]^{3+}$
	8	Bicapped trigonal prism	$PuBr_3$, $[AmCl_2(H_2O)_6]^+$
	9	Tricapped trigonal prism	UCl_3, $AmCl_3$ (also La–$GdCl_3$)
	9	Irregular	$(NH_4)U(SO_4)_2(H_2O)_4$
+4	4	Distorted	$U(NPh_2)_4$
	5	Distorted *tbp*	$U_2(NEt_2)_8$
	6	Octahedral	UCl_6^{2-}, UCl_4(HMPA)$_2$
	8	Cubic(O_h)	$(Et_4N)_4[U(NCS)_8]$
		Dodecahedral	$[Th(ox)_4]^{4-}$, $Th(S_2CNEt_2)_4$
		Fluorite structure	ThO_2, UO_2
		Square antiprism	ThI_4(s), U(acac)$_4$, $(NH_4)_2UF_6$, $Cs_4[U(NCS)_8]$
	9	Capped square antiprism	Th(trop)$_4\cdot H_2O$
	10	Bicapped square antiprism	$K_4Th(ox)_4\cdot 4H_2O$
	10	?	An(trop)$_5^-$ (An = Th or U)
	12	Irregular icosahedral	$[Th(NO_3)_6]^{2-}$ [b]
		distorted cubo-octahedral	$An(BH_4)_4$ (Np, Pu[c])
	14	Complex	$An(BH_4)_4$ (Th, Pa, U[c])
+5	6	Octahedral	UF_6^-, α-UF_5(infinite chain)
	7		β-UF_5
	8	Cubic(O_h)	Na_3AnF_8(An = Pa, U, No)
	9	Complex	PaF_7^{2-} in K_2PaF_7
+6	6	Octahedral	AnF_6,[d] Li_4UO_5(distorted), UCl_6
	6–8	See text	AnO_2^{2+} complexes
	8	?	$M^I_2UF_8$

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[a] For detailed discussion of crystal structures, many of which are more complicated, see A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, 1984.

[b] S. M. Bowen *et al., Inorg. Chem.*, 1982, **21**, 261.

[c] N. M. Edelstein *et al., J. Am. Chem. Soc.*, 1980, **102,** 620.

[d] E. P. Zeer *et al., Chem. Phys. Lett.*, 1983, **100**, 24.

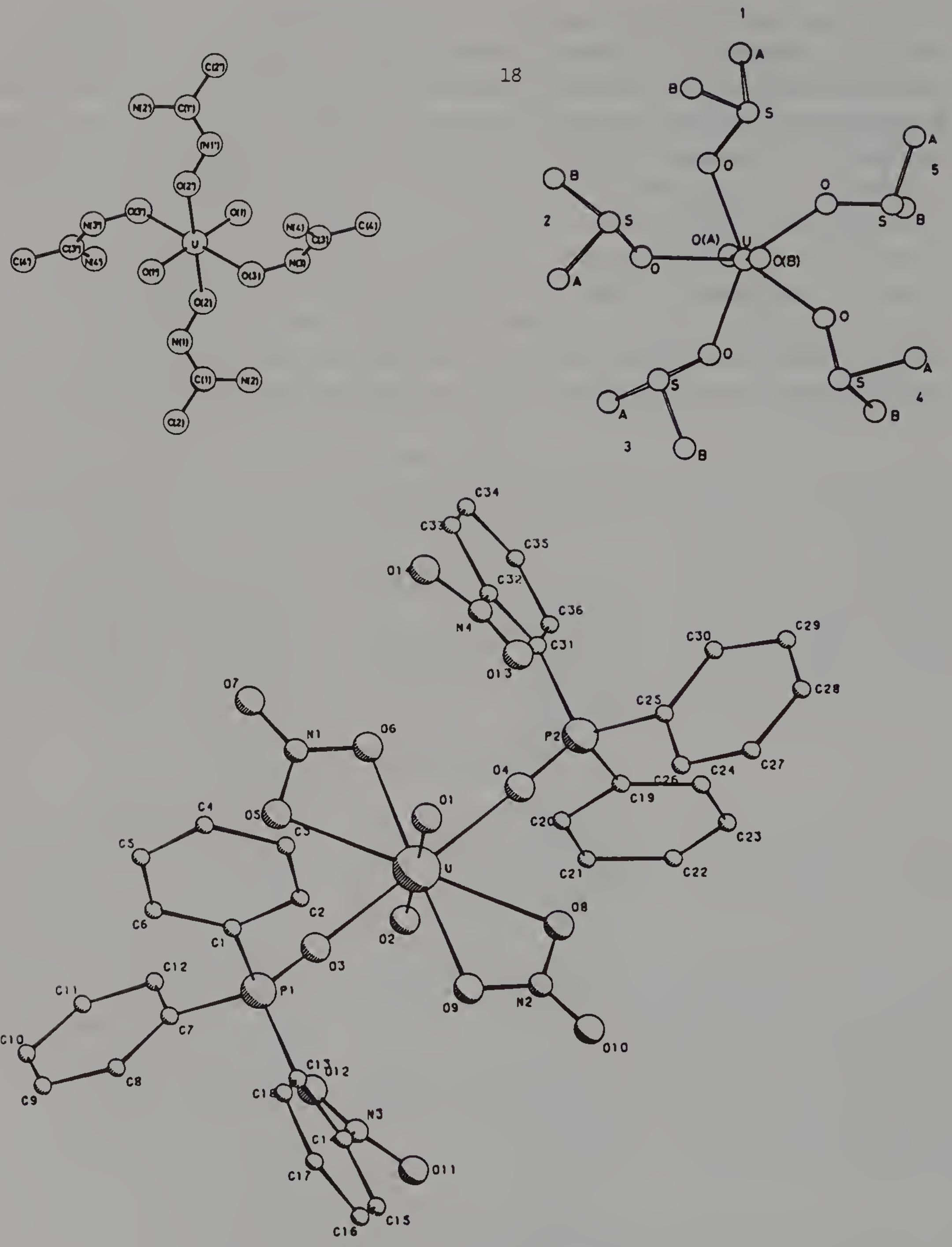

FIG. 21-2. Some representative UO_2^{2+} complex structures. (a) $[UO_2(acetamidoxime)_4]^{2+}$ (ref. 11), (b) $[UO_2(DMSO)_5]^{2+}$ (ref. 12), and (c) $UO_2(NO_3)_2(Ph_3PO)_2$ (ref. 16.)

earlier reports to the contrary notwithstanding [see footnote (*d*) to Table 21-7].

The stereochemistry of the AnO_2^{2+} complexes, especially for uranium, has been greatly studied and varies considerably. The overall pattern is that the axial O—U—O unit is surrounded by 4–6 ligand atoms in or close to an equatorial plane, so as to provide tetragonal, pentagonal, or hexagonal bipyramidal coordination. The six-coordinate species are least common; examples are provided by the amidoxime complexes, $UO_2[RC(NH_2)NO]_4$ (Fig. 21-2).[11] Seven-coordination is found for species such as the cation in $[UO_2(DMSO)_5](ClO_4)_2$[12] (Fig. 21-2), the $[UO_2F_4(H_2O)]^{2-}$ ion,[13] or the uranyl β-diketonate adducts, $UO_2(RCOCHCOR)_2L$ ($L = H_2O$ or EtOH).[14]

The eight-coordinate AnO_2^{2+} complexes are the most numerous and there are many important examples. Some of these have an essentially flat equatorial six ring, for example, the anion in $Na[UO_2(O_2CCH_3)_3]$,[15] the $UO_2(NO_3)_2(Ph_3PO)_2$ molecule,[16] or the $UO_2(O_2CR)_2(H_2O)_2$ molecules,[17] but puckering may well occur in other cases.[18]

21-7. Organometallic Chemistry[19]

While there are a few organometallic compounds of other actinide elements, the overwhelming majority are those of uranium, along with a smaller number formed by thorium. We shall therefore focus on the uranium compounds, with subsidiary mention of others as appropriate. The field is a relatively young one having begun only in 1956 with Wilkinson's preparation of Cp_3UCl, followed in 1962 by Fischer's reports of some additional cyclopentadienyl compounds of U and Th, and then in 1968 by Streitwieser's preparation of $(C_8H_8)_2U$. The first compounds with U—C σ bonds were reported only in 1972.

Allyl Complexes. For Th and U, the homoleptic allyls (or 2-methylallyls), which are unstable above 0°C, may be prepared by the reaction:

$$AnCl_4 + 4(\text{allyl})MgX \longrightarrow M(\text{allyl})_4 + 4MgXCl$$

The allyl groups are bound in an η^3 fashion, and may be displaced by reactions with HX or ROH to give, for example, $U(C_3H_5)_3X$ or $[U(C_3H_5)_3(OR)]_2$. More stable An—allyl linkages are known in compounds that also contain η^5-Cp or η^5-Cp* ligands.

Cyclopentadienyl Compounds. These constitute the largest and most varied class. In addition to those of C_5H_5 (Cp) itself, there are a number of MeC_5H_4,[20] Me_5C_5 (Cp*), and indenyl[21] compounds. The bonding of the Cp rings

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[11] E. G. Witte *et al., Inorg. Chim. Acta,* 1984, **94,** 323.

[12] J. M. Harrowfield *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 393.

[13] T. C. W. Mack and W.-H. Yip, *Inorg. Chim. Acta,* 1985, **109,** 131.

[14] D. T. Haworth and M. Das, *Inorg. Chim. Acta,* 1985, **110,** L3.

[15] D. H. Templeton *et al., Acta Cryst, C,* 1985, **41,** 1439.

[16] U. Casellato *et al., Inorg. Chim. Acta,* 1985, **110,** 41.

[17] G. Micera *et al., Inorg. Chim. Acta,* 1985, **109,** 135.

[18] L. J. Candle *et al., Inorg. Chim. Acta,* 1985, **110,** 91; W. I. Azeez and A. I. Abdulla, *Inorg. Chim. Acta,* 1985, **110,** 15.

[19] For extensive references see K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc.,* 1987, **109,** 3195.

[20] A. Zalkin and J. G. Brennan, *Acta Cryst. C,* 1985, **41,** 1295.

[21] J. Goffart *et al., J. Organometal. Chem.,* 1981, **209,** 281; *Acta Cryst. B.,* 1982, **38,** 2400.

to the metals is basically dative and rather polar in character and there is some f-orbital participation.[22]

With Cp itself, there are compounds of the types Cp_4An (for U, Th, Pa, and Np), Cp_3An (for U, Th, Pu, Am, Cm, Bk, and Cf), Cp_2AnX (for U, Th, and Bk), Cp_3AnX (for U, Th, and Np), and $CpAnX_3$ (for U, Th, and Np). It should be noted that because of the varying chemical properties of the An elements, preparative methods often differ from one element to another.

The compound Cp_3U[23] can be made in a number of ways:

$$UCl_3 + 3KCp \xrightarrow[\text{reflux}]{\text{benzene}} Cp_3U + 3KCl$$

$$Cp_4U + K \xrightarrow[\text{reflux}]{\text{benzene}} Cp_3U + KCp$$

$$U + 3\,CpH \longrightarrow Cp_3U + \tfrac{3}{2}H_2$$

It is a strong Lewis acid and forms adducts with a variety of donors including diphenylacetylene.[24a] The structure of the THF adduct[24b] is shown in Fig. 21-3; the Cp ring centroids and the THF oxygen atom define a distorted tetrahedron. The thorium compound[24c] $Th[C_5H_3(SiMe_3)_2]_3$, a rare example of Th^{III}, is blue and paramagnetic.

The Cp_4U molecule, obtained by reaction of UCl_4 with KCp, has four pentahapto rings in an essentially tetrahedral array about the metal atom.

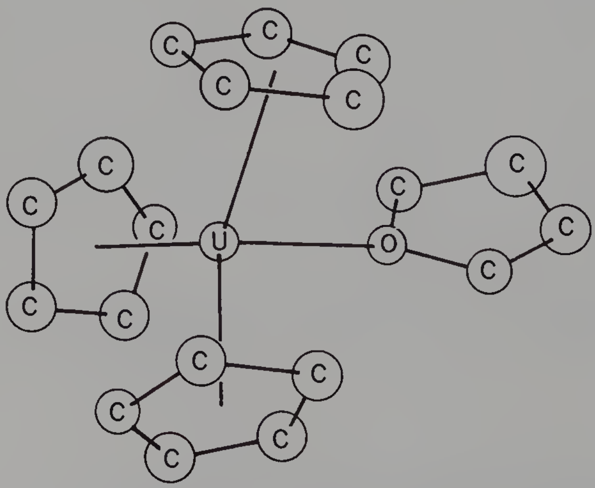

FIG. 21-3. The structure of $(\eta^5\text{-}C_5H_5)_3U(C_4H_8O)$ (cf. ref. 24b).

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[22] B. E. Bursten and A. Fang, *Inorg. Chim. Acta*, 1985, **110,** 153.

[23] B. Kanellakopulos *et al., J. Organomet. Chem.*, 1980, **24,** 507; P. Zanella *et al., Inorg. Chim. Acta*, 1980, **44,** L155; Y. Mugnier *et al., J. Chem. Soc. Chem. Commun.*, **1982,** 257; T. J. Marks *et al., J. Am. Chem. Soc.*, 1982, **104,** 1860.

[24a] M. Ephritikhine *et al., J. Chem. Soc. Chem. Commun.*, **1987,** 494.

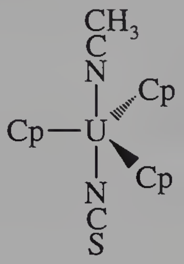
[24b] H. J. Wasserman *et al., J. Organomet. Chem.*, 1983, **254,** 305.

[24c] P. C. Blake *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 1148.

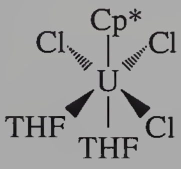
The Cp_3UX compounds are the most generally important cyclopentadienyl compounds. The chloride is best prepared by the reaction

$$UCl_4 + 3TlCp \xrightarrow{DME} Cp_3UCl + 3TlCl$$

The Cp rings do not behave ionically, but the Cl is labile, allowing ready synthesis of many other Cp_3UX compounds. There is even ionization in aqueous solution to give $Cp_3U(H_2O)_2^+$, which forms precipitates with many anions.[25] Many other synthetic methods are known for Cp_3UX as well as $(RCp)_3AnX$[26] compounds and X may be virtually any anion. In some cases adduct formation occurs to give five-coordinate *tbp* products, as in $Cp_3U(NCS)(CH_3CN)$ (21-I) or in $Cp_3AnX_2^-$ complexes.[27]



(21-I)



(21-II)

The Cp_2AnX_2 compounds are rather unstable, and "Cp_2UCl_2" is in fact a mixture of Cp_3UCl and $CpUCl_3(DME)$ when prepared in DME.[28] However, some genuine Cp_2UX_2 compounds do exist, for example, $Cp_2U(NEt_2)_2$ and $Cp_2U(BH_4)_2$.

The $CpAnX_3$ compounds generally exist as diadducts [cf. $CpUCl_3(DME)$, cited previously] and are not widely used.

The Cp* (i.e., Me_5C_5) compounds differ in many ways from their Cp analogues, including having generally improved solubility and crystallizability. Perhaps the most significant major difference is that $Cp^*_2UCl_2$ (unlike its Cp analogue) is stable and has an extensive chemistry leading to a great variety of other $Cp^*_2UX_2$ compounds.[29] The compound $Cp^*_2UCl_2$ forms adducts with donors, $Cp^*_2UCl_2L$; L may be pyrazole, but in addition to the simple adduct pyrazole also gives an unusual product[30] in which both nitrogen atoms of the $C_3H_3N_2^-$ anion are bound, as shown in Fig. 21-4. There is also the compound $Cp_3U(C_3H_3N_2)$, which has a pz^- ligand bound in the same unusual way.[31]

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[25] R. D. Fischer *et al., J. Organomet. Chem.*, 1982, **238,** 99.

[26] A. Dormond, *J. Organomet. Chem.*, 1983, **256,** 47.

[27] K. W. Bagnall *et al., J. Chem. Soc. Dalton Trans.*, **1982,** 1999.

[28] T. J. Marks *et al., J. Am. Chem. Soc.*, 1979, **101,** 2656.

[29] T. J. Marks *et al., J. Am. Chem. Soc.*, 1981, **103,** 2206, 6650; 1984, **106,** 2907; R. G. Finke *et al., J. Organomet. Chem.*, 1982, **229,** 179; P. Reeb *et al., J. Organomet. Chem.*, 1982, **239,** Cl; R. R. Ryan *et al., J. Am. Chem. Soc.*, 1985, **107,** 501; R. R. Ryan *et al., Organometallics*, 1986, **5,** 90.

[30] C. W. Eigenbrot, Jr., and K. N. Raymond, *Inorg. Chem.*, 1982, **21,** 2653.

[31] C. W. Eigenbrot, Jr., and K. N. Raymond, *Inorg. Chem.*, 1981, **20,** 1553.

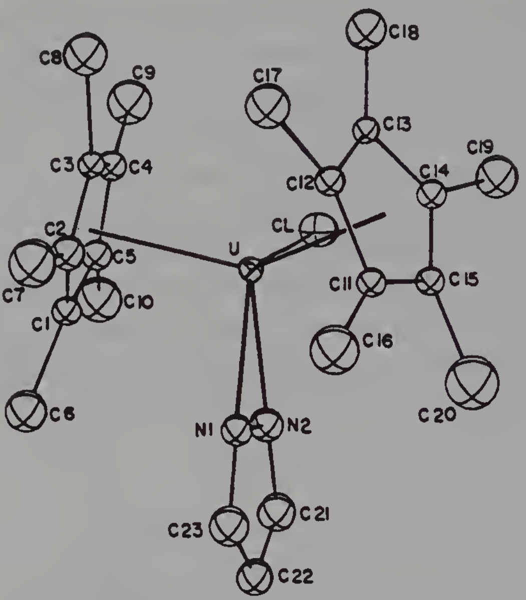
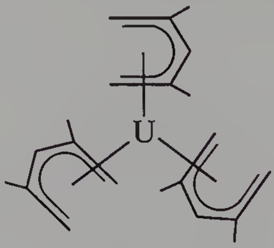


FIG. 21-4. The structure of $(C_5Me_5)_2UCl(C_3H_3N_2)$ (cf. ref. 30).

Compounds of the type Cp_2^*UX are also known,[32] as are Cp^*UX_3 species,[33] such as $Cp^*UCl_3(THF)_2$, which has the structure shown in (21-II).

A few open pentadienyl compounds, such as $U(2,4\text{-}C_7H_{11})_3$ have been reported[34] and are believed to have tris-η^5 coordination, as in (21-III).



(21-III)

Until recently there was little indication of stable actinide compounds with neutral arene rings, but with hexamethyl benzene it has been possible to isolate several such compounds of U^{III} and U^{IV}, e.g., $(C_6Me_6)U(AlCl_4)_3$.[35]

Cyclooctatetraene Compounds. The green, pyrophoric compound $U(C_8H_8)_2$, known as *uranocene*, was first prepared in 1968 by the reaction

$$UCl_4 + 2K_2C_8H_8 \longrightarrow U(C_8H_8)_2 + 4KCl$$

but it can also be made from C_8H_8 and finely divided uranium, and in other ways. Its molecular structure, Fig. 21-5, is that of a sandwich with perfect D_{8h} symmetry. The Th, Pa, Np, and Pu analogues are all known. In addition,

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[32] R. G. Finke *et al.*, *J. Chem. Soc. Chem. Commun.*, **1981**, 232; R. G. Finke *et al.*, *J. Am. Chem. Soc.*, 1981, **103**, 1873; T. J. Marks *et al.*, *Organometallics.*, 1982, **1**, 170.

[33] T. J. Marks *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 4692.

[34] R. D. Ernst *et al.*, *J. Organomet. Chem.*, 1983, **255**, 311.

[35] F. A. Cotton and W. Schwotzer, *Organometallics*, 1987, **6**, 1275.

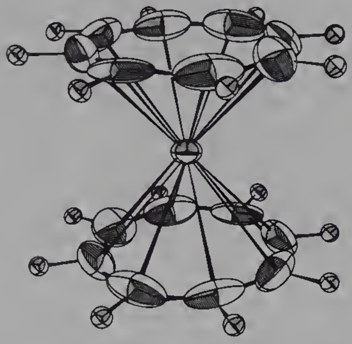

FIG. 21-5. The molecular structure of $An(C_8H_8)_2$ compounds (An = U and Th).

a host of compounds with substituted cyclooctatetraene rings, have also been made.[36] The thorocene chemistry has been almost as thoroughly studied as that of uranocene.[37]

The $An(C_8H_8)_2$ compounds and their derivatives are exceedingly sensitive to O_2, H_2O, and other protic reagents, although $U(C_8H_8)_2$ is only slowly hydrolyzed by water to UO_2 and isomers of C_8H_{10}. Half-sandwich C_8H_8 compounds of thorium have also been made[38] and characterized,[39] for example, by the reaction:

$$Th(C_8H_8)_2 + ThCl_4 \xrightarrow{THF} 2Th(C_8H_8)Cl_2(THF)_2$$

A great deal of effort has been expended to understand the bonding in the $An(C_8H_8)_2$ compounds. The crucial issues are the degree of covalence in the bonding and, particularly, how much *f*-orbital participation there is. Qualitatively, just in terms of orbital symmetry, uranocene might be considered an *f*-orbital analogue of ferrocene, as indicated in Fig. 21-6. The picture that is emerging from a combination of calculations[40] and experimental[41] studies is that there is appreciable covalence, but that the 6*d* orbitals probably play at least as great a role as the 5*f* orbitals. The exact role of the 5*f* orbitals, however, remains elusive.[42]

Actinide Alkyls and Aryls. Simple alkyls, AnR_x or AnR_x^{n-}, have been sought by many workers with little success. The only well-defined species is found[43] in $[Li(TMEDA)]_3[Th(CH_3)_7]\cdot TMEDA$, which contains a seven-coordinate $Th(CH_3)_7^{3-}$ complex to which the Li atoms are attached. The compound is stable at 20°C for many hours. There is also $Th(CH_2Ph)_4$, which is relatively stable, but probably has some multihapto bonding.

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[36] A. Streitwieser, Jr., *et al., Inorg. Chem.*, 1981, **20,** 3086; *Organometallics,* 1982, **1,** 618; 1983, **2,** 1873.

[37] C. Levanda and A. Streitwieser, Jr., *Inorg. Chem.*, 1981, **20,** 656.

[38] A. Streitwieser, Jr., *et al., J. Am. Chem. Soc.*, 1980, **102,** 2128.

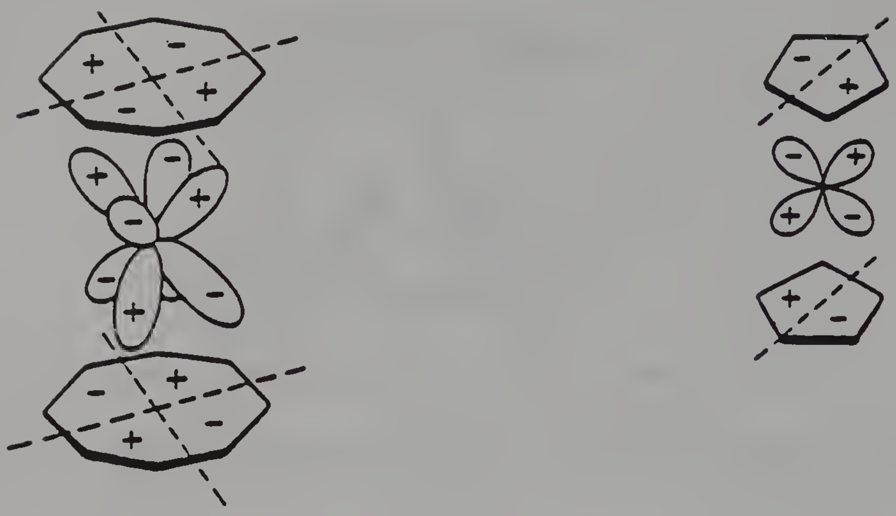
[39] A. Zalkin *et al., Inorg. Chem.*, 1980, **19,** 2560.

[40] N. Rösch and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, 1983, **105,** 7237; N. Rösch, *Inorg. Chim. Acta,* 1984, **94,** 297.

[41] J. C. Green *et al., Organometallics,* 1983, **2,** 1707.

[42] B. R. McGarvey, *Can. J. Chem.*, 1984, **62,** 1349.

[43] T. J. Marks *et al., J. Am. Chem. Soc.*, 1984, **106,** 6841.



(a) (b)

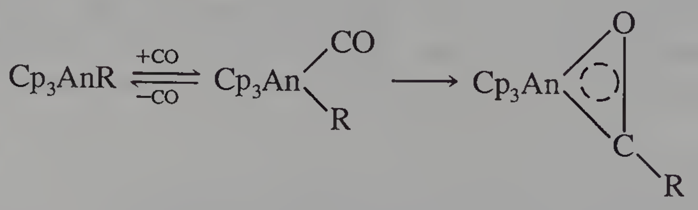
FIG. 21-6. A comparison of the major bonding modes in (a) an $An(C_8H_8)_2$ and (b) an $M(C_5H_5)_2$ molecule.

Moderately stable methyl and benzyl compounds of Th and U can be prepared when chelating diphosphines are also present,[44] as in the following scheme.

$$AnCl_4 + 2dmpe \longrightarrow AnCl_4(dmpe)_2 \xrightarrow{4RLi} AnR_4(dmpe)_2 \quad R = CH_3 \text{ and } CH_2Ph$$

Thermally stable methyl compounds can also be obtained when $(Me_3Si)_2N$ ligands are present, for example, $An(CH_3)[N(SiMe_3)_2]_3$ (An = Th and U).[45]

However, it is with the Cp_3AnR (An = Th, U, and Np) and homologous compounds containing substituted cyclopentadienyl groups, especially Cp*, that the important, stable An—C σ bonds are to be found. The Th—R bonds are rather strong,[46] and vary with R much as do other M—C bonds. Both photo and thermal decomposition pathways are multiple and complex.[47] Unlike *d*-block alkyls, decomposition by β-hydride elimination is not a major route. Such compounds undergo migratory insertion reactions[48] with CO, RNC, or SO_2, as shown in the following equations:



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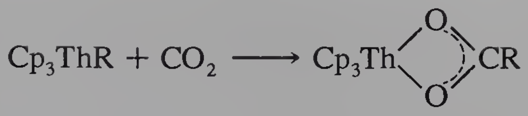
[44] R. A. Andersen *et al., Organometallics,* 1984, **3,** 293.

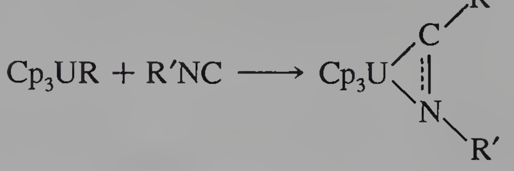
[45] R. A. Andersen *et al., J. Am. Chem. Soc.*, 1981, **103,** 4063; *Inorg. Chem.*, 1981, **20,** 2991.

[46] T. J. Marks *et al., Organometallics,* 1985, **4,** 352.

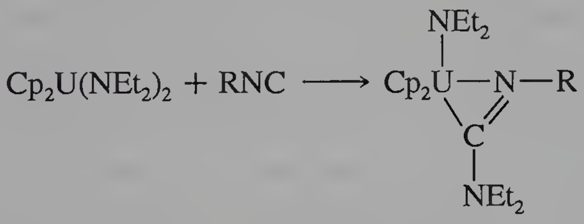
[47] T. J. Marks *et al., J. Am. Chem. Soc.*, 1982, **104,** 1860; E. Klähne *et al., J. Organomet. Chem.*, 1980, **201,** 399; M. Burton *et al., J. Organomet. Chem.*, 1982, **229,** 21.

[48] L. Arnaudet *et al., J. Organomet. Chem.*, 1981, **214,** 215; G. Paolucci *et al., J. Organomet. Chem.*, 1984, **272,** 363; T. J. Marks *et al., J. Am. Chem. Soc.*, 1984, **106,** 3484; K. C. Moloy and T. J. Marks, *Inorg. Chim. Acta,* 1985, **110,** 127; P. Zanella *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 96.



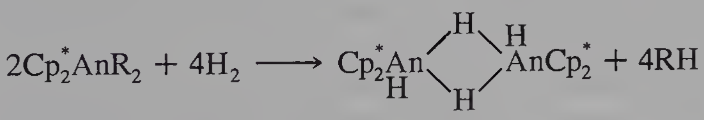


The η^2-bonding of the CO and RNC insertion products is characteristic of these actinide compounds, although it has some parallels in the organometallic chemistry of the *d*-block elements. There are similar insertions into An—NR$_2$ bonds[49] to give products with η^2 ligands, namely,

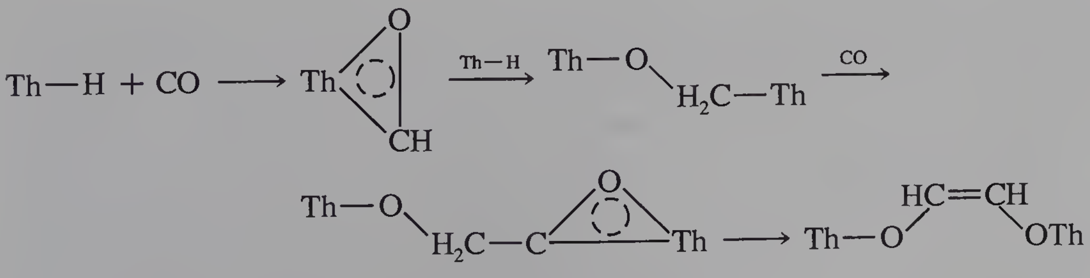


With the Cp* ligand there is considerable chemistry of the Th and U compounds of the type Cp$_2^*$AnR$_2$.[50] These compounds behave similarly to their Cp$_3$AnR analogues in undergoing migratory insertion reactions with CO and RNC to give η^2-products.

Organoactinide Hydrides. The Cp$_2^*$AnR$_2$ compounds (An = Th and U) react with hydrogen to afford dinuclear dihydrides[50]:



The hydrogen in these molecules is rather hydridic and the compounds undergo a host of rapid and interesting reactions with alcohols, ketones, and halocarbons. With CO at low temperature there is insertion into the An—H bond to give η^2-formyls,[51] but these are converted at higher temperatures[52] into the remarkable bridged species, as shown in the following reaction scheme (where Th carries two Cp*):



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[49] A. Dormond *et al., J. Chem. Soc. Chem. Commun.*, **1985**, 1231.

[50] T. J. Marks *et al., J. Am. Chem., Soc.*, 1981, **103**, 4755, 6650.

[51] T. J. Marks *et al., J. Am. Chem. Soc.*, 1981, **103**, 6959; K. G. Moloy and T. J. Marks, *J. Am. Chem. Soc.*, 1984, **106**, 7051.

[52] T. J. Marks *et al., Organometallics*, 1982, **1**, 1723.

Actinide Carbonyls. The carbonyl $U(CO)_6$ can exist below 20 K and its CO stretching frequency of 1961 cm^{-1} implies appreciable $U \rightarrow CO$ π bonding; it is kinetically labile. The only U—CO bond stable at ambiant temperature is formed when $(Me_3SiC_5H_4)_3U$ reversibly absorbs CO to give $(Me_3SiC_5H_4)_3UCO$. It exhibits $\nu(CO)$ at 1976 cm^{-1} but is too labile to be isolated.[53]

CHEMISTRY OF INDIVIDUAL ELEMENTS

21-8. Actinium

Actinium was originally isolated from uranium minerals in which it occurs in traces, but it is now made on a milligram scale by neutron capture in radium (Table 21-2). The actinium +3 ion is separated from the excess of radium and isotopes of Th, Po, Bi, and Pb formed simultaneously by ion-exchange elution or by solvent extraction with thenoyltrifluoroacetone.

The general chemistry of Ac^{3+} in both solid compounds and solution, where known, is very similar to that of lanthanum, as would be expected from the similarity in position in the Periodic Table and in radii (Ac^{3+}, 1.10; La^{3+}, 1.06 Å) together with the noble gas structure of the ion. Thus actinium is a true member of Group IIIB(3), the only difference from lanthanum being in the expected increased basicity. The increased basic character is shown by the stronger absorption of the hydrated ion on cation-exchange resins, the poorer extraction of the ion from concentrated nitric acid solutions by tributyl phosphate, and the hydrolysis of the trihalides with water vapor at ~1000°C to the oxohalides AcOX; the lanthanum halides are hydrolyzed to oxide by water vapor at 1000°C.

The crystal structures of actinium compounds, where they have been studied, for example, in AcH_3, AcF_3, Ac_2S_3, and AcOCl, are the same as those of the analogous lanthanum compounds.

The study of even milligram amounts of actinium is difficult owing to the intense γ-radiation of its decay products that rapidly build up in the initially pure material.

21-9. Thorium

The element is widely distributed in Nature. The principal commercial ore is *monazite sands* (Section 20-6), from which it is extracted by a complex process culminating in a solvent extraction from strongly acid solution.

The chemistry is almost exclusively that of oxidation state IV; some typical compounds are listed in Table 21-8. There are a few compounds which appear to be genuine, but of uncertain nature, in formal oxidation states II and III, namely, ThS, Th_2S_3, $ThI_2(CH_3CN)_2$, and ThI_2.[54]

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[53] R. A. Andersen *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 335.

[54] N. Kumar and D. G. Tuck, *Inorg. Chem.*, 1983, **22**, 1951.

TABLE 21-8
Some Thorium Compounds

Compound	Form	mp (°C)	Properties
ThO_2	White, crystalline; fluorite structure	3220	Stable, refractory, soluble in HF + HNO_3
ThN	Refractory solid	2500	Slowly hydrolyzed by water
ThS_2	Purple solid	1905	Metal like; soluble in acids
$ThCl_4$	Tetragonal white crystals	770	Soluble in and hydrolyzed by H_2O, Lewis acid
$Th(NO_3)_4 \cdot 5H_2O$	White crystals, orthorhombic		Very soluble in H_2O, alcohols, ketones, ethers
$Th(IO_3)_4$	White crystals		Precipitated from 50% HNO_3, very insoluble
$Th(C_5H_7O_2)_4$	White crystals	171	Sublimes in a vacuum 160°C
$Th(BH_4)_4$	White crystals	204	Sublimes in a vacuum about 40°C
$Th(C_2O_4)_2 \cdot 6H_2O$	White crystals		Precipitated from up to 2 *M* HNO_3

Binary Compounds. The oxide (ThO_2) forms on ignition of oxo acid salts or the hydroxide; the latter is strictly basic, though it readily gives colloidal dispersions. A highly insoluble peroxide of variable composition can be precipitated by addition of H_2O_2 to solutions of the salts. All four halides are known as white, crystalline solids, sublimable (except ThF_4) in vacuum at ~600°C. The bromide has potential utility as a luminescent material.[55] The fluoride is precipitated from solution as a hydrate, which can be dehydrated to ThF_4 in a stream of HF, or the anhydrous ThF_4 can be prepared directly by treating ThO_2 with HF(g) at 600°C. Similarly, CCl_4 reacts with ThO_2 to give $ThCl_4$. *Oxohalides* ($ThOX_2$) are formed by reactions of ThO_2 with ThX_4 at 600°C.

The halides are Lewis acids and form many complexes with amines, ketones and a variety of other donors, in which coordination numbers of 7, 8, 9, and even 10 are reached.[56] Many complexes with chelating agents such as hydroxamic acids[57] are also known.

Various borides, sulfides, carbides, nitrides, etc., have been obtained by direct interaction of the elements at elevated temperatures. Like other actinide and lanthanide metals, thorium also reacts at elevated temperatures with hydrogen. Products with a range of compositions can be obtained, but two definite phases, ThH_2 and Th_4H_{15}, have been characterized.

Other Salts and Complexes. Salts of oxo anions, especially

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[55] R. Guillaumont, *Radiochim. Acta,* 1983, **32,** 129.

[56] C. Bombieri *et al., Inorg. Chem. Acta,* 1984, **95,** 237, 251; C. E. F. Rickard and D. C. Woollard, *Acta Cryst., B,* 1980, **36,** 292; A. C. M. Al-Daher and K. W. Bagnall, *J. Less-Common Met.,* 1985, **108,** 257.

[57] W. L. Smith and K. N. Raymond, *J. Am. Chem. Soc.,* 1981, **103,** 3341.

$Th(NO_3)_4 \cdot 5H_2O$ and $Th(SO_4)_2 \cdot 8H_2O$,[58] are important and easily obtained from aqueous solution. The nitrate is particularly useful as it is soluble in alcohols, ketones, ethers, and esters as well as water. Many other thorium salts are precipitated from aqueous solution, for example, the hydroxide, peroxide, fluoride, iodate, oxalate, and phosphate; the last four give precipitates even from strongly acid (6 *M*) solutions and provide useful separations of thorium from elements other than those having +3 or +4 cations with similar properties.

The Th^{4+} ion is larger and hence more resistant to hydrolysis than other +4 ions but at pH's above three complex, polymeric hydrolysis products are formed. However, the high charge makes Th^{4+} very susceptible to forming complexes and even with weakly basic anions association to species such as $Th(NO_3)^{3+}(aq)$, $ThCl_2^{2+}(aq)$, or $Th(HSO_4)(SO_4)^+(aq)$ occurs readily.

Many crystalline complex compounds with high coordination numbers can be isolated such as $K_4Thox_4 \cdot 4H_2O$ (CN = 10, bicapped square antiprism), $K_2Th(NO_3)_6 \cdot 8H_2O$ (CN = 12, icosahedron), $Th(MoO_4)_2$ (CN = 8, square antiprism),[59] $(NEt_4)_4[Th(NCS)_8]$ (CN = 8, cube),[60] $Th(SO_4)_2 \cdot 8H_2O$ (CN = 10, bicapped square antiprism),[58] and many others. The compounds $Th(CH_3BH_3)_4L_n$ (L = Et_2O or THF) have complex dinuclear structures.[61] There are also numerous neutral complexes formed by 8-quinolinol, β-diketones, dithiocarbamates, carbamates, and so on.

21-10. Protactinium[62]

While protactinium is present at less than the parts per million level in uranium ores, this is still the major source because it can be extracted from the residues accumulated in large-scale production of uranium. There are extreme technical difficulties because of colloid formation but more than 100 g have been isolated.

The main oxidation state is V, but there is no Pa^{5+} aquo ion because of hydrolysis to species such as $PaO(OH)^{2+}$ and $PaO(OH)_2^+$ or the formation of complexes with virtually all anions. The fluoro complexes, PaF_6^-, PaF_7^{2-}, and PaF_8^{3-} are of greatest importance and many solids containing them have been isolated. Other stable complexes are formed with $C_2O_4^{2-}$, SO_4^{2-}, citrate, tartrate, β-diketones, and so on.

In the solid state, an important Pa^V compound is the oxide (Pa_2O_5) obtained by ignition of most other compounds in air. On further heating it gives lower oxide phases and ultimately PaO_2.

The pentahalides are all known. The chloride sublimes at 160°C in vacuum

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[58] J. Habash and A. J. Smith, *Acta Crystallogr.*, 1983, **29C,** 413.

[59] T. L. Cremers, *Acta Crystallogr.*, 1983, **39C,** 1165.

[60] P. Charpin *et al.*, *Acta. Crystallogr.*, 1983, **39C,** 190.

[61] N. Edelstein *et al.*, *Inorg. Chem.*, 1985, **24,** 2896.

[62] D. Brown, in *Actinides in Perspective,* N. M. Edelstein, Ed., Pergamon Press, Oxford, 1982, p. 343.

even though it has a polymeric structure consisting of infinite chains of irregular pentagonal bipyramidal $PaCl_7$ units sharing edges. It is soluble in THF but readily hydrolyzes to oxo chlorides such as Pa_2OCl_8 or $Pa_2O_3Cl_4$.

The oxidation state IV can be obtained in aqueous solution by reduction of Pa^V with Cr^{2+} or Zn/Hg but Pa^{IV} is rapidly reoxidized by air. Solid compounds include PaO_2, PaF_4, and $PaCl_4$, and chloro, bromo, and other complexes have been characterized. The esr spectra suggest that Pa^{IV} is a $5f^1$ rather than a $6d^1$ ion.

21-11. Uranium

The existence of the element was recognized by Klaproth in 1789, but only in 1841 did Peligot actually isolate the metal itself. However, it was not until the discovery of uranium fission by Meitner, Hahn, and Strassmann in 1939 that it became commercially important. Its most important ores are *uraninite* (usually called *pitchblend,* and approximating to UO_2) and uranium vanadates.

Oxides. The main ones are UO_2 (brown-black and highly nonstoichiometric), U_3O_8 (greenish-black), and UO_3 (orange-yellow). All of them dissolve readily in nitric acid to give the UO_2^{2+} ion. On addition of H_2O_2 to uranyl solutions a pale yellow peroxide, best formulated as $(UO_2^{2+})(O_2^{2-})(H_2O)_2$, is formed, while the action of NaOH and H_2O_2 gives the stable salt $Na_4[UO_2(O_2)_3]$. The trioxide is best prepared by the decomposition of uranyl nitrate or "ammonium uranate" (see below). From UO_3, the other oxides can be obtained by the reactions

$$3UO_3 \xrightarrow{700°C} U_3O_8 + \tfrac{1}{2}O_2$$

$$UO_3 + CO \xrightarrow{350°C} UO_2 + CO_2$$

Uranates. The fusion of uranium oxides with alkali or alkaline earth carbonates, or thermal decomposition of salts of the uranyl acetate anion, gives orange or yellow materials generally referred to as uranates, for example,

$$2UO_3 + Li_2CO_3 \longrightarrow Li_2U_2O_7 + CO_2$$

$$Li_2U_2O_7 + Li_2CO_3 \longrightarrow 2Li_2UO_4 + CO_2$$

$$Li_2UO_4 + Li_2CO_3 \longrightarrow Li_4UO_5 + CO_2$$

Addition of aqueous NH_3 to $UO_2(NO_3)_2$ solutions affords the so-called ammonium diuranate. This is mainly a hydrated uranyl hydroxide containing NH_4^+. Below 580°C it gives UO_3 and above, U_3O_8.

Uranates do not contain discrete ions such as UO_4^{2-}. They have octahedral U^{VI} with unsymmetrical oxygen coordination such that two U—O bonds are short (~1.92 Å), constituting a sort of uranyl group, with other longer U—O bonds in the plane normal to this UO_2 axis linked into chains or layers. However, Na_4UO_5 has strings of UO_6 octahedra sharing opposite corners.

Uranium Halides. The principal halides are listed in Table 21-9. In addition to those listed, there are several intermediate fluorides, namely, U_2F_9, U_3F_{13}, U_4F_{17}, and U_5F_{22}, of which only the first has been structurally characterized. It is a genuine mixed oxidation state, U^{IV}/U^{V}, compound.[63]

Fluorides. Uranium trifluoride, which may be obtained by reduction of UF_4 with H_2 or by reaction of UF_4 with UN at 950°C is a high-melting, nonvolatile solid. It resembles the lanthanide trifluorides in being insoluble in water or dilute acids.

The *tetrafluoride,* also insoluble in water, can be prepared in several ways, *inter alia,* the following:

$$UO_2 \xrightarrow[500\text{–}600°C]{C_2Cl_4F_2} UF_4$$

$$NH_4UF_5 \xrightarrow{500°C} UF_4$$

It can also be precipitated in hydrated form from aqueous solutions of U(IV).

The *pentafluoride,* which exists in two (α and β) crystalline modifications, melts to give an electrically conducting liquid. It may be obtained[64] from UF_6 by reduction with PF_3 as well as other reductants (see later). It reacts with alkali fluorides and NaOEt to form $M[UF_6]$ and $U_2(OEt)_{10}$, respectively, and dissolves in donor solvents to form saltlike products, $[UF_4L_{3,4}][UF_6]$, L = DMF, DMSO, and MeCN.

Uranium hexafluoride is the most important fluoride and is made on a large scale, since it is the compound used in gas diffusion plants for the separation of uranium isotopes. It is made by the reactions:

$$UO_2 + 4HF = UF_4 + 2H_2O$$

$$3UF_4 + 2ClF_3 = 3UF_6 + Cl_2$$

$$Cl_2 + 3F_2 = 2ClF_3$$

The hexafluoride forms colorless crystals (mp 64.1°C) with a vapor pressure of 115 mm at 25°C. It is a powerful fluorinating agent (e.g., it converts CS_2

TABLE 21-9
Uranium Halides[a]

+3	+4	+5	+6
UF_3, green	UF_4, green	UF_5, white-blue	UF_6, colorless
UCl_3, red	UCl_4, green	U_2Cl_{10}, red-brown	UCl_6, green
UBr_3, red	UBr_4, brown	UBr_5, dark red	
UI_3, black	UI_4, black		

[a] Other fluorides are known (see text).

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[63] P. G. Eller *et al., Inorg. Chim. Acta,* 1979, **37,** 129.
[64] T. A. O'Donnell *et al., J. Fluorine Chem.,* 1983, **23,** 97.

to SF_4) and is rapidly hydrolyzed by water. It reacts with CO under irradiation to give UF_5.[65]

Uranium hexafluoride may be used to prepare UF_5 and UF_4 by the following reactions (X = Cl and Br)[66]:

$$UF_6 + Me_3SiX \longrightarrow Me_3SiF + \tfrac{1}{2}X_2 + UF_5$$

$$UF_6 + 2Me_3SiX \longrightarrow 2Me_3SiF + X_2 + UF_4$$

Chlorides. Uranium trichloride as an unsolvated solid is generally insoluble in solvents with which it does not react and therefore rather intractable for synthetic purposes.[67] The same is true of the U^{III} bromide and iodide, which are much less stable. They are made by passing HCl, HBr, or CH_3I over UH_3. To obtain a synthetically useful form of UCl_3 it is necessary to reduce UCl_4 in a solvent such as THF with NaH or sodium naphthalide.[68] With this $UCl_3(THF)_x$ or its THF solutions, a number of U^{III} compounds can be prepared.[68,69] The hydrate, $UCl_3 \cdot 7H_2O$, is known and has the same structure as its $LnCl_3 \cdot 7H_2O$ analogues.[70]

The *tetrachloride* is readily obtained by liquid-phase chlorination of UO_3 by refluxing with hexachloropropene. The primary product is believed to be UCl_6, which decomposes thermally. Uranium tetrachloride is soluble in polar organic solvents and in water. It is the usual starting material for synthesis of other U^{IV} compounds. Various adducts of UCl_4 are formed with oxygen and nitrogen donors having two to seven ligand molecules, and having a variety of structures. Thus $UCl_4(CH_3CN)_4$ is a nearly ideal dodecahedron,[71] while $UCl_4(DMSO)_3$ is in fact $[UCl_2(DMSO)_6][UCl_6]$, and $UCl_4(Me_3PO)_6$ is $[UCl(OPMe_3)_6]Cl_3$. With bulky neutral ligands octahedral complexes are obtained: *cis*-$UCl_4(OPPh_3)_2$ and *trans*-$UCl_4(HMPA)_2$. The complex $U(NCS)_4$ adds three $Me_3CCONMe_2$ ligands to give a pentagonal bipyramidal seven-coordinate complex, with all NCS^- (two axial) coordinated through nitrogen.[72] The reduction of UCl_4 with *t*-C_4H_9Li in alkane solvents leads to poorly defined but catalytically active U^{III} hydride complexes.[73]

Uranium tetrabromide resembles UCl_4, but the iodide has a unique chain structure[74] (like that of $ZrCl_4$, p. 779). It is obtained by direct reaction of U and I_2, but if heated too much it readily decomposes to UI_3.

Uranium *hexachloride* can be made by chlorination of a mixture of U_3O_8 and carbon at 380°C, and in other ways.[75] The green crystals sublime in

[65] C. W. Halstead and P. G. Eller, *Inorg. Synth.*, 1982, **21,** 162.

[66] D. Brown *et al.*, *J. Less-Common Met.*, 1983, **92,** 149.

[67] T. J. Marks *et al.*, *Organometallics* 1982, **1,** 170.

[68] R. B. Anderson, *Inorg. Chem.*, 1979, **18,** 1507; D. C. Moody and J. D. Odom, *J. Inorg. Nucl. Chem.*, 1979, **41,** 533.

[69] D. C. Moody *et al.*, *Inorg. Chem.*, 1982, **21,** 3856.

[70] J. Drozdzynski, *Inorg. Chim. Acta,* 1985, **109,** 79.

[71] F. A. Cotton *et al.*, *Acta Crystallogr.*, 1984, **40C,** 1186.

[72] K. W. Bagnall *et al.*, *J. Chem. Soc. Dalton Trans.*, **1982,** 19.

[73] W. J. Evans *et al.*, *Inorg. Chem.*, 1982, **21,** 2565.

[74] J. C. Taylor *et al.*, *Inorg. Chem.*, 1980, **19,** 672.

[75] K. Redeiss and W. Sawodny, *Z. Naturforsch.*, 1982, **37B,** 524.

vacuum. In CH_2Cl_2 solution it slowly decomposes to the red-brown volatile crystalline *pentachloride* (U_2Cl_{10}), which can also be made by chlorination of UCl_4. In the crystal U_2Cl_{10} has a structure similar to Ta_2Cl_{10} or Mo_2Cl_{10}. It forms a volatile complex with Al_2Cl_6 of stoichiometry $UAlCl_8$. Both halides are rapidly hydrolyzed by water.

Halogeno Complexes. All the halides can form halogeno complexes, those with F^- and Cl^- being the best known. They can be obtained by interaction of the halide and alkali halides in melts or in solvents such as $SOCl_2$, or in the case of fluorides sometimes in aqueous solution.

Fluoro complexes of U^{IV} are numerous; the UF_7^{3-} and UF_8^{4-} are more common, but the octahedral UF_6^{2-} ion is also known.

Although U^V is usually unstable (see later) in aqueous solution, UF_5 dissolves in 48% HF to give blue solutions that are only slowly oxidized in air and from which $(H_3O)UF_6 \cdot 1.5H_2O$ can be crystallized. By addition of Rb or Cs fluoride, the blue salts MUF_6 (M = Rb or Cs) can be formed.

For U^{VI} the ions UF_7^- and UF_8^{2-} can be made by the reactions

$$UF_6 + NaF = NaUF_7$$

$$UF_6 + 2NOF = (NO)_2UF_8$$

The alkali metal heptafluorouranates(VI) decompose on heating, for example,

$$2NaUF_7 \overset{>100°C}{\rightleftharpoons} UF_6 + Na_2UF_8$$

$$Na_2UF_8 \xrightarrow{>300°C} 2NaF + UF_6$$

Chloro complexes of U^{III}, U^{IV}, and U^V, are known,[76] such as K_2UCl_5, KU_2Cl_7, $NH_4UCl_4 \cdot 5H_2O$ (a useful U^{III} reagent), K_2UCl_6, $(Me_4N)UCl_6$, and $(Me_4N)_3UCl_8$. The pentachloride U_2Cl_{10} reacts with PCl_5 to give $[PCl_4]^+[UCl_6]^-$.

When U_3O_8 is boiled with hexachloropropene a dark red complex of trichloroacryloyl chloride (L) of stoichiometry UCl_5L is formed. Other adducts can be made from this by displacement reactions with, for example, $SOCl_2$.

Uranium and other actinide *pseudohalide* complexes can be made, for example, when UCl_4 is treated with KSCN in MeCN giving the $[U(NCS)_8]^{4-}$ ion.

Oxohalides. The stable uranyl compounds UO_2X_2 are soluble in water. They are made by reactions such as

$$UCl_4 + O_2 \xrightarrow{350°C} UO_2Cl_2 + Cl_2$$

$$UO_3 + 2HF \xrightarrow{400°C} UO_2F_2 + H_2O$$

$$U_3O_8 + 3Cl_2 = 3UO_2Cl_2 + O_2$$

$$UO_2Cl_2 \xrightarrow{450°C} (UO_2)_2Cl_3 \xrightarrow{500°C} UO_2Cl$$

UO_2Cl_2 forms an adduct with 2 mol of $OPPh_3$.

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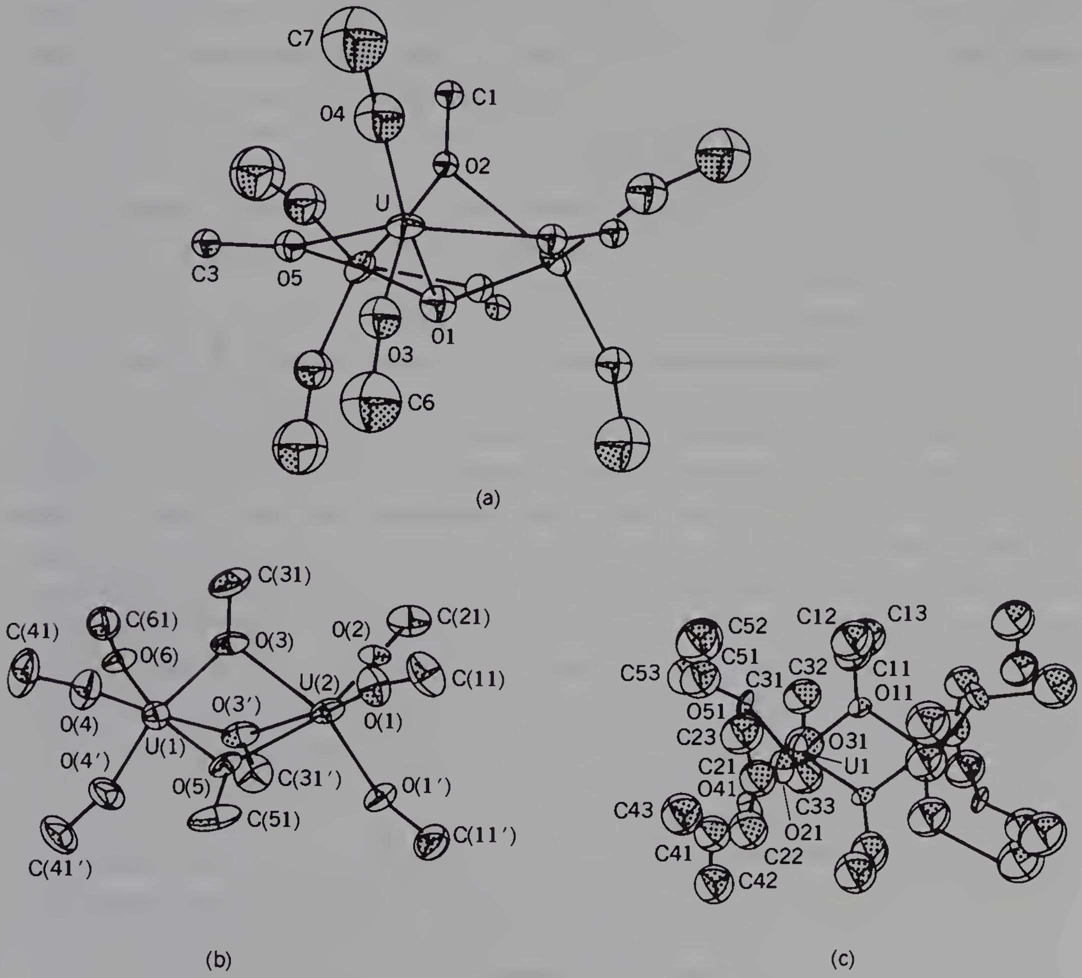
[76] J. Drozdzynski, *Inorg. Chim. Acta,* 1979, **32,** L83.

There are two oxo fluorides, UO_2F_2 and UOF_4, both of which are polymeric solids with F bridges.[77]

Other Uranium Compounds. Uranium reacts directly with most nonmetals (B, C, Si, N, P, As, Sb, S, Se, Te, etc.) to form semimetallic solids; the silicides and the sulfide (US) are chemically inert and used as refractories.

A binary compound of unusual importance as a source material is the hydride (UH_3) (Section 3-14).

Uranium forms many *alkoxides* in oxidation states IV to VI. Those of U^{IV} are usually dimeric or trimeric,[78] with structures such as those shown in Fig. 21-7. With R = $C(CF_3)_3$ or $CH(CF_3)_2$ in THF, mononuclear, volatile $U(OR)_4(THF)_2$ compounds have been obtained.[79] Uranium(VI) alkoxides of the types $UO_2(OR)_2$ and $U(OR)_6$ are known. The compound $U(OMe)_6$ can be used for laser-induced isotope enrichment.[80]



(a)

(b)

(c)

FIG. 21-7. Structures of some U^{III}, U^{IV}, and U^{V} alkoxides. (a) $U_3O(OCMe_3)_{10}$; (b) $U_2(OCMe_3)_9$; (c) $U_2(OCHMe_2)_{10}$. Outer methyl groups are omitted in (a) and (b).

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[77] J. H. Holloway *et al., J. Chem. Soc. Dalton Trans.*, **1982,** 1355, 1635.

[78] F. A. Cotton *et al., Inorg. Chim. Acta,* 1984, **95,** 207; *Inorg. Chem.*, 1984, **23,** 4211.

[79] R. A. Andersen, *Inorg. Nucl. Chem. Lett.*, 1979, **15,** 57.

[80] T. J. Marks *et al., J. Am. Chem. Soc.*, 1979, **101,** 1036.

A number of *amido* compounds, such as the $U(NR_2)_4$ compounds, which may be monomeric (R = Ph) or dimeric (R = Et), are known. They react characteristically with CS_2, COS, and CO_2 to give dithiocarbamates, and so on, which have coordination number 8. A variety of $(Me_3Si)_2N$ compounds are also known,[81] such as $U(NR_2)_3$, $HU(NR_2)_3$, $CH_3U(NR_2)_3$, and $BH_4U(NR_2)_3$. There are thorium analogues of a number of these.

Uranium in oxidation states III and IV has quite extensive chemistry with BH_4^- and also with $BH_3CH_3^-$.[82a] The compound $U(BH_4)_4$, which has full T_d symmetry (all BH_4^- are η^3) decomposes on heating in solution to give $U(BH_4)_3$. This can also be made[82b] by interaction of UH_3 and B_2H_6 in THF: it forms numerous adducts, such as $U(BH_4)_3(THF)_3$, $U(BH_4)_3(dmpe)_2$, and $U(BH_4)_3[Ph_2Ppy]_2$. $U(BH_4)_4$, reacts with ethers to give a structurally diverse series of products depending on the ether; examples are monomeric $U(BH_4)_4(THF)_2$, $U(BH_4)_3(i\text{-}Pr_2O)_2U(\mu,\eta^4\text{-}BH_4)U(BH_4)_4$, and $[U(BH_4)_4(Et_2O)]_\infty$. The methyl analogue, $U(BH_3CH_3)_4$, for which Th and Np homologues exist, has comparable behavior. There are other $An(BH_4)_4$ compounds with An = Pa, Th, Np, and Pu with similar properties to those of $U(BH_4)_4$,[83a] but there are also unexpected structural differences. The dimethoxyethane adduct $UH(BH_4)_3(dme)$ is unique in having a U—H bond.[83b]

Uranium(IV) gives many eight-coordinate complexes, both neutral,[84] for example, $U(acac)_4$ or $U(oxine)_4$, and anionic,[85] for example, $[U(NCS)_8]^{4-}$, $[U(NCSe)_8]^{4-}$, as well as the 7-coordinate $[U(NCS)_5bipy]^-$.

Aqueous Chemistry. This is quite complicated owing to extensive complexation as well as hydrolytic reactions which lead to polymeric ions under appropriate conditions. The formal potentials for 1 *M* $HClO_4$ have been given in Table 21-5. In the presence of other anions the values differ: thus for the U^{4+}/U^{3+} couple in 1 *M* $HClO_4$ the potential is -0.631 V, but in 1 *M* HCl it is -0.640 V. The simple ions and their properties are also listed in Table 21-6. Because of hydrolysis, aqueous solutions of uranium salts have an acid reaction that increases in the order $U^{3+} < UO_2^{2+} < U^{4+}$. The main hydrolyzed species of UO_2^{2+} at 25°C are UO_2OH^+ $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$, but the system is a complex one and the species present depend on the medium; at higher temperatures the monomer is most stable but the rate of hydrolysis to UO_3 of course increases. The solubility of large amounts of UO_3 in UO_2^{2+} solutions is also attributable to formation of UO_2OH^+ and polymerized hydroxo-bridged species.

The U^{3+} ion, which is readily obtained in perchlorate or chloride solutions by reduction of UO_2^{2+} electrolytically or with zinc amalgam, is a powerful

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[81] R. A. Andersen *et al., Inorg. Chem.,* 1981, **20,** 622, 2991.

[82a] A. Zalkin *et al., Inorg. Chem.,* 1987, **26,** 2868.

[82b] D. Maennig and H. Nöth, *Z. Anorg. Allg. Chem.,* 1986, **543,** 66.

[83a] N. M. Edelstein *et al., J. Am. Chem. Soc.,* 1980, **102,** 620.

[83b] D. Baudry *et al., J. Chem. Soc. Chem. Commun.,* **1987,** 739.

[84] D. G. Tuck *et al., Inorg. Chim. Acta.,* 1985, **109,** 19.

[85] R. O. Wiley and T. M. Brown, *Inorg. Chim. Acta,* 1985, **109,** 23.

reducing agent. Its oxidation by I_2 or Br_2 occurs by an outer-sphere mechanism. The solutions of U^{3+} in 1 *M* HCl are stable for days, but in more acid solution, spontaneous oxidation occurs more rapidly. The hydrate $UF_3 \cdot H_2O$ and $U_2(SO_4)_3 \cdot 5H_2O$ can be obtained from fluoride and sulfate solutions, respectively. $(NH_4)U(SO_4)_2 \cdot (H_2O)_4$ is a crystalline hydrate that can be handled in air. The U^{III} is nine-coordinate but the arrangement does not correspond to any regular prototype.[86]

The U^{4+} ion is only slightly hydrolyzed in molar acid solutions:

$$U^{4+} + H_2O \rightleftharpoons U(OH)^{3+} + H^+ \qquad K_{25^\circ C} = 0.027 \ (1\ M\ HClO_4, NaClO_4)$$

but it can also give polynuclear species in less acid solutions.

The U^{4+} ion gives insoluble precipitates with F^-, PO_4^{3-}, and IO_3^- from acid solutions (cf. Th^{4+}).

Although the UO_2^+ ion is extremely unstable towards disproportionation (Section 21-4), its aqueous chemistry has been much studied by special techniques (e.g., stopped-flow methods). In DMSO it is more stable, both thermodynamically and kinetically (half-life, ~0.5 h).

The UO_2^{2+} ion in aqueous solution is entirely stable and forms many complexes (see later). It can be reduced to U^{IV}, for example by Cr^{2+}; in the reverse process, use of ^{18}O tracer has shown that some oxidants (PbO_2, H_2O_2, and MnO_2) give almost entirely $U(^{18}O)_2^{2+}$, while O_2 and O_3 give $U(^{16}O^{18}O)^{2+}$.

Uranyl Compounds. The most common uranium compounds are those containing the linear, symmetrical UO_2^{2+} ion. This ion readily adds 4–6 donors in its equatorial plane to give structures such as those shown in Fig. 21-2. The number of known complexes of UO_2^{2+} is enormous, and virtually every kind of oxygen donor ligand as well as many nitrogen donors and even sulfur donors[87] have been found in such complexes.

One of the most important uranyl complexes is the nitrate, which crystallizes with six, three, or two molecules of water, depending on whether it is obtained from dilute, concentrated, or fuming nitric acid. In each case, there are two bidentate nitrate ions and two water molecules coordinated equatorially. The anhydrous compound can be obtained by the reactions

$$U + N_2O_4(l) \xrightarrow{MeCN} UO_2(NO_3)_2 \cdot N_2O_4 \cdot 2MeCN \xrightarrow{163^\circ C} UO_2(NO_3)_2$$

The nitrate is of major importance because the extraction of uranyl nitrate from aqueous nitric acid into nonpolar solvents is a classic method for separating and purifying the element. Typically, phosphate esters, such as $[(C_4H_9)(C_2H_5)CHCH_2O]_2P(O)(OH)$, are used and the extracted species is $UO_2(NO_3)_2[(RO)_2PO_2]_2$.[88] An analogous Ph_3PO complex has been established by X-ray crystallography.[89] Uranyl ion also forms carbonato complexes, such

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[86] J. I. Bullock *et al., Inorg. Chem. Acta,* 1980, **43**, 101.
[87] D. L. Perry *et al., Inorg. Chem.,* 1982, **21**, 237.
[88] A. E. Lemire *et al., Inorg. Chem Acta,* 1985, **110**, 237.
[89] N. W. Alcock *et al., J. Chem. Soc. Dalton Trans.,* **1982**, 25.

as $UO_2(CO_3)_3^{4-}$ that play a prominent role in the extraction of uranium from its ores.[90]

Other uranyl salts are given by organic acids, sulfate, halides, and so on; the water-soluble acetate in the presence of an excess of sodium acetate in dilute acetic acid gives a crystalline precipitate of $NaUO_2(OCOCH_3)_3$. There is considerable current research on the use of cyclic hexadentate and related ligands to form strong complexes with the UO_2^{2+} ion.[91]

One of the characteristic features of UO_2^{2+} compounds is fluorescence, and uranyl oxalate is used as an actinometer.

21-12. The Transuranium Elements, Np, Pu,[92] and Am

Though several isotopes of each of these elements are known, only a few (listed in Table 21-2) have been obtained in macroscopic amounts. Both ^{237}Np and ^{239}Pu are available on a large (~kilogram) scale from spent uranium fuel rods of reactors, but the technical problems in working with above-tracer amounts of these highly radioactive and (especially for Pu) toxic[93] elements are extremely formidable. Nevertheless, a number of effective separation methods have been developed.[94] The principles upon which separation procedures are based are the following:

1. *Stabilities of Oxidation States.* The stabilities of the major ions involved are: $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+} > AmO_2^{2+}$; $Am^{3+} > Pu^{3+} \gg Np^{3+}, U^{4+}$. It is thus possible (see also Table 21-5) by choice of suitable oxidizing or reducing agents to obtain a solution containing the elements in different oxidation states; they can then be separated by precipitation or solvent extraction. For example, Pu can be oxidized to PuO_2^{2+} while Am remains as Am^{3+}—the former could be removed by solvent extraction or the latter by precipitation of AmF_3.

2. *Extractability into Organic Solvents.* As noted previously, the MO_2^{2+} ions can be extracted from nitrate solutions into organic solvents. The M^{4+} ions can be extracted into tributyl phosphate in kerosene from 6 *M* nitric acid solutions; the M^{3+} ions can be similarly extracted from 10 to 16 *M* nitric acid; and neighboring actinides can be separated by a choice of conditions.

3. *Precipitation Reactions.* Only M^{3+} and M^{4+} give insoluble fluorides or phosphates from acid solutions; the higher oxidation states either give no

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[90] E. T. Strom *et al., J. Am. Chem. Soc.*, 1981, **103**, 1255; I. Grenthe *et al., Inorg. Chem.*, 1981, **20**, 463.

[91] P. Lagrange *et al., Inorg. Chem.*, 1985, **24**, 80; L. M. Vallarino *et al., Inorg. Chim. Acta*, 1985, **110**, L1; S. Shinkai *et al., J. Chem. Soc. Chem. Commun.*, **1986**, 233.

[92] J. M. Cleveland, *The Chemistry of Plutonium*, American Nuclear Society, LaGrange Park, Illinois, 1979 (encyclopedic coverage of all phases of Pu chemistry with literature references); W. T. Carnall and G. R. Choppin, Eds. *Plutonium Chemistry* (ACS Symposium Series, No. 216), American Chemical Society, Washington, D.C., 1983.

[93] J. C. Nenot and H. Metivier, *Inorg. Chim. Acta*, 1984, **94**, 165.

[94] For further details see the 4th edition of this text, and various compendia cited in the General References at the end of the chapter.

precipitate or can be prevented from precipitation by complex formation with sulfate or other ions.

4. *Ion-Exchange Procedures.* Although ion-exchange procedures, both cationic and anionic, can be used to separate the actinide ions, they are best suited for small amounts of material.

To illustrate briefly the practical employment of these principles on a large scale, the following processes may be mentioned.

1. *The hexone* [$MeC(O)CH_2CHMe_2$] *method,* in which both U and Pu are oxidized to the AnO_2^{2+} ions, which are then extracted into an organic solvent by the hexone, leaving the fission products in the aqueous layer. Uranium is then separated from Pu by selectively (SO_2) reducing the latter to Pu^{4+} and solvent extracting only the UO_2^{2+}.
2. *The tributyl phosphate extraction method,* where control of the concentration of nitric acid from 6 to 16 *M* allows control of the transfer of various actinide ions into kerosene containing 30% $(C_4H_9O)_3PO$.
3. *The lanthanum fluoride cycle* in which hexone extraction along with LaF_3 as a carrier precipitate are used.

Compounds of Np, Pu, and Am

Oxides. The important oxides are the *dioxides,* obtained by heating nitrates or hydroxides in air. They are isostructural with UO_2 but PuO_2 is nonstoichiometric unless roasted in air at 1200°C. No AnO_3 compounds are known though corresponding hydrated substances, for example, $NpO_3 \cdot 2H_2O$, can be made. Only americium gives a lanthanide-like oxide (Am_2O_3).

Halides. These are listed in Table 21-10. While their preparations and properties show much similarity to those of the uranium halides, there is a steady decrease in stability of the higher oxidation states with increasing atomic number (which continues in the succeeding elements). In short, the "actinide" concept becomes more and more valid.

TABLE 21-10
Halides of Np, Pu, and Am[a]

+2[b]	+3	+4	+6
	NpF_3, purple-black	NpF_4, green	NpF_6, orange, mp 55.1°C
	PuF_3, purple	PuF_4, brown	PuF_6, red-brown, mp 51.6°C
	AmF_3, pink	AmF_4, tan	
	$NpCl_3$, white	$NpCl_4$, red-brown	
	$PuCl_3$, emerald		
$AmCl_2$, black	$AmCl_3$, pink		
	$NpBr_3$, green	$NpBr_4$, red-brown	
	$PuBr_3$, green		
$AmBr_2$, black	$AmBr_3$, white		
	NpI_3, brown		
	PuI_3, green		
AmI_2, black	AmI_3, yellow[b]		

[a] Certain oxohalides $M^{III}OX$, $M^{V}OF_3$, and $M^{VI}O_2F_2$ are known.

[b] R. G. Haire *et al.*, *J. Less-Common Met.*, 1983, **93**, 339.

The fluorides MF_3 and MF_4 can be precipitated from aqueous solutions in hydrated form. The hexafluorides have been greatly studied because they are volatile; the melting points and stabilities decrease in the order $U > Np > Pu$. Plutonium hexafluoride is so very much less stable than UF_6 that at equilibrium, the partial pressure of PuF_6 is only 0.004% of the fluorine pressure. Hence PuF_6 formed by fluorination of PuF_4 at 750°C must be quenched immediately by a liquid nitrogen probe. The compound also undergoes self-destruction by α-radiation damage, especially in the solid; it must also be handled with extreme care owing to the toxicity of Pu.

Neptunium hexafluoride has a $5f^1$ configuration according to esr and absorption spectra, the octahedral field splitting the sevenfold orbital degeneracy of the $5f$ electron and leaving a ground state that has only spin degeneracy. This quenching of the orbital angular momentum is similar to that in the first-row *d*-transition group. It provides further evidence for the closeness of the energy levels of the $5f$ and the valence electrons in actinides, in contrast to the much lower energies of the $4f$ electrons in lanthanides.

Other Compounds. A substantial number of compounds, particularly of plutonium, are known, and most of them closely resemble their uranium analogues. The hydride systems of Np, Pu, and Am are more like that of thorium than that of uranium and are complex. Thus nonstoichiometry up to $MH_{2.7}$ is found in addition to stoichiometric hydrides such as PuH_2 and AmH_2.

As with uranium, many complex salts are known [e.g., Cs_2PuCl_6, $NaPuF_5$, $KPuO_2F_3$, $NaPu(SO_4)_2 \cdot 7H_2O$, and $Cs_2Np(NO_3)_6$].

Aqueous Chemistry. The formal reduction potentials of Np, Pu, and Am were given in Table 21-5 and information on the ions in Table 21-6. Solutions of the IV to VI oxidation states undergo spontaneous reduction because of their own α radiation.

For Np the potentials of the four oxidation states are separated (like U) but unlike the chemistry of U, the NpO_2^+ ion is comparatively stable. For Pu, however, the potentials are close and at 25°C in 1 *M* $HClO_4$ we have

$$K = \frac{[Pu^{VI}][Pu^{III}]}{[Pu^{V}][Pu^{IV}]} = 10.7$$

which indicates that measurable amounts of all four states can be present. The Am ions that can exist in appreciable concentrations are Am^{3+}, AmO_2^+ and AmO_2^{2+}, with Am^{3+} being the usual state in acid solution. However, for 1 *M* basic solution the $Am(OH)_4$–$Am(OH)_3$ couple has a value of +0.5 V, nearly 2 V less than for the Am^{4+}/Am^{3+} couple in acid solution. Thus pink $Am(OH)_3$ can be readily converted into black $Am(OH)_4$ or hydrous AmO_2 by the action of hypochlorite.

As with uranium, the solution chemistry is complicated owing to hydrolysis and polynuclear ion formation, complex formation with anions other than perchlorate, and disproportionation reactions of some oxidation states. The tendency of ions to displace a proton from water increases with increasing charge and decreasing ion radius, so that the tendency to hydrolysis increases in the same order for each oxidation state, that is, $Am > Pu > Np > U$ and

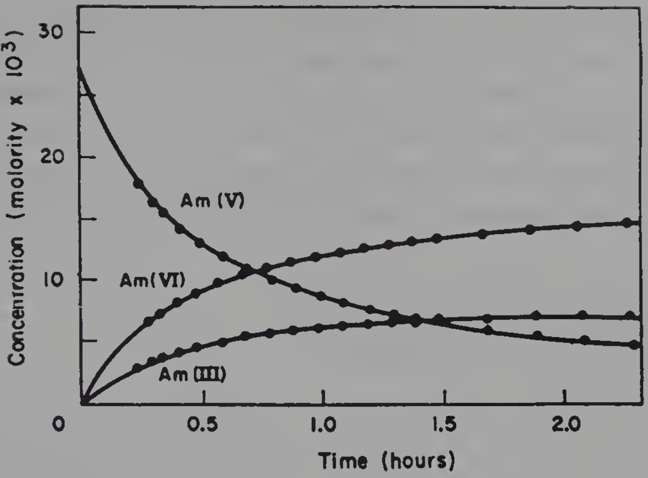

FIG. 21-8. Disproportionation of AmO_2^+ in 6 *M* perchloric acid at 25°C. Net reaction $3AmO_2^+ + 4H^+ = 2AmO_2^{2+} + Am^{3+} + 2H_2O$. (Reproduced by permission from J. P. Coleman, *Inorg. Chem.*, 1963, **2,** 53.)

$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$; simple ions such as NpO_2OH^+ or $PuOH^{3+}$ are known, in addition to polymeric species that in the case of plutonium can have molecular weights up to 10^{10}.

The complexing tendencies decrease, on the whole, in the same order as the hydrolytic tendencies. The formation of complexes shifts the oxidation potentials, sometimes influencing the relative stabilities of oxidation states; thus the formation of sulfate complexes of Np^{4+} and NpO_2^{2+} is strong enough to cause disproportionation of NpO_2^+. The disproportionation reactions have been studied in some detail; Figs. 21-8 and 21-9 illustrate some of the complexities involved.

Typical of these disproportionations are the following at low acidity:

$$3Pu^{4+} + 2H_2O \rightleftharpoons PuO_2^{2+} + 2Pu^{3+} + 4H^+$$

$$2Pu^{4+} + 2H_2O \rightleftharpoons PuO_2^+ + Pu^{3+} + 4H^+$$

$$PuO_2^+ + Pu^{4+} \rightleftharpoons PuO_2^{2+} + Pu^{3+}$$

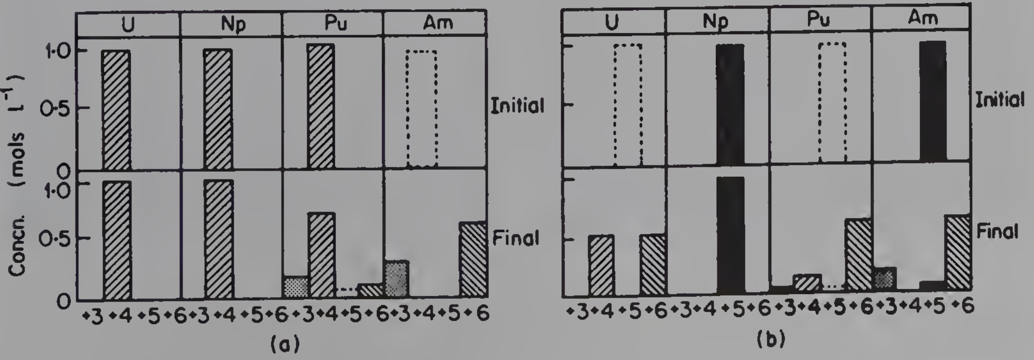

FIG. 21-9. Disproportionation reactions of (a) tetrapositive (b) pentapositive ions in 1 *M* acid at 25°C. (Reproduced by permission from J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, Methuen, London, 1957.)

Carbonate complexes are of importance, in part because of their role in the transport of these elements in natural waters, and they have accordingly been studied in detail.[95] Other complexes of these elements are being studied in order to find specific sequestering agents, especially for Pu.[96] A tetraaza (N_4) ligand that has an extremely high complexity constant ($>10^{52}$) for Pu^{IV} has been found, and it may have some use in scavenging Pu from body tissues, and elsewhere.

21-13. The Trans-Americium Elements

We shall discuss here all the elements from curium on. The isotope ^{242}Cm was first isolated among the products of α bombardment of ^{239}Pu, and its discovery actually preceded that of americium. Isotopes of the other elements were first identified in products from the first hydrogen bomb explosion (1952) or in cyclotron bombardments. Although Cm, Bk, and Cf have been obtained in macro amounts (Table 21-2), much of the chemical information has been obtained on the tracer scale. The remaining elements have been characterized only on the tracer scale or even, for elements 100 to 105, employing only about 10 atoms.

For these elements the correspondence of the actinide and the lanthanide series becomes most clearly revealed. The position of curium corresponds to that of gadolinium where the *f* shell is half-filled. For curium the +3 oxidation state is the normal state in solution, although unlike gadolinium, a solid tetrafluoride CmF_4 has been obtained. Berkelium has +3 and +4 oxidation states, as would be expected from its position relative to terbium, but the +4 state of terbium does not exist in solution, whereas for Bk it does. Although CfF_4 and CfO_2 have been made, the remaining elements have only the +3 and +2 states. The great similarity between the +3 ions of Am and the trans-americium elements has meant that the more conventional chemical operations successful for the separation of the previous actinide elements are inadequate and most of the separations require the highly selective procedures of ion-exchange discussed later; solvent extraction of the M^{3+} ions from 10 to 16 *M* nitric acid by tributyl phosphate also gives reasonable separations.

Ion exchange has been the principal and indispensable tool in the isolation of all the elements from curium on. By detailed comparison with the elution of lanthanide ions and by extrapolating data for the lighter actinides such as Np^{3+} or Pu^{3+}, the order of elution of the heavier actinides can be accurately forecast. Even a few *atoms* of the element can be identified because of the characteristic nuclear radiation.

The main problems in the separations are (*a*) separation of the actinides as a group from the lanthanide ions (which are formed as fission fragments in the bombardments which produce the actinides) and (*b*) separation of the actinide elements from one another.

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[95] L. Maya, *Inorg. Chem.*, 1984, **23**, 3926; I. Grenthe *et al.*, *Inorg. Chem.*, 1986, **25**, 1679.
[96] K. N. Raymond *et al.*, *Inorg. Chem.*, 1985, **24**, 605.

The former problem can be solved by the use of concentrated hydrochloric acid as eluting agent; since the actinide ions form chloride complexes more easily, they are desorbed first from a cation-exchange resin, thus effecting a *group* separation; conversely, the actinides are more strongly adsorbed on anion-exchange resins.

The actinide ions are effectively separated from each other by elution with citrate or similar eluant; some typical elution curves in which the relative positions of the corresponding lanthanides are also given are displayed in Fig. 21-10. It will be noted that a very striking similarity occurs in the spacings of corresponding elements in the two series. There is a distinct break between Gd and Tb and between Cm and Bk, which can be attributed to the small change in ionic radius occasioned by the half-filling of the 4*f* and 5*f* shells, respectively. The elution order is not always as regular as that in Fig. 21-10. With some complexing agents (e.g., thiocyanate) more complicated elution orders are found, but nevertheless useful purifications (e.g. of Am) can be developed.

After separation by ion exchange, the actinides may be precipitated by fluoride or oxalate in macroscopic amounts or collected on an insoluble fluoride precipitate for trace quantities.

Curium. Solid curium compounds are known, for example, CmF_3, CmF_4, $CmCl_3$, $CmBr_3$, white Cm_2O_3 (mp 2265°C), and black CmO_2. Where X-ray structural studies have been made—and these are difficult, since amounts of the order of 0.5×10^{-6} g must be used to avoid fogging of the film by radioactivity and because of destruction of the lattice by emitted particles—the compounds are isomorphous with other actinide compounds.

In view of the position of Cm in the actinide series, numerous experiments have been made to ascertain whether Cm has only the +3 state in solution; no evidence for a lower state has been found. Concerning the +4

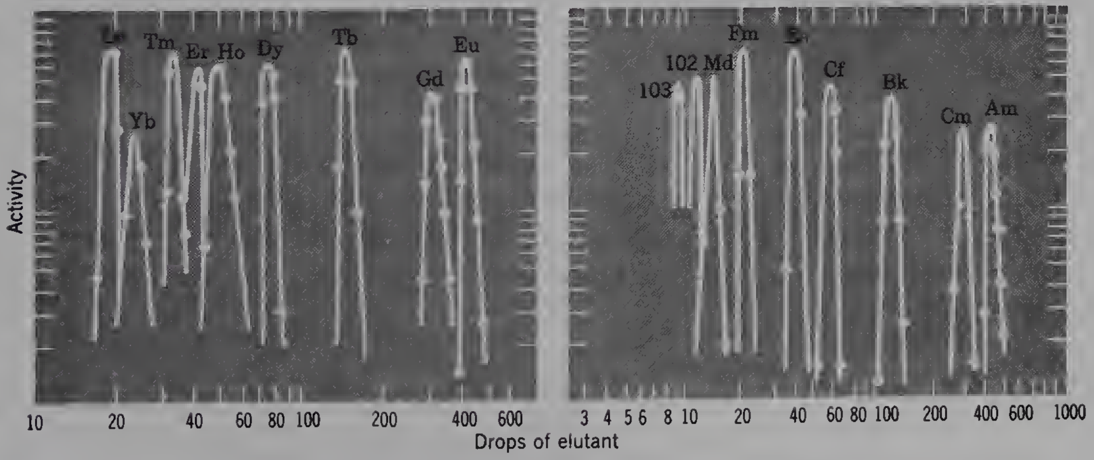

FIG. 21-10. Elution of lanthanide +3 ions (left) and actinide +3 ions (right) from Dowex 50 cation-exchange resin. Buffered ammonium 2-hydroxybutyrate was the eluant. The predicted positions of elements 102 and 103 (unobserved here) are shown by broken lines. (Reproduced by permission from J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, Methuen, London, 1957.)

state, the potential of the Cm^{4+}/Cm^{3+} couple must be greater than that of Am^{4+}/Am^{3+}, which is 2.6 to 2.9 V, so that solutions of Cm^{4+} must be unstable. When CmF_4, prepared by dry fluorination of CmF_3, is treated with 15 *M* CsF at 0°C, a pale yellow solution is obtained that appears to contain Cm^{4+} as a fluoro complex. The solution exists for only an hour or so at 10°C owing to reduction by the effects of α radiation; its spectrum resembles that of the isoelectronic Am^{3+} ion.

The solution reactions of Cm^{3+} closely resemble those of the lanthanide and actinide +3 ions, and the fluoride, oxalate, phosphate, iodate, and hydroxide are insoluble. There is some evidence for complexing in solution, although the complexes appear to be weaker than those of preceding elements.

Magnetic measurements on CmF_3 diluted in LaF_3 and also the close resemblance of the absorption spectra of CmF_3 and GdF_3 support the hypothesis that the ion has the $5f^7$ configuration.

Berkelium.[97] As the analogue of Tb, berkelium could be expected to show the +4 state and does so, not only in solid compounds but also in solution. Thus Bk^{3+} solutions can be oxidized by BrO_3^-, and the Bk^{4+} ion can be coprecipitated with Ce^{4+} or Zr^{4+} as phosphate or iodate. The ion can also be extracted (cf. Ce^{4+}) by hexane solutions of bis(2-ethylhexyl) hydrogen phosphate or similar complexing agents. Berkelium(IV) is a somewhat weaker oxidant than Ce^{IV}.

Among the variety of solid Bk compounds known, more than two dozen have been structurally characterized, for example, BkO_2 (fluorite structure), Bk_2O_3, BkF_4, BkX_3 (X = F, Cl, Br, and I), and BkOX (X = Cl, Br, and I), as well as various chalcogenides. The oxides and halides generally resemble their lanthanide analogues. There are also two known organoberkelium compounds, Cp_3Bk and $[Cp_2BkCl]_2$.

Californium. The compounds CfF_4 and CfO_2 are well characterized and in the +3 state there are halides, the oxide, sulfide, oxohalides, and Cp_3Cf. The compounds $CfBr_2$ and CfI_2 are also known.

TABLE 21-11
The Elements with $Z \geq 100$

Element	Half-life	No. of Atoms Made
$^{255}_{100}Fm$	20.1 h	10^{11}
$^{256}_{101}Md$	77 m	10^6
$^{255}_{102}No$	3.1 m	10^3
$^{256}_{103}Lr$	31 s	10
$^{260}_{104}X^a$	~20 ms	~10
$^{261}_{105}X^a$	~ 2 m	~10

[a] Name and symbol not yet officially adopted.

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[97] J. R. Peterson and D. E. Hobart, *Adv. Inorg. Chem. Radiochem.*, 1984, **28,** 29.

Einsteinium. Several isotopes have been made[98] and the following compounds prepared: Es_2O_3, $EsCl_3$, $EsBr_3$, EsI_3, EsOCl, $EsCl_2$, $EsBr_2$, and EsI_2. A little bit is known about the solution chemistry.

Fermium and Beyond.[99] For these elements, as shown in Table 21-11, only submicrogram quantities (down to 10 atoms or fewer!) have been made, and their chemistry is known only in solution. For elements 106 and 107 no chemical properties whatever are yet known.

For elements 104 to 107 there is as yet no agreement on names though rutherfordium and hahnium have frequently been used for the first two.

Finally, we note that although there have been proposals by theoreticians that *superheavy* elements ($Z \geqq 110$) may have long enough half-lives to be dealt with, there is as yet no evidence for them either in Nature or in the laboratory.[100]

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[98] S. A. Kulyukhin *et al., Inorg. Chim. Acta,* 1985, **110,** 25.

[99] E. K. Hulet, *J. Inorg. Nucl. Chem.,* 1980, **42,** 79; *Radiochim. Acta,* 1983, **32,** 7.

[100] J. V. Kratz, *Radiochim. Acta,* 1983, **32,** 25.

4

SURVEY OF SELECTED AREAS

Chapter Twenty Two

Transition Metal Carbon Monoxide Compounds

22-1. Introduction

The bonding in MCO groups has been described in Section 2-8. This chapter now surveys in detail the types and properties of carbon monoxide compounds formed by metals. The stoichiometries of many, though not all, of them can be reconciled with the *noble gas formalism* or *18-electron rule* (Section 2-1), which is merely a phenomenological way of formulating the tendency of the metal atom to use its valence orbitals, nd, $(n + 1)s$, and $(n + 1)p$, as fully as possible in forming bonds to ligands. It is of considerable utility in the design of new compounds, but by no means is it infallible. There are numerous exceptions, even among CO compounds, {e.g., $V(CO)_6$ and $[Mo(CO)_2(diphos)_2]^+$} and it fails entirely for other classes, such as $M(dipy)_3$ and $M(S_2C_2R_2)_3$ species.

In metal carbonyl chemistry, group homology is often very pronounced [e.g., the extreme similarity of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$], but not always. In later groups, there are marked differences at each step, the most obvious being the absence[1] of any stable Pd or Pt analogues of $Ni(CO)_4$, or any Rh or Ir analogues of $Co_2(CO)_8$.

Polynuclear metal carbonyls frequently show a form of fluxionality based on movements of CO ligands between terminal and bridging positions (Section 22-4). In many cases interchanges of nonequivalent CO groups within $M(CO)_x$ units are also very facile. A particularly dramatic example is provided by $Fe(CO)_5$, a trigonal bipyramidal molecule. It is a general tendency of *tbp* molecules to display axial/equatorial exchange, but $Fe(CO)_5$ does so with virtually no activation energy (≤ 8 kJ mol^{-1}), presumably by the Berry process (Fig. 29-10)[2]

22-2. Preparation of Metal Carbonyls

Homoleptic (Binary) Carbonyls. Direct reaction of a metal with CO is feasible only for nickel (which, when finely divided, will react at 25°C) and

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[1] F. Calderazzo *et al., Inorg. Chem.*, 1984, **23,** 3030.

[2] G. Blyholder and J. Springs, *Inorg. Chem.*, 1985, **24,** 224.

iron (only at high temperatures and pressures). In all other cases the carbonyls are prepared from metal compounds under reductive conditions. Common reducing agents are sodium, aluminum alkyls, or CO itself, sometimes mixed with hydrogen. The detailed procedures, however, are so enormously varied that we can give here only a few illustrative examples.

Dicobalt octacarbonyl is prepared by the reaction at 250 to 300 atm pressure and 120 to 200°C:

$$2CoCO_3 + 2H_2 + 8CO \longrightarrow Co_2(CO)_8 + 2CO_2 + 2H_2O$$

The general method for other carbonyls is to treat a metal halide, usually in suspension in an organic solvent such as THF, with carbon monoxide at 200 to 300 atm pressure and temperatures up to 300°C in the presence of a reducing agent. A variety of reducing agents have been employed—electropositive metals like Na, Al, or Mg, trialkylaluminums, copper, or the sodium ketyl of benzophenone (Ph_2CONa). The detailed course of the reactions is not well known, but when organometallic reducing agents are employed it is likely that unstable organo derivatives of the transition metal are formed as intermediates.

The quantitative reaction

$$W(CH_3)_6 + 9CO \longrightarrow W(CO)_6 + 3(CH_3)_2CO$$

supports this assumption.

Vanadium carbonyl is best obtained by the following reaction sequence,[3] in which the role of the cyclooctatetraene (COT) is uncertain, but essential.

$$VCl_3 + Na(\text{excess}) + CO(1\text{ atm}) \xrightarrow[40°C]{\text{THF, COT}} NaV(CO)_6 \xrightarrow[\text{then sublime}]{\text{acid}} V(CO)_6$$

In many cases CO itself can act as the reductant. Thus $Os(CO)_5$, and $Re_2(CO)_{10}$ are obtained by the action of CO at ~300°C and ~300 atm on OsO_4 and Re_2O_7, respectively. Interestingly, NH_4ReO_4 reacts with CO under much milder conditions.[4]

The binuclear carbonyl $Fe_2(CO)_9$ is obtained as orange mica-like plates by photolysis of $Fe(CO)_5$ in hydrocarbon solvents. The green $Fe_3(CO)_{12}$ is best made by acidification of a polynuclear carbonylate anion (see later), which in turn is obtained from $Fe(CO)_5$ by the action of organic amines such as triethylamine.

Compounds with M—M multiple bonds (Section 23-13) characteristically react with CO and other π-acid ligands to sever the M—M bond and produce carbonyl (or other) products.[5] In some cases complete reduction leads to a binary carbonyl[6]:

$$Ru_2(O_2CCH_3)_4Cl + CO(70\text{ atm}) \longrightarrow Ru_3(CO)_{12}$$

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[3] F. Calderazzo and G. Pampaloni, *J. Organomet. Chem.*, 1983, **250**, C33.

[4] F. Calderazzo and R. Poli, *Gazz. Chim. Ital.*, 1985, **115**, 573.

[5] R. A. Walton, *ACS Symp. Ser.*, 1981, No. 155, 212.

[6] F. A. Cotton *et al.*, *Synth. React. Inorg. Met. Org. Chem.*, 1985, **15**, 637.

while in others, illustrated by the following reactions, more complex processes and products are observed[7,8]:

$$\mathrm{Re_2Cl_4(PEt_3)_4 + CO(120\ atm) \longrightarrow Re(CO)_2Cl_2(PEt_3)_2 + Re(CO)_3Cl(PEt_3)_2 + Re(CO)_4Cl(PEt_3)}^{7}$$

$$\mathrm{Mo_2Cl_4(PR_3)_4 + CO(1\ atm) \longrightarrow Mo(CO)_4(PR_3)_2 + Mo(CO)_3Cl_2(PR_3)_2}$$

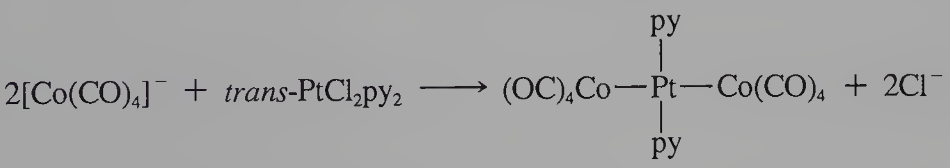
Mixed Metal Polynuclear Carbonyls. Designed syntheses of these are desirable, but not always available. Procedures in which potential constituents are mixed and caused to react randomly to give a more or less statistical mixture of all possible products are generally unattractive because separation is usually difficult and inefficient, even by chromatography. For lack of anything better, however, many mixed metal carbonyl compounds are currently obtainable only by such reactions.

The most widely applicable basis for rational synthesis depends on the reaction of carbonylate anions with metal carbonyl halides causing elimination of halide ion. The general reaction may be represented by

$$[\mathrm{M}_n(\mathrm{CO})_x]^- + \mathrm{XM'(CO)}_y \xrightarrow{\pm z\mathrm{CO}} \mathrm{M}_n\mathrm{M'(CO)}_{x+y\pm z} + \mathrm{X}^-$$

We describe both of these classes of compound in detail presently, but the following reactions may be cited to illustrate this synthetic approach, which is so designed that like metal atoms cannot react with each other:

$$\mathrm{[Mn(CO)_5]^- + BrRe(CO)_5 \longrightarrow (OC)_5MnRe(CO)_5 + Br^-}$$



$$2\mathrm{[Co(CO)_4]^-} + trans\text{-}\mathrm{PtCl_2py_2} \longrightarrow \mathrm{(OC)_4Co}\!-\!\underset{\substack{|\\ \mathrm{py}}}{\overset{\substack{\mathrm{py}\\ |}}{\mathrm{Pt}}}\!-\!\mathrm{Co(CO)_4} + 2\mathrm{Cl^-}$$

A variation on this procedure, leading to mixed metal carbonyl hydrides, is illustrated by the following:

$$\mathrm{Os_3(CO)_{12} + Re(CO)_5^-} \xrightarrow{\text{then H}^+} \mathrm{H_3ReOs_3(CO)_{12}}$$

$$\mathrm{Ru_3(CO)_{12} + Co(CO)_4^-} \xrightarrow{\text{then H}^+} \mathrm{HCoRu_3(CO)_{13}}$$

22-3. Structures of Metal Carbonyls

Mononuclear Carbonyls. These compounds (listed in Table 22-1) are all hydrophobic liquids or volatile solids, soluble to varying degrees in nonpolar solvents. The M—C—O chains are essentially linear, and these compounds obey the 18-electron rule [except $\mathrm{V(CO)_6}$].

$V(CO)_6$. Because this mononuclear species does not achieve an 18-electron

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[7] F. A. Cotton *et al., Inorg. Chem.*, 1986, **25,** 1021.

[8] F. A. Cotton *et al., J. Organomet. Chem.*, 1981, **217**, C14.

TABLE 22-1
Mononuclear Binary Metal Carbonyls

Compound	Color and form	Structure[a]	Comments
$V(CO)_6$	Blue-black[b] solid; dec 70°C; subl in vacuum	Octahedral,[c] V—C = 2.008(3)	Paramagnetic ($1e^-$); yellow orange in solution
$Cr(CO)_6$ $Mo(CO)_6$ $W(CO)_6$	Colorless crystals; all subl readily	Octahedral: Cr—C = 1.913(2) Mo—C = 2.06(2) W—C = 2.06(4)	
$Fe(CO)_5$[d]	Yellow liquid; mp −20.5°C bp 103°C	*tbp;* Fe—C = 1.810(3)ax, 1.833(2)eq	
$Ru(CO)_5$[d]	Colorless liquid; mp −16 to −17°C	*tbp* (by ir)	Very volatile and difficult to obtain pure
$Os(CO)_5$[d]	Colorless liquid; mp 2.0 to 2.5°C	*tbp* (by ir)	Very volatile and difficult to obtain pure
$Ni(CO)_4$	Colorless liquid; mp −25°C	Tetrahedral Ni—C = 1.838(2)	Very toxic; musty smell; flammable; decomposes readily to metal

[a] M—C bond lengths are in Angstroms. Figures in parentheses are error estimates, occurring in the least significant digit.

[b] For a discussion of the color (blue-black solid, yellow solution) and the electronic structure, cf. D. C. Ellis *et al.*, *J. Am. Chem., Soc.*, 1983, **105**, 2308.

[c] See text for discussion of possible distortions.

[d] R. K. Pomeroy *et al.*, *Organometallics*, 1983, **2**, 693.

configuration, the possibility that it might dimerize arises; however, this does not happen under normal conditions, although by cocondensing V atoms and CO at about 10K, a substance that may have a $(OC)_5V(\mu\text{-}CO)_2V(CO)_5$ structure is obtained. For an octahedral structure the d^5 configuration gives a $^2T_{2g}$ ground state that should be subject to Jahn–Teller distortion. In the vapor, electron diffraction results are consistent with O_h symmetry, albeit with large vibrational amplitudes. The crystal structure at 244K is built of octahedral molecules showing only marginal distortion from O_h symmetry, and the magnetic moment corresponds to one unpaired electron. However, at 66K there is a phase transition and antiferromagnetic exchange is observed, until at 4.2K all paramagnetism is lost; dimer formation is not believed to occur, however.

Cr$(CO)_6$, *Mo*$(CO)_6$, *W*$(CO)_6$. These constitute the only complete family of carbonyls that are all stable and in common use. No polynuclear Group VIB(6) carbonyls are known.

Fe$(CO)_5$, *Ru*$(CO)_5$, *Os*$(CO)_5$. These form the only other complete set, but the Ru and Os compounds are difficult to prepare, unstable, and seldom encountered.

Ni$(CO)_4$. This is the only binary carbonyl formed by the Ni, Pd, Pt group that is stable under normal conditions, although there is evidence for $Pd(CO)_4$ and $Pt(CO)_4$ in noble gas matrices at ~20K.

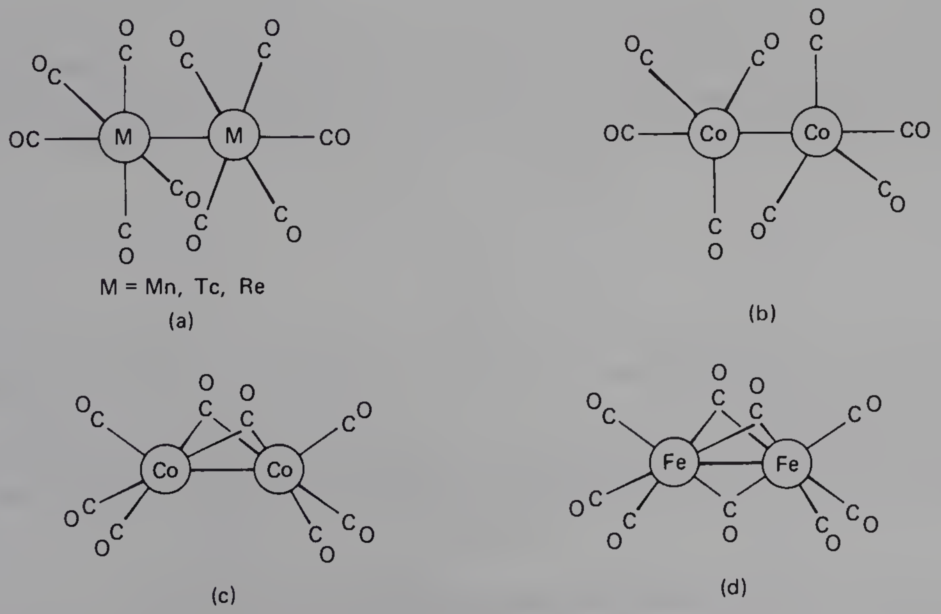
TABLE 22-2
Binuclear Binary Metal Carbonyls

Compound	Color and form	Structure	Comments
$Mn_2(CO)_{10}$	Yellow; mp. 154°C	$(OC)_5MM(CO)_5$, with D_{5d} symmetry	Sublime readily; weak, reactive M—M bonds
$Tc_2(CO)_{10}$	White; mp. 160°C		
$Re_2(CO)_{10}$	White, mp. 177°C		
$Fe_2(CO)_9$	Shiny golden plates	Confacial bioctahedron	Insoluble in organic media
$Ru_2(CO)_9$	Dark orange; dec at *RT*	Uncertain[a]	Loses CO to give $Ru_3(CO)_{12}$
$Os_2(CO)_9$	Orange yellow; mp 64–67°C	Uncertain[a]	Decomposes in few days at −20°C.

[a] See text.

Binuclear Carbonyls. These are listed in Table 22-2. $Mn_2(CO)_{10}$ (as well as its Tc and Re congeners) and $Co_2(CO)_8$ are the simplest molecules satisfying the 18-electron rule that these metals can form because they have odd atomic numbers. Thus $Mn(CO)_5$ and $Co(CO)_4$ are radicals with 17-electron configurations, but by dimerizing through the formation of M—M single bonds, they complete their valence shells. In the case of the $M_2(CO)_{10}$ molecules, the formation of this bond completes the structure, which is that shown in Fig. 22-1(a). For $Co_2(CO)_8$ the situation is more interesting, and the $(OC)_4Co—Co(CO)_4$ structure, Fig. 22-1(b) is only one of three that exist in equilibrium in solution. The structure of another one is shown in Fig. 22-1(c), while the structure of the third isomer is unknown. The crystalline compound contains molecules of structure (c) only, and this structure predominates in solution at low temperature.

Dicobalt octacarbonyl, $Co_2(CO)_8$, provides the first example encountered



(a)

(b)

(c)

(d)

FIG. 22-1. The structures of dinuclear metal carbonyls.

in this discussion of the occurrence of bridging carbonyl groups, and more important, of their occurrence in pairs. Moreover, the occurrence of two forms of $Co_2(CO)_8$ illustrates the following important principle of carbonyl structure; the two structural units (22-Ia) and (22-Ib) represent equally acceptable ways of distributing the two CO groups insofar as they each give the metal atoms the same formal electron count. The relative stabilities of the two arrangements are unlikely to differ greatly, and the preference shown in any given molecule for one or the other is not generally predictable. Doubtless steric considerations are pertinent, since the bridged form gives each metal atom a higher coordination number; this may explain why $Mn_2(CO)_{10}$ has no detectable amount of a bridged isomer. In the case of $Co_2(CO)_8$, bridged and nonbridged structures differ by only a few kilojoules per mole in free energy, and a close balance of this kind is not uncommon.

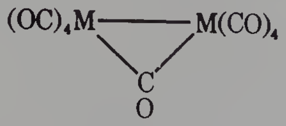
(22-Ia)

(22-Ib)

The Tc and Re analogues of $Mn_2(CO)_{10}$, as well as the mixed species $MnRe(CO)_{10}$, are quite stable, and $Re_2(CO)_{10}$ is relatively common, whereas no Rh or Ir analogues of $Co_2(CO)_8$ exist in normal circumstances, though it has been shown that under high pressures of CO, $Rh_4(CO)_{12}$ (see later) dissociates reversibly according to the equation[9]

$$Rh_4(CO)_{12} + 4CO = 2Rh_2(CO)_8$$

The structure of $Fe_2(CO)_9$ is shown in Fig. 22-1(d). This very symmetrical molecule (D_{3d} symmetry) has three bridging CO groups. An alternative, in the spirit of the discussion of (22-Ia) and (22-Ib), would be a singly bridged structure (22-II). There is no evidence for this in $Fe_2(CO)_9$ under any circumstances, but this appears to be the structure of $Os_2(CO)_9$ and probably of $Ru_2(CO)_9$ as well.



(22-II)

While most metal-to-metal bonds in binuclear (and higher nuclearity) carbonyls can be regarded as homopolar, some (rare) cases of dative bonding are known, as in $Cp^*(OC)_2Ir \rightarrow W(CO)_5$.[10]

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[9] F. Oldani and G. Bor, *J. Organomet. Chem.*, 1985, **279**, 459.

[10] R. K. Pomeroy *et al.*, *Organometallics*, 1985, **4**, 250.

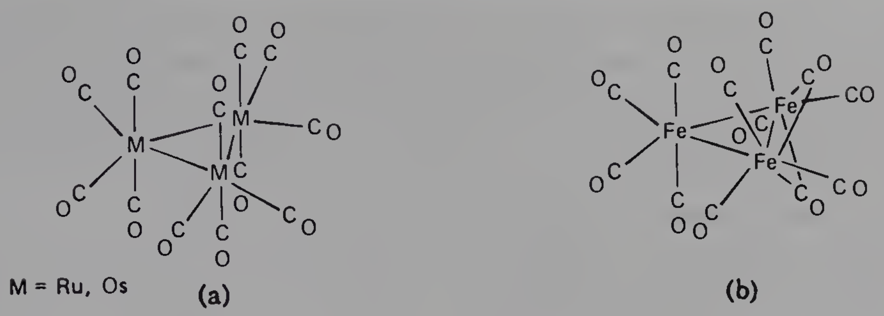

FIG. 22-2. The structures of $M_3(CO)_{12}$ molecules.

Trinuclear Carbonyls. The principal trinuclear carbonyls are of the $M_3(CO)_{12}$ type. They are formed by Fe, Ru, and Os and include not only the homonuclear ones but mixed ones, for example, $FeRu_2(CO)_{12}$ and $Fe_2Os(CO)_{12}$. All have the structure shown in Fig. 22-2(a) except $Fe_3(CO)_{12}$, which has a structure approximately as shown in Fig. 22-2(b). The former contains only terminal CO groups and has D_{3h} symmetry (in the homonuclear cases), whereas the $Fe_3(CO)_{12}$ structure is a highly unsymmetrical one.* It can be thought of as derived from the D_{3h} structure by the rotation of one CO group on each of two metal atoms into bridging positions across the bond between those two atoms, with accompanying rotations of the residual $Fe(CO)_3$ moieties containing those metal atoms. It is, however, even more complex than this, since the CO bridges are not symmetrical. We return to this point in Section 22-4.

Tetranuclear Carbonyls. There is an enormous number of tetranuclear species containing CO groups along with other ligands. We discuss here only the three homoleptic species, $M_4(CO)_{12}$, with M = Co, Rh, and Ir. These are the most stable binary carbonyls formed by the two latter elements. There are two structures for these molecules, each consisting of a tetrahedron of metal atoms. For $Ir_4(CO)_{12}$ the deployment of CO groups [Fig. 22-3(a)] is such as to conserve the full symmetry of a tetrahedron: there are three terminal CO groups on each metal atom with each Ir—C bond approximately trans to an Ir—Ir bond. For the Co and Rh compounds the structure has lower

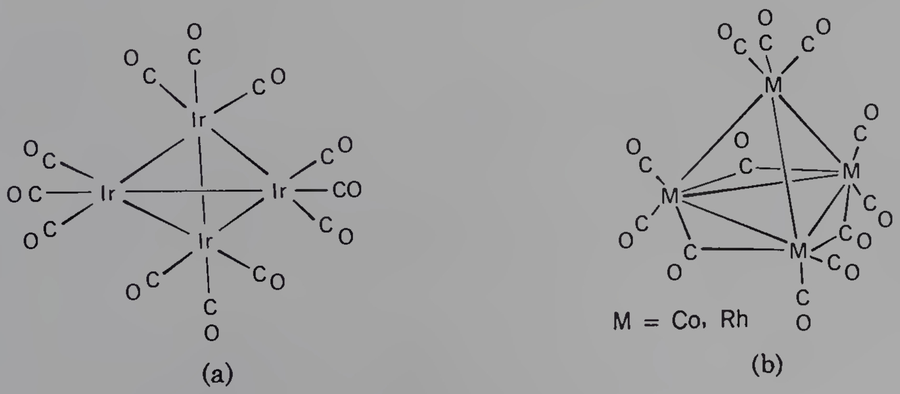

FIG. 22-3. The two structures for $M_4(CO)_{12}$ carbonyls.

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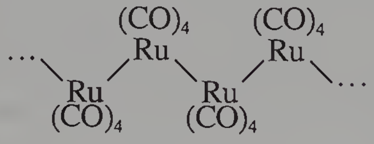
*For structure in solution see N. Binstead *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987**, 1330.

symmetry [Fig. 22-3(b)]. One metal atom has three terminal CO groups, as in $Ir_4(CO)_{12}$, but the remaining nine CO groups occupy both symmetrical bridging positions and terminal positions around the triangle formed by the other three metal atoms; the molecule has C_{3v} symmetry. Five mixed species $M_nM'_{4-n}(CO)_{12}$ are also known, and ir spectra (see Section 22-5) show that they all have structures of the type shown in Fig. 22-3(b).

Larger Polynuclear Carbonyls. In dealing with still larger metal carbonyls, the focus shifts more and more to the nature of the metal cluster itself. Its inherent properties determine the character and chemistry of the compound with the presence of CO groups—or other ligands—on the surface taking a place of secondary interest. For this reason, the larger species, called *high-nuclearity metal carbonyl clusters* are discussed in detail in Chapter 23, along with other types of metal atom cluster compounds and other classes of compounds that contain metal–metal bonds.

It is more appropriate to mention here that there appears to be only one possible example of a polymeric carbonyl, namely, $[Ru(CO)_4]_n$,[11] obtained by photolysis of concentrated solutions of $Ru_3(CO)_{12}$ under 1 atm of CO; a reasonable, though unproved, structure for this is (22-III).



(22-III)

22-4. Additional Structural and Bonding Features; Fluxionality

In addition to the linear M—C—O group, which is the commonest structural unit to be found in carbon monoxide compounds of the metallic elements, a number of other arrangements can occur when two or more metal atoms are present.

The four principal geometrical arrangements of a CO ligand relative to two or more metal atoms are shown schematically in Fig. 22-4. In (a) we see the symmetrical bridge in which the two M—C bonds are of equal length and the CO axis is perpendicular to the M—M axis. It should be stressed that most structural data on metal carbonyls are obtained by X-ray crystallographic studies, and in the solid state intermolecular contacts can cause small distortions of this ideal geometry (of C_{2v} symmetry). This situation is similar to that pertaining to "linear" M—C—O units, which often have M—C—O angles of only 170° (or even less) because of packing forces, but are nevertheless to be regarded as linear in describing both the molecular structure and the bonding.

In Fig. 22-4(b) is an unsymmetrical bridge, which differs from (a) in two respects: the two M—C distances are significantly different (M'---C being

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[11] W. R. Hastings and M. C. Baird, *Inorg. Chem.*, 1986, **25**, 2913.

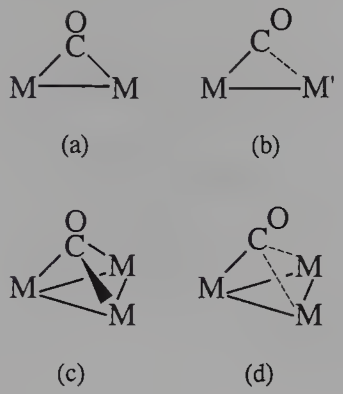

FIG. 22-4. Four important structural modes for attachment of the CO ligand to two or three metal atoms.

longer) and the M—C—O and M′—C—O angles are quite different, with the former being more nearly linear. The question of how best to describe the bonding for these "semibridging" CO groups will be discussed presently.

In Fig. 22-4(c) we have a triply bridging μ_3-CO group, in which the ideal symmetry is C_{3v}, with the CO unit lying along the threefold axis of symmetry. The less symmetrical arrangement shown in Fig. 22-4(d) differs from the symmetrical one in much the same way as (b) differs from (a), and again a bonding explanation for such a geometry is often problematical.

Semibridging CO Groups. This term can be applied to all structures of the types shown in Fig. 22-4(b) and (d), and commonly is.[12] While there may be many reasons for the occurrence of these unsymmetrical systems, there are three types that are most common and most easily interpreted.

1. *Cyclic Sets of Semibridging CO's.* It has already been noted that each of the nonbridged and symmetrically double-bridged arrangements (22-Ia) and (22-Ib), respectively, gives the metal atoms the same formal electron count and that the arrangements appear, in general, to differ little in inherent stability. In many cases it appears that not only are these two limiting forms of similar stability, but all the intermediate, symmetrical stages by which one can be converted to the other are also of similar energy. This idea is represented graphically in Fig. 22-5, which shows three possible ways in which the energy might vary as a function of the degree of bridge formation. In case *A* the unbridged structure constitutes the preferred minimum and the fully bridged structure a less stable minimum; all symmetric intermediate stages of bridge formation are less stable. Situation *B* is similar to *A* except that the relative stabilities of the fully bridged and nonbridged structures are reversed. In case *C* the most stable conformations are those in which the bridges are incompletely formed. All these intermediate stages maintain a balanced charge distribution over the M—M unit because the two CO groups have at all points achieved equal but the opposite degrees of bridge formation.

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[12] R. H. Crabtree and M. Lavin, *Inorg. Chem.*, 1986, **25**, 805, R. Hoffmann *et al., J. Am. Chem. Soc.*, 1980, **102**, 2576; M. Bénard *et al., Nouv. J. Chim.*, 1984, **8**, 149.

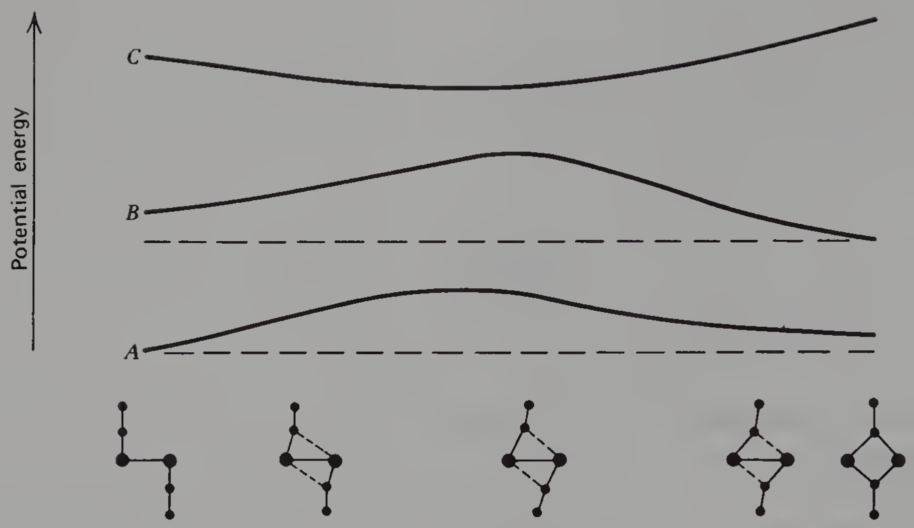
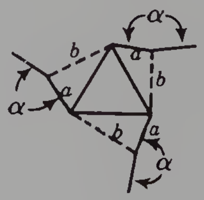


FIG. 22-5. Some ways in which the potential energy of an $M_2(CO)_2$ group may vary as a function of the degree of bridge formation.

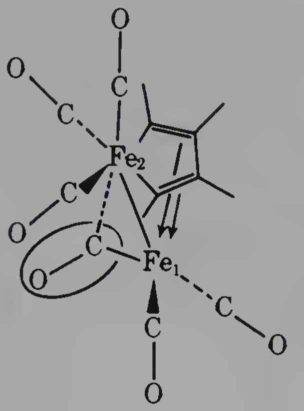
Case *C* is probably the least likely of the three shown in Fig. 22-5, but it is not logically impossible, since it occurs in the case of $Fe_3(CO)_{12}$ where the two bridges across one Fe—Fe bond are formed incompletely but in the balanced way indicated by the sketches in Fig. 22-5.

The partial formation of bridges in such a way as to keep the metal atoms equivalent is "a game any number can play," provided the system is cyclic. Thus for an equilateral triangle of metal atoms an arrangement of the sort shown in (22-IV) is "balanced" and just such an arrangement, with mean values of $a \approx 1.82$ Å, $b \approx 2.28$ Å, and $\alpha \approx 155°$ is found in the carbonylate anion $[Fe_4(CO)_{13}]^{2-}$ (see Section 22-6). In $Rh_4(CO)_{12}$, on the other hand, $a = b$ and we have a set of fully formed bridges.



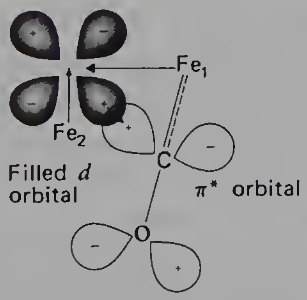
(22-IV)

2. *Semibridging CO's in Inherently Unsymmetrical Environments.* In a number of cases only one CO group is semibridging, and in a few there are two, but they are both closest to the same metal atom. Obviously such cases do not represent the sort of situation just discussed: equivalence of the metal atoms is not possible. In the majority of these cases an explanation for the semibridging posture of one or more CO ligands can be given in terms of an inequality of metal atom charges caused by the distribution of the other ligands in the molecules. A typical example is shown in (22-V), where the circled



(22-V)

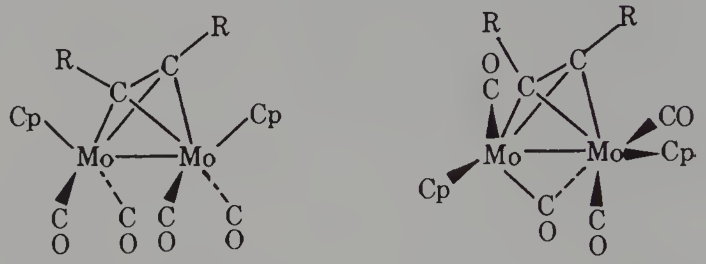
CO group is distinctly bent ($Fe_1—C—O \approx 165°$) and the two Fe—C distances are ~1.80 and ~2.35 Å; the former distance is approximately normal for a terminal CO group, but the latter is too short to be merely a nonbonded contact. This may be explained in the following way. Ignoring for the moment the presence of the Fe—Fe bond, we can count electrons around each iron atom in the following way: Fe_1 has 8 electrons of its own, acquires 6 more from the three CO groups and 4 more from the double bonds; this gives it 18. Fe_2 has 8 electrons of its own, plus 6 from the three CO groups, and only 2 more from the two Fe—C bonds. This gives it only 16. If each metal atom is to have an 18-electron valence shell, the Fe—Fe bond must be considered as a dative bond and written as $\overset{+}{Fe_1} \rightarrow \overset{-}{Fe_2}$ with resultant separation of charges. The semibridging CO group then serves to mitigate this charge separation by taking charge from Fe_2 in the way shown in (22-VI). Electron density passes from a filled $d\pi$ orbital of Fe to the π^* orbital of the CO group. A related type of CO group is found in the M—M triply bonded $(C_5Me_5)Cr_2(CO)_4$ species, where the CO groups lie over the M≡M bond and electron density from the M≡M bond partially drifts into the carbon atom $p\pi$ orbitals.



(22-VI)

3. *Semibridging CO's Caused by Steric Crowding.* There are a few cases in which a lone semibridging CO group occurs without any apparent electronic cause or function. It is presumed that the CO group is forced into this position

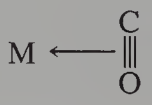
by steric crowding in the molecule. Perhaps the most unambiguous examples are provided by molecules of formula $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(RC{\equiv}CR)$, which might have been expected to have the symmetric structure (22-VIIa), whereas they actually have the unsymmetrical, twisted structure (22-VIIb). In this structure one CO group is apparently forced into the vicinity of the Mo—Mo bond, opposite to the bridging RC≡CR group, to allow the Cp rings to move away from the R groups. Once there, however, this CO group experiences an electronic interaction such that its CO stretching frequency is lowered (to ~1840 cm^{-1}) just as in cases 1 and 2.



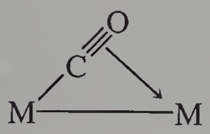
(a) (b)

(22-VII)

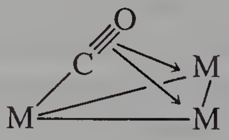
Side-on Bonding of CO.[13] While this is not known in the simple form shown in (22-VIII) it occurs as shown in (22-IX) and (22-X), both of which have CNR analogues. The compounds $Mn_2(CO)_5(dppm)_2$ and $Mn_2(CO)_4(CN\text{-}tolyl)(dppm)_2$ have the type of structure shown in (22-IX). In order for the right-hand Mn atom to reach the 18-electron configuration, donation of a pair of π electrons from the C—X (X = O and NR) may be invoked.[14] The bridging ligand is thus a 4-electron donor ($2\sigma + 2\pi$). Examples of CO (or CNR) serving as 6-electron donors ($2\sigma + 4\pi$), as in (22-X) are provided by $(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_7$[15] and two documented isocyanide cases, $Fe_3(CO)_9(CN\text{-}t\text{-}Bu)_5$[16a] and $Nb_3Cl_8(CN\text{-}t\text{-}Bu)_5$.[16b] There is even a case where the non-π-acid ligand (CH_3CN) behaves in the same way, namely, $Fe_3(CO)_9(CH_3CN)$.[17]



(22-VIII)



(22-IX)



(22-X)

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[13] C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem.*, 1984, **23,** 219.

[14] A. J. Deeming and S. Donovan-Mtunzi, *Organometallics*, 1985, **4,** 693.

[15] W. A. Herrmann *et al., J. Am. Chem. Soc.*, 1981, **103,** 1692.

[16a] M. I. Bruce *et al., J. Chem. Soc. Chem. Commun.*, **1982,** 353.

[16b] F. A. Cotton and W. J. Roth, *J. Am. Chem. Soc.*, 1983, **105,** 3734.

[17] H. D. Kaesz *et al., J. Am. Chem. Soc.*, 1979, **101,** 7260.

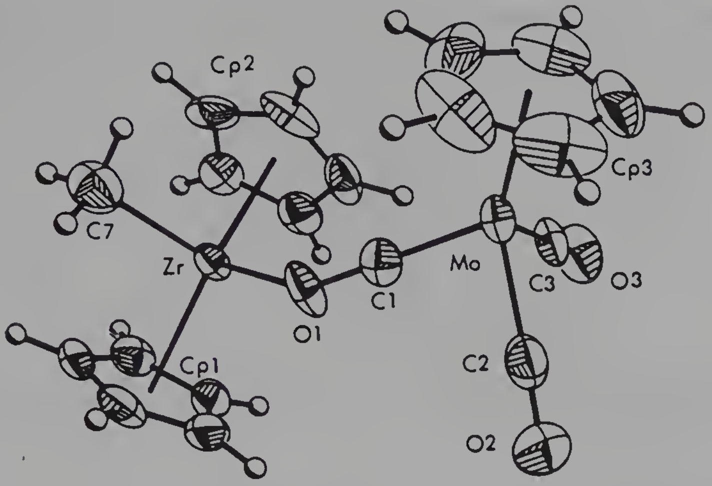
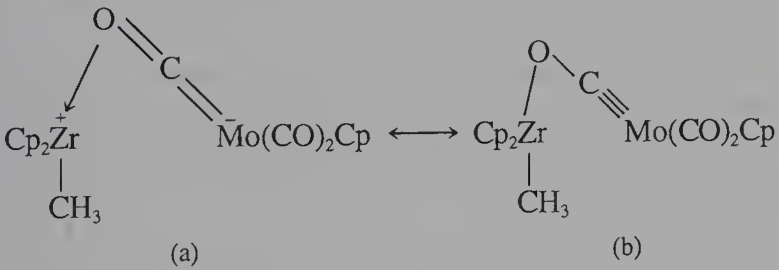


FIG. 22-6. The molecular structure of $Cp(OC)_2MoCOZr(CH_3)Cp_2$ (reproduced by permission from ref. 18).

Oxygen-to-Metal Bonds.[13] In all of the bonding modes so far discussed the CO is attached to the metal atom or atoms entirely, or mainly, through the carbon atom, with little or no direct oxygen-to-metal bonding. There are, however, some instances where oxygen-to-metal bonding is strong and unambiguous. The compound shown in Fig. 22-6 is a clear example, but there are at least six others,[18] of the same general kind, that is, with a MCO → M′ grouping. The C—O—M′ groups are not in general linear. The proper formulation of the bonding poses problems; the structural data suggest considerable covalence, as in (22-XI), but ionic dissociation occurs in moderately



(22-XI)

polar solvents such as CH_3CN. In the case of $(OC)_5VCOVCp'_2$, where the VCOV unit is strictly linear with V—C = 1.90 Å and V—O = 2.08 Å, the V—O bond is thought to be primarily electrostatic.[19]

The ability of bridging CO groups to serve as donors toward Lewis acids such as $AlCl_3$ has long been known.[13] More recently, stronger, essentially covalent interactions with transition metal atoms have been observed, as in

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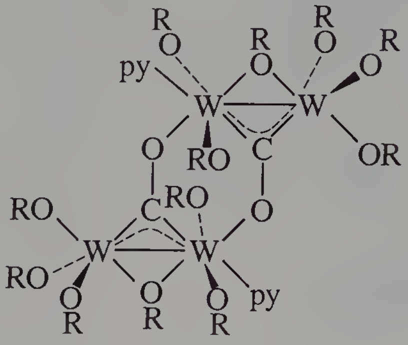
[18] J. R. Norton *et al.*, *Inorg. Chem.*, 1985, **24,** 1389.

[19] W. C. Trogler *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 6292.

the tetranuclear compound[20] shown in (22-XII), and in the compound $[Cp_2Mo_2(CO)_2](\mu\text{-}CO)_2(TiCp^*)_2$.[21]



(22-XII)

22-5. Vibrational Spectra of Metal Carbonyls[22]

Although in recent years ^{13}C nmr spectra have become increasingly valuable, it is still true that infrared (ir) spectroscopy (with occasional use of Raman spectroscopy) is the preeminent physical method for characterizing metal carbonyls. We shall now survey and illustrate the principal ways of employing ir spectra.

Detection of Bridging CO Groups. For neutral molecules, bridging CO groups absorb in the range 1700 to 1860 cm^{-1} and terminal ones generally absorb at higher frequencies (1850–2125 cm^{-1}). Figure 22-7 illustrates how these properties may be used to infer structures. It is evident that $Fe_2(CO)_9$ has strong absorption bands in both the terminal and the bridging regions. From this alone it could be inferred that the structure must contain both types of CO groups; X-ray study shows that this is so. For $Os_3(CO)_{12}$ several structures consistent with the general rules of valence can be envisioned; some of these would have bridging CO groups, while one [that shown in Fig. 22-2(a), the actual one] does not. The ir spectrum alone, Fig. 22-7(b), shows that no structure with bridging CO groups is acceptable, since there is no absorption band below 2000 cm^{-1}.

In using the positions of CO stretching bands to infer the presence of bridging CO groups, it is necessary to keep certain conditions in mind. The frequencies of terminal CO stretches can be quite low if (*a*) there are a number of ligands present that are good donors but poor π acceptors, or (*b*) there is a net negative charge on the molecule. In either case, back-donation to the CO groups becomes very extensive, thus increasing the M—C bond orders, decreasing the C—O bond orders, and driving the CO stretching frequencies

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[20] M. H. Chisholm *et al., Organometallics,* 1985, **4,** 986.

[21] E. J. M. de Boer *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 1666.

[22] See P. S. Braterman, *Metal Carbonyl Spectra,* Academic Press, New York, 1975, and S. F. A. Kettle, *Top. Cur. Chem.,* 1977, **71,** 111, for more technical discussions of all points relating to carbonyl spectra.

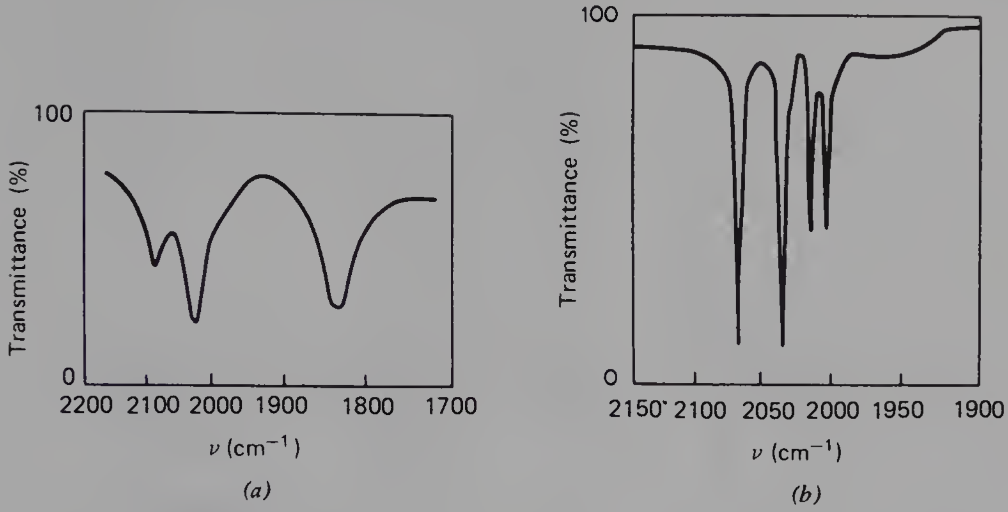

FIG. 22-7. The ir spectra in the CO stretching region of (a) solid $Fe_2(CO)_9$ and (b) $Os_3(CO)_{12}$ in solution. Note the greater sharpness of the solution spectrum. The most desirable spectra are those obtained in nonpolar solvents or in the gas phase. (Data from F. A. Cotton, in *Modern Coordination Chemistry,* J. Lewis and R. G. Wilkins, Eds., Wiley-Interscience, New York, 1960, and D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *Inorg. Chem.*, 1965, **4**, 166.)

down. Thus in $Mo(dien)(CO)_3$ one of the CO stretching bands is as low as 1760 cm^{-1} and in the $Fe(CO)_4^{2-}$ ion there is a band at 1790 cm^{-1}.

Molecular Symmetry from the Number of Bands. Because there is a direct relationship between the symmetry of a molecule and the number of ir active CO stretching modes, it is often possible to determine the arrangement of CO groups by comparing the observed spectrum with the number of bands predicted for each of several possible structures.

To illustrate the procedure, consider the cis and trans isomers of an $ML_2(CO)_4$ molecule. Figure 22-8 shows the approximate forms of the CO stretching vibrations and also indicates those that are expected to absorb ir radiation, when only the symmetry of the $M(CO)_4$ portion of the molecule is considered. When L = $(C_2H_5)_3P$, the two isomeric compounds can be isolated. One has four ir bands (2016, 1915, 1900, and 1890 cm^{-1}) and is thus the cis isomer; the other shows only one strong band (1890 cm^{-1}) and is thus the trans isomer.

It may also be noted that since no major interaction is to be expected between the CO stretching motions in two $M(CO)_4$ groups if they are connected only through the two heavy metal atoms, $Os_3(CO)_{12}$ should have the four-band spectrum of a *cis*-$ML_2(CO)_4$ molecule, and as seen in Fig. 22-8 it does.

Bond Angles from Relative Intensities. In some cases, isomers can be distinguished by the relative intensities of bands, even when both isomers give the same number of bands. This can be illustrated by the two isomeric ions whose structures are shown in Fig. 22-9 and spectra in Fig. 22-10. Each isomer gives two bands, due to the symmetric and antisymmetric modes of

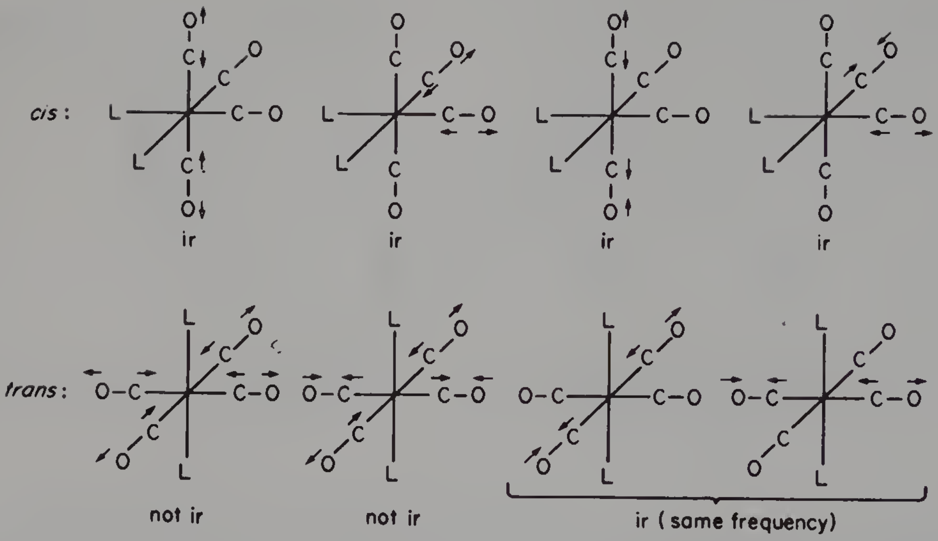

FIG. 22-8. Schematic indication of the forms of the CO stretching vibrations of *cis*- and *trans*-$ML_2(CO)_4$ molecules. For the cis isomer all four are distinct and can absorb ir radiation. For the trans-isomer, two are equivalent and have the same frequency, forming a degenerate vibration; only this form can absorb ir radiation.

vibration. We now use two general rules. First, for reasons discussed later, it is certain that the symmetric, or in-phase, stretching mode gives a higher frequency, ν_{sym}, than the antisymmetric mode, ν_{asym}. Second, even though the two CO oscillators are somewhat coupled in energy (else both ν_{sym} and ν_{asym} would be the same) each one makes a vectorial contribution to the total intensity that is nearly independent of the other. If we make the approximation that they are totally independent, we can simply do vector addition of the individual dipole vectors **r** as shown in Fig. 22-11, to get the vector dipoles **R** for the modes.

Since the intensities of ν_{sym} and ν_{asym} are proportional to $\mathbf{R}^2_{sym}$ and $\mathbf{R}^2_{asym}$, respectively, the ratio of the two band intensities is given by

$$\frac{I(1)}{I(2)} = \frac{\mathbf{R}^2_{sym}}{\mathbf{R}^2_{asym}} = \frac{(2\mathbf{r}\cos\theta)^2}{(2\mathbf{r}\sin\theta)^2} = \text{cotan}^2\theta$$

It is now clearly possible to calculate from the intensity ratios the OC—Mo—CO angles for the species giving rise to spectra A and B of Fig.

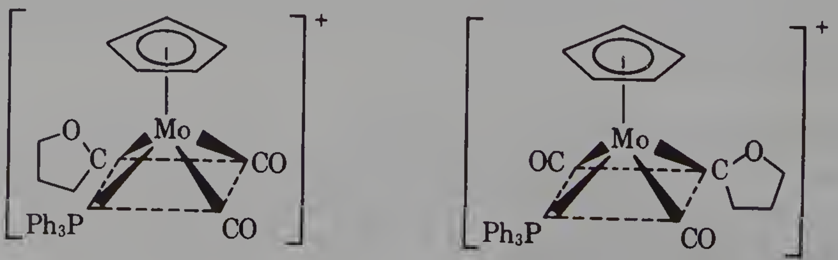

FIG. 22-9. The two isomers of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2PPh_3C_4H_6O]^+$.

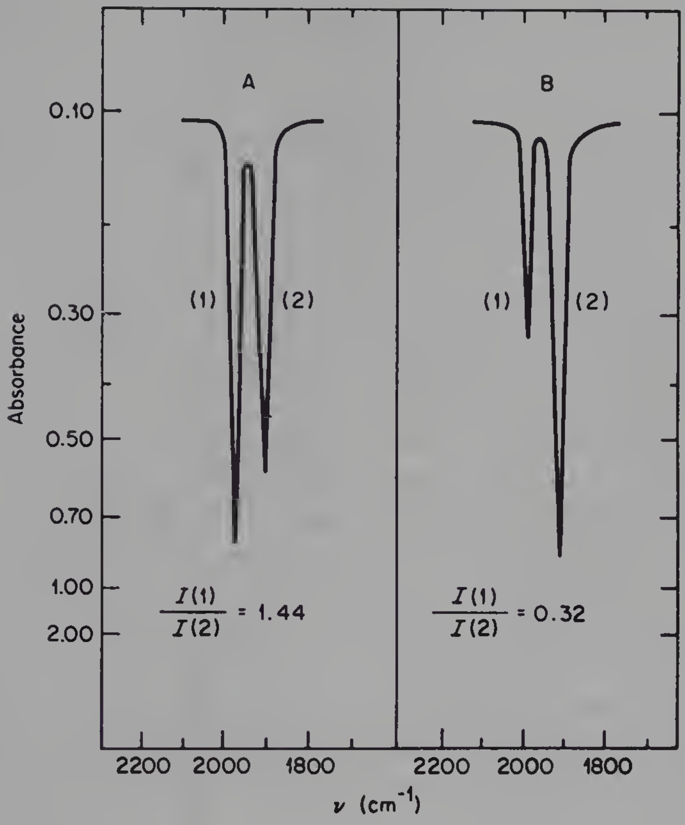

FIG. 22-10. The CO stretching bands and their relative intensities for the two cations of Fig. 22-9. (Data from F. A. Cotton and C. M. Lukehart, *J. Am. Chem. Soc.*, 1971, **93,** 2672, and other studies.)

22-10, namely,

$$2\theta_A = 2\sqrt{\text{arc cotan } 1.44} = 79°$$

$$2\theta_B = 2\sqrt{\text{arc cotan } 0.32} = 121°$$

We see that the isomer giving spectrum A must be the cis isomer and the one giving spectrum B must be the trans isomer.

Mixtures of Conformers or Other Isomers. The number of bands in the carbonyl stretching region for certain molecules can often be used to show that two conformational isomers are present. Thus in the molecule

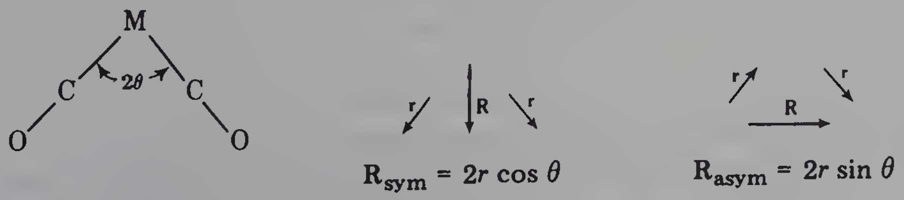

FIG. 22-11. Diagrams showing how the dipole vectors (**r**) of individual CO groups combine to give the dipole vectors **R** for the symmetric and the antisymmetric modes of vibration of an $M(CO)_2$ moiety.

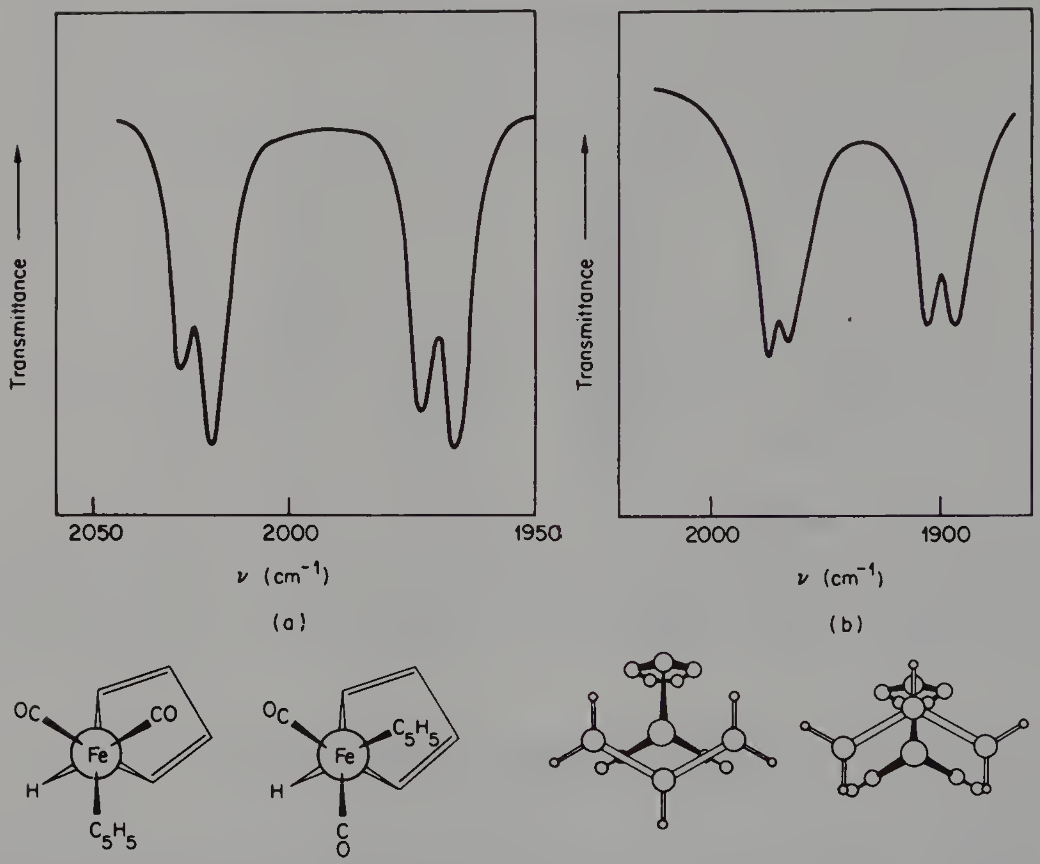

FIG. 22-12. Infrared spectra that demonstrate the presence of conformational isomers. (a) For the molecule $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$. (Data from F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, 1969, **91,** 7523.) (b) For the molecule $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_3H_5$(Data from R. B. King, *Inorg. Chem.*, 1966, **5**, 2242, and A. Davison and W. C. Rode, *Inorg. Chem.*, 1967, **6,** 2124.)

$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ one would tend to expect only two bands because of the symmetric and the antisymmetric modes. In fact, there are four bands [Fig. 22-12(a)]. This shows that there must be nearly equal populations of two conformations, presumably those shown below the spectrum. Similarly, for $(\eta^5\text{-}C_5H_5)Mo(CO)_2C_3H_5$, the appearance of two sets of bands indicates the presence of the two conformers shown below the spectrum [Fig. 22-12(b)].

Force Constants; Prediction and Assignment of Spectra. Even the simpler and more symmetrical metal carbonyl molecules, for example, $Ni(CO)_4$ or $Mo(CO)_6$, would pose a serious challenge with respect to a full analysis of the entire vibrational spectrum. In such a complete analysis, we should require experimental values for all vibrational modes, from which a set of force constants for all internal bond stretching and bending coordinates would be derived. Fortunately, for metal carbonyls, an understanding, with predictive potential, of the CO stretching frequencies, which are the vibrations of greatest interest and use, can be obtained with less effort. This is because the CO stretching modes are so much higher in energy and so weakly coupled with other vibrations that they can be treated separately. This situation is termed "energy factoring" of the complete vibrational equations.

The way in which advantage is normally taken of this inherent energy factoring is by use of a scheme called the Cotton–Kraihanzel method, or, sometimes, the Cotton–Kraihanzel force field (CKFF). The CKFF treats the CO stretching modes only and ignores their interactions with low frequency vibrations such as M—C stretches and M—C—O wags (both in the 300–600-cm^{-1} range) and C—M—C bends ($\leq 200\ \text{cm}^{-1}$). It also employs observed values of the ν_{CO}, whereas, in a rigorous treatment, these would have to be corrected for anharmonicity (20–30 cm^{-1}). Both of these approximations work not only because the neglected effects are relatively small but because they vary little from one ν_{CO} to another within the same molecule, or among similar molecules. Nonetheless, the CK force constants for CO stretching are not "absolute" although they stand in the correct relationship to one another.

The CKFF can include the coupling between the vibrations of the adjacent CO groups in a fully correct way, but often employs some approximate ratios between them in order to reduce the number of independent parameters. While the relationships have a basis in bonding theory, they are nevertheless also empirical, and more recently, a modification of the CK method that employs different empirical relationships has proven highly successful.[23]

The CO stretching force constants obtained by the CK method, or a modification thereof, conform to, and afford a quantitative expression for our understanding of how substituents in metal carbonyls affect M—CO back-bonding, as a function of their own capacity to compete with the CO ligand for metal $d\pi$ electrons. Thus, in *cis*-$\text{Mo(CO)}_4\text{py}_2$, there are four observed ν_{CO} frequencies, as noted in Fig. 22-8, all of which are observed in the ir. Using a CKFF these may be fitted by the set of force constants given in Fig. 22-13. Three features of these results are noteworthy. (1) $k_1 < k_2$, in accord with the fact that the CO's trans to py can get a larger share of $d\pi$ electrons, thus

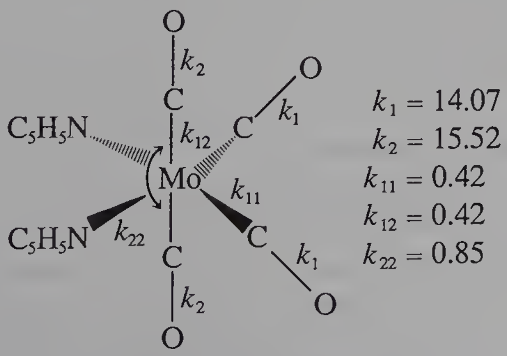

FIG. 22-13. A *cis*-$\text{Mo(CO)}_4\text{py}_2$ molecule with the full set of distinct CO stretching constants (k_1, k_2) and CO/CO interaction constants (k_{11}, k_{22}, k_{12}) denoted, all in units of md/Å. In the CKFF used, the relationships, $k_{11} = k_{12} = \frac{1}{2}k_{22}$, were imposed.

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[23] J. A. Timney, *Inorg. Chem.*, 1979, **18,** 2502.

lowering the CO bond order. The CO groups trans to each other compete with each other and therefore get less $d\pi$ electron density. (2) The interaction constants are all positive, which means physically that when one CO is stretched it is more difficult to stretch any of the others. The physical basis for this is that a stretched CO has a weaker C—O bond in which a lower-lying π^* orbital will attract more metal $d\pi$ density, thus making less $d\pi$ density available for its neighbors. The neighbors therefore have enhanced C—O bond strength and are thus harder to stretch. (3) The type of effect noted in point (2) will be roughly twice as important for a pair of *trans* CO groups that compete for two $d\pi$ orbitals than for a pair of *cis* CO groups that share only one $d\pi$ orbital. This is the basis for the constraining condition $k_{22} = 2k_{11} = 2k_{12}$.

22-6. Carbonylate Anions

A large number of anionic metal carbonyl species, $M_x(CO)_y^{z-}$, are known. In many cases they can be fully protonated to give the metal carbonyl hydrides, $H_zM_x(CO)_y$; we shall discuss carbonyl hydrides in detail in Chapter 24 along with many other examples of M—H bonds.

Metal carbonylate anions can be obtained in a number of ways, as illustrated by the following reactions:

$$\begin{aligned}
Fe(CO)_5 + 3NaOH(aq) &\longrightarrow Na[HFe(CO)_4](aq) \\
&\qquad + Na_2CO_3(aq) + H_2O \\
Co_2(CO)_8 + 2Na/Hg &\xrightarrow{THF} 2Na[Co(CO)_4] \\
Mn_2(CO)_{10} + 2Li &\xrightarrow{THF} 2Li[Mn(CO)_5] \\
Mo(CO)_6 + KI &\xrightarrow{\text{diglyme}} [K(\text{diglyme})_3]^+[Mo(CO)_5I]^- \\
&\qquad + CO \\
2Co^{2+}(aq) + 11CO + 12OH^- &\xrightarrow{KCN(aq)} 2[Co(CO)_4]^- \\
&\qquad + 3CO_3^{2-} + 6H_2O \\
M_2Cl_{10} + CO(1\text{ atm}) + \text{reductant} &\xrightarrow{25°C} M(CO)_6^- \qquad (M = Nb, Ta)
\end{aligned}$$

$$[\text{reductant} = LiC_{10}H_8, \text{ or } NaC_{10}H_8{}^{24}, \text{ or } Mg + Zn + py^{25}]$$

The simpler carbonylate ions, like the binary carbonyls, obey the noble gas formalism, and their stoichiometries can thus be predicted. The ions are usually fairly readily oxidized by air; the alkali metal salts are soluble in water, from which they can be precipitated by large cations such as $[Co(NH_3)_6]^{3+}$

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[24] J. E. Ellis *et al.*, *Organometallics*, 1983, **2**, 388.

[25] F. Calderazzo *et al.*, *Inorg. Chem.*, 1983, **22**, 1865.

or $[Ph_4As]^+$. Moreover, the structures of these simple anions appear to correspond to those of the stoichiometrically analogous neutral carbonyls. Thus, $Fe(CO)_4^{2-}$ and $Co(CO)_4^-$, like $Ni(CO)_4$, have a regular tetrahedral structure,[26] while $V(CO)_6^-$ and $Nb(CO)_6^-$ are, like $Cr(CO)_6$ and $Mo(CO)_6$, octahedral. Substituted carbonylate anions,[27] for example, $[Nb(CO)_4(dppe)]^-$, are also known.

In addition to the anions already mentioned, where the 18-electron rule is satisfied as much as possible by CO groups, with only the minimum (one or two) negative charges, there is a class of highly reduced or "super-reduced" carbonylate anions,[28a] of which $[M(CO)_5]^{3-}$ (M = V, Nb, and Ta), $[M(CO)_4]^{4-}$ (M = Cr, Mo, and W), and $M(CO)_4^{3-}$ (M = Mn and Re) are examples. These are synthesized by employing very powerful reducing agents (usually alkali metals) under strongly basic conditions. The Cr, Mo, and W salts[28b] $Na_2M(CO)_5$ induce disproportionation of CO_2 by the reaction $Na_2M(CO)_5 + 2CO_2 \rightarrow M(CO)_6 + Na_2CO_3$.

In addition to mononuclear carbonylate anions, a variety of polynuclear species have been obtained. The iron carbonylate ions, which have been much studied, are obtained by the action of aqueous alkali or Lewis bases on binary carbonyls or in other ways, for example,

$$Fe_2(CO)_9 + 4OH^- \longrightarrow [Fe_2(CO)_8]^{2-} + CO_3^{2-} + 2H_2O$$

$$2Fe_3(CO)_{12} + 7OH^- \longrightarrow [Fe_3(CO)_{11}]^{2-} + [HFe_3(CO)_{11}]^- + 2CO_3^{2-} + 3H_2O$$

$$Fe(CO)_5 + Et_3N \xrightarrow{H_2O,\,80^\circ C} [Et_3NH][HFe_3(CO)_{11}]$$

$$[HFe_3(CO)_{11}]^- + Fe(CO)_5 \longrightarrow [HFe_4(CO)_{13}]^- + 3CO$$

The $Fe_2(CO)_8^{2-}$ ion has a direct Fe—Fe bond with no bridges; the structure is essentially that shown in Fig. 22-1(b). The $HFe_3(CO)_{11}^-$ ion has the structure shown in Fig. 22-14(a), which can be considered analogous to that of $Fe_3(CO)_{12}$ with one bridging CO group replaced by a bridging H^-. The structure of the $Fe_4(CO)_{13}^{2-}$ ion varies somewhat from compound to compound. In one case, Fig. 22-13(b), three semibridging CO groups that approach the symmetrical μ-CO geometry are found while in a different salt the bridges are opened up almost to the extent of being true terminal CO groups.[29]

The chemistry of the $[Fe(CO)_4]^{2-}$ ion has been extensively studied. Figure 22-15 shows some of its reactions, which may be taken as typical for metal carbonylate anions. It will be seen that for the most part, these reactions are consequences of the nucleophilicity of the carbonylate anion. The compound $Na_2Fe(CO)_4 \cdot 1.5$ dioxane can be used in a pseudo-Grignard type of chemistry

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[26] G. Doyle and D. Van Engen, *J. Organomet. Chem.*, 1985, **280**, 253.
[27] K. Bachmann and D. Rehder, *J. Organomet. Chem.*, 1984, **276**, 177.
[28a] J. E. Ellis *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 672.
[28b] N. J. Cooper *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 2956.
[29] H. D. Kaesz *et al.*, *Organometallics*, 1985, **4**, 149.

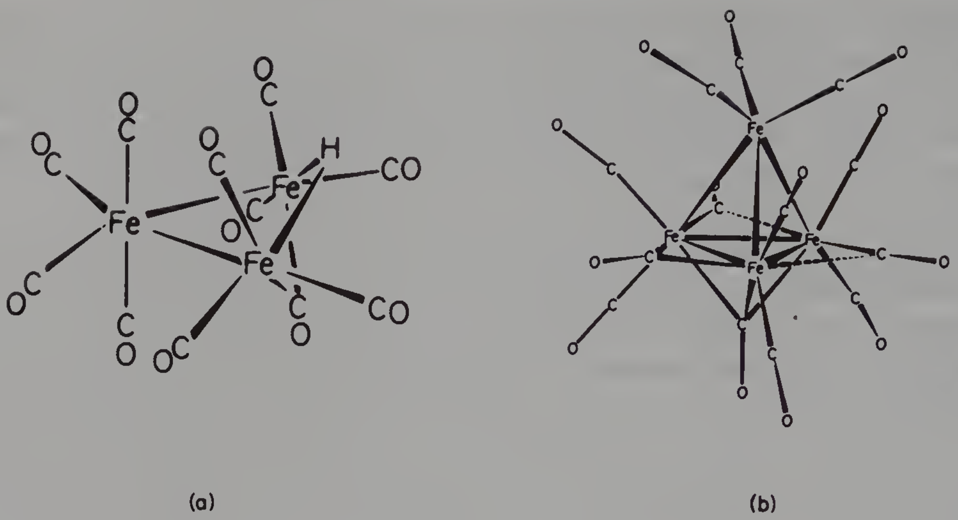
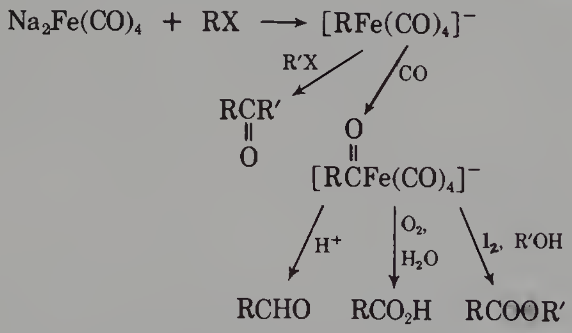


FIG. 22-14. The structures of (a) the $[HFe_3(CO)_{11}]^-$ ion and (b) the $[Fe_4(CO)_{13}]^{2-}$ ion.

to synthesize aldehydes, ketones, acids, and esters from alkyl halides as in the following reactions:



There is now a large number of polynuclear carbonylate anions formed particularly by Co, Rh, and Pt. Since these are of interest more because they are metal atom cluster species than because of their chemistry as carbonylate anions, the subject is discussed in Chapter 23.

In addition to the small homoleptic carbonyl anions such as $Co(CO)_4^-$, there are a number of important ones that contain η^5-C_5H_5 (Cp). All of these are readily obtainable in solution and useful as preparative reagents. Their reactivity depends on two factors. First, their inherent nucleophilicity (basicity) is a fundamental property. For the common carbonyl anions the following order of relative basicities has been established[30]:

$$CpFe(CO)_2^- \ (7 \times 10^7) > CpNi(CO)^- \ (5.5 \times 10^6)$$
$$> CpW(CO)_3^- \ (550) > Mn(CO)_5^- \ (77) > CpMo(CO)_3^- \ (67)$$
$$> CpCr(CO)_3^- \ (4) > Co(CO)_4^- \ (1)$$

Second, because the solvents normally used are only moderately polar, these anions engage in varying degrees of ion pairing with the cations present, and

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[30] R. B. King, *J. Am. Chem. Soc.*, 1966, **88**, 5121.

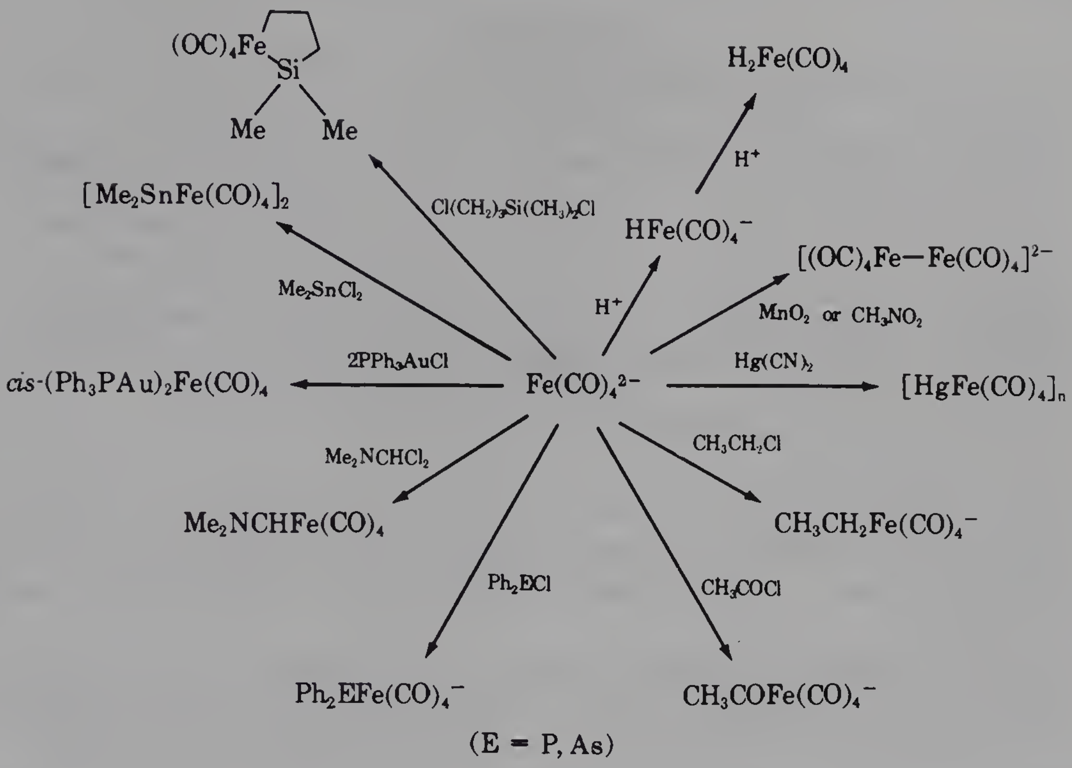


FIG. 22-15. Some reactions of $[Fe(CO)_4]^{2-}$

this can cause distortions of their structures and changes in their reactivities,[31a] for example in alkyl group migrations to coordinated CO (Section 27-6). Similar interactions with alkyl ammonium ions[31b] lead to interactions of the type MCO—HN.

22-7. Metal Carbonyl Halides

Carbonyl halides $M_x(CO)_yX_z$ are known for most of the elements forming binary carbonyls but also for Pd, Pt, and Au, which do not form binary carbonyls; Cu^I and Ag^I carbonyl halides also exist.

The carbonyl halides are obtained either by the direct interaction of metal halides and carbon monoxide, usually at high pressure, or from the cleavage by halogens of polynuclear carbonyls, for example,

$$Mn_2(CO)_{10} + Br_2(l) \xrightarrow{40°C} 2Mn(CO)_5Br \underset{\text{CO 150 atm}}{\overset{\text{in petroleum 120°C}}{\rightleftharpoons}} [M(CO)_4Br]_2 + 2CO$$

$$RuI_3 + 2CO \xrightarrow{220°C} [Ru(CO)_2I_2]_n + \tfrac{1}{2}I_2$$

$$2PtCl_2 + 2CO \longrightarrow [Pt(CO)Cl_2]_2$$

[31a] M. Y. Darensbourg, *Prog. Inorg. Chem.*, 1985, **33**, 221.

[31b] F. Calderazzo *et al.*, *J. Organomet. Chem.*, 1985, **296**, 1; C. H. Cheng *et al.*, *Organometallics*, 1987, **6**, 868.

TABLE 22-3
Some Examples of Carbonyl Halide Complexes

Compound	Form	mp (°C)	Comment
$Mn(CO)_5Cl$	Pale yellow crystals	Sublimes	Loses CO at 120°C in organic solvents; can be substituted by pyridine, etc.
$[Re(CO)_4Cl]_2$	White crystals	Dec >250	Halogen bridges cleavable by donor ligands or by CO (pressure)
$[Ru(CO)_2I_2]_n$	Orange powder	Stable >200	Halide bridges cleavable by ligands
$[Pt(CO)Cl_2]_2$	Yellow crystals	195; sublimes	Hydrolyzed by H_2O; PCl_3 replaces CO
$W_2(CO)_8Br_4$[a]	Red-orange crystals	Decomposes	Loses one CO to form $W_2(CO)_7Br_4$
$Mo_2(CO)_8I_4$	Red crystals	Decomposes	Disproportionates easily

[a] F. A. Cotton *et al., Inorg. Chem.*, 1985, **24**, 514.

The reaction of metal atoms with oxalyl chloride, $(COCl)_2$, is a newly discovered route to $[Re(CO)_4Cl]_2$, $[Ru(CO)_3Cl_2]_2$, $[Rh(CO)_2Cl]_2$, and $Pt(CO)_2Cl_2$.[32]

A few examples of the halides and some of their properties are listed in Table 22-3. Carbonyl halide anions are also known; they are often derived by reaction of ionic halides with metal carbonyls or substituted carbonyls:

$$M(CO)_6 + R_4N^+X^- \xrightarrow{\text{diglyme}} R_4N^+[M(CO)_5X]^- + CO \quad M = \text{Cr, Mo, and W}$$

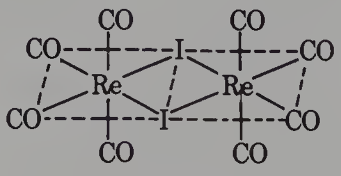
$$Mn_2(CO)_{10} + 2R_4N^+X^- \longrightarrow (R_4N^+)_2[Mn_2(CO)_8X_2]^{2-} + 2CO$$

$$(R_4N^+)_2[Mn_2(CO)_8X_2]^{2-} + 2R_4N^+Y^- \longrightarrow 2(R_4N^+)_2[Mn(CO)_4XY]^-$$

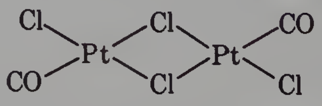
$$M(CO)_4\text{bipy} + 2KCN \longrightarrow K_2[M(CO)_4(CN)_2] + \text{bipy} \quad M = \text{Cr, Mo, and W}$$

Carbonyl fluorides are rare, the best characterized being $[Re(CO)_5F]ReF_5$ and a compound whose structure shows that it is not actually a carbonyl fluoride but $[Re(CO)_6][Re_2F_{11}]$.[33]

When carbonyl halides are di- or polymeric they are nearly always halogen bridged, as in (22-XIII) to (22-XV), but there are a few exceptions, such as the $[Pt_2X_4(CO)_2]^{2-}$ ions in which there is a Pt—Pt bond with no bridges, or the $[Pd_2X_4(CO)_2]^{2-}$ ions in which there are μ-CO groups.[34]



(22-XIII)



(22-XIV)

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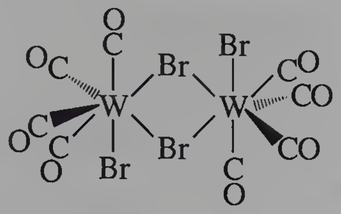
[32] M. L. H. Green *et al., Polyhedron*, 1985, **4**, 869.
[33] J. H. Holloway *et al., J. Chem. Soc. Dalton Trans.*, **1987**, 741.
[34] P. L. Goggin *et al., J. Chem. Soc. Chem. Commun.* **1981**, 1077.

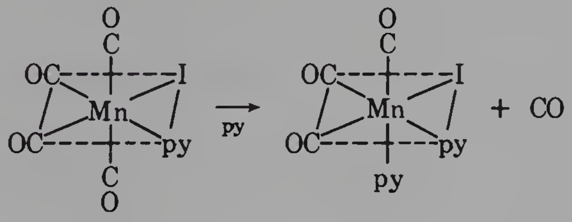


(22-XV)

As with halogen-bridged species generally, donors such as pyridine , phosphines or isocyanides can break the bridges, as illustrated by the reaction

$$[Mn(CO)_4I]_2 + 4py \longrightarrow 2Mn(CO)_3Ipy_2 + 2CO$$

The initial product of the cleavage in this reaction is (22-XVI), but the reaction can proceed further, and the product (22-XVII) is isolated. This occurs because in (22-XVI) two of the CO groups are trans to each other,



(22-XVI) (22-XVII)

thus will be competing across the metal atoms for the same metal π-bonding orbitals. Hence in the presence of any ligand like a nitrogen, phosphorus, or arsenic donor, of *lower* π bonding requirement or capacity compared to CO, one of the trans CO groups will be displaced. It follows that the two pyridine (or other) ligands inserted must appear in the cis position to each other.

22-8. Reactions of Metal Carbonyls

The number of carbonyls and the variety of their reactions is so enormous that only a few types of reaction can be mentioned. For $Mo(CO)_6$ and $Fe(CO)_5$, Fig. 22-16 gives a suggestion of the extensive chemistry that any individual carbonyl typically has. Other examples are encountered in succeeding chapters. A discussion of reaction mechanisms can be found in Section 29-8.

CO Substitution Reactions. An important general class of reactions of carbonyls comprises those in which CO groups are displaced by other ligands. These may be individual donor molecules, with varying degrees of back-acceptor ability themselves [e.g., PX_3, PR_3, $P(OR)_3$, SR_2, NR_3, OR_2, RNC] or unsaturated organic molecules such as C_6H_6 or cycloheptatriene. Derivatives of organic molecules are discussed in Chapter 26.

The more or less classical substitution reactions shown in Fig. 22-16 are

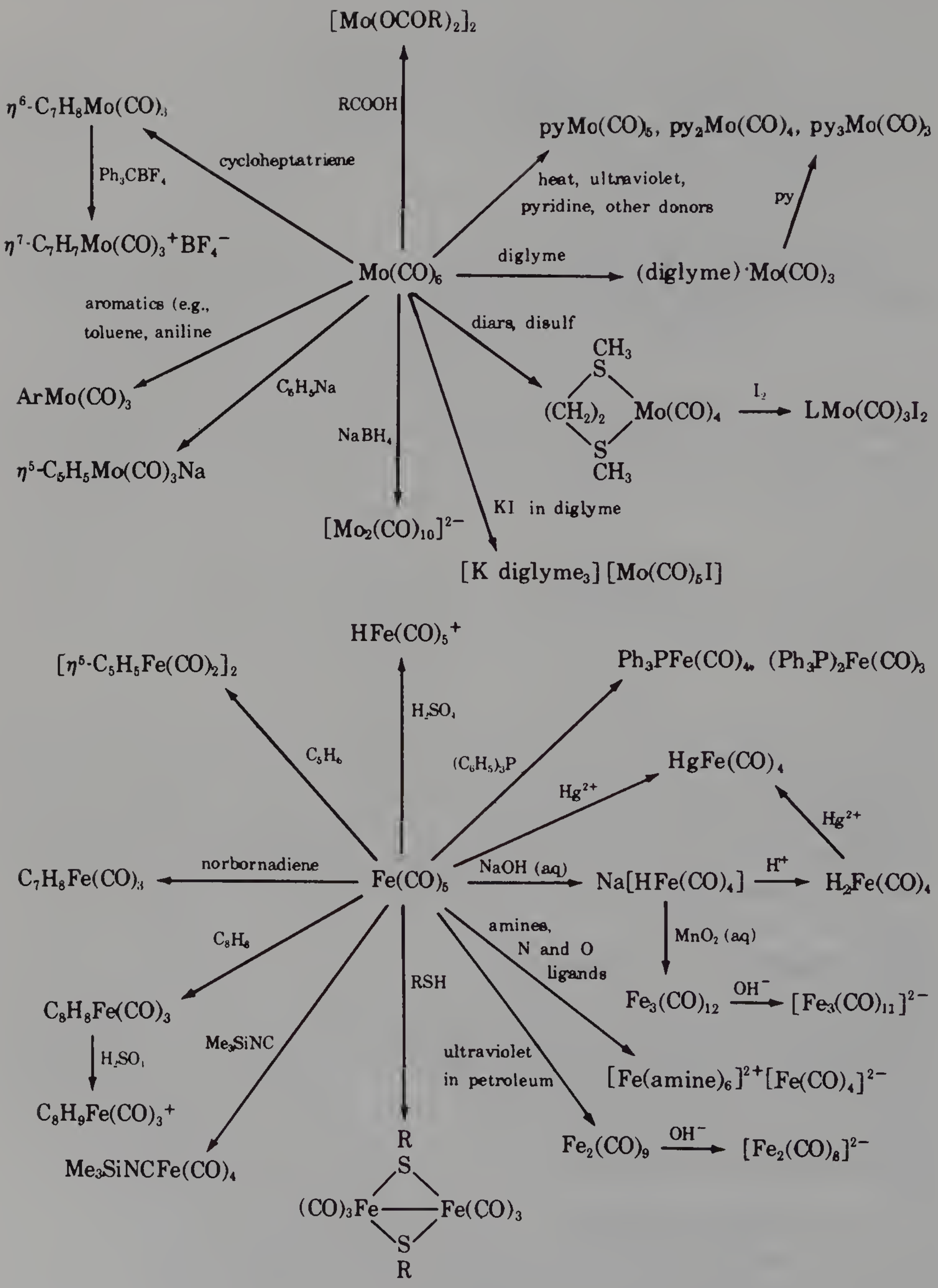


FIG. 22-16. Some reactions of molybdenum and iron carbonyls.

mainly thermal reactions. In many cases they are not clean, as when $Fe(CO)_5$ reacts with Ph_3P to give a mixture of products. In other cases, thermal reactivity may be too slow. In some cases catalysis of thermal reactions by PdO or $CoCl_2 \cdot 2H_2O$ is effective,[35] although the mode of action of these catalysts is obscure.

$V(CO)_6$. Relative to the rather sluggish thermal reactivity of most metal carbonyls, $V(CO)_6$ can be called hyperreactive because of a rapid associative S_N2 pathway.[36] For example, for reactions of the type

$$M(CO)_6 + PR_3 \longrightarrow M(CO)_5PR_3 + CO$$

the relative rates for M = V and Cr are in the ratio of $\sim 10^{10}$. The compound $^*Cp_2VCO$ also exchanges with labelled CO rapidly by an associative mechanism. In addition, while $Cr(CO)_6$ reacts with harder bases such as acetone, py, and MeCN to give simple substitution products $Cr(CO)_{6-n}L_n$, the reaction with $V(CO)_6$ proceeds rapidly to disproportionation products such as $[VL_6^+][V(CO)_6^-]$. The exceptional reactivity of $V(CO)_6$ is connected with its being a 17-electron system, which generally though not always is far more labile than a comparable 18-electron system (see Section 29-8).

Photochemical Reactions of Metal Carbonyls. In recent years increasing attention has been given to photochemical reactions, which often occur cleanly and easily where corresponding thermal routes are messy or unavailable. These derive from two main types of primary photo process: (1) photoejection of a CO ligand; (2) M—M bond scission. Virtually every metal carbonyl can undergo loss of one CO group to generate a reactive intermediate. This may be attributed to the fact the lowest photoexcited states are those resulting from $\pi \rightarrow \sigma^*$ transitions, which weaken one or more CO bonds, leading to CO loss. On the other hand, nearly all M—M bonds have a strongly absorbing $\sigma \rightarrow \sigma^*$ transition, the excitation of which will generate $M(CO)_x$ radicals.[37a]

The photogeneration of $M(CO)_5$ from $M(CO)_6$, M = Cr, Mo, and W, has been extensively studied.[37b] These 16-electron $M(CO)_5$ fragments react avidly with any available donor to form $M(CO)_5L$ species, and where L is a chelating bidentate ligand, rapid continuation to afford the $M(CO)_4L$ product can occur. The $M(CO)_5$ fragments will even combine with species normally regarded as having negligible donor capacity, for example, Ne, SF_6, Ar, Kr, Xe, and CH_4; although these products cannot normally be isolated, $Cr(CO)_5Xe$ has been

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[35] M. O. Albers *et al., J. Chem. Educ.,* 1986, **63,** 444; N. J. Colville *et al., J. Chem. Soc. Chem. Commun.,* **1984,** 1307.

[36] F. Basolo *et al., J. Am. Chem. Soc.,* 1986, **108,** 6046.

[37a] See P. Rushman and T. L. Brown, *J. Am. Chem. Soc.,* 1987, **109,** 3632.

[37b] J. J. Turner *et al., J. Chem. Soc. Chem. Commun.,* **1983,** 1355; A. J. Lees *et al., Inorg. Chem.,* 1985, **24,** 2942; F.-W. Grevels *et al., Inorg. Chem.,* 1985, **24,** 418; A. J. Downs *et al., Inorg. Chem.,* 1985, **24,** 275; E. Weitz *et al., J. Am. Chem. Soc.,* 1985, **107,** 1432; 1986, **108,** 4721.

characterized at $-100°C$ by ir spectrometry and $M(CO)_5en$, M = Cr, Mo and W, isolated.[37c]

Turning now to M—M bond photolysis, we note that this process may often be accompanied by CO ejection, thus leading to more complex reactions,[38] and also that species such as $(C_5H_5)_2Mo_2(CO)_6$ and $(C_5H_5)_2Fe_2(CO)_4$ as well as binary carbonyls such as $Mn_2(CO)_{10}$ can be photolyzed to metal-based radicals. It may also be noted that such radicals are also obtainable by photolysis of the M—H bonds in metal carbonyl hydrides, such as $HMn(CO)_5$.[39] However, we shall focus here on the well-studied processes:

$$M_2(CO)_{10} \xrightarrow{h\nu} 2M(CO)_5 \qquad M = \text{Mn and Re}$$

Once generated, these radicals have several important ways of reacting,[40] other than recombination, which they do at nearly the diffusion-controlled rate. One of these is with organic halides to abstract a halogen atom[41]:

$$Mn(CO)_5 + CCl_4 \longrightarrow ClMnCO_5 + CCl_3$$

They can also undergo substitution by phosphines, arsines, and so on. There is good evidence[40] that this proceeds associatively, that is, through a 19-electron intermediate that then expells CO

$$Mn(CO)_5 + PPh_3 \longrightarrow [Mn(CO)_5PPh_3] \longrightarrow Mn(CO)_4PPh_3 + CO$$

When photolysis of $Mn_2(CO)_{10}$ is carried out in a large excess of a basic ligand like pyridine, there is an overall disproportionation reaction that proceeds through a large number of intermediates.[42]

$$Mn_2(CO)_{10} \xrightarrow[\text{excess py}]{336\,\text{nm}} [Mn(CO)_3py_3^+][Mn(CO)_5^-] + 2CO$$

In the case of $Co_2(CO)_8$ there is also reactivity attributable to radical intermediates, $Co(CO)_4$, which can be generated thermally at relatively low temperatures.[43]

Nucleophilic Attack on CO. An important general reaction for M—CO units is nucleophilic attack at the carbon atom. Such reactions, especially with H^- or OH^- as nucleophile, have been intensively studied since these reactions provide a model for those involved in the water gas shift and other reactions between CO in water or in alcohols (Chapter 28).

The most important reactions are those with oxygen nucleophiles, H_2O, OH^-, ROH, and RO^-, which react to produce the types of products shown

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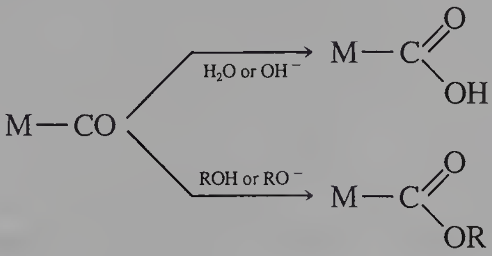
[37c] D. E. Marx and A. J. Lees *Inorg. Chem.*, 1987, **26**, 2254.
[38] K. Yasufuku *et al.*, *Organometallics*, 1985, **4**, 2174.
[39] J. J. Turner *et al.*, *Inorg. Chem.*, 1983, **22**, 3259.
[40] T. R. Herrinton and T. L. Brown, *J. Am. Chem. Soc.*, 1985, **107**, 5700.
[41] T. L. Brown *et al.*, *Organometallics*, 1985, **4**, 42.
[42] D. R. Tyler *et al.*, *Inorg. Chem.*, 1986, **25**, 2976.
[43] G. Palzi et al., *Coord. Chem. Rev.*, 1984, **53**, 37.

in the following equations, where M is used to represent a metal atom together with all other, nonreacting ligands:



The susceptibility of the CO group to such attacks is enhanced by overall positive charge on the M—CO unit, and proceed more rapidly with the better nucleophiles RO^- and OH^-. Both the hydroxocarbonyl and alkoxocarbonyl adducts are in general readily attacked by acids[44] to regenerate the M—CO compound, but some of the hydroxocarbonyl species can also react with base with proton loss to give $M—CO_2^-$.

The dicationic carbonyl complexes $(IrX(dppe)_2(CO)]^{2+}$ react with both H_2O and OH^-, as well as with MeO^- and MeOH (in the presence of Et_3N) to give CO_2^-, C(O)OH, and C(O)OMe products.[45]

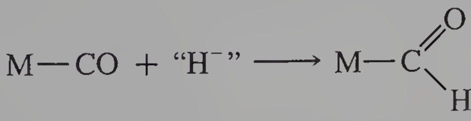
Other examples of reactions that have been studied in detail[46] are the following:

$$[CpMo(CO)_3(PPh_3)]^+ \xrightarrow{Et_4NOH} trans\text{-}CpMo(CO)_2(PPh_3)CO_2H$$

$$M(CO)_5 + MeO^- \longrightarrow [M(CO)_4(CO_2Me)]^- \quad M = \text{Fe, Ru, and Os}$$

$$M_3(CO)_{12} + NaOMe \longrightarrow Na[M_3(CO)_{11}CO_2Me] \quad M = \text{Fe, Ru, and Os}$$

The *hydride ion* is also an excellent nucleophile (introduced as, for example, BH_4^- or BEt_3H^-), and gives rise to formyl complexes (Section 25-3):



These can often be decarbonylated to give the hydride MH. Another reaction leading to hydrides is by decarboxylation of $M—CO_2H$, for example, the classic preparation of the $Fe(CO)_4H^-$ ion:

$$Fe(CO)_5 + OH^- \longrightarrow (OC)_4FeCO_2H^- \xrightarrow{-CO_2} Fe(CO)_4H^-$$

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[44] A. J. Deeming *et al.*, *J. Chem. Soc. Dalton Trans.*, **1985,** 857.

[45] M. A. Lilga and J. A. Ibers, *Organometallics,* 1985, **4,** 590; T. B. Brill *et al.*, *Organometallics,* 1986, **5,** 2259.

[46] D. H. Gibson *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 1125; P. C. Ford *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 585, 2355.

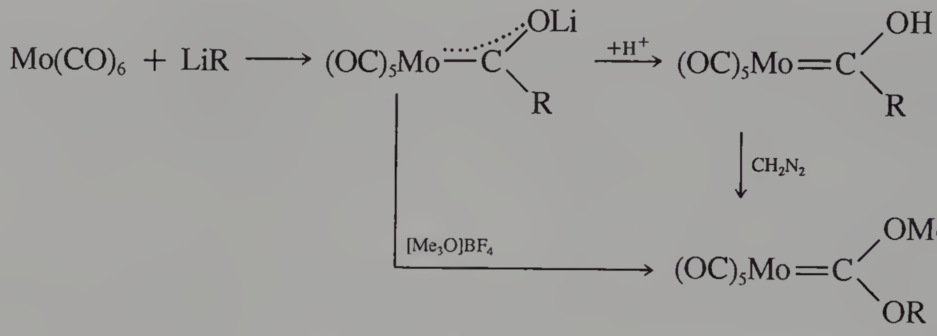
Ammonia, amines, dialkylamides,[47] and phosphides[48] also nucleophilically attack M—CO groups, as illustrated by the following reactions:

$$[\mathrm{CpFe(CO)_3}]^+ + \mathrm{H_2NCH_2CH_2NMe_2} \xrightarrow{-\mathrm{H}^+} \mathrm{CpFe(CO)_2CONHCH_2CH_2NMe_2}$$

$$[(\eta\text{-}\mathrm{C_6Me_6})\mathrm{Mn(CO)_3}]^+ + \mathrm{C_6H_{11}NH_2} \xrightarrow{-\mathrm{H}^+} (\eta\text{-}\mathrm{C_6Me_6})\mathrm{Mn(CO)_2CONHC_6H_{11}}$$

$$[\mathrm{Cp^*Fe(CO)_3}]^+ + \mathrm{LiPRR'} \longrightarrow \mathrm{Cp^*Fe(CO)_2C(O)PRR'} + \mathrm{Li}^+$$

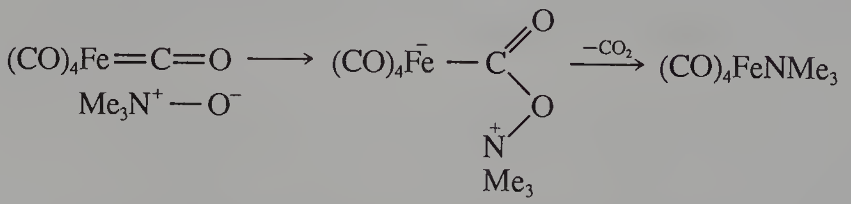
Reactions with lithium alkyls are especially important since they lead, via the following representative sequence, to carbene complexes (Section 25-7).



The acyl tetracarbonylferrates obtained from $\mathrm{Fe(CO)_5}$ are useful reagents for synthesis of ketones by attack of R′X on the anion:

$$\mathrm{Fe(CO)_5} + \mathrm{LiR} \longrightarrow \mathrm{Li^+[(OC)_4Fe{-}C(O)R]^-} \xrightarrow{\mathrm{RX}} \mathrm{RCOR'}$$

Finally, the interaction of tertiary amine oxides ($\mathrm{R_3NO}$) with carbonyls results in conversion of CO to $\mathrm{CO_2}$.[49] This is a useful means of providing a labile site on metal carbonyls, since the amine can be readily displaced:



Electrophilic Attacks. As noted previously, strong Lewis acids such as $\mathrm{BX_3}$ or $\mathrm{AlX_3}$ can give adducts that have C—O—$\mathrm{EX_3}$ groups, while there can also be strong interaction with ion carbonylate anions of the type M—C—O→MS_n,[13,31] where M can be an alkali metal, Mg^{2+}, and so on, solvated by THF, crown ethers, pyridine, or similar ligands.

In addition, however, electrophilic attacks by H^+, Me^+, and other carbocations can occur, expecially with bridging CO groups, adding to the CO with the highest coordination.[13] An example is the reaction

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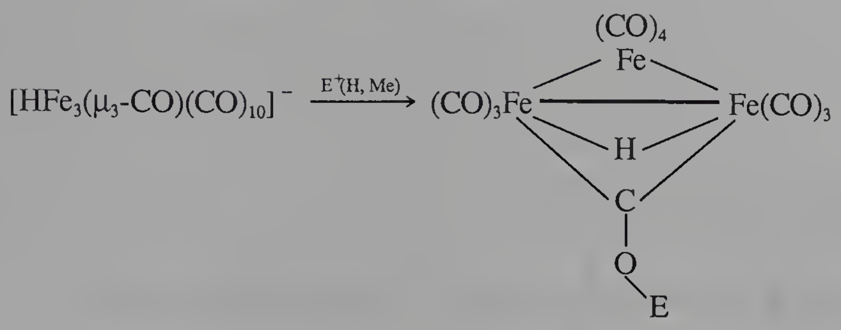
[47] R. J. Angelici *et al., Organometallics,* 1984, **3,** 1523.

[48] L. Weber *et al., Organometallics,* 1985, **4,** 2097.

[49] F. Basolo *et al., Organometallics,* 1987, **6,** 1538.



The nature of electrophilic attacks may, in certain cases, depend on the nature of the carbocation reagent.[50]

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Buckingham, J., *et al.*, Eds. *Dictionary of Organometallic Compounds* Chapman Hall, London, 1984, 3 Vols with supplements. Lists CAS numbers, preparations and physical properties.

Sikora, D. J., *et al., Adv. Organomet. Chem.*, 1986, **25,** 318 (CO derivatives of Ti, Zr and Hf).

Wender, I. and P. Pino, *Organic Syntheses via Metal Carbonyls,* Vols. 1, 2, Wiley, New York, 1968, 1977.

Wilkinson, G., F. G. A. Stone, and E. W. Abel, Eds., *Comprehensive Organometallic Chemistry,* Pergamon Press, Oxford, 1982 (see appropriate chapters for each element).

Wilkinson, G., R. D. Gillard, and J. A. McCleverty, Eds., *Comprehensive Coordination Chemistry,* Pergamon Press, Oxford, 1987 (some carbon monoxide compounds containing additional ligands are treated under individual metals).

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[50] See, for example, G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1981,** 2496; **1983,** 1557.

Chapter Twenty Three

Metal-to-Metal Bonds and Metal Atom Clusters

23-1. Introduction

As is well known, one of the most important concepts in chemistry, and perhaps the greatest one in inorganic chemistry, is the concept of the coordination complex, which was developed by Alfred Werner in the decades around 1900. This concept enabled Werner to make sense of an enormous amount of experimental data that had no explanation in the structural and bonding theory that had been worked out previously for compounds of carbon and other main group elements.

The essential idea in the coordination theory of Werner is that a metal ion surrounds itself with ligands and that the nature of the ligands, the character of the metal–ligand bonds, and the geometrical arrangement of the ligands around the metal atom determine the physical and chemical properties of the compound. There is no place in the Wernerian scheme for direct bonding between metal atoms.

Werner recognized the existence of polynuclear complexes, of course, and devoted a great many papers to the elucidation of their properties. However, these were viewed simply as a conjunction of two or more mononuclear complexes having some shared ligand atoms. The properties of these complexes were still attributed to the metal–ligand interactions, and direct metal-to-metal (M—M) interactions were not considered. This approach was entirely justified because in the compounds being considered there were no direct M—M interactions of chemical significance.

A few compounds containing metal–metal bonds and metal atom clusters had actually been isolated in the middle of the nineteenth century[1] and were known to, but not understood by, Werner and his contemporaries. It was only with the application of X-ray crystallographic techniques during the late 1930s and 1940s that the existence of metal–metal bonds (e.g., in $W_2Cl_9^{3-}$ and MoO_2) and metal atom clusters (of the $Mo_6Cl_8^{4+}$ type) was recognized.

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[1] For a more detailed historical account see F. A. Cotton, *J. Chem. Educ.*, 1983, **60,** 713.

Even so, it was not until the early 1960s that some sense of the possible generality of such chemistry began to develop. A key step was the discovery of the $[Re_3Cl_{12}]^{3-}$ ion, since this led to the first general discussion of the existence of the entire class of "metal atom cluster" compounds.

A metal atom cluster may be defined as a group of two or more metal atoms in which there are substantial and direct bonds between the metal atoms. Thus a metal atom cluster complex is more than just an ordinary polynuclear complex, and it is unfortunate that occasionally some authors have used the term "cluster" indiscriminately to designate polynuclear complexes of the classical (Werner) type in which there is no significant amount of direct M—M bonding. There are, of course, some borderline cases, that is, compounds in which the metal-to-metal distances and other properties are such that one cannot say unequivocally whether M—M bonding is "chemically significant." That does not negate the value of recognizing the existence of an enormous number of true, unambiguous metal atom cluster compounds in which the M—M bonds are as important as, or more important than, any other bonds in determining the chemistry and properties of the substance. The term "cluster" should be reserved for such compounds.

The history briefly sketched would be incomplete without mentioning the emergence of another class of cluster compounds, namely, those of the metal carbonyl type. It was with the structure determination of $Fe_2(CO)_9$ in 1938 that the close (~2.5 Å) approach of metal atoms in a polynuclear carbonyl-type compound was first observed. Perhaps the most crucial observation in establishing the reality and importance of M—M bonds in this area was the determination of the $Mn_2(CO)_{10}$ structure, where for the first time in the carbonyl field a direct M—M bond unsupported by any bridges was seen. There are now scores of such cluster-type compounds comprising neutral carbonyls, carbonylate anions, carbonyl hydrides, isocyanides, phosphitcs, and many mixed organocarbonyl-type molecules.

The two general types of metal cluster compound, which may be loosely called the "lower halide" type and the "carbonyl" type, differ from each other in many ways, and there is very little in the way of chemical reactions to interrelate them. This chapter discusses both types in some detail, but separately. The lack of any established relationship between them means that this can be done quite conveniently.

The discussion of the noncarbonyl-type clusters is concerned mainly with understanding their electronic structures. This is so closely related to the problem of M—M multiple bonds that we then move directly to that topic, and finally to a discussion of the close relationships between the clusters and the M—M multiple bonds.

We also include in this chapter a discussion of the "one-dimensional" solids in which the stacking pattern leads to the formation of infinite chains of metal atoms closely enough bonded to engender metallic properties.

At least a few examples of each of the types of compound discussed in this chapter have been encountered earlier in the presentation of the chemistry of individual elements. The objectives here, however, are to give a unified view, to introduce a number of additional examples, and to deal with questions of bonding that cut across the chemistry of a number of elements.

We have restricted this chapter to those species in which there are clearly direct M—M bonds. There are other species, such as the Fe_4S_4 aggregates in ferredoxins, which are often called "cluster compounds" and in which *some* direct M—M bonding may well exist. We have elected, perhaps somewhat arbitrarily, to discuss them in other places (e.g., under bioinorganic chemistry, Chapter 30, for the ferredoxin species).

We also omit from this chapter the metal cluster compounds formed by copper and gold. In each case, these compounds are of types peculiar to the element that forms them and they have been described under the chemistry of copper and gold, respectively.

METAL CARBONYL CLUSTERS[2]

Reference has already been made to the fact that there are two broad classes of metal atom cluster compounds: The "carbonyl" type and the "halide" type. There may also be designated, respectively, low-valence and high-valence types.[3] The carbonyl, or low-valence, types contain metal atoms in formal valence states -1 to $+1$, have carbonyl groups (usually many of them) to help stabilize these low oxidation states, and they contain relatively long M—M bonds) (>2.80 Å). They are formed mainly by the later transition metals, including those of the first transition series (i.e., Fe, Co, and Ni) as well as by the heavier ones. The high-valence clusters are formed by the earlier transition metals, and are restricted to the metals of the second and third transition series (i.e., Nb, Ta, Mo, W, and Re).

At present the study of carbonyl-type clusters is an extremely active field; hundreds of compounds are known already and more are reported every month. The present rampant accumulation of facts has temporarily outrun our ability to develop theories and correlations. In attempting to survey the field, then, there is no unique, fundamental way to organize the wealth of facts.

In this book we can do no more than give a broad survey and mention some illustrative compounds. In so doing, it is convenient to present the descriptive chemistry under two headings: (1) low-nuclearity carbonyl clusters (LNCC), which are those with three or four metal atoms; (2) high-nuclearity carbonyl clusters (HNCC), which are those with five or more metal atoms, each forming at least one M—M bond.

It may be noted that carbonyl cluster compounds, like simpler metal car-

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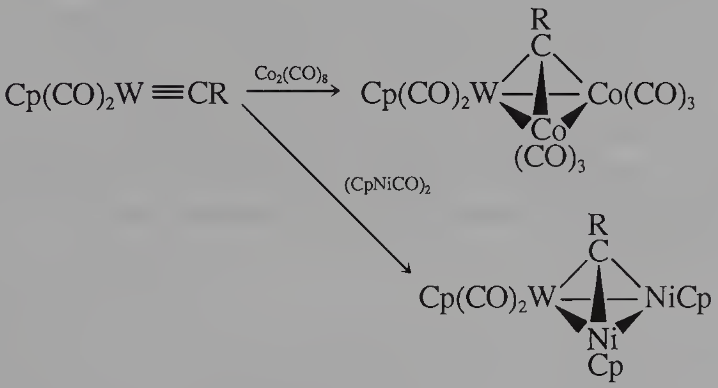
[2] B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.*, 1981, **24,** 225; H. Vahrenkamp, *Adv. Organomet. Chem.*, 1983, **22,** 169; R. D. Adams and I. T. Horvath, *Prog. Inorg. Chem.*, 1985, **33,** 127; P. Braunstein, *Nouv. J. Chim.*, 1986, **10,** 365.

[3] F. A. Cotton, in *Inorganic Chemistry: Toward the 21st Century,* M. H. Chisholm, Ed. (ACS Symposium Series, No. 211), American Chemical Society, Washington, DC, 1983, p. 209.

bonyls, also have some nitrosyl analogues,[4] although this is, as yet, a small area. It is also important to note that mixed metal clusters, for example, $H_2FeRu_2Os(CO)_{13}$, are very numerous and some can be obtained by designed syntheses.[5]

For both LNCCs and HNCCs the most common method of synthesis is some sort of thermally driven process, quite often a pyrolysis, and thus design and selectivity tend to be absent much of the time. However, some recent work, especially with LNCCs has concentrated on developing more deliberate approaches to specific, predictable target molecules, and doubtless further progress will be made. As an illustration we may cite the use of $Cp(CO)_2W{\equiv}CR$, which can react (like an alkyne) with various dimetal species to generate tetrahedral clusters (see also Section 25-11) in which the CR group also appears,[6] namely,



Anionic and Hydrido Clusters. Many of the carbonyl cluster species are anions (cations being virtually unknown) or hydrido species, or both. The relationships of these to each other and to neutral clusters in terms of electron count are the same as in simpler metal carbonyls, namely, one CO can be replaced by two hydrogen atoms, one H and one negative charge, or two negative charges. Protonation or deprotonation reactions are usually simple and rapid, and cause no change in the cluster structure, although there are exceptions; an example is

$$[Os_6(CO)_{18}]^{2-} \xrightarrow{+H^+} [Os_6(CO)_{18}H]^- \xrightarrow{+H^+} Os_6(CO)_{18}H_2$$

The fact that many large clusters are relatively strong polyacids has made their isolation and characterization more difficult since several species at different stages of ionization may coexist.

The locations of the hydrogen atoms in the hydrido clusters (and in some cases even the total number present) are often difficult to ascertain. There are, however, cases where clear results have been obtained, either directly by neutron diffraction, or less directly by X-ray diffraction coupled with steric

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[4] W. L. Gladfelter, *Adv. Organomet. Chem.*, 1985, **24,** 41.

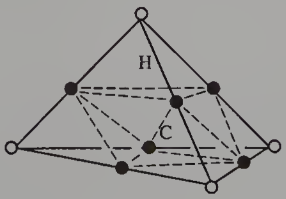
[5] W. L. Gladfelter and G. L. Geoffroy, *Adv. Organomet. Chem.*, 1980, **18,** 207.

[6] F. G. A. Stone, in *Inorganic Chemistry: Toward the 21st Century,* M. H. Chisholm, Ed. (ACS Symposium Series, No. 211), 1983, p. 383.

considerations. In $[FeRu_3(CO)_{13}H]^-$ a neutron diffraction study has shown that one Ru—Ru edge of the metal atom tetrahedron is symmetrically bridged by the hydrogen atom.[7] Similarly,[8] in $Re_3H_3(CO)_{11}PPh_3$ there is an essentially symmetrical hydrogen bridge on each edge, and in $Os_4H_4(CO)_{11}P(OMe)_3$ four edges are bridged, in the pattern shown in (23-I).

(23-I)

For the $[Co_6H(CO)_{15}]^-$ ion it has been shown by neutron diffraction that the hydrogen atom resides at the geometric center of the slightly distorted octahedron of cobalt atoms.[9] In a number of other cases, there has been evidence (from either neutron or X-ray diffraction, as well as from spectroscopy) that hydrogen atoms reside inside M_6 octahedra. Examples include $[Ru_6H(CO)_{18}]^-$ and $[Ni_{12}H_2(CO)_{21}]^{2-}$.[10] In $[Os_{10}(C)(H)(CO)_{24}]^-$ there is a hydrogen atom in a tetrahedral cavity,[11] while the C atom occupies the central octahedral cavity, as indicated in (23-II). Carbido clusters are discussed further in Section 23-5.



(23-II)

23-2. Low-Nuclearity (M_3 and M_4) Clusters

Triatomic Clusters. While linear M_3 clusters exist, and are not unimportant, the majority of M_3 clusters are triangular, and only this type will be discussed here. There are so many triatomic clusters, many of which are heteronuclear, that space permits discussion of only a few illustrative examples. The chemistry derived from the $M_3(CO)_{12}$ clusters (M = Fe, Ru, and Os), especially where M = Os, has been particularly well studied and can be used to illustrate some of the types of reactions that are possible.[12]

The $M_3(CO)_{12}$ clusters themselves, represented as (23-III) (where CO groups

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[7] T. F. Koetzle *et al., Inorg. Chem.*, 1981, **20,** 3823.

[8] R. Bau *et al., J. Organomet. Chem.*, 1981, **213,** 63.

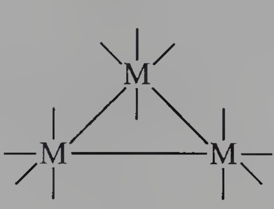
[9] R. Bau *et al., J. Am. Chem. Soc.*, 1981, **103,** 1458.

[10] G. Longoni *et al., Inorg. Chem.*, 1983, **22,** 1595.

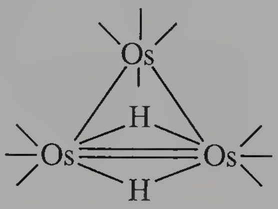
[11] J. Lewis *et al., J. Chem. Soc. Chem. Commun.*, **1982,** 754.

[12] R. D. Adams and I. T. Horvath, *Prog. Inorg. Chem.*, 1985, **33,** 127, where further details on these and other LNCCs will be found.

are denoted simply by lines), are electronically saturated, namely, they have a sufficient number of electrons to provide each metal atom with an 18-electron, closed shell configuration. In such systems there must be a total of 48 electrons, assuming that each M—M bond is of order 1. As will be discussed further later, the $H_2Os_3(CO)_{10}$ cluster can be derived from $Os_3(CO)_{12}$. This is an example of an unsaturated system; it possesses a total of only 46 electrons. From the structure (23-IV) in which one edge of the Os_3 triangle is shorter (2.60 Å) than the others (2.88 Å) and bridged by hydrogen atoms, it is inferred that there is one Os═Os double bond, thus allowing all Os atoms to achieve formal 18-electron configurations.



(23-III)

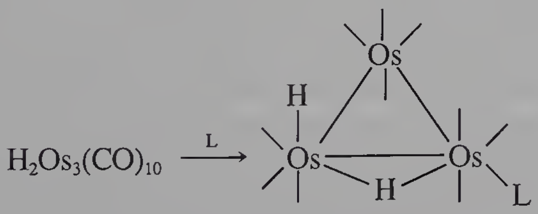


(23-IV)

While the $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ clusters are somewhat unreactive, they can be converted into more reactive derivatives, from which a large amount of interesting chemistry can then be developed. Three important points of departure are the following:

1. By replacement of one or two CO ligands with CH_3CN; these substituted species are then relatively reactive by loss of CH_3CN toward, *inter alia,* olefins. Some of the chemistry for the osmium system is summarized in Fig. 23-1. Similar reactions occur for $Ru_3(CO)_{12}$.[13]

2. Reaction of $Os_3(CO)_{12}$ with H_2 under pressure displaces two CO groups, giving $H_2Os(CO)_{10}$, which, as already mentioned, is unsaturated and reactive towards a variety of reagents,[14] such as Lewis bases:



3. Treatment of $Os_3(CO)_{12}$ with KOH in MeOH gives the $[HOs_3(CO)_{11}]^-$ ion, which can be converted via reactions such as those shown in Fig. 23-2 into a methyl derivative. This methyl compound is electronically unsaturated (46 electrons) and responds to this by developing a strong interaction between one C—H bond and an adjacent osmium atom (see Section 24-8 for "agostic" hydrogen atoms). This peculiar methyl compound is actually in equilibrium

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[13] G. A. Foulds *et al., J. Organomet. Chem.,* 1985, **296,** 147.

[14] Compare S. G. Shore *et al., J. Am. Chem. Soc.,* 1983, **105,** 655; *Inorg. Chem.,* 1982, **21,** 627, 1958; *Organometallics,* 1986, **5,** 1041.

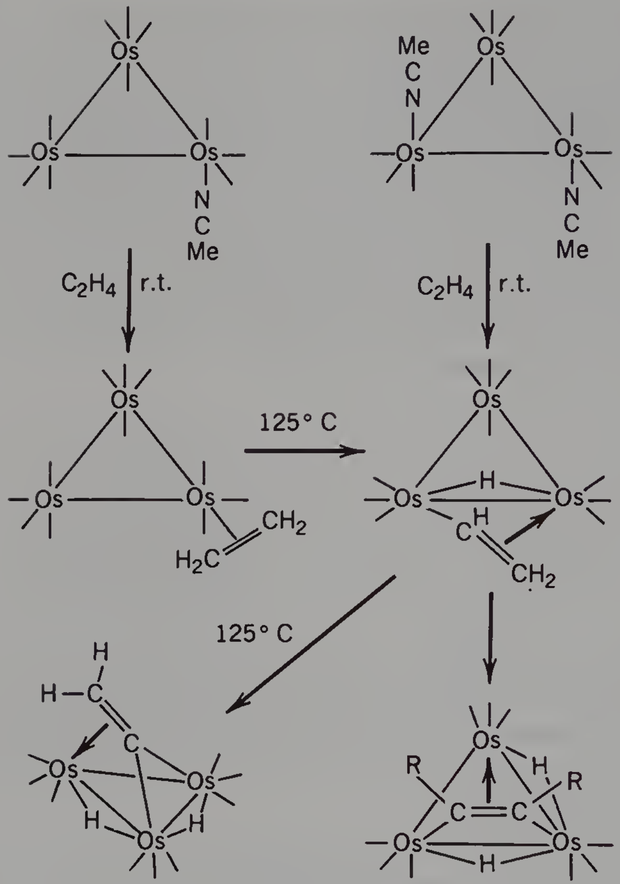
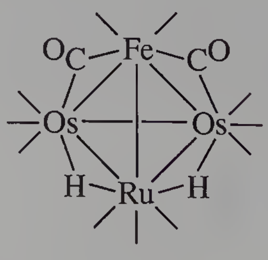


FIG. 23-1. Some reactions of $Os_3(CO)_{11}(MeCN)$ and $Os_3(CO)_{10}(MeCN)_2$.

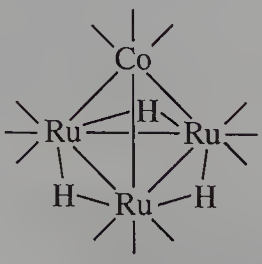
with the methylene bridged isomer (which is a 48 electron species) and the latter has been isolated from solution and crystallographically characterized. On loss of CO it forms a stable CH-capped cluster.

Four-Atom Clusters. These are very numerous, particularly in heteronuclear form. The majority of them display tetrahedral structures and the best known homonuclear prototypes are the $M_4(CO)_{12}$ (M = Co, Rh, and Ir) molecules (see Fig. 22-3). In these the 18-electron rule is satisfied for each metal atom through the formation of six M—M single bonds and the total electron count is 60. Some representative heteronuclear analogues are shown as (23-V) and (23-VI); these are also 60 electron systems.

The compound $H_4Re_4(CO)_{12}$ has only 56 electrons but nevertheless has a



(23-V)



(23-VI)

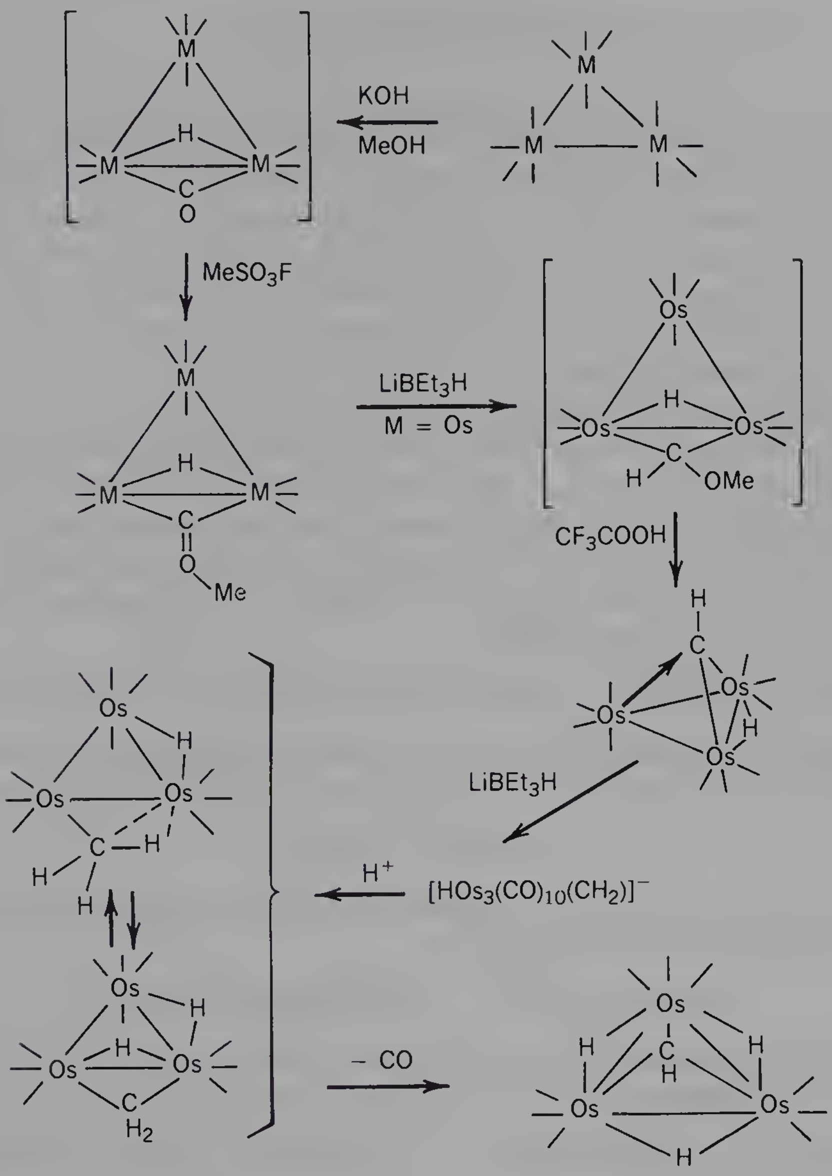
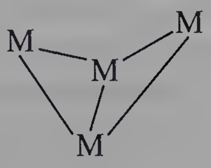


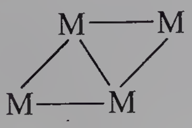
FIG. 23-2. Some reactions of $Os_3(CO)_{12}$ and, in part, of its Fe and Ru analogues.

regular tetrahedral Re_4 core. Since this structure precludes the existence of discrete, localized Re═Re double bonds [comparable to the Os—Os bond in $H_2Os_3(CO)_{10}$] both resonating double bonds or the formation of three-center (face) bonding have been proposed.

Besides the tetrahedral geometry, four-atom clusters are known with butterfly (23-VII) and planar (23-VIII) structures[15] as well as still others.



(23-VII)



(23-VIII)

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[15] F. W. B. Einstein *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 338.

23-3. Isoelectronic and Isolobal Relationships

The LNCCs, though small, are extremely numerous. In seeking relationships among them, so that their design and synthesis may be tackled in a systematic way and their properties better understood, two major concepts have been employed. Seemingly diverse metal–ligand fragments, L_xM and $L_y'M'$, may have fundamental similarities because they are either isoelectronic, isolobal, or both. An appreciation of these relationships and how they can serve to predict chemical and structural similarities is also of importance in organometallic chemistry, generally.

Isoelectronic Relationships. This concept is a relatively familiar one, having been invoked in many other contexts earlier. For present purposes, let us simply provide a few examples that are pertinent to metal atom cluster chemistry. Some of them derive directly from the isoelectronic relationships already noted in connection with simple metal carbonyl molecules.

1. Species of the same or similar composition containing metal atoms from the same group are isoelectronic:

$$Mn(CO)_5/Re(CO)_5 \qquad CpMo(CO)_3/CpW(CO)_3 \qquad Co(CO)_3/Ir(CO)_3$$

2. Species with the same or similar ligands containing metal atoms from different groups with suitable change in net charge are isoelectronic

$$Fe(CO)_3^-/Co(CO)_3$$

3. Species in which NO is substituted for CO, with proper charge adjustment, if necessary, are isoelectronic

$$NiNO/Co(CO)_2 \qquad CpFe(NO)R/CpCo(CO)R$$

4. The replacement of one CO ligand by two electrons or two H atoms gives isoelectronic species

$$Fe_5C(CO)_{15}/[Fe_5C(CO)_{14}]^{2-} \qquad [Re_6C(CO)_{19}]^{2-}/[Re_6C(CO)_{18}H_2]^{2-}$$

5. A special case, where we have to anticipate the coverage of Chapter 27, is based upon the fact that arene ligands such as C_6H_6 and $C_5H_5^-$ are six-electron donors. Thus, we have sets of isoelectronic species such as

$$C_6H_6Cr/C_5H_5Mn/Cr(CO)_3 \qquad \text{or} \qquad C_5H_5Ni/C_6H_6Co$$

Isolobal Relationships.[16] Two molecular fragments are isolobal if the number, symmetry properties, shapes, and approximate energies of their frontier orbitals are the same. They may or may not also be isoelectronic. For example, the HB and HC fragments are isolobal (but not isoelectronic), whereas the H_2C^- and H_2N moieties are both isolobal and isoelectronic. These relationships are illustrated in Fig. 23-3. As shown there the symbol $\underset{\circ}{\longleftrightarrow}$ is used to express isolobality. Also shown in Fig. 23-3 is the idea that we may

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[16] R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.

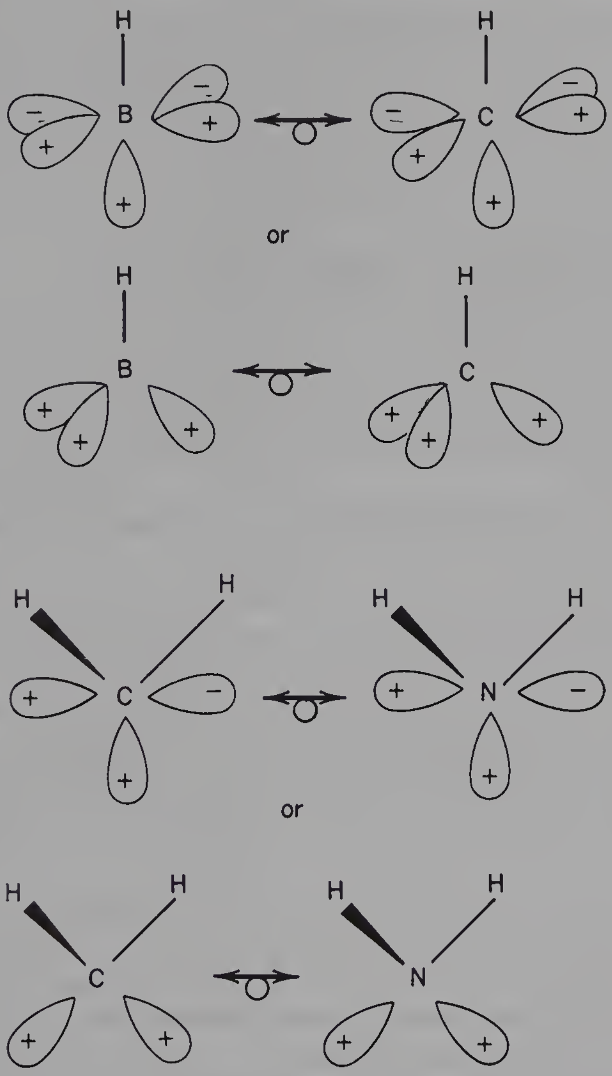

FIG. 23-3. Some simple examples of isolobal species. Each pair is represented in two ways: above, with least hybridization; below, with fullest hybridization.

choose to picture the isolobality in more than one way. Thus, for the HB and HC fragments, we can either envision one *sp* hybrid orbital whose axis is colinear with the H—B or H—C bond, plus two *p* orbitals perpendicular to this axis, or we may envision a state of maximal hybridization, where the frontier orbitals in each case are three of the four in a set of sp^3 tetrahedral hybrids. The orbitals whose similarity is critical in determining isolobality are called the *frontier orbitals*.

The illustrations of isolobality given in Fig. 23-3 may seem so obvious as to be trivial, but the concept gains power when generalized to more disparate systems. Consider, for example, the species shown in Fig. 23-4. The practical import of these isolobalities is that, in general we may expect the existence of stable, isostructural molecules in which one component is replaced by another that is isolobal to it. If the two fragments are also isoelectronic, in the sense that the ratio of the number of electrons in frontier orbitals to the

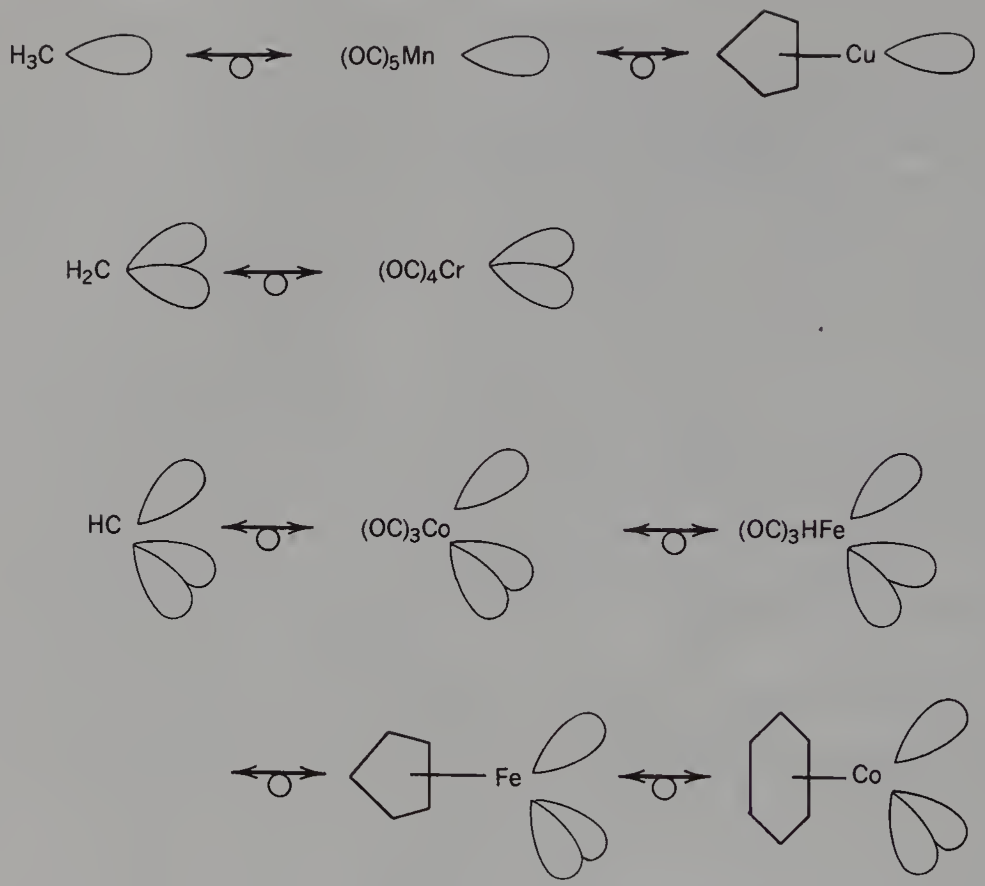

FIG. 23-4. Some more general examples of isolobal species.

number of frontier orbitals is the same, then the net charges on the two species will be the same. If not, the addition or deletion of electrons in one case will result in different net charges.

As an illustration of this, all of the following clusters may be regarded as related by isolobal replacements; in each case, there is a tetrahedral core:

$$Co_4(CO)_{12} \qquad Co_3FeH(CO)_{12} \qquad C_5H_5NiCo_3(CO)_9$$
$$C_6H_6Co_4(CO)_9 \qquad HCCo_3(CO)_9 \qquad PCo_3(CO)_9$$

23-4. High-Nuclearity Carbonyl Clusters (HNCCs)[17]

We include under this heading clusters with five or more metal atoms, each forming at least one M—M bond. The first HNCC, $Rh_6(CO)_{16}$, was structurally elucidated by Corey, Dahl, and Beck in 1963; today there is an enormous number of them and we can sketch only a few of the main facts. In addition to their intrinsic interest, these large clusters, especially the very largest ones, are of importance because they may be expected to show properties verging on those of bulk metals.[18] They provide one approach to an-

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[17] M. D. Vargas and J. N. Nichols, *Adv. Inorg. Chem. Radiochem.*, 1986, **30**, 123.
[18] P. P. Edwards *et al.*, *Nature* (*London*), 1985, **314**, 231.

swering the question: How large does a particle of metal have to be before bulk metal properties begin to appear?

Structural Patterns for HNCCs. The structural diversity found among HNCCs is impressive, but four major types can be recognized:

1. Closed polyhedra; the octahedron is particularly common, examples being $[Os_6(CO)_{18}]^{2-}$, $Rh_6(CO)_{16}$, and $Ru_6(CO)_{18}H_2$. In some of these a hetero atom such as C, N, or H may be encapsulated, for example, $[Co_6(CO)_{15}H]^-$. Other polyhedra found less commonly are the trigonal bipyramid, found in $[Ni_5(CO)_{12}]^{2-}$, $Ni_3Mo_2(CO)_{13}$, and $Os_5(CO)_{16}$, the trigonally distorted octahedron (a trigonal antiprism) as in $[Ni_6(CO)_{12}]^{2-}$, and occasionally, the cube.
2. Close-packed arrays, in which the metal atoms are grouped much as they are (or even exactly) in bulk metal. Rhodium and Pt (see later) provide many examples of these.
3. Stacked triangular arrays, as in the $[Ni_3(CO)_6]_n^{2-}$ ($n = 2$–5) species, and similar platinum ones.
4. Rafts, that is, large, triangulated, planar nets. Thus far this sort of structure has been found only for some osmium species (see later).

In all of these types of structure triangular faces are exposed and a very common mode of cluster enlargement is by capping one or more of these faces by another metal atom [e.g., by an $M(CO)_3$ group], thus generating a tetrahedron fused to the main or central unit. An example is $Os_7(CO)_{21}$. There are also many cases where an additional metal atom (plus some ligands) may associate itself with one of the edges of a polyhedral or close-packed central array.

Methods of Synthesis. These are largely of empirical origin and mechanistic insight is, in general, but with exceptions, rather limited and superficial. Isolobal analogies have so far proven much less useful for HNCCs than for LNCCs. The building up of HNCCs requires the generation of reactive fragments that can combine to form the HNCCs, and these fragments may be produced either thermally (or sometimes photolytically) or by reduction processes.

Pyrolysis reactions provide syntheses that are perhaps the least rational, but sometimes quite efficient. The entire field of osmium HNCCs was opened up by vacuum pyrolysis of $Os_3(CO)_{12}$, and by optimizing conditions high yields of selected products [e.g., 60% of $Os_6(CO)_{18}$] can be obtained. A useful modification of pyrolytic syntheses is often to first replace one or two CO groups, under mild conditions, by pyridine or CH_3CN (much more labile ligands) and then conduct a pyrolysis reaction. For example, the following preparation[19] proceeds in 65% yield:

$$Os_3(CO)_{11}py \xrightarrow[64\ h]{250°C} \xrightarrow[extract]{acetone} \xrightarrow{+PPN^+} (PPN)_2[Os_{10}(CO)_{24}C]$$

This same example also illustrates the fact that pyrolysis methods of synthesis are quite prone to give carbido clusters.

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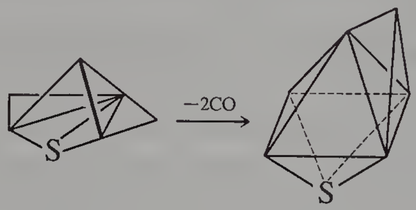
[19] J. Lewis *et al., J. Chem. Soc. Dalton Trans.,* **1982,** 2099.

Thermal reactions of a milder nature may also be employed. The use of partially substituted starting materials provides a means to enlarge medium size clusters. Thus, $Os(CO)_4H_2$ reacts to displace CH_3CN ligands from $Os_6(CO)_{18-n}(MeCN)_n$ species to give heptanuclear clusters, $Os_7(CO)_nH_2$ ($n = 20$, 21, and 22).

Another mild type of thermal pathway for synthesis of larger clusters utilizes ligands that have unshared electron pairs. Among a number of examples that might be chosen[20,21] we can cite reactions between a cluster containing one or more labile ligands and a cluster with capping sulfur atom whose lone pair can come into play:

$$Os_3(CO)_{10}(MeCN)_2 + Os_3(CO)_{10}S \xrightarrow{-CO,\ 2MeCN}$$



$Os_6(CO)_{19}S$ $Os_6(CO)_{17}S$

The majority of the HNCCs containing the cobalt and nickel subgroups are prepared by reductively generating reactive anionic intermediates that condense. For example, $Co_4(CO)_{12}$ is converted by treatment with alkali metals in THF to the $[Co_6(CO)_{15}]^{2-}$ ion. Similarly, the action of strong, basic reductants (Na/THF, $NaBH_4$/THF) on $Ni(CO)_4$ leads to cluster anions such as $[Ni_5(CO)_{12}]^{2-}$, $[Ni_6(CO)_{12}]^{2-}$, $[Ni_9(CO)_{18}]^{2-}$, or $[Ni_{12}(CO)_{21}]^{4-}$ depending on the exact conditions.

These reductive pathways are particularly suitable for making clusters that encapsulate hetero atoms, simply by introducing a suitable source of these atoms, such as CCl_4 for C, C_2Cl_6 for C_2, H_2S for S, or Ph_3As for As.

Carbonyl metallates may also react with neutral carbonyls containing a different metal to produce heteronuclear products, namely;

$$[Rh_6(CO)_{15}]^{2-} + Ni(CO)_4 \xrightarrow{-3CO} [Rh_6Ni(CO)_{16}]^{2-}$$

$$[Pt_3(CO)_6]^{2-} + 3Fe(CO)_5 \xrightarrow{-6CO} [Fe_3Pt_3(CO)_{15}]^{2-}$$

Even simple metal halides may react with carbonyl anions. A good example is provided by the following reaction in which the largest characterized metal cluster compound[22] is produced.

$$[Ni_6(CO)_{12}]^{2-} + PtCl_2 \longrightarrow [Ni_{38}Pt_6(CO)_{48}H_2]^{4-}$$

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[20] R. D. Adams *et al., Organometallics,* 1984, **3,** 623.

[21] H. Vahrenkamp and E. J. Wucherer, *Angew. Chem. Int. Ed. Engl.,* 1981, **20,** 680.

[22] A. Ceriotti *et al., Angew. Chem. Int. Ed. Engl.,* 1985, **24,** 697.

23-5. Hetero Atoms in Metal Atom Clusters[23]

We have already cited in passing some examples of clusters in which nonmetallic atoms are present, not simply as ligands, but either as constituents of the cluster framework or occupying the internal volume of the cluster (i.e., encapsulated). In this section we shall discuss the presence of hetero atoms more fully.

The elements that can appear as encapsulated atoms[24] include hydrogen as in $[HCo_6(CO)_{15}]^-$ as noted in Section 23-1, phosphorus, in $[Rh_9P(CO)_{22}]^{2-}$, arsenic in $[Rh_{10}As(CO)_{22}]^{3-}$, sulfur in $[Rh_{17}S_2(CO)_{32}]^{3-}$, but N and especially C are the most common, and each of them will now be discussed more fully. A sharp distinction between framework and encapsulated C (or N) atoms cannot always be made, as illustrated by the situation in certain M_4C "butterfly" structures, such as those shown below in Fig. 23-5.

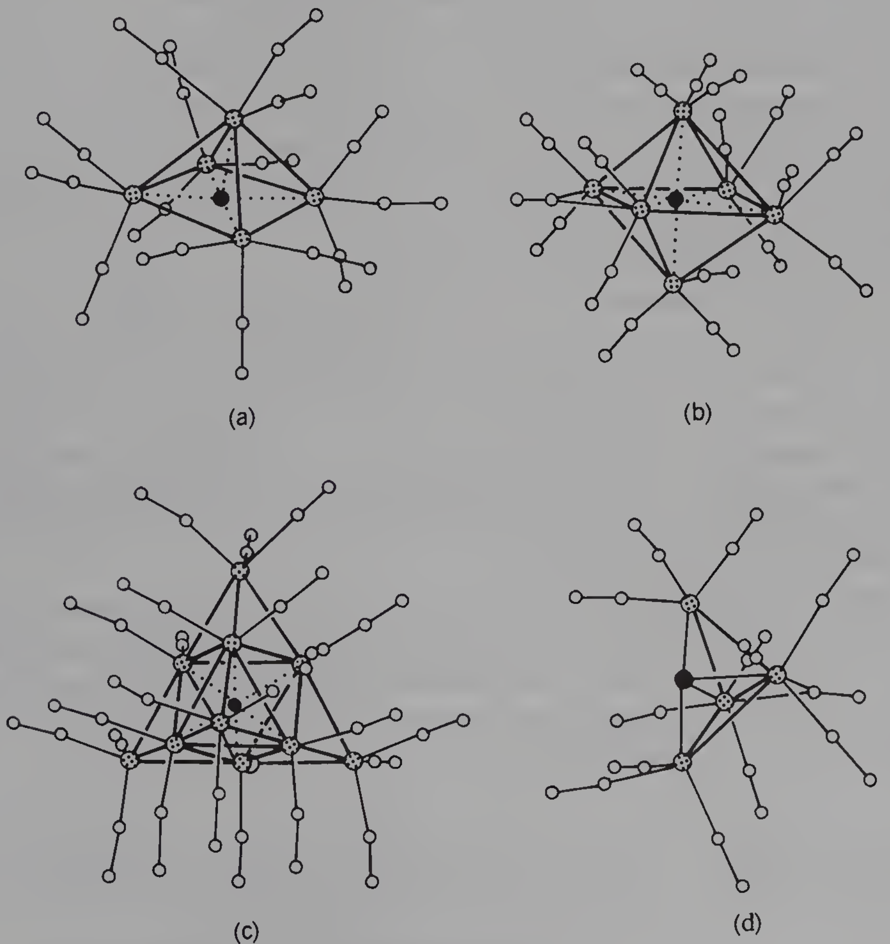

FIG. 23-5. The structures of some representative carbido carbonyl cluster species. (a) $Fe_5C(CO)_{15}$, (b) $Ru_6C(CO)_{17}$, (c) $[Os_{10}C(CO)_{24}]^{2-}$, and (d) $Fe_4C(CO)_{13}$.

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[23] J. N. Nicholls, *Polyhedron*, 1984, **3**, 1307.

[24] J. L. Vidal, *Inorg. Chem.*, 1981, **20**, 243.

Carbide-Containing Clusters.[25] Scores of these are known; they are formed by the metals iron, ruthenium, osmium, cobalt, rhodium, nickel, and rhenium. Some mixed metal species, for example, $[RhFe_4C(CO)_{14}]^-$ are also known. As a general rule a discrete carbon atom can be considered to contribute four electrons to the total skeletal electron count. The majority contain discrete carbon atoms, but several are known that contain C_2 units in which, judging by the C—C distances, a C—C bond exists; examples are $[Co_{11}C_2(CO)_{22}]^{3-}$ with C—C = 1.62 Å and $Rh_{12}C_2(CO)_{25}$ with C—C = 1.48 Å.

An interesting series of mixed metal clusters containing encapsulated C_2 (C—C, ~1.48 Å) are the anions $[Co_3Ni_7(CO)_xC_2]^{n-}$ with (x, n) combinations of (16,2), (16,3), and (15,3). These contain scrambled sets of 10 metal atoms arranged in a distorted form of cubic close packing.[26]

The earliest carbido cluster to be recognized was $Fe_5C(CO)_{15}$, shown in Fig. 23-5 (a). The Ru and Os analogues with similar structures are now known. Octahedral species with a carbon atom in the center were next to be recognized, the first having been $Ru_6C(CO)_{17}$, Fig. 23-5 (b), and a number of larger ones are now well characterized, for example, $[Os_{10}C(CO)_{24}]^{2-}$, Fig. 23-5 (c). The truly encapsulated carbon atoms are relatively unreactive and it is the smaller cluster, $Fe_4C(CO)_{13}$, [Fig. 23-5 (d)] that has shown the greatest chemical activity, as summarized in Fig. 23-6. Clearly, the exposed carbon atom in the Fe_4C system can be thought of as a possible model for a surface carbon atom in heterogeneous catalytic processes.

The synthetic chemistry for carbido metal carbonyl clusters is not very systematic. Many of them are obtained by pyrolysis of precursors or by refluxing precursors for long periods in high boiling solvents. The source of the carbido carbon atom has been shown by tracer studies to be the CO ligands via a disproportionation process, 2CO = "C" + CO_2. While this appears to be the most usual source of the carbido atoms, it is not the only possible one. For $[Rh_6C(CO)_{15}]^{2-}$ and $[Co_6C(CO)_{15}]^{2-}$ it has been shown that the sources are $CHCl_3$ and CCl_4, respectively.

Nitride-Containing Clusters.[4] Just as CO is the most common source of C atoms in carbido clusters, so also is NO (or NO^+) capable of furnishing N atoms to form nitrido clusters, and most nitrido clusters have been obtained in that way. In all cases nitrosyl clusters are thought to be intermediates. Some examples are the following:

$$[H_3Ru_4(CO)_{12}]^- + NO^+ \longrightarrow HRu_4N(CO)_{12} + H_3RuN(CO)_{11}$$

$$2[Fe(CO)_3NO]^- + 3Fe_3(CO)_{12} \longrightarrow 2[Fe_4N(CO)_{12}]^- + 3Fe(CO)_5 + 2CO_2 + CO$$

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[25] M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.*, 1981, **28,** 203; J. S. Bradley, *Adv. Organomet. Chem.*, 1983, **22,** 1; D. F. Shriver *et al., Inorg. Chem.*, 1987, **26,** 2943.

[26] A. Arrigoni *et al., J. Organomet. Chem.*, 1985, **296,** 243.

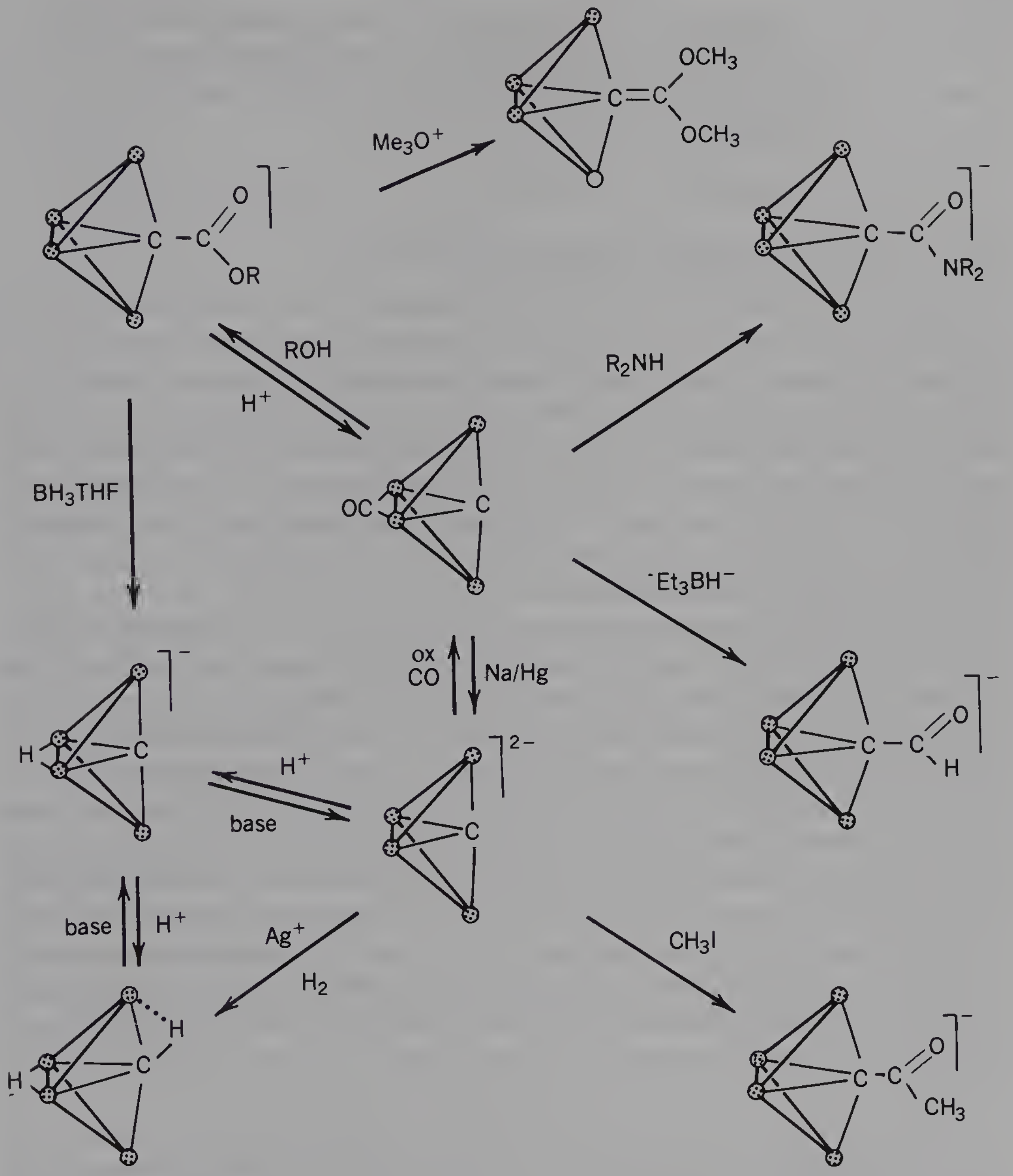
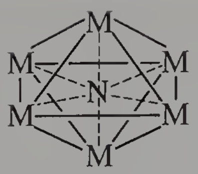


FIG. 23-6. A schematic summary of the reactions of $Fe_4C(CO)_{13}$ (adapted from J. S. Bradley, ref. 25).

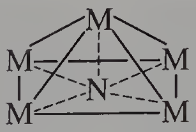
There are a few other reactions in which N_3^- or NCO^- supply the N atom, namely,

$$2Ru_3(CO)_{12} + N_3^- \longrightarrow [Ru_6N(CO)_{16}]^- + 8CO + N_2$$

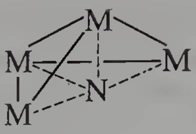
As with the carbido clusters, structures tend to be based on a N-centered octahedron, or fragments thereof, as in (23-IX) to (23-XI), namely, $[Ru_6N(CO)_{16}]^-$, $[Ru_5N(CO)_{14}]^-$, and $[Fe_4N(CO)_{12}]^-$.



(23-IX)



(23-X)



(23-XI)

23-6. Electron Counting Schemes for HNCCs

The HNCCs are large, often structurally complex, and most of them contain the heavier (2nd and 3rd series) transition metals. For these reasons, they are not amenable to conventional interpretations of their electronic structures nor, *a fortiori,* to rigorous quantum mechanical calculations. Instead much effort has been devoted to seeking relationships between their structures and the number of electrons available for cluster bonding. All of these large clusters are regarded as electron deficient in the sense that there are insufficient electrons to permit the assignment of an electron-pair bond between each adjacent pair of metal atoms.

For polyhedral clusters (sometimes called deltahedral, because the faces are all triangles resembling the Greek letter delta) the ancestor of all electron counting schemes is the correlation proposed by Wade between borane (or carborane) cages and metal carbonyl cages. Wade first drew attention to the similarity of an $M(CO)_3$ unit and a BH (or CH) unit, a relationship that we would now call isolobality. He then proposed that the $2n + 2$ rule for *closo* boranes (Section 6-9) would also apply to *closo* metal cluster species such as $[Os_6(CO)_{18}]^{2-}$, and that $2n + 4$ and $2n + 6$ electron counts would, similarly, be appropriate for stable M_n clusters with *nido* and *arachno* structures. Hydrogen atoms are assumed to contribute one electron each, an interstitial carbon atom four electrons, and so forth. In addition to the isolobal relationship of metal clusters to boranes and carboranes, other support for Wade type of correlations is provided by some calculations for metal clusters themselves.[27]

Subsequently, several more elaborate or differently derived treatments of the relationships between structure and electron count for large clusters have appeared.[28–34] Space does not permit us to present a detailed discussion of this rather complex body of material. We shall restrict the discussion to the basic ideas proposed by Wade, plus a few added rules that will be useful in subsequent sections.[35]

[27] A. J. Stone, *Inorg. Chem.*, 1981, **20,** 563 and earlier references therein.

[28] P. W. Fowler and W. W. Porterfield, *Inorg. Chem.*, 1985, **24,** 3511.

[29] R. G. Woolley, *Nouv. J. Chim.*, 1981, **5,** 441; *Chem. Phys. Lett.*, 1980, **71,** 135.

[30] B. K. Teo, *Inorg. Chem.*, 1985, **24,** 1627.

[31] D. M. P. Mingos, *Inorg. Chem.*, 1985, **24,** 114.

[32] B. K. Teo, *Inorg. Chem.*, 1985, **24,** 115.

[33] D. M. P. Mingos, *J. Chem. Soc. Chem. Commun.*, **1985,** 1352.

[34] R. L. Johnston and D. M. P. Mingos, *Inorg. Chem.*, 1986, **25,** 1661.

[35] M. McPartlin, *Polyhedron,* 1984, **3,** 1279.

While the number of skeletal electron pairs, denoted S, is at the root of the correlation procedures, discussions found in the literature are often couched in terms of other, related parameters, particularly the *total electron count* (TEC). The TEC is obtained from the formula by adding the following contributions:

1. The number of valence electrons for each metal atom. For example, in an Os_6 cluster, $6 \times 8 = 48$.
2. Two electrons for each CO group, regardless of its structural type (terminal, μ_2, or μ_3).
3. One electron for each negative charge.
4. The number of valence electrons for each hetero and/or interstitial atom. For example, 1 for H, 4 for C, 5 for P. Column 2 of Table 23-1 presents some examples of total electron counts.

Let us now ask how we could predict the correct total electron count, as just defined, for a stable cluster of known structure (i.e., *closo, nido,* or *arachno*). To do this for metal carbonyl clusters it is postulated that in addition to the electrons necessary for skeletal bonding each metal atom will also have 12 nonskeletal electrons. The basis for this assumption is that in the pyramidal $M(CO)_3$ unit each M—CO bond will comprise two formally "carbon σ" electrons that are donated to the metal atom and two formally "metal" π electrons that backbond, at least partially, to the CO ligand. Thus, in predicting the *total electron count* for a *closo* polyhedral cluster of n vertices, the result would be $12n + 2(n + 1)$. Similarly, for *nido* and *arachno* clusters that are derived from an n-vertex polyhedron (their *parent polyhedron*) by removal of one or two vertices, respectively, there will be 12 and 24 fewer total electrons, respectively.

The predictions for TEC can therefore be stated in the following equations (where n is the number of vertices in the *parent* polyhedron for the *nido* and *arachno* cases—not the actual number of metal atoms in the cluster itself):

closo	$12n + 2(n + 1)$
nido	$12(n - 1) + 2(n + 1)$
arachno	$12(n - 2) + 2(n + 1)$

In practice, these relations are often employed "in reverse" so to speak. From the actual TEC (easily derived from the formula as already explained)

TABLE 23-1

Examples of Correlating Structures with Total Electron Count on a Wade's Rules Basis

Cluster	Total electron count (TEC)	No. of skeletal electron pairs (S)	Vertices of parent polyhedron	Structural conclusion
$Rh_6(CO)_{16}$	$(9 \times 6) + (2 \times 16) = 86$	$\frac{1}{2}[86 - (6 \times 12)] = 7$	6	*Closo*
$Os_5(CO)_{16}$	$(5 \times 8) + (2 \times 16) = 72$	$\frac{1}{2}[72 - (5 \times 12)] = 6$	5	*Closo*
$Os_5C(CO)_{15}$	$(5 \times 8) + (2 \times 15) + 4 = 74$	$\frac{1}{2}[74 - (5 \times 12)] = 7$	6	*Nido*
$[Fe_4C(CO)_{12}]^{2-}$	$(4 \times 8) + (2 \times 12) + 4 + 2 = 62$	$\frac{1}{2}[62 - (4 \times 12)] = 7$	6	*Arachno*
$[H_3Ru_4(CO)_{12}]^-$	$(4 \times 8) + (2 \times 12) + 3 + 1 = 60$	$\frac{1}{2}[60 - (4 \times 12)] = 6$	5	*Nido*

12*e* are subtracted for each metal atom and the number of skeletal pairs (S) thus determined. On the basis that ($S + 1$) pairs are required for a polyhedron of S vertices, one may select the most likely structure or structures. Some illustrations will make this procedure clear.

For $Rh_6(CO)_{16}$ the TEC is $(9 \times 6) + (2 \times 16) = 86$. The number of skeletal pairs (S) will be obtained by subtracting 6×12 from 86 and dividing by 2; the result is 7. Since the number of vertices of the parent polyhedron is $S - 1$, we conclude that this will be a six-vertex polyhedron (e.g., an octahedron). Since there are six metal atoms, we conclude that a *closo* structure, probably an octahedron, is appropriate. This is correct. In general 86-electron clusters consisting of six metal atoms are octahedral.

To present more concisely some further examples, we employ Table 23-1. The $Rh_6(CO)_{16}$ example just discussed is included in the table to help illustrate the way it works. The $Os_5(CO)_{16}$ cluster affords another example of how a *closo* structure (a trigonal bipyramid) is correctly predicted.

The next two examples in Table 23-1, $Os_5C(CO)_{15}$ and $[Fe_4C(CO)_{12}]^{2-}$ show how *nido* and *arachno* structures are predicted. The *nido* structure already shown in Fig. 23-5(a) for the iron analogue, $Fe_5C(CO)_{15}$, is derived by removal of one vertex from the parent polyhedron, which is an octahedron. The $[Fe_4C(CO)_{12}]^{2-}$ cluster should be isostructural with the $Fe_4C(CO)_{13}$ cluster, whose structure has been shown in Fig. 23-5(d). It is derived from a parent octahedron by removal of two vertices.

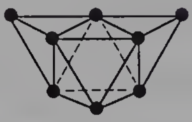
The final example in Table 23-1 illustrates the point that a tetrahedron is treated as a trigonal bipyramid that is missing one vertex, that is, as a *nido* structure. While this may seem artificial, it is not illogical and it is necessary in order to maintain consistency with the general rules.

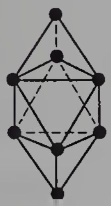
The Capping Rule. Many carbonyl-type clusters consist of a central polyhedron to which one or more additional metal atoms are appended by placement over a triangular face. These appended metal atoms are called capping atoms. The electron counting rules we have discussed can be extended to cover such structures by the rule that the addition of a capping atom does not change the skeletal electron requirement for the central cluster. Thus, the addition of a capping atom simply increases the total electron count by 12 electrons.

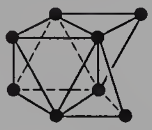
The $Os_7(CO)_{21}$ cluster provides a simple illustration. The TEC is given by $(7 \times 8) + (21 \times 2)$, namely, 98. Subtracting $7 \times 12 = 84$, we obtain $S = 7$, which implicates a six-vertex central polyhedron. This is consistent with there being a *closo* six-atom deltahedron (namely, an octahedron) capped on one face—which is, indeed, the actual structure of $Os_7(CO)_{21}$. Correct results are similarly obtained for $[Os_8(CO)_{22}]^{2-}$, which is a bicapped octahedron (23-XII) and $[Os_{10}C(CO)_{24}]^{2-}$, which is a tetracapped octahedron. For the latter, a capsule summary of the analysis is as follows:

TEC: $(8 \times 10) + 4 + (2 \times 24) + 2 = 134$
S: $\frac{1}{2}[134 - (12 \times 10)] = 7$

A final word about the capping rule concerns a limitation. The $[Os_8(CO)_{22}]^{2-}$ cluster has the bicapped structure shown in (23-XII). However, two other, isomeric bicapped M_8 structures (23-XIII) and (23-XIV), are possible and the capping rule *per se* cannot predict which one to expect, nor can any other rule presently known. The *trans*-capped structure (23-XIII), is known in $[Re_8C(CO)_{24}]^{2-}$, but no example of (23-XIV) has yet been reported. It may be that when the steric requirements of the CO groups are considered, this cis-capped arrangement is, for that reason, not possible.


(23-XII)


(23-XIII)


(23-XIV)

23-7. HNCCs of the Fe, Ru, and Os Group

These elements, especially osmium, are prolific formers of HNCCs, the structures of which can generally be well understood by employing the electron counting rules presented in Section 23-6. Indeed, we have drawn heavily on these compounds in introducing the rules. There are a number of iron and ruthenium analogues to the 5- and 6-atom clusters of osmium, but no larger clusters of these two elements are as yet established.

By far the greatest number of cluster species is formed by osmium; there

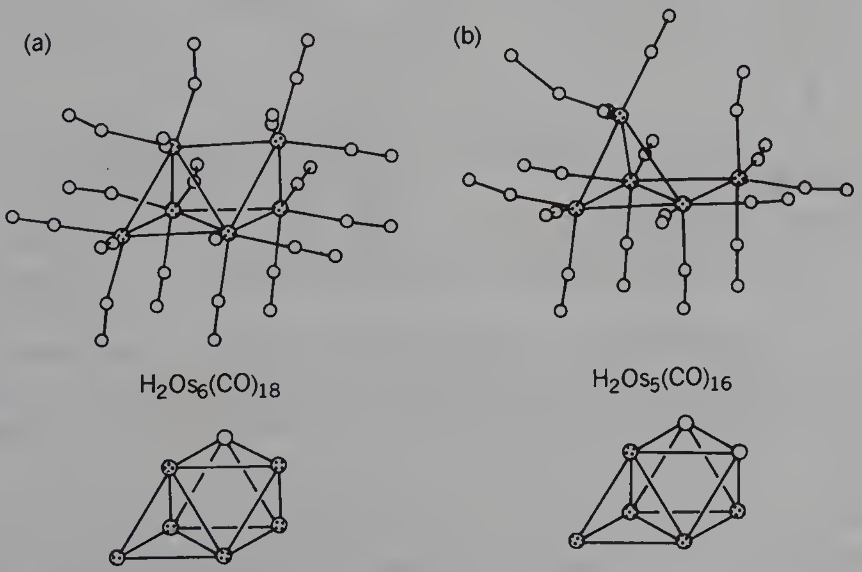


FIG. 23-7. Two osmium clusters whose structures illustrate the capping of incomplete polyhedra. (a) capping of a *nido* polyhedron, (b) capping of an *arachno* polyhedron. (Reproduced by permission from ref. 35.)

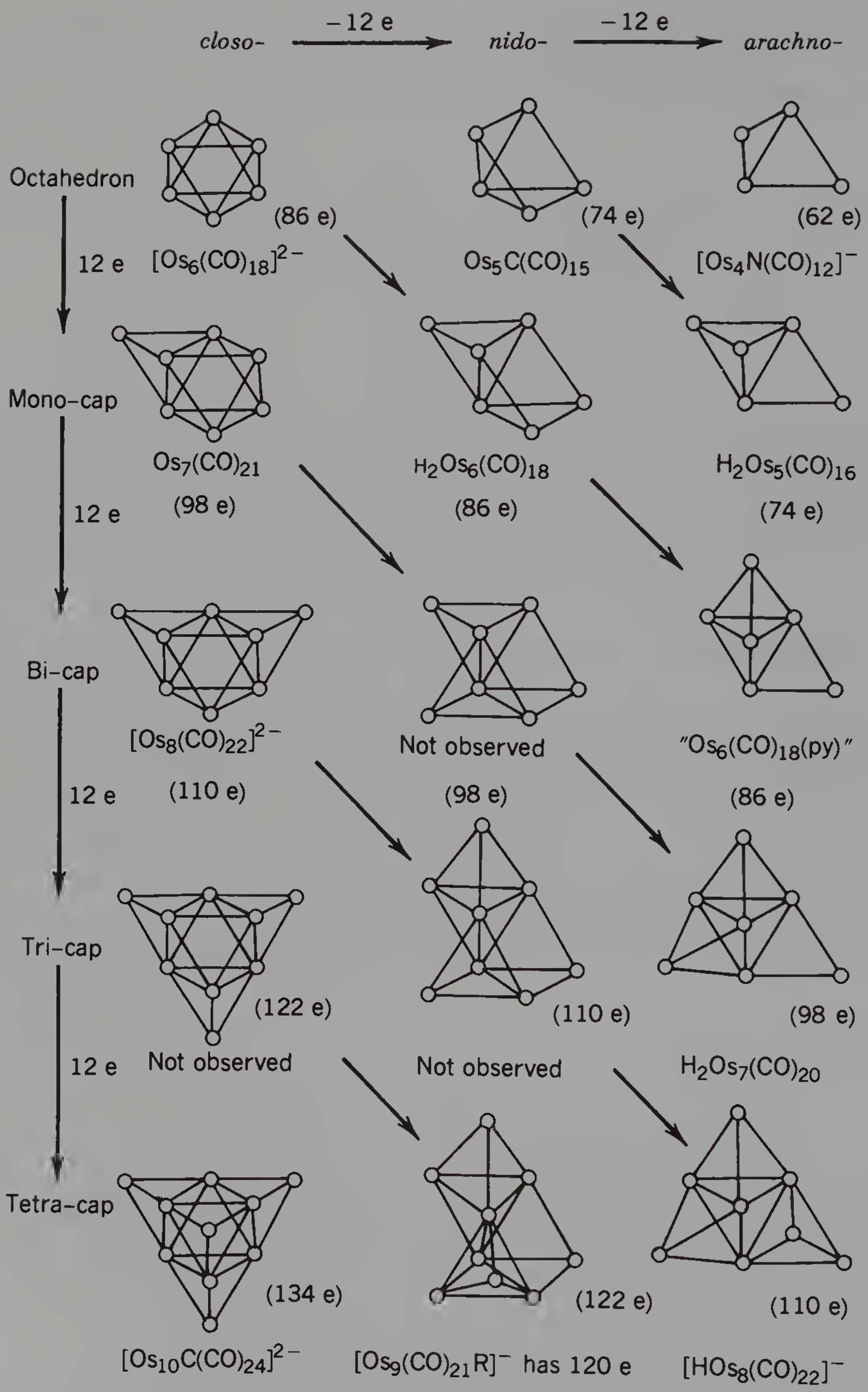


FIG. 23-8. Structures and total electron counts for osmium clusters with $S = 7$. Structures related by the diagonal arrows are alternatives for the same total electron count. (Reproduced by permission from ref. 35.)

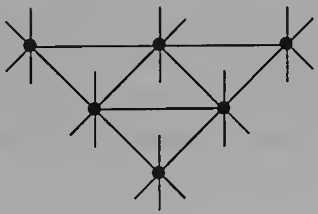
are so many that only a few illustrative examples can be mentioned here. In illustrating the capping rule several examples of structures derived by capping of the octahedron were cited. While it was noted that with two (or more) caps several alternatives are equally possible under the rule, there are even further possibilities, and osmium clusters provides good examples of them.

This first became apparent when the structure of $H_2Os_6(CO)_{18}$ was determined. It has the same electron count as $[Os_6(CO)_{18}]^{2-}$, obviously, but it does *not* have the same structure. As shown in Fig. 23-7 its structure can be regarded as a capped square pyramid. This, however, is also consistent with the electron counting rules. By moving one $Os(CO)_3$ out of the cluster we delete 12*e*, but the remaining $Os_5(CO)_{15}$ unit still has $S = 7$ and should therefore be a *nido* octahedron. By now using the deleted $Os(CO)_3$ unit to cap this, we require no change in the central square pyramid. The general implication of this example is that in addition to a set of Os_{6+n} clusters obtainable by adding n caps to an octahedron, there will be another set of structures obtainable by adding $(n + 1)$ caps to the square pyramid—and equally in accord with the rules.

The principle can be extended further. A set of structures can be derived by capping an *arachno* parent with $S = 7$. This is the way to account for the structure of $H_2Os_5(CO)_{16}$, also shown in Fig. 23-7. The entire set of relationships can be summarized by the chart presented in Fig. 23-8.

Osmium also lends itself to the formation of numerous heteronuclear clusters.[36]

A final aspect of osmium cluster chemistry concerns the type called *rafts*. The principal example is $Os_6(CO)_{17}[P(OMe)_3]_4$,[37] which is formally a substitution product of $Os_6(CO)_{21}$. The structure, shown schematically in (25-XV), is easily understood electronically, with every Os—Os bond being a 2*c*-2*e* bond, and each metal atom having an 18-electron configuration.



(23-XV)

23-8. HNCCs of Cobalt, Rhodium, and Iridium

Cobalt forms clusters with from 5 to at least 16 metal atoms and rhodium forms them with 5 to at least 22 metal atoms. The number of iridium clusters is more limited.

Rhodium HNCCs are particularly prone to adopt structures having an interstitial rhodium atom within a polyhedron of rhodium atoms.[38] The most prominent structure of this type is that for the $[Rh_{13}(CO)_{24}H_n]^{(5-n)-}$ species, which is shown in Fig. 23-9a. This metal atom arrangement is precisely a fragment of a hexagonal close-packed array. By additions to it larger clusters are built up, as also shown in Fig. 23-9.

Rhodium also forms an unusually large number of clusters containing en-

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[36] R. D. Adams *et al., Inorg. Chem.*, 1986, **25,** 4, 1623; *J. Am. Chem. Soc.*, 1986, **108,** 3518.

[37] J. Lewis *et al., J. Chem. Soc. Chem. Commun.*, **1982,** 640.

[38] B. T. Heaton *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 1375.

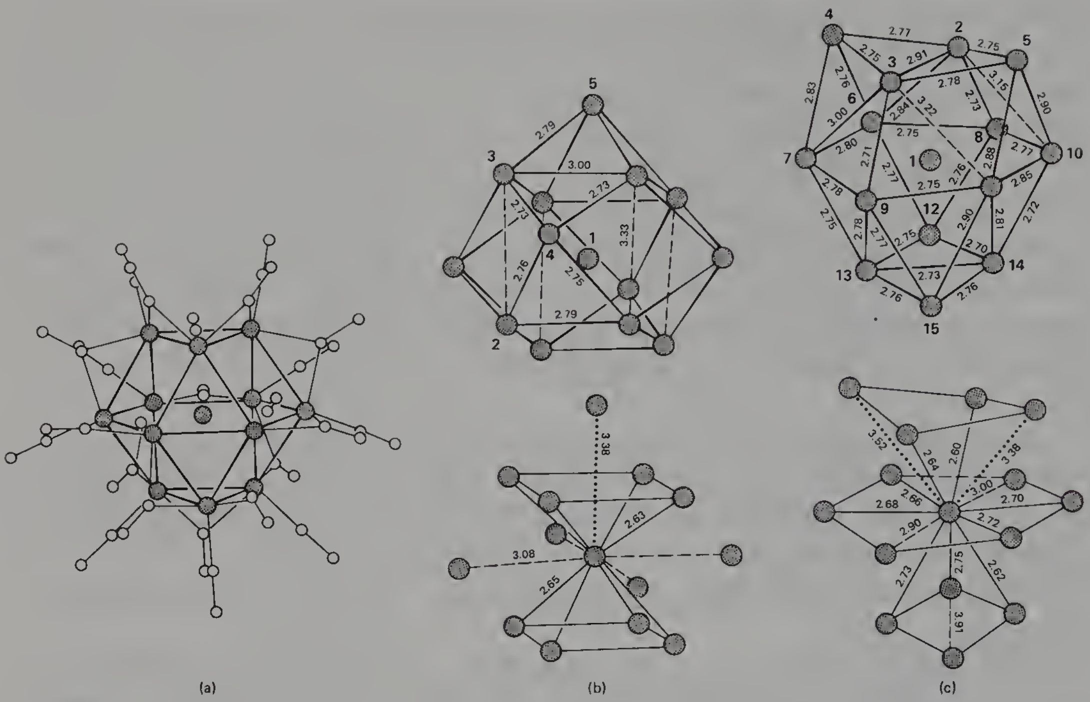

FIG. 23-9. The configurations of the metal atom cores in three high-nuclearity rhodium clusters that have internal metal atoms: (a) $Rh_{13}(CO)_{24}H_{2,3}]^{3,2-}$, (b) $[Rh_{14}(CO)_{25}]^{4-}$, and (c) $[Rh_{15}(CO)_{27}]^{3-}$.

capsulated hetero atoms as, for example, the $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ species, whose skeletal structure is shown in Fig. 23-10, and a number that contain carbon atoms.[39] It also forms both smaller, for example, $Rh_6(CO)_{16}$, and larger, for example, $Rh_{12}H_2(CO)_{25}$, clusters that have no encapsulated atoms. The Rh_{12} species has a very novel structure in which two Rh_6 octahedra are linked together to form an Rh_6 octahedron between them.[40] Finally, rhodium

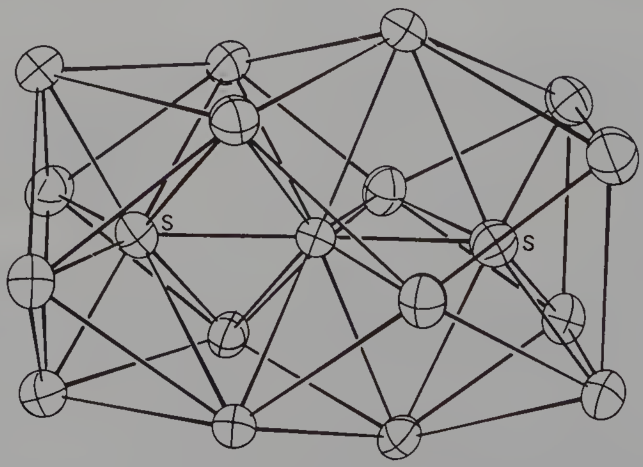

FIG. 23-10. Diagram of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$, omitting the carbon monoxide ligands.

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[39] S. Martinengo *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 1837.
[40] G. Ciani *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985**, 1757.

also forms many mixed metal clusters, especially with platinum. The $[PtRh_8(CO)_{19}]^{2-}$ ion consists of two octahedra fused together, with the Pt atom at one of the shared vertices.[41]

23-9. HNCCs of Nickel, Palladium, and Platinum

These metals are prolific formers of HNCCs. The earliest studies dealt mainly with the clusters of Ni and Pt in which $M_3(\mu\text{-}CO)_3(CO)_3$ units are stacked to form columns; there are no Pd analogues of these. In more recent years, numerous other structural types of clusters have been found for all three metals, and this is currently an active research area.

Nickel Clusters. The first ones to be recognized were $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$, whose structures are shown in Fig. 23-11. Both are generated by reduction of $Ni(CO)_4$ with alkali metals in THF or with alkali hydroxides in methanol. Note that $[Ni_5(CO)_{12}]^{2-}$ does not obey the electron counting rules previously explained; unlike $[Os_5(CO)_{12}]^{2-}$ (which has 72 electrons and does) it has 76 electrons and would be predicted to have an *arachno* structure based on a seven-vertex parent polyhedron. By oxidation of $[Ni_6(CO)_{12}]^{2-}$ with $FeCl_3$, the $[Ni_9(CO)_{18}]^{2-}$ ion is obtained almost quantitatively. It has a structure in which one more $Ni_3(CO)_6$ unit is added to the $[Ni_6(CO)_{12}]^{2-}$ structure, but eclipsed to one face; the result is thus an octahedron and a trigonal prism with a common triangular face.[42]

Larger nickel clusters with different structures are stabilized by introduction of interstitial carbon atoms. Reaction of $[Ni_6(CO)_{12}]^{2-}$ with CCl_4 produces the $[Ni_8(CO)_{16}C]^{2-}$, $[Ni_9(CO)_{17}C]^{2-}$, and $[Ni_{10}(CO)_{18}C]^{2-}$ species, the first two of which have been structurally characterized.[43] The Ni_8 species has a square antiprism of metal atoms. The Ni_9 cluster has a cap on one square face and

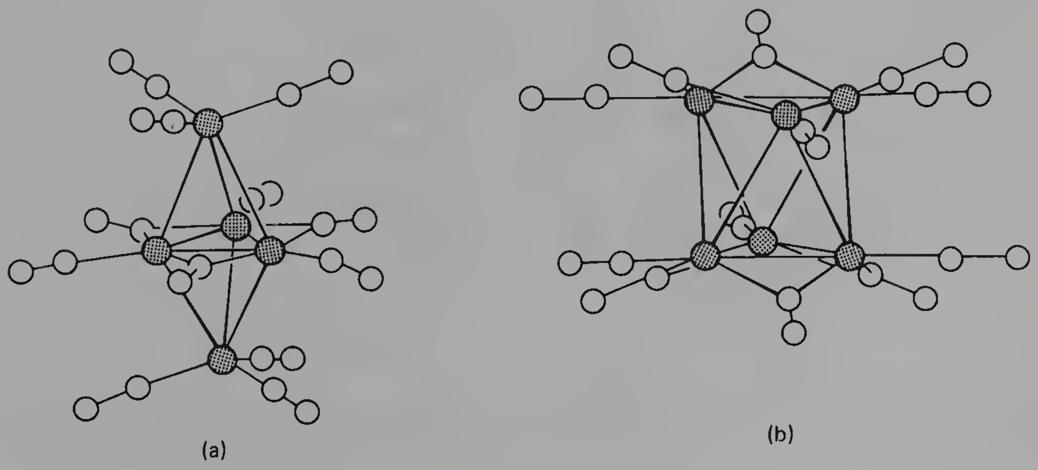

FIG. 23-11. The structures of the nickel carbonylate ions (a) $[Ni_5(CO)_{12}]^{2-}$ and (b) $[Ni_6(CO)_{12}]^{2-}$.

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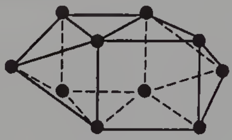
[41] A. Fumagalli *et al., Inorg. Chem.,* 1986, **25,** 592.
[42] L. F. Dahl *et al., Organometallics,* 1986, **5,** 1764.
[43] G. Longoni *et al., Inorg. Chem.,* 1985, **24,** 117.

presumably the Ni_{10} species has a cap on the other square face as well. The reaction of $[Ni_6(CO)_{12}]^{2-}$ with C_2Cl_6 affords $[Ni_{10}(CO)_{16}C_2]^{2-}$ in which there is a C_2 unit with C—C = 1.40 Å. The 10 nickel atoms are arranged as in (25-XVI).[44] When this cluster anion is treated with Ph_3P it is quantitatively converted to the $[Ni_{16}(CO)_{23}(C_2)_2]^{4-}$ ion which consists of a large polyhedral metal atom cage within which are two separate C_2 units (C—C = 1.38 Å).[45] The structure is shown in Fig. 23-12.



(23-XVI)

Palladium Clusters. Palladium clusters with a mixture of CO and phosphine ligands have been established within the past few years. The species $Pd_7(CO)_7(PMe_3)_7$ and $Pd_{10}(CO)_{18-n}(PMe_3)_n$ contain a central Pd_6 octahedron with one or four capping atoms, while $Pd_{23}(CO)_{22}(PEt_3)_{10}$ has an extraordinary structure based on a cubooctahedron with one encapsulated Pd atom, a cap on each square face and four edge-bridging Pd atoms.[46]

Platinum Clusters. There are two broad classes:

1. Columnar species, $[Pt_3(CO)_6]_n^{2-}$ (n = 2–5), which are built up by stacking planar $Pt_3(CO)_6$ units. Structures of three of these are shown in Fig. 23-13. The details of these structures are curious and not easily explained.[47] The

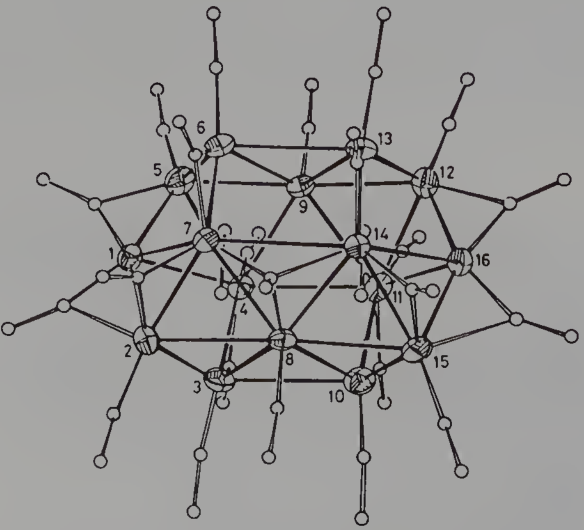


FIG. 23-12. The structure of the $[Ni_{16}(CO)_{23}(C_2)_2]^{2-}$ ion. (Reproduced by permission from ref. 45.)

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[44] G. Longoni *et al.*, *J. Chem. Soc. Chem. Commun.* **1985,** 181.

[45] G. Longoni *et al.*, *J. Chem. Soc. Chem. Commun.* **1985,** 1402.

[46] Yu. T. Struchkov *et al.*, *J. Organomet. Chem.*, 1986, **301,** C35.

[47] R. Hoffmann *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 5968.

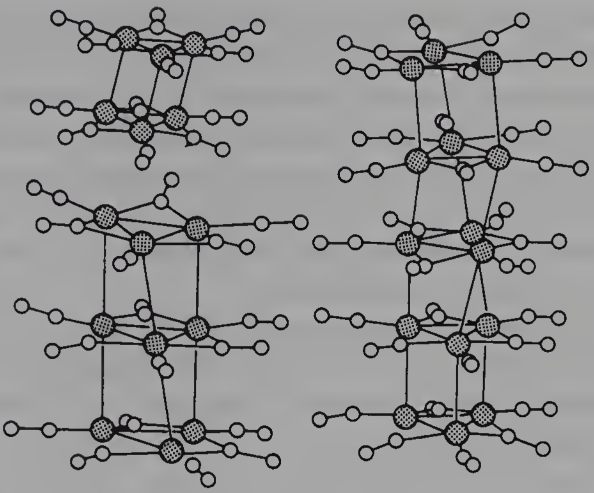

FIG. 23-13. The structures of $[Pt_3(CO)_6]_n^{2-}$ ions with n = 2, 3, and 5.

stacking is essentially prismatic rather than antiprismatic but in addition there are offsets and slight twists from one layer to the next. It has been speculated that these seemingly irregular structures result from a compromise between the competing effects of Pt—Pt bonding and nonbonded repulsions, although the avoidance of antiprismatic stacking where a larger number of interlayer Pt—Pt bonds could be formed is puzzling. The intratriangle Pt—Pt distances (~2.65 Å) are much shorter than the interlayer ones (~3.05 Å).

2. Three large platinum carbonyl anions, $[Pt_{19}(CO)_{22}]^{4-}$, $[Pt_{26}(CO)_{32}]^{3-}$, and $[Pt_{38}(CO)_{44}H_x]^{2-}$ (where the value of x is uncertain). The last two consist of approximately cubic close-packed arrays of platinum atoms,[48] and can be

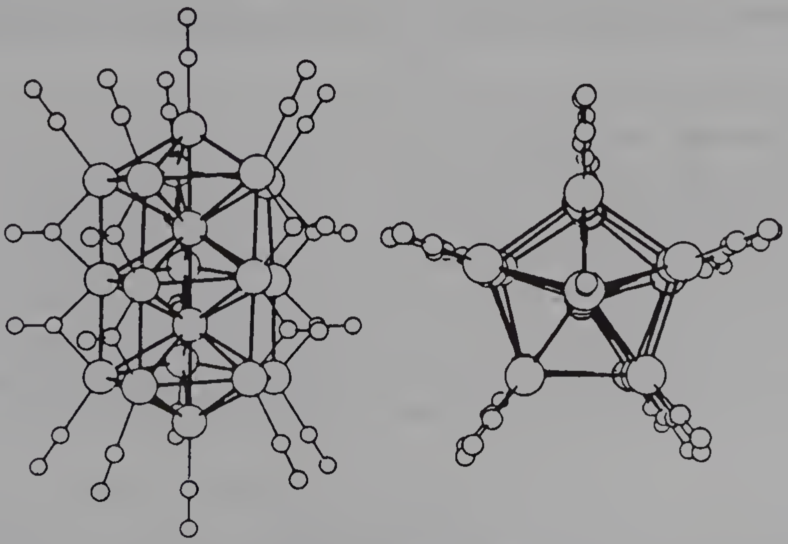

FIG. 23-14. Two views of the $[Pt_{19}(CO)_{22}]^{4-}$ ion, which has idealized D_{5h} symmetry. (Reproduced by permission from ref. 49.)

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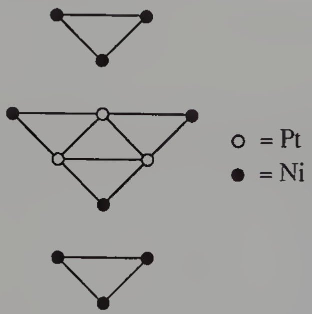
[48] L. F. Dahl, private communication.

thought of almost as small chunks of the metal solubilized by a coating of CO groups together with the negative charge and/or hydrogen atoms. These two platinum cluster anions come closest of all known metal atom clusters to approaching the borderline between molecular and bulk metal properties. The $[Pt_{19}(CO)_{22}]^{4-}$ ion has the remarkable structure shown in Fig. 23-14; this fivefold (D_{5h}) symmetry is not related to close-packed structures found in bulk metals, but it is similar to that reported for certain microcrystalline materials such as whiskers and dendrites.[49]

We may note, finally, that nickel and platinum form various mixed clusters, some very large, as in the case of the $[Ni_{38}Pt_6(CO)_{48}H_{6-n}]^{n-}$ ions. A medium size cluster, $[Ni_9Pt_3(CO)_{21}H]^{3-}$ has been structurally characterized.[50] The metal framework is as shown in (23-XVII).



(23-XVII)

All three metals also form smaller clusters with isocyanides,[51] namely, Ni_4L_6, Ni_4L_7, Pd_3L_6, and Pt_3L_6.

LOWER HALIDE AND CHALCOGENIDE CLUSTERS

Among the lower halides and chalcogenides of the transition elements are many compounds containing metal atom clusters, other types of arrays with M—M bonds, and multiple bonds between metal atoms. The majority of these have been mentioned in Chapters 18 to 20. Our purposes here are to review this information in a general way, to comment on the bonding in this class of clusters, and to describe a few additional aspects of metal atom cluster chemistry. We shall then (Sections 23-13 and 23-14) turn to multiple bonds in dinuclear species. There are two predominant structural types among clusters of this class: octahedral and triangular, each of which will now be discussed.

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[49] L. F. Dahl *et al., J. Am. Chem. Soc.*, 1979, **101,** 6110.

[50] G. Longoni *et al., J. Organomet. Chem.*, 1986, **301,** C5.

[51] C. G. Francis *et al., Inorg. Chem.*, 1984, **23,** 3680; M. Green *et al., J. Chem. Soc. Dalton Trans.*, **1980,** 2095.

23-10. Octahedral Metal Halide and Chalcogenide Clusters

There are two principal types of octahedral clusters, as shown in Fig. 23-15, which differ in how the bridging nonmetal atoms are arranged. In (a) there are eight μ_3-X atoms capping the faces, while in (b) there are 12 μ_2-X atoms spanning the edges. In each case there are generally six additional ligand atoms lying along the extensions of the fourfold axes of the octahedron.

To understand the bonding in such clusters it is not generally fruitful (although it works out in a few cases) to think in terms of localized M—M bonds. Instead, a molecular orbital approach is more effective, but for such large systems there are serious practical difficulties and a variety of approximations have been employed.[52] While the results of different calculations show discrepancies in detail, they give a generally consistent overall picture. The M—M bonding is based essentially on the overlap of metal *d* orbitals. A good example is provided by the results shown in Fig. 23-16 for the Mo_6X_8 type cluster. The number of cluster electrons in the examples chosen, $Mo_6Cl_8^{4+}$ and $Mo_6S_8^{4-}$, is 24. While the exact energies and level ordering cannot be taken literally, the general picture is reliable and has as its key feature the filling of a set of bonding molecular orbitals by 24 electrons. In effect, there is one electron pair per octahedron edge and a set of 12 Mo—Mo single bonds can be envisioned.

Similar calculations on the $[Nb_6Cl_{12}]^{2+}$ system predict that there are the following occupied bonding orbitals: $a_{1g}^2\, t_{2g}^6\, t_{1u}^6\, a_{2u}^2$. The total number of bonding electrons is only 16 so that a mean Nb—Nb bond order of only $\frac{2}{3}$ is predicted. This is in accord with the fact that the Nb—Nb distances in $[Nb_6Cl_{12}]^{2+}$ are ~2.90 Å while the Mo—Mo distances in $[Mo_6Cl_8]^{4+}$ are ~2.60 Å.

The M_6X_{12} type clusters of niobium and tantalum can be oxidized to $[M_6X_{12}]^{3+}$ and $[M_6X_{12}]^{4+}$ species, which have 1 or 2 electrons fewer than the number

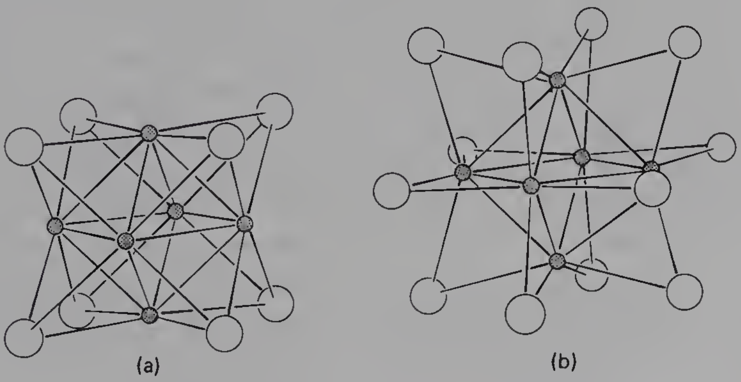

FIG. 23-15. The two prototypal structures for octahedral cluster species. (a) the M_6X_8 type, (b) the M_6X_{12} type.

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[52] B. E. Bursten *et al., Isr. J. Chem.*, 1980, **19**, 132; R. G. Woolley, *Inorg. Chem.*, 1985, **24**, 3519.

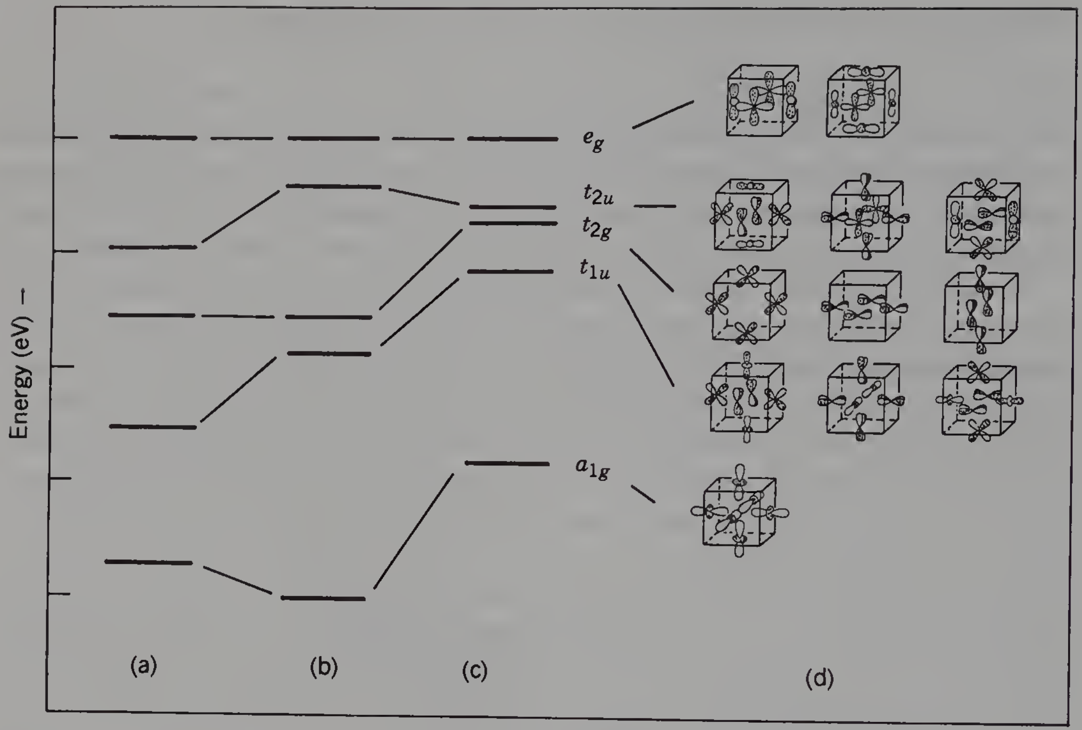

FIG. 23-16. Bonding molecular orbitals and their energies for Mo_6X_8 systems by several calculations. (a) SCF-SW-Xα for $[Mo_6Cl_{14}]^{2-}$; (b) Fenske–Hall for $[Mo_6Cl_{14}]^{2-}$; (c) extended Huckel for $[Mo_6S_8]^{4-}$; (d) diagrams of the molecular orbitals. (Based on results given in refs. 52 and 63).

needed to completely occupy all cluster bonding orbitals.[53] It is also notable that several $Zr_6I_{12}C^{2+}$ compounds are known in which a carbon atom is encapsulated.[54]

In addition to the numerous octahedral cluster compounds formed by Zr, Nb, Ta, Mo, and W, there is another relatively large group formed by rhenium.[55] Besides Re_6 species in compounds such as $Re_2Se_8Cl_2$, Re_2Te_5, $Na_2Re_3S_6$, and $Sr_2Re_6S_{11}$, there are Mo—Re mixed clusters in $Mo_2Re_4S_8$ and $Mo_2Re_4Se_8$.

Several interesting examples of clusters that can usefully be regarded as partial octahedra (i.e., as *nido* and *arachno* structures) are known.[56] The $Mo_5Cl_{13}^{2-}$ ion has a structure which may be described as that of the $Mo_6Cl_{14}^{2-}$ ion with an MoCl unit missing. The $[Mo_4Cl_{12}]^{3-}$ ion exists in two isomeric forms. One has a planar Mo_4 cluster which can be derived from an octahedron by deleting two trans Mo atoms; it is not, however, square but rectangular. The other "butterfly" isomer is similar to an iodo species, $[Mo_4I_{11}]^{2-}$, and both may be regarded as fragments of an octahedron obtained by removing two adjacent Mo atoms.

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[53] N. Bricevic *et al., J. Chem. Soc. Dalton Trans.*, **1985**, 455.

[54] J. D. Smith and J. D. Corbett, *J. Am. Chem. Soc.*, 1985, **107**, 5704.

[55] F. Klaiber *et al., J. Solid State Chem.*, 1983, **46**, 112; L. Leduc *et al., Acta Crystallogr.*, 1983, **C39**, 1503.

[56] B. A. Aufdembrink and R. E. McCarley, *J. Am. Chem. Soc.*, 1986, **108**, 2474; T. C. Zietlow and H. B. Gray, *Inorg. Chem.*, 1986, **25**, 631.

Chevrel Phases.[57] These are ternary molybdenum chalcogenides, named for Roger Chevrel who was the first (1971) to recognize and characterize them structurally. Their general formula is $M_xMo_6X_8$, where M represents one or several of the following: a vacancy, a rare earth element, a transition or main group metallic element (e.g., Pb, Sn, Cu, Co, Fe), and X may be S, Se, or Te. The idealized structure of $PbMo_6S_8$ is shown in Fig. 23-17. It is easily seen that one component of the structure, packed together with the Pb atoms in a CsCl pattern, is an Mo_6S_8 unit that has the type of structure shown in Fig. 23-15. These Mo_6S_8 units are linked together because some of the S atoms are bonded to the external coordination sites of their neighbors.

The binary phase (Mo_6S_8) contains quite distorted Mo_6 octahedra, elongated on a threefold axis to become trigonal antiprisms. This can be attributed to the fact that there are only 20 cluster electrons. This number is insufficient to form a full set of Mo—Mo bonds, that is, to populate all the 12 bonding orbitals indicated in Fig. 23-16, resulting in a distorted octahedron with somewhat longer Mo—Mo bonds compared to the 24-electron clusters. In the compounds containing additional metal atoms, some electrons are added to

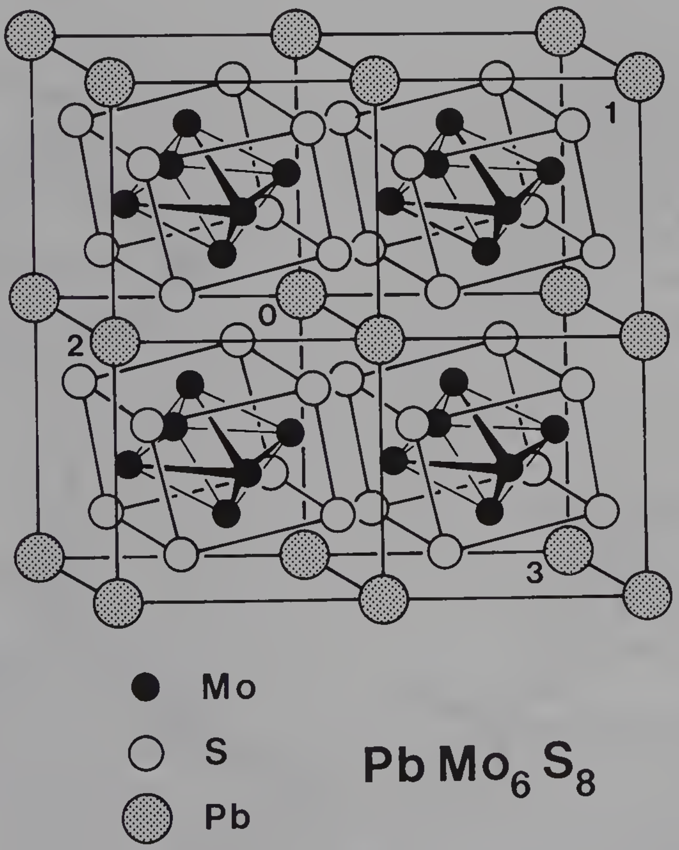

FIG. 23-17. The idealized structure of a representative Chevrel compound.

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[57] F. S. Delk and M. J. Sienko, *Inorg. Chem.*, 1980, **19**, 1352; J. D. Corbett, *J. Solid State Chem.*, 1981, **39**, 56.

the Mo_6 core and it becomes more regular in structure with shorter Mo—Mo bonds.[58]

The Chevrel phases have aroused great interest because they display remarkable superconductivity, as well as some other notable physical properties. Their superconductivity is exceptional in its persistence in the presence of magnetic fields, a property that is obviously important if superconductivity is to be exploited in making powerful magnets. In recent years a great many chemical variations on the basic MMo_6X_8 composition have been devised, for example, compounds such as $Mo_6Br_6S_3$, which contains $Mo_6(\mu_3\text{-}Br)_4(M_3\text{—}S)_4$ units.[59]

23-11. Triangular Clusters

Triangular clusters come in a great variety of structural types, many of which have been cited in Chapter 19.

For rhenium in oxidation state III there is a type of cluster not known for any other element (Fig. 19-D-2), in which there are Re=Re double bonds.

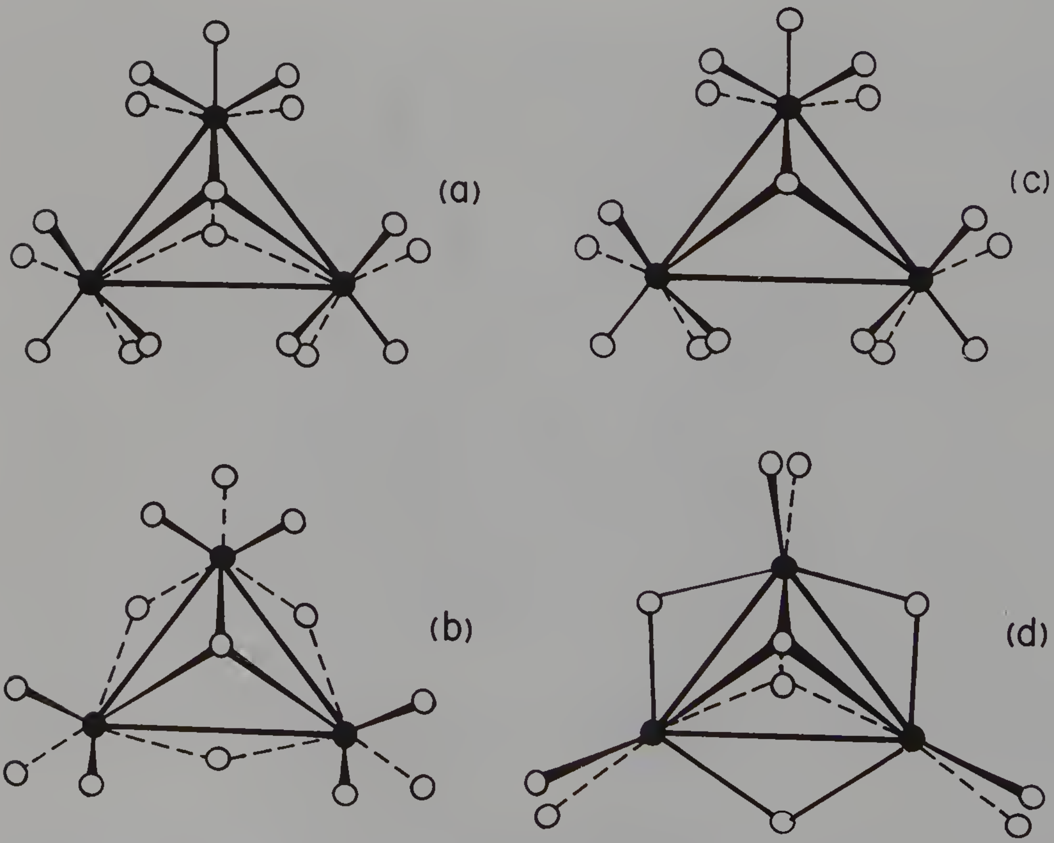

FIG. 23-18. Four of the most important types of trinuclear cluster structures. Solid circles are metal atoms and open circles nonmetal (ligand) atoms.

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[58] W. Hönle *et al.*, *J. Solid State Chem.*, 1983, **49**, 157.
[59] C. Perrin *et al.*, *Acta Crystallogr.*, 1983, **C39**, 415.

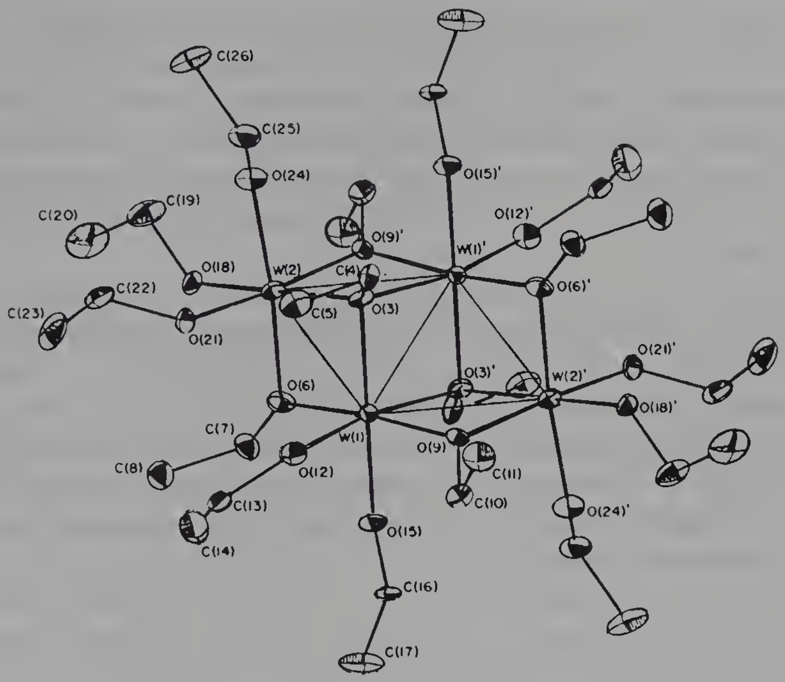

FIG. 23-19. The $W_4(OEt)_{16}$ molecule. (Reproduced by permission from ref. 61.)

These were the first M–M double bonds to be recognized and are still the only ones known in metal clusters of this class with nuclearity three or higher.

Numerous trinuclear cluster compounds are formed by molybdenum, and to a lesser but significant extent by tungsten and niobium. Four principal types are known, and their structures are shown schematically in Fig. 23-18. In all of these the M—M bond orders are in the range $\frac{2}{3}$ to 1. For molybdenum particularly, there are numerous mixed oxides in which the type of structure shown in Fig. 23-18(b) features prominently.[60]

As a kind of extension of this particular type of trinuclear structure, there are numerous compounds that contain two such units fused together on a common edge to give either a discrete molecule[61] as in $W_4(OEt)_{16}$ (Fig. 23-19), and Mo_4O_8 (Oi-Pr)$_4$py$_4$ or extended arrays of such a unit, joined by shared nonmetal atoms, as in MNb_4Cl_{11} (Fig. 19-B-8) or certain mixed oxides of molybdenum[62] such as $Ba_{1.14}Mo_8O_{16}$.

23-12. Solid State Extended Arrays

In traditional solid state chemistry M—M bonding was not observed because the compounds studied were mainly oxides and halides containing the metal atoms in their higher (or highest) oxidation states, where they do not form

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[60] C. C. Torardi and R. E. McCarley, *Inorg. Chem.*, 1985, **24**, 476.

[61] M. H. Chisholm *et al., J. Am. Chem. Soc.*, 1981, **103**, 6093.

[62] R. E. McCarley, *Inorganic Chemistry: Toward the 21st Century*, M. H. Chisholm, Ed. (ACS Symposium Series, No. 211), American Chemical Society, Washington, DC, 1983, p. 273.

M—M bonds. In recent years investigations of chalcogenides, oxides, and halides in which the oxidation states of the metal atoms are kept low have revealed the existence of a new realm of solid state materials in which M—M bonding plays a widespread and essential role. We have already referred to some solid state systems such as the Chevrel phases, in which metal atom clusters occur. We now draw attention to substances containing infinite arrays of M—M bonds.

Among the newest and most interesting systems are some ternary oxides of lower-valent molybdenum that contain infinite chains of octahedral clusters fused on opposite edges.[62] This type of structure is similar to those found in the lower halides of scandium (Section 20-12) and the lanthanides (Section 20-15). The compounds that display such structures are $NaMo_4O_6$, $Ba_5(Mo_4O_6)_8$, and $Sc_3Zn_5(Mo_4O_7)_4$. At the present time a thorough understanding of the electronic structures of these chains of edge-sharing octahedra has not been achieved. It is evident, however, from the Mo—Mo distances that bond orders in the vicinity of 1 are present.

Another type of extended array is also built up of octahedra, but with the

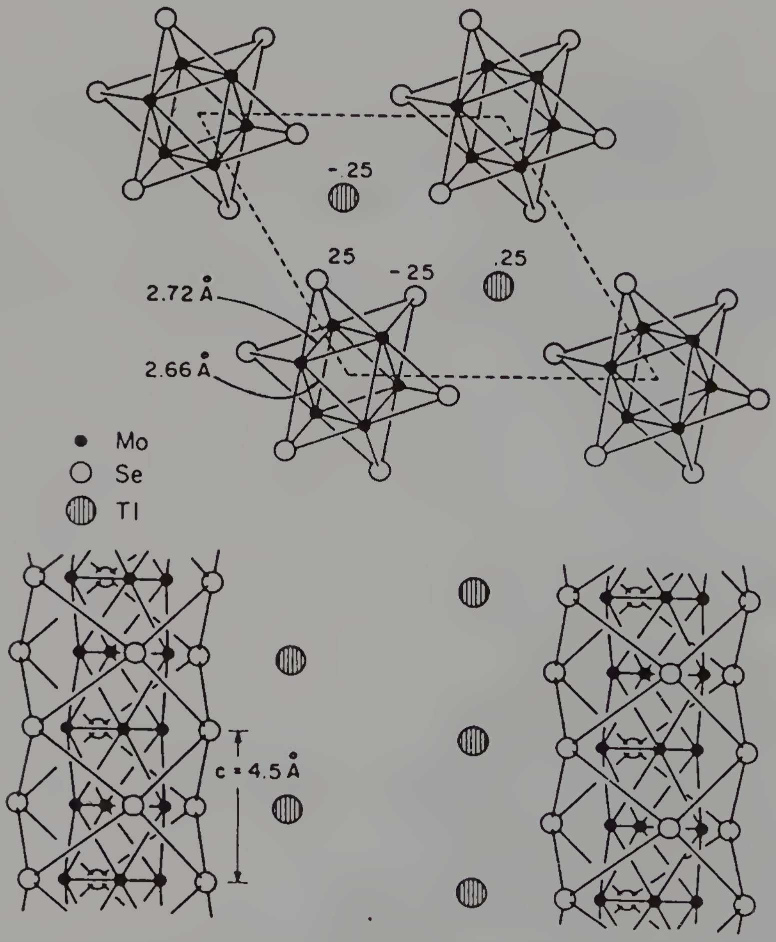


FIG. 23-20. Two views of the structures of $Tl_2Mo_6Se_6$. (Reproduced by permission from ref. 63.)

sharing of opposite faces.[63] Discrete units containing two and three fused octahedra provide transitional structures[64] leading to the limiting case of infinite stacks of octahedra, as shown in Fig. 23-20. Compounds having such infinite stacks are of the type $M_2Mo_6X_6$, in which X = S, Se, or Te and M = In, Na, or K. The electronic structure of these stacks can be formulated in terms of energy band theory.[63]

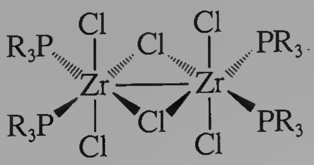
COMPOUNDS WITH M—M MULTIPLE BONDS

There is now a very large number of dinuclear compounds in which the metal atoms are united by bonds of orders 2 to 4.[65] Many have been mentioned in Chapters 18 and 19. Our purpose here is to deal with them as a class and to provide an overview of the nature of M—M multiple bonds.

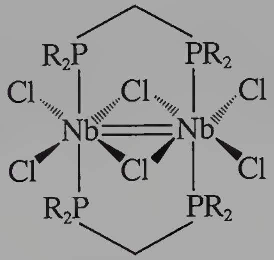
23-13. Major Structural Types

The number of different structural contexts in which M—M multiple bonds are found is very large, and we shall restrict this discussion to four that occur frequently.

1. *Edge-Sharing Bioctahedra.* These are very numerous and may in principle exhibit M—M bond orders of 1 to 3, by overlap of pairs of metal *d* orbitals, as shown in Fig. 23-21. Examples of single (σ^2) and double ($\sigma^2\pi^2$) bonds are provided by molecules such as (23-XVIII) and (23-XIX). In the



(23-XVIII)



(23-XIX)

case where two d^4 metal atoms interact, there will also be a net double bond because both the δ and δ* orbitals will be filled. The existence of a triple bond in this context, however, is problematical. The energy level diagram in Fig. 23-21 shows the δ orbital to be more stable than δ*, but when the different

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[63] T. Hughbanks and R. Hoffmann, *J. Am. Chem. Soc.*, 1983, **105**, 1150, and references to experimental papers given therein.

[64] R. Chevrel *et al.*, *J. Solid State Chem.*, 1980, **34**, 247; C. Perrin and M. Sergent, *J. Chem. Res. (S)*, **1983**, 38.

[65] F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Wiley, New York, 1982; M. H. Chisholm *et al.*, *Polyhedron*, 1987, **6**, 665 *et seq.*

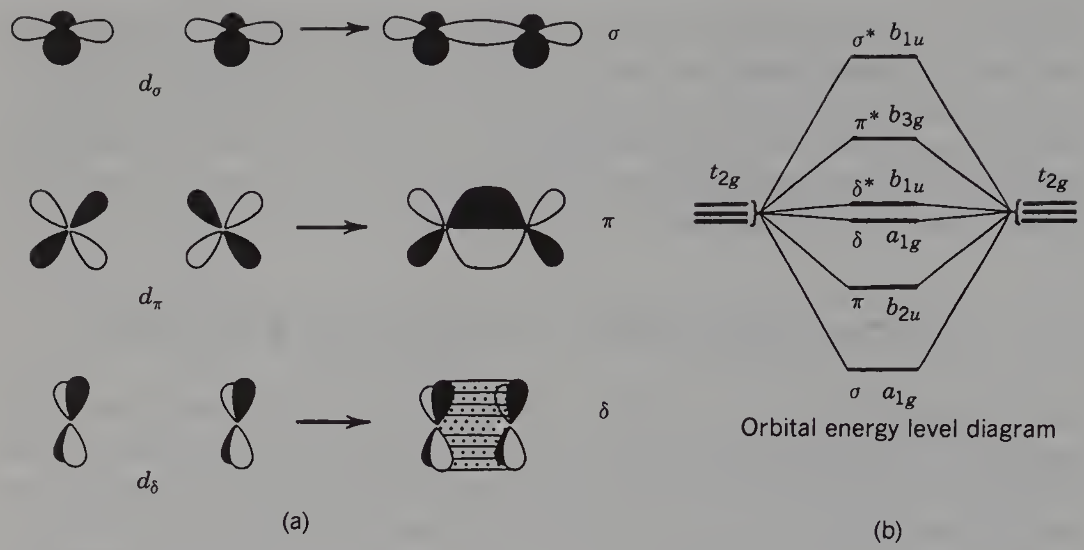
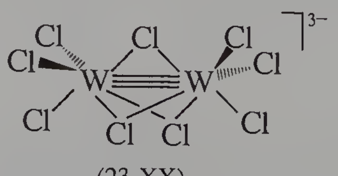


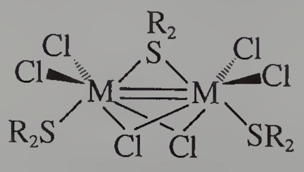
FIG. 23-21. (a) The three d–d overlaps that can be expected in an edge-sharing bioctahedral structure. (b) The pattern of energy levels expected when only the direct overlaps are considered.

interactions of these two orbitals with ligand orbitals are taken into account, the order may be, and in most cases probably is, reversed.[66] Thus, in a d^3–d^3 system the bond order may be 1 rather than 3, and there is some evidence for this.[67] Whatever the order of the δ and δ* orbitals, they are generally close in energy; in some cases they are so close that a singlet state (δ^2 or δ^{*2}) and a triplet state ($\delta\delta^*$) are only a few hundred cm^{-1} apart, and spin-state equilibria are observed.[68]

2. *Face-Sharing Bioctahedra.* What we can now recognize as the first example of a M—M triple bond was discovered within this structural context, namely, the W≡W bond in the $[W_2Cl_9]^{3-}$ ion (23-XX). As we have already noted in Section 19-B-5, the very important Nb^{III} and Ta^{III} complexes of general type (23-XXI) have M—M double bonds.



(23-XX)



(23-XXI)

3. *Tetragonal Prismatic Structures.* These provide the largest and most thoroughly investigated group of compounds with M—M bonds up to quadruple. The prototypal examples are the $[Re_2Cl_8]^{2-}$ and $[Mo_2Cl_8]^{4-}$ ions, whose general, idealized structure is shown in (23-XXII). To understand the M—M bonding possibilities within this structural context we first consider the five

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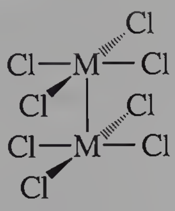
[66] R. Hoffmann *et al., J. Am. Chem. Soc.*, 1980, **102,** 4555; F. A. Cotton *et al., J. Am. Chem. Soc.*, 1981, **103,** 5078.

[67] F. A. Cotton *et al., J. Am. Chem. Soc.*, 1986, **108,** 971.

[68] F. A. Cotton *et al., J. Am. Chem. Soc.*, 1985, **107,** 7438.



(23-XXII)

possible overlaps of the *d* orbitals on two metal atoms, as shown in Fig. 23-22. The relative values of the three types of overlap shown, σ, π, and δ, decrease in that order and thus the ordering of bonding and antibonding orbitals might be expected to appear as in the column labeled M_2 of Fig. 23-23.

When four ligand atoms are brought up to each metal atom to give the arrangement shown in (23-XXII), the order of the MO's is modified. If we define the M—M axis as the *z* direction and the M—L bond axes as $\pm x$ and $\pm y$, the eight lobes of the two $d_{x^2-y^2}$ orbitals will become engaged in the formation of metal-to-ligand σ bonds. Therefore one member of the δ set of M_2 drops to lower energy and becomes an MLσ orbital; at the same time one member of the δ* pair rises in energy and becomes an MLσ* orbital. The exact extent to which these MLσ and MLσ* orbitals move relative to the other M—M bonding and antibonding orbitals will vary from case to case, and the arrangement shown in the M_2L_8 column of Fig. 23-23 is only one of many possibilities. In any case, however, the MLσ orbital will be filled by electrons that contribute to M—L bonding and will play no further role in M—M bonding.

The remaining orbitals that result primarily from M—M overlaps are the MMσ, MMπ (a degenerate pair), and MMδ orbitals. In a case where the metal atoms each have four *d* electrons to contribute, we can fill these four orbitals and obtain a metal–metal quadruple bond, the configuration of which

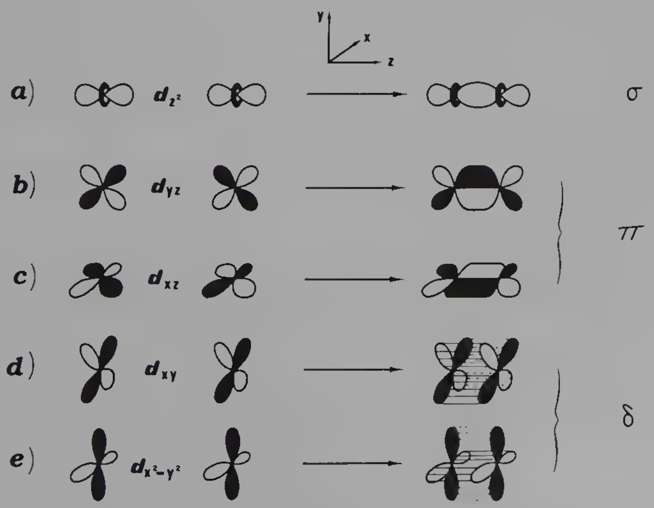


FIG. 23-22. The σ, π, and δ overlaps between two sets of *d* orbitals on adjacent metal atoms with the internuclear axis as the *z* axis.

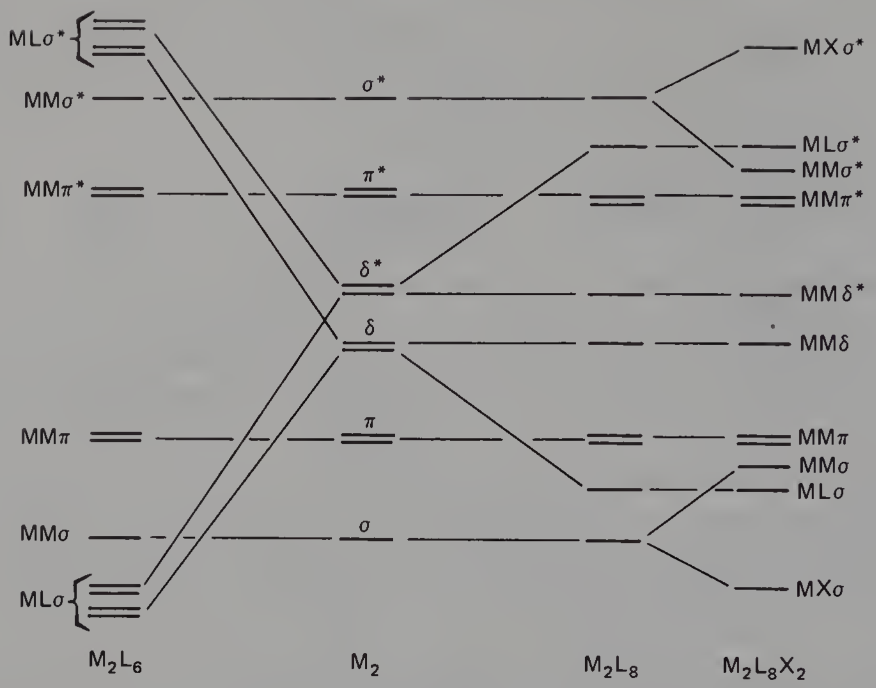
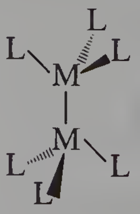


FIG. 23-23. Energy level diagrams showing schematically how *d*-orbital overlaps between two metal atoms (M_2) can be modified by bonding of ligands to give triple bonds in M_2L_6, strong quadruple bonds in M_2L_8, and weaker quadruple bonds in $M_2L_8X_2$.

is $\sigma^2\pi^4\delta^2$. Such a bond has two characteristic properties: (1) it is very strong, therefore very short, and (2) because of the angular properties of the d_{xy} orbitals that overlap to form the δ bond, it has an inherent dependence on the angle of internal rotation. The δ bond is strongest (d_{xy}–d_{xy} overlap maximizes) when the two ML_4 halves have an eclipsed relationship. However, L ⋯ L nonbonded repulsions are also maximized in this conformation. Therefore, the rotational conformation about a quadruple bond might in some cases be expected to be twisted somewhat away from the exactly eclipsed one. Indeed, the d_{xy}–d_{xy} overlap decreases only slightly through the first few degrees of rotation, so that little δ-bond energy is lost by small rotations. Several examples of rotations of up to 20° have been observed; the majority of quadruple bonds are essentially eclipsed, however.

We shall discuss quadruple bonds, and others that arise within this structural context more fully later.

4. *Trigonal Antiprismatic Structure.* The fourth major structural pattern among compounds with M—M multiple bonds is that shown in (23-XXIII).



(23-XXIII)

The bonding possibilities here may be examined by again referring to Fig. 23-23. The approach of six ligands in the manner shown in (23-XXIII) (an ethanelike pattern) causes all the δ and δ^* orbitals to shift their energies, as shown, and leaves three M—M bonding type orbitals, σ and (doubly degenerate) π. Thus, this particular structural context is especially favorable for the formation of triple bonds with $\sigma^2\pi^4$ configurations. Compounds belonging to this class are formed mainly by molybdenum(III) and tungsten(III), and they have been discussed in detail in Chapter 19-C.

23-14. Quadruple Bonds

Since the existence of a quadruple bond was first recognized and explained in 1964 in the case of the $[Re_2Cl_8]^{2-}$ ion, hundreds of compounds containing such bonds have been prepared. They are formed by the elements Cr, Mo, W, Tc, and Re, and important examples have been discussed under the chemistry of each of these elements.

Theoretical and spectroscopic studies have provided a more thorough and sophisticated description of the bonding, but the simple orbital overlap picture presented in Section 23-13 remains qualitatively valid, except possibly with respect to the role of the σ component of the bond, which may be less important than previously thought.[69] For the crucial δ and π components, however, all theoretical and experimental results are in accord.

The δ interaction in the quadruple bond is undoubtedly its most interesting aspect, especially when both the δ (bonding) and δ^* (antibonding) orbitals are considered. Because the δ orbital is only weakly bonding and the δ^* orbital only weakly antibonding (and hence the separation between them is very small) a number of interesting chemical and spectroscopic consequences ensue.

The most characteristic spectroscopic feature of all quadruply bonded species is an absorption band in the visible region due to the excitation of an electron from a singlet $\sigma^2\pi^4\delta^2$ ground state to give a singlet $\sigma^2\pi^4\delta\delta^*$ excited state. Although these transitions are relatively weak considering that they are quantum mechanically allowed (the weakness is traceable to the small orbital overlap in the δ bond) they are intense enough to confer strong, characteristic colors on the species in which they occur. The characteristic royal blue of $[Re_2Cl_8]^{2-}$, intense red of $[Mo_2Cl_8]^{4-}$, and yellow of $Mo_2(O_2CCH_3)_4$ are due to $\delta \rightarrow \delta^*$ transitions at 7000, 5250, and 4350 Å, respectively. An important fact about these transitions, however, is that their energies are determined more by interelectronic repulsive forces (correlation energies) than by orbital energy differences. In Mo_2^{4+} species, the total transition energy of ~18,000 cm^{-1} is, crudely speaking, the sum of about 6000 cm^{-1} orbital energy difference and 12,000 cm^{-1} electron correlation energy.[70]

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[69] E. M. Kober and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1985, **107,** 7199.

[70] F. A. Cotton *et al., Inorg. Chem.*, 1985, **24,** 177.

Because of the weakness of the δ bond, the gain or loss of electrons from δ or δ* orbitals has only a slight effect on the strength of the M—M bond. One interesting consequence of this is that the M—M bond length may be influenced as much or more by the change in effective atomic charge when an electron is removed from a δ or δ* orbital.[71] This is most dramatically evident in the following series of structures[72]:

$Re_2Cl_4(PMe_2Ph)_4$	$\sigma^2\pi^4\delta^2\delta^{*2}$	2.241(1) Å
$[Re_2Cl_4(PMe_2Ph)_4]^+$	$\sigma^2\pi^4\delta^2\delta^{*1}$	2.218(1) Å
$[Re_2Cl_4(PMe_2Ph)_4]^{2+}$	$\sigma^2\pi^4\delta^2\delta^{*0}$	2.215(1) Å

As the δ* electrons are removed the formal bond order changes from 3.0 through 3.5 to 4.0, but the changes in Re—Re distance are very small. This is because at the same time the oxidation state of the metal atoms is also increasing, which causes the *d* orbitals to contract and thus the overlap in the π bonds becomes poorer. This bond weakening effect approximately offsets the strengthening that would be expected when antibonding electrons are lost. In the case of $[Tc_2Cl_8]^{3-}$ versus $[Tc_2Cl_8]^{2-}$ there is actually a lengthening of the Tc—Tc bond by about 0.03 Å when the δ* electron is lost.[71]

The most direct way to evaluate the contribution made by the δ electrons to the M—M bond length is by observing the change in M—M distances as a molecule of type (23-XXII) is twisted from the eclipsed toward the staggered rotational conformation. This should cause the δ bond strength to go from its maximum to zero. A series of structures of Mo_2Cl_4(diphosphine)$_2$ molecules in which there are differing twist angles has shown that the total loss of the δ component of the bond corresponds to a lengthening of about 0.10 Å.[73] Thus, of the entire bond length difference between an Mo—Mo single bond (~2.60 Å) and the quadruple bonds (~2.10 Å) only ~20% is due to the δ component.

23-15. Other Bond Orders in the Tetragonal Context

Because of the nearly nonbonding character of both δ and δ* orbitals, both deletion and addition of either one or two electrons to the $\sigma^2\pi^4\delta^2$ configuration might be expected to occur easily. On this basis, species that are structurally within the tetragonal prismatic framework having bond orders of 3 and 3.5 as well as 4 may be expected, as indicated schematically in Fig. 23-24. Species of all the types represented there are known. Representative species with $\sigma^2\pi^4$ and $\sigma^2\pi^4\delta^1$ configurations are the phosphonato-bridged $[Mo_2(HPO)_4)_4]^{2-}$ and sulfato-bridged $[Mo_2(SO_4)_4]^{3-}$ ions.[74] The $Re_2Cl_4(PMe_2Ph)_4$ and $[Re_2Cl_4(PMe_2Ph)_4]^+$ species discussed in the previous section provide exam-

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[71] F. A. Cotton, *Chem. Soc. Rev.*, 1983, **12,** 35.
[72] F. A. Cotton *et al., J. Am. Chem. Soc.*, 1983, **105,** 4950.
[73] F. A. Cotton *et al., Inorg. Chem.*, 1985, **24,** 4384.
[74] V. M. Miskowski *et al., J. Am. Chem. Soc.*, 1986, **108,** 959.

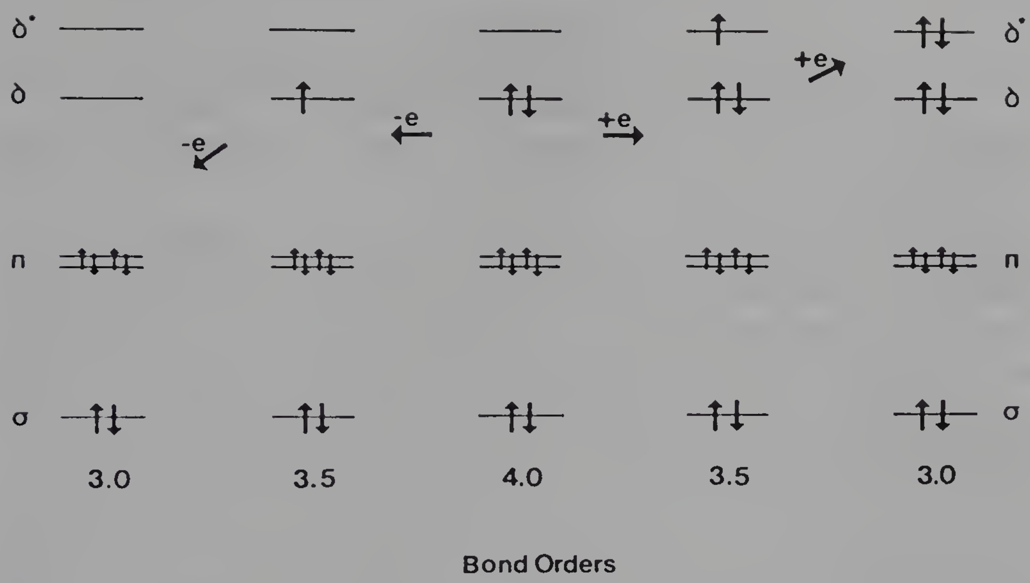

FIG. 23-24. A schematic representation of how changes in the occupation of the δ and δ* orbitals change the M—M bond order.

ples of the so-called electron-rich bonds of orders 3.0 and 3.5, respectively. It is interesting to note that the presence of δ* electrons in $Re_2Cl_4(PR_3)_4$ compounds, as indicated schematically in Fig. 23-24, receives direct, quantitative support from the photoelectron spectrum of $Re_2Cl_4(PMe_3)_4$, where the δ* and δ ionizations, of equal intensity occur at 5.7 and 6.6 eV, respectively.[75]

The addition of two electrons to the δ* orbitals occurs also in a number of triply bonded diosmium compounds,[76] of which the $[Os_2Cl_8]^{2-}$ and $[Os_2Br_8]^{2-}$ ions, are the simplest examples.[77] The presence of the two δ* electrons means that there should be no inherent barrier to rotation about the Os—Os bond; in beautiful accord with this it is found that the conformations of both $[Os_2X_8]^{2-}$ ions are within 1 to 4° of being exactly staggered.

The addition of further electrons to the set of antibonding orbitals shown in Fig. 23-23 occurs in a great variety of dinuclear complexes formed by the metals Os, Ru, Rh, Ir, and Pt.[76] Selected examples of these and their bond lengths and bond orders are given in Table 23-2. Further details on many of these compounds are to be found in Chapter 19-F to 19-H.

23-16. Relation of Clusters to Multiple Bonds

Although it has been convenient to discuss cluster and multiply bonded binuclear species separately, it is also necessary to point out the relationship between them. There is, in a formal way, continuous gradation from clusters to high M—M bond orders.

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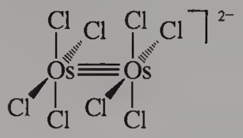
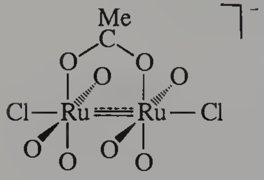
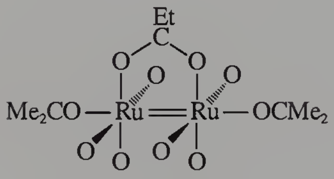
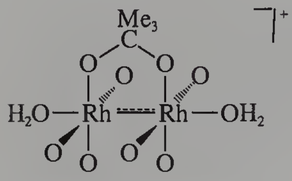
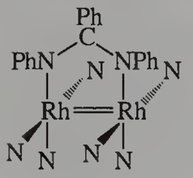
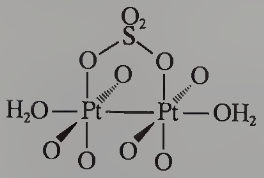
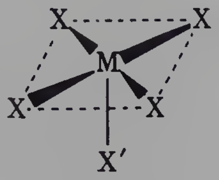
[75] D. L. Lichtenberger *et al., J. Am. Chem. Soc.,* 1986, **108,** 953.
[76] F. A. Cotton and R. A. Walton, *Struct. Bonding, Berlin,* 1985, **62,** 1.
[77] F. A. Cotton *et al., J. Am. Chem. Soc.,* 1986, **108,** 4850.

TABLE 23-2
Some Compounds with Electron Rich M—M Bonds[a]

Compound	Electron configuration	Bond order	Bond length (Å)	Notes
	$\sigma^2\pi^4\delta^2\delta^{*2}$	3	2.182(1)	*b*
	$\sigma^2\pi^4\delta^2\delta^{*}\pi^{*2}$	2½	2.267(2)	*c*
	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$	2	2.260(3)	*d*
	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*3}$	1.5	2.316(2)	*c*
	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$	1	2.389(1)	*e*
	$\sigma^2\delta^4\delta^2\delta^{*2}\pi^{*4}$	1	2.461(1)	*f*

[a] In structures with bridging ligands, only one is shown in full.
[b] See ref. 77; conformation is staggered.
[c] See ref. 65.
[d] G. Wilkinson *et al., J. Chem.Soc., Dalton Trans.*, **1985,** 2321.
[e] J. L. Bear *et al., J. Am. Chem. Soc.*, 1985, **107,** 7195.
[f] See ref. 76.

To appreciate this we note first that the local ligand environment of a metal atom is much the same in the M_6X_8, M_6X_{12}, M_3X_9 clusters and in the X_4MMX_4 quadruply bonded dimers. In each case a metal atom is coordinated by a square set of ligands; the MX_4 group is generally slightly pyramidal, with the ligands forming the base. In addition, there is a tendency in all cases for a fifth ligand to occupy a position along the four-fold axis of this pyramid, just below the base. We have in each case, the structural element (23-XXIV).



(23-XXIV)

The four structural types just mentioned are obtained by combining such elements in different ways, the differences being in the extent and type of bridging by the X groups. In both the octahedral clusters all X ligands are bridges, triple ones in M_6X_8, and double ones in M_6X_{12}. In M_3X_9 only two of the four X ligands are bridges, and in X_4MMX_4 none are bridges.

These structural differences go hand in hand with differences in the way in which M—M bonds are formed. In the MX_4 or MX_4X' unit the metal atom has available four *d* orbitals with which to form M—M bonds, as shown earlier. Let us suppose we are also dealing with a specific group, such as MoX_4^{2-} or ReX_4^-, in which the metal atom also has four electrons available. What are the possible ways in which these four orbitals and four electrons may be used? At one extreme we have the possibility of forming four single bonds to four other metal atoms. This is, in fact, exactly what happens in the Mo_6X_8 type cluster. At the other extreme the four orbitals and four electrons may all be used to form one quadruple bond to one other metal atom, as in $[Mo_2X_8]^{4-}$ and $[Re_2X_8]^{2-}$. There is then the intermediate case in which two double bonds are formed; this is what ocurs in the Re_3X_9 systems. This set of three species is indicated by (23-XXVa) to (23-XXVc).

M_6X_8 ··············	M_3X_9 ··················	M_2X_8
Four M—M single bonds per M	Two M—M double bonds per M	One M—M quadruple bond per M
(a)	(b)	(c)

(23-XXV)

The question of what determines the relative stabilities of these possible arrangements has not been answered in detail. It is likely that avoidance of excessively high total charge plays a part. This could explain why $[Mo_6Cl_{14}]^{2-}$ and $[Mo_2Cl_8]^{4-}$ are stable, but not the molybdenum analogue of $[Re_3Cl_{12}]^{3-}$, since that would be $[Mo_3Cl_{12}]^{6-}$, with perhaps too much negative charge for stability. With rhenium the known chloro compounds are $[Re_2Cl_8]^{2-}$ and $[Re_3Cl_{12}]^{3-}$, but the rhenium analogue of $[Mo_6Cl_{14}]^{2-}$, which would be $[Re_6Cl_{14}]^{4+}$, has not been seen. Interestingly, the compound $Na_4Re_6S_{10}(S_2)$ has recently been discovered and shown to contain an $[Re_6S_8]^{2+}$ unit to which four S^{2-} ligands and two S_2^{2-} ligands, each of which bridges to an adjacent cluster, are coordinated in the six outer positions. By substituting S^{2-} for Cl^-, the unacceptably high charge on a central $[Re_6Cl_8]^{10+}$ has been avoided. Thus for Re^{III} the entire set of structures (23-XXVa) to (23-XXVc) is known.

The possibility that the X_3M units of $X_3M{\equiv}MX_3$ might also be able to form tetrahedral $(X_3M)_4$ molecules in an obvious, analogous idea, but to date there has been no report of such a compound.

23-17. One-Dimensional Solids[78]

The substances of interest in this section are mainly those in which planar complexes of platinum and iridium are arranged in infinite stacks in the crystals, as illustrated in Fig. 23-25 for $[Pt(CN)_4]^n$ ions in several of the important compounds. In this way chains of metal atoms are created and there is direct bonding between the metal atoms, so that a kind of one-dimensional metal can be created if the metal atoms approach one another closely enough.

We discuss first the compounds that have been most intensively studied, namely, $K_2Pt(CN)_4{\cdot}3H_2O$ and its partly oxidized derivatives. These are listed in Table 23-3. As indicated, $K_2Pt(CN)_4{\cdot}3H_2O$ itself does *not* have interesting properties. It is white and a nonconductor of electricity. The platinum valence is integral (+2.0) and the Pt---Pt distances are so long that no significant M—M bonding would be expected. As long ago as 1842 it was observed that under oxidizing conditions one could obtain what appeared to be bronze-colored forms of this compound, and the bronze specimens were later found to be electrical conductors. It has since been shown that these bronze, conducting materials contain about 0.3 Br^- or Cl^- ions per Pt and that the oxidation number of Pt in them is therefore about 2.3. As Table 23-3 shows,

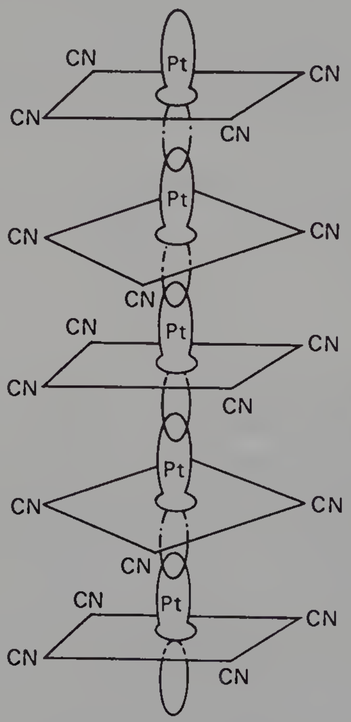


FIG. 23-25. Diagram of the stacking of $[Pt(CN)_4]^{n-}$ ions showing how metal d_{z^2} orbitals can overlap. Note alternating 45° rotation.

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[78] P. Monceau, Ed., *Electronic Properties of Inorganic Quasi-One-Dimensional Compounds. Part I. Theoretical. Part II. Experimental.* Reidel, Dordrecht, 1985; J. M. Williams, *Adv. Inorg. Chem. Radiochem.*, 1983, **26,** 235.

TABLE 23-3
Some Tetracyanoplatinate Compounds with Stacked Anions

Complex	Pt valence	Pt—Pt (Å)	Color	Conductivity (Ω^{-1} cm^{-1})
Pt metal	0	2.775	Metallic	~9.4×10^4
$K_2[Pt(CN)_4]\cdot 3H_2O$	+2.0	3.48	White	5×10^{-7}
$K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$	+2.3	2.88	Bronze	4–830
$K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$	+2.3	2.87	Bronze	~200
$K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$	+2.25	2.96	Bronze	~70–100
$Cs_2[Pt(CN)_4](FHF)_{0.39}$	+2.39	2.83	Gold	Unknown

this fractional oxidation is accompanied by an enormous decrease in the stacking distance, so that Pt—Pt separations approach to within 0.11 Å of those in metallic platinum. Detailed calculations show that a kind of one-dimensional band structure is set up and that electrical conductance and other metallic properties result from this. The calculations suggest that the observed stoichiometries give optimum M—M bonding. The electrical conductivity arises from partial filling of a band, just as in the normal three-dimensional case.

The substances containing ~0.3 Cl or 0.3 Br in the crystals are sometimes called Krogmann salts. The partial oxidation of $[Pt(CN)_4]^{2-}$ may also be done in such a way as to obtain a cation-deficient product like $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$, as also indicated in Table 23-3.

Besides the $[Pt(CN)_4]^{n-}$ ($n < 2$) cases, which, it should be emphasized, we have covered only superficially, there are several other established examples of good one-dimensional conductors that appear to be basically similar but have been less thoroughly investigated.

Partial oxidation of $[Pt(ox)_2]^{2-}$ by nitric acid, Cl_2, H_2O_2, or other agents yields copper-colored needles containing the $[Pt(ox)_2]^{\sim 1.64-}$ ion, many cation-deficient salts of which, for example, $Mg_{0.82}[Pt(ox)_2]\cdot xH_2O$, have been isolated and studied. Pt—Pt distances in these compounds are in the range 2.80 to 2.85 Å, and their properties are comparable to those of the cyano compounds.

Halo carbonyliridate compounds containing, in effect, partially oxidized Ir^I have also been shown to form one-dimensional conductors.[79] Ir^I is, of course, isoelectronic with Pt^{II}, but the greater spatial extension of the *d* orbitals of Ir^I might be expected to allow stronger interactions and better band formation at similar internuclear distances. Thus far these compounds are very incompletely characterized as compared to the cyanoplatinum ones. They include "$Ir(CO)_3X$" (X = Cl, Br), which are evidently nonstoichiometric and have iridium in a mean oxidation state >1, and salts of the type $M^I_xIr(CO)_2Cl_2$ ($0.5 < x < 1.0$). There are indications that the latter have stacked structures, but details are still fuzzy.

Certain nonstoichiometric mixed platinum oxides (e.g., $Na_xPt_3O_4$, 0 <

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[79] A. H. Reis, Jr., in *Extended Linear Chain Compounds,* J. S. Miller, Ed., Plenum Press, New York, 1982, Vol. I, p. 157.

$x < 1$) have complex structures with chains of Pt atoms running in all three crystal directions and Pt—Pt distances of ~2.80 Å. This is broadly reminiscent of the structure of $Hg_{2.86}AsF_6$ (Section 16-5).

In conclusion it should be noted that structures in which planar complexes are arranged in stacks to give infinite chains of metal atoms are not uncommon in the coordination chemistry of d^8 metals; a few have already been mentioned (Section 19-H-4). In these cases the optical properties of the crystals are usually quite anisotropic, with strong absorption bands polarized in the direction of the metal atom chains, but the M—M distances are long (3.2–3.5 Å), and there is no intrinsic electrical conductivity. We have already mentioned the completely stoichiometric salts of $[Pt(CN)_4]^{2-}$. Other examples of such substances include Magnus's green salt $[Pt(NH_3)_4][PtCl_4]$ and a number of analogous compounds such as $[Pt(NH_2Me)_4[PtBr_4]$, as well as $Rh(CO)_2(acac)$ and bis(dimethylglyoximato)nickel.

Additional References

Bruce, M. I. *Coord. Chem. Rev.*, 1987, **76,** 1 (ruthenium carbonyl clusters).

Deeming, A. J., *Adv. Organomet. Chem.*, 1986, **26,** 1 (triosmium cluster chemistry).

Gates, B. C., L. Guczi and H. Knözinger, *Metal Clusters in Catalysis*, Elsevier, Amsterdam, 1986.

Haggin, J., *Chem. Eng. News*, 1987, Mar. 2, p. 9 (clusters in catalysis).

Lavisne, G. and H. D. Kaesz, *Stud. Surf. Sci. Catal.*, 1986, **29,** 43 (reactivity of clusters and relevence to catalysis).

McPartlin, M., *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 853 (computer graphics of clusters).

Sappa, E., *et al.*, *Progr. Inorg. Chem.*, 1987, **35,** 438 (butterfly clusters of Group VIII elements).

Chapter Twenty Four

Transition Metal Compounds with Bonds to Hydrogen

Complexes of transition metals with M—H bonds[1a–d] are of critical importance in many stoichiometric and catalytic reactions (Chapters 27 and 28), while the formation of M—H bonds on metallic heterogeneous catalysts such as Fe, Co, Ni, Pd, or Pt is involved in hydrogenations, hydrocarbon cracking, and so on.

The first complexes to be made, by Hieber and by Blanchard in the 1930s, were $HCo(CO)_4$ and $H_2Fe(CO)_4$, but their structures and the nature of the M—H bond was not known until much later. The discovery of Cp_2ReH in 1955 initiated modern studies as this molecule allowed the M—H stretching region in the ir spectrum to be identified, at $\sim 2000\ cm^{-1}$, while the ^1H nmr spectrum showed a line on the high field side of Me_4Si. The molecule also demonstrated for the first time that metal atoms in complexes could be protonated:

$$Cp_2ReH + H^+ \rightleftharpoons Cp_2ReH_2^+$$

The compound is as basic as ammonia. Hundreds of hydrido compounds are now known for the *d* group elements, lanthanides, and actinides. The most common supporting ligands are CO, PR_3, and Cp but cyano compounds like $[HCo(CN)_5]^{3-}$ and some nitrosyls, for example, $[CpW(NO)(H)_2]_2$,[2] carborane,[3] and sulfur ligand[4] complexes exist. Complexes with non-π-bonding ligands are rare, the best example being the stable $[RhH(NH_3)_5]^{2+}$, while

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[1a] G. G. Hlatky and R. H. Crabtree, *Coord. Chem. Rev.*, 1985, **65,** 1 (an extensive review with much data; 292 references).

[1b] R. G. Pearson, *Chem. Rev.*, 1985, **85,** 41 (M—H bond acidity, thermodynamic data).

[1c] D. S. Moore and S. D. Robinson, *Chem. Soc. Rev.*, 1983, 415 (general review).

[1d] R. G. Teller and R. Bau, *Struct. Bonding, Berlin,* 1981, **44,** 1 (exhaustive crystallographic data including M—H—C and other interactions).

[2] P. Legdzins *et al., Organometallics,* 1985, **4,** 1263.

[3] R. B. Maynard and R. N. Grimes, *J. Am. Chem. Soc.*, 1982, **104,** 5983.

[4] P. M. Boorman *et al., Inorg. Chem.*, 1985, **24,** 2989; D. D. Sellman and L. Zapf, *Z. Naturforsch.*, 1985, **B40,** 380.

$[CrH(H_2O)_5]^{2+}$ has only a short lifetime. Only a few paramagnetic hydrides are known, for example, $IrH_2Cl_2(P\textit{i}\text{-}Pr_3)_2$ and $TaH_2Cl_2(dmpe)_2$.[5]

24-1. Characterization of Hydride Complexes

The characterization by X-ray diffraction sometimes presents considerable difficulty since H atoms in the presence of heavy atoms are commonly not seen due to scattering problems. Neutron diffraction studies, where H is observed directly, have been made in relatively few cases. Accordingly hydrides are commonly identified by ir and ^1H nmr spectra. The M—H stretches lie in the region 2300 to 1600 cm^{-1} and the bends 900 to 600 cm^{-1}. The ^1H nmr spectra can have lines in the region δ −1 to −60 but usually ~−5 to −35 ppm.* There is little correlation between nmr line positions and stretching frequencies and M—H bond lengths. In phosphorus ligand complexes coupling of ^1H and ^{31}P often gives useful structural information but in 5 and 7 or higher coordinate species nonrigidity (Chapter 29) is commonly observed, for example, in $Cr(H)_2[P(OMe)_3]_5$.[6] It is often difficult to determine by nmr the number of hydrogen atoms bound to the metal by integration due to differences in relaxation times between M—H and ligand protons. The former tend to have long relaxation times and hence one way is to compare the signal of L_nMH_m against that of a standard M—H compound; another way is to have sufficiently long pulse delay times in the FT nmr.[7]

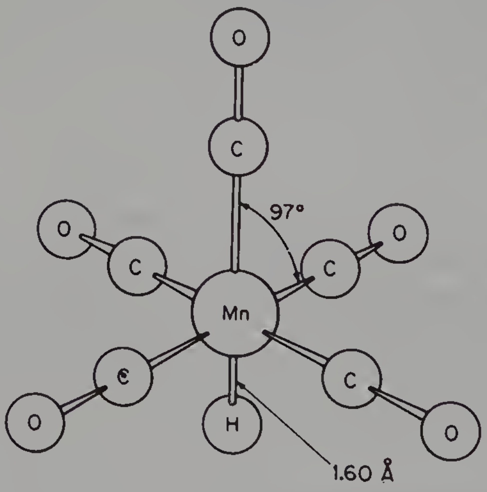

FIG. 24-1. The structure of the $HMn(CO)_5$ molecule, showing both the stereochemical activity of the hydrogen atom and the metal-to-hydrogen distance, which approximates to the sum of normal covalent radii.

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[5] P. Mura, *J. Am. Chem. Soc.*, 1986, **108**, 351; A. P. Sattelberger *et al.*, *Inorg. Chem.*, 1987, **26**, 2430.

*In $W_2H(\mu\text{-}CPh)(\mu\text{-}C_4Me_4)(OCHMe_2)_2$ the ^1H nmr peak is 20 ppm *downfield* from Me_4Si; M. H. Chisholm *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985,** 861.

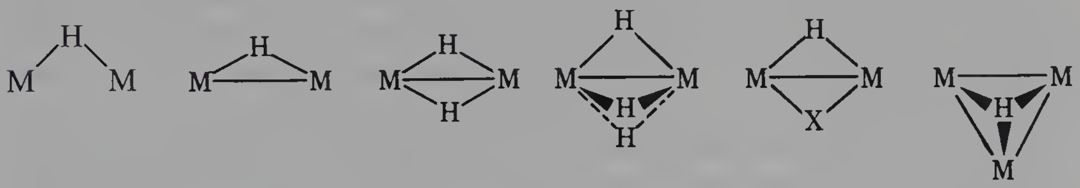
[6] S. D. Ittel *et al.*, *Organometallics*, 1985, **4,** 18.

[7] R. H. Crabtree *et al.*, *Inorg. Chem.*, 1985, **24,** 1949.

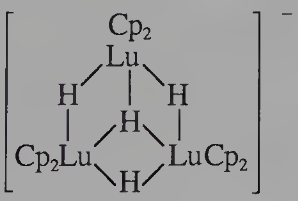
An early difficulty in interpreting wide line nmr data of solids indicated that the H atoms occupied little space, but reinterpretation coupled with X-ray and neutron diffraction data now show that the H atom occupies a normal bond position where M—H distances are approximately the sum of the covalent radii of H and M, that is, 1.6 to 1.7 Å. An example is shown in Fig. 24-1.

Hydrogen Bridges. The first evidence that hydrogen could act as a bridge between two metals came from nmr spectra of $[Cp(CO)_3W]_2H^+$ where the ^1H spectrum showed satellites due to coupling with both ^{184}W(spin $\frac{1}{2}$) atoms symmetrically.

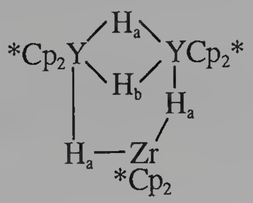
Many bridged species have been confirmed by diffraction, ir, and Raman methods[8a] as well as by nmr.[8b] The following are representative types:



More complicated bridge systems have been found in yttrium and lanthanide compounds,[8c] for example, (24-I) and (24-II):



(24-I)



(24-II)

More representative examples are $[(\mu\text{-H})(\mu\text{-Cl})_2Mo_2Cl_6]^{3-}$, $[\mu\text{-HW}_2(CO)_{10}]^-$, $(\mu\text{-H})_2Re_2(CO)_8$, $Mo_2(H)_2(\mu\text{-H})_2(PMe_3)_6$, $[{*CpIr}(\mu\text{-H})_3Ir{*Cp}]^+$, and $Re_2(H)_4(\mu\text{-H})_4(PR_3)_4$.

Cluster compounds (Chapter 23) often have μ_2 or μ_3 bridges and in addition there can be bridges between different atoms as in $[(CO)_5Cr(\mu\text{-H})Fe(CO)_4]^-$.[9]

It now seems clear[10] that no linear single bridges M—H—M occur and that all are *inherently bent.* The M(μ-H)M bond angles range from ~78 to 124°; M—H—M asymmetric stretching frequencies are ~1700 cm^{-1}. Due to the ease of deformation of the bridge, the species may have variable configurations depending on the nature of the counter ion, the ligands, and the metal.

Although many compounds clearly have M—M bonds supporting the bridge, a few cases of unsupported bridges have been established,[10] for ex-

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[8a] N. Sheppard *et al., Inorg. Chem.,* 1986, **25,** 2846; U. A. Jayasooviya *et al., Inorg. Chem.,* 1986, **25,** 2850, 2853.

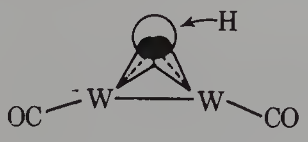
[8b] P. Legzdins *et al., J. Am. Chem. Soc.,* 1986, **108,** 7971.

[8c] W. J. Evans *et al., Organometallics,* 1986, **5,** 263.

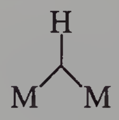
[9] M. Y. Darensbourg *et al., J. Am. Chem. Soc.,* 1984, **106,** 456.

[10] R. Bau *et al., Organometallics,* 1985, **4,** 1590.

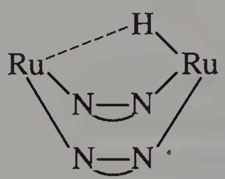
ample, in $[Ph_4P][HW_2(CO)_{10}]$ where W---W = 3.34 Å and WHW = 123.4°. In the species with M—M bonds there appears to be orbital overlap in the center of the MHM triangle (24-III) and in the unsupported cases, a closed 3*c*-2*e* bond (24-IV).



(24-III)



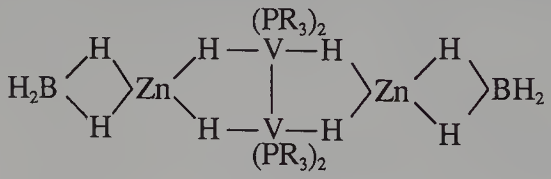
(24-IV)



(24-V)

Although the majority of single bent bridges are symmetrical a few unsymmetric ones have been found, for example, in $[Et_4N][Mo_2(\mu\text{-}H)(CO)_9\text{-}PPh_3]$ and $dppe_2Pt(\mu\text{-}H)_2PtHdppe_2$ and there is one unique case of a "semi-bridged" hydride in a pyrazole (N—N) ruthenium complex (24-V) where Ru—Ru = 3.166, Ru---H = 2.05 and Ru—H = 1.68 Å.

Finally, bridges between transition and nontransition metals have been confirmed in numerous complexes containing BH_4^-, AlH_4^-, and $AlMe_3$ that are discussed in Section 24-10. Carboranes can also show M—H—B bridges[11] while a more complicated system involves zinc (24-VI).[12]



(24-VI)

24-2. Synthetic Methods

Compounds with M—H bonds can be synthesized in a variety of ways of which the following are the main types of reaction.

1. *Action of Hydride Sources on Metal Complexes.* The hydride sources can be organic compounds such as alcohols, aldehydes, sugars, and formaldehyde, that have readily transferable H atoms, water, NH_4^+, or hydrido anions such as BH_4^-, AlH_4^-, and so on. Note that the latter ions may in some cases give boro- or alumino hydride complexes (Section 24-10) and the transition metal hydride is obtained only on hydrolysis.

Representative syntheses are

$$trans\text{-}PtCl_2(PEt_3)_2 \xrightarrow{\text{KOH–EtOH}} trans\text{-}PtClH(PEt_3)_2$$

$$FeI_2(CO)_4 \xrightarrow[\text{THF}]{\text{NaBH}_4} FeH_2(CO)_4$$

$$Rh^{3+}(aq) + SO_4^{2-} + NH_3 + Zn \longrightarrow [Rh(NH_3)_5H]SO_4$$

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[11] M. F. Hawthorne *et al., J. Am. Chem. Soc.,* 1985, **107,** 932.

[12] K. G. Caulton *et al., J. Am. Chem. Soc.,* 1983, **105,** 6163; F. A. Cotton *et al., Inorg. Chem.,* 1985, **24,** 1510.

2. *Reactions Involving Molecular Hydrogen.* Hydrogen can add to coordinately unsaturated compounds (Chapter 27) especially those of Rh^I, Ir^I, and Pt^{II}; in the presence of bases H_2 may undergo heterolytic cleavage.[13a]

$$RhCl(PPh_3)_3 + H_2 \rightleftharpoons RhCl(H)_2(PPh_3)_3$$

$$RuCl_2(PPh_3)_2 + H_2 + Et_3N \longrightarrow RuClH(PPh_3)_3 + Et_3NHCl$$

Hydrogenolyses of alkyls, alkoxides, or dialkylamides can be induced:

$$Cp_2ZrMe_2 \xrightarrow[60\text{ atm}]{H_2,\ 80°C} Cp_2ZrH_2 + 2CH_4$$

$$WMe_6 + 3PMe_3 \xrightarrow[1\text{ atm}]{H_2} WH_4(PMe_3)_3 + 6CH_4$$

$$(Ph_3P)_2Rh[N(SiMe_3)_2] \xrightarrow[1\text{ atm}]{H_2} (Ph_3P)_2RhH + (Me_3Si)_2NH$$

Whereas some hydrogenolyses may proceed via initial oxidative-addition of H_2 followed by reductive-elimination, this is *not* possible for d^0 species such as $Cp_2Zr^{IV}Me_2$. Hence in such cases heterolytic attack by hydrogen involving the vacant metal coordination site must occur *cf.*, Section 20-11.[13b]

The hydrogenation of alkene or alkyne complexes (Chapter 28) can also lead to removal of ligand, for example,

$$[Rh(COD)(PPh_3)_2]^+ \xrightarrow{H_2,\text{ solvent, S}} [Rh(H)_2(PPh_3)_2S_2]^+ + C_8H_{16}$$

$$Ru(COD)(COT) \xrightarrow{H_2,\ PCy_3} RuH_6(PCy_3)_2 + C_8H_{16}$$

where in both cases the metal has undergone oxidative-addition.

Direct interaction and cleavage of M—M bonds by H_2 is useful for certain carbonyl hydrides, for example,

$$Co + 4CO + \tfrac{1}{2}H_2 \xrightarrow[150°C]{50\text{ atm}} HCo(CO)_4$$

$$Mn_2(CO)_{10} + H_2 \xrightarrow[200°C]{200\text{ atm}} 2HMn(CO)_5$$

Finally, H_2 addition to multiple bonds is possible as in the reaction

$$Ta_2Cl_6(PMe_3)_4 + H_2 \longrightarrow (\mu\text{-}H)_2Ta_2Cl_6(PMe_3)_4$$

where there is a Ta═Ta bond.[14]

3. *Reactions of Hydrogen Compounds HX.* These can add also oxidatively, for example,

$$trans\text{-}IrCl(CO)(PPh_3)_2 + HSiCl_3 = IrCl(H)(SiCl_3)(CO)(PPh_3)_2$$

$$trans\text{-}PtCl_2(PEt_3)_2 + HCl = PtCl_3H(PEt_3)_2$$

Complexes that have lone pairs or putative lone pairs can be protonated by

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[13a] P. J. Brothers, *Progr. Inorg. Chem.*, 1981, **28,** 1.

[13b] J. Schwartz *et al., J. Am. Chem. Soc.*, 1982, **104,** 1846; G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1981,** 1204.

[14] A. P. Sattelberger *et al., Inorg. Chem.*, 1982, **21,** 4179.

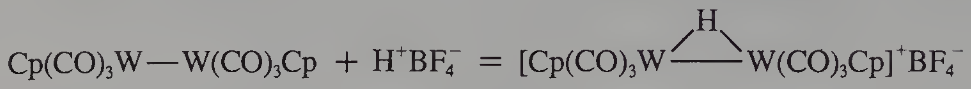
strong acids with noncoordinating anions, for example,

$$Cp_2MoH_2 + H^+BF_4^- = Cp_2MoH_3^+BF_4^-$$

$$Fe(CO)_3(PPh_3)_2 + H_2SO_4 \longrightarrow HFe(CO)_3(PPh_3)_2^+HSO_4^-$$

$$Co(CO)_4^- + H^+ \rightleftharpoons HCo(CO)_4$$

$$Ni[P(O\text{-}p\text{-tol})_3]_4 + H^+ \rightleftharpoons HNi[P(O\text{-}p\text{-tol})_3]_4^+$$



$$Cp(CO)_3W{-}W(CO)_3Cp + H^+BF_4^- = [Cp(CO)_3W\overset{H}{\frown}W(CO)_3Cp]^+BF_4^-$$

Weak acids such as H_2O, MeOH, or MeCN can also in some cases add oxidatively, for example,

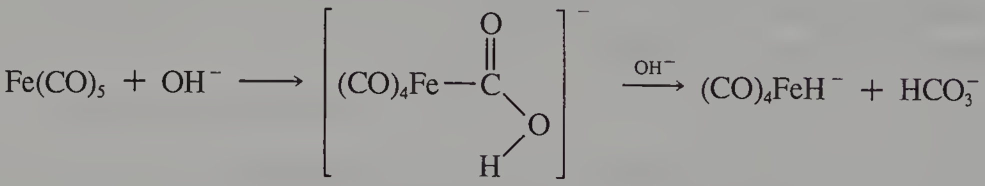
$$Ru(styrene)_2(PPh_3)_2 + H_2O = RuH(OH)(PPh_3)_2 + 2\ styrene$$

$$WH_2(PMe_3)_5 + MeOH = WH_3(OMe)(PMe_3)_4 + PMe_3$$

4. *Intramolecular Hydrogen Transfers.* There are many examples of the formation of M—H bonds by intramolecular transfers. These can occur in the decomposition of metal alkyls (Chapter 25) and in the so-called *ortho*-metallation reaction in which M—H and M—C bonds are formed (Section 27-9), for example,

$$IrH(CO)(PPh_3)_3 \xrightarrow{\Delta} Ir(H)_2CO(PPh_3)_2(o\text{-}C_6H_4PPh_2)$$

Intramolecular H-transfers occur in nucleophilic attacks on CO[15a] (Section 22-8), for example,



$$Cr(CO)_6 + OH^- \longrightarrow [(\mu\text{-H})Cr_2(CO)_{10}]^-$$

Another example is the oxidative addition:

$$Mo(N_2)_2(dppe)_2 + MeCH{=}CH_2 \rightleftharpoons MoH(\eta^3\text{-}CH_2CHCH_2)(dppe)_2 + 2N_2$$

5. *Intermolecular Hydride Transfers.* A common way of making hydrido bridged species is the interaction of a hydride complex with another complex, one being anionic or cationic and one having solvent occupied sites or easily displaced ligands.[15b] Some examples are

$$[CpMo(CO)_3]^+ + HMo(CO)_3Cp \longrightarrow \{[Cp(CO)_3Mo]_2(\mu\text{-H})\}^+$$

$$Cp_2MoH_2 + [Rh(H)_2(PR_3)_2(Me_2CO)]^+ \xrightarrow{-Me_2CO} [Cp_2Mo(\mu\text{-H})_2Rh(H)_2(PR_3)_2]^+$$

$$[HCr(CO)_5]^- + AuCl(PPh_3) \xrightarrow{-Cl^-} (Ph_3P)Au(\mu\text{-H})Cr(CO)_5$$

[15a] T. J. McNeese *et al., Inorg. Chem.,* 1985, **24,** 3465.

[15b] See, for example, L. M. Venanzi *et al., Organometallics,* 1986, **5,** 1785.

24-3. Chemical Behavior of Hydrido Compounds

The hydride ligand has both a very high trans influence (shown by long M—L distances in *trans* H—M—L compounds) and also a strong trans effect which means that ligands in trans positions to H commonly undergo facile substitution.

1. *Acidity.* The factors that affect the protonic or hydridic behavior of compounds with M—H bonds are generally similar to those determining this behavior in non-transition metal compounds as exemplified by BH_3, CH_4, NH_3, OH_2, and FH.[1b,16a] The most important factors in complexes are the strength of the M—H bond and the nature of the ligands. For a reaction

$$L_nMH \rightleftharpoons L_nM^- + H^+$$

the key is the stability of the conjugate base, that is, the electronic structure of the anion. Strong π bonding of the ligand L will stabilize ML_n^- by delocalization of negative charge and this is why the most acidic hydrides are those with CO or PF_3 as ligands. Substitution of CO by a poorer π acid can dramatically reduce the pK_A as the following examples in H_2O show:

$HCo(CO)_4$	Strong acid	$HV(CO)_6$	Strong acid
$HCo(CO)_3(PPh_3)$	$pK_A = 7.0$	$HV(CO)_3PPh_3$	$pK_A = 6.8$

There are, of course hydrides that are essentially neutral, for example, $HRuCl(CO)_2(PPh_3)_2$, while the basic hydrides either have lone pairs as in Cp_2ReH mentioned earlier, or are electron rich as in the d^8 and d^{10} complexes such as those of Ru^0, Rh^I, or Pt^{II} that can undergo not only protonations but oxidative-additions of a variety of molecules (Chapter 27).

Three other points can be noted:

(a) In all discussions of acidity, it must always be remembered that the acidity depends on the solvent[16b] and the extent, consequently, of dissociation.

(b) The hydrides of early transition metals tend to be hydridic; 2nd and 3rd row *d* metal compounds are usually less acidic than their 1st row analogues.

(c) Bridging hydrides are more acidic than terminal hydrides on the same metal atom in a polynuclear compound.

2. *Hydrogen Migration Reactions.* Metal hydrides undergo a very wide range of hydrogen migration reactions sometimes called insertion reactions (Chapter 27), which is not surprising considering that in organic chemistry H is known to migrate much better than, for example, CH_3. A representative

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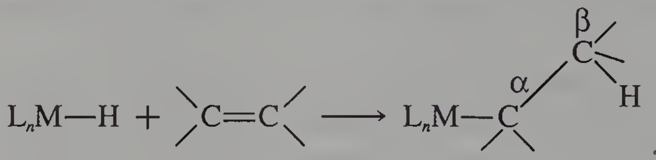
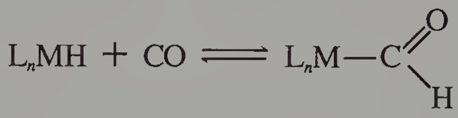
[16a] B. E. Bursten and M. G. Galter, *Organometallics*, 1984, **3**, 895.

[16b] J. R. Norton *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 2257.

selection is listed in Fig. 24-2. Perhaps the most important of these is that involving C=C bonds to generate metal-carbon bonds by the so-called β-hydride transfer—a 1,2 insertion—that is discussed in more detail in Sections 24-8, 25-4, 25-5, and 27-8.



In view of the importance of the insertion of CO into M—R bonds to give acyls (Chapter 27) and of direct conversions of CO and H_2 directly into organic products (Chapter 28) there has been considerable speculation on the possibility of an initial reaction to give a formyl



This reaction is also discussed in detail in Section 27-6. Although insertions

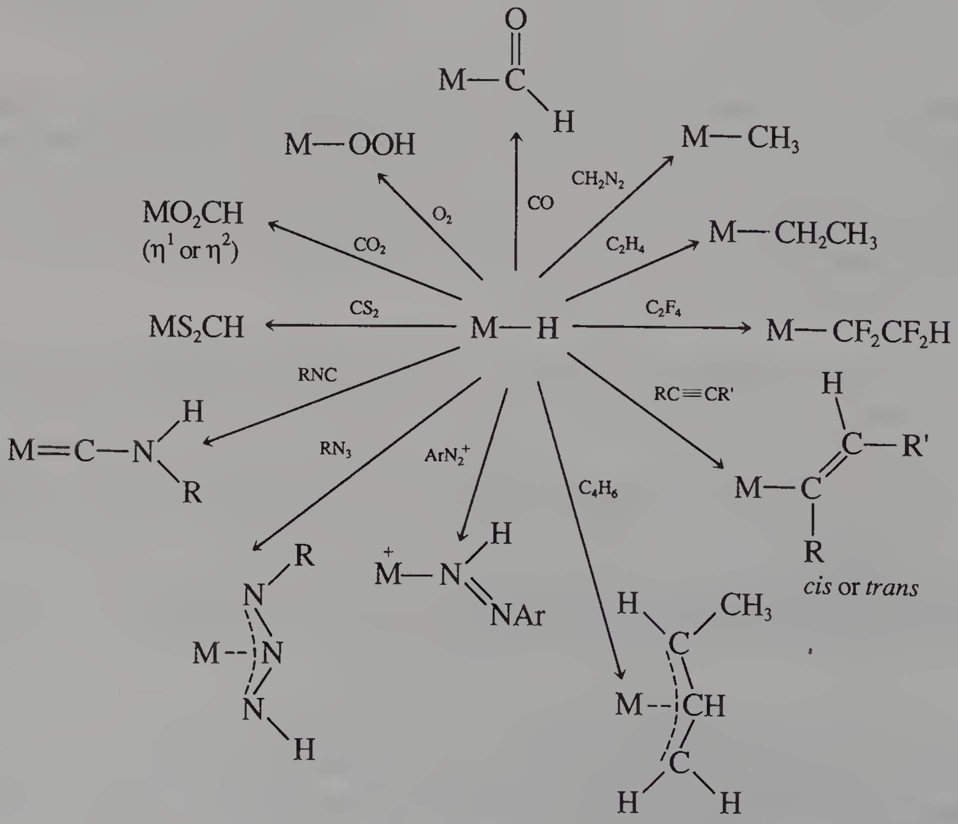


FIG. 24-2. Some intramolecular hydrogen transfer or insertion reactions. These can be designated as 1,1, 1,2, 1,3, or 1,4 shifts depending on which atom of the substrate the H atom migrates to. Bridging hydrides can also undergo insertions.

with SO_2 are established, further reactions can also occur here:[17]

$$\text{*CpMo(CO)}_3\text{H} \xrightarrow{SO_2} \text{*CpMo(CO)}_3\text{SO}_2\text{H} + [\text{*CpMo(CO)}_3]_2(\mu\text{-S}_2\text{O}_4)$$
$$\text{*Cp}_2\text{MoH}_2 \xrightarrow{SO_2} \text{*Cp}_2\text{MoS}_2\text{O}_3 + \text{H}_2\text{O}$$

Transfers from hydrido carbonylate anions are discussed in Section 24-6.

3. *Other Reactions.* Interaction of L_nMH with halogens or halogen compounds usually gives the corresponding halides. The radical reaction with CCl_4

$$L_nMH + CCl_4 \longrightarrow L_nMCl + CHCl_3$$

can be used as a simple test for the presence of M—H bonds; the reactivity decreases $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$.

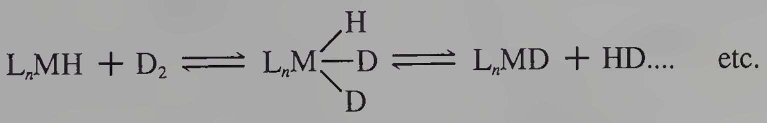
Hydride abstraction is achieved by use of trityltetrafluoroborate, for example,

$$RuH_2(PR_3)_4 + Ph_3CBF_4 \longrightarrow [RuH(PR_3)_4]BF_4 + Ph_3CH$$

Other electrophiles such as H^+ or Ag^+ may behave similarly. Hydrogen atoms can also be removed by strong bases, KH, LiR, KOMe, $LiNR_2$, and so on, to give, formally, anionic species although these are often associated:

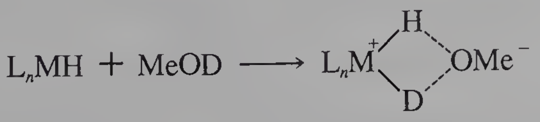
$$Cp_2ReH + LiBu \longrightarrow Li[ReCp_2] + BuH$$
$$CoH[P(OMe)_3]_4 + KH \longrightarrow K\{Co[P(OMe)_3]_4\} + H_2$$
$$H_4Ru_4(CO)_{12} + OMe^- \rightleftharpoons [H_3Ru_4(CO)_{12}]^- + MeOH$$

Exchange reactions between M—H and H_2, H_2O, and ROH proceed in some cases by oxidative-addition reactions



$$L_nMH + D_2 \rightleftharpoons L_nM(H)(D)_2 \rightleftharpoons L_nMD + HD\text{....} \qquad \text{etc.}$$

but in others by protonation[18a]



$$L_nMH + MeOD \longrightarrow L_n\overset{+}{M}(H)(D)\cdots OMe^-$$

Elimination reactions between metal hydrides and metal alkyls, alkoxides or dialkylamides[18b] can generate metal–metal bonds in reactions of the type

$$L_nMH + L_mM'R \longrightarrow L_nMM'L_m + RH$$

[17] G. L. Kubas and R. R. Ryan, *Polyhedron,* 1986, **1/2,** 473.

[18a] P. L. Gaus *et al., J. Am. Chem. Soc.,* 1984, **106,** 4752.

[18b] See J. R. Norton *et al., J. Am. Chem. Soc.,* 1987, **109,** 3945 and also ref. 26b.

24-4. Mononuclear Polyhydrides

A large number of neutral, cationic, or anionic compounds that have 3 to 9 hydrogen atoms are called polyhydrides; they usually have tertiary phosphines or Cp groups as ligands but some homoleptic hydrido anions are known, as discussed later. Some representative polyhydrides are Cp_2TaH_3, $CrH_4(dmpe)_2$, $WH_6(PR_3)_3$, $ReH_8(PR_3)^-$, and $RuH_6(PR_3)_2$. The phosphine complexes have been especially well studied and numerous structures determined.[19] Note, however, that some polyhydride species may need to be reformulated with coordinated H_2 molecules (see Section 24-7).

As well as by $LiAlH_4$ or $NaBH_4$ reductions of phosphine or other metal halides under H_2, with hydrolysis of intermediate boro- or aluminohydride complexes, polyhydrides can be obtained by hydrogenolysis of high-valent alkyls or olefin complexes. The polyhydrides may be obtained in various oxidation states up to the highest for a given element; for example, there are species from $ReH_3(PR_3)_4$ to $[ReH_8(PR_3)]^-$. Most of the polyhydrides are nonrigid according to nmr studies. The hydride $TaH_4(dmpe)_2$[20] is paramagnetic (cf. ref. 5).

Polyhydrides undergo several unusual reactions.

1. Attack by *electrophilic reagents* such as H^+, Cu^+, Ag^+, or $HgCl_2$ can give cationic species some of which have $M(\mu\text{-}H)M'$ bonds.[21] The following are examples:

$$WH_6(PR_3)_3 \xrightarrow[MeCN]{HBF_4} [WH_2(MeCN)_3(PR_3)_3]^{2+} + 2H_2$$

$$IrH_3(PR_3)_3 \underset{NEt_3}{\overset{HBF_4}{\rightleftharpoons}} IrH_4(PR_3)_3^+ \underset{H_2}{\overset{N_2,\ CH_2Cl_2}{\rightleftharpoons}} IrH_2(PR_3)_3^+$$

$$ReH_7(PR_3)_2 \xrightarrow{AgPF_6} \{Ag[ReH_7(PR_3)_2]_2\}^+$$

$$IrH_3(PR_3)_2 \xrightarrow[MeCN]{CuPF_6} \{Cu(\mu\text{-}H)_2[IrH(PR_3)_2]_2\}^+$$

$$OsH_6(PR_3)_2 \xrightarrow{HgCl_2} Cl_2HgOsH_6(PR_3)_2$$

For coordinately unsaturated hydrides, protonation can occur at the metal,

$$WH_4(PR_3)_4 \xrightarrow{H^+} [WH_5(PR_3)_4]^+$$

but for the coordinately saturated ones such as $WH_6(PR_3)_3$ this is *not* possible and protonation may occur at the M—H bond to give a linear or bent M—H---H^+ or possibly $M(\eta^2\text{-}H_2)^+$ species, which then loses H_2. Note also that BF_4^- can undergo F^- abstraction leading to hydrido–fluoro complexes.

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[19] For references see R. Poilblanc *et al., Organometallics,* 1985, **4,** 1722, 1727.

[20] A. P. Sattelberger *et al., Inorg. Chem.,* 1984, **23,** 1718.

[21] R. A. Walton *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 67; R. H. Crabtree *et al., Inorg. Chem.,* 1984, **23,** 354; K. G. Caulton *et al., J. Am. Chem. Soc.,* 1985, **107,** 1759; N. G. Connelly *et al., J. Chem. Soc. Dalton Trans.,* **1984,** 2003.

2. *Nucleophilic reagents* such as NaH, KH, or LiR can give anionic species:

$$WH_6(PMe_3)_3 \xrightarrow{\text{NaH + (15-C-5)}} [Na(15\text{-}C\text{-}5)][WH_5(PMe_3)_3]$$

$$OsH_4(PR_3)_3 \xrightarrow{\text{KH, THF}} K[OsH_3(PR_3)_3]$$

This potassium salt[22] has $K_2Os_2H_6(PR_3)_6$ dimers with the ion pair monomer bound into dimers by a H bridge from K^+ to one H in the next unit,[22] while $Li[WH_5(PMe_3)_3]$[23] is a tetramer (Fig. 24-3).

3. Photolysis of polyhydrides[24] causes loss of H_2, and the reactive species so formed may pick up other ligands, for example,

$$MoH_4(\text{diphos})_2 \xrightarrow[N_2]{h\nu} Mo(N_2)_2(\text{diphos})_2 + 2H_2$$

$$ReH_5(PR_3)_3 \xrightarrow{h\nu} ReH_2(PR_3)_2 \xrightarrow{\text{COT}} (\eta^4\text{-}C_8H_{10})ReH_3(PR_3)_2$$

Cyclometallation of the phosphine can also occur.

4. Although polyhydrides are usually stable to hydrolysis, $^*CpTaH_4(dmpe)$ is hydridic and, like B or Al hydrides, is solvolyzed in methanol to give $^*CpTa(OMe)_4$.[25]

5. Interaction of Al_2Me_6 with $ReH_5(PR_3)_3$ or $ReH_7(PR_3)$ gives rise to aluminate species that have $Re(\mu\text{-}H)_3AlMe_2$ or $Re(\mu\text{-}H)_2AlMe_2$ bridges (cf.

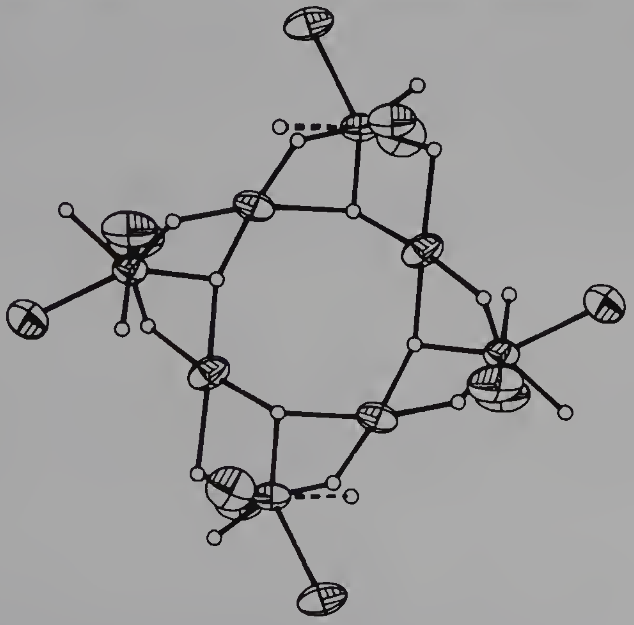

FIG. 24-3. The structure of the petroleum soluble compound $\{Li[WH_5(PMe_3)_3]\}_4$ showing W(μ-H)Li and W(μ_3-H)Li bridges. Each W atom has two terminal hydrides and three PMe_3 ligands (Me groups omitted). Dashed lines indicate unlocated hydrides. (Reproduced by permission from G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1987**, 837.)

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[22] K. G. Caulton *et al., J. Am. Chem. Soc.*, 1985, **107,** 5111.
[23] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 837.
[24] See, for example, K. G. Caulton *et al., Organometallics,* 1985, **4,** 514.
[25] J. M. Mayer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1982, **104,** 2157.

AlH_4^- complexes Section 24-10)[26a]; eliminations with alkoxides, e.g., Cu(OMe), can also give mixed metal species.[26b]

6. As with other hydrides, insertion reactions occur with small molecules. Thus $WH_6(PMe_3)_3$ reacts rapidly with CO_2 to give $WH_2(\eta^1\text{-}O_2CH)(\eta^2\text{-}O_2CH)(PMe_3)_3$, which is fluxional for the uni- and bidentate formato groups,[27] probably via initial loss of H_2 to give $WH_4(PMe_3)_3$.

7. Several polyhydride species especially of Re and Ir can participate in so-called alkane C—H activation reactions (Section 27-9). Thus $Ir(H)_5(P\textit{i}\text{-}Pr_3)_3$ promotes H—D exchange with deuterobenzene or 3,3-dimethylbutene[28] while rhenium hydrides can dehydrogenate cycloalkanes, react with alkenes, and so on.[29] The hydride $Ir(H)_5(P\textit{i}\text{-}Pr_3)_3$ will convert *n*-hexane into hex-1-ene at 45°C using 3,3-dimethylbutene as a hydrogen acceptor.

24-5. Homoleptic Polyhydrido Anions

The first well-characterized hydrido anion was $[ReH_9]^{2-}$, Fig. 24-4, made by reduction of ReO_4^- with Na in ethanol. In 1926, however, Weichselfelder prepared some little understood species by the interaction of Grignard reagents with metal halides. The iron complex, has been characterized by X-ray crystallography and shown to be $FeH_6(MgX)_4(THF)_8$, which contains the octahedral $[FeH_6]^{4-}$ ion [Fig. 24-5(a)]. This ion, which is isoelectronic with ReH_9^{2-} is surrounded by a tetrahedral array of solvated $MgX(THF)_2^+$ units lying over four of the octahedral faces. The Mg---HFe distances, 2.045 Å, suggest ionic bonding.[30]

A variety of solvent insoluble hydrides have been obtained by interaction of metals such as Ru, Co, Rh, Ni, or Pt with LiH or NaH at high tempera-

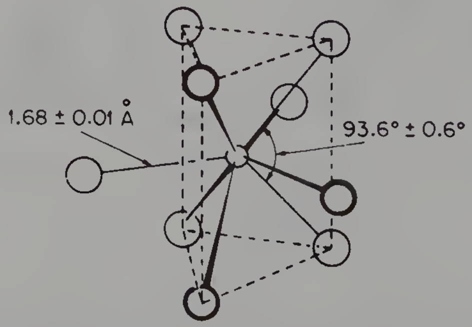
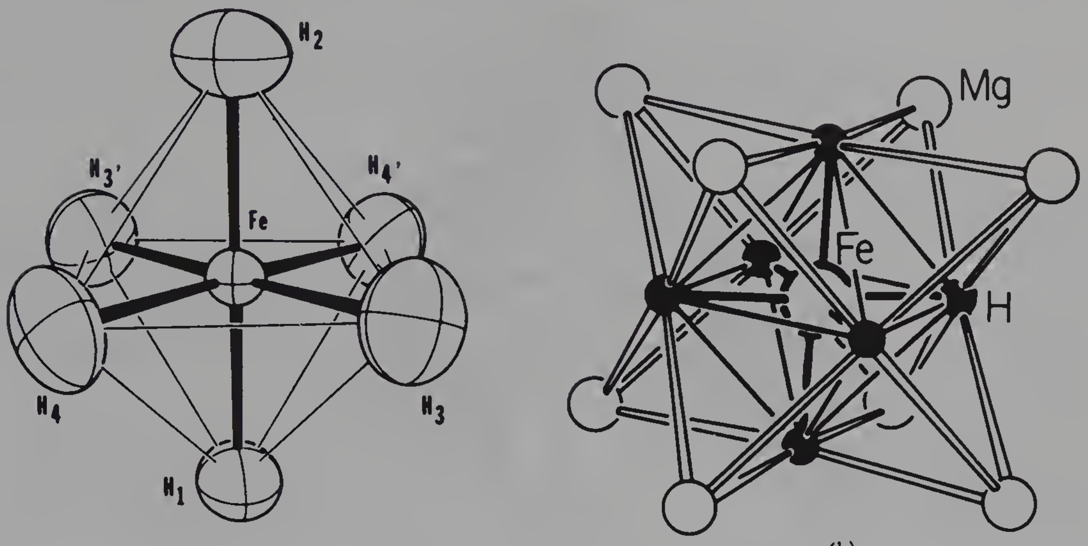


FIG. 24-4. The structure of ReH_9^{2-}; the Re—H distance of 1.68 Å is consistent with the sum of single bond radii (Re = 1.28 Å).

[26a] K. G. Caulton *et al., J. Am. Chem. Soc.*, 1984, **106,** 8128.
[26b] K. G. Caulton *et al., J. Am. Chem. Soc.*, 1987, **109,** 3489.
[27] D. Lyons and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, **1985**, 587.
[28] J. W. Faller and H. Felkin, *Organometallics*, 1985, **4,** 1488.
[29] H. Felkin *et al., Tetrahedron Lett.*, **1985,** 1999.
[30] R. O. Moyer, Jr., *et al., Inorg. Chem.*, 1985, **24,** 3890.



(a) (b)

FIG. 24-5. (a) The structure of the $[FeH_6]^{4-}$ ion in $FeH_6(MgX)_4(THF)_8$. [Reprinted with permission from R. Bau *et al., Inorg. Chem.*, 1984, **23**, 2833. Copyright (1984) American Chemical Society.] (b) The structural unit of Mg_2FeH_6 which has the K_2PtCl_6 type structure. [Reprinted with permission from K. Yvon *et al., Inorg. Chem.*, 1984, **23**, 1953. Copyright (1984) American Chemical Society.]

tures.[30,31] Some of these are nonstoichiometric but others are stoichiometric and believed to contain ions such as square $[PtH_4]^{2-}$ and octahedral $[RuH_6]^{4-}$. The green crystalline analogue of the soluble iron hydride, Mg_2FeH_6, has octahedral low-spin $[FeH_6]^{4-}$ ions according to Mössbauer, Raman and ir spectra [Fig. 24-5(b)]. The ternary hydride systems are of interest because of their potential for hydrogen storage (Chapter 3).

24-6. Carbonyl Hydrides[1b,32] and Hydrido Anions

As noted earlier $HCo(CO)_4$ and $H_2Fe(CO)_4$ were the first known hydrides. Carbonyl hydrides and carbonylate anions have been intensively studied in part because they are intermediates in many metal catalyzed reactions involving CO and H_2. The structure of $HMn(CO)_5$ has been shown in Fig. 24-1.

Some compounds and their properties are shown in Table 24-1. The iron and cobalt carbonyl hydrides form pale yellow solids or liquids at low temperatures and in the liquid state begin to decompose above ~ −10 and −20°C, respectively; they are relatively more stable in the gas phase, however, particularly when diluted with carbon monoxide. They have revolting odors and are readily oxidized by air. The carbonyl hydride, $HMn(CO)_5$, is appreciably more stable.

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[31] W. Bronger *et al., Z. Anorg. Allg. Chem.*, 1984, **516**, 35; *J. Less-Common. Met.*, 1986, **116**, 9; K. Yvon *et al., Inorg. Chem.*, 1985, **24**, 4177, 1986, **25**, 3590.

[32] C. J. Eyermann and A. Chung-Phillips, *J. Am. Chem. Soc.*, 1984, **106**, 7437.

TABLE 24-1
Some Carbonyl Hydrides and Their Properties

Compound	Form	Mp (°C)	M—H stretching frequency (cm^{-1})	^1H nmr δ(ppm)	Comment
$HMn(CO)_5$	Colorless liquid	−25	1783	−7.5	Stable liquid at 25°C; weakly acidic
$H_2Fe(CO)_4$	Yellow liquid, colorless gas	−70		−11.1	Decomposes at −10°C giving H_2 + (red)$H_2Fe_2(CO)_8$
$H_2Fe_3(CO)_{11}$	Dark red liquid			−15.0	
$HCo(CO)_4$	Yellow liquid, colorless gas	−26	~1934	−10.0	Decomposes above mp giving H_2 + $Co_2(CO)_8$
$HW(CO)_3(\eta\text{-}C_5H_5)$	Yellow crystals	69	1854	−7.5	Stable short time in air
$[HFe(CO)_3(PPh_3)_2]^+$	Yellow			−7.6	Formed from $Fe(CO)_3(PPh_3)_2$ in conc H_2SO_4

The hydrides are usually obtained by acidification of carbonylate or substituted carbonylate anions (Section 22-6). In the case of highly reduced anions[33] like $Na_3Ta(CO)_5$, interaction with BH_4^- in EtOH–THF may be adequate to give $[HM(CO)_5]^{2-}$.

Polynuclear cluster hydrides can be made similarly, but special methods may be used, for example,[34]

$$Fe(CO)_5 + Et_3N \xrightarrow{H_2O,\ 80°C} [Et_3NH][HFe_3(CO)_{11}]$$

$$[HFe_3(CO)_{11}]^- + Fe(CO)_5 \longrightarrow [HFe_4(CO)_{13}]^- + 3CO$$

$$[HRu(CO)_4]^- \xrightarrow{CO,\ H_2O} [HRu_3(CO)_{11}]^-$$

$$[HFe(CO)_4]^- + (THF)Mo(CO)_5 \longrightarrow [HFeMo(CO)_9]^-$$

The anionic hydrido carbonyls[35a] have been much studied because of their intermediacy in catalytic reactions like the water gas shift, reduction of organic substances, and other reactions.[35b] Thus chromium group hydrides $[HM(CO)_4PR_3]^-$ are highly efficient H-transfer agents and for reactions with alkyl halides a reactivity order was established: *cis*-$[HW(CO)_4PR_3]^-$ > *cis*-$[HCr(CO)_4PR_3]^-$ > $[HW(CO)_5]^-$ > $[CpV(CO)_3H]^-$ > $[HCr(CO)_5]^-$ > $[HRu(CO)_4]^-$ > *trans*-$HFe(CO)_3PR_3$ ≫ $[HFe(CO)_4]^-$, which resembles the order of nucleophilicity of carbonylate anions due to R. B. King (Section 22-6).

Ion-pair formation with the cation is important for both carbonylate and

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[33] G. F. P. Warnock and J. E. Ellis, *J. Am. Chem. Soc.*, 1984, **106,** 5016.

[34] See S. G. Shore *et al., Organometallics,* 1984, **3,** 201; M. Y. Darensbourg *et al., J. Am. Chem. Soc.,* 1984, **106,** 456.

[35a] See, for example, M. Y. Darensbourg *et al., J. Am. Chem. Soc.,* 1986, **108,** 2617; 1987, **109,** 3313.

[35b] See, for example, J. C. Kao *et al., Organometallics,* 1985, **4,** 83.

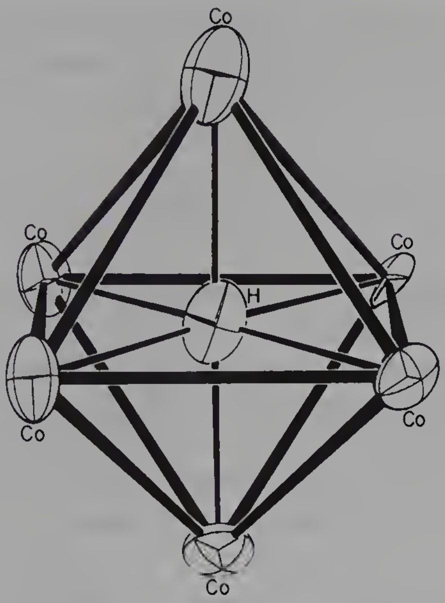

FIG. 24-6. The structure of the HCo_6 core of the ion $[HCo_6(CO)_{15}]^-$ by neutron diffraction, where H is encapsulated Co—H = 1.8 Å. [Reprinted with permission from R. Bau *et al., J. Am. Chem. Soc.,* 1981, **103,** 1458. Copyright (1981) American Chemical Society.]

hydrido carbonylate anions and in many reactions may determine the reaction pathway.

On treatment with amines, $HCo(CO)_4$ has been shown to form a strong ion pair $[R_3NH][Co(CO)_4]$[36a] and this fact, coupled with the ability of NH_4^+ or R_3NH^+ ions to protonate[36b] metal species may account for the importance of amines as cocatalysts that promote carbonylation reactions, one example being the rhodium catalyzed synthesis of acetic anhydride (Chapter 28).

The cluster hydrido anions are discussed in more detail in Chapter 23, but suffice it to say here that they may have M—H, (μ_2—H), or (μ_3—H) groups and that edge—terminal H-exchanges occur.

In certain clusters, for example, the ion $[HCo_6(CO)_{15}]^-$ made by protonation of $[Co_6(CO)_{15}]^{2-}$, the H-atom is in the center of a Co_6 unit[37] (Fig. 24-6). In rhodium clusters, for example, $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$, $n = 2$ and 3, one of the hydrogen atoms is encapsulated and ^1H nmr spectra show that this atom interacts with all 13 Rh atoms (^{103}Rh, spin $\frac{1}{2}$) and is thus migrating within the cluster.

24-7. Molecular Hydrogen Compounds

The possibility of binding of H_2 molecules was considered many years ago by E. Singleton in connection with the nature of "$RuH_4(PPh_3)_2$", which readily lost H_2 in its reactions. Also, the oxidative-addition reaction of molecular hy-

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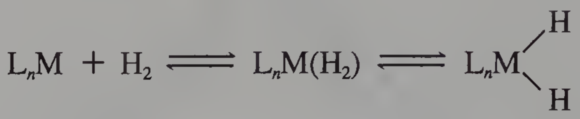
[36a] F. Calderazzo *et al., J. Chem. Soc. Chem. Commun.,* **1981,** 181.
[36b] L. Manojlovic-Muir *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 1725.
[37] R. Bau *et al., J. Am. Chem. Soc.,* 1981, **103,** 1458.

drogen with many d^8 complexes such as $IrCl(CO)(PPh_3)_2$ (Chapter 27), implied a close approach of the H_2 molecule to the metal atom before cleavage of the H—H bond occurs to form two new M—H bonds.[38a]



$$L_nM + H_2 \rightleftharpoons L_nM(H_2) \rightleftharpoons L_nM\begin{smallmatrix}\diagup H\\ \diagdown H\end{smallmatrix}$$

Since the recent recognition of molecular hydrogen complexes such equilibria are now known to be feasible.[38b]

As well as a variety of unstable species characterized spectroscopically at low temperature[38c] many stable η^2-H_2 complexes are now established. These may be neutral or cationic but are invariably octahedral.[39a,b]

The first one, by G. J. Kubas, $W(\eta^2\text{-}H_2)(CO)_3(P\textit{i}\text{-}Pr_3)_3$,[39a] Fig. 24-7, was made by reduction of the corresponding halide under H_2. Neutron diffraction gives the H—H distance as 0.84 Å (0.75 Å by X-ray diffraction), which can be compared with the distance of 0.74 Å in molecular hydrogen. The ir stretch for H—H is at 2690 cm^{-1} and the ^1H nmr peak ~ -4 ppm.

Solid state magic-angle spinning nmr spectra allow H—H distances to be estimated[40a] and show that rapid rotation of H_2 about the W—(H_2) bond may occur. Solution nmr spectra allow a distinction to be made between M—H and $M(H_2)$ since the ^1H nuclei in M—H_2 relax faster (T_1) than in M—H by a factor of ~500.[40b]

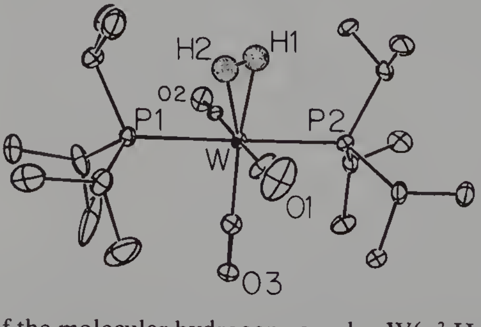


FIG. 24-7. The structure of the molecular hydrogen complex $W(\eta^2\text{-}H_2)(CO)_3(P\textit{i}\text{-}Pr_3)_2$. Hydrogen atoms on phosphine omitted. [Reprinted with permission from G. J. Kubas *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 451. Copyright (1984) American Chemical Society.] (See also ref. 39a.)

[38a] See, for example, R. Eisenberg *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 5315. See also Y. Jean *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 6587; P. J. Hay, *J. Am. Chem. Soc.*, 1987, **109**, 705.

[38b] C. Bianchini *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 5548.

[38c] See, for example, M. Poliakoff *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 3645.

[39a] G. G. Kubas *et al.*, *Polyhedron*, 1986, **5**, 473; *J. Am. Chem. Soc.*, 1986, **108**, 1339, 2294, 7000.

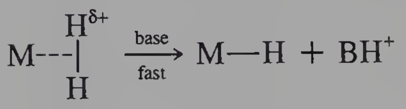
[39b] R. H. Morris *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 5581 and references therein; F. M. Conroy-Lewis and S. J. Simpson, *J. Chem. Soc., Chem. Commun.*, **1986**, 506; A. R. Siedle *et al.*, *Inorg. Chem.*, 1986, **25**, 3412.

[40a] K. W. Zilm, *J. Am. Chem. Soc.*, 1986, **108**, 7837; R. D. Farlee *et al.*, *Inorg. Chem.*, 1987, **26**, 1381.

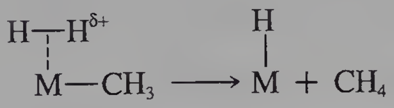
[40b] R. H. Crabtree *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 3124, 4032.

It can now be asked whether polyhydrides have all M—H bonds or whether η^2-H_2 groups are involved. In some cases[40c], it is clear that M—H bonds alone are present, for example, in $Os(H)_4(PPh_3)_3$ and $Ir(H)_5\,[P(cyclohexyl)_3]_3$. Other polyhydride compounds have been shown to contain η-H_2 groups, examples being $Ru^{II}(H)_2(H_2)(PPh_3)_3$ and $[Ir^{III}(H)_2(H_2)_2(Pcy_3)_2]^+$. It is possible that there may be differences in the solid state (M—H) and in solution ($M—H_2$) and examples may be $CpNbH_3$ and $WH_6(PPh_2i\text{-}Pr)_3$. The bonding as $M\leftarrow H_2$ is evidently favored by low π basicity and strong σ acidity of the ML_n system: that is the metal is rather electron poor.

It is quite possible that dihydrogen complexes as such are intermediates in oxidative-addition reactions of H_2 and in reactions such as[40d]



$\mathrm{M}\text{---}\overset{\mathrm{H}^{\delta+}}{\underset{\mathrm{H}}{|}} \xrightarrow[\text{fast}]{\text{base}} \mathrm{M{-}H} + \mathrm{BH}^+$ for example $\mathrm{RuCl_2(PPh_3)_3} \xrightarrow{\mathrm{H_2,\ Et_3N}} \mathrm{RuClH(PPh_3)_3}$

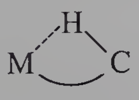


$\overset{\mathrm{H{-}H}^{\delta+}}{\mathrm{M{-}CH_3}} \longrightarrow \overset{\mathrm{H}}{\overset{|}{\mathrm{M}}} + \mathrm{CH_4}$ for example $\mathrm{WMe_6(PMe_3)} \xrightarrow{\mathrm{H_2,\ PMe_3}} \mathrm{WH_4(PMe_3)_4}$

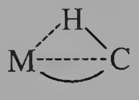
24-8. Metal–Hydrogen Interactions with C—H Groups[1d,41]

There is now compelling evidence that transition metal complexes may bind to C—H (or Si—H and N—H) groups on ligands to give M···H—C "hydrogen-bonding" type interactions. The term "agostic" has been coined by M. L. H. Green for such hydrogen atoms. These interactions may well precede hydrogen transfers from ligands to metals to form M—H bonds in reactions such as *o*-metallations and alkyl decomposition reactions, either intra- or intermolecular, whether as actual intermediates or merely transition states.

There are two main types of M···H—C interactions referred to as open (24-VII) or closed (24-VIII), the difference being that in the latter case there is also M—C interaction.



(24-VII)



(24-VIII)

1. *Open Interactions.*[41a,b] The interaction appears to arise between an electron deficient metal center and a C—H bond of an alkyl group or a phenyl group. Examples of *ortho* hydrogen atoms on phenyl rings of a phosphine being near to a metal and occupying a coordination site have long been known. An early example was $RuCl_2(PPh_3)_2$ (16*e*) where interaction with C—H would tend to move the complex to an 18*e* configuration (24-IX). More recently

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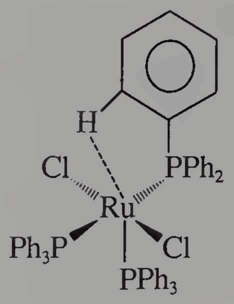
[40c] See, e.g., R. H. Morris *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 3780.

[40d] R. H. Crabtree *et al.*, *Inorg. Chim. Acta*, 1986, **125**, L7.

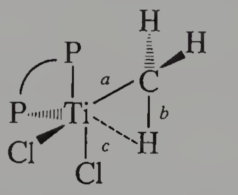
[41a] O. Eisenstein and Y. Jean, *J. Am. Chem. Soc.*, 1985, **107**, 1177; 1986, **108**, 1457.

[41b] N. J. Fitzpatrick and M. A. McGinn, *J. Chem. Soc. Dalton Trans.*, **1985**, 1637.



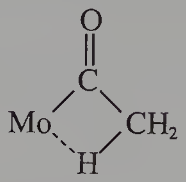
(24-IX)

severe distortions of alkyl groups in compounds such as $dmpeCl_3TiCH_3$[42] (24-X), the acyl $(dtc)_2(CO)(PMe_3)_2MoCOCH_3$ (24-XI),[43] bridging alkyl groups,[44] for example in $Mn_2(CH_2R)_2(\mu\text{-}CH_2R)_2(PMe_3)_2$ (24-XII), and benzyls, have been observed.

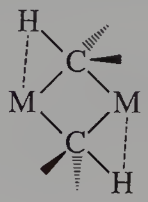


$a = 2.149$ Å
$b = 1.00$ Å
$c = 2.03$ Å

(24-X)



(24-XI)



(24-XII)

Such interactions—or *rather the distortions* and apparent close approach to metal of a hydrogen—could be described as donation of electron density from the C—H bond to give a 3*c*-2*e* bond and some MO calculations purport to show this.[45]

However, (*a*) electron deficiency at the metal is *not* sufficient in itself as no M—H interactions are found in $(Me_3P)_2Mn(CH_2R)_2$,[44] (*b*) other theory[41a] indicates that the distorted structures arise from electronic reorganization of the M—C bonds rather than M···H—C interactions. It may also be noted that while low C—H stretching frequencies have sometimes been taken to indicate M···H—C interaction, there is a low C—H stretch (2750 cm^{-1}) in $Cp(Me_3P)_2VCH_3$ and $(CO)_5MnCH_3$ but *no* "agostic" hydrogen.[46] Distortions have also been observed in carbene and carbyne complexes[47] on clusters.

As mentioned earlier interactions of this type may precede H-transfer from alkyl groups to the metal. One case studied in detail[48] is the cluster $HOs_3(CO)_{10}CH_3$ (24-XIII) (Section 23-2) where there is an equilibrium be-

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[42] M. L. H. Green *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 1629.

[43] E. Carmona *et al., J. Am. Chem. Soc.*, 1984, **106,** 3214.

[44] See, for example, G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1983,** 2631; P. W. Jolly *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 555; R. H. Grubbs *et al., J. Am. Chem. Soc.*, 1986, **108,** 6402.

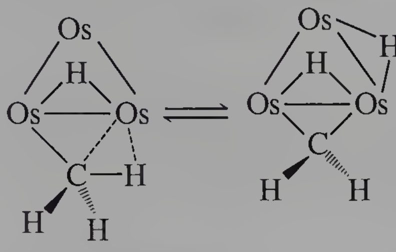
[45] K. Morokuma *et al., J. Am. Chem. Soc.*, 1984, **106,** 4625.

[46] J. H. Teuben *et al., Organometallics*, 1985, **4,** 946; M. A. Andrews *et al., J. Am. Chem. Soc.*, 1983, **105,** 2262.

[47] See, for example, T. P. Fehlner *et al., J. Am. Chem. Soc.*, 1985, **107,** 5563.

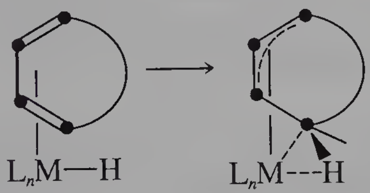
[48] J. R. Shapley *et al., J. Am. Chem. Soc.*, 1986, **108,** 1316.

tween an unsymmetric bridging methyl (most are symmetrical, Chapter 25) and a (μ-CH_2) hydride.



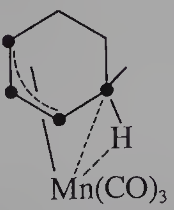
(24-XIII)

2. *Closed M···H—C interactions.*[41b] This class differs from the previous one in that it involves allylic or cycloalkenyl systems (Chapter 26) where the metal atom attempts to achieve an 18*e* configuration by M···H—C 2*e*-3*c* bond formation. Several metal diene hydrides do *not* possess the structure (24-XIV) but have the η^3-allyl structure (24-XV) with M···C and M···H—C inter-

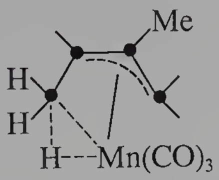


(24-XIV) (24-XV)

action. Examples[49] include protonated diene complexes such as (η^3-C_8H_{13})Ru[P(OMe)$_3$]$^+$, and manganese cyclohexenyls and allyls such as (24-XVI) and (24-XVII). These compounds have unusual features.

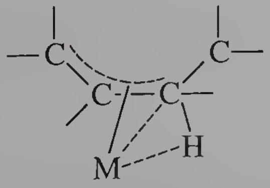


(24-XVI)



(24-XVII)

1. X-ray and neutron diffraction studies for the system (24-XVIII) show that the C—H bond is elongated and that both M···C and M···H distances



(24-XVIII)

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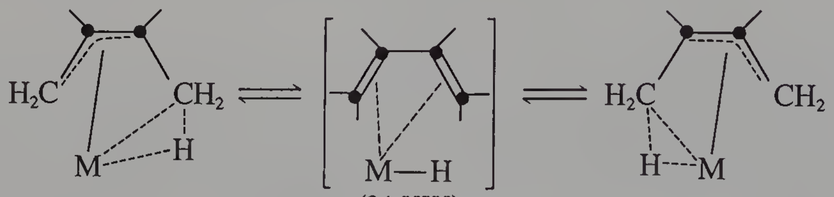
[49] M. Brookhart *et al., Organometallics,* 1985, **4,** 1365; *J. Am. Chem. Soc.,* 1985, **107,** 1443; E. Singleton *et al., Organometallics,* 1984, **3,** 1851; C. G. Kreuter *et al., Angew. Chem. Int. Ed. Engl.,* 1985, **24,** 502; D. L. Lichtenberger and G. E. Kellogg, *J. Am. Chem. Soc.,* 1986, **108,** 2560.

are short; thus in $\{(\eta^3\text{-}C_8H_{13})Fe[P(OMe)_3]_3\}^+$, Fe···H = 1.874 Å and the stretched C—H = 1.164 Å.[50]

2. The nmr studies show independent fluxional processes leading to exchange and equilibrations.

(a) Exchanges occur between H at the ends of the allylic system (24-XIX) via diene–hydride intermediates.

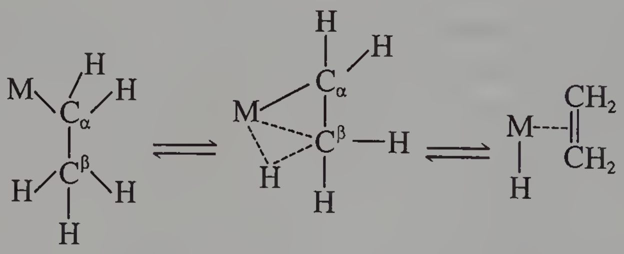


(24-XIX)

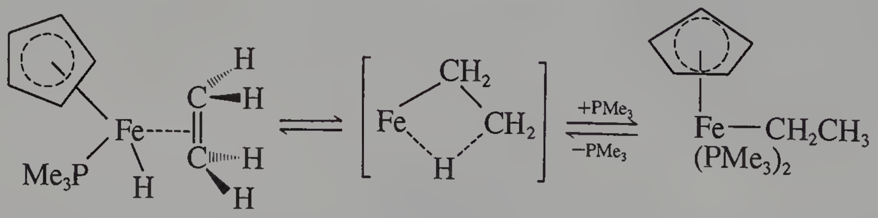
(b) In the ring systems the ML$_n$ group migrates around the ring via hydride shifts from ring to metal and a diene hydride intermediate.

(c) The L groups equilibrate by rotation.

Finally, note the close relation between these agostic systems and the β-hydride transfer in alkyl decompositions and synthesis from MH + olefin:



Two observations are of interest. First, there are exchanges between M—H and C_2H_4 that are considered to proceed via an agostic interaction[51]:



Second, a model for the transition state in this β-hydride transfer is provided by study of the salt isolated from the protonation of a cobalt ethylene complex;

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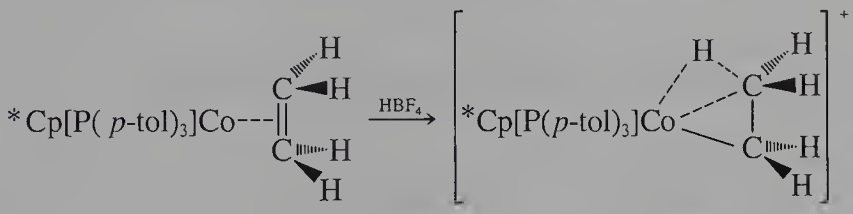
[50] J. M. Williams *et al.*, *J. Am. Chem. Soc.*, 1980, **102,** 981.

[51] M. L. H. Green and L-L. Wong, *J. Chem. Soc. Chem. Commun.*, **1984,** 1442; N. J. Hazel *et al.*, *J. Chem. Soc. Chem. Commun.*, **1984,** 1663.

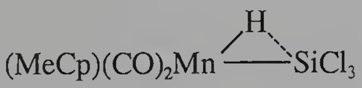
the nmr spectrum of the ion (24-XX) shows the unique H at δ −12.67 ppm and the crystal structure confirms the 3*c*-2*e* interaction.[52]



(24-XX)

24-9. Other M···H—X Interactions[1d,53]

Compounds are now known in which similar M···H—X interactions have been confirmed and 3*c*-2*e* bonds proposed. These include B, Si, Ge, and N



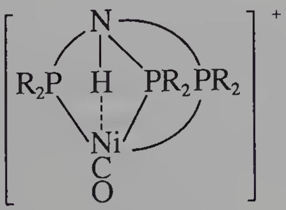
(24-XXI)

ligands. A specific example is (24-XXI), which has been compared directly with a "normal" $SiCl_3$ group in $CpFe(CO)_2SiCl_3$.[54a]

A bridged species[54b] with Ti—H—Si—Ti bonds is $Cp_2Ti(\mu\text{-}H)(\mu\text{-}H\text{—}SiHPh)TiCp_2$, but this bridge is more akin to those of BH_4^- or AlH_4^- complexes discussed later, or to the zinc complex 24-VI.

It may be noted in such silyls that the Si atom has vacant orbitals to accept electron density from M—H, thereby becoming essentially five-coordinate. The oxidative-addition of R_3SiH to transition metals involved in hydrosilation reactions of alkenes may well proceed by such transition states or intermediates.

Finally, there are some indications of M···H—N interactions in certain quaternized ligands. Thus in $[Ni(CO)npH]^+$, np = $N(CH_2CH_2PPh_2)_3$ (24-XXII) the N—H stretching frequencies seem to be lowered substantially.



(24-XXII)

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[52] R. B. Cracknell *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986,** 1005. See also M. J. McGlinchey *et al.*, *Organometallics,* 1987, **6,** 2201.

[53] U. Schubert *et al.*, *Organometallics,* 1987, **6,** 469; R. J. P. Corriu *et al.*, *Organometallics,* 1984, **3,** 1272; E. Singleton *et al.*, *Organometallics,* 1987, **6,** 2014.

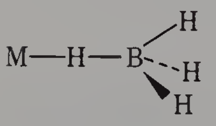
[54a] U. Schubert *et al.*, *Z. Anorg. Allg. Chem.*, 1984, **519,** 916.

[54b] J. F. Harrod *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 4059.

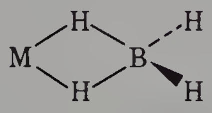
However, the N—H distance is normal but the Ni···H distance of 1.95 Å could indicate some weak interaction.[55a] There are also agostic M···X—C, X = F, Br, and I interactions.[55b]

24-10. Complexes of Borohydrides and Aluminohydrides

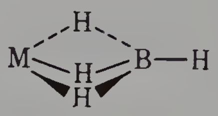
Borohydride Compounds.[1d,56] The *tetrahydridoborate ion* (BH_4^-) forms compounds with most metallic elements, acting as a 2, 4, or 6*e* donor, in species with M—H—B bridges of the types (a to c). There is, so far, only one example of side-on bonding as in (d).[57a]



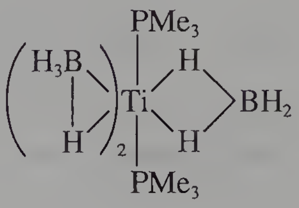
(a)



(b)



(c)



(d)

Some specific examples are $U(BH_4)_3dmpe_2$,[57b] $Y(BH_4)_3(THF)_3$, $(Ph_3P)_2CuBH_4$, and $Al(BH_4)_3$. They are usually made by interaction of a halide with Li or $NaBH_4$ in an ether or by interaction of BH_3THF as in the reaction[58]

$$[HCr(CO)_5]^- + BH_3(THF) \longrightarrow [Cr(CO)_5BH_4]^-$$

The most common form of binding is η^2, type (b).

Unidentate η^1-BH_4 is rare but occurs in triphos$CuBH_4$ and $(MePh_2P)_3CuBH_4$ [though $(Ph_3P)_2CuBH_4$ is η^2] and in $dmpe_2HFeBH_4$.[59] Although M—H—B is usually linear, some examples of bent M—H—B bonds are known.[60] The η^3 type is also rare but is found in Ti and Zr compounds $M(BH_4)_3$, and some others.[61]

Bridge complexes of the types (24-XXIIIa,b,c, and d) are also uncommon but one case is $Co^{I}_{2}(\mu\text{-}BH_4)_2(\mu\text{-diphos})_2$[62] with type (a) bridges. In (μ-

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[55a] S. Midollini *et al., Inorg. Chem.*, 1984, **23,** 922.

[55b] R. M. Catala *et al., J. Chem. Soc. Chem. Commun.*, **1987,** 261.

[56] R. N. Grimes, Ed., *Metal Interactions with Boron Clusters,* Plenum Press, New York, 1982; C. M. Housecroft and T. P. Fehlner, *Adv. Organomet. Chem.*, 1982, **21,** 57; R. N. Grimes, *Adv. Inorg. Chem. Radiochem.*, 1983, **26,** 55; T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77,** 263; N. N. Greenwood, *Pure Appl. Chem.*, 1983, **55,** 1415.

[57a] J. A. Jensen and G. S. Girolami, *J. Chem. Soc. Chem. Commun.*, **1986,** 1160.

[57b] A. Zalkin *et al., Inorg. Chem.*, 1984, **23,** 4143.

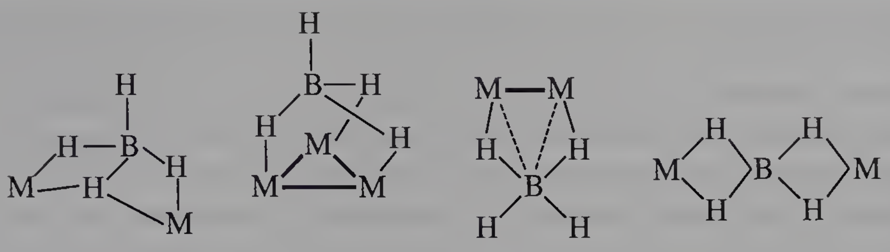
[58] M. Y. Darensbourg *et al., J. Am. Chem. Soc.*, 1982, **104,** 6961.

[59] M. V. Baker and L. D. Field, *J. Chem. Soc. Chem. Commun.*, **1984,** 996.

[60] T. F. Koetzle *et al., J. Am. Chem. Soc.*, 1981, **103,** 5165; R. Bau *et al., Inorg. Chim. Acta,* 1986, **114,** L27.

[61] J. C. Green, *Inorg. Chem.*, 1986, **25,** 2718; D. Hohl and N. Rösch, *Inorg. Chem.*, 1986, **25,** 2711; C. E. Housecroft and T. P. Fehlner, *Inorg. Chem.*, 1986, **25,** 404.

[62] D. G. Holah *et al., J. Chem. Soc. Chem. Commun.*, **1983,** 1308.



(a) (b) (c) (d)

(24-XXIII)

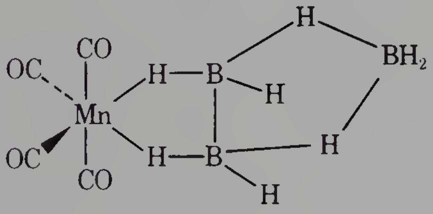
H)Fe$_3$(CO)$_9$(μ_3-BH$_4$) the μ_3-BH$_4$ (b) acts as a 6*e* donor to the cluster,[63] which is isoelectronic with H$_3$Fe$_3$(CO)$_9$(μ_3-CH).

An iridium complex has the third type (c) with a M—M bond[64a] while type (d), μ,η^2 occurs in (triphosRu)$_2$BH$_4$.[64b]

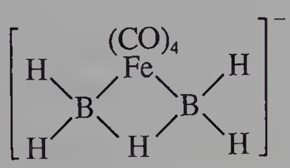
Borohydride complexes are sometimes nonrigid in solution though elevated temperatures may be required. In η^2 and η^3 complexes the bridge and terminal H atoms exchange.[65] The migration of BH$_4$ between metal atoms has also been invoked[66] in a HB(μ-H)$_3$Hf(μ-H)$_3$Hf system. However, in [(*c*-C$_5$H$_9$)$_3$P]$_2$H$_3$Os(η^2-BH$_4$) at 90°C the hydrogen atoms of the OsH$_2$B bridge exchange rapidly only with Os—H.[67]

Cyanoborohydride complexes can be M—NCBH$_3$ or M—H—B(H)$_2$CN—M.[68]

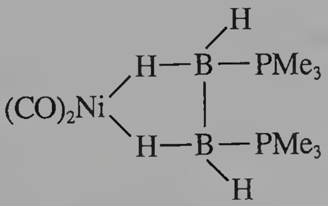
Polyborane anions also give a variety of complexes; one example, from B$_3$H$_8^-$ is (24-XXIV). Many of the compounds of the higher borane anions have M—B and/or B—B bonds as well as M—H—B links as in (24-XXV) and (24-XXVI). Also in HFe$_4$(μ_4-BH$_2$)(CO)$_{12}$ there is evidently a close three-



(24-XXIV)



(24-XXV)



(24-XXVI)

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[63] T. P. Fehlner *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 4633.

[64a] R. G. Bergman, *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 3508.

[64b] L. M. Venanzi *et al.*, *Inorg. Chem.*, 1986, **25**, 3335.

[65] D. J. Wink and N. J. Cooper, *J. Chem. Soc. Dalton Trans.*, **1984**, 1257.

[66] M. D. Fryzuk *et al.*, *Inorg. Chem.*, 1985, **24**, 4316.

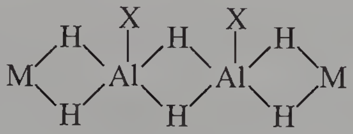
[67] J. L. Spencer *et al.*, *J. Chem. Soc. Chem. Commun.*, **1984**, 1362.

[68] B. E. Robertson *et al.*, *Inorg. Chem.*, 1984, **23**, 2391; K. W. Morse *et al.*, *Inorg. Chem.*, 1986, **25**, 3113.

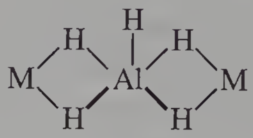
center FeBH bond.[69] These compounds have been discussed[70] in Section 6-13.

Aluminohydride Complexes.[71] Although $LiAlH_4$ like $NaBH_4$ has commonly been used as a reducing agent or source of H^- in reactions with metal halides, until recently few complexes had been isolated.

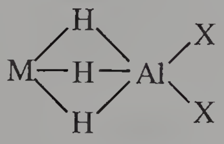
Structural determination and ^{27}Al nmr spectra show that they are quite different from BH_4^- complexes in that the Al atom is usually five-coordinate as in (24-XXVIIa,b, and c). Related compounds have been made by interaction of Me_3Al with transition metal hydrides. The compounds have units of the following types:



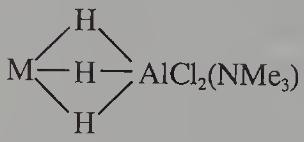
(a) X = H or OR



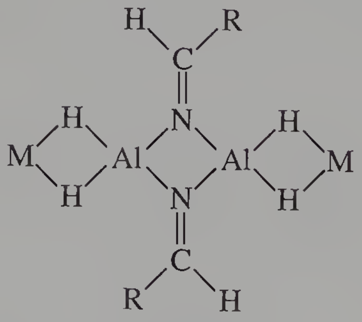
(b)



(c) X = H or CH_3



(d)



(e)

(24-XXVII)

As noted previously, the synthesis of polyhydrides in reactions such as that of $WCl_4(PMe_3)_3$ with $LiAlH_4$ initially gives aluminohydride complexes, which give the polyhydride only on hydrolysis. A typical example is the reaction[72]

$$RuCl_2(PMe_3)_4 + 2LiAlH_4 \xrightarrow{Et_2O} [fac\text{-}(Me_3P)_3HRuAlH_4]_2$$

When reactions are carried out in THF, cleavage of the ring occurs leading to compounds with an AlO*n*-Bu group as in (a) above.[73]

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[69] T. P. Fehlner *et al., J. Am. Chem. Soc.*, 1982, **104**, 1111.

[70] Some recent references are N. N. Greenwood *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 795; R. T. Baker, *Inorg. Chem.*, 1986, **25**, 109; J. D. Kennedy, *Inorg. Chem.*, 1986, **25**, 111.

[71] A. R. Barron and G. Wilkinson, *Polyhedron*, 1986, **5**, 1897.

[72] A. R. Barron and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, **1986**, 287.

[73] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1986**, 279.

The single-bridged complexes are made by removal of AlH_3 (as its adduct) with $Me_2NCH_2CH_2NMe_2$. Thus $[(Me_3P)_3H_3WAlH_4]_2$ gives $(Me_3P)_3H_3W(\mu\text{-}AlH_5)WH_3(PMe_3)_3$.[73]

The compounds are nonrigid and the behavior depends on the geometry around the metal. There is no exchange between $M(\mu\text{-}H)_2Al$ and the terminal Al—H. Where there are H atoms on the transition metal, exchange occurs between M—H and $M(\mu\text{-}H)_2Al$ as well as between Al—H and $Al(\mu\text{-}H)_2Al$.

The methyl aluminum complexes[26a] are made by reactions like

$$ReH_7(PMe_2Ph)_2 + \tfrac{1}{2}Al_2Me_6 \longrightarrow ReH_6AlMe_2(PMe_2Ph)_2 + CH_4$$

Some singly bridged compounds, for example, $Cp_3Zr—H—AlEt_3$ are also known. It may be noted that Me_3Al can also interact with halides to give compounds[74] such as $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$, $Cp_2Mo(\mu\text{-}Me)_2AlMe_2$, and $Cp_2(Me_3P)_2RhAlMe_3$.

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[74] J. M. Mayer and J. C. Calabrese, *Organometallics,* 1984, **3,** 1292; P. M. Maitlis *et al., Organometallics,* 1983, **2,** 1724.

Chapter Twenty-Five

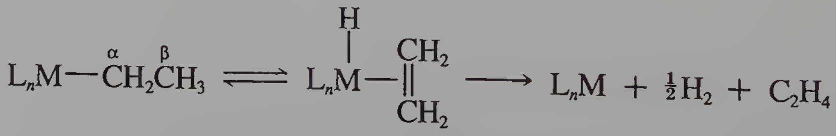
Compounds with Transition Metal Single, Double, and Triple Bonds to Carbon

TRANSITION METAL–CARBON SINGLE BONDS

25-1. Introduction

Following Edward Frankland's discovery of zinc alkyls in 1849, numerous attempts were made to prepare transition metal analogues; although evidence was obtained for unstable species in solution at low temperatures, no compounds could be isolated. However, in 1907, Pope and Peachy isolated $(Me_3PtI)_4$, which was shown, some 50 years later, to have a Pt_4I_4 cubane structure with μ_3-I groups and three methyl groups on platinum. Other stable compounds were not obtained until the 1950s and these had η-C_5H_5, CO, or PR_3 ligands present, one example being $(\eta\text{-}C_5H_5)Mo(CO)_3CH_3$.

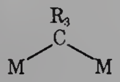
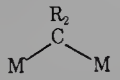
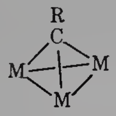
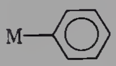
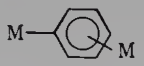
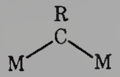
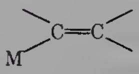
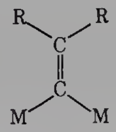
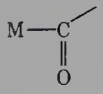
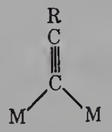
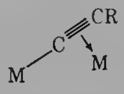
The failure to isolate stable compounds led to the assumption that transition metal-to-carbon bonds were intrinsically weak, and indeed some MO calculations purported to show that overlap of sp^3 hybridized carbon orbitals with any combination of *d, s,* and *p* metal orbitals was small. It was also considered that the presence of π-bonding ligands could improve this overlap and lead to stronger bonds. In fact, the lability of alkyls such as $Fe(C_2H_5)_2$ is a result of facile decomposition pathways involving H transfers. The situation provided a classic case of confusion of thermodynamic and kinetic stability. The stability of alkyls having Cp, CO, or PR_3 groups present is a result of the blocking by firmly held ligands of coordination sites needed for H transfers, for example, in the β-H transfer where two sites are involved in the hydrido ethylene intermediate:



$$L_nM-\overset{\alpha}{C}H_2\overset{\beta}{C}H_3 \rightleftharpoons L_n\overset{\overset{H}{|}}{M}-\underset{CH_2}{\overset{CH_2}{\|}} \longrightarrow L_nM + \tfrac{1}{2}H_2 + C_2H_4$$

The use of bulky alkyls or aryls and of groups without β-hydrogens allows isolation of stable alkyls such as $Cr(CH_2SiMe_3)_4$ or $Os(o\text{-}MeC_6H_4)_4$.

TABLE 25-1
Summary of Major Types of Transition Metal-to-Carbon Bonds Excluding π Complexes

Carbon Hybridization	Ligand			
	Terminal		Bridging [a]	
sp^3	M—R_3	Alkyl		Three-center μ-alkyl
				μ_2-Alkylidene [b]
				μ_3-Alkylidyne
sp^2		Aryl		
	M=CR_2	Carbene or alkylidene		μ_2-Alkylidyne
		Vinyl		μ-Vinylidene
		Acyl		
sp	M≡CR	Carbyne or alkylidyne		
	M—C≡CR	Acetylide		
	M=C=CR	Vinylidine		

[a] M. F. Lappert, *et al., Chem. Rev.*, 1983, **83,** 135.
[b] J. E. Hahn, *Prog. Inorg. Chem.*, 1984, **31,** 205.

Transition metal-carbon single bond energies[1] are in the region ~120 to 160 kJ mol^{-1} and quite comparable to those with non-transition elements. The difference made by the presence of vacant orbitals utilizable in decomposition reactions is illustrated by the thermal stability of $PbMe_4$ (bp 200°C). By contrast, $TiMe_4$ is unstable above ~ −50°C despite the Ti—C bond energy being higher, 259.4 kJ mol^{-1}, than the Pb—C energy, 167.4 kJ mol^{-1}. Completion of octahedral coordination of Ti^{IV} by addition of bipyridyl or similar ligands substantially increases the thermal stability; for example, $TiMe_4$bipy is stable at ~15°C.

The thermal stability of homoleptic alkyls (MR_n) can vary enormously. Most compounds are air sensitive, probably initially undergoing insertion of O_2 to give MOOR groups, which then decompose by radical pathways. Hydrolysis by water or acids and hydrogenolysis to give alkanes are usually facile.

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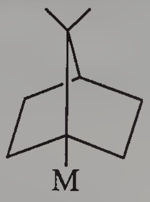
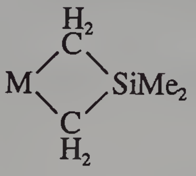
[1] J. A. Connor, *Top. Curr. Chem.*, 1977, **71,** 71; J. Halpern, *Acc. Chem. Res.*, 1982, **15,** 238.

Table 25-1 summarizes the major types of M—C and also M═C and M≡C bonds; it will be noted that bridge as well as terminal bonds are possible; the bridged species usually have the bridged alkyl supported by a metal–metal bond.

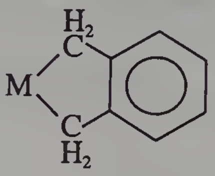
As noted previously, alkyls that have no readily transferable β-hydrogen atoms are unusually thermally stable; methyl compounds are also more stable than, say, ethyls, since they have no β hydrogen and must decompose homolytically or by α-H transfer (see below). Examples of "stabilizing" alkyls are 1-norbornyls[2a] (25-I), trimethylsilylmethyl (—CH_2SiMe_3), neopentyl (—CH_2CMe_3)[2b], benzyl (—CH_2Ph), and metallacycles such as (25-II) and (25-III).[3a] The ylids,[3b] (25-IV) to (25-VII) represent another class of metallacycles.



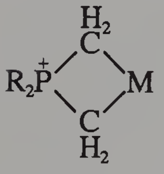
(25-I)



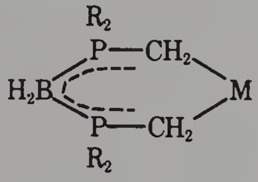
(25-II)



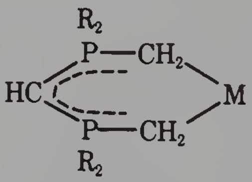
(25-III)



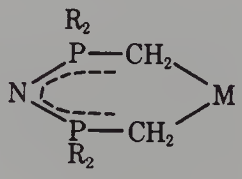
(25-IV)



(25-V)



(25-VI)



(25-VII)

25-2. Compound Types

The main classes of compounds are the following:

1. *Mononuclear.* Examples are $Ti(CH_2Ph)_4$, Mn(1-norbornyl)$_4$, WMe_6, and $OsPh_4$. Note that although *o*-xylylidenes can give compounds such as (25-VIII) this ligand can bind as a 4*e* bis(alkene) (25-IXa) or as a 6*e* bis (allyl) (25-IXb).[4a] Many oxo alkyls, $O{=}MR_n$, O_2MR_n, and so on, are known,[4b] as well as a few compounds of the type $(RN)_nMR_m$[4c] and NMR_n.

[2a] K. H. Theopold *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 1491; H. B. Abrahamson *et al.*, *Organometallics*, 1984, **3**, 1379; K. H. Thiele *et al.*, *Z. Anorg. Allg. Chem.*, 1985, **527**, 85.

[2b] J. L. Atwood *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 747.

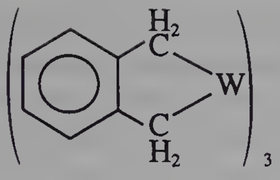
[3a] P. Diversi *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 477.

[3b] H. Schmidbauer *et al.*, *Organometallics*, 1983, **2**, 257; *Angew. Chem. Int. Ed. Engl.*, 1983, **22**, 907 (236 references).

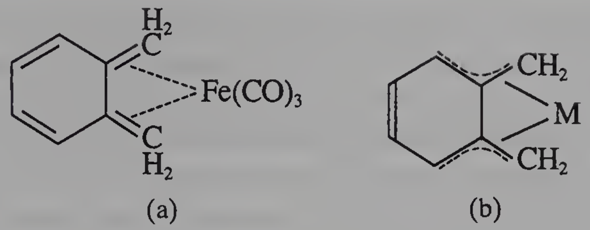
[4a] M. F. Lappert *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 893; R. G. Bergman *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 5834, 5846.

[4b] J. E. Bercaw, *J. Am. Chem. Soc.*, 1986, **108**, 5347; G. Wilkinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 169.

[4c] G. Wilkinson *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 1398; J. A. Osborn *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987**, 129.



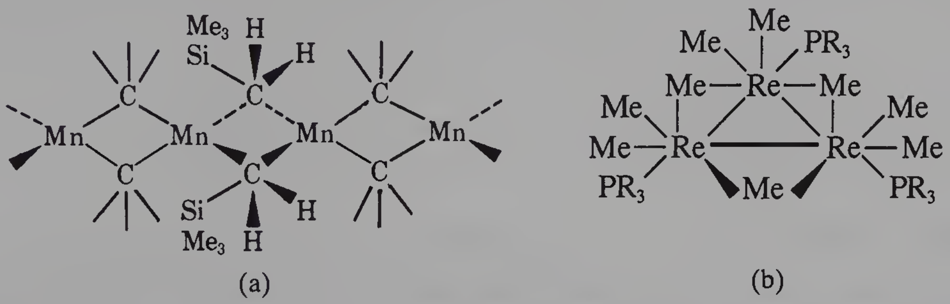
(25-VIII)



(25-IX)

2. *Binuclear with Metal–Metal Bonds.* Examples are $Mo_2(CH_2SiMe_3)_6$ and $Ru_2(CH_2CMe_3)_6$ that have similar structures with alkyl end groups and M≡M triple bonds.

3. *Bi- or Polynuclear with Alkyl Bridges.*[5a] Examples are (25-Xa) where Mn^{II} is tetrahedral (cf. $BeMe_2$ or $BeCl_2$) and the triangular $Re_3(\mu\text{-}Me)_3Me_6(PEt_2Ph)_3$, which has Re—Re bonds (25-Xb).



(25-X)

Apart from rhenium, only molybdenum and tungsten give cluster alkyls[5b] and these may have alkoxide groups, as in $W_4(p\text{-tol})_2(O\text{-}i\text{Pr})_{10}$.

In some bridged alkyls there may be distortion due to agostic interaction (Section 24-8)[5c].

4. *Alkylate Anions.* Alkyls or aryls MR_n that are coordinately unsaturated can behave as Lewis acids and give alkylate anions (cf. $AlMe_3$ and $[AlMe_4]^-$). They may be mononuclear, $[Co(C_6F_5)_4]^{2-}$, or dinuclear $[Mo_2Me_8]^{4-}$. The lithium "salts" are most commonly obtained by use of excess lithium alkyl on the metal halide or acetate. The Li atom may be solvated by THF, dioxan, tmed, or similar ligands, as in $(Li\ tmed)_3[ThMe_7]$ and $(Li\ tmed)_2[{}^*CpLuMe_3]$.[6] In *nonsolvated* species strong interaction between Li^+ and the hydrogen atoms of alkyl groups bound to the metal is commonly found as in lithium alkyls themselves (Section 4-8).

The most useful alkylate anions are those of copper, which have extensive use in organic syntheses.

[5a] M. F. Lappert *et al., Chem. Rev.*, 1983, **83,** 135.

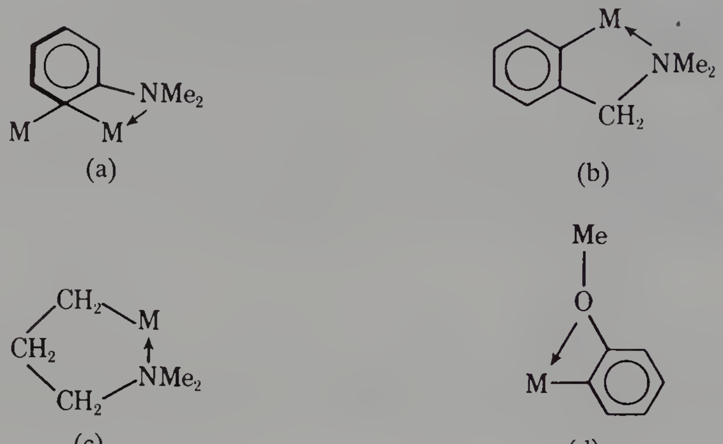
[5b] M. H. Chisholm *et al., J. Am. Chem. Soc.*, 1987, **109,** 3146; T. Saito *et al., Inorg. Chem.*, 1987, **26,** 1362.

[5c] B. E. Bursten and R. H. Cayton, *Organometallics,* 1986, **5,** 1051.

[6] T. J. Marks *et al., J. Am. Chem. Soc.*, 1984, **106,** 6841; H. Schumann *et al., J. Organomet. Chem.*, 1984, **276,** C5.

5. *Ligand Stabilized Alkyls.* There are hundreds of compounds that have π-bonding or π-complexing ligands occupying coordination sites. For substitution-inert octahedral species of Cr^{III}, Co^{III}, and Rh^{III}, compounds with non-π-bonding ligands can be made, for example, $CrPh_3(THF)_3$,[7a] $[CrR(H_2O)_5]^{2+}$,[7b] and $[RhC_2H_5(NH_3)_5]^{2+}$.

If the alkyl or aryl group has an attached donor function, additional stability can arise through coordination. Examples of such groups[7c] are (25-XIa–d).



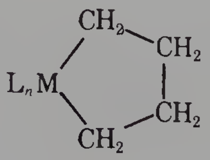
(a) (b)

(c) (d)

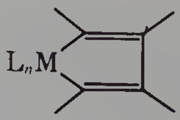
(25-XI)

Finally, note that when aryls have ortho substituents such as CH_3 or *t*-Bu, the compounds may be much more thermally stable than the corresponding phenyls and less reactive due to steric factors. A good example is the high stability and low reactivity of $Os(o\text{-}MeC_6H_4)_4$ compared to $OsPh_4$.[8] The mesityl group, 2,4,6-trimethylphenyl has been much used for this purpose.

6. *Metallacycles.*[9] Typical metallacycles are (25-XII) and (25-XIII). Saturated ring compounds such as (25-XII) are sometimes more thermally stable than the corresponding dialkyls especially for heavier transition metals such as Pt in compounds of the type $(R_3P)_2M(CH_2)_n$, $n = 3$–6.[10] Others such as



(25-XII)



(25-XIII)

[7a] S. I. Khan and R. Bau, *Organometallics,* 1983, **2,** 1896.

[7b] A. Bakac *et al., Inorg. Chem.,* 1986, **25,** 3360; H. Cohen *et al., Inorg. Chem.,* 1985, **24,** 4158.

[7c] See, for example, W. H. Risen, Jr., *et al., Inorg. Chem.,* 1985, **24,** 2312.

[8] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1987,** 557.

[9] S. D. Chapell and D. J. Cole-Hamilton, *Polyhedron,* 1982, **1,** 739; E. Lindner, *Adv. Heterocyclic Chem.,* 1986, **39,** 238.

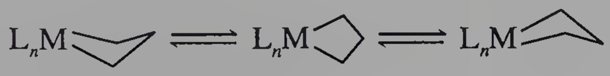
[10] G. Erker *et al., Organometallics,* 1985, **4,** 2059; *Angew. Chem. Int. Ed. Engl.,* 1986, **25,** 364; M. I. Steigerwald and W. A. Goddard III, *J. Am. Chem. Soc.,* 1985, **107,** 5027; J. T. Burton and R. J. Puddephat, *Organometallics,* 1987, **6,** 951.

those of the earlier metals, for example, $Cp_2Ti(CH_2)_4$ commonly decompose at fairly low temperatures to give ethylene.

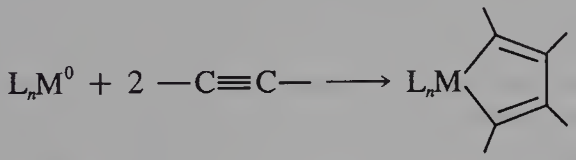
Although they can be formed using dimagnesium reagents, $(XMg)_2(CH_2)_n$, and in cyclometallations (Section 27-9), they are also formed in reactions with ethylene, especially for the early transition metals, where two molecules can react in insertion reactions

$$L_nM \xrightarrow{C_2H_4} L_nM(\eta^2\text{-}C_2H_4) \xrightarrow{C_2H_4} L_nM(C_4H_8)$$

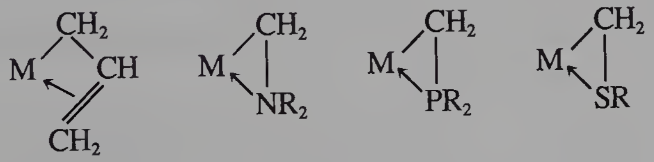
The saturated metallacycles have quite a low activation energy for ring puckering:



Unsaturated macrocycles[11] of type (25-XIII) are commonly formed in reactions of acetylenes, which undergo oxidative coupling[12]:

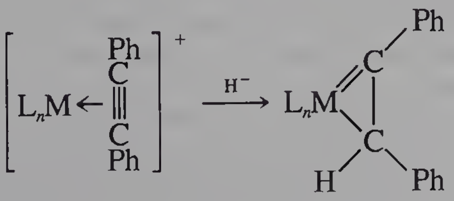


Other metallacycles are those with η^2-ligands where the ligand is acting as a $3e$ donor. Some examples are the following:



(25-XIV)

The η^1 complexes for these ligands are also known as in $M—CH_2PR_2$ or $M—CH_2NR_2$. The allyl (25-XIV) is a special case discussed in Section 26-5. Vinyls are normally η^1 but can be obtained in the η^2 form (25-XV), where there is a long and a short M—C bond, by H^- attack on a $4e$ alkyne complex cation[13a] (see also Section 26-3).



(25-XV)

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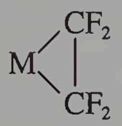
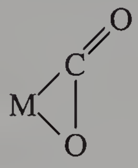
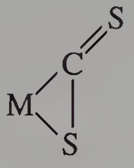
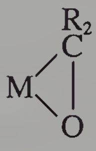
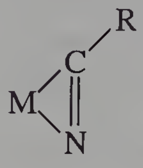
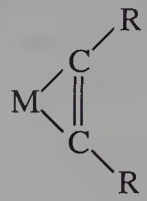
[11] M. H. Chisholm and J. A. Heppert, *Adv. Organomet. Chem.*, 1986, **26,** 97 (1,3 di-tungsten cyclobutadienes); J. R. Bleeke and W-J. Peng, *Organometallics,* 1987, **6,** 1576.

[12] See, for example, Y. Wakatsuki *et al., J. Am. Chem. Soc.*, 1983, **105,** 1907.

[13a] S. R. Allen *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 435.

The η^2 binding of various small molecules like C_2H_4, CO_2, CS_2, ketones,[13b] aldehydes,[13b] nitriles,[13c] and alkynes can also be regarded as giving a metallacycle by oxidative-addition reactions (see Section 27-3, Table 27-1). Examples are

7. *Other Types. Halogeno methyls* (M—CH_2X) can react with methanol to give *methoxymethyls* M—CH_2OMe[14a] that can be also η^2-C,O. More important are *hydroxymethyls*,[14b] M—CH_2OH, of which $[IrH(CH_2OH)(PMe_3)_4]^+$ is an example. These species can be made by interaction of M—H with formaldehyde and are probable intermediates in interactions of CO and H_2 (Chapter 28).

Acetylides.[15] Examples are $[Ni(C{\equiv}CR)_4]^{2-}$ and $Cp(CO)_3Cr(C{\equiv}CPh)$. The triple bond in the acetylides can bind via its π bonds as an acetylene (Section 26-3) giving bridges, for example, $[{}^*Cp_2Zr\text{-}\mu(C{\equiv}CPh)]_2$. The C≡C bond is very susceptible to attack by electrophiles, leading *inter alia* to vinylidene, alkylidene, and alkylidyne compounds as discussed later.

Cyclopropyls. A few have been made by decarbonylation[16a] of the acyl M—$C(O)C_3H_5$; similar are η^1-cyclopropenyls.[16b]

Cyclohexyls.[16c] Relatively few are known but some are remarkably stable, for example, $Os(c\text{-}C_6H_{11})_4$ and $Cr(c\text{-}C_6H_{11})_4$.

Fluoroalkyls and Aryls. There are many compounds with CF_3, CF_2CF_2H, C_6F_5, and so on, groups and some chlorinated compounds that are often more thermally stable than hydrocarbon analogues.[17] This is probably not so much due to stronger M—C bonds (M—C_F bonds are usually shorter than analogous M—C_H bonds) but because of lack of the decomposition pathways involving H transfers that are available to hydrocarbon compounds.

[13b] H. Taube *et al., J. Am. Chem. Soc.*, 1986, **108,** 8223; J. A. Gladysz *et al., J. Am. Chem. Soc.*, 1986, **108,** 8268.

[13c] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 2017.

[14a] J. R. Moss *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 1495; G. Erker *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 1403.

[14b] D. L. Thorn, *Organometallics*, 1986, **5,** 1897; S. L. Van Voorhees and B. B. Wayland, *Organometallics*, 1985, **4,** 1887; J. A. Gladysz *et al., J. Am. Chem. Soc.*, 1986, **108,** 1455, *et seq.*

[15] R. Nast, *Coord. Chem. Rev.*, 1982, **47,** 89; K. R. Birdwhistell, and J. L. Templeton, *Organometallics,* 1985, **4,** 2062; G. Erker *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 463; A. J. Carty *et al., Inorg. Chem.*, 1987, **26,** 3201.

[16a] N. L. Jones and J. A. Ibers, *Organometallics*, 1983, **2,** 490.

[16b] R. P. Hughes *et al., J. Am. Chem. Soc.*, 1982, **104,** 4846.

[16c] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 557.

[17] For CF_3 derivatives see: R. J. Lagow and J. A. Morrison, *Adv. Inorg. Chem. Radiochem.*, 1980, 23, 178.

Benzyls may have a normal σ bond but can also be η^3 as an allyl (Section 26-5).[18]

Silicon analogues[19] of the alkyls have long been known, one example being $Cp(CO)_3WSiMe_3$. Silyl compounds are intermediates in the hydrosilation reaction of alkenes (Section 29-11).

25-3. Acyls[20]

Compounds with an acyl or formyl group are especially important as they are formed in reactions of CO such as

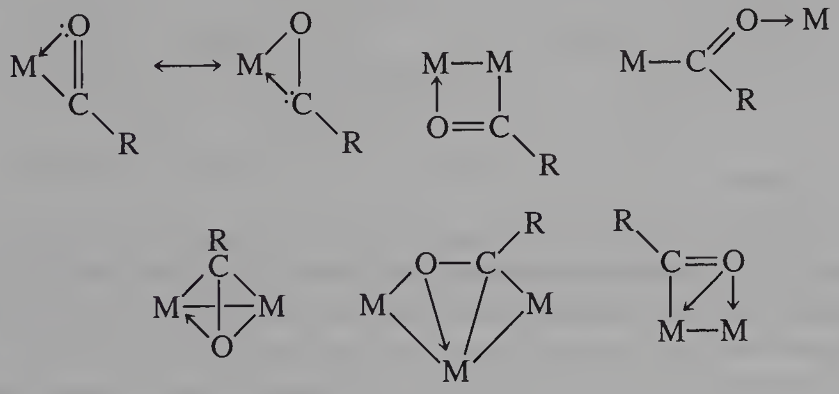
$$(CO)_5MnCH_3 + CO \longrightarrow (CO)_5MnC(O)CH_3$$

that are discussed in Chapters 27 and 28. They can also sometimes be made by oxidative-addition of aldehydes[21]:

$$RhCl(PMe_3)_3 + RCHO \longrightarrow (Me_3P)_3Rh(H)(RCO)$$

Acylate anions can be made by nucleophilic attacks of lithium alkyls on metal carbonyls (Section 22-8), for example, $W(CO)_6 + LiR \rightarrow Li[(CO)_5WC(O)R]$. They are precursors of alkylidenes (Section 25-7).

Acyl groups have several bonding modes in addition to η^1 as follows[22]:



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[18] See, for example, I. P. Rothwell *et al., Organometallics,* 1985, **4,** 902.

[19] L. A. Oro *et al., Organometallics,* 1986, **5,** 1519; T. D. Tilley *et al., Organometallics,* 1987, **6,** 473; *J. Am. Chem. Soc.,* 1987, **109,** 945, 2049; J. A. Gladysz, *Acc. Chem. Res.,* **1984,** 326; B. J. Aylett, *Adv. Inorg. Chem. Radiochem.,* 1982, **25,** 1; D. H. Berry and J. H. Mitstifer, *J. Am. Chem. Soc.,* 1987, **109,** 3777; K. H. Pannell *et al., Organometallics,* 1987, **6,** 2085.

[20] R. Hoffmann *et al., J. Am. Chem. Soc.,* 1985, **107,** 4440; *Organometallics,* 1985, **4,** 404 (bonding and many references).

[21] D. Milstein, *Organometallics,* 1982, **1,** 1549.

[22] η^1: J. L. Templeton *et al., J. Am. Chem. Soc.,* 1986, **108,** 4632.

η^2: T. D. Tilley *et al., J. Am. Chem. Soc.,* 1986, **108,** 5355; M. D. Curtis, *J. Am. Chem. Soc.,* 1986, **108,** 1550; T. J. Marks *et al., J. Am. Chem. Soc.,* 1986, **108,** 56; J. R. Norton *et al., J. Am. Chem. Soc.,* 1985, **107,** 7952.

μ_2: T. Adatia *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 1206, 1206; G. L. Geoffroy *et al., Organometallics,* 1984, **3,** 846; H. D. Kaesz *et al., J. Am. Chem. Soc.,* 1984, **106,** 5926; *Inorg. Chem.,* 1984, **23,** 4640; D. Seyferth and C. M. Archer, *Organometallics,* 1986, **5,** 2572.

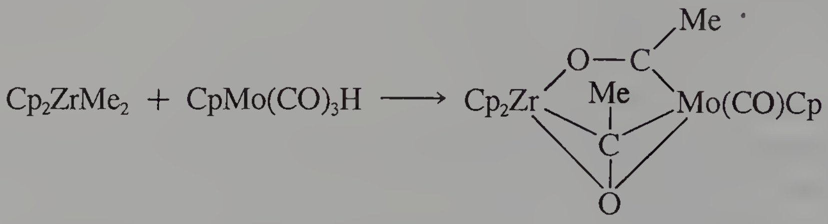
μ_3: J. R. Shapley *et al., J. Am. Chem. Soc.,* 1984, **106,** 1144; J. C. Jeffery and J. G. Lawrence-Smith, *J. Chem. Soc. Chem. Commun.,* **1985,** 275.

Note that the η^2 species can also be considered as an *oxoalkylidene* and that acyls of oxophilic elements like Ti, Zr, Hf, Th, and U have behavior that best accords with this view.

The bridge species can be made by reactions such as

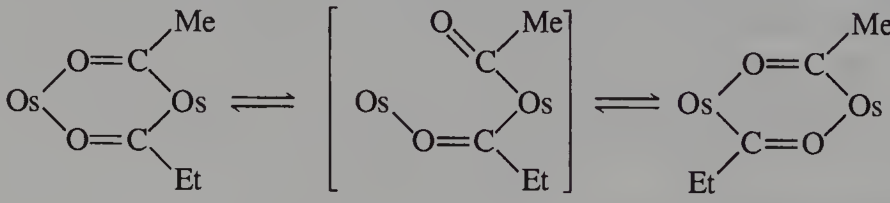
$$[Fe_2(CO)_8]^{2-} \xrightarrow{CH_3I} [Fe_3(CO)_9\mu_3\text{-}CH_3CO]^-$$

$$Cp(CO)_3WC(O)Me + [CpW(CO)_3]^+ \longrightarrow [Cp(CO)_3W\text{-}C(Me)OW(CO)_3Cp]^+$$



and by insertion of CO into μ-alkylidenes.

In binuclear species with two RCO bridges *vic–gem* isomerization can occur via ring opening:



gem *vic*

The μ_3,η^2 cluster species can undergo C—O cleavage by electrophilic attack at oxygen or by nucleophilic attack at carbon to give other clusters.

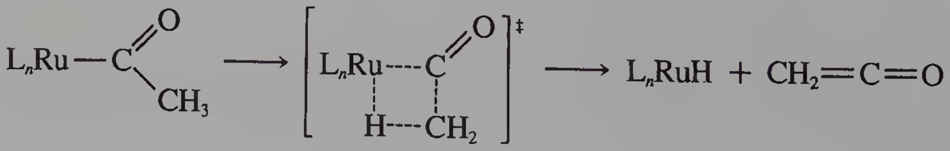
Formyls. The reaction of CO with M—H bonds to give formyls has been noted in Section 24-3 and is discussed in Section 27-6.

Stable anionic formyls are commonly made by hydridic attacks[23a] on metal, carbonyls,

$$L_nM\text{—}CO \xrightarrow{H^-} [L_nMC(H)O]^-$$

but some cationic, neutral and bridging species are also known.

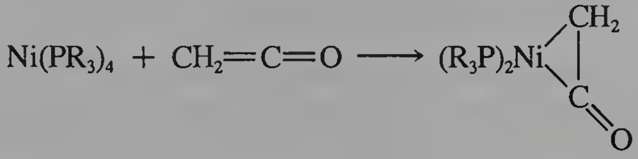
Although acyls may have β-H atoms, only recently has a β-hydride transfer been recognized[23b]:



[23a] See, for example, D. L. Thorn and D. C. Roe, *Organometallics,* 1987, **6,** 617; C. P. Casey *et al., Organometallics,* 1985, **4,** 143; P. A. Kongshaug and R. G. Miller, *Organometallics,* 1987, **6,** 372.

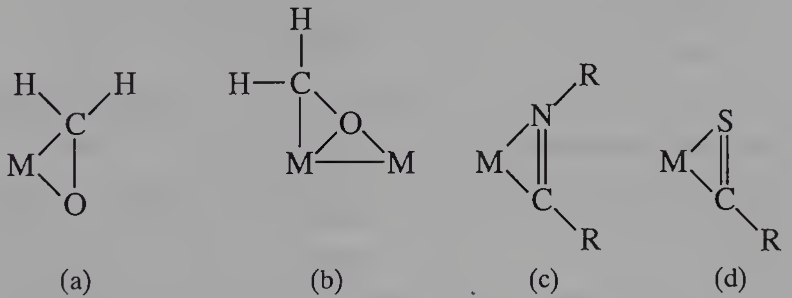
[23b] S. I. Hommeltoft and M. C. Baird, *J. Am. Chem. Soc.,* 1985, **107,** 2545.

Other species related to acyls are η^2- or μ-*ketenes,*[24a] for example,



Formaldehyde complexes (25-XVIa and b),[24b] (cf. ref. 13b) can be made from CH_2O or $(CH_2O)_n$.

Finally, there are η^2-iminoacyls (25-XVIc)[24c] made by insertion of isocyanides into M—C bonds, *thioacyls* (25-XVId), *alkoxycarbonyls* M—C(O)OR formed by nucleophilic attacks of RO^- on M—CO groups (Section 22-8),[24d] *diazoalkanes* $M—C(=N_2)R$,[24e] and η^2-thioaldehydes, η^2-(SCHR).[24f]



(25-XVI)

25-4. Synthetic Methods for M—C Bonds

Compounds with M—C bonds can be obtained in innumerable ways, some of which are unique. The following are a few examples.

1. *Alkylation by Other Metal Alkyls.* Transition metal halides, acetates, alkoxides, and so on, can be alkylated by Grignard reagents or alkyls and aryls of Li, Mg, Zn, Al, Sn, and Hg.

It is often better to use acetates or alkoxides than halides and to use dialkylmagnesium rather than Grignard reagents. In a few cases, oxides, notably Re_2O_7 or OsO_4 can be used.[25] Mercury and tin alkyls commonly give only partial alkylation but sometimes the reactions are stereoselective.[26] Alu-

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[24a] A. Miyashita *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 850.

[24b] J. A. Gladysz *et al., Organometallics,* 1986, **5,** 956; G. Erker *et al., J. Am. Chem. Soc.,* 1986, **108,** 2251; C. Floriani *et al., Organometallics,* 1986, **5,** 2425; G. D'Alfonso *et al., Organometallics,* 1987, **6,** 194 (μ_3); K. R. Pörschke *et al., Angew. Chem. Int. Ed. Engl.,* 1987, **26,** 919.

[24c] E. K. Barefield *et al., Organometallics,* 1987, **6,** 454.

[24d] C. Bianchini *et al., Organometallics,* 1986, **5,** 1670.

[24e] S. I. Murahashi *et al., Organometallics,* 1986, **5,** 356.

[24f] S. L. Buchwald *et al., J. Am. Chem. Soc.,* 1987, **109,** 1590; J. A. Gladysz *et al., Organometallics,* 1987, **6,** 1150.

[25] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 2167.

[26] R. J. Cross and J. Gemmill, *J. Chem. Soc. Dalton Trans.,* **1984,** 199, 205.

minum alkyls usually transfer only *one* alkyl group, for example,

$$WCl_6 + 6AlMe_3 = WMe_6 + 6AlCl_2Me$$

The alkylation reactions are often complicated; solvent effects are very important and traces of oxygen can have substantial effects on yields. Use of magnesium alkyls can sometimes give Mg salts of alkylate anions which, on oxidation give the neutral alkyl,[25] for example,

$$Re_2O_7 \xrightarrow{MgMe_2} (Me_4ReO)_2Mg(THF)_4 \xrightarrow{-2e} 2Me_4ReO + Mg^{2+}$$

2. *Interaction of Sodium Salts of Anions with Alkyl or Aryl Halides.* This is a useful method when sodium salts of carbonylate or other anions are available. Examples are

$$CpW(CO)_3^-Na^+ + CH_3I = CpW(CO)_3Me + NaI$$

$$Mn(CO)_5^-Na^+ + CH_3I = CH_3Mn(CO)_5 + NaI$$

This method can also be used to synthesize acyls and compounds with bonds to Si, Ge, and Sn, for example,

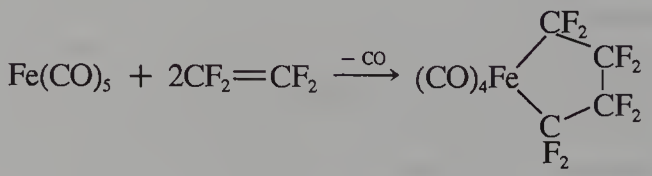
$$CpW(CO)_3^-Na^+ + ClSiMe_3 = CpW(CO)_3SiMe_3 + NaCl$$

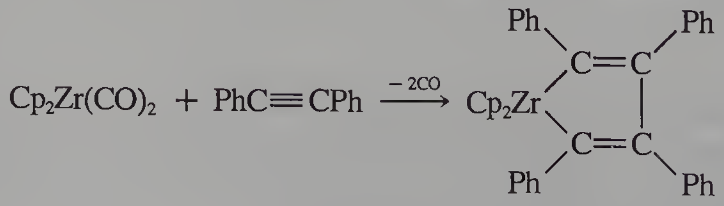
3. *Oxidative-Addition Reactions.* For metal complexes that can undergo the oxidative-addition reaction (Chapter 27), this is a useful method for synthesis of alkyls, aryls, acyls, and compounds with bonds to other elements. Typical reactions are

$$IrCl(CO)(PPh_3)_2 + CH_3I = Ir(CH_3)(Cl)(I)(CO)(PPh_3)_2$$

$$IrCl(CO)(PPh_3)_2 + Me_3O^+BF_4^- = [Ir(Me)(Cl)(CO)(PPh_3)_2]^+BF_4^- + Me_2O$$

Metal–carbon bonds can also be formed in *oxidative coupling reactions*,[27] for example,





4. *Metal Atom Reactions.*[28] The cocondensation of metal vapors with alkyl or aryl halides can be regarded as a type of oxidative-addition reaction.

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[27] See, for example, D. J. Sikora and M. D. Rausch, *J. Organomet. Chem.*, 1984, **276**, 21.

[28] R. D. Riecke *et al.*, *Organometallics*, 1983, **2**, 377.

Examples are

$$Pd + CF_3I = (PdICF_3)_n$$

$$Pd + RX + 2PR_3 = PdR(X)(PR_3)_2$$

$$Ni + C_6F_5Br + C_6H_5Me \longrightarrow NiBr_2 + (C_6F_5)_2Ni(\eta\text{-}C_6H_5Me)$$

5. *Insertion Reactions.* Reactions of compounds with C═C, C≡C, C═N, and so on, bonds with metal complex hydrides have been discussed in Chapter 24, while other insertions especially of CO are discussed in Chapter 27. Typical examples are

$$[Rham_5H]^{2+} + CH_2{=}CH_2 \longrightarrow [Rham_5C_2H_5]^{2+}$$

$$CpFe(CO)_3CH_3 + CO \longrightarrow Cp(CO)_3FeC(O)CH_3$$

$$Cp_2W(CO) + MeNCO \longrightarrow Cp_2\overline{W[C(O)N(Me)C}(O)]$$

6. *Elimination Reactions.* These are the reverse of insertion reactions. They involve the elimination from appropriate compounds such as acyls, carboxylates, sulfinates, azo compounds, or hydrides of CO, CO_2[29a], SO_2, N_2, H_2, and so on, by the action of heat or light with the concomitant formation of a metal-to-carbon σ bond. Examples are

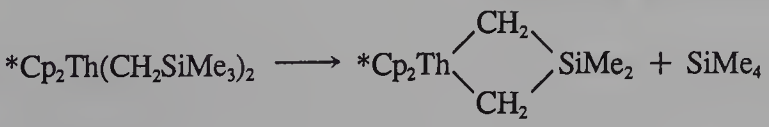
$$Ni(bipy)(CO_2Ph)_2 \longrightarrow Ni(bipy)Ph_2 + 2CO_2$$

$$CpFe(CO)_2SO_2R \longrightarrow CpFe(CO)_2R + SO_2$$

$$PtHCl(PEt_3)_2 + PhN_2^+ \xrightarrow{KOH} (Et_3P)_2PtCl(N{=}NPh) \longrightarrow (Et_3P)_2PtClPh + N_2$$

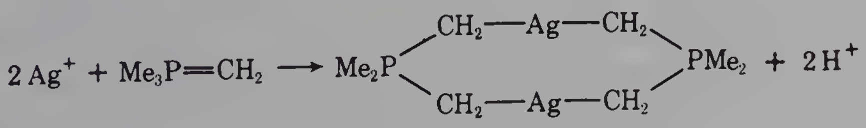
Other eliminations are *cyclometallations*[29b] (cf. Section 27-9), for example,

$$(Ph_3P)_3RhMe \xrightarrow{\Delta} (Ph_3P)_2\overline{Rh-C_6H_4P}Ph_2 + CH_4$$



7. *Ylid Syntheses.*

(*a*) From trimethylphosphanemethylene:



(*b*) From phosphonium salts and lithium alkylate anions:

$$4Me_4PCl + Li_4[Mo_2Me_8] = Mo_2[(CH_2)_2PMe_2]_4 + 8CH_4 + 4LiCl$$

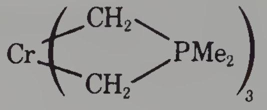
[29a] G. B. Deacon *et al., Adv. Organomet. Chem.*, 1986, **25**, 257.

[29b] See, for example, T. J. Marks *et al., J. Am. Chem. Soc.*, 1986, **108**, 40.

(*c*) From lithium phosphonium methylide and metal salts:

$$Me_4PCl + 2MeLi = Me_2P(CH_2)_2Li + LiCl + 2CH_4$$

$$3Me_2P(CH_2)_2Li + CrCl_3(THF)_3 =$$



$$+ 3LiCl$$

(*d*) From phosphanes:

$$[Cp_2W(C_2H_4)]^+ \xrightarrow[PF_6]{MeI} [Cp_2W(C_2H_4)Me]^+ \xrightarrow[-C_2H_4]{+PMe_2Ph} [Cp_2W(H)(CH_2PMe_2Ph]^+$$

(*e*) From ylids and carbonyl compounds:

$$MnBr(CO)_5 + Ph_3PCCPPh_3 \longrightarrow (CO)_4BrMn{-}C{\equiv}CPPh_3 + PPh_3$$

$$Ph_3PCr(CO)_5 + Ph_3P{=}CH_2 \longrightarrow (CO)_5CrCH_2PPh_3 + PPh_3$$

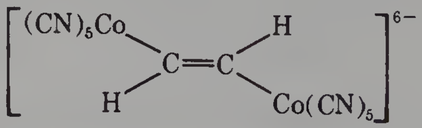
8. *Paramagnetic Metal Ion–Free-Radical Reactions.* These involve interaction of paramagnetic complex ions, examples being:

$$[Cr(H_2O)_6]^{2+} + t\text{-}BuOOH = [Cr(t\text{-}Bu)(H_2O)_5]^{2+}$$

$$[Cr(H_2O)_6]^{2+} + CHCl_3 = [Cr(H_2O)_5Cl]^{2+} + [Cr(H_2O)_5CHCl_2]^{2+}$$

$$Co(dmgH)_2py + CCl_4 = Cl_3CCo(dmgH)_2py + ClCo(dmgH)_2py$$

$$[Co(CN)_5]^{3-} + HC{\equiv}CH =$$



9. *Radical Oxidations.* These are possible in selected cases,[30] for example,

$$Co^{II}sal_2en + MeNHNH_2 \xrightarrow{O_2,\ py} MeCo^{III}sal_2en(py) + N_2$$

25-5. Decomposition Reactions

We have already mentioned decomposition pathways in connection with thermal stability of alkyls or aryls.

There are two major thermal reaction paths (*a*) homolytic dissociation to give radicals,[31a] (*b*) hydrogen transfer reactions.[31b] The difference between these can be illustrated by the decomposition of two similar alkyls, only one of which has a readily transferable β-hydrogen atom: $Bu_3PCuCH_2CH_2CH_2CH_3$ and $Bu_3PCuCH_2CMe_2Ph$. The former decomposes to give Cu, H_2, but-1-ene, and butane; the latter gives as products $PhCMe_3$, $PhCHMe_2$, $PhCH_2C(Me){=}CH_2$, and $(PhMe_2CCH_2\text{-})_2$, which can come only from homolytic fission of the Cu—C bond and subsequent radical reactions.

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[30] E. G. Samsel and J. K. Kochi, *Inorg. Chem.*, 1986, **25**, 2450.

[31a] See, for example, E. Gretz and A. Sen, *J. Am. Chem. Soc.*, 1986, **108**, 6038.

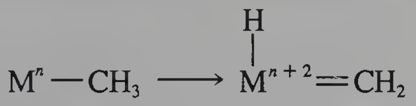
[31b] For references see T. J. Marks *et al.*, *Organometallics*, 1987, **6**, 232.

Photochemical decomposition[31c] occurs by both homolysis and H transfers; the radicals can sometimes be utilized to initiate polymerizations, for example, of styrene.

α-Hydride Transfer. Methyl compounds such as $TaMe_5$ or WMe_6 decompose thermally to give CH_4 and polymeric material:

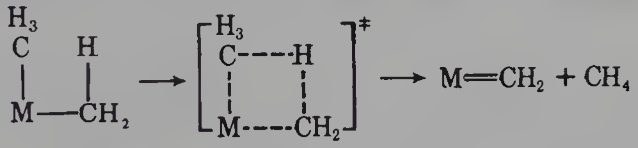
$$WMe_6 \longrightarrow 3CH_4 + \text{“}W(CH_2)_3\text{”}$$

Since the metal atom here is in its maximum oxidation state there is no possibility for an intramolecular oxidative-addition



$$M^n{-}CH_3 \longrightarrow \overset{\displaystyle H}{\overset{|}{M^{n+2}}}{=}CH_2$$

Hence the decomposition occurs either by way of a four-center transition state:



or possibly by a radical route. Such a four-center state could well arise from agostic distortion of CH_3 groups (Section 24-8) either on the electron deficient metal center or in bridging intermediates if the reaction is binuclear. A prime example of α-H transfer has been noted (Section 24-8), namely,

$$(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CH_3) \rightleftharpoons (\mu\text{-}H)_2Os_3(CO)_{10}(\mu\text{-}CH_2)$$

In some decompositions the $M{=}CH_2$ intermediate can be trapped,[32] for example,

$$(ArO)_2TaMe_3 \xrightarrow{h\nu} (ArO)_2Ta({=}CH_2)Me$$

Abstractions of α-hydrogen atoms can occur with strong bases or with $(C_6H_5)_3C^+$ and leads to alkylidene or alkylidyne compounds, for example,

$$[Cp_2TaMe_2]^+ \xrightarrow{OMe^-} Cp_2MeTa{=}CH_2$$

$$Cp(NO)(PPh_3)ReCH_2R \xrightarrow{Ph_3C^+} [Cp(NO)(PPh_3)Re{=}CHR]^+$$

β-Hydride Transfer. This is unquestionably the most important transfer reaction, occurring not only for alkyls, but also for acyls and alkoxides,[33] for

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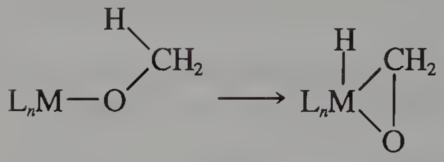
[31c] D. B. Pourreau and G. L. Geoffroy, *Adv. Organomet. Chem.*, 1985, **24**, 249; H. G. Alt, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 766.

[32] See, for example, J. C. Green *et al.*, *Organometallics*, 1985, **4**, 1302; L. R. Chamberlain and I. P. Rothwell, *J. Chem. Soc. Dalton Trans.*, **1987**, 163.

[33] H. E. Bryndza *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 4805; J. D. Atwood *et al.*, *Organometallics*, 1986, **5**, 390.

example,



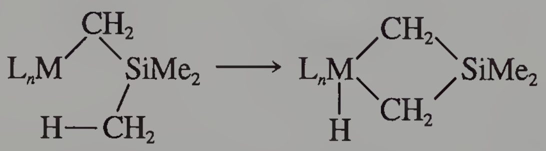
The reaction is especially important in the reverse direction for the synthesis of M—C bonds:

$$L_nMH + MeCH{=}CH_2 \rightleftharpoons L_nMCH_2CH_2Me$$

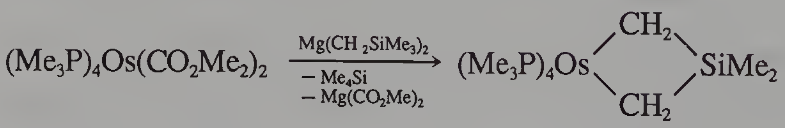
This reaction will be discussed in more detail in Chapter 27 but has also been discussed in connection with agostic hydrogen atoms (Section 24-8).

Many metal complexes have been studied, especially those of platinum(II)[34] such as $(R_3P)_2PtR'_2$ and the free energy of activation for elimination has been obtained for $(COD)Pt(CH_2CH_3)_2$ labeled with ^{13}C.

γ-Hydride Transfer. Gamma transfer leads to the formation of a metallacycle[35]:

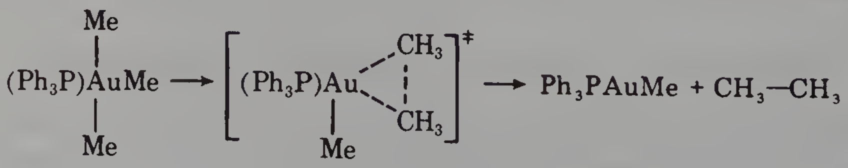


As noted previously when more than one alkyl is present on the metal, elimination of alkane can occur, for example,



δ-and ϵ-Hydride Transfers. These transfers are rarer than those previously mentioned, but examples are known.[31b,36]

Intramolecular Reductive-Eliminations. These are the reverse of oxidative-addition reactions (Section 28-3). They may be reversible in some cases. An example of an irreversible reductive-elimination is the reaction in Me_2SO



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[34] H. E. Bryndza, *J. Chem. Soc. Chem. Commun.*, **1985,** 1696; H. A. Brune *et al., Chem. Ber.*, 1984, **117,** 2803; G. M. Whitesides *et al., Organometallics,* 1985, **4,** 1550; 1986, **5,** 1473, 1481; T. J. Marks *et al., J. Am. Chem. Soc.*, 1986, **108,** 7275.

[35] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 877; P. Diversi *et al., J. Organomet. Chem.*, 1984, **269,** 285.

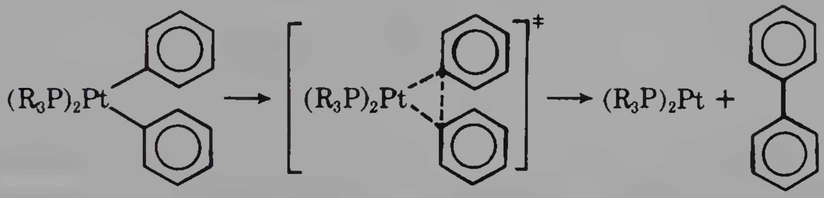
[36] For references see R. H. Reamy and G. M. Whitesides, *J. Am. Chem. Soc.*, 1984, **106,** 81; D. J. Cole-Hamilton *et al., J. Chem. Soc. Dalton Trans.*, **1982,** 1867; A. C. Skapski *et al., Organometallics,* 1986, **5,** 1744.

If the same reaction is carried out in benzene or decalin it proceeds by an *inter*molecular pathway.

Reductive coupling of alkyl groups can also be induced by oxidation, and in such cases paramagnetic intermediates are clearly involved:

$$\mathrm{Et_2Nibipy} \xrightarrow{-e} \mathrm{Et_2Nibipy^+} \longrightarrow \mathrm{C_4H_{10}}$$

Under normal circumstances no radicals or ions appear to be involved, and the concerted reaction is probably initiated by vibrational modes bringing the carbon atoms of the alkyl groups into close proximity. Aryls similarly decompose, possibly via a transition state such as (25-XVII).



(25-XVII)

The decomposition of alkyl hydrides is of particular interest because of the relation to processes involved in catalytic hydrogenations. For $\mathrm{Os(CO)_4H(CH_3)}$, *inter*molecular elimination occurs, but for the complexes *cis*-$\mathrm{PtH(R)(PPh_3)_2}$, kinetic studies show that alkane elimination is *intra*molecular, with the rate-determining step being, for example,

$$cis\text{-}\mathrm{PtH(CH_3)(PPh_3)_2} \longrightarrow \mathrm{Pt(PPh_3)_2} + \mathrm{CH_4}$$

The reactivity decreases for the R groups in the order

$$\mathrm{C_6H_5} > \mathrm{C_2H_5} > \mathrm{CH_3} > \mathrm{CH_2CH{=}CH_2}$$

In some other cases more complicated behavior is found, and in the decomposition of $(\eta\text{-Me}_5\mathrm{C}_5)_2\mathrm{ZrH}(t\text{-Bu})$, the elimination involves the cyclopentadienyl ring.

25-6. Other Reactions of M—C Bonds

1. *Insertions.* Many small molecules will insert into the M—C bond. These reactions are discussed in detail in Chapter 27. The most important reaction is that with CO to give acyls.

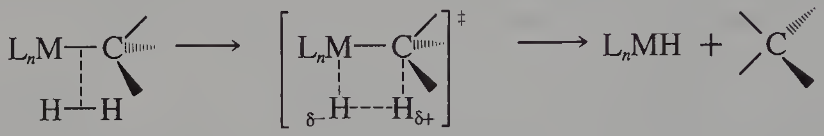
2. *Hydrogenolysis.* Interaction of alkyls or aryls with hydrogen normally gives alkane and a metal hydride which, in the absence of stabilizing ligands, may decompose further. The reaction is one of the key steps in catalytic hydrogenation of alkenes and alkynes (Chapter 28). For compounds with the metal in lower oxidation states the reaction proceeds via initial oxidative-addition of hydrogen followed by H transfer to the α-carbon:

$$\mathrm{L}_n\mathrm{MR} + \mathrm{H_2} \rightleftharpoons \mathrm{L}_n\mathrm{M(H)_2R} \longrightarrow \mathrm{L}_n\mathrm{MH} + \mathrm{RH}$$

However, in many cases where the metal is in a high oxidation state, oxidative-addition of H_2 is impossible (cf. the decomposition of WMe_6 noted earlier), as in the reaction of the tungsten(VI) complex[37]:

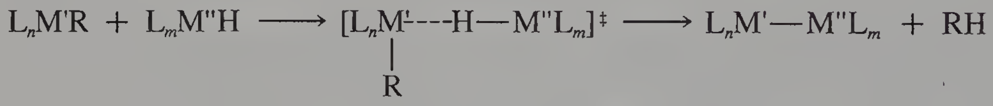
$$WMe_6(PMe_3) + 5H_2 + 3PMe_3 \longrightarrow WH_4(PMe_3)_4 + 6CH_4$$

In such cases, although a molecular hydrogen complex (Section 24-7) may be an intermediate, there must be elimination via a four-center transition state (25-XVIII)



(25-XVIII)

More complicated reactions can, however, occur; for example, with $Cp(PPh_3)CoMe_2$,[38] where the final stage is binuclear



$$L_nM'R + L_mM''H \longrightarrow [\underset{\displaystyle R}{\underset{|}{L_nM'}}\text{---}H\text{—}M''L_m]^\ddagger \longrightarrow L_nM'\text{—}M''L_m + RH$$

Many examples of such interactions of metal hydrides and metal alkyls (and also L_nMNR_2 and L_nMOR) are known.

3. *Alkyl Exchange Reactions.* Interaction of alkyls with, for example, halides, can lead to exchanges,[39] an example being

$$(Me_3P)_2(PhN)ReMe_3 + (Me_3P)_2(PhN)ReCl_3 \longrightarrow (Me_3P)_2(PhN)ReCl_2Me + (Me_3P)_2(PhN)ReClMe_2$$

Such bimolecular reactions may involve ligand dissociation to allow bridge halide or alkyl intermediates to be formed.

4. *Electrophilic Cleavage.*[40] Attacks by halogens or HX usually proceed via the reactions

$$\begin{tikzcd} & L_nMX + RH \\ L_nMR \arrow[ur, "HX"] \arrow[dr, "X_2"'] & \\ & L_nMX + RX \end{tikzcd}$$

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[37] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.*, **1981,** 1204; J. E. Bercaw *et al., J. Am. Chem. Soc.*, 1985, **107,** 4670.

[38] A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, **103,** 2488.

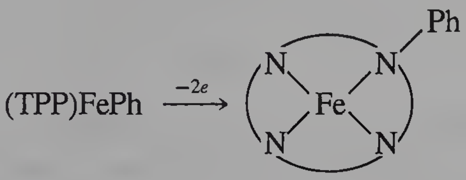
[39] J. D. Scott and R. J. Puddephatt, *Organometallics,* 1983, **2,** 1643; G. Wilkinson *et al., Polyhedron,* 1982, **1,** 31; R. G. Bergman *et al., J. Am. Chem. Soc.*, 1980, **102,** 4948.

[40] T. C. Flood, *Top. Stereochem.*, 1981, **12,** 37; H. Brunner, *Adv. Organomet. Chem.*, 1980, **18,** 151.

Extensive studies of the stereochemistry at both C and at M has been performed using optically active compounds. For example,[41] cleavage of (+)-(*S*)-CpRe(NO)(PPh_3)Me with HX shows >99% retention of configuration at Re, although halogens give racemic mixtures.

5. *Electron Transfer Cleavage.* Oxidation electrochemically or chemically can lead to loss of alkane by coupling reactions, for example as noted above for Et_2Nibipy.

In some cases migration of an aryl or alkyl group to ligand[42] occurs, as in the reaction of the tetraphenylporphyrin compound:



TRANSITION METAL-TO-CARBON MULTIPLE BONDS[43]

Complexes that have M═C bonds were first prepared by E. O. Fischer and his students by the interaction of acylate anions (Section 22-8) with electrophiles. These compounds were 18-electron species in low oxidation states where :CR_2 could be considered to replace :CO as in $(CO)_5CrCR_2$. These have been called *carbene complexes.* Subsequently, compounds in high oxidation states such as $Cl_2H(PR_3)_3Ta^V(CHCMe_3)$ with 10 to 16 electrons have been made, commonly by α-hydrogen removal from alkyl groups. These have been termed *alkylidene complexes.* The IUPAC convention now recommends that the term carbene should be restricted to free CR_2 and that all complexes should be termed alkylidenes (see Table 25-1). Similarly, it is recommended that "alkylidyne" includes (M≡CR) "carbyne" complexes.

Alkylidenes are involved in many stoichiometric and catalytic reactions some of which will be discussed in Chapter 28.

ALKYLIDENE COMPLEXES

25-7. Low-Valent Alkylidene or Carbene Complexes

Carbene complexes commonly have CO or PR_3 ligands and the most intensively studied are those of Cr, Mo, and W. Although they could be formulated as having a M═C double bond (25-XIXa) other canonical forms evidently

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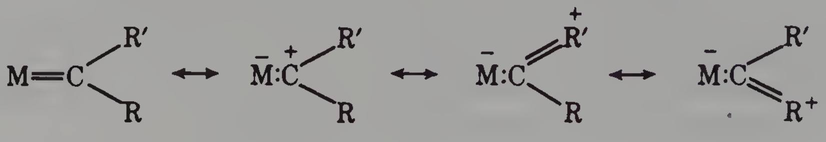
[41] J. A. Gladysz *et al., Inorg. Chem.,* 1984, **23,** 4022.

[42] K. M. Kadish *et al., J. Am. Chem. Soc.,* 1984, **106,** 4472.

[43] K. H. Dotz *et al., Transition Metal Carbene Complexes,* Verlag Chemie, Weinheim, 1983; K. H. Dotz, *Angew. Chem. Int. Ed. Engl.,* 1984, **23,** 587; F. J. Brown, *Prog. Inorg. Chem.,* 1980, **27,** 1 (reactions); T. E. Taylor and M. B. Hall, *J. Am. Chem. Soc.,* 1984, **106,** 1576; H. Nakatsuji *et al., J. Am. Chem. Soc.,* 1984, **106,** 5592 (bonding).

are involved (25-XIXb-d). Many of the earlier known complexes have OR or NR_2 groups attached to carbon, and electron flow from lone pairs on O or N leads to a contribution of the type (25-XIXc,d) through O—C or N—C $p\pi \rightarrow p\pi$ bonding. However, several complexes without such groups are known.

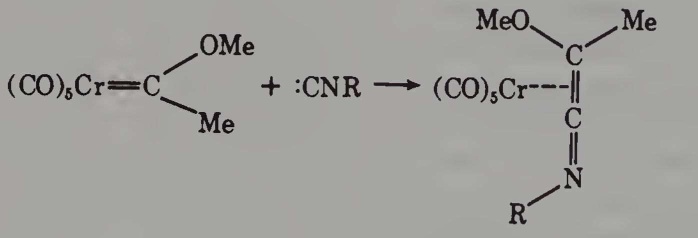


(a) (b) (c) (d)

(25-XIX)

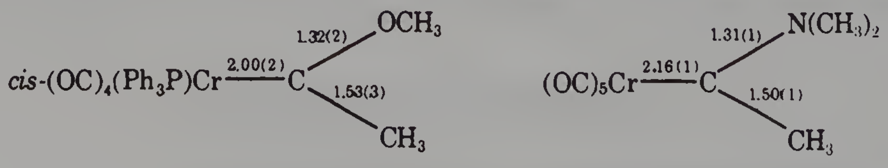
In the high-valent *alkylidenes* the $M{=}CR_2$ bond is best regarded as being formed by donation of π electron density from a filled sp^2 orbital on C to an empty orbital on the metal. The reactions of *alkylidenes* suggest that the C atom bound to the metal is *nucleophilic* and the compounds can be compared to phosphanemethylenes, cf. $L_nM{=}CH_2$ and $R_3P{=}CH_2$.

In the *carbene complexes,* the C atom bound to the metal is *electrophilic* and is readily attacked by nucleophilic reagents as in the following reaction:



Ketenimine complex

The structures of many carbene compounds have been determined, representative examples being (25-XXa,b). The M—CRR′ grouping is *always*



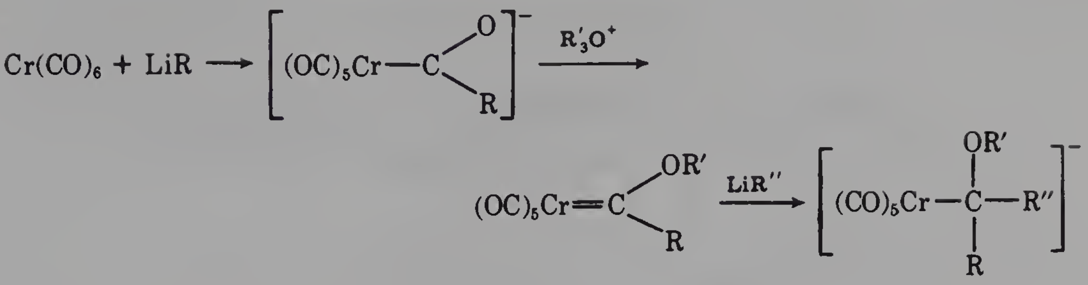
(a) (b)

(25-XX)

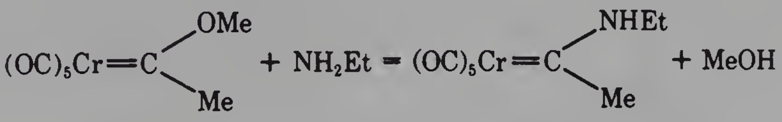
planar, and the M—C distances indicate considerable shortening consistent with multiple-bond character. The C—O and C—N distances are also shortened, as expected with π bonding.

The compounds can be synthesized by a wide variety of reactions; some examples are the following:

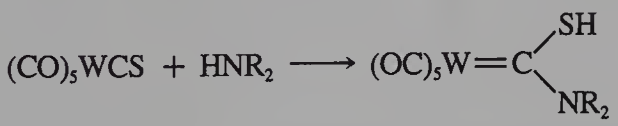
1. *From Metal Carbonyls.* Electrophilic attacks on acylate anions give alkoxo carbenes



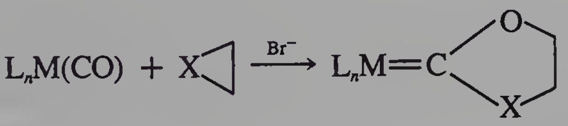
Note that this reaction is not universal; thus $[(CO)_4FeC(O)R]^-$ in some solvents tends to alkylate at the metal.[44] Other carbenes can be obtained in exchange reactions, for example,



Nucleophilic attacks can also be made on thiocarbonyls[45]:

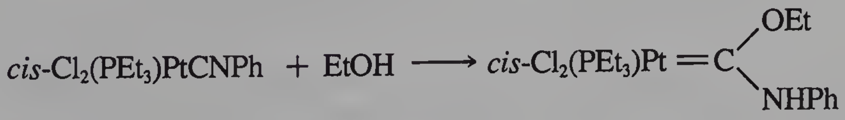


while cyclic compounds can be made by Br^- catalyzed reactions:

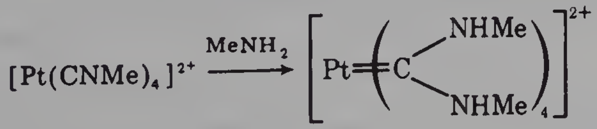


X = O, N

2. *Nucleophilic Attacks on Coordinated Isocyanides.* These reactions were discussed in Section 8-11 but an example is



Unidentate, chelate, bis, and tetrakis alkylidenes can be so obtained. An example is the reaction that gives a square, formally platinum(II) complex:



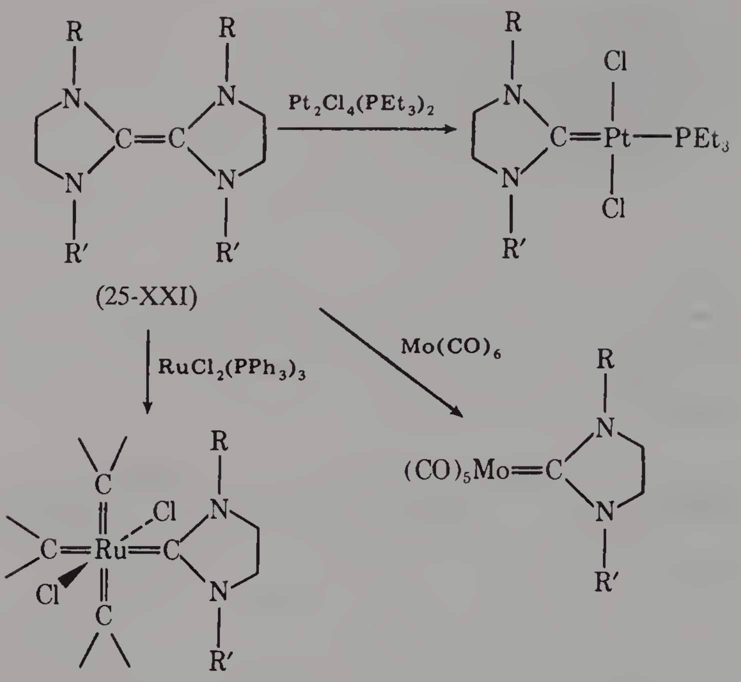
3. *Cleavage of Electron-Rich Alkenes.*[46] These alkenes are of the type (25-XXI) and react as follows:

---

[44] M. F. Semmelhack and R. Tamura, *J. Am. Chem. Soc.*, 1983, **105,** 4099.

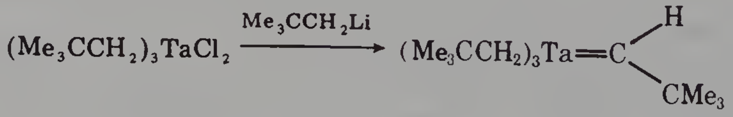
[45] R. J. Angelici *et al., Inorg. Chem.*, 1981, **20,** 118; *Inorg. Chim. Acta*, 1985, **100,** 57.

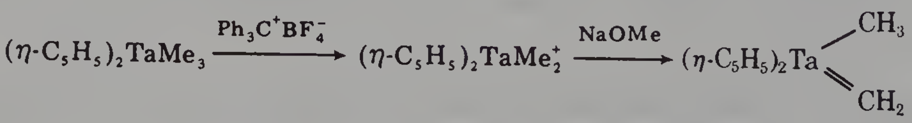
[46] M. F. Lappert *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2355.

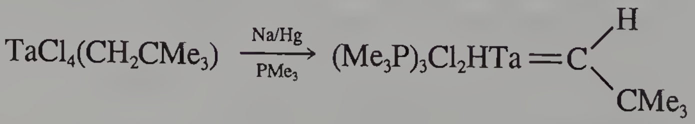

(25-XXI)

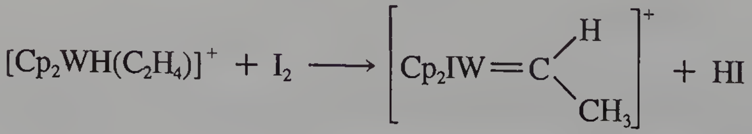
25-8. High-Valent Alkylidene Complexes

The most studied compounds are those of Nb, Ta, Mo, and W but compounds of other transition metals, for example Ti and Fe, are known. They are obtained mainly in reactions in which α-hydrogen atoms of alkyl groups are either adventitiously or deliberately removed.[47] Some typical examples are


$$(Me_3CCH_2)_3TaCl_2 \xrightarrow{Me_3CCH_2Li} (Me_3CCH_2)_3Ta{=}C\begin{matrix}H\\CMe_3\end{matrix}$$


$$(\eta\text{-}C_5H_5)_2TaMe_3 \xrightarrow{Ph_3C^+BF_4^-} (\eta\text{-}C_5H_5)_2TaMe_2^+ \xrightarrow{NaOMe} (\eta\text{-}C_5H_5)_2Ta\begin{matrix}CH_3\\{=}CH_2\end{matrix}$$


$$TaCl_4(CH_2CMe_3) \xrightarrow[PMe_3]{Na/Hg} (Me_3P)_3Cl_2HTa{=}C\begin{matrix}H\\CMe_3\end{matrix}$$


$$[Cp_2WH(C_2H_4)]^+ + I_2 \longrightarrow \left[Cp_2IW{=}C\begin{matrix}H\\CH_3\end{matrix}\right]^+ + HI$$

There are, however, many other methods, such as the following:

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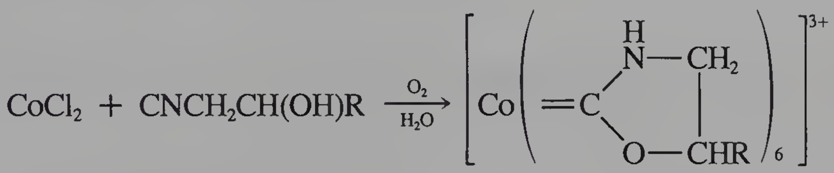
[47] See, for example, R. R. Schrock *et al.*, *J. Am. Chem. Soc.*, 1983, **105,** 4942; G. A. Miller and N. J. Cooper, *J. Am. Chem. Soc.*, 1985, **107,** 709; J. A. Osborn *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985,** 793.

1. Reactions of diazomethane or other diazo compounds[48a] R_2CN_2, for example,

$$OsCl(NO)(PR_3)_3 + CH_2N_2 \longrightarrow CH_2{=}OsCl(NO)(PR_3)_2$$

2. Oxidation of isocyanide compounds



3. Halogenated alkylidenes can be obtained by reduction of Fe^{III} porphyrins in the presence of CCl_4 or other chlorinated hydrocarbons (this may explain the toxicity of such compounds); for example, the tetraphenylporphyrin complex reacts as follows:

$$(TPP)FeCl + CCl_4 \xrightarrow[\text{MeOH}]{\text{Zn, etc.}} (TPP)Fe{=}CCl_2$$

A similar reaction using CI_4 leads to the "cumulene" (TPP)-Fe=C=Fe(TPP).[48b]

Many CF_2 species[49] are also known, sometimes derived by F^- abstraction from CF_3 groups, for example,

$$Cp(Ph_3P)COFeCF_3 + BF_3 \xrightarrow{SO_2(l)} [Cp(Ph_3P)COFe{=}CF_2]BF_4$$

4. From imminium salts[50] by reactions of the types

$$[W(CO)_5]^{2-} + Me_2N{=}CPh_2^+ \longrightarrow [(CO)_5W{-}C(Ph)_2NMe_2]^- \xrightarrow{2H^+} (CO)_5W{=}CPh_2 + Me_2NH_2^+$$

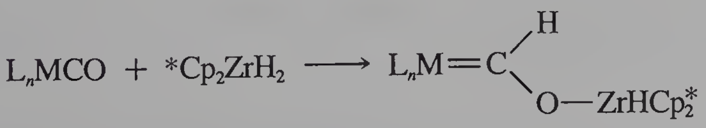
$$[Fe(CO)_4]^{2-} + 2Me_2N{=}CH_2^+ \longrightarrow (CO)_4Fe{=}C(H)NMe_2 + NMe_3$$

5. From —CH_2X compounds[51] by reactions such as

$$^*Cp(CO)(PPh_3)FeCH_2OMe \xrightarrow[-\text{MeOH}]{H^+} [^*Cp(CO)(PPh_3)Fe{=}CH_2]^+$$

$$Cp(CO)_2FeCH_2Cl \xrightarrow[CH_2Cl_2]{AgPF_6} [Cp(CO)_2Fe{=}CH_2]^+$$

6. From interaction of metal hydride and carbonyl compounds of oxophilic elements[52]:



[48a] See M. P. Doyle, *Acc. Chem. Res.*, 1986, **19**, 348; W. R. Roper *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987**, 563.

[48b] D. Mansuy *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 207.

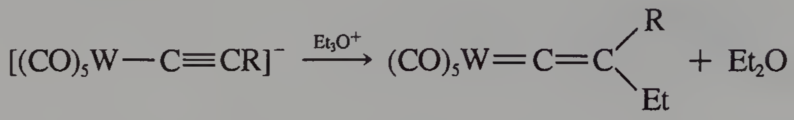
[49] A. M. Crespi and D. F. Shriver, *Organometallics*, 1985, **4**, 1830.

[50] N. J. Cooper *et al.*, *J. Am. Chem. Soc.*, 1981, **103**, 238.

[51] J. Guerchais and D. Astruc, *J. Chem. Soc. Chem. Commun.*, **1985**, 835; T. W. Bodnar and A. R. Cutler, *Organometallics*, 1985, **4**, 1558.

[52] J. E. Bercaw *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 5178.

Metallocumulenes.[53] Acetylides can react with electrophiles, one example being



$$[(CO)_5W{-}C{\equiv}CR]^- \xrightarrow{Et_3O^+} (CO)_5W{=}C{=}C(R)(Et) + Et_2O$$

to give *vinylidenes* or *alkenylidenes*. These in turn can be converted on electrophilic attack to alkylidynes to be discussed later:

$$(CO)_5W{=}C{=}CH(R) \xrightarrow[Me_4NI]{CF_3SO_3H} I(CO)_4W{\equiv}CCH_2R$$

The reaction of electrophile E,

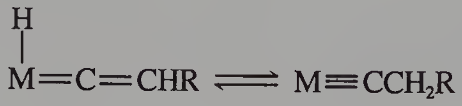
$$M{=}C{=}CR_2 \underset{base}{\overset{E}{\rightleftharpoons}} W{\equiv}C{-}CER_2$$

is a general one.

A similar conversion[54a] involves initial oxidative-addition of an acetylene and H transfer,

$$(R_3P)_2ClRh(PhC{\equiv}CH) \rightleftharpoons L_nRh(H)(C{\equiv}CPh) \xrightarrow{py} L_n(py)Rh{=}C{=}C(H)Ph$$

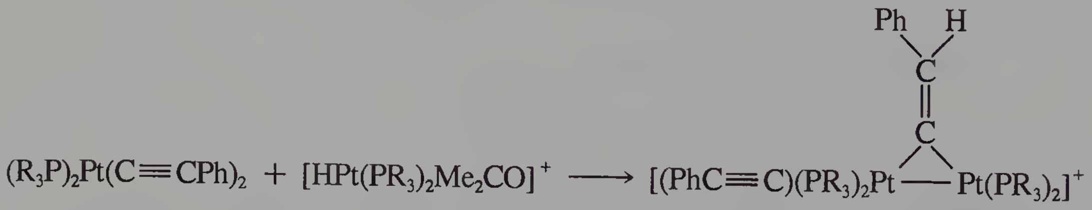
and in certain cases the reaction



$$\overset{\displaystyle H}{\overset{|}{M}}{=}C{=}CHR \rightleftharpoons M{\equiv}CCH_2R$$

may be reversible.[54b]

Bridging vinylidenes[55] can also be obtained, for example,



The interrelationship between species with M—C, M═C, and M≡C bonds are illustrated by Scheme 25-1.

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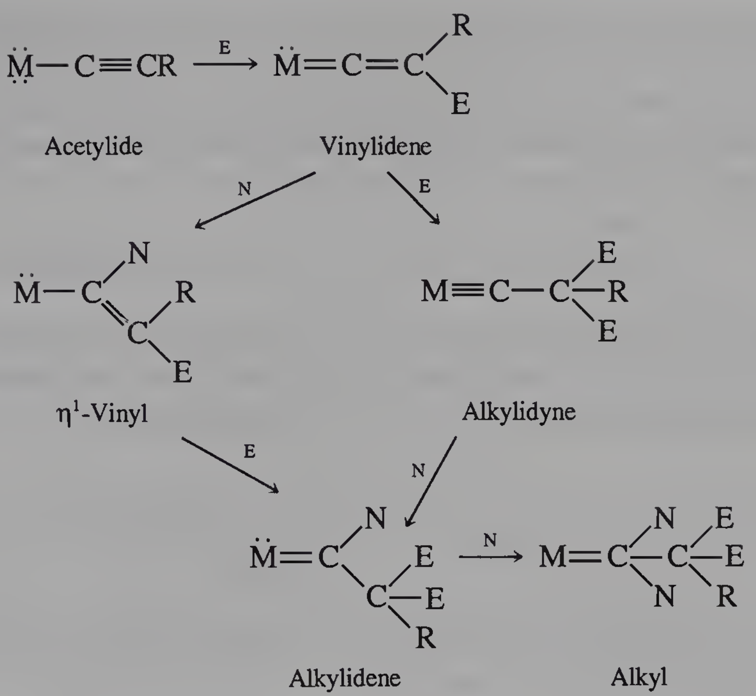
[53] See, for example, A. Mayr *et al., J. Am. Chem. Soc.*, 1984, **106,** 1517; K. R. Birdwhistell and J. L. Templeton, *Organometallics*, 1985, **4,** 2062; H. Werner *et al., J. Chem. Soc. Chem. Commun.*, **1987,** 852.

[54a] H. Werner *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 406; J. L. Templeton *et al., J. Am. Chem. Soc.*, 1985, **107,** 4474.

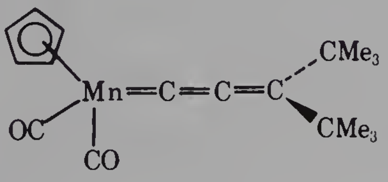
[54b] A. Höhn and H. Werner, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 737.

[55] C. M. Lukehart *et al., J. Am. Chem. Soc.*, 1984, **106,** 3050.



Scheme 25-1

Other types of cumulenes are the *allenylidenes* (25-XXIIa) and *heterocumulenes* such as (25-XXIIb).[56]



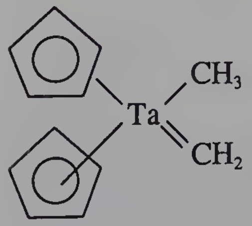
(a)

$[(CO)_5W{=}C{=}N{=}CR_2]^+$

(b)

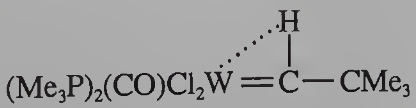
(25-XXII)

The structures of numerous alkylidenes have been determined. In $Cp_2Ta(CH_3)(CH_2)$ (25-XXIII) a direct comparison of M═C and M—C bond lengths is possible. In alkylidenes the M═CH angles are generally small, down to 78°, while the M═C—R angles are large, up to 170°. An example



C—Ta = 2.246 Å
C═Ta = 2.026 Å

(25-XXIII)



$(Me_3P)_2(CO)Cl_2W{=}\overset{H}{C}{-}CMe_3$

(25-XXIV)

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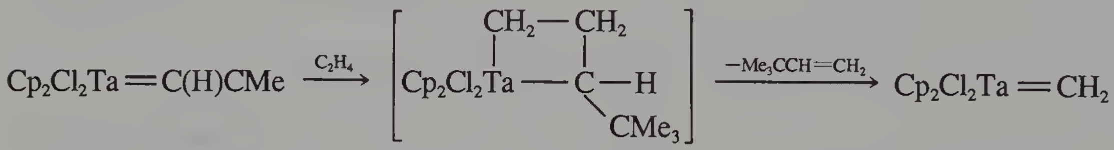
[56] H. Fischer *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985,** 537; H. Fischer *et al.*, *Organometallics*, 1986, **5,** 2187; F. Seitz and M. S. Wrighton, *Inorg. Chem.*, 1987, **26,** 64.

of a distorted species is (25-XIV) where a sort of agostic interaction may be involved.[57]

Methylidenes.[58a] As noted previously, several stable compounds are known, but unstable ones such as Mo=CH_2 species obtained by action of MeLi on $MoCl_5$ can be used as CH_2 transfer agents.[58b] Methylidene can also insert into M—C bonds[59]

$$[Cp_2W(Ph)CH_2]^+ \xrightarrow{MeCN} [Cp_2W(CH_2Ph)MeCN]^+$$

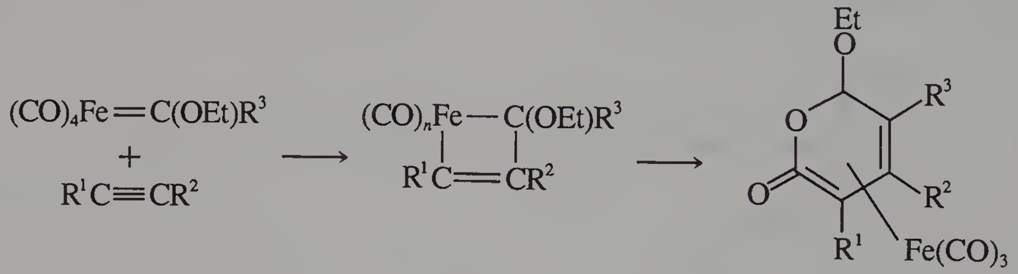
Other Reactions. Alkylidenes are intermediates in the alkene metathesis reaction (Section 28-16), which involves addition of a C=C bond across an M=C bond to give a metallacycle. A model for the system is



Alkylidenes of the type $(t\text{-}BuCH_2O)_2Br_2W{=}CHR$ can also react with ketones in a Wittig-type reaction (Section 11-12)[60a]:

$$W{=}CR_1R_2 + R_3R_4CO \longrightarrow W{=}O + R_1R_2C{=}CR_3R_4$$

Acetylenes can also react[60b]:



ALKYLIDYNE COMPLEXES

25-9. Low-Valent Alkylidynes or Carbynes

Compounds with M≡CR bonds are similar to carbenes and can be made from them by the reaction:

$$cis\text{-}(OC)_4(Me_3P)Cr{=}CMe(OMe) \xrightarrow[\text{pentane}]{BX_3}$$

$$(OC)_3(Me_3P)XCr{\equiv}CMe + CO + (BX_2OMe)$$

---

[57] M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, 1983, **22,** 1574.

[58a] E. A. Carter and W. A. Goddard III, *J. Am. Chem. Soc.*, 1986, **108,** 2180, 4746; J. E. Bercaw *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 5347; R. H. Grubbs *et al.*, *J. Am. Chem. Soc.*, 1987, **109,** 4880.

[58b] T. Kaufmann *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1984, **23,** 532.

[59] Y. Stenstrøm and W. M. Jones, *Organometallics*, 1986, **5,** 178; P. Jernakoff and N. J. Cooper, *Organometallics*, 1986, **5,** 747.

[60a] J. A. Osborn *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986,** 531.

[60b] M. F. Semmelhack *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 5363.

Structural studies on carbyne complexes show that in some cases the W—C—C group is not linear [e.g., *trans*-$I(CO)_4W{\equiv}CPh$ has an angle of 162°], whereas in other compounds [e.g., *trans*-$I(CO)_4Cr{\equiv}CCH_3$] the Cr—C—C group is linear. The force constants for M≡C bonds are comparable to those for M≡N compounds.

25-10. Alkylidynes

These are obtained in deprotonation of alkylidenes having a C—H group as in the reaction (dmp = N,N′-dimethylpiperazine)

$$(Me_3CCH_2)_3Ta{=}C(H)CMe_3 \xrightarrow[\text{dmp}]{\text{BuLi}} (\text{Li dmp})[(Me_3CCH_2)_3Ta{\equiv}CCMe_3]$$

or by direct α-elimination via a methyl compound:

$$WCl_2(PMe_3)_4 \xrightarrow{AlMe_3} trans\text{-}W(CH)Cl(PMe_3)_4$$

Other syntheses include electrophilic attacks on isocyanides:

$$(dppe)_2ClRe(CNR) \xrightarrow{H^+} [(dppe)_2ClRe{\equiv}CN(H)R]^+$$

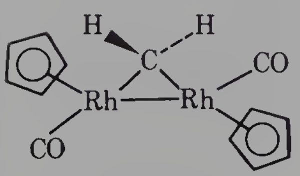
Many different types of compound are now known,[61] examples being $(RO)_3WC$*t*-Bu, $[Cl_4WC$*t*-Bu$]^-$, (*t*-$BuCH_2)_3WC$*t*-Bu, and *trans*-$(Me_3P)_2W(CH_2CMe_3)(CHCMe_3)(CCMe_3)$, which has W—C, W=C and W≡C bonds.

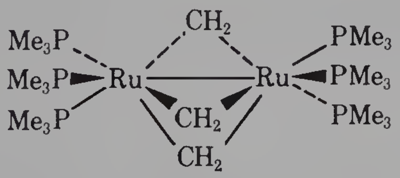
Alkylidynes are intermediates in alkyne metathesis, just as alkenes are in alkene metathesis (Section 28-17); a model step is simple reversible cleavage[62]:

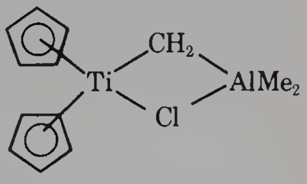
$$W_2(Ot\text{-}Bu)_6 + MeC{\equiv}CMe \rightleftharpoons 2(t\text{-}BuO)_3W{\equiv}CMe$$

25-11. Bridging Alkylidenes and Alkylidynes[63]

μ-Alkylidenes. The simplest bridge group is CH_2 and some representative examples are (25-XXV) to (25-XXVII).[64a] Compounds like (25-XXV) that


(25-XXV)


(25-XXVI)


(25-XXVII)

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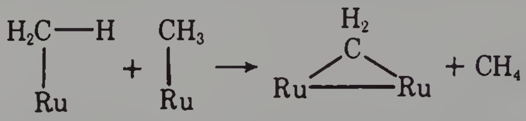
[61] See, for example, R. R. Schrock *et al., Acc. Chem. Res.*, 1986, **19,** 342; *Organometallics*, 1985, **4,** 1937; A. L. Pombeiro *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 246; A. Mayr *et al., J. Am. Chem. Soc.*, 1986, **108,** 6079.

[62] M. H. Chisholm *et al., Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 446.

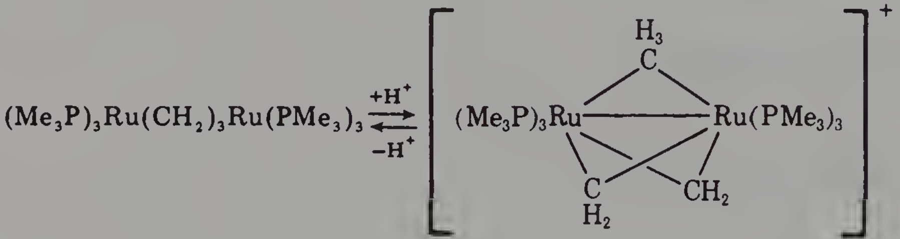
[63] J. E. Hahn, *Prog. Inorg. Chem.*, 1984, **31,** 205; W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20,** 160; M. F. Lappert *et al., Chem. Rev.*, 1983, **83,** 135; M. Pfeffer *et al., J. Am. Chem. Soc.*, 1986, **108,** 4222 (μ-CH_2); M. D. Curtis *et al., J. Am. Chem. Soc.*, 1987, **109,** 3603 (μ-CAr_2).

[64a] See, for example, W. A. Herrmann *et al., J. Organomet. Chem.*, 1983, **250,** 319.

have a metal-metal bond can be referred to as *dimetallacyclopropanes*.[64b] Some of these compounds, such as (25-XXVI) and (25-XXVII) can be obtained in alkylation reactions, the former by interaction of $[Ru_3O(CO_2Me)_6(PMe_3)_3]^+$ with MeLi presumably via an α-H transfer:



The ruthenium compound shows the relation between bridging methyl and bridging CH_2 compounds since protonation of (μ-CH_2) gives (μ-CH_3).

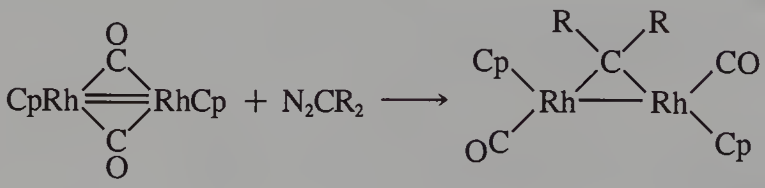


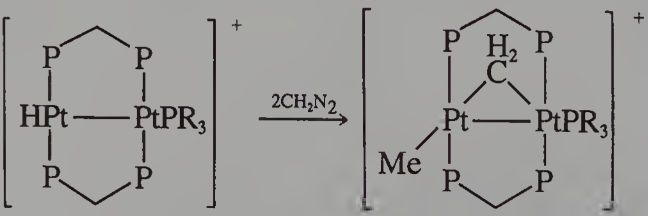
Aluminum trimethyl produces CH_2-bridged species in certain cases,[65] as in (25-XXVII) by the reaction

$$Cp_2TiCl_2 + 2AlMe_3 \longrightarrow Cp_2Ti(\mu\text{-}Cl)(\mu\text{-}CH_2)AlMe_2 + CH_4 + AlClMe_2$$

There are two general methods of synthesis of compounds with single bridges:

1. Interaction of CH_2N_2 or other diazo compounds[66a] with complexes having metal–metal bonds, as in these examples:

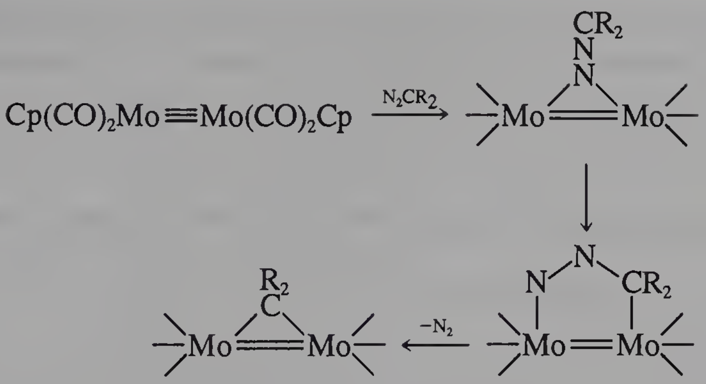




[64b] See, for example, R. J. Puddephatt *et al., Organometallics,* 1985, **4,** 1400.

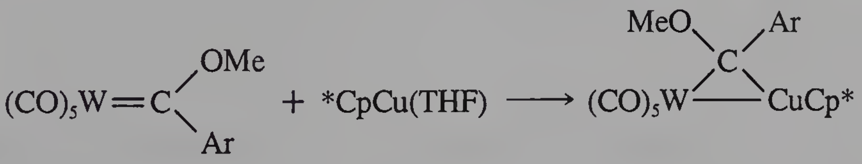
[65] F. N. Tebbe *et al., Inorg. Chem.,* 1982, **21,** 2900. See also D. Wingbermühle *et al., Angew. Chem. Int. Ed. Engl.,* 1986, **25,** 910; J. Schwartz *et al., Organometallics,* 1987, **6,** 1346.

[66a] See, for example, M. D. Curtis *et al., Organometallics,* 1986, **5,** 2283.



N-alkyl-*N*-nitrosoureas and ylids like $Ph_3P{=}CH_2$ can also be used as $:CR_2$ sources.

2. Carbene complexes can react with other metal complexes that have weakly bound ligands, for example,

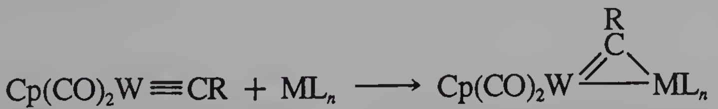


This method has been developed by F. G. A. Stone and co-workers[66b] for synthesis of a wide range of binuclear and cluster compounds not only from alkylidenes but also, as noted next, alkylidynes. Other methods include

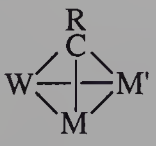
$$[Fe_2(CO)_8]^{2-} + CH_2I_2 \longrightarrow (CO)_4Fe(\mu\text{-}CH_2)Fe(CO)_4 + 2I^-$$

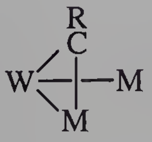
$$Os_3(CO)_{12} \xrightarrow{BH_4^-} [Os_3(CHO)(CO)_{11}]^- \xrightarrow{H^+} (\mu\text{-}CH_2)Os_3(CO)_{11}$$

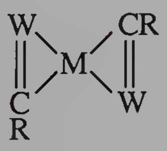
μ-Alkylidynes. As just noted a general synthesis involves reactions such as

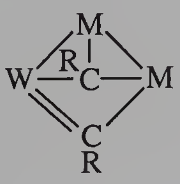


A wide range of core structures can be obtained. Some examples of the core structures involved are









In addition, there are species with RC—CR or RC=CR groupings.

μ-Alkylidyne compounds can be obtained by loss of hydrogen from com-

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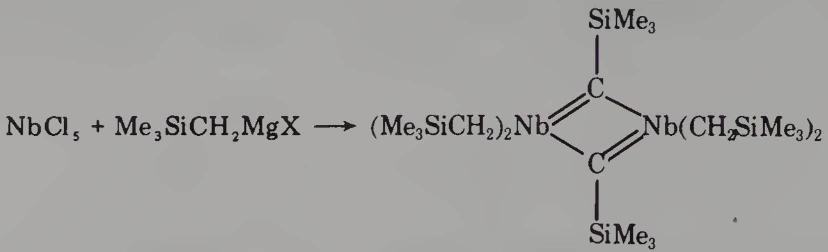
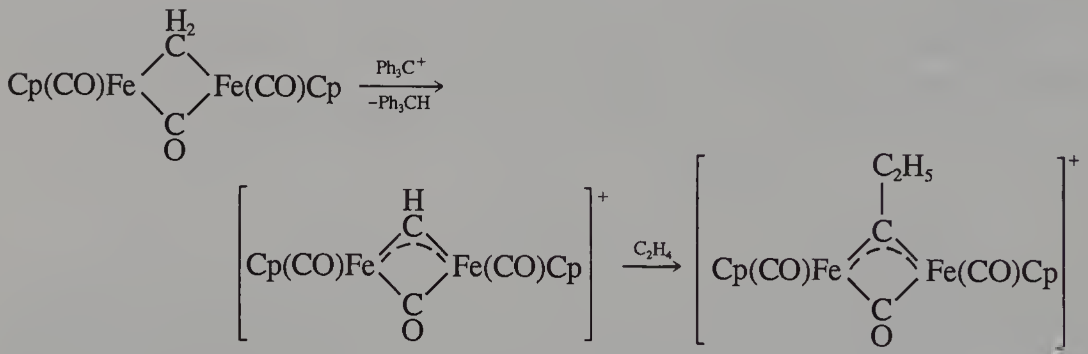
[66b] F. G. A. Stone *et al.*, *J. Chem. Soc. Dalton Trans.*, **1987**, 2219, and earlier papers; *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 89.

pounds with alkyl groups that have weakly acidic methylene hydrogen atoms,[67a] for example, (25-XXVIII) is formed in Grignard reactions.

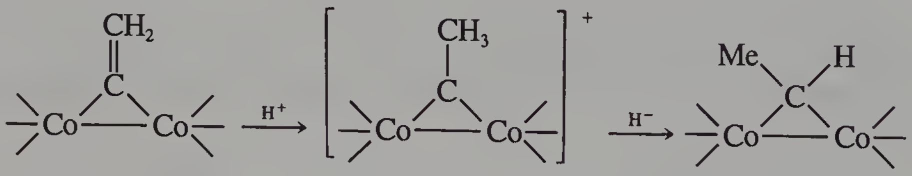


(25-XXVIII)

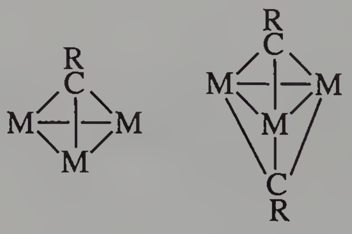
Note also the following sequence,[67b] especially the reaction with ethylene:



Bridges can also be obtained by H^+ additions to μ-vinylidene species,[68] for example to $[Cp(CO)_2CO]_2(\mu\text{-}CCH_2)$,



The niobium compound (25-XXVIII) is one of a class of compounds that have M_2C_2 cores and can be termed *1,3-metallacyclobutadienes.* Another major class of bridged species are μ_3-alkylidynes of types (25-XXIXa and b).



(a) (b)

(25-XXIX)

[67a] M. H. Chisholm *et al., J. Am. Chem. Soc.,* 1985, **107,** 5116; *Organometallics,* 1987, **6,** 1065; N. G. Connelly *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 14, 16.

[67b] C. P. Casey *et al., J. Am. Chem. Soc.,* 1986, **108,** 4043.

[68] E. N. Jacobsen and R. G. Bergman, *J. Am. Chem. Soc.,* 1985, **107,** 2023.

Many cobalt compounds[69] of the first type are known; $(\mu_3\text{-CH})Co_3(CO)_9$ is made by the action of $CHCl_3$ on $Co_2(CO)_8$. They have an extensive chemistry including redox reactions. There appears to be delocalization of electron density in the region of the apical C atom that allows transmission of electronic effects between the Co atoms and R groups.

It seems best to regard the C atom as having *sp* rather than sp^3 hybridization although formally the latter is convenient.

μ-CR groups can also be formed in alkyne cleavages[70] (cf. Sections 26-4 and 28-16).

For additional references see the list in Chapter 26.

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[69] B. H. Robinson *et al., Organometallics,* 1986, **5,** 1122 et seq.; P. T. Chesky and M. B. Hall, *Inorg. Chem.*, 1981, **103,** 4419.

[70] J. R. Shapley *et al., Organometallics,* 1984, **3,** 1595.

Chapter Twenty Six

Compounds of Transition Metals with Alkenes, Alkynes, and Delocalized Hydrocarbon Systems

ALKENE COMPLEXES

Although the first transition metal hydrocarbon complex, $K[PtCl_3(C_2H_4)]$, was made by Zeise in Copenhagen in 1827, the true nature of the bonding of the ethylene molecule was not settled until the 1950s. The general features and bonding have been discussed in Chapter 2. Although C_2H_4 is normally η^2, the bridged species, $^*Cp_2Yb(\mu,\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$[1a] and $[(R_3P)_2Cl_3Zr]_2(\mu,\eta^2\text{-}C_2H_4)$[1b] are known.

26-1. Types of Alkene Complexes

1. *Nonconjugated Alkenes.* Complexes are formed with all types of alkene and substituted alkenes, including cyclic ones. Nonconjugated polyenes generally function as having independent C═C bonds. Cyclic alkenes such as cycloocta-1,5-diene can give chelate complexes such as $(COD)PtCl_2$. Formation constants for alkene complexes of Cu^+, Ag^+, $PdCl_3^-$, $Rh^I(acac)$, $Cu(bipy)^+$, and a few other metal ions or complex ions are known for various alkenes; ethylene has the highest constant.[2a]

Although alkene complexes, like those of CO or RNC, are normally found in low oxidation states, some compounds with metals in high oxidation states can be isolated, for example, *cis*-$(C_2H_4)OWCl_2(PMe_2Ph_2)_2$.[2b] Unstable complexes in high oxidation states are intermediates in alkene metathesis reactions (Chapter 28). It might be noted in this connection that an example of an alkene–carbene complex has been isolated.[2c]

[1a] C. J. Burns and R. A. Andersen, *J. Am. Chem. Soc.*, 1987, **109**, 915.

[1b] F. A. Cotton and P. A. Kibala, *Polyhedron*, 1987, **6**, 645.

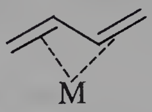
[2a] V. Schurig, *Inorg. Chem.*, 1986, **25**, 945; M. Munakata *et al.*, *Inorg. Chem.*, 1986, **25**, 2622.

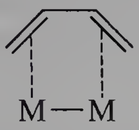
[2b] J. M. Mayer *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 3545.

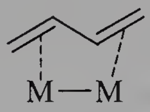
[2c] K. H. Dotz *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 812.

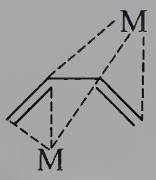
2. *Conjugated Alkenes.*[3a] Probably the most important conjugated diene is *buta-1,3-diene,* which can bind in several different ways as follows:

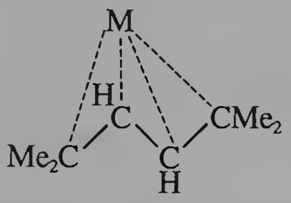

η^4-*s-cis*

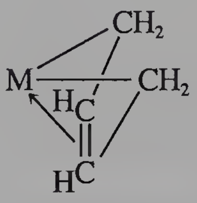

η^4-*s-trans*


μ,η^4-*s-cis*


μ,η^4-*s-trans*

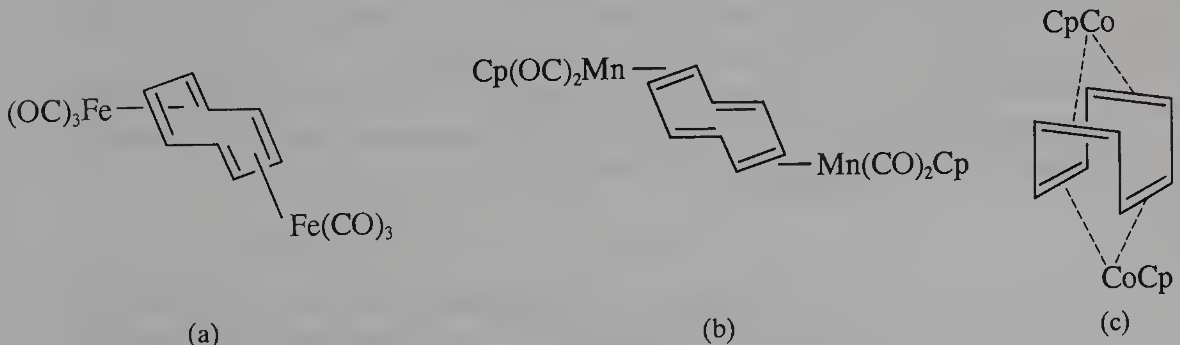

(26-I)


(26-II)


(26-III)

The η^4-*s-cis* is usually more stable than η^4-*s-trans* but the reverse is known in one case, $CpMo(NO)(\eta^4\text{-}C_4H_6)$.[3b] The "sandwich" form (26-I) found in a rhodium chelate phosphine complex has η^3 bonding as from a *cis*-$C_4H_6^{2-}$ ligand[3c] while (26-II) found in $CpMo(NO)C_4H_2Me_4$ has a twisted transoidal, nonplanar diene with the central atoms closer to Mo than the outer ones. The bent cisoid metallocyclopent-3-ene structure (26-III) occurs in some Zr, Hf, and Ta complexes.[3d,e]

In complexes of cyclic alkenes like cycloheptatriene or cyclooctatetraene, not all the C═C bonds may be involved in bonding. Thus in $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ there is one nonbonded C═C, while C_8H_8[4] can bind in η^2, η^4, η^6, and η^8 modes as well as acting as a bridge in at least five ways, three of which are (26-IV, a–c).



(a) (b) (c)

(26-IV)

[3a] C. G. Kreiter, *Adv. Organomet. Chem.*, 1986, **26,** 297; G. Erker *et al., Organometallics,* 1986, **5,** 1023; *Adv. Organomet. Chem.*, 1985, **24,** 1.

[3b] P. Legzdins *et al., J. Am. Chem. Soc.*, 1986, **108,** 3843.

[3c] M. D. Fryzuk *et al., J. Am. Chem. Soc.*, 1985, **107,** 8259.

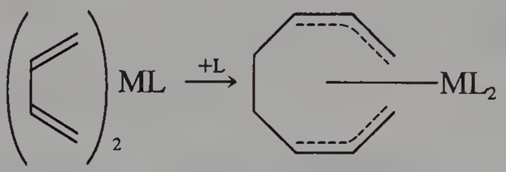
[3d] A. Nakamura *et al., J. Am. Chem. Soc.*, 1985, **107,** 2410.

[3e] J. H. Teuben *et al., Organometallics,* 1987, **6,** 459.

The $Fe(CO)_3$ moiety is particularly prone to bind η^4 and its alkene complexes have been much used in organic synthesis.[5]

In $C_8H_8Fe(CO)_3$, however, the ring is pseudoaromatic and can undergo Friedel–Crafts reactions like ferrocene (Section 26-10) and is fluxional (Section 29-15).

Butadiene interactions with certain elements, notably palladium, have a great tendency to lead to allyl complexes (Section 26-5) and a coupling reaction can also occur[6] for some Fe, Ru, and Os complexes:

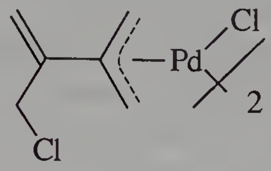


Magnesium–butadiene reagent,[3d,7] $Mg(C_4H_6)(THF)_2$, formally (2-butene-1,4-diyl)magnesium, is useful in synthesis of diene complexes from halides, for example,

$$MnCl_2 + PMe_3 + (C_4H_6)_2Mg \longrightarrow (\eta^4\text{-}C_4H_6)_2MnPMe_3 + MgCl_2$$

3. Cumulenes such as allenes ($R_2C{=}C{=}CR_2$)[8] can form complexes usually η^2, but like dienes, certain metals can give allyls, for example,

$CH_2{=}C{=}CH_2 + PdCl_2(PhCN)_2 \longrightarrow$



For other cumulenes, such as *ketenes,*[9] $R_2C{=}C{=}O$, the bonding depends on the metal. In electron-rich systems, η^2-C,C is favored, while oxophilic metals Ti, Zr, V, and so on, give η^2-C,O bonding.

Although ketene complexes can be made by displacement from ethylene complexes, a bridged ketene (trimetallacyclopentanone!) and a η^2-ketene can be made from alkylidenes by CH_2 transfers[10a]

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[4] W. E. Geiger *et al., J. Am. Chem. Soc.,* 1986, **108,** 7454; A. Salzer *et al., Organometallics,* 1986, **5,** 2413; H. P. Lüthi and C. W. Bauschlicher Jr., *J. Am. Chem. Soc.,* 1986, **108,** 2096.

[5] A. J. Pearson, *Acc. Chem. Res.,* 1980, **13,** 463.

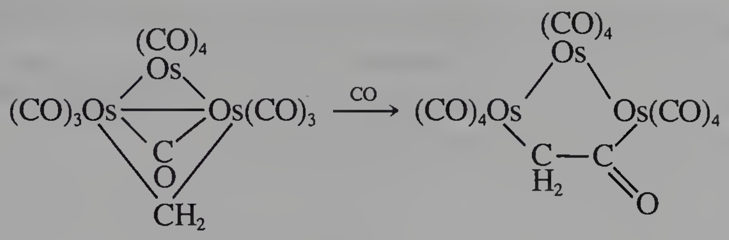
[6] R. Roulet *et al., Organometallics,* 1985, **4,** 2001.

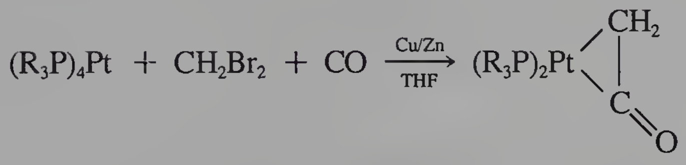
[7] S. S. Wreford *et al., Organometallics,* 1982, **1,** 1506.

[8] M. R. White and P. J. Stang, *Organometallics,* 1983, **2,** 1654; L. S. Hegedus *et al., Organometallics,* 1983, **2,** 1658; A. J. L. Pambeiro *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 1125.

[9] C. P. Casey and J. M. O'Connor, *J. Am. Chem. Soc.,* 1983, **105,** 2919; R. H. Grubbs *et al., J. Am. Chem. Soc.,* 1986, **108,** 1427; C. Floriani *et al., J. Chem. Soc. Dalton Trans.,* **1987,** 1789.

[10a] G. L. Geoffroy *et al., J. Am. Chem. Soc.,* 1983, **105,** 4104; A. Myashita *et al., Organometallics,* 1985, **4,** 1463.





Ketenes can also undergo more complex reactions including deoxygenation to μ-vinylidenes, decarbonylation as above to μ-alkylidenes, and coupling reactions.[10b]

26-2. Synthesis and Reactions of Alkene Complexes

Some syntheses have been noted in earlier sections but the main general methods are

1. Substitution of CO in metal carbonyls or of weakly held ligands, for example,

$$\mathrm{Ag^+ + alkene} \rightleftharpoons [\mathrm{Ag\ alkene}]^+$$

$$\mathrm{Cl_2Pd(RCN)_2 + COD} \longrightarrow \mathrm{Cl_2Pd(COD) + 2RCN}$$

$$\mathrm{Cr(CO)_6 + C_7H_8} \longrightarrow (\eta^6\text{-}\mathrm{C_7H_8})\mathrm{Cr(CO)_3 + 3CO}$$

2. From halides or other compounds in the presence of reducing agents or by use of anionic species (cf., $MgC_4H_6(THF)_2$ cited previously),

$$\mathrm{RuCl_3(aq)} + 2\ \text{cyclohexadiene} \xrightarrow[\mathrm{EtOH}]{\mathrm{Zn}} (\eta^6\text{-}\mathrm{C_6H_6})\mathrm{Ru}(\eta^4\text{-}\mathrm{C_6H_8})$$

$$\mathrm{Ni(acac)_2 + COD} \xrightarrow{\mathrm{Al}t\text{-}\mathrm{Bu_3}} \mathrm{(COD)_2Ni}$$

$$\mathrm{(R_3P)_2PtCl_2 + C_2H_4} \xrightarrow{\mathrm{NaBH_4}} \mathrm{(R_3P)_2Pt(C_2H_4)}$$

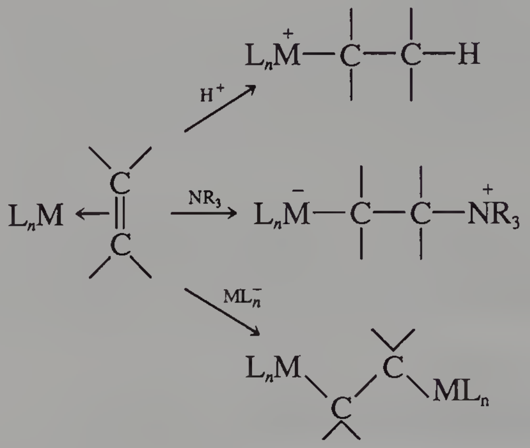
3. Cocondensation of metal vapors with alkenes:

$$\mathrm{Fe + 2COD} \longrightarrow \mathrm{Fe(COD)_2}$$

The formation of alkene complexes in β-hydride transfers of alkyl groups has been discussed (Section 24-8); β-hydride abstraction by Ph_3C^+ is also well established.[10c] The formation of alkene complexes in nucleophilic attacks on carbocyclic complexes is noted later (Section 26-15).

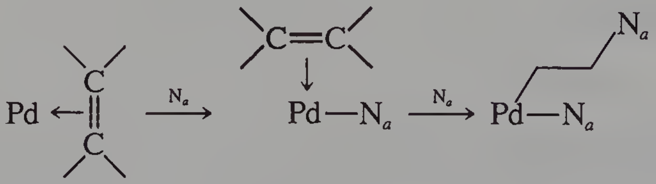
[10b] See T. F. Koetzle *et al.*, *Inorg. Chem.*, 1985, **24**, 1492.
[10c] J. A. Gladysz *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 1757.

Reactions of Alkene Complexes. The most important reactions are those involving hydride transfers to generate alkyls that are discussed (Sections 24-3, 24-8, and 25-4). Coordinated alkenes can also be attacked by a variety of nucleophiles[11a] and electrophiles[11b] for example,

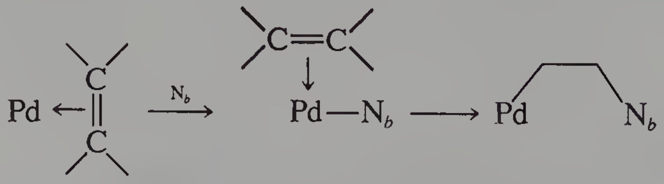


The most important is probably the attack by water on C_2H_4 coordinated to Pd in the Wacker process (Section 28-20). For Pd there are two classes of nucleophiles:

1. Those adding with external trans attack where there is no migration from the metal (OH, OR, and NR_3)



2. Those where metal-to-ligand migration does occur (H, alkyl, aryl)



Diene and polyene complexes can also be attacked, for example, by Me, H, or OMe to give alkyls (see also Sections 24-8 and 26-15).[11c,d]

[11a] See, for example, R. C. Busk, R. J. Angelici, *J. Am. Chem. Soc.*, 1986, **108**, 2735; J. E. Bäckvall *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 4369; M. Green *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 771. M. Rettig *et al.*, *Organometallics*, 1987, **6**, 1211.

[11b] M. J. McGlinchey *et al.*, *Organometallics*, 1987, **6**, 2201.

[11c] M. F. Semmelhack and H. T. M. Le, *J. Am. Chem. Soc.*, 1984, **106**, 2715.

[11d] W. Beck *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 734.

ALKYNE AND ALKYNE-DERIVED COMPLEXES[12a,b]

26-3. Alkyne Complexes

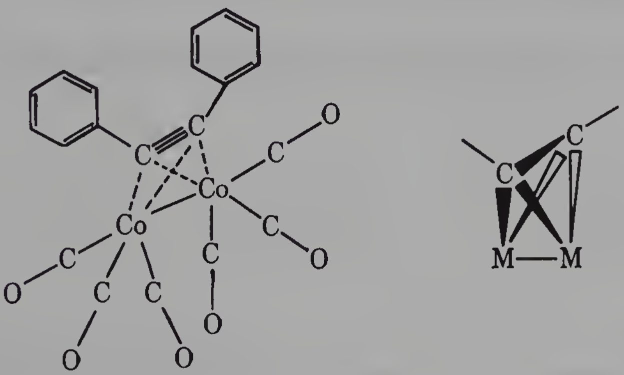
Alkynes can be bound to metals using one or both sets of π bonds, as 2, 3, or 4*e* donors and as bridges. The bonding has been discussed in Chapter 2.[13]

The two extremes of η^2 bonding (*a*) alkene type π bonding or (*b*) metallacyclopropanelike are illustrated in Fig. 26-1. In some η^2-species,[14] as in alkene complexes, the barriers to rotation about the metal to C—C bond center can be determined.

In type (b) the C—C bond lengths are longer than in type (a), ranging from 1.285 Å in $Cp_2Ti(CO)(Ph_2C_2)$ to 1.32 Å in $(Ph_3P)_2Pt(Ph_2C_2)$; in all cases the R groups bend away from the metal.

Three-electron donation occurs in complexes such as $[CpMo(CO)_2(Me_2C_2)]^+$ or $O{=}ReI(Me_2C_2)_2$ and 4*e* donation in $^*CpCl_2Nb(C_2H_2)$ and in both types, two sets of π orbitals are involved in bonding.[15a]

Acetylene bridges of several types are known. Although the bonding in (26-Va) could be conceived as donation from two sets of π bonds at 90°, structural evidence suggests rehybridization to form relatively strong σ bonds in a M_2C_2 unit (26-Vb). Cobalt compounds, $Co_2(CO)_8(C_2R_2)$ have been particularly well studied.[12b,15b]



(a) (b)

(26-V)

[12a] P. Braunstein, *Chem. Rev.*, 1983, **83,** 203.

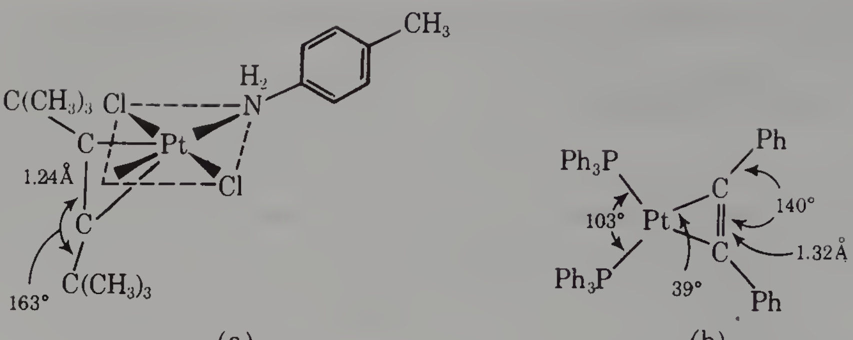
[12b] G. Palyi *et al.*, in *Stereochemistry in Organometallic and Inorganic Compounds,* Vol. 1, I. Bernal, Ed., Elsevier, Amsterdam, 1986 (Co).

[13] See also R. Hoffmann *et al., Inorg. Chem.*, 1982, **21,** 466.

[14] M. Green *et al., J. Chem. Soc. Dalton Trans.*, **1984,** 2747; J. L. Templeton *et al., J. Am. Chem. Soc.*, 1987, **109,** 1401.

[15a] J. M. Meyer *et al., J. Am. Chem. Soc.*, 1985, **107,** 7454; M. D. Curtis and J. Real, *Organometallics,* 1985, **4,** 940; M. Bénard *et al., Inorg. Chem.*, 1986, **25,** 1830.

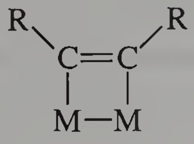
[15b] B. H. Robinson *et al., Organometallics,* 1987, **6,** 1470, 1479.



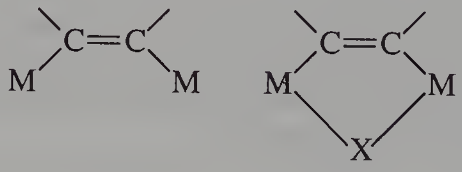
(a) (b)

FIG. 26-1. (a) The structure of a platinum complex in which the alkyne fills essentially the same role as an alkene. (b) The structure of a complex in which diphenylacetylene can be regarded as a divalent bidentate ligand.

Other bridge forms[16a] are (26-VI), which can be called a dimetallacyclobutane, and (26-VII*a* and *b*), a dimetallated alkene.[16b]



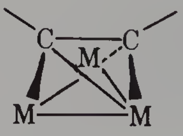
(26-VI)

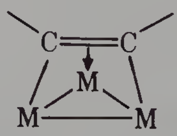


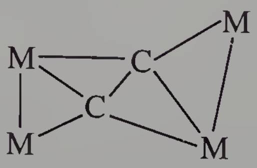
(a) (b)

(26-VII)

In clusters, bridges of the following types are known[16c]:







These species can of course be considered as M_2C_2, M_3C_2, and so on, clusters.

Acetylene complexes are made by reactions such as the following:

$$Cp_2Rh_2(CO)_3 + CF_3C{\equiv}CCF_3 \longrightarrow Cp_2Rh_2(CO)_2(CF_3C_2CF_3)$$

$$Pt(PPh_3)_3 + RC{\equiv}CR \longrightarrow (Ph_3P)_2Pt(RC{\equiv}CR) + PPh_3$$

$$Co_2(CO)_8 + RC{\equiv}CR \longrightarrow Co_2(CO)_6(\mu\text{-}RC{\equiv}CR) + 2CO$$

$$Ni(1,5\text{-}COD)_2 + RC{\equiv}CR \longrightarrow (1,5\text{-}COD)_2Ni_2(\mu\text{-}RC{\equiv}CR)$$

[16a] J. T. Mague, *Organometallics*, 1986, **5**, 981; R. S. Dickson *et al.*, *Organometallics*, 1986, **5**, 1435.

[16b] S. J. Higgins and B. L. Shaw, *J. Chem. Soc. Chem. Commun.*, **1986**, 1629.

[16c] D. Sutton *et al.*, *Inorg. Chem.*, 1986, **25**, 1631; M. I. Bruce *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 701; L. Manojlovic-Muir *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 6527 (μ_3, η^2).

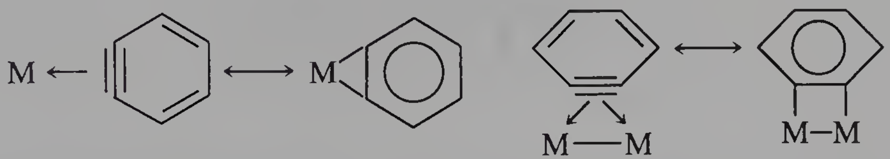
Acetylenes will also add across certain metal triple bonds, as in the reaction

$$Cp_2Mo_2(CO)_4 + RC{\equiv}CR' \longrightarrow Cp_2Mo_2(CO)_4(\mu\text{-}RC{\equiv}CR')$$

Some complexes can be obtained by reduction of halides in the presence of acetylenes, for example,

$$Cp_2MoCl_2 + C_2H_2 \xrightarrow{Na/Hg} Cp_2Mo(C_2H_2)$$

Benzyne complexes[17] have η^2- or μ-C_6H_4 groups (26-VIII*a* and *b*).



(a) (b)

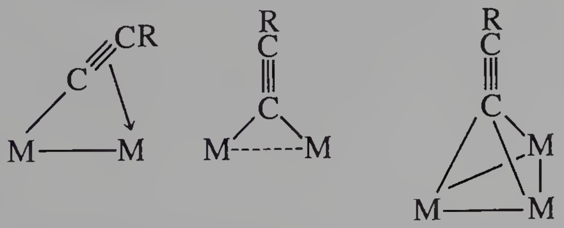
(26-VIII)

They may be obtained by dehydrogenation of benzene by cluster compounds or of phenyl groups bound to a metal or by reactions such as

$$\text{diphosClNi}(o\text{-}BrC_6H_4) \xrightarrow{Na/Hg} \text{diphos Ni}(\eta^2\text{-}C_6H_4)$$

$$Re(o\text{-}C_6H_4Me)_4 + 2PMe_3 \longrightarrow (Me_3P)_2(o\text{-}C_6H_4Me)_2Re(\eta^2\text{-}C_6H_3Me) + C_6H_5Me$$

Acetylides can form bridged complexes of the types[18]



26-4. Alkyne-Derived Compounds

Alkynes quite often react with metal carbonyls and complexes such as $PdCl_2(PhCN)_2$ with easily displacable ligands and in doing so undergo complex reactions by transfers and couplings to give carboxylic or metallacyclic systems often incorporating CO where CO is present.

Some relatively simple reactions involve nucleophilic attacks,[11c,19] for example,

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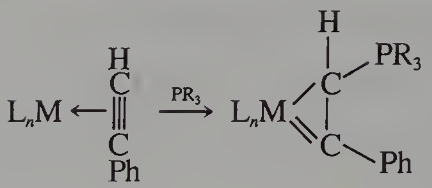
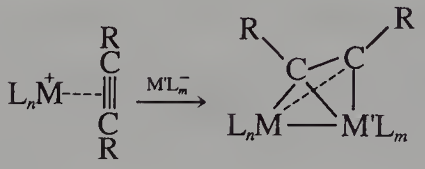
[17] I. P. Rothwell *et al., J. Am. Chem. Soc.*, 1987, **109,** 6471; M. A. Bennett *et al., Organometallics*, 1985, **4,** 1992.

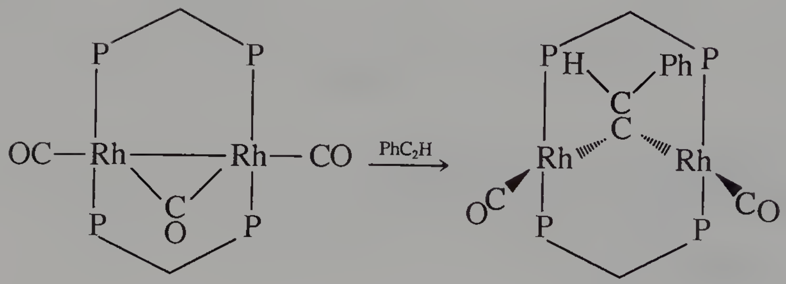
[18] N. Naldini *et al., J. Organomet. Chem.*, 1985, **279,** C42.

[19] J. L. Templeton *et al., J. Am. Chem. Soc.*, 1985, **107,** 6956; D. H. Berry and R. Eisenberg, *J. Am. Chem. Soc.*, 1985, **107,** 7181.

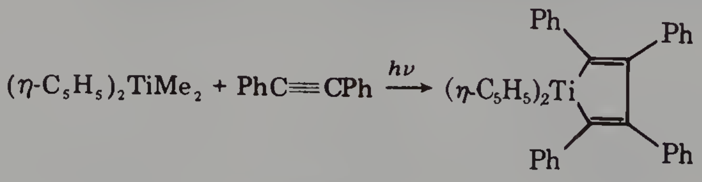


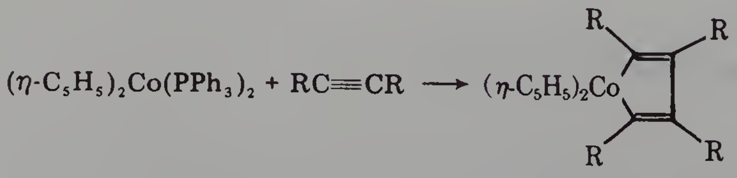
η²-Vinyl

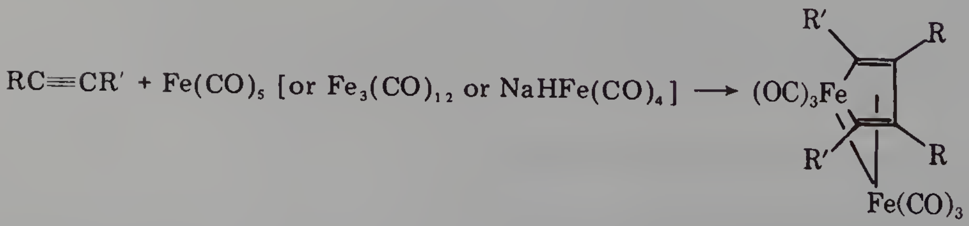




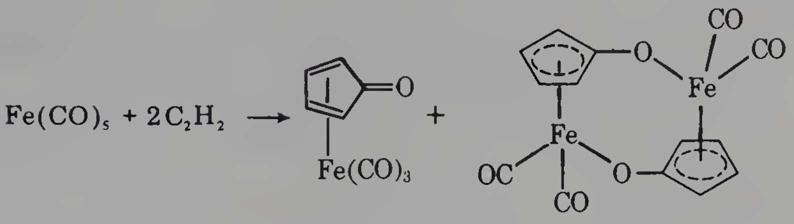
Examples of more complicated reactions are

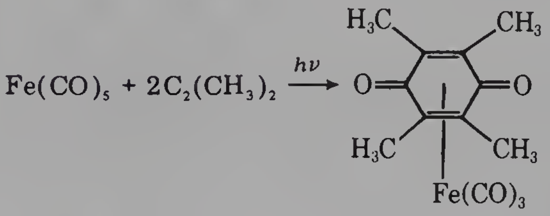






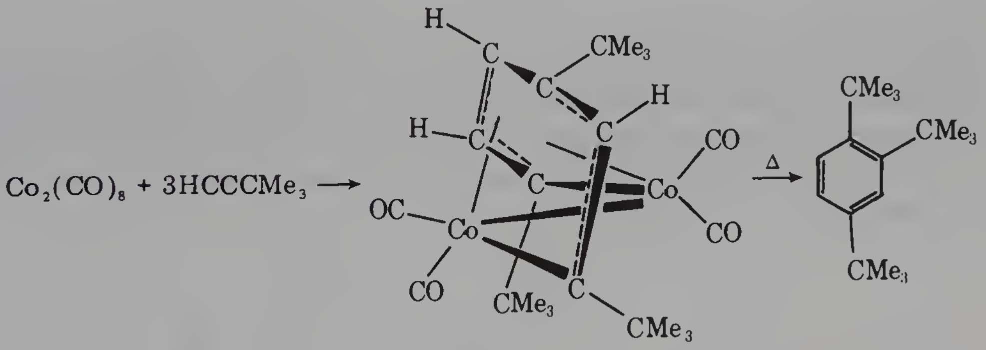
R, R' = H, CH_3, Ph, or OH





Many of the cyclopentadienone and quinone complexes can, of course be made directly from a metal carbonyl and the cyclic ketone itself.

There are many cases in which still more complex organic ligands are elaborated from alkyne starting materials. An example of a "flyover"-type complex is (26-IX) and the reaction sequences leading from C_2 through C_4 and C_6 to C_8 bridges have been studied in detail.[20] The flyovers commonly involve allylic bonding (Section 26-5).



(26-IX)

As well as forming complexes alkynes can react sometimes catalytically with metal complexes to give polyacetylenes and other products in [2 + 2] or [2 + 2 + 2] cycloadditions (Scheme 26-1). Many of these reactions proceed *via* unsaturated metallacycles.[21]

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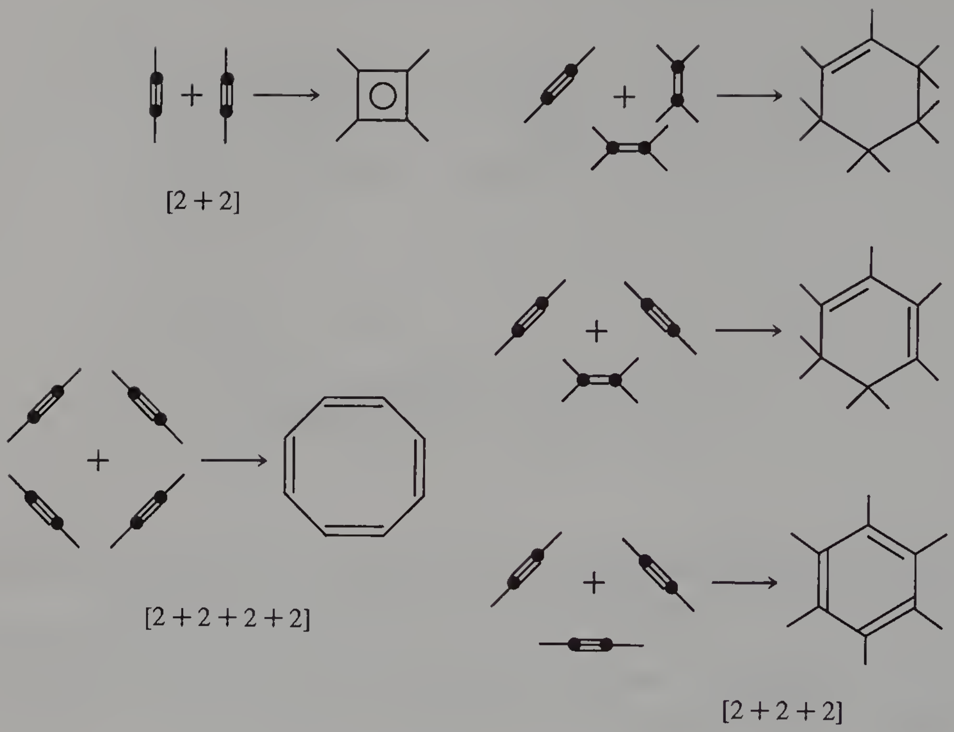
[20] See M. Casarin *et al., Inorg. Chem.*, 1986, **25,** 511; M. Green *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 657; cf. also H. Werner *et al., J. Organometal. Chem.*, 1985, **287,** 247; R. A. Jones *et al., Organometallics,* 1987, **6,** 506.

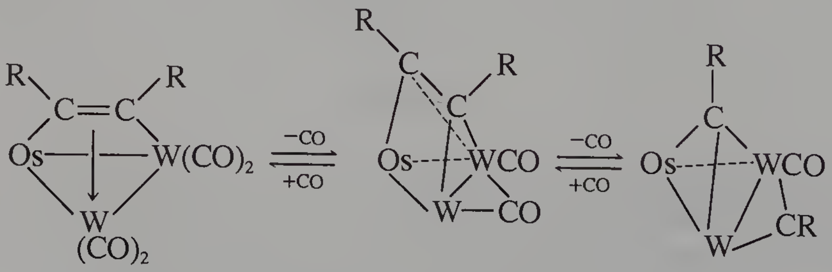
[21] See, for example, K. P. C. Vollhardt, *Acc. Chem. Res.*, 1984, **17,** 539; Y. Wakatsuki *et al., J. Am. Chem. Soc.*, 1983, **105,** 1907; B. L. Booth *et al., J. Organomet. Chem.*, 1985, **293,** 103; E. Singleton *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 1680. See D. E. Wigley *et al., J. Am. Chem. Soc.*, 1987, **109,** 6525, for arene complex of Ta.



Scheme 26-1

Acetylene Cleavage. Acetylene cleavage is, of course, of necessity involved in alkyne metathesis reactions (Section 28-16). Stoichiometric cleavages to give alkylidyne complexes have been fully characterized in a number of cases.

An example on a W_2Os cluster involves the reversible reactions (some ligands omitted)[22]



ALLYL AND RELATED COMPLEXES

26-5. Allyls

Allylic complexes have delocalized three-carbon open or closed moieties bound to a metal. They can be considered as arising from a η^1-allyl by further

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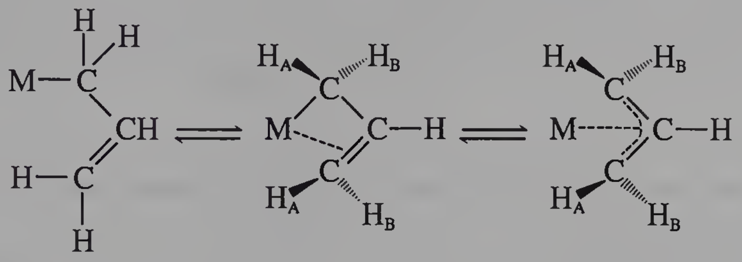
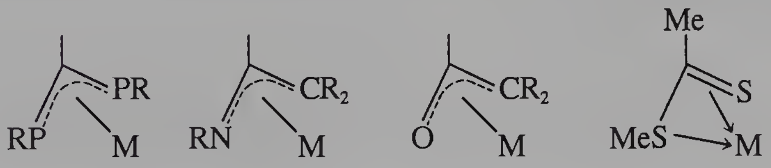
[22] Y. Chi and J. R. Shapley, *Organometallics*, 1985, **4**, 1900 and references therein.

binding of the C═C π bond and indeed both η^1- and η^3-allyls are known and nonrigid behavior (Section 29-15) arises from this equilibrium in some cases.



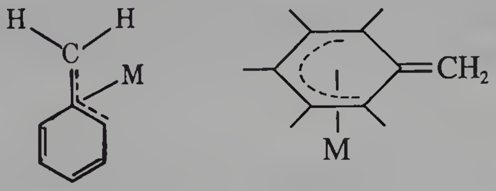
Heteroallyls[23] are (26-Xa, b, and c); like η^3-allyls they are 3*e* donor ligands. However, a structurally similar ligand (26-Xd) [MeC(S)SMe] acts as a 4*e* ligand.[24]



(a) (b) (c) (d)

(26-X)

By use of a double bond in the aromatic ring, benzyls[25] can also act as η^3, 3*e* donor ligands (26-XIa) but here there is a further possibility (26-XIb) where the exocyclic double bond is slightly bent and twisted (cf. cyclohexadienyls, Section 26-15).

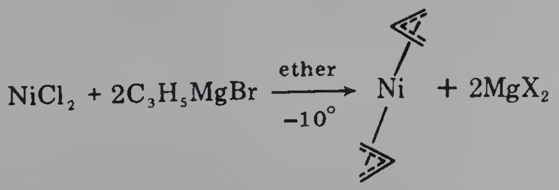


(a) (b)

(26-XI)

The allyl complexes can be made in several ways:

1. *From Allyl Grignard Reagents or Allyl Halides.* Examples are the following:



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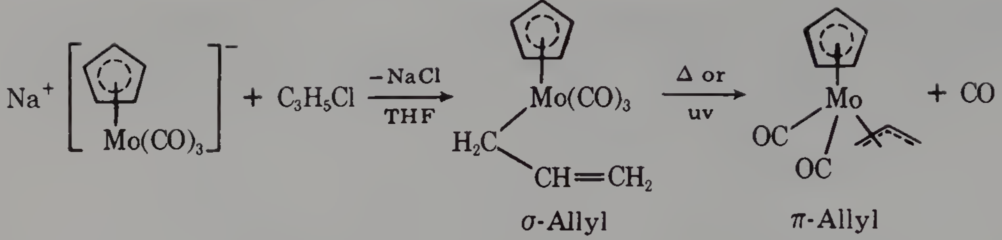
[23] R. Appel *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 420; M. Green *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 422; R. G. Bergman *et al., J. Am. Chem. Soc.*, 1987, **109,** 2022.

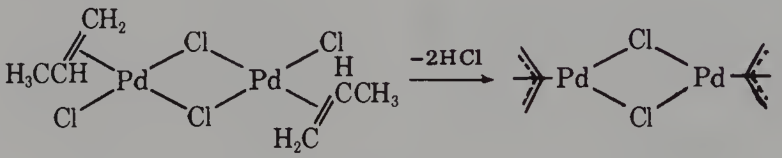
[24] W. A. Schenk *et al., Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 971.

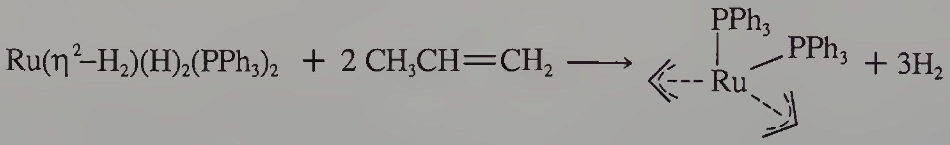
[25] G. Pályi *et al., J. Am. Chem. Soc.*, 1986, **108,** 3344.



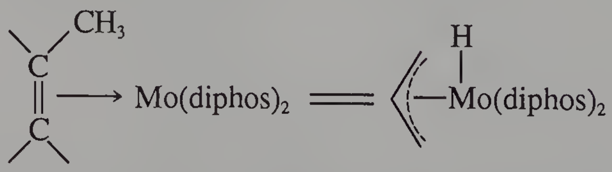
Note that the second example shows the initial formation of a σ- or η^1-allyl that is subsequently converted into a η^3-allyl with loss of CO. There are numerous examples of $\eta^1 \rightleftharpoons \eta^3$ allylic conversions involving displacement of CO, PR_3, Cl^-, or other ligands.

2. *By Hydrogen Transfer from Alkene Complexes and Loss of HCl or H_2.* In some cases direct interaction of an alkene gives an allyl through loss of allylic hydrogen atoms:

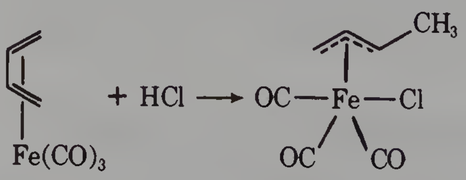


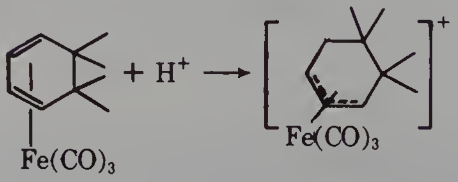


The latter reaction proceeds by way of the transfer of hydrogen from propylene (see also Section 27-9) in an oxidative-addition reaction, since such reactions have been observed spectroscopically in certain cases, for example, the reversible reaction

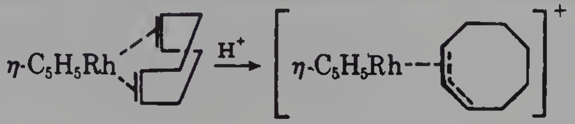


3. *Protonation of 1,3-Diene Complexes*. Two examples are

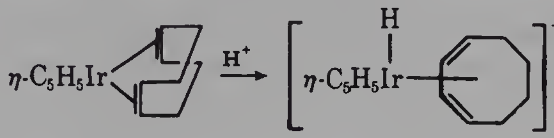




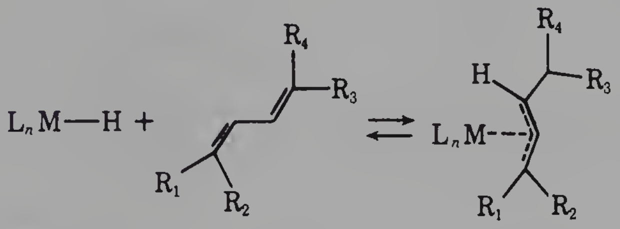
There can also be differences in behavior depending on the metal; for example, for the Co and Rh cycloocta-1,5-diene complexes, protonation occurs on the ring, namely,



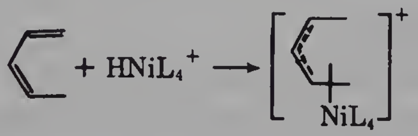
whereas for the Ir analogue an Ir—H bond is formed and the 1,5-diene isomerizes to a coordinated 1,3-diene, namely,



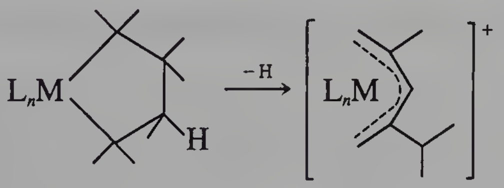
4. *Hydrogen Transfer from MH to Dienes*. This is a common reaction,



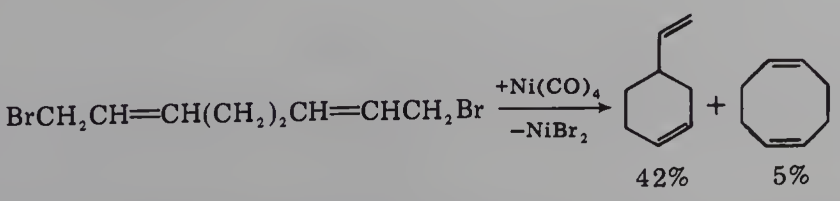
a specific example being



5. *Hydrogen Abstraction From Metallacycles*. Abstraction of a β-hydrogen from Rh, Ir, and Pd metallacycles by Ph_3C^+ is regiospecific[26]:



Allyl complexes are intermediates in a great variety of reactions, some of which are mentioned elsewhere in the text. Cobalt, and especially Pd, are very prone to form allyls and there are many Pd catalyzed diene transformations that proceed via allyl intermediates.[27] Allyls are involved in cyclization reactions such as



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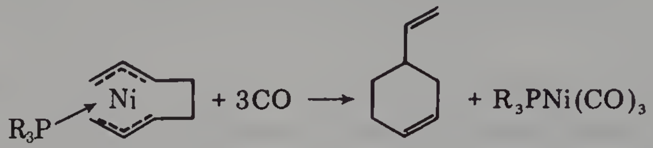
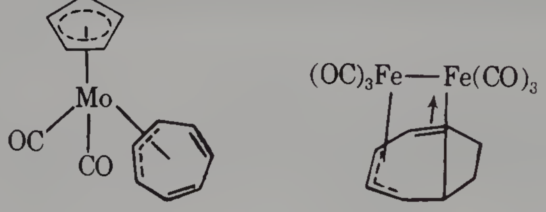
[26] P. Diversi *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984,** 2517.
[27] P. W. Jolly, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 283.

The participation of an η^3-allylnickel species in this reaction is strongly supported by the isolation of an intermediate and its further reaction with CO as in



η^3-Allylmetal groups are also found in a wide variety of compounds containing more complex ligands, and as building blocks in more elaborate structures (26-XII*a* and *b*).



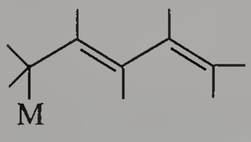
(a) (b)

(26-XII)

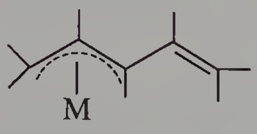
26-6. Dienyl Compounds

Pentadienyls.[28a,b] These are open chain compounds similar to allyls but derived from the anion $CH_2{=}CH{-}CH{=}CH{-}CH_2^-$ instead of $CH_2{=}CH{-}CH_2^-$. The transition metal complexes are made by the action of the metal halides or complex halides, acetates, and so on, with sodium or zinc pentadienyls.

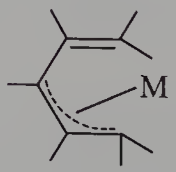
Various bonding modes are possible, η^1, η^3, and η^5:



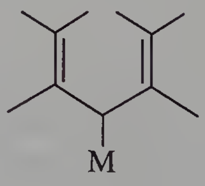
η^1(*cis* +*trans*)



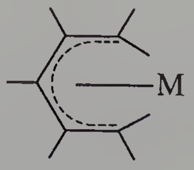
syn-η^3



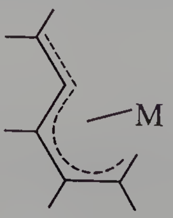
anti-η^3



η^1-C_3



η^5–U

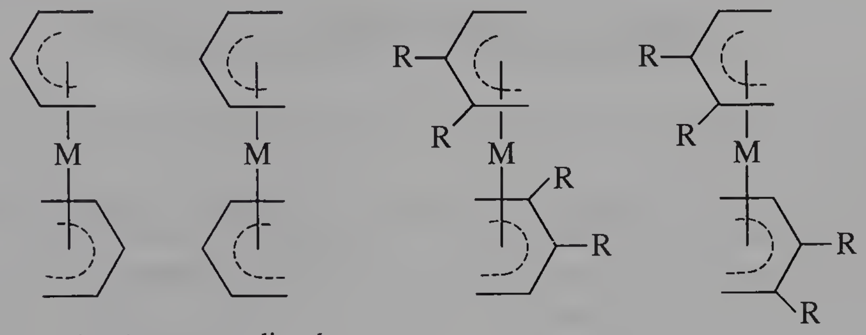


η^5-S(sickle)

[28a] S.-M. Peng *et al.*, *Organometallics*, 1987, **6**, 2094; J. R. Bleeke *et al.*, *J. Am. Chem. Soc*, 1987, **109**, 417; *Organometallics*, 1987, **6**, 486; P. Powell, *Adv. Organomet. Chem.*, 1986, **26**, 125.

[28b] R. D. Ernst *et al.*, *Organometallics*, 1987, **6**, 848, 854.

The most studied are the 2,4-dimethylpentadienyls. The η^5 compounds show considerable similarity to the η^5-cyclopentadienyls (Section 26-9) and compounds that have a sandwich-type structure are known for several elements. The unsubstituted compounds may have isomers such as (26-XIIIa and b) while the substituted compounds have isomers of the types (26-XIIIc and d).



anti eclipsed (a) *syn* eclipsed (b) (26-XIII) (c) (d)

Although most η^5 compounds are of the U type, in bis(2,4-$Me_2C_5H_5$)$MoPEt_3$, there is one U and one η^5-S ligand. This S–U situation is reminiscent of *cis* and *trans*-butadiene complexes.

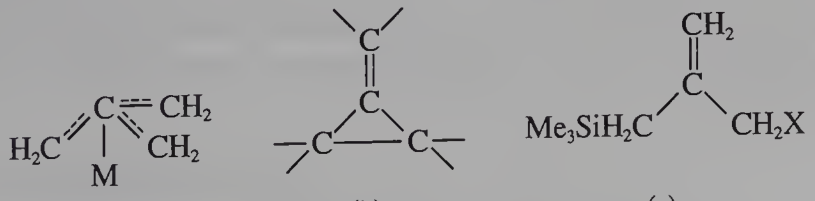
The η^3 compounds can be obtained in direct reactions or from $\eta^5 \rightarrow \eta^3$ conversions, for example,

$$(\eta^5\text{-L})Mn(CO)_3 + PMe_3 \longrightarrow (\eta^3\text{-L})Mn(CO)_3PMe_3$$

An example is $Fe(PMe_3)_2(\eta^3\text{-}C_5H_7)_2$. Monopentadienyls[28b] corresponding to η^5-C_5H_5 compounds (Section 26-10) are also known, an example being $C_7H_{11}Fe(CO)_3^+$.

26-7. Trimethylenemethane Complexes[29]

Although not directly related to compounds discussed previously, we include these η^4 compounds in this section. These are compounds with a $C(CR_2)_3$ group acting as a $4e$ donor (e.g., 26-XIVa). Examples are



(a) (b) (c)

(26-XIV)

$Os[\eta^4\text{-}C(CH_2)_3](CO)_2(PPh_3)$ and $[Mo[\eta^4\text{-}C(CH_2)_3](CO)_2Cp^*]^+$. The $C(CH_2)_3$ group is pyramidal and in some cases bound symmetrically with the central

[29] R. D. W. Kemmitt *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 1201; *J. Chem. Soc. Dalton Trans.*, **1986,** 1411, 1603; R. Aumann and J. Uphoff, *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 357.

M—C bond shorter than the outer M—C bonds; in other cases, unsymmetrical bonding has been confirmed.

The compounds can be derived from methylenecyclopropanes (26-XIVb) or compounds of type (26-XIVc).

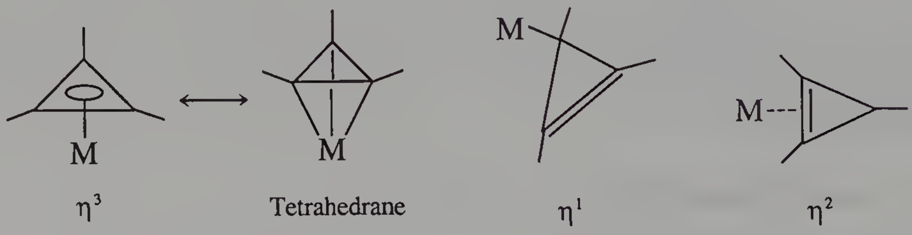
CARBOCYCLIC π COMPLEXES

The general features and bonding in these compounds were discussed in Chapter 2.

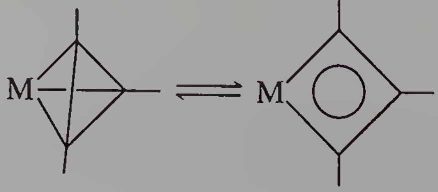
The first carbocyclic compound to be recognized, dicyclopentadienyl iron (II) or ferrocene, was shown to have a sandwich structure with η^5- or π-bonded rings. The only true sandwich compounds with parallel rings are those of the types $(\eta\text{-}C_5H_5)_2M$ and $(\eta\text{-}C_5H_5)_2M^+$; others like $(\eta\text{-}C_5H_5)_2TiCl_2$ have rings at an angle. True sandwich compounds are also formed by arenes [e.g., $(C_6H_6)_2Cr$], by the $C_7H_7^+$ and $C_8H_8^{2-}$ ions in $(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)V$ or $(\eta\text{-}C_8H_8)_2U$, respectively, and by some heterocyclic compounds.

26-8. Three-Membered Rings

Cyclopropenyl compounds[30a,b] derived from $C_3R_3^+$ usually have a symmetrical η^3 ring but may also be η^1 or η^2:

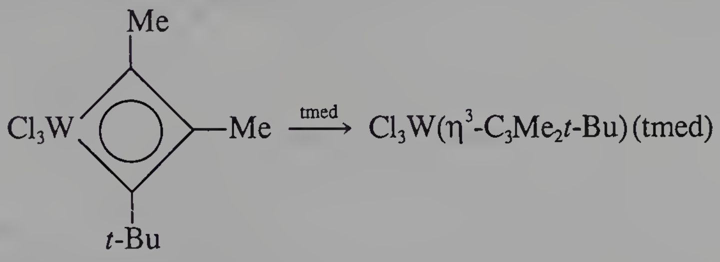


The η^3 type can also be formulated as metallatetrahedranes and in some cases the bond distances are closer to this form than to η^3. An example is $^*CpCl_2(Me_3P)W[C_3Me(CMe_3)_2]$.[30b] In certain cases the ring may show dynamic behavior. Although these C_3 compounds could be intermediates in acetylene metathesis (Section 29-16), involving a transformation to a metallacyclobutadiene,



[30a] R. P. Hughes *et al., Organometallics,* 1985, **4,** 2055, 797, 789; C. A. Ghilardi *et al., J. Organomet. Chem.,* 1985, **295,** 377; S. Midollini *et al., Angew. Chem. Int. Ed. Engl.,* 1986, **25,** 833.
[30b] M. R. Churchill and J. C. Feltinger, *J. Organomet. Chem.,* 1985, **290,** 375.

which is a valence isomer; this seems not to happen. However, addition of donors to a planar metallacyclobutadiene can yield the η^3-cyclopropenyl.[31]

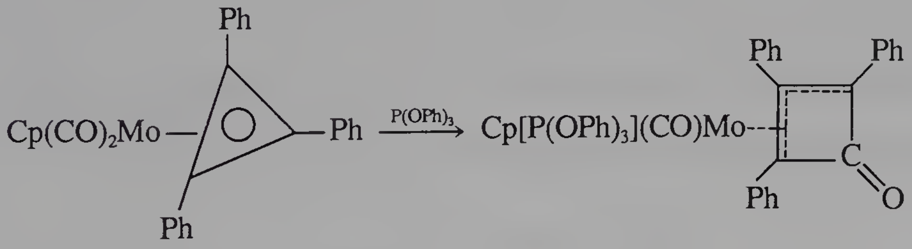


The compounds are usually made by reactions such as

$$Ph_3C_3PF_6 + Mo(CO)_3(MeCN)_3 \longrightarrow [(\eta^3\text{-}Ph_3C_3)Mo(CO)_2(MeCN)_2]^+$$

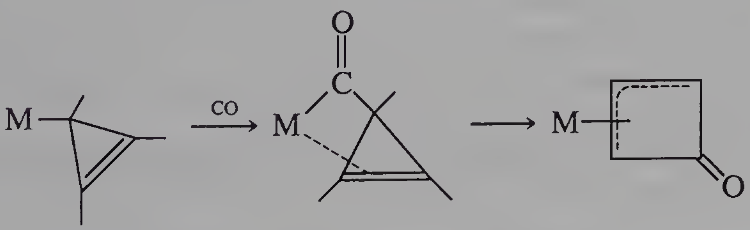
$$Ph_3C_3X + Ni(CO)_4 \longrightarrow (\eta^3\text{-}Ph_3C_3)Ni(CO)_2X$$

The ring can undergo expansion by CO insertion to give *oxocyclobutenyl* (26-XV),



(26-XV)

which has an η^3 allylic grouping, probably via an intermediate η^1 species which then inserts:



26-9. Four-Membered Rings

Cyclobutadiene (C_4H_4) is antiaromatic and unstable in the free state, but it can be stabilized by bonding to a metal atom with suitable electron configuration. The first such compound prepared was the Ni compound obtained as in Fig. 26-2. This chloride can then be reduced in the presence of bipyridine

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[31] R. R. Schrock *et al.*, *Organometallics*, 1986, **5**, 25.

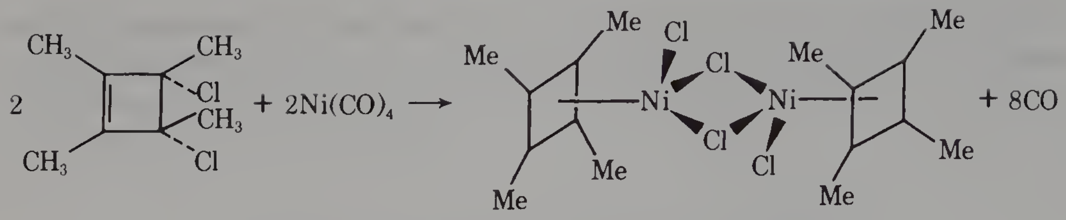
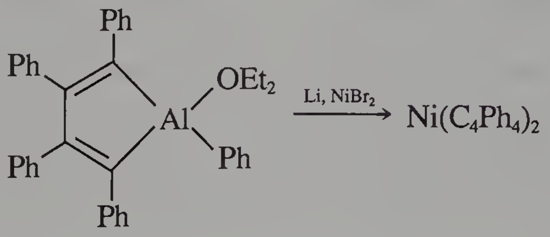


FIG. 26-2. The preparation and structure of $[(CH_3C)_4NiCl_2]_2$.

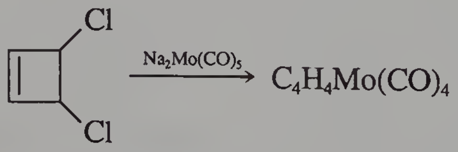
to give the Ni^0 complex (Me_4C_4)Nibipy. A true sandwich compound has been obtained as a blue solid resistant to air, water, and carbon monoxide:



Cyclobutadienyl compounds may also be formed in reactions of acetylenes,[32a] for example,

$$Mn(NO)(CO)_4 + 2PhC{\equiv}CPh \longrightarrow Ph_4C_4Mn(NO)(CO)_2 + 2CO$$

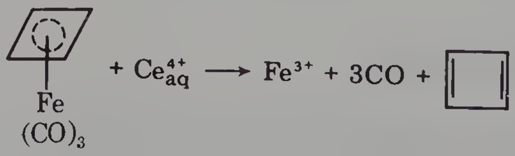
Unsubstituted compounds can be made by reactions such as



In $C_4H_4Fe(CO)_3$ and $CpCoC_4H_4$ there are square rings but in other cases distortions can be present.[32b]

Like the C_5H_5 ring in ferrocene and $CpMn(CO)_3$ (see later), the C_4H_4 ring undergoes typical aromatic electrophilic substitution reactions. There is quite an extensive organic chemistry of the derivatives.

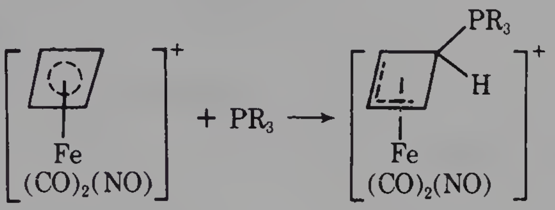
Finally, it is possible to obtain free cyclobutadiene for use in *in situ* organic reactions by oxidative decomposition:



[32a] See, for example, A. Albinati *et al.*, *J. Chem. Soc. Dalton Trans.*, **1984**, 2637; L. Brammer *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986,** 1226.

[32b] R. E. Davis and P. E. Riley, *Inorg. Chem.*, 1980, **19,** 674; I. S. Butler *et al.*, *Inorg. Chem.*, 1986, **25,** 1009.

Cationic C_4H_4 compounds can also be obtained, and nucleophilic addition to the C_4H_4 ring in the cation $C_4H_4Fe(CO)_2NO^+$ gives an *exo*-η^3-allyl (cf. attacks on other rings, Section 26-15).



26-10. Five-Membered Rings

Cyclopentadienyl compounds are by far the most important of all carbocyclic π complexes, and the C_5H_5 ligand or substituted derivatives such as $MeC_5H_4^-$ or $Me_5C_5^-$ are widely used. The C_5H_5 group is commonly abbreviated as Cp, Me_5C_5 as *Cp, and other substituted species as Cp′ or Cp″.

The synthetic methods for C_5H_5 compounds depend on the fact that cyclopentadiene is a weak acid (p$K_a \sim 20$) and with strong bases gives salts of the symmetrical cyclopentadienide ion, $C_5H_5^-$.

The most general method is the formation of the sodium salt by action of Na or NaH on C_5H_6 in THF and the subsequent reaction of this solution with metal halides, carbonyls, and so on,

$$2C_5H_6 + 2Na = 2C_5H_5^- + 2Na^+ + H_2 \qquad \text{(main reaction)}$$

$$3C_5H_6 + 2Na = 2C_5H_5^- + 2Na^+ + C_5H_8$$

$$FeCl_2 + 2C_5H_5Na = (\eta\text{-}C_5H_5)_2Fe + 2NaCl$$

$$W(CO)_6 + C_5H_5Na = Na^+[(\eta\text{-}C_5H_5)W(CO)_3]^- + 3CO$$

Excess of a strong organic base can also be used as an acceptor for HCl, for example,

$$2C_5H_6 + CoCl_2 + 2Et_2NH \xrightarrow{THF} Cp_2Co + 2Et_2NH_2Cl$$

Some direct interactions of C_5H_6 or dicyclopentadiene with metals or metal carbonyls gives the complex, for example,

$$2C_5H_6(g) + Mg(s) \xrightarrow{\Delta} Cp_2Mg + H_2$$

$$Fe(CO)_5 + C_{10}H_{12} \longrightarrow [CpFe(CO)_2]_2$$

Although η^5 is the common bonding mode η^3 , η^1, and bridging species are well established.[33] In some cases the $\eta^5 \rightleftharpoons \eta^3 \rightleftharpoons \eta^1 \rightleftharpoons \eta^0$ system may be

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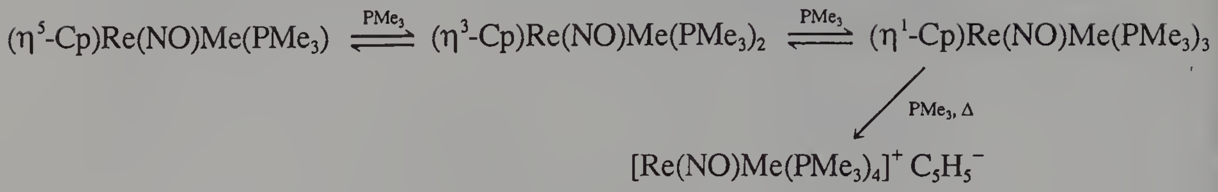
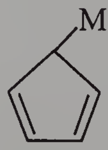
[33] J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87,** 308 (106 ref); A. L. Reingold *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 2460, (η^3); C. Floriani *et al.*, *Inorg. Chem.*, 1987, **26**, 1871; G. K. Anderson *et al.*, *Organometallics*, 1987, **6**, 1440.

reversible, for example,

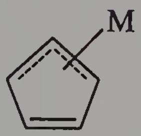


$$\begin{tikzcd}(\eta^5\text{-Cp})Re(NO)Me(PMe_3) \arrow[r, shift left, "PMe_3"] & (\eta^3\text{-Cp})Re(NO)Me(PMe_3)_2 \arrow[l, shift left] \arrow[r, shift left, "PMe_3"] & (\eta^1\text{-Cp})Re(NO)Me(PMe_3)_3 \arrow[l, shift left] \arrow[d, "PMe_3, \Delta"] \\ & & [Re(NO)Me(PMe_3)_4]^+ C_5H_5^-\end{tikzcd}$$

The other types in addition to η^5 are

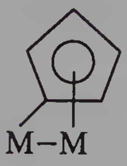


η^1



η^3

μ



$\mu,\eta^1,\eta^5C_5H_4$

The η^1 species such as $(\eta^5\text{-Cp})_3Zr(\eta^1\text{-Cp})$ are nonrigid "ring whizzers" (Section 29-15).

Di-η^5-cyclopentadienyls. Since the anion functions as a uninegative ligand, the compounds are of the type $[Cp_2M]X_{n-2}$, where the oxidation state of the metal M is n and X is a uninegative ion. Hence in the II oxidation state we obtain neutral, sublimable, and organic solvent-soluble molecules like Cp_2Fe and Cp_2Cr, and in III, IV, and V oxidation states species such as Cp_2Co^+, Cp_2TiCl_2, and Cp_2NbBr_3, respectively. Some representative compounds are given in Table 26-1.

Neutral compounds are known for V, Cr, Mn, Fe, Co, and Ni. The Mn (Section 2-14) and Ti (Section 18-A-5) compounds are anomalous. Although Cp_2Mn does have the sandwich structure, it behaves as an ionic cyclopentadienide and is, for example, miscible in all proportions with Cp_2Mg, whereas Cp_2Fe and the others are not; it and its substituted analogues have unusual magnetic properties.[34]

The neutral species can undergo electron transfer reactions to give species such as Cp_2Cr^- or Cp_2Cr^+ and ferrocene is often used as a standard in electrochemical studies.

Except for Cp_2Ru and Cp_2Os the second and third row elements do not form stable isolable Cp_2M compounds and conventional syntheses may lead to hydrides such as Cp_2ReH or Cp_2WH_2 by H abstraction. A "rhenocene" is a dimer with a Re—Re bond.[35a] Some very reactive species like "Cp_2W" may exist as intermediates that have carbenelike behavior and have been trapped in matrices at low temperature.[35b]

Many studies on *pentamethylcyclopentadienyls* have been made, partly be-

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[34] F. H. Kohler *et al., J. Am. Chem. Soc.*, 1986, **108,** 3281.

[35a] P. Pasman and J. J. M. Snel, *J. Organomet. Chem.*, 1984, **276,** 387.

[35b] R. N. Perutz *et al., Inorg. Chem.*, 1982, **21,** 3647.

TABLE 26-1
Some Di-η^5-cyclopentadienyl Metal Compounds[a]

Compound	Appearance; mp (°C)	Unpaired electrons	Other properties
$(\eta^5\text{-}C_5H_5)_2Fe$	Orange crystals; 174	0	Oxidized by $Ag^+(aq)$, dil. HNO_3; $Cp_2Fe = Cp_2Fe^+$ $E^0 = 0.3$ V (vs. SCE)[b]; stable thermally to >500°C
$(\eta^5\text{-}C_5H_5)_2Cr$	Scarlet crystals; 173	2	Very air sensitive; soluble in HCl giving C_5H_6 and blue cation, probably $[\eta^5\text{-}C_5H_5CrCl(H_2O)_n]^+$
$(\eta^5\text{-}C_5H_5)_2Ni$	Bright green; dec at 173	2	Fairly air stable as solid; oxidized to Cp_2Ni^+; NO gives CpNiNO; Na/Hg in C_2H_5OH gives $CpNiC_5H_7$
$(\eta^5\text{-}C_5H_5)_2Co^+$	Yellow ion in aqueous solution	0	Forms numerous salts and a stable, strong base (absorbs CO_2 from air); thermally stable to ~400°C
$(\eta^5\text{-}C_5H_5)_2TiCl_2$	Bright red crystals; 230	0	Slightly soluble in H_2O giving Cp_2TiOH^+; C_6H_5Li gives $Cp_2Ti(C_6H_5)_2$; reducible to Cp_2TiCl; Al alkyls give polymerization catalyst
$(\eta^5\text{-}C_5H_5)_2WH_2$	Yellow crystals; 163	0	Moderately stable in air, soluble benzene, etc.; soluble in acids giving $Cp_2WH_3^+$ ion

[a] Note that Cp_2M compounds are known for some main group elements (ref. 39c) and divalent lanthanides (J. C. Green *et al.*, *Organometallics*, 1987, **6**, 712).

[b] Substitution by electron donating or electron withdrawing groups changes the potential, for example, $^*Cp_2Fe$ 0.95, $(CF_3C_5H_4)_2Fe$, −0.23.[37b]

cause there are no hydrogen atoms on the ring that can be displaced, partly because the compounds are often more stable as well as differing in their chemical and electronic properties.[36] Methyl substitution increases the covalency, enhancing the ligand field strength of the ring. Thus $^*Cp_2Mn$ is low spin in contrast to other Cp_2Mn compounds. The $^*Cp_2M$ compounds are also more easily oxidized due to the electron donating properties of CH_3 groups. Phenyls,[37a] $C_5(CO_2Me)_5^-$,[37b] and CF_3[37c] derivatives have been less studied. For phenyls steric factors are probably important, for example, in stabilizing $(C_5Ph_5)_2Ni^{2+}$ relative to Cp_2Ni^{2+}.

Angular Compounds.[38] Except for neutral Cp_2M compounds, and their cations, other compounds such as Cp_2TiCl_2, Cp_2ReH, and $Cp_2Mn(PMe_3)$ have

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[36] See, for example, J. L. Robbins *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 1882; B. L. Ramakrishna *et al.*, *Inorg. Chem.*, 1986, **25**, 1364.

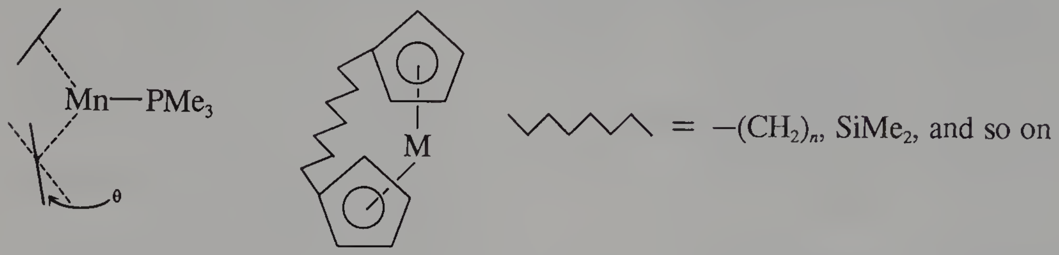
[37a] J. L. Atwood *et al.*, *Organometallics*, 1986, **5**, 635; A. L. Rheingold *et al.*, *Organometallics*, 1986, **5**, 1116; N. G. Connelly *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 1613; *J. Am. Chem. Soc.*, 1986, **108**, 6219; W. Kläui and L. Ramachev, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 97.

[37b] A. G. Davies *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 1873.

[37c] P. G. Gassman and C. H. Winter, *J. Am. Chem. Soc.*, 1986, **108**, 4228.

[38] I. Omae, *Coord. Chem. Rev.*, 1982, **42**, 31; R. C. Fay *et al.*, *Organometallics*, 1983, **2**, 44, 48; F. Rettig *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 6510.

non-parallel rings. These rings may also be "tilted" that is, the ring plane is not orthogonal to the metal-to-ring center axis (26-XVIa)[39a]:



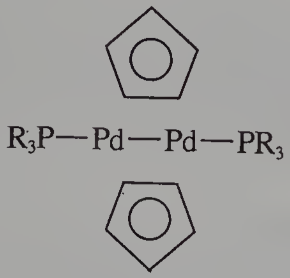
(a) (b)

(26-XVI)

Other commonly bent species, especially when the chains are short are the *metalloceneophanes* (26-XVIb).[39b]

Angular sandwiches are also formed by tin, lead, and other main group elements.[39c]

Bridging Cyclopentadienyls. A few examples are known where $C_5H_5^-$ acts as a 4*e* ligand as in (26-XVII).[40]



(26-XVII)

Ionic Cyclopentadienides. The sodium salts noted previously and compounds of electropositive metals such as Mg, Ca, Sr, Y, and the lanthanides are typically very reactive toward air, water, and other substances with protonic hydrogen atoms.

Some divalent compounds such as Cp_2Mg have a ferrocenelike structure that is the most favored on electrostatic grounds although, however, $^*Cp_2Eu$, Cp_2Ba, and Cp_2Sr are bent.[39c,41] Structure is *not* a criterion of bond type in cyclopentadienyl compounds.

[39a] G. Wilkinson *et al., J. Am. Chem. Soc.*, 1984, **106,** 2033.

[39b] U. T. Mueller-Westerhoff, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 702.

[39c] H. F. Schaefer III *et al., J. Am. Chem. Soc.*, 1985, **107,** 7239; R. Blom *et al., J. Chem. Soc. Chem. Commun.*, **1987,** 768.

[40] See R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, 1982, **21,** 711.

[41] W. J. Evans *et al., Organometallics*, 1986, **5,** 1285.

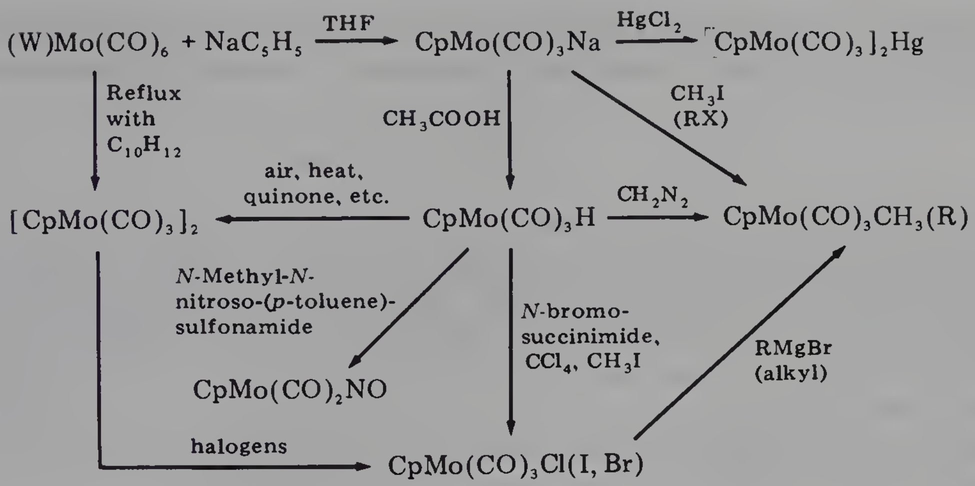


FIG. 26-3 Some reactions of monocyclopentadienyl compounds of molybdenum and tungsten. For similar reactions of $CpFe(CO)L^+$ and $CpOs(CO)L^+$ see G. L. Geoffroy *et al.*, *Organometallics*, 1986, **5**, 1337; M. Rosenblum, *J. Organomet. Chem.*, 1986, **300**, 191. A number of oxo species such as $^*CpReO_3$ $^*Cp_3Re_3(\mu\text{-}O)_6^{2+}$ and $[^*CpVCl(\mu\text{-}O)]_4$ are known; see W. A. Herrmann *et al.*, *Polyhedron*, 1987, **6**, 1165; P. Hofmann *et al.*, *Inorg. Chem.*, 1986, **25**, 4470; F. Bottomley *et al.*, *Organometallics*, 1986, **5**, 2165.

Monocyclopentadienyls.[42a,b] There is an extensive chemistry of cyclopentadienyls that have only one ring. Some typical syntheses are shown in Fig. 26-3. The carbonylate anions $CpM(CO)_3^-$, M = Cr, Mo, and W are isolobally analogous to Cp^- and these fragments can replace each other.[42b]

A particularly widely used compound is the iron carbonyl made by the reaction

$$Fe(CO)_5 + C_{10}H_{12} \xrightarrow{200°C} [CpFe(CO)]_2(\mu\text{-}CO)_2$$

This carbonyl-bridged dimer can be cleaved by sodium to give the anion $CpFe(CO)_2^-$, which is one of the strongest of organometallic nucleophiles (for nucleophilic orders of carbonylate anions see Section 22-6). The $CpMn(CO)_2$ moiety is also useful for stabilizing many unstable molecules.[43]

Accurate studies on $CpMn(CO)_3$, $CpCo(CO)_2$, and on $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ show that there is some interruption of the conjugated π system in the ring by the other ligands leading to short and long C—C bonds.[44]

Reactions of the C_5H_5 Ring. The C—C bond orders in $\eta^5\text{-}C_5H_5$ compounds resemble those of benzene. Most cyclopentadienyl compounds do not, however, survive the reaction conditions involved in aromatic substitution and similar reactions.

[42a] H. Werner, *Angew. Chem. Int. Ed. Engl.*, 1983, **22**, 92; R. Hoffmann *et al.*, *Organometallics*, 1982, **1**, 180.

[42b] P. Hofmann and H. R. Schmidt, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 837; P. Härter *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 839; J. E. Bercaw *et al.*, *Organometallics*, 1987, **6**, 922.

[43] See, for example, W. Kaim, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 856.

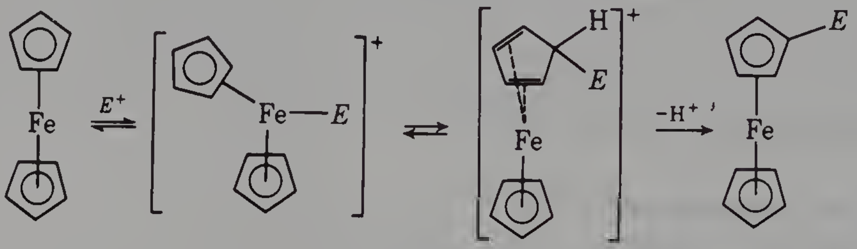
[44] J. W. Chinn Jr., and M. B. Hall, *J. Am. Chem. Soc.*, 1983, **105**, 4930.

For *ferrocene,* which to a large extent does survive, there is a vast organic chemistry. It undergoes Friedel–Crafts acylation, sulfonation, and metallation by butyllithium,[45a] and so on. A recent example[45b] is the reaction

$$Cp_2Fe + CO_2 \xrightarrow{AlCl_3} CpFeC_5H_4CO_2H$$

The Friedel–Crafts acylation occurs 3 × 10^6 times faster than with benzene. *Cymantrene* or η-$C_5H_5Mn(CO)_3$, also has an extensive derivative chemistry.

In certain reactions of the molecules the metal atom is directly involved. One example is the intramolecular bonding of ferrocene alcohols, another is protonation by very strong acids to give the cation Cp_2FeH^+ with bent rings. The protonation of Cp_2Ni is discussed later (Section 26-14). Electrophilic attacks on Cp_2Fe and $CpMn(CO)_3$ have been suggested to proceed via initial attack on the metal with rearrangements as in the following:

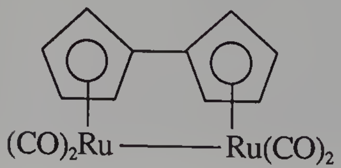


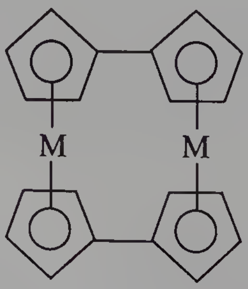
However, it seems more likely that the electrophile attacks the ring in the *exo* position with the *endo* H then moving to the metal and being subsequently lost, as ferrocene is such a weak base. This mechanism is not possible for benzene.

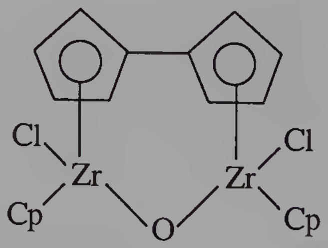
For the monocyclopentadienyl, $CpCo(PMe_3)_2$, the metal atom is extremely nucleophilic and gives the hydride $[CpCoH(PMe_3)_2]^+$ with acids as weak as H_2O or MeOH. It also reacts with acyl chlorides to give $[CpCo(COR)(PMe_3)_2]^+$.

Other Five-Membered Ring Compounds. Substituted cyclopentadienyls such as indenyl give similar ranges of compounds to Cp.

Fulvalenes[46a] can give species such as







[45a] W. R. Cutler *et al., Organometallics,* 1985, **4,** 2196.

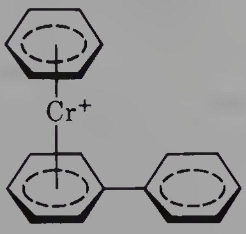
[45b] D. Astruc *et al., Organometallics,* 1986, **5,** 2505.

[46a] G. Gambarotta and M.-Y. Chiang, *Organometallics,* 1987, **6,** 897; J. W. Egan, Jr., and J. L. Petersen, *Organometallics,* 1986, **5,** 906; W. A. Herrmann *et al., Angew. Chem. Int. Ed. Engl.,* 1986, **25,** 288; K. P. C. Volhardt *et al., Inorg. Chem.,* 1986, **25,** 1846.

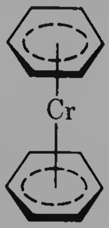
Paracyclophanes can similarly give π complexes,[46b] while there is a variety of complexes of other fused ring systems[47] such as azulenes.

26-11. Six-Membered Rings[48a]

Like the C_5H_5 ion, benzene has six π electrons, but although some Cr compounds were first made by Hein in 1919 by interaction of PhMgBr and $CrCl_3$ they were formulated as "polyphenyl" compounds. They actually contain C_6H_6, or biphenyl, η^6 bound as in (26-XVIII).



(26-XVIII)



(26-XIX)

The prototype neutral compound *dibenzenechromium* [$(C_6H_6)_2Cr$ (26-XIX) has also been obtained from the Grignard reaction of $CrCl_3$, but a more effective method of wider applicability to other metals is the direct interaction of an aromatic hydrocarbon and metal halide in the presence of Al powder as a reducing agent and halogen acceptor and $AlCl_3$ as a Friedel–Crafts-type activator. Although the neutral species are formed directly in the case of Cr, the usual procedure is to hydrolyze the reaction mixture with dilute acid, which gives the cations $(C_6H_6)_2Cr^+$, $(\text{mesitylene})_2Ru^{2+}$, and so on. In several cases these cations can be reduced to the neutral molecules by reducing agents such as hypophosphorous acid.

Dibenzenechromium, which forms dark brown crystals, is much more sensitive to air than is ferrocene, with which it is isoelectronic; it does not survive the reaction conditions of aromatic substitution. Structural studies on arene complexes show that the C—C bond lengths are usually equivalent. However, there are small but significant differences[48b] in $(Me_6C_6)Cr(CO)_3$.

Some benzenoid complexes may be obtained by cyclization of doubly substituted acetylenes, namely,

$$(C_6H_5)_2Mn + 6CH_3C{\equiv}CCH_3 \longrightarrow [C_6(CH_3)_6]_2Mn$$

As well as *d*-block transition metals, Ga, In, Tl, and Bi form complexes such

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[46b] H. Schmidbauer *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 1089.

[47] See, for example, T. A. Albright *et al.*, *J. Am. Chem. Soc.*, 1983, **105**, 3396; K. Jonas *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 928.

[48a] E. L. Muetterties *et al.*, *Chem. Rev.*, 1982, **82**, 499. For examples see A. Ludi *et al.*, W. C. Trogler *et al.*, *Organometallics*, 1987, **6**, 20, 94.

[48b] B. P. Byers and M. B. Hall, *Inorg. Chem.*, 1987, **26**, 2186.

as $[\{(C_6H_6)_2Ga\}GaCl_4]_2$,[49a] while lanthanide and uranium arenes, for example, $Sm(\eta^6\text{-}C_6Me_6)(\eta^2\text{-}AlCl_4)_3$, are also known.[49b]

Arenes also form a variety of mono complexes,[50a] that can be made by reactions such as

$$C_6H_6 + Mn(CO)_5Cl + AlCl_3 \longrightarrow [C_6H_6Mn(CO)_3][AlCl_4] + 2CO$$

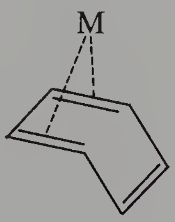
$$C_6H_6 + Cr(CO)_6 \longrightarrow C_6H_6Cr(CO)_3 + 3CO$$

$$Co + 2C_6F_5Br + C_6H_5Me \xrightarrow{\text{cocondense}} (\eta\text{-}MeC_6H_5)Co(C_6F_5)_2$$

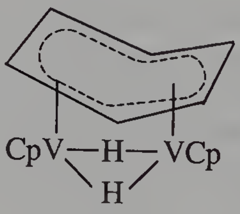
Many studies have been made on the cyclopentadienyl arenes such as $^*CpRuAr^+$ and $CpFeAr^{0,+}$. Since the Fe^I species have 19 electrons they can act as electron reservoirs with ionization potentials similar to potassium.[50b]

Phenyl compounds,[51] such as $PhPR_2$, PPh_3, and BPh_4^- can be π bonded in compounds such as $[RuH(\eta^6\text{-}PhPPh_2)(PPh_3)_2]^+$ and $(C_7H_8)Rh(\eta^6\text{-}PhBPh_3)$.

Other Arene Bonding Modes. While η^6 arenes may sometimes have small boat-form deformations, well-defined species with η^2 and η^4 bonding are known. η^4-Arenes of the type (26-XX) that are dienelike are intermediates in homogeneous catalytic reactions such as hydrogenation (Chapter 28) and are implicated in arene exchange reactions.[52]



(26-XX)



(26-XXI)

η^2-Arene complexes of Ni, Cu, Ag, Re[53a] and Os,[53b] are known, e.g., $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$. In $Ag(B_{11}CH_{12}) \cdot 2C_6H_6$, the silver ion lies above one carbon of the benzene ring in an essentially η^1-mode.[53c]

[49a] H. Schmidbauer *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 234, 338, *Organometallics*, 1987, **6,** 2266; F. Frank *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 74.

[49b] F. A. Cotton and W. Schwotzer, *J. Am. Chem. Soc.*, 1986, **108,** 4657; *Organometallics*, 1987, **6,** 1275.

[50a] See, for example, C. D. Hoff *et al.*, *Organometallics*, 1986, **5,** 2529.

[50b] See, for example, A. M. McNair and K. R. Mann, *Inorg. Chem.*, 1986, **25,** 2519; D. Astruc, *Acc. Chem. Res.*, 1986, **19,** 377; R. G. Sutherland *et al.*, *J. Organomet. Chem.*, 1986, **302,** 307.

[51] J. J. Frizzell *et al.*, *J. Organomet. Chem.*, 1985, **284,** 243; A. L. Beauchamp *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 6848.

[52] W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1986, **108,** 4814; J. W. Hull and Jr., W. L. Gladfelter, *Organometallics*, 1984, **3,** 605; T. G. Traylor *et al.*, *J. Am. Chem. Soc.*, 1984, **106,** 4445.

[53a] J. R. Sweet and W. A. G. Graham, *Organometallics*, 1983, **2,** 135.

[53b] W. D. Harmon and H. Taube, *J. Am. Chem. Soc.*, 1987, **109,** 1883.

[53c] C. A. Reed *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 5955.

Bridging arenes can be symmetrical between two metals in triple-decker sandwiches (Section 26-14), μ, η^2, η^2 as in $\{[Os(NH_3)_5]_2\ C_6H_6\}^{4+}$[53b] or nonplanar as in (26-XXI).[53d] η^4-Benzene can also bridge as in $Pd_2(C_6H_6)_2(AlCl_4)_2$ (cf. 26-XVII p. 1174).

26-12. Seven- and Eight-Membered Rings

Complexes of the cycloheptatrienyl ion ($C_7H_7^+$) are relatively scarce.[54] They can be obtained by reactions such as

$$C_7H_8Mo(CO)_3 + Ph_3C^+BF_4 \longrightarrow [\eta\text{-}C_7H_7Mo(CO)_3]^+BF_4^- + Ph_3CH$$

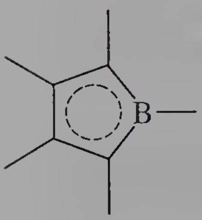
$$\eta\text{-}C_5H_5V(CO)_4 + C_7H_8 \xrightarrow{\text{reflux}} (\eta\text{-}C_5H_5)V(\eta\text{-}C_7H_7)$$

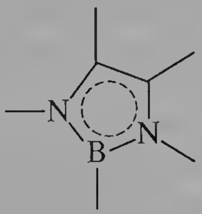
The cyclooctatetraenide ion ($C_8H_8^{2-}$) has 10 π electrons and can be made as its Li salt by metallation of C_8H_8 with BuLi. Interaction with Ce, Th, and U tetrahalides gives neutral species $(\eta^8\text{-}C_8H_8)_2M$ that can be referred to as bis(π-[8] annulenes).[55] η^8-Binding to other metals such as Zr and V is also known.[56]

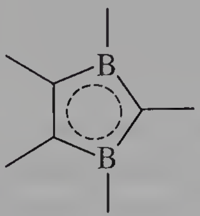
26-13. Metal Compounds of Heterocycles

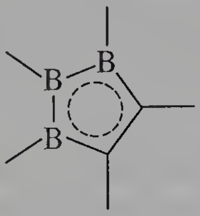
Heterocycles with sufficient aromatic character can form π complexes:

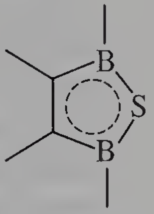
Boron.[57] Borabenzenes and heterocyclic units such as the following can act as ligands in compounds such as $(CO)_3Fe[2\text{-}EtC_4H_3BPh]$ and in multi-decker sandwiches to be discussed later:

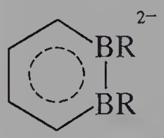












[53d] K. Jonas *et al.*, *J. Am. Chem. Soc.*, 1983, **105,** 5480; *Angew. Chem. Int. Ed. Engl.*, 1983, **22,** 620.

[54] See D. A. Brown *et al.*, *Organometallics*, 1986, **5,** 152, 158; I. S. Butler *et al.*, *Inorg. Chem.*, 1987, **6,** 32.

[55] A. Streitwieser Jr., *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 7786.

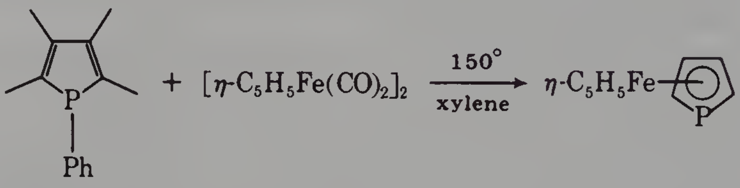
[56] R. N. Grimes *et al.*, *J. Am. Chem. Soc.*, 1983, **105,** 2079.

[57] G. E. Herberich and H. Ohst, *Adv. Organomet. Chem.*, 1986, **25,** 199; W. Siebert *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1985, **24,** 943; G. E. Herberich *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 642; *J. Organomet. Chem.*, 1986, **308,** 153.

Borazines (Section 6-15) give arenelike compounds such as $(B_3N_3R_6)Cr(CO)_3$. Metallocarborane complexes have been discussed (Section 6-13).

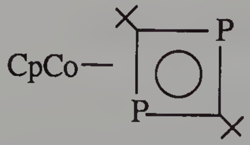
Nitrogen. The pyrrolate anion[58a] gives η^1 and η^5 compounds such as $(C_4H_4N)Mn(CO)_3$ [cf. $CpMn(CO)_3$] and azaferrocene, $CpFe(C_4H_4N)$. However, interaction[58b] of $FeCl_2$ and C_4H_4NNa in THF gives a polymeric solid which is a useful source material; thus bipyridine gives $bipy_2Fe(\eta^1\text{-}C_4H_4N)_2$.

Phosphorus. *Phosphaferrocenes*[59a] have been made by reactions involving cleavage of a P—Ph bond in a λ_3-phosphole



but more striking is $^*CpFe(\eta^5\text{-}P_5)$, which is a green solid made by refluxing P_4 and $[^*CpFe(CO)_2]_2$ in xylene.[59b]

A four-membered ring compound (26-XXII) is made by interaction of $CpCo(C_2H_4)_2$ with $P{\equiv}CCMe_3$.[59c]



(26-XXII)

Here the P atoms can additionally act as donors.

Arsenabenzene and related compounds can give analogues of $(C_6H_6)_2Cr$.[60]

Sulfur. Thiophen[61] gives both η^1 (*S*-bonded) and η^5-complexes such as $(\eta^5\text{-}C_4H_4S)Cr(CO)_3$ and $[CpRu(PPh_3)_2(\eta^1\text{-}C_4H_4S)]^+$ and such complexes provide models for thiophen chemisorption.

Silicon. A variety of silacyclopentadiene complexes are known, for example, (26-XXIII), with the ring acting as a η^4-diene rather than as a delocalized system.[62a] Other heteroalkenes such as 1,3-diphospha metallabutadienes also give complexes, for example, (26-XXIV).[62b]

[58a] F. Basolo *et al.*, *J. Organomet. Chem.*, 1985, **296,** 83; H. Felkin and J. Zakrzewski, *J. Am. Chem. Soc.*, 1985, **107,** 3374; A. L. Rheingold *et al.*, *Organometallics*, 1987, **6,** 196.

[58b] W. K. Reagan and L. T. Radonovich, *J. Am. Chem. Soc.*, 1987, **109,** 2193.

[59a] F. Matthey *et al.*, *Inorg. Chem.*, 1984, **23,** 3455; *Struct. Bonding, Berlin*, 1983, **55,** 153; R. M. G. Roberts *et al.*, *Inorg. Chem. Acta*, 1987, **126,** 61, 67.

[59b] J. Scherer and T. Brück, *Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 59.

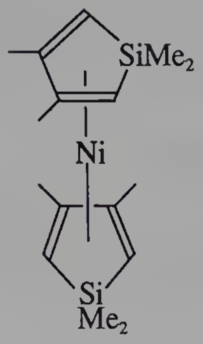
[59c] P. Binger *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 441; J. F. Nixon *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987,** 844.

[60] C. Elschenbroich *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 571; A. J. Ashe III *et al.*, *Angew Chem. Int. Ed. Engl.*, 1987, **26,** 229.

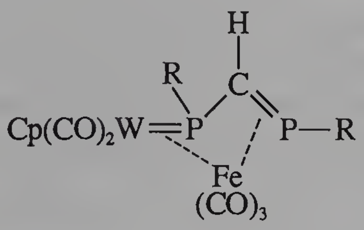
[61] T. B. Rauchfuss *et al.*, *Organometallics*, 1985, **4,** 1909; R. J. Angelici *et al.*, *Organometallics*, 1987, **6,** 591, 1146, 1897.

[62a] J. P. Corriu *et al.*, *Organometallics*, 1987, **6,** 1398.

[62b] H. H. Karsch *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1986, **25,** 455.



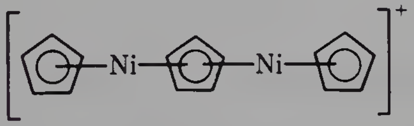
(26-XXIII)



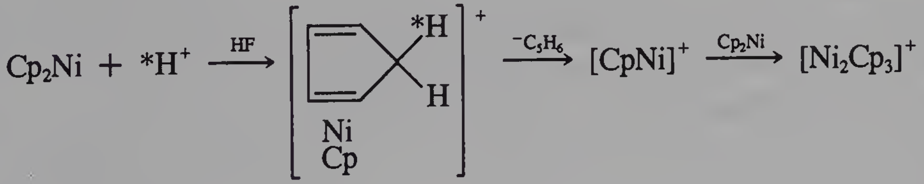
(26-XXIV)

26-14. Multidecker Sandwich Compounds[63]

Lewis acids such as BF_3 react with Cp_2Ni to give a stable cationic species that proved to be a triple-decker sandwich (26-XXV). The mechanism of formation, in which the π-C_5H_5 rings are labilized, appears to be similar to that involved in electrophilic attacks on ferrocene discussed earlier, with the initial addition being *exo*:



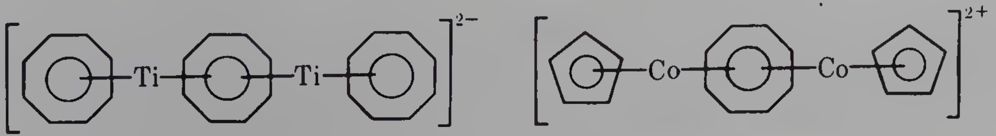
(26-XXV)



The intermediate $CpNiC_5H_6^+$ ion is stable in liquid HF solution for only a few minutes; nmr study confirms that the added proton is exo. The cation $[C_5H_5Ni]^+$ can be isolated as its BF_4^- or SbF_6^- salt, and these salts react quantitatively with $(C_5H_5)_2Ni$ to give the triple-decker cation.

Just as Cp_2M or Ar_2M compounds tend to follow the 18-electron rule, polynuclear sandwich compounds may follow a 30 or 34 total electron rule.

Other types of "triple deckers" with 5, 6, or 8 membered rings are now known, for example, (26-XXVI*a* and *b*).



(a) (b)

(26-XXVI)

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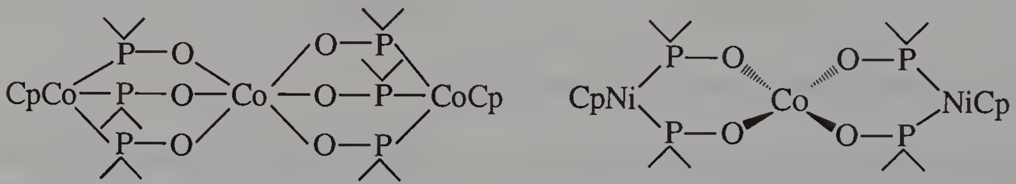
[63] J. K. Burdett and E. Canadell, *Organometallics,* 1985, **4,** 805; W. M. Lamanna *et al., J. Am. Chem. Soc.,* 1986, **108,** 2096; *Organometallics,* 1987, **6,** 1583.

The triple-decker $CpV(\mu,\eta^6\text{-}C_6H_6)VCp$ obtained by interaction of $CpV(C_3H_5)_2$ and cyclohexa-1,3-diene, violates this rule in having only 26*e*.[64a]

Other types that are not, strictly speaking, triple deckers are compounds obtained by reactions of phosphites,[64b] for example,

$$Cp_2Co \xrightarrow[90\text{–}130°C]{HP(O)(OMe)_2} Cp_2Co_3[OP(OMe)_2]_6$$

These have structures such as (26-XXVII*a* and *b*) (R groups omitted for clarity), where the metals are bridged by M—P—O—M bonds; thio analogues[64c] also exist.



(a) (b)

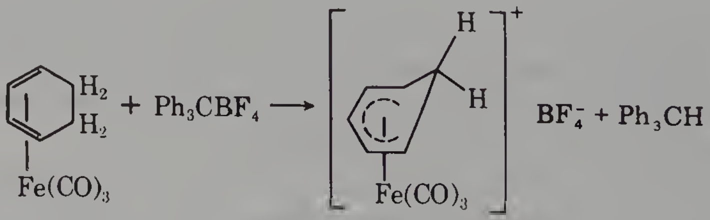
(26-XXVII)

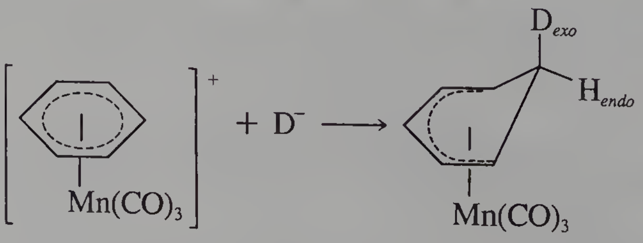
26-15. Partially Delocalized Carbocyclic Systems

Some compounds have been mentioned previously that have a carbocycle bound to a metal by only a three-carbon allylic grouping, for example, η^3-C_5H_5.

We now consider another class of compounds that may have 6, 7, 8, or more carbon atoms that give rise to η(1–5)dienyl systems, the most important of which are η*(1–5)cyclohexadienyls.* These have also been noted previously (Section 24-8) in connection with agostic hydrogen atoms.

η(1–5)-Cyclohexadienyls. These are formed by hydride transfer reactions, either H abstraction or addition as in the following reactions:

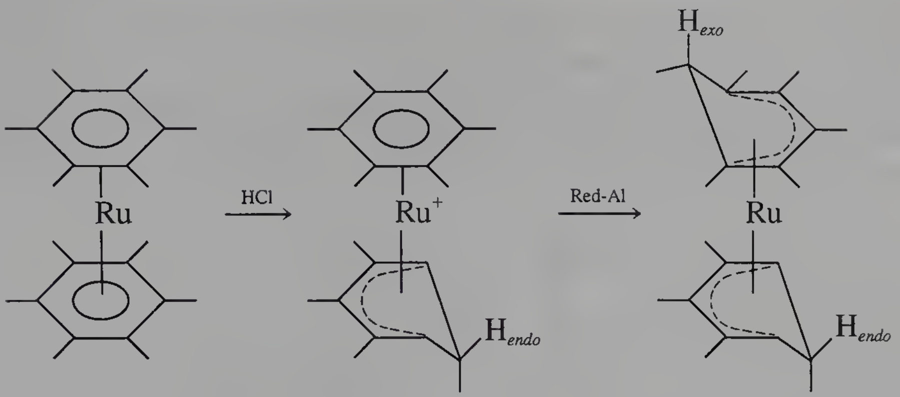




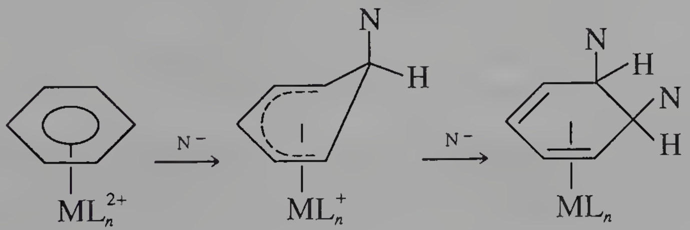
[64a] K. Jonas *et al., Angew. Chem. Int. Ed. Engl.,* 1986, **25,** 927.

[64b] E. Román. E. *et al., Polyhedron,* 1986, **5,** 917.

[64c] W. Kläui *et al., Inorg. Chem.,* 1986, **25,** 4125.



Note that in the reactions of $(C_6Me_6)_2Ru$ protonation first gives H_{endo} (ir stretch ~2950 cm^{-1}) in the cation which, on nucleophilic attack by H^- gives H_{exo} (ν ~2750 cm^{-1}.[65] Hydride ion attack on 2+ cations can give double hydride addition first to the η(1–5)dienyl, then to the diene complex,[66] for example,



There has been much discussion on the initial nucleophilic[66,67] attack on the arene ring—whether N^- first goes on the metal and whether *exo* or *endo* products are formed.

Both of the latter types have been observed and the result appears to depend on electronic features of the complex, the nucleophilicity of the reagent, and solvent polarity. In the great majority of cases, however, the addition is stereospecifically *exo*.

A special type of hexadienyls are those where the CH_2 or CHR groups are replaced by C=O,[68] C=NR, $C=CR_2$, or $SiMe_2$. In all of these compounds, the five C atoms over which there is electron delocalization are essentially planar with the $>CH_2$, >CO, and so on, groups bent out of the plane away from the metal, largely because of electronic factors. The $C_6H_5O^-$ compounds have been simply made from phenol

$$RuH_2(PPh_3)_4 + C_6H_5OH \longrightarrow [\eta(1\text{–}5)C_6H_5O]RuH(PPh_3)_2 + H_2 + 2PPh_3$$

and can be termed π-phenoxo species (Section 12-11).

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[65] A. W. Hanson *et al., J. Am. Chem. Soc.*, 1984, **106,** 818.

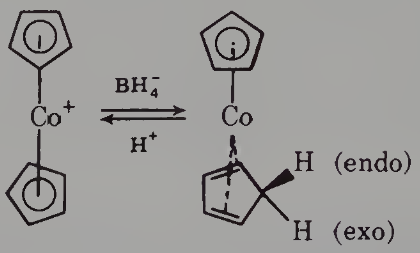
[66] See M. Brookhart and A. Lukacs, *J. Am. Chem. Soc.*, 1984, **106,** 4161; S. L. Grundy and P. M. Maitlis, *J. Organomet. Chem.*, 1984, **272,** 265; D. Astruc *et al., Nouv. J. Chim.*, 1985, **9,** 41; D. A. Sweigart *et al., J. Am. Chem. Soc.*, 1985, **107,** 2388; W. T. Robinson *et al., Organometallics,* 1983, **2,** 1497.

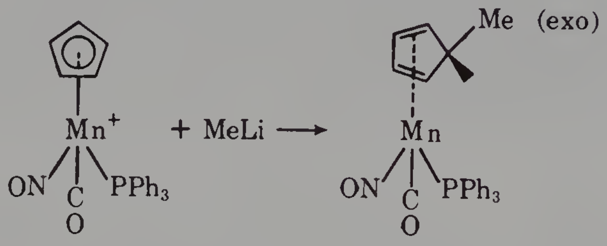
[67] See T. A. Albright and B. K. Carpenter, *Inorg. Chem.*, 1980, **19,** 3092; D. A. Brown *et al., J. Organomet. Chem.*, 1985, **293,** 235.

[68] L. Dahlenberg and N. Hoeck, *J. Organomet. Chem.*, 1985, **284,** 129.

Nucleophilic attacks on seven-membered cycloheptatriene complex cations leads to η(1–5) cycloheptadienyls.[69]

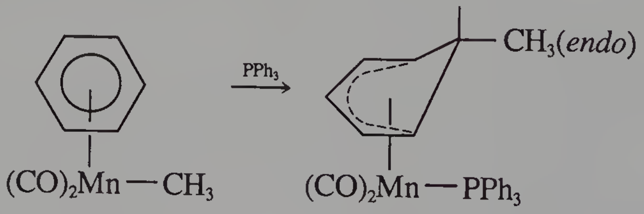
Nucleophilic Attacks on Cyclopentadienyl Compounds. These have also been much studied.[70] They lead to diene complexes via exo attack of the nucleophile on the ring:



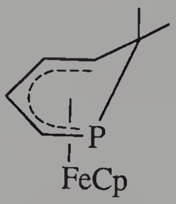


In the complex $(\eta^4\text{-}C_5H_6)ReH_3(PPh_3)_2$ the *endo* hydrogen atoms exchange with the H on Re, probably via a η^3-cycloallylic intermediate.[71]

Migrations of groups from the metal to $\eta^5\text{-}C_5H_5$ rings and η^6-arenes[72] are known, for example,



Finally, partially delocalized heterocycles are known, for example, (26-XXVIII).[73]



(26-XXVIII)

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[70] J. W. Faller *et al., Inorg. Chem.,* 1980, **19,** 2857; S. G. Davies *et al., J. Chem. Soc. Dalton Trans.,* **1983,** 1805.

[71] W. D. Jones and J. H. Maguire, *Organometallics,* 1985, **4,** 951.

[72] M. Brookhart *et al., Organometallics,* 1986, **5,** 1745; D. P. Eyman *et al., Organometallics,* 1986, **5,** 2559.

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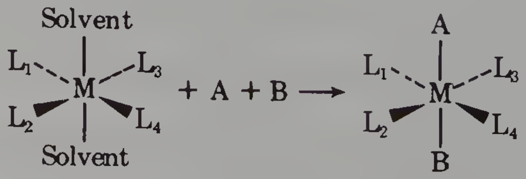
Chapter Twenty-Seven

Oxidative-Addition and Migration (Insertion) Reactions

There are two important reactions involved in the synthesis of organic compounds by stoichiometric or catalyzed reactions involving CO, H_2, alkenes, arenes, and so on. These reactions, called oxidative-addition and insertion, are normally intramolecular. This implies that the reacting molecules or groups are coordinated to the metal although this has not always been unequivocally proved. Attacks on coordinated ligands by nucleophiles or electrophiles could be involved in certain reactions. The latter types of reactions have been considered elsewhere for CO, Section 22-8; NO, Section 10-10; N_2, Section 10-9; RNC, Section 8-11; alkenes, Section 26-2; and RCN, Section 10-11.

If two substances A and B are to react at a metal atom contained in a complex in solution, clearly there must be vacant sites for their coordination. In heterogeneous reactions the surface atoms of metals, metal oxides, halides, and so on, are necessarily *coordinately unsaturated;* but when even intrinsically coordinately unsaturated complexes such as square d^8 species are in solution, solvent molecules will occupy the remaining sites and these will have to be displaced by reacting molecules, thus:



In five- or six-coordinated metal complexes, coordination sites may be made available by dissociation of one or more ligands either thermally or photochemically. Examples of thermal dissociations are

$$\mathrm{RhH(CO)(PPh_3)_3} \underset{}{\overset{-\mathrm{PPh_3}}{\rightleftharpoons}} \mathrm{RhH(CO)(PPh_3)_2} \underset{}{\overset{-\mathrm{PPh_3}}{\rightleftharpoons}} \mathrm{RhH(CO)(PPh_3)}$$

The iridium analogue, $IrH(CO)(PPh_3)_3$, does not catalyze the reactions that the Rh species does at 25°C, but does so when dissociation is induced either by heat or by uv irradiation.

Dissociation may also be promoted by a change in oxidation state as in oxidative-addition reactions discussed later. Thus, although the complex $RhCl(PPh_3)_3$ (Section 19-G-2) is not appreciably dissociated in solution, under hydrogen it gives *cis*-$RhH_2Cl(PPh_3)_3$, which can dissociate one PPh_3 to provide a vacant site:

$$Rh^{I}Cl(PPh_3)_3 \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} Rh^{III}Cl(H)_2(PPh_3)_3 \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} RhCl(H)_2(PPh_3)_2$$

Sites may be made more readily available by the use of ligands with high trans effects. For example, the reaction

$$PtCl_4^{2-} + C_2H_4 \longrightarrow [PtCl_3C_2H_4]^- + Cl^-$$

is quite slow, but it is accelerated by addition of tin(II) chloride, which forms $[PtCl_3(SnCl_3)]^{2-}$ where the Cl trans to $SnCl_3$ is labilized.

For phosphorus ligands (Sections 2-10 and 11-18) in particular, steric effects are especially important, and compounds with bulky ligands have a greater tendency to dissociate. This is illustrated by the equilibria:

$$NiL_4 \rightleftharpoons NiL_3 + L \qquad K_d(25°C, \text{benzene})$$

where for $P(p\text{-}OC_6H_4Me)_3$, whose cone angle is 128°, $K_d = 6 \times 10^{-10}\ M$, whereas for $PMePh_2$ (136°) $K_d = 5 \times 10^{-2}\ M$ and for PPh_3 (145°) dissociation appears to be complete and no $Ni(PPh_3)_4$ could be detected in solution.

Steric effects of bulky ligands are by no means confined to dissociative equilibria but often have a determining influence on reactions such as oxidative-addition and in catalytic reactions. It is, however, not always easy to distinguish between steric and electronic effects in substituted phosphine ligands.

It was noted in Chapter 2 that many compounds of π-bonding ligands such as CO or PPh_3 obey the noble gas or 18-electron rule. It has been considered that in many catalytic reactions 16- and 18-electron species are involved. However, this is an oversimplification, since in many catalytic cycles discussed in Chapter 28, coordinately unsaturated 14-electron species [e.g., $RhCl(PPh_3)_2$] are involved. The postulation of the involvement of only even-electron, diamagnetic species also overlooks the fact that many catalytic and stoichiometric reactions that were originally thought to proceed by 2-electron steps are, in fact, *radical reactions* involving 1-electron changes. This is especially true for oxidative-addition reactions discussed later, but some insertion reactions and carbonyl substitution reactions are also radical in character.

27-1. The Acid–Base Behavior of Metal Atoms in Complexes

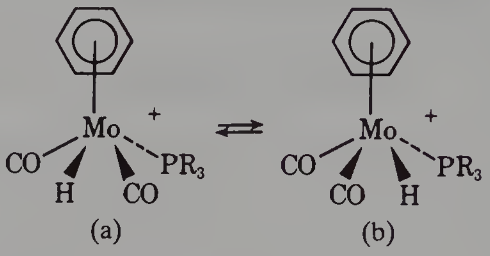
Protonation and Lewis Base Behavior. In electron-rich complexes the metal atom may have substantial nonbonding electron density located on it and consequently may be attacked by H^+ or other electrophiles.

An example of protonation at the metal is

$$(\eta\text{-}C_5H_5)_2HRe + H^+ \rightleftharpoons (\eta\text{-}C_5H_5)_2H_2Re^+$$

Similar angular compounds with lone pairs, Cp_2MoH_2 and Cp_2WH_2, can be readily protonated, but ferrocene, which has its electrons essentially in bonding orbitals, is an exceedingly weak base and can be protonated only by very strong acids.

Arene compounds of Cr, Mo, and W such as $(\eta\text{-}C_6H_6)Mo(CO)_2PPhMe_2$ are protonated by trifluoroacetic acid and the cis–trans isomers (27-I) are fluxional molecules.



(27-I)

Many metal carbonyls, phosphine, and phosphite complexes, including cluster compounds, can be protonated, and often salts may be isolated. Examples are

$$Fe(CO)_5 + H^+ \rightleftharpoons FeH(CO)_5^+$$

$$Ni[P(OEt)_3]_4 + H^+ \rightleftharpoons NiH[P(OEt)_3]_4^+$$

$$Ru(CO)_3(PPh_3)_2 + H^+ \rightleftharpoons RuH(CO)_3(PPh_3)_2^+$$

$$Os_3(CO)_{12} + H^+ \rightleftharpoons HOs_3(CO)_{12}^+$$

The acidification of carbonylate anions can be regarded similarly, for example,

$$Mn(CO)_5^- + H^+ \rightleftharpoons HMn(CO)_5$$

Both 18- and 16-electron compounds that have lone pairs can also form adducts with Lewis acids such as BF_3, for example,

$$(\eta\text{-}C_5H_5)_2ReH + BF_3 \rightleftharpoons (\eta\text{-}C_5H_5)_2ReHBF_3$$

$$IrCl(CO)(PPh_3)_2 + BF_3 \rightleftharpoons IrCl(CO)(PPh_3)_2BF_3$$

In view of the discussion of oxidative-addition in Section 27-3, it may be noted that these protonations (cf. $NH_3 + H^+ \rightleftharpoons NH_4^+$) can be considered as *formal oxidations,* for example, $Cp_2ReH_2^+$ has Re^V, while $[FeH(CO)_5]^+$ has Fe^{II}, rather than just as base–acid reactions.

27-2. Acceptor Properties or Lewis Acidity of Complexes

Coordinately unsaturated compounds, whether transition metal or not, can generally add neutral or anionic nucleophiles, for example,

$$PF_5 + F^- \rightleftharpoons PF_6^-$$

$$TiCl_4 + 2OPCl_3 \longrightarrow TiCl_4(OPCl_3)_2$$

but it is important to note that even when they are electron rich, coordinately unsaturated species may show Lewis acid *as well as* Lewis base behavior, for example,

$$\textit{trans}\text{-IrCl(CO)(PPh}_3)_2 + \text{CO} \rightleftharpoons \text{IrCl(CO)}_2(\text{PPh}_3)_2$$

$$\text{PdCl}_4^{2-} + \text{Cl}^- \rightleftharpoons \text{PdCl}_5^{3-}$$

That is, 16-electron species can add a ligand to become 18-electron species—the reverse of dissociation as discussed previously.

27-3. Oxidative-Addition; Reductive-Elimination

When a complex behaves *simultaneously* as Lewis acid and as Lewis base we have the so-called oxidative-addition reaction, which can be written generally as

$$L_yM^n + XY \longrightarrow L_yM^{n+2}(X)(Y)$$

The reverse reaction can be termed *reductive-elimination.* These terms merely describe the reaction and *have no mechanistic implication.* The mechanisms can be extremely complicated and vary with the nature of the metal–ligand systems and the reactant that is oxidatively added.

For the addition reactions to proceed, we must have (*a*) nonbonding electron density on the metal M, (*b*) two vacant coordination sites on the complex L_yM to allow formation of two new bonds to X and Y, and (*c*) a metal M with its oxidation states separated by two units.

Many reactions of compounds even of nonmetals, not usually thought of as oxidative-additions, may be so designated, for example,

$$(\text{CH}_3)_2\text{S} + \text{I}_2 \rightleftharpoons (\text{CH}_3)_2\text{SI}_2$$

$$\text{PF}_3 + \text{F}_2 \rightleftharpoons \text{PF}_5$$

$$\text{SnCl}_2 + \text{Cl}_2 \rightleftharpoons \text{SnCl}_4$$

The most studied reactions for transition metals are those of complexes of metals with the d^8 and d^{10} electron configuration, notably, Fe^0, Ru^0, Os^0; Rh^{I}, Ir^{I}; Ni^0, Pd^0, Pt^0, and Pd^{II}, and Pt^{II}. An especially well-studied complex is the square *trans*-IrCl(CO)(PPh$_3$)$_2$ (Section 19-G-2), which undergoes reactions such as

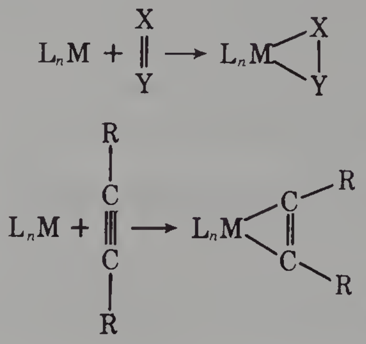
$$\textit{trans}\text{-Ir}^{\text{I}}\text{Cl(CO)(PPh}_3)_2 + \text{HCl} \rightleftharpoons \text{Ir}^{\text{III}}\text{HCl}_2\text{(CO)(PPh}_3)_2$$

It will be noted that:

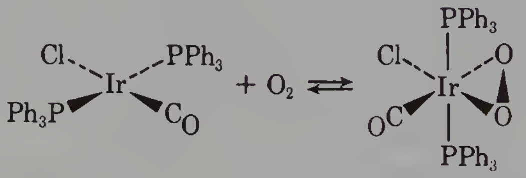
1. Oxidative-addition to 16-electron systems such as the coordinately unsaturated square complexes of Rh^{I}, Ir^{I}, or Pt^{II} produces 18-electron systems. The reverse of such reactions (i.e., reductive-elimination) would reduce an 18-electron system to a 16-electron one.

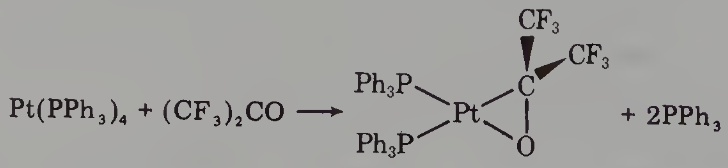
2. In additions of molecules such as H_2, HCl, or Cl_2, two new bonds to the metal are made and the H—H, H—Cl, or Cl—Cl bond is broken. How-

ever, molecules that contain *multiple bonds* may be added oxidatively *without* cleavage to form new complexes that have three-membered rings. The addition can be looked on as the breaking of one component of the multiple bond, while leaving the others intact, that is,



Specific examples are





3. Compounds with 18-electrons cannot undergo oxidative-addition reactions without expulsion of a ligand. This merely means that otherwise the most stable coordination number in the oxidized state would be exceeded. The following cases supplement the last example:

$$\mathrm{Ru^0(CO)_3(PPh_3)_2 + I_2 = Ru^{II}(I)_2(CO)_2(PPh_3)_2 + CO}$$

$$\mathrm{Mo^0(CO)_4bipy + HgCl_2 = Mo^{II}Cl(HgCl)(CO)_3bipy + CO}$$

In some cases the oxidative-addition can be photoassisted, the reaction probably involving initial photodissociation, then oxidative-addition to a coordinately unsaturated species. Table 27-1 lists molecules that can be oxidatively added either with bond breaking for X—Y molecules or without for those involving multiple bonds.

For addition to 16-electron complexes where no ligand loss is involved, there may be an equilibrium reaction

$$\mathrm{L_yM^n + XY \rightleftharpoons L_yM^{n+2}XY}$$

TABLE 27-1
Examples of Substances That Can Be Added Oxidatively[a]

Atoms separate	Atoms remain attached
X—X	O_2
H_2, Cl_2, Br_2, I_2, $(SCN)_2$, RSSR	SO_2
C—C	$CF_2{=}CF_2$, $(CN)_2C{=}C(CN)_2$
$Ph_3C{-}CPh_3$, $(CN)_2$, C_6H_5CN, $MeC(CN)_3$, cyclopropanes	
H—X	$RC{\equiv}CR'$ RNCS
HCl, HBr, HI, $HClO_4$, C_6F_5OH, C_6H_5SH, PH_3, H_2S, H_2O, CH_3OH	RNCO
NH_3, $C_6F_5NH_2$, C_4H_4NH, $HC{\equiv}CR$, C_5H_6, CH_3CN, HCN, HCO_2R, C_6H_6, C_6F_5H, $HSiR_3$, $HSiCl_3$	$RN{=}C{=}NR'$
$H{-}B_{10}C_2HPMe_2$, $H{-}B_5H_8$, CH_4, RCHO	
C—X	$RCON_3$
CH_3I, C_6H_5I, CH_2Cl_2, CCl_4	$R_2C{=}C{=}O$
CH_3COCl, $C_6H_5CH_2COCl$ C_6H_5COCl, CF_3COCl	CS_2
RCN, RCO_2R', ROR' R_2S	$(CF_3)_2CO$, $(CF_3)_2CS$, CF_3CN
M—X	
Ph_3PAuCl, $HgCl_2$, MeHgCl, R_3SnCl, R_3SiCl, $RGeCl_3$ H_8B_5Br, Ph_2BX	
Ionic	
$PhN_2^+BF_4^-$, $Ph_3C^+BF_4^-$	

[a] Oxidative-addition of C—H bonds of arenes and alkanes is discussed in Section 27-9. For discussion of the reaction

$$M(CH_2{=}CH_2) \rightleftharpoons HM(CH{=}CH_2)$$

see R. Hoffmann *et al.*, *Organometallics*, 1986, **5**, 1841.

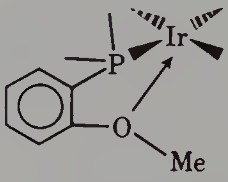
Whether the equilibrium lies on the reduced or the oxidized side depends very critically on (*a*) the nature of the metal and its ligands, (*b*) the nature of the added molecule XY and of the M—X and M—Y bonds so formed, and (*c*) the medium in which the reaction is conducted. Qualitatively, for the addition to proceed, $E_{MX} + E_{MY}$ must exceed $E_{XY} + P$, where E_{MX} and E_{MY} are the free energies of the new bonds to the metal, E_{XY} is the free energy for bond dissociation of XY, and P is the promotional energy for oxidation of the metal. Usually only E_{XY} is known.

The higher oxidation states are usually more stable for the heavier than for the ligher metals, so that, for example, Ir^{III} species are generally more stable than Rh^{III} species. For the ligands, *factors that tend to increase the electron density on the metal make for an increase in oxidizability*. For example, in the reactions of square iridium(I) complexes with carboxylic acids, for example,

$$trans\text{-}\mathrm{Ir^{I}X(CO)L_2} + \mathrm{RCO_2H} \rightleftharpoons \mathrm{Ir^{III}HX(O_2CR)(CO)L_2}$$

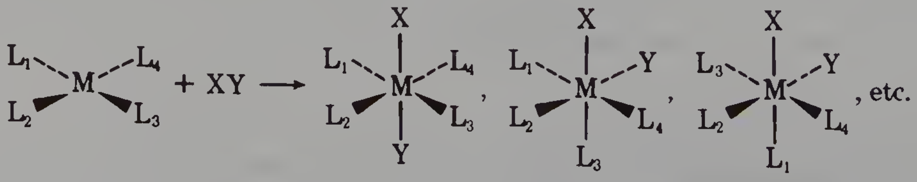
the equilibria lie further to the $\mathrm{Ir^{III}}$ side in the order X = Cl < Br < I and in the orders L = $\mathrm{PPh_3} < \mathrm{PMePh_2} < \mathrm{PMe_2Ph} < \mathrm{PMe_3}$ and L = $\mathrm{P}(p\text{-}\mathrm{FC_6H_4})_3 < \mathrm{P}(p\text{-}\mathrm{MeC_6H_4})_3$. There is no direct correlation to be expected between the $\mathrm{p}K_a$ of various acids HX *in water* and the propensity to add to metals. For example, $\mathrm{HCO_2H}$ ($\mathrm{p}K_A$ 3.75) and $\mathrm{CH_3COSH}$ ($\mathrm{p}K_A$ 3.33) have similar acidities, but on addition to $\mathrm{Pt(PPh_3)_4}$ the formic acid adduct is very unstable, whereas the thioacetic acid adduct is quite stable. This difference is evidently due to the greater affinity of platinum for sulfur than for oxygen. Hence both the acidity and the polarizability of the conjugate base are important.

Steric properties of ligands are also important. For example, very bulky ligands such as PEt*t*-$\mathrm{Bu_2}$ tend to decrease the ease of oxidative-addition, whereas the substitution of an *o*-methoxy group on a phenylphosphine increases the nucleophilicity of the metal by donation (27-II):



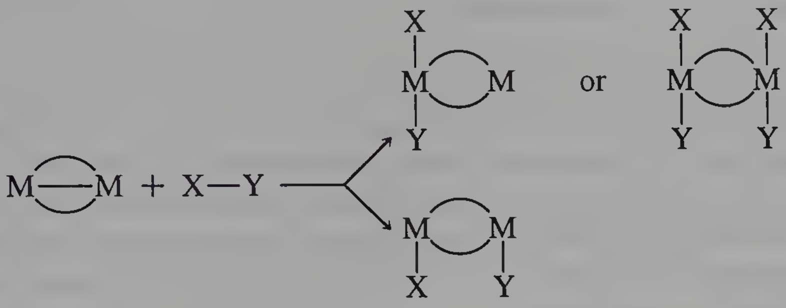
(27-II)

When the XY molecule adds without severance of X from Y, the two new bonds to the metal are necessarily in cis positions, but when X and Y are separated, the product may be one or more of several isomers with either *cis-* or *trans-*MX and -MY groups, for example,

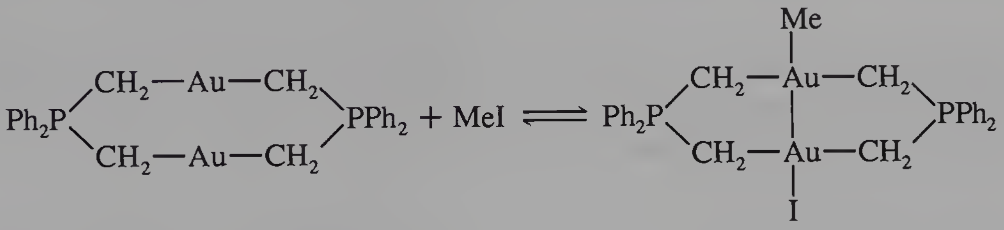


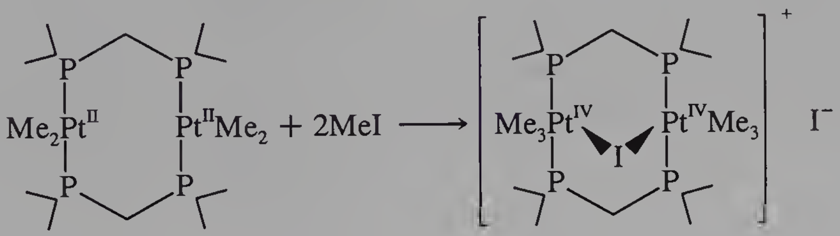
The final product will be the isomer or isomer mixture that is the most stable thermodynamically under the conditions used. The ligands, solvent, temperature, pressure, and so on, will have a decisive influence on this. The nature of the final product does not necessarily give a guide to the initial product of the reaction, since isomerization of the initial product may also occur.

Additions to Bimetallic Species. Only monomeric species have been considered so far. Oxidative-additions can, however, proceed at more than one metal center in bi- or polynuclear complexes. Compounds that have bridge groups, with or without a metal-metal bond, can add to one or to both metals.[1] Thus we may have



Addition to give MX and MY results in formal one-electron oxidation of each metal. Two examples are





Oxidative-additions can also occur with metal-metal multiple bonds,[2] for example,

$$\begin{tikzcd}
(RO)_3Mo^{III}{\equiv}Mo^{III}(OR)_3 \arrow[r, "ROOR"] \arrow[dr, "2Cl_2"'] & (RO)_4Mo^{IV}{=}Mo^{IV}(OR)_4 \\
& Mo_2(OR)_6Cl_4
\end{tikzcd}$$

27-4. Addition of Specific Molecules

Hydrogen Addition. The addition of hydrogen is a special case in that despite the high H—H bond energy (450 kJ mol^{-1}), oxidative-addition often

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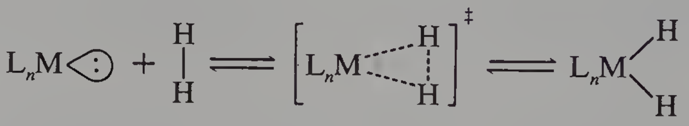
[1] B. Bosnich *et al., Inorg. Chem.,* 1985, **24,** 2338; R. J. Puddephatt *et al., Organometallics,* 1985, **4,** 1198, 1221; J. V. Caspar *et al., J. Am. Chem. Soc.,* 1985, **107,** 6718; W. D. McGhee and R. G. Bergman, *J. Am. Chem. Soc.,* 1986, **108,** 5261; A. L. Balch *et al., Inorg. Chem.,* 1987 **26,** 1836.

[2] G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 2711; F. A. Cotton *et al., Inorg. Chem.,* 1986, **25,** 287.

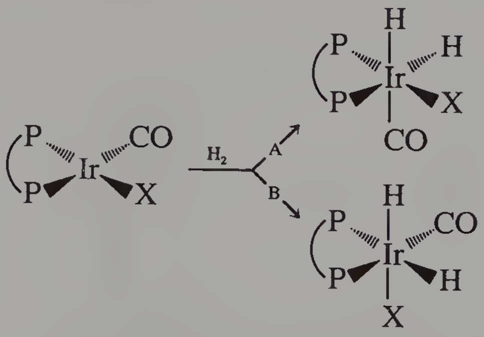
occurs with great facility. The reactions are commonly reversible at 25°C and 1-atm pressure, the hydrogen being readily removed by sweeping with N_2 or Ar or by evacuation, for example,

$$\mathrm{IrCl(CO)(PPh_3)_2} + \mathrm{H_2} \rightleftharpoons \mathrm{Ir(H)_2Cl(CO)(PPh_3)_2}$$

There has been extensive discussion of the mechanism of addition.[3] It now seems likely that a molecular hydrogen complex (Section 24-7) is initially formed, the σ* orbital playing an acceptor role. Electron density flowing into this σ* orbital will then lead to polarization, weakening, and cleavage of the H—H bond and formation of two *cis*-M—H bonds via a concerted, three-center addition mechanism:

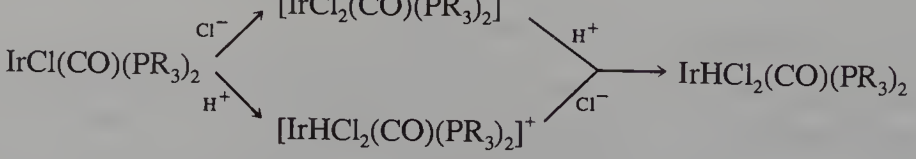


With chelate ligands present on the metal, there is a product dependence on whether the incoming H_2 molecule is aligned with the P—Ir—CO axis (A) or with the P—Ir—X axis (B), that is,



HX Additions. In the addition of HCl or HBr to *trans*-$\mathrm{IrCl(CO)(PPh_3)_2}$ in nonpolar solvents such as benzene, cis addition is also found, suggesting a concerted mechanism. If wet solvents or polar solvents such as DMF or benzene–methanol are used, cis–trans mixtures are obtained.

In polar solvents, where HX is dissociated, there are two possible pathways—initial attack by H^+ or by X^-, namely,



Kinetic studies[4] on $\mathrm{IrCl(CO)(PR_3)_2}$ compounds in methanol have confirmed initial attack by Cl^-. Here, protonation by CF_3SO_3H, where the anion is noncoordinating, gives $\mathrm{[IrHCl_2(CO)(PR_3)_2MeOH]^+}$. However, although $\mathrm{IrCl(COD)(PEtPh_2)_2}$ is also attacked by Cl^-, the compound is immediately

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[3] See, for example, R. Eisenberg *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 2963; J. San Filippo, Jr., *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 8049.

[4] R. G. Pearson and C. T. Kresge, *Inorg. Chem.*, 1981, **20**, 1878.

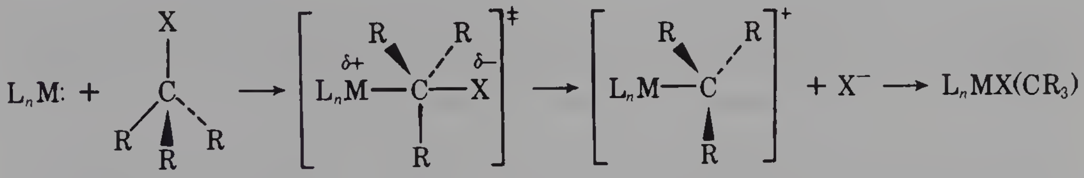
protonated—presumably because of lower intrinsic basicity, which is increased on coordination of Cl^-.

The five-coordinate intermediates are fluxional and hence the stereochemistry of the final product is determined by thermodynamic stability.

Organic Halides. There has also been much study of addition of alkyl and aryl halides[5] as well as of acyl halides[6a] and CH_2Cl_2,[6b] to a variety of complexes of different metals. There are no simple generalizations about mechanisms. In oxidative-additions of *halogens* themselves, the initial interaction is probably the formation of a M---X—X charge transfer complex[7a] (Section 14-7) and the same is doubtless true for halogen compounds[7b].

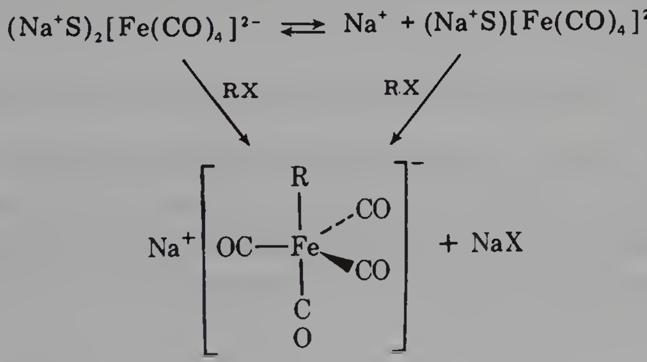
There are two main mechanisms, S_N2 or radical.

1. In reactions of *trans*-$IrCl(CO)(PPh_3)_2$ and similar compounds with CH_3I, $PhCH_2X$, and so on, the mechanism is evidently S_N2:



A polar transition state appears to be involved, since there is promotion by polar solvents. Such reactions ought to proceed with *inversion* of configuration when an optically active halide is used, and this has been observed in a few cases. There are also substantial steric and electronic effects of the phosphines.

Additions to the anion $Fe(CO)_4^{2-}$ as solvent-separated ion pairs in THF or *N*-methylpyrollidone *appear* to be S_N2, namely,



2. Radical pathways, chain or nonchain, have been established in some reactions, especially where these are induced by irradiation as in that of phen $Pt^{II}Me_2$ with RI.

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[5] G. Ferguson *et al.*, *Organometallics*, 1984, **4**, 1169; R. H. Hill and R. J. Puddephatt, *J. Am. Chem. Soc.*, 1985, **107**, 1218; P. J. Stang *et al.*, *Organometallics*, 1984, **3**, 1133.

[6a] M. A. Bennett *et al.*, *Inorg. Chem.*, 1981, **20**, 323.

[6b] Y. Yoshida *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985**, 1137; L. F. Dahl *et al.*, *Organometallics*, 1986, **5**, 630; M. Lattman *et al.*, *Organometallics*, 1986, **5**, 2383; T. B. Marder *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987**, 1543.

[7a] G. van Koten *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 5010.

[7b] See R. H. Crabtree *et al.*, *Organometallics*, 1987, **6**, 2241.

The chain mechanism involves $1e$ rather than $2e$ steps:

$$L_nM + R^{\cdot} \longrightarrow L_nMR^{\cdot} \xrightarrow{RX} L_nMXR + R^{\cdot}$$

The nonchain process is probably initiated by electron transfer to alkyl halide:

$$L_nM + RX \longrightarrow L_nM^{+\cdot}RX^{-\cdot} \longrightarrow L_nMX^{\cdot} + R^{\cdot} \longrightarrow L_nMXR$$

The majority of simple bromides and iodides react with Ir^{I}, Pd^{0}, and Pt^{0} by one-electron paths, although CH_3I, $C_6H_5CH_2Cl$, and $CH_2{=}CH{-}CH_2Cl$ seem generally nonradical. The halide C_6H_5X with Pt^{0} (but *not* Ir^{I}) and $CH_2{=}CHX$ with Pt^{0}, Pd^{0} (but not Ir^{I}) again are nonradical. Radical paths have not been observed for Rh^{I}.

The reaction

$$Mo(CO)_2(diphos)_2 + 2RX = R{-}R + [Mo(CO)_2(diphos)_2X]X$$

proceeds by a radical reaction involving also a paramagnetic Mo^{I} species:

$$L_nMo + RX \longrightarrow L_nMo^{+} + RX^{-\cdot}$$

$$RX^{-\cdot} \longrightarrow R^{\cdot} + X^{-}$$

It must be stressed that in many cases it is not easy to be certain of the pathway and that traces of oxygen, adventitious paramagnetic impurities, or light can seriously affect the reactions.

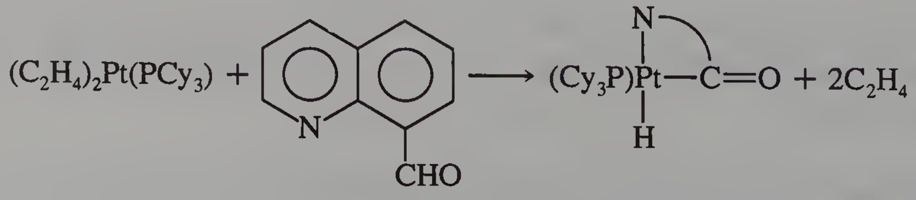
It is possible too that in the presence of oxygen, peroxo intermediates can be formed with ROO· radicals being involved.[8]

Additions of Some Other Molecules. There are few established reactions where *water*[9] or *alcohols*[10] add, for example,

$$Pt(PR_3)_2 + H_2O \rightleftharpoons PtH(OH)(PR_2)_2 \rightleftharpoons [PtH(PR_3)_2solv]^{+}OH^{-}$$

$$WH_2(PMe_3)_5 + MeOH \longrightarrow WH_3(OMe)(PMe_3)_4 + PMe_3$$

Aldehydes[11] are also usually difficult to add as H and RCO. Although PhCHO does not add to $IrCl(CO)(PPh_3)_2$ the chelating effect of the aldehyde o-$Ph_2PC_6H_4CHO$[12a] drives the reaction to completion and a similar *chelate assisted addition* is the reaction[12b]



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[8] See, for example, G. Fergusen *et al.*, *J. Chem. Soc. Chem. Commun.*, **1983,** 267.

[9] P. K. Monaghan and R. J. Puddephatt, *Organometallics*, 1984, **3,** 444; D. Milstein *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 6387.

[10] G. Wilkinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981,** 395.

[11] C. A. Tolman *et al.*, *J. Am. Chem. Soc.*, 1979, **101,** 1742.

[12a] E. F. Landvatter and T. B. Rauchfuss, *Organometallics*, 1982, **1,** 506.

[12b] W. M. Risen, Jr., *et al.*, *J. Organomet. Chem.*, 1985, **284,** 409.

Addition of formaldehyde[13] can occur also, for example,

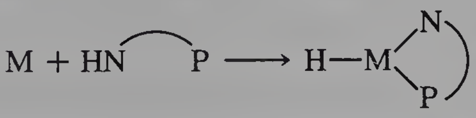
$$\mathrm{IrCl(PMe_3)_3 + HCHO \longrightarrow IrH(CHO)Cl(PMe_3)_3}$$

Sulfur compounds, R_2S, RSH and H_2S, can add,[14] for example,

$$\mathrm{IrCl(CO)(PR_3)_2 + H_2S \longrightarrow IrClH(SH)(CO)(PR_3)_2}$$

$$\mathrm{RhCl(PPh_3)_2 + H_2S \longrightarrow [(Ph_3P)_2ClHRh]_2(\mu\text{-}SH)_2}$$

Relatively few additions of NH bonds from *amines* have been established except where chelate assisted[15a]:



However, ammonia[15b] adds to $\mathrm{IrCl(C_2H_4)_2(PEt_3)_2}$ to give $\mathrm{[(Et_3P)_2HIr(\mu\text{-}NH_2)]_2^{2+}}$ with loss of ethylene. Acetonitrile (and other weak acids) can add to strongly basic complexes, giving $\mathrm{HMCH_2CN}$.[16]

Reductive-Elimination.[17] Where reactions are reversible, the principle of microscopic reversibility indicates that reductive-elimination should follow the same path and be intramolecular.

This is unlikely to be so for compounds formed by radical additions and it need not necessarily be so for compounds that cannot be obtained by oxidative-additions.

For *hydrogen* on monomeric species[18a] such as $\mathrm{RhCl(PR_3)_3}$ reductive-elimination is intramolecular, and this is probably true also for binuclear hydrides,[18b] for example,

$$\mathrm{[Pt_2(H)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+ \xrightarrow[-H_2]{PR_3} [Pt_2H(PR_3)(\mu\text{-}dppm)_2]^+}$$

Although oxidative-addition of C—H bonds in alkanes is unfavorable (Section 27-8) some compounds with *cis* H and R groups are known; they are much less stable than those with *trans* H—M—R groups. In the two reactions

$$cis\text{-}\mathrm{H(CH_3)Co[P(OR)_3]_4 \longrightarrow CH_4 + Co[P(OR)_3]_4^+}$$

$$cis\text{-}\mathrm{H(H)Co[P(OR)_3]_4 \longrightarrow H_2 + Co[P(OR)_3]_4^+}$$

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[13] D. L. Thorn, *Organometallics,* 1982, **1,** 197.

[14] L. H. Pignolet *et al., Inorg. Chem.,* 1984, **23,** 44; E. Wenkert *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 1390; B. R. James *et al., Inorg. Chim. Acta,* 1986, **121,** L7.

[15a] D. Hedder and D. M. Roundhill, *Inorg. Chem.,* 1986, **25,** 9.

[15b] A. L. Casalnuovo *et al., Inorg. Chem.,* 1987, **26,** 971.

[16] C. A. Tolman *et al., J. Am. Chem. Soc.,* 1979, **101,** 1742; W. D. McGhee and R. G. Bergman, *J. Am. Chem. Soc.,* 1986, **108,** 5621.

[17] D. Millstein, *Acc. Chem. Res.,* 1984, **17,** 221.

[18a] D. L. Packett and W. C. Trogler, *J. Am. Chem. Soc.,* 1986, **108,** 5036; D. A. Wink and P. C. Ford, *J. Am. Chem. Soc.,* 1986, **108,** 4838; J. D. Petersen *et al., Inorg. Chem.,* 1986, **25,** 247.

[18b] R. H. Hill and R. J. Puddephatt, *J. Am. Chem. Soc.,* 1983, **105,** 5797.

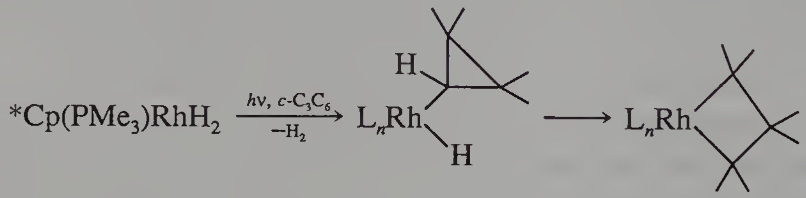
the rate of methane elimination is three orders of magnitude faster than that of hydrogen.

However, these eliminations can be far from simple.[19] Thus $Cp_2WH(Me)$ is *intra*molecular in dilute, but *inter*molecular in concentrated solution.[20] Intermolecular eliminations can, of course be studied in reactions of the type[21]

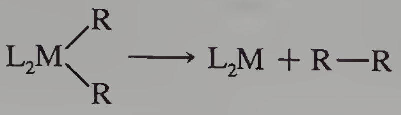
$$RMn(CO)_4L + HMn(CO)_4L \longrightarrow \text{products}$$

but in reactions where CO groups are present, not only alkanes but aldehydes may be formed and the mechanisms are complex and condition dependent. Similarly for *cis*-$Os(CO)_4HR$ the decomposition can be *intra*- or *inter*molecular, while *cis*-$Os(CO)_4Me_2$ decomposes by a radical reaction and *cis*-$Os(CO)_4Et_2$ by β-hydride transfer.[22]

Some special cases are known where elimination does not occur but rearrangements can happen[23]:

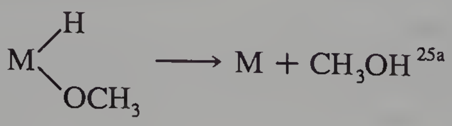


The eliminations of *cis*-dialkyls and aryls, especially of d^8 metals, notably Pt^{II} has been particularly well studied[24]:

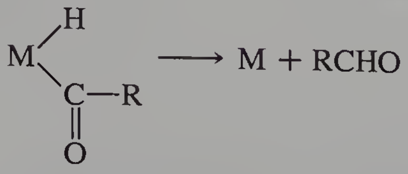


$$L_2M{<}^{R}_{R} \longrightarrow L_2M + R{-}R$$

Reductive-eliminations are involved in many catalytic reactions, some examples being



$$M{<}^{H}_{OCH_3} \longrightarrow M + CH_3OH^{25a}$$



$$M{<}^{H}_{C(=O)-R} \longrightarrow M + RCHO$$

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[19] J. Halpern, *Acc. Chem. Res.*, 1982, **15,** 332.

[20] J. R. Norton *et al., J. Am. Chem. Soc.*, 1985, **107,** 727.

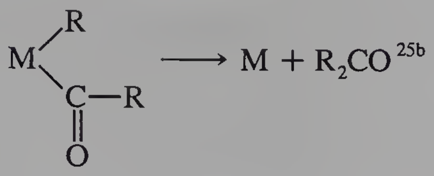
[21] J. Halpern *et al., Organometallics,* 1985, **4,** 34.

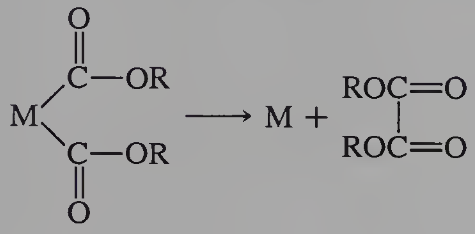
[22] J. R. Norton *et al., Organometallics,* 1985, **4,** 1376.

[23] R. A. Periana and R. G. Bergman, *J. Am. Chem. Soc.*, 1984, **106,** 7272.

[24] K. Tatsumi *et al., J. Am. Chem. Soc.*, 1984, **106,** 8181; G. M. Whitesides *et al., Inorg. Chem.*, 1982, **21,** 2162.

[25a] D. Milstein, *J. Am. Chem. Soc.*, 1986, **108,** 3525.





A stoichiometric example of ketone elimination is the decomposition of $Ru(CO)_2R_2(PR'_3)_2$

27-5. Migration (Insertion) Reactions[26]

The concept of "insertion" is of wide applicability in chemistry when defined as a reaction wherein any atom or group of atoms is inserted between two atoms initially bound together:

$$L_nM{-}X + YZ \longrightarrow L_nM{-}(YZ){-}X$$

Some representative examples are

$$R_3SnNR_2 + CO_2 \longrightarrow R_3SnOC(O)NR_2$$

$$Ti(NR_2)_4 + 4CS_2 \longrightarrow Ti(S_2CNR_2)_4$$

$$R_3PbR' + SO_2 \longrightarrow R_3PbOS(O)R'$$

$$[(NH_3)_5RhH]^{2+} + O_2 \longrightarrow [(NH_3)_5RhOOH]^{2+}$$

$$(CO)_5MnCH_3 + CO \longrightarrow (CO)_5MnCOCH_3$$

An early example (Berthelot, 1869) is

$$SbCl_5 + 2HC{\equiv}CH \longrightarrow Cl_3Sb(CH{=}CHCl)_2$$

Although not all insertion reactions are reversible, some are. The reverse reaction is termed *extrusion*.

The term "insertion" carries no mechanistic implications. Such reactions are usually transfer reactions involving cis sites where a group such as an alkyl or aryl, hydride, alkoxide, dialkylamide, and so on, is transferred to a coordinated ligand. Some representative examples are shown in Table 27-2. Insertions may be termed 1,1, 1,2, 1,3, 1,4, and so on depending on the atom

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[25b] D. R. Saunders and R. J. Mawby, *J. Chem. Soc. Dalton Trans.*, **1984,** 2133.

[26] T. Ziegler *et al., J. Am. Chem. Soc.*, 1986, **108,** 612 (theoretical study of H and CH_3 migration, many references).

TABLE 27-2
Some Representative Insertion or Group Transfer Reactions

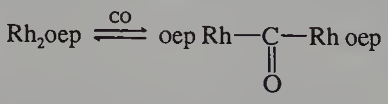
"Inserted" molecule	Bond	Product
CO	M—CR$_3$	MCOCR$_3$
	M—OH	MCO$_2$H
	M—NR$_2$	MCONR$_2$
CO$_2$	M—H	MO$_2$CH
	M—R	MC(O)OR
	M—NR$_2$	MOC(O)NR$_2$
	M—OH, M—OR	MOCO$_2$H(R)
CS$_2$	M—M	MSC(S)M
	M—H	MS$_2$CH and MSC(S)H
C$_2$H$_4$	M—H	MC$_2$H$_5$
C$_2$F$_4$	M—H	MCF$_2$CF$_2$H
RC≡CR′	M—H	MC(R)=CH(R′) cis or trans
CH$_2$=C=CH$_2$	M—R	M(η^3-allyl)
SnCl$_2$	M—M	MSn(Cl$_2$)M
RNC	M—H	MCH=NR
	M—R′	MCR′=NR
	M—η^3-C$_3$H$_5$	MC(=NR)(CH$_2$CH=CH$_2$)
RNCS	M—H	M(RNCHS)
RN=C=NR	M—H	M(RNCHNR)
SO$_2$	M—C	MS(R)O$_2$ or MOS(O)R
	M—M	MOS(O)M
	M—(η^3-C$_3$H$_5$)	MSO$_2$CH$_2$CH=CH$_2$
SO$_3$	M—CH$_3$	M—OSO$_2$CH$_3$
O$_2$	M—H	M—OOH
	M—CR$_3$	M—OOCR$_3$, MOCR$_3$[a]
S$_8$	M—CR$_3$	MSCR$_3$[b]
CH$_2$N$_2$	M—Cl	MCH$_2$Cl[c]

[a] I. P. Rothwell *et al.*, *Inorg. Chim. Acta*, 1986, **120**, 81.

[b] P. Legzdins *et al.*, *Organometallics*, 1987, **6**, 7.

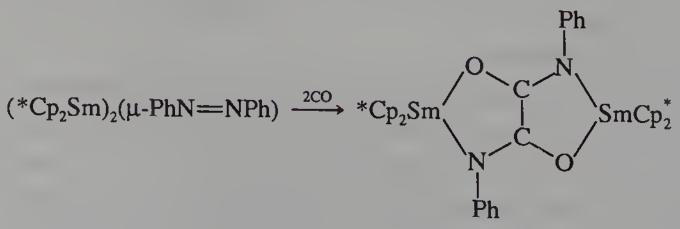
[c] R. McCrindle *et al.*, *J. Chem. Soc., Chem. Commun.*, **1986**, 943.

Note: Carbon monoxide can also cleave M—M bonds (B. B. Wayland *et al.*, *Organometallics*, 1986, **5**, 1059)



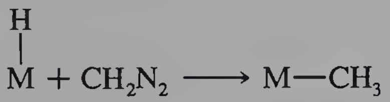
$$\mathrm{Rh_2oep} \underset{}{\overset{\mathrm{CO}}{\rightleftharpoons}} \mathrm{oep\,Rh{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Rh\,oep}$$

and also N=N bonds (W. J. Evans and D. K. Drummond, *J. Am. Chem. Soc.*, 1986, **108**, 7440)

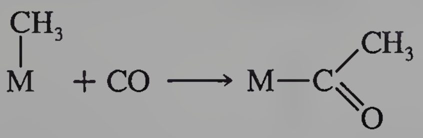


to which the migrating group is transferred. Thus we have

1,1



$$\overset{\displaystyle H}{\overset{|}{M}} + CH_2N_2 \longrightarrow M{-}CH_3$$



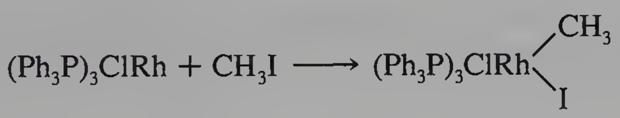
1,2 $$M{-}H + CF_2{=}CF_2 \longrightarrow M{-}CF_2CF_2H$$

$$M{-}R + O_2 \longrightarrow M{-}O{-}OR$$

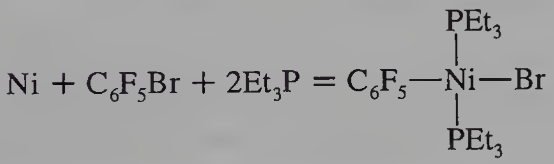
1,3 $$M{-}H + N_2CHR \longrightarrow M{-}N{-}NCH_2R$$

1,4 $$M{-}H + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow M{-}CH_2CH{=}CHCH_3$$

Note that oxidative-addition as discussed in the last section *could* be defined as insertion, for example,



where the Rh atom could be said to be inserted between CH_3 and I. A number of oxidative-addition reactions of metals have indeed been termed "insertions," for example,



$$Ni + C_6F_5Br + 2Et_3P = C_6F_5{-}\underset{\underset{\displaystyle PEt_3}{|}}{\overset{\overset{\displaystyle PEt_3}{|}}{Ni}}{-}Br$$

However, we define insertion reactions as those showing *no change in the formal oxidation state of the metal.*

27-6. Insertion of Carbon Monoxide[26,27]

The most intensively studied insertion reactions are those of CO into metal-to-carbon bonds to form acyls: such phenomena have great catalytic and industrial importance (Chapter 28).

Mechanistic studies have been made using mainly $CH_3Mn(CO)_5$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ or related compounds. With ^{14}CO as tracer, it has been shown that (*a*) the CO molecule that becomes the acyl-carbonyl is *not* derived from external CO but is one already coordinated to the metal atom, (*b*) the

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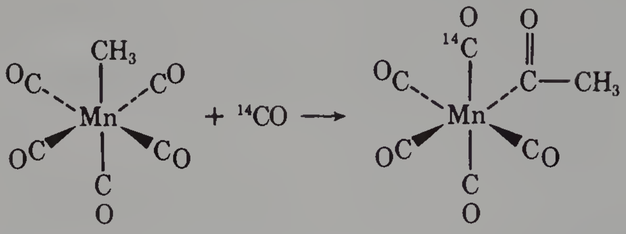
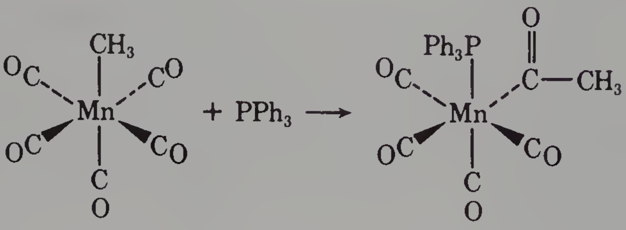
[27] G. Erker, *Acc. Chem. Res.*, 1984, **17,** 103 (for Cp_2ZrR_2 etc.); G. K. Andersen and R. J. Cross, *Acc. Chem. Res.*, 1984, **17,** 67 (in square complexes).

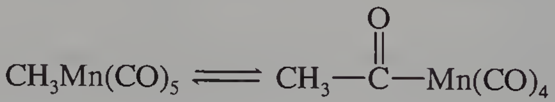
incoming CO is added cis to the acyl group, that is,



(*c*) the conversion of alkyl into acyl can be effected by addition of ligands other than CO, for example,



The first step involves an equilibrium between the octahedral alkyl and a five-coordinate acyl, probably square pyramidal with a basal acetyl group[28a]:



$$CH_3Mn(CO)_5 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-Mn(CO)_4$$

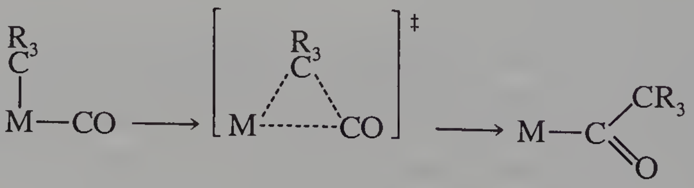
The coordinately unsaturated acyl then adds the incoming ligand L (CO, PPh$_3$[*], etc.) to re-form an octahedral complex

$$CH_3COMn(CO)_4 + L \rightleftharpoons CH_3COMn(CO)_4L$$

The barrier for the migration reaction has been estimated[28b] as 70.2 kJ mol^{-1}, while the unsaturated intermediate is ~41.3 kJ mol^{-1} less stable than MeCOMn(CO)$_5$.

It may be noted that since five-coordinate intermediates can undergo molecular rearrangements, more than one isomer of final products, for example, CH$_3$COMn(CO)$_4$L, may be formed.

The CO insertion reaction is a 1,2-migration of an alkyl group to a coordinated CO ligand in a cis position, proceeding through a three-center transition state:



[28a] S. C. Wright and M. C. Baird, *J. Am. Chem. Soc.*, 1985, **107,** 6899.

[28b] F. V. Axe and D. S. Marynick, *Organometallics,* 1987, **6,** 572.

[*] Dependence on the cone angle of PR$_3$ has been shown in CO insertion into (diars)Fe(CO)$_2$Me$^+$, C. R. Jablonski and Y. P. Wang, *J. Organomet. Chem.*, 1986, **301,** C49.

In several studies of complexes in which chiral groups are present, it was found that alkyl transfer proceeds with *retention of configuration.* One example is the insertion of CO into the Fe—C bond of $(\eta\text{-}C_5H_5)Fe(CO)_2R$ ($R = CHDCHDCMe_3$) on reaction with PPh_3.

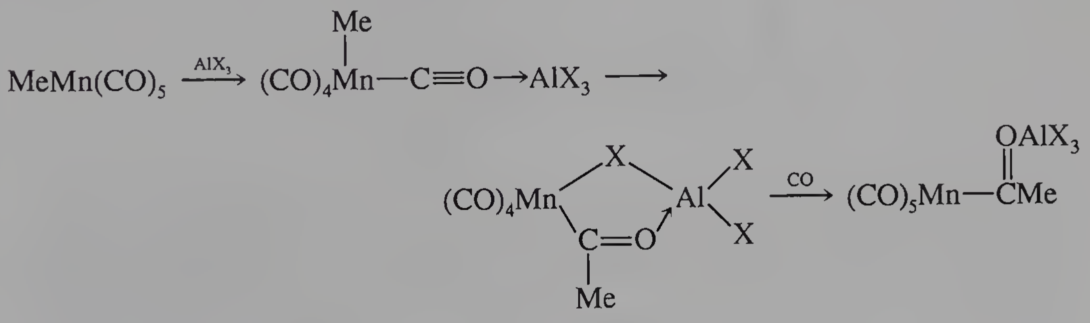
Promotion of Alkyl Migration. The alkyl migration to CO can be speeded up in various ways.

1. There can be solvent participation[29a,b] for example in the preequilibria, especially with polar solvents, and rate increases up to 10^4 have been observed.

$$CH_3Mn(CO)_5 \underset{-S}{\overset{+S}{\rightleftharpoons}} CH_3COMn(CO)_4S \xrightarrow{+L} CH_3COMn(CO)_4L$$

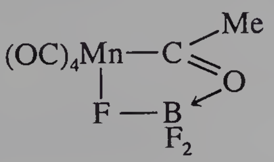
In some cases equilibrium and rates have been measured.

2. Rate increases of orders of magnitude can be obtained by addition of Lewis acids like BF_3 or $AlCl_3$ or in heterogeneous systems by Lewis acid sites on alumina,[29a,30] that complex with the acyl group and thus drive the reaction probably via steps of the type

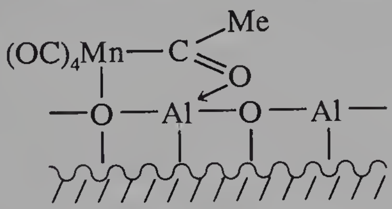


(27-III)

An intermediate of type (27-III) has been characterized for $AlBr_3$. Other intermediates could be (27-IV) and on surfaces (27-V).



(27-IV)



(27-V)

The use of amphoteric ligands like $Ph_2PN(R)AlR'_2$ may have a similar function.[31a] Silicon–oxygen bond formation is a driving force in the interaction of $MnR(CO)_5$ with Ph_2PSiMe_3.[31b]

[29a] See, for example, J. D. Cotton and R. D. Markwell, *Organometallics,* 1985, **4,** 937; J. R. Norton *et al., J. Am. Chem. Soc.,* 1986, **108,** 33.

[29b] T. C. Flood and K. D. Campbell, *J. Am. Chem. Soc.,* 1984, **106,** 2583.

[30] D. F. Shriver *et al., Inorg. Chem.,* 1982, **21,** 1272; H. Brunner *et al., Organometallics,* 1983, **2,** 1595; M. Ichikawa *et al., J. Am. Chem. Soc.,* 1985, **107,** 7216.

[31a] J. A. Labinger *et al., Organometallics,* 1983, **2,** 733.

[31b] J. A. Gladysz *et al., Organometallics,* 1986, **5,** 936.

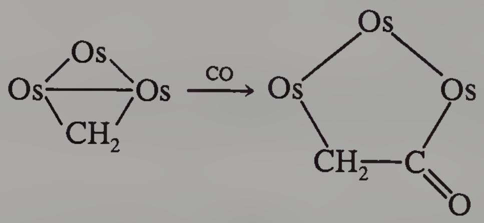
3. Migration can be initiated by electrochemical[32] or chemical oxidation with Ag^+ or Ce^{IV},[33] where transfer is more facile in the oxidized state, for example,

$$\begin{tikzcd}
\mathrm{Cp(PR_3)(CO)Fe{-}Me} \arrow[r, leftrightarrow, "\mathrm{MeCN}"] \arrow[d, shift left, "-e"] & \mathrm{Cp(PR_3)(MeCN)Fe{-}COMe} \arrow[d, shift left, "+e"] \\
\mathrm{Cp(PR_3)(CO)Fe{-}Me^+} \arrow[r, rightleftharpoons, "\mathrm{MeCN}"] \arrow[u, shift left, "+e"] & \mathrm{Cp(PR_3)(MeCN)Fe{-}COMe^+} \arrow[u, shift left, "-e"]
\end{tikzcd}$$

Hydride migration from MH to CO is also facilitated by Cu^{II} oxidation.[34]

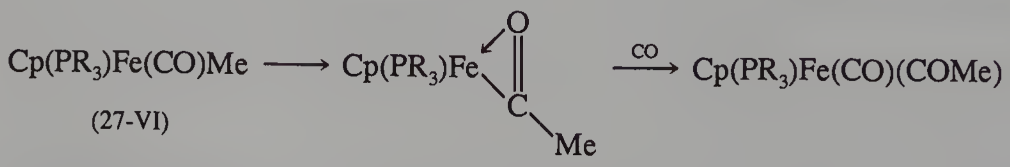
4. Protonic acids may facilitate transfer but there is dependency on solvent. Thus $CpFe(CO)_2Me$ is normally unreactive but with 1% HBF_4 in CH_2Cl_2 insertion of CO is much more rapid at 1-atm pressure.[35]

5. Many catalytic reactions involving CO are promoted by halide ions,[36] especially iodide. Study of osmium clusters where the actual insertion is



shows that in $[Os_3(CO)_{10}(\mu\text{-}CH_2)\mu\text{-}X]^-$ the rate is over 10^2 times faster than in $Os_3(CO)_{10}\mu\text{-}CH_2$. This may be attributed to the acyls being better electron acceptors than alkyls or alkylidenes (μ-CH_2) here and thus better able to stabilize the electron density injected by X^-.

Finally, there is the question whether insertion can occur without alkyl migration, possibly via η^2-acyl intermediates.[37] At very high pressure (400 bar) the stereospecificity of CO insertion is >90% for the chiral species (27-VI),



(27-VI)

which suggests this is possible.

Insertion of CO into M—H bonds. The insertion reactions of M—H

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[32] M. J. Therien and W. C. Trogler, *J. Am. Chem. Soc.*, 1987, **109**, 5127.

[33] D. L. Reger and E. Mintz, *Organometallics*, 1984, **3**, 1759.

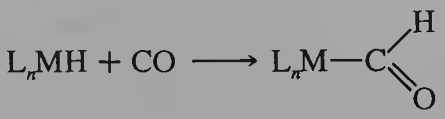
[34] M. C. Baird *et al.*, *Organometallics*, 1983, **2**, 465.

[35] F. C. Forschner and A. R. Cutler, *Organometallics*, 1985, **4**, 1247.

[36] E. Earle and C. R. Jablonski, *J. Chem. Soc. Dalton Trans.*, **1986**, 2137; E. D. Morrison and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1985, **107**, 3541 (see also for C_2H_4 insertion, J. R. Norton *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 7325).

[37] G. Cardaci *et al.*, *Inorg. Chem.*, 1984, **23**, 2936; H. Brunner and H. Vogt, *Chem. Ber.*, 1981, **114**, 2186.

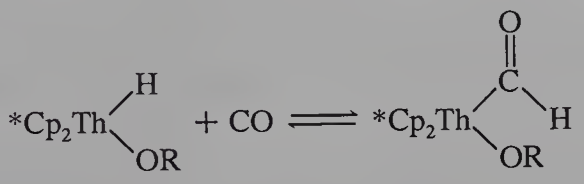
bonds have been discussed (Chapter 24), but that involving CO is best discussed here. The reaction comparable to acyl formation, that is, to give formyl,



$$L_nMH + CO \longrightarrow L_nM{-}C(H){=}O$$

has been greatly discussed as a potential first step in the Fischer–Tropsch reduction of CO by H_2 (Chapter 28).

For *d* group transition metal species the reaction is thermodynamically unfavorable. Thus for early transition metals the MH + CO reaction is generally endothermic, whereas MR + CO is exothermic. The difference resides in the fact that M—H bonds are stronger than M—C bonds by up to ~120 kJ mol^{-1}. For actinides the difference is only ~60 kJ mol^{-1} and for this reason one of the few direct insertions is



where the formyl, like the acyl in actinides, has carbenelike character.[38]

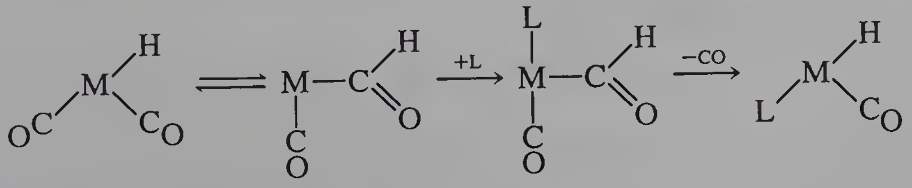
Another direct insertion, probably a radical reaction, is that of HRh(oep) to give the formyl.[39] For most *d* group elements, insertion is uncertain. The reaction

$$HMn(CO)_5(g) + CO(g) = (CO)_5MnCHO \qquad \Delta H \sim +20 \text{ kJ mol}^{-1}$$

is very unfavorable, even more so when the entropy contribution of CO is included.[40] Calculations for the $[(CO)_4FeH]^-$ to $[(CO)_3FeCHO]^-$ reaction also show that the hydride is more stable by between 92 to 184 kJ mol^{-1}.[41]

However, kinetic studies of $XM(CO)_n$ compounds[42a] indicates that when X = H, the rate of CO substitution reactions is much faster than when X = Cl or CH_3 so that we can clearly have *kinetically* significant amounts of a formyl intermediate.

Rapid substitution occurs only for first row transition elements and ruthenium:



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[38] K. G. Moloy and T. J. Marks, *J. Am. Chem. Soc.*, 1984, **106**, 7051.

[39] S. L. Van Voorhees and B. B. Wayland, *Organometallics*, 1985, **4**, 1887.

[40] J. A. Connor *et al.*, *Organometallics*, 1982, **1**, 1166.

[41] G. Blyholder *et al.*, *Organometallics*, 1985, **4**, 1371.

[42a] R. G. Pearson *et al.*, *Inorg. Chem.*, 1981, **20**, 2741.

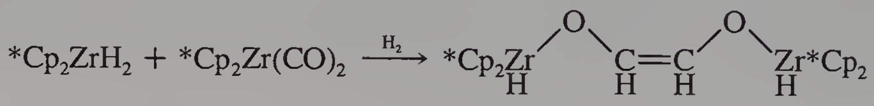
Attempts to speed up H migration to CO by use of Lewis acids[42b], which is effective for CH_3 migrations does *not* lead to formyls but to reactions such as

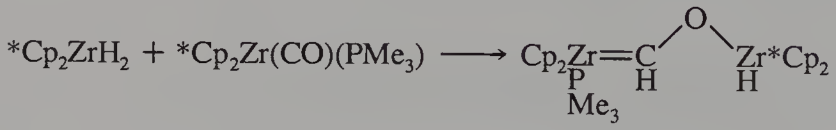
$$(CO)_5MnH + BCl_3 \rightleftharpoons (CO)_5Mn—H—BCl_3$$

While formyl formation provides one model for Fischer–Tropsch reactions there has been much study of *bimolecular hydride transfer reactions* in order to form C—H bonds from CO. Generally, reactions of the type

$$L_nMH_m + L_nM(CO)_m \longrightarrow \text{products}$$

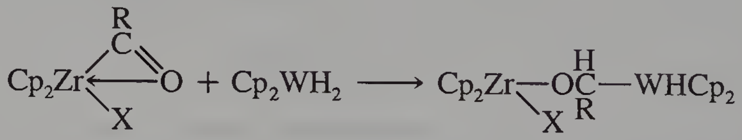
are very complicated. Certain transfer reactions are established,[43] some examples being





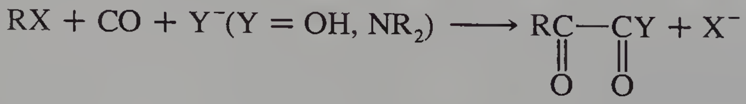
Some of these reactions, and similar ones involving lanthanides and actinides, are probably promoted by the oxophilic nature of the metal atom.

Another similar example involving a η^2-acyl[44] is



Other Aspects of CO Insertion Reactions.

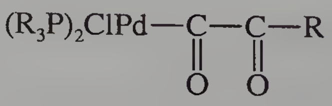
1. Reactions of the type



$$RX + CO + Y^-(Y = OH, NR_2) \longrightarrow \underset{\substack{\parallel \\ O}}{RC}—\underset{\substack{\parallel \\ O}}{C}Y + X^-$$

are known to be catalyzed by $Co_2(CO)_8$ and palladium compounds and are probably important in oxalate synthesis (Chapter 28).

Although compounds such as



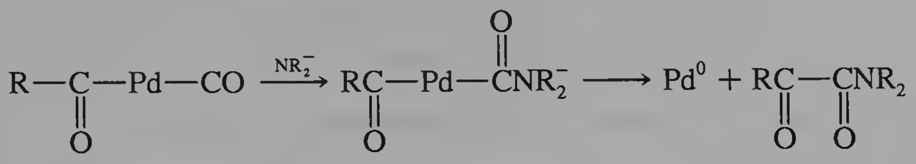
$$(R_3P)_2ClPd—\underset{\substack{\parallel \\ O}}{C}—\underset{\substack{\parallel \\ O}}{C}—R$$

[42b] D. F. Shriver *et al., Organometallics,* 1982, **1,** 1624.

[43] See, for example, J. E. Bercaw *et al., J. Am. Chem. Soc.,* 1984, **106,** 5179; *Organometallics,* 1984, **3,** 278; W. J. Evans *et al., J. Am. Chem. Soc.,* 1985, **107,** 1671; C. E. Summer and G. O. Nelson, *J. Am. Chem. Soc.,* 1984, **106,** 432; C. Moisé *et al., Organometallics,* 1985, **4,** 1051; J. Halpern *et al., J. Am. Chem. Soc.,* 1986, **108,** 345.

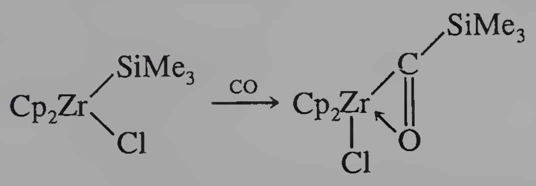
[44] K. G. Caulton *et al., Inorg. Chim. Acta,* 1985, **96,** 161; S. Stella and C. Floriani, *J. Chem. Soc. Chem. Commun.,* **1986,** 1053.

can be made from the oxalyl chloride, there is *no* evidence[45] for a "double insertion" and the reaction apparently involves a nucleophilic attack and reductive-elimination:



$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}Pd{-}CO \xrightarrow{NR_2^-} R\underset{\underset{O}{\|}}{C}{-}Pd{-}\overset{\overset{O}{\|}}{C}NR_2^- \longrightarrow Pd^0 + R\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}NR_2}$$

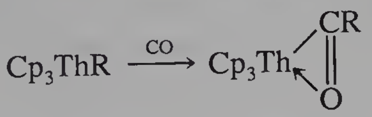
2. Although so far few examples are known, CO can insert into metal-silicon bonds,[46] for example,



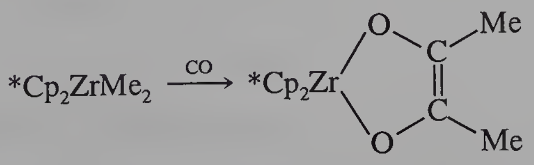
3. Other CO insertions are those into alkoxides[47a] (MOR), dialkylamides[47b] (MNR_2), and some, but not all, hydroxymethyls[48] (MCH_2OH).

For the alkoxide $(Ph_3P)_2Ir(CO)(OMe)$ the intermediate $[Ir(CO)_3(PPh_3)_2]^+$ OMe^- has been identified and "insertion" therefore proceeds via nucleophilic attack rather than intramolecular transfer. However, true transfer is evident for $(dppe)Pt(OMe)_2$ and (dppe)PtMe(OMe) where the rate is much faster for OMe migration than for Me migration; the products have MePt[C(O)OMe] units.

4. For certain types of compounds insertion may give η^2 rather than η^1 acyls; this is particularly so for oxophilic metals such as early transition metals and for thorium[49] for example,



More complicated reactions can also occur involving reductive coupling, for example,[50]



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[45] A. Yamamoto *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 3235; A. Sen *et al.*, *Organometallics*, 1984, **3**, 866; *J. Am. Chem. Soc.*, 1984, **106**, 1506.

[46] T. D. Tilly, *J. Am. Chem. Soc.*, 1987, **109**, 2049; *J. Chem. Soc. Chem. Commun.*, **1987**, 793.

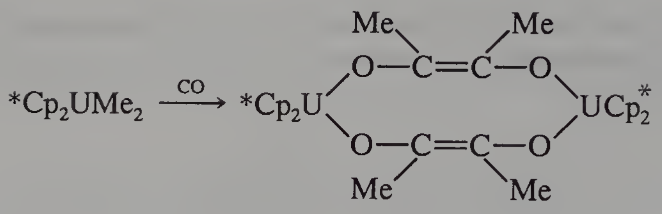
[47a] M. R. Churchill *et al.*, *Organometallics*, 1985, **4**, 2179; H. E. Bryndza, *Organometallics*, 1985, **4**, 1686.

[47b] H. E. Bryndza, *Organometallics*, 1985, **4**, 939.

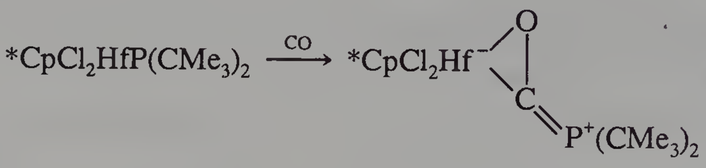
[48] G. D. Vaughn and J. A. Gladysz, *Organometallics*, 1984, **3**, 1596.

[49] T. J. Marks *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 7051.

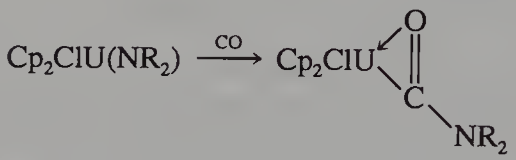
[50] P. Hofmann *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 712; K. Tatsumi *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 4467.



Other CO insertions into M—P[51] and M—N[52] bonds are



Carboxyphosphide



With compounds containing more than one alkyl group CO insertions can lead to elimination of ketones by reductive-elimination, for example,

$$\mathrm{WMe_6} \xrightarrow{\mathrm{CO}} \mathrm{WMe_5(COMe)} \xrightarrow{-\mathrm{Me_2CO}} \mathrm{WMe_4} \xrightarrow{\mathrm{CO}} \cdots \mathrm{W(CO)_6} + 3\mathrm{Me_2CO}$$

27-7. Transfers to Other Molecules

Carbon Dioxide. These reactions, which probably involve CO_2 complexes as intermediates are known with alkyls,[52,53] hydrides,[54a] dialkylamides, dialkylphosphides,[54b] alkoxides,[54c] and with ethylene complexes.[54d] Examples are

$$[\mathrm{(CO)_5WMe}]^- + \mathrm{CO_2} \longrightarrow [\mathrm{(CO)_5WO(CO)Me}]^-$$

$$[\mathrm{CO)_5WOR}]^- + \mathrm{CO_2} \longrightarrow [\mathrm{(CO)_5WOC(O)OR}]^-$$

$$\mathrm{Cp_3ThR} + \mathrm{CO_2} \longrightarrow \mathrm{Cp_2Th(\eta^2\text{–}O_2CR)}$$

$$\mathrm{WH_6(PMe_3)_3} + \mathrm{CO_2} \longrightarrow \mathrm{H_2(Me_3P)_3W(\eta^2\text{–}O_2CH)(\eta^1\text{–}O_2CH)}$$

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[51] J. E. Bercaw *et al., J. Am. Chem. Soc.*, 1985, **107,** 4670.

[52] T. J. Marks *et al., J. Am. Chem. Soc.*, 1981, **103,** 2206; K. J. Ahmed and M. H. Chisholm, *Organometallics*, 1986, **5,** 185; G. L. Hillhouse *et al., Organometallics* 1987, **6,** 1522.

[53] D. J. Darensbourg *et al., Inorg. Chem.*, 1987, **26,** 977.

[54a] D. Lyons and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, **1985,** 587; H. G. Moloy and T. J. Marks, *Inorg. Chim. Acta*, 1985, **110,** 127; C. Floriani *et al., J. Am. Chem. Soc.*, 1985, **107,** 6278; J. L. Templeton *et al., Inorg. Chem.*, 1986, **25,** 2883; B. P. Sullivan and T. J. Meyer, *Organometallics*, 1986, **5,** 1500.

[54b] M. H. Chisholm *et al., Inorg. Chem.*, 1987, **26,** 3087.

[54c] D. J. Darensbourg *et al., J. Am. Chem. Soc.*, 1987, **109,** 290.

[54d] H. Hoberg *et al., Angew. Chem. Int. Ed. Engl.*, 1987, **26,** 153.

Sometimes the reactions are reversible[55a]:

$$\mathrm{Bu_3SnH + CO_2 \xrightleftharpoons{115\text{–}175^\circ C} Bu_3SnO_2CH}$$

In the reaction with $\mathrm{WCl_2(PMePh_2)_4}$, oxygen transfer from CO_2 occurs[55b]:

$$\mathrm{W^{II}Cl_2(PMePh_2)_4 + CO_2 \longrightarrow W^{IV}Cl_2(O)(CO)(PMePh_2)_2 + 2\ PMePh_2}$$

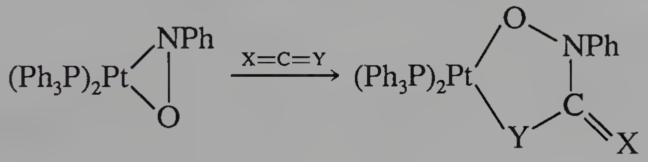
This oxidative-addition is tantamount to an insertion of W into the C—O bond.

For dialkylamides of early transition metals, the insertions again are not intramolecular but are catalyzed by traces of amines so that we have the sequence:

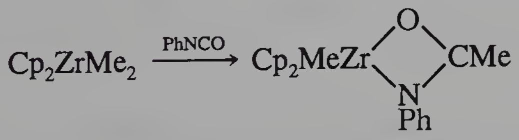
$$\mathrm{Me_2NH + CO_2 \rightleftharpoons Me_2NCO_2H}$$

$$\mathrm{L_\mathit{n}MNMe_2 + Me_2NCO_2H \rightleftharpoons L_\mathit{n}MO_2CNMe_2 + HNMe_2}$$

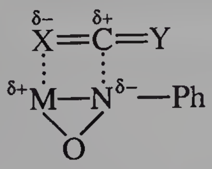
Cumulenes X═C═Y other than CO_2, such as C_3O_2, CS_2, PhNCO, PhNCS, and $\mathrm{Ph_2C{=}C{=}O}$, can also undergo insertions[56] such as



$$\mathrm{(Ph_3P)_2(CO)_2(NO)WH \xrightarrow{C_3O_2} L_\mathit{n}W{-}C(CHO){=}C{=}O}$$



These reactions proceed by dipolar transition states, for example,



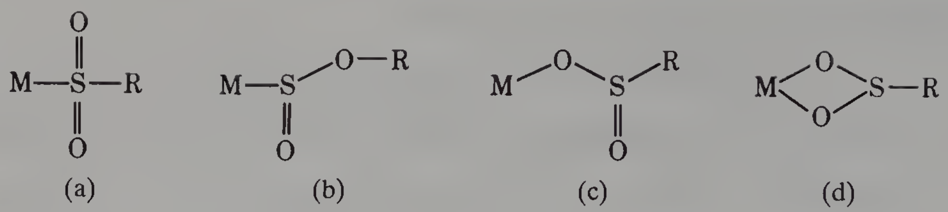
Sulfur Dioxide.[57] Unlike CO insertion, where only an acyl can be obtained, the products from SO_2 insertion can vary; although the usual product is the *S*-sulfinate (27-VIa), the *O*-alkyl-*S*-sulfoxylate (27-VIb), the *O*-sulfinate (27-VIc), or the *O,O′*-sulfinate (27-VId) may be formed.

[55a] J. W. Rathke *et al., Organometallics,* 1985, **4,** 1893.

[55b] J. M. Meyer *et al., J. Am. Chem. Soc.,* 1987, **108,** 2826.

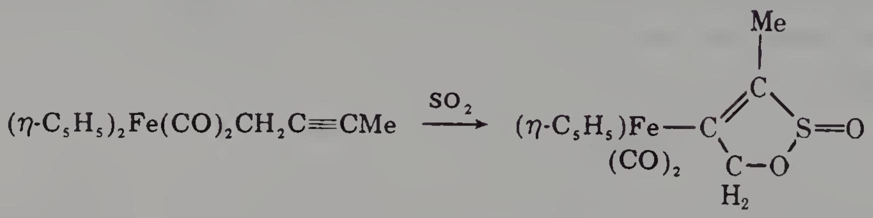
[56] See, for example, C. Floriani *et al., Inorg. Chem.,* 1985, **24,** 654; G. L. Hillhouse, *J. Am. Chem. Soc.,* 1985, **107,** 7772.

[57] G. J. Kubas *et al., Polyhedron,* 1986, **5,** 473; *Organometallics,* 1985, **4,** 2012; D. J. Darensbourg and G. Grötsch, *J. Am. Chem. Soc.,* 1985, **107,** 7473.

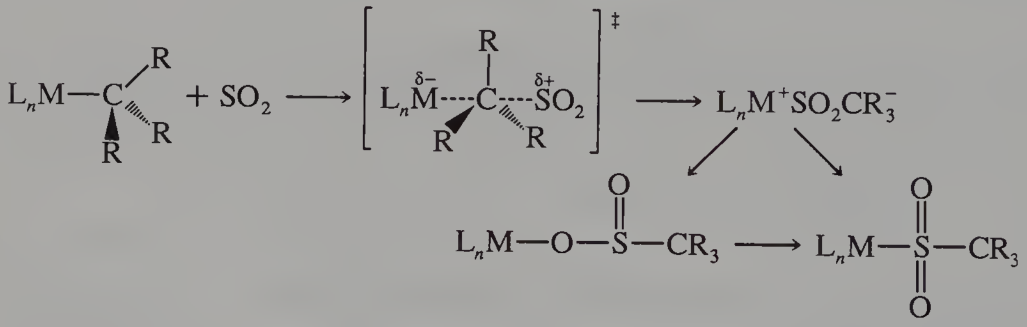


(27-VI)

A further type of reaction is



The insertion of SO_2 appears to proceed by several different mechanisms, one of which involves *exo* S_E2 attack, as follows:



The insertion of SO_2 into the R—Co groups of cobaloximes (Section 18-F-4) is a radical chain reaction of the type

$$R{-}Co = R^{\cdot} + Co^{\cdot}$$

$$Co^{\cdot} + SO_2 \longrightarrow CoSO_2^{\cdot}$$

$$CoSO_2^{\cdot} + RCo \longrightarrow CoSO_2R + Co^{\cdot}$$

Nitric Oxide.[58] This ancient reaction was discovered by Frankland in his original studies on zinc alkyls. Insertions of nitric oxide into metal–methyl bonds of metal alkyls depends on whether the alkyl is diamagnetic or paramagnetic. If it is diamagnetic, the reaction involves a radical intermediate (27-VII),

(27-VII)

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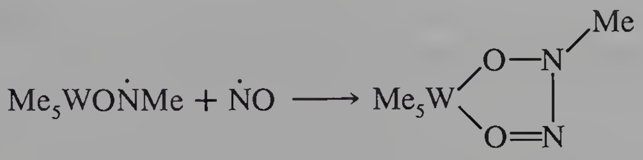
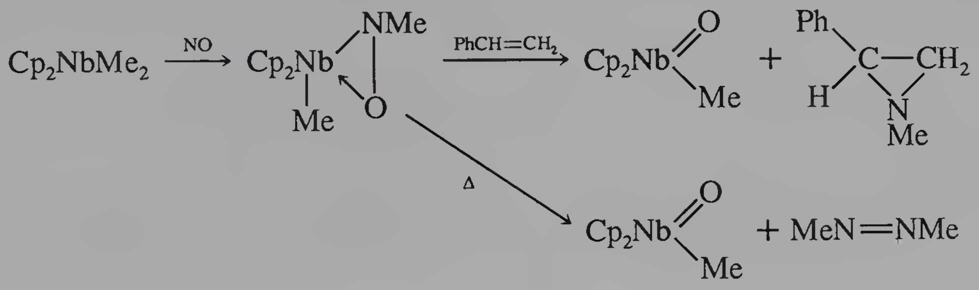
[58] C. Floriani *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 445; K. K. Pandey, *Coord. Chem. Rev.*, 1983, **51,** 69; J. M. McCleverty *et al., J. Chem. Soc. Dalton Trans.*, **1985,** 405; R. G. Bergman *et al., J. Am. Chem. Soc.*, 1984, **106,** 7462; B. N. Diel *et al., J. Organomet. Chem.*, 1985, **284,** 257.

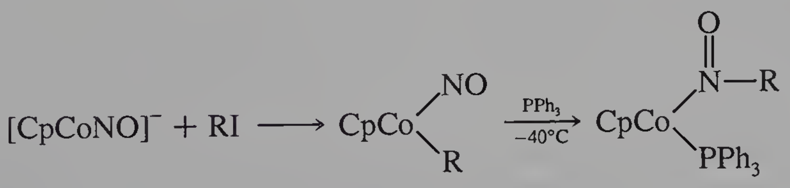
which reacts rapidly with the radical NO to generate an *N*-methyl,*N*-nitrosohydroxylaminato group:



However, a paramagnetic alkyl such as $ReOMe_4$ or Cp_2NbMe_2 cannot so react because the initial species *must* be diamagnetic. This intermediate, which may have an η^2-ONMe group, decomposes with formation of a M=O bond, while the nitrene, MeN, dimerizes to MeN=NMe. The nitrene can be trapped by an olefin to give an aziridene, namely,



Nitric oxide insertion can be studied spectroscopically in reactions such as



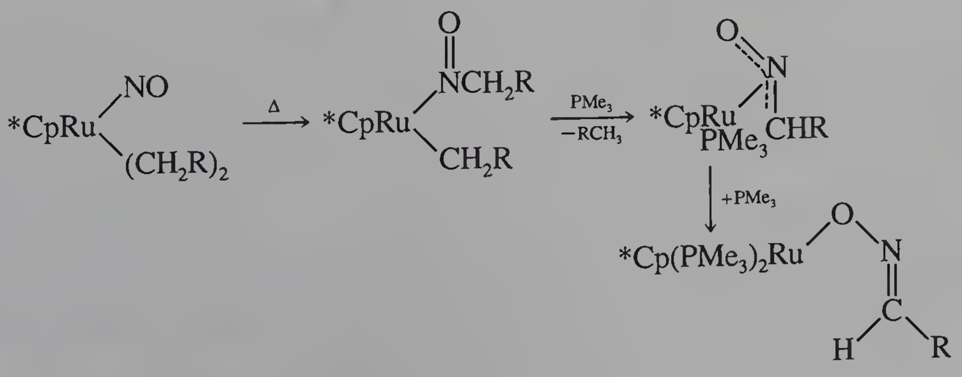
(27-VIII)

$$CpFeMe_2NO \xrightarrow{PMe_3} Cp(Me_3P)FeMe(\eta^1\text{-}N(O)R)$$

and the structure of (27-VIII) confirmed by X-ray study. A nitrosyl alkyl was also obtained by the reaction[59]

$$^*CpCl_2RuNO \xrightarrow{Al(CH_2R)_3} {}^*CpRu(NO)(CH_2R)_2$$

This can then undergo further reaction



O-Oximate

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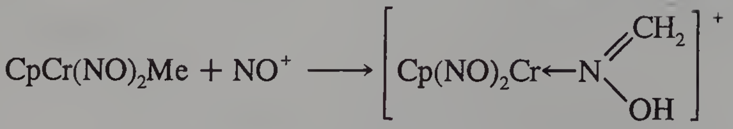
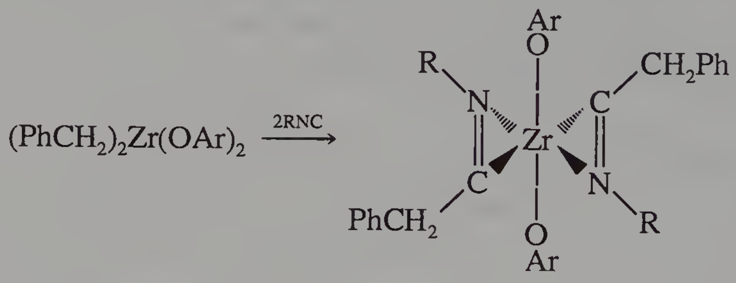
[59] M. D. Seidler and R. G. Bergman, *J. Am. Chem. Soc.*, 1984, **106**, 6110.

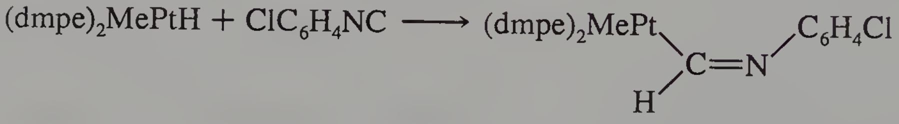
Finally, NO^+ insertions are also known,[60] for example,

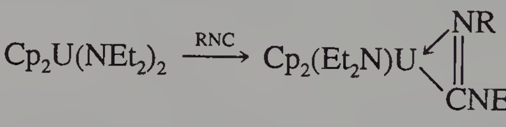


η¹-Formaldoxime

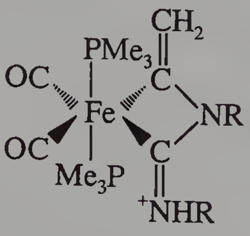
Isocyanide. Insertion of RNC into MH or MC bonds leads to imino compounds such as η^1- or η^2-iminoacyls. Some examples[61] are



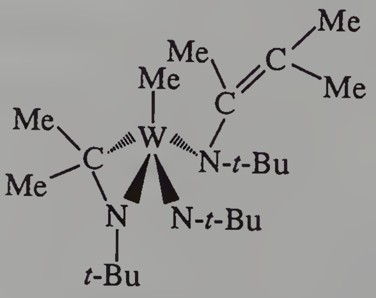




More complicated reactions[62] may occur. Thus $(Me_3P)(CO)_2IFeMe$ gives (27-IX) by way of insertions and coupling, while WMe_6 and *t*-BuNC by a complex series of reactions including C—N cleavage to give (27-X)



(27-IX)



(27-X)

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[60] K. P. C. Vollhard *et al., J. Am. Chem. Soc.,* 1986, **108,** 516; P. Legzdins *et al., J. Am. Chem. Soc.,* 1986, **108,** 317.

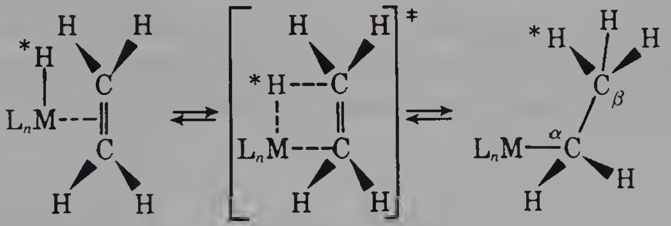
[61] I. P. Rothwell *et al., J. Am. Chem. Soc.,* 1985, **107,** 1072; W. D. Jones and W. P. Kosar, *Organometallics,* 1986, **5,** 1823; N. A. Bailey *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 2127; M. D. Curtis and J. Real, *J. Am. Chem. Soc.,* 1986, **108,** 4668; C. Cardacci *et al., Inorg. Chem.,* 1987, **26,** 84; J. DuPont *et al., Organometallics,* 1987, **6,** 899.

[62] C. Cardacci *et al., J. Chem. Soc. Chem. Commun.,* **1984,** 650; G. Wilkinson *et al., J. Chem. Soc. Dalton Trans.,* **1981,** 2088.

27-8. Insertions of Alkenes and C—C Unsaturated Compounds

The reaction of transition metal hydrido and alkyl complexes with alkenes and other unsaturated substances is of prime importance in catalytic reactions such as hydrogenation, hydroformylation, and polymerization (Chapter 28). It is one of the major methods for synthesizing metal-to-carbon bonds. We have already discussed the importance of the reverse of the reaction, the β-hydride transfer–alkene elimination reaction in the decomposition of metal alkyls (Section 25-5) and the probability of "agostic" interactions in the transfer (Section 24-8) of hydrogen atoms.

The insertion is considered to be a concerted intramolecular process involving a planar cyclic transition state, the result being a cis addition to the C=C bond;



(27-1)

Note that in the hydrido alkene complex two coordination sites are involved, whereas in the product alkyl, only one is involved. Thus the stability of alkyls (Section 25-1) depends on blocking of the coordination site required for β-hydride transfer. Some stable hydrido alkene complexes are known; where the groups are trans, hydrogen transfer will be difficult without thermal or photochemical isomerization, possibly via ligand dissociation, to give cis species, for example,[63a]

$$\textit{trans}\text{-HRh}(\text{C}_2\text{H}_4)(\text{P}i\text{-Pr}_3)_2 \rightleftharpoons \textit{cis}\text{-HRh}(\text{C}_2\text{H}_4)(\text{P}i\text{-Pr}_3)_2 \rightleftharpoons \text{EtRh}(\text{P}i\text{-Pr}_3)_2$$

The first step in the transfer is coordination of alkene,

$$\text{L}_n\text{MH} + \text{RCH}{=}\text{CH}_2 \rightleftharpoons \text{L}_n\text{MH}(\text{RCH}{=}\text{CH}_2)$$

but such equilibria have been observed only rarely.[63a,b]

The equilibrium constants are probably similar to those for nonhydridic complexes and will depend on the steric and electronic nature of the alkene as well as on the metal–ligand system. Alk-1-enes have constants ~50 times those for alk-2-enes.

The transfer process can, in favorable cases, be studied by the special ^{1}H nmr techniques of magnetization transfer and coalescence. The complex $\text{HRh}(\text{C}_2\text{H}_4)(\text{P}i\text{-Pr}_3)_2$ above is one example; another studied kinetically in con-

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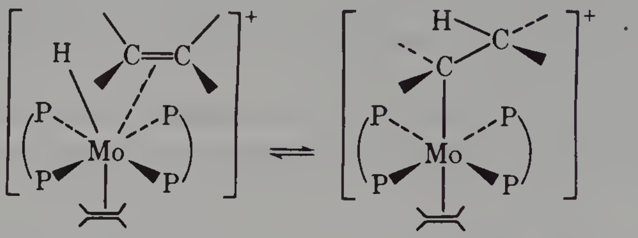
[63a] D. C. Roe, *J. Am. Chem. Soc.*, 1983, **105**, 7770.
[63b] M. L. H. Green and L-L. Wong, *J. Chem. Soc. Dalton Trans.*, **1987**, 411.

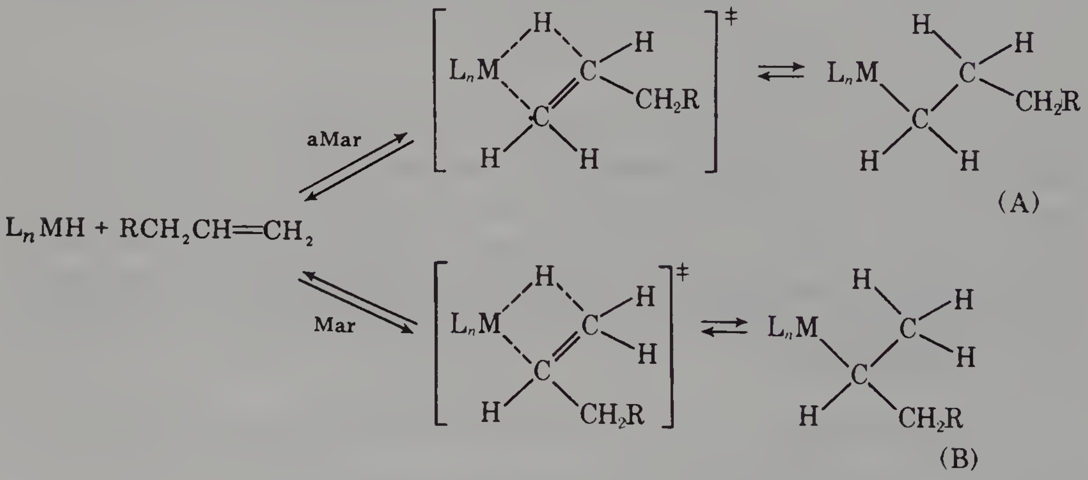
siderable detail[63c] is

$$^{*}Cp_2Nb(H)(CH_2{=}CHR) \rightleftharpoons {}^{*}Cp_2NbCH_2CH_2R$$

Here, it was possible to show that a fractional positive charge develops on the β-carbon in the transition state and that hydrogen migrates more nearly as H^- than as H^+. A third example is the protonation of $Mo(diphos)_2(C_2H_4)_2$ and the equilibrium



With alkenes other than ethylene, addition of M—H to the double bond in either the Markovnikov or the anti-Markovnikov direction, may occur, generating either a branched or linear alkyl group*:



aMar = anti-Markovnikov
Mar = Markovnikov

When the anti-Markovnikov reaction is reversed and alkene eliminated, the original alk-1-ene must be formed, but because of rotation about the C—C bond, the *same* hydrogen need not necessarily be removed from the β-carbon, and the possibility of H atom exchange arises. Using a deuterium complex L_nMD, it can be shown that L_nMH is formed by exchange, since the appearance of the high field line of H bound to metal can be observed, for example,

$$RhD(CO)(PPh_3)_2 + RCH{=}CH_2 \rightleftharpoons RhH(CO)(PPh_3)_2 + RCD{=}CH_2$$

[63c] N. M. Doherty and J. E. Bercaw, *J. Am. Chem. Soc.*, 1985, **107,** 2670.

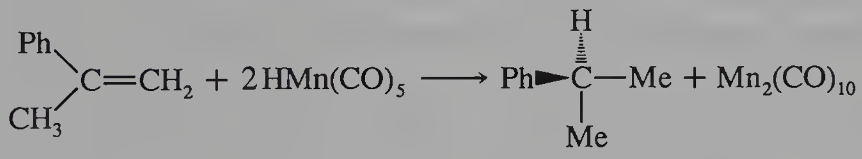
*For secondary-normal alkyl isomerizations and rearrangements on Ir^{III} see detailed studies by M. A. Bennett and G. T. Crisp, *Organometallics,* 1986, **5,** 1792, 1800.

For the secondary or branched chain alkyl (B), formed by Markovnikov addition, there are *two* possibilities for elimination. If the H atom transferred from the β-CH_3 group, again the original alk-1-ene is formed, but if it is transferred from the β-CH_2 of the CH_2R group, then alk-2-ene is formed.

Thus Markovnikov addition provides a mechanism whereby alk-1-enes can be *isomerized* to *cis–trans*-alk-2-enes. Many metal hydrido species [e.g., $HCo(CO)_4$ and $HRh(CO)(PPh_3)_3$, or metal halide complexes plus a hydride source] will isomerize alk-1-ene to alk-2-ene catalytically.

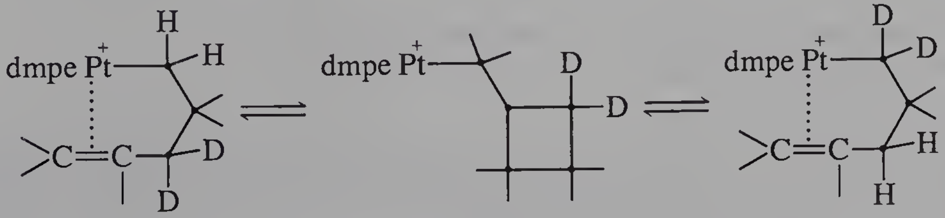
The effects of steric factors on the stability of alkyl intermediates in isomerization and other reactions are discussed in Section 28-10.

Finally, note that whereas the hydride–alkene interactions normally appear to proceed via nonradical pathways, in some cases a free-radical mechanism is certainly involved[64]. This is so for the reaction of α-methylstyrene and butadiene with $HMn(CO)_5$:



The radical $^{\bullet}Mn(CO)_5$ is involved, and chemically induced dynamic nuclear polarization effects were observed when the reaction was followed by nmr at 70°C. The reaction between $PtHCl(PR_3)_2$ and some acetylenes also appears to be radical initiated.

The insertion of alkene into metal-to-carbon bonds has long been an assumption in the most favored mechanism for Ziegler–Natta polymerization of alkenes (Section 28-13). However, until recently there have been few clear cut instances of well defined stoichiometric reactions. A rather special case where reversible insertion was observed is in the chelating complex system[65]



A reaction more comparable to that in Ziegler–Natta polymerization is[66]

$$*Cp_2LuMe + CH_2{=}CHMe \rightleftharpoons *Cp_2LuCH_2CHMe_2$$

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[64] M. C. Baird *et al., J. Am. Chem. Soc.,* 1987, **109,** 1995; R. M. Bullock and E. G. Samsel, *J. Am. Chem. Soc.,* 1987, **109,** 6542.

[65] T. C. Flood and S. P. Bitler, *J. Am. Chem. Soc.,* 1984, **106,** 6076.

[66] P. L. Watson and G. W. Parshall, *Acc. Chem. Res.,* 1985, **18,** 51; see also J. E. Bercaw *et al., J. Am. Chem. Soc.,* 1987, **109,** 203; C. J. Burns and R. A. Andersen, *J. Am. Chem. Soc.,* 1987, **109,** 915.

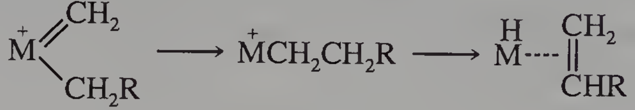
while C_2H_4 can be inserted[67]:

$$Cp(PPh_3)Ru(Ph)(C_2H_4) \longrightarrow Cp(PPh_3)RuCH_2CH_2Ph \xrightarrow{\beta\text{-H transfer}} Cp(PPh_3)RuH(CH_2CHPh)$$

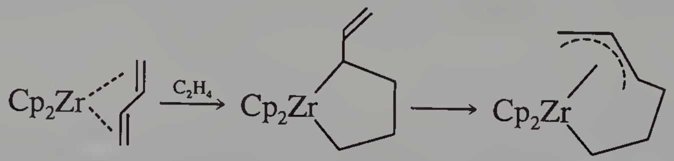
The lutetium or ytterbium methyls provide an excellent model for Ziegler–Natta catalysis as they polymerize C_2H_4 very rapidly (see Section 28-13 for further discussion). The *o*-metallated M—C bond (Section 27-9) can also undergo insertions of alkenes as well as other molecules like CO, RNC, and alkynes.[68]

Finally, other related insertions may be noted:

1. An alkyl migration to an alkylidene,[69]



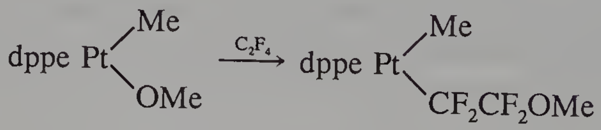
2. Insertion of ethylene into a diene, which proceeds via a metallacycle,[70]



3. 1,2 Insertion of an alkyne,[71]

$$(Ph_3P)(acac)NiMe + RC{\equiv}CR \longrightarrow (Ph_3P)(acac)Ni{-}C(R){=}C(Me)R$$

4. 1,2 Insertion of C_2F_4 into an alkoxide,[72]



27-9. Cleavage of C—H Bonds; Alkane "Activation;" Cyclometallation Reactions

The cleavage of C—H bonds is such an important area of oxidative-addition reactions that we treat it separately. There are the following main types of reactions involving C—H bond cleavage.

1. Oxidative-addition of C—H in compounds with acidic or weakly acidic hydrogen atoms.

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[67] H. Lehmkuhl *et al., Z. Naturforsch.*, 1984, **39B**, 1052.

[68] R. D. O'Sullivan and A. W. Parkins, *J. Chem. Soc. Chem. Commun.*, **1984**, 1165; L. N. Lewis and J. F. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 2728.

[69] P. Jernakoff and N. J. Cooper, *J. Am. Chem. Soc.*, 1984, **106**, 3026. For H migration see M. J. Winter and H. L. Bozec *et al., J. Chem. Soc. Chem. Commun.*, **1986**, 1185, 1182.

[70] G. Erker *et al., Angew. Chem. Int. Ed. Engl.*, 1981, **20**, 914.

[71] J. M. Huggins and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, **103**, 3002.

[72] H. E. Bryndza *et al., Organometallics*, 1984, **3**, 1603.

2. Hydrogen transfers from alkyl groups to give M—H and M—C bonds; α, β, and γ transfers have been discussed previously (Section 25-5).
3. Hydrogen transfers from hydrogen atoms on aryl rings in cyclometallation reactions.
4. Oxidative-additions of arenes and alkanes.

The cleavage of C—H bonds has sometimes been referred to as activation of C—H bonds and has been much studied in the hope of obtaining useful organic products directly from alkanes, especially methane. However, the thermodynamics of such direct conversion gives little hope for economic syntheses such as

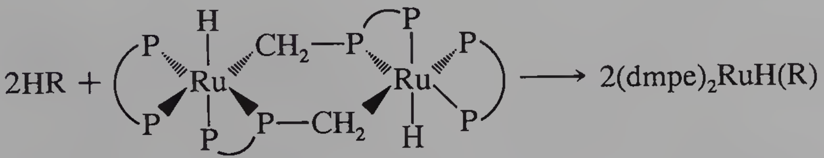
$$CH_4 + CO \longrightarrow CH_3CHO$$

although photochemical reactions of this type are known (see ref 91). The main thrust for developing useful catalytic reactions of methane is almost certainly going to have to rely on selective combustion, heterogeneously catalyzed, to give not only CO and H_2 but ethylene, acetylene, and other small hydrocarbon molecules.

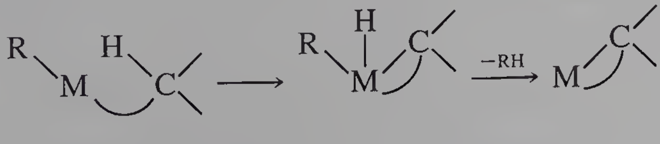
Oxidative-Addition of Weak Acids. Compounds such as RC≡CH, $HC(CN)_3$, CH_3NO_2, CH_3CN, or cyclopentadiene can add oxidatively with C—H cleavage:

$$Ir(diphos)_2Cl + CH_3CN \rightleftharpoons IrClH(CH_2CN)(diphos)_2$$

The more basic the metal complex, the more facile the addition. Complexes that add CH_3CN, CH_3COCH_3 and arenes are the dmpe ones of Fe, Ru, and Os.[16] These react not so much as an oxidative-addition, although this may be involved, but as a reaction in which there is H^+ attack on the M—C bond of the deprotonated bridging $CH_2P(Me)CH_2CH_2PMe_2$ ligand:



Cyclometallation Reactions.[73] These are intramolecular C—H cleavage reactions that can be considered as oxidative-additions sometimes resulting in MH + MC bonds but sometimes giving only MC bonds when the hydride can be transferred to, say, an alkyl group or hydride, which is then eliminated as alkane or hydrogen, respectively, for example,



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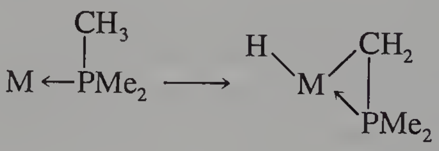
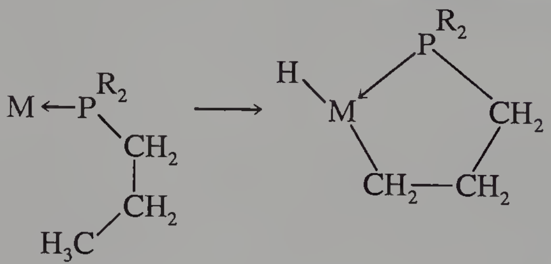
[73] E. C. Constable, *Polyhedron*, 1984, **3,** 1037; P. E. Garrou, *Chem. Rev.*, 1981, **81,** 229; I. Omae, *Coord. Chem. Rev.*, 1980, **32,** 235; M. A. Bennett *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987,** 1613; J. E. Bercaw *et al. Organometallics* 1987, **6,** 1219; J. A. D. Jeffreys *et al.*, *Organometallics* 1987, **6,** 1553; D. J. Cole-Hamilton *et al.*, *Polyhedron*, 1987, **6,** 1709.

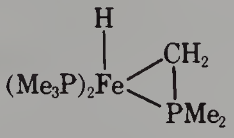
There are three main classes of reaction that lead to the formation of 3, 4, 5, or 6 membered rings.

1. The sp^3 hybridized carbon, for example, a CH_3 group, is attached to a phosphine, cyclopentadienyl, or other ligand:

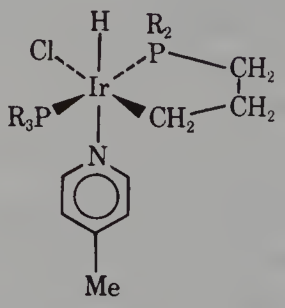




Some specific examples[74] are the compounds (27-XI) and (27-XII)

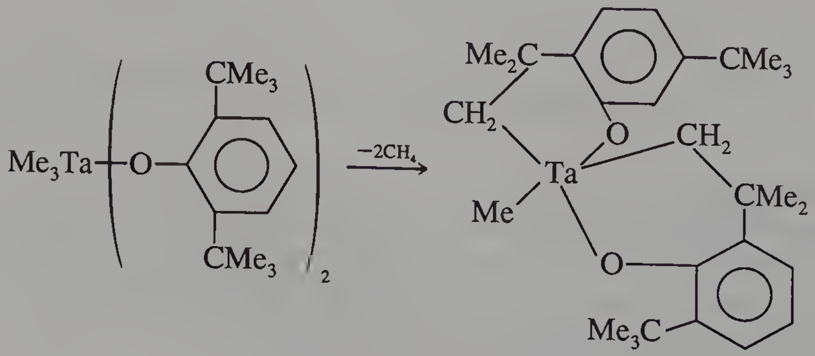


(27-XI)

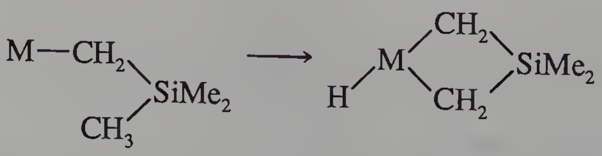


(27-XII)

and the reaction



2. Metal alkyls also can undergo cyclization[75] (see Section 25-5):



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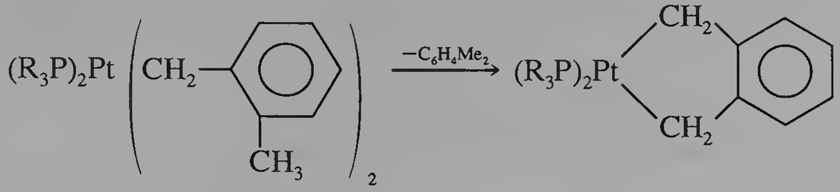
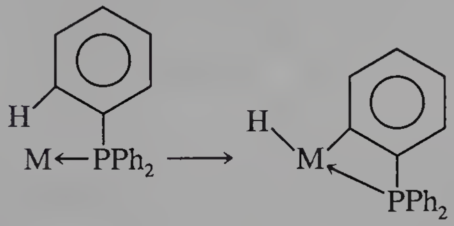
[74] For references see I. P. Rothwell *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 1502; T. C. Flood *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 1346.

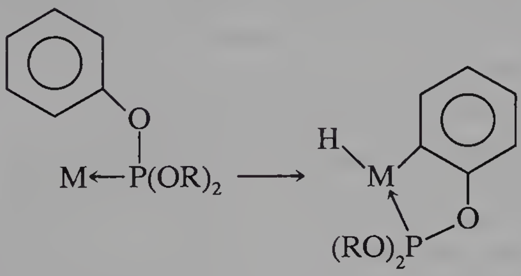
[75] S. D. Chappell and D. J. Cole-Hamilton, *Polyhedron*, 1982, **1**, 739; *J. Chem. Soc. Dalton Trans.*, **1983**, 1051; P. Diversi *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 803.

A slightly different specific example is

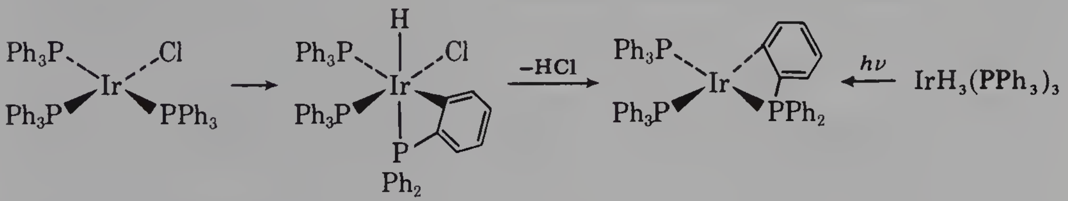


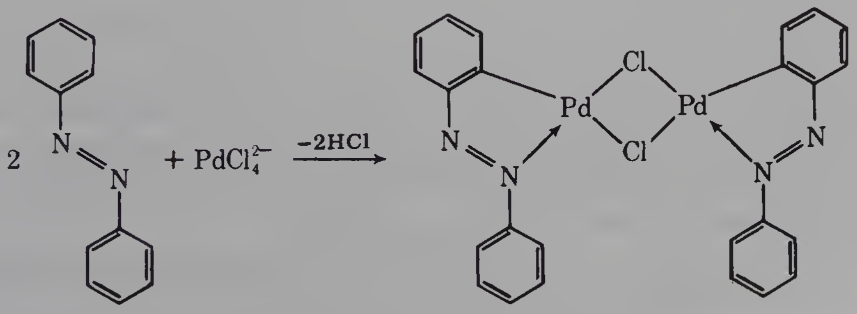
3. The *ortho* hydrogen of an aryl group in compounds such as aryl phosphines or phosphites,[76a] azobenzene, and other *N*-donors,[76b] arylketones, and carboxylic acids,[77] and so on, can be transferred (or lost), for example,





This is probably the most common type and is usually termed *orthometallation.* It may be noted that *insertion reactions,* for example, with C_2H_4, or RNC are feasible with the M—C bond.[76a,c] Some examples of cyclometallations are





[76a] L. N. Lewis and J. F. Smith, *J. Am. Chem. Soc.*, 1986, **108,** 2728.

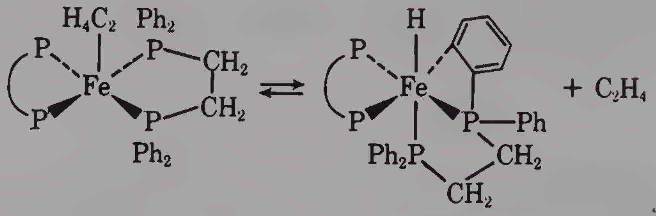
[76b] A. Chakravorty *et al., Inorg. Chem.*, 1987, **26,** 3359; J. Sales *et al., J. Chem. Soc. Dalton Trans.*, **1986,** 1785; J. Selbin *et al., Inorg. Chem.*, 1986, **25,** 1842.

[76c] W. D. Jones and W. P. Kosar, *J. Am. Chem. Soc.*, 1986, **108,** 5640.

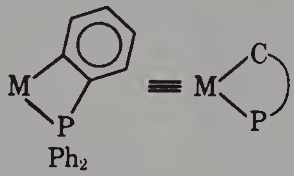
[77] P. M. Maitlis *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 770; M. F. McGuigan and L. H. Pignolet, *Inorg. Chem.*, 1982, **21,** 253.

In a few cases the reactions may be reversible[78a]:

$$^{*}Cp_2Th(CH_2SiMe_3)_2 \rightleftharpoons {}^{*}Cp_2Th[(CH_2)_2SiMe_2] + SiMe_4$$



For triphenylphosphine a convenient designation is the following:

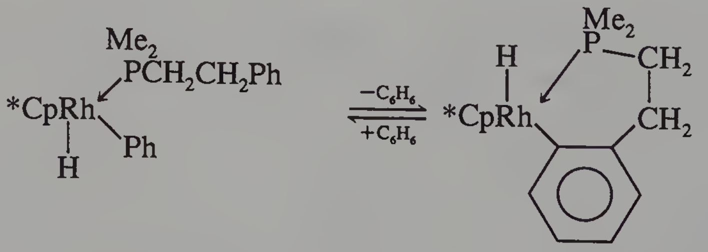


The complex $RuHCl(PPh_3)_2$, which is a 16-electron system, can catalyze the exchange of D_2 for the ortho H atom of PPh_3, whereas for the 18-electron $RuHCl[P(OPh)_3]_4$ the exchange is slow and is prevented by excess of $P(OPh)_3$. Deuteration studies[76a,78b] also show that there is a rapid equilibration of D and H between the hydride and ortho aryl sites:

$$RuDCl(PPh_3\text{-}d_1)_3 \rightleftharpoons RuHCl[PPh_3\text{-}d_2]$$

Deuterium exchange has also been observed with the ortho aryl position and also with C—H of the acetylacetonate in $Rh(acac)[P(OPh)_3]_2$.[79a]

In all of these cyclometallations, the initial step probably involves "agostic" M--H—C interactions. Finally, the kinetics and thermodynamics of intramolecular reactions of the type discussed here have been compared with similar reactions that are *inter*molecular by nmr study of the equilibrium[2]



The intermediate, $^{*}CpRh(Me_2PCH_2CH_2Ph)$, a 16*e* species shows a kinetic preference for *inter*molecular reaction with benzene (see following reaction) over intramolecular cycloaddition. However, there is a moderate thermodynamic preference for intramolecular reaction.

Finally, as noted earlier, CO, RNC, and alkynes can insert into the M—C bonds of orthometallated species.[68,79b]

[78a] T. J. Marks *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 6805.

[78b] See, for example, L. N. Lewis, *Inorg. Chem.*, 1985, **24**, 4433.

[79a] B. C. Whitmore and R. Eisenberg, *J. Am. Chem. Soc.*, 1984, **106**, 3225.

[79b] J. DuPont *et al.*, *Organometallics*, 1987, **6**, 899; M. Pfeffer *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987**, 565.

Reactions of Free Hydrocarbons.[80] Arenes[81] are more reactive than alkanes and often react at elevated temperatures or photochemically. Some examples have been noted earlier but others are

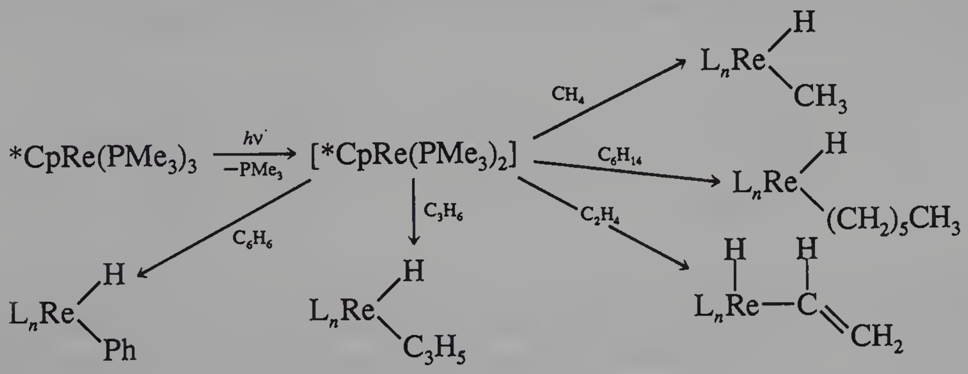
$$Cp_2TaH + C_6H_6 = Cp_2Ta(H)_2Ph$$

$$Cp_2WH_2 \xrightarrow[-H_2]{h\nu} [Cp_2W] \xrightarrow{C_6H_6} Cp_2WHPh$$

$$(\eta^6\text{-}C_6H_6)Os(C_2H_4)PMe_3 \overset{PMe_3}{\rightleftharpoons} [(Me_3P)_2Os(C_2H_4)\eta^2\text{-}C_6H_6] \xrightarrow{PMe_3} (Me_3P)_3(C_2H_4)OsHPh$$

The rate-determining step with arene oxidative-addition appears to be formation of a η^2-arene. A number of polyhydride complexes such as $IrH_5(PMe_3)_2$ will also catalyze H—D exchange in arenes via intermediate hydrido phenyls.

Much more difficult to attack than aromatic C—H bonds are *sp*^{3} hybridized C—H bonds in alkanes. However, a number of basic metal complexes such as $^*CpRe(PMe_3)_3$, $CpIr(PMe_3)H(c\text{-}C_6H_{11})$,[82a] $^*CpIr(CO)_2$,[82b] and $FeH_2(dmpe)_2$[82c] can undergo photochemical reactions such as the following*:



all of which evidently involve 16*e* or other very reactive species.

Dehydrogenations of alkanes have also been achieved in the presence of an olefin such as 3,3-dimethylbutene as hydrogen acceptor, sometimes catalytically, by polyhydrides of Re, Ru, and Ir, $MH_n(PR_3)_m$,[83] and by cationic complexes[84] such as $[IrH_2(PPh_3)_2(H_2O)_2]^+$. Other reactions include ring open-

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[80] A. E. Shilov, *Activation of Saturated Hydrocarbons by Transition Metal Complexes,* Reidel, Dordrecht, 1984; R. G. Bergman *et al., J. Am. Chem. Soc.,* 1987, **109,** 3143; M. L. Deem, *Coord. Chem. Rev.,* 1986, **74,** 101; R. H. Crabtree, *Chem. Rev.,* 1985, **85,** 245; J. E. Bercaw *et al., J. Am. Chem. Soc.,* 1987, **109,** 203.

[81] See, for example, H. Werner *et al., Angew. Chem. Int. Ed. Engl.,* 1986, **25,** 1091; W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.,* 1986, **108,** 4814; T. C. Flood *et al., J. Am. Chem. Soc.,* 1986, **108,** 7964.

[82a] D. Sutton *et al., J. Am. Chem. Soc.,* 1986, **108,** 3107; T. T. Wenzel and R. G. Bergman, *J. Am. Chem. Soc.,* 1986, **108,** 4856.

[82b] J. K. Hoyano and W. A. Graham, *J. Am. Chem. Soc.,* 1983, **105,** 7179.

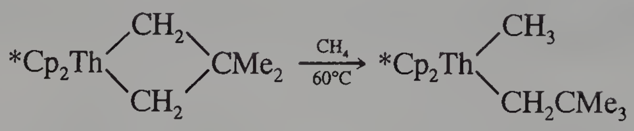
[82c] M. V. Baker and C. D. Field, *J. Am. Chem. Soc.,* 1987, **109,** 2825.

*With cyclopropane, C—C cleavage can also occur: see R. H. Crabtree, *J. Am. Chem. Soc.,* 1986, **108,** 7222; R. A. Periana and R. G. Bergman, *J. Am. Chem. Soc.,* 1986, **108,** 7346.

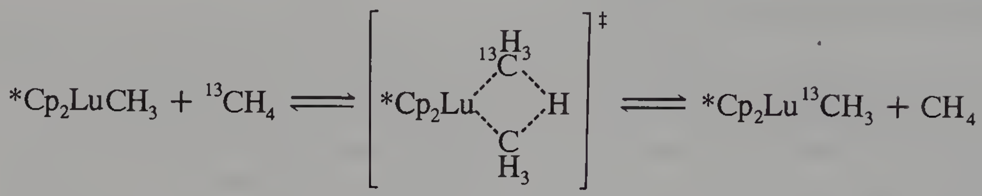
[83] H. Felkin *et al., J. Chem. Soc. Chem. Commun.,* **1986,** 801; M. Ephritikine, *Nouv. J. Chim.,* 1986, **10,** 9.

[84] R. H. Crabtree *et al., Organometallics,* 1987, **6,** 696.

ing of a metallacycle,[85]

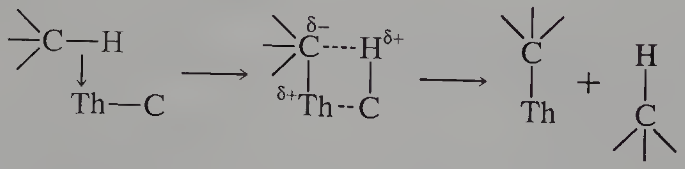


and exchange reactions,[86a] for example,



(27-XIII)

In view of the oxidation state of the lanthanide and actinide elements in these complexes, oxidative-addition is an unlikely process and a transition state such as (27-XIII) may be involved, or a sequence as in equation (27-2)[86b]



(27-2)

The same problem arises with hydrogenolysis of alkyls or MH—D_2 exchange[86c] for Ti, Zr, or Th^{IV} compounds where oxidative-addition is impossible and a similar polar transition state must be invoked.

Weak coordination of CH_4 or H_2 to the metal atoms that are strong Lewis acids is quite conceivable as a first step in these and similar reactions with arenes and Me_4Si.

Reactions similar to these proceed heterogeneously on surfaces such as those of nickel or other metals.[87]

Alkanes can react with $[PtCl_6]^{2-}$ in some cases to give halogenated alkanes as well as alkyls such as $[RPtCl_5]^{2-}$.[88]

Methane can be chlorinated by $CuCl_2$ at elevated temperatures and on other metals, Al_2O_3, SiO_2, and so on.[89]

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[85] C. M. Fendrick and T. J. Marks, *J. Am. Chem. Soc.*, 1986, **108,** 425.

[86a] P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, 1985, **18,** 51.

[86b] J-Y. Saillard *et al.*, *J. Am. Chem. Soc.*, 1986, **108,** 4327.

[86c] J. L. Petersen *et al.*, *Organometallics*, 1985, **4,** 1929.

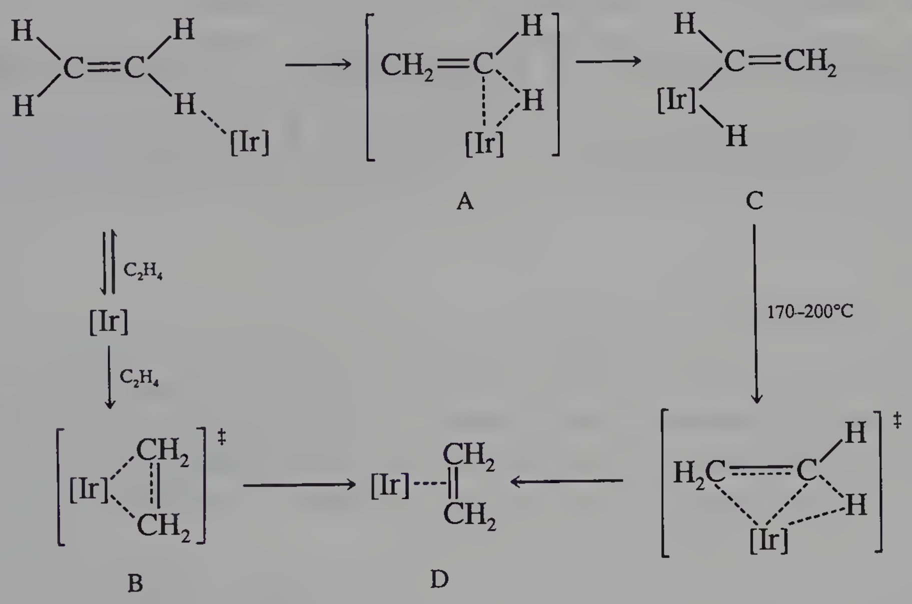
[87] J-Y. Saillard and R. Hoffmann, *J. Am. Chem. Soc.*, 1984, **106,** 2006 (has many references to C—H reactions).

[88] G. B. Shul'pin *et al.*, *J. Organometal. Chem.*, 1984, **275,** 139.

[89] J. Schwartz, *Acc. Chem. Res.*, 1985, **18,** 302; G. A. Olah *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 7097.

Hydrogen transfers from alkenes* and from metal alkyls have been discussed previously.

It may be noted that it is possible that coordination prior to H transfer may *not* be required in view of studies using *CpIr(PMe_3) made *in situ* by heating *CpIr(PMe_3)H(c-C_6H_{11}). The reaction with ethylene can give either an ethylene (D) or a vinyl complex (C) via proposed transition states (B) and (A), respectively.[90]



Finally, note that under photolysis, n-pentane, cyclohexane, and benzene will react with RhCl(CO)(PMe_3)$_2$ catalytically with modest turnovers to give the aldehyde, alcohol, and carboxylic acid.[91]

Additional References

Albright, T. A., Burdett, J. K., and Whangbo, M. H., *Orbital Interactions in Chemistry,* Wiley, New York, 1985 (considers oxidative-additions and migrations).

Collman, J. P., L. S. Hegedus, J. R. Norton, and R. G. Fink, *Principles and Applications of Organotransition Metal Chemistry,* 2nd ed., University Science Books, Mill Valley, CA, 1987.

Halpern, J., *Pure Appl. Chem.,* 1986, **58,** 575 (radical reactions in organic and bioorganometallic chemistry).

Low, J. J. and Goddard III, W. A., *Organometallics,* 1986, **5,** 109 (theory, oxidative-additions).

Mimoun, H., *New. J. Chem.,* 1987, **11,** 513 (activation of CH_4 not involving synthesis gas).

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*For addition of C_2H_4 as μ-vinyl and μ-H see C. Ting and L. Messerle, *J. Am. Chem. Soc.,* 1987, **109,** 6506.

[90] P. O. Stoutland and R. G. Bergman, *J. Am. Chem. Soc.,* 1985, **107,** 4581.

[91] T. Sakemura and M. Tanaka, *J. Chem. Soc. Chem. Commun.,* **1987,** 758.

Chapter Twenty Eight

Homogeneous Catalytic Synthesis of Organic Chemicals by Transition Metal Complexes

28-1. Introduction

Most organic chemicals produced in bulk quantities are oxygenated compounds such as alcohols, ketones, and carboxylic acids, and hydrocarbons such as ethylene, propylene, and butadiene that may be polymerized to higher olefins, which include polyethylene, polypropylene, and rubbers. Many are used as starting materials for other syntheses.

In the early part of this century, coal and coal tar products were the main source of these products via acetylene (from calcium carbide), but as the petroleum and natural gas industries developed, ethylene, obtained by cracking, and other alkenes became major sources for organic synthesis. However, in recent years, synthesis gas derived methanol has increasingly become the starting point for many other bulk chemicals.

In most conversions starting from methane or petroleum fractions, transition metals or their compounds are used as catalysts, heterogeneously on oxide, carbon or other supports, or where necessary in order to obtain greater selectivity, in homogeneous solution.

The whole area of catalyzed reactions has been intensively studied and has generated a vast patent literature as well as a great many papers in scientific journals. In particular, the discovery of the low pressure polymerization of ethylene and propylene by Ziegler and Natta led not only to technical syntheses of polyalkenes and rubbers, but also to the wide use of aluminum alkyls as alkylating agents and reductants for metal complexes. Similarly, the discovery by Smidt of palladium-catalyzed oxidation of alkenes stimulated an enormous growth in the use of palladium complexes for a variety of catalytic and stoichiometric reactions of organic compounds.

The term "catalyst" is ambiguous and requires careful use. In heterogeneous reactions—where, for example, a gas mixture is passed over a solid that evidently undergoes no change—the term may have some point insofar as it means a substance added to accelerate a reaction. However, homogeneous catalytic reactions in solution are commonly very complex and proceed by way of linked chemical reactions in a closed cycle involving different metal species. The concept of one particular species being "the catalyst," even if it is the one added to initiate or accelerate the reaction, has no real validity.

This chapter deals mainly with homogeneous reactions, since many of these can be studied mechanistically and spectroscopically, and in certain favorable cases intermediates in the reaction cycles, isolated or otherwise, are characterized. The principles on which our understanding of these reactions are based are mainly coordinative unsaturation, oxidative-addition, and insertion reactions and attacks on coordinated ligands by electrophiles or nucleophiles that have been discussed in earlier chapters. Some of these principles doubtless have applicability in heterogeneous catalysis and there have been attempts to correlate and interrelate the mechanisms of both homo- and heterogeneous catalysis.[1]

From the industrial point of view, heterogeneous systems have great practical advantages over homogeneous ones, notably because of the ease of separation of products from any excess of reactants and from the catalyst. However, a number of industrial homogeneous processes have been developed because they may give much higher selectivity in reactions, operate under milder conditions of temperature and pressure, or have other technical advantages.

Two other points may be noted:

1. It is sometimes difficult with homogeneous reactions to be certain that the reaction is so, and not catalyzed heterogeneously by decomposition products, or reaction vessel surfaces. Several tests have been devised.[2] For example, in platinum complex catalyzed reactions any metallic platinum can be poisoned by mercury, while a soluble unsaturated polymer is hydrogenated only by homogeneous catalysts.

2. Attempts to overcome the technical problems in using homogeneous reactions are (a) phase transfer reactions where the catalyst is in the aqueous and substrate and products are an organic phase; (b) the supporting of well-defined homogeneous catalysts on surfaces that may in addition be functionalized to act as ligands (Section 28-18). Both still encounter difficulties, particularly the latter.

We begin with reactions of CO and H_2 whose mixtures, obtained by partial combustion of hydrocarbons, are called "synthesis gas"; this gas is now the major starting point for many bulk chemicals. Before doing so, some comment on the direct use of alkanes, especially methane from natural gas, is appropriate. As noted in the Section 27-9, on alkane C—H bond "activation," direct syntheses are currently not practical and may never become so. How-

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[1] See, for example, J. J. Rooney, *J. Mol. Catal.*, 1985, **31**, 147.

[2] G. M. Whitesides *et al.*, *Organometallics*, 1985, **4**, 1819 and references quoted.

ever, improved methods of methane oxidation[3] can give not only synthesis gas but C_2H_4, C_2H_2, CH_3OH, and other products; butanes have long been used as a source for acetic acid. Selective chlorinations of CH_4 can give CH_3Cl (Section 27-9) and although CH_3Cl can be readily converted into other products, the necessity for recycling HCl in vast quantities and the resulting corrosion problems almost certainly eliminate this route on economic grounds. Hence, in the near future direct oxidation of methane seems to be the most practical alternative to syngas conversions.

REACTIONS OF CARBON MONOXIDE AND HYDROGEN[4]

The nickel catalyzed conversion of CO and H_2 to methane was discovered by Sabatier and Senderens but the best known names are those of Fischer and Tropsch who first described the conversion into oxygenated products as well as hydrocarbons using heterogeneous iron catalysts. Much of the early work on "carbonylation" reactions was carried out in Germany by Fischer, Tropsch, Reppe, Roehlen, and others. In recent years these reactions have been studied as potential routes to organic chemicals once again from coal, rather than natural gas or petroleum.

28-2. Synthesis Gas and the Water Gas Shift Reaction

Mixtures of CO, H_2, and CO_2 may be obtained by (*a*) controlled oxidation or catalytic steam "re-forming" of CH_4, or light petroleums (naptha, C_6–C_8), (*b*) gasification of coal with oxygen and/or steam at ~1500°C. Carbon dioxide is removed by scrubbing with monoethanolamine or by arsenite solutions, from which it can be recovered. The ratios of H_2 and CO vary in the different routes $CH_4 + O_2$, ~1.8; $CH_4 + H_2O$, ~3; naphthas and coal + O_2, ~0.9.

Carbon monoxide may also be contained in dilute concentration in nitrogen from blast furnaces or air oxidation of coke and can be recovered by complexing with $CuAlCl_4$ in aromatic solvents. A critical prerequisite for use of synthesis gas or CO in most reactions catalyzed by transition metals is that sulfur compounds such as H_2S or COS formed from sulfur compounds in natural hydrocarbons or coal be first removed, for example, by heterogeneous nickel treatment.

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[3] R. Pitchai and K. Kliev, *Cat. Rev. Sci. Eng.*, 1986, **28,** 13; N. R. Foster, *Appl. Catal.*, 1985, **19,** 1; G. J. Hutchings *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987,** 1388.

[4] R. P. A. Sneeden, *Comprehensive Organometallic Chemistry,* Vol. 8, Pergamon Press, New York, 1982; J. Falbe, *Carbon Monoxide in Organic Synthesis,* Springer-Verlag, Berlin, 1970; J. Falbe, Ed., *New Syntheses with Carbon Monoxide,* Springer-Verlag, Berlin, 1980; I. Wender and P. Pino, Eds., *Organic Synthesis via Metal Carbonyls,* Vol. 1, 1968, Vol. 2, 1976, Wiley, New York; R. A. Sheldon, *Chemicals from Synthesis Gas,* Reidel, Dordrecht, 1983; W. Keim, Ed., *Catalysis in C-1 Chemistry,* Reidel, Dordrecht, 1983; B. D. Dombek, *Advances in Catalysis,* Vol. 32, Academic Press, New York, 1983; C. D. Chang, *Chemical Industry Series, Vol. 10. Hydrocarbons from Methanol,* Dekker, New York, 1983.

It is possible to obtain pure hydrogen or CO or to change the synthesis gas composition by the *water gas shift* (*WGS*) *reaction:*

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_2 \qquad \Delta H^0_{298°C} = -41.2 \text{ kJ mol}^{-1}$$
$$\Delta G^0_{298°C} = -28.5 \text{ kJ mol}^{-1}$$

If liquid water is present, however, the reaction is mildly endothermic

$$CO_{(g)} + H_2O_{(l)} \rightleftharpoons CO_2 + H_{2(g)} \qquad \Delta H^0_{298°C} = +2.8 \text{ kJ mol}^{-1}$$
$$\Delta G^0_{298°C} = -19.9 \text{ kJ mol}^{-1}$$

but nevertheless highly favored because of the large positive entropy change.

Although the shift is normally used for H_2 generation heterogeneously over iron–chromium and zinc–copper oxide catalysts, there has been much study of homogeneous systems with liquid water present.[5a] These have used carbonyls or carbonyl complexes of Mo, W, Fe, Ru, Rh, Ir, and so on, in acidic or basic solutions. A typical cycle in alkaline aqueous methanol is Scheme 28-1. Another similar cycle using an iridium dipyridyl derivative is shown in Fig. 28-1. However, none of the various homogeneous systems are sufficiently rapid to be of use commercially. Carbon monoxide–water systems can be used to replace hydrogen in a number of reactions such as reduction or hydroformylation[5b] via an *in situ* shift, but again this is not particularly useful as generally expensive CO is converted to cheap CO_2.

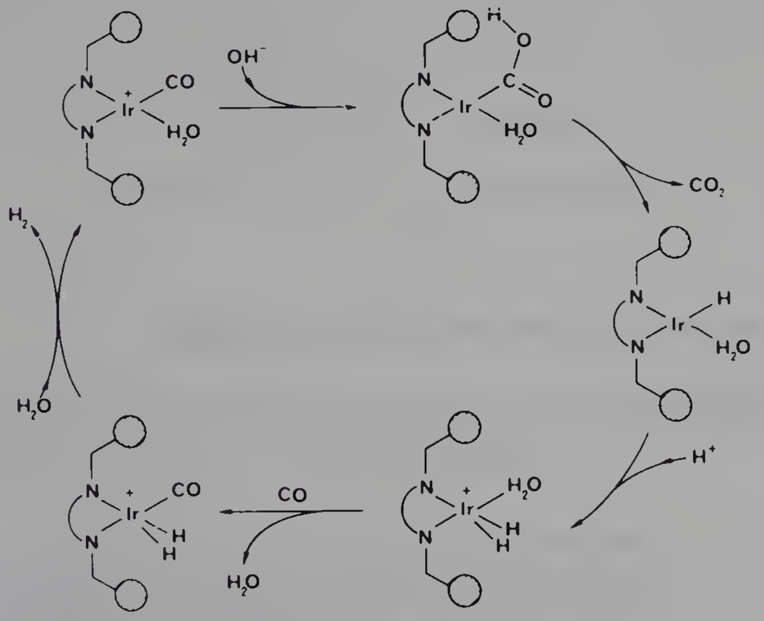
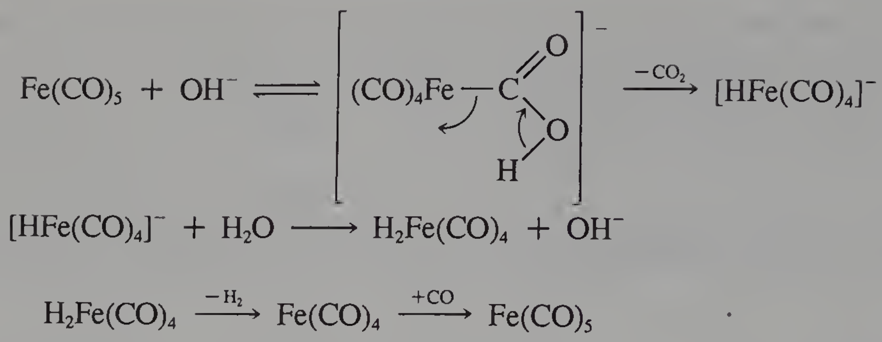


FIG. 28-1. Homogeneous water gas shift cycle. [Reproduced by permission from J. P. Collin, R. Ruppert, and J. P. Sauvage, *Nouv. J. Chim.*, 1985, **9**, 395.]

[5a] T. Tanaka *et al., Organometallics,* 1986, **5**, 724.

[5b] See, for example, P. Kalck *et al., J. Chem. Soc. Chem. Commun.*, **1987**, 146.



$$Fe(CO)_5 + OH^- \rightleftharpoons [(CO)_4Fe{-}C(O)OH]^- \xrightarrow{-CO_2} [HFe(CO)_4]^-$$

$$[HFe(CO)_4]^- + H_2O \longrightarrow H_2Fe(CO)_4 + OH^-$$

$$H_2Fe(CO)_4 \xrightarrow{-H_2} Fe(CO)_4 \xrightarrow{+CO} Fe(CO)_5$$

Scheme 28-1

Some important reactions of H_2, CO and MeOH are shown in Figs. 28-2 and 28-5.

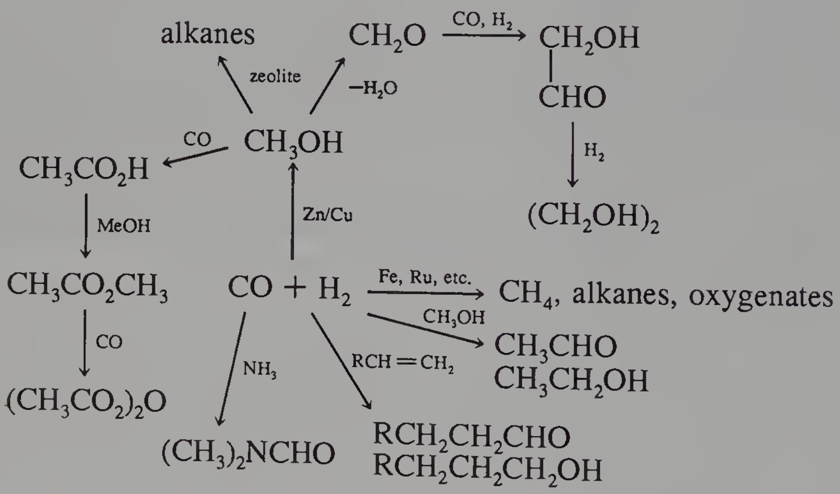


FIG. 28-2. Some synthesis gas and methanol reactions.

28-3. Reduction of Carbon Monoxide by Hydrogen[6]

This reaction has been much studied, and some thermodynamic data (Table 28-1) show that only the reduction to methane is favorable. Nevertheless,

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[6] R. B. Anderson, H. Köbel, and M. Ralek, *The Fischer–Tropsch Synthesis*, Academic Press, New York, 1984; M. E. Dry, in *Applied Industrial Catalysis*, Vol. 2, B. E. Leach, Ed., Academic Press, New York, 1983; R. G. Herman, Ed., *Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals*, Plenum Press, New York, 1982; R. A. Sheldon, in *Catalysis by Metal Complexes*, Vol. 3, R. Ugo and B. R. James, Eds, Reidel, Dordrecht, 1983; G. Henrici Olivé and S. Olivé, *Chemistry of Catalytic Hydrogenation of Carbon Monoxide*, Springer-Verlag, Berlin, 1984; R. B. Anderson, *J. Phys. Chem.*, 1986, **90**, 4806 (CO and CO_2). Am. Chem. Soc. Symp. Ser. No. 328, 1987 (industrial C-1 processes).

TABLE 28-1
Thermodynamic Data for CO–H_2 Reactions (at 500°K)[a]

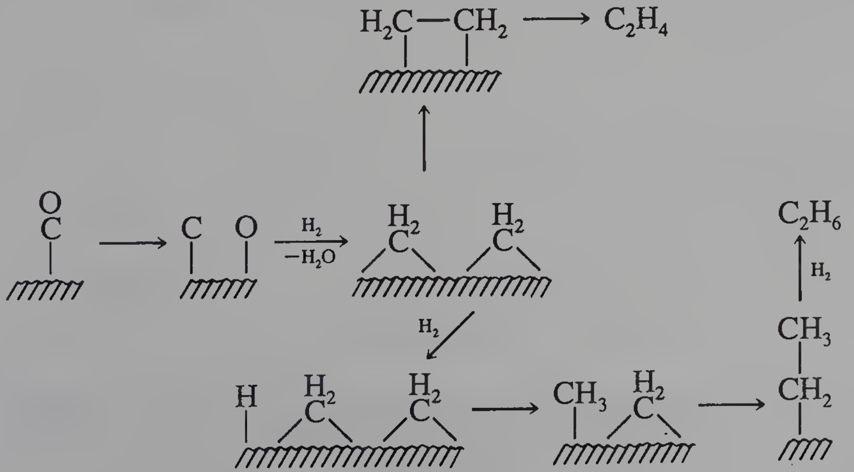
Reaction	ΔG kJ mol^{-1}	Log K_p
$CO + 3H_2 = CH_4 + H_2O$	−96.22	10.065
$CO + H_2 = HCHO$	50.62	−5.293
$CO + 2H_2 = CH_3OH$	21.23	−2.222
$2CO + 3H_2 = \begin{matrix} CH_2OH \\ \vert \\ CH_2OH \end{matrix}$	65.92	−6.891

[a] From D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, *The Thermodynamics of Organic Compounds,* Wiley, New York, 1969. Methanation of CO_2 is also feasible, $CO_2 + 4H_2 = CH_4 + 2H_2O(l)$ $\Delta H_{298} = -252.9$ kJ mol^{-1} as is the reduction to formates (D. J. Darensbourg and C. Ovalles, *Inorg. Chem.*, 1986, **25,** 1603, and *J. Am. Chem. Soc.*, 1987, **109,** 3330.

reduction of CO by H_2 to give alcohols is feasible using appropriate catalysts.

The Fischer–Tropsch synthesis is a heterogeneous reaction of H_2 and CO catalyzed by various metals such as Fe, Co, Ni, or Ru on alumina or other support and by cobalt–chromium and other oxides. Using different catalysts and varying the conditions, either CH_4, liquid hydrocarbons, high molecular weight waxy hydrocarbons, methanol, higher alcohols, olefins, and so on, can be obtained. Nickel is best for methanation, cobalt for higher alkanes; Rh tends to give EtOH, MeCHO, and $MeCO_2H$.

Since CO and H_2 have to be obtained from coal or oil, the use of Fischer–Tropsch catalysis for manufacture of synthetic fuels is uneconomic and only in South Africa, where coal is cheap and there is strategic necessity is the process used; however, a Shell catalyst is said to give a waxy product that can be upgraded to diesel and jet fuel.[7]



Scheme 28-2

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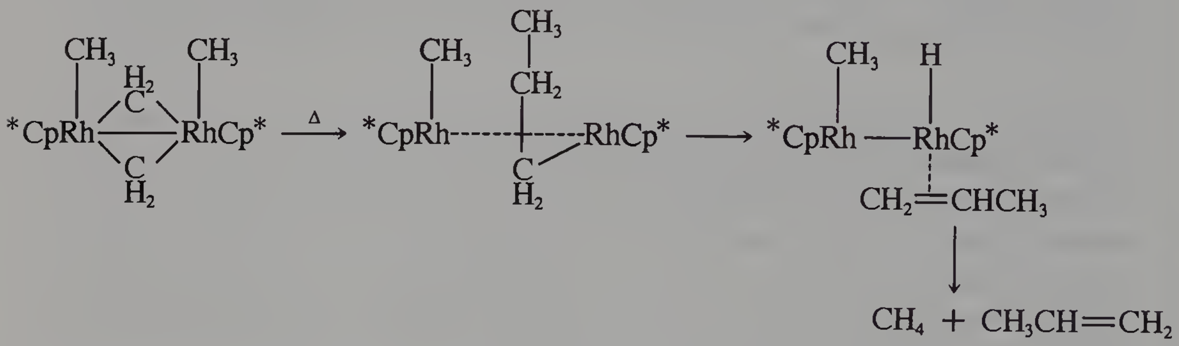
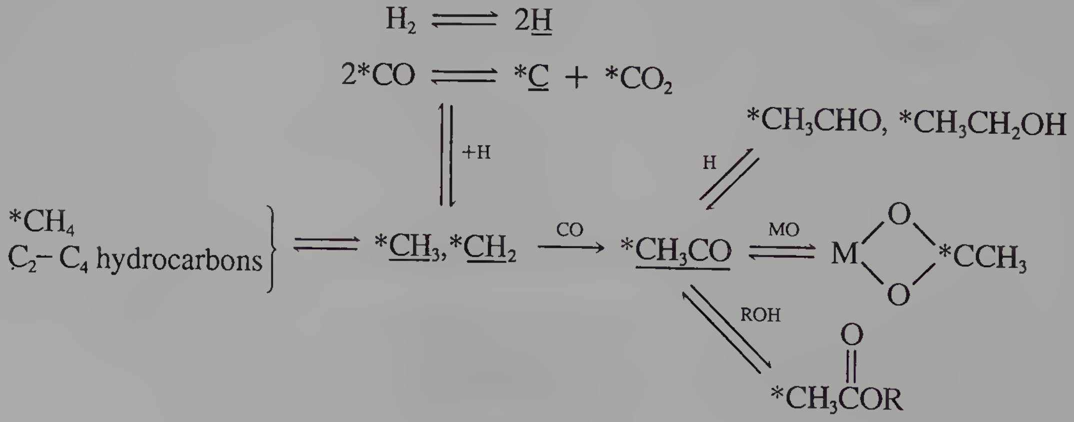
[7] Shell Science and Technology, November 1985.

There has been extensive speculation on the mechanism of reduction of CO by H_2.[6,8a,b] Fischer and Tropsch originally proposed that surface carbide formed from dissociation of carbon monoxide* (which is known to occur quite readily on metal surfaces) gave rise on hydrogenation to CH_2 groups which then initiated the reaction. Modeling studies using the interaction of CH_2N_2 with Fe, Ru, Co, Ni, and Pd surfaces gave C_2 to C_{18} alkanes and monolefins.[9] The use of CO + H_2 under the same conditions gave similar products. The mechanism proposed involved addition across M—M bonds to form μ-alkylidene and further reaction, Scheme 28-2. Simple molecular models[8b] have also been developed using μ-alkylidene complexes, for example,



Surface intermediates with —OCH_3, —CH_2OH, and —CH_2 groups have been identified. For Rh—Ti on SiO_2, ^{13}C labeling studies show that surface C leads to CH_3, CH_2, and CH_3CO moieties and to ethanol and other C_2 products as in Scheme 28-3.[10]



Scheme 28-3

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[*] For CO cleavage on complexes see M. H. Chisholm *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 717; R. P. Planalp and R. A. Andersen, *J. Am. Chem. Soc.*, 1983, **105**, 7774.

[8a] C. K. Rofer-De Pooter, *Chem. Rev.*, 1981, **81**, 447.

[8b] W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, 1982, **21**, 117 (organometallic aspects).

[9] R. G. Copperthwaite *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987**, 541; H. Bock *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 1068.

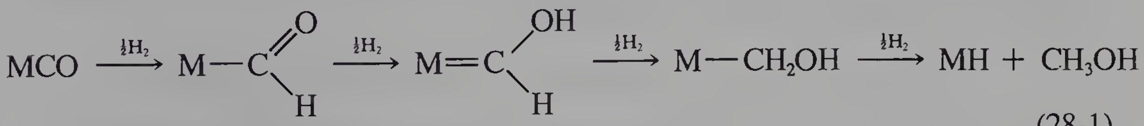
[10] M. Ichikawa and T. Fukushima, *J. Chem. Soc. Chem. Commun.*, **1985**, 321; G. L. Geoffroy *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 1315.

Synthesis of Oxygenated Compounds. We have just noted that rhodium can give C_2 species. The formation of *methanol* (Table 29-1) over Zn—Cu oxides on supports, or other catalysts under relatively mild conditions (30–50 atm, 100–250°C) is carried out on a large scale[11] and is undoubtably the most important reaction of synthesis gas. Methanol from natural gas via $CO + H_2$ also provides a route to petroleum hydrocarbons since it can be converted to them over the high silica zeolites; a plant operates in New Zealand,[12a] but again the reason is probably strategic.

The mechanism of the reaction has been proposed to proceed via Me_2O and dimethyl oxonium ylid ($Me_2O^+CH_2^-$) on the surface, but this is still under discussion.[12b]

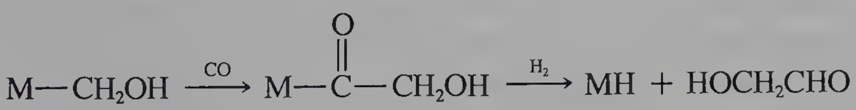
There have been extensive efforts to develop homogeneous reductions of CO by H_2 directly to more desirable products like ethylene glycol or formate esters,[13a], but so far, none has proved economically viable. Most of these reactions have involved metal carbonyls or substituted carbonyls sometimes with two or more metals, high temperatures, 200°C or more, and high pressures, up to 3000 atm. Solvents such as sulfolane, crown ethers, acetic acid, or fused melts of, for example, $[Bu_4P]Br$[13b] have been used. One problem of such systems is that although catalysis probably proceeds on a mononuclear or possibly binuclear species, the reaction conditions are such as to lead to clusters that effectively remove active catalyst. Thus in polyalcohol syntheses using $Rh(acac)(CO)_2$,[14] clusters such as $[Rh_5(CO)_{15}]^-$ are present as well as $[Rh(CO)_4]^-$.

For homogeneous reactions many schemes have been proposed, almost all of which involve an initial formyl group and its further reduction, eq. 28-1,



(28-1)

and/or reduction with CO insertions



$$M{-}CH_2OH \xrightarrow{CO} M{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2OH \xrightarrow{H_2} MH + HOCH_2CHO$$

[11] F. Marschner and F. W. Moeller, in *Applied Industrial Catalysis,* Vol. 2, B. E. Leach, Ed., Academic Press, New York 1983; R. H. Hoeppener *et al., Appl. Catal.,* 1986, **25,** 109; R. Sapienza, *et al., Polyhedron,* 1986, **5,** 249.

[12a] G. J. Hutchings, *Chem. Br.,* **1987,** 762.

[12b] C. D. Chang *et al., J. Chem. Soc. Chem. Commun.,* **1987,** 1320; R. Hunter *et al., J. Chem. Soc. Chem. Commun.,* **1987,** 1369.

[13a] B. D. Dombek, *Adv. Catal.,* 1983, **32,** 325; Y. Kiso and K. Saeki, *J. Organomet. Chem.,* 1986, **309,** C26.

[13b] J. F. Knifton, *et al., Organometallics,* 1984, **3,** 62.

[14] J. L. Vidal and W. E. Walker, *Inorg. Chem.,* 1980, **19,** 896. See also Y. Ohgomori *et al., J. Chem. Soc. Chem. Commun.,* **1987,** 829 (use of $RhX(CO)(PCy_3)_2$).

If the initial formation of a CHO group is assumed, and, as discussed in Section 27-6, there are some difficulties, then logical catalytic cycles can be constructed, though precisely what happens in reactions at high temperature and pressure is a matter for speculation unless spectroscopic data taken under reaction conditions in high pressure cells are available. One such cycle is shown in Fig. 28-3.

A vast amount of work using organometallic compounds as models[8b] has been done in order to justify some of the proposals that are mostly based on eq. 28-1.[15a]

Interactions of metal carbonyl species with transition metal hydrido species have given many interesting compounds but little or no $\mathrm{CH_4}$, $\mathrm{CH_3OH}$, and so on.

Reductions using hydridic reagents such as $\mathrm{LiBH_2Et_2}$, $\mathrm{NaAlH_2Et_2}$, and $\mathrm{BH_3}$, have been used to generate formyl species, while these have been treated with $\mathrm{H^+}$ or $\mathrm{Me^+}$ and reduced. Such stoichiometric reactions can be done successively;[15b] for example, CO can be converted to pentanoic acid starting from $\mathrm{[Cp(Me_3P)(CO)_2Fe]^+}$.

Other typical stoichiometric sequences[16] are

$$\mathrm{Os_3(CO)_{12}} \xrightarrow{\mathrm{KBH(O\mathit{i}-Pr)_3}} \mathrm{Os_3(CO)_{11}CHO} \xrightarrow[\mathrm{Me_3O^+}]{\mathrm{H^+}} \mathrm{Os_3(CO)_{11}(\mu\text{-}CH_2)} \xrightarrow{\mathrm{H_2}} \mathrm{CH_4}$$

$$\mathrm{{}^*Cp(NO)Re(CO)_2^+} \xrightarrow{\mathrm{NaAlEt_2H_2}} \mathrm{{}^*Cp(NO)(CO)ReCH_2OH}$$

$$\textit{trans}\text{-}\mathrm{[Ru(CO)_2dppe_2]^{2+}} \xrightarrow{\mathrm{NaHB(OEt)_3}} \textit{trans}\text{-}\mathrm{[Ru(CHO)(CO)dppe_2]^{2+}}$$

Model systems probably closest to those involved in the catalytic reactions are those where $\mathrm{H^+}$ and $\mathrm{H^-}$ are transferred between platinum group metal complexes intermolecularly,[17] for example,

$$\mathrm{Cp(NO)(CO)Re} + \mathrm{HRu(CO)_4^-} \longrightarrow \mathrm{Cp(NO)(CO)ReCHO}$$

$$\mathrm{[HRu_3(CO)_9dppe]^-} + \mathrm{[Ru(CO)_2dppe_2]^+} \longrightarrow \textit{trans}\text{-}\mathrm{[Ru(CHO)(CO)dppe_2]^+}$$

Ion pairing may have a profound effect; for example, the $\mathrm{K^+}$ but not the $\mathrm{Na^+}$ salts are reactive (Section 22-6). The prevention of ion pairing may well be the reason why large cations, and chelating or strongly donating solvents are often required in catalytic reactions.

In addition, systems with two different metals show some synergic effects and it is possible that different metal species have a different function. Thus catalytic studies using Ru and Rh compounds with an iodide promoter give

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[15a] See D. Milstein *et al., J. Am. Chem. Soc.,* 1986, **108,** 1338, 3525.

[15b] See, for example, A. R. Cutler *et al., J. Am. Chem. Soc.,* 1985, **107,** 3130; S. L. Brown and S. G. Davies, *J. Chem. Soc. Chem. Commun.,* **1986,** 84.

[16] G. L. Geoffroy *et al., J. Am. Chem. Soc.,* 1984, **106,** 2559; D. J. Cole-Hamilton *et al., J. Chem. Soc. Dalton Trans.,* **1985,** 387.

[17] B. D. Dombek and A. M. Harrison, *J. Am. Chem. Soc.,* 1983, **105,** 2485; D. S. Barratt and D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.,* **1985,** 1559.

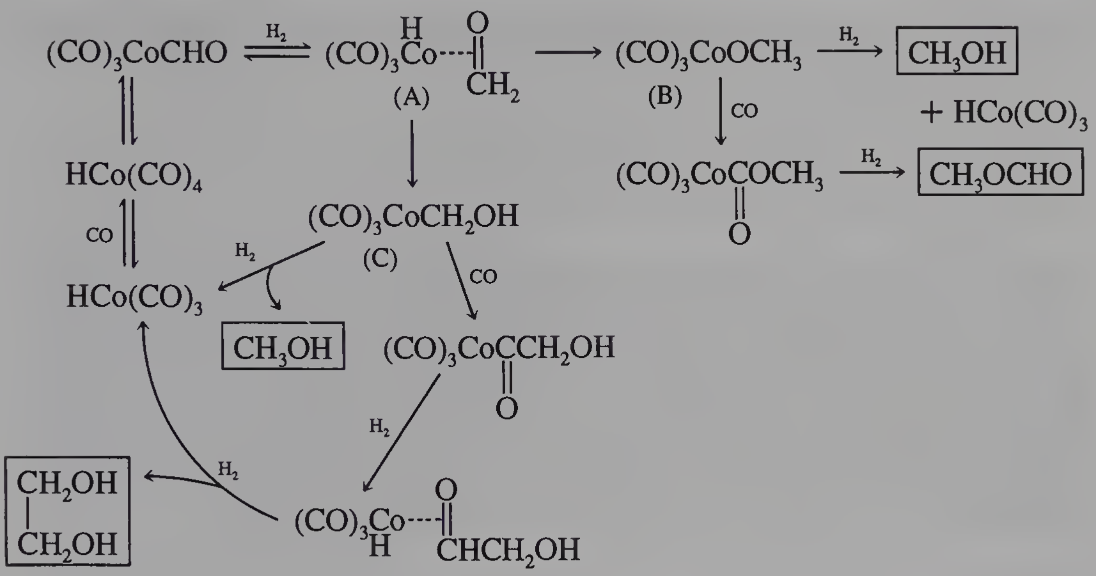


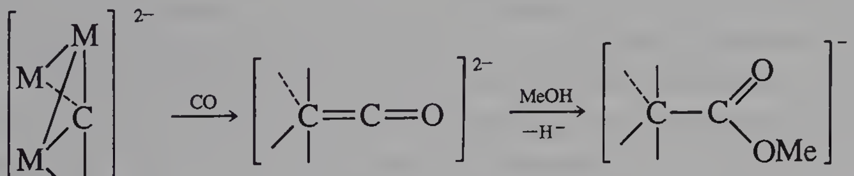
FIG. 28-3. C_1 and C_2 syntheses using $Co_2(CO)_8$ as cycle precursor (adapted from H. M. Feder and J. M. Rathke, *Ann. N.Y. Acad. Sci.*, 1980, **333,** 45). Note that H transfer to coordinated formaldehyde A, can give a methoxide B, or a hydroxymethyl C, either of which can then be reduced by H_2 or can insert CO the product of which is then reduced. The $HCo(CO)_3$ is recycled.

glycol where the reduction

$$L_nRh—CO + HRuL'_m \longrightarrow Rh—CHO$$

is proposed.[18a]

Models based on clusters with exposed carbido groups (Section 23-5) have also been studied[18b]:



(CO groups omitted)

28-4. Hydroformylation of Unsaturated Compounds[19]

The hydroformylation of unsaturated compounds discovered by Otto Roelen of Ruhrchemie in 1938 is an important reaction that is homogeneous; its mechanism is now known with some certainty.

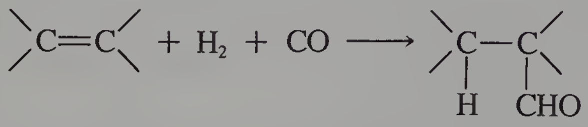
The name "hydroformylation" stems from the nature of the reaction, which

[18a] B. D. Dombek, *Organometallics*, 1985, **4,** 1707.

[18b] D. F. Shriver *et al.*, *Organometallics*, 1987, **6,** 1377.

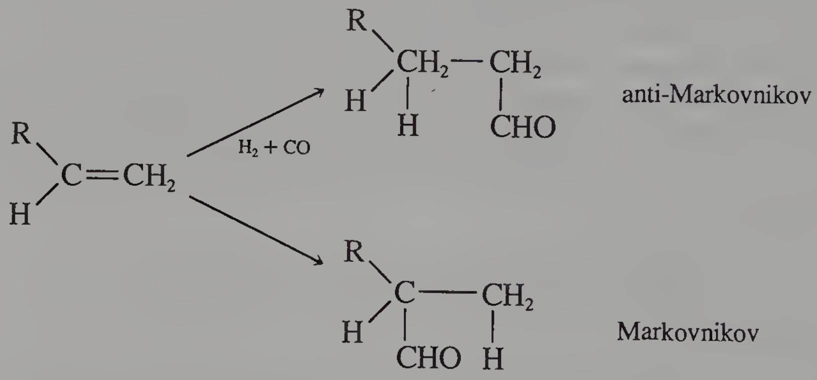
[19] B. Cornils, in *New Synthesis with Carbon Monoxide,* J. Falbe, Ed., Springer-Verlag, Berlin, 1980; D. Antolovic and E. R. Davidson, *J. Am. Chem. Soc.*, 1987, **109,** 5828.

formally involves adding H and the formyl group (CHO) derived from H_2 and CO to an olefin:



The reaction is also known as the *oxo* reaction. The main use is in the conversion of propylene, and higher alk-1-enes into aldehydes and alcohols.

The original reaction used cobalt as the catalyst, and the commerical process requires a high temperature (150°–180°C) and pressure (>200 atm). It produces a mixture, roughly 3:1, of both linear and branched-chain aldehydes or alcohols. These products are formally the products from anti-Markovnikov or Markovnikov addition (Section 27-8), respectively, namely,



The Co process is technically difficult to operate because the hydrocarbonyl, $HCo(CO)_4$, participating in the catalyst cycle, is volatile and must be separated from the alcohol products, and the Co must be recovered as sulfate and recycled. Another disadvantage is that ~15% of the alkene is lost by hydrogenation; condensation and ketone by-products are also formed.

A Shell modification using trialkylphosphine addition allowed greater selectivity and lower reaction pressures (see use of PPh_3 later). Using Et_3P and $CO:H_2 = 1:2$ fairly high yields of formate esters can also be obtained[20]

The main steps in the mechanism, first elucidated by D. S. Breslow and R. F. Heck are as follows:

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \tag{28-2}$$

$$RCH{=}CH_2 + HCo(CO)_3 \rightleftharpoons RCH_2CH_2Co(CO)_3 \tag{28-3}$$

$$RCH_2CH_2Co(CO)_3 + CO \rightleftharpoons RCH_2CH_2COCo(CO)_3 \tag{28-4}$$

$$RCH_2CH_2COCo(CO)_3 + H_2 \longrightarrow RCH_2CH_2CHO + HCo(CO)_3 \tag{28-5}$$

where eq. 28-3 involves the β-hydrogen transfer to coordinated olefin, eq. 28-4 the insertion of CO to form acyl, and eq. 28-5 the acyl cleavage by

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[20] C. D. Wood and P. E. Garrou, *Oganometallics,* 1984, **3,** 170.

hydrogen. The last step could also be intermolecular,

$$RCOCo(CO)_3 + HCo(CO)_4 \xrightarrow{CO} RCHO + Co_2(CO)_8$$

which is established in stoichiometric reactions[21] and where kinetic data for the overall reaction suggest that the slow step is complexing of alkene. However, high pressure spectroscopic studies of catalytic systems[22] suggest that hydrogen cleavage as in (28-5) occurs.

The replacement of Co by Rh has allowed development of processes which operate under much milder conditions, below 100°C and at only a few atmospheres pressure, and which produce aldehyde with no loss of alkene by hydrogenation. The key to high selectivity is the use of triphenylphosphine in large excess, which gives a >95% straight chain, that is, anti-Markovnikov product. The process is used for $CH_3CH{=}CH_2$ to *n*-butyraldehyde, allyl alcohol[23a] to butanediol, and maleic anhydride to 1,4-butanediol, tetrahydrofuran and γ-butyrolactone.

A modification uses $P(p\text{-}C_6H_4SO_3)_3^{3-}$ in a two phase system (Section 28-18).

The rhodium system based on $RhH(CO)(PPh_3)_3$ (Section 19-G-2) has allowed a fairly detailed picture of the mechanism to be obtained,[23b] Fig. 28-4.

The initial step is attack of the alkene on the 16-electron species $RhH(CO)(PPh_3)_2$ (A in Fig. 28-4), which leads to the alkyl complex B. The latter then undergoes CO addition and insertion to form the acyl derivative C, which subsequently undergoes oxidative-addition of molecular hydrogen to give the dihydridoacyl complex D.

The last step, which is the only one in the cycle that involves a change in oxidation state of the metal, is probably rate determining. The final steps are another H transfer to the carbon atom of the acyl group in D, followed by loss of aldehyde and regeneration of the four-coordinate species A. An excess of CO over H_2 inhibits the hydroformylation reaction, probably through the formation of five-coordinate dicarbonyl acyls, E, which cannot react with hydrogen.

To obtain very high selectivity for the formation of *n*-aldehyde, very high concentrations of triphenylphosphine are required, evidently to maintain bisphosphine species in the cycle and to suppress dissociation to give monophosphine species. The high selectivity results from the formation of a straight-chain alkyl in species B, and this is promoted, by the large cone angle of the bulky *trans*-PPh_3 ligands; at low phosphine concentrations the straight and branch chain aldehydes are formed in a 3:1 ratio as in the unmodified cobalt system. The steric effect is discussed further in connection with hydrogenations using $RhH(CO)(PPh_3)_3$ (Section 28-10).

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[21] C. D. Hoff *et al., J. Am. Chem. Soc.*, 1985, **107,** 666; J. Azran and M. Orchin, *Organometallics*, 1984, **3,** 197.

[22] L. Markó *et al., Organometallics*, 1986, **5,** 209.

[23a] D. Bryant *et al., Chem. Ind. (Dekker)*, 1985, **22,** 151.

[23b] See M. Chanon *et al., J. Mol. Catal.*, 1985, **32,** 27.

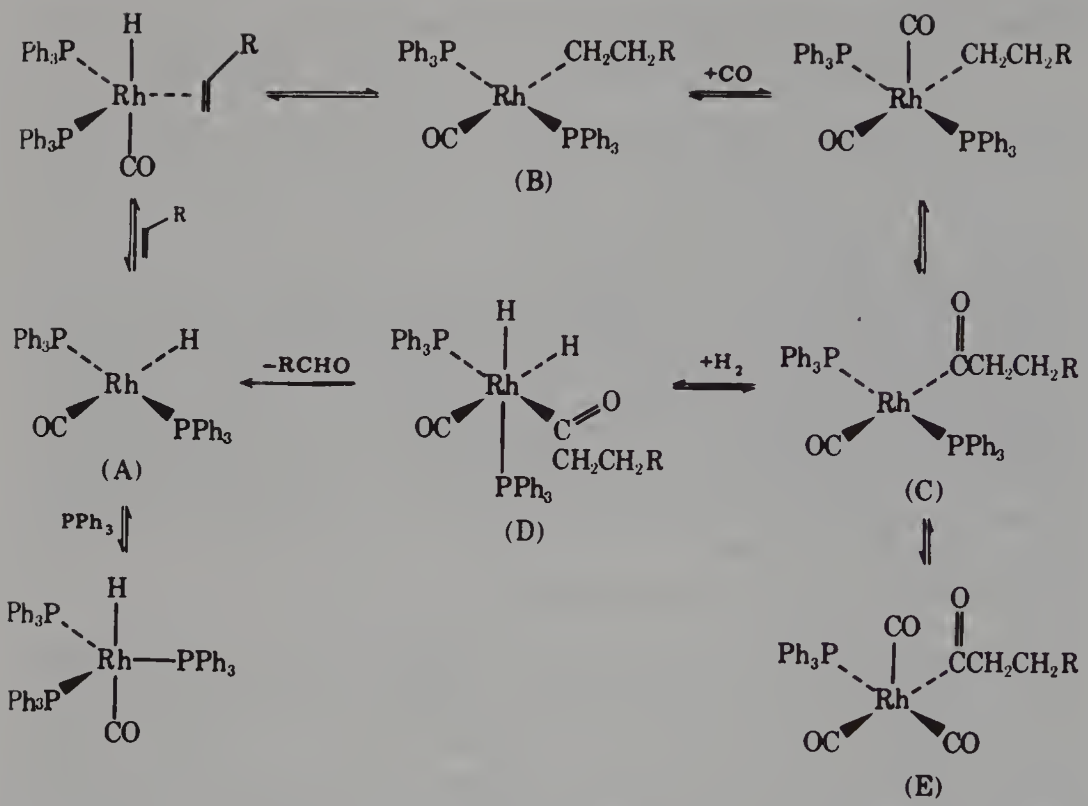

FIG. 28-4. Simplified catalytic cycle for hydroformylation using rhodium complexes. Note that the configurations of complexes are not known with certainty and that five-coordinate species are fluxional. Rhodium can be added as $Rh(acac)(CO)(PPh_3)$, $HRh(CO)(PPh_3)$, or similar complexes. The solvent in C_2H_4 or $CH_3CH{=}CH_2$ hydroformylation is the aldehyde trimer which is in equilibrium with aldehyde.

The intermediates shown in Fig. 28-4 are too unstable for isolation. However, detailed nmr studies[24] have confirmed some of them while it has proved possible either by use of C_2F_4, which gives stable species such as $Rh(C_2F_4H)(CO)(PPh_3)_2$, or by using the similar but more stable iridium compounds, to characterize analogues for most of the species in the cycle.

The mechanism is considerably more complicated than Fig. 28-4 indicates. Some Ph_3P cleavage occurs (Section 11-18), with $n\text{-}C_3H_7PPh_2$ and, under certain conditions, phosphido bridged carbonyl clusters being formed.[25]

A wide variety of unsaturated substances can be hydroformylated, but conjugated alkenes (e.g., butadiene) may give a number of products including hydrogenated monoaldehydes. Use of chelating phosphines allows selective hydroformylation of butadiene to pentanal.[26] The mechanism differs from

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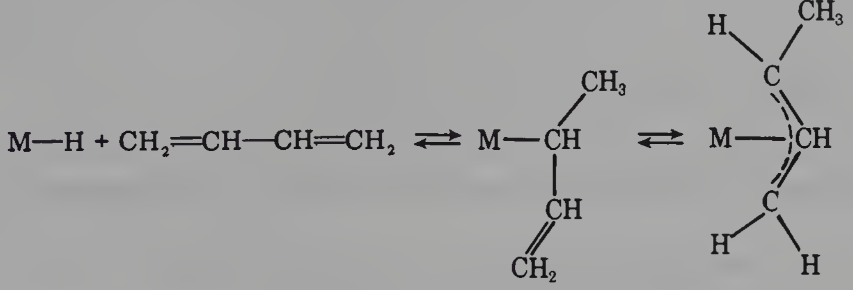
[24] J. M. Brown and A. G. Kent, *J. Chem. Soc. Chem. Commun.*, **1982**, 723.

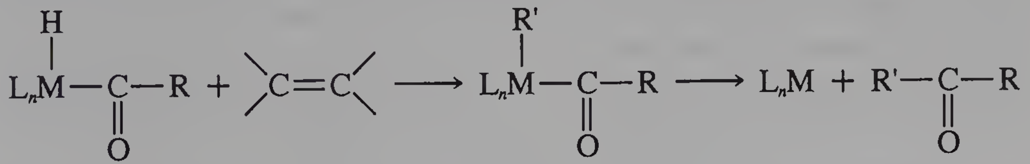
[25] H. L. Pelt *et al.*, *J. Mol. Chem.*, 1985, **33**, 119; A. G. Abatjoglou *et al.*, *Organometallics*, 1984, **3**, 923; for P—C bond cleavage and relevance in catalysis see also P. E. Garrou, *Chem. Rev.*, 1985, **85**, 117.

[26] P. W. N. Van Leeuwen and C. F. Roobeck, *J. Mol. Catal.*, 1985, **31**, 345.

that for monoalkenes since addition of M—H to conjugated dienes leads to an allylic species, which may be present as σ-bonded or η^3-allyls, for example,

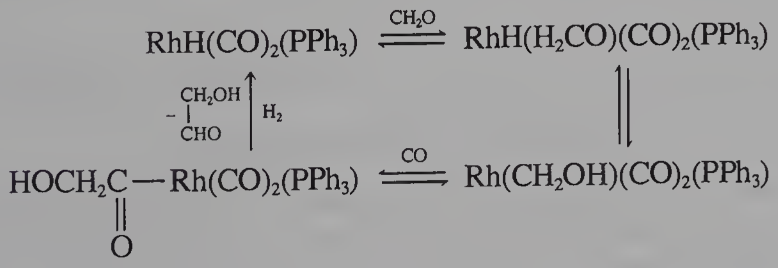


Hydroformylation can also be achieved using ruthenium complexes such as $Ru(CO)_3(PPh_3)_2$, by platinum–tin catalysts[27a] where $PtH(CO)(SnCl_3)(PPh_3)_2$ appears to act similarly to $RhH(CO)(PPh_3)_3$, and by $PtH(Ph_3PO)(Ph_2POH)(PPh_3)$ made from $Pt(COD)_2$, PPh_3, and Ph_2POH.[27b] The latter system yields ketones when under high ethylene pressure. Ketone formation can also be observed in other systems and occurs by the sequence:



This will be favored by low CO and high alkene concentration. The use of optically active phosphines has allowed asymmetric hydroformylation with prochiral alkenes (see Section 28-10).[27c]

The hydroformylation of *formaldehyde*,[28] a route to ethylene glycol via glycolaldehyde, may be easier than the direct route from CO and H_2. One reaction involves the same rhodium catalyst used for alkenes in a cycle:



The similarity to the direct CO—H_2 reduction cycles noted earlier is obvious. Small amounts of amines are added to catalyze the H-transfer from coordinated formaldehyde to give the formyl and from this, the hydroxymethyl

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[27a] H. Ruegg *et al., J. Organomet. Chem.*, 1986, **316**, 233; G. Moretti *et al., J. Mol. Catal.*, 1987, **39**, 177.

[27b] P. W. N. M. van Leeuwen *et al., J. Chem. Soc. Chem. Commun.*, **1986**, 31.

[27c] See, for example, P. Pino *et al., J. Organomet. Chem.*, 1985, **296**, 281.

[28] J. Kollar, *Chem. Tech.*, 1984, 504; M. Marchionna and G. Longoni, *Organometallics*, 1987, **6**, 606; *J. Chem. Soc. Chem. Commun.*, **1987**, 1097.

compound. Amines are commonly used as "promoters" because of their facile H^+ transfer ability

$$R_3NH^+ \rightleftharpoons R_3N + H^+$$

Other examples of amine promotion are noted later.

28-5. Reductive Carbonylation of Alcohols and Other Compounds[29]

Interaction of synthesis gas with alcohols, carboxylic acids, esters, and so on, can lead to the next higher analogue, for example,

$$CH_3OH + CO + 2H_2 \xrightarrow[180°C,\ 200\ atm]{Co_2(CO)_8} CH_3CH_2OH + H_2O$$

$$MeCO_2Me + CO + H_2 \longrightarrow MeCHO + MeCO_2H$$

The reaction is sometimes called *homologation* or even hydroformylation although the latter is best used only for alkenes. The most studied reaction has been with MeOH. Cobalt, Fe, or Ru carbonyls, usually with iodides and often phosphines as cocatalysts, have been used. There has been much speculation on possible mechanisms. One suggested sequence is the following:

$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4$$

$$HCo(CO)_4 + MeOH \longrightarrow MeOH_2^+ + [Co(CO)_4]^- \qquad (28\text{-}6)$$

$$MeOH_2^+ + Co(CO)_4^- \longrightarrow MeCo(CO)_4 + H_2O \qquad (28\text{-}7)$$

$$MeCo(CO)_4 + CO \longrightarrow MeCOCo(CO)_4$$

$$MeCOCo(CO)_4 + H_2 \longrightarrow MeCHO + HCo(CO)_4$$

or

$$MeCOCo(CO)_4 + HCo(CO)_4 \longrightarrow MeCHO + Co_2(CO)_8$$

$$MeCHO + H_2 \longrightarrow MeCH_2OH$$

Although acetyls are doubtless intermediates,[30a] the steps (28-6) and (28-7) are dubious. Since iodides appear to be essential for the rapid reactions of Co and Ru[30b,c] it seems certain that as in the acetic acid process discussed

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[29] G. Braca *et al., Aspects Homog. Catal.*, 1984, **5,** 241; *J. Mol. Catal.*, 1985, **32,** 291; M. E. Fakeley and R. A. Head, *Appl. Catal.*, 1983, **5,** 3; E. Dreut, Am. Chem. Soc. Symp. Ser. No. 328 American Chemical Society, Washington, DC, p. 154, 1987.

[30a] J. T. Martin and M. C. Baird, *Organometallics,* 1983, **2,** 1073.

[30b] M. Hidai *et al., Organometallics,* 1983, **2,** 292.

[30c] R. W. Wegman and D. C. Busby, *J. Mol. Catal.*, 1985, **32,** 125; *J. Chem. Soc. Chem. Commun.,* **1986,** 322.

in Section 28-6, we have

$$CH_3OH + HI \rightleftharpoons CH_3I + H_2O$$

followed by

$$L_nM \xrightarrow{CH_3I} L_nMCH_3^+I^- \xrightarrow{CO} L_nMC(O)CH_3^+I^- \xrightarrow{H_2} L_nM + HI + CH_3CHO$$

The homologation of acetic to propionic acid, which uses homogeneous ruthenium–iodide catalysis, probably involves the initial conversion of CH_3CO_2H to acetyl iodide[30d]

$$CH_3CO_2H + HI \rightleftharpoons CH_3COI + H_2O$$

in the overall reaction

$$CH_3CO_2H + CO + 2H_2 \xrightarrow[>4000\ \text{psi}]{220°\text{C}} CH_3CH_2CO_2H + H_2O$$

A different system[31] where oxygen is removed as CO_2 is $Fe(CO)_5$ and *N,N'*-dimethylpiperidine in *N*-methyl pyrollidone, with the overall reaction

$$CH_3OH + 2CO + H_2 \xrightarrow{200°\text{C},\ 300\ \text{atm}} CH_3CH_2OH + CO_2$$

The individual steps proposed are

$$CH_3OH + CO \overset{NR_3}{\rightleftharpoons} CH_3OCHO \overset{NR_3}{\rightleftharpoons} CH_3NR_3^+ + HCO_2^-$$

$$Fe(CO)_5 + H_2 + NR_3 \rightleftharpoons [HFe(CO)_4]^- + CO + R_3NH^+$$

$$R_3NH^+ + HCO_2^- \xrightarrow{Fe(CO)_5} H_2 + CO_2 + NR_3$$

$$[HFe(CO)_4]^- + HCO_2CH_3 \longrightarrow CH_3FeH(CO)_4 + HCO_2^-$$

$$CH_3NR_3^+ + [HFe(CO)_4]^- \longrightarrow CH_3FeH(CO)_4 + NR_3$$

$$\begin{tikzcd}
& & CH_4 + Fe(CO)_5 & \\
CH_3FeH(CO)_4 \arrow[r, dash, "CO"] & {} \arrow[ur] \arrow[dr] & & \\
& & CH_3COFeH(CO)_4 \arrow[r, "CO"] & CH_3CHO + Fe(CO)_5 \arrow[d, "H_2 \quad \text{or} \quad {[HFe(CO)_4]^-}"] \\
& & & CH_3CH_2OH
\end{tikzcd}$$

A key feature is *methyl* transfer from alkylammonium ions to metal carbonylate anions (cf. H^+ transfer from R_3NH^+), which has been studied kinetically. Thus $[Mn(CO)_5]^-$ is 2.7 times as nucleophilic towards Me_4N^+ as is $[HFe(CO)_4]^-$.

[30d] J. F. Knifton, *J. Mol. Catal.*, 1981, **11**, 91.

[31] J. W. Rathke *et al.*, *Organometallics*, 1984, **3**, 708.

CARBONYLATION REACTIONS

Reactions using CO in the presence of water (a synthesis gas equivalent via the WGS), alcohols, amines, and so on, are generally called carbonylations. Various syntheses are summarized in Fig. 28-5.

28-6. Methanol and Methyl Acetate[32]

High pressure, high temperature carbonylation of methanol to acetic acid and of methyl acetate to the anhydride were first developed by W. Reppe using CoI_2 as catalyst precursor.

As in the case of hydroformylation, use of rhodium allows much lower pressures and temperatures to be used and Monsanto developed a process using wet methanol that operates at ~30-atm pressure and ~180°C; in view of the corrosive nature Hastalloy or zirconium reactors have to be used.

The key feature is the use of iodide as cocatalyst.[33] When the methanol has ~5% water, acetic acid is produced but there is some methyl acetate in

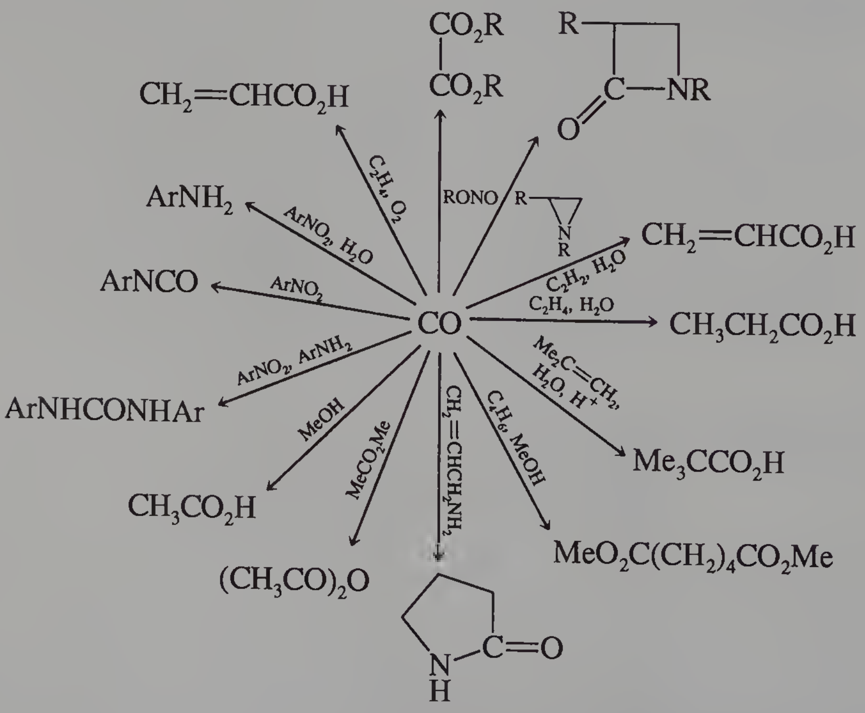

FIG. 28-5. Some carbonylation reactions. Reppe reactions involve CO + H_2O or CO + ROH. Koch reactions involve CO + H_2O in strongly acidic solution. Oxidative carbonylations may involve O_2, NO, or ROOR.

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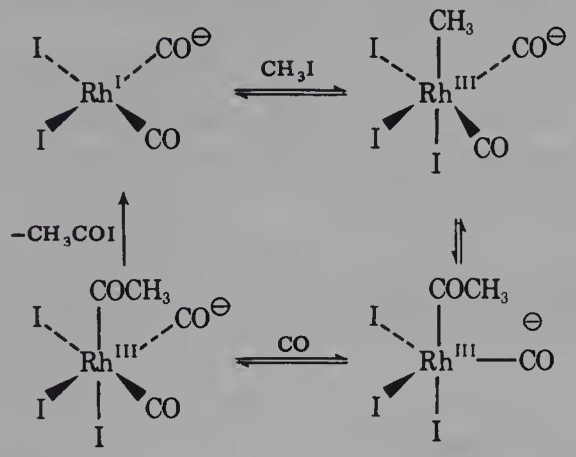
[32] T. W. Deklava and D. Forster, *Adv. Catal.* 1986, **34,** 81; R. T. Eby and T. C. Singleton, in *Applied Industrial Catalysis,* Vol. 1, B. E. Leach, Ed., Academic Press, New York, 1983; M. E. Fakeley and R. A. Head, *Appl. Catal.*, 1983, **5,** 3.

[33] D. J. Drury, *Aspects Homog. Catal.*, 1984, **5,** 197 (iodide promoted catalyses).

Methyl Iodide Generation

$$CH_3OH + HI \longrightarrow CH_3I + H_2O \qquad A_1$$
$$CH_3OC(O)CH_3 + LiI \longrightarrow CH_3I + Li^+O_2CH_3^- \qquad B_1$$



Product Generation

$$CH_3C(O)I + H_2O \longrightarrow CH_3CO_2H + HI \qquad A_2$$
$$CH_3C(O)I + LiO_2CCH_3 \longrightarrow (CH_3CO)_2O + LiI \qquad B_2$$

FIG. 28-6. The similar cycles for synthesis of (A) acetic acid by carbonylation of methanol with ~ 5% water, (B) acetic anhydride by carbonylation of dry methanol or more conveniently methyl acetate. The oxidative-addition of CH_3I is believed to be rate determining. The final step need not require elimination of acetyl iodide, which is then attached nucleophilically by H_2O or acetate ion, but only this nucleophilic attack on $[Rh(COMe)I_3(CO)_2]^-$ followed by elimination of HI or LiI for acetic acid or anhydride synthesis, respectively.

equilibrium in the system

$$CH_3CO_2H + CH_3OH \rightleftharpoons CH_3CO_2CH_3 + H_2O$$

When the methanol is dry, acetic anhydride is formed due to carbonylation of the methyl acetate formed.

The catalytic cycles for both acetic acid and acetic anhydride synthesis are very similar as shown in Fig. 28-6.

In the MeOH—H_2O medium, CH_3I is generated (added initially of course to start reaction) by reaction A_1, while in methyl acetate it is formed by reaction B_1.[34]

The only major difference in the two cycles is the nucleophile, either H_2O or $CH_3CO_2^-$, which either attack acetyl iodide liberated in a reductive-elimination or, directly attack the pentultimate complex *cis*-$[Rh(COMe)I_3(CO)_2]^-$. In both cases the rate-determining step is believed to be oxidative-addition of CH_3I to *cis*-$[RhI_2(CO)_2]^-$. The only intermediate isolated from a model system[35] is the ion $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$, which reacts with CO to give

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[34] See R. Wegman and D. C. Busby, *J. Chem. Soc. Chem. Commun.*, **1986,** 332.

[35] B. E. Mann *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 728.

$[Rh^{III}(COMe)I_3(CO)_2]^-$. The latter has *trans* CO groups; the isomeric species in Fig. 29-6 has *cis*-CO groups and presumably cannot be detected as it loses acetyl iodide so rapidly.

Higher alcohols can be converted to the acids like methanol but the rates are MeOH ≫ EtOH > *n*-PrOH.[36]

The anhydride process[37] uses LiI together with a nitrogen base such as *N*-methylimidazole and a chromium compound such as $Cr(CO)_6$ as promoter.

Interaction of methyl acetate with H_2 and CO under similar reaction conditions gives ethylidene diacetate:

$$2(CH_3CO)_2O + H_2 \longrightarrow CH_3CH(O_2CMe)_2 + CH_3CO_2H$$

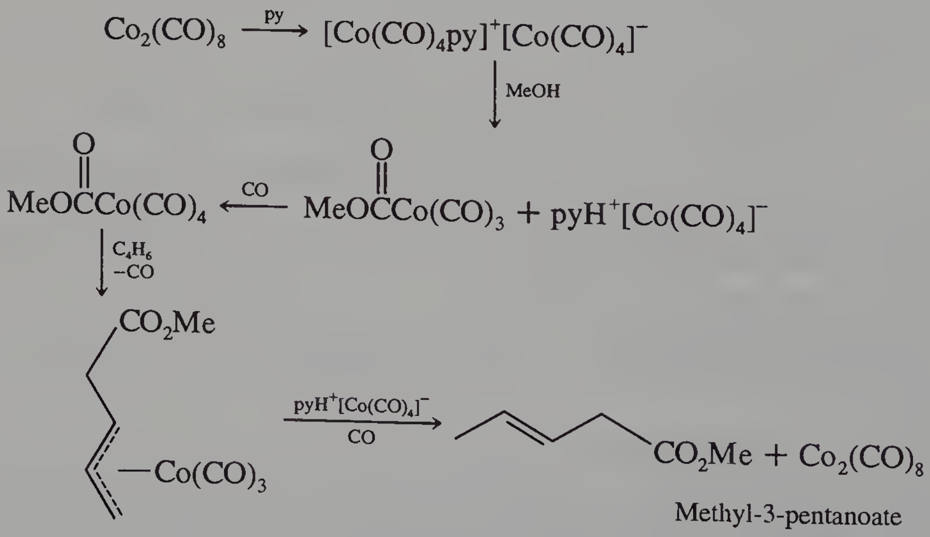
Reductive carbonylation of esters can also be catalyzed by CoI_2–LiI as noted earlier.[30c]

28-7. Adipic Ester Synthesis

A possible commercial process is the carbonylation of butadiene catalyzed by $Co_2(CO)_8$ and pyridine at ~300 atm.

$$CH_2{=}CH{-}CH{=}CH_2 + 2MeOH + 2CO \longrightarrow MeO_2C(CH_2)_4CO_2Me$$

The ester can be hydrolyzed to adipic acid (used in Nylon 6). Some separate steps in this reaction have been identified[38] as in Scheme 28-4.



Scheme 28-4

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[36] T. W. Deklava and D. Forster, *J. Am. Chem. Soc.*, 1985, **107,** 3568; *J. Mol. Catal.*, 1985, **33,** 269.

[37] Halcon International, British Patents 1468940, 1538783; see C. E. Hickey and P. M. Maitlis, *J. Chem. Soc. Chem. Commun.*, **1984,** 1609.

[38] D. Milstein and J. H. Huckaby, *J. Am. Chem. Soc.*, 1982, **104,** 6150.

28-8. Other Carbonylation Reactions

Carbon monoxide can be used for the deoxygenation of nitro arenes,[39] where Fe, Ru, or Rh complexes are catalysts, for example,

$$2\mathrm{PhNO_2} + 4\mathrm{CO} = \mathrm{PhN{=}NPh} + 4\mathrm{CO_2}$$

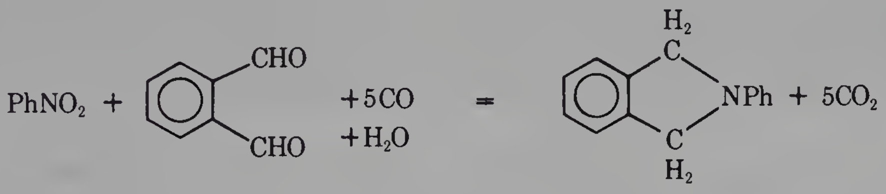
$$\mathrm{PhNO_2} + 3\mathrm{CO} = \mathrm{PhNCO} + 2\mathrm{CO_2}$$

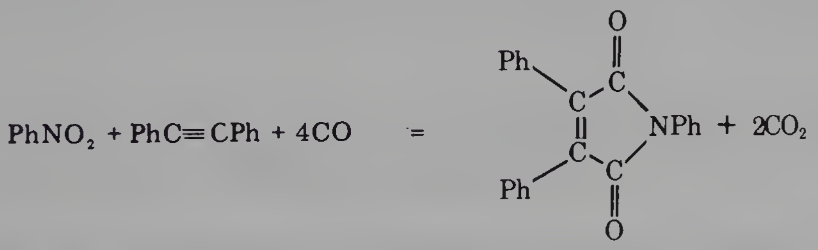
The first step in these reactions is probably the formation of a nitrene complex:

$$\mathrm{RNO_2} + \mathrm{M(CO)}_n \xrightarrow{2\mathrm{CO}} \mathrm{RNM(CO)}_n + 2\mathrm{CO_2}$$

The RN moiety then undergoes further reactions such as hydrogenation to anilines, CO insertion, or dimerization.

In the presence of trapping agents such as aldehydes or acetylenes, this deoxygenation reaction provides a means for synthesis of nitrogen compounds, for example,





Oxidative carbonylations are discussed in Section 28-19.

28-9. Decarbonylation Reactions

The insertion of CO into M—C bonds to give acyl is reversible, as we have seen earlier (Section 27-6). However, CO can be irreversibly removed from organic molecules, and these reactions commonly proceed via acyl intermediates. Thus aldehydes, acyl, and aroyl halides, and so on, can be decarbonylated either stoichiometrically or catalytically by complexes such as $\mathrm{RhCl(PPh_3)_3}$ or $\mathrm{RhCl(CO)(PPh_3)_2}$.[40a]

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[39] G. L. Geoffroy *et al., J. Am. Chem. Soc.*, 1987, **109,** 3936; S. Cenini *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 784; R. A. Sanchez-Delgado *et al., J. Mol. Catol.*, 1986, **36,** 283.

[40a] B. R. James and C. G. Young, *J. Organomet. Chem.*, 1985, **285,** 321; J. A. Kampmeier *et al., Organometallics*, 1986, **5,** 823.

Examples of stoichiometric decarbonylations are

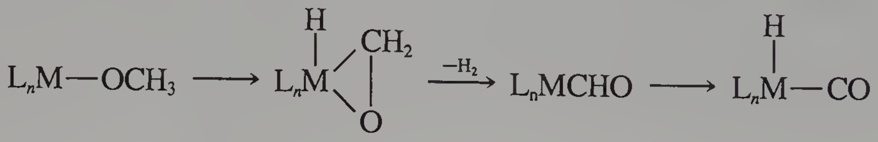
$$\mathrm{RhCl(PPh_3)_3 + RCOCl \longrightarrow RhCl_2(COR)(PPh_3)_2 \rightleftharpoons RhRCl_2(CO)(PPh_3)_2}$$
$$\mathrm{\longrightarrow RCl + RhCl(CO)(PPh_3)_2}$$

$$\mathrm{Cp(CO)_2FeC(O)R + RhCl(PPh_3)_3 = Cp(CO)(PPh_3)FeR}$$
$$\mathrm{+ RhCl(CO)(PPh_3)_2 + CO}$$

The decarbonylations have been well studied both kinetically and from the stereochemical point of view. The principal steps in decarbonylation of acyl chlorides or of aldehydes involve oxidative-addition of RCOCl or RCHO to give an acyl, followed by migration of R to the metal and subsequent reductive-elimination of RCl or RH.

With triphenylphosphine the rhodium system is catalytic only > 200°, but using $[\mathrm{Rh(dppp)_2}]\mathrm{BF_4}$, dppp = 1,3-bis(diphenylphosphino)propane,[40b] much more efficient catalytic decarbonylation can be achieved.

It is convenient to note here that a common reaction of alcohols with transition metal halides in the presence of phosphines is decarbonylation and sometimes dehydrogenation. These reactions proceed via alkoxide intermediates, which then undergo β-H transfers, for example,



CATALYTIC ADDITION OF MOLECULES TO C—C MULTIPLE BONDS

28-10. Homogeneous Hydrogenation of Unsaturated Compounds[41]

It has been known for more than 40 years that molecular hydrogen can be "activated" homogeneously by solutions of ions such as $\mathrm{Ag^+}$ or $\mathrm{MnO_4^-}$ or by complexes such as $\mathrm{Cu^{2+}}$ in quinoline or $\mathrm{Co^{2+}}$ in aqueous cyanide. Certain of these species can be used as catalysts for the slow reduction of unsaturated substances. Although the intermediacy of species with M—H bonds was often postulated, proof was not obtained, and indeed in the $\mathrm{Co^{2+}—CN^-}$ system free radicals appear to be involved.

[40b] H. H. Wang and L. H. Pignolet, *Inorg. Chem.*, 1980, **19**, 1470.

[41] B. R. James, *Homogeneous Hydrogenation*, Wiley, New York, 1973; P. N. Rylander, *Catalytic Hydrogenation in Organic Synthesis*, Academic Press, New York, 1979; L. H. Pignolet, Ed., *Homogeneous Catalysis by Metal Phosphine Complexes*, Plenum Press, New York, 1983; *Houben Weyl Meth. der Org. Synth.*, 4th ed., Vol. IV 1c, Reduktion, Part 1, G. Thieme, Stuttgart, 1981.

The first rapid and practical system for the homogeneous reduction of alkenes, alkynes, and other unsaturated substances at 25°C and 1-atm pressure used the complex $RhCl(PPh_3)_3$ (Section 19-G-2) sometimes known as Wilkinson's catalyst. Subsequently many other tertiary phosphine complexes have been studied as catalysts for hydrogenations of alkenes, alkynes, aromatics, and heterocycles like quinoline. They may be either neutral like $RuHCl(PPh_3)_3$ or cationic like $[Rh\text{diene}(PPh_3)_2]^+$ or $[RuH(PMe_2Ph)_5]^+$. There are three main types of compound:

1. Those without a metal–hydride bond such as $RhCl(PPh_3)_3$ and $[RhS_2(PR_3)_3]^+$ (S = solvent), which react, usually reversibly, with molecular hydrogen.
2. Those with an M—H bond such as $RhH(CO)(PPh_3)_3$ or $RuHCl(PPh_3)_3$, which do not usually react with H_2.
3. *f*-Block element hydrides such as $(^*Cp_2LuH)_2$, where catalytic cycles do *not* involve oxidative-addition reactions.

Hydrogenation catalysts from non-platinum group metals are known. Thus arene chromium tricarbonyls[42a] will hydrogenate dienes, alkynes, and so on, while $ReH_7(PCy_3)_2$ will selectively hydrogenate acenaphthylene[42b]; lanthanide catalysts are discussed later. Although all the previously mentioned catalysts operate via nonradical processes, a few systems are known that do involve radical reactions.[42c]

Reversible *cis*-Dihydrido Catalysts. In benzene the distorted square d^8 complex $RhCl(PPh_3)_3$ is red. Despite the steric bulk of the phosphine, it dissociates to only a small extent at 25°C[43]:

$$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3 \qquad K = 2.3 \times 10^{-7}\,M$$

but dimerization to an orange, halogen-bridged species can occur, especially at higher temperatures

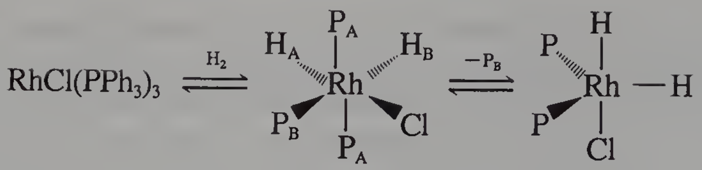
$$RhCl(PPh_3)_3 \rightleftharpoons (Ph_3P)_2Rh(\mu\text{-}Cl)_2Rh(PPh_3)_2 + 2PPh_3 \quad K = 3 \times 10^{-4}\,M$$

The complex reacts with alkenes to a small extent, the constant for ethylene being the largest

$$RhCl(PPh_3)_3 + C_2H_4 \rightleftharpoons RhCl(C_2H_4)(PPh_3)_2 + PPh_3 \qquad K = 0.4$$

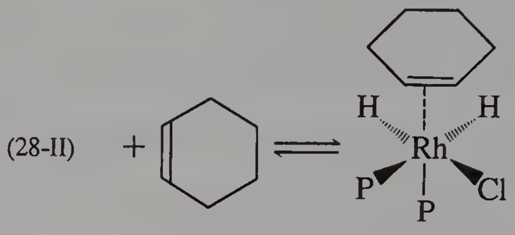
Under hydrogen $RhCl(PPh_3)_3$ solutions rapidly become yellow and ^1H and ^{31}P nmr studies[44a] show that an octahedral dihydride (28-I) is first formed but, due to the strong trans effect of H, this rapidly dissociates at room temperature to give a fluxional five-coordinate rhodium(III) species (28-II).

[42a] M. Sodeoka and M. Shipasaki, *J. Org. Chem.* 1985, **50,** 1147.
[42b] K. G. Caulton *et al., Organometallics,* 1985, **4,** 1149.
[42c] R. Eisenberg *et al., J. Am. Chem. Soc.* 1986, **108,** 5345.
[43] D. A. Wink and P. C. Ford, *J. Am. Chem. Soc.*, 1987, **109,** 436.
[44a] J. M. Brown *et al., J. Chem. Soc. Chem. Commun.*, **1984,** 914, 915.

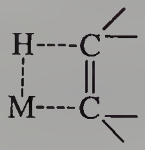


(28-I) (28-II)

This species then coordinates alkene, for example, cyclohexene. The complex (28-III) with *cis* phosphines is the most favored on steric grounds and has a hydride trans to PPh_3, thus labilized and readily transferable. In the actual transfer the best overlap occurs when M—H and C═C bonds are coplanar in the four-center transition state (28-IV). Note that when the *cis* phosphine geometry is enforced by use of a chelate diphosphine, hydride transfer to coordinated alkene is very rapid. Detailed studies[44b] of transfer in the system



(28-III)



(28-IV)

$$trans\text{-}HRh(C_2H_4)(PPr_3)_2 \rightleftharpoons cis\text{-}HRh(C_2H_4)(PPr_3)_2 \rightleftharpoons EtRh(PPr_3)_2$$

indicate that the complex with *cis* phosphines is the active one. When a rhodium complex with a rigid *trans* diphosphine was studied only slow transfer of hydrogen to alkenes was observed.[44a]

After the first transfer to the alkyl, a second transfer via a three-center transition state, that is, a reductive-elimination, gives alkane. The cycle is shown in Fig. 28-7 but the process is actually much more complicated since the equilibria are dependent on phosphine, alkene and rhodium concentrations, temperature, and pressure.

Finally, it may be noted that complexes with alkyl phosphines which are more basic and less sterically hindered than aryl complexes are generally less active due to a lower tendency to dissociation. The steric bulk of the ligand (Section 2-10) influences the dissociative equilibria, the orientation and com-

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[44b] D. D. Roe, *J. Am. Chem. Soc.* 1983, **105**, 7770.

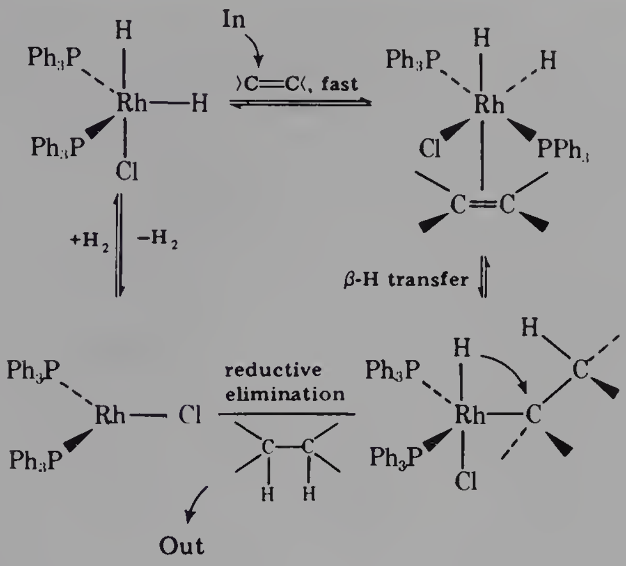
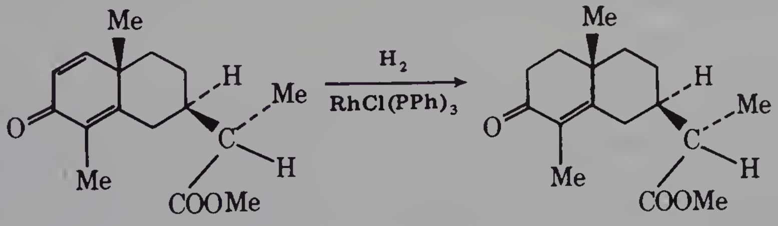


FIG. 28-7. Simplified catalytic cycle for hydrogenation of C=C bonds by species derived from $RhCl(PPh_3)_3$ or from $[(alkene)_2RhCl]_2 + PR_3$. Possible solvent coordination is disregarded. Cycle shows only major species involved for millimolar rhodium concentrations with large alkene concentrations under ambient conditions. Similar cycles operate for cationic species where the *cis*-dihydrido species are of the type $[Rh(H)_2(PR_3)_2S_2]^+$, S = solvent. For calculations on the potential energy profile for the cycle see N. Koga *et al.*, *J. Am. Chem. Soc.*, 1987, **109,** 3455.

plexing of the unsaturated substrate (whose steric factors are also of importance), and finally, the stability of the intermediate alkyls (see later).

A consequence of steric interactions is that highly selective hydrogenations are possible, one example being



Finally, in contrast to heterogeneous catalysis, where scattering of deuterium throughout the molecule usually results, D_2 is added to the one bond and remains there.

Although Ir^I complexes such as *trans*-$IrCl(CO)(PPh_3)_2$ (Section 19-G-1) take up hydrogen reversibly, the octahedral species [e.g., $Ir(H)_2Cl(CO)(PPh_3)_2$] so formed do not eliminate a neutral ligand. Hence they have no vacant site for coordination of unsaturated substances and cannot act as hydrogenation catalysts at 25°C and atmospheric pressure, although they may do so when phosphine dissociation is promoted thermally or photochemically.

Monohydrido Complexes. Compounds such as $RuHCl(PPh_3)_3$, $RhH(CO)(PPh_3)_3$, $RhH(dph)_2$ (dph = dibenzophosphole), and

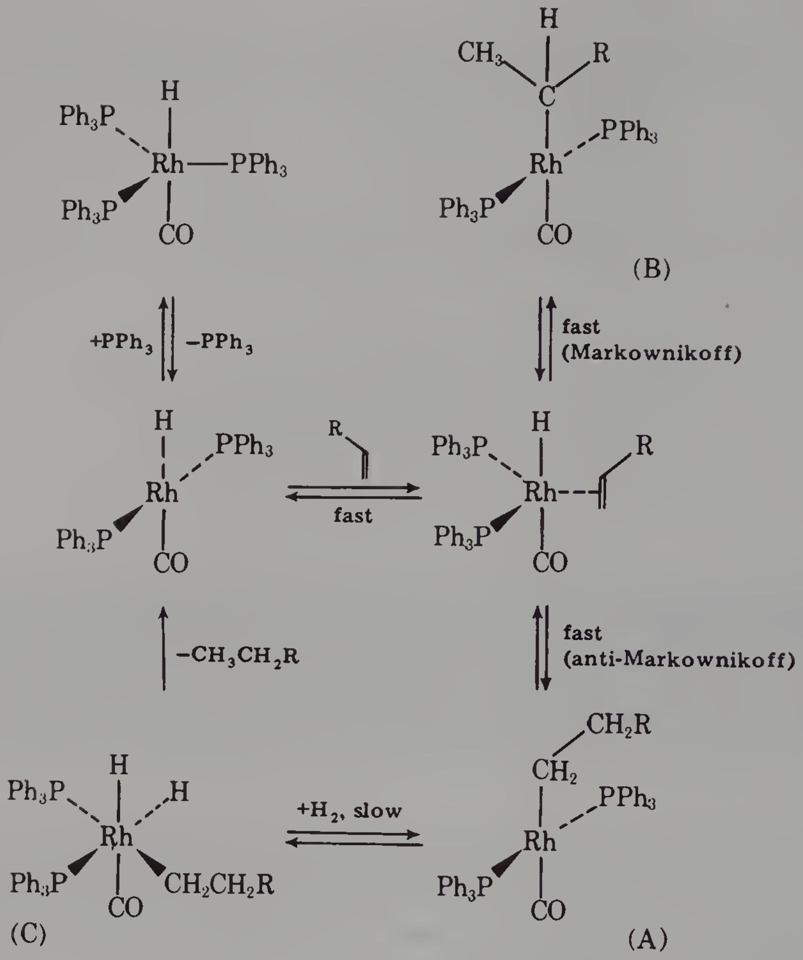


FIG. 28-8. Catalytic cycle of hydrogenation and isomerization of alk-1-enes by $RhH(CO)(PPh_3)_3$ at 25°C and 1 atm pressure.

$IrH(CO)(PPh_3)_3$, which have a bound hydrogen, also act as hydrogenation catalysts. The hydride $RhH(PPh_3)_3$ is a much more active catalyst than $RhCl(PPh_3)_3$. Compounds such as $RuCl_2(PPh_3)_3$ or $RuCl_2(CO)(PPh_3)_2$ undergo hydrogenolysis[45] to hydrido species in the presence of hydrogen halide acceptors, for example,

$$RuCl_2(PPh_3)_3 + H_2 + Et_3N = RuHCl(PPh_3)_3 + Et_3NHCl$$

In these cases the catalytic cycle differs from that discussed previously. The cycle for $RhH(CO)(PPh_3)_3$ is shown in Fig. 28-8. The complex dissociates in benzene, and both isomerization and hydrogenation of alk-1-enes are suppressed by addition of excess PPh_3. By contrast, $CoH(CO)(PPh_3)_3$ catalyzes hydrogenation only at ~150°C and 150-atm hydrogen, and $IrH(CO)(PPh_3)_3$ will hydrogenate alkenes at ~50°C.

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[45] P. J. Brothers, *Prog. Inorg. Chem.*, 1981, **28**, 1.

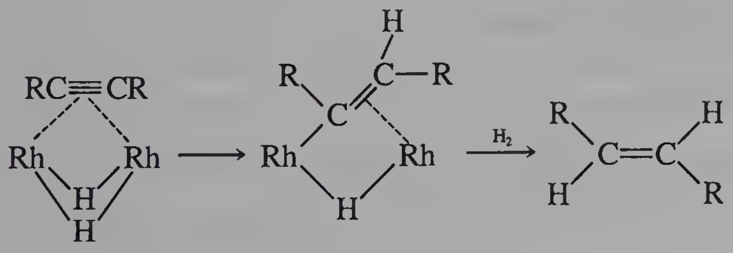
The hydrogenation of alkenes by $RhH(CO)(PPh_3)_3$ is unusual in that there is a high selectivity for the hydrogenation of alk-1-ene compared to alk-2-ene. We noted (Section 27-8) that alk-1-ene can react with a metal-hydrogen bond in either a Markovnikov or an anti-Markovnikov fashion and that a secondary branched or a primary straight-chain alkyl, respectively, is produced. An alk-2-ene can, of course, give only a branched-chain alkyl. We can now explain the selectivity as follows. In the square species A and B of Fig. 29-8 the bulky triphenylphosphine groups are in trans positions, and the result is that a primary alkyl (i.e., $Rh—CH_2CH_2R$) will experience much less steric interaction than will a more bulky alkyl, for example, $Rh—CH(CH_3)CH_2R$. The lowered stability of a secondary alkyl complex means that such a species would undergo the reverse β-hydrogen transfer reaction to give olefin more easily; hence the alkyl would have a shorter lifetime in solution—so short, in fact, that it would not live long enough to undergo the slow rate-determining oxidative-addition of hydrogen to give species C. That the secondary alkyl complex is formed simultaneously with the primary alkyl complex from alk-1-ene is shown by comparability of the rates of isomerization (alk-1-ene to alk-2-ene) and hydrogenation.

Similar steric factors introduced by bulky PPh_3 groups are also important in the hydroformylation reaction of alkenes that is also catalyzed by the same system (Section 28-4) and which, in the presence of a large excess of PPh_3 gives high selectivity for *n*-aldehyde formation. Steric effects of bulky ligands have been observed in several other cases, for example, the preferential formation of *n*-alkyl from acyl in the reaction

$$(Ph_3P)_2Cl_2IrCOR \rightleftharpoons (Ph_3P)_2Cl_2Ir(CO)R$$

Other related systems that have been studied in great detail include rhodium carborane cluster species, such as $Rh^{I}(C_2B_9H_{11})(PPh_3)_2$, which show very facile reversibility of the HRh^{III} alkyl formation and relatively slow elimination of alkane.[46]

The phosphite clusters $\{HRh[P(OR)_3]_2\}_3$ catalyze alkene hydrogenation, allegedly without fragmentation[47] while the dimer $Rh_2(\mu\text{-}H)_2[P(O\textit{i}\text{-}Pr)_3]_4$ hydrogenates alkynes via μ-acetylene complexes[48]:



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[46] M. F. Hawthorne *et al., J. Am. Chem. Soc.*, 1984, **106**, 7444.

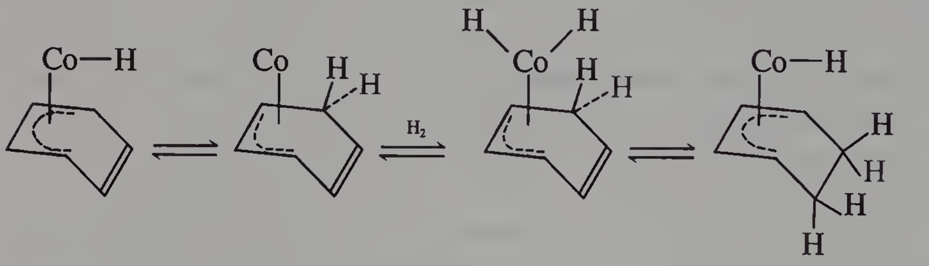
[47] E. L. Muetterties *et al., Inorg. Chem.*, 1980, **19**, 370.

[48] E. L. Muetterties *et al., J. Am. Chem. Soc.*, 1983, **105**, 3546.

Hydrogenation of *aromatic hydrocarbons*[49] can also be effected by phosphine or phosphite complexes. One system studied in detail is $(\eta^3\text{-}C_3H_5)Co[P(OMe)_3]_3$ where cis stereoselectivity in the cyclohexane products is observed. The true catalytic species is the hydride formed on hydrogenolysis,

$$(\eta^3\text{-}C_3H_5)CoP_3 \xrightarrow[-P]{H_2} HCoP_2 + C_3H_8$$

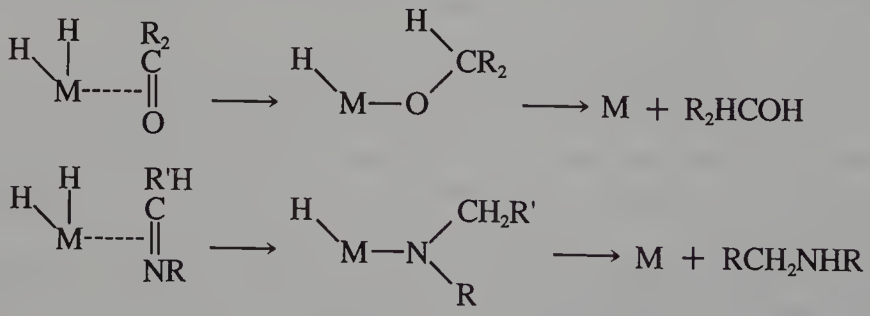
which with, say benzene, forms first the species $HCoP_2(\eta^4\text{-}C_6H_6)$; Hydrogen-transfer then gives $\eta^3\text{-}C_6H_7$ and further hydrogenated species (phosphine omitted):



and so on

$(\eta^4\text{-}C_6H_6)$ $(\eta^3\text{-}C_6H_7)$ $(\eta^4\text{-}C_6H_8)$

Hydrogenation of Other Unsaturated Groups. By use of phosphine or dipyridyl complexes of various types, $R_2C{=}O$, $RHC{=}NR'$, $RN{=}NR'$, and NO_2 groups may be reduced though often not as readily as $C{=}C$ or $C{\equiv}C$ bonds. The ketones[50a] are hydrogenated via alkoxide intermediates and imines[50b] via dialkylamide intermediates, namely,



In both cases the substrate must be bound η^2 for transfer of hydrogen to occur.

Asymmetric Hydrogenation.[51] The development of the catalytic hydrogenation system based on $RhCl(PPh_3)_3$ and methods for the resolution of optical isomers of tertiary phosphines occurred around the same time (1965),

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[49] See G. T. Palmer and F. Basolo, *J. Am. Chem. Soc.*, 1985, **107**, 3122; J. Halpern *et al.*, *J. Organomet. Chem.*, 1985, **296**, 115.

[50a] E. Farnetti *et. al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 746; J. Blum *et al. J. Mol. Catal.*, 1984, **26**, 327.

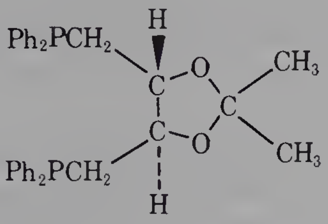
[50b] G. Wilkinson *et al.*, *Polyhedron*, 1986, **5**, 1625; see also M. R. Dubois *et al.*, *Organometallics*, 1986, **5**, 951; *J. Am. Chem. Soc.*, 1987, **109**, 283 (various nitrogen compounds); D. E. Linn, Jr., and J. Halpern, *J. Am. Chem. Soc.*, 1987, **109**, 2969 (ketones and arenes).

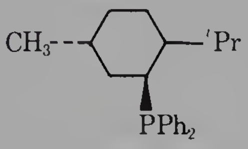
[51] J. M. Brown, *Angew. Chem. Int. Ed. Engl.*, 1987 **26**, 190; C. R. Landis and J. Halpern, *J. Am. Chem. Soc.*, 1987, **109**, 1746.

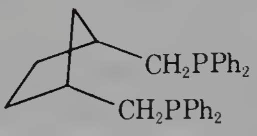
and this led to the possibility of asymmetric catalytic hydrogenations of prochiral unsaturated substances with C=C, C=O, C=N, bonds.

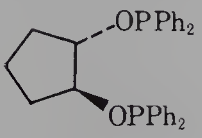
Tertiary phosphine ligands can have chirality either at the P atom, at a carbon atom on a group attached to the P atom, or at both. A third class has an axial element of chirality only.

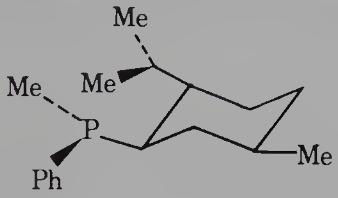
Some representative ligands are *o*-anisylcyclohexylmethylphosphine, (− or +)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane (28-V), usually abbreviated to (+ or −)DIOP, which is readily obtained from the appropriate tartaric acid, neomenthyldiphenylphosphine (28-VI), and compound (28-VII) abbreviated to (+)-camphos. The ligand *trans*-1,2-bis(diphenylphosphinoxo)cyclopentane (28-VIII) is particularly useful for substrates without functional groups. The methyl ligand (28-IX) is an example similar to (28-VI) but chiral at both P and C. Compound (28-X) is an example of axial chirality. Water soluble asymmetric phosphines for reductions in two phase systems have also been made.[52a]

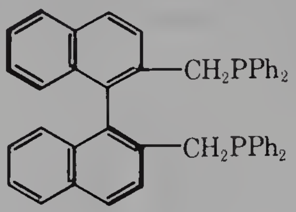

(28-V)


(28-VI)

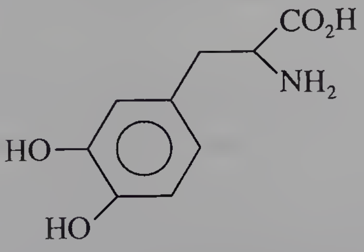

(28-VII)

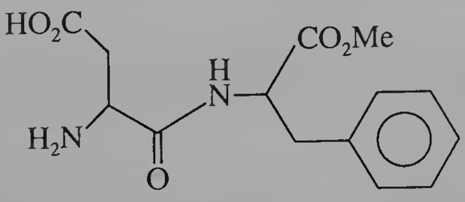

(28-VIII)


(28-IX)


(28-X)

The most important reduction has been for prochiral alkenes of the type $R'CH{=}C(NHR_2)CO_2R''$ that can be converted to chiral amino acids with optical purities >95% at quite rapid rates. The drug used for treatment of Parkinson's disease, L-DOPA (28-XI) and the sweetner aspartame (28-XII)


(28-XI)


(28-XII)

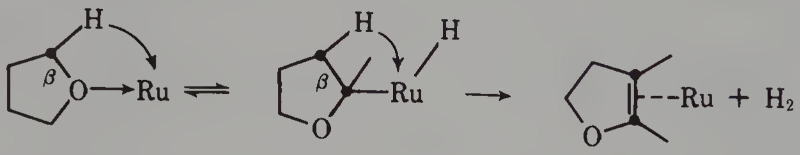
[52a] D. Sinou *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986,** 202; *J. Mol. Catal.*, 1986, **36,** 319.

have been made this way, while L-menthol production began in Japan in 1983.[52b]

Asymmetric catalysis is a kinetic phenomenon where the chiral ligand discriminates the prochiral features of the bound substrate by differences in reaction rates associated with the formation of one or other of the product enantiomers. The mechanism is outlined in Fig. 28-9. The enantioselective step is the oxidative-addition of H_2 to the four-coordinate diastereomer substrate catalyst complexes that are in rapid dissociative equilibria. The *major enantiomer of the product* arises from the *minor substrate-catalyst diastereomer* even though this cannot always be detected by virtue of its higher reactivity towards hydrogen. The large increase in reaction rate for the minor diastereomer arises from the increased stability of the corresponding dihydrido intermediate, that is, the enantioselective step is under product control.

Asymmetric hydrogenation has been achieved for C═C bonds also using ruthenium catalysts while enantioselective hydrosilation, hydrocyanation, hydroformylation of alkenes, isomerization of allylamines, and so on, have also been achieved using chiral phosphine complexes.

Transfer Hydrogenations.[53] The above reductions use molecular hydrogen but other hydride sources such as alcohols, including CH_3OH,[54a] dioxan, and THF can be used in homogeneous transfer hydrogenations. The hydrogen donor must be able to coordinate to the metal, and β-hydrogen transfer or 1,2-shifts similar to those described earlier are doubtless involved, for example,



Typical transfer reactions use rhodium-tertiary phosphine complexes such as $RhCl(PPh_3)_3$ with dioxane. The overall transfer reaction is merely tantamount to breaking C—H bonds in one molecule and forming them in another, namely,

Ketones and other unsaturated substances can also be reduced by transfer hydrogenation. Thus $RuCl_2(PPh_3)_3$ in methanol will reduce cyclohexanone to

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[52b] See A. Nakamura, *J. Organomet. Chem.*, 1984, **272**, V.

[53] R. A. W. Johnstone *et al.*, *Chem. Rev.*, 1985, **85**, 129 (heterogeneous).

[54a] T. A. Smith and P. M. Maitlis, *J. Organomet. Chem.*, 1985, **289**, 385; D. Beaupère *et al.*, *Nouv. J. Chim.*, 1986, **10**, 493.

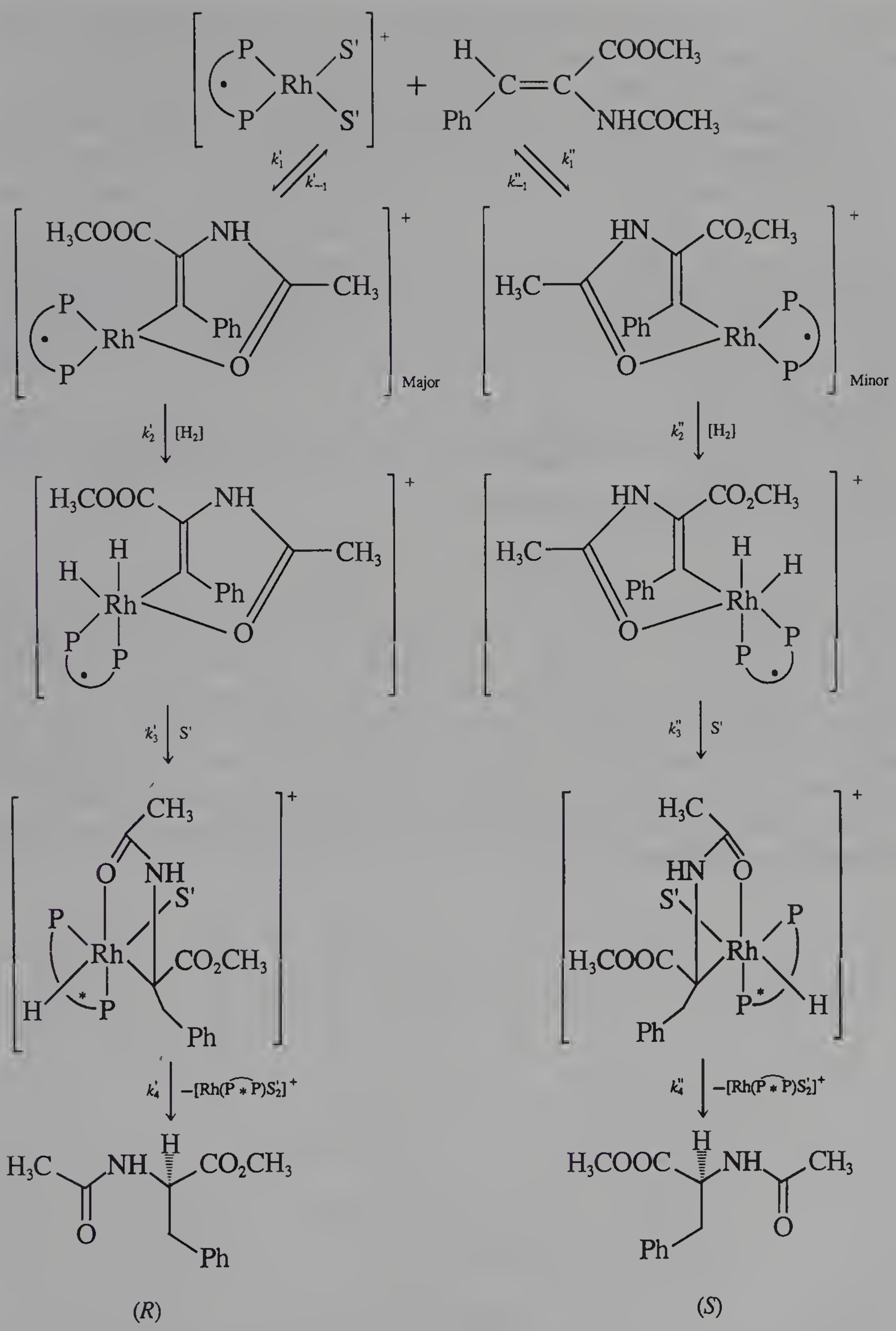


FIG. 28-9. Mechanism of asymmetric hydrogenation of prochiral precursors using rhodium complexes with chiral diphosphine ligands. [Reproduced by permission from B. Bosnich, *Chem. Br.*, **1984,** 808.] See also J. M. Brown and D. Parker, *Organometallics,* 1982, **1,** 950; J. D. Oliver and D. P. Riley, *Organometallics,* 1983, **2,** 1032; J. Halpern, *Pure Appl. Chem.*, 1983, **55,** 99. Iridium analogues are kinetically more stable than rhodium ones and can be isolated in selected cases (J. M. Brown *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 575).

cyclohexanol, the solvent being oxidized to methyl formate. Asymmetric transfer hydrogenation[54b] uses Rh or Ru complexes of chiral phosphines.

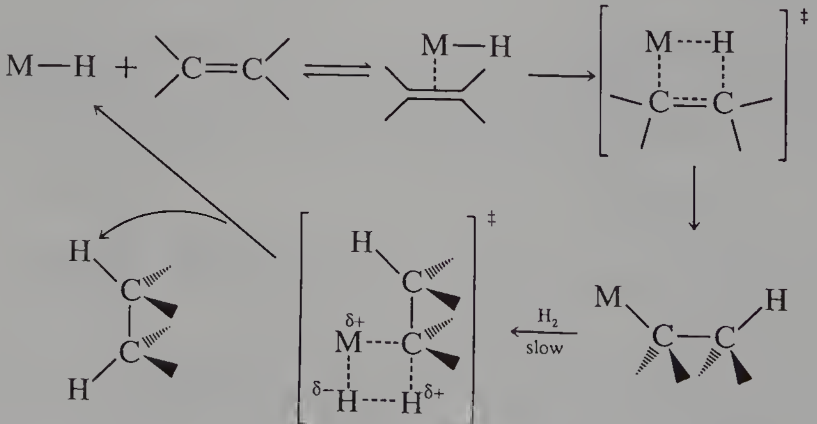
Hydrogenations by *f*-Block Complexes.[55] As discussed in Chapters 20 and 21, the lanthanide and actinide elements form hydrides, alkyls, and so on, especially in pentamethylcyclopentadienyl compounds, examples being $[(Me_5C_5)_2ThH_2]_2$ and the "chelate" $[Me_4C_5(SiMe_2)C_5Me_4LuH]_2$. Some of these compounds are extremely active for hydrogenation of alkenes and alkynes. A comparison for $(^*Cp_2LuH)_2$ with some representative *d*-block phosphine complexes under similar conditions shows that the turnover numbers per hour at 25°C, 1 atm for hex-1-ene are $(Cp_2LuH)_2$, 120,000; $[Ir(COD)(P\textit{c}\text{-hex}_3)(py)]PF_6$, 6400; $[Rh(COD)(PPh_3)_2]PF_6$, 4000; $RuHCl(PPh_3)_3$, 3000; $RhCl(PPh_3)_3$, 650.

It is clear that oxidative-addition of H_2 cannot be involved as this would require lanthanides in +5 oxidation states. The hydrogenation thus doubtless proceeds by dissociation to a monomer,

$$(^*Cp_2LuH)_2 \rightleftharpoons 2^*Cp_2LuH$$

which then interacts with alkene undergoing insertion to give an alkyl; the latter then undergoes hydrogenolysis similar to that with, for example, Cp_2TiMe_2 where again oxidative-addition of H_2 is impossible. The cycle is shown in Scheme 28-5. Alkynes appear to be hydrogenated in two steps and there is some evidence for selectivity, for example, $[(Me_4C_5(SiMe_2)C_5Me_4)NdH]_2$ hydrogenates mainly the exo double bond in limonene.

In the absence of hydrogen, the same compounds initiate alkene polymerization (see Section 28-13).



Scheme 28-5

[54b] See, for example F. Morandini and O. Piccolo, *J. Catal.*, 1985, **94**, 292; P. Kvintovics *et al.*, *J. Chem. Soc. Chem. Commun.*, **1986**, 1810.

[55] T. J. Marks *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 8111, 8103.

28-11. Hydrosilation of Unsaturated Compounds

The hydrosilation (cf. hydroboration, Section 6-14) or hydrosilylation reaction is similar to hydrogenation except that H and SiR_3 from a silane $HSiR_3$, are added across a double bond. Olefins usually give the terminal product:

$$RCH{=}CH_2 + HSiR_3 = RCH_2CH_2SiR_3$$

The reaction was first discovered using chloroplatinic acid as catalyst, and H_2PtCl_6 in alcohols is commonly referred to as Speier's catalyst. It is effective in extremely low concentration (10^{-5} to 10^{-8} mol of Pt/mol of reactant). The reaction is used in silicone technology in various ways; for example, hydrosilation of acrylonitrile allows incorporation of C_2H_4CN groups into rubbers for self-sealing fuel tanks and for cross-linking reactions in the curing of gums to elastomers.

The reaction may proceed by the initial formation of platinum(II) olefin complexes—indeed such complexes can be used directly—which then undergo addition as shown in Fig. 28-10. The stoichiometric oxidative-addition of silanes to compounds such as $RhCl(PPh_3)_3$ or *trans*-$IrCl(CO)(PPh_3)_2$ provides evidence for the first step, for example,[56a]

$$IrCl(CO)(PPh_3)_2 + R_3SiH = IrCl(H)(SiR_3)(CO)(PPh_3)_2$$

The addition of chiral silanes shows that the addition occurs with retention of configuration. However, the insertion of C_2H_4 into an Fe—Si bond photochemically suggested this insertion as one alternative.[56b]

Hydrosilation can also be catalyzed by complexes such as $RhCl(PPh_3)_3$ but

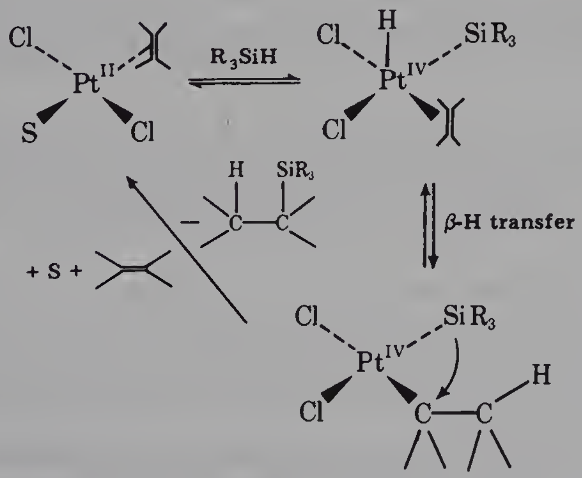
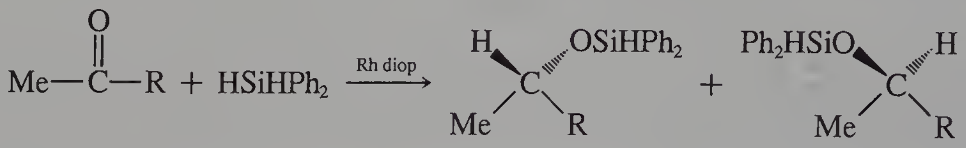


FIG. 28-10. Simplified cycle for hydrosilation of alkenes by platinum complexes (S = solvent).

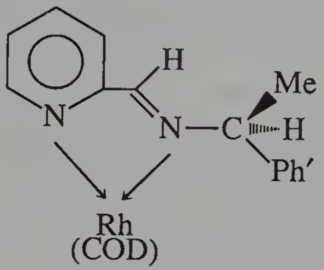
[56a] S. R. Stobart *et al.*, *J. Am. Chem. Soc.*, 1984, **106**, 1314.
[56b] C. L. Randolf and M. S. Wrighton, *J. Am. Chem. Soc.*, 1986, **108**, 3366.

initiation by O_2 or t-BuO_2H suggests that radical paths are involved.[56c] In Pt catalyzed studies, however, it appears that platinum colloids may be involved; for H_2PtCl_6 in isopropanol, which is very active, these have a size ~830 Å.[57]

In addition to C=C bonds, C≡C, C=O, and C=N bonds can be hydrosilated. The use of optically active phosphine complexes allows prochiral ketones such as acetophenone to be silated with 32% optical induction,



but complexes of Schiff bases such as (28-XIII) are much better than phosphine



(28-XIII)

complexes since the asymmetric substituent interacts directly (rather than indirectly as with DIOP) with the adjacent metal positions.[58]

28-12. Hydrocyanation of Alkenes[59]

Various complexes of Cu, Ni, or Pd, especially $Ni[P(o\text{-}C_6H_4Me)_3]_4$ are active for addition of HCN to alkenes and alkynes.[60] Although HCN is a weak acid it will add oxidatively to $RhCl(PPh_3)_3$, $Pt(PPh_3)_3$, $Ni[P(OR)_3]_4$, for example,

$$NiL_4 + HCN \underset{+L}{\overset{-L}{\rightleftharpoons}} NiH(CN)L_3 \underset{+L}{\overset{-L}{\rightleftharpoons}} NiH(CN)L_2$$

The hydride can then react with alkene as in the cycle shown in Scheme 28-6[61]:

[56c] R. V. Parrish *et al., J. Chem. Soc. Dalton Trans.,* **1980,** 308; R. A. Faltynek, *Inorg. Chem.,* 1981, **20,** 1357.

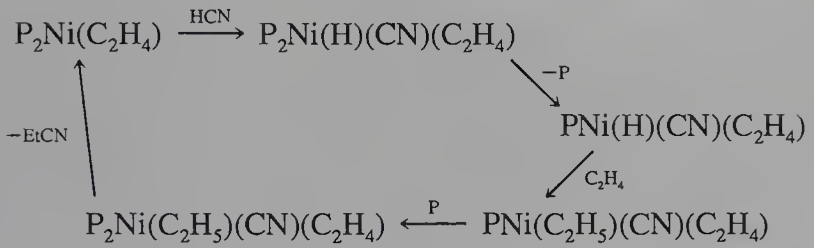
[57] L. N. Lewis and N. Lewis, *J. Am. Chem. Soc.,* 1986, **108,** 7228. See also L. Lukevics *et al., Organometallics,* 1987, **6,** 1410.

[58] H. Brunner *et al., J. Organomet. Chem.,* 1986, **300,** 395; *Organometallics,* 1986, **5,** 739.

[59] B. R. James, *Comprehensive Organometallic Chemistry,* Vol. 8, Pergamon Press, Oxford, 1980, p. 285; C. A. Tolman, *J. Chem. Educ.* 1986, **63,** 199; *Adv. Catal.,* 1985, **33,** 1.

[60] P. Perlmutter *et al., J. Chem. Soc. Chem. Commun.,* **1985,** 4; P. Teyssié *et al., J. Mol. Catal.,* 1985, **31,** 183.

[61] R. J. McKinney and D. C. Roe, *J. Am. Chem. Soc.,* 1986, **108,** 5167; J. E. Bäckvall and O. S. Andell, *Organometallics,* 1986, **5,** 2350; W. R. Jackson and P. Perlmutter, *Chem. Br.,* **1986,** 338.



Scheme 28-6

The most important use is hydrocyanation of butadiene or acrylonitrile as a route to adiponitrile or succinonitrile that are used to make hexamethylenediamine or 1,4-diaminobutane for synthesis of nylons. The reaction of butadiene, which is complicated and can give mixtures due to HCN addition either Markovnikov or anti-Markovnikov to one or both double bonds has been studied in detail.[61,62] While the first addition,

$$CH_2{=}CH{-}CH{=}CH_2 + HCN \longrightarrow CH_2{=}CH{-}CH_2{-}CH_2CN + CH_2{=}CN{-}CH(CN)CH_3$$

can proceed without addition of Lewis acids, these are required for the second addition and also for improved distribution of linear, anti-Markovnikov products and for longer catalyst life. Thus for propylene the percentage linear product was 71% with or without $AlCl_3$ or $ZnCl_2$ but ~89% using BPh_3. The effect is evidently due to complexing of the CN groups on nickel to give a bulky ligand which then alters the direction of addition of H to alkene (cf. hydroformylation with bulky ligands, Section 28-4). The structure of a model, $Cp(CO)_2Fe(CN{\rightarrow}BPh_3)$, has been determined. Thus we have

$$HNi(CN)[P(tol)_3] + BPh_3 \rightleftharpoons HNi(CNBPh_3)[P(tol)_3]$$

Alkynes can also be hydrocyanated to α, β-unsaturated nitriles by heating alkyne, acetone cyanhydrin (as HCN source), and $Ni[P(OPh)_3]_4$ in refluxing toluene.

POLYMERIZATION, OLIGOMERIZATION, AND METATHESIS REACTIONS OF ALKENES AND ALKYNES

28-13. Ziegler–Natta Polymerization of Ethylene and Propylene[63]

The discovery by K. Ziegler that hydrocarbon solutions of $TiCl_4$ in the presence of Et_3Al give heterogeneous suspensions that polymerize ethylene at 1-

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[62] J. D. Druliner, *Organometallics,* 1984, **3,** 205; C. A. Tolman, *Organometallics,* 1984, **3,** 33.

[63] W. Keim *et al., Comprehensive Organometallic Chemistry,* Vol. 8, Pergamon Press, Oxford, 1982, p. 371; K. H. Reichart, in *Transition Metal Catalysed Polymerisation,* R. P. Quirk, Ed., Horwood, Chichester, 1983; F. J. Karol and H. L. Hsieh, *Catal. Rev. Sci. Eng.,* 1984, **26,** 557; K. Y. Choi and W. H. Ray, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.,* **1985,** C25; P. Pino and B. Rotzinger, *Macromol. Chem. Phys. Suppl.,* 1984, **7,** 41; I. Pasquon and U. Gianini, in *Catalysis,* Vol. 6, J. R. Anderson and M. Boudart, Eds., Springer, Berlin 1984; P. C. Barbe *et al., Adv. Polym. Sci.,* 1986, **81,** 1.

atm pressure has led to an extremely diverse chemistry in which aluminum alkyls are used to generate transition metal–alkyl species. At about the same time it was found by the Phillips Petroleum Company that specially activated chromium oxides on an alumina support also polymerize ethylene when they are suspended in inert hydrocarbon solvents. A more effective process for C_2H_4 operated in the gas phase by Union Carbide uses alumina treated with $(\eta\text{-}C_5H_5)_2Cr$. These processes produce a linear high density polyethylene that differs from the low density, branched polyethylene produced by free-radical polymerization at very high pressure (Imperial Chemical Industries). Modification of the gas phase process now allows low density polyethylene and polypropylene to be produced.[64a]

The Ziegler–Natta system is heterogeneous, and the active metal species is a fibrous form of $TiCl_3$ formed *in situ* from $TiCl_4$ and $AlEt_3$. Many improvements in the catalyst have been described in patents.

For propylene the titanium systems can produce stereoregular polypropylene called isotactic, syndiotactic, or atactic depending on the position of the methyl groups.[64b] The commercially important isotactic polymer can be represented by (28-XIV), where most of the CH_3 groups are on one side—this gives a higher melting point.

(28-XIV)

Polymerization by homogeneous catalysts is also known and these may produce polymers with different stereosequences. An example[64b] is the system $Cp_2TiPh_2 + (AlMeO)_n$ while a similar zirconium system is an extremely active catalyst.[65a] In homogeneous solutions, cations are believed to be the active metal species involved,[65b] for example, $Cp_2ZrMe(THF)^+$.

There have been two main mechanistic proposals (Fig. 28-11). The first due to Cossee and Arlman involves insertion of C_2H_4 or C_3H_6 into a titanium–alkyl group initially formed on the surface by aluminum alkyl. The stereoregularity of polypropylene is considered to arise because of the nature of sterically hindered sites on the $TiCl_3$ lattice. For many years, the insertion mechanism has been uncertain largely because of the absence of any systems in which alkyl transfer to coordinated alkene could be proved. The situation has now been resolved (*a*) by direct proof of insertion, (*b*) by elimination of the carbene route. First, the carbene route Fig. 28-11(b) can be excluded by kinetic isotope effects and deuteration studies show no deuterium incorporation into an α-M—CH(D) group as would be expected.[66]

[64a] *Chem. Eng. News* 1986, March 31, p. 15.

[64b] J. A. Ewen, *J. Am. Chem. Soc.*, 1984, **106,** 6355.

[65a] W. Kaminsky, *et al.*, *Angew. Chem. Int. Ed. Engl.*, 1985, **24**, 507.

[65b] R. F. Jordan *et al.*, *J. Am. Chem. Soc.*, 1987, **109,** 4111.

[66] R. H. Grubbs *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 337.

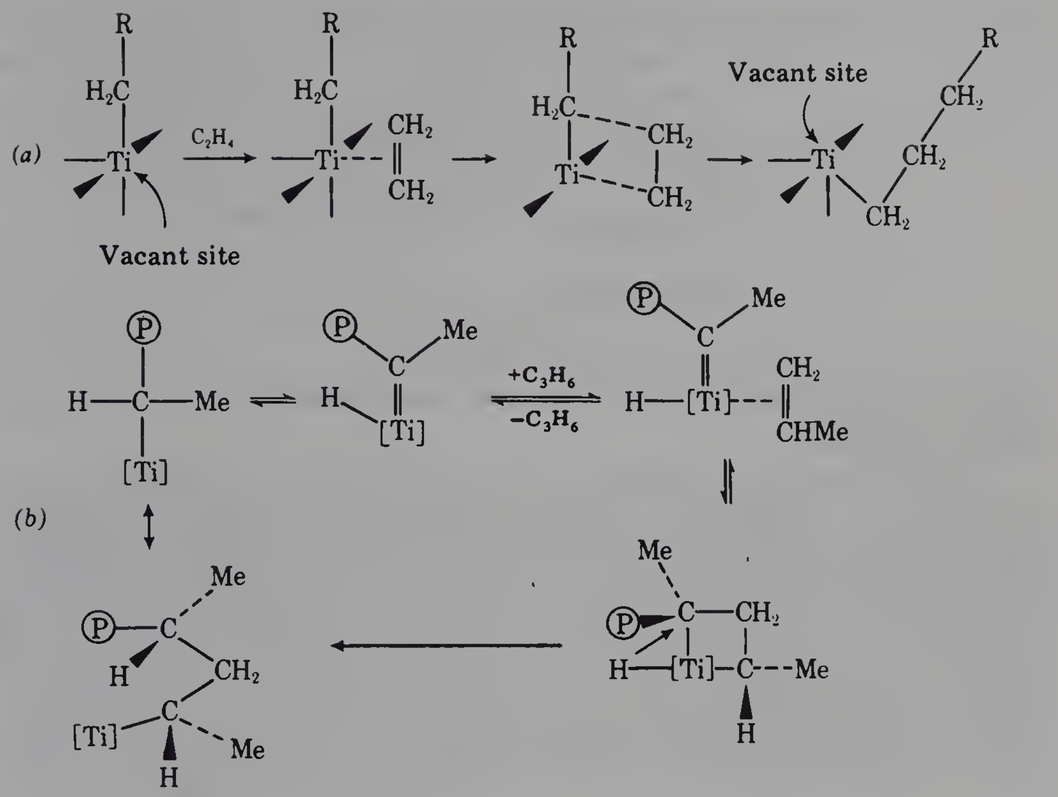
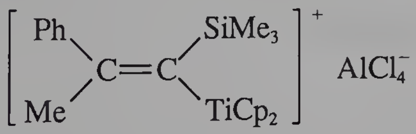


FIG. 28-11. (a) The Cossee–Arlman mechanism involving alkyl migration to coordinated alkene. (b) Proposed carbene mechanism.

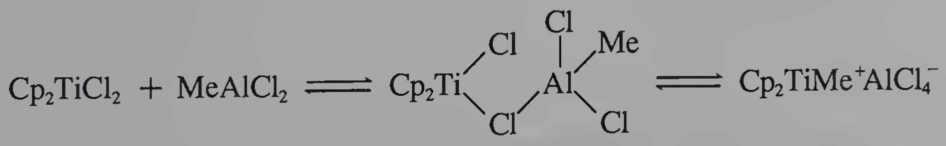
Second, direct insertions have been established.[67]

In Cp_2TiCl_2—$MeAlCl_2$ systems using PhC≡$CSiMe_3$ as a surrogate, the



(28-XV)

insertion product (28-XV) was established and it was concluded that the active titanium species is the ion-pair $Cp_2TiMe^+ \cdot AlCl_4^-$:



The bridged chloro complex was isolated and the structure determined.

Other evidence comes from proof of insertions in lanthanide alkyls,[68a,b] for example, $^*Cp_2MMe$, and hydrides, for example, $(^*Cp_2MH)_2$, that are extremely active catalysts for ethylene polymerization and provide sound models

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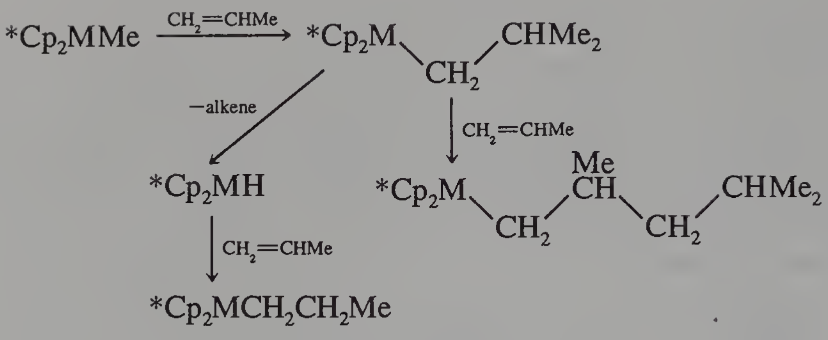
[67] J. J. Eisch *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 7219.

[68a] P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, 1985, **18**, 51.

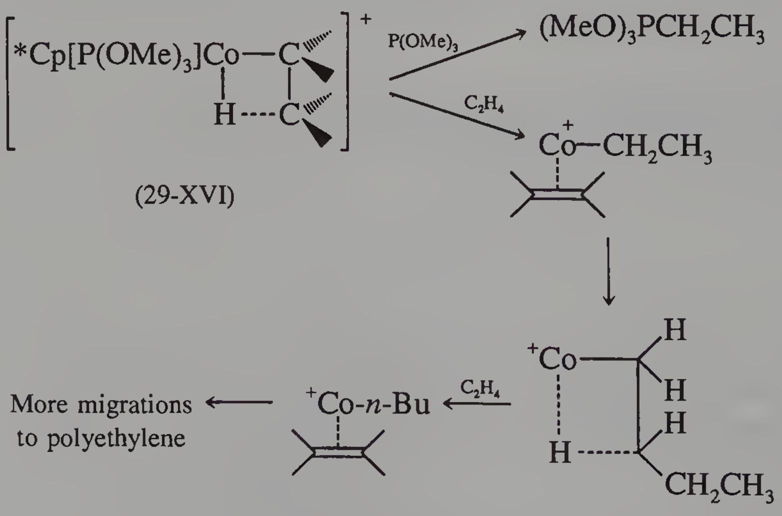
[68b] T. J. Marks *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 8091, 8103.



Scheme 28-7

for the Ziegler–Natta system. Thus insertions such as those in Scheme 28-7 can be confirmed.

Other aspects of the titanium system, such as the control of the degree of polymerization by addition of hydrogen, which leads to hydrogenolysis of the M—C bond and other steps, are simulated by the lanthanide complexes.[68a] It also seems that agostic hydrogen interactions are involved and facilitate alkyl migration to coordinated alkene.[69] Thus study of the species (28-XVI), that has an H-bridged structure (*cf.* 24-XX, p. 1117) shows that alkyl migration is facile and that effective ethylene polymerization occurs as in Scheme 28-8. No actual alkene–alkyl complexes were observed directly and the agostic bridged structures appear to be the "resting state" of the catalyst.



(29-XVI)

Scheme 28-8

28-14. Oligomerization and Related Reactions[70]

Alk-1-enes, conjugated alkenes such as butadiene, fuctionalized alkenes, and acetylenes of many types can be dimerized, trimerized, and so on, to give linear, cyclic, and more complex products. These transformations can be

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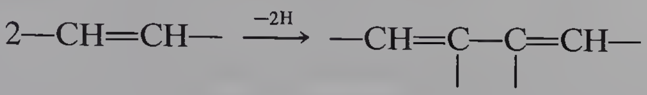
[69] G. F. Schmidt and M. Brookhart, *J. Am. Chem. Soc.*, 1985, **107,** 1443.

[70] W. Keim *et al., Comprehensive Organometallic Chemistry,* Vol. 8, Pergamon Press, Oxford, 1980, p. 371; P. W. Jolly, *ibid,* p. 615, 671; S. Pillai *et al., Chem. Rev.*, 1986, **86,** 353 (C_2H_4 and C_3H_8 dimerization).

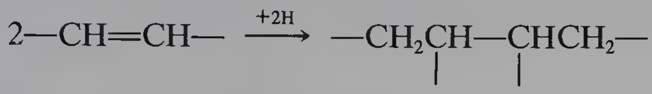
achieved by metal complexes + aluminum alkyls or by phosphine complexes such as $CoH(N_2)(PPh_3)_3$. Acrylonitrile and methylacrylate can be dimerized by reduced Ru species.

Dimerization can occur oxidatively (i.e., with loss of hydrogen atoms),



$$2\text{—CH=CH—} \xrightarrow{-2\text{H}} \text{—CH=}\underset{|}{\text{C}}\text{—}\underset{|}{\text{C}}\text{=CH—}$$

or reductively (i.e., with addition of hydrogen atoms),

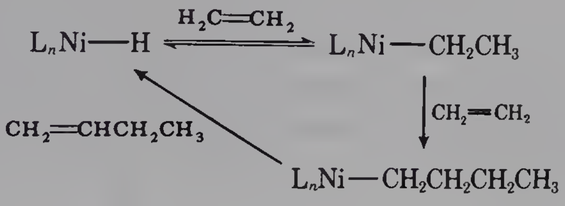


$$2\text{—CH=CH—} \xrightarrow{+2\text{H}} \text{—CH}_2\underset{|}{\text{C}}\text{H—}\underset{|}{\text{C}}\text{HCH}_2\text{—}$$

as well as by simple addition of one monomer to another.

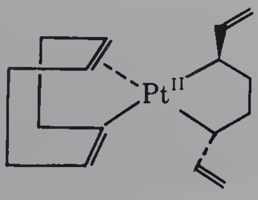
There are related reactions in which two different alkenes are codimerized. Thus hexa-1,4-diene is obtained by reaction of C_2H_4 and butadiene using rhodium trichloride in ethanolic HCl or by nickel complexes. Ethylene and propylene can be codimerized using π-allyl nickel halides + $AlCl_3$.

The mechanism of most of these reactions probably involves alkyl transfers to coordinated alkenes coupled with β elimination as in the nickel catalyzed dimerization of ethylene, Scheme 28-9. However, some oligomerizations involve alkylidene intermediates.



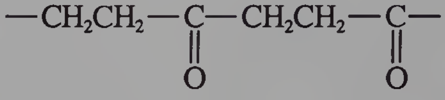
Scheme 28-9

The conversion of 1,3-dienes such as isoprene and the copolymerization of styrene and buta-1,3-diene to rubbers are carried out by anionic (initiated by lithium alkyls) or aqueous emulsion (initiated by Fe^{2+} and peroxodisulfate) polymerization, respectively. However, 1,3-dienes may be dimerized or trimerized by nickel complexes. Thus $Ni(cod)_2$ causes cyclotrimerization of buta-1,3-diene to cyclododecatriene, whereas in the presence of tertiary phosphines, only dimers are formed. The mechanism of these reactions, which involve allylic intermediates is well understood and intermediate complexes have been characterized for both nickel and platinum reactions, one example being the metallacyclic complex (28-XVII) derived from $Pt(cod)_2$ and buta-



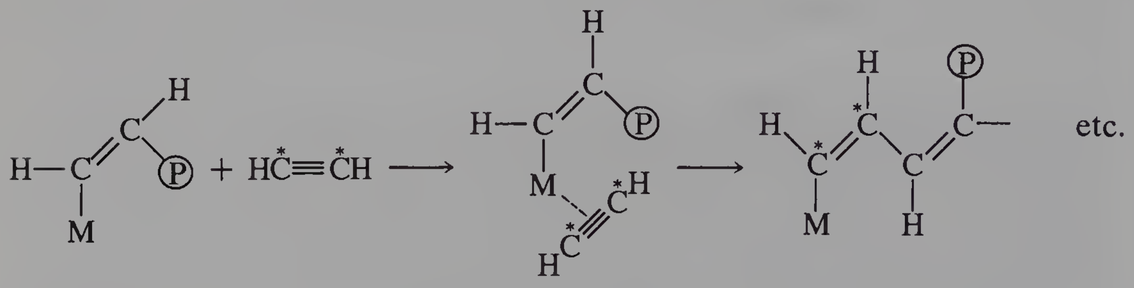
(28-XVII)

diene. Finally, copolymerization of C_2H_4 and CO is catalyzed by $[Pd(MeCN)(PPh_3)_3]^+BF_4^-$ where alternate insertion of CO and C_2H_4 into M alkyl leads to chains.[71]



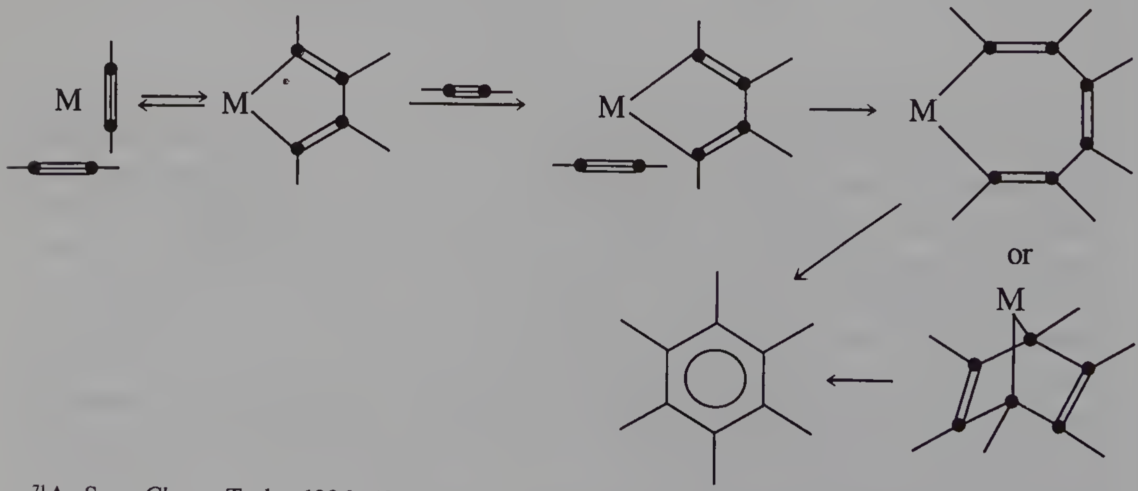
$$-CH_2CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_2-\underset{\underset{O}{\|}}{C}-$$

Polymerization and oligomerization of *acetylenes*[72] can be most complicated. Acetylene itself can be polymerized by Ti(O*n*-Bu)$_4$ + $AlEt_3$ in toluene to give a *cis-trans*oid isomer where the mechanism appears to be insertion similar to ethylene polymerization:



Labeling with ^{13}C shows that *C═*C bonds are in the polymer, which would *not* be the case if metathesis (Section 29-16) was involved—this would give *C—*C.[73]

However, polymerization of PhC≡CH by WCl_6 or by $(CO)_5W{=}CPh(OMe)$ does appear to proceed by alkylidene intermediates.[74] Acetylenes can also be trimerized[75] to arenes by $NbCl_5$ or $TaCl_5$ and by complexes such as $CpCo(\eta^6\text{-}C_6Me_6)$ or *CpRh(COD). These trimerizations proceed by cycles involving acetylene complexes and metallacycle formation along the lines of the sequence[76]



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[71] A. Sen, *Chem. Tech.*, **1986,** 48.

[72] T. Masuda *et al.*, *Macromol.*, 1985, **18,** 2109; *Acc. Chem. Res.*, 1984, **17,** 51; W. Keim and P. W. Jolly, ref. 70, p. 410, 649; R. E. Colburn and K. P. C. Vollhard, *J. Am. Chem. Soc.*, 1986, **108,** 5474; J. L. Davidson *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985,** 1474.

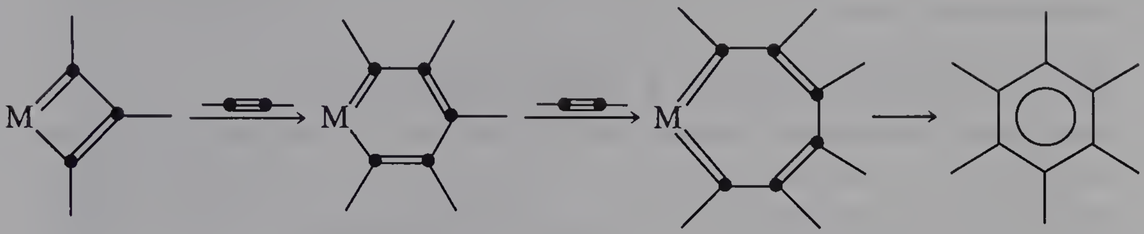
[73] T. C. Clarke *et al.*, *J. Am. Chem. Soc.*, 1983, **105,** 7797.

[74] C-C. Han and T. J. Katz, *Organometallics*, 1985, **4,** 2186; G. L. Geoffroy *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 6739.

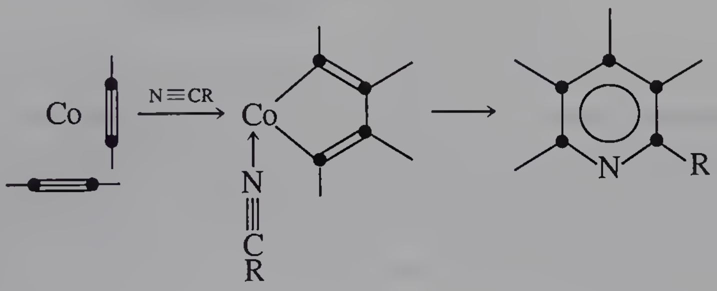
[75] See, for example, B. L. Booth *et al.*, *J. Organomet. Chem.*, 1985, **293,** 103.

[76] See, for example, R. R. Schrock *et al.*, *Inorg. Chem.*, 1985, **4,** 5999.

or, via alkylidenes

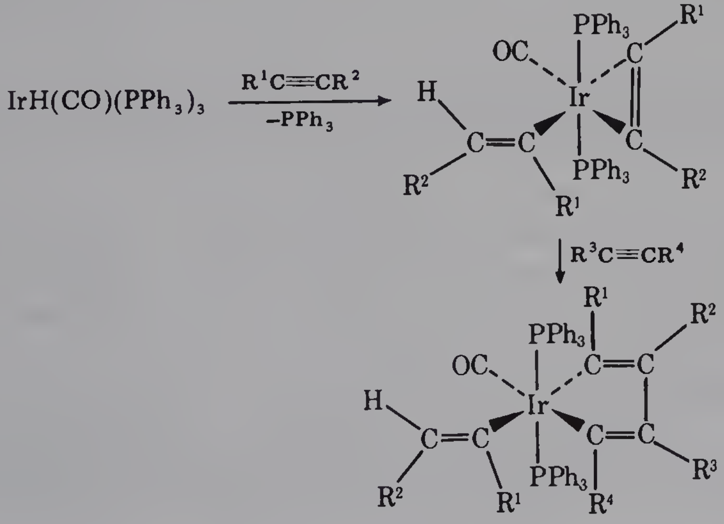


It may be noted the *nitriles* (RC≡N) may be similarly polymerized or copolymerized with acetylenes to give pyridines.[77] Pyridine synthesis can proceed as follows (ligands omitted):



where the cobalt catalyst precursor is $(\eta^5\text{-}C_5H_5)Co(diene)$.

The formation of metallacycles in acetylene reactions has long been known and many complexes characterized, for example,



REACTIONS INVOLVING C—C BOND CLEAVAGE

There are three main classes of reactions that involve cleavage of carbon-carbon bonds.

1. Single C—C bonds in strained hydrocarbons.
2. C═C bond cleavage in metathesis of alkenes.
3. C≡C bond cleavage in metathesis of alkynes.

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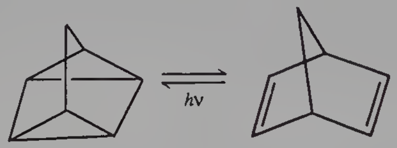
[77] H. Bönnemann *et al.*, *Angew, Chem. Int. Ed. Engl.*, 1985, **24**, 248; *New J. Chem.*, 1987, **11**, 549; G. Vitulli *et al.*, *J. Organomet. Chem.*, 1986, **307**, C35.

Both 2 and 3 involve alkylidene or alkylidyne complexes, whereas 1 involves oxidative-additions.

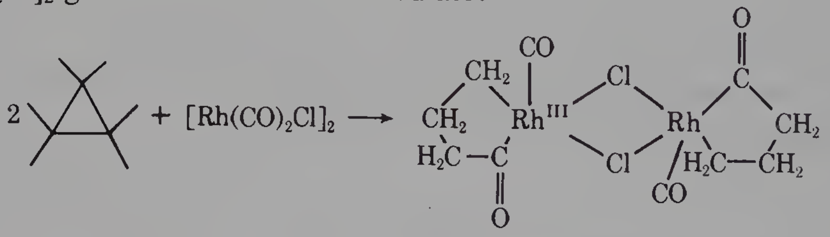
28-15. Valence Isomerizations of Strained Hydrocarbons

A number of complexes, notably of Rh^I, Pd^0, and Ni^0 will induce valence isomerizations in strained hydrocarbons. Because of the possibility of developing energy storage systems such as the interconversion of quadricyclene into norbornadiene this reaction has been of special interest:

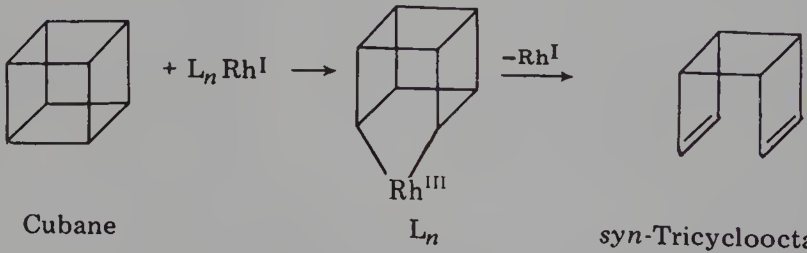


The forward reaction[78] is catalyzed, for example, by $PdCl_2$(norbornadiene) while the norbornadiene → quadricyclene photoisomerization[79] is sensitized by an iridium(III) *o*-metallated complex, $[(bipy)_2Ir(2,2'\text{-bipyrid-3-yl-}C^3,N^1)]^{2+}$.

Most reactions of this type are considered to proceed by oxidative-addition and cleavage of the C—C bond. For cyclopropane the reaction with $[Rh(CO)_2Cl]_2$ gives an isolable intermediate:



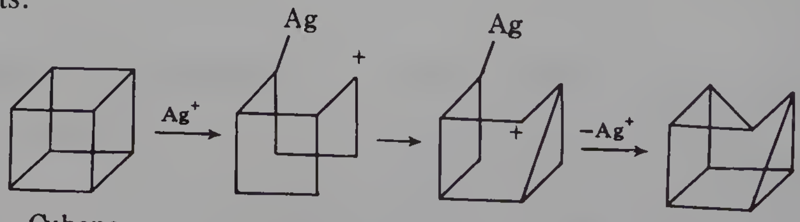
A few other intermediates have been isolated. With noncarbonyl complexes [e.g., $RhCl(PPh_3)_3$] the reaction is held to proceed as



Cubane

syn-Tricyclooctadiene

The Ag^+ ion also catalyzes such isomerizations, but these reactions proceed by electrophilic cleavage of C—C bonds followed by carbonium ion rearrangements:



Cubane

Cuneane

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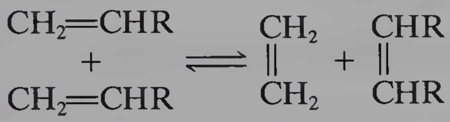
[78] A. Basu *et al., J. Chem. Soc. Dalton Trans.*, **1987,** 1797; C. Kutal *et al., Inorg. Chem.*, 1987, **26,** 3258.

[79] P. A. Grutsch and C. Kutal, *J. Am. Chem. Soc.*, 1986, **108,** 3108.

There are other reactions featuring C—C bond cleavages, for example, in skeletal rearrangements of 1,4-dienes catalyzed by nickel phosphine complexes. The statement made that these metal-catalyzed rearrangements "violate the Woodward–Hoffmann rules" is erroneous because these rules pertain only to concerted processes. The catalysts provide alternative, nonconcerted pathways.

28-16. Alkene and Alkyne Metathesis

Alkenes.[80] The metathesis or dismutation reaction of alkenes is reversible and can be extremely rapid:



$$\begin{matrix} CH_2{=}CHR \\ + \\ CH_2{=}CHR \end{matrix} \rightleftharpoons \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + \begin{matrix} CHR \\ \| \\ CHR \end{matrix}$$

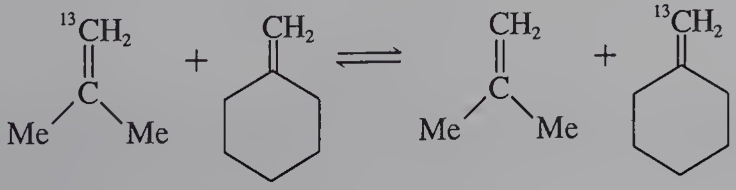
It was first discovered by Banks and Bailey in heterogeneous systems where olefins were passed at 150 to 500° over $Mo(CO)_6$ or $W(CO)_6$ deposited on Al_2O_3, silica-supported metals, and so on. Later a wide variety of homogeneous catalysts of Mo and W have been used, typical catalysts being $WCl_6 + EtAlCl_2 + EtOH$, $Mo(py)_2(NO)_2Cl_2 + AlR_3$, and $MoCl_6 + AlCl_3$ in chlorobenzene. Rhenium oxide (Re_2O_7) on Al_2O_3 is also very effective for metathesis of functionized alkenes.

There was much initial speculation on the mechanism but one involving metal alkylidenes, first suggested by the French chemists Herrisson and Chauvin, is now fully established by experiments involving direct reaction of alkenes with alkylidene complexes, complicated kinetic and alkene-crossing studies and trapping of alkylidene intermediates. In early studies, it was far from clearly recognized that traces of oxygen may have been important. It is now established that high-valent metal species, *particularly of d^2 configuration* (assuming the alkylidene ligand is taken as CR_2 and not CR_2^{2-}) are active but need to be *stabilized by π-donor* ligands such as oxo, imido, or alkoxo.

We cannot deal with the vast amount of research on models for the various mechanisms proposed and merely summarize the main conclusions.

There are two key steps: (*a*) generation of the initial alkylidene intermediate, (*b*) the propagation via alkylidene–alkene exchange.

1. Proof that alkylidenes are involved comes from the study of well-characterized alkylidenes that initiate the reaction (28-8)



(28-8)

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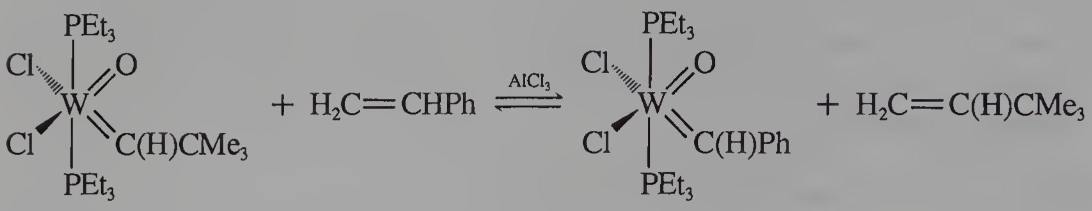
[80] K. J. Ivin, *Olefin Metathesis,* Academic Press, New York, 1983; R. H. Grubbs, *Comprehensive Organometallic Chemistry,* Vol. 8, Pergamon Press, Oxford, 1982, p. 499; R. L. Banks, *Chem. Tech.,* **1986,** 112; R. R. Schrock *et al., J. Organomet. Chem.,* 1986, **300,** 249; *J. Am. Chem. Soc.,* 1986, **108,** 2771; F. Volatron and O. Eisenstein, *J. Am. Chem. Soc.,* 1986, **108,** 2173.

which is catalyzed by $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$ and also of the reaction (28-9)

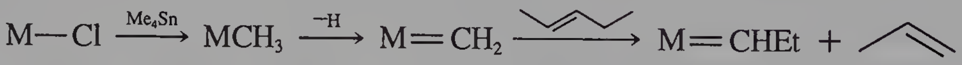


(28-9)

where the exchanged alkylidene complex could be observed. Photochemical exchange can also be shown[81]:

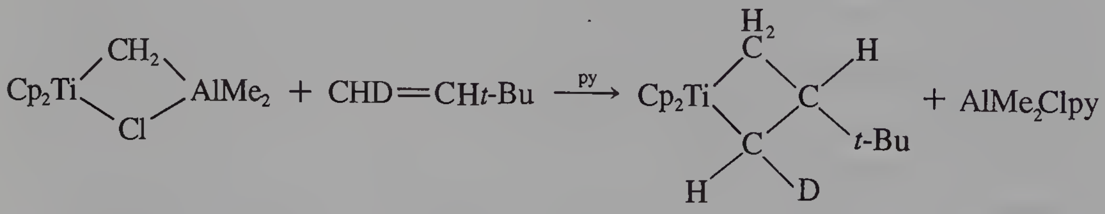
$$(CO)_5W{=}CPh_2 + CH_2{=}CPh(C_6H_4OMe) \xrightarrow{h\nu} (CO)_5W{=}C(Ph)(C_6H_4OMe) + Ph_2C{=}CH_2$$

2. The generation of the alkylidene would appear mostly to occur by α-H abstraction from an alkyl, itself made from transition metal halide by alkylating agent:



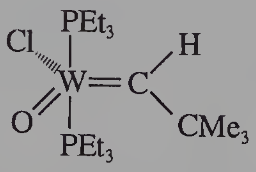
Models for *alkylidene–alkene complexes* have also been studied.[82]

3. The intermediacy of metallacyclobutanes is supported by their isolation in the reaction:



This metallacycle acts as a metathesis catalyst.

In reactions such as that involved for the tungsten compound noted previously, it appears that the Lewis acid acts to remove a ligand, producing a vacant site, since the related five-coordinate species (28-XVIII) reacts only



(28-XVIII)

slowly without Lewis acid. The catalytic systems are thus chain reactions of the type proceeding by an alkylidene complex and a four-center transition state.

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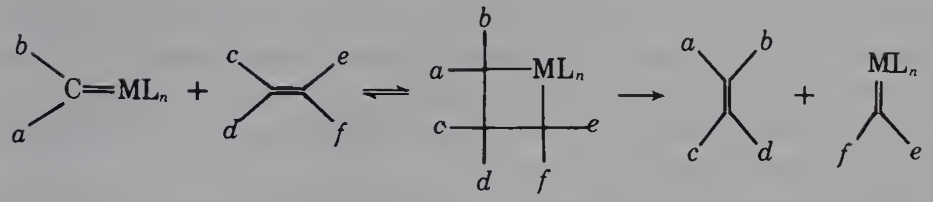
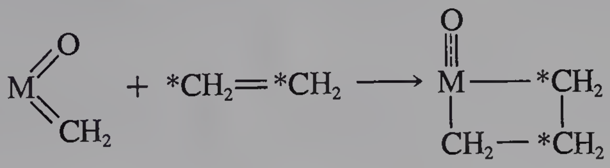
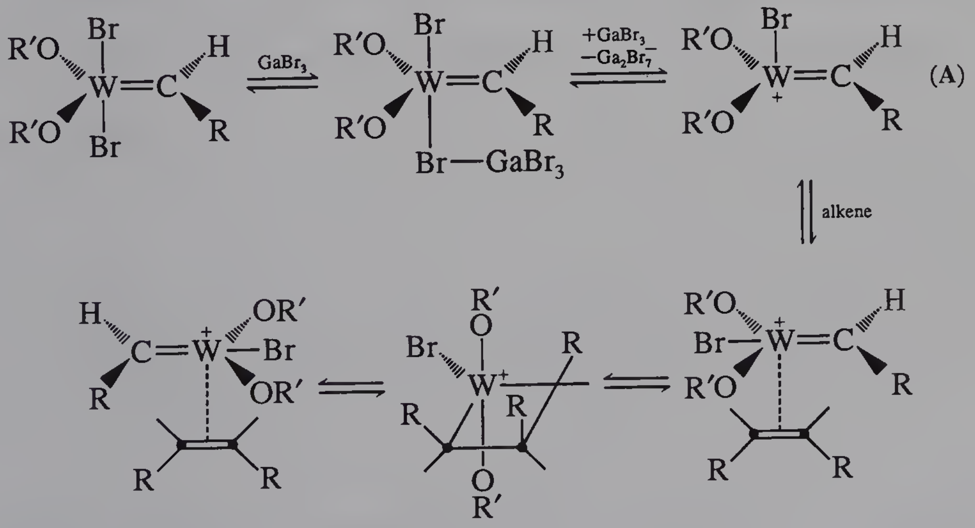
[81] L. K. Fong and N. J. Cooper, *J. Am. Chem. Soc.*, 1984, **106**, 2595.
[82] J. L. Templeton *et al.*, *Organometallics*, 1985, **4**, 2102.



Theoretical studies[83] of the intermediacy of oxo species both in complexes and on surfaces suggest that M═O groups may play an important role in favoring the formation of metallacycles because of the possibility of conversion of a double bond to a triple bond MO group, that is,



It is *not,* however, essential to have M═O species involved since $WX_2(CHR)(OCH_2R)_2$, X = Cl, Br, and R = *t*-Bu can be converted by Lewis acids such as AlX_3 and GaX_3 to give very active catalysts (Fig. 28-12).[84] This involves the alkylidene cation A for which nmr data show the two OCH_2t-Bu groups to be diastereotopic—A is thus chiral. The alkene then approaches A via the vacant site when suprafacial interaction of alkene and M═C π orbitals leads to formation of a metallacycle B, which has a plane of symmetry.



(B)

FIG. 28-12. Alkene metathesis by cationic tungsten(IV) alkylidene in presence of Lewis acids according to J. Kress and J. A. Osborn, ref. 84. R′O = *t*-$BuCH_2O$; the counter anion is $Ga_2Br_7^-$.

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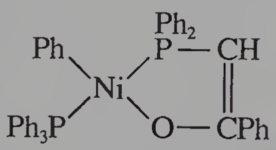
[83] A. K. Rappé and W. A. Goddard, III. *J. Am. Chem. Soc.*, 1982, **104,** 448.

[84] J. A. Osborn *et al., J. Am. Chem. Soc.*, 1987, **109,** 899, 3953; *J. Mol. Catal.*, 1986, **36,** 1; K. Tanaka *et al., J. Am. Chem. Soc.*, 1987, **109,** 2422.

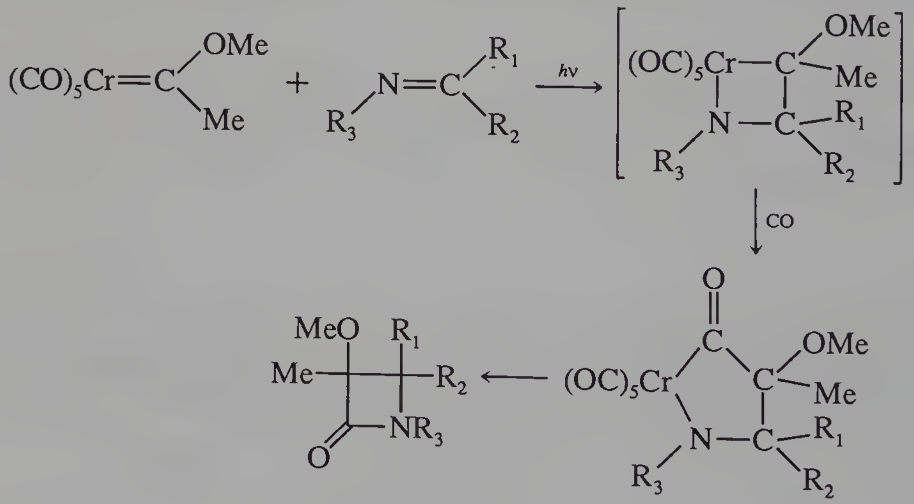
Ligand rearrangement *must* accompany metallacycle formation and hence a *cis* alkene reacting to give a *cis* alkene product should occur with inversion of alkylidene catalyst chirality. A *cis* alkene giving a trans product occurs with retention of configuration. It thus seems *essential* to have an *electrophilic* metal site for metathesis to occur.

There are commercial processes on a relatively small scale for metathesis of alkenes. The most important is the Shell Higher Olefin Process (SHOP) in which metathesis is coupled with oligomerization and isomerization to convert ethylene into C_{10} to C_{20} alkenes as intermediates for agrochemicals, detergents, and so on.[85a] The oligomerization uses nickel complexes of the type[85b] (28-XIX) with a rhenium on Al_2O_3 metathesis step for converting internal alkene and ethylene to alk-1-ene. Dienes such as 1,5-hexadiene and 1,5-decadiene are similarly obtained by metathesis from C_2H_4 and cycloocta-1,5-diene or cyclooctene.



(28-XIX)

Finally, it may be noted that a photocatalyzed synthesis of lactams from imines also may proceed via a metallacycle[86] as in Scheme 28-10.



Scheme 28-10

Alkynes.[87a] Molybdenum, W, and Re alkylidyne complexes similar to those involved in alkene metathesis can metathesize alkynes via cyclobutadiene intermediates. Functionized alkynes are difficult or impossible to me-

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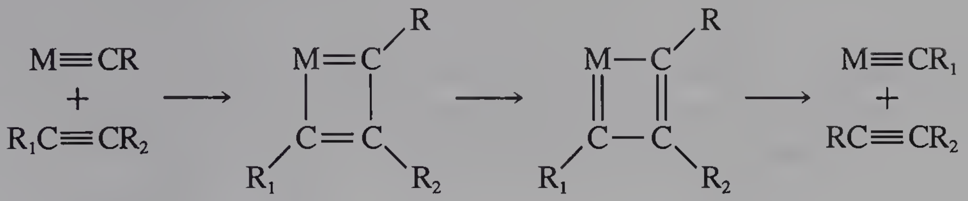
[85a] E. F. Lutz, *J. Chem. Educ.*, 1986, **63,** 202.

[85b] W. Keim *et al., Organometallics,* 1986, **5,** 2356; *New J. Chem.*, 1987, **11,** 531.

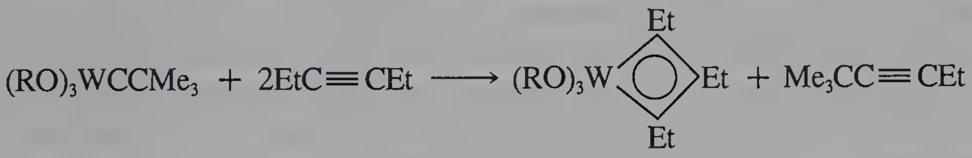
[86] L. S. Hegedus *et al., J. Am. Chem. Soc.*, 1987, **109,** 1101.

[87a] R. R. Schrock *et al., J. Mol. Catal.*, 1985, **28,** 1; *Organometallics,* 1986, **5,** 398, 1411, 1508.

tathesize. Thus we have



Tungstenocyclobutadiene complexes of the type proposed as intermediates have been characterized, for example, where R is the bulky aryloxide —O(2,6—C_6H_3*i*-Pr_2).



The metathesis of *nitriles,*[87b] where the C≡N rather than the C≡C bond is cleaved or of carbodiimides[87c] where N=C bonds in RN=C=NR′ are cleaved, are quite similar; four-membered *N*-heterocyclic rings are formed in both cases.

OTHER ASPECTS OF CATALYTIC REACTIONS

28-17. Cluster Compounds in Catalysis[88]

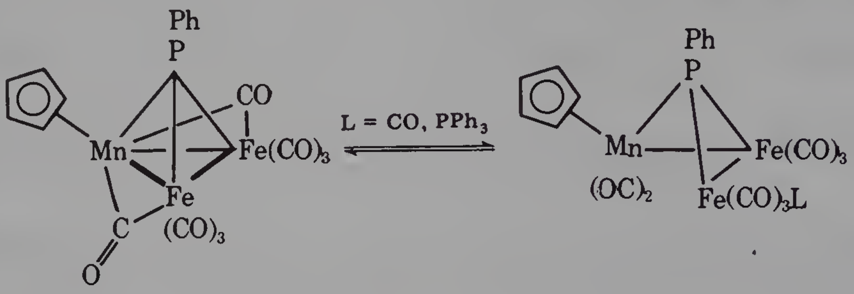
In previous sections the catalytic reactions have involved mononuclear species. However, there has been much study of metal clusters (Chapter 23), mainly carbonyl containing ones, as catalyst precursors in homogeneous solution as well as on supports (cf. next section) in all manner of catalytic reactions. In carbon monoxide reactions it is far from clear whether clusters are really involved since the conditions used, high temperature and pressure, may be such as to cause cluster fragmentation. This would give the active mononuclear species that actually do the catalysis. Thus in the CO + H_2 conversion to ethylene glycol by rhodium complexes, anionic rhodium carbonyl clusters are certainly formed but catalysis actually may be due to, say, $HRh(CO)_4$ in small but catalytically significant amounts in equilibrium with the bulk of the metal in cluster species.

[87b] J. H. Freudenberger and R. R. Schrock, *Organometallics,* 1986, **5,** 398.

[87c] K. Weiss *et al., J. Mol. Catal.,* 1986, **36,** 159.

[88] B. C. Gates *et al.*, Eds., *Metal Clusters in Catalysis,* Elsevier, Amsterdam, 1986; W. L. Gladfelter *et al., J. Am. Chem. Soc.,* 1986, **108,** 553; G. Balavoine *et al., Organometallics,* 1986, **5,** 203; E. Sappa *et al., J. Chem. Soc. Dalton Trans.,* **1986,** 23.

The opening of clusters to provide vacant sites is also possible, for example,



In the hydrogenation of alkenes in DMF using a non-cluster ion $[Ru_3O(CO_2Me)_6(H_2O)_3]^+$ precursor,[89] also only one ruthenium site is active in the species $[HRu_3O(CO_2Me)_5DMF_3]^+$. Clusters such as $\{HRh[P(OR)_3]_2\}_x$, $x = 2,3$, while active for hydrogenation of alkenes, doubtless dissociate to the 14*e* species $HRh[P(OR)_3]_2$. The same may apply to hydrogenation of acetylenes, RNC, and RCN using $Ni_3(CNCMe_3)_7$.

There is no doubt, however, that many interesting reactions do occur on

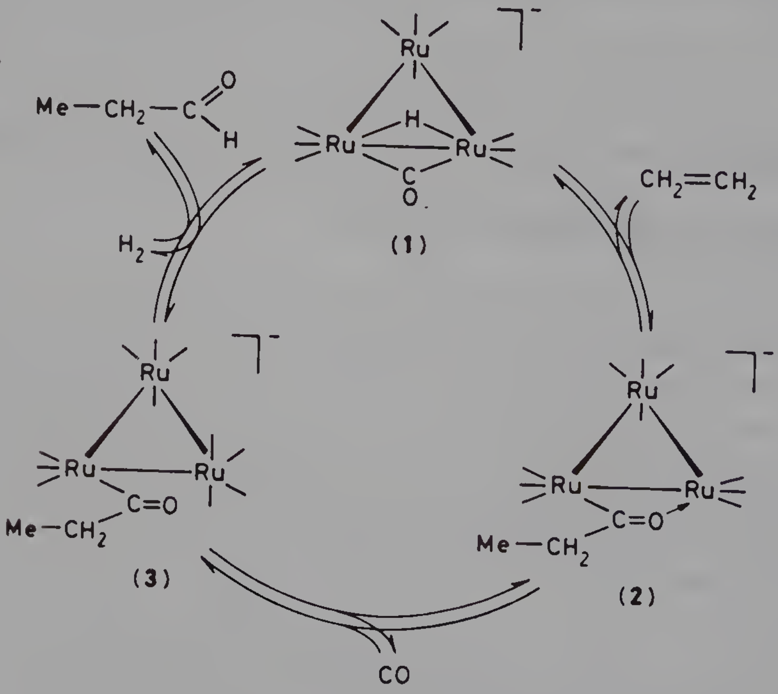


FIG. 28-13. Hydroformylation of ethylene using the cluster anion $[HRu_3(CO)_{11}]^-$ **1** as catalyst precursor. [Reprinted by permission from G. Süss-Fink and G. Herrmann, *J. Chem. Soc. Chem. Commun.*, **1985,** 735.] Deuterium labeling studies confirm that the Ru_3 clusters remain intact. Note that C_2H_4 reacts with the electrophilic C atom of the bridge in **1** to give a μ_2,η^2(C, O)-propionyl **2,** which with more CO becomes η^1 in **3.** Hydrogenolysis of the acyl gives propionaldehyde and **1** again.

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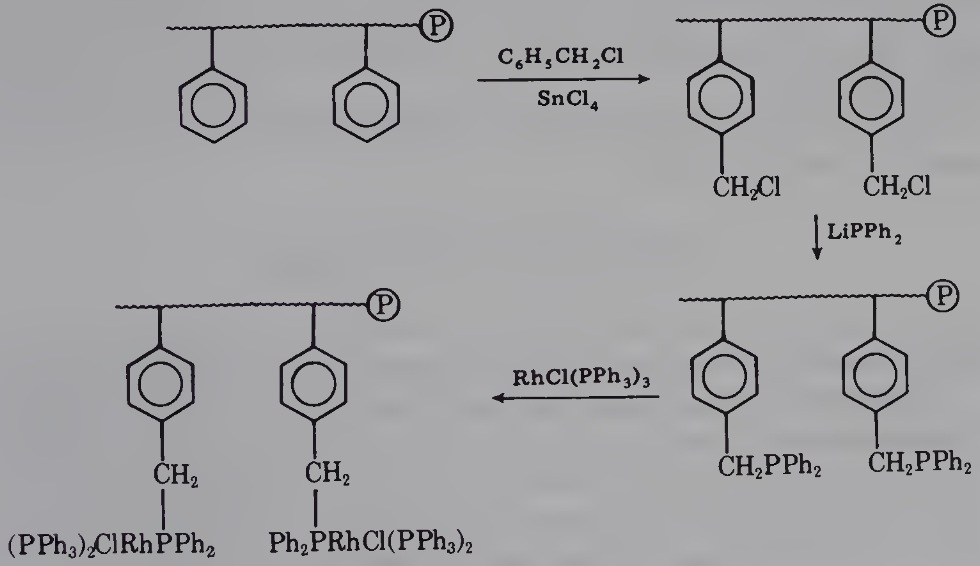
[89] S. A. Fouda and G. L. Rempel, *Inorg. Chem.*, 1979, **18,** 1.

clusters,[90a] and in a few cases true cluster catalysis is established.[90b] Thus isotopic labeling studies of hydroformylation of ethylene using $[Ru_3H(CO)_{11}]^-$ clearly shows that the reaction proceeds via intact clusters although catalysis decays after only ~300 cycles. The proposed reaction scheme is shown in Fig. 28-13, which should be compared with the normal oxo mechanism in Fig. 28-4.

28-18. Supported Homogeneous and Phase Transfer Catalysis

A major difficulty associated with all homogeneous catalytic systems is separation of products from reactants and catalyst. Since homogeneous systems often allow much greater selectivity in reactions, attempts have been made to achieve similar benefits by "heterogenizing" known homogeneous catalysts.[91a] This has been done by incorporating tertiary phosphine, pyridine, thiol, or other ligands into styrenedivinylbenzene or other polymeric materials, as well as by supporting complexes on carbon, silica, alumina, ion-exchange resins, or molecular sieves.

The anchoring of phosphines to polymers is usually done by first chloromethylating phenyl rings of the polymer by chloromethyl ethers, then reacting the chloro polymers with $LiPPh_2$. The functionalized polymer is exchanged with a typical homogeneous catalyst as follows:



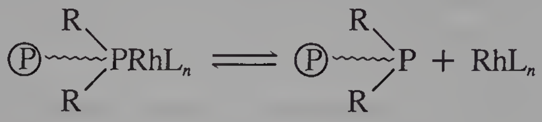
Asymmetric reductions can also be carried out by incorporation of DIOP-type ligands.

[90a] See R. D. Adams and I. T. Horvath, *Prog. Inorg. Chem.*, 1985, **33,** 127.

[90b] G. Süss-Fink and G. Hermann, *J. Chem. Soc. Chem. Commun.*, **1985,** 735. See also J. L. Zuffa and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1986, **108,** 4669; see also R. A. Sanchez-Delgado *et al., Inorg. Chem.*, 1987, **26,** 1866.

[91a] C. U. Pittman, *Comprehensive Organometallic Chemistry,* Vol. 8, Pergamon Press, Oxford, 1982, p. 553. F. R. Hartley, *Supported Metal Complexes, a New Generation of Catalysts,* Reidel, Dordrecht, 1985.

Although many reactions (hydrogenation, hydroformylation and hydrosilation[91b] of olefins, methanol carbonylation, etc.), can be carried out, often with high selectivity, supported catalysts also have disadvantages. First, if reactions are carried out in solution there may well be an equilibrium,

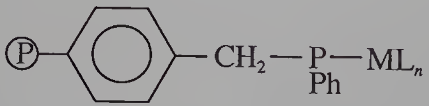


so that leaching of a metal complex from the support can occur. With purely gaseous reactants this is not likely. The other disadvantage is that neither the environment nor indeed the nature of the metal on the surface is known with certainty or easy to control.

A study of $RhCl(PPh_3)_3$ on a divinylbenzene–styrene polymer by the extended X-ray absorption fine structure (EXAFS) technique suggests that although the bond distances are similar to those in $RhCl(PPh_3)_3$, aggregation to form binuclear species has occurred. This could account for the lowered activity in selective hydrogenation.

Further developments are to use organic-solvent-soluble functionalized polymers with PPh_2 groups or to incorporate transition metal ions or complex ions into ion-exchange resins such as sulfonated polystyrene. In the latter type of support, rhodium containing domains can react with CO to form $Rh^I(CO)_2$ species.[92a] Liquid phase polymers, for example, polyethyleneimine, allow hydrogenation of $C{\equiv}C$, $C{=}O$, and $C{\equiv}N$ bonds[92b] on coordination to metal.

Finally, another method of anchoring metal species uses phosphido groups bound to a support, that is,



This appears to give stronger binding to polymers than other methods.[93]

Semipermeable Membranes and Two-Phase Systems. Another approach to separation of products from homogeneous systems is to use reverse osmosis with selectively permeable membranes. Certain polyamides or polyimides can allow small molecules to permeate under reverse osmosis conditions while retaining metal complexes. Thus the equilibrium

$$RuH_2(PPh_3)_4 + N_2 \rightleftharpoons RuH_2(N_2)(PPh_3)_3 + PPh_3$$

can be shifted to the right by removal of PPh_3. Similarly, adiponitrile obtained

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[91b] A. L. Prignano and W. C. Trogler, *J. Am. Chem. Soc.*, 1987, **109,** 3586.

[92a] W. M. Risen, Jr., *et al., Inorg. Chem.*, 1984, **23,** 3597; cf. R. Prins. *J. Am. Chem. Soc.*, 1985, **107,** 3139.

[92b] E. Bayer and W. Schumann, *J. Chem. Soc. Chem. Commun.*, **1986,** 949.

[93] R. A. Jones and M. H. Seeberger, *J. Chem. Soc. Chem. Commun.*, **1985,** 373.

by hydrogenation of 1,4-dicyanobutene with $RhCl(PPh_3)_3$ can be separated from the complex.

Another alternative is the use of two-phase systems in which the catalyst is in one phase and the substrate and products are in another; a phase transfer catalyst such as a long-chain amine may be required. Two-phase catalytic hydrogenation, carbonylation,[94a] and hydroformylation reactions have been achieved using water-soluble compounds derived from functionalized phosphines of various types. Some specific examples are the following. Hydrogenation of arenes and heterocyclic compounds is catalyzed under ambient conditions with $[RhCl\ diene]_2$ in hexane as the organic phase with a quaternary ammonium salt, $[Bu_4N]HSO_4$, in the aqueous phase at pH 7.4 to 7.6.[94b]

The carbonylation of benzyl bromide[95] to phenylacetic acid uses $[Co(CO)_4]^-$ in $H_2O—CH_2Cl_2$ or $H_2O—C_6H_6$; the main steps are

$$\begin{tikzcd}
PhCH_2Br + [Co(CO)_4]^- \arrow[r, "-Br^-"] & PhCH_2CO(CO)_4 \arrow[d, shift right, "+CO"'] \\
PhCH_2CO_2H + [Co(CO)_4]^- & PhCH_2COCo(CO)_4 \arrow[l, "OH^-"'] \arrow[u, shift right]
\end{tikzcd}$$

An important commercial use[96] is rhodium hydroformylation of olefins using $P(C_6H_4SO_3)_3^{3-}$. This has the advantage over the PPh_3 system (Section 28-4) where there is difficulty in removing aldehydes $>C_4$ by distillation since this leads to catalyst decomposition.

Conversion of aromatic nitro compounds to anilines can also be carried out using $Fe_3(CO)_{12}$ in aqueous NaOH–benzene with $PhCH_2NEt_3^+Cl^-$.

OXIDATION REACTIONS[97]

The catalytic oxidations of alkanes, alkenes, and other substances are of enormous technical and biological importance and only the briefest treatment can be given here.

Stoichiometric oxidations can be carried out by (*a*) metal ions or complexes

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[94a] H. Alper, *J. Organomet. Chem.*, 1986, **300,** 1.

[94b] K. R. Janoszklewicz and H. Alper, *Can. J. Chem.*, 1984, **62,** 1031.

[95] H. des Abbayes *et al.*, *Organometallics*, 1983, **2,** 1730.

[96] Ph. Kalck *et al.*, *New J. Chem.*, 1987, **11,** 601.

[97] H. Mimoun, *Comprehensive Coordination Chemistry*, Vol. 6, Pergamon Press, Oxford, 1987, Chapter 61.3; *Angew. Chem. Int. Ed. Engl.*, 1982 **21,** 734; H. Mimoun, R. A. Sheldon and P. B. Brindley, in *The Chemistry of Peroxides*, S. Patai, Ed., Wiley, New York, 1983; R. A. Sheldon and J. K. Kochi, *Metal Catalysed Reactions of Organic Compounds*, Academic Press, New York, 1981; *Applied Industrial Catalysis*, Vol. 3, B. E. Leach, Ed., Academic Press, New York 1984; R. A. Sheldon, *Bull. Soc. Chem. Belg.*, 1985, **94,** 651; W. J. Mijs and C. R. H. I. de Jonge Eds., *Organic Syntheses by Oxidation with Metal Compounds*, Plenum Press, New York, 1986.

that are themselves oxidants, for example, Ce^{4+} or $Pb(O_2CMe)_4$; (*b*) metal or nonmetal species with M=O bonds such as CrO_3, OsO_4, NO_2, or PhIO[98a]; (*c*) metal species with peroxo groups $M(O_2)$ from H_2O_2 or O_2[98b]; (*d*) molecular oxygen. The problem with using O_2, the cheapest oxidant, is that oxidations are usually radical in nature and commonly nonselective while the problem with oxidations using metal oxidants is one of reoxidation to obtain a catalytic system.

28-19. Oxidative Carbonylations[99a]

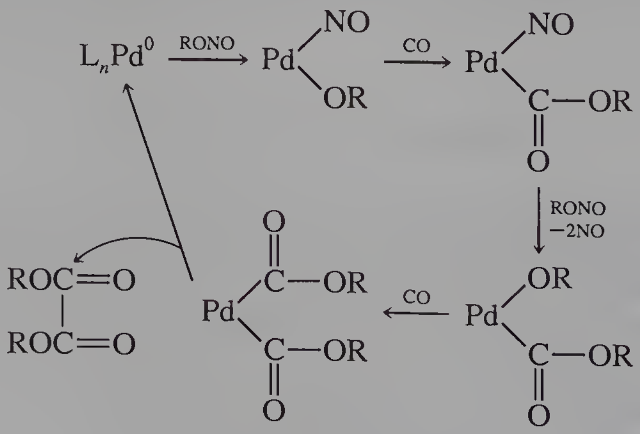
These are reactions involving CO, a substrate and an oxidizing agent. Probably the most important reaction is that used for oxalate ester synthesis; the ester can be used as a precursor for ethylene glycol.[99b]

There are both homogeneous and heterogeneous processes[99c] developed by Ube Chemical Co. The latter uses palladium on carbon with NO as the oxygen carrier in a two-step gas phase reaction at low pressure:

$$2NO + 2ROH + \tfrac{1}{2}O_2 = 2RONO + H_2O$$

$$2RONO + 2CO = (CO_2R)_2 + 2NO$$

The likely reaction cycle in homogeneous solution involves oxidative-addition of RONO and CO insertion with a final reductive-elimination of dialkyl oxalate as shown in Scheme 28-11.



Scheme 28-11

[98a] See, for example, M. J. Nappa and C. A. Tolman, *Inorg. Chem.*, 1985, **24**, 4711.

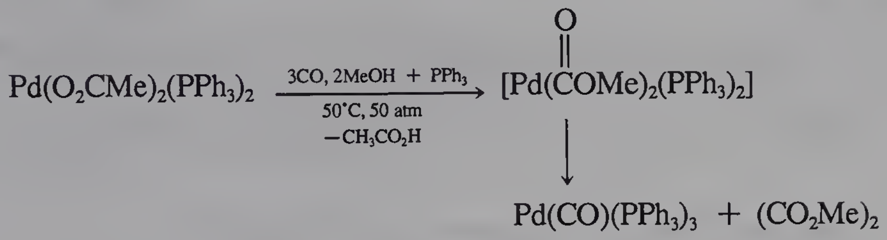
[98b] See H. Sugimoto and D. T. Sawyer, *J. Am. Chem. Soc.*, 1985, **107**, 5712.

[99a] See H. S. Kesling Jr., (A.C.S. Symp. Ser. No. 328) American Chemical Society, Washington, DC, 1987. See H. E. Bryndza *et al.*, *J. Chem. Soc. Chem. Commun.*, **1985**, 977.

[99b] D. L. King and J. H. Groto, *Chem. Tech.*, **1985**, 244.

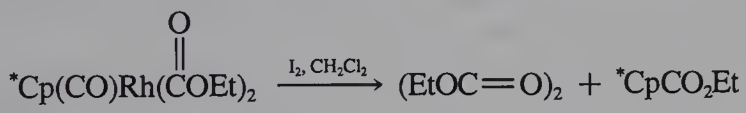
[99c] S. Uchiumi and M. Yamashita, *J. Jpn. Petr. Inst.*, 1982, **25**, 197.

Support has been provided by (*a*) study of the reaction



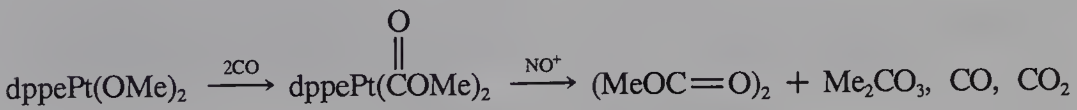
$$Pd(O_2CMe)_2(PPh_3)_2 \xrightarrow[\substack{50^\circ C,\ 50\ atm \\ -CH_3CO_2H}]{3CO,\ 2MeOH\ +\ PPh_3} [Pd(\overset{\overset{\Large O}{\|}}{C}OMe)_2(PPh_3)_2] \longrightarrow Pd(CO)(PPh_3)_3 + (CO_2Me)_2$$

(*b*) by stoichiometric oxidative coupling of a rhodium bis(alkoxycarbonyl) using I_2 as oxidant[100]



$$^*Cp(CO)Rh(\overset{\overset{\Large O}{\|}}{C}OEt)_2 \xrightarrow{I_2,\ CH_2Cl_2} (EtOC{=}O)_2 + {}^*CpCO_2Et$$

(*c*) by the sequence

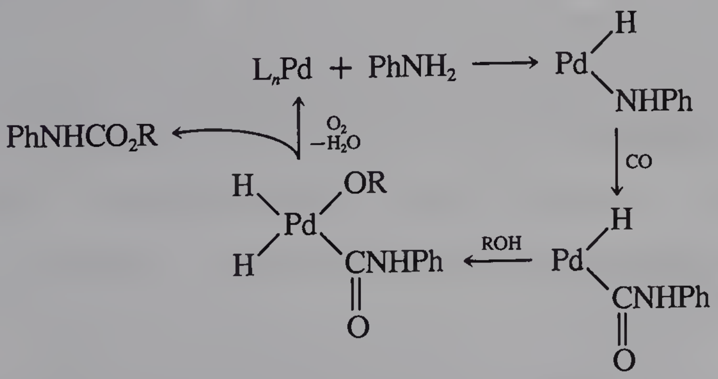


$$dppePt(OMe)_2 \xrightarrow{2CO} dppePt(\overset{\overset{\Large O}{\|}}{C}OMe)_2 \xrightarrow{NO^+} (MeOC{=}O)_2 + Me_2CO_3,\ CO,\ CO_2$$

The oxidative carbonylation of aniline (Asahi Chemical) produces alkylphenylcarbamate[101a]

$$PhNH_2 + CO + EtOH + \tfrac{1}{2}O_2 \xrightarrow[83\ atm]{165^\circ} PhNHCO_2Et + H_2O$$

but it is not clear whether the reaction is homogeneous since Pd black and NaI in EtOH convert aniline to ethylphenylcarbamate highly selectively. A possible sequence, Scheme 28-12, involves oxidative-addition of aniline. The reaction can be done at ambient temperature and pressure using $PdCl_2$ with



Scheme 28-12

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[100] P. L. Burk *et al.*, *Organometallics*, 1984, **3**, 493.

[101a] S. Fukuoka *et al.*, *Chem. Tech.*, **1984**, 670; see also S-I. Murahashi *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987**, 125.

$CuCl_2$ as reoxidant (see Wacker process later) in HCl [or using $Pd(O_2CMe)_2$ in acetic acid].[101b]

Finally, there are oxidative carbonylations employing di-*t*-butylperoxide and Cu–Pd catalysts for dimethylcarbonate synthesis.[101c]

$$2MeOH + (t\text{-}BuO)_2 + CO \longrightarrow O{=}C(OMe)_2 + 2t\text{-}BuOH$$

28-20. Palladium Catalyzed Oxidation of Ethylene[102]

In the last section palladium was used in "oxypalladation" reactions but the earliest catalytic use of palladium is the Wacker process, which linked together the previously known individual reactions

$$\begin{array}{rcl} C_2H_4 + PdCl_2 + H_2O & \longrightarrow & CH_3CHO + Pd + 2HCl \\ Pd + 2CuCl_2 & \longrightarrow & PdCl_2 + 2CuCl \\ 2CuCl + 2HCl + \frac{1}{2}O_2 & \longrightarrow & 2CuCl_2 + H_2O \\ \hline C_2H_4 + \frac{1}{2}O_2 & \longrightarrow & CH_3CHO \end{array}$$

The oxidation of ethylene by palladium(II)–copper(II) chloride solution is essentially quantitative and only low Pd concentrations are required; the process can proceed either in one stage or in two stages—in the latter case the reoxidation by O_2 is done separately.

Oxidation of alkenes of the type $RCH{=}CHR'$ or $RCH{=}CH_2$ gives ketones, for example, acetone from propene.

When media other than water are used, different but related processes operate. Thus in acetic acid ethylene gives vinyl acetate, whereas vinyl ethers may be formed in alcohols; there are usually competing reactions giving unwanted side products. There has been much industrial study of such processes, and both homogeneous and heterogeneous syntheses of vinyl acetate have been commercialized. The latter process (Hoechst) involves direct oxidation over a palladium–gold catalyst containing alkali acetate on a support:

$$C_2H_4 + CH_3CO_2H + \tfrac{1}{2}O_2 = CH_2{=}CHCO_2CH_3 + H_2O$$

In the reaction in aqueous solution containing chloride ion, the initial equilibria appear to be

$$[PdCl_4]^{2-} + C_2H_4 \rightleftharpoons [PdCl_3(C_2H_4)]^- + Cl^-$$

$$[PdCl_3(C_2H_4)]^- + H_2O \rightleftharpoons PdCl_2(H_2O)(C_2H_4) + Cl^-$$

[101b] H. Alper and F. W. Hartstock, *J. Chem. Soc. Chem. Commun.*, **1985,** 1141.

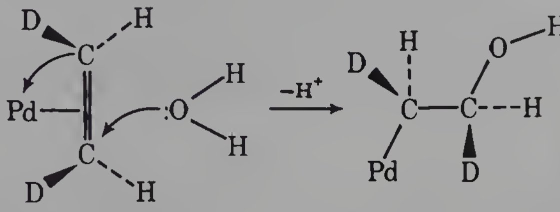
[101c] G. E. Morris *et al.*, *J. Chem. Soc. Chem. Commun.*, **1987,** 410, 411.

[102] J. Tsuji, *Synthesis,* 1984, 369; J. E. Bäckvall, *Angew. Chem. Int. Ed. Engl.*, 1983, **22,** 335; N. Gragor and P. M. Henry, *J. Am. Chem. Soc.*, 1981, **102,** 681.

There is *nucleophilic attack by external water* on the neutral complex $PdCl_2(H_2O)(C_2H_4)$

$$Cl_2(H_2O)Pd(C_2H_4) + H_2O \rightleftharpoons [Cl_2(H_2O)Pd{-}CH_2CH_2OH]^- + H^+$$

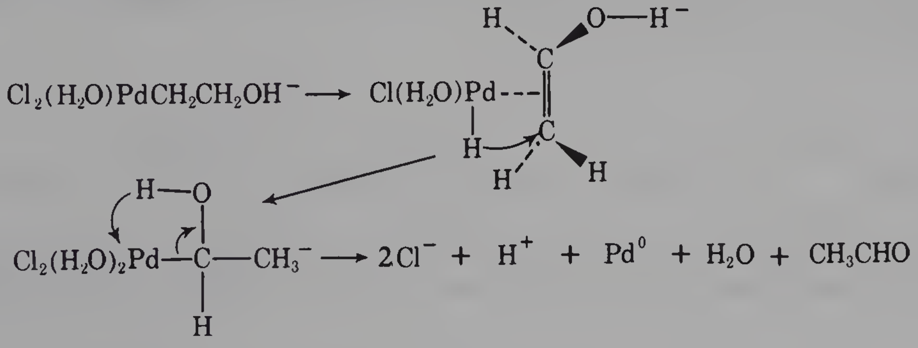
Deuteration studies show that the stereochemistry of the addition is trans, that is,



This reaction is then followed by the rate-determining step:

$$Cl_2(H_2O)Pd\text{-}CH_2CH_2OH + H_2O \rightleftharpoons Cl(H_2O)_2PdCH_2CH_2OH + Cl^-$$

The hydroxoalkyl then isomerizes by β-hydride transfers, finally eliminating acetaldehyde as follows:



Similar mechanisms can be written involving CH_3CO_2H and alcohols as nucleophiles in these media.

The mechanism for the oxidation of Pd metal by Cu^{II} chloro complexes is not well understood, but electron transfer via halide bridges is probably involved. The extremely rapid air oxidation of Cu^{I} chloro complexes is better known and probably proceeds through an initial oxygen complex,

$$CuCl_2^- + O_2 \rightleftharpoons ClCuO_2 + Cl^-$$

followed by formation of radicals such as O_2^-, OH, or HO_2,

$$ClCuO_2 + H_3O^+ \longrightarrow CuCl^+ + HO_2 + H_2O$$

As with Ziegler and Natta's discovery, recognition of the reactivity of palladium complexes has led to a deluge of patents and papers involving all manner of organic substances and types of reactions other than oxidations including additions, carbonylations, and polymerizations.[103]

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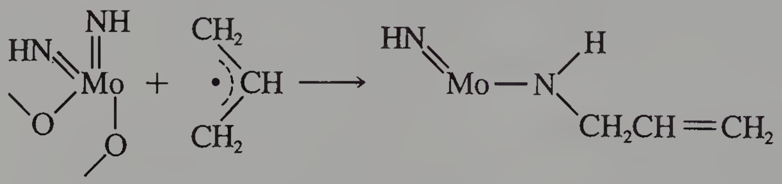
[103] See, for example, B. Trost and T. R. Verhoeven, *Comprehensive Organometallic Chemistry*, Vol. 8, Pergamon Press, Oxford, 1982, p. 799; B. Åkermark and K. Zetterberg, *J. Am. Chem. Soc.*, 1984, **106,** 5560.

28-21. Acrylonitrile Synthesis[104]

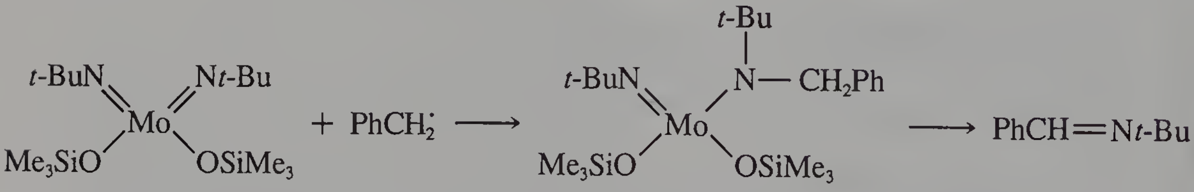
The ammonia–propylene oxidation catalyzed by Bi_2O_3—MoO_3 at 400°C is the main route to acrylonitrile

$$CH_2{=}CHCH_3 + NH_3 + \tfrac{3}{2}O_2 = CH_2{=}CHCN + 3H_2O$$

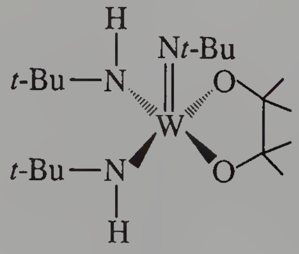
It appears that the rate-determining step is the formation of an allyl radical on the surface, which may migrate to the N atom of an imido group:



Compounds with diimido groups, for example, $Cr(Nt\text{-}Bu)_2(OSiMe_3)_2$ have been used in attempts[104] to develop models for the C—N bond formation using benzyl radicals (which behave similarly to allyl radicals) from toluene and benzoyl peroxide, for example,



Another model compound studied was the distorted *tbp* pinacolate (28-XX).



(28-XX)

Another direct oxidation is that of HCN to oxamide catalyzed by $Cu(NO_3)_2$ in acetic acid at 50 to 80° and 1 atm:

$$2HCN + \tfrac{1}{2}O_2 + H_2O \longrightarrow (CONH_2)_2$$

which provides a means of converting waste HCN to fertilizer. If the reaction is run in MeCN instead of $MeCO_2H$, cyanogen is formed, presumably because the Cu^I acetonitrile complex is less able to catalyze the hydration step.

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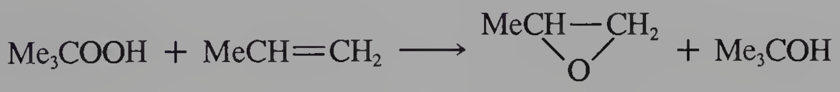
[104] D. M. T. Chan and W. A. Nugent, *Inorg. Chem.*, 1985, **24**, 1422; R. K. Grasselli, *J. Chem. Educ.*, 1986, **63**, 216.

28-22. Oxygen Transfers from Peroxo and Oxo Species

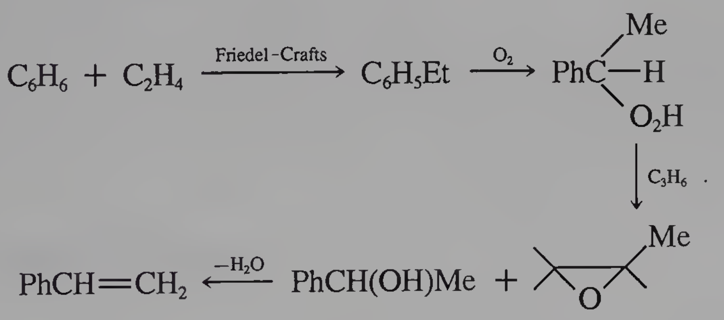
An important commercial oxidation using *t*-butylhydroperoxide (made by O_2 oxidation of isobutane) is the epoxidation of propylene using molybdate catalysts:

$$2Me_3CH + 1.5\,O_2 = Me_3COOH + Me_3COH$$

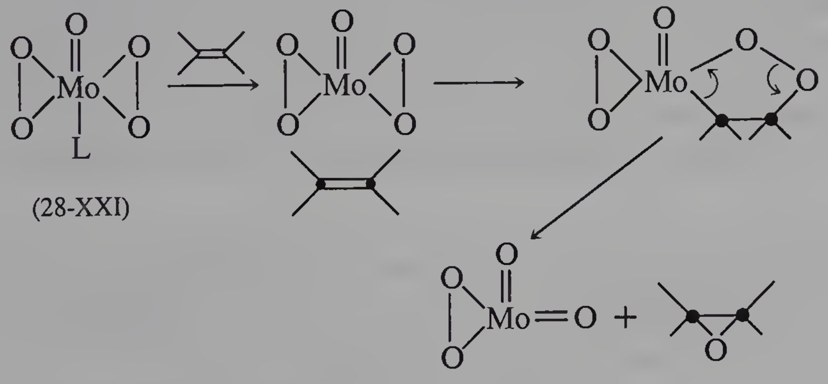


$$Me_3COOH + MeCH{=}CH_2 \longrightarrow \underset{\diagdown O \diagup}{MeCH{-}CH_2} + Me_3COH$$

Three times as much *t*-butanol as propylene oxide is produced, but this can be used to synthesize methacrylic acid (for methylmethacrylate polymers) and *t*-BuOMe as a gasoline supplement. Simultaneous production of propylene oxide and styrene is possible by the sequence



Peroxomolybdate species are involved in the reaction and the steps can be modeled using a well-characterized complex (28-XXI), where L = hexamethylphosphoramide. Similar vanadium complexes also oxidize various substrates probably via a radical mechanism.[105]



(28-XXI)

Another important application of *t*-BuO_2H is that using titanium alkoxides in diethyltartrate as chiral solvent, in the presence of molecular sieves to remove water (Sharpless oxidations), for the epoxidation of allylic alcohols.[106]

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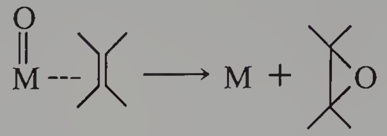
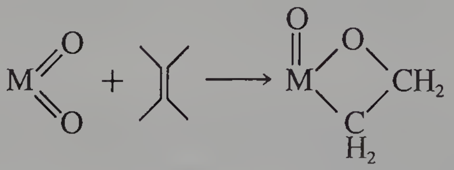
[105] R. D. Bach *et al., J. Am. Chem. Soc.*, 1984, **106**, 6098.

[106] K. B. Sharpless, *Chem. Br.*, **1986**, 38; *J. Org. Chem.* 1986, **51**, 1922; K. A. Jørgensen *et al., J. Am. Chem. Soc.*, 1987, **109**, 3240.

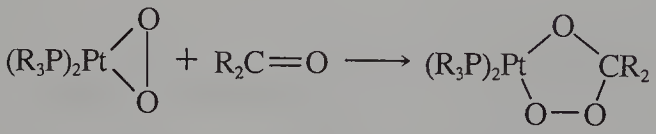
Epoxidations of alkenes is achieved *stoichiometrically* by a variety of metal complexes, such as FeCl(TPP) or [Cr $sal_2en]^+$, using PhIO or OCl^- as oxidants.[107] These reactions are believed to proceed via interactions of the types





where M═O bonds are formed by the oxidant. Similarly alkanes can be hydroxylated by iron and manganese porphyrins, for example, $Mn(CO_2Me)TPP$ + PhIO.[108a,b] Such systems have been much studied as models[108b] for cytochrome P_{450} (see Chapter 30).

Many metals that form η_2-O_2 species (Section 12-10) have also been studied[109a] for oxidations such as



as have μ peroxo species such as those of cobalt(III).[109b]

It is clear that in many of the oxidations, metal complexes with MOOH or MOOR groups are intermediates. A number of such compounds have been fully characterized [e.g., (28-XXI)] including those of platinum group metals such as $diphosPtCF_3(OOH)$, diphosPtH(OOR), and $(Ph_3P)_2PtPh(OOBu)$.[110]

The alkyl peroxo species are formed by initial O_2 insertion into M—C bonds, although sometimes cleavage may occur as in the reaction[111]

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[107] K. A. Jørgenson, *J. Am. Chem. Soc.*, 1987, **109,** 698; K. S. Suslik *et al., J. Am. Chem. Soc.*, 1987, **109,** 2818; Y. Misrakami *et al., J. Am. Chem. Soc.*, 1985, **107,** 6415; J. K. Kochi *et al., J. Am. Chem. Soc.*, 1986, **108,** 2309; C. L. Hill *et al., Inorg. Chem.*, 1987, **26,** 1602; D. Mansuy *et al., Nouv. J. Chim.*, 1985, **9,** 771; J. P. Collman *et al., J. Am. Chem. Soc.*, 1986, **108,** 2588; J. S. Valentine *et al., J. Am. Chem. Soc.*, 1986, **108,** 5006.

[108a] T. C. Bruice *et al., J. Am. Chem. Soc.*, 1987, **109,** 3428; D. Mansuy *et al., J. Chem. Soc. Chem. Commun.*, **1986,** 341.

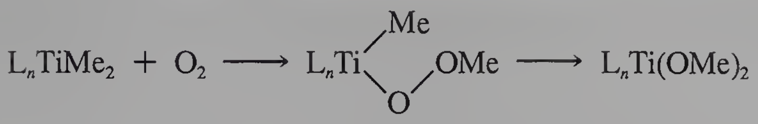
[108b] J. T. Groves *et al., J. Am. Chem. Soc.*, 1986, **108,** 3837.

[109a] R. Ugo *et al., J. Am. Chem. Soc.*, 1980, **102,** 3745; M. Kubota *et al., J. Am. Chem. Soc.*, 1985, **107,** 4558.

[109b] S. A. Bedell and A. E. Martell, *J. Am. Chem. Soc.*, 1985, **107,** 7907; G. Read and M. Urgelles, *J. Chem. Soc. Dalton Trans.*, **1986,** 1383.

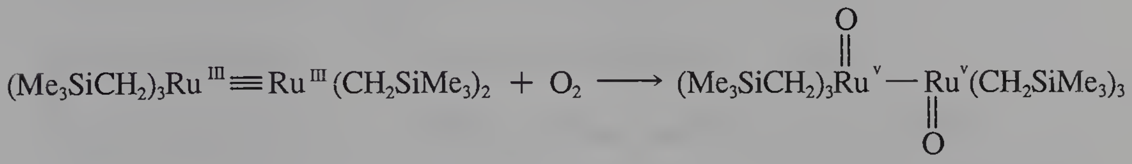
[110] L. Randaccio *et al., Inorg. Chem.*, 1983, **22,** 3706; G. Strukul and R. A. Michelin, *J. Am. Chem. Soc.*, 1985, **107,** 7563; R. S. Drago *et al., J. Am. Chem. Soc.*, 1985, **107,** 2898; E. P. Talsi *et al., J. Chem. Soc. Chem. Commun.*, **1985,** 1768.

[111] T. V. Lubben and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1985, **107,** 701.



$$L_nTiMe_2 + O_2 \longrightarrow L_nTi(Me)(O{-}OMe) \longrightarrow L_nTi(OMe)_2$$

Direct cleavage of the O—O bonds of oxygen to give M=O species that can epoxidize alkenes has been established in the reaction:[112]



$$(Me_3SiCH_2)_3Ru^{III}{\equiv}Ru^{III}(CH_2SiMe_3)_3 + O_2 \longrightarrow (Me_3SiCH_2)_3Ru^{V}(=O){-}Ru^{V}(=O)(CH_2SiMe_3)_3$$

Porphyrin or phenanthroline complexes of Ru^{VI} will catalytically epoxidize olefins.[113]

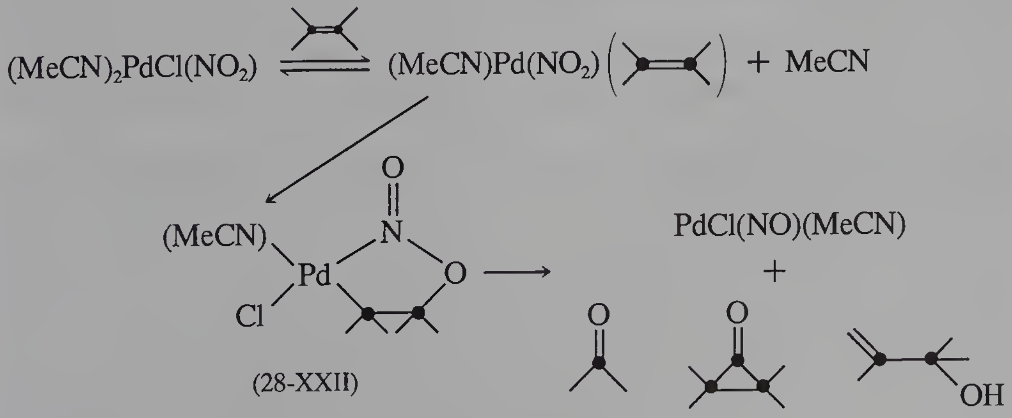
28-23. Oxygen Transfers from NO_2 Groups

Oxidations can be catalyzed by nitro compounds of cobalt, rhodium, and other metals in which oxyen atoms are transferred to a substrate and $M—NO_2$ is reduced to M—NO,[114a,b] for example,

$$trans\text{-}Ni(NO_2)_2(PEt_3)_2 + CO \longrightarrow Ni(NO_2)(NO)(PEt_3)_2 + CO_2$$

$$Ru(NO_2)_2(CO)_2(PPh_3)_2 + PPh_3 \longrightarrow Ru(NO)_2(PPh_3)_2 + CO_2 + CO + Ph_3PO$$

More interesting, however, are those where an oxygen atom is transferred to alkenes, RNC, CS_2, and so on. For the complex $PdCl(NO_2)(MeCN)_2$[114b] the metallacyclic intermediate (28-XXII) was isolated when the alkene was norbornadiene.



(28-XXII)

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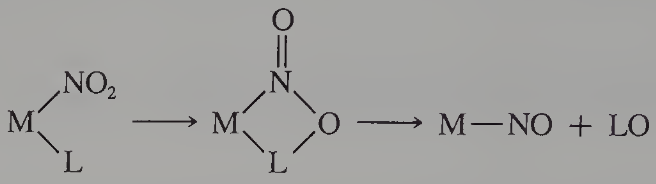
[112] G. Wilkinson *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 2711.

[113] C. L. Bailey and R. S. Drago, *J. Chem. Soc. Chem. Commun.*, **1987**, 179.

[114a] R. D. Feltham *et al.*, *Inorg. Chem.*, 1983, **22**, 3318; F. Mares *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 3545.

[114b] B. L. Feringa, *J. Chem. Soc. Chem. Commun.*, **1986**, 909; J. E. Bäckvall and A. Heumann, *J. Am. Chem. Soc.*, 1986, **108**, 7107.

In other oxidations, metallacycles may be formed, but other mechanisms are possible.[114b]



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Chapter Twenty Nine

Reaction Mechanisms of Transition Metal Complexes

29-1. Introduction

Processes in which complexes undergo ligand exchange, oxidation, reduction, or rearrangement of the coordination sphere are the bases for the chemical properties of all the metallic elements. A delineation of the mechanisms by which these processes occur is therefore vital to a full understanding and interpretation of the chemistry of complexes. However, the design and interpretation of experiments capable of providing mechanistic information is a very difficult and subtle task, and not all interesting reactions make good subjects for kinetic and mechanistic study. One of the important criteria in choosing reactions for kinetic study is that they have rates convenient for measurement by the available techniques.

Whether a reaction has a rate convenient for measurement depends on what type of technique can be applied. The techniques can be classified into three broad categories; reaction rates for which they are generally used are indicated by the half-times:

1. Static methods ($t_{1/2} \geqslant 1$ min).
2. Flow or rapid-mixing techniques (1 min $\geqslant t_{1/2} \geqslant 10^{-3}$ s).
3. Relaxation methods ($t_{1/2} \leqslant 10^{-1}$ s).

The static methods are the classical ones in which reactants are mixed simply by pouring them both into one vessel, and the progress of the reaction is followed by observation of the time variation of some physical or chemical observable (e.g., light absorption, gas evolution, pH, isotopic exchange). Flow and rapid mixing techniques differ mainly in achieving rapid mixing (in $\sim 10^{-3}$ s) of the reactants but use many of the same observational techniques as in static measurements. Relaxation methods depend on either (*a*) creating a single disturbance in a state of equilibrium in a very short period of time (usually by a temperature or pressure jump) and following the process of relaxation to an equililbrium state by a combination of spectrophotometric and fast electronic recording devices, or (*b*) continuous disturbances by ultrasonic waves or radiofrequency signals in the presence of a magnetic field (i.e., nmr). The latter methods are capable of following the very fastest reactions, and in many cases rate constants up to the limit ($\sim 10^{10}\ s^{-1}$) set by diffusion processes have been measured by ultrasonic methods.

It should be noted that nmr has the unique capability of following certain processes in which there is no net chemical or physical change, provided they involve the passage of observable nuclei among two or more sites in each of which their chemical shift is different. In this way certain rapid intramolecular rearrangements can be studied that would otherwise not even be seen.

The *direct* result of a kinetic study can at best be a *rate law,* that is, an equation showing how the velocity v of a reaction at a given temperature and pressure and in a given medium varies as a function of the concentration of the reactants. Certain constants, k_i, called *rate constants,* will appear in the rate law. For example, a rate law for the reaction

$$A + B = C + D$$

might be

$$v = k_a[A] + k_{ab}[A][B] + k'_{ab}[A][B][H^+]^{-1}$$

This would mean that the reaction occurs by three detectable paths, one influenced only by [A], a second influenced by [A] and [B], and a third that depends also on pH. The third term shows that not only A and B, but also $[OH^-]$ (since this is related inversely to $[H^+]$), participates in the activated complex when this path is followed.

The ultimate purpose of a rate and mechanism study is usually to *interpret* the rate law correctly so as to determine the correct *mechanism* for the reaction. By "mechanism," we mean a specification of what species actually combine to produce activated complexes, and what steps occur before and/or after the formation of the activated complex.*

Another preliminary point to be stressed is the difference between the kinetic and thermodynamic properties (especially "stability" in the loose sense) of a complex. The ability of a particular complex to engage in reactions that result in replacing one or more ligands in its coordination sphere by others is called its *lability.* Those complexes for which reactions of this type are very rapid are called *labile,* whereas those for which such reactions proceed only slowly or not at all are called *inert.* It is important to emphasize that these two terms refer to rates of reactions and should not be confused with the terms "stable" and "unstable," which refer to the thermodynamic tendency of species to exist under equilibrium conditions. A simple example of this distinction is provided by the $[Co(NH_3)_6]^{3+}$ ion, which will persist for days in an acid medium because of its kinetic inertness or lack of lability even though it is thermodynamically unstable, as the following equilibrium constant shows:

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ = [Co(H_2O)_6]^{3+} + 6NH_4^+ \qquad K \sim 10^{25}$$

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*We assume that the reader is familiar with the basic concepts of chemical kinetics as taught, for example, in undergraduate physical chemistry courses.

In contrast, the stability of $[Ni(CN)_4]^{2-}$ is extremely high,

$$[Ni(CN)_4]^{2-} = Ni^{2+} + 4CN^- \qquad K \sim 10^{-22}$$

but the rate of exchange of CN^- ions with isotopically labeled CN^- added to the solution is immeasurably fast by ordinary techniques. Of course this lack of any necessary relation between thermodynamic stability and kinetic lability is to be found generally in chemistry, but its appreciation here is especially important.

Although the use of nonaqueous media is mandatory for reactions of metal carbonyls (Section 29-8), water is by far the commonest solvent for most coordination chemistry and studies of kinetics and mechanisms are also carried out in that solvent. However, in recent years there have been a number of kinetic studies employing other media (DMSO, DMF, etc.) since data so obtained can, indirectly, elucidate the behavior in aqueous media, as well as having intrinsic interest.[1] We shall restrict the discussion here to aqueous media, however.

This chapter mainly emphasizes the processes occurring in the more classical types of complexes as they are formed and react in aqueous solution or in similarly polar solvents. However, we shall also devote attention to some mechanistic problems peculiar to the metal carbonyls, and we discuss in some detail the types of intermolecular rearrangement involved in the phenomena known variously as stereochemical nonrigidity, fluxionality, polytopal rearrangement, and ligand scrambling.

LIGAND REPLACEMENT REACTIONS

29-2. Classification of Mechanisms

Three basic classes of mechanism are generally considered, as illustrated in the following equations:

$$M-X \rightleftharpoons [M + X] \xrightarrow{Y} M-Y \qquad \textit{Dissociative}\,(D) \quad (29\text{-}1)$$

$$M-X + Y \rightleftharpoons \left[M\begin{matrix}<X\\<Y\end{matrix}\right] \longrightarrow M-Y + X \qquad \textit{Associative}\,(A) \quad (29\text{-}2)$$

$$M-X + Y \rightleftharpoons M-X\cdots Y \rightleftharpoons M-Y\cdots X \longrightarrow M-Y + X \qquad \textit{Interchange}\,(I) \quad (29\text{-}3)$$

The I mechanism entails a concerted exchange of X and Y between the inner and outer coordination shells of the metal atom. However, there are two

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[1] A. E. Merbach *et al.*, *Inorg. Chem.*, 1984, **23**, 4341.

subclasses of interchange mechanism, I_a and I_d, depending on the relative importance of incipient M—Y bond formation and M—X bond breaking, as discussed later.

D Mechanism. This can be difficult to identify unambiguously since a rate dependence on Y may be observed even though M—X bond breaking is the essential mechanistic step. To see how this might happen, consider the reaction shown in eq. 29-4.

$$ML_6 + L' \longrightarrow ML_5L' + L \qquad (29\text{-}4)$$

If it occurs by a D mechanism there is a transient intermediate (ML_5). This intermediate is assumed to live long enough to be able to discriminate between potential ligands in its vicinity, including the one just lost (L), the new one (L′), and also solvent molecules (S). The rate need *not* be independent of [L′] even though M—L dissociation is complete before M—L′ bond formation, since at very low [L′] there will be competition by L and L′ for the intermediate and only at high [L′] will the rate be the same regardless of the identity or concentration of L′.

To see the basis for the last statement, we write out the steps explicitly:

$$ML_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5 + L \qquad (29\text{-}5a)$$

$$ML_5 + L' \xrightarrow{k_2} ML_5L' \qquad (29\text{-}5b)$$

By employing the well-known steady state approximation for [ML_5], we obtain for the rate law:

$$R = \frac{k_1k_2[ML_6][L']}{k_{-1} + k_2[L']} \qquad (29\text{-}6a)$$

The rate clearly depends in general on [L′] as well as on [ML_6], but when [L′] becomes very large k_{-1} becomes negligible compared to $k_2[L']$, and $k_2[L']$ may be canceled from the numerator and denominator, leaving

$$R_{[L']\to\infty} = k_1[ML_6] \qquad (29\text{-}6b)$$

I_d Mechanism. This is the dissociative interchange mechanism. The transition state involves considerable extension of an M—L bond (but not its complete rupture), together with some incipient interaction with the incoming ligand L′. This incipient interaction can be described as a kind of weak complex ML_6,L′, which positions the new ligand L′ to enter the (first) coordination sphere immediately on the departure of L. We may represent this by the scheme in eq. 29-7.

$$ML_6 + L' \xrightarrow{K} ML_6,L' \xrightarrow{k} [L_5M \cdots L,L']^{\ddagger} \longrightarrow ML_5L' + L \qquad (29\text{-}7)$$

The species ML_6,L′ is called an *outer-sphere complex* or, if ML_6 is a cation and L′ an anion, an *ion pair.*

I_a Mechanism. This is the associative interchange mechanism. Again, there is interchange of ligands between the inner and next-nearest coordination spheres, but here the interaction between M and L′ is much more advanced in the transition state; $M \cdots L'$ bonding is important in defining the activated complex.

A Mechanism. In this extreme there is a fully formed intermediate complex ML_6L', which then dissociates.

In the real world there are processes whose mechanisms define a continuous gradation from D through increasingly associated interchanges to A. In any given real case it is difficult and often futile to try to give an exact description; the experimental criteria are seldom if ever definitive. The experimental data that do provide the best clues to the mechanistic type for a reaction are the following.

Rate Law. A first-order rate law is sometimes indicative of a unimolecular (dissociative) reaction and a second-order rate law indicative of a bimolecular (associative) reaction, but the use of such evidence requires great caution. We have already seen (eqs. 29-5 and 29-6) that the rate of a purely dissociative process may show a dependence on [L′]. For I_d processes such a dependence is always expected. The rate law for the process represented in eq. 29-7 must be eq. 29-8 because of the rapid preequililbrium formation of the outer-sphere complex ML_6,L'.

$$R = Kk[ML_6][L'] \tag{29-8}$$

A second and very common situation is solvent participation. That is, there may be a "hidden" step in which solvent, especially an excellent nucleophile like water, present at a concentration of ~55 *M*, participates:

$$ML_6 + H_2O \longrightarrow ML_5(H_2O) + L \qquad \text{Slow} \tag{29-9a}$$

$$ML_5(H_2O) + L' \longrightarrow ML_5L' + H_2O \qquad \text{Fast} \tag{29-9b}$$

The rate law might show *no* dependence on L′, but the process by which the first step proceeds could still be a highly *associative* one.

We may also mention here the process of conjugate base formation. Whenever a rate law containing the factor [OH^-] is found, there is a question whether OH^- actually attacks the metal atom in a genuinely associative-type mechanism or whether it appears in the rate law because it rapidly deprotonates a ligand forming a conjugate base (CB) which then reacts as in the sequence of eqs. 29-10.

$$[Co(NH_3)_5Cl]^{2+} + OH^- = [Co(NH_3)_4(NH_2)Cl]^+ + H_2O \qquad \text{Fast} \tag{29-10a}$$

$$[Co(NH_3)_4(NH_2)Cl]^+ \xrightarrow[\text{then } H^+]{+Y^-} [Co(NH_3)_5Y]^{2+} + Cl^- \qquad \text{Slow} \tag{29-10b}$$

In summary, rate laws must be interpreted with extreme caution.

Activation Parameters. By studying a reaction over a temperature range, one can evaluate the enthalpy and entropy changes required to form the activated complex, $\Delta H^\ddagger$ and $\Delta S^\ddagger$. A more difficult but increasingly common experiment[2,3] is to measure the rate as a function of pressure and from the equation $(\partial \ln k/\partial P)_T = \Delta V^\ddagger/RT$ determine the volume of activation $\Delta V^\ddagger$. These three quantities $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger$ can be valuable guides to visualizing the transition state, but they too must be used judiciously. For example, a reaction with large positive values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ and a positive $\Delta V^\ddagger$ can scarcely be other than dissociative, but things are not often so one sided, as will be seen later.

Other Criteria. The many other data that are sometimes helpful include the dependence of rate on ionic strength and on solvent composition.. The latter approach, however, often creates more problems than it solves. Careful measurement of trends in rates and activation parameters during variance of the incoming ligand L′ or observation of the properties (e.g., steric hindrance) of the nonreplaceable ligands can sometimes be informative.

29-3. Water Exchange Rates

With the powerful techniques now available to measure very fast reaction rates, it has been possible to accumulate data on the rates of exchange of coordinated water with bulk water for nearly all known aqua ions. Similar solvent exchange rates have been measured for a number of cations in other solvents such as DMSO and DMF. For the important aqueous systems, the results are summarized in Fig. 29-1. The challenge of explaining these rates, which cover about 15 orders of magnitude [not to mention $Rh(H_2O)_6^{3+}$ and $Ir(H_2O)_6^{3+}$ where the rates are 1 to 3 orders slower than those plotted] has attracted many workers.

For the alkali and alkaline earth ions, it appears that a mechanism of the D or I_d type holds throughout. Within each group the rate of exchange increases with size, and for M^+ and M^{2+} ions of similar size, the one of lower charge exchanges more rapidly. Since M—OH_2 bond strength should increase with charge and decrease with the size of the metal ion, these correlations suggest that the transition state for the exchange reaction is attained by breaking an existing M—OH_2 bond to a much greater extent than a new one is formed. For sets such as (Al^{3+}, Ga^{3+}, In^{3+}), (Sc^{3+}, Y^{3+}), and (Zn^{2+}, Cd^{2+}, Hg^{2+}) a predominantly dissociative mechanism also seems secure.

With the transition metal ions, however, the picture is confused. Until relatively recently it was generally agreed that the mechanism was essentially dissociative throughout and the failure of the rates to display smooth variations as a function of radius within the +2 and +3 groups seemed to be explainable

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[2] R. van Eldik, Ed., *Inorganic High Pressure Chemistry, Kinetics and Mechanisms,* Elsevier, Amsterdam, 1986.

[3] R. van Eldik, *Angew. Chem. Int. Ed. Engl.,* 1986, **25,** 673; S. Suvachittanont, *J. Chem. Educ.,* 1983, **60,** 150; D. A. Palmer and H. Kelm, *Coord. Chem. Rev.,* 1981, **36,** 89; A. E. Merbach, *Pure Appl. Chem.,* 1982, **54,** 1479.

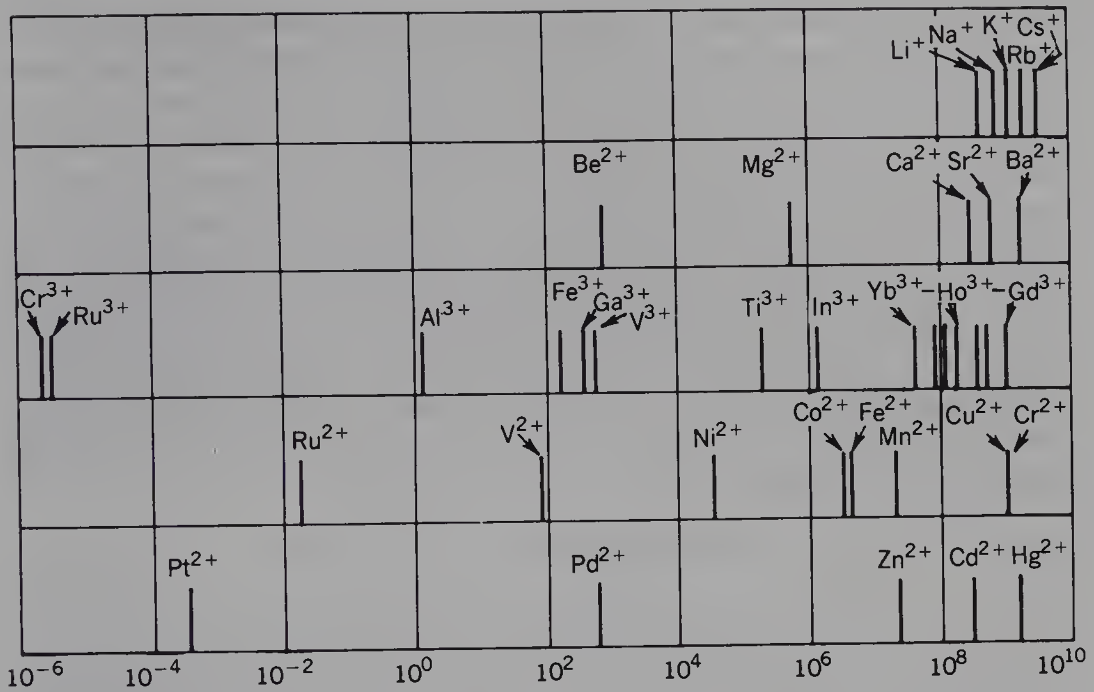

FIG. 29-1. Characteristic rate constants (s^{-1}) for substitution of inner-sphere water molecules on various metal ions (Adapted from M. Eigen, *Pure Appl. Chem.*, 1963, **6,** 105 with addition of data from other sources.)

by invoking variations in ligand field stabilization energies and, for Cr^{2+} and Cu^{2+}, dynamic Jahn–Teller effects. More recently, measurements of $\Delta V^{\ddagger}$ have given rise to controversy. For the water exchange reaction for M^{2+} ions of the first transition series, the measured volumes of activation are positive for Fe^{2+}, Co^{2+}, and Ni^{2+}, but negative for V^{2+} and Mn^{2+}, whereas a dissociative mechanism would be expected to lead always to $\Delta V^{\ddagger} > 0$. However, it may (or may not) be too naive to consider that only the sign of $\Delta V^{\ddagger}$ is needed to diagnose a mechanism, since the net, measured value is made up of several contributions, which may differ in sign.[4] At this stage, the mechanistic question is undecided for some ions, although a dissociative process doubtless occurs in many cases.

29-4. Formation of Complexes from Aqua Ions

Extensive studies of the rates at which an aqua ion combines with a ligand to form a complex have revealed the following general rules:

1. The rates for a given ion show little or no dependence (less than a factor of 10) on the identity of the ligand.
2. The rates for each ion are practically the same as the rate of water exchange for that ion, usually ≤ 10 times slower.

A reasonable explanation for these observations is that the formation re-

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[4] K. E. Newman and K. M. Adamson-Sharpe, *Inorg. Chem.*, 1984, **23**, 3818.

actions proceed in two steps, the first being formation of the aqua ion–ligand outer-sphere complex, followed by elimination of H_2O from the aqua ion in the same manner as in the water-exchange process for that same metal aqua ion. Thus, from a study of volumes of activation for the formation of bipy and terpy complexes of Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}, a gradual changeover from an I_a to an I_d mechanism (as for water exchange) is indicated.[5] In the cases of Co^{2+} and Ni^{2+}, the mechanism is presumably that described by eq. 29-7, with $L = H_2O$ and L' representing bipy or another incoming ligand.

The rate law for this process would be that of eq. 29-11a. Under the usual experimental conditions $[L']$ is small and K is usually small, and the experimental rate law will appear to be that of eq. 29-11b with an apparent second-order rate constant k_{app}, which is really the product of K and the true dissociative interchange constant k.

$$R = \frac{Kk[M(H_2O)_6][L']}{1 + K[L']} \qquad (29\text{-}11a)$$

$$R = k_{app}[M(H_2O)_6][L'] = Kk[M(H_2O)_6][L'] \qquad (29\text{-}11b)$$

When the outer-sphere association constant K has been measured or estimated, k can be determined as k_{app}/K. The resulting values of k are usually very similar to the water-exchange rate constant for the $M(H_2O)_6^{n+}$ ion; the activation enthalpies and entropies are also essentially the same. Thus once the outer-sphere complex $M(H_2O)_6,L'$ has been formed, a dissociative loss of one H_2O is the rate-controlling step, just as with the water-exchange process. As an illustration, the value of k_{app} for the formation of $Ni(CH_3PO_3)^+$ is 2.9×10^5 M^{-1} s^{-1}, and the outer-sphere association constant K has an estimated value of 40 M^{-1}; from these one obtains $k = 7 \times 10^3$ s^{-1}. A direct measurement by ultrasonic relaxation gave 15×10^3 s^{-1}. These values of k may be compared to the rate constant for water exchange k_{ex}, which is 30×10^3 s^{-1}. It is not unreasonable that k_{ex} should be 2 to 4 times greater than k for the complex, since there is a statistical factor favoring the presence of an outer-sphere water molecule in the right place to move in as an inner-sphere water molecule leaves.

Anation Reactions. It appears that ligand displacement reactions (eq. 29-12) rarely proceed directly. Instead, especially in aqueous solution, X is first replaced by H_2O; then Y attacks the aqua complex (eq. 29-13) in a reaction called an anation reaction. Although these reactions resemble the processes of forming complexes from aqua ions in the sense that a ligand replaces H_2O in the first coordination sphere, they cannot necessarily be assumed to have similar mechanisms. Indeed, the varying character of the other n ligands L may well cause great variations in mechanism. Anation reactions have proved

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[5] R. Mohr and R. van Eldik, *Inorg. Chem.*, 1985, **24**, 3396.

difficult to elucidate for a number of reasons—for example, the formation of ion pairs (outer-sphere complexes).

$$[L_nMX] + Y \longrightarrow [L_nMY] + X \qquad (29\text{-}12)$$

$$[L_nM(H_2O)] + Y \longrightarrow [L_nMY] + H_2O \qquad (29\text{-}13)$$

To avoid the ion-pairing problem, an anionic complex such as $[Co(CN)_5(H_2O)]^{2-}$ may be used. Studies of anations of this ion have shown that the mechanisms all involve a rate-determining I_d step that is essentially at the pure D limit (eq. 29-14a), giving an intermediate $Co(CN)_5^{2-}$ ion having a long enough lifetime to discriminate between various ligands present in the solution.

$$Co(CN)_5H_2O^{2-} = Co(CN)_5^{2-} + H_2O \qquad (29\text{-}14a)$$

$$Co(CN)_5^{2-} + X^- = Co(CN)_5X^{3-} \qquad (29\text{-}14b)$$

Volumes of activation have provided evidence in favor of I_d or I_a mechanisms in other cases, despite possible complications from ion pairing that might occur in a preliminary step. The following results were reported for several reactions:

$$[Co(NH_3)_5(H_2O)]^{3+} + Cl^- \longrightarrow [Co(NH_3)_5Cl]^{2+} + H_2O$$
$$\Delta V^\ddagger = 1.4 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$$

$$[Co(NH_3)_5(H_2O)]^{3+} + SO_4^{2-} \longrightarrow [Co(NH_3)_5SO_4]^+ + H_2O$$
$$\Delta V^\ddagger = 2.3 \pm 1.8 \text{ cm}^3 \text{ mol}^{-1}$$

$$[Rh(NH_3)_5(H_2O)]^{3+} + Cl^- \longrightarrow [Rh(NH_3)_5Cl]^{2+} + H_2O$$
$$\Delta V^\ddagger = 3.0 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$$

$$[Cr(NH_3)_5(H_2O)]^{3+} + NCS^- \longrightarrow [Cr(NH_3)_5NCS]^{2+} + H_2O$$
$$\Delta V^\ddagger = -4.9 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$$

The first three small positive $\Delta V^\ddagger$ values are consistent with an I_d mechanism when compared with the value of 1.2 ± 0.2 cm^3 mol^{-1} for the water-exchange reaction of $[Co(NH_3)_5(H_2O)]^{3+}$, where an I_d mechanism is indicated by much other evidence. The negative $\Delta V^\ddagger$ for the chromium complex suggests an I_a mechanism in that case.

29-5. Aquation and Base Hydrolysis

The replacement of a ligand by H_2O is called *aquation,* as illustrated in eq. 29-15 for a pentammine cobalt(III) complex.

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^- \qquad (29\text{-}15)$$

The rates of such reactions are pH dependent and generally follow the rate law

$$v = k_A[L_5CoX] + k_B[L_5CoX][OH^-] \qquad (29\text{-}16)$$

In general, k_B (for *base hydrolysis*) is some 10^4 times k_A (for *acid hydrolysis*).

Acid Hydrolysis. Since the entering ligand is H_2O, present in high ($\sim 55.5M$) and essentially constant concentration, the first term in eq. 28-16 tells us nothing about how H_2O participates in forming the transition state. To obtain information on whether the process is associative or dissociative is difficult and requires indirect approaches. A few examples of the type of study used, and the conclusions implied (but *not* proved) are the following:

1. The variation of rates with the identity of X correlates well with the variation in thermodynamic stability of the complexes. This indicates that breaking the Co—X bond is important in reaching the transition state.

2. In a series of complexes where X is a carboxylate ion, there is not only the correlation of higher rates with lower basicity of the RCO_2^- group, but an *absence* of any slowing down due to increased size of R, after due allowance for the basicity effect. For an I_d mechanism, increased size of R should decrease the rate, at least if the attack were on the same side as X, although an attack on the *opposite* side is not excluded by these data.

3. For an extreme D mechanism the five-coordinate intermediate $Co(NH_3)_5^{3+}$ would be generated, and its behavior would be independent of its source. When the ions Hg^{2+}, Ag^+, and Tl^{3+} were used to assist in removal of Cl^-, Br^-, and I^- because of their high affinity for these halide ions, the ratio $H_2{}^{18}O/H_2{}^{16}O$ in the product was studied. For a genuine $Co(NH_3)_5^{3+}$ intermediate this ratio should be >1 and constant regardless of the identity of X. When the assisting cation was Hg^{2+} the ratio 1.012 was observed for all three $[Co(NH_3)_5X]^{3+}$ ions, indicating the existence of $Co(NH_3)_5^{3+}$ as an intermediate. However, with Ag^+ the ratio varied (1.009, 1.007, and 1.010) indicating that $Co(NH_3)_5^{3+}$ does not have a completely independent existence in this case. For Tl^{3+} the ratios were 0.996, 0.993, and 1.003, showing considerable deviation from a pure D mechanism. In these experiments there is, however, the question of whether the entering water molecule in the assisted aquations comes from the bulk of the solvent or from the coordination sphere of the assisting metal ion. Thus like many another mechanistic study, this one is tricky to interpret.

4. A means of generating $Co(NH_3)_5^{3+}$ has been found by using the reaction 29-17, where azide is the sixth ligand:

$$[Co(NH_3)_5N_3]^{2+} + HNO_2 = [Co(NH_3)_5N_3NO]^{3+} + OH^-$$
$$= Co(NH_3)_5^{3+} + N_2 + N_2O \qquad (29\text{-}17)$$

The relative rates of reaction of this with various anions (e.g., Cl^-, Br^-, SCN^-, F^-, HSO_4^-, and $H_2PO_4^-$) and with H_2O were studied. The agreement between these results and those in the reaction 29-18:

$$Co(NH_3)_5(H_2O)^{3+} + X^- = Co(NH_3)_5X^{2+} + H_2O \qquad (29\text{-}18)$$

was close, thus indicating that 29-18 also involves the intermediate $Co(NH_3)_5^{3+}$ or something of similar reactivity. By the principle of microscopic reversibility, this intermediate must also participate in the reverse of 29-18, that is, in the hydrolysis reaction itself. However, other experiments are considered to show that the usual aquation reactions (e.g., that of $[Co(NH_3)_5NO_3]^{2+}$) *cannot* proceed through the same intermediate as that generated by oxidation of $[Co(NH_3)_5N_3]^{2+}$.

For the reaction 29-19, where L—L represents a bidentate amine, it has been found that the rate is increased by increasing bulk of the ligands, a result not in agreement with an I_a mechanism but consistent with an I_d mechanism.

$$[Co(L\text{—}L)_2Cl_2]^+ + H_2O = [Co(L\text{—}L)_2Cl(H_2O)]^{2+} + Cl^- \qquad (29\text{-}19)$$

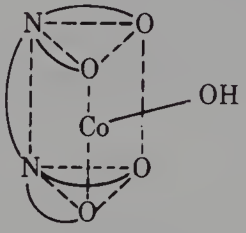
Another class of hydrolyses that have been extensively studied are those of *trans*-Co^{III} en_2AX species, in which the leaving group is X^-. The variation in rates and stereochemistry (cis or trans) of products as functions of the nature of A have been examined, and certain informative correlations established. When A is NH_3 or NO_2^- the data indicate that the mechanism is I_a, whereas for A = OH^-, Cl^-, N_3^-, and NCS^- an I_d mechanism is postulated. The assignments of mechanism in these cases depend heavily on detailed consideration of the stereochemical possibilities for the intermediates or activated complexes; thus they are indirect though apparently reliable.

Base Hydrolysis. Interpretation of the term $k_B[L_5CoX][OH^-]$ in eq.29-16 is not unequivocal. The "obvious" inference that there is an A mechanism, with OH^- making a nucleophilic attack on the metal atom, is not generally favored because it would require postulating that OH^- is a uniquely effective nucleophile, and there is no evidence for this.

As an alternative, a dissociative conjugate base (see Section 29-2) mechanism, D-CB, is generally preferred. The validity of a D-CB mechanism can be examined in terms of three aspects of the overall process: (1) the acid–base behavior of the reacting complex, (2) the structure of the five-coordinate intermediate, (3) the ability of the amido or hydroxo group, which results from deprotonation of an amino or H_2O ligand, to stabilize such an intermediate.

The D-CB mechanism, of course, requires that the reacting complex have at least one protonic hydrogen atom on a nonleaving ligand and that the rate of reaction of this hydrogen be fast compared to the rate of ligand displacement. It has been found that the rates of proton exchange in many complexes subject to rapid base hydrolysis are in fact some 10^5 times faster than the hydrolysis itself [e.g., in $Co(NH_3)_5Cl^{2+}$ and Co $en_2NH_3Cl^{2+}$]. Such observations are in keeping with the D-CB mechanism but afford no positive proof of it.

In complexes having no protonic hydrogen, acceleration by base should not be observed according to the D-CB mechanism. This is in general true (as for 2,2′-bipyridine complexes, for example), but in a few cases a reaction of the first-order in OH^- is observed nonetheless. One of these is the hydrolysis of $Co(EDTA)^-$ by OH^-. The formation of the seven-coordinate intermediate (29-I) has been proposed, since it is also found that the complex racemizes with a first-order dependence on OH^-, but with a rate faster than that of hydrolysis. The seven-coordinate species could revert to $Co(EDTA)^-$ again without hydrolysis occurring, but with concomitant racemization.



(29-I)

A number of experiments support the idea that the conjugate base does react dissociatively to produce a reactive, five-coordinate intermediate with a lifetime sufficient for its reactivity to be independent of its origin, and for its characteristic pattern of discrimination among available entering ligands to be manifested. It is a common feature of base hydrolysis of the simpler Co^{III} ammine systems (e.g., $Co\ en_2AX$) that there is considerable stereochemical change. For example,

$$\Lambda\text{-}cis\text{-}[Co\ en_2Cl_2]^+ + OH^- \longrightarrow [Co\ en_2Cl(OH)]^+ + Cl^-$$

63% *trans*

21% Λ-*cis*

16% Δ-*cis*

This sort of result is best accommodated by postulating a *tbp* intermediate, on which the attack of H_2O can occur in several ways, each leading to one of these isomers. One possible intermediate, and the lines of attack on it, are shown in Fig. 29-2. If loss of X were to leave a square pyramidal intermediate, it seems more likely that there would be complete retention of stereochemistry.

Some results obtained in nonaqueous solvents also support the D-CB mechanism. Thus in DMSO reactions of the type

$$Co\ en_2NO_2Cl^+ + Y^- = Co\ en_2NO_2Y^+ + Cl^-$$

$$(Y = N_3^-, NO_2^-, \text{or } SCN^-)$$

are slow, with half-times in hours, but when traces of OH^- or piperidine are added the half-times are reduced to minutes. Since it was also shown that

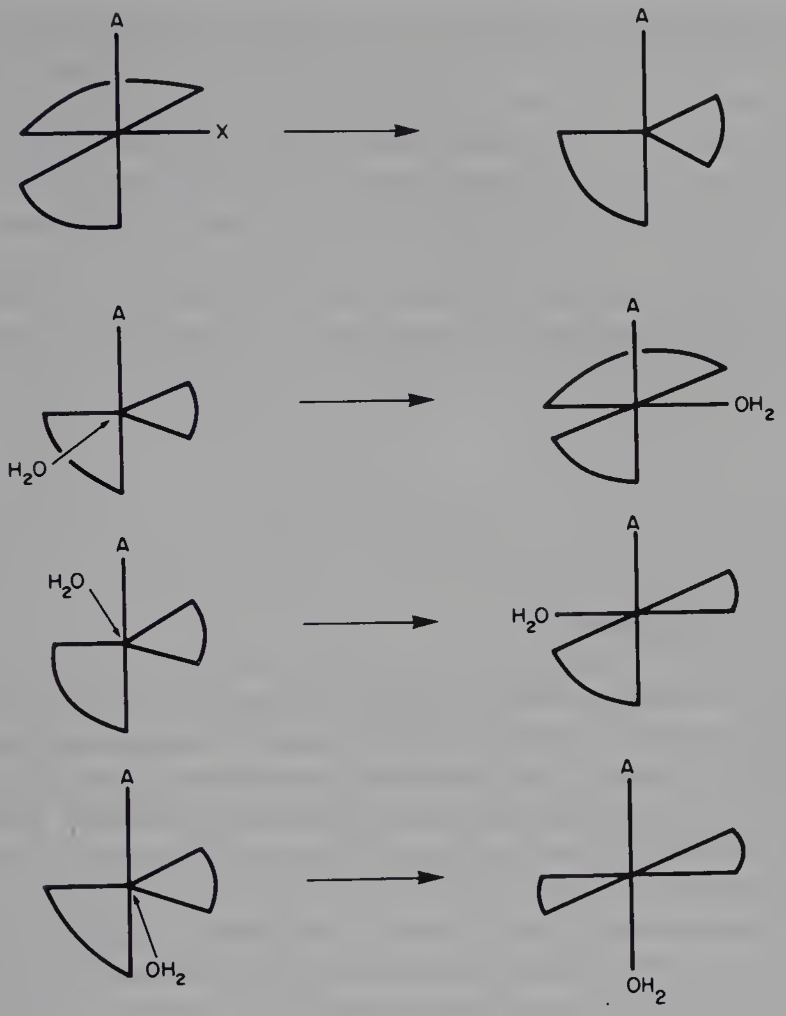


FIG. 29-2. Possible means by which a *tbp* intermediate in base hydrolysis by the D-CB mechanism could yield three isomeric products.

reaction of Co $en_2NO_2OH^+$ with Y^- is slow, an A mechanism with this as an intermediate is ruled out, and a genuine conjugate-base mechanism must prevail here.

Further interesting evidence for the conjugate base (though it does not bear on whether the actual aquation is D or A) comes from a study of the activity of OOH^- in base hydrolysis. Since OOH^- is a weaker base but a better nucleophile toward metal ions than OH^-, base hydrolysis by OOH^- compared to OH^- should proceed more slowly if its function is to form the conjugate base by removing a proton, but faster if it attacks the metal in a genuine A process. Experimental data are in agreement with the former.

Finally, there is the question of why the conjugate base so readily dissociates to release the ligand X. In view of the very low acidity of coordinated amines, the concentration of the conjugate base is a very small fraction of the total concentration of the complex. Thus its reactivity is enormously greater, by a factor far in excess of the mere ratio of k_B/k_A. It can be estimated that the ratio of the rates of aquation of $[Co(NH_3)_4NH_2Cl]^+$ and $[Co(NH_3)_5Cl]^{2+}$ must be $> 10^6$. Two features of the conjugate base have been considered in efforts to account for this reactivity. First, there is the obvious charge effect. The conjugate base has a charge that is one unit less positive than the complex from which it is derived, but it seems unlikely that the charge effect, in itself, can account for the enormous rate difference involved. It has been proposed that the amide ligand could labilize the leaving group X by a combination of electron repulsion in the ground state and a π-bonding contribution to the stability of the five-coordinate intermediate, as suggested in eq. 29-20. However, this proposal is subject to criticism and the question remains open.

(29-20)

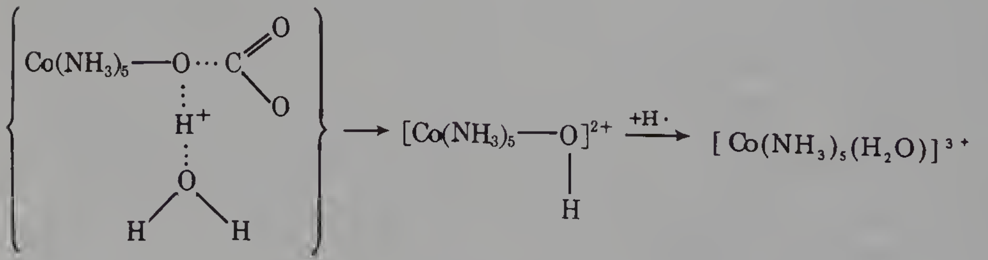
29-6. Attack on Ligands

The chemistry of organometallic compounds of the transition metals is replete with important reactions in which reagents attack the ligands rather than the metal atom (see Chapters 25–28) and the ligand attacks are also of importance in metal carbonyl chemistry (see Section 22-8). Such pathways are relatively uncommon in classical coordination compounds, but there are some well-documented cases.

One well-known case is the aquation of carbonato complexes. When isotopically labeled water ($H_2{}^*O$) is used, it is found that no *O gets into the coordination sphere of the ion during aquation,

$$[Co(NH_3)_5OCO_2]^+ + 2H_3{}^*O^+ \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + 2H_2{}^*O + CO_2$$

The most likely path for this reaction involves proton attack on the oxygen atom bonded to Co followed by expulsion of CO_2 and then protonation of the hydroxo complex (eq. 29-21).



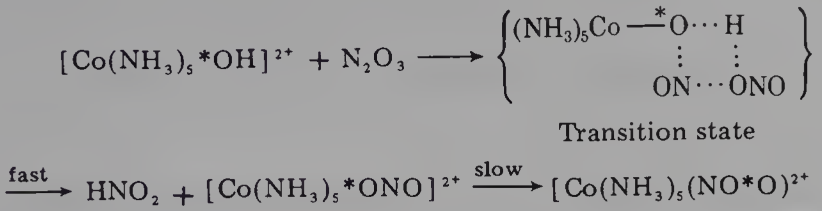
(29-21)

Transition state

Similarly, in the reaction of NO_2^- with pentaammineaquocobalt(III) ion, isotopic labeling studies show that the oxygen originally in the bound H_2O

turns up in the bound NO_2^-. This remarkable result is explained by the reaction sequence 29-22.

$$2NO_2^- + 2H^+ = N_2O_3 + H_2O \tag{29-22a}$$



$$[Co(NH_3)_5{*}OH]^{2+} + N_2O_3 \longrightarrow \left\{\begin{array}{ccc}(NH_3)_5Co\text{—}\overset{*}{O} & \cdots & H\\ \vdots & & \vdots\\ ON & \cdots & ONO\end{array}\right\}_{\text{Transition state}}$$

$$\xrightarrow{\text{fast}} HNO_2 + [Co(NH_3)_5{*}ONO]^{2+} \xrightarrow{\text{slow}} [Co(NH_3)_5(NO{*}O)]^{2+} \tag{29-22b}$$

29-7. Reactions of Square Complexes

Square complexes are of major importance for Ni^{II}, Pd^{II}, Pt^{II}, Rh^{I}, Ir^{I}, and Au^{III}. The overwhelming majority of mechanistic studies have been done on complexes of Pt^{II} because so much is known about its chemistry, and reactions generally proceed at convenient rates. For example, Ni^{II} and Pd^{II} complexes typically react 10^6 and 10^5 times more rapidly, respectively, although in special cases, such as CN^- exchange in $[M(CN)_4]^{2-}$ species, these relative rates may vary.[6] Gold(III) complexes react $\sim 10^3$ times faster and are subject to easy reduction. The qualitative rate relationships are all understandable. For Ni^{II} the tendency to increase its coordination number to 5 [e.g., $Ni(CN)_5^{3-}$ is isolable] is great; for Pd^{II} the metal ligand bonds are weaker than for Pt^{II}; for Au^{III} the greater positive charge on the metal attracts the attacking nucleophile. All available data suggest, however, that the mechanistic results for Pt^{II} apply generally to square complexes of the other elements.

Mechanism of Ligand-Displacement Reactions. Because of the low coordination number, these occur almost entirely by associative pathways.

For reactions in aqueous solution of the type 29-23 the rate law takes the general form 29-24. It is believed that the second term corresponds to a genuine A reaction of Y with the complex, and the first term represents a two-step path in which one Cl^- is first replaced by H_2O (probably also by an A mechanism) as the rate-determining step followed by relatively fast replacement of H_2O by Y.

$$PtL_nCl_{4-n} + Y = PtL_nCl_{3-n}Y + Cl^- \tag{29-23}$$

$$v = k[PtL_nCl_{4-n}] + k'[PtL_nCl_{4-n}][Y] \tag{29-24}$$

It has been found that the rates of reaction 29-23 for the series of four complexes in which L = NH_3 and Y = H_2O vary by only a factor of 2. This is a remarkably small variation, since the charge on the complex changes from -2 to $+1$ as n goes from 0 to 3. Since Pt—Cl bond breaking should become more difficult in this series, whereas the attraction of Pt for a nu-

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[6] J. J. Pesek and W. R. Mason, *Inorg. Chem.*, 1983, **22**, 2958.

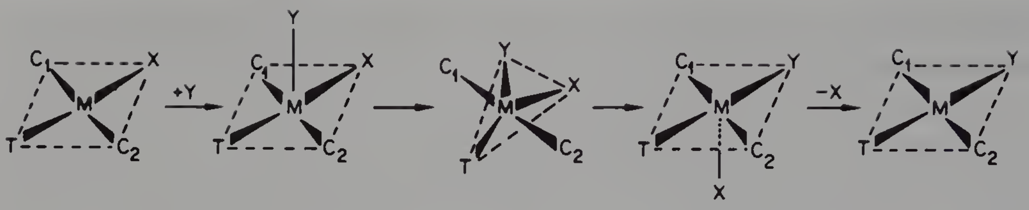


FIG. 29-3. The course of ligand displacement at a planar complex and the *tbp* five-coordinate structure.

cleophile should increase in the same order, the virtual constancy in the rate argues for an A process in which both Pt—Cl bond breaking and Pt···OH_2 bond formation are of comparable importance.

Other evidence for associative pathways is provided by (1) the uniformly negative entropies and volumes of activation, and (2) marked dependence of rates on the nature of both entering and leaving groups. The activation parameters are negative for both the first- and second-order paths, consistent with associative solvent attack in the former, rather than a true first-order (or dissociative) pathway.

A general representation of the stereochemical course of displacement reactions of square complexes is given in Fig. 29-3. This process is entirely stereospecific: cis and trans starting materials lead, respectively, to cis and trans products.

The order of the rate constants k' in eq. 29-24 establishes an order of nucleophilicity for the entering ligands towards Pt^{II}, which is substantially invariant whatever the other three ligands may be, and also, so far as is known, for other metals:

$$PR_3 > I^-, SCN^-, N_3^- > NO_2^- > Br^- > py > NH_3, Cl^- > H_2O > OH^-$$

This order bears no correlation with protonic basicity, but is related to the polarizability or softness of the ligands.

We have stressed the stereospecificity of ligand displacement reactions. In order to explain the well-known tendency of traces of free ligands to catalyze cis-trans isomerization in planar complexes, a two-stage mechanism, shown in Fig. 29-4, must be invoked.

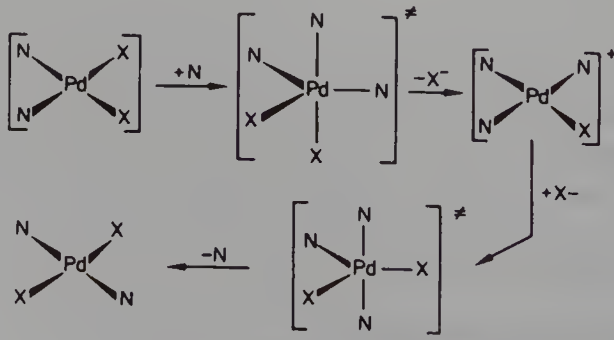
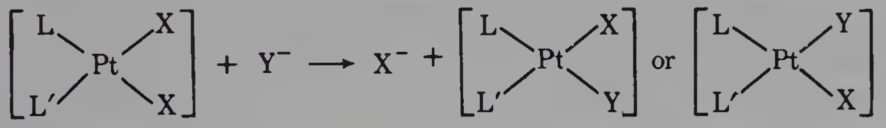


FIG. 29-4. Two-state mechanism for the catalytic isomerization of *cis*-[Pd(amine)$_2$X$_2$] complexes to the corresponding trans isomers.

It may also be noted that recent studies[7] of water exchange for $[Pd(H_2O)_4]^{2+}$ and $[Pt(H_2O)_4]^{2+}$ show negative values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in each case, thus suggesting associative mechanisms.

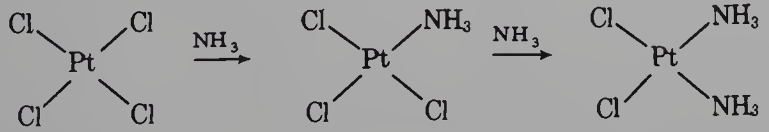
The trans Effect. It has long been known that ligand exchange reactions in square complexes show distinct preferences for the site trans to one ligand rather than another. Consider, for example, a reaction of the type 29-25, where two isomeric products are possible. From results on this and other related reactions, an extensive series of ligands has been arranged in order of their tendency to facilitate substitution in the position trans to themselves. This phenomenon is known as the *trans effect,* and the approximate ordering of ligands is


(29-25)

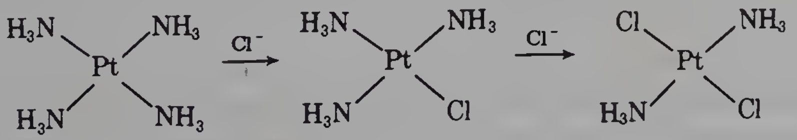
$$\mathrm{CO,\ CN^-,\ C_2H_4 > PR_3,\ H^- > CH_3^- > C_6H_5^-,\ NO_2^-,\ I^-,\ SCN^-}$$
$$\mathrm{> Br^-,\ Cl^- > py,\ NH_3,\ OH^-,\ H_2O}$$

This order spans a factor of 10^6 in rate and holds for all square planar platinum complexes thus far examined.

The trans effect series has proved very useful in rationalizing known synthetic procedures and in devising new ones. As an example, consider the synthesis of the cis and trans isomers of $[Pt(NH_3)_2Cl_2]$. The synthesis of the cis isomer is accomplished by treatment of the $[PtCl_4]^{2-}$ ion with ammonia (reaction 29-26).


(29-26)

Since Cl^- has a greater trans-directing influence than does NH_3, substitution of NH_3 into $[Pt(NH_3)Cl_3]^-$ is least likely to occur in the position trans to the NH_3 already present; thus the cis isomer is favored. The trans isomer is made by treating $[Pt(NH_3)_4]^{2+}$ with Cl^- (reaction 29-27).


(29-27)

Here the superior trans-directing influence of Cl^- causes the second Cl^- to enter trans to the first one, producing *trans*-$[Pt(NH_3)_2Cl_2]$.

All theorizing about the trans effect must recognize that since it is a kinetic phenomenon, depending on activation energies, the stabilities of both the ground state and the activated complex are relevant. It is in principle possible

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[7] A. E. Merbach *et al., Inorg. Chem.,* 1985, **24,** 1719.

for the activation energy to be affected by changes in one or the other of these energies or by changes in both.

The influence of one ligand on the strength of the bond to the ligand that is trans to it is called the *trans influence;* it is a ground state property and can be evaluated from bond lengths or M—L stretching frequencies. Trans influence is attributable to the fact that two trans ligands will both depend on the participation of one metal orbital, and the more one ligand preempts this orbital, the weaker will the bond to the other ligand be. The order of some important ligands with regard to their trans influence is

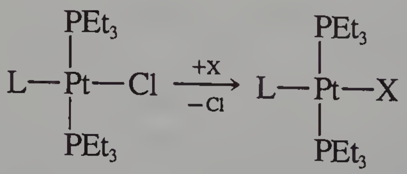
$$H^- > PR_3 > SCN^- > I^-, CH_3^-, CO, CN^- > Br^- > Cl^- > NH_3 > OH^-$$

This sequence is generally similar to the trans effect sequence, with certain striking exceptions, such as the positions of CN^- and CO. This can be traced to the ability of these, and some other ligands, to produce a trans effect by participating in π bonding in the transition state, as illustrated in Fig. 29-5. The π bonding draws electron density away from the directions in which Y and X must be in the transition state. A likely order of π-bonding ability of ligands is

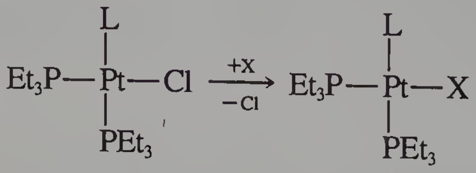
$$C_2H_4, CO > CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^-$$

When this sequence and the trans influence sequence above are both considered, the net trans effect sequence can be rationalized, more or less.

Cis Effects. Cis ligands have little effect electronically on reaction rates (at most a factor of 3), but can be important sterically because of their proximity to the site of replacement. This is well illustrated by the following examples:



$$\begin{array}{c} PEt_3 \\ | \\ L{-}Pt{-}Cl \\ | \\ PEt_3 \end{array} \xrightarrow[-Cl]{+X} \begin{array}{c} PEt_3 \\ | \\ L{-}Pt{-}X \\ | \\ PEt_3 \end{array} \qquad (29\text{-}28)$$



$$\begin{array}{c} L \\ | \\ Et_3P{-}Pt{-}Cl \\ | \\ PEt_3 \end{array} \xrightarrow[-Cl]{+X} \begin{array}{c} L \\ | \\ Et_3P{-}Pt{-}X \\ | \\ PEt_3 \end{array} \qquad (29\text{-}29)$$

In reactions of the type 29-28 changing L from phenyl to mesityl causes only a 30-fold lowering in the rate, whereas in reactions of type 29-29 the deceleration is by a factor of nearly 10^5.

Other Reaction Types.[8] There are two other classes of reactions for square complexes. In view of the fact that they are in general coordinately unsaturated (four-coordinate rather than six-coordinate) and also electroni-

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[8] R. J. Cross, *Chem. Soc. Rev.*, 1985, **14**, 197.

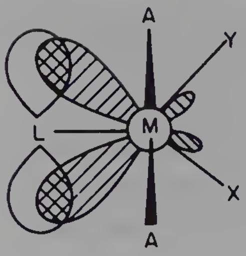


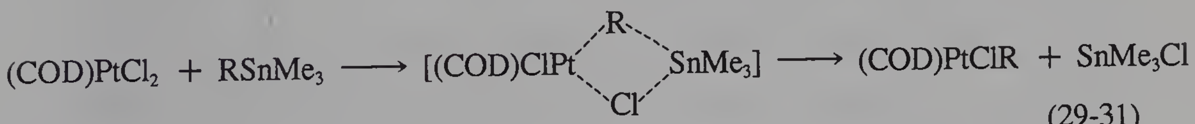
FIG. 29-5. Postulated *tbp* five-coordinate activated complex for reaction of Y with *trans*-MA_2LX, to displace X.

cally unsaturated (16 electrons rather than 18), it is entirely reasonable that they undergo oxidative-addition reactions. In some cases the adduct is of low stability and decomposes by reductive-elimination. Thus, in a two-step fashion, ligand exchange can be effected, as illustrated in eq. 29-30.

$$PtMeCl(PR_3)_2 \xrightarrow{+Cl_2} PtMeCl_3(PR_3)_2 \xrightarrow{-MeCl} PtCl_2(PR_3)_2 \qquad (29\text{-}30)$$

Of course, in many cases the adduct is stable and oxidative-addition in itself constitutes an important reaction type. Oxidative-additions and reductive-eliminations have already been discussed with respect to organometallic chemistry and catalysis in Chapter 27.

Finally, in some cases the ligand exchange reaction is most usefully viewed as an electrophilic attack upon a metal–carbon bond. An example is shown in eq. 29-31.



$$(COD)PtCl_2 + RSnMe_3 \longrightarrow [(COD)ClPt\overset{R}{\underset{Cl}{\diamond}}SnMe_3] \longrightarrow (COD)PtClR + SnMe_3Cl \qquad (29\text{-}31)$$

29-8. Metal Carbonyl Reactions

The discussion here will be restricted to certain mechanistic aspects of CO replacement reactions. For other aspects of the reactivity of metal carbonyls, see Chapters 22 (especially Section 22-8), 27 and 28. We shall also focus here on octahedral metal carbonyl systems, since these provide excellent opportunities to examine stereoselectivity and they have been the most thoroughly studied. It may be mentioned that in some ways mechanistic study of metal carbonyl reactions is easier than for the complexes discussed earlier in this chapter. For instance, the compounds are generally soluble in nonpolar, nonligating solvents, and ion-pair formation is seldom a problem.

Reactions of the hexacarbonyls of Cr, Mo, and W with a variety of ligands (29-32a) have been extensively studied, and in general they follow a two-term rate law (29-32b). The first term corresponds to an essentially limiting D

$$M(CO)_6 + L \longrightarrow M(CO)_5L + CO \qquad (29\text{-}32a)$$

$$-\frac{d[M(CO)_6]}{dt} = k_1[M(CO)_6] + k_2[M(CO)_6][L] \qquad (29\text{-}32b)$$

process in which an $M(CO)_5$ intermediate is formed. Coordinately unsaturated intermediates are, in general, far more common and important in the reactions of metal carbonyls than in those of the conventional ionic complexes. The thermodynamic parameters of activation for the first-order path with L = $PhCH_2NH_2$ are $\Delta H_1^\ddagger = 150 \pm 12$ kJ mol^{-1} and $\Delta S_1^\ddagger = +80 \pm 37$ J deg^{-1} mol^{-1}, both of which are in good accord with the idea of a dissociative mechanism.

The transition state for the bimolecular pathway is more difficult to define unequivocally. For the same ligand $PhCH_2NH_2$, the activation parameters are $\Delta H_2^\ddagger = 113 \pm 8$ kJ mol^{-1} and $\Delta S_2^\ddagger = -16 \pm 24$ J deg^{-1} mol^{-1}. These values and other evidence suggest that the second reaction pathway is a dissociative interchange I_d, in which M—CO bond breaking is well advanced in the activated complex but at the same time the ligand L is closely associated with the $M(CO)_6$ molecule.

Reactions of molecules of the types $M(CO)_5L$ (M = Cr, Mo, and W; L = a neutral ligand) and $M(CO)_5X$ (M = Mn, Re; X = Cl, and Br) display interesting stereospecificities. The basic feature is that they react thermally by dissociative pathways with a marked preference for dissociation of a ligand cis to L or X. Each *cis* CO group is ~10 times more labile than the *trans* CO group. Therefore, in general, substitution reactions give cis products, as in eqs. 29-33 and 29-34.

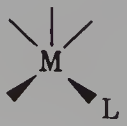
$$Mo(CO)_5PR_3 + PR_3 \longrightarrow \textit{cis}\text{-}Mo(CO)_4(PR_3)_2 + CO \qquad (29\text{-}33)$$

$$Mn(CO)_5Br + PR_3 \longrightarrow \textit{cis}\text{-}Mn(CO)_4Br(PR_3) + CO \qquad (29\text{-}34)$$

In some cases, where steric considerations favor the trans isomer, isomerization occurs. Studies of *cis*-$M(CO)_4(^{13}CO)PR_3$ (M = Cr and W) have shown that the isomerization to the trans isomers is an intramolecular process. In the tungsten case the low $\Delta H^\ddagger$ (36 kJ mol^{-1}) and highly negative $\Delta S^\ddagger$ (−220 J mol^{-1} deg^{-1}) indicate an internal twist mechanism (see Section 29-13), but for the Cr compounds ($\Delta H^\ddagger = 111$ kJ mol^{-1}, and $\Delta S^\ddagger = 8$ J mol^{-1} deg^{-1}) the mechanism is uncertain.[9]

The preference for cis dissociation may be attributed mainly to the fact that (29-II) is more stable than (29-III) when X or L is less of a π acid than CO, although other factors may contribute.

The formation and stability of (29-II) rather than (29-III) is clearly shown



(29-II)

(29-III)

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[9] D. J. Darensbourg and R. L. Gray, *Inorg. Chem.*, 1984, **23**, 2993.

by reactions of the type 29-35,

$$LM(CO)_5 + {}^*CO \longrightarrow cis\text{-}LM(CO)_4({}^*CO) + CO \qquad (29\text{-}35)$$

where the principle of microscopic reversibility requires that if incoming CO ends up cis to L, the outgoing CO must have come from a cis position. With other entering ligands L′, the products are mainly cis as in 29-36,

$$LM(CO)_5 + L' \longrightarrow cis\text{-}M(CO)_4LL' + CO \qquad (29\text{-}36)$$

although the reaction conditions employed in actual preparations often lead to considerable isomerization to the trans isomers, which are generally more thermodynamically stable.

The stereoselectivity of reactions 29-35 or 29-36 tells nothing about whether the intermediate (29-II) is rigid in the sense that the remaining four CO groups do not interchange among themselves. It is likely that they do so fairly rapidly. In the absence of a ligand L that is different from CO, scrambling definitely occurs as shown by the fact that *cis*-$Mo(CO)_4({}^{13}CO)(C_5H_{10}NH)$ reacts with ^{13}CO to afford a statistical mixture of *cis*- and *trans*-$Mo(CO)_4({}^{13}CO)_2$.

Preferential labilization of a cis ligand coupled with retention of the configuration (29-II) in the five-coordinate intermediate has some interesting consequences and applications. For example, it provides a convenient synthesis of *cis*-$Mo(CO)_4L_2$ species under conditions so mild that racemization is negligible. The compound *cis*-$Mo(CO)_4(C_5H_{10}NH)_2$ is easily prepared free of trans isomer. It then reacts smoothly (40°C; 10–15 min) with L to give *cis*-$Mo(CO)_4L(C_5H_{10}NH)$ and then *cis*-$Mo(CO)_4L_2$. In each step the weakest bond, Mo—N, is preferentially broken and the remaining noncarbonyl ligand controls the stereochemistry.

Ligand displacement reactions (eq. 29-37) also occur dissociatively,[10] as shown by their large positive values of $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger$. From the values of $\Delta H^\ddagger$ for both the forward and reverse reactions, the relative strengths of various Cr—L bonds have been determined[11]:

$$PBu_3 >> P(OPh)_3 > PPh_3 \approx CO > AsPh_3 > py$$

$$Cr(CO)_5L + CO = Cr(CO)_6 + L \qquad (29\text{-}37)$$

Because the initial dissociative step is rate determining in most reactions of metal carbonyls, kinetic study of thermal reactions reveals little or nothing about subsequent steps. By employing flash photolysis to instantaneously generate the five-coordinate intermediate, the recombination or ligand entry phase of the reactions can be followed. Thus, the competition between ring reclosure and substitution (eq. 29-38) has been studied in detail.[12]

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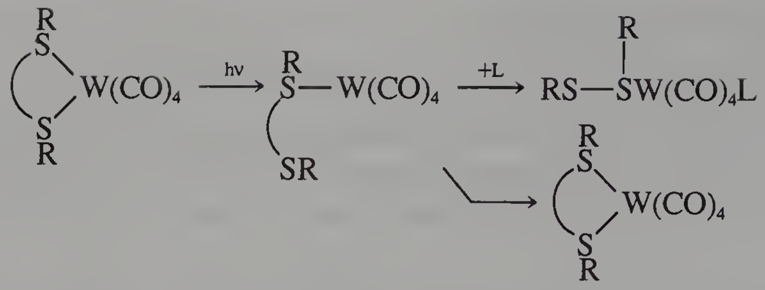
[10] R. van Eldik *et al.*, *Inorg. Chem.*, 1986, **25**, 1914.
[11] M. J. Wovkulich and J. D. Atwood, *Organometallics*, 1982, **1**, 1316.
[12] G. R. Dobson *et al.*, *Inorg. Chem.*, 1985, **24**, 2179.



(29-38)

Reactions of Binuclear Carbonyls. The thermal reactions of molecules such as $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are also governed by dissociative mechanisms with preferred cis labilization. This is illustrated by the stereospecific reactions 29-39 and 29-40, where L = PPh_3.

$$Mn_2(CO)_{10} + L \longrightarrow ax\text{-}L(OC)_4MnMn(CO)_5 + CO \tag{29-39a}$$

$$\text{rate} = k_1[Mn_2(CO)_{10}] + k_2[L][Mn_2(CO)_{10}] \tag{29-39b}$$

$$ax\text{-}L(OC)_4MnMn(CO)_5 + L \longrightarrow ax,ax\text{-}L(OC)_4MnMn(CO)_4L + CO \tag{29-40a}$$

$$R = k_3[Mn_2(CO)_9L] \tag{29-40b}$$

It is found that $k_3 = 50k_1$. These results can be explained by the scheme in Fig. 29-6. One $Mn(CO)_5$ group has a cis labilizing effect on the other, but the first entering ligand L is too bulky to remain in the cis position, and there is prompt rearrangement to the trans (axial) position. The cis labilizing effect of L causes $Mn_2(CO)_9L$ to lose CO at least 50 times faster than $Mn_2(CO)_{10}$, but for steric reasons the second L cannot enter the open site. Carbon monoxide transfer via a bridged intermediate occurs rapidly, and the second L therefore substitutes on the second Mn atom.

Similarly, $Ru_3(CO)_{12}$ reacts with PPh_3 to give only 1,2,3-$Ru_3(CO)_9L_3$ with no detectable mono- or disubstituted intermediates, and the process is zero

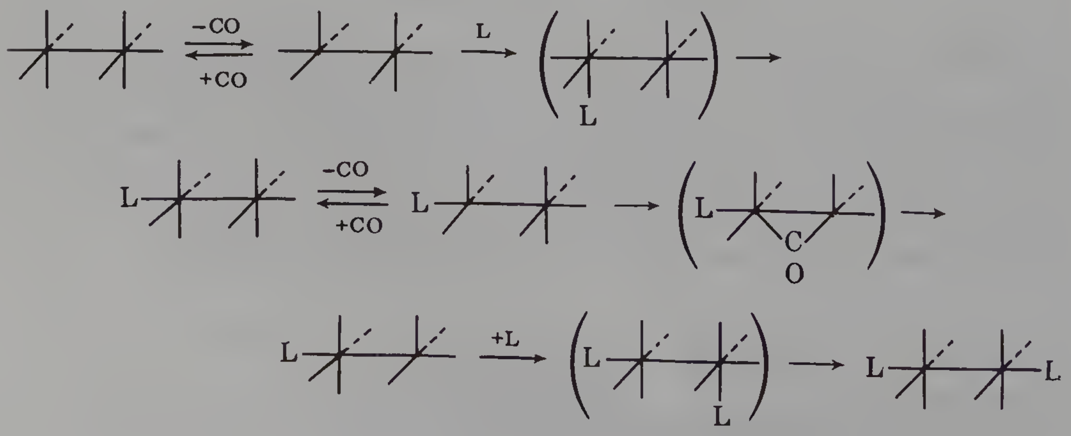
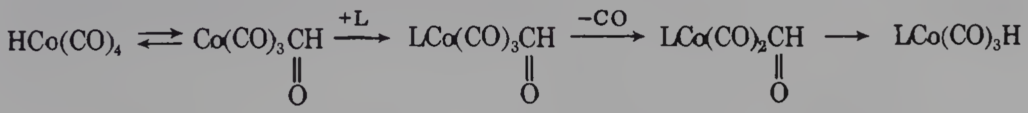


FIG. 29-6. A scheme to account for the course of reactions (29-39) and (29-40).

order in PPh_3. However, with L = $P(OPh)_3$, which is a poorer cis labilizer, the intermediates can be obtained.

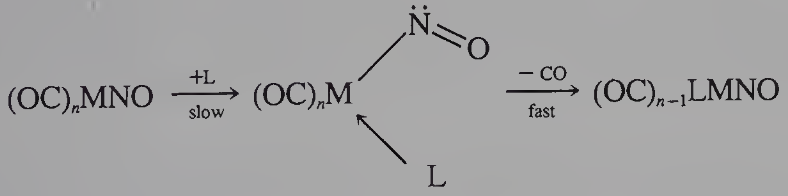
Some metal carbonyl hydrides, for example, $HMn(CO)_5$ and $HCo(CO)_4$, are exceptionally reactive toward ligands that replace a CO group. This has been attributed to a special mechanism involving hydride migration; for example,



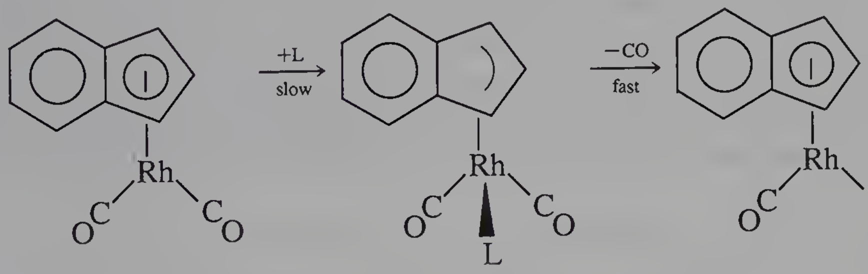
$$HCo(CO)_4 \rightleftarrows Co(CO)_3\underset{\overset{\|}{O}}{C}H \xrightarrow{+L} LCo(CO)_3\underset{\overset{\|}{O}}{C}H \xrightarrow{-CO} LCo(CO)_2\underset{\overset{\|}{O}}{C}H \longrightarrow LCo(CO)_3H$$

The intermediates here, which contain a formyl group, are similar to the reaction products in the case of the alkyl migration reaction.

Associative Reactions. While D or I_d paths predominate in the nonradical reactions of metal carbonyls, presumably because of the extremely unfavorable nature of the 20-electron configuration that a true A reaction would entail, there are special cases where an A mechanism does operate.[13] These cases are understandable because they depend on the presence of a ligand that can donate either *n* or *n*-2 electrons. The conversion of this ligand from the *n* mode to the *n*-2 mode allows the additional bond to be formed. The most important of these bimodal ligands are NO and Cp (or, better, indenyl) groups. Reactions (29-41) and (29-42) illustrate the situation.



(29-41)



(29-42)

Species with 17 Electrons. It has been well established that 17-electron carbonyl molecules undergo ligand substitution reactions with exceptional rapidity. The only stable 17-electron species is $V(CO)_6$. It has been thoroughly studied and all of its reactions, which on average proceed ~10^{10} times faster than similar reactions of $Cr(CO)_6$, display second-order kinetics and have associative mechanisms.[14] It is not known why this tremendous rate enhancement occurs.

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[13] F. Basolo, *Inorg. Chim. Acta*, 1985, **100**, 33.

[14] F. Basolo *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 6046.

Other 17-electron species are known only as short-lived intermediates that must be generated and studied by special techniques. The $Co(CO)_4$,[15] $Co(CO)_3L$, $Mn(CO)_5$, $Re(CO)_5$, $Mn(CO)_4L$ radicals, and other similar ones have been extensively studied. They appear to react mainly by associative paths. Methods of generating them include pulse radiolysis,[16] flash photolysis and electrochemical oxidation.[17] In some of the systems studied by the last method, it has been shown[17] that a radical chain mechanism operates, namely,

$$(OC)_nML \xrightarrow{-e} (OC)_nML^+$$

$$(OC)_nML + \xrightarrow[-L]{+L'} (OC)_nML'^+$$

$$(OC)_nML'^+ + (OC)_nML \longrightarrow (OC)_nML' + (OC)_nML^+$$

ELECTRON TRANSFER PROCESSES[18]

The electron transfer processes can be divided into two main classes: (1) those in which the electron transfer effects no net chemical change, and (2) those in which there is a chemical change. The former, called *electron-exchange* processes, can be followed only indirectly, as by isotopic labeling or by nmr. The latter are the usual oxidation–reduction reactions and can be followed by many standard chemical and physical methods. The electron-exchange processes are of interest because of their particular suitability for theoretical study.

There are two well-established general mechanisms for electron transfer processes. In the first, called the *outer-sphere mechanism,* each complex retains its own full coordination shell, and the electron must pass through both. This, of course, is a purely formal statement in that we do not imply that the "same" electron leaves one metal atom and arrives at the other. In the second case, the *inner-sphere mechanism,* the two complexes form an intermediate in which at least one ligand is shared, that is, belongs simultaneously to both coordination shells.

In some cases a reaction may proceed partly by each type of path. A documented example is

$$V^{2+}(aq) + VO^{2+}(aq) \longrightarrow 2V^{3+}(aq)$$

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[15] G. Palyi *et al., Coord. Chem. Rev.,* 1984, **53,** 37 (90 refs.).

[16] A. Wojcicki *et al., Inorg. Chim. Acta,* 1985, **105,** 147.

[17] J. K. Kochi *et al., J. Am. Chem. Soc.,* 1982, **104,** 3034.

[18] H. Taube, *Science,* 1984, **226,** 1028 (Taube's Nobel Lecture; an excellent personal history); *Progress in Inorganic Chemistry,* Vol. 30 1983, review articles by C. Creutz, J. F. Endicott *et al.,* J. H. Espenson, A. Haim, T. J. Meyer, and N. Sutin on various aspects of electron transfer reactions.

where at ~25°C an outer-sphere path accounts for ~$\frac{1}{3}$ of the product and an inner-sphere path, via a $[VOV]^{4+}$ intermediate, accounts for the rest.

29-9. Outer-Sphere Reactions

The outer-sphere mechanism is certain to be the correct one when *both* species participating in the reaction undergo ligand-exchange reactions more slowly than they participate in the electron transfer process. An example is the reaction

$$[Fe^{II}(CN)_6]^{4-} + [Ir^{IV}Cl_6]^{2-} \longrightarrow [Fe^{III}(CN)_6]^{3-} + [Ir^{III}Cl_6]^{3-}$$

where both reactants are classified as inert ($t_{1/2}$ for aquation in 0.1 M solution > 1 ms), but the redox reaction has a rate constant of ~10^5 L mol^{-1} s^{-1} at 25°C.

For electron exchange reactions a plot of free energy versus reaction coordinate has the symmetrical form shown in Fig. 29-7. The free energy of activation, $\Delta G^\ddagger$, can be expressed as the sum of four contributions:

$$\Delta G^\ddagger = RT \ln \frac{kT}{hZ} + \Delta G_a^\ddagger + \Delta G_o^\ddagger + \Delta G_i^\ddagger \qquad (29\text{-}43)$$

The first term, standard in absolute reaction rate theory, takes account of the loss of motional energy in forming the collision complex; it can be calculated. The term $\Delta G_a^\ddagger$ is the free energy change caused by increased repulsion between the reactants of like charge at the distance of contact in the collision complex. The free energy of the rearrangement of solvent layers outside the first coordination spheres of the reacting species is represented by $\Delta G_o^\ddagger$. Finally, $\Delta G_i^\ddagger$ represents the free energy of internal rearrangement within the first coordination spheres of each of the reacting species. The first two free energy terms, $\Delta G_a^\ddagger$ and $\Delta G_o^\ddagger$, are much the same for systems involving reactants with the same charges and the same ligands in the first coordination sphere. It is $\Delta G_o^\ddagger$ that leads to the vast differences in reaction rates that can

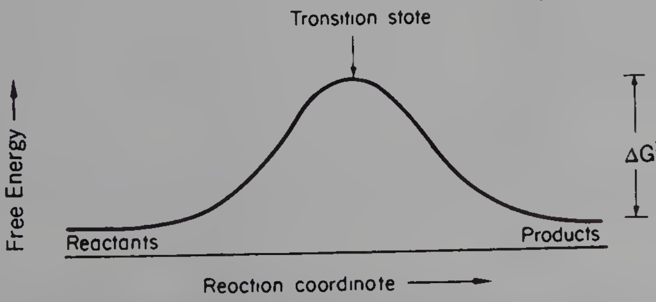

FIG. 29-7. Graph of energy versus reaction coordinate for an electron-exchange reaction in which reactants and products are identical.

be seen in the data of Table 29-1. Let us consider in detail why this term, $\Delta G_o^\ddagger$, exists.

The M—L bond lengths in two reacting species, say $[M(H_2O)_6]^{2+}$ and $[M(H_2O)_6]^{3+}$, are different. The lowest energy pathway for electron transfer, however, requires that after the collision complex has been formed, these two sets of M—L distances become equal. The reason for this is as follows. Suppose for an M^{II}—M^{III} exchange the electron jumped while both ions were in their normal configurations. This would produce an M^{II} complex with bonds compressed *all the way* to the length appropriate to an M^{III} complex and an M^{III} complex with the bonds lengthened *all the way* to the length of those in the M^{II} complex. This would be the zenith of energy, and as the bonds readjusted, the energy of the exchanging pair would drop to the initial energy of the systems. However, this zenith of energy is obviously higher than it would be if the reacting ions first adjusted their configurations so that each met the other one *only halfway* and then exchanged the electron. The more the two reacting species differ initially in their sizes, the higher will be the contribution of $\Delta G_i^\ddagger$ to the total free energy of activation.

Turning now to a detailed examination of Table 29-1, we can see how this simple concept comes into play. At the top of the table are electron exchange reactions between octahedral species that proceed very rapidly. In all these cases, the exchanging species differ by one t_{2g} electron. In accord with well-known concepts from ligand field theory, a t_{2g} electron has little effect on the strength (and hence length) of an M—L bond, unless π bonding is important,

TABLE 29-1
Some Outer-Sphere Electron-Exchange Reactions

Reacting pair	Electron configuration	Rate (L mol^{-1} s^{-1} at 25°C)	Difference in M—L bond lengths (Å)
$[Fe(bipy)_3]^{2+/3+}$	t_{2g}^6/t_{2g}^5	$>10^6$	0.00 ± 0.01
$[Mn(CN)_6]^{4-/3-}$	t_{2g}^5/t_{2g}^4		Very small
$[Mo(CN)_8]^{4-/3-}$	[a]		
$[W(CN)_8]^{4-/3-}$	[a]		
$[IrCl_6]^{3-/2-}$	t_{2g}^6/t_{2g}^5		
$[Os(bipy)]^{2+/3+}$	t_{2g}^6/t_{2g}^5		
$[Fe(CN)_6]^{4-/3-}$	t_{2g}^6/t_{2g}^5	$\sim10^5$	
$[Ru(en)_3]^{2+/3+}$	t_{2g}^6/t_{2g}^5	4×10^4	
$[Ru(NH_3)_6]^{2+/3+}$	t_{2g}^6/t_{2g}^5	4×10^3	0.04 ± 0.01[b]
$[Ru(H_2O)_6]^{2+/3+}$	t_{2g}^6/t_{2g}^5	20[c]	0.09 ± 0.02[b]
$[Fe(H_2O)_6]^{2+/3+}$	$t_{2g}^4e_g^2/t_{2g}^3e_g^2$	4	0.14 ± 0.02[b]
$[MnO_4]^{2-/1-}$	[a]	$>10^3$	
$[Coen_3]^{2+/3+}$	$t_{2g}^3e_g^2/t_{2g}^6$	$\sim10^{-4}$	0.18 ± 0.02
$[Co(NH_3)_6]^{2+/3+}$			
$[Co(C_2O_4)_3]^{4-/3-}$			

[a] Not octahedral, but the change in electronic configuration occurs in a nonbonding orbital.
[b] H.-B. Bürgi *et al.*, *Inorg. Chem.*, 1982, **21**, 3936.
[c] A. E. Merbach *et al.*, *J. Am. Chem. Soc.*, 1985, **107**, 312.

which is not the case in these systems. Thus, in all these cases we might reasonably expect that the $\Delta G_i^\ddagger$ term is small. For the $[Fe(bipy)_3]^{n+}$ and several other species, structural results have been obtained showing directly that the M—L bond length difference is indeed very small.

The series of systems $[Ru(NH_3)_6]^{2+/3+}$, $[Ru(H_2O)_6]^{2+/3+}$, and $[Fe(H_2O)_6]^{2+/3+}$ provides an excellent illustration of the influence of the M—L bond length change, since the rates of electron exchange decrease markedly while at the same time the bond length differences increase.

In the $MnO_4^{2-/1-}$ system, the electron exchanged is not in a strictly nonbonding orbital and thus some enhancement of $\Delta G_i^\ddagger$ is expected. In fact, this system poses a number of unresolved problems, especially regarding the volume of activation.[19]

The slowness of the several $Co^{2+/3+}$ electron exchange processes has occasioned much discussion over the years, with the fact that these involve a large difference in spin quantum number between the two species having been given much attention. For a time, these $Co^{2+/3+}$ exchanges were thought to be slow because of "spin forbiddenness." Recent work does not support this.[20] It appears that the slowness of these exchanges is simply attributable to the very large (~0.2 Å) difference in Co—N bond lengths, which adds ~60 kJ mol^{-1} to $\Delta G^\ddagger$.

In electron transfer reactions between two dissimilar ions, in which there is a net decrease in free energy, the rates are generally higher than in comparable electron-exchange processes. In other words, one factor favoring rapid electron transfer is the thermodynamic favorability of the overall reaction. This generalization seems to apply not only to the outer-sphere processes now under discussion but also to the inner-sphere mechanism to be discussed shortly.

In several cases the rate constants for reactions in Table 29-1 have been found to depend on the identity and concentration of cations present in the solution. The general effect is an increase in rate with an increase in concentration of the cations, but certain cations are particularly effective. The general effect can be attributed to the formation of ion pairs, which then decrease the electrostatic contribution to the activation energy. Certain specific effects, found, for example, in the MnO_4^-–MnO_4^{2-}, and $[Fe(CN)_6]^{4-}$–$[Fe(CN)_6]^{3-}$ systems, are less easily interpreted with certainty. The effect of $[Co(NH_3)_6]^{3+}$ on the former is thought to be due to ion pairing, greatly enhanced by the high charge. There is no evidence that the cations participate in the actual electron transfer, though this may be so in some cases.

It is also known that when the reactants in an electron transfer reaction differ in chirality, stereoselective preferences can be observed.[21]

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[19] L. Spiccia and T. W. Swaddle, *J. Chem. Soc. Chem. Commun.*, **1985**, 67.

[20] D. Geselowitz and H. Taube, *Adv. Inorg. Bioinorg. Mech.*, 1982, **1**, 391; P. Braun and R. van Eldik, *J. Chem. Soc. Chem. Commun.*, **1985**, 1349.

[21] P. Osvath and A. G. Lappin, *J. Chem. Soc. Chem. Commun.*, **1986**, 1056.

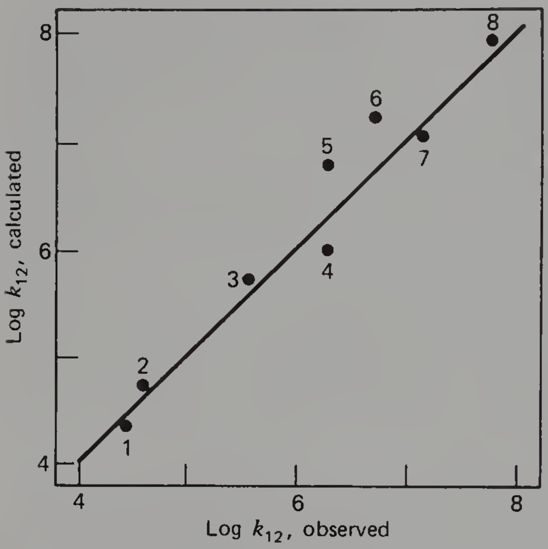

FIG. 29-8. Rate constants calculated from the Marcus cross relation versus measured constants: 1, $Mo(CN)_8^{3-}$–$Fe(CN)_6^{4-}$; 2, $Fe(CN)_6^{3-}$–$W(CN)_8^{4-}$; 3, $IrCl_6^{2-}$–$Fe(CN)_6^{4-}$; 4, $IrCl_6^{2-}$–$Mo(CN)_8^{4-}$; 5, Ce^{IV}–$Fe(CN)_6^{4-}$; 6, $Mo(CN)_8^{3-}$–$W(CN)_8^{4-}$; 7, Ce^{IV}–$Mo(CN)_8^{4-}$; 8, $IrCl_6^{2-}$–$W(CN)_8^{4-}$.

The Marcus Theory. The expression given in eq. 29-43 for the $\Delta G^{\ddagger}$ of an electron exchange reaction provides the basis for a successful quantitative treatment developed mainly by R. A. Marcus. A particularly valuable part[22] of the Marcus theory is the *Marcus cross relation,* which can be stated as follows:

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{29-44}$$

where k_{12} and K_{12} are the rate and equilibrium constants for a given electron transfer reaction, and k_{11} and k_{22} are the rate constants for the "component" electron-*exchange* reactions (for which, of course, $K_{11} = K_{22} = 1$). The factor f is defined by eq. 29-45, where Z is the collision frequency for hypothetically uncharged reactant ions.

$$\log f = \frac{(\log K_{12})^2}{4 \log(k_{11}k_{22}/Z^2)} \tag{29-45}$$

Figure 29-8 plots some observed values of k_{12} against those calculated by eq. 29-44. Clearly the agreement is remarkably good, considering that four orders of magnitude are covered. However, there are some unresolved problems with the theory. It is known, for example, that it gives poorer and poorer agreement as the value of K_{12} increases. This is illustrated by the data in Table 29-2, for two reactions with quite negative values of ΔG. It should be emphasized, however, that the Marcus cross relation is often justifiably in-

TABLE 29-2

Reaction	ΔG(kJ mol^{-1})	k_{12} Observed	k_{12} Calculated
$Fe^{III} + V^{II} \rightarrow Fe^{II} + V^{III}$	-96	3×10^4	1×10^6
$Fe^{III} + U^{III} \rightarrow Fe^{II} + U^{IV}$	-135	7×10^5	1×10^9

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[22] L. E. Bennett *et al., Inorg. Chem.,* 1983, **22,** 553.

voked to supply corroboration for an outer-sphere mechanism, provided cases with large negative ΔG values are avoided.

29-10. Ligand-Bridged (Inner-Sphere) Reactions[23]

The ligand-bridged reaction is illustrated schematically in eq. 29-46.

$$MX^{m+} + N^{n+} \longrightarrow \underset{\text{Precursor complex}}{[M^{m+}\text{—}X\text{—}N^{n+}]} \longrightarrow \underset{\text{Successor complex}}{[M^{(m-1)+}\underset{a}{\text{—}}X\underset{b}{\text{—}}N^{(n+1)+}]} \longrightarrow \text{products} \qquad (29\text{-}46)$$

The essential features of the mechanism are

1. A bridged binuclear complex, the *precursor complex,* is formed first by sharing some ligand X, which may use different atoms, even quite remote ones, to form the bonds to M and N. The formation of this complex requires N^{n+} to lose (at least) one of its initial ligands (not shown) to make room for the new bond to X.
2. A net electron transfer from N^{n+} to M^{m+} takes place giving the *successor complex.*
3. The *successor complex* collapses to give the products of the reaction.

In the recognition of this mechanism and pioneering studies of it by H, Taube and his students, reactions of the type 29-47 played a key role.

$$[Co(NH_3)_5X]^{2+} + Cr^{2+}(aq) + 5H^+ = [Cr(H_2O)_5X]^{2+} + Co^{2+}(aq) + 5NH_4^+ \qquad (29\text{-}47)$$

($X = F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NCS^-, N_3^-, PO_4^{3-}, P_2O_7^{4-}, CH_3CO_2^-, C_3H_7CO_2^-$, crotonate, succinate, oxalate, and maleate)

The significance and success of these experiments rest on the following facts. The Co^{III} complex is not labile though the Cr^{II} aqua ion is, whereas in the products the $[Cr(H_2O)_5X]^{2+}$ ion is not labile but the Co^{II} aqua ion is. It is found that the transfer of X from $[Co(NH_3)_5X]^{2+}$ to $[Cr(H_2O)_5X]^{2+}$ is quantitative. The most reasonable explanation for these facts is a mechanism such as that illustrated in 29-48.

$$\begin{tikzcd}
Cr^{II}(H_2O)_6^{2+} + Co^{III}(NH_3)_5Cl^{2+} \arrow[r] & {[(H_2O)_5Cr^{II}ClCo^{III}(NH_3)_5]^{4+}} \arrow[d, shift left, "\text{electron transfer}"] \\
Cr(H_2O)_5Cl^{2+} + Co(NH_3)_5(H_2O)^{2+} \arrow[d, "{H^+,\ H_2O}"] & {[H_2O)_5Cr^{III}ClCo^{II}(NH_3)_5]^{4+}} \arrow[l] \arrow[u, shift left] \\
Co(H_2O)_6^{2+} + 5NH_4^+ &
\end{tikzcd} \qquad (29\text{-}48)$$

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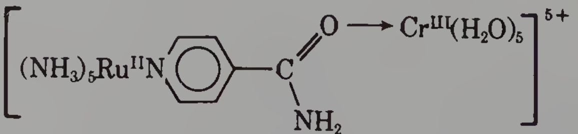
[23] A. Haim, *Prog. Inorg. Chem.*, 1983, **30**, 273 (an in-depth review).

Since all Cr^{III} species, including $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5Cl^{2+}$, are substitution inert, the quantitative production of $Cr(H_2O)_5Cl^{2+}$ must imply that electron transfer, $Cr^{II} \rightarrow Co^{III}$, and Cl^- transfer from Co to Cr are mutually interdependent acts, neither possible without the other. Postulation of the binuclear, chloro-bridged intermediate appears to be the only chemically credible way to explain this.

In reactions between Cr^{2+} and CrX^{2+} and between Cr^{2+} and $Co(NH_3)_5X^{2+}$, which are inner sphere, the rates decrease as X is varied in the order $I^- > Br^- > Cl^- > F^-$. This seems reasonable if ability to "conduct" the transferred electron is associated with polarizability of the bridging group, and it was once thought that this order might be diagnostic of the mechanism. However, the opposite order is found for $Fe^{2+}/Co(NH_3)_5X^{2+}$ and $Eu^{2+}/Co(NH_3)_5X^{2+}$ reactions; the $Eu^{2+}/Cr(H_2O)_5X^{2+}$ reactions give the order first mentioned, thus showing that the order is not simply a function of the reducing ion used.

In these classic examples of the inner-sphere mechanism it is the transfer of the bridging ligand X from cobalt to chromium that provides the definitive evidence for its operation. Although such a transfer may usually be expected, and usually occurs, it should be carefully noted that it is not an essential feature; it was not mentioned in the list of the three essential steps given earlier. Whether in the successor complex it is bond *a* or bond *b* (or both) that breaks depends on their relative strengths and labilities. Of course, if bond *b* breaks, there is no ligand transfer, hence no easy, direct proof that the precursor complex did indeed exist. An example in which bond *b* breaks is afforded by the reduction of $Ru(NH_3)_5[NC_5H_4C(NH_2)O]^{3+}$, where the large ligand is nicotinamide coordinated to Ru^{III} by its pyridine nitrogen atom, by Cr^{2+} (aq), which attaches to the amido oxygen atom to form the precursor complex. After electron transfer we have the successor complex (29-IV).

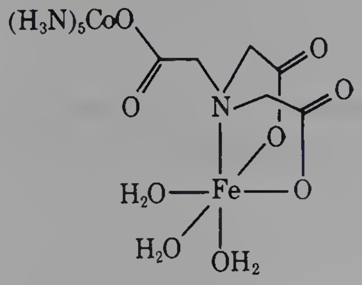


(29-IV)

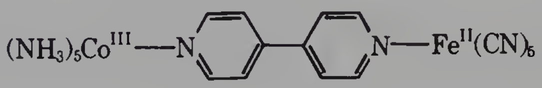
The rate of Ru^{II}—N bond cleavage is even slower than that of Cr^{III}—O bond cleavage; consequently the reaction products are $Ru(NH_3)_5[NC_5H_4C(NH_2)O]^{2+}$ and Cr^{3+}(aq) and there is no transfer of the bridging ligand.

Actually, in the example just cited, the really unusual and interesting feature is that the successor complex is so stable that it is an observable intermediate. This is a rare situation, but there are other examples. For the reaction of $[Fe(CN)_6]^{3-}$ with $[Co(CN)_5]^{3-}$ the bridged anion $[(NC)_5Fe{-}CN{-}Co(CN)_5]^{6-}$ can be precipitated as its barium salt.

There are also reactions in which the precursor complex is stable enough to constitute an observable intermediate. Among these are (29-V), which forms in the reduction of $Co(NH_3)_5(NTA)$ by Fe^{2+}(aq) and has a half-life of ~5 s, and (29-VI) formed in the reduction of $[Co(NH_3)_5(4,4'\text{-bipyridyl})]^{3+}$ by the $[Fe(CN)_5(H_2O)]^{3-}$ ion. An intermediate with half-life <0.1 s, believed to be the precursor complex, has also been observed in the reaction of $V^{IV}O(EDTA)$ with $V^{II}(EDTA)$.

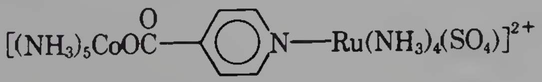


(29-V)



(29-VI)

A series of complexes in which the rates of electron transfer as such (i.e., the conversion of the preformed precursor complex to the successor complex) can be studied is typified by (29-VII), which contains Co^{III} and Ru^{II}. The +3 cation containing Co^{III} and Ru^{III} can be prepared and isolated. When redissolved and treated with Eu^{II} or $[Ru(NH_3)_6]^{2+}$, extremely rapid oxidation by an outer-sphere mechanism at Ru occurs to give the +2 ion (29-VII), whose conversion to the successor Co^{II}, Ru^{II} complex can then be observed.[24] Picosecond (ps) pulsed excitation affords another method of generating a precursor complex whose rate of electron transfer can then be monitored.[25]



(29-VII)

There is also the subtle question of the "intimate" mechanism of electron transfer by the inner-sphere path, that is, a detailed idea of how electron density is shifted from the reductant to the oxidant, once the bridged binuclear intermediate has been formed. Basically, two types of "intimate" mechanism have been considered:

1. A "chemical" mechanism, in which an electron is transferred to the bridging group, thus reducing it to a radical anion, whereupon an electron-hopping process eventually carries the electron to the oxidant metal ion.
2. A tunneling mechanism, whereby the electron simply passes from reductant to oxidant by quantum-mechanical tunneling through the barrier constituted by the bridging ligand.

In using organic bridging groups to investigate this question, the problem early arises of distinguishing between adjacent and remote attack by the reductant on the potential bridging group. In the case of benzoate ion as bridging group, attack must be on the coordinated carboxyl group, and there

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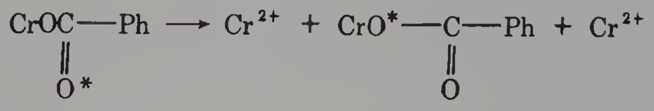
[24] S. K. S. Zawacky and H. Taube, *J. Am. Chem. Soc.*, 1981, **103**, 3379; K. Wieghardt *et al.*, *Inorg. Chem.*, 1984, **23**, 3435.

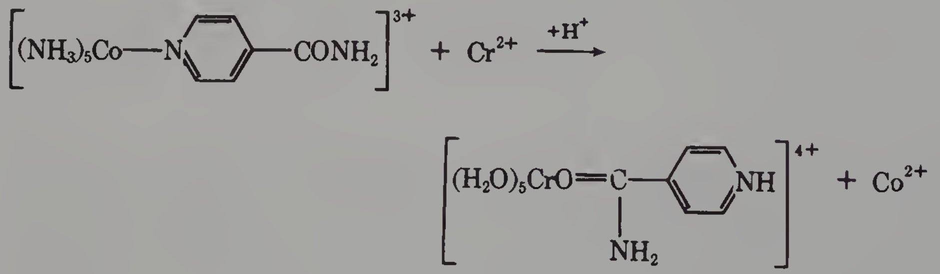
[25] P. M. Rentzepis *et al.*, *J. Am. Chem. Soc.*, 1982, **104**, 7400.

is evidence to show that it actually occurs on the carbonyl oxygen atom, as shown here:

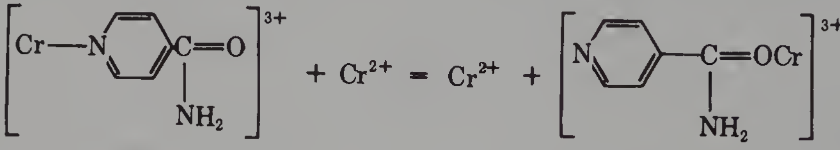


$$\mathrm{Cr}\overset{}{\underset{\mathrm{O^*}}{\mathrm{OC}}}\!\!\!\!\!\overset{}{\underset{}{}}\text{—Ph} \longrightarrow \mathrm{Cr^{2+}} + \mathrm{CrO^*}\text{—}\underset{\mathrm{O}}{\overset{}{\mathrm{C}}}\text{—Ph} + \mathrm{Cr^{2+}}$$

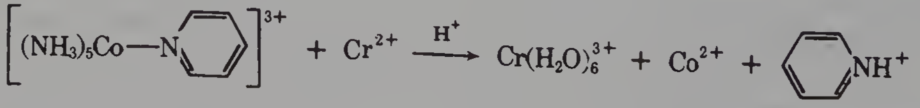
A definitive example of remote attack is provided by reaction 29-49. The evidence required to prove remote attack here is more elaborate than might at first sight be suspected. The mere fact that the $\mathrm{Cr^{III}}$ product contains the amide-bound ligand does not assure that remote attack occurred as the rate-determining step. It is necessary to exclude the possibility that (29-VIII) might initially be formed and then isomerized by unreacted $\mathrm{Cr^{2+}}$, as illustrated. In fact, the equilibrium represented is established only very slowly, and it lies well to the left (pyridine being a much better ligand than an amide). In addition, reaction 29-50 proceeds much more slowly than reaction 29-49, and exclusively by an outer-sphere mechanism; all chromium appears as $\mathrm{Cr(H_2O)_6^{3+}}$. Thus direct remote attack seems certain in the case of the *p*-amido ligand.



(29-49)

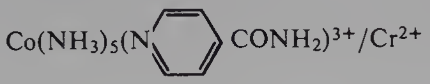
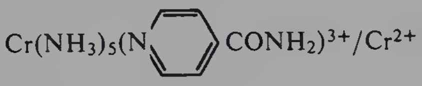


(29-VIII)



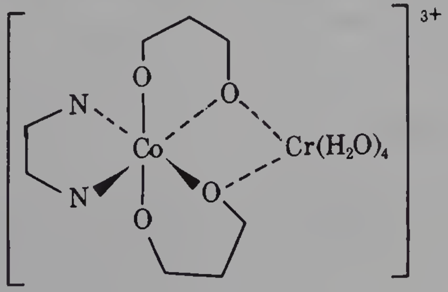
(29-50)

An indication that the chemical intimate mechanism can be operative in remote attack is afforded by the rate data in the accompanying tabulation. The first two pairs of reactions are inner sphere but presumably involve tunneling as the intimate mechanism. They indicate that tunneling to $\mathrm{Co^{3+}}$ is characteristically 10^6 times faster than to $\mathrm{Cr^{3+}}$. The small rate ratio in the last pair of reactions then strongly implies that the rates are primarily set by the rate of reduction of the bridging ligand, this rate being only a second-order function of what metal ion is attached to the far end.

Reactants	Rate ratio, Co/Cr
$Co(NH_3)_5F^{2+}/Cr^{2+}$	$\sim 10^6$
$Cr(NH_3)_5F^{2+}/Cr^{2+}$	
$Co(NH_3)_5OH^{2+}/Cr^{2+}$	$\sim 10^6$
$Cr(NH_3)_5OH^{2+}/Cr^{2+}$	
	~ 10
	

Doubly Bridged Inner-Sphere Transfer. Only a few electron transfer reactions are known to proceed through doubly bridged intermediates, and the factors conducive to such a pathway are not well understood. An early example was reduction of *cis*-$Co(en)_2(N_3)_2^+$ or its tetraammine analogue by Cr^{2+}. Approximately 1.2 and 1.4 azide ligands per Cr^{III} are found in the respective products, which would seem to require the frequent occurrence of double-bridge formation with subsequent transfer of the bridges, though this is not mandatory.

It has been shown that the reduction of $Co(acac)_2(en)^+$ by Cr^{2+} gives the following product distribution for the Cr^{3+} species: $Cr(H_2O)_6^{3+}$, 31%; $Cr(H_2O)_4(acac)^{2+}$, 38%; and $Cr(H_2O)_2(acac)_2^+$, 31%. It can be concluded that the reduction goes about equally by each of three paths: (1) outer sphere to produce $Cr(H_2O)_6^{3+}$, (2) singly bridged inner sphere to transfer one (acac), (3) doubly bridged inner sphere, to give $Cr(H_2O)_2(acac)_2^+$ with the transition state looking roughly as in (29-IX). Curiously, the reduction of $Co(acac)_3$ by Cr^{2+} takes place 66% by the outer-sphere path, 34% by a singly bridged path, and not to any detectable extent by the doubly bridged path.



(29-IX)

29-11. Other Electron Transfer Reactions

Two-Electron Transfers. There are some elements that have stable oxidation states differing by two electrons, without a stable state in between. It has been shown that in the majority of these cases, if not in all, two-electron transfers occur. The Pt^{II}–Pt^{IV} system (discussed briefly later) and the Tl^{I}–Tl^{III} system have been studied in some detail. For the latter in aqueous perchlorate solution the rate law is

$$v = k_1[Tl^+][Tl^{3+}] + k_2[Tl^+][TlOH^{2+}]$$

In the presence of other anions more complicated rate laws are found, indicating that two-electron transfers occur through various Tl^{3+} complexes.

A number of other redox reactions also appear to proceed by two-electron transfers, examples being:

$$Sn^{II} + Tl^{III} \longrightarrow Sn^{IV} + Tl^{I}$$
$$Sn^{II} + Hg^{II} \longrightarrow Sn^{IV} + Hg^{0}$$
$$V^{II} + Tl^{III} \longrightarrow V^{IV} + Tl^{I}$$

All these reactions are *complementary,* meaning that in the overall stoichiometry the oxidant gains and the reductant loses two electrons.

Noncomplementary Reactions. Reactions of a noncomplementary type, that is, the number of electrons gained by one ion of one species is not equal to the number lost by one ion of the other, must have multistep mechanisms, since ternary activated complexes are not likely and are not supported by any experimental evidence. This, in turn, means that some relatively unstable intermediate must be generated. For example, the overall reaction of Fe^{2+} with Tl^{3+} (eq. 29-51) might have as its initial step either a one-electron transfer to generate Fe^{3+} and the unstable Tl^{2+} or a two-electron transfer to generate Tl^+ and the unstable Fe^{4+}. It has been reported that the addition of Fe^{3+} reduces the rate of reaction, but the addition of Tl^+ is without effect. These and other observations indicate the mechanism to be that of eqs. 29-52a and 29-52b.

$$Tl^{3+}(aq) + 2Fe^{2+}(aq) \longrightarrow Tl^+(aq) + 2Fe^{3+}(aq) \qquad (29\text{-}51)$$
$$Fe^{2+}(aq) + Tl^{3+}(aq) \longrightarrow Fe^{3+}(aq) + Tl^{2+}(aq) \qquad (29\text{-}52a)$$
$$Fe^{2+}(aq) + Tl^{2+}(aq) \longrightarrow Fe^{3+}(aq) + Tl^+(aq) \qquad (29\text{-}52b)$$

Another noncomplementary reaction that has been studied is 29-53,

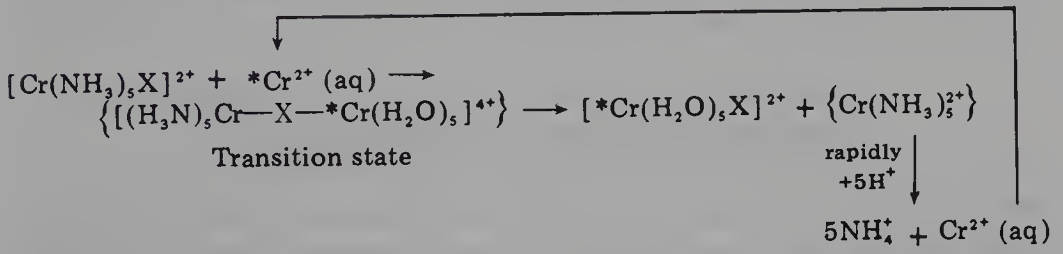
$$Sn^{II} + 2Fe^{III} \longrightarrow Sn^{IV} + 2Fe^{II} \qquad (29\text{-}53)$$

where the evidence shows successive one-electron transfers with Sn^{III} as the transient intermediate. Although this reaction is very slow when ClO_4^- is the only available anion, in the presence of halide ions it is still first order in Fe^{3+} but goes much faster, perhaps because of intermediate oxidation of halide ions to species such as X_2^-. The cluster ion $Ta_6Cl_{12}^{3+}$ is an effective catalyst, presumably because it has three successive oxidation levels (+2, +3, +4) conveniently accessible. Thus the following mechanism has been proposed:

$$Fe^{3+} + Ta_6Cl_{12}^{3+} \longrightarrow Fe^{2+} + Ta_6Cl_{12}^{4+}$$
$$Ta_6Cl_{12}^{4+} + Sn^{2+} \longrightarrow Sn^{4+} + Ta_6Cl_{12}^{2+}$$
$$Fe^{3+} + Ta_6Cl_{12}^{2+} \longrightarrow Fe^{2+} + Ta_6Cl_{12}^{3+}$$

Ligand Exchange via Electron Exchange. When a metal atom forms cations in two oxidation states, one giving labile complexes and the other inert complexes, substitution reactions of the latter can be accelerated by the presence of trace quantities of the former. For example, the reactions of type 29-54 that are catalyzed by a trace of Cr^{2+} must occur as shown in eq. 29-55, in view of the complete retention of X by Cr^{III} while the NH_3's are completely lost.

$$[Cr(NH_3)_5X]^{2+} + 5H^+ = [Cr(H_2O)_5X]^{2+} + 5NH_4^+ \qquad (29\text{-}54)$$
$$(X = F^-, Cl^-, Br^-, I^-)$$



(29-55)

There are various other cases, especially the $[Cr(H_2O)_5X]^{2+}—[Cr(H_2O)_6]^{2+}$ exchanges, in which retention of the X groups shows that they must be bridges in the activated complex. Also, when Fe^{3+} is reduced by Cr^{2+} in the presence of halide ions, the chromium(III) is produced as $[Cr(H_2O)_5X]^{2+}$. Similar phenomena are found also in the Co^{II}–Co^{III} aqua system and fairly generally in Pt^{II}–Pt^{IV} systems.

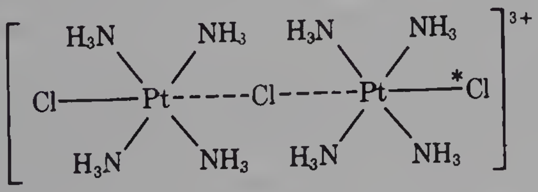
Platinum(II) catalyzes the exchange of chloride ion with $[Pt(NH_3)_4Cl_2]^{2+}$ in accordance with the following rate law:

$$v = k[Pt^{II}][Pt^{IV}][Cl^-]$$

The mechanism proposed to explain this is

$$Pt(NH_3)_4^{2+} + {}^*Cl^- = Pt(NH_3)_4{}^*Cl^+ \text{ (fast preequilibrium)}$$

$$Pt(NH_3)_4Cl_2^{2+} + Pt(NH_3)_4{}^*Cl^+ \longrightarrow$$



$$\longrightarrow Pt(NH_3)_4Cl^+ + Pt(NH_3)_4{}^*ClCl^{2+}$$

The structure of the proposed activated complex, or intermediate, is very plausible, being quite comparable to the structures found in crystals of several compounds containing equal molar quantities of Pt^{II} and Pt^{IV} (see Fig. 19-H-1). There is also considerable kinetic evidence corroborating this mechanism. It is likely that traces of Pt^{II} generated by adventitious reducing agents (traces of other metal ions, organic matter, etc.) or photochemically play a role in many reactions of Pt^{IV} complexes. It is also known that traces of other metals, notably Ir, which have several oxidation states, can catalyze Pt^{IV} reactions.

Reductions by Hydrated Electrons. The hydrated electron is a powerful reducing agent with a redox potential estimated to be -2.7 V. It is an ephemeral species with a half-life of $<10^{-3}$ s, but it may be generated by pulse radiolysis at roughly millimolar concentrations. It reacts very rapidly, generally with second-order rate constants of 10^8 to 5×10^{10}, which indicate that the reactions are at or near the diffusion-controlled limit. Because of its great reducing power and great speed, the hydrated electron is highly useful for generating in aqueous media unstable low-valent cations whose decomposition or reaction kinetics can then be studied.

STEREOCHEMICAL NONRIGIDITY

Most molecules have a single, well-defined nuclear configuration. The atoms execute approximately harmonic vibrations about their equilibrium positions, but in other respects the structures may be considered rigid. There are, however, a significant number of cases in which molecular vibrations or intramolecular rearrangements carry a molecule from one nuclear configuration into another. When such processes occur at a rate permitting detection by at least some physical or chemical method, the molecules are designated as *stereochemically nonrigid*. In some cases the two or more configurations are not chemically equivalent and the process of interconversion is called *isomerization* or *tautomerization*. In other cases the two or more configurations are chemically equivalent, and this type of stereochemically nonrigid molecule is called *fluxional*.

The rearrangement processes involved in stereochemically nonrigid molecules are of particular interest when they take place rapidly, although there is a continuous gradation of rates and no uniquely defined line of demarcation can be said to exist between "fast" and "slow" processes. The question of the speed of rearrangement most often derives its significance when considered in relation to the *time scale* of the various physical methods of studying molecular structure. In some of these methods, such as electronic and vibrational spectroscopy and gas phase electron diffraction, the act of observation of a given molecule is completed in such an extremely short time ($<10^{-11}$ s) that processes of rearrangement may seldom if ever be fast enough to influence the results. Thus for a fluxional molecule, where all configurations are equivalent, there will be nothing in the observations to indicate the fluxional character. For interconverting tautomers the two (or more) tautomers will each be registered independently, and there will be nothing in the observations to show that they are interconverting.

It is the technique of nmr spectroscopy that most commonly reveals the occurrence of stereochemical nonrigidity, since its time scale is typically in the range 10^{-2} to 10^{-5} s. The rearrangements involved in stereochemically nonrigid behavior are rate processes with activation energies. When these activation energies are in the range 25 to 100 kJ mol^{-1} the rates of the rearrangements can be brought into the range of 10^2 to 10^5 s^{-1} at temperatures between +150 and −150°C. Thus by proper choice of temperature, many such rearrangements can be controlled so that they are slow enough at lower temperatures to allow detection of individual molecules, or environments within the molecules, and rapid enough at higher temperatures for the signals from the different molecules or environments to be averaged into a single line at the mean position. Thus by studying nmr spectra over a suitable temperature range, the rearrangement processes can be examined in much detail.

29-12 Stereochemically Nonrigid Coordination Compounds

Coordination polyhedra are usually thought of in essentially static terms, that is, as if there are no intramolecular interchanges of ligands. In many cases, especially for octahedral complexes, this is valid, but there is a growing body of evidence that nonrigidity, particularly fluxionality, is not uncommon. In fact, for five-coordinate complexes and most of those with coordination numbers of 7 or higher, nonrigidity is the rule rather than the exception.

A common type of fluxional behavior is the inversion of pyramidal molecules (Fig. 29-9). In the cases of NH_3 (Section 10-2) and other simple noncyclic amines the activation energies, which are equal to the difference between the energies of the pyramidal ground configurations and the planar transition states, are quite low (24–30 kJ mol^{-1}) and the rates of inversion extremely high (e.g., 2.4×10^{10} s^{-1} for NH_3). Actually in the case of NH_3 the inversion occurs mainly by quantum mechanical tunnelling through the barrier rather than by passage over it. In most cases, however, passage over a barrier (i.e., a normal activated rate process) is operative. With phosphines, arsines, R_3S^+, and R_2SO species the barriers are much higher (>100 kJ mol^{-1}), and inversions are slow enough to allow separation of enantiomers in cases such as RR′R″P and RR′SO.

Among four-coordinate transition metal complexes fluxional behavior based on planar tetrahedral interconversions is of considerable importance. This is especially true of nickel(II) complexes, where planar complexes of the type $Ni(R_3P)_2X_2$ have been shown to undergo planar ⇌ tetrahedral rearrangements with activation energies of about 45 kJ mol^{-1} and rates of ~10^5 s^{-1} at about room temperature.

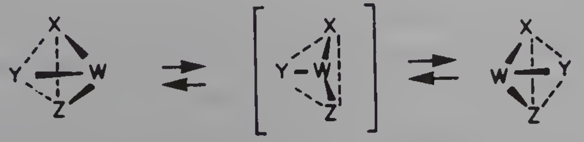


FIG. 29-9. The inversion of a pyramidal molecule WXYZ. Note that if X, Y, and Z are all different, the *invertomers* are enantiomorphous.

Trigonal Bipyramidal Molecules. A class of fluxional molecules of great importance are those with a *tbp* configuration. Because of their importance and the great amount of information on them, they are discussed here at some length. When all five appended groups are identical single atoms, as in AB_5, the symmetry of the molecule is D_{3h}. The two apical atoms B_1 and B_2 (Fig. 29-10) are equivalent but distinct from the three equatorial atoms B_3, B_4, B_5, which are equivalent among themselves. In general, experiments such as measuring nmr spectra of B nuclei, which can sense directly the kind of environmental difference represented by B_1, B_2 versus B_3, B_4, B_5, should indicate the presence of two sorts of B nuclei in *tbp* molecules. In many cases, for example, the ^{13}C spectrum of $Fe(CO)_5$, and the ^{19}F spectrum of PF_5 (to name the two cases where such observations were first made), all five B nuclei appear to be equivalent in the nmr spectrum, even though other experimental data with a shorter time scale, such as diffraction experiments and vibrational spectroscopy, confirm the *tbp* structure.

All the ligands in the nmr spectrum in these cases appear to be equivalent because they pass rapidly between the axial and equatorial sites. Theory shows that if two nuclei occupying sites whose resonance frequencies ν_1 and ν_2 differ by $\Delta\nu\ s^{-1}$ change places at a frequency greater than $\Delta\nu\ s^{-1}$, only one resonance at $\frac{1}{2}(\nu_1 + \nu_2)$ will be observed. Obviously a ligand can move from an axial to an equatorial site only if there is a simultaneous shift of a ligand from an equatorial site to an axial one. With this in mind, it is then clear that there are only two types of intramolecular* exchange processes possible: (1) those in which each step involves only one axial and one equatorial ligand, and (2) those in which both axial ligands simultaneously exchange with two equatorial ones. In cases for which direct evidence has been obtained, the second type of process (2-for-2 exchange) is indicated.

It is important to realize that the nmr experiment can never do more than distinguish between two algebraically different permutations (i.e., 1-for-1, or 2-for-2, as above); it can never reveal the detailed pathways of the atoms. Two plausible, idealized pathways have been suggested for the 2-for-2 rearrangement of a *tbp* molecule. One of them, first suggested by R. S. Berry in 1960, is shown in Fig. 29-10. Not only do the *tbp* and *sp* configurations of an

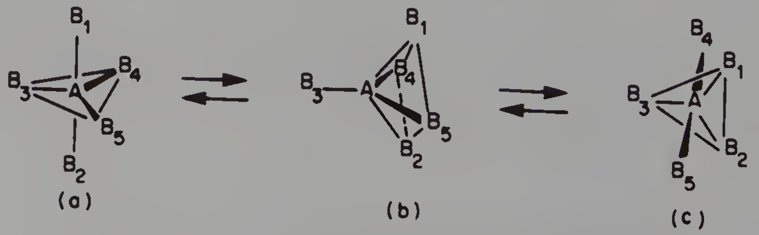


FIG. 29-10. The *tbp*–*sp*–*tbp* interconversion, the so-called Berry mechanism or pseudorotation for five-coordinate molecules.

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*In both PF_5 and $Fe(CO)_5$ the persistence of ^{31}P—^{19}F and ^{57}Fe—^{13}C coupling rules out dissociative or bimolecular processes, and there is no reason to doubt that the overwhelming majority if not all fluxional *tbp* molecules rearrange intramolecularly.

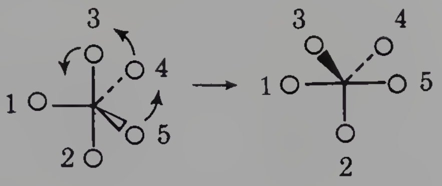

FIG. 29-11. The turnstile rotation.

AB_5 molecule tend to differ little in energy, but, as Berry pointed out, they can also be interconverted by relatively small and simple angle deformation motions and in this way axial and equatorial vertices of the *tbp* may be interchanged. As shown in Fig. 29-10, the *sp* intermediate (b) is reached by simultaneous closing of the B_1AB_2 angle from 180° and opening of the B_4AB_5 angle from 120° so that both attain the same intermediate value, thus giving a square set of atoms, B_1, B_2, B_4, B_5, all equivalent to each other. This *sp* configuration may then return to a *tbp* configuration in either of two ways, one of which simply recovers the original while the other, as shown, places the erstwhile axial atoms B_1, B_2 in equatorial positions and the erstwhile equatorial atoms B_4, B_5 in the axial positions. Note that B_3 remains an equatorial atom and also that the molecule after the interchange is, effectively, rotated by 90° about the A—B_3 axis. Because of this apparent, but not real rotation, the Berry mechanism is often called a pseudorotation and the atom B_3 is called the pivot atom. Of course, the process can be repeated with B_4 or B_5 as the pivot atom, so that B_3 too will change to an axial position.

A second process that also results in a 2-for-2 exchange, called the "turnstile rotation" for obvious reasons, is shown in Fig. 29-11. As already noted, no choice between these is possible on the basis of the nmr spectra themselves for an AB_5 molecule. However, theoretical work[26] on PF_5 and other species has consistently favored the Berry process.

Systems with Coordination Number 6 or More. The octahedron is usually rather rigid, and fluxional or rapid tautomeric rearrangements generally do not occur in octahedral complexes unless metal-ligand bond breaking is involved. Among the few exceptions are certain iron and ruthenium complexes of the type $M(PR_3)_4H_2$. The cis and trans isomers of $Fe[PPh(OEt)_2]_4H_2$, for example, have separate, well-resolved signals at −50°C that broaden and collapse as the temperature is raised until at +60°C there is a single sharp multiplet indicative of rapid interconversion of the two isomeric structures. The preservation of the ^{31}P–^{1}H couplings affords proof that the rearrangement process is nondissociative. The distortion modes postulated to account for the interconversions are shown in Fig. 29-12. The rearrangement of "octahedral" bis and tris chelate complexes is considered in the next section.

Stereochemical nonrigidity, especially if it is fluxional, seems likely to be consistently characteristic of complexes with coordination numbers of 7 or greater. All seven-coordinate complexes so far investigated by nmr techniques

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[26] C. J. Marsden, *J. Chem. Soc., Chem. Commun.*, **1984,** 401.

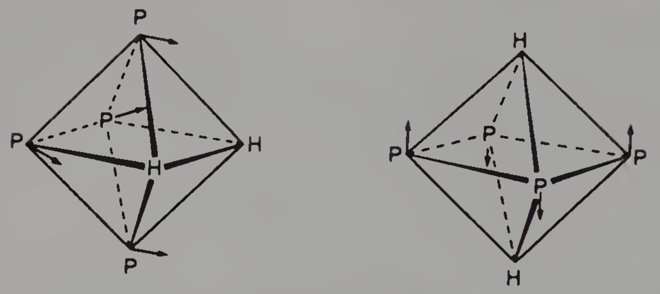

FIG. 29-12. The types of distortion postulated to lead to interconversion of cis and trans isomers of $Fe[PPh(OEt)_2]_4H_2$.

have shown ligand-atom equivalence even though there is no plausible structure for a seven-coordinate complex that would give static or instantaneous equivalence.[27]

Eight-coordinate structures are usually, but not invariably, fluxional. The dodecahedral structure, which is one of the commonest, has two distinct subsets of ligands, but these can easily interchange by rearrangement of the dodecahedron to a square antiprism, and then back, as shown in Fig. 29-13. The fundamental feature of this process is the opening of one or more edges shared by adjacent triangular faces to generate one or more square faces, followed by reclosing of edges in a different way. In this case, two such triangle–square–triangle transformations occur; the Berry process can be viewed as entailing only one such process for each step. There are other systems (e.g., icosahedral carboranes) in which this simple step may provide a basis for polytopal rearrangements.

In the case of nine-coordinate species, where the ligands adopt the D_{3h} capped trigonal prism arrangement shown in Fig. 29-14, there is also an easy pathway for interchanging ligands of the two sets, and for species such as ReH_9^{2-}, $ReH_8PR_3^-$, and $ReH_7(PR_3)_2$ attempts to detect the presence of hydrogen atoms in two different environments by nmr have failed. Figure 29-14 shows the probable form of the rearrangement that causes the rapid exchange.

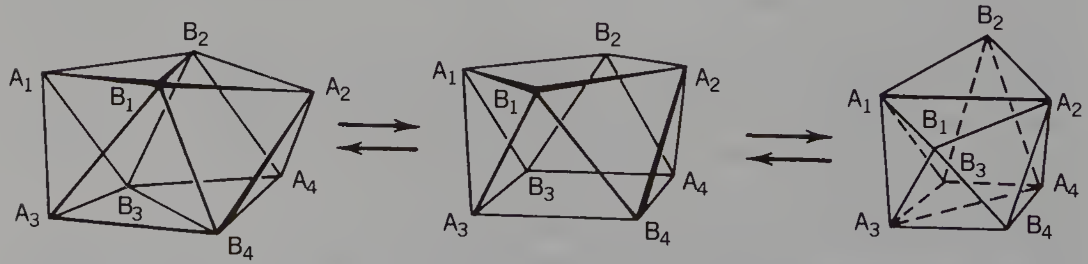

FIG. 29-13. Interconversion of A and B vertices of a dodecahedron by way of a square antiprism intermediate or transition state.

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[27] S. S. Wreford *et al.*, *Organometallics*, 1982, **1**, 935.

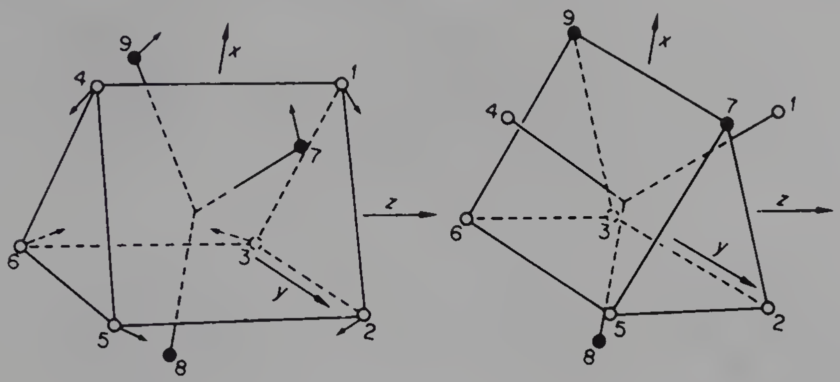


FIG. 29-14. The postulated pathway by which the ligands may pass from one type of vertex to the other in the D_{3h} tricapped trigonal prism.

29-13. Isomerization and Racemization of Trischelate Complexes

Trischelate complexes exist in enantiomeric configurations Λ and Δ about the metal atom (Fig. 2-3), and when the chelating ligand is unsymmetrical (i.e., when it has two different ends), there are also geometrical isomers, cis and trans. Each geometrical isomer exists in enantiomeric forms; thus there are four different molecules.

In the case of tris complexes with symmetrical ligands, the process of inversion (interconversion of enantiomers) is of considerable interest. When the metal ions are of the inert type, it is often possible to resolve the complex; then the process of racemization can be followed by measurement of optical rotation as a function of time. Possible pathways for racemization fall into two broad classes: those without bond rupture and those with bond rupture.

There are two pathways without bond rupture that have been widely discussed. One is the trigonal, or Bailar, twist and the other is the rhombic, or Ray-Dutt, twist, in Fig. 29-15(a) and (b), respectively. Twist processes are, of course, not confined to chelate complexes. It has already been noted (p. 1302) that some *cis*-$M(CO)_4(PR_3)_2$ complexes are believed to isomerize in this way.

There are several plausible dissociative pathways, in which a five-coordinate intermediate of either *tbp* or *sp* geometry is formed. One which seems likely in some cases is shown in Fig. 29-15(c). While associative pathways entailing a seven-coordinate intermediate with a coordinated solvent molecule have been hypothesized, there is no evidence for their actual occurrence.

While unequivocal determination of rearrangement pathways is usually impossible, experimental data can often *exclude* certain possibilities. For example, in the racemization of $[Cr(C_2O_4)_3]^{3-}$ a ring-opening path is virtually demanded since *all* oxalate oxygen atoms exchange with solvent water at a rate faster than that for oxalate exchange but almost equal to that of racemization.

A considerable amount of effort has been devoted to $M(dike)_3$ complexes

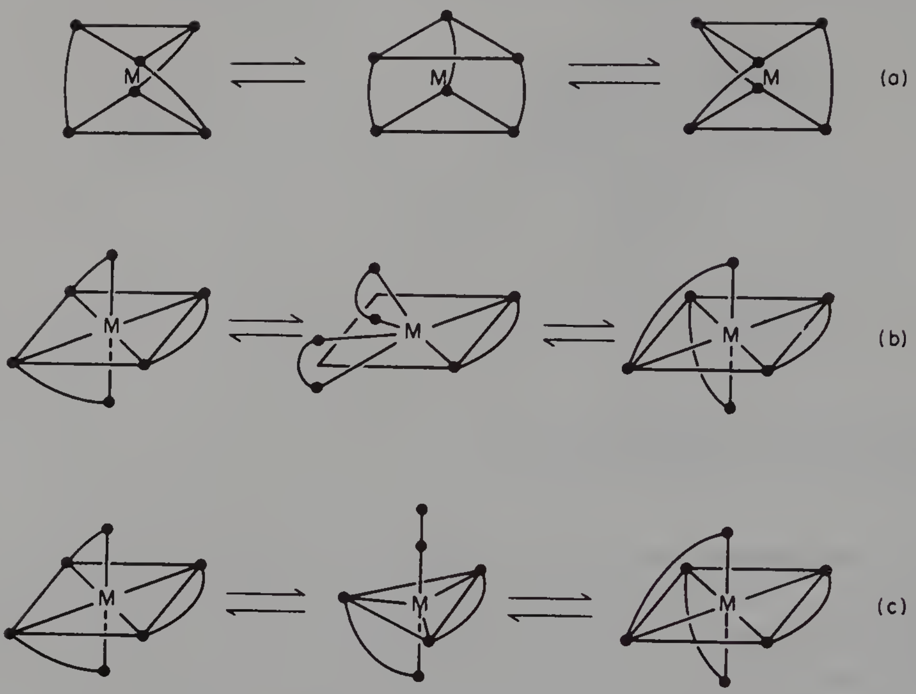
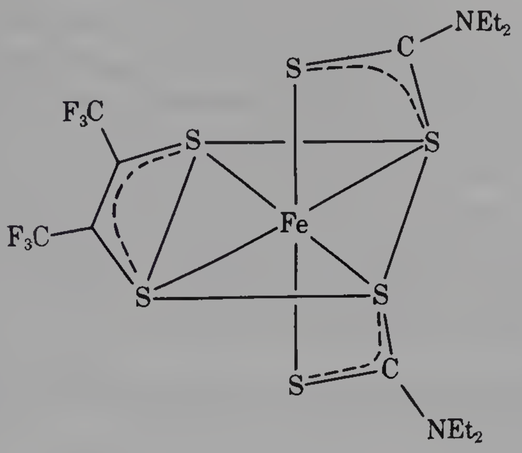


FIG. 29-15. Three possible modes of intramolecular racemization of a trischelate complex. (a) trigonal twist, (b) rhombic twist, (c) one of several ring-opening paths.

because by using unsymmetrical diketonate ligands, the processes of isomerization and racemization can be studied simultaneously. Since isomerization can occur *only* by a dissociative pathway, it is often possible to exploit well-designed experiments to yield information on the pathways for both isomerization and racemization.

To illustrate the approach, let us consider some of the data and deductions for the system $Co[CH_3COCHCOCH(CH_3)_2]_3$, measured in C_6H_5Cl. It was found that both the isomerization and the racemization are intramolecular processes, which occur at approximately the same rate and with activation energies that are identical within experimental error. It thus appears likely that the two processes have the same transition state. This excludes a twist mechanism as the principal pathway for racemization. Moreover, it was found that isomerization occurs mainly with inversion of configuration. This imposes a considerable restriction on the acceptable pathways. Detailed consideration of the stereochemical consequences of the various dissociative pathways, and combinations thereof, leads to the conclusion that for this system the major pathway is through a *tbp* intermediate with the dangling ligand in an axial position as in Fig. 29-15(a).

Evidence for the trigonal twist mechanism has been obtained in a few complexes in which the "bite" of the ligand is small, thus causing the ground state configuration to have a small twist angle ϕ, as defined in Fig. 1-7. The complex (29-X) is an example. A twist mechanism is preferred in these cases



(29-X)

because the structure is considerably distorted away from an octahedral configuration of sulfur atoms toward a trigonal prismatic configuration. Thus the transition state, which is trigonal prismatic, is probably more energetically accessible than it would be if the complex had an essentially regular octahedral ground configuration.

29-14. Metal Carbonyl Scrambling[28]

It has now been conclusively shown that di- and polynuclear metal carbonyl compounds have a marked general tendency to engage in a type of fluxional behavior called *carbonyl scrambling.* This type of behavior arises because of some of the inherent properties of metal to CO bonding. As shown in Section 22-4, especially in Fig. 22-5, the energy of a binuclear system consisting of two metal atoms and two CO groups does not in general vary a great deal (<30 kJ mol^{-1}) over the entire range of configurations from that in which there is one terminal CO ligand on each metal atom to that in which both CO groups are forming symmetrical bridges. The important thing that we now add to the picture presented in Fig. 22-5 is an emphasis on the symmetricality of the system, so that we can take case A from Fig. 22-5 and obtain Fig. 29-16. In this case the terminal arrangement is more stable than the bridging one, so that the overall process allows CO (A) to pass from the left metal atom to the one on the right while CO (B) is simultaneously making exactly the opposite journey. This sort of process may also occur around a three-membered ring (or even a larger one). The converse case, where a bridged arrangement is more stable than the terminal one, as in curve B of Fig. 22-5, may also be recognized. Concerted processes of this type account for most of the known cases in which CO groups are scrambled over a skeleton of two or more metal atoms. Let us examine a few illustrations.

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[28] F. A. Cotton and B. E. Hanson, in *Rearrangements in Ground and Excited States,* P. de Mayo, Ed., Academic Press, New York, 1980, p. 379.

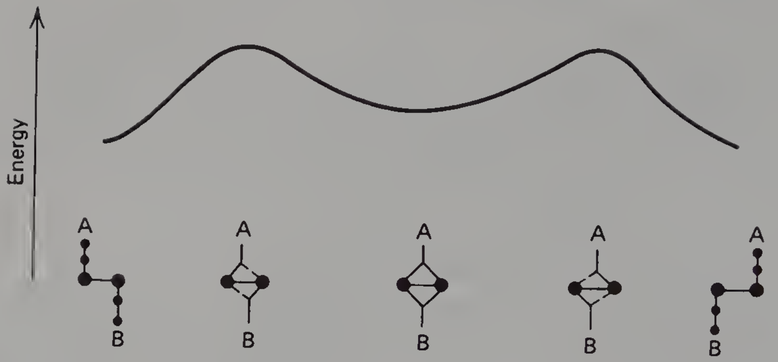
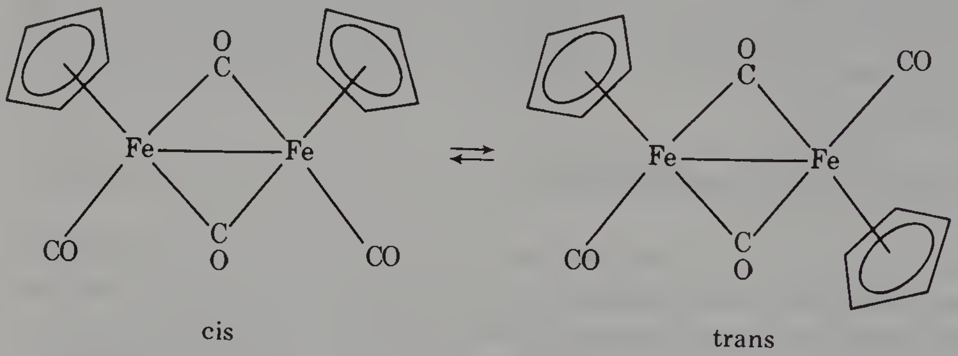


FIG. 29-16. Potential energy curve for the concerted exchange of two CO ligands groups via a bridging intermediate.

The $Cp_2Fe_2(CO)_4$ molecule ($Cp = \eta\text{-}C_5H_5$) exists in solution as a mixture of cis and trans isomers with bridging CO groups, as shown in eq. 29-56. The ^1H nmr resonances for the rings should appear at different positions and, as shown in Fig. 29-17, this is observed at −70°C. However, at +28°C only a single sharp signal at the intermediate position is seen. Clearly, between −70°C and room temperature some process by which the cis and trans isomers are interconverted becomes very rapid. This process cannot be a simple rotation because of the central rigid ring system. The nmr spectrum of the ^{13}C



(29-56)

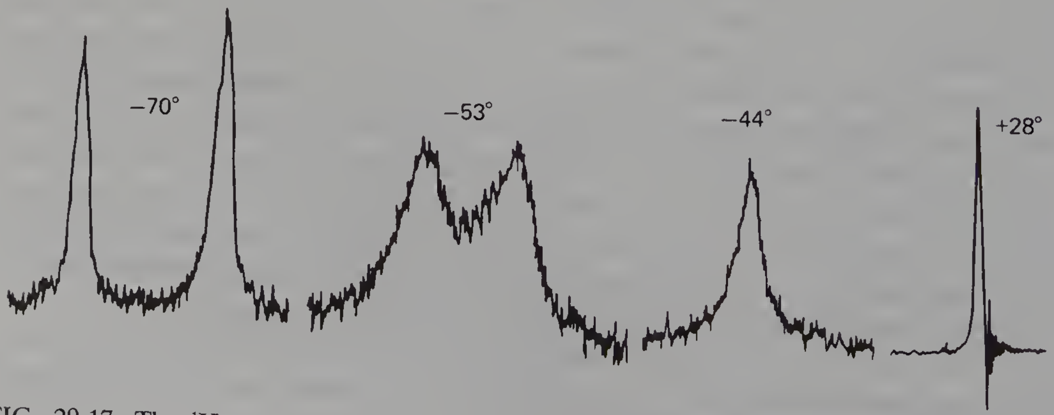
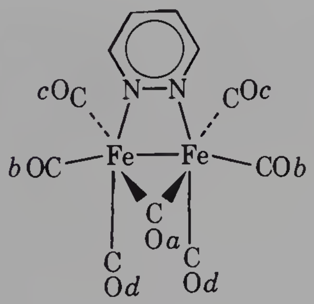


FIG. 29-17. The ^1H nmr spectra of the system *cis*- and *trans*-$[\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ at several temperatures.

atoms of the CO groups shows that the cis–trans interconversion is accompanied by interchange of the CO groups between bridging and terminal positions. The explanation for both these processes is that the CO bridges open in a concerted way to give a nonbridged $Cp(OC)_2Fe—Fe(CO)_2Cp$ intermediate in which rotation about the Fe—Fe bond takes place. This rotation will be followed by a reclosing of bridges, but that may happen to produce either a cis or a trans isomer, regardless of which one was present before bridge opening. In addition, the CO groups that swing into bridge positions need not be the same ones that were there at the outset, so that bridge/terminal interchange will also result.

Another example of CO scrambling is provided by the molecule (29-XI), which has four different types of CO group, *a–d,* as indicated. In a ^{13}C nmr spectrum, only at −139°C or lower are all the different resonances seen. When the temperature is raised to about −60°C only two resonances, in an intensity ratio of 5:2, are seen. This is because the five approximately coplanar CO groups (types *a, b,* and *c*) are rapidly cycling around over the five available sites, as in Fig. 29-18(a). Between −60°C and room temperature, this two-line spectrum collapses to a one-line spectrum as the five in-plane CO groups come into rapid exchange with the other two, probably by a process in which each set of three *a, b,* and *c* carbonyl groups on each iron atom rapidly rotates as in Fig. 29-18(b). The combined effect of both rapid processes is to move all CO groups over all seven sites rapidly, thus making them all appear



(29-XI)

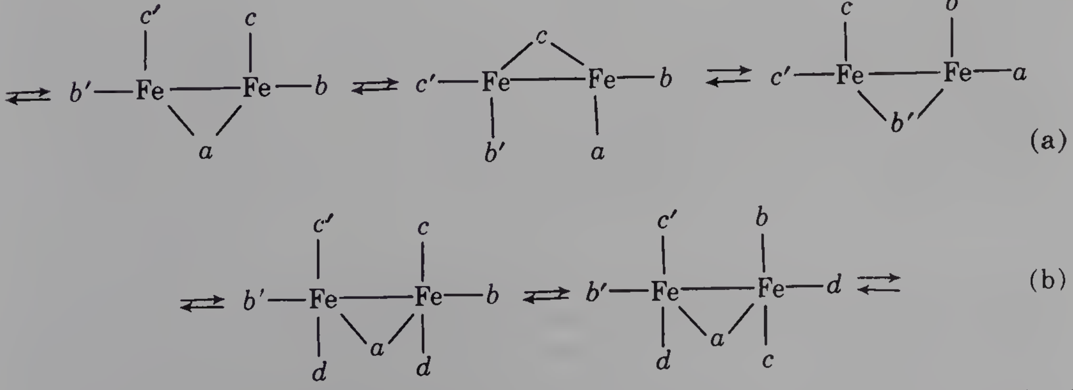


FIG. 29-18. (a) Cyclic mode of rearrangement of the five coplanar CO groups. (b) Mode of rearrangement of three terminal CO groups on the same iron atom.

equivalent in the nmr spectrum, even though there are four distinct types at any instant.

This example introduces another rather common type of CO scrambling process, namely, localized rotation of the CO groups in an $M(CO)_3$ unit that is bound to some other portion of a large molecule. In virtually every known case, this rotation will occur rapidly below the decomposition temperature of the compound, regardless of whether there is any internuclear scrambling of the CO groups. However, the activation energies, and hence the temperatures of onset, for these localized rotations vary considerably. A rather nice example is provided by $Os_6(CO)_{18}$ (a bicapped tetrahedron), in which the three distinct types of $Os(CO)_3$ unit exhibit coalescence temperatures of ~ −100, −10, and +40°C. It has not been possible to determine which signal is associated with each type of $Os(CO)_3$ group, however.

Carbonyl scrambling is also observed in metal carbonyl hydrides, where it may or may not be associated with scrambling of H atoms. For example, in the clusters $H_2FeRu_3(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$, the processes shown in Fig. 29-19, in which only CO groups move, can explain the observed changes in the ^{13}C nmr spectra.[29] On the other hand in

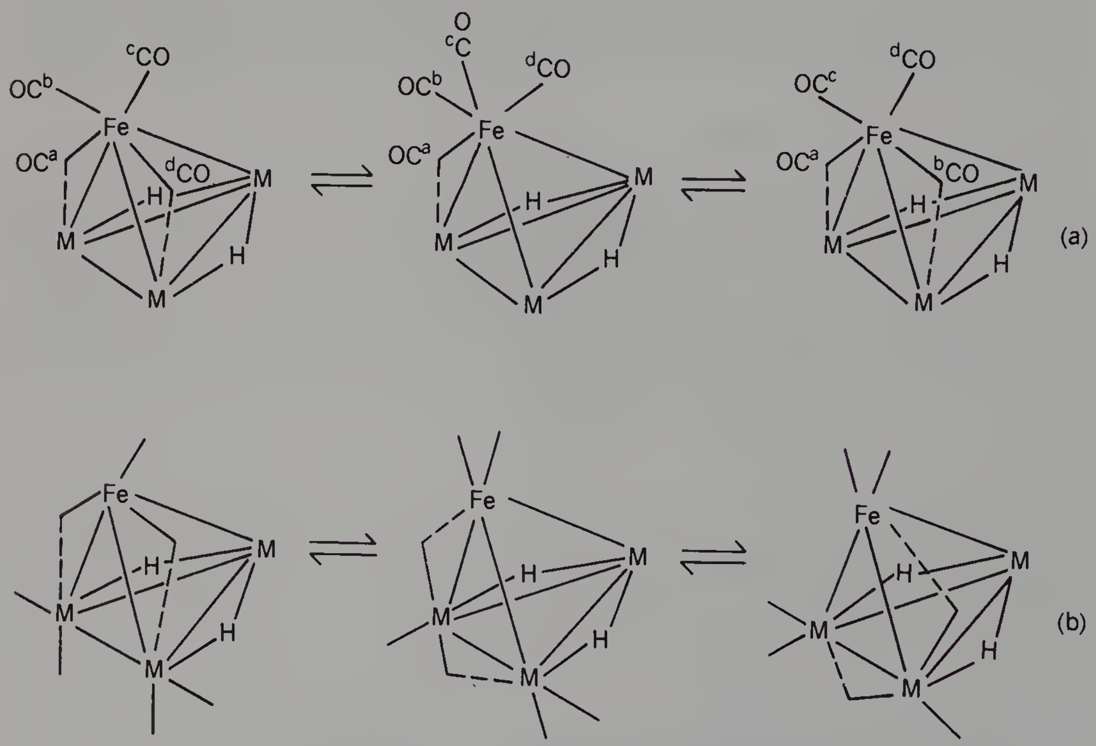


FIG. 29-19. Schematic representations of two CO scrambling processes believed to occur in $H_2FeM_3(CO)_{13}$ molecules. (a) Localized scrambling on the Fe atom. (b) Circulation of CO groups around one triangular face.

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[29] W. L. Gladfelter and G. L. Geoffroy, *Inorg. Chem.*, 1980, **19**, 2579.

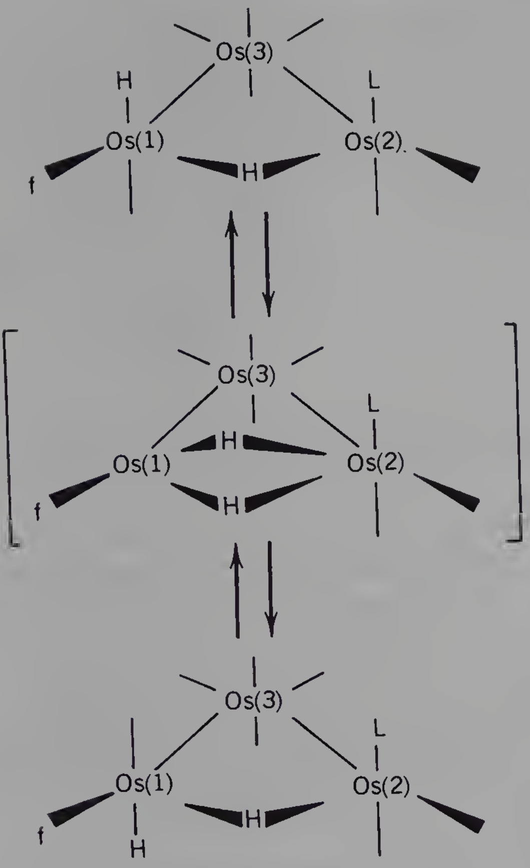

FIG. 29-20. A fluxional process proposed for $H_2Os_3(CO)_{10}L$ molecules in which both H atoms and CO groups engage in concerted movements.

$H_2Os_3(CO)_{10}L$ compounds, the process shown in Fig. 29-20, in which concerted CO and H rearrangements take place, has been invoked.[30]

Cluster Rotation within CO Shells. It is well known that in molecules such as $Fe_3(CO)_{12}$ and $Rh_4(CO)_{12}$, where there are several structurally nonequivalent types of CO groups, the ^{13}C nmr spectrum at higher temperatures shows only one signal. This indicates that all CO groups pass through all of the different types of sites rapidly. In the case of $Rh_4(CO)_{12}$ the signal in the fast exchange regime also shows unequivocally that these CO groups "see" each of the four Rh atoms equally. It is easily possible to explain these results by the repeated occurrence of the sorts of processes just discussed. For each of these molecules the key step would be the concerted opening of CO bridges to give intermediates that contain only terminal groups, followed by the reclosing of bridges using other CO groups and spanning other edges of the Fe_3 or Rh_4 cluster. It has been pointed out, however, that for these two cases, and some others, a different mechanism could also account for the ^{13}C nmr results.[31]

This alternative mechanism is based on the notion that the set of 12 CO groups is packed around the central cluster of metal atoms in such a way as

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[30] J. B. Keister and J. R. Shapley, *Inorg. Chem.*, 1982, **21,** 3304.

[31] B. F. G. Johnson and R. E. Benfield, in *Transition Metal Clusters*, B. F. G. Johnson, Ed., Wiley, New York, 1980, p. 471.

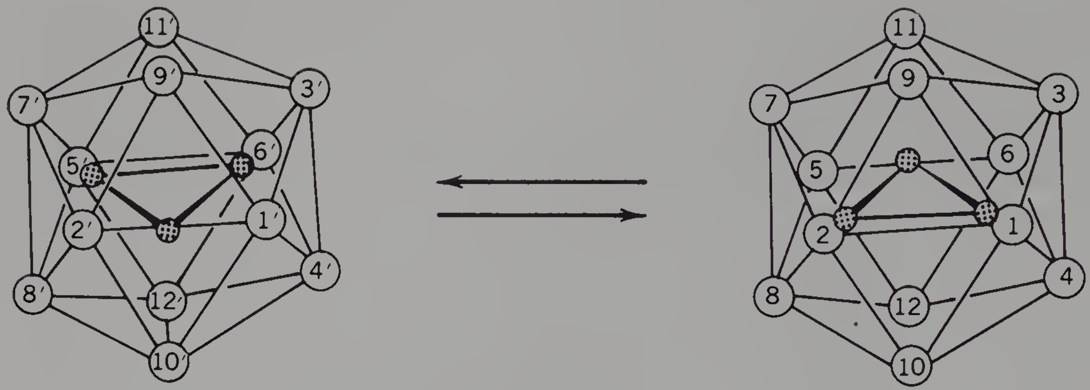

FIG. 29-21. An idealized view of the structure of $Fe_3(CO)_{12}$, where the set of CO groups is represented as a regular icosahedron and the two orientations for the Fe_3 cluster are shown.

to define a distorted icosahedron. Since the central cluster has only a few of the symmetry elements of a regular icosahedron, its presence inside the icosahedron leads to small, symmetry-lowering distortions. However, if we imagine that the cluster as a whole can reorient within the shell of the CO groups, accompanied by small readjustments of the distortions from full icosahedral symmetry, we have a mechanism for rendering all of the CO groups equivalent on a time-average basis. At the present time, no experiment has yet been devised to distinguish between this mechanism and the more conventional ones for molecules in solution.

In the crystalline state, however, there is experimental evidence showing that at least limited reorientations of metal clusters within shells of CO groups do occur. The clearest example is provided by $Fe_3(CO)_{12}$, crystals of which are disordered as shown in Fig. 29-21. Magic-angle spinning ^{13}C nmr spectra between 31 and −121°C show that the Fe_3 cluster flips between these two orientations at room temperature but is frozen into one or the other at lower temperatures.[32] This has the effect of averaging the bridge CO resonances with a pair of the terminal ones, as well as averaging the other terminal resonances in pairs. In crystalline $Co_4(CO)_{12}$ the situation is a little more complicated, but at least one form of rotation of the Co_4 cluster within the shell of CO groups occurs.[33] In both of these cases, the proposal of cluster rotation within a fixed shell of CO groups is based on the reasonable assumption that because of intermolecular forces the CO shell itself is immobile.

29-15. Fluxional Organometallic Compounds[34]

Fluxionality is characteristic of certain classes of organometallic compound and is found sporadically in others. The phenomenon is seen characteristically

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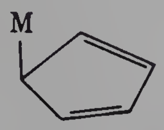
[32] B. E. Hanson *et al.*, *Inorg. Chem.*, 1986, **25**, 4062.

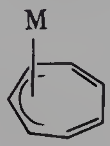
[33] B. E. Hanson and E. C. Lisic, *Inorg. Chem.*, 1986, **25**, 716.

[34] B. E. Mann, in *Comprehensive Organometallic Chemistry*, Vol. 3, pp. 89–171, Pergamon Press, Oxford, 1982.

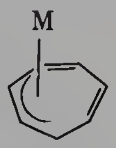
in compounds containing conjugated cyclic polyolefins such as cyclopentadienyl, cycloheptadienyl, or cyclooctatetraene, to name the three most common ones, attached to a metal atom through at least one but less than all of their carbon atoms, as illustrated by the partial structures (29-XII) to (29-XVI).



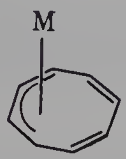
(29-XII)



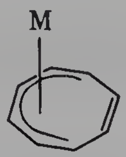
(29-XIII)



(29-XIV)



(29-XV)



(29-XVI)

In each of these structures there are several structurally different ring carbon atoms and hydrogen atoms; thus complex nmr spectra would be expected. For example, the (η^1-C_5H_5)M system (29-XII) should have a complex downfield multiplet of the AA′BB′ type and relative intensity 4 for the four olefinic H atoms and an upfield multiplet of relative intensity 1 for the H atom attached to the same carbon atom as the metal atom. In fact, at room temperature, nearly all compounds containing moieties of these kinds exhibit only one sharp singlet in the ^{1}H or ^{13}C spectrum for the entire organic ligand. The explanation for this is that at higher temperatures the place of attachment of the metal atom to the ring is shifting rapidly over some or all members of the set of such equivalent points, thus conferring time-average equivalence on the C and H atoms. Two such hopping processes for the (η^1-C_5H_5)M case are illustrated in Fig. 29-22. Because of the nature of the motion of the ring relative to the metal atom, these systems are commonly called "ring whizzers."

In each of the ring whizzer systems full characterization requires experimental information on three points: (1) proof of structure for the type of configuration in which the molecule rests between hops; (2) estimates of the rate of hopping at various temperatures, from which activation parameters can be obtained; (3) a knowledge of the pathway used in the hopping process. As the (η^1-C_5H_5)M case shows, there is usually more than one set of jumps that can be considered a priori plausible.

On all these points information is provided by nmr spectra recorded at lower temperatures. When a temperature is reached such that the spectrum remains the same at still lower temperature, it is generally safe to assume that this spectrum (the slow-exchange spectrum) can be used to infer the structure of the molecule between jumps. In dozens of cases structural moieties of the types (29-XII) to (29-XVI) were expected, and their presence was

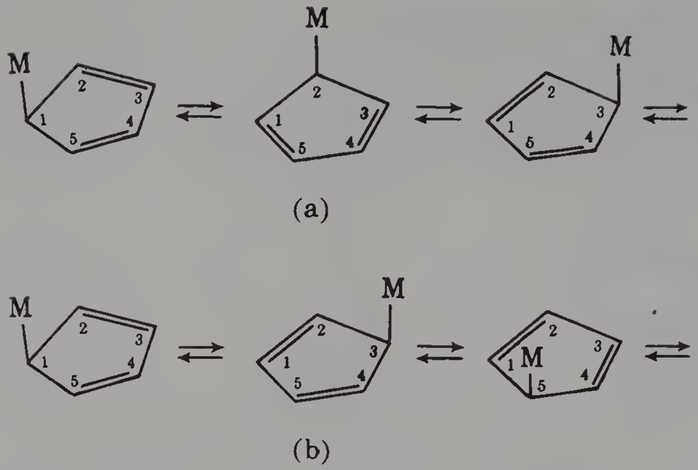


FIG. 29-22. Two rearrangement pathways for a (η^1-C_5H_5)M moiety. (a) 1,2 shifts. (b) 1,3 shifts.

confirmed in this way. Of course X-ray study of the crystalline compounds can usually also be carried out, and in every case the X-ray and low-temperature nmr results have been in agreement. If nmr spectra are then recorded at 10 to 20°C temperature intervals between the slow-exchange limit and the higher temperatures and each one is matched to a computer-calculated spectrum for a given rate of rearrangement, the activation parameters can be evaluated by plotting the rates and temperatures in the usual ways.

In quite a few cases it can be shown that the appearance of the intermediate spectra is different for different hopping patterns (such as the 1,2 shifts and 1,3 shifts in Fig. 29-22), and a decision can therefore be made between them. In all cases of (η^1-C_5H_5)M systems, observations of this kind coupled with other data have favored the 1,2-shift pathway. For the homologous (η^1-C_7H_7)M systems more diversity has been found. When M = $Re(CO)_5$, only 1,2 shifts are observed, but when M = (η^5-C_5H_5)$Ru(CO)_2$ both 1,2 and 1,3 shifts occur, although the former predominate.[35] In the case of Ph_3Sn(η^1-C_7H_7) the fluxional pathway entails 1,5 shifts.

For systems of types (29-XIII), (29-XIV), and (29-XV), only 1,2 shifts have been observed. For systems of type (29-XVI) there is again some diversity. For the (η^6-1,3,5,7-$Me_4C_8H_4$)$M(CO)_3$ molecules, with M = Cr, Mo, and W, only 1,2 shifts have been detected, but in the (η^6-C_8H_8)$M(CO)_3$ molecules, the predominent pathway is by 1,3 shifts, with 1,2 shifts accounting for only about 30% of the jumps.

In the case of (29-XVII) the usual nmr line shape experiment fails to detect the 1,3-shift interconversion shown, indicating either that it does not occur at all or that it has an activation energy greater than ~80 kJ mol^{-1}. A spin saturation experiment has indicated that this process does in fact take place

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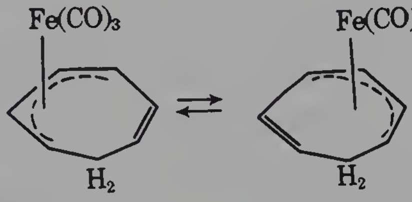
[35] D. M. Heinekey and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104,** 915.

with a free energy of activation of 85 to 95 kJ mol^{-1} for several substituted derivatives.[36]

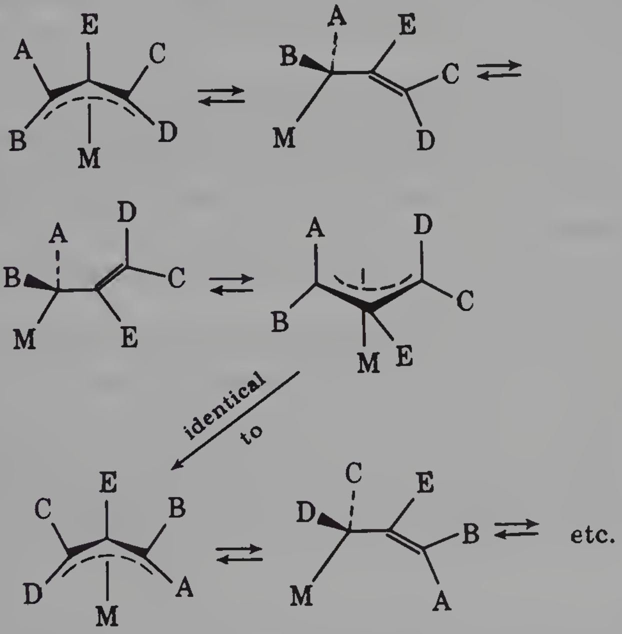


(a) (b)

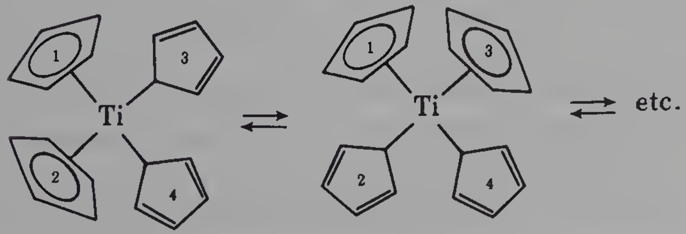
(29-XVII)

Allyl complexes are characteristically fluxional, the principal pathway being the η^3-η^1-η^3 process shown in eq. 29-57.

There are also compounds in which ligands exchange their modes of bonding. This is illustrated, for example, by $Ti(\eta^1\text{-}C_5H_5)_2(\eta^5\text{-}C_5H_5)_2$ as shown in eq. 29-58.



(29-57)



(29-58)

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[36] T. A. Albright *et al., Organometallics*, 1982, **1**, 419.

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Chapter Thirty

Bioinorganic Chemistry

30-1. Introduction

Although biochemistry involves extremely elaborate organic molecules (and also many simple ones) and the array of organic reactions that occur is dazzling in its scope and subtlety, it is important to recognize that biochemistry is not merely an elaboration of organic chemistry. Without the participation of the metallic elements and some others that are not normally involved in organic chemistry, life—at least in its present form—would not exist. The inorganic chemist, especially the coordination chemist, has a contribution to make to the understanding of life that is just as essential, though smaller in scope, as that of the organic chemist. This chapter gives an overview of the principal ways in which metals and some other elements participate in biochemical processes.

About 30 elements are recognized as essential to life.[1] Some are required in bulk, or at least macroscopic amounts, in essentially all forms of life: H, Na, K, Mg, Ca, C, N, O, P, S, and Cl. The others occur in trace (or ultratrace) quantities, although Fe, Cu, and Zn are at the top end of this "trace" scale and are, apparently, also essential to all, or at least most, forms of life. The remaining elements that are required by at least a few life forms are Li, B, F, Si, V, Cr, Mn, Co, Ni, As, Se, Mo, I, and W.

One of the major roles played by metallic elements in biochemistry is in *metalloenzymes*. This term is applied to enzymes that not only require the participation of a metal ion at the active site to function but bind that metal ion (or ions) strongly even in the resting state. Known metalloenzymes now number several hundred. The role of the metal atoms in enzymic catalysis is currently an active subject of research. The details doubtless differ from case to case, but it appears that in many cases the metal ion is held in an enforced stereochemistry (the entatic state), which enhances its capacity to bind and/or activate the substrate.[2]

Metalloenzymes may be considered as a subclass (the largest) of the *me-*

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[1] E. Frieden, *J. Chem. Educ.*, 1985, **62**, 917.

[2] R. J. P. Williams, *J. Mol. Catal.*, 1986, 1, (review issue).

talloproteins, that is, proteins that incorporate one or more metal atoms as a normal part of their structures. This includes, then, not only enzymes but respiratory proteins like hemoglobin and myoglobin, electron transport proteins such as cytochromes and ferredoxins, and metal storage proteins.

In many but not all cases it is possible to remove the metal atoms and then restore them (or replace them by others) without collapse of the overall protein structure. The protein from which the metal ions have been removed is called the *apoprotein,* the use of this term usually (though perhaps not invariably) implying that the active metalloprotein can be recovered on restoration of the metal ions.

We shall not attempt to cover even superficially all the elements known to be involved in bioinorganic chemistry. Instead, we discuss only those that are presently recognized to be most important or about which most is known. Based on one or both of these criteria, the element iron comes most readily to mind, and we treat it first, then proceed to briefer discussions of several other elements.

THE BIOCHEMISTRY OF IRON

Iron is truly ubiquitous in living systems. Its versatility is unique. It is at the active center of molecules responsible for oxygen transport and electron transport and it is found in, or with, such diverse metalloenzymes as nitrogenase, various oxidases, hydrogenases, reductases, dehydrogenases, deoxygenases, and dehydrases. In many cases little if anything is known beyond that fact that it is there (hence a vast field of research lies waiting). In others the function is known but knowledge about the molecular structure is scanty.[3] On the other hand in some of the most important cases, such as hemoglobin, ferredoxins, and cytochromes, we know the molecular structures and electronic properties of the active sites in considerable detail.

Not only is iron involved in an enormous range of functions, it also is found in the whole gamut of life forms from bacteria to man. Iron is extremely abundant in the earth's crust and it has two readily interconverted oxidation states; doubtless these properties have led to evolutionary selection for use in many life processes. Table 30-1 shows the principal forms in which iron is found in the human body.

The next few sections treat the biochemistry of iron under two broad headings: storage and transport, and function. The latter is broken into a number of topics because of the great diversity of function and the widely differing chemistries of the iron-containing species.

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[3] J. W. Whittaker and E. I. Solomon, *J. Am. Chem. Soc.*, 1986, **108,** 835; L. Que, Jr., *J. Chem. Educ.*, 1985, **62,** 938.

TABLE 30-1
Distribution of Iron-Containing Proteins in a Normal Adult

Protein	Molecular weight of protein	Amount of protein (g)	Amount of iron (g)	% of total body iron	Nature of iron heme (H) or nonheme (N)	Number of iron atoms bound per molecule	Valence state	Function
Hemoglobin	64,500	750	2.60	65	H	4	Fe^{2+}	Oxygen transport in plasma
Myoglobin	17,000	40	0.13	6	H	1	Fe^{2+}	Oxygen storage in muscle
Transferrin	76,000	20	0.007	0.2	N	2	Fe^{3+}	Iron transport via plasma
Ferritin	444,000	2.4	0.52	13	N	0–4,500	Fe^{3+}	Iron storage in cells
Hemosiderin	Not known	1.6	0.48	12	N	5000	Fe^{3+}	Iron storage in cells
Catalase	280,000	5.0	0.004	0.1	H		Fe^{2+}	Metabolism of H_2O_2
Cytochrome *c*	12,500	0.8	0.004	0.1	H	1	Fe^{2+}/Fe^{3+}	Terminal oxidation
Peroxidase	44,100				H			Metabolism of H_2O_2
Cytochromes and oxidase			0.02	<0.5	H		Fe^{2+}/Fe^{3+}	Terminal oxidation
Flavoprotein dehydrogenases, oxidases, and oxygenases					N		Fe^{2+}	Oxidation reactions, incorporation of molecular oxygen

30-2. Iron Storage and Transport

As Table 30-1 indicates, there are known to be two principal iron-storage compounds in the human body: ferritin and hemosiderin. Hemosiderin appears to be rather variable in composition and properties and is poorly understood compared to ferritin. It is not discussed further here.

Ferritin.[4] Ferritin serves as a depot in which surplus iron can be stored within cells in nontoxic form and from which it can be released in usable form as required, either within that cell itself or in other cells of the organism. It is widely distributed throughout the various organs of all mammals, especially high concentrations being found in liver, spleen, and bone marrow. It is also found in plants and bacteria.

Ferritin consists of a shell of protein surrounding a core that contains the iron. The diameter of the essentially spherical core varies from 40 to 88 Å and may contain up to 4500 iron atoms. The core is quasicrystalline (it gives an X-ray diffraction pattern) and has a composition approximating closely to $(FeOOH)_8 \cdot FeO \cdot H_2PO_4$. The diffraction pattern of the core is rather similar to that of a substance called ferrihydrite, $5Fe_2O_3 \cdot 9H_2O$, which is formed by slow addition of NH_4OH to a solution of ferric nitrate at 80 to 90°C. The structure is based on a close-packed array of oxide ions and OH^- ions, with iron atoms in octahedral interstices. The phosphate is not a part of the bulk structure, but appears instead to play some role in covering the $(FeOOH)_x$ particles and perhaps attaching them to each other and to the protein sheath. The magnetic behavior of ferritin has been extensively studied, and data from Mössbauer spectroscopy are also available. The ferric ions are present in high-

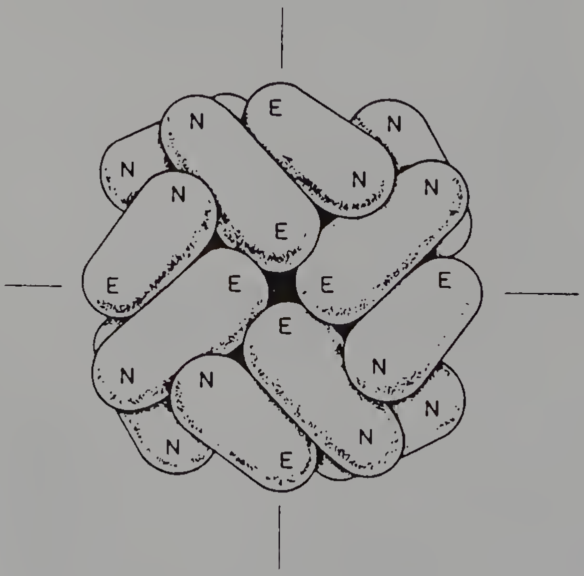

FIG. 30-1. A schematic diagram of the packing of the 24 subunits that form the protein sheath of horse spleen ferritin. The view is down one fourfold axis.

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[4] See S. J. Lippard *et al., J. Am. Chem. Soc.,* 1987, **109,** 3337 and references herein.

spin form and are subject to strong antiferromagnetic coupling, as would be expected for the type of structure just discussed.

The X-ray crystal structure of the protein sheath—called the apoferritin—from horse spleen has been established at 2.8 Å resolution. It is made up of 24 subunits, each of which is a polypeptide chain coiled so as to form a slightly prolate spheroid or lozenge. The arrangement of the lozenges, shown in Fig. 30-1 is very symmetrical; it has full cubic symmetry, with fourfold, threefold, and twofold axes (point group O) and forms face centered cubic crystals.

The manner in which iron enters and leaves ferritin is still poorly understood. The core can be formed *only* from aqueous iron(II), so that oxidation accompanies (or follows) incorporation. Iron release is controlled by the protein shell and can occur very rapidly when necessary.

Transferrin.[5] This molecule carries ingested iron from the stomach and introduces it into the iron metabolic processes of the body. As iron passes from the stomach (which is acidic) into the blood (pH ~ 7.4) it is oxidized to Fe^{III} in a process catalyzed by the copper metalloenzyme ceruloplasmin, then picked up by transferrin molecules. These are proteins with a molecular weight of ~80,000 and they contain two similar but not identical sites that bind iron tightly but reversibly in the presence of certain anions, mainly CO_3^{2-} or HCO_3^-. The details of the nature of these binding sites are still unknown. The binding constant is $\sim 10^{26}$; therefore transferrin is an extremely efficient scavenger of iron, removing it from such stable complexes as those with phosphate or citrate. Transferrin then becomes bound to the cell wall of an immature red cell, which requires iron, and the transfer is made under control of a complex mechanism for transporting the iron through the cell membrane.

Transferrin also carries iron to ferritin *in vitro* and the process of transfer is a complex one requiring ATP and ascorbic acid and proceeding via Fe^{II}. The nature of the binding sites of transferrin has not been established, but tyrosine, histidine, and the carbonate ion have been suggested as ligands, rather than two hydroxamate ligands that are well established in the bacterial iron transport ligands, discussed next.

Bacterial Iron Transport.[6] The agents responsible for iron transport into and within bacteria have been intensively studied, and many structural and chemical details have been firmly established. The problem is that iron is not spontaneously available to aerobic organisms in an aqueous environment because of the very low solubility of ferric hydroxide ($pK_{sp} \approx 38$). Thus Fe^{3+} ions at a pH of ~7 have a molar concentration of only $\sim 10^{-18}$, and simple diffusion into cells could never suffice to supply their needs. Indeed, simple inward diffusion would not occur, since iron is already more concentrated than this in the living cell. Therefore special chelating agents called

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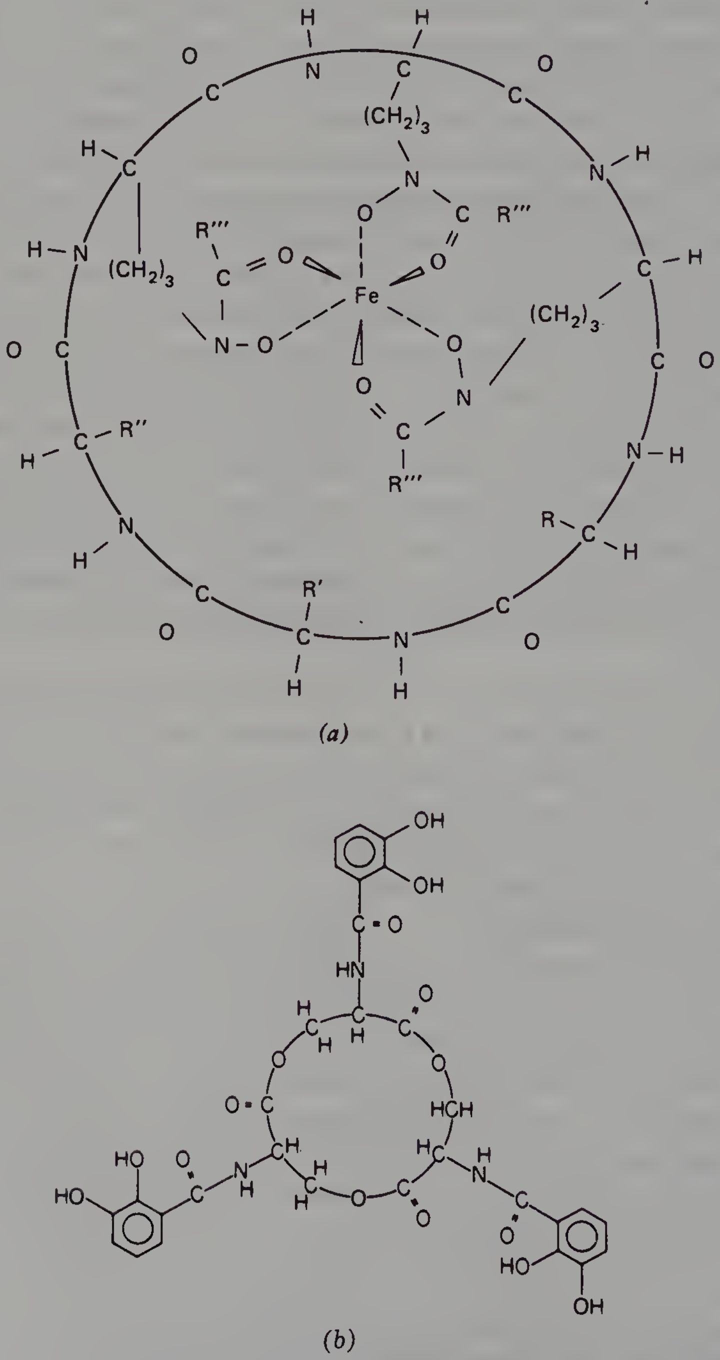
[5] N. D. Chasteen, *Adv. Inorg. Biochem.*, 1983, **5**, 201.

[6] J. B. Nielands *et al.*, *Adv. Inorg. Biochem.*, 1983, **5**, 137; *Struct. Bonding* (*Berlin*), 1984, **58**, 1–107 (reviews of siderophores).

siderophores are produced by bacteria and ejected into their environment to gather iron and transfer it through the cell wall into the cell. In some cases it appears that the iron is released by the chelator at the wall and it passes through alone, whereas in others the entire complex enters the cell.

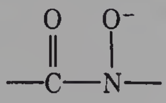
The siderophores are rather diverse chemically but have in common the use of chelating, oxygen-donor-type ligands; only in one case is nitrogen known to be a donor atom. A very large fraction of the siderophores that


(a)

(b)

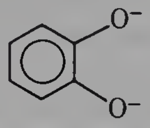
FIG. 30-2. (a) An iron ferrichrome complex. (b) An enterobactin.

have been characterized employ hydroxamate moieties (30-I) as the ligating units. For example, a type of siderophore called a *ferrichrome* consists of a cyclic hexapeptide in which three successive amino acid residues have side chains ending in hydroxamate groups. These three hydroxamate groups bind iron by forming a trischelate octahedral complex [Fig. 30-2(a)].



$—C(=O)—N(O^-)—$

(30-I)



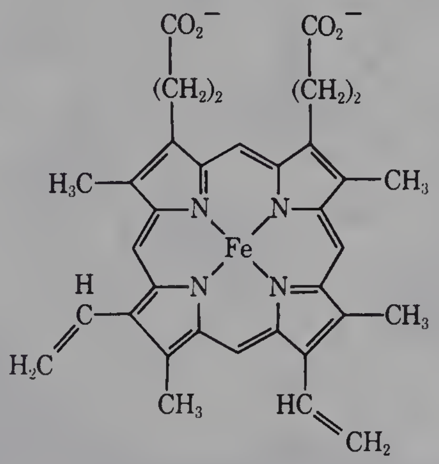
(30-II)

Another type of siderophore, especially common in prokaryotes such as enteric bacteria, is called an *enterobactin;* the ligating units are catecholate anions (30-II) that also chelate very effectively. The chemistry of the enterobactin shown in Fig. 30-2(b) has been studied in some detail.[7]

The siderophores form Fe^{3+} complexes that are very stable thermodynamically (i.e., they have very high formation constants). It has been estimated that the enterobactin in Fig. 30-2 complexes Fe^{3+} with a formation constant of $\geq 10^{45}$. However, these complexes are kinetically labile, and of course such lability is essential so that iron can be easily taken up before transport and released afterward.

30-3. Hemoglobin and Myoglobin[8,9]

Myoglobin (Mb) consists of one polypeptide chain (globin) with one heme group [the iron–porphyrin complex shown as (30-III)] embedded therein. The peptide chain contains 150 to 160 amino acid residues, the precise number



(30-III)

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[7] K. N. Raymond *et al., J. Am. Chem. Soc.,* 1985, **107,** 6920.

[8] R. E. Dickerson and I. Geis, *Hemoglobin,* Benjamin/Cummings, Menlo Park, California 1983; H. F. Bunn and B. G. Forget, *Hemoglobin: Molecular, Genetic and Clinical Aspects,* Saunders, Philadelphia, 1986.

[9] K. S. Suslick and T. J. Reinert, *J. Chem. Educ.,* 1985, **62,** 974.

depending on the species in which it is found. Hemoglobin (Hb), with a molecular weight of 64,500, consists of four myoglobin-like subunits; these four are similar but not all identical, two being α units and the other β units. Neither the α nor the β units of hemoglobin have amino acid sequences that match the sequence in myoglobin, but nevertheless the ways in which the chains are coiled to give three-dimensional structures (tertiary structure) are quite similar. In each subunit of hemoglobin and in myoglobin, the iron atom is also bonded to the nitrogen atom from the imidazole side chain of a histidine residue. Figure 30-3 gives a schematic representation of the β subunit of hemoglobin; its essential features are typical of α subunits and myoglobin as well.

According to this description, the iron atoms in Hb and Mb when no oxygen is present (the deoxy forms) would be five-coordinate. In fact, there is probably a water molecule loosely bonded in the sixth position (i.e., trans to the histidine nitrogen atom) to complete a distorted octahedron. The iron atom

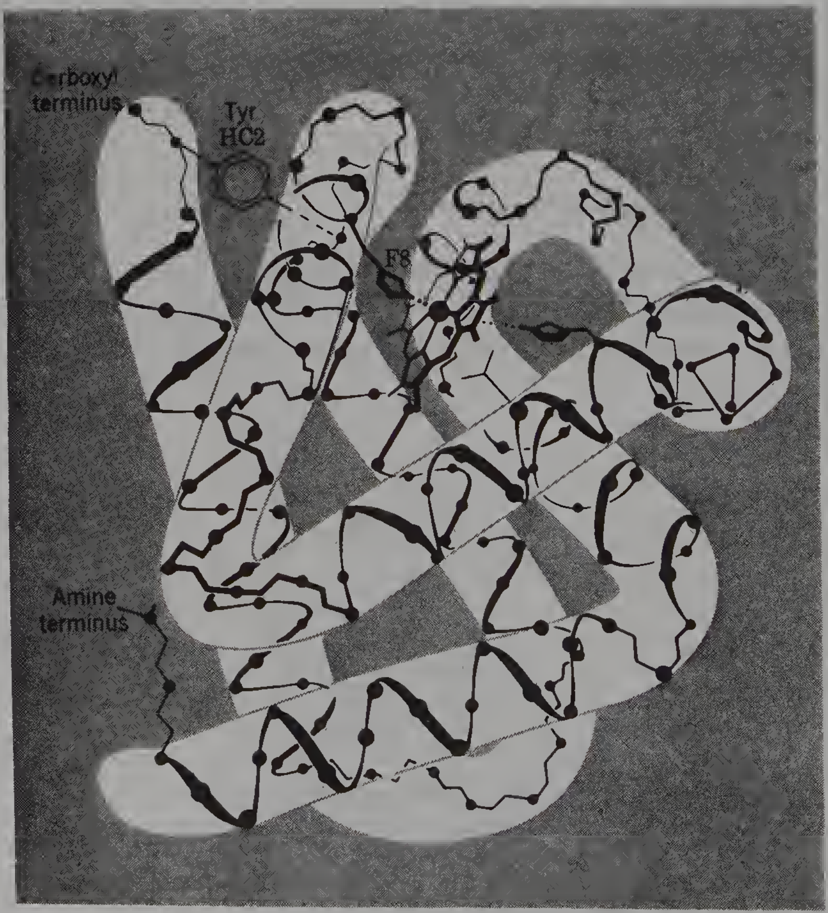


FIG. 30-3. A schematic representation of one of the four subunits of hemoglobin. The continuous black band represents the peptide chain, and the various sections of helix are evident. Dots on the chain represent the α-carbon atoms. The heme group can be seen at upper right center with the iron as a large dot. The coordinated histidine side chain is labeled F8 (meaning the eighth residue of the F helix). (This figure was adapted from one kindly supplied by M. Perutz.)

is out of the porphyrin plane toward the histidine by 0.5 Å. In both deoxy-Mb and deoxy-Hb the iron atoms are high-spin Fe^{II}, with four unpaired electrons.

The function of both Hb and Mb is to bind oxygen, but their physiological roles are very different. Hemoglobin picks up oxygen in the lungs and carries it to tissues via the circulatory system. Cellular oxygen is bound by myoglobin molecules that store it until it is required for metabolic action, whereupon they release it to other acceptors. Hemoglobin has an additional function, however, and that is to carry CO_2 back to the lungs; this is done by certain amino acid side chains, and the heme groups are not directly involved. Because the circumstances under which Hb and Mb are required to bind and release O_2 are very different, the two substances have quite different binding constants as a function of O_2 partial pressure (Fig. 30-4).

Hemoglobin is not simply a passive carrier of oxygen but an intricate molecular machine. This may be appreciated by comparing its affinity for O_2 to that of myoglobin. For myoglobin (Mb) we have the following equilibrium:

$$\mathrm{Mb} + \mathrm{O_2} = \mathrm{MbO_2} \qquad K = \frac{[\mathrm{MbO_2}]}{[\mathrm{Mb}][\mathrm{O_2}]}$$

If f represents the fraction of myoglobin molecules bearing oxygen and P represents the equilibrium partial pressure of oxygen, it follows that

$$K = \frac{f}{(1 - f)P} \qquad \text{and} \qquad f = \frac{KP}{1 + KP}$$

This is the equation for the hyperbolic curve labeled Mb in Fig. 30-4. Hemoglobin with its four subunits has more complex behavior; it approximately

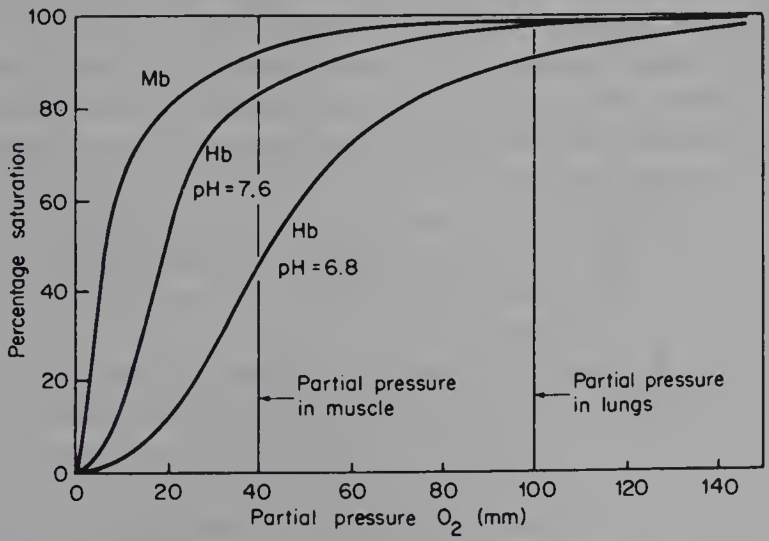


FIG. 30-4. The oxygen-binding curves for myoglobin (Mb) and hemoglobin (Hb), showing also the pH dependence (Bohr effect) for the latter.

follows the equation

$$f = \frac{KP^n}{1 + KP^n} \qquad n \approx 2.8$$

where the exact value of n depends on pH. Thus for hemoglobin the oxygen binding curves are sigmoidal as shown in Fig. 30-4. The fact that n exceeds unity can be ascribed physically to the increase caused by attachment of O_2 to one heme group in the binding constant for the next O_2, which in turn increases the constant for the next one and so on. This is called cooperativity. Just as a value of $n = 1$ would represent the lower limit of no cooperativity, a value of $n = 4$ would represent the maximum of cooperativity, since it would imply that only Hb and $Hb(O_2)_4$ would be participants in the equilibrium.

It will be seen that although Hb is about as good an O_2 binder as Mb at high O_2 pressure, it is much poorer at the lower pressures prevailing in muscle, hence passes its oxygen on to the Mb as required. Moreover, the need for O_2 is greatest in tissues that have already consumed oxygen and simultaneously produced CO_2. The CO_2 lowers the pH, thus causing the Hb to release even more oxygen to the Mb. The pH sensitivity (called the Bohr effect) and the progressive increase of the O_2 binding constants in Hb are due to interactions between the subunits; Mb behaves more simply because it consists of only one unit. It is clear that each of the two is essential in the complete oxygen transport process. Carbon monoxide, PF_3, and a few other substances are toxic because they become bound to the iron atoms of Hb instead of O_2; their effect is one of competitive binding.

Nature of the Heme–Dioxygen Binding. Because of the size and complexity of both myoglobin and hemoglobin it has not been easy to establish either the structural or the electronic character of the bonding of O_2 to heme. However, it now seems clear from X-ray studies on both $Mb(O_2)$ and $Hb(O_2)_4$ that O_2 binds in an end-on-bent geometry, with an Fe—O—O angle of ~130°. The structure of the O_2 adduct of a model compound (of the type shown in Fig. 30-5) also has a bent Fe—O—O chain. Interestingly, in the CO adduct of the same model compound the Fe—C—O chain is linear, whereas in CO complexes of hemoglobins the Fe—C—O chains are bent. This is apparently a result of steric forces; the O_2 binding site in hemoglobin is shaped to accomodate a bent Fe—O—O chain and therefore forces the Fe—C—O chain to be bent as well. Since this is unfavorable, the steric forces constitute a defence against CO, although only a partial one.

Given that the end-on-bent geometry is correct, the proper electronic formulation of the oxygenated iron–porphyrin complex must next be considered. It has long been known that $Mb(O_2)$ and $Hb(O_2)_4$ are diamagnetic. This is consistent with either a singlet O_2 molecule coordinated to a low-spin Fe^{II} or with a $Fe^{III}—O_2^-$ formulation provided that for the latter we postulate that there is strong magnetic coupling between the one unpaired electron that a low-spin octahedral Fe^{III} complex would have and the odd electron expected

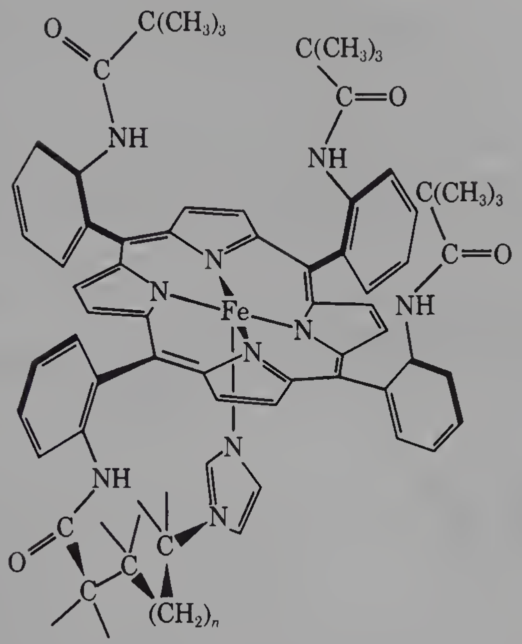
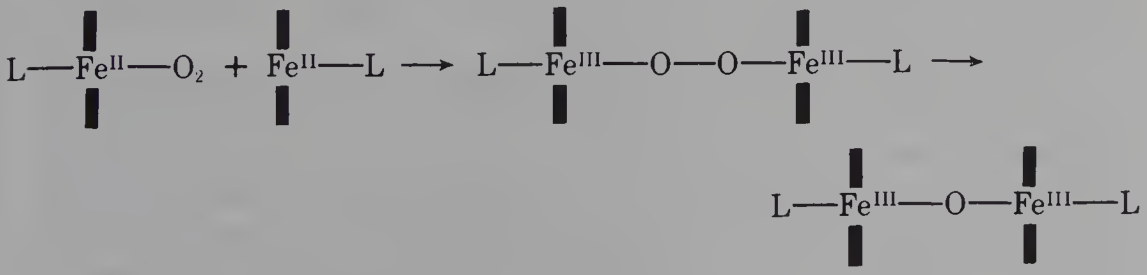


FIG. 30-5. One of the "picket fence" models for a heme–protein oxygen carrier.

for an O_2^- ion. The credibility of such a coupling is supported by the fact that the $Cr(TPP)(py)O_2$ molecule (TPP = tetraphenylporphyrin) has a magnetic moment of 2.7 BM, indicative of only two unpaired electrons. This can be attributed to pairing (or very strong antiferromagnetic coupling) of the odd electron on O_2^- with one of the three *d* electrons of Cr^{III}.

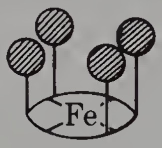
Model Systems. These have been mentioned several times, and it is appropriate to say a few words about how they are designed. They are intended to mimic the natural oxygen-carrying heme proteins while avoiding the difficulties introduced in the study of the natural systems by the great size and other inconvenient properties of the large proteins. The models contain an iron–porphyrin complex but attempt to simulate the role of the protein in simpler ways. It has been fully appreciated for a long time that if only a simple iron–porphyrin complex is used oxygen reacts in an irreversible manner with two such hemelike units, as represented schematically in 30-1.



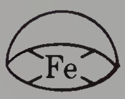
(30-1)

In nature this is prevented because individual heme units are attached to the bulky globin (protein) molecules and the close approach required for oxygen bridging is impossible. In the model systems the bimolecular reaction is usually precluded by some kind of steric hindrance, deliberately introduced in one of several ways.*

1. The "picket fence" approach, in which three or four large groups stand around the iron atom on the side where oxygen is to be bound (30-IV), has been widely exploited. A real example of a "picket fence" model is shown in Fig. 30-5.
2. "Strapped" models (30-V) in which one chain extends over the iron atom, but leaves room for the O_2.
3. "Roofed" models (30-VI) in which there is more complete enclosure of the binding site.



(30-IV)



(30-V)

(30-VI)

As an alternative to steric hindrance, the rate of oxidation can also be markedly reduced by use of low temperatures (~ −50°) and dilute solutions (~10^{-4} *M*), but it is usually so advantageous to be able to work at ordinary temperatures that the steric hindrance approach is preferable.

Cooperativity in Hemoglobin. The critical importance of cooperativity in the process of oxygenation of Hb has been emphasized. Although the details may still require extension and refinement, the mechanism of the cooperativity is known, *grosso modo.* A key feature of it is the behavior of an individual iron–porphyrin complex as it goes from the deoxy to the oxygenated state. In the deoxy state the heme complex is distinctly domed, with the iron atom ~0.5 Å out of the porphyrin mean plane and with the Fe—N bond to histidine *F*8 some 8° off of perpendicular, as shown in Fig. 30-6. When an oxygen molecule becomes bound the iron comes into, or nearly into, the porphyrin plane and the Fe—N bond becomes more nearly perpendicular. These changes in the local structure of the heme unit are entirely in accord with our understanding of the coordination chemistry involved and were anticipated by inorganic chemists. They form the "trigger" for the cooperativity mechanism, which we now consider.

The movements just described impose changes upon the conformation of the protein which are large in the immediate region, as shown in Fig. 30-7, but extend even to remote parts of the subunit. Changes at the periphery then influence the conformations of the protein chains in adjacent subunits of Hb so as to make them more receptive to an O_2 molecule. In a widely discussed though perhaps oversimplified model, each subunit is postulated to have two available allosteric (Greek for differently shaped) conformations: a *T* form which has low O_2 affinity and an *R* form which has ~100 times the

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*See ref. 9 for a gallery of model compounds.

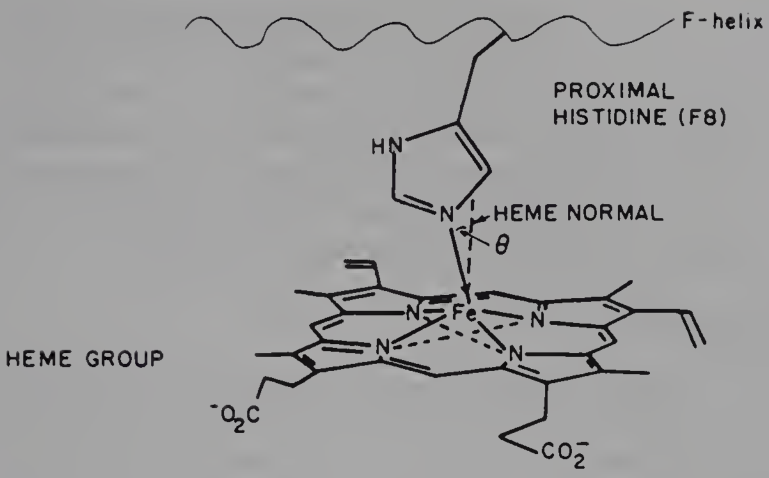

FIG. 30-6. The structure of the deoxy heme group.

O_2 affinity of the *T* form. Once O_2 is bound to a given subunit it is locked into the *R* conformation and its interactions with its neighbors favor the conversion of those neighboring subunits to their *R* forms as well. The details of the subunit interactions are complex and still a subject for research.

The ability of a heme unit to bind O_2 is annulled if its iron atom becomes oxidized to Fe^{III}. This oxidation occurs in living creatures but there is reductive machinery in the red blood cells to reconvert to the Fe^{II} state. In the event

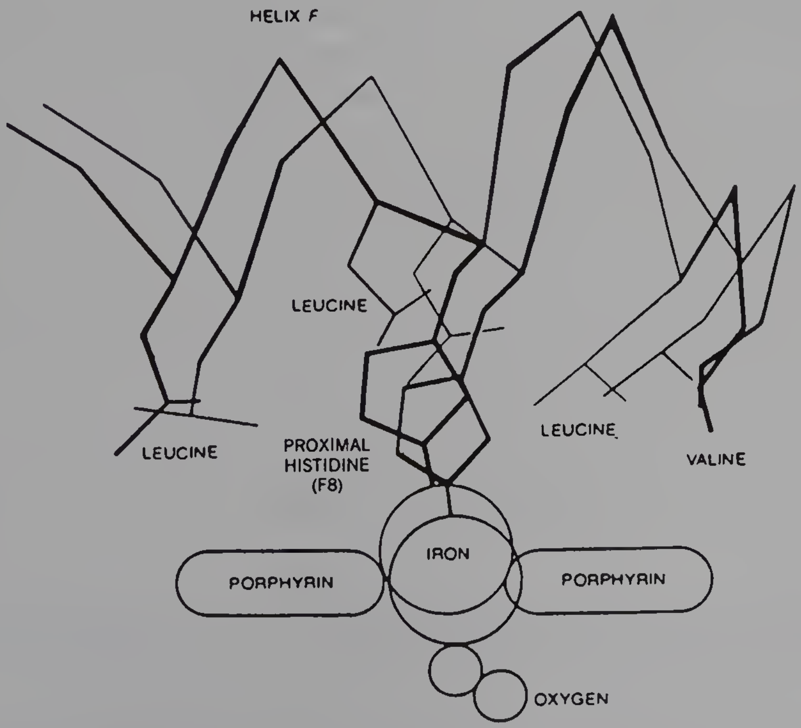

FIG. 30-7. The movements in the heme group and those induced in the adjacent protein chain upon oxygenation.

this machinery fails, a disease called methemoglobinemia results.[10] Because the Fe^{III} containing Hb subunits have a structure very similar to that of the oxygenated subunit, they trigger the cooperative process of oxygen binding by the remaining subunits. However, because the *R* conformation of these oxidized units is permanent, the ability of the other *oxygenated* subunits to release their O_2 is seriously impaired and the entire tetrameric Hb molecule, not just the oxidized subunits, becomes nonfunctional.

30-4. Cytochromes[11]

Cytochromes are heme proteins that act as electron carriers, linking the oxidation of substrates to the reduction of O_2, as shown schematically in Fig. 30-8. Cytochromes are found in all aerobic forms of life. They are small (MW ~ 12,000) molecules, and they operate by shuttling of the iron atom between Fe^{II} and Fe^{III}. The classification of cytochromes is complex because there are many different types and the historical development of notation has not been entirely systematic. They can be broadly divided into types *a, b,* and *c* according to the type of porphyrin they contain. We shall restrict this discussion almost entirely to those of type *c*, for which the porphyrin, and its mode of attachment to the protein are shown in Fig. 30-9(a). Also shown, in Fig. 30-9(b), is a view of the three-dimensional (tertiary) structure of a typical cytochrome *c*. The iron–porphyrin unit is seen edge-on lodged in a pocket

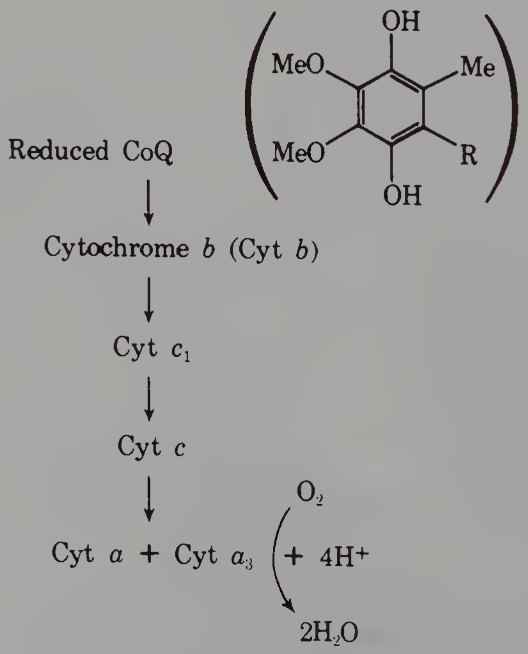

FIG. 30-8. A scheme showing the sequence of cytochromes (Cyt) that intervene between coenzyme Q (CoQ) and the reduction of dioxygen to water.

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[10] N. M. Senozan, *J. Chem. Educ.*, 1985, **62,** 181.

[11] T. E. Meyer and M. D. Kamen, *Adv. Protein Chem.*, 1982, **35,** 105–212; G. R. Moore *et al.*, *Adv. Inorg. Bioinorg. Mech.*, 1984, **3,** 1–96.

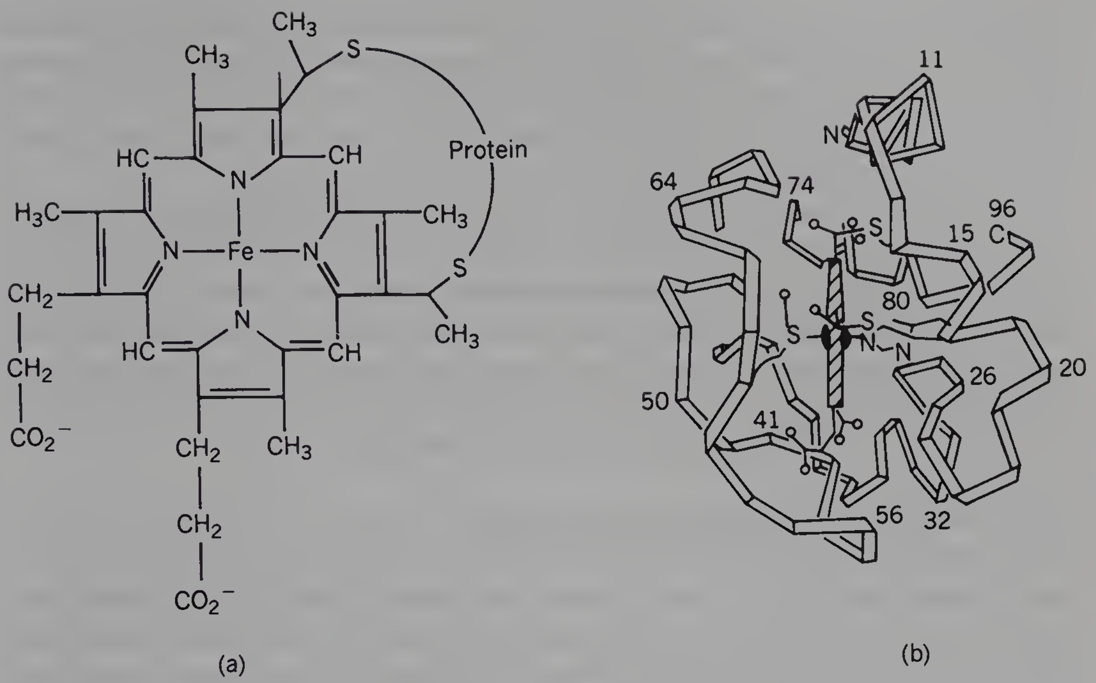

FIG. 30-9. (a) The iron porphyrin unit in cytochromes *c*. (b) A schematic view of the tertiary structure of cytochrome C_{555} from *Chlorobium thiosulfatophilum*. The "ribbon" represents the peptide chain.

created by the folding of the peptide chain. The iron atom is ligated on both sides of the porphyrin plane by the $CH_2CH_2SCH_3$ side chain of a methionine and a nitrogen atom of a histidine. The rest of the pocket is lined by hydrophobic side chains and only a small part of the rim of the porphyrin ring is at or near the exposed surface of the molecule.

To return to Fig. 30-8, we see that electrons originating with reduced coenzyme Q (CoQ) are accepted by a cytochrome *b* and proceed through a series of intermediate cytochromes until, at the end, four electrons are delivered at an appropriate potential to carry out the reduction of O_2 to water.

The redox potentials of the intervening cytochromes gradually increase to cover the gap stepwise between that for the oxidation of reduced CoQ and that for reduction of dioxygen. To do this the cytochromes have distinctive structures and properties. In Cyt *b*, Cyt c_1, and Cyt *c* the heme group is the same as that in hemoglobin and myoglobin. In Cyt *b* the heme is not covalently attached to the protein, but is held only by ligation to the iron atom. In Cyt c_1 and Cyt *c* the heme is covalently connected by thioether linkages [Fig. 30-9(a)], and the iron atom is coordinated by protein side chains [Fig. 30-9(b)].

Cytochrome *a* and Cyt a_3 exist together as a complex, sometimes called *cytochrome oxidase,* and they contain a heme with several different substituents on the periphery of the porphyrin ring. Cytochrome a_3 also contains copper, which goes from Cu^{II} to Cu^{I} and thus transfers an electron from the heme of Cyt a_3 to the dioxygen molecule.

Mechanistic details of the way in which cytochromes *c* participate in electron transfer processes have been sought in studies both of self-exchange reactions and in reactions of the cytochromes *c* with nonbiological redox reagents, mainly substitution-inert transition metal complexes. In general, the processes are outer-sphere reactions that can be accounted for by the Marcus theory (Section 29-9).

Cytochrome *c* seems to be one of the most ancient of biomolecules, having evolved in essentially its present form more than 1.5 billion years ago, even though it is present in all animals and plants, including those that have appeared more recently. It has been found that the cytochrome *c* of any eucaryotic species (one having cells with nuclei) will react with the cytochrome oxidase of any other species, thus confirming that this electron transfer chain has resisted evolutionary change for a very long time.

30-5. Other Iron–porphyrin Biomolecules

The heme unit, that is, iron–protoporphyrin IX and closely related derivatives, has shown the capacity, through the long process of evolutionary change and selection, to be an extraordinarily versatile chemical species. We have already seen that it serves as an oxygen carrier (in which case it is oxygenated rather than oxidized) and as an electron transfer agent (in cytochromes) where the Fe^{II}/Fe^{III} couple is the key element. In addition, heme or hemelike units engage in much more energetic processes whereby oxidation states of IV and perhaps even V are involved. The question of oxidation state V is still being debated, however, because the same number of oxidizing equivalents, which some workers propose to account for in this way, can also be attributed to Fe^{IV} together with a radical cation residing somewhere on the porphyrin ligand.

The three major types of enzymes to be mentioned here are peroxidases, catalases, and cytochrome P_{450} enzymes. The first two are conveniently considered together.

Peroxidases and Catalases.[12,13] Peroxidases catalyze the oxidation of a variety of substrates by peroxides, mainly H_2O_2. Catalases catalyze decomposition of H_2O_2 (and some other peroxides) to H_2O and O_2. They have many similarities, both in structure and in aspects of their mechanisms. They both have high-spin ferric heme groups lodged deeply in rather large protein molecules, with a histidine nitrogen atom constituting the fifth ligand. The sixth position may be occupied by a water molecule in the resting enzyme. There is growing evidence that a $(porph)Fe^{IV}{=}O$ species is a key intermediate in peroxidases[14] and catalases.

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[12] J. E. Frew and P. Jones, *Adv. Inorg. Bioinorg. Mech.*, 1984, **3,** 175–212.

[13] H. B. Dunford, *Advances in Inorganic Biochemistry*, Vol. 4, Elsevier, Amsterdam, 1982, pp. 41–68.

[14] R. Weiss *et al., Chem Commun.*, **1986,** 93.

The catalytic activity of peroxidase entails the following steps, where *P* represents the resting enzyme and AH a reducing substrate:

$$\mathrm{P} + \mathrm{H_2O_2} \longrightarrow \text{compound I} + \mathrm{H_2O}$$

$$\text{compound I} + \mathrm{AH} \longrightarrow \text{compound II} + \mathrm{A^{\cdot}}$$

$$\text{compound II} + \mathrm{AH} \longrightarrow \mathrm{P} + \mathrm{A^{\cdot}}$$

Compound I has an oxidation level two units higher than P, but it reverts to *P* in two one-electron steps. There is evidence to suggest (but not prove) that compounds I and II can be more specifically formulated as follows:

$$\underset{\mathrm{P}}{\mathrm{Fe^{III}}} \xrightarrow{\mathrm{H_2O_2}} \underset{\mathrm{I}}{(\mathrm{R^{\cdot+}})\mathrm{Fe^{IV}{=}O}} \xrightarrow{\mathrm{AH}} \underset{\mathrm{II}}{\mathrm{Fe^{IV}{-}OH^+}}$$

The $\mathrm{R^{\cdot+}}$ represents a π-cation radical formed on the porphyrin ligand.

Cytochrome P_{450} Enzymes.[15] These are heme-containing oxygenases; they catalyze the introduction of oxygen atoms from O_2 into substrates. Of the many possible substrates the most important are molecules in which C—H groups are converted to C—OH groups. While much remains to be learned, it is now clear that the catalytic cycle entails a species in which the iron atom attains a high (IV or V) oxidation number. The coordination sphere of the iron atom includes, in addition to the porphyrins, one sulfur atom, but whether the sixth position is occupied by a water molecule or is vacant in the resting enzyme is still uncertain.

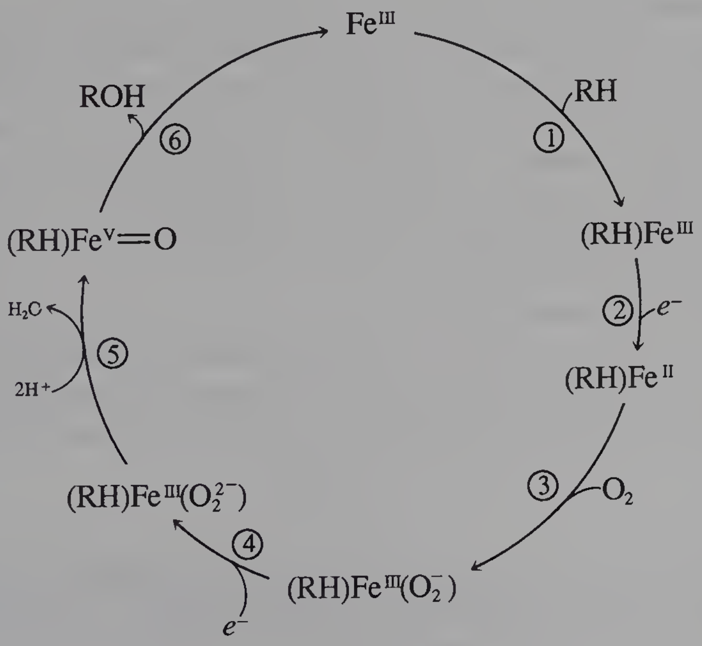

FIG. 30-10. A catalytic cycle for cytochrome P_{450} enzyme.

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[15] J. T. Groves, *Adv. Inorg. Biochem.* 1979, **1,** 119; F. P. Guengerich and T. L. Macdonald, *Acc. Chem. Res.,* 1984, **17,** 9; J. T. Groves, *J. Chem. Educ.,* 1985, **62,** 928.

Although studies of the actual P_{450} enzyme have been numerous and important, studies of model systems have been of enormous importance in developing an overall picture of the catalytic cycle.[16]

The key features of the presently accepted catalytic cycle for a cytochrome P_{450} enzyme are summarized in Fig. 30-10. In step (1) the substrate is bound, at or near the iron atom, and in step (2) reduction is effected by another enzymatic system. In step (3) the $(RH)Fe^{II}$ species binds an O_2 molecule, much as hemoglobin or myoglobin would do. In step (4) another one-electron reduction occurs to give an iron(III) peroxo complex. In step (5), this complex loses H_2O to give the crucial high-oxidation-state intermediate, written as $(RH)Fe^{V}{=}O$.

Whether this intermediate should be viewed as a true iron(V) complex or as an iron(IV) complex closely associated with a π-radical cation on the porphyrin ligand is again (as in the case of peroxidases) still an open question. In any event, this intermediate then collapses (not necessarily in one step) to give ROH and regenerate the enzyme in its initial condition.

30-6. Other Natural Oxygen Carriers[17]

In certain lower animals there are respiratory metalloproteins that differ considerably from hemoglobin. The two most important (or at least best known) metalloproteins are hemerythrins and hemocyanins. The latter are dicopper compounds and will be mentioned in Section 30-9.

Hemerythrins.[18] In a great variety of marine worms the oxygen-carrying molecules are iron-bearing proteins, but they do not contain porphyrins. They are substances called hemerythrins and it appears that the active sites are all very similar. The essential structural unit is a single-chain protein of ~113 amino acid residues, which contains two atoms of iron. Most often the *in vivo* operating systems consist of eight such units associated to form a tertiary structure with fourfold symmetry, but there are also a number of species containing trimers of the basic unit.[19]

Hemerythrins differ functionally from hemoglobin in two major ways. They show little or no cooperativity, and two iron atoms are employed to bind one O_2 molecule. Kinetic studies[20] suggest a similarity to hemoglobin, namely, that in the deoxy form hemerythrin has one iron coordination site unoccupied, or occupied by a very weakly held group.

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[16] T. G. Traylor *et al., J. Am. Chem. Soc.*, 1985, **107,** 5537; J. T. Groves and J. A. Gilbert, *Inorg. Chem.*, 1986, **25,** 123; J. T. Groves and Y. Watanabe, *J. Am. Chem. Soc.*, 1986, **108,** 507; E. M. Gaul and R. J. Kassner, *Inorg. Chem.*, 1986, **25,** 3734.

[17] A. E. Martell *et al, Chem. Rev.*, 1984, **84,** 137.

[18] R. G. Wilkins and P. C. Harrington in, *Advances in Inorganic Biochemistry*, Vol. 5, E. C. Theil, G. L. Eichhorn, and L. G. Marzilli, Eds., Elsevier, New York, 1983, pp. 51–85; A. G. Sykes, in *Adv. Inorg. Bioinorg. Mech.*, 1982, **1,** 154–167.

[19] J. L. Smith *et al., Nature (London)*, 1983, **303,** 86.

[20] G. D. Armstrong and A. G. Sykes, *Inorg. Chem.*, 1986, **25,** 3725.

Deoxyhemerythrin has a magnetic susceptibility and a Mössbauer spectrum indicating that both iron atoms in each pair are high-spin iron(II) ions. It has also been established by chemical and spectroscopic means that when hemerythrin binds O_2, it forms an $Fe_2^{III}(O_2^{2-})$ type of complex in which there is antiferromagnetic coupling between nonequivalent ferric ions. The peroxo state of the bound O_2 is very clearly shown by the resonance Raman spectrum where ν(O—O) is found at 844 cm^{-1}, a value typical for the O—O single bond of peroxides. When the oxygenated hemerythrin is treated with anionic ligands (L^-) such as NCS^-, N_3^-, CN^-, or F^-, one of the so-called methemerythrins is formed:

$$Fe_2^{III}(O_2^{2-}) + L^- + H_2O \longrightarrow Fe_2^{III}(L^-) + OH^- + O_2H^-$$

Much has been learned about the two-iron active site of hemerythrins by X-ray crystallography,[21] and other physical methods such as EXAFS[22] and various forms of spectroscopy.[23,24] The X-ray crystallographic results provide a complete picture of the entire metalloprotein as well as details of the iron

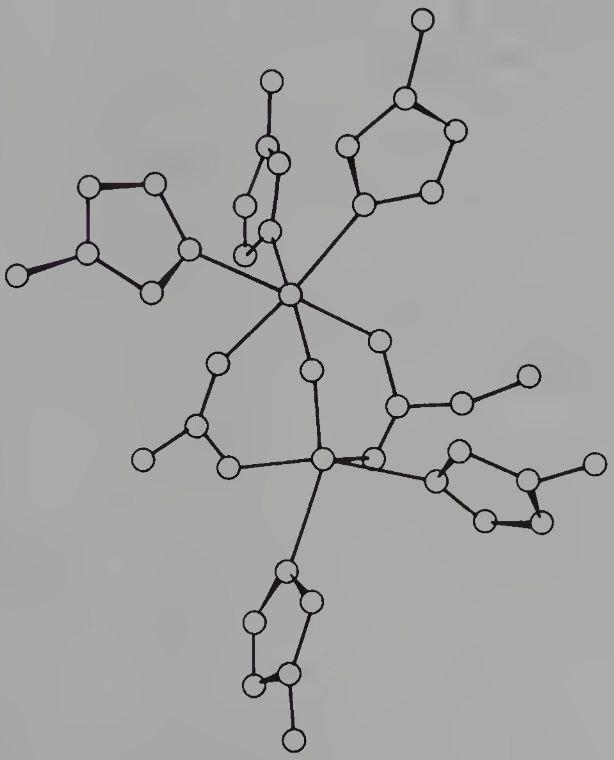

FIG. 30-11. The structure of the two-iron site in methemerythrin. The five terminal ligands are all imidazole groups from histidine residues and the bridging carboxyl groups belong to an aspartate and a glutamate residue. The Fe···Fe distance is ~3.21 Å.

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[21] R. E. Stenkamp *et al., J. Am. Chem. Soc.*, 1984, **106,** 618.

[22] E. A. Stern *et al., J. Am. Chem. Soc.*, 1983, **105,** 1919.

[23] J. Sanders-Loehr *et al., J. Am. Chem. Soc.*, 1986, **108,** 2437.

[24] R. C. Reem and E. I. Solomon, *J. Am. Chem. Soc.*, 1987, **109,** 1216.

atom environment, but so far the X-ray studies have dealt only with methemerythrin and azido methemerythrin, which are not the active form of the molecule. In the methemerythrin species the iron atoms are both Fe^{III} and one of the bridges between them is an oxygen atom. Figure 30-11 shows the reported structure of azidomethemerythrin. To become active, the iron atoms must both be reduced to Fe^{II} and the bridging O atom protonated to become μ-OH.

In the active form, hemerythrin is believed to function in the manner shown in Fig. 30-12. The substrate O_2 enters the sixth coordination site on the lower iron atom and becomes reduced to a hydroperoxo group, which is held by a hydrogen bond to the bridging oxygen atom. The steps that follow this during *in vivo* activity of hemerythrin are still obscure, however.

Our understanding of hemerythrin has been enhanced by the characterization and study of several interesting model systems for the two-iron site of hemerythrin.[25,26] These are schematically represented by (30-VII). These model

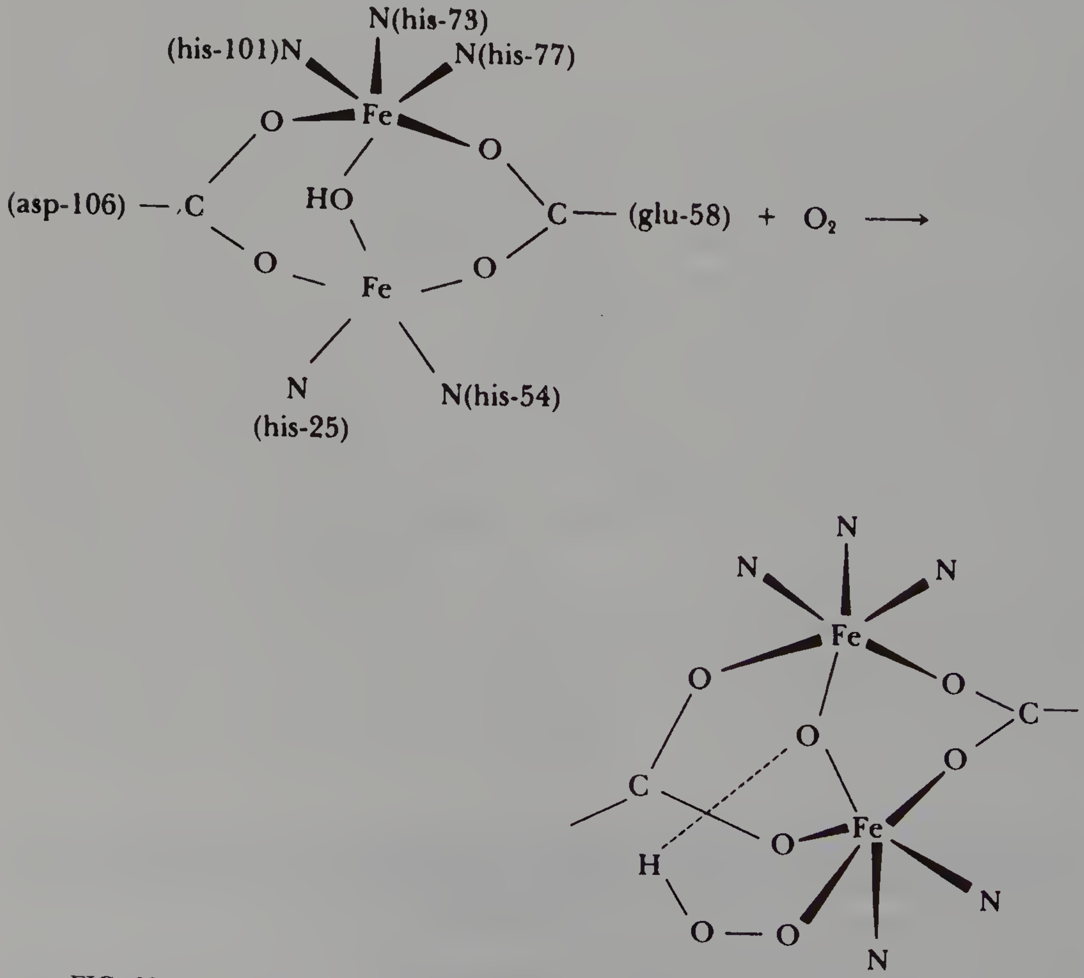

FIG. 30-12. A possible description of the mode of oxygen binding by hemerythrin.

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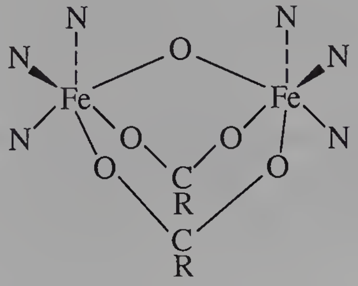
[25] S. J. Lippard *et al., J. Am. Chem. Soc.*, 1984, **106,** 3653; *Inorg. Chem.*, 1985, **24,** 2156.
[26] K. Wieghardt *et al., Inorg. Chem.*, 1985, **24,** 1230.

primarily the iron–iron interaction but not the oxygen-binding function since they have no unoccupied coordination sites or readily displaced ligands.



(30-VII)

30-7. Iron–Sulfur Proteins[27]

These are relatively low molecular weight compounds consisting of peptide chains bound through cysteine sulfur atoms to redox centers that consist either of one iron atom or a cluster of iron and sulfur atoms, the latter often being called "inorganic" sulfur atoms to distinguish them from the sulfur atoms of the cysteine residues. The term *rubredoxin* is used for those with one iron atom, while those containing clusters are called *ferredoxins* or *high-potential iron proteins* (HiPIPs). Each of these will now be discussed. Schematic structures for all of them are presented in Fig. 30-13.

Rubredoxins are found in anaerobic bacteria where they are believed to participate in biological redox reactions. They are relatively low molecular weight proteins (~6000) containing only one iron atom. In the best characterized rubredoxin, from the bacterium *Clostridium pasturianum,* the iron atom, which is normally in the III oxidation state, is surrounded by a distorted tetrahedron of cysteinyl sulfur atoms. The Fe—S distances range from 2.24 to 2.33 Å, and the S—Fe—S angles from 104 to 114°. When the Fe(III) is reduced to Fe(II) there is a slight (0.05 Å) increase in the Fe—S distances but the essentially tetrahedral coordination is maintained. Mössbauer spectroscopy has shown that the iron is in the high-spin condition in both oxidation states. Inorganic chemists have prepared and studied $[Fe(SR)_4]^{2-}$ and $[Fe(SR)_4]^-$ complexes as models to help understand the properties of the rubredoxins.

Ferredoxins and high-potential iron proteins are also relatively small proteins (6000–12,000) in which the redox centers, clusters of two, three, or four iron atoms, each with an equal number of sulfur atoms (so-called inorganic sulfur) are held in place by bonds from cysteine sulfur atoms to iron. The structures of the clusters are shown in Fig. 30-13. In each case, an approximate tetrahedron of sulfur atoms is completed about *each* iron atom by the sulfur atoms of cysteine residues of the peptide.

The two-iron cluster, complete with its attached cysteine sulfur atoms, can be described as two FeS_4 tetrahedra sharing on edge (Fig. 30-13). In

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[27] F. Armstrong, *Adv. Inorg. Bioinorg. Mech.*, 1982, **1**, 65; T. G. Spiro, Ed., *Iron–Sulfur Proteins,* Wiley, New York, 1982.

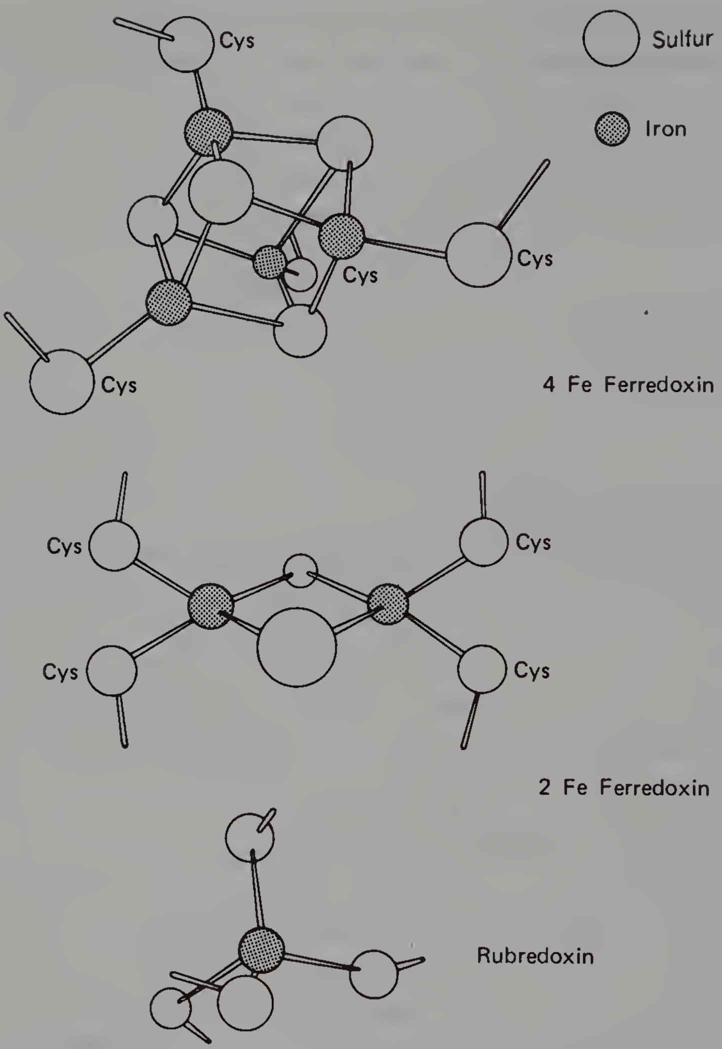

FIG. 30-13. Structures of the 4Fe—4S centers and 2Fe—2S centers in ferredoxins and the 1 Fe center in rubredoxin.

a convenient brief notation, the two-iron clusters can be represented as [2Fe–2S]$^{n+}$. They have relatively simple behavior. Their normal state is [2Fe–2S]$^{2+}$ (meaning that both iron atoms are ferric) but they can be reduced at potentials similar to that of the standard hydrogen electrode to [2Fe–2S]$^{+}$.

Spectroscopic evidence of several kinds shows unambiguously that in the [2Fe–2S]$^{+}$ cluster the added electron is localized on one iron atom, so that one Fe^{II} and one Fe^{III} are present. In the [2Fe–2S]$^{2+}$ cluster the Fe to Fe distance is only 2.72 Å and the two high-spin (d^5) iron atoms have their magnetic moments so strongly coupled antiferromagnetically that the cluster is diamagnetic. Upon reduction, this coupling persists and the [2Fe–2S]$^{+}$ cluster has only one unpaired electron. This is very helpful since it means that epr detection is quite easy.

The four-iron centers, [4Fe–4S]$^{n+}$ appear to be more common than the two-iron centers and have more complex behavior. In biological systems they have three oxidation levels, giving them charges of +3, +2, or +1, but in any given system, only one pair of these is employed. For those systems called *ferredoxins* (abbreviated Fd), the normally isolated substance contains a diamagnetic $[4Fe{-}4S]^{2+}$ cluster; this can be reversibly reduced at ~0.0 V (vs. the hydrogen electrode) to $[4Fe{-}4S]^{+}$, which has one unpaired electron. These four-iron ferredoxins obviously behave much like the ferredoxins that contain two-iron clusters.

For the systems called high potential iron–sulfur proteins (HiPIPs) the operative redox couple, at $\sim +0.75$ V (vs. the hydrogen electrode), is between the $[4Fe{-}4S]^{3+}$ and $[4Fe{-}4S]^{2+}$ clusters. The redox behavior of both Fd's and HiPIPs is summarized in the following reaction:

$$\begin{array}{ccccc} [4Fe{-}4S]^{3+} & \underset{-e}{\overset{+e}{\rightleftharpoons}} & [4Fe{-}4S]^{2+} & \underset{-e}{\overset{+e}{\rightleftharpoons}} & [4Fe{-}4S]^{+} \\ S = \frac{1}{2} & & S = 0 & & S = \frac{1}{2} \\ & \sim +350 \text{ mV} & & \sim -400 \text{ mV} & \\ & \text{HiPIP couple} & & \text{Fd couple} & \end{array}$$

In this scheme the potentials are given in millivolts (mV) against the standard calomel electrode, which is the usual practice in the research literature.

The existence of three-iron clusters is now well documented,[28] but their behavior is at present poorly understood. There is direct X-ray information in at least one case concerning the structure of such a cluster in a crystalline ferredoxin. However, their biological significance is still being debated, and it may be that in at least some cases they are not present *in vivo,* but arise by degradation of [4Fe–4S] clusters during isolation procedures.

The study of ferredoxin and HiPIP biochemistry provides a classic example of how inorganic chemists can often use model systems to throw light on complex biological processes. It has been possible to synthesize compounds containing $[Fe_4S_4(SR)_4]^{x-}$ anions that are very similar in many aspects (especially structurally) to the $[4Fe{-}4S]^{n+}$ clusters as they are bonded to four crysteinyl sulfur atoms of the peptide chain. It is even possible, by treating ferredoxins with solutions of mercaptides (RS^-) to extract the $[4Fe{-}4S]^{2+}$ clusters from the protein and capture them as $[Fe_4S_4(SR)_4]^{2-}$ anions. Efforts to synthesize model [2Fe–2S] clusters have been hampered by the fact that these tend to dimerize spontaneously to [4Fe–4S] clusters. The synthesis of model [3Fe–3S] clusters has also been problematical.[29]

While the study of model, protein-free clusters has been enormously productive in advancing our understanding of the natural biomolecules, it is important to appreciate that many aspects of cluster behavior are strongly affected by their environment, particularly by whether they are within the protein environment or relatively exposed in solution. The protein environment immediately surrounding the clusters is hydrophobic, whereas the model

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[28] H. Beinert and A. J. Thomson, *Arch Biochem. Biophys.* 1983, **222,** 333.

[29] D. Coucouvanis *et al., J. Am. Chem. Soc.,* 1984, **106,** 7998.

systems such as $[Fe_4S_4(SR)_4]^{n-}$, being ionic, must be surrounded in solution by a more or less polar environment. This has a marked effect on their electrochemical behavior. Since it is, of course, their redox activity which is their biological *raison d'etre,* this is an important point.[30]

Another important point having to do with cluster environment is the following. Both HiPIP and Fd are normally isolated with the $[4Fe–4S]^{2+}$ cluster. For Fd, reversible, one-electron reduction occurs at −400 mV, but reversible oxidation to the 3+ level has never been accomplished. For HiPIPs, conversely, reversible, one-electron oxidation occurs readily, but reduction can be achieved only under forcing conditions having no relevance to the biological situation. Unquestionably, however, the $[4Fe–4S]^{2+}$ clusters in the two types of compounds are the same. What, then, causes the marked difference in their redox behavior?

Two hypotheses are under consideration. One focuses on the number of hydrogen bonds from surrounding protein NH groups to cysteinyl sulfur atoms: there appear to be about twice as many of these for a Fd than for a HiPIP. Thus, reduction (the introduction of negative charge) would be preferred for an Fd. A second hypothesis is that oxidation and reduction of the $[4Fe–4S]^{2+}$ cluster lead to different sorts of structural deformations, and that the protein conformations about the cluster in Fd's and HiPIPs differ so as to favor the reductively induced changes in the Fd case and the oxidatively induced changes in the HiPIP case. This is a fascinating question which will, no doubt, be resolved as better structural data are obtained and, perhaps, as model systems become better characterized.

THE BIOCHEMISTRY OF OTHER METALS

30-8. Zinc

Zinc is now recognized to be essential to all forms of life, and a large number of diseases and congenital disorders have been traced to zinc deficiency. In the adult human body there are 2 to 3 g of zinc, as compared to 4 to 6 g of iron and only ~250 mg of copper. Biochemists were somewhat slow to appreciate the presence and importance of zinc because it is colorless, nonmagnetic, and generally, not as easily noticed as iron and copper.

In 1940 carbonic anhydrase was shown to be a zinc enzyme, and in 1955 carboxypeptidase became the second recognized zinc enzyme. Since then more than 80 other zinc enzymes have been reported, and functionally they are of many kinds, including alcohol dehydrogenases, aldolases, peptidases, carboxypeptidases, proteases, phosphatases, transphosphorylases, a transcarbamylase, and DNA- and RNA-polymerases.[31] We discuss here only two

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[30] T. Tanaka *et al., Inorg. Chem.,* 1984, **23,** 518.

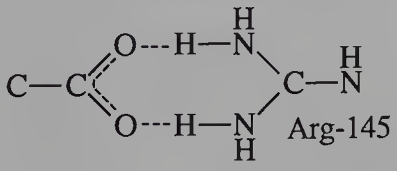
[31] F. Y. Wu and C. Wu, in *Advances in Inorganic Biochemistry,* Vol. 3, G. L. Eichhorn and L. G. Marzilli, Eds., Elsevier, New York, 1981, pp. 143–166; T. G. Spiro, Ed., *Zinc Enzymes,* Wiley, New York, 1983; R. J. P. Williams, *Polyhedron,* 1987, **6,** 61.

of the zinc enzymes, namely, carboxypeptidase and carbonic anhydrase, since our structural and kinetic knowledge for these is extensive and throws considerable light on the role played by the zinc ion in these chemical reactions.

Carboxypeptidase A. This type of enzyme, with a molecular weight of ~34,600, catalyzes the hydrolysis of the terminal peptide bond at the carboxyl end of proteins and other peptide chains. It is also effective toward correspondingly placed ester linkages. There is a marked preference for peptide bonds in which the side chain of the terminal residue is aromatic or a branched aliphatic chain. Carboxypeptidase A's (CPAs) have been found in the pancreas of many mammals including man, but most studies have been carried out on the bovine enzyme.

The overall structure of the bovine CPA has been determined by X-ray crystallography. The zinc ion is coordinated by two histidine nitrogen atoms and an oxygen atom from the carboxyl side chain of a glutamate residue, with a water molecule completing a roughly tetrahedral arrangement. The conformation of the molecule is such as to create a groove in which the zinc ion is found and nearby a pocket that contains no binding groups but is of the right size to accommodate the large nonpolar side chains mentioned previously.

By combining the structural information with indications from a variety of chemical studies, it has been possible to devise hypotheses about the mechanism of catalysis. Several key points are generally agreed to. (1) The carbonyl oxygen atom of the peptide or ester link that is to undergo hydrolysis becomes coordinated to the zinc atom. This polarizes it in the $^{-}O—C^{+}$ sense, thus making the carbon atom more prone to nucleophilic attack. The arginine-145 residue forms a strong hydrogen-bonded linkage (30-VIII) to the terminal carboxyl group. This accounts for the specificity of the enzyme for catalyzing hydrolysis of the terminal residue at the carboxyl end of a peptide. It also results in a good fit of a large nonpolar side chain on the terminal residue into an available hydrophobic pocket. At this point, the so-called Michaelis complex has been formed. Beyond this, there has been considerable controversy as to how bond scission and generation of products is accomplished. Currently, however, the scheme shown in Fig. 30-14 seems to have the greatest credibility, though not universal acceptance.[32]



(30-VIII)

A key point in favor of this scheme is that it can account for the accepted fact that following the Michaelis complex, another metastable complex (or

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[32] M. W. Makinen *et al., Adv. Inorg. Biochem.*, 1984, **6**, 1.

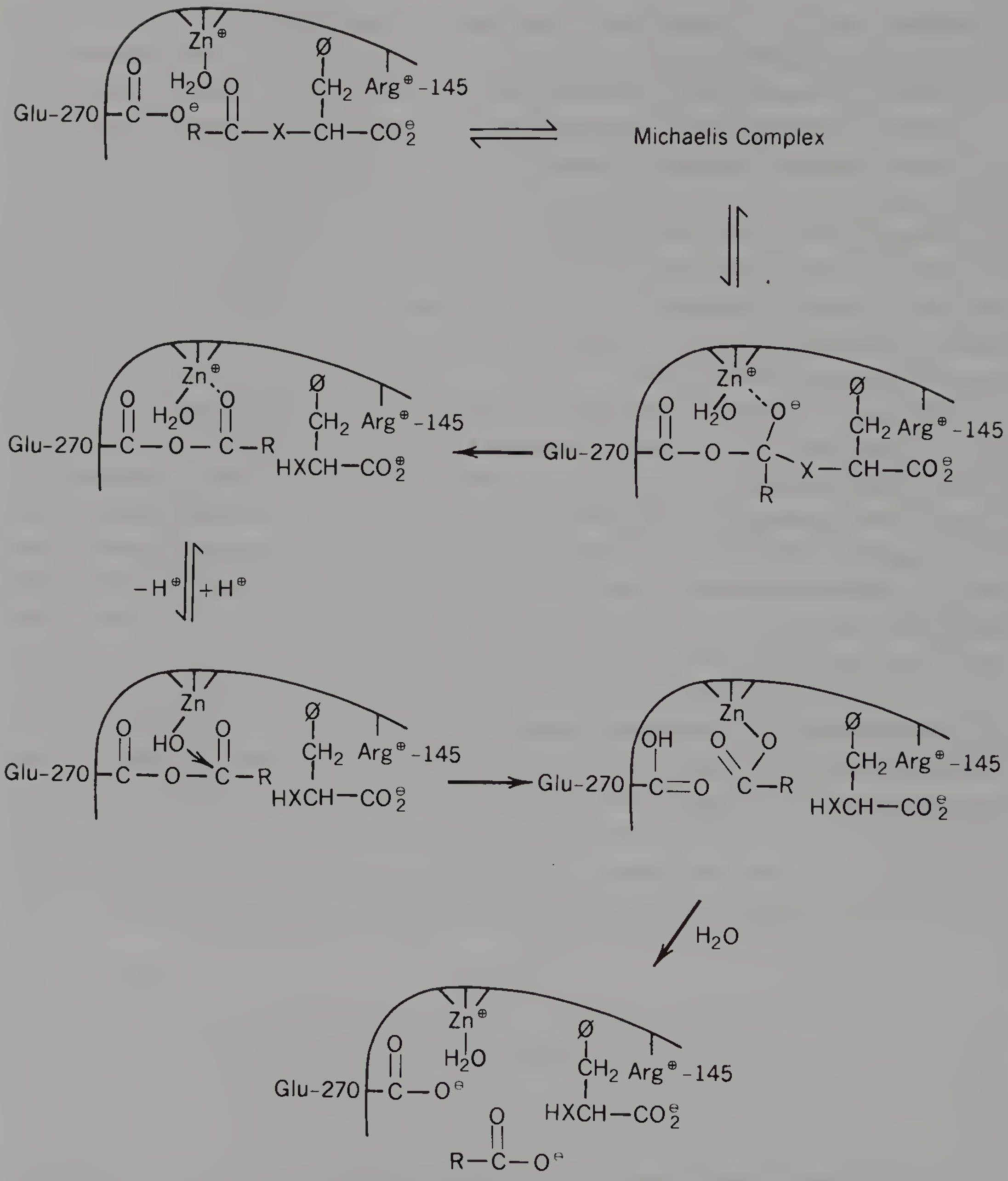

FIG. 30-14. A possible mechanism for the action of carboxypeptidase. X represents either O or NH, and the steps are not all written so as to be balanced with respect to protons.

intermediate) is formed, and only then is the product complex formed, from which the products, RCO_2^- + $HOCR'HCO_2^-$ or RCO_2^- + $H_3NCR'HCO_2^-$, promptly dissociate, leaving the enzyme ready for the next cycle. This second complex must be one of the species in which there is an intermediate anhydride involving the carboxyl group of Glu-270. It is to be noted that another key step in the mechanism is the generation of a Zn—OH group, which is responsible directly for the attack on the carbonyl carbon atom. The zinc ion thus serves twice as a Lewis acid: once in binding and polarizing the carbonyl group and again in enhancing the acidity of the bound water molecule so that it can become the necessary OH nucleophile. There is indirect evidence for the occurrence of this Zn—OH attack on the mixed anhydride intermediate from study of model systems.[33]

Carbonic Anhydrase.[34] As noted elsewhere (Section 8-5), the reaction

$$CO_2(aq) + H_2O = H_2CO_3$$

is slow; yet many physiological processes require rapid equilibration of CO_2 with HCO_3^- and H_2CO_3 at physiological pH, which is ~7.0. Therefore, enzymes called carbonic anhydrases are found in nearly all phyla, and all appear to contain zinc.

Human carbonic anhydrase has a molecular weight of ~30,000 and occurs in two similar but not identical forms. The molecular structures of both are known from X-ray crystallography. A schematic indication of one of them (the other is very similar) appears in Fig. 30-15. The zinc ion lies in a deep pocket, and is coordinated by three histidine imidazole nitrogen atoms. The enzyme enhances the rate of the hydration reaction in either direction by a factor of 10^6 or more.

The enzyme-catalyzed reaction rates are pH dependent in a way that indicates the existence of a group in the enzyme with a pK_A of ~7 that must be deprotonated to give that form of the enzyme E, which is required for hydration of CO_2. Conversely, an acid form EH^+ is required for the reverse reaction. It is necessary to assume that the substrate for dehydration is HCO_3^-, since the pH dependence of dehydration is the inverse of that for

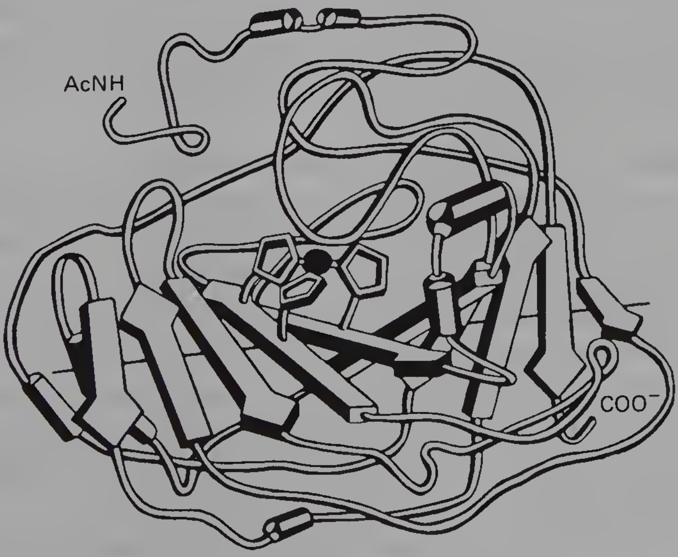

FIG. 30-15. A schematic diagram of the tertiary structure of carbonic anhydrase. The coordination of the zinc ion (black filled circle) by three histidine imidazole groups is highlighted.

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[33] J. T. Groves and J. R. Olson, *Inorg. Chem.*, 1985, **24,** 2717.

[34] S. Lindskog, *Adv. Bioinorg. Chem.*, 1982, **4,** 116.

hydration. A reaction involving only neutral species, $CO_2 + H_2O$ to give H_2CO_3, would not give such a relationship. A four-step mechanism that appears to satisfy all available evidence is shown in eq. 30-2.

$$\mathrm{E} + \mathrm{CO_2} \rightleftharpoons \mathrm{E}\cdots\mathrm{CO_2} \underset{\mathrm{H_2O}}{\overset{\mathrm{H_2O}}{\rightleftharpoons}} \mathrm{EH^+}\cdots\mathrm{HCO_3^-} \rightleftharpoons \mathrm{EH^+} + \mathrm{HCO_3^-} \rightleftharpoons \mathrm{E} + \mathrm{H^+} + \mathrm{HCO_3^-} \quad (30\text{-}2)$$

All available data now show that the activity-linked group in the enzyme with a pK_A of 7 is an H_2O molecule coordinated to the zinc ion. In short, the initial complex of CO_2 with the active site is a $ZnOH\cdots CO_2$ complex, where the CO_2 is doubtless positioned by several other interactions so that the oxygen atom of ZnOH approaches the carbon atom of CO_2. The nature of the pocket in which the zinc ion is found lowers the otherwise much higher pK_A of the $ZnOH_2$ group to ~7, while at the same time leaving the coordinated OH^- sufficiently nucleophilic to attack the carbon atom of the CO_2. The immediate product of this attack is the HCO_3^- ion, and this, in turn, must be the substrate in the reverse reaction.

In effect, the enzyme makes the fast reaction $CO_2 + OH^- = HCO_3^-$ the major pathway of hydration at a pH of 7, whereas normally the slow reaction of CO_2 with H_2O would predominate at a pH of 7 and the reaction with OH^- would not become dominant until pH 10 or greater. The importance of a Zn—OH group in providing a potent attacking nucleophile is in harmony with the proposed importance of a similar feature of the carboxy–peptidase mechanism. A difference between the two, however, is that here it must be assumed that hydrogen bonding to the two CO_2 oxygen atoms polarizes the C=O bonds so as to enhance the positive character of the carbon atom, whereas in carboxypeptidase the zinc atom was also involved in the polarization of the C=O group.

Metallothioneins.[35] These relatively low molecular weight (6100 dalton) cysteine-rich proteins are found in mammals, invertebrates, (e.g., crabs), fungi, and yeast. About one third of the ~60 amino acids in the peptide chain are cysteines, and this confers on metallothioneins a remarkable capacity to bind metals such as zinc, copper, cadmium, and mercury, which have an affinity for thiolate ligands. It is believed that this metal-binding capacity, which allows the complexation of seven metal ions per molecule enables metallothioneins to serve as detoxifying agents (especially against Cd) but they may also play more intricate metabolic roles. Metallotheoneins are the only biomolecules known to normally contain cadmium.

The structure of a Zn/Cd metallothionein from rat liver has recently been reported.[36] It contains 61 amino acids and consists of an α domain (residues 30–61, including 11 cysteines) and a β domain (residues 1–29, 9 cysteines). In each domain there is a set of three metal atoms forming a triangular array

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[35] D. C. Dalgarno and I. M. Armitage, *Adv. Inorg. Biochem.*, 1984, **6,** 113.

[36] W. F. Furey *et al., Science*, 1986, **231,** 704.

(M···M = ~4.1 Å) with an additional separate metal atom in the α domain. Each metal atom is coordinated by an approximately tetrahedral set of four cysteine sulfur atoms.

30-9. Copper[37]

Copper is the third most abundant metallic element in the human body, following iron and zinc, and it is important in all other forms of life as well. Table 30-2 gives an overview of the major classes of copper-containing biomolecules, with emphasis on function and occurrence.

TABLE 30-2
Major Types of Copper Proteins

	Occurrence	Function
"Blue" electron carriers		
Azurin Plastocyanin Stellacyanin Umecyanin	Algae, green leaves and other plants	Electron transfer (photosynthesis)
"Blue" Oxidases (reducing O_2 to H_2O)		
Laccase	Tree, fungal	Oxidation of phenols and diamines
Ceruloplasmin	Human, animal serum	Weak oxidase activity, Fe and Cu transport
Ascorbate oxidase	Plants	Oxidation of L-Ascorbic Acid ?
"Nonblue" Oxidases (reducing O_2 to H_2O_2)		
Amine oxidase[a]	Most animals, etc.	Elastin, collagen formation
Galactose oxidase	Molds	Galactose oxidation
Oxygen Carrier		
Hemocyanin	Molluscs and arthropods	Oxygen transport
Copper Monooxygenases		
Phenol *o*-monooxygenase (Tyrosinase)	Animal skin, melanoma, insects, plants	Tyrosine oxidation pigment (melanin) formation
Dopamine β-Hydroxylase	Adrenals	Converts dopamine to norepinephrine
Copper Dioxygenase		
Quercetinase	Fungal	Quercetin oxidative cleavage
Others		
Superoxide dismutase[b]	Red blood cells of animals	O_2^- detoxification?
Cytochrome *c* oxidase[c]	Mitochondria	Terminal oxidase ($O_2 \rightarrow H_2O$)

[a] Contains pyridoxal phosphate as well as copper.
[b] Contains zinc as well as copper.
[c] Contains heme as well as copper.

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[37] T. G. Spiro, Ed., *Copper Proteins*, Wiley–Interscience, New York, 1981; K. Karlin and J. Zubieta, Eds., *Copper Coordination Chemistry*, Vols. 1 and 2, Adenine Press, Guilderland, New York, 1982, 1984; E. I. Solomon *et al.*, *Struct. Bonding* (*Berlin*), **1983, 53,** 1.

Another classification scheme, which is of particular interest to the bioinorganic chemist, is based on the type of copper center present.[38] The four types to be considered are listed, along with their chief characteristic properties in Table 30-3.

While many copper biomolecules contain copper in only one form (e.g., "blue" or normal), there are also numerous cases where several different types of copper are present, and this can provide difficulties in working out their mode of action. This is commonly true for copper oxidases. For example, ascorbate oxidase contains eight copper atoms, one normal, three blue, and two coupled binuclear sites.

The "normal" copper(II) sites are those in which the Cu^{2+} ion is coordinated by a square set of ligands, usually nitrogen atoms (commonly those of histidine imidazole groups) with one or two additional ligands occupying more distant coordination sites above and below this plane. Since this is just the sort of tetragonal environment that generally prevails in normal copper(II) complexes, such sites have familiar spectral characteristics.

The "blue" copper(II) sites[39] must entail an environment quite unlike those in ordinary tetragonal copper(II) complexes. Numerous sophisticated spectroscopic studies, both of biomolecules themselves and of model systems, have been made in an effort to discover the key features of such sites, but many aspects of the problem remain unclear. In the final analysis, the most important data will be descriptions, based on X-ray crystallographic studies of the structures of the "blue" proteins, of the copper coordination spheres. Thus far, only one such result is available, namely, for a plastocyanin. This, as shown in Fig. 30-16, has a highly unusual geometry for Cu^{II}. Because of the structural data available for it, plastocyanin has proved to be a very attractive subject for the study of biological electron transfer kinetics,[40] although others have been studied as well.[41]

Returning now to the "blue" copper site shown in Fig. 30-16, we note that

TABLE 30-3
Types of Copper Sites in Biomolecules

Type	Main characteristics
Copper(I)	Colorless; diamagnetic; epr silent
Normal copper(II)	Visible and epr spectra typical of tetragonally coordinated Cu^{2+}
"Blue" copper(II)	The epr shows abnormally small A_{11}; very intense absorption ($\epsilon \sim 5000\ M^{-1}\ cm^{-1}$) at ~600 nm
Coupled $(Cu^{II})_2$	Abnormal visible spectrum; diamagnetic and epr silent

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[38] B. Reinhammer, *Adv. Inorg. Biochem.*, 1979, **1,** 91.
[39] D. R. McMillan, *J. Chem. Educ.*, 1985, **62,** 997.
[40] A. G. Sykes, *Chem. Soc. Rev.*, 1985, **14,** 283.
[41] A. G. Sykes *et al.*, *Inorg. Chem.*, 1986, **25,** 3730.

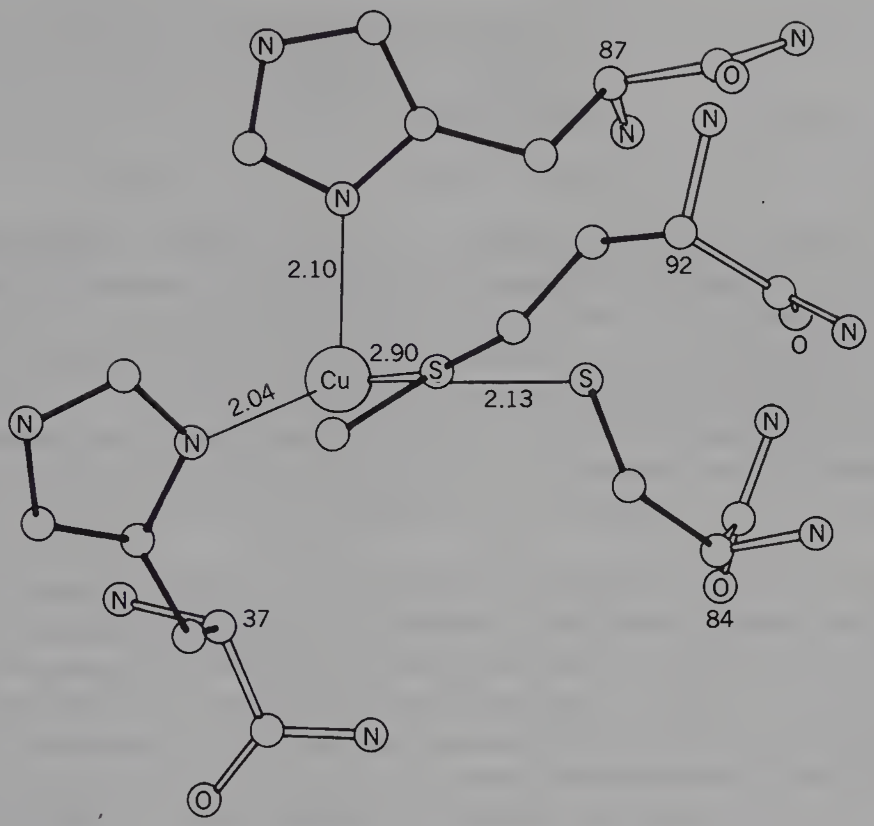

FIG. 30-16. The "blue" copper site in plastocyanin as determined by X-ray crystallography. The Cu–ligand bond lengths are given in Angstroms.

the coordination is extremely unsymmetrical. The angles range from 85 to 137°, while one Cu—S bond is exceptionally long and the other unusually short. The strong visible absorption, which gives rise to the intense blue color, can be assigned to a S → Cu charge-transfer transition localized in this bond.

There are currently many experimental studies appearing[42] and in progress on "blue" copper proteins, including X-ray crystallographic studies on additional ones, such as azurin.

A series of SCF-Xα-SW calculations on approximations to the plastocyanin blue copper site[43] have shown that the epr spectrum can be accounted for, particularly through strong delocalization of the unpaired electron into the $p\pi$ orbital of the cysteine sulfur atom. Undoubtedly the time when these "blue" sites will be pretty well understood is not far off.

For the coupled binuclear type of site, no detailed structural data are yet available for a biological molecule although several studies on hemocyanins are proceeding. Such sites evidently arise[44] when an O_2 molecule is bound by two proximate Cu^I atoms to give a species such as that shown schematically as (30-IX), in which X is a bridging ligand (of unknown identity) that is mainly

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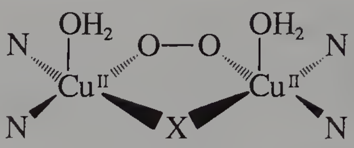
[42] S. I. Chan *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 5755.

[43] E. I. Solomon *et al.*, *J. Am. Chem. Soc.*, 1985, **107,** 4519.

[44] K. D. Karlin and Y. Gultnek, *J. Chem. Educ.*, 1985, **62,** 983.



(30-IX)

responsible for strong antiferromagnetic coupling leading to a diamagnetic, epr silent ground state. The unusual spectral features are mainly charge-transfer bands from the peroxo ligand to the metal atoms.

We now turn to some of the biomolecules that incorporate one or more of the types of active copper sites just discussed.

Superoxide Dismutase (CuZn SOD).[45] Several enzymes that catalyze the dismutation of the superoxide ion (eq. 30-3) are known.

$$2O_2^- + 2H^+ \longrightarrow H_2O_2 + O_2 \qquad (30\text{-}3)$$

Some contain iron or manganese at the active site, but the one that is by far the most thoroughly investigated consists of two identical subunits, each of which has a molecular weight of ~16,000 and contains one copper and one zinc atom. The structure of the active site of the bovine enzyme has been well defined by X-ray crystallography,[46] and is shown schematically in Fig. 30-17. We have here an unambiguous example of a normal copper site.

There is no doubt that the copper atom is the active center, while the zinc atom plays a supportive, structural role, possibly that of maintaining the bridging imidazole group of histidine-61 in place. The zinc can be replaced by Co, Cd, or Cu with 70 to 100% retention of activity, but without copper

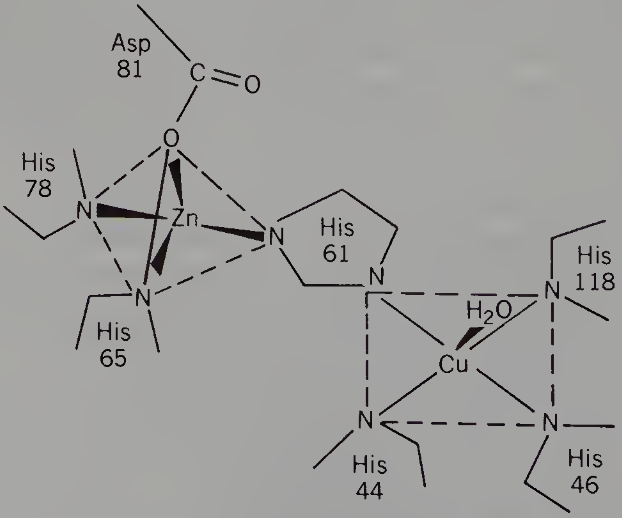


FIG. 30-17. Schematic drawing of the active site of bovine superoxide dismutase.

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[45] I. Fridovich, *Adv. Inorg. Biochem.*, 1979, 1, **67;** J. S. Valentine and D. M. de Freitas, *J. Chem. Educ.*, 1985, **62,** 990.

[46] J. S. Richardson *et al. J. Mol. Biol.*, 1982, **160,** 187.

there is no activity. It appears plausible, though not certain, that the catalytic cycle may be expressed by the following equations:

$$(\mathrm{HisH})_3\mathrm{Cu^{II}}(\mathrm{His^-})\mathrm{Zn} + \mathrm{O_2^-} + \mathrm{H^+} \longrightarrow (\mathrm{HisH})_3\mathrm{Cu^{I}} + (\mathrm{HisH})\mathrm{Zn} + \mathrm{O_2}$$

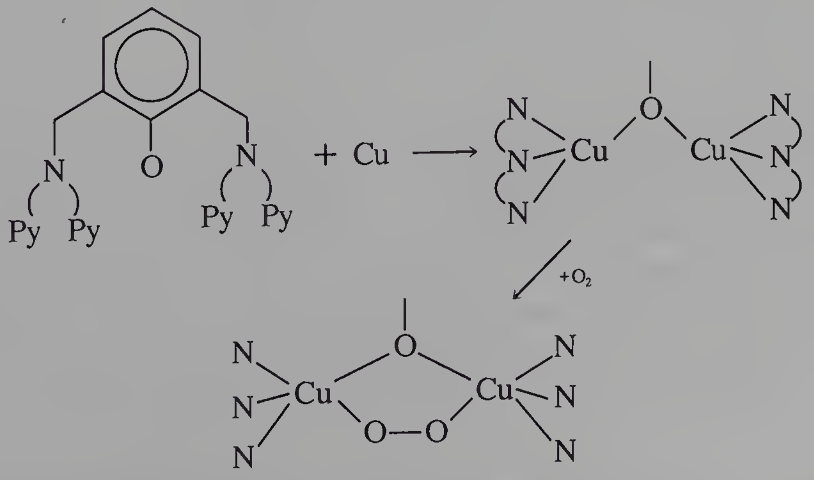
$$(\mathrm{HisH})_3\mathrm{Cu^{I}} + \mathrm{O_2^-} + \mathrm{H^+} \longrightarrow (\mathrm{HisH})_3\mathrm{Cu^{II}}(\mathrm{His^-})\mathrm{Zn} + \mathrm{H_2O_2}$$

Hemocyanins. These respiratory proteins are found in the lymph of most (but not all) animals in the phyla Mollusca and Arthropoda (e.g., squid, cuttlefish, octopus, lobsters, and crabs). Unlike mammalian hemoglobin, they are not confined to special cells. They are very large, with molecular weights of between 4.5×10^5 and 9×10^6, but they consist of subunits. Each subunit contains a pair of Cu atoms, and they can bind one O_2 molecule per pair of Cu atoms. Hemocyanins generally display cooperativity in O_2 binding, presumably through subunit interactions, but no mechanism has yet been suggested for this.

The colorless deoxy form contains $\mathrm{Cu^I}$ while the blue oxy form contains $\mathrm{Cu^{II}}$, which, however, gives no epr signal. The hemocyanins clearly afford clearcut examples of the copper(I) type site in their deoxy form and of the coupled $(\mathrm{Cu^{II}})_2$ type site in their oxygenated form.

An X-ray study[47] of the hemocyanin from a spiny lobster at 3.2 Å resolution gives a general view of the protein structure and some indication (though not yet atomic details) of the dicopper site of the deoxy molecule. The copper atoms appear to be 3.8 ± 0.4 Å apart and each one is ligated by three amino acid residues, though there is no indication of a bridging ligand. The Cu···Cu distance is in accord with earlier estimates (3.39–3.67 Å) from various EXAFS measurements.

Keen interest in the nature of coupled $(\mathrm{Cu^{II}})_2$ sites together with delays in obtaining X-ray structural data because of the large size of the biomolecule has lead to a considerable amount of work on synthetic model systems. An illustrative example[48] (*cf.* p. 773) is provided by the following system:



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[47] W. P. J. Gaykema *et al., Nature (London)*, 1984, **309**, 23.

[48] K. D. Karlin *et al., J. Am. Chem. Soc.*, 1984, **106**, 3372; 1985, **107**, 5828.

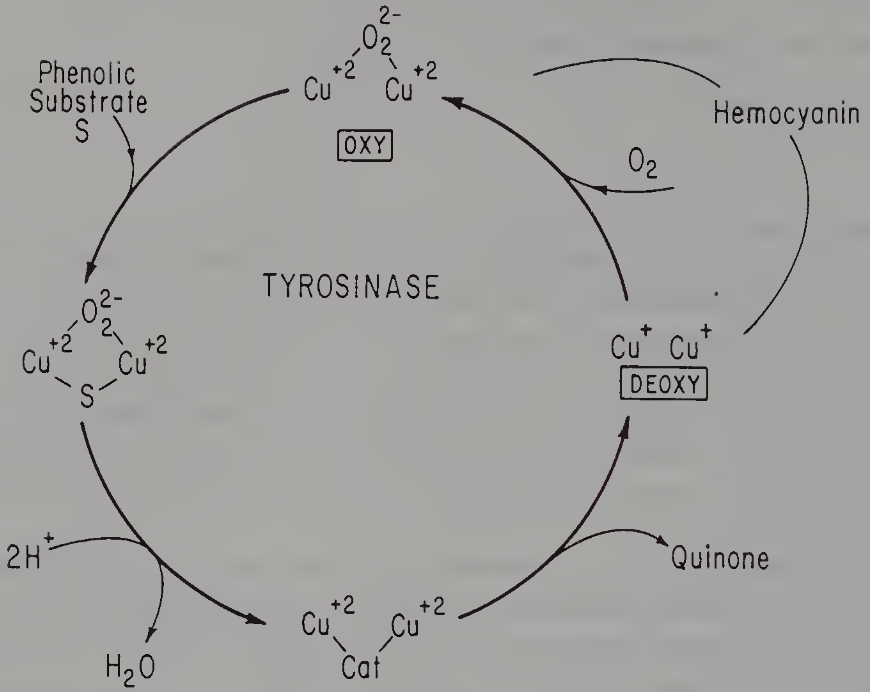
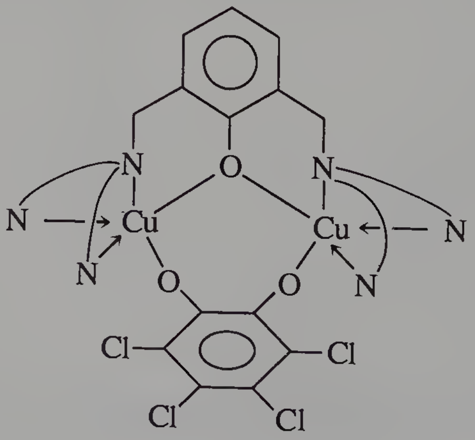


FIG. 30-18. A proposed catalytic cycle for the role of tyrosinase in oxidizing phenol to *o*-quinone. Cat = catecholate dianion.

The two-copper site found in the hemocyanins, or something very similar, occurs also in tyrosinase, which catalyzes oxidation of phenols to *o*-phenyldiols. It is reasonable to assume that there is a catalytic cycle of the type shown in Fig. 30-18. That the hemocyanins can fulfill only one segment of this entire cycle is due at least in part to the fact that the dicopper site is deeply buried. A model compound for the postulated intermediate catechol complex (30-X) has been prepared and studied structurally.[49]



(30-X)

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[49] K. D. Karlin *et al.*, *Inorg. Chem.*, 1985, **24**, 3725.

Oxidases. These are widespread and of many types,[45,50] but none has yet been characterized by X-ray crystallography. They are the most difficult to study for the bioinorganic chemist since they contain copper sites of all four types (the Cu^I and coupled Cu_2^{II} sites being, of course related by redox reactions).

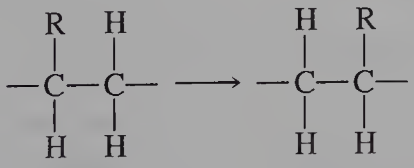
Laccases have molecular weights that vary with the source, from 60,000 to 110,000. They contain one normal copper site, one blue copper site, and one coupled Cu_2^{II} site—four copper atoms in all. Laccases catalyze the oxidation of a number of diamines and diphenols and during the course of the reaction the coupled Cu_2^{II} site binds oxygen and transfers it to substrate, while the normal center carries out electron transfer. The role of the blue center is not yet known.

Ceruloplasmins are found in the blood of mammals, birds, reptiles and amphibians. Human ceruloplasmin has a molecular weight of ~150,000 and contains saccharide units as well as protein. The copper is present in all types of sites.

Other Oxidases. Important oxidases include ascorbate oxidase, which catalyzes oxidation of ascorbic acid (vitamin C) to dehydroascorbic acid, galactase oxidase, and various amine oxidases. Detailed characterization of the copper sites in these is still underway, although it is definitely known that ascorbate oxidase has sites of all types.

30-10. Cobalt

Cobalt has only one important biochemical role, as far as we know at present, namely, in vitamin B_{12}.[51] This vitamin is a cofactor for a number of enzymes, virtually all of which catalyze a reaction of the type 30-4.



$$-\overset{\displaystyle R}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}- \longrightarrow -\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle R}{\underset{\displaystyle H}{C}}- \qquad (30\text{-}4)$$

The adult human body contains 2 to 5 mg of vitamin B_{12} and its derivatives, mainly in the liver. A feature of great significance is that in nearly every case the foregoing type of reaction occurs so that there is no exchange between the migrating hydrogen atom and those in the solvent water.

The structure of vitamin B_{12}, which is known conclusively from X-ray crystallography as well as chemical studies, is shown in Fig. 30-19. The bond to the 5′ carbon atom of the deoxyribose moiety is labile, and the ligand attached to cobalt at that coordination site is variable. The vitamin is quite

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[50] B. Mondovi and P. Riccio, *Adv. Inorg. Biochem.*, 1984, **6**, 225.

[51] D. Dolphin, Ed., *B12*, Vol. 1 and 2, Wiley, New York, 1982.

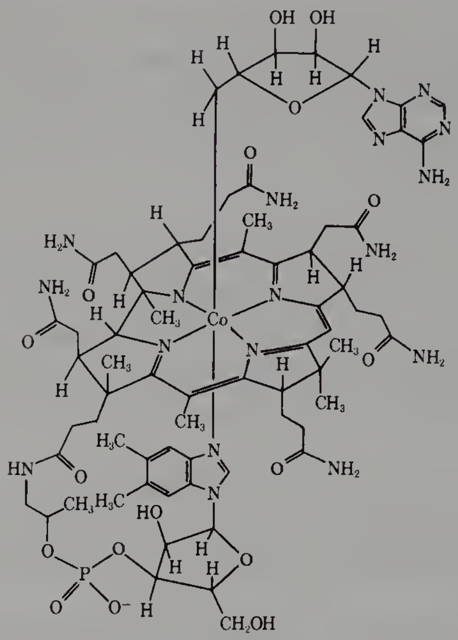

FIG. 30-19. The structure of vitamin B_{12} coenzyme. Note the Co—C bond to the 5′ carbon atom of the adenosyl moiety.

commonly isolated in a form called cyanocobalamin, in which CN occupies this position. The similarity to the porphyrin ring systems of the tetradentate ring, called a *corrin* ring, should be obvious, but there is a key difference, namely, that one of the bridges between pyrrole rings is a direct ring-to-ring bond instead of an HC or CH_3C unit. The reason why the corrin system rather than a porphyrin one is employed may be that its greater flexibility[52] leads to steric forces that eject the 5′-deoxyadenosyl radical, thus initiating the catalytic cycle (as discussed later), but other explanations have been suggested.

There are many B_{12}-dependent enzymes, which differ in the substrate upon which they operate,[53] but the role of coenzyme B_{12} appears uniformly to be the same: by means of Co—C homolytic bond cleavage a formal Co^{II} form of the coenzyme and the adenosyl radical are formed.[54] The relative importance of various factors in enhancing the homolytic Co—C bond cleavage is still to be determined.[55] However, once this step has occurred the adenosyl radical (denoted later as $RCH_2^{\cdot}$) accepts a hydrogen atom from the substrate (SH) to generate a substrate radical ($S^{\cdot}$). The enzyme causes this to rearrange to the product radical ($P^{\cdot}$) and this then abstracts a hydrogen atom from RCH_3 to give product PH and the coenzyme is recovered, ready for another cycle. The details of the enzyme-catalyzed conversion, $S^{\cdot} \rightarrow P^{\cdot}$, are still in need of

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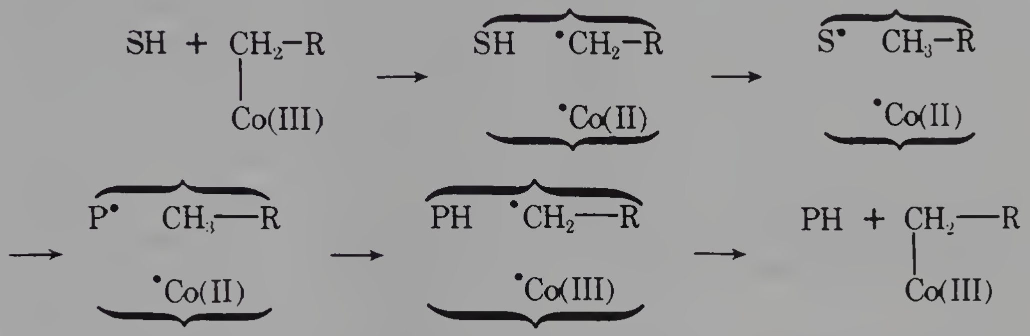
[52] M. K. Geno and J. Halpern, *J. Am. Chem. Soc.*, 1987, **109**, 1238.

[53] J. M. Pratt, *Chem. Soc. Rev.*, 1985, **14**, 161.

[54] J. Halpern, *Science*, 1985, **227**, 869.

[55] M. F. Summers *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 566.

clarification. This general sequence of events is summarized in the following scheme where the curly brackets indicate intermediates whose association is mediated by the enzyme:



One other aspect of cobalt "biochemistry" that should be mentioned is that Co^{2+} can be substituted for Zn^{2+} in a number of enzymes without gross change in activity; carboxypeptidase and carbonic anhydrase are good examples. So far as is known this does not happen in Nature, but it serves as a useful tool for the enzymologist, since the Co^{2+} ion with its spectroscopic and magnetic properties is a useful probe of the enzyme active site.[56]

30-11. Molybdenum and Tungsten

Until the recent discovery of tungsten-containing enzymes (*vide infra*), molybdenum was the only transition metal below the first transition series that was known to be essential in living systems, and molybdenum is still the only heavy transition metal of known wide-spread occurrence.[57] It is an essential trace element for many plants, and also occurs in higher animals, including humans.

Molybdenum is principally known for its role in biological nitrogen chemistry. Table 30-4 lists several of the enzymes that contain molybdenum. They are all very large molecules and for this reason no X-ray structure has yet been completed, although several are underway. The main methods of study have been EXAFS and esr spectroscopy.[58] It appears that molybdenum participates in the action of these enzymes in the form of *cofactors,* which are relatively small molecules that can be detached more or less intact from the large enzyme molecule. For nitrogenase the cofactor also contains iron and is referred to as the iron–molybdenum cofactor (FeMoco), but there appears to be a common molybdenum cofactor (Mo-co) for all the other molybdenum enzymes, or at least for all nitrate reductases.

Nitrogenases. This type of enzyme is found in blue-green algae, in free-living bacteria, and in bacteria that have a symbiotic relationship with leg-

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[56] I. Bertini *et al., Acc. Chem. Res.,* 1983, **16,** 272; *Adv. Inorg. Biochem.,* 1984, **6,** 71; *Inorg. Chem.,* 1985, **24,** 301.

[57] T. G. Spiro, Ed., *Molybdenum Enzymes,* Wiley, New York, 1985.

[58] S. P. Cramer, *Adv. Inorg. Bioinorg. Mech.,* 1983, **2,** 259.

TABLE 30-4
Some Enzymes That Contain Molybdenum

Enzyme	Source	Molecular weight	Number of Mo atoms	Iron and sulfur content	Reaction catalyzed
Nitrogenase	Bacteria; blue-green algae	220,000	2	30Fe, 30S	$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$
		60,000	0	4Fe, 4S	
Nitrate reductase	[a]	200,000–360,000	1 or 2	Cytochrome *b*	$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$
Xanthine oxidase	Cow's milk	275,000	2	8Fe, 8S	Xanthine + $H_2O \rightarrow$ uric acid + $2H^+ + 2e$
Xanthine dehydrogenase	Chicken liver	300,000	2	8Fe, 8S	Same as above
Aldehyde oxidase	Rabbit liver	270,000	2	8Fe, 8S	$RCHO + H_2O \rightarrow RCO_2H + 2H^+ + 2e^-$
Sulfite oxidase	Cow liver	11,000	2	2 Heme	$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$

[a] Fungi, *E. coli,* spinach, and others.

uminous plants, converting N_2 to NH_3 in the soil. The general composition of the *C. pasteurianum* nitrogenase appears to be typical. It consists of two distinct proteins, both of which are essential for activity. The smaller part, called the iron protein, is extemely air sensitive and consists of two apparently identical subunits with a combined molecular weight of ~60,000. There is only one [4Fe–4S] cluster of the ferredoxin type shared by these two subunits. The larger protein has four subunits, 2α and 2β, and has a total molecular weight of ~220,000. One $\alpha_2\beta_2$ molecule contains 2Mo, ~30Fe, and ~30 "inorganic" S atoms, which are believed to be arranged to form four [4Fe–4S] clusters and two Mo—Fe—S clusters of undefined composition. The [4Fe–4S] clusters do *not* resemble ferredoxin clusters in their epr or electronic absorption spectra, but it is not known why.

In 1977 it was shown that all of the molybdenum together with some iron and some sulfur could be isolated from the large protein as an extremely insoluble, and extremely air-sensitive substance with a molecular weight of 1000 to 1500. This is called the iron–molybdenum cofactor (FeMoco) and contains 2 Mo, 6 to 8 Fe, and ≤6 S atoms. Vigorous efforts are being made to establish its composition more exactly and to determine its structure, but

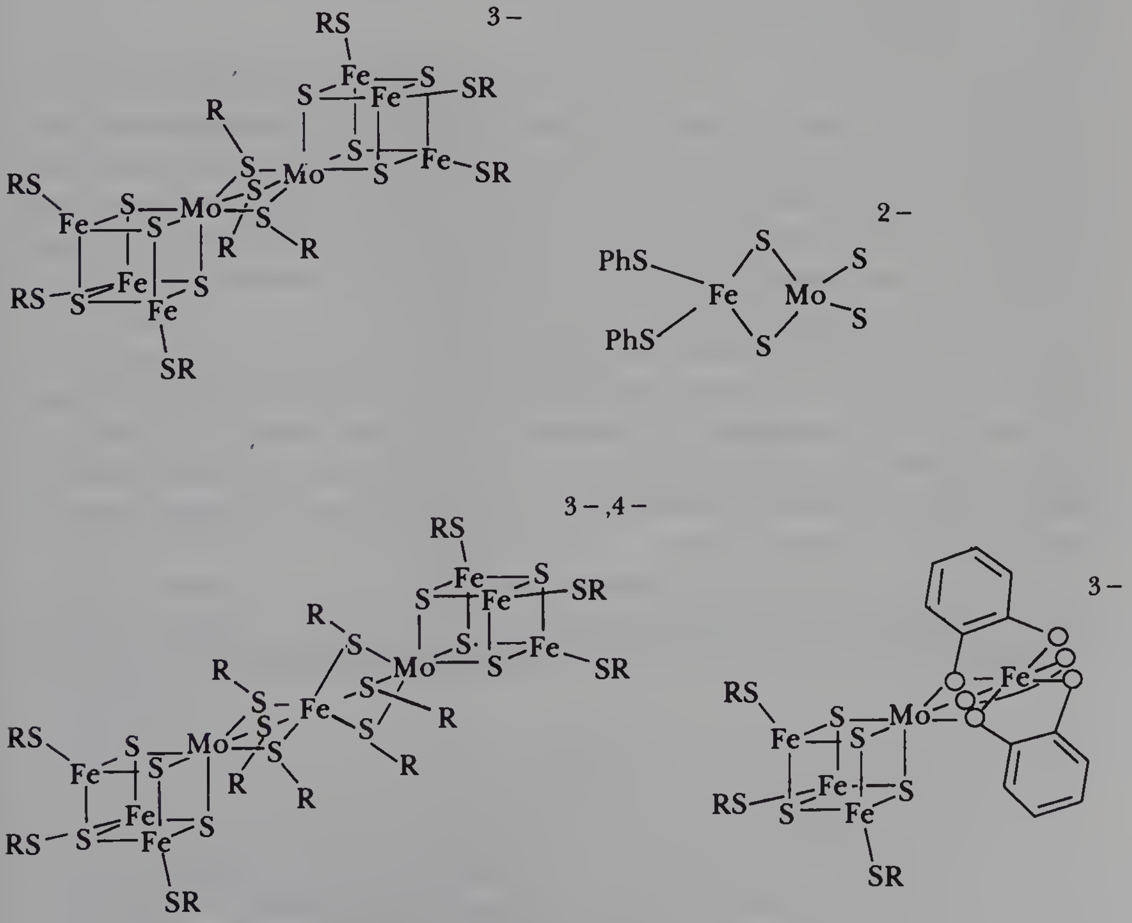

FIG. 30-20. Some species that have been prepared and studied as possible models for the FeMoco.

it is not a tractable material. The EXAFS studies indicate that it contains some sort of Fe—Mo—S cluster species in which the Mo atom is coordinated by at least three and probably four sulfur atoms. This has sparked a great deal of synthetic work to produce model cluster compounds[59] whose EXAFS characteristics might resemble those of FeMoco. Some of these models are shown in Fig. 30-20. While some notable EXAFS similarities have been observed, there are no models that have any functional verisimilitude. For example, none of the models duplicate the electrochemistry of the real FeMoco.[60]

Tungsten.[61] There are a few bacterial enzymes with endogenous tungsten, all of them formate dehydrogenases (FDHs). They catalyze the reversible reaction

$$CO_2 + 2H^+ + 2e \longrightarrow HCO_2H$$

The majority of bacterial FDHs, however, are molybdenum enzymes. The chemistries of the Mo and W FDHs, though not known in great detail, appear to be very similar.

30-12. Miscellaneous Other Elements

As noted in Section 30-1, at least 30 elements play some role in life processes. In earlier parts of this chapter several of the most important elements have been discussed in moderate detail. Extended discussion of calcium could also have been justified because of its widespread fundamental importance in biochemistry.[62] It serves in structural materials (bones, teeth, and shells), as a regulator, and as a cofactor for some enzymes. For reasons of space, we have elected to omit detailed coverage, however.

Another element whose biochemical importance is being increasingly recognized is selenium.[63] It is now recognized to be an essential trace nutrient and is present, for example, in glutathione peroxidase, an enzyme important in the metabolism of hydroperoxides. It also has emerged as a significant anticarcinogen. However, the chemistry *per se* is still not understood, and no more will be said about it here.

We do wish to conclude by summarizing some important recent developments concerning three transition metals, V, Cr, and Ni, whose chemical behavior in life processes is currently becoming reasonably well defined.

[59] R. H. Holm, *Chem. Soc. Rev.*, 1981, **10,** 455.

[60] F. A. Schultz *et al., J. Am. Chem. Soc.*, 1985, **107,** 5364.

[61] E. I. Solomon *et al., Biochem. Biophys. Res. Commun.* 1984, **121,** 1042.

[62] R. P. Robin, G. B. Weiss, and J. W. Putney, Eds., *Calcium in Biological Systems,* Plenum Press, New York, 1985; E. Carafoli and J. T. Penniston, *Sci. Am.*, 1985, **253,** No. 5, p. 70; C. K. Schauer and O. P. Anderson, *J. Am. Chem. Soc.*, 1987, **109,** 3646.

[63] G. F. Combs, Jr., *Fed. Proc.*, 1985, **44,** 2561; T. Jukes, *Nature* (*London*), 1985, **316,** 673.

Vanadium.[64] It is known that vanadium in extremely small amounts is a nutritional requirement for many types of organism, possibly including higher animals. However, specific chemical information is only now beginning to emerge, except in one case where macroscopic concentrations are observed.

The longest known example of vanadium biochemistry is probably the accumulation of vanadium, in special cells called vanadophores, by certain lower marine organisms called tunicates. They concentrate it by a factor of $\sim 10^6$ over its level in the surrounding marine environment.[65a] EXAFS results show that most of it is present as V^{III} surrounded by an octahedral array of oxygen atoms, although esr detectable VO^{2+} is also present in small amounts. Whether it is present simply as $V(H_2O)_6^{3+}$ ions and why it is so accumulated remain open questions.[65b]

Vanadium may also serve in place of molybdenum in the nitrogenase enzymes of certain free-living, nitrogen-fixing bacteria.[66] The V-containing form of the enzyme is encoded by different genes, but is generally similar to the common molybdenum form. Thus, it consists of a protein containing only iron and another containing both iron and vanadium. The latter, which contains 2 vanadium atoms and 23 iron atoms, as well as 20 atoms of acid-labile sulfur, is a cofactor comparable to the FeMoco of the Mo enzyme (see Section 30-11).

Vanadium is also accumulated by the fungus *Amanita muscaria,* and has been isolated from a seaweed.

Chromium. This element was recognized as an essential trace element for rats as early as 1955, and for humans in 1975. There may be a number of biological roles for it, but the one that is most definite concerns glucose tolerance.[67] Chromium is found in a molecule called the *glucose tolerance factor,* where it is present as Cr^{III} along with the amino acids glycine, cysteine, and glutamic acid. Nicotinic acid is also present. Attempts to establish its structure or to make active model compounds[68] have thus far failed and its detailed nature and mode of action remain unknown.

Nickel.[69] Only recently has the biological importance of nickel been recognized. Although its widespread occurrence in bacterial hydrogenases may be of greatest long-term importance, its presence in jack bean *urease* is historically the most remarkable example.

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[64] W. Boyd and K. Kusten, *Advances in Inorganic Biochemistry,* G. L. Eichhorn and L. G. Marzelli, Eds., Elsevier, New York, Vol. 6, 1984, pp. 311–365; R. Cammack, *Nature* (*London*), 1986, **322,** 312.

[65a] K. O. Hodgson *et al., Inorg. Chem.,* 1986, **25,** 470.

[65b] See C. J. Hawkins *et al., Inorg. Chem.,* 1987, **26,** 627.

[66] R. L. Robson *et al., Nature,* (*London*), 1986, **322,** 388; J. M. Arber *et al., Nature* (*London*) 1987, **325,** 372.

[67] P. O'Brien *et al., Polyhedron,* 1985, **4,** 1.

[68] W. E. Broderick and J. I. Legg, *Inorg. Chem.,* 1985, **24,** 3724.

[69] A. J. Thomson, *Nature* (*London*), 1982, **298,** 602.

Urease[70] from jack beans was the first enzyme to be crystallized and was for many years held to be a pure polypeptide, but nearly 50 years later (1975) it was shown to contain tightly bound nickel, which is essential to activity. Urease catalyzes the hydrolysis of urea to ammonia and carbonic acid. There is little doubt that the urea molecule becomes bound to the nickel atom at one or more crucial stages, but the details are still a matter of speculation. Urease is a rather large entity, consisting of six identical subunits, each containing two nickel atoms.

Several types of bacteria are already known to have nickel-containing hydrogenases, which catalyze the reaction $2H_2 + O_2 = 2H_2O$ (or $H_2 = 2H^+ + 2e$), the reduction of sulfate ion, the production of methane, and perhaps other reductive processes. Chemical insight into the role of nickel is just beginning to develop, but already it is known that Ni^{III} plays a critical role in most if not all.[71] The Ni^{III} can be detected by its epr spectrum. The type of coordination that stabilizes this unusual state (by giving the Ni^{III}/Ni^{II} couple a low redox potential) is not known yet, but sulfur atoms are believed to be in the coordination sphere. It would seem that rapid progress in characterizing these enzymes is in the offing.

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APPENDICES

Appendix 1

Units and Fundamental Constants

The most widely sanctioned set of units, the Système Internationale d'Unités or SI set, is summarized here. In this book (as elsewhere, and for good reason*) this system has been only partially adopted. Thus, we use joules (instead of calories) but retain other earlier units, most importantly, Angstroms, atmospheres, and degrees Celsius. A table of useful conversion factors is found inside the front cover.

Also presented in this appendix is a list of some fundamental constants frequently required by inorganic chemists.

Basic SI Units

Physical Quantity	Name of Unit	Symbol for Unit
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Luminous intensity	candela	cd
Amount of substance	mole	mol

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*A. W. Adamson, *J. Chem. Educ.*, 1978, **55**, 634.

Derived SI Units

Physical quantity	Name of unit	Symbol for unit	Definition of unit
Energy	Joule	J	$\mathrm{kg\ m^2s^{-2}}$
Force	Newton	N	$\mathrm{kg\ m\ s^{-2} = J\ m^{-1}}$
Power	Watt	W	$\mathrm{kg\ m^2s^{-3} = J\ s^{-1}}$
Pressure	Pascal	Pa	$\mathrm{kg\ m^{-1}s^{-2} = N\ m^{-2}}$
Electric charge	Coulomb	C	A s
Electric potential difference	Volt	V	$\mathrm{kg\ m^2s^{-3}A^{-1} = J\ A^{-1}s^{-1}, J/C}$
Electric resistance	Ohm	Ω	$\mathrm{kg\ m^2s^{-3}A^{-2} = V\ A^{-1}}$
Electric capacitance	Farad	F	$\mathrm{A^2s^4kg^{-1}m^{-2} = A\ s\ V^{-1}}$
Magnetic flux	Weber	Wb	$\mathrm{kg\ m^2s^{-2}A^{-1} = V\ s}$
Inductance	Henry	H	$\mathrm{kg\ m^2s^{-2}A^{-2} = V\ s\ A^{-1}}$
Magnetic flux density	Tesla	T	$\mathrm{kg\ s^{-2}A^{-1} = V\ s\ m^{-2}}$
Frequency	Herz	Hz	$\mathrm{Hz = s^{-1}}$
Customary temperature, *t*	Degree Celsius	°C	$t[°\mathrm{C}] = T[\mathrm{K}] - 273.15$

Fundamental Constants

Quantity	Symbol	Value	SI unit
Speed of light in vacuum	c	$2.997\,925 \times 10^{8}$	$\mathrm{m\ s^{-1}}$
Elementary charge	e	$1.602\,189 \times 10^{-19}$	C
Planck constant	h	$6.626\,18 \times 10^{-34}$	J s
Avogadro constant	N_A	$6.022\,04 \times 10^{23}$	$\mathrm{mol^{-1}}$
Atomic mass unit	1u	$1.660\,566 \times 10^{-27}$	kg
Electron rest mass	$\mathrm{m_e}$	$0.910\,953 \times 10^{-30}$	kg
Proton rest mass	$\mathrm{m_p}$	$1.672\,649 \times 10^{-27}$	kg
Neutron rest mass	$\mathrm{m_n}$	$1.674\,954 \times 10^{-27}$	kg
Faraday constant	F	$9.648\,46 \times 10^{4}$	$\mathrm{C\ mol^{-1}}$
Rydberg constant	$\mathrm{R_\infty}$	$1.097\,373 \times 10^{7}$	$\mathrm{m^{-1}}$
Bohr radius	$\mathrm{a_0}$	$0.529\,177 \times 10^{-10}$	m
Electron magnetic moment	μ_e	$9.284\,83 \times 10^{-24}$	$\mathrm{J\ T^{-1}}$
Proton magnetic moment	μ_p	$1.410\,617 \times 10^{-26}$	$\mathrm{J\ T^{-1}}$
Bohr magneton	μ_B	$9.274\,08 \times 10^{-24}$	$\mathrm{J\ T^{-1}}$
Nuclear magneton	μ_N	$5.050\,82 \times 10^{-27}$	$\mathrm{J\ T^{-1}}$
Molar gas constant	R	$8.314\,41$	$\mathrm{J\ mol^{-1}\ K^{-1}}$
Molar volume of ideal gas (stp.)	V_m	$0.022\,413\,8$	$\mathrm{m^3\ mol^{-1}}$
Boltzmann constant	k	$1.380\,662 \times 10^{-23}$	$\mathrm{J\ K^{-1}}$

Appendix 2

Ionization Enthalpies of the Atoms

Definition: The ionization enthalpies of an atom X are the enthalpies of the processes

$$X(g) = X^+(g) + e^-(g) \qquad \Delta H^0_{\text{ion}}(1)$$

$$X^+(g) = X^{2+}(g) + e^-(g) \qquad \Delta H^0_{\text{ion}}(2), \text{ and so on}$$

Older chemical literature commonly uses the term "ionization potential," which is $-\Delta H^0_{\text{ion}}$, usually expressed in electron-volts.

Values of $\Delta H^{\circ}_{\text{ion}}$ (n) (kJ mol^{-1})

	First	Second	Third	Fourth
1 H	1311			
2 He	2372	5249		
3 Li	520.0	7297	11,810	
4 Be	899.1	1758	14,850	21,000
5 B	800.5	2428	2394	25,020
6 C	1086	2353	4618	6512
7 N	1403	2855	4577	7473
8 O	1410	3388	5297	7450
9 F	1681	3375	6045	8409
10 Ne	2080	3963	6130	9363
11 Na	495.8	4561	6913	9543
12 Mg	737.5	1450	7731	10,540
13 Al	577.5	1817	2745	11,580
14 Si	786.3	1577	3228	4355
15 P	1012	1903	2910	4955
16 S	999.3	2260	3380	4562
17 Cl	1255	2297	3850	5160
18 Ar	1520	2665	3950	5771
19 K	418.7	3069	4400	5876
20 Ca	589.6	1146	4942	6500
21 Sc	631	1235	2389	7130
22 Ti	656	1309	2650	4173
23 V	650	1414	2828	4600
24 Cr	652.5	1592	3056	4900

Values of $\Delta H^\circ_{\text{ion}}$ (n) (kJ mol^{-1}) (*Continued*)

	First	Second	Third	Fourth
25 Mn	717.1	1509	3251	
26 Fe	762	1561	2956	
27 Co	758	1644	3231	
28 Ni	736.5	1752	3489	
29 Cu	745.2	1958	3545	
30 Zn	906.1	1734	3831	
31 Ga	579	1979	2962	6190
32 Ge	760	1537	3301	4410
33 As	947	1798	2735	4830
34 Se	941	2070	3090	4140
35 Br	1142	2080	3460	4560
36 Kr	1351	2370	3560	
37 Rb	402.9	2650	3900	
38 Sr	549.3	1064		5500
39 Y	616	1180	1979	
40 Zr	674.1	1268	2217	3313
41 Nb	664	1381	2416	3700
42 Mo	685	1558	2618	4480
43 Tc	703	1472	2850	
44 Ru	710.6	1617	2746	
45 Rh	720	1744	2996	
46 Pd	804	1874	3177	
47 Ag	730.8	2072	3360	
48 Cd	876.4	1630	3615	
49 In	558.1	1820	2705	5250
50 Sn	708.2	1411	2942	3928
51 Sb	833.5	1590	2440	4250
52 Te	869	1800	3000	3600
53 I	1191	1842		
54 Xe	1169	2050	3100	
55 Cs	375.5	2420		
56 Ba	502.5	964		
57 La	541	1103	1849	
72 Hf	760	1440	2250	3210
73 Ta	760	1560		
74 W	770	1710		
75 Re	759	1600		
76 Os	840	1640		
77 Ir	900			
78 Pt	870	1791		
79 Au	889	1980		
80 Hg	1007	1809	3300	
81 Tl	588.9	1970	2880	4890
82 Pb	715.3	1450	3080	4082
83 Bi	702.9	1609	2465	4370
84 Po	813			
86 Rn	1037			
88 Ra	509.1	978.6		
89 Ac	670	1170		

Appendix 3

Enthalpies of Electron Attachment (Electron Affinities) of Atoms

Definition: The enthalpy of electron attachment pertains to the process:

$$X(g) + e^- = X^-(g) \qquad \Delta H^0_{EA}$$

Older chemical literature commonly uses the term "electron affinity," defined as $-\Delta H^0_{EA}$.

Values of ΔH^0_{EA} (kJ mol^{-1})[a,b]

Z	Atom	$-\Delta H^0_{EA}$
1	H	72.77
3	Li	59.8(6)
5	B	27
6	C	122.3
7	N	*ca.* 0
8	O	141.1(3)
9	F	328.0(3)
11	Na	52.7(5)
13	Al	45
14	Si	132.2
15	P	71(1)
16	S	200.42(5)
17	Cl	348.8(4)
19	K	48.36(5)
33	As	77(5)
34	Se	194.96(3)
35	Br	324.6(4)
37	Rb	46.89(5)
51	Sb	101(5)
52	Te	190.15(3)
53	I	295.3(4)
55	Cs	45.5(2)
79	Au	222.8(1)

Values of ΔH^0_{EA} (kJ mol^{-1})[a,b] (*Continued*)

Z	Atom	$-\Delta H^0_{EA}$
83	Bi	97(2)
84	Po	183(30)
85	At	270(20)

[a] All taken from H. Hotop and W. C. Lineberger, *J. Phys. Chem. Reference Data,* 1975, **4,** 539, which should be consulted for sources and background.

[b] All alkaline earth and noble gas atoms have $\Delta H^0_{EA} > 0$.

Appendix 4

Ionic Radii

One of the major factors in determining the structures of the substances that can be thought of, at least approximately, as made up of cations and anions packed together, is ionic size, especially the ratio of radii of the two or more ions present.

It is obvious from the nature of wave functions that no ion or atom has a precisely defined radius. The only way radii can be assigned is to determine how closely the centers of two atoms or ions actually approach each other in solid substances and then to assume that such a distance is equal or closely related to the sum of the radii of the two atoms or ions. Even this procedure is ambiguous. Further assumptions are required to get an empirically useful set of radii. Early efforts to do this were made by Goldschmidt and by Pauling. Their results satisfy the minimum requirements of being additive, internally consistent, and showing physically reasonable trends (e.g., increasing with Z for members of a group in the Periodic Table and decreasing with the degree of ionization for the cations of a given metallic element). However, it must be kept in mind that there is no absolute way to say where one ion ends and the neighboring one begins. Moreover, ions are undoubtedly somewhat elastic and their apparent radii can vary with environment, particularly with coordination number.

With the advent of relatively accurate experimental electron density maps based on high-precision X-ray diffraction methods, it became possible to see more realistically how electron density actually varies along the line between adjacent nuclei in an ionic crystal. An example is provided by LiF, as shown in Fig. A4-1. It can be seen that neither the Goldschmidt (G) nor, *a fortiori,* the Pauling (P) radii for Li^+ are at the minimum (M) of electron density. Thus these radii could be said to be "wrong" in an absolute sense, even though the complete sets to which they belong display internal consistency.

Recently, with the insight afforded by electron density maps and with an enormously larger base of data, new efforts to establish tables of ionic radii have been made, the most successful being those of Shannon and Prewitt. In Table A4-1 are listed a selection of these radii. For some additional values and detailed discussion of how these radii were derived, see footnotes to the table. There are many important trends and correlations to be found among

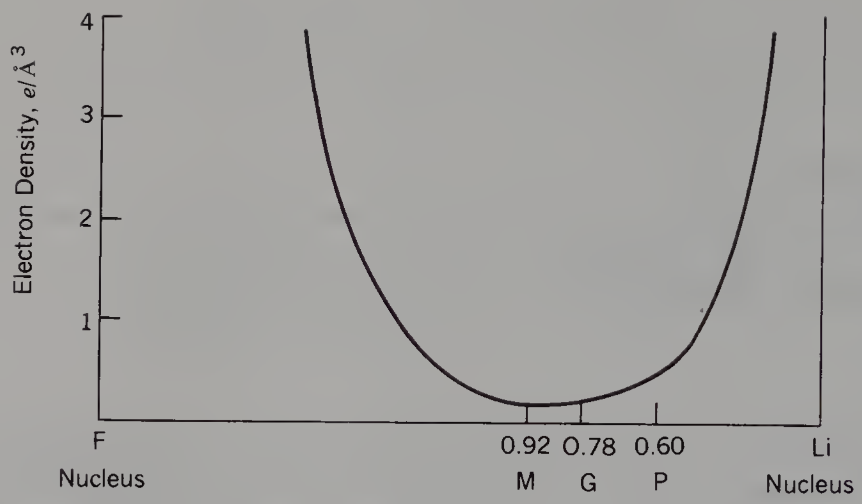

FIG. A4-1. A plot of experimentally measured electron density between adjacent F and Li nuclei in LiF. The Pauling and Goldschmidt radii of Li^+ are indicated by P and G, while M denotes the actual minimum (adapted from H. Krebs, *Fundamentals of Inorganic Crystal Chemistry,* McGraw-Hill, New York, 1968).

these results. Several of the principal ones are

1. For a cation that displays several coordination numbers (C.N.), the radius increases with increasing C.N.
2. For a given vertical group (e.g., the alkalis or alkaline earths) the radii increase with *Z* for a given coordination number.
3. For an isoelectronic series such as Na^+, Mg^{2+}, Al^{3+}, and Si^{4+}, the radii decrease with increasing charge.
4. For any element with several oxidation numbers, for example, Ti^{2+}, Ti^{3+}, and Ti^{4+}, the radius decreases with increasing charge.
5. For each of the various transition series, ions of the same charge show an overall trend towards decreasing radii with increasing *Z*. However, in the *d* block, these trends are not smooth, for reasons given in accounts of ligand field theory. The behavior of the lanthanide and actinide radii is discussed in Chapters 20 and 21, respectively.
6. For transition metals that can have both high- and low-spin states, for example, Fe^{2+}, the radius is larger for the high-spin ion.

TABLE A4-1
Ionic Radii[a,b] (Å)

Ion	C.N.[c]	Radius	Ion	C.N.[c]	Radius
A. *Alkali and Alkaline Earth Cations*					
Li^+	4	0.73	Fr^+	6	1.94
	6	0.90	Be^{2+}	4	0.41
	8	1.06		6	0.59
Na^+	4	1.13	Mg^{2+}	4	0.71
	6	1.16		6	0.86
	8	1.32		8	1.03
	12	1.53	Ca^{2+}	6	1.14

TABLE A4-1 (*Continued*)

Ion	C.N.[c]	Radius	Ion	C.N.[c]	Radius
K^+	4	1.51		8	1.26
	6	1.52		10	1.37
	8	1.65		12	1.48
	10	1.73	Sr^{2+}	6	1.32
	12	1.78		8	1.40
Rb^+	6	1.66		10	1.50
	8	1.75		12	1.58
	10	1.80	Ba^{2+}	6	1.49
	12	1.86		8	1.56
	14	1.97		10	1.66
Cs^+	6	1.81		12	1.75
	8	1.88	Ra^{2+}	8	1.62
	10	1.95		12	1.84
	12	2.02			
B. *Group IB (11)*					
Cu^+	2	0.60	Ag^+	8	1.42
	4	0.74	Au^+	6	1.51
	6	0.91	Cu^{2+}	4	0.71
Ag^+	2	0.81		4 (sq)	0.71
	4	1.14		6	0.87
	4 (sq)	1.16	Au^{3+}	4 (sq)	0.82
	6	1.29		6	0.99
C. *Group IIB (12)*					
Zn^{2+}	4	0.74	Cd^{2+}	12	1.45
	6	0.88	Hg^{2+}	2	0.83
	8	1.04		4	1.10
Cd^{2+}	4	0.92		6	1.16
	6	1.09		8	1.28
	8	1.24			
D. *Other Non-Transition Metal Ions*					
NH_4^+	6	1.61 (?)	Tl^{3+}	8	1.12
Tl^+	6	1.64	Sb^{3+}	6	0.90
	8	1.73	Bi^{3+}	6	1.17
	12	1.84	Sc^{3+}	6	0.89
Pb^{2+}	6	1.33		8	1.01
	8	1.43	Y^{3+}	6	1.04
	10	1.54	C^{4+}	4	0.29
	12	1.63	Si^{4+}	4	0.40
B^{3+}	4	0.25		6	0.54
Al^{3+}	4	0.53	Ge^{4+}	4	0.53
	6	0.68		6	0.67
Ga^{3+}	4	0.61	Sn^{4+}	4	0.69
	6	0.76		6	0.83
In^{3+}	4	0.76		8	0.95
	6	0.94	Pb^{4+}	4	0.79
	8	1.06		6	0.92
Tl^{3+}	4	0.89		8	1.08
	6	1.03			

TABLE A4-1 (*Continued*)

Ion	C.N.[c]	Radius	Ion	C.N.[c]	Radius
E. *First Transition Series Metals*					
Ti^{2+}	6	1.00	Ni^{2+}	6	0.83
V^{2+}	6	0.93	Ti^{3+}	6	0.81
Cr^{2+}	6 (LS)	0.87	V^{3+}	6	0.78
	6 (HS)	0.94	Cr^{3+}	6	0.76
Mn^{2+}	4 (HS)	0.80	Mn^{3+}	6 (LS)	0.72
	6 (LS)	0.81		6 (HS)	0.79
	6 (HS)	0.97	Fe^{3+}	4 (HS)	0.63
Fe^{2+}	4 (HS)	0.77		6 (LS)	0.69
	6 (LS)	0.75		6 (HS)	0.79
	6 (HS)	0.92	Co^{3+}	6 (LS)	0.69
Co^{2+}	4 (HS)	0.72		6 (HS)	0.75
	6 (LS)	0.79	Ni^{3+}	6 (LS)	0.70
	6 (HS)	0.89		6 (HS)	0.74
Ni^{2+}	4	0.69	Ti^{4+}	6	0.75
	4 (sq)	0.63			
F. *Second Transition Series Elements*					
Pd^{2+}	4 (sq)	0.78	Rh^{3+}	6	0.81
	6	1.00	Nb^{4+}	6	0.82
Nb^{3+}	6	0.86	Mo^{4+}	6	0.79
Mo^{3+}	6	0.83	Ru^{4+}	6	0.76
Ru^{3+}	6	0.82	Rh^{4+}	6	0.74
G. *Third Transition Series Elements*					
Pt^{2+}	4 (sq)	0.74	W^{4+}	6	0.80
	6	0.94	Re^{4+}	6	0.77
Ta^{3+}	6	0.86	Os^{4+}	6	0.78
Ir^{3+}	6	0.82	Ir^{4+}	6	0.77
Hf^{4+}	6	0.85	Pt^{4+}	6	0.77
Ta^{4+}	6	0.82	Th^{4+}	6	1.08
H. *Anions*					
F^-	2	1.15	O^{2-}	8	1.28
	4	1.17	S^{2-}	6	1.70
	6	1.19	Se^{2-}	6	1.84
Cl^-	6	1.67	Te^{2-}	6	2.07
Br^-	6	1.82	OH^-	2	1.18
I^-	6	2.06		3	1.20
O^{2-}	2	1.21		4	1.21
	3	1.22		6	1.23
	4	1.24	N^{3-}	4	1.32
	6	1.26			

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[a] Selected from R. D. Shannon, *Acta Crystallogr.*, 1976, **A32,** 751. This article gives radii for many other ions and also for other coordination numbers.

[b] For lanthanide and actinide radii, see Tables 20-1 and 21-1.

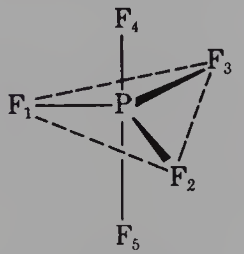
[c] Unannotated 6 means octahedral; no particular geometry is implied for other numbers unless stated [e.g., 4 (sq) means square]; LS and HS mean low spin and high spin, respectively.

Appendix 5

Basic Concepts of Molecular Symmetry; Character Tables

A5-1. Symmetry Operations and Elements

When we say that a molecule has *symmetry,* we mean that *certain parts of it can be interchanged with others without altering either the identity or the orientation of the molecule.* The interchangeable parts are said to be equivalent to one another by symmetry. Consider, for example, a trigonal bipyramidal molecule such as PF_5 (A5-I). The three equatorial P—F bonds, to F_1, F_2, and F_3, are equivalent. They have the same length, the same strength, and the same type of spatial relation to the remainder of the molecule. Any permutation of these three bonds among themselves leads to a molecule indistinguishable from the original. Similarly, the axial P—F bonds, to F_4 and F_5, are equivalent. *But,* axial and equatorial bonds are different types (e.g., they have different lengths), and if one of each were to be interchanged, the molecule would be noticeably perturbed. These statements are probably self-evident, or at least readily acceptable, on an intuitive basis; but for systematic and detailed consideration of symmetry, certain formal tools are needed. The first set of tools is a set of *symmetry operations.*



(A5-I)

Symmetry operations are geometrically defined ways of exchanging equivalent parts of a molecule. There are four kinds which are used conventionally and these are sufficient for all our purposes.

1. Simple rotation about an axis passing through the molecule by an angle $2\pi/n$. This operation is called a *proper rotation* and is symbolized $\mathbf{C}_n$. If it is

repeated n times, of course the molecule comes all the way back to the original orientation.

2. Reflection of all atoms through a plane that passes through the molecule. This operation is called *reflection* and is symbolized $\boldsymbol{\sigma}$.

3. Reflection of all atoms through a point in the molecule. This operation is called *inversion* and is symbolized **i**.

4. The combination, in either order, of rotating the molecule about an axis passing through it by $2\pi/n$ and reflecting all atoms through a plane that is perpendicular to the axis of rotation is called *improper rotation* and is symbolized $\mathbf{S}_n$.

These operations are *symmetry operations if, and only if,* the appearance of the molecule is *exactly* the same after one of them is carried out as it was before. For instance, consider rotation of the molecule H_2S by $2\pi/2$ about an axis passing through S and bisecting the line between the H atoms. As shown in Fig. A5-1, this operation interchanges the H atoms and interchanges the S—H bonds. Since these atoms and bonds are equivalent, there is no physical (i.e., physically meaningful or detectable) difference after the operation. For HSD, however, the corresponding operation replaces the S—H bond by the S—D bond, and vice versa, and one can see that a change has occurred. Therefore, for H_2S, the operation $\mathbf{C}_2$ is a symmetry operation; for HSD it is not.

These types of symmetry operation are graphically explained by the diagrams in Fig. 5A-2, where it is shown how an arbitrary point (0) in space is affected in each case. Filled dots represent points above the xy plane and open dots represent points below it. Let us examine first the action of proper rotations, illustrated here by the $\mathbf{C}_4$ rotations, that is, rotations by $2\pi/4 = 90°$. The operation $\mathbf{C}_4$ is seen to take the point 0 to the point 1. The application of $\mathbf{C}_4$ twice, designated $\mathbf{C}_4^2$, generates point 2. Operation $\mathbf{C}_4^3$ gives point 3 and, of course, $\mathbf{C}_4^4$, which is a rotation by $4 \times 2\pi/4 = 2\pi$, regenerates the original point. The set of four points, 0, 1, 2, 3 are permutable, cyclically, by repeated $\mathbf{C}_4$ proper rotations and are equivalent points. It will be obvious

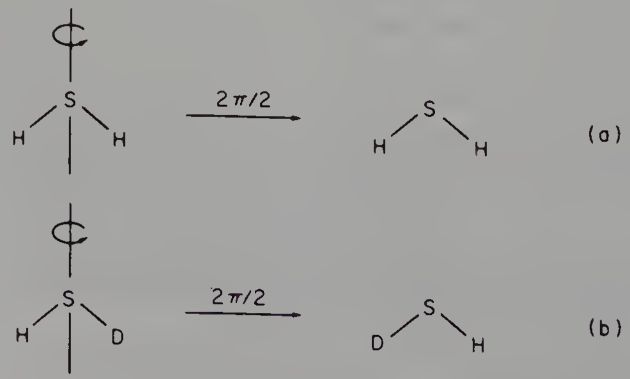


FIG. A5-1. The operation $\mathbf{C}_2$ carries H_2S into an orientation indistinguishable from the original, but HSD goes into an observably different orientation.

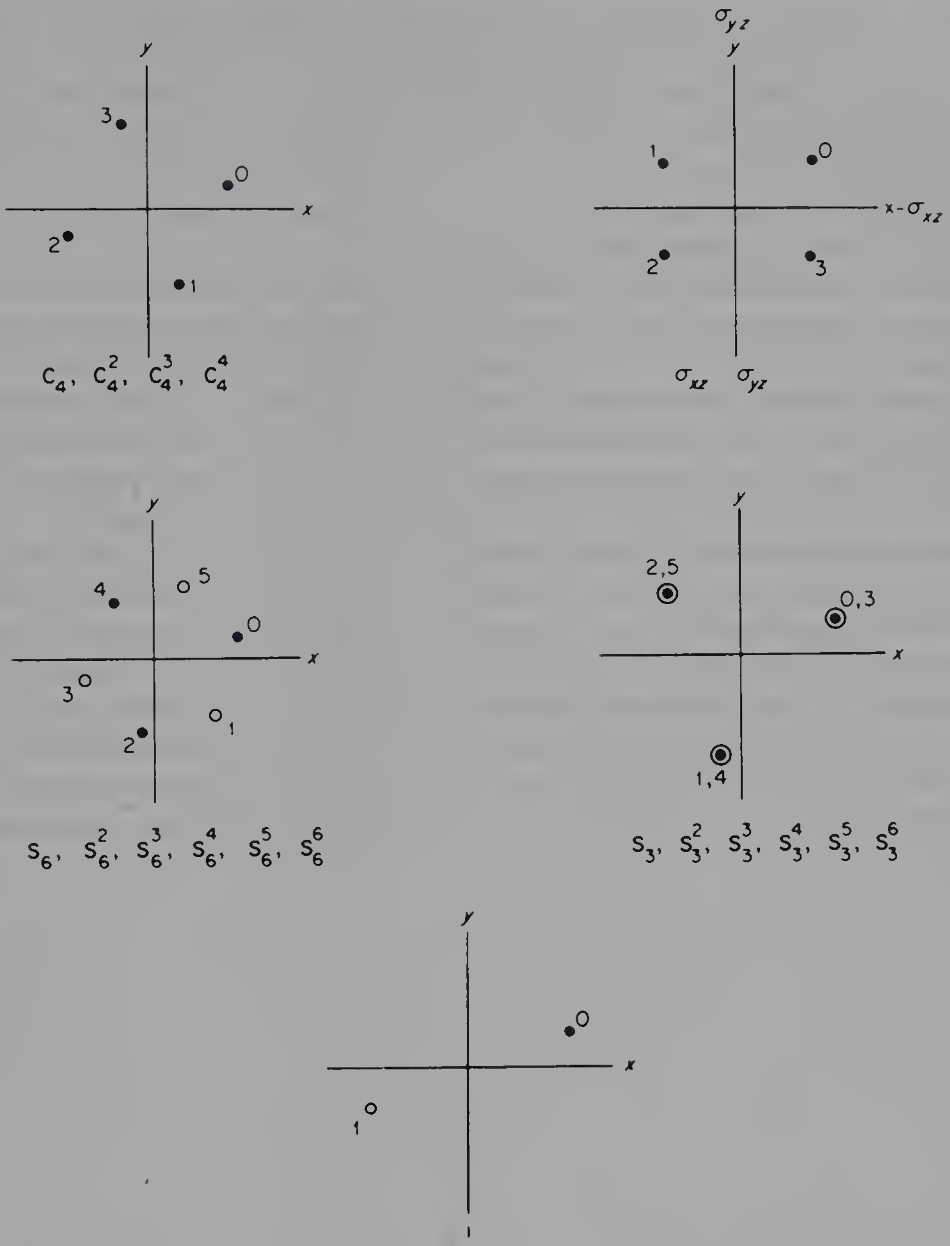


FIG. A5-2. The effects of symmetry operations on an arbitrary point, designated 0, thus generating sets of points.

that in general repetition of a $\mathbf{C}_n$ operation will generate a set of n equivalent points from an arbitrary initial point, provided that point lies off the axis of rotation.

The effect of reflection through symmetry planes perpendicular to the xy plane, specifically, $\boldsymbol{\sigma}_{xz}$ and $\boldsymbol{\sigma}_{yz}$ is also illustrated in Fig. A5-2. The point 0 is related to point 1 by the $\boldsymbol{\sigma}_{yz}$ operation and to the point 3 by the $\boldsymbol{\sigma}_{xz}$ operation. By reflecting either point 1 or point 3 through the second plane, point 2 is obtained.

The set of points generated by the repeated application of an improper rotation will vary in appearance depending on whether the order of the operation, $\mathbf{S}_n$, is even or odd, order being the number n. A crown of n points, alternately up and down, is produced for n even, as illustrated for $\mathbf{S}_6$. For n odd there is generated a set of $2n$ points which form a right n-sided prism, as shown for $\mathbf{S}_3$.

Finally, the operation **i** is seen to generate from point 0 a second point, 1, lying on the opposite side of the origin.

Let us now illustrate the symmetry operations for various familiar molecules as examples. As this is done it will be convenient to employ also the concept of *symmetry elements.* A symmetry element is an *axis* (line), *plane*, or *point* about which symmetry operations are performed. The existence of a certain symmetry operation implies the existence of a corresponding symmetry element, and conversely, the presence of a symmetry element means that a certain symmetry operation or set of operations is possible.

Consider the ammonia molecule (Fig. A5-3). The three equivalent hydrogen atoms may be exchanged among themselves in two ways: by proper rotations, and by reflections. The molecule has an axis of threefold proper rotation; this is called a C_3 axis. It passes through the N atom and through the center of the equilateral triangle defined by the H atoms. When the molecule is rotated by $2\pi/3$ in a clockwise direction H_1 replaces H_2, H_2 replaces H_3, and H_3 replaces H_1. Since the three H atoms are physically indistinguishable, the numbering having no physical reality, the molecule after

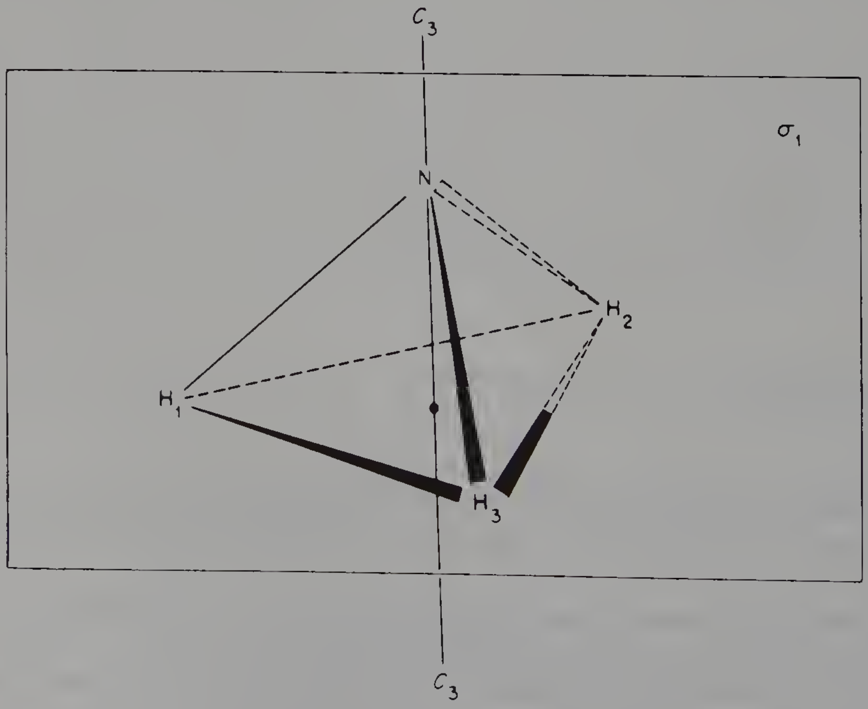


FIG. A5-3. The ammonia molecule, showing its threefold symmetry axis C_3, and one of its three planes of symmetry σ_1, which passes through H_1 and N and bisects the H_2—H_3 line.

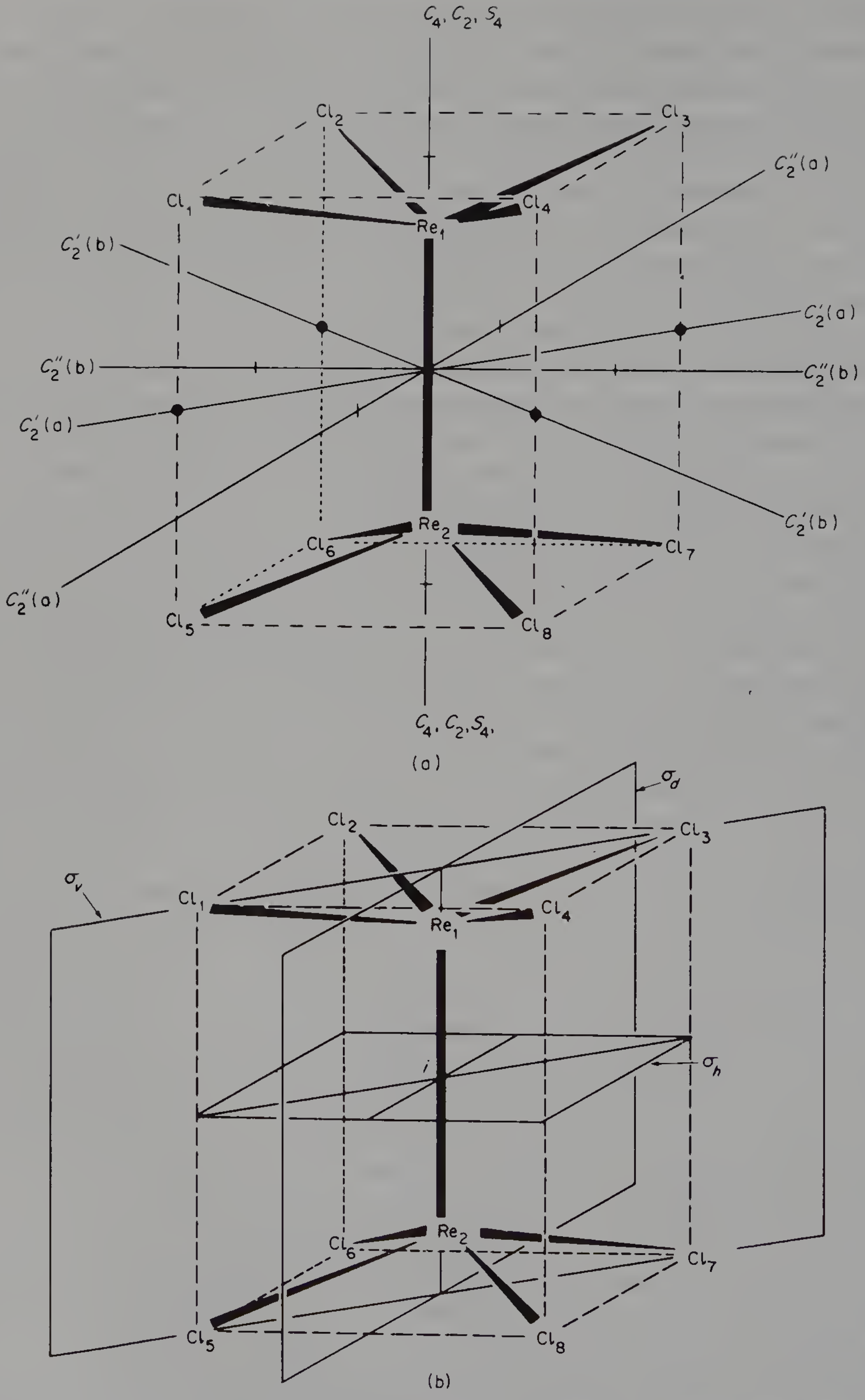
rotation is indistinguishable from the molecule before rotation. This rotation, called a $\mathbf{C}_3$ or threefold proper rotation, is a symmetry operation. Rotation by 2 × $2\pi/3$ also produces a configuration different, but physically indistinguishable, from the original and is likewise a symmetry operation; it is designated $\mathbf{C}_3^2$. Finally, rotation by 3 × $2\pi/3$ carries each H atom all the way around and returns it to its initial position. This operation, $\mathbf{C}_3^3$, has the same net effect as performing no operation at all, but for mathematical reasons it must be considered as an operation generated by the C_3 axis. This, and other operations which have no net effect, are called *identity* operations and are symbolized by **E**. Thus, we may write $\mathbf{C}_3^3 = \mathbf{E}$.

The interchange of hydrogen atoms in NH_3 by reflections may be carried out in three ways; that is, there are three planes of symmetry. Each plane passes through the N atom and one of the H atoms, and bisects the line connecting the other two H atoms. Reflection through the symmetry plane containing N and H_1 interchanges H_2 and H_3; the other two reflections interchange H_1 with H_3, and H_1 with H_2.

Inspection of the NH_3 molecule shows that no other symmetry operations besides these six (three rotations, $\mathbf{C}_3$, $\mathbf{C}_3^2$, $\mathbf{C}_3^3 = \mathbf{E}$, and three reflections, $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$, $\boldsymbol{\sigma}_3$) are possible. Put another way, the only symmetry elements the molecule possesses are C_3 and the three planes that we may designate σ_1, σ_2, and σ_3. Specifically, it will be obvious that no sort of improper rotation is possible, nor is there a center of symmetry.

As a more complex example, in which all four types of symmetry operation and element are represented, let us take the $Re_2Cl_8^{2-}$ ion, which has the shape of a square parallepiped or right square prism (Fig. A5-4). This ion has altogether six axes of proper rotation, of four different kinds. First, the Re_1–Re_2 line is an axis of fourfold proper rotation, C_4, and four operations, $\mathbf{C}_4$, $\mathbf{C}_4^2$, $\mathbf{C}_4^3$, $\mathbf{C}_4^4 \equiv \mathbf{E}$, may be carried out. This same line is also a C_2 axis, generating the operation $\mathbf{C}_2$. It will be noted that the $\mathbf{C}_4^2$ operation means rotation by 2 × $2\pi/4$, which is equivalent to rotation by $2\pi/2$, that is, to the $\mathbf{C}_2$ operation. Thus the C_2 axis and the $\mathbf{C}_2$ operation are implied by, not independent of, the C_4 axis. There are, however, two other types of C_2 axis that exist independently. There are two of the type that passes through the centers of opposite vertical edges of the prism, C_2' axes, and two more that pass through the centers of opposite vertical faces of the prism, C_2'' axes.

The $Re_2Cl_8^{2-}$ ion has three different kinds of symmetry plane [see Fig. A5-4(b)]. There is a unique one that bisects the Re—Re bond and all the vertical edges of the prism. Since it is customary to define the direction of the highest proper axis of symmetry, C_4 in this case, as the vertical direction, this symmetry plane is horizontal and the subscript h is used to identify it, σ_h. There are then two types of vertical symmetry plane, namely, the two that contain opposite vertical edges, and two others that cut the centers of the opposite vertical faces. One of these two sets may be designated $\sigma_v^{(1)}$ and $\sigma_v^{(2)}$, the v implying that they are vertical. Since those of the second vertical set bisect



(a)

(b)

FIG. A5-4. The symmetry elements of the $Re_2Cl_8^{2-}$ ion. (a) The axes of symmetry. (b) One of each type of plane and the center of symmetry.

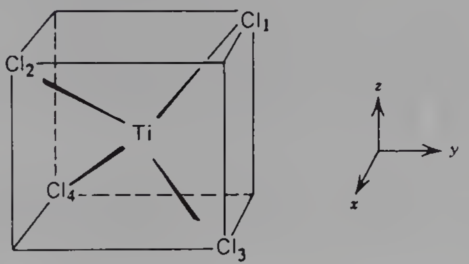
the dihedral angles between those of the first set, they are then designated $\sigma_d^{(1)}$ and $\sigma_d^{(2)}$, the *d* standing for dihedral. Both pairs of planes are vertical and it is actually arbitrary which are labeled σ_v and which σ_d.

Continuing with $Re_2Cl_8^{2-}$, we see that an axis of improper rotation is present. This is coincident with the C_4 axis and is an S_4 axis. The $\mathbf{S}_4$ operation about this axis proceeds as follows. The rotational part, through an angle of $2\pi/4$, in the clockwise direction has the same effect as the $\mathbf{C}_4$ operation. When this is coupled with a reflection in the horizontal plane, $\boldsymbol{\sigma}_h$, the following shifts of atoms occur:

$Re_1 \longrightarrow Re_2$ $\quad Cl_1 \longrightarrow Cl_6$ $\quad Cl_5 \longrightarrow Cl_2$
$Re_2 \longrightarrow Re_1$ $\quad Cl_2 \longrightarrow Cl_7$ $\quad Cl_6 \longrightarrow Cl_3$
$Cl_3 \longrightarrow Cl_8$ $\quad Cl_7 \longrightarrow Cl_4$
$Cl_4 \longrightarrow Cl_5$ $\quad Cl_8 \longrightarrow Cl_1$

Finally, the $Re_2Cl_8^{2-}$ ion has a center of symmetry *i* and the inversion operation **i** can be performed.

In the case of $Re_2Cl_8^{2-}$ the improper axis S_4 might be considered as merely the inevitable consequence of the existence of the C_4 axis and the σ_h, and, indeed, this is a perfectly correct way to look at it. However, it is important to emphasize that there are cases in which an improper axis S_n exists without independent existence of either C_n or σ_h. Consider, for example, a tetrahedral molecule as depicted in (A5-II), where the $TiCl_4$ molecule is shown inscribed in a cube and Cartesian axes, *x*, *y*, and *z* are indicated. Each of these axes is an S_4 axis. For example, rotation by $2\pi/4$ about *z* followed by reflection in the *xy* plane shifts the Cl atoms as follows:



(A5-II)

$Cl_1 \longrightarrow Cl_3$ $\quad Cl_3 \longrightarrow Cl_2$
$Cl_2 \longrightarrow Cl_4$ $\quad Cl_4 \longrightarrow Cl_1$

Note, however, that the Cartesian axes are not C_4 axes (though they are C_2 axes) and the principal planes (namely, *xy*, *xz*, *yz*) are not symmetry planes. Thus we have here an example of the existence of the S_n axis without C_n or σ_h having any independent existence. The ethane molecule in its staggered configuration has an S_6 axis and provides another example.

A5-2. Symmetry Groups

The complete set of symmetry operations that can be performed on a molecule is called the *symmetry group* for that molecule. The word "group" is used here not as a mere synonym for "set" or "collection," but in a technical, mathematical sense, and this meaning must first be explained.

Introduction to Multiplying Symmetry Operations. We have already seen in passing that if a proper rotation $\mathbf{C}_n$ and a horizontal reflection $\boldsymbol{\sigma}_h$ can be performed, there is also an operation that results from the combination of the two which we call the improper rotation $\mathbf{S}_n$. We may say that $\mathbf{S}_n$ is the product of $\mathbf{C}_n$ and $\boldsymbol{\sigma}_h$. Noting also that the order in which we perform $\boldsymbol{\sigma}_h$ and $\mathbf{C}_n$ is immaterial,* we can write

$$\mathbf{C}_n \times \boldsymbol{\sigma}_h = \boldsymbol{\sigma}_h \times \mathbf{C}_n = \mathbf{S}_n$$

This is an algebraic way of expressing the fact that successive application of the two operations shown has the same effect as applying the third one. For obvious reasons, it is convenient to speak of the third operation as being the product obtained by multiplication of the other two.

This example is not unusual. Quite generally, any two symmetry operations can be multiplied to give a third. For example, in Fig. A5-2 the effects of reflections in two mutually perpendicular symmetry planes are illustrated. It can be seen that one of the reflections carries point 0 to point 1. The other reflection carries point 1 to point 2. Point 0 can also be taken to point 2 by way of point 3 if the two reflection operations are performed in the opposite order. But a moment's thought will show that a direct transfer of point 0 to point 2 can be achieved by a $\mathbf{C}_2$ operation about the axis defined by the line of intersection of the two planes. If we call the two reflections $\boldsymbol{\sigma}(xz)$ and $\boldsymbol{\sigma}(yz)$ and the rotation $\mathbf{C}_2(z)$, we can write:

$$\boldsymbol{\sigma}(xz) \times \boldsymbol{\sigma}(yz) = \boldsymbol{\sigma}(yz) \times \boldsymbol{\sigma}(xz) = \mathbf{C}_2(z)$$

It is also evident that

$$\boldsymbol{\sigma}(yz) \times \mathbf{C}_2(z) = \mathbf{C}_2(z) \times \boldsymbol{\sigma}(yz) = \boldsymbol{\sigma}(xz)$$

and

$$\boldsymbol{\sigma}(xz) \times \mathbf{C}_2(z) = \mathbf{C}_2(z) \times \boldsymbol{\sigma}(xz) = \boldsymbol{\sigma}(yz)$$

It is also worth noting that if any one of these three operations is applied twice in succession, we get no net result or, in other words, an identity operation, namely;

$$\boldsymbol{\sigma}(xz) \times \boldsymbol{\sigma}(xz) = \mathbf{E}$$

$$\boldsymbol{\sigma}(yz) \times \boldsymbol{\sigma}(yz) = \mathbf{E}$$

$$\mathbf{C}_2(z) \times \mathbf{C}_2(z) = \mathbf{E}$$

---

*This is, however, a special case; in general, order of multiplication matters as noted later.

Introduction to a Group. If we pause here and review what has just been done with the three operations $\sigma(xz)$, $\sigma(yz)$, and $C_2(z)$, we see that we have formed all the nine possible products. To summarize the results systematically, we can arrange them in the annexed tabular form. Note that we have added seven more multiplications, namely, all those in which the identity operation **E** is a factor. The results of these are trivial, since the product of any other, nontrivial operation with **E** must be just the nontrivial operation itself, as indicated.

	E	$C_2(z)$	$\sigma(xz)$	$\sigma(yz)$
E	**E**	$C_2(z)$	$\sigma(xz)$	$\sigma(yz)$
$C_2(z)$	$C_2(z)$	**E**	$\sigma(yz)$	$\sigma(xz)$
$\sigma(xz)$	$\sigma(xz)$	$\sigma(yz)$	**E**	$C_2(z)$
$\sigma(yz)$	$\sigma(yz)$	$\sigma(xz)$	$C_2(z)$	**E**

The set of operations **E**, $C_2(z)$, $\sigma(xz)$, and $\sigma(yz)$ evidently has the following four interesting properties:

1. There is one operation **E**, the identity, that is the trivial one of making no change. Its product with any other operation is simply the other operation.
2. There is a definition of how to multiply operations: we apply them successively. The product of any two is one of the remaining ones. In other words, this collection of operations is self-sufficient, all its possible products being already within itself. This is sometimes called the property of *closure.*
3. Each of the operations has an *inverse,* that is, an operation by which it may be multiplied to give **E** as the product. In this case, each operation is its own inverse, as shown by the occurrence of **E** in all diagonal positions of the table.
4. It can also be shown that if we form a triple product, this may be subdivided in any way we like without changing the result, thus

$$\begin{aligned} &\sigma(xz) \times \sigma(yz) \times C_2(z) \\ &= [\sigma(xz) \times \sigma(yz)] \times C_2(z) = C_2(z) \times C_2(z) \\ &= \sigma(xz) \times [\sigma(yz) \times C_2(z)] = \sigma(xz) \times \sigma(xz) \\ &\qquad = \mathbf{E} \end{aligned}$$

Products that have this property are said to obey the *associative law* of multiplication.

The four properties just enumerated are of fundamental importance. They are the properties—and the *only* properties—that any collection of symmetry operations must have to constitute a *mathematical group.* Groups consisting of symmetry operations are called *symmetry groups* or sometimes *point groups.* The latter term arises because all the operations leave the molecule fixed at a certain point in space. This is in contrast to other groups of symmetry operations, such as those that may be applied to crystal structures in which individual molecules move from one location to another.

The symmetry group we have just been examining is one of the simpler groups; but nonetheless, an important one. It is represented by the symbol C_{2v}; the origin of this and other symbols is discussed later. It is not an entirely representative group in that it has some properties that are *not* necessarily found in other groups. We have already called attention to one, namely, that each operation in this group is its own inverse; this is actually true of only three kinds of operation: reflections, twofold proper rotations, and inversion **i**. Another special property of the group C_{2v} is that all multiplications in it are *commutative;* that is, every multiplication is equal to the multiplication of the same two operations in the opposite order. It can be seen that the group multiplication table is symmetrical about its main diagonal, which is another way of saying that all possible multiplications commute. In general, multiplication of symmetry operations is *not* commutative, as subsequent discussion will illustrate.

For another simple, but more general, example of a symmetry group, let us recall our earlier examination of the ammonia molecule. We were able to discover six and only six symmetry operations that could be performed on this molecule. If this is indeed a complete list, they should constitute a group. The easiest way to see if they do is to attempt to write a multiplication table. This will contain 36 products, some of which we already know how to write. Thus we know the result of all multiplications involving **E**, and we know that

$$\mathbf{C}_3 \times \mathbf{C}_3 = \mathbf{C}_3^2$$

$$\mathbf{C}_3 \times \mathbf{C}_3^2 = \mathbf{C}_3^2 \times \mathbf{C}_3 = \mathbf{E}$$

It will be noted that the second of these statements means that $\mathbf{C}_3$ is the inverse of $\mathbf{C}_3^2$ and vice versa. We also know that **E** and each of the $\boldsymbol{\sigma}$'s is its own inverse. So all operations have inverses, thus satisfying requirement 3.

To continue, we may next consider the products when one $\boldsymbol{\sigma}_v$ is multiplied by another. A typical example is shown in Fig. A5-5(a). When point 0 is reflected first through $\sigma^{(1)}$ and then through $\sigma^{(2)}$, it becomes point 2. But point 2 can obviously also be reached by a clockwise rotation through $2\pi/3$, that is, by the operation $\mathbf{C}_3$. Thus we can write

$$\boldsymbol{\sigma}^{(1)} \times \boldsymbol{\sigma}^{(2)} = \mathbf{C}_3$$

If, however, we reflect first through $\sigma^{(2)}$ and then through $\sigma^{(1)}$, point 0 becomes point 4, which can be reached also by $\mathbf{C}_3 \times \mathbf{C}_3 = \mathbf{C}_3^2$. Thus we write

$$\boldsymbol{\sigma}^{(2)} \times \boldsymbol{\sigma}^{(1)} = \mathbf{C}_3^2$$

Clearly the reflections $\boldsymbol{\sigma}^{(1)}$ and $\boldsymbol{\sigma}^{(2)}$ do not commute. The reader should be able to make the obvious extension of the geometrical arguments just used

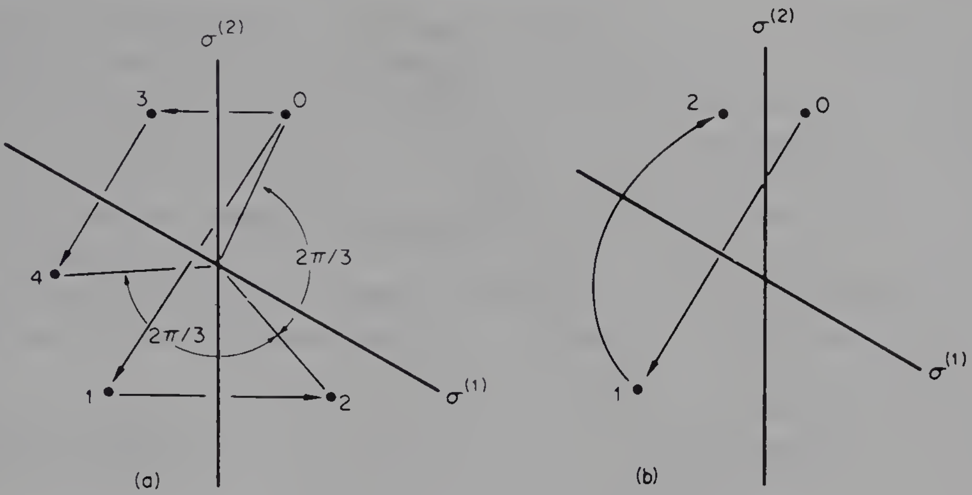


FIG. A5-5. The multiplication of symmetry operations (a) reflection times reflection and (b) reflection followed by C_3.

to obtain the following additional products:

$$\boldsymbol{\sigma}^{(1)} \times \boldsymbol{\sigma}^{(3)} = \mathbf{C}_3^2$$

$$\boldsymbol{\sigma}^{(3)} \times \boldsymbol{\sigma}^{(1)} = \mathbf{C}_3$$

$$\boldsymbol{\sigma}^{(2)} \times \boldsymbol{\sigma}^{(3)} = \mathbf{C}_3$$

$$\boldsymbol{\sigma}^{(3)} \times \boldsymbol{\sigma}^{(2)} = \mathbf{C}_3^2$$

There remain, now, the products of $\mathbf{C}_3$ and $\mathbf{C}_3^2$ with $\boldsymbol{\sigma}^{(1)}$, $\boldsymbol{\sigma}^{(2)}$, and $\boldsymbol{\sigma}^{(3)}$. Figure A5-5(b) shows a type of geometric construction that yields these products. For example, we can see that the reflection $\boldsymbol{\sigma}^{(1)}$ followed by the rotation $\mathbf{C}_3$ carries point 0 to point 2, which could have been reached directly by the operation $\boldsymbol{\sigma}^{(2)}$. By similar procedures all the remaining products can be easily determined. The complete multiplication table for this set of operations is given here.

	$\mathbf{E}$	$\mathbf{C}_3$	$\mathbf{C}_3^2$	$\boldsymbol{\sigma}^{(1)}$	$\boldsymbol{\sigma}^{(2)}$	$\boldsymbol{\sigma}^{(3)}$
$\mathbf{E}$	$\mathbf{E}$	$\mathbf{C}_3$	$\mathbf{C}_3^2$	$\boldsymbol{\sigma}^{(1)}$	$\boldsymbol{\sigma}^{(2)}$	$\boldsymbol{\sigma}^{(3)}$
$\mathbf{C}_3$	$\mathbf{C}_3$	$\mathbf{C}_3^2$	$\mathbf{E}$	$\boldsymbol{\sigma}^{(3)}$	$\boldsymbol{\sigma}^{(1)}$	$\boldsymbol{\sigma}^{(2)}$
$\mathbf{C}_3^2$	$\mathbf{C}_3^2$	$\mathbf{E}$	$\mathbf{C}_3$	$\boldsymbol{\sigma}^{(2)}$	$\boldsymbol{\sigma}^{(3)}$	$\boldsymbol{\sigma}^{(1)}$
$\boldsymbol{\sigma}^{(1)}$	$\boldsymbol{\sigma}^{(1)}$	$\boldsymbol{\sigma}^{(2)}$	$\boldsymbol{\sigma}^{(3)}$	$\mathbf{E}$	$\mathbf{C}_3$	$\mathbf{C}_3^2$
$\boldsymbol{\sigma}^{(2)}$	$\boldsymbol{\sigma}^{(2)}$	$\boldsymbol{\sigma}^{(3)}$	$\boldsymbol{\sigma}^{(1)}$	$\mathbf{C}_3^2$	$\mathbf{E}$	$\mathbf{C}_3$
$\boldsymbol{\sigma}^{(3)}$	$\boldsymbol{\sigma}^{(3)}$	$\boldsymbol{\sigma}^{(1)}$	$\boldsymbol{\sigma}^{(2)}$	$\mathbf{C}_3$	$\mathbf{C}_3^2$	$\mathbf{E}$

The successful construction of this table demonstrates that the set of six operations does indeed form a group. This group is represented by the symbol

C_{3v}. The table shows that its characteristics are more general than those of the group C_{2v}. Thus it contains some operations that are not, as well as some which are, their own inverse. It also involves a number of multiplications that are not commutative.

A5-3. Some General Rules for Multiplication of Symmetry Operations

In the preceding section several specific examples of multiplication of symmetry operations have been worked out. On the basis of this experience, the following general rules should not be difficult to accept:

1. The product of two proper rotations must be another proper rotation. Thus although rotations can be created by combining reflections [recall: $\boldsymbol{\sigma}(xz) \times \boldsymbol{\sigma}(yz) = \mathbf{C}_2(z)$], the reverse is not possible.
2. The product of two reflections in planes meeting at an angle θ is a rotation by 2θ about the axis formed by the line of intersection of the planes (recall: $\boldsymbol{\sigma}^{(1)} \times \boldsymbol{\sigma}^{(2)} = \mathbf{C}_3$ for the ammonia molecule).
3. When there is a rotation operation $\mathbf{C}_n$ and a reflection in a plane containing the axis, there must be altogether n such reflections in a set of n planes separated by angles of $2\pi/2n$, intersecting along the C_n axis (recall: $\boldsymbol{\sigma}^{(1)} \times \mathbf{C}_3 = \boldsymbol{\sigma}^{(2)}$ for the ammonia molecule).
4. The product of two $\mathbf{C}_2$ operations about axes that intersect at an angle θ is a rotation by 2θ about an axis perpendicular to the plane containing the two C_2 axes.
5. The following pairs of operations always commute:
   - (*a*) Two rotations about the same axis.
   - (*b*) Reflections through planes perpendicular to each other.
   - (*c*) The inversion and any other operation.
   - (*d*) Two $\mathbf{C}_2$ operations about perpendicular axes.
   - (*e*) $\mathbf{C}_n$ and $\boldsymbol{\sigma}_h$, where the $\mathbf{C}_n$ axis is vertical.

A5-4. A Systematic Listing of Symmetry Groups, with Examples

The symmetry groups to which real molecules may belong are very numerous. However they may be systematically classified by considering how to build them up using increasingly more elaborate combinations of symmetry operations. The outline that follows, though neither unique in its approach nor rigorous in its procedure, affords a practical scheme for use by most chemists.

The simplest nontrivial groups are those of order 2, that is, those containing but one operation in addition to **E**. The additional operation must be one that is its own inverse; thus the only groups of order 2 are

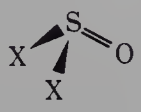
$$C_s\text{: } \mathbf{E}, \boldsymbol{\sigma}$$

$$C_i\text{: } \mathbf{E}, \mathbf{i}$$

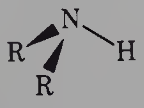
$$C_2\text{: } \mathbf{E}, \mathbf{C}_2$$

The symbols for these groups are rather arbitrary, except for C_2 which, we shall soon see, forms part of a pattern.

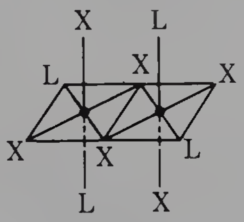
Molecules with C_s symmetry are fairly numerous. Examples are the thionyl halides and sulfoxides (A5-III), and secondary amines (A5-IV). Molecules having a center of symmetry as their *only* symmetry element are quite rare; two types are shown as (A5-V) and (A5-VI). The reader should find it very challenging, though not impossible, to think of others. Molecules of C_2 symmetry are fairly common, two examples being (A5-VII) and (A5-VIII).



(A5-III)



(A5-IV)



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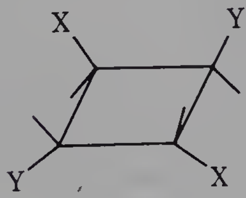
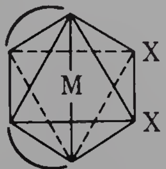


(A5-VI)

(A5-VII)

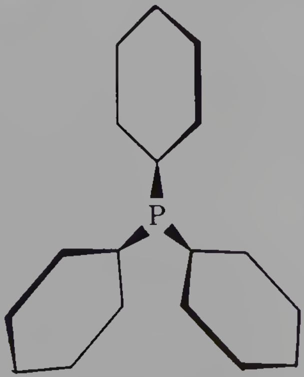


(A5-VIII)

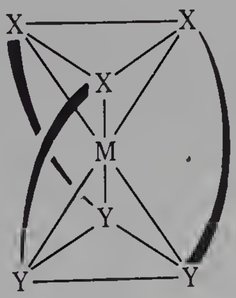
The Uniaxial or C_n Groups. These are the groups in which all operations are due to the presence of a proper axis as the sole symmetry element. The general symbol for such a group, and the operations in it, are

$$C_n\text{: } \mathbf{C}_n, \mathbf{C}_n^2, \mathbf{C}_n^3, \cdots \mathbf{C}_n^{n-1}, \mathbf{C}_n^n \equiv \mathbf{E}$$

A C_n group is thus of order n. We have already mentioned the group C_2. Molecules with pure axial symmetry other than C_2 are rare. Two examples of the group C_3 are shown in (A5-IX) and (A5-X).

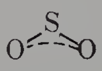


(A5-IX)



(A5-X)

The C_{nv} Groups. If in addition to a proper axis of order n there is also a set of n vertical planes, we have a group of order $2n$, designated C_{nv}. This type of symmetry is found quite frequently and is illustrated in (A5-XI) to (A5-XV), where the values of n are 2 to 6.

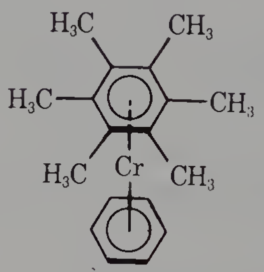


(A5-XI)

(A5-XII)

(A5-XIII)

(A5-XIV)



(A5-XV)

The C_{nh} Groups. If in addition to a proper axis of order n there is also a horizontal plane of symmetry, we have a group of order $2n$, designated C_{nh}. The $2n$ operations include $\mathbf{S}_n^m$ operations that are products of $\mathbf{C}_n^m$ and $\boldsymbol{\sigma}_h$ for n odd, to make the total of $2n$. Thus for C_{3h} the operations are

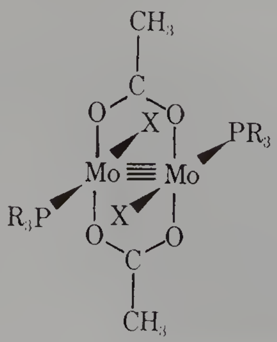
$$\mathbf{C}_3,\ \mathbf{C}_3^2,\ \mathbf{C}_3^3 \equiv \mathbf{E}$$

$$\boldsymbol{\sigma}_h$$

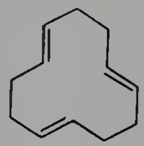
$$\boldsymbol{\sigma}_h \times \mathbf{C}_3 = \mathbf{C}_3 \times \boldsymbol{\sigma}_h = \mathbf{S}_3$$

$$\boldsymbol{\sigma}_h \times \mathbf{C}_3^2 = \mathbf{C}_3^2 \times \boldsymbol{\sigma}_h = \mathbf{S}_3^5$$

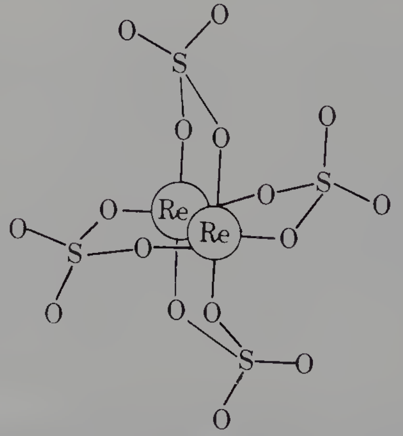
Molecules of C_{nh} symmetry with $n > 2$ are relatively rare; examples with n = 2, 3, and 4 are shown in (A5-XVI) to (A5-XVIII).



(A5-XVI)

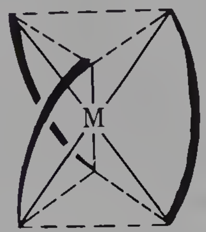


(A5-XVII)



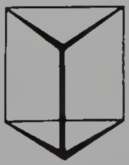
(A5-XVIII)

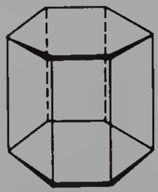
The D_n Groups. When a vertical C_n axis is accompanied by a set of n C_2 axes perpendicular to it, the group is D_n. Molecules of D_n symmetry are, in general, rare, but there is one very important type, namely, the trischelates (A5-XIX) of D_3 symmetry.

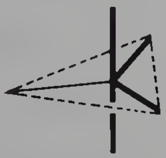


(A5-XIX)

The D_{nh} Groups. If to the operations making up a D_n group we add reflection in a horizontal plane of symmetry, the group D_{nh} is obtained. It should be noted that products of the type $\mathbf{C}_2 \times \boldsymbol{\sigma}_h$ will give rise to a set of reflections in vertical planes. These planes *contain* the C_2 axes; this point is important in regard to the distinction between D_{nh} and D_{nd}, mentioned next. The D_{nh} symmetry is found in a number of important molecules, a few of which are benzene (D_{6h}), ferrocene in an eclipsed configuration (D_{5h}), $Re_2Cl_8^{2-}$, which we examined previously, (D_{4h}), $PtCl_4^{2-}$ (D_{4h}), and the boron halides (D_{3h}) and PF_5(D_{3h}). All right prisms with regular polygons for bases as illustrated in (A5-XX) and (A5-XXI), and all bipyramids, as illustrated in (A5-XXII) and (A5-XXIII), have D_{nh}-type symmetry.

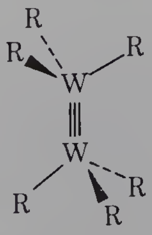

(A5-XX)


(A5-XXI)

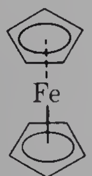

(A5-XXII)


(A5-XXIII)

The D_{nd} Groups. If to the operations making up a D_n group we add a set of vertical planes that bisect the angles between pairs of C_2 axes (note the distinction from the vertical planes in D_{nh}), we have a group called D_{nd}. The D_{nd} groups have no σ_h. Perhaps the most celebrated examples of D_{nd} symmetry are the D_{3d} and D_{5d} symmetries of $R_3W{\equiv}WR_3$ and ferrocene in their staggered configurations (A5-XXIV) and (A5-XXV).



(A5-XXIV)



(A5-XXV)

Two comments about the scheme so far outlined may be helpful. The reader may have wondered why we did not consider the result of adding to the operations of C_n *both* a set of $n\sigma_v$'s and a σ_h. The answer is that this is simply another way of getting to D_{nh}, since a set of C_2 axes is formed along the lines of intersection of the σ_h with each of the σ_v's. By convention, and in accord with the symbols used to designate the groups, it is preferable to proceed as we did. Second, in dealing with the D_{nh}-type groups, if a horizontal plane is found, there must be only the n vertical planes *containing* the C_2 axis. If dihedral planes were also present, there would be, in all $2n$ planes and hence, as shown previously, a principal axis of order $2n$, thus vitiating the assumption of a D_n type of group.

The S_n Groups. Our scheme has, so far, overlooked one possibility, namely, that a molecule might contain an S_n axis as its only symmetry element (except for others that are directly subservient to it). It can be shown that for n odd, the groups of operations arising would actually be those forming the group C_{nh}. For example, take the operations generated by an S_3 axis:

$$\mathbf{S}_3$$

$$\mathbf{S}_3^2 \equiv \mathbf{C}_3^2$$

$$\mathbf{S}_3^3 \equiv \boldsymbol{\sigma}_h$$

$$\mathbf{S}_3^4 \equiv \mathbf{C}_3$$

$$\mathbf{S}_3^5$$

$$\mathbf{S}_3^6 \equiv \mathbf{E}$$

Comparison with the list of operations in the group C_{3h} shows that the two lists are identical.

It is only when n is an even number that new groups can arise that are not already in the scheme. For instance, consider the set of operations generated by an S_4 axis:

$$\mathbf{S}_4$$

$$\mathbf{S}_4^2 \equiv \mathbf{C}_2$$

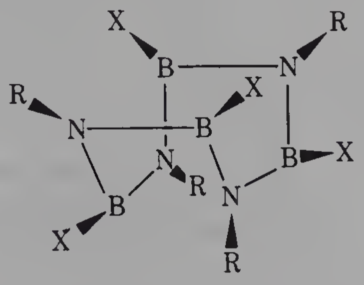
$$\mathbf{S}_4^3$$

$$\mathbf{S}_4^4 \equiv \mathbf{E}$$

This set of operations satisfies the four requirements for a group and is not a set that can be obtained by any procedure previously described. Thus S_4, S_6, and so on are new groups. They are distinguished by the fact that they contain no operation that is not an $\mathbf{S}_n^m$ operation, even though it may be written in another way, as with $\mathbf{S}_4^2 \equiv \mathbf{C}_2$ above.

Note that the group S_2 is not new. A little thought will show that the operation $\mathbf{S}_2$ is identical with the operation **i**. Hence the group that could be called S_2 is the one we have already called C_i.

An example of a molecule with S_4 symmetry is shown in (A5-XXVI). Molecules with S_n symmetries are not very common.



(A5-XXVI)

Linear Molecules. There are only two kinds of symmetry for linear molecules. There are those represented by (A5-XXVII), which have identical ends. Thus, in addition to an infinitefold rotation axis C_∞, coinciding with the molecular axis, and an infinite number of vertical symmetry planes, they have a horizontal plane of symmetry and an infinite number of C_2 axes perpendicular to C_∞. The group of these operations is $D_{\infty h}$. A linear molecule with different ends (A5-XXVIII), has only C_∞ and the σ_v's as symmetry elements. The group of operations generated by these is called $C_{\infty v}$.

A—B—C—B—A (A5-XXVII)

A—B—C—D (A5-XXVIII)

A5-5. The Groups of Very High Symmetry

The scheme followed in the preceding section has considered only cases in which there is a single axis of order equal to or > 3. It is possible to have symmetry groups in which there are several such axes. There are, in fact, seven such groups, and several of them are of paramount importance.

The Tetrahedron. We consider first a regular tetrahedron. Figure A5-6 shows some of the symmetry elements of the tetrahedron, including at least one of each kind. From this it can be seen that the tetrahedron has altogether 24 symmetry operations, which are as follows:

There are three S_4 axes, each of which gives rise to the operations $\mathbf{S}_4$, $\mathbf{S}_4^2 \equiv \mathbf{C}_2$, $\mathbf{S}_4^3$, and $\mathbf{S}_4^4 \equiv \mathbf{E}$. Neglecting the $\mathbf{S}_4^4$'s, this makes $3 \times 3 = 9$.

There are four C_3 axes, each giving rise to $\mathbf{C}_3$, $\mathbf{C}_3^2$ and $\mathbf{C}_3^3 \equiv \mathbf{E}$. Again omitting the identity operations, this makes $4 \times 2 = 8$.

There are six reflection planes, only one of which is shown in Fig. A5-6, giving rise to six $\boldsymbol{\sigma}_d$ operations.

Thus there are 9 + 8 + 6 + one identity operation = 24 operations. This group is called T_d. It is worth emphasizing that despite the considerable amount of symmetry, there is no inversion center in T_d symmetry. There are,

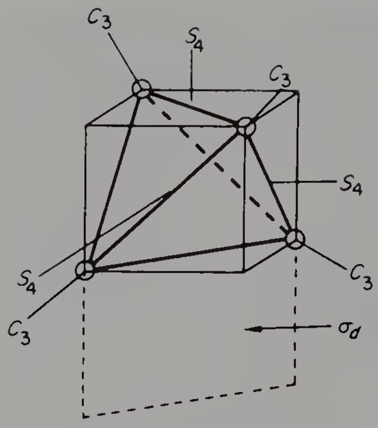
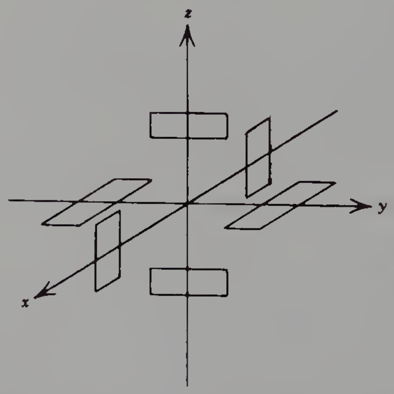


FIG. A5-6. The tetrahedron, showing some of its essential symmetry elements. All S_4 and C_3 axes are shown, but only one of the six dihedral planes σ_d.

of course, numerous molecules having full T_d symmetry, such as CH_4, SiF_4, ClO_4^-, $Ni(CO)_4$, and $Ir_4(CO)_{12}$, and many others where the symmetry is less but approximates to it.

If we remove from the T_d group the reflections, it turns out that the $\mathbf{S}_4$ and $\mathbf{S}_4^3$ operations are also lost. The remaining 12 operations (**E**, four $\mathbf{C}_3$ operations, four $\mathbf{C}_3^2$ operations and three $\mathbf{C}_2$ operations) form a group, designated T. This group in itself has little importance, since it is very rarely, if ever, encountered in real molecules. However, if we then add to the operations in the group T a different set of reflections in the three planes defined so that each one contains two of the C_2 axes, and work out all products of operations, we get a new group of 24 operations (**E**, four $\mathbf{C}_3$, four $\mathbf{C}_3^2$, three $\mathbf{C}_2$, three $\boldsymbol{\sigma}_h$, **i**, four $\mathbf{S}_6$, four $\mathbf{S}_6^5$) denoted T_h. This, too, is rare, but it occurs in some "octahedral" complexes in which the ligands are planar and arranged as in (A5-XXIX). The important feature here is that each pair of ligands on each of the Cartesian axes is in a different one of the three mutually perpendicular planes, *xy*, *xz*, and *yz*. Real cases are provided by $W(NMe_2)_6$ and several $M(NO_3)_6^{n-}$ ions in which the NO_3^- ions are bidentate.



(A5-XXIX)

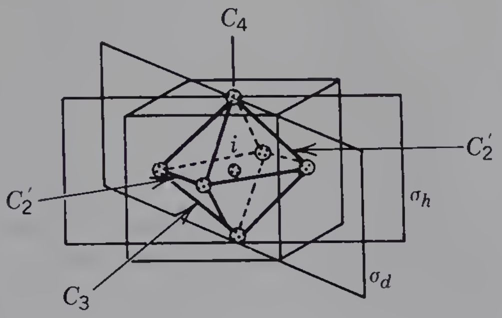


FIG. A5-7. The octahedron and the cube, showing one of each of their essential types of symmetry element.

The Octahedron and the Cube. These two bodies have the same elements, as shown in Fig. A5-7, where the octahedron is inscribed in a cube, and the centers of the six cube faces form the vertices of the octahedron. Conversely, the centers of the eight faces of the octahedron form the vertices of a cube. Figure A5-7 shows one of each of the types of symmetry element that these two polyhedra possess. The list of symmetry operations is as follows:

There are three C_4 axes, each generating $\mathbf{C}_4$, $\mathbf{C}_4^2 \equiv \mathbf{C}_2$, $\mathbf{C}_4^3$, $\mathbf{C}_4^4 \equiv \mathbf{E}$. Thus there are $3 \times 3 = 9$ rotations, excluding $\mathbf{C}_4^4$'s.

There are four C_3 axes giving four $\mathbf{C}_3$'s and four $\mathbf{C}_3^2$'s.

There are six C_2' axes bisecting opposite edges, giving six $\mathbf{C}_2'$'s.

There are three planes of the type σ_h and six of the type σ_d, giving rise to nine reflection operations.

The C_4 axes are also S_4 axes and each of these generates the operations $\mathbf{S}_4$, $\mathbf{S}_4^2 \equiv \mathbf{C}_2$ and $\mathbf{S}_4^3$, the first and last of which are not yet listed, thus adding $3 \times 2 = 6$ more to the list.

The C_3 axes are also S_6 axes and each of these generates the new operations $\mathbf{S}_6$, $\mathbf{S}_6^3 \equiv \mathbf{i}$, and $\mathbf{S}_6^5$. The **i** counts only once, so there are then $(4 \times 2) + 1 = 9$ more new operations.

The entire group thus consists of the identity $+ 9 + 8 + 6 + 9 + 6 + 9 = 48$ operations. This group is denoted O_h. It is, of course, a very important type of symmetry since octahedral molecules (e.g. SF_6), octahedral complexes [$Co(NH_3)_6^{3+}$ and $IrCl_6^{3-}$], and octahedral interstices in solid arrays are very common. There is a group O, which consists of only the 24 proper rotations from O_h, but this, like T, is rarely if ever encountered in Nature.

The Pentagonal Dodecahedron and the Icosahedron. These bodies (Fig. A5-8) are related to each other in the same way as are the octahedron and the cube, the vertices of one defining the face centers of the other, and vice versa. Both have the same symmetry operations, a total of 120! We shall not list them in detail but merely mention the basic symmetry elements: six C_5 axes; ten C_3 axes, fifteen C_2 axes, and fifteen planes of symmetry. The group of 120 operations is designated I_h and is often called the icosahedral group.

There is one known example of a molecule that is a pentagonal dodecahedron, viz., dodecahedrane, $C_{12}H_{12}$. The icosahedron is a key structural unit

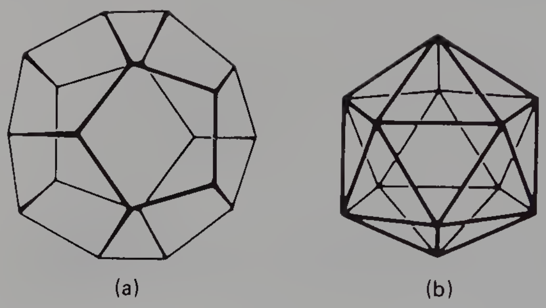


FIG. A5-8. The two regular polyhedra having I_h symmetry. (a) The pentagonal dodecahedron and (b) the icosahedron.

in boron chemistry, occurring in all forms of elemental boron as well as in the $B_{12}H_{12}^{2-}$ ion.

If the symmetry planes are omitted, a group called *I* consisting of only proper rotations remains. This is mentioned purely for the sake of completeness, since no example of its occurrence in Nature is known.

A5-6. Molecular Dissymmetry and Optical Activity

Optical activity, that is, rotation of the plane of polarized light coupled with unequal absorption of the right- and left-circularly polarized components, is a property of a molecule (or an entire three-dimensional array of atoms or molecules) that is not superposable on its mirror image. When the number of molecules of one type exceeds the number of those that are their nonsuperposable mirror images, a net optical activity results. To predict when optical activity will be possible, it is necessary to have a criterion to determine when a molecule and its mirror image will not be identical, that is, superposable.

Molecules that are not superposable on their mirror images are called *dissymmetric*. This term is preferable to "asymmetric," which means "without symmetry," whereas dissymmetric molecules can and often do possess some symmetry, as will be seen.*

A compact statement of the relation between molecular symmetry properties and dissymmetric character is: *a molecule that has no axis of improper rotation is dissymmetric.*

This statement includes and extends the usual one to the effect that optical isomerism exists when a molecule has neither a plane nor a center of symmetry. It has already been noted that the inversion operation **i** is equivalent to the improper rotation $\mathbf{S}_2$. Similarly, $\mathbf{S}_1$ is a correct although unused way of representing $\boldsymbol{\sigma}$, since it implies rotation by $2\pi/1$, equivalent to no net rotation, in conjunction with the reflection. Thus $\boldsymbol{\sigma}$ and **i** are simply special cases of improper rotations.

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*Dissymmetry is sometimes called chirality, and dissymmetric chiral, from the Greek word χειρ for hand, in view of the left-hand/right-hand relation of molecules that are mirror images.

However, even when σ and i are absent, a molecule may still be identical with its mirror image if it possesses an $\mathbf{S}_n$ axis of some higher order. A good example of this is provided by the (—RNBX—)$_4$ molecule shown in (5A-XXVI). This molecule has neither a plane nor a center of symmetry, but inspection shows that it can be superposed on its mirror image. As we have noted, it belongs to the symmetry group S_4.

Dissymmetric molecules either have no symmetry at all, or they belong to one of the groups consisting only of proper rotation operations, that is, the C_n or D_n groups. (Groups T, O, and I are, in practice, not encountered, though molecules in these groups must also be dissymmetric.) Important examples are the bischelate and trischelate octahedral complexes (A5-VIII), (A5-X), and (A5-XIX).

Index