Organometallic Compounds

VOLUME TWO

The Transition Elements

ORGANOMETALLIC COMPOUNDS

by

G. E. COATES M.A., D.Sc., F.R.I.C.
Professor of Chemistry in the University of Durham

M. L. H. GREEN Ph.D., M.A.
Fellow and Tutor in Inorganic Chemistry, Balliol College, Oxford

K. WADE B.Sc., Ph.D.
Lecturer in Chemistry in the University of Durham

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M. L. H. GREEN

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Preface to the Third Edition, Volume Two

The very great expansion of transition metal chemistry during the last ten years is reflected in the large increase of space devoted to transition elements in the present edition of this book when compared to the earlier editions.

Classification of the organic derivatives of the transition metals by the type of ligands is now more appropriate than classification by Periodic Group. This arises since the chemistry of a given class tends to be dominated more by the nature of the organic group – particularly when this effectively occupies several co-ordination positions – than by the metal itself. In order to compensate, to some extent, for this underestimate of metal influence, classification of metal compounds by the metal is given in the subject index.

Where it is considered appropriate a major topic is treated first in a relatively general manner followed by a more detailed description of some particular chemistry or ideas. It is intended that the more general sections will serve to introduce the field to undergraduates without there being burdensome detail. The rather pictorial treatment of the description of the bonding in these complexes is especially arranged for this purpose.

There has been no attempt made to cover the literature comprehensively although the majority of the more important references are given. Also there has not been space to discuss the often fascinating history of some of the compounds and ideas in this field. Generally, work known to be erroneous is omitted without comment. There are, however, instances where a partially incorrect paper may contain useful information; for example, the method of preparation of a compound which is incorrectly formulated, in these cases the reference is given. It is therefore necessary for the reader to look at all the references given to a particular compound or statement, in order to understand the present situation and ascertain the accuracy of the text. Since reference is given to all the work discussed few names are mentioned in the text.

I am deeply grateful to the many people who have helped in the production of this book. I wish to express my thanks to Professor G. E. Coates, Dr R. J. P. Williams and Dr D. J. Jones who have read and improved parts of the book, and particularly to Dr D. F. Evans and Dr L. Pratt who have read the book at manuscript and proof stages and who have made substantial corrections and improvements. I would also like to thank Messrs J. R. Sanders, W. E. Lindsell and M. G. Swanwick for helping to check the text and references and prepare indexes.

Finally, I should like to thank my wife for the very considerable assistance she has given me in the writing and production of this book.

M. L. H. G.

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Introduction to Volume Two

During the second half of the last century, when the foundations of the organometallic chemistry described in Volume I were being laid, it was generally held that the transition elements were unable to form organic derivatives. Early in the present century methyl platinum compounds were made (Pope and Peachy [1]) and an extensive organic chemistry of gold(III) was developed (Gibson [2]) mainly in the 1930's. During the 1940's the organic chemistry of the transition elements comprised little more than the gold and platinum compounds, the olefin complexes of platinum and palladium which were not understood, and Hein's phenylchromium compounds (1919–1931) – which were quite mysterious.

There was a dramatic change in the early 1950's, following the now famous discovery of ferrocene or biscyclopentadienyliron, $(C_5H_5)_2Fe$, simultaneously by Miller, Tebboth and Tremaine [3] and by Kealy and Pauson [4]. Ferrocene was quickly recognized as an entirely new type of compound in which a metal atom is bound to aromatic rings in a previously unknown way (Wilkinson, Rosenblum, Whiting and Woodward [5], 1952; Fischer and Pfab [6], 1952).

Since the early fifties there has been a great deal of work on the organic derivatives of transition metals and many exciting new types of compounds have been isolated and studied.

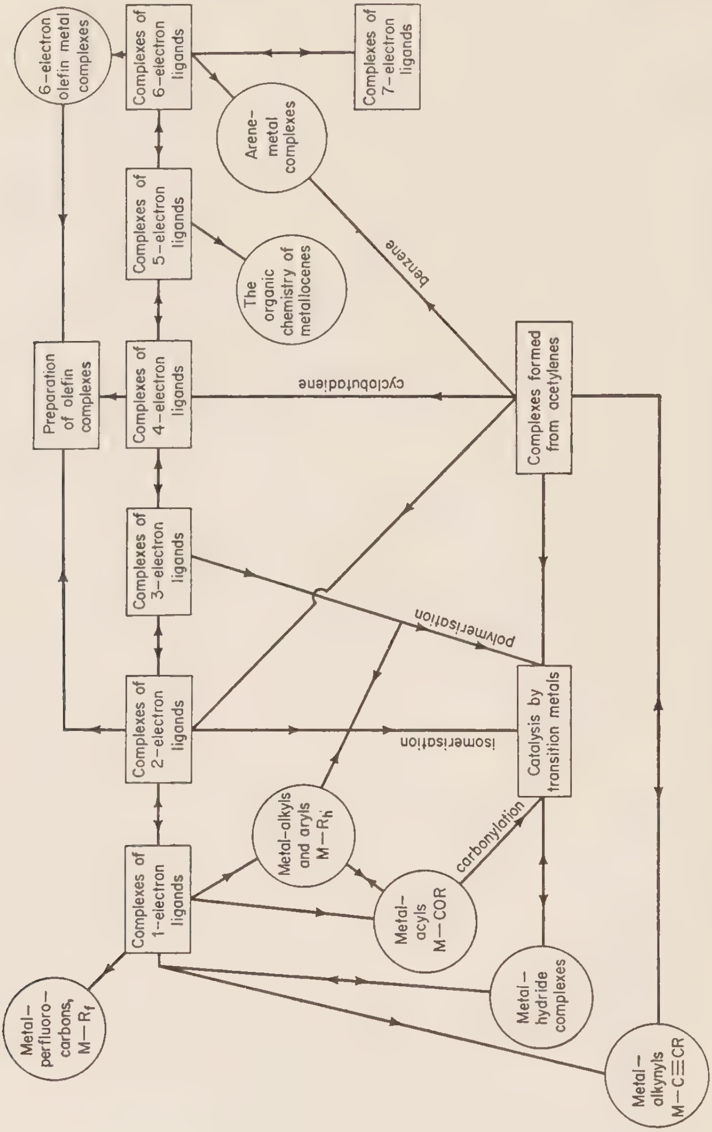
Classification

The compounds discussed in the following chapters are classified by the organic ligands attached to the metal according to the number of electrons which are formally considered to arise from the ligand and which take part in the formation of the metal–ligand bond. This classification and a plan of the following chapters are shown in the table and in the chart below.

A classification of organic groups which act as ligands to transition metals

Number of electrons	Name of class	Example of organic group
1	Yl	Alkyl or aryl groups, compare $Cl^\bullet$, $CN^\bullet$ and $H^\bullet$.
2	Alkene	Ethylene, compare carbon monoxide
3	Enyl	π-Allyl, compare nitric oxide
4	Diene	Cyclobutadiene, butadiene
5	Dienyl	π-Cyclopentadienyl
6	Triene	Benzene, cycloheptatriene
7	Trienyl	π-Cycloheptatrienyl

The basis of the above classification is the 18-electron rule and it is appropriate to discuss this rule here.



Plan of chapters and major topics in this book: the chapter titles are in the square boxes.

The 18-electron rule

The large majority of the transition metal complexes with metal–carbon organic, –carbonyl or –hydride ligands isolable at room temperature can be regarded as having 18 electrons in their valence shell. This is the empirical basis of the rule ‘a valence shell containing 18 electrons gives stable complexes’. It is argued in Chapter 7 that the greater stability associated with the 18-electron valence shell may arise both from thermodynamic and kinetic factors.

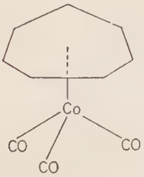
In order to test the application of the 18-electron rule to a compound it is necessary to count the number of electrons which are formally in the valence shell of the metal atom. This is most easily achieved in the following manner:

(*a*) Take the number of electrons in the valence shell of the uncomplexed metal atom and add or subtract electrons according to the total charge on the metal complex. Thus iron in a unipositive cation has $8 - 1 = 7$ electrons, in a neutral compound has 8 electrons and in a uninegative anion has 9 electrons.

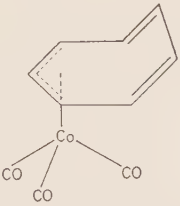
(*b*) Sum the number of electrons which the ligands formally contribute to the metal, according to the classification of ligands given above. Add this sum to the metal electrons from (*a*).

To exemplify this procedure we consider first the complex cation $[\pi\text{-}C_5H_5Fe(CO)_2C_2H_4]^+$ which does not require further structural evidence before the electrons can be counted. The electrons come from $Fe^+ = 7$; $\pi\text{-}C_5H_5 = 5$; $(CO)_2 = 4$; $C_2H_4 = 2$; the total is therefore 18 electrons. Another example is $\pi\text{-}C_5H_5(Me)_2Re(C_5H_5Me)$; in this case the structure of the ReC_5H_5Me group must be known before we can unambiguously count electrons. The electrons arise from $Re = 7$; $\pi\text{-}C_5H_5 = 5$; $Me_2 = 2$; and, since X-ray diffraction shows that the methylcyclopentadiene ligand has all four diene carbons bonded to the metal, $C_5H_5Me = 4$; again the total = 18 electrons. Contrast this complex with the cyclopentadiene complex $\pi\text{-}C_5H_5Re(CO)_2C_5H_6$ in which the cyclopentadiene group is only bonded to the metal by one carbon–carbon double bond (see p. 23).

Finally, consider the complex $C_7H_7Co(CO)_3$ whose structure is unknown but may be *predicted* using the 18-electron rule. At first sight the complex appears to be a $7 + 9 + 6 = 22$ electron complex. It is therefore proposed that the C_7H_7 ring only contributes three electrons to the cobalt, rather than seven, and that instead of being the π-cycloheptatrienyl complex, I.1, it is the π-enyl complex I.2:



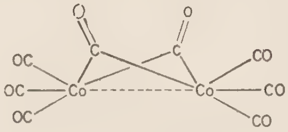
I.1



I.2

A problem in the counting of electrons may arise with complexes containing metal–metal bonds. In complexes for which X-ray diffraction clearly shows there to be metal–metal bonding, e.g. $(CO)_5Mn—Mn(CO)_5$, the bond is represented by an *unbroken* line. In these complexes each metal atom acts as a one-electron ligand to the other.

Those complexes which contain bridging ligands between two metal atoms are *assumed* to contain a metal–metal bond when this is required by the 18-electron rule and if it is suggested by experiment, for example by magnetic data. Both dicobalt octacarbonyl, I.3, and the binuclear complex $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ have two bridging carbonyl groups and they are diamagnetic. It is therefore normally assumed that spin-pairing between the metal atoms occurs via a metal–metal bond, otherwise the metal atoms would have an odd, 17-electron environment. However, spin-pairing may possibly occur by mechanisms other than direct metal–metal interaction; for example via a bridging ligand. A metal–metal interaction which is *postulated* solely on the basis of magnetic data or the 18-electron rule is therefore represented by a *dotted* line in this book (see I.3).



I.3

(*i*) *The basis of the 18-electron rule*

The change in energy of the 4*s*, 4*p* and 3*d* orbitals with increasing atomic number across the first long series of the transition elements is given in Figure 1. This figure shows several points of interest:

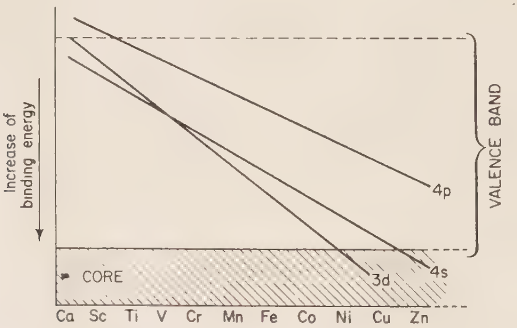


Fig. 1. The change in energy of the 3*d*, 4*s* and 4*p* orbitals of the first transition series (after Phillips and Williams [7])

(*a*) For scandium and titanium the 3*d* orbitals are rather high in energy and are unlikely to be very important in metal–ligand bonding.

(*b*) Across the series V, Cr, Mn, Fe, Co the 3*d* orbitals decrease in energy more rapidly than the 4*s* and 4*p* orbitals, yet all three types of orbitals are fairly close in energy and are of suitable energy to be important in metal–ligand bonding.

(*c*) Across the series Ni, Cu, Zn the *d* orbitals continue to decrease in energy and at Cu and Zn they are best regarded as core electrons, that is they are no longer 'valence electrons' and cannot be expected to make significant contributions to the metal–ligand bonding.

It should also be noted that for all the transition metals the effect of a positive charge on the metal is to lower the energy of all the orbitals. More important, however, is the increase in the separation between the 3*d* orbitals and the 4*s*, 4*p* orbitals. From these observations we may, in a very qualitative manner, understand the occurrence and limitations of the 18-electron rule, as follows.

When the energies of the 3*d*, 4*s* and 4*p* orbitals are fairly close together and are suitable for metal–ligand bonding, i.e. when the orbitals are in the valence band, then the maximum bonding occurs when they are all filled, and this is of course the case when the metal atom has an 18-electron environment. It follows from (*b*) that the low (and negative) oxidation states of the metals V, Cr, Fe and Co would be expected to obey an 18-electron rule. In the case of Ni then, it makes little difference whether we regard the 3*d* orbitals as valence or core orbitals since in both cases there remain the valence 4*s* and 4*p* orbitals which, when filled, would give tetrahedral nickel complexes, e.g. $Ni(CO)_4$.

(*ii*) *Exceptions to the 18-electron rule*

It follows from (*a*) and (*c*) above, that the 18-electron rule would be expected to break down for transition metals in low oxidation states at both ends of the transition series, either because the 3*d* orbitals are too high (Ti) or too low (Cu) in energy. This is indeed the case and there are no known 18-electron complexes of Ti and few of Cu.

It can be seen also that the 18-electron rule will tend to break down when the first-row transition metals are in a high oxidation state. There may also be steric limitations to the formation of 18-electron complexes in high oxidation states – consider for example the hypothetical cation $[Cr(CO)_9]^{6+}$. Steric limitations may also explain why vanadium forms the monomeric, paramagnetic and 17-electron hexacarbonyl, $V(CO)_6$, rather than the dimeric complex $[V(CO)_6]_2$ which would be diamagnetic and would obey the 18-electron rule.

It is observed that nickel frequently forms complexes in which it has a 16-electron environment, e.g. in square-planar complexes such as

$(PR'_3)_2NiR_2$. Also, copper sometimes and gold frequently form 14-electron complexes, of the type PR_3MR. These observations can be understood in terms of Figure 1 as follows.

Across the series Co, Ni, Cu and Zn the 3*d* orbitals go into the metal core and the energy separation between the 4*s* and 4*p* orbitals becomes greater. As the difference of energy of the 4*s* and 4*p* orbitals increases, the 4*s* orbital becomes more important in bonding whilst the 4*p* orbitals become less significant. The stepwise removal of two of the three 4*p* orbitals may account for the occurrence of stable complexes of Co, Ni and Cu in which the metals have 18-, 16- and 14-electron environments respectively.

It should be noted that all the above arguments apply also to the second and third *d*-block transition series and that differences between the *relative* energies of the n*s*, n*p* and (n — 1)*d* orbitals may also be significant. For example there is an increase in the separation between the n*s* and n*p* orbitals in the series Cu, Ag and Au. This may account for the apparently greater stability of the 14-electron gold complexes PR_3AuR compared to that of the copper analogues.

Finally, it is emphasized that the 18-electron rule is unsophisticated and provides no detailed insight into the chemistry of organometallic complexes.

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CHAPTER ONE

Two-electron ligands

A. Classification

The model 2-electron ligand is ethylene, and all olefinic compounds which bind to a metal atom using *one* C=C system can be treated as 2-electron ligands. Those olefins which have more than one C=C system but which are *unconjugated* may be regarded as potential chelating 2-electron ligands. Thus cyclo-octa-1,5-diene and cyclododeca-1,5,9-triene are classified as a two × 2-electron ligand and as a three × 2-electron ligand respectively. These unconjugated olefins are therefore distinguished from *conjugated* olefins such as butadiene and cycloheptatriene which are classified as 4- and 6-electron ligands respectively. This distinction is made since there are considerable differences between the chemistry of the two classes of olefins as ligands.† These differences are discussed in Chapter 3.

In Table 1 examples are given of a variety of olefins which act as 2-electron or $n \times 2$-electron ligands. This table shows that complexes of these ligands are widespread amongst the transition metals with a preponderance towards the metals with larger numbers of *d*-electrons. Although there is a difference between the chemical properties of the complexes with 2-electron olefins and conjugated olefins as ligands, the preparative routes for both classes of complexes are closely related. Therefore the *preparations* of olefin–metal complexes for all classes of olefin ligand are considered together.

B. The preparation of olefin–transition metal complexes

Olefin–metal complexes are usually prepared by the treatment of a metal complex with an olefin. There is usually displacement of another ligand from the metal which in the simplest cases may be just a solvent molecule. Although the first stage in most reactions of olefins with metal complexes is the formation of a metal–olefin bond, there may follow a variety of reactions such as: isomerization of the olefin, hydrogen transfer, loss or addition of hydrogen, or polymerization of the olefin. Thus the products of the reaction of olefins with metal complexes may be organometallic compounds which contain hydrocarbon ligands of very different nature from the parent olefin. For example, cyclohexene may give π-cyclohexenyl metal complexes (p. 41), cyclopentadiene frequently affords π-cyclo-

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† An olefin may belong to more than one class of ligand. Examples are given on pp. 9, 10, 12, and 197.

Table 1 *Examples of two-electron ligands*

No. of $>C{=}C<$ groups bound, $= n$	Name of olefin	Metals which form complexes with the olefin
Monodentate $n = 1$	Ethylene(a)	Cr, Mo, W, Mn, Re, Fe, Rh, Ni, Pd, Pt, Ag
unconjugated	Propene	Mo, W, Mn, Fe, Cu, Ag (b)
	Cyclohexene	Mn, Pd, Ag
	Cis-cyclo-octene	Ag as in $2C_8H_{14}AgNO_3$ [3]
	Norbornadiene (c)	Cu as in $(C_7H_8CuCl)_4$
conjugated	Styrene	Pt, Pd
	Stilbene	W as in $PhCH{=}CHPhW(CO)_5$ [4]
	Acrylonitrile	Fe as in $C_2H_3CNFe(CO)_4$ [55]
	Acrolein	Fe as in $CH_2{=}CHCHOFe(CO)_4$ [57]
	Acrylic acid esters	Fe as in $CH_2{=}CHCOORFe(CO)_4$ [57]
	Butadiene	Fe, Ag as in $C_4H_6(AgNO_3)_2$ [5] $C_4H_6Fe(CO)_4$ and $C_4H_6(Fe(CO)_4)_2$ [24]
	Cyclopentadiene	Re, Ag as in π-$C_5H_5Re(CO)_2C_5H_6$ [67], $C_5H_6AgClO_4$ [20]
	Cyclohexa-1,3-diene	Mn as in π-$C_5H_5Mn(CO)_2C_6H_8$ [6]
Bidentate $n = 2$	Cyclo-octa-1,5-diene	Cr, Mo, W, Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au (b)
	Norbornadiene (c)	Cr, Mo, W, Mn, Fe, Ru, Co, Rh, Ir, Pd, Pt, Cu, Ag (b)
	Cyclohexa-1,4-diene	in $C_6H_8Fe(CO)_3$
	Hexa-1,5-diene	W, Pd, Pt, Ag (b)
	Dicyclopentadiene	Mn, Re, Pd, Pt, Cu, Rh, Ag (b)
	Dimethyldivinylsilane	$C_6H_{12}Si\ Mo(CO)_4$ [7]
Tridentate $n = 3$	Cyclododeca-1,5,9-triene	Fe, Ni, Pd as in $C_{12}H_{18}Fe(CO)_3$, ($n=2$), $C_{12}H_{18}PdCl_2$, ($n = 2$) [8] and $C_{12}H_{18}Ni$, ($n = 3$) [34]

(*a*) Examples are *sym*-$(CH_3)_3C_6H_3Cr(CO)_2C_2H_4$, red, 100° [9]; $[\pi\text{-}C_5H_5Mo(\text{and }W)(CO)_3C_2H_4]^+PF_6^-$, yellow [37]; $[C_2H_4Mn(CO)_5]^+ClO_4^-$, yellow [10, 11]; π-$C_5H_5Mn(CO)_2C_2H_4$, yellow, 125° [27]; $[(C_2H_4)_2Re(CO)_4]^+\ AlCl_4^-$, white [38]; $C_2H_4Fe(CO)_4$, yellow [12]; $[\pi\text{-}C_5H_5Fe(CO)_2C_2H_4]^+PF_6^-$, yellow [37]; π-$C_5H_5Rh(C_2H_4)_2$, orange [64, 65]; $[(C_2H_4)_2RhCl]_2$, orange-red, 115° d [18]; $(PR_3)_2NiC_2H_4$ [13]; $[C_2H_4PtCl_2]_2$, orange [47]; $(C_2H_4)_2PtCl_2$, yellow [14]; $C_2H_4PtCOCl_2$, white [94]; $C_2H_4(AgNO_3)_2$ white, stable below $-30°$ [15].

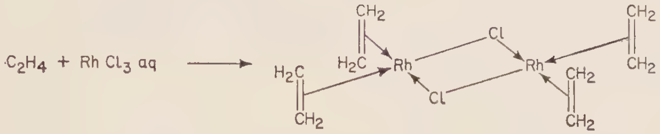
(*b*) Detailed references are available in reviews [1,2]

(*c*) Bicyclo-2,2,1-heptadiene.

pentadienyl complexes, and with metal hydrides, olefins may give alkyl complexes. In this section, only those reactions which give olefin complexes are considered but references to those reactions between olefins and metal complexes which give organometallic complexes containing ligands other than olefins are given separately at the end of this section. Some typical preparations are discussed below.

(*a*) *Displacement of solvent ligands*

The treatment of many metal salts either in solution or in the solid state may give smooth addition of the olefin to the complex. The famous Zeise's salt, first isolated in 1827 [16], is prepared by bubbling ethylene through an aqueous solution of potassium tetrachloroplatinate(II) from which the yellow crystals of the complex, $K^+[C_2H_4PtCl_3]^-.H_2O$, are precipitated. The reaction is catalysed by tin(II) chloride [17]. The bis-ethylene rhodium complex, 1.1, is similarly prepared [18].



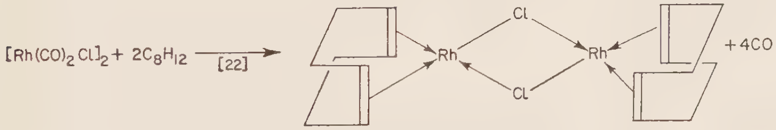
1.1

Aqueous solutions of silver nitrate or perchlorate also react rapidly with olefins. It has been noted that the addition of fluoroboric acid to silver nitrate gives a surprisingly large increase in ethylene adsorption and it was suggested that this may be due to a lowering of the degree of hydration of the silver ion in solution [19]. Non-aqueous solvents such as alcohols, acetone or acetic acid have been used in these reactions and, in the case of hydrolytically unstable complexes such as $C_5H_6AgClO_4$, benzene or ether solutions are used [20].

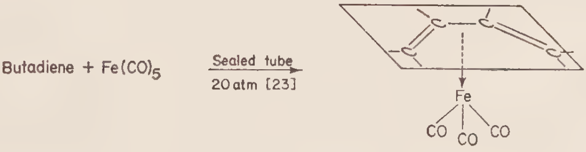
The butadiene complexes of the copper(I) halides are prepared by the direct reaction of anhydrous copper(I) halides with butadiene at −10°, in the absence of solvents [21]. Also, the complexes $[\text{Olefin PdCl}_2]_2$, where the olefin is straight chain, may be prepared by direct interaction at room temperature of palladium dichloride and the olefin in a liquid state [21*a*].

(*b*) *Preparations from metal carbonyls*

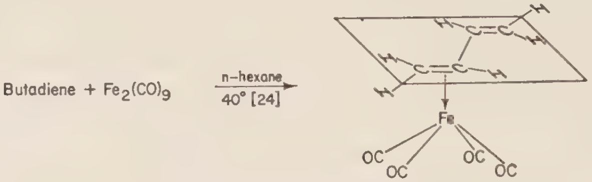
Many metal carbonyls undergo easy replacement of some of their carbon monoxide ligands. Direct reaction between the olefin and the metal carbonyl frequently occurs at room temperature or at slightly higher temperatures, e.g.



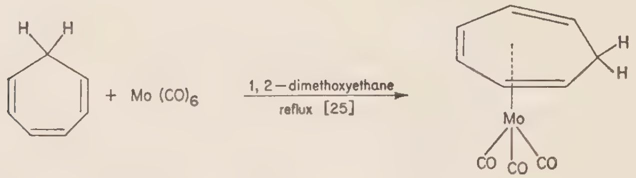
For the more volatile olefins such as butadiene, high-pressure conditions may be used,



contrast the reaction,



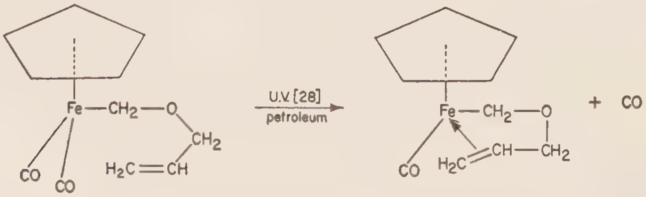
With the hexacarbonyls of chromium, molybdenum and tungsten, ethers which can act as weak ligands, such as 1,2-dimethoxyethane, may be necessary, e.g.



Irradiation of solutions of metal carbonyls in the presence of an olefin is frequently a very good method of effecting substitution of the carbonyl ligands. Indeed photochemical techniques are often more advantageous than thermal reactions – any unstable intermediates produced are formed at lower temperatures and therefore are less liable to decompose to unwanted products. Thermal and photolytic reactions may yield different products. Generally, photochemical substitutions proceed by a dissociative (S_N1) mechanism whereas thermal reactions may proceed by either S_N1 or associative (S_N2) mechanisms [26]. Thus photochemical techniques have been used to effect substitution when thermal substitution by an associative mechanism is difficult or impossible, e.g.

$$C_2H_4 + C_5H_5Mn(CO)_3 \xrightarrow[\text{petroleum [27]}]{\text{U.V.}} C_5H_5Mn(CO)_2C_2H_4 + CO$$

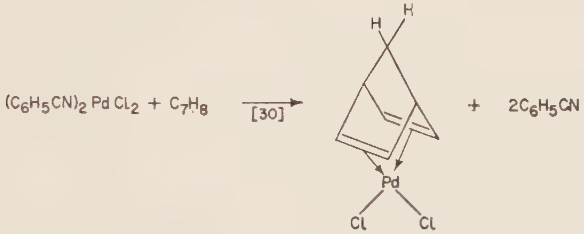
and where gentle conditions are necessary,



For the Group VI carbonyls replacement of 2, 3 or 4 carbon monoxides by olefin ligands has been achieved. However, the substitution of four carbon monoxide ligands has only been found with chelating ligands; metal–tricarbonyl systems are usually markedly resistant to substitution. In the case of iron pentacarbonyl, only one or two carbonyl groups may be displaced whilst for nickel tetracarbonyl the substitution of all four carbonyls is possible but has only been observed with chelate ligands such as duraquinone [29] (see Chapter 8).

(*c*) *Less common preparative routes*

Ligands other than carbon monoxide which may be displaced by olefins include the labile ligand benzonitrile [31], e.g.



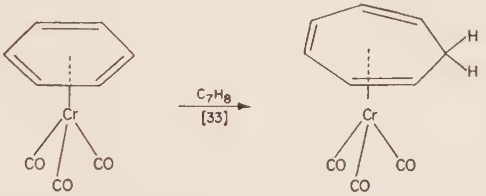
and the closely related ligand acetonitrile [31*a*],

$$(MeCN)_3W(CO)_3 \xrightarrow[\text{diene}]{\text{triene or}} (\text{triene})W(CO)_3 \text{ or } (\text{diene})W(CO)_4$$

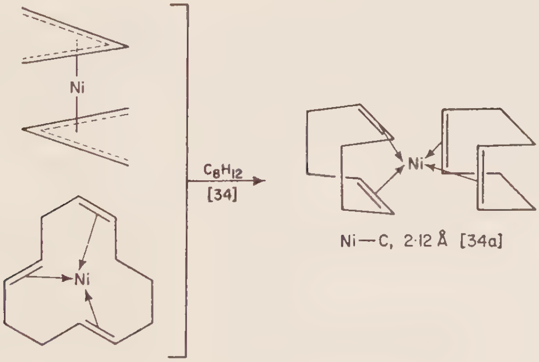
hydrocarbon ligands such as other olefins,

$$[C_2H_4PtCl_2]_2 + \text{Olefin} \xrightarrow[{[32]}]{} [\text{Olefin } PtCl_2]_2 + C_2H_4$$

and even benzene

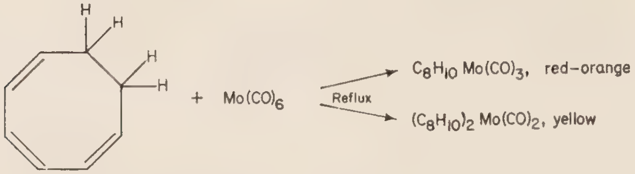


In particular, the ligands in bis-π-allyl nickel and cyclododeca-1,5,9-triene nickel are readily displaced.



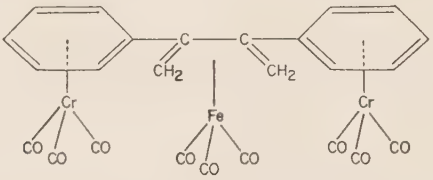
Ni—C, 2·12 Å [34a]

It may be noted that even in the case of conjugated olefins, the number of available electrons on an olefin by no means solely dictates the stoicheiometry of the olefin–metal product. Thus the reactions on pp. 9, 10 show butadiene acting as a 2- and 4-electron ligand towards iron, and cycloocta-1,3,5-triene may act as a 4- or 6-electron ligand [35], e.g.,



With phenyl-substituted butadienes, both arene and diene systems may complex to the metal:

$$CH_2{=}C(C_6H_5)C(C_6H_5){=}CH_2 + Fe(CO)_5 + Cr(CO)_6 \xrightarrow[\text{[36]}]{\text{reflux}}$$



The replacement of halide ligands, to give cationic olefin complexes, may be achieved using Lewis acids which complex the displaced halide ion and thus prevent the reverse displacement of the olefin ligand,

$$\pi\text{-}C_5H_5Mo(CO)_3Cl + AlCl_3 + C_2H_4 \xrightarrow[\text{[37]}]{\text{benzene}} [\pi\text{-}C_5H_5Mo(CO)_3C_2H_4]^+ AlCl_4^-$$

In some cases disubstitution products are found [38],

$$Re(CO)_5Cl + AlCl_3 + 2C_2H_4 \xrightarrow[\text{[38]}]{\text{cyclohexane}} [Re(CO)_4(C_2H_4)_2]^+ AlCl_4^-$$

Reductive olefination method. A general but as yet little-used route to metal olefin complexes, analogous to a preparative method employed for metal carbonyls, is the reaction of a suitable metal salt with an alkylating agent, such as Grignard reagents or trialkylaluminiums, in the presence of an olefin:

$$\begin{tikzcd}
\text{Metal halide} + RCH_2CH_2MgX \arrow[r, "\text{ether}"] & \underset{\text{unstable alkyl intermediate}}{[M(CH_2CH_2R)_x.nEt_2O]} \arrow[dl, "\text{u.v.} +"', "\text{olefin}"] \\
\text{Zero valent metal olefin complex} &
\end{tikzcd}$$

The pure olefin complex, (cyclo-octa-1,3,5-triene)(cyclo-octa-1,5-diene) iron, $C_8H_{10}FeC_8H_{12}$, has been prepared in 13% yield by this route [39]; the analogous Ru and Os complexes have been reported [39*a*]. Cyclododeca-1,5,9-triene nickel may be prepared similarly using trialkylaluminiums as the reducing agents [40].

Other preparations of olefin–metal complexes may be found on pp. 51, 211, 296. Also described elsewhere in the text are the reactions of olefins to give alkyl (p. 66), π-enyl (pp. 41–43, 66) and arene (p. 171) complexes.

C. A molecular orbital description of the bonding in organometallic complexes.

(*a*) *General comments*†

It is difficult to describe the bonding of unsaturated organic ligands to transition metal atoms in a conventional classical valence bond fashion. Thus it is necessary to employ the techniques of molecular orbital theory. The application of M.O. theory to these complexes falls into two parts. The first part, which is rigorous, is concerned with the symmetry of the complexes and of the possible molecular orbitals. The second part, which is largely concerned with the energies and relative energies of the molecular orbitals in the complexes, is more complicated: elaborate mathematics is necessary and approximations must be made. Fortunately, for fairly symmetrical molecules, we can often gain useful insight into the nature of the ligand–metal bonding by application of the relatively simple symmetry arguments.

(*b*) *Symmetry considerations*

The consideration of the symmetry of a molecule followed by the application of group theory enable us to determine which orbitals of the metal and ligands are allowed to combine to give molecular orbitals. Metal and ligand orbitals which transform in the same way under the symmetry operations of the group to which the compound belongs are capable of doing this. It turns out that we shall be chiefly concerned with two types of symmetry element. If the organometallic compound has a rotational axis of symmetry perpendicular to the plane of the organic ligand and passing through the metal, then this axis is by convention called the z-axis. Using this axis, the ligand and metal orbitals may frequently‡ be classified as σ-, π- or δ-orbitals (see Table 2).

As also shown in Table 2 the metal orbitals may be further resolved in

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† This general section serves as an introduction to the method of description of the bonding in all π-bonding ligands. It is placed here since the π-bonding 2-electron ligands are the first to be considered.

‡ This classification only applies if the symmetry of rotation of the molecule is >2.

their symmetry classification by consideration of their behaviour on inversion through the centre of symmetry. Those orbitals which change sign on inversion are called odd or ungerade (u); those which do not change sign are called even or gerade (g). This further classification assists in the consideration of the bonding of centrosymmetric molecules, such as ferrocene.

Table 2 *Symmetry classification of metal orbitals*

Symmetry with respect to rotation about the z-axis		Symmetry with respect to rotation about the z-axis *and* inversion at the metal nucleus	
Symmetry	Metal orbitals	Symmetry	Metal orbitals
σ	s, d_{z^2}, p_z	σ_g	s, d_{z^2}
		σ_u	p_z
π	d_{xz}, d_{yz}, p_y, p_x	π_g	d_{xz}, d_{yz}
		π_u	p_x, p_y
δ	$d_{x^2-y^2}, d_{xy}$	δ_g	$d_{x^2-y^2}, d_{xy}$

Since only those ligand and metal orbitals which have the same symmetry properties can overlap to form bonds, we may by symmetry considerations determine the fairly small number of combinations of ligand and metal orbitals which may give bond formation. It should be noted that we are restricting ourselves to the highest occupied and lowest unoccupied orbitals.

(*c*) *Energies of the molecular orbitals*

Theoretical calculations of M.O. energy levels, for molecules of the complexity of most organometallic complexes, at best involve numerous approximations. There are however rough rules which are partially successful in determining the orders of energy levels. Firstly, a large overlap of orbitals of similar energy leads to a high degree of stabilization. Secondly, the closer the original orbitals are in energy, the more stable the resulting M.O. will be. The energy of an atomic orbital is taken as equal in magnitude to the ionization potential for an electron occupying it, as obtained from spectral data. To obtain the energy of ligand M.O.s simple Huckel calculations are usually employed. Finally, experimental evidence about the relative energies of the M.O.s is obtained from spectral and magnetic data.

D. A description of the bonding of 2-electron ligands to transition metals

Ethylene will serve as an example of a typical 2-electron hydrocarbon ligand. Ethylene, like carbon monoxide and tertiary phosphines, belongs to that class of ligand which does not often co-ordinate readily with traditional acceptor molecules (Lewis acids, e.g. BF_3), but which forms quite stable complexes with transition metals which have some available *d*-electrons. Furthermore these ligands, unlike NH_3 for example, all have vacant, or potentially vacant, low-lying orbitals.

It is postulated for ligands like ethylene that bonding with the metal involves both a simple σ-co-ordinate link and also a back-donation of the metal electrons to the ligand. The σ-co-ordinate bond is the reason for the classification of ethylene as a 2-electron ligand.

Consider the bonding of the ethylene in Zeise's salt, $K^+[C_2H_4PtCl_3]^-$, which X-ray studies have shown the structure of the anion to be that given in Figure 2. The anion has C_{2v} symmetry; the directions of the x-, y- and z-axes are shown. The ethylene electrons which are involved in the σ-bonding of the H_2C—CH_2 system are considered *not* to be involved in the ethylene–metal bonding. If φ_1 and φ_2 are the carbon $2p_\pi$ orbitals, the π-M.O.s of ethylene are

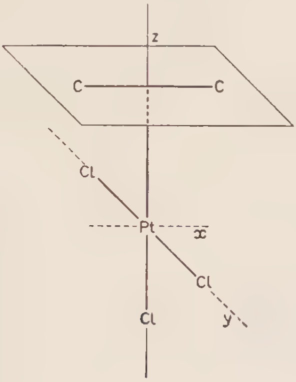

Fig. 2. Structure of the anion $[C_2H_4PtCl_3]^-$ [41]

$$\psi_1 = \varphi_1 + \varphi_2 \quad \text{and} \quad \psi_2 = \varphi_1 - \varphi_2$$

The symmetry of these orbitals and those of the platinum in the group C_{2v} are given in Table 3 (unlike the general classification in Table 2, the

Table 3 *The transformation properties of the group* C_2H_4M *according to the svmmetry group* C_{2v}

Symmetry	Ligand orbitals	Metal orbitals	Rotational symmetry
A_1	ψ_1	$s, p_z, d_{z^2},$ $d_{x^2-y^2}$	σ
B_1	ψ_2	p_x, d_{xz}	π

$d_{x^2-y^2}$ orbital has a σ-rotational symmetry since the anion has rotational symmetry lower than C_3). Pictorial representations of the various ligand and metal orbital combinations are shown in Figure 3. The extent to which these individual combinations are important is not exactly known and the bonding is usually represented as shown in Figure 4, in which the combinations of metal orbitals of σ-symmetry and those of π-symmetry are represented by two hybrid metal orbitals.† This bonding description is satisfactory in so far as it is compatible with the observed structure and interprets the lowering of the C=C stretching frequency of 60–150 cm^{-1} observed when olefins co-ordinate to transition metals. Thus the removal of electrons from the bonding π-orbital of the ethylene and the placing of electrons into the antibonding π*-orbital of the ethylene would weaken the C=C bond. There is some X-ray evidence which suggests that the C=C

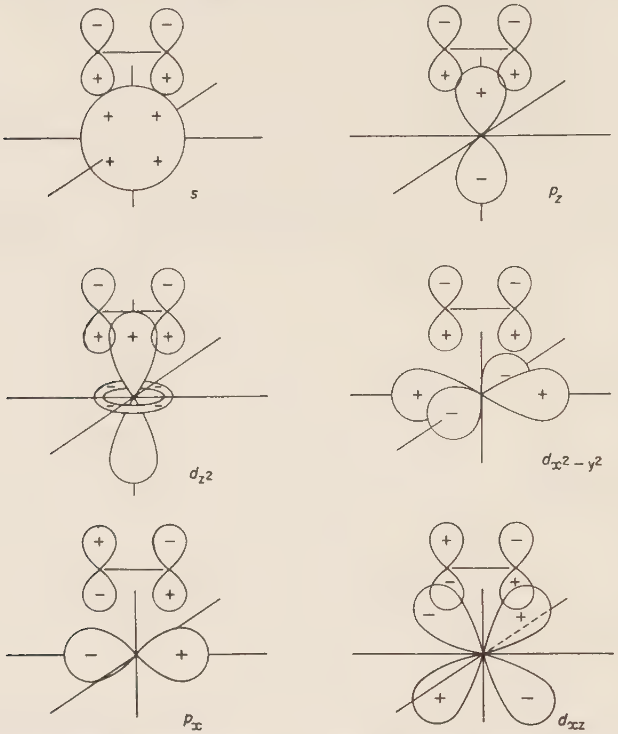

Fig. 3. Diagrammatic representation of types of orbital overlap between ethylene $2p_z$ = atomic orbitals and n*s*, n*p* and (n − 1)*d* orbitals of a transition metal

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† Because of a different choice of axes, this description of the ethylene–metal bonding differs in labelling from the description commonly found in the literature [42]. Our choice of the z-axis is simply to emphasize the resemblances between the bonding of the 2-electron ligand to the metal and that of the metal-ligand bonds of other hydrocarbon ligands.

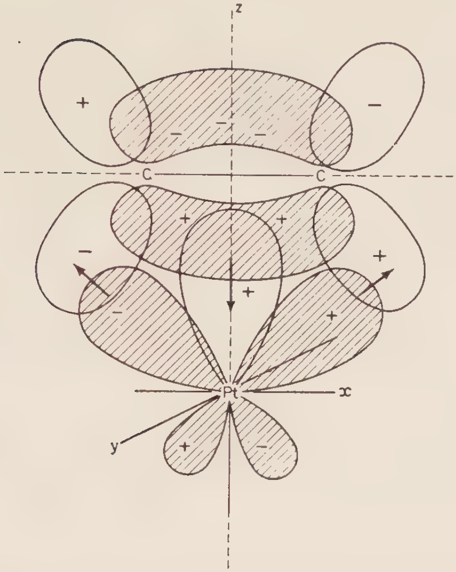


Fig. 4. Conventional representation of the metal–olefin bond; this description was originally proposed by Dewar and in a modified form by Chatt [42]

distance is increased on co-ordination; it remains unsure how reliable this evidence is (see section F(*b*)). It should be noted that other more conventional pictorial representations of the bonding of ethylene to a metal

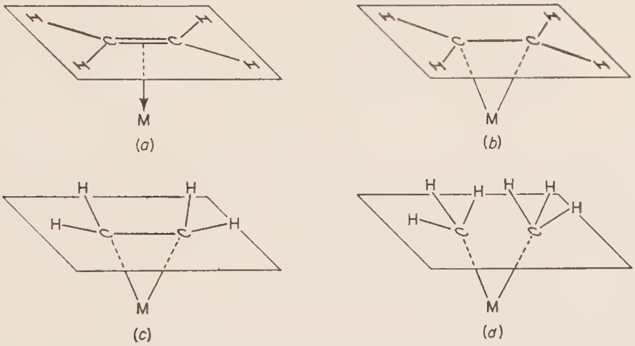
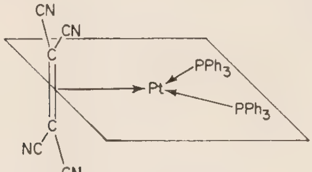
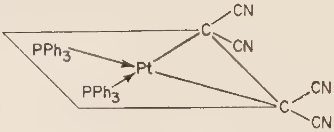


Fig. 5. (*a*) and (*b*) Representations of the olefin metal bond where the ethylene carbon–hydrogen bonds are sp^2 hybridized. (*c*) Ethylene carbon–hydrogen bonds show some sp^3 character. (*d*) Two methyl groups bonded to a metal atom

(such as are shown in Figure 5) are alternatives in the light of an M.O. approach but may be used to emphasize the relative importance of the contribution to the ligand–metal bond of the σ-bonding (*a*) or the π-bonding (*b*). However, should X-ray or neutron diffraction studies show that the configuration around the ethylene carbons is essentially tetrahedral (Figure 5(*c*)), then it would be more useful to think of the ligand–metal bond as equivalent to that of two metal–σ-alkyl bonds (*d*). A molecule where such bonding problems arise is $(Ph_3P)_2Pt(C_2(CN)_4)$ [43]. If it has structure A the tetracyanoethylene group may be regarded as a π-bonding ligand like CO, but if the olefinic carbons are coplanar with the PtP_2 system, B, the analogy with molecules such as $(R_3P)_2Pt(CH_3)_2$ may be more useful.

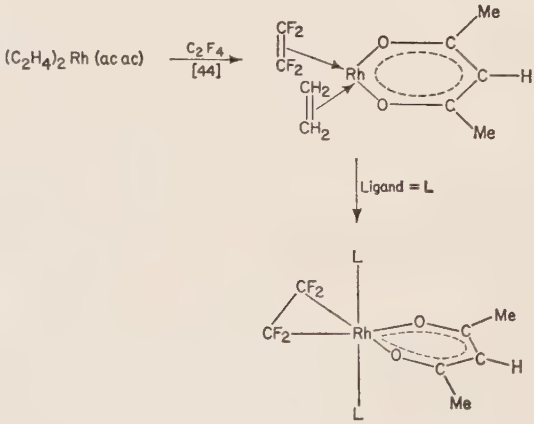


A



B

It should be noted that in the π-bonding structure A the platinum is formally in the zero oxidation state whilst in B it is in a +2 state. Other examples where the same problem arises are the tetracyanoethylene complexes *trans*-$(Ph_3P)_2MCOCl(C_2(CN)_4)$, where M = Rh or Ir [43*a*], the perfluoropropene complex $(Ph_3P)_2Pt(CF_3CF{=}CF_2)$ [43*b*] and some tetrafluoroethylene complexes, viz.



$$(Ph_3P)_2\,NiC_2H_4 \xrightarrow[[44]]{C_2F_4} (PPh_3)_3\,NiC_2F_4$$

The donor properties of tetrafluoroethylene and tetracyanoethylene would be expected to be very much reduced compared to those of ethylene, due to the high electronegativity of fluorine and of the cyanide group. For the same reason, the acceptor properties of these ligands would be expected to be considerably enhanced. It may be that these ligands bind to metal atoms mainly by back-donation from the metal to π^*-ligand orbitals (π-bonding), which in the extreme case is tantamount to a σ-bonded 3-membered ring as shown in Figure 5(*c*). Such an extreme situation has in fact been proposed for all the above tetracyanoethylene and fluoro-olefin complexes and for some unstable C_2F_4–Pt complexes [45]. In the case of the perfluoropropene complex the geminal coupling constant of the CF_2 group in the fluorine resonance spectrum is 200 c./sec. which is consistent with an sp^3 hybridized state for the CF_2 carbon. This is in agreement with a square-planar Pt(II) formulation of type B.

The X-ray structure of the fumaric acid iron tetracarbonyl complex, 1.2 [45*a*], shows that the carboxyl groups are bent out of the C=C axis, away from the $Fe(CO)_4$ group. Thus the C–COOH bond shows a little greater *p*-character than sp^2 and there is probably a considerable back-donation from the $Fe(CO)_4$ group to the $p\pi^*$-orbitals of the C=C system.

1.2

E. General comments on 2-electron ligands

The similarity between the carbonyl– and ethylene–metal bond has been noted earlier and indeed there is considerable analogy between the chemistry of metal carbonyls and metal–olefin complexes. Thus ethylenic ligands frequently complex with metals which are in a low oxidation state and which are formally rich in electrons. Of course, filled *d* orbitals of suitable energy are required for back-donation to the olefin ligand. For this reason olefin complexes are not found with the higher oxidation state complexes, e.g. the higher chlorides, of the Group IV–VII metals. Again, olefin complexes of Pt(IV) are unknown whilst for the d^8 Pt(II) they are amongst the most stable known.

In many complexes, the stability of the olefin–metal bond depends markedly on the other ligands attached to the metal. Copper(I) chloride forms more stable complexes than copper(I) bromide [46], whilst for the complex anions $[C_2H_4PtX_3]^-$, the stability of the ethylene–platinum bond falls in the order $X = Cl > Br > I > NO_2 > SCN > CN$ [47]. In the series *trans*-$C_2H_4PtCl_2L$, the order of stability L = quinoline > pyridine > ammonia > thiourea > ethylene is found [48]. The first series may be explained in terms of decreasing stability with increasing multiple bond character of the ligand. Thus the *trans* ligand causes, by competition, a lessening of back-donation from the metal to the ethylene (π-bonding).† Stability constant data over a range of temperatures have been determined for the system,

$$\text{Olefin} + [PtX_4]^{2-} \rightleftharpoons [\text{olefin } PtX_3]^- + X^-$$

where many olefins such as unsaturated ammonium ions, e.g. $CH_2{=}CHCH_2NH_3^+$ or unsaturated alcohols, e.g. $CH_2{=}CHCH_2OH$ were used, and X = Cl or Br [48*b*]. These olefin complexes are found to have stability constants comparable with those found for the heavier halogen ligands. The data showed that the bromide complexes were less stable than the corresponding chlorides, however, the enthalpy data suggested that the Pt–olefin bond was stronger in the bromo- than the chloro-complexes. In agreement the olefin–Pt stretch was found to be slightly higher (5–10 cm^{-1}) in the bromide complexes. The greater strength of the olefin–Pt bond in the bromides is explained by the argument that the $PtBr_3^-$ ion would be a poorer σ-acceptor and a better π-donor than $PtCl_3^-$.

It was also argued from these equilibrium studies that the π-acceptor capacity of an olefin is more important than its σ-donor capacity in the formation of the platinum–olefin bond.

Suggestive evidence for the above statement comes from the observation that the enthalpies of formation of the platinum complexes of olefins $olenNH_3^+$ decrease with increasing ionization potential of the olefins $olenCH_3$ [48*b*.] Thus the lower in energy the π-electrons of the olefin the more stable the resulting olefin–platinum complex. If the π-electrons of the olefin are of lower energy than the platinum acceptor orbitals, this observation suggests increased π-bond strength.

(*a*) *Infrared studies*

The lowering of the C=C stretch on co-ordination of olefins to transition metals has already been mentioned (p. 16). A normal co-ordinate analysis on Zeise's salt and the deutero analogue assigns the Pt–olefin stretch at 405–407 cm^{-1} [49]; this gives a force constant of 2·23 mdynes/Å. Also it

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† It should be noted that the possible mechanisms of *trans* effects are still debated and the relative importance of the various mechanisms is not known. This subject has been reviewed recently [48*a*].

is shown that the C=C stretch is coupled with the in-plane CH_2 scissor vibration so that the lowering of the C=C stretch upon co-ordination can only be a qualitative measure of the Pt–olefin bond strength. It is interesting to note that most of the other fundamental frequencies of ethylene co-ordinated to platinum show little change from the free ligand [50].

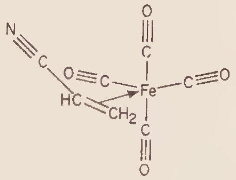
Similarly, infrared studies of a series of 4-substituted pyridine–N-oxide complexes *trans*-4-$RC_5H_4NO{\rightarrow}PtC_2H_4Cl_2$ show that the C=C stretching frequency is markedly dependent on the nature of the substituent, R, and shifts to lower frequencies with increasing electron-releasing properties of the substituent [50*a*]. It is suggested that the lowering of the C=C stretch indicates greater back-donation to the π^*-orbitals and hence a stronger metal–ethylene bond.

In the case of complexes of metals with substituted ethylenes as ligands, it appears that electron-releasing, alkyl (*non-conjugating*) substituents weaken the olefin–metal bond. Thus complexes of 2-butenes with platinum are less stable than the ethylene complex. The *cis*-butene isomer is more stable than the *trans*-isomer, and generally *cis*-isomers appear to be the more stable [51, 52]. In the case of complexes of cyclic olefins with platinum, there is an increase of the stability constant with increasing ring strain [53]. This observation is consistent with the argument that an increase in the olefin–metal bond strength would increase the length of the C=C bond and thus decrease the ring strain.

(*b*) *Effect of olefin substituents*

Stability constant studies show that *conjugated* >C=C< systems such as in crotonic acid form less stable complexes than ethylene with platinum and silver [52, 54]. Conversely, substituents which conjugate with the bonding C=C system appear to stabilize the olefin–metal bond in the case of iron. Thus although a number of 'unconjugated-olefin'–iron tetracarbonyl complexes are known [54*a*], e.g. $CH_2{=}CHClFe(CO)_4$, they are often less thermally stable than conjugated olefin analogues. A considerable number of 'conjugated-olefin'–iron tetracarbonyl complexes are known, e.g. $(RCH{=}CHX)Fe(CO)_4$, where X = CN [55], COOR, CHO, and $-CH{=}CH_2$ [56, 58, 59] have been prepared. The X-ray structure of

$CH_2{=}CHCN + Fe(CO)_5 \longrightarrow$



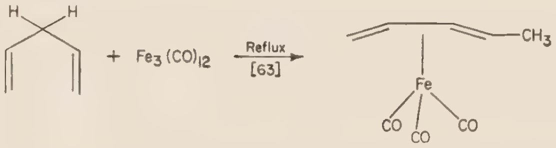
Fe—C 2·09, 2·1Å

1.3

the acrylonitrile complex, 1.3, shows that the $CH_2{=}CH$—system is π-bonded to the iron [60].

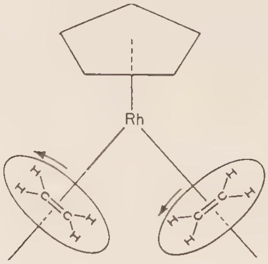
The presence of substituents in substituted ethylenes can affect the olefin–metal bond strength by, for example, steric interactions or by changing the energies of the C=C π and π^*-orbitals. In the case of conjugating substituents, a considerable change in the energies of the π- and π^*-orbitals would be expected. It has been argued for the olefin–iron tetracarbonyl complexes that the apparent increase in olefin–metal bond strength for conjugated olefins (there are no thermodynamic data) occurs because the energies of the olefin electrons more nearly match the energies of the iron electrons than in the case of ethylene and non-conjugated olefins [61, 62] (see Figure 13, p. 67).

Some unconjugated two × 2-electron olefins isomerize when they react with a metal complex forming complexes containing 4-electron, conjugated olefin ligands. Presumably in these cases the conjugated olefin forms the more stable complex. There is, however, little quantitative evidence to support the view that complexes with conjugated olefins are more stable than those with chelated olefins.



(c) The rotation of ethylene about the ligand–metal bond

The description of the ethylene bond given above is of a metal–olefin double bond. Some elegant variable-temperature proton magnetic resonance studies [64] on the complex π-$C_5H_5Rh(C_2H_4)_2$ (1.4) [65] have shown that the ethylene groups rotate about the metal–ethylene σ-axis with a rotational energy barrier of $\sim$6 kcal. However, the ethylene ligands do not readily exchange with free ethylene and it therefore appears that ethylene has a choice of metal orbitals with which to combine, so that as it

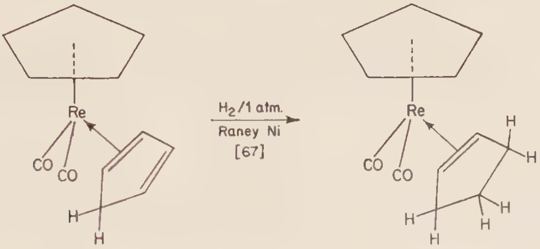


1.4

rotates it is always bonded to the metal although some orientations may be favoured [65*a*].

(*d*) *Chemical properties*

The stability of olefin–metal complexes to oxidation and reduction varies widely. In many cases the resistance of the co-ordinated C=C to reduction is markedly higher than that of the free olefin. Thus in the reduction of the π-cyclopentadiene complex, 1.5, only the free C=C bond is reduced.



1.5

There are however exceptions, for example, the reaction

$$(C_2H_4PtCl_2)_2 + 4H_2 \longrightarrow 2Pt + 4HCl + 2C_2H_6$$

proceeds quantitatively at room temperature [47].

Olefin–metal complexes are frequently labile, especially those of copper, silver and gold, and treatment of most olefin–metal complexes with ligands such as tertiary phosphines results in the displacement of the olefin. In the square-planar acetylacetonate complex (acac)Rh$(C_2H_4)_2$ the ethylenes readily exchange with free ethylene – as is also found in the square-planar platinum–olefin complexes [17]. In these planar molecules exchange of olefins may involve olefin attack on the exposed metal atom, via a five-co-ordinated intermediate [65, 66].

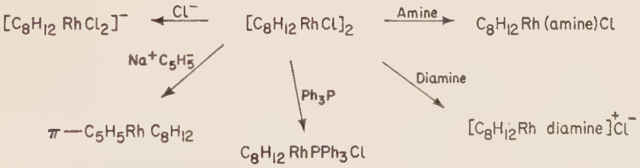
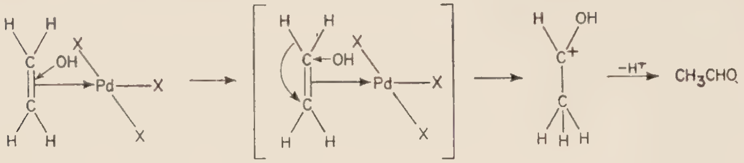


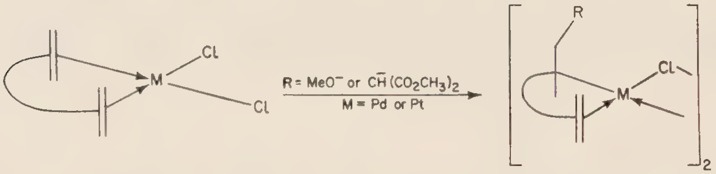
Fig. 6. Bridge cleavage reactions of cyclo-oct-1,5-diene rhodium chloride dimer

A number of complexes containing bridged halogen systems, e.g. [(olefin)$_2$RhCl]$_2$, readily react with donor ligands to undergo bridge cleavage rather than displacement of the olefin [22, 68]. Examples are shown in Figure 6.

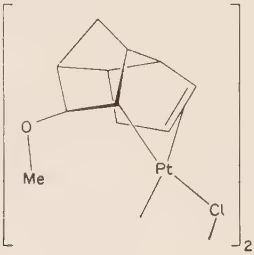
Another fairly common property of co-ordinated 2-electron ligands is their susceptibility to nucleophilic attack, an example being the industrially important oxidation of ethylene to acetaldehyde, for which the following mechanism has been proposed [69] (see p. 339). Other examples are the reduction of π-ethylene complexes to σ-alkyls by complex Group III



hydrides (see p. 66), and the attack of the methoxide [70] or ethylmalonate ion [71] on two × 2-electron ligand–palladium complexes, i.e.

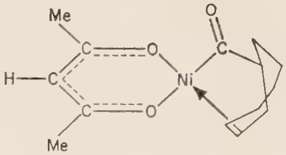


When the diene is dicyclopentadiene, reduction and proton magnetic resonance studies suggest that the product of attack by the OMe^- ion has the structure, 1.6 [72]. This structure has been confirmed by X-ray analysis [72*a*].



1.6

The cyclo-octenyl complex, 1.6*a*, which is prepared from bis-cyclo-octa 1,5-diene nickel and acetylacetone has a rather similar structure [72*b*] with the ligand forming both a σ-, and a π-bond to the metal.†



1.6*a*

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† Further examples of these σ-, π-complexes may be found in the references [72*a*, 72*d*].

F. Particular complexes of metals with 2-electron ligands

(*a*) *Copper, silver and gold*

The olefin complexes of Cu(I) and Ag(I) are readily formed but they are more labile and probably less stable thermodynamically than most of the related complexes known for other metals. Stability constant data for the equilibrium,

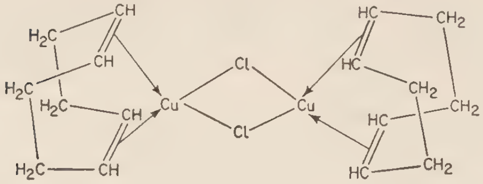
$$Ag(H_2O)_n + L \rightleftharpoons Ag(H_2O)_nL^+$$

where L = substituted ammonium ions, e.g. $CH_2{=}CHCH_2NH_3^+$, and unsaturated alcohols, e.g. $CH_2{=}CHCH_2OH$, show that the olefins form complexes of stability comparable to those formed by acetate and fluoride ions and of much lower stability than for example bromine or amines [72*c*]. The lower stability of the olefin complexes of Cu(I) and Ag(I) may be due both to the low energy of the metal donor n*d* orbitals and to the reduced availability of their acceptor n*p* orbitals.

The olefin complexes of these metals are often readily decomposed in aqueous solution and Cu(I)–olefin complexes are conveniently prepared by reduction of ethanolic solutions of copper(II) halides and the olefin with SO_2 [73]. Distribution studies of olefins between carbon tetrachloride and aqueous solutions of silver and copper salts show that the Cu(I)–olefin complexes have considerably higher stability constants than the analogous silver complexes [74]. Evidence for a relatively weak olefin–metal bond in the complexes of both metals comes from infrared and Raman spectra which show that usually the stretching frequency of the co-ordinated C=C is lowered by only 50–60 cm^{-1} compared with a lowering of ~120 cm^{-1} found for most olefin–platinum complexes. In the acrolein complex $[(CH_2{=}CHCHO)CuCl]_x$ the C=C stretch is lowered by 90 cm^{-1} [74*a*].

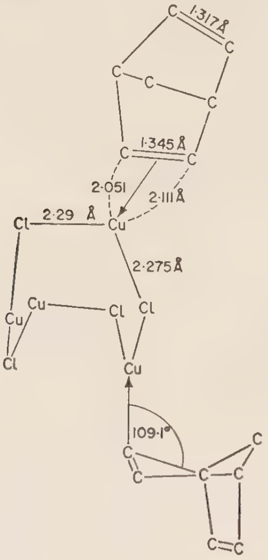
Despite their lability, many of the silver–olefin complexes may be isolated as their nitrate or perchlorate salts and, in most cases, the ratio of co-ordinated C=C groups to the metal atom is 1 : 1. However, the stoicheiometry of the isolated olefin complexes does not necessarily indicate the nature of the species in solution. For example, in solution norbornadiene forms a 1 : 1 complex with Ag(I), whilst the solids isolated from the solution may have the stoicheiometry $C_7H_8(AgNO_3)_2$ [30] or $C_7H_8AgNO_3$ [53, 30].

Cyclo-octa-1,5-diene acts as a bidentate ligand to Cu(I) in the complex $[C_8H_{12}CuCl]_2$. X-ray studies show the structure, 1.7, where the copper atoms have a tetrahedral environment and the cyclo-octa-1,5-diene has the boat form [75]. The complex $(C_8H_{12})_2CuClO_4$ which has a copper : cyclo-octa-1,5-diene ratio of 1 : 2 has been reported; its structure is unknown [75*a*].



1.7

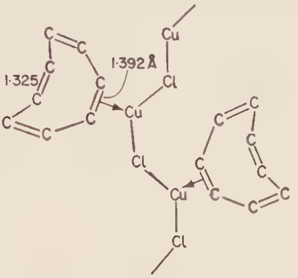
The crystal structure [76] of the norbornadiene complex $(C_7H_8CuCl)_4$, 1.8, shows the tetrameric nature of the molecule with the Cu and Cl atoms



1.8

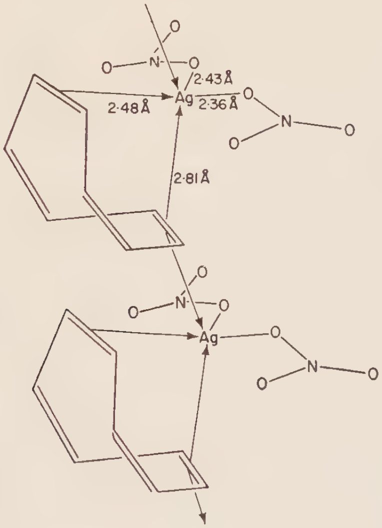
forming an 8-membered tub-shaped ring. Only one C=C of the olefin co-ordinates to each copper atom. The copper atom has a distorted trigonal planar environment similar to the cyclo-octatetraene structures discussed below and unlike the cyclo-octa-1,5-diene complex. Two other features of the structure of the norbornadiene tetramer are of interest. Firstly the bond distance of the co-ordinated C=C is *not* significantly longer than that found for the C=C of the free olefin although the stretching frequency is lowered by about 100 cm^{-1}. This suggests that the infrared spectrum might be a rather more sensitive indication than X-ray distances of the degree of olefin–metal bonding. Secondly, the co-ordinated C=C is not quite symmetrically bound to the copper atom. Such asymmetry is found for a number of olefin complexes of copper and silver which suggests that it may arise from the nature of the metal–olefin bond rather than from steric requirements of the olefin or from crystal forces.

The structure of cyclo-octatetraene Cu(I) chloride, 1.9, consists of continuous chains formed by the copper and chlorine atoms with one C=C system closely bonded to each Cu(I) atom [77]. Again the C=C system is essentially coplanar with the Cu and adjacent Cl atoms. A chain structure



1.9

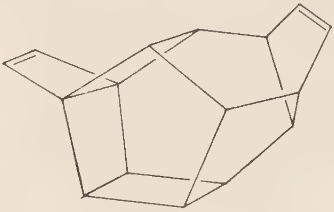
is also found for the complex $C_8H_8AgNO_3$ in which the silver ion interacts with two non-adjacent C=C systems of each cyclo-octatetraene molecule, 1.10. The short distance found between the silver ion and one of the oxygens of the nitrate group suggests that there is some covalent bonding. The



1.10

C=C distances in the cyclo-octatetraene do not appear to be lengthened [78]. The norbornadiene complex $C_7H_8(AgNO_3)_2$ is similar to the cyclo-octatetraene complex 1.10, in that it consists of Ag–NO_3 chains linked by the olefin [78*a*]. In refluxing solutions of silver salts in cyclo-octatetraene the cyclo-octatetraene may dimerize forming a number of isomeric olefins

$(C_8H_8)_2$. The structure of a cyclo-octatetraene dimer: silver nitrate complex isolated from these solutions has been studied [79]; the ligand has the structure, 1.11, and each silver ion appears to be closely associated with the double bonds of two different dimer molecules. The structure of a humulene silver nitrate complex has been determined by X-ray analysis and is given in 1.11*a* [79*a*]. A silver–bullvalene complex has been prepared and the rather interesting crystal structure determined by X-ray diffraction [79*b*] is shown in 1.11*b*.



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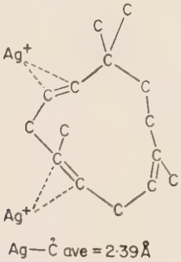
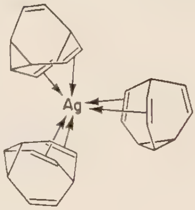
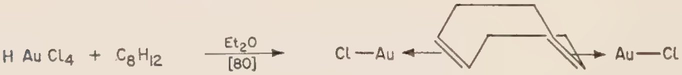


1.11*a*



1.11*b*

Cyclo-octa-1,5-diene forms complexes with Au(I) and Au(III) [80], e.g.



There is also evidence for the complex $C_8H_{12}AuCl_3$ [80]. With norbornadiene, complexes such as $C_7H_8Au_2Cl_4$,$(C_7H_8)_2Au_2Cl_4$ are formed. It is suggested they are mixed Au(I)–Au(III) derivatives, e.g. C_7H_8—Au—Cl—$AuCl_3$ [80*a*]. A series of complexes LAuCl where L is a cyclic olefin have been described and their C=C stretch is ~120 cm^{-1} lower than in the free olefin [80*b*].

Complexes with benzene. Silver salts such as $AgClO_4$ readily dissolve in benzene. Conductivity measurements suggest that ion-pairs $C_6H_6Ag^+ClO_4^-$ are present [81], and indeed the benzene–silver bond energy appears to be of the same order as in ordinary covalent bonds [82]. Related complexes of Cu(I), Hg(I) and Ga(I) are known. The structures of the complexes $C_6H_6AgClO_4$ and $C_6H_6CuAlCl_4$ are shown in Figure 7.

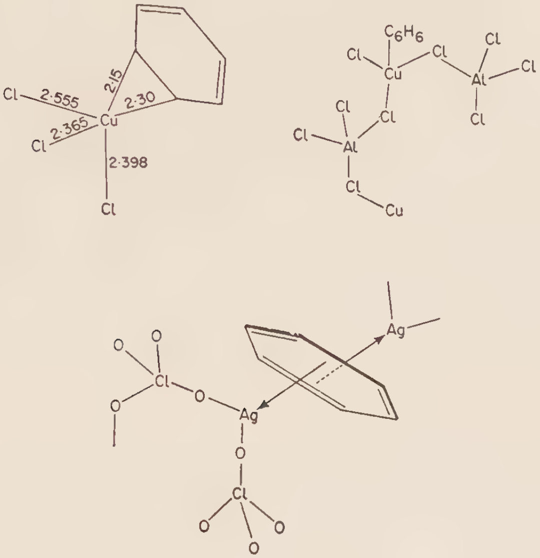


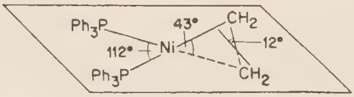
Fig. 7

The Cu(I) complex has a corrugated sheet structure formed by the copper and the $AlCl_4^-$ ions [83]. The benzene forms a π-type bond with the copper through *one* carbon–carbon bond only and the plane of the benzene ring is above the copper atom. The three Cu–Cl distances are between 2·3 and 2·6 Å, which are about the distances expected for single covalent bonds. Thus to a first approximation, the copper atom has a tetrahedral environment. It is interesting that the co-ordinated C=C distance is 1·35 Å, being *shorter* than the other C=C of the ring (1·43 Å). Possibly there is back-donation from the copper into ring anti-bonding orbitals which extend mainly over the 'unbonded' carbon atoms. In contrast the analogous silver complex $C_6H_6AgAlCl_4$ has been found to have infinite planar sheets in which the silver is five-co-ordinate. Each benzene bonds at its edge to only one silver atom and the plane of the ring makes an angle of 98° with the C=C–Ag plane: the Ag–C lengths are 2·92 and 2·47 ± 0·06 Å [82*a*].

As shown in Figure 7, the silver–benzene complex forms chains where the silver atoms are bound to two benzene rings, thus C_6H_6—Ag—C_6H_6—Ag—. Again only two carbon atoms of a ring are bonding to one silver atom, and the plane of the ring makes an angle of 101° with the C=C–Ag^+ plane [82].

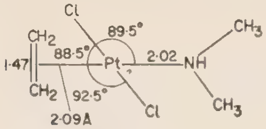
(*b*) *Nickel, palladium and platinum*

Platinum–olefin complexes were amongst the earliest known organometallic complexes and Zeise's salt, $K^+[C_2H_4PtCl_3]^-.H_2O$, was first described in 1827 [16]. Many olefin complexes of Pt(II) and Pd(II) are known and they fall into two classes, the monomeric complexes, e.g. [olefin $MCl_3]^-$, [*cis*-diolefin MCl_2] or [*trans*-olefin MCl_2 (donor ligand)], and the dimeric complexes with bridging halogens, e.g. [olefin $MCl_2]_2$ or $[(\text{olefin})_2MCl]_2$. Nickel–olefin complexes are less stable and few are known at present (see p. 11). For a given olefin ligand the general order of stability Pt > Pd > Ni is found. The crystal structure of $(Ph_3P)_2NiC_2H_4$, 1.11*c*, shows that the plane through the NiCC atoms is inclined to the plane through the NiP_2 atoms by 12° [83*a*].



1.11*c*

The olefin–platinum complexes are usually square-planar, as shown by X-ray studies and the isolation of all three isomers of $C_2H_4PtClBrNH_3$ [84]. The structure of Zeise's salt is given in Figure 2. In this structure and



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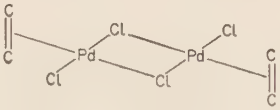
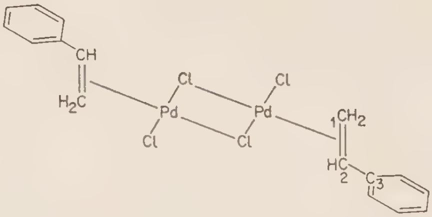


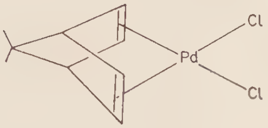
1.13

that of *trans*-$C_2H_4PtCl_2(NH(CH_3)_2)$, 1.12 [85], the C=C system of the ethylene is symmetrically bound to the platinum. The C=C distances appear to be longer than is found in free ethylene, in agreement with the observed decrease in C=C stretching frequency of 120 cm^{-1}. The X-ray determinations of the structures of the dimeric complex $(C_2H_4PdCl_2)_2$, 1.13 [86], and of the styrene analogue $(C_6H_5CH{=}CH_2PdCl_2)_2$, 1.14, [86],



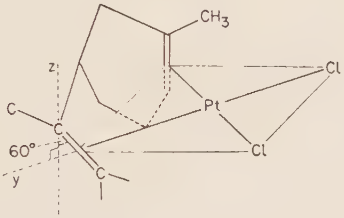
1.14

show the expected configuration for the co-ordinated C=C—Pd system. The C=C distances for the two styrene ligands of ~1·45 Å, are apparently longer than those found for the free ligand. A rather anomalous situation arises with the complexes $C_7H_8PdCl_2$, and dipentene $Pt(II)Cl_2$. The X-ray structure of the norbornadiene complex 1.15 [87] determined at



1.15

−140°C [88], shows that the distances of the co-ordinated C=C systems (1·360 ± 0·01 Å) are not significantly longer than those found in the free ligand although the C=C stretching frequency is lowered by about



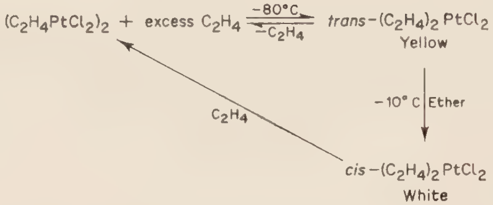
1.16

100 cm^{-1}. Similarly for the dipentene complex, 1.16, the carbon–carbon distances are normal within the limits of accuracy of the determination [89].

Thus it appears that although the C=C stretching frequency is invariably lowered on co-ordination of the olefin, the C=C distance may not be detectably longer. In these complexes there is a heavy metal near the C=C carbons and also there may be large-amplitude rotational oscillations of the co-ordinated C=C system about the C=C metal bond [90]; it may be that the small observed increases in the C=C distances of the olefin on co-ordination are not significant within the experimental error, and that the co-ordinated C=C bond is at the most only *very slightly* longer than in the free olefin.

As also shown in 1.14, in the styrene complex the C=C system is asymmetrically bound to the metal with the palladium atom nearer the terminal $=CH_2$ group. The C_1, C_2, C_3 plane is, however, still perpendicular to the plane of the $(PdCl)_2$ system. Another kind of asymmetry is found in the dipentene complex 1.16, in that one C=C bond is tipped 60° in the plane normal to the plane of the $PdCl_2$ atoms and perpendicular to the y-axis. The former distortion may arise from the asymmetry of the π- and π*-orbitals of the free styrene whereas the distortion of the dipentene ligand is presumably due to steric requirements of the dipentene.

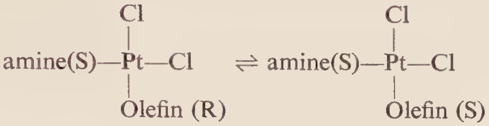
Trans effects. In these square-planar olefin complexes, ligands which are *trans* to the olefin readily undergo displacement reactions [91, 92, 93]. The *trans* effect of ethylene is apparent in the greater stability of the white *cis*-bis-ethylene complex *cis*-$(C_2H_4)_2PtCl_2$ compared with the very unstable yellow *trans*-isomer [48, 14]. The *trans*-isomer readily isomerizes to the *cis*-isomer in ether solution [94].



Also *cis*-(1-octene)$_2$PtCl$_2$ is readily prepared [95] whilst no *trans*-isomer was detected.

The greater instability of the *trans*-bis-ethylene isomer may arise since both ethylenes require back-donation from the same metal orbitals. It is interesting that in the styrene–palladium complex and in Zeise's salt, the M–Cl bonds *trans* to the C=C ligands are longer than those *trans* to a chlorine ligand. On the other hand in *trans*-$C_2H_4PtCl_2(NH(CH_3)_2)$ no relative lengthening of the Pt–N is found. Since the nitrogen is bound to the platinum by a predominantly σ-bond whereas the M–Cl bonds may have some π-character as well, the differential lengthening suggests that the ethylene ligand has a more marked *trans*-effect on the metal π-orbitals than on the metal σ-orbitals. It follows that the greater the back-donation of the metal to the olefin (i.e. the stronger the olefin–metal bond) the less will be the electron–electron repulsion between the metal-orbitals and the chlorine *p*-electrons. Thus an increase of olefin–metal bond strength should give rise to an increase in metal–chlorine bond strength. On the basis of this argument, and a study of the metal–chlorine stretching frequencies for the series of *cis*-complexes (olefin)$_2$PtCl$_2$, the following order of olefin–metal bond strengths for the olefin ligands has been found, $(CO)_2 >$ norbornadiene > cyclo-octatetraene > cyclo-octa-1,5-diene > bis-ethylene > dicyclopentadiene > dipentene [94].

A number of optical isomers of olefin–platinum complexes have been prepared and resolved [94*a*, 94*b*]. The *cis*- and *trans*-isomers of the general formulation 1.17 and 1.18 have been prepared where L = R- or S-α-phenethylamine. There is the very interesting observation that if an olefin with symmetry different from C_{2v} or D_{2h} is equilibrated with the *cis*-isomer, 1.17, then the olefin becomes an asymmetric centre and diastereoisomers are generated which can be resolved by fractional crystallization. In other words the constant for the following equilibrium is $\neq 1$ [94*a*].



$$\begin{array}{c} \text{Cl} \\ | \\ \text{amine(S)—Pt—Cl} \\ | \\ \text{Olefin (R)} \end{array} \rightleftharpoons \begin{array}{c} \text{Cl} \\ | \\ \text{amine(S)—Pt—Cl} \\ | \\ \text{Olefin (S)} \end{array}$$

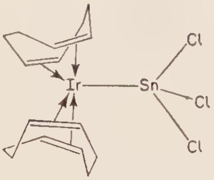
1.17 1.18

Diastereoisomers are not formed in the case of the *trans*-isomer. It is suggested that the *cis*-isomer shows a preference for a given optical isomer by virtue of interaction between the olefin ligand and the optically active amine.

Finally, it may be noted that, since the changes in stretching frequencies of C=C systems on co-ordination may depend on factors other than just the effect of the olefin–metal bond (for example steric changes in the olefin and vibrational coupling effects), small differences (10–20 cm^{-1}) between the relative lowering of ν(C=C) on co-ordination to a particular metal are not reliable indications of relative metal–olefin bond strengths.

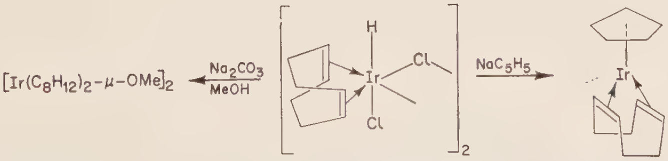
(*c*) *Rhodium, iridium, ruthenium, osmium and rhenium*

Whilst rhodium forms a number of stable complexes with 2-electron olefins (p. 23) [95*a*], at present only a few olefin complexes of iridium are known. Well-characterized complexes include the unusual cyclo-octa-1,5-diene hydride $C_8H_{12}IrHCl_2$ [95*b*], the norbornadiene complex $(C_7H_8)_2IrSnCl_3$ [96] and the related complex 1.19, whose structure has been determined by X-ray diffraction [96*a*].



1.19

The hydride complex undergoes a number of bridge cleavage reactions [95*b*], viz.



A number of stable polymeric complexes of Ru(II) of general stoicheiometry $[\text{Diene RuX}_2]_n$, where X = halogen, are known [30]. Their negligible solubility suggests that they are polymeric and it is proposed that the ruthenium is six-co-ordinate with halogen bridges. In accord with the proposal of bridging halogens, treatment of the ruthenium complexes with donor ligands may give the complexes (Diene)RuX_2L; however, some strong ligands such as pyridine may also replace the diene. The complexes [$RuCl_2$(CO)diene]$_2$, where diene = C_7H_8 or C_8H_{12}, have been prepared by addition of the diene to ethanolic solutions of ruthenium–carbonyl species [96*b*]. In both the ruthenium complexes ν(C=C) falls on co-ordination by about 130 cm^{-1}.

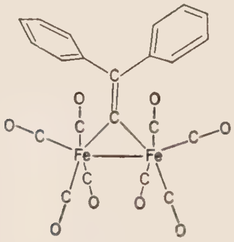
The only reported unconjugated olefin complexes of osmium are cycloocta-1,5-diene complexes $OsCl_2PPh_2Et$ [97] and $[Os(C_8H_{12})Cl_2]_x$ [98]. For rhenium a few olefin complexes are known such as the cyclopentadiene derivative π-$C_5H_5Re(CO)_2C_5H_6$ (p. 23) which may be compared to the π-$C_5H_5Mn(CO)_2$ olefin analogues (p. 125).

It is to be expected that many more olefin complexes of these metals will prove to be stable since these metals are already well known to form low-oxidation state complexes with other ligands such as carbon monoxide.

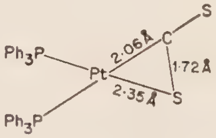
It is worth noting again that 2-electron ligands such as ethylene form stable complexes with *electron-rich* transition metals, and hence for those metals with fewer *d*-electrons, the formation of olefin–metal complexes is favoured when the metal is in a low oxidation state.

(*e*) *Miscellaneous*

When a solution of diphenylketene and $Fe(CO)_5$ in benzene are irradiated the complex, 1.19*a*, is formed. The crystal structure shows that a unique bridging carbon system is formed [98*b*].



1.19*a*

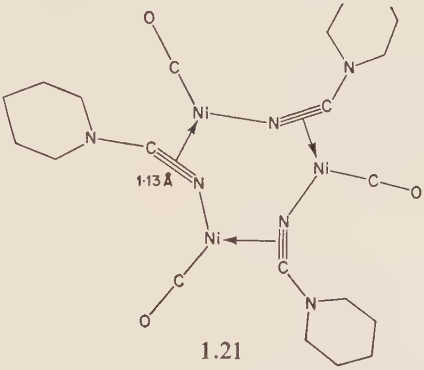


1.20

Carbon disulphide has been found to act as a 2-electron ligand to platinum in the complex 1.20 [99].

Related complexes with carbon oxysulphide, COS, or phenylthiocyanate, as in $(Ph_3P)_2PtSC$—NPh have also been isolated and are thought to contain similar C=S–Pt bonds. There is evidence for a π-bonding C=O system in the complex $(Ph_3P)_2PtOC(CF_3)_2$ [43*b*].

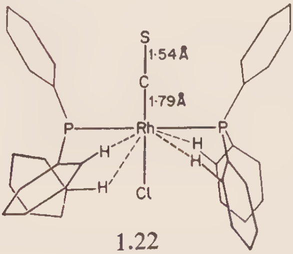
A piperidine-N-carbonitrile nickel carbonyl complex, 1.21, has been reported [100] whose structure has been found to contain (π–C^-=N)-nickel systems, [101], as shown.



1.21

The formal description of the bonding in these C=X metal complexes may be considered to be essentially analogous to that given for the C=C–metal system. However, since there is a difference of electronegativity between C and X there will be distortion of the π- and π^*-orbitals and it would therefore be expected that the M–X and M–C distances would be unequal.

Finally mention should be made of the 2-electron ligand carbon monosulphide, CS. This ligand forms complexes with transition metals and may be considered to be similar to carbon monoxide; an example is shown in 1.22 [102].



1.22

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CHAPTER TWO

Three-electron ligands

Hydrocarbon ligands which π-bond to a transition metal by a conjugated system and which contribute three electrons in the formation of the ligand–metal bond are called π-enyl ligands.†

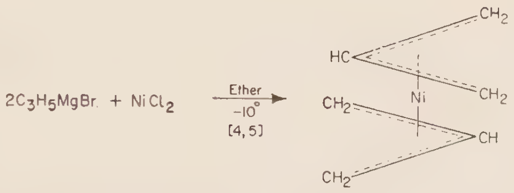
The simplest 3-electron ligand is the π-allyl group, π-C_3H_5. As discussed later (p. 212) the allyl group may also bond to metals as a 1-electron ligand, in a manner analogous to alkyl ligands; in this case the allyl ligand is called a σ-allyl group, σ-C_3H_5.

A. Preparation of π-enyl complexes

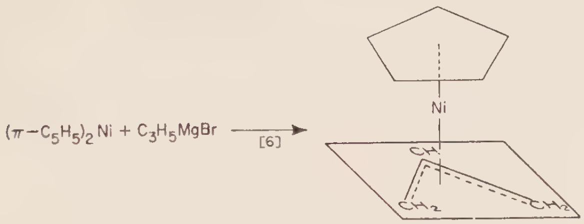
There are several general routes available.

(*a*) *From allyl Grignard reagents*

Pure π-allyl complexes are best prepared by treatment of suitable metal salts with allyl Grignard reagents such as freshly prepared allyl magnesium bromide.



Mixed π-allyl complexes may also be prepared by this route [34], e.g.



(*b*) *From allyl halides and allyl alcohols*

Allyl halides react with a variety of anionic metal complexes forming π-allyl metal bonds. The reactions are thought to proceed via a σ-allyl intermediate. Suitable anions are the metal carbonyl anions,

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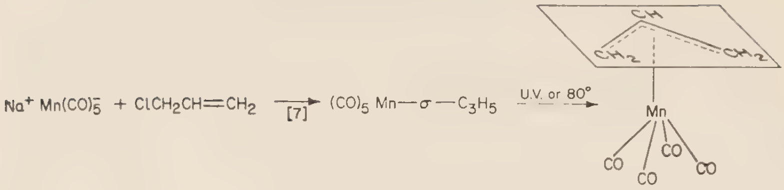
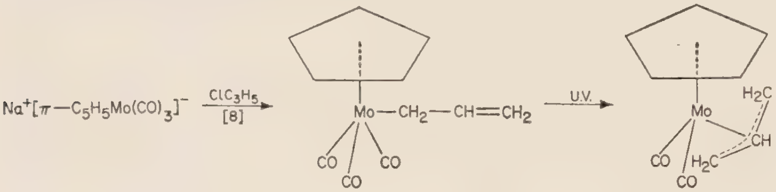
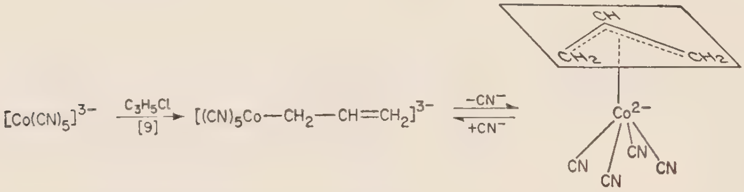
† Also called π-allylic ligands; there are several reviews of π-enyl complexes [1,2,3,31]



or π-cyclopentadienyl carbonyl anions,



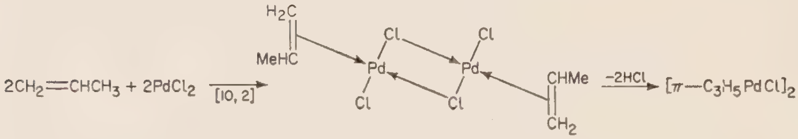
or the pentacyanocobaltate anion,

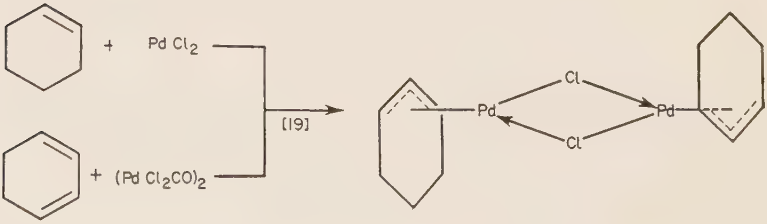


Allyl halides and alcohols will also react directly with metal compounds; examples are shown in Figure 8.

(*c*) *From olefins*

The formation of π-enyl complexes from a mono-olefin probably proceeds via the prior formation of an unstable olefin–metal complex, followed by the loss of a hydrogen atom. The reaction may be compared to that of allyl halides which lose the halogen. Examples are





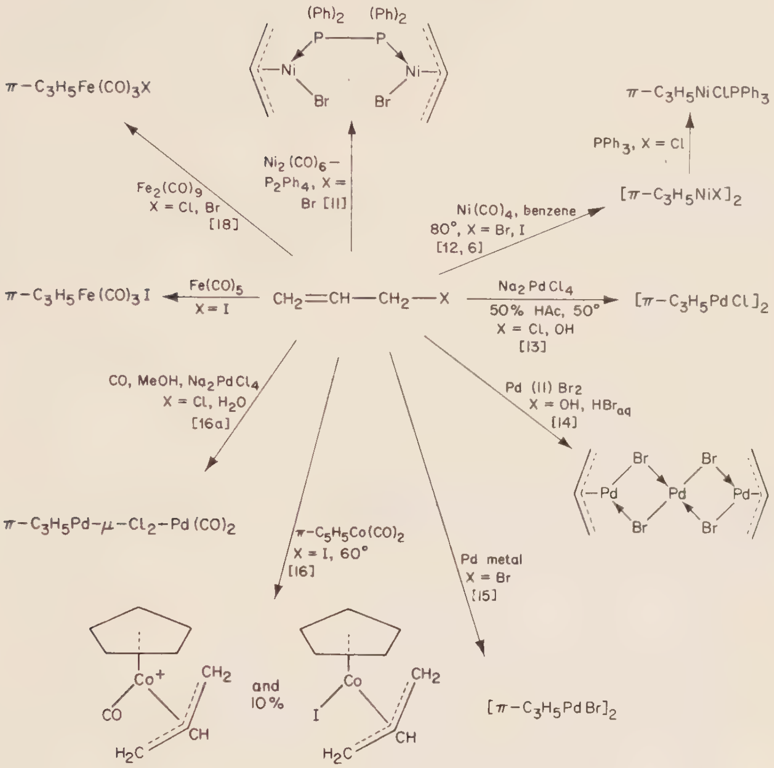
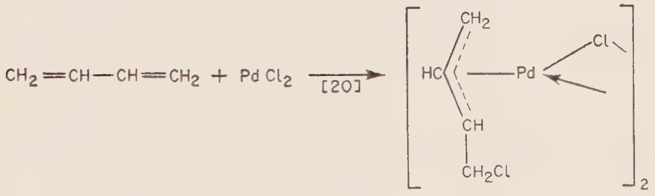
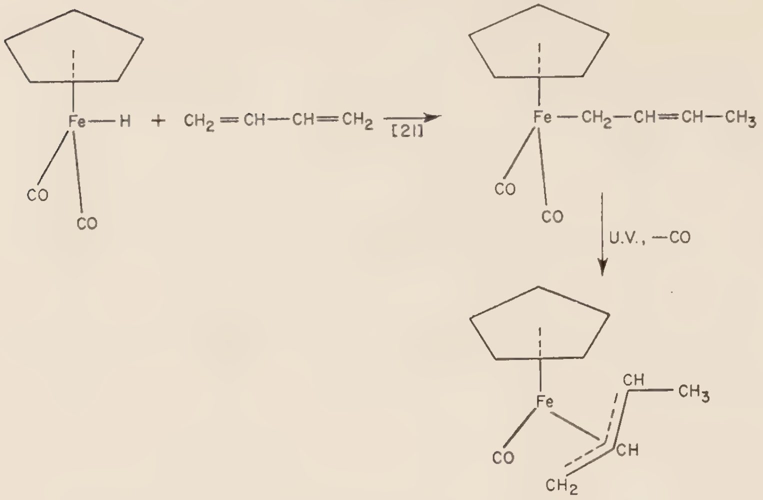


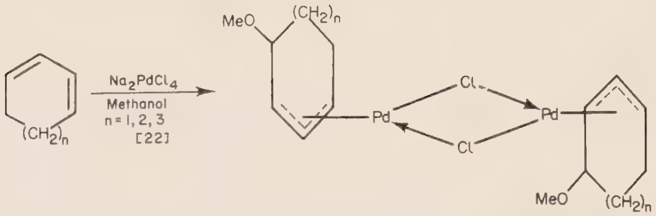
Fig. 8. The preparation of some π-enyl complexes from allyl halides

With diene olefins, the formation of a π-enyl ligand requires the addition to the diene of another group. Thus in the above equation a hydrogen atom has been acquired, presumably from the solvent, by a cyclohexa-1,3-diene, whilst the equations below show the addition of a chlorine or hydrogen atom to butadiene. The addition of $[(CN)_5CoH]^{3-}$ to butadiene is discussed on pp. 323–325.

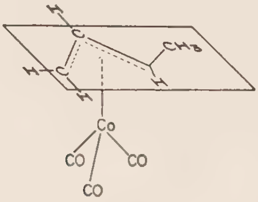




A large number of methoxy-substituted π-enyl complexes of palladium have been made by treatment of methanolic solutions of Na_2PdCl_4 with cyclic-1,3-dienes [22], viz.,

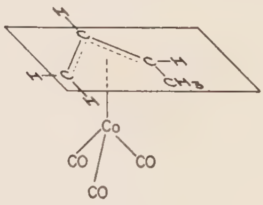


Obviously, substituted π-enyl complexes *only* may be prepared from diene olefins. In the above addition of π-$C_5H_5(CO)_2Fe$—H to butadiene mainly the 1,4-addition product is obtained. Similarly the 1,4-addition product is found with $Co(CO)_4H$ and butadiene. In this case a σ-but-2-enyl intermediate is not isolated and the reaction proceeds immediately to the π-methylallyl cobalt tricarbonyl which is isolated as a mixture of the



"Syn"

2.1



"Anti"

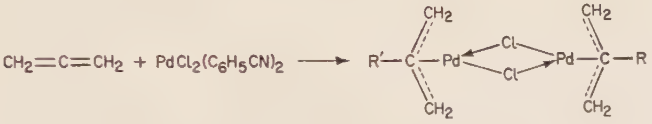
2.2

geometrical isomers, 2.1 and 2.2. The *syn*-isomer is more stable and may be obtained from the *anti*-isomer by equilibration at 80° [23].

The protonation of neutral diene metal complexes giving π-enyl metal cations is another preparative route, closely related to those above (see p. 66).

(*d*) *From allenes*

Treatment of bis-benzonitrile palladium dichloride with allene affords a variety of π-enyl complexes depending on the stoicheiometry of the reaction, and on the solvent [24, 25].

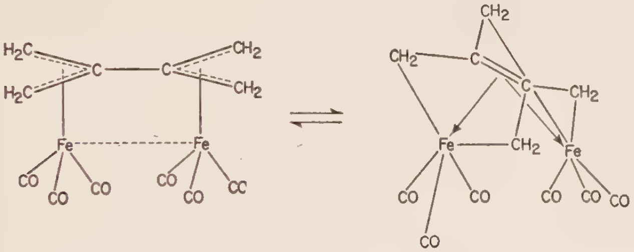


R and R′ may be Cl or —C(CH$_2$Cl)=CH$_2$

The addition of the allene to the palladium chloride complex is reversible in so far that treatment of the 2-chloropropenyl complex, i.e. where $R = R' = Cl$, with tertiary phosphines such as Ph_3P gives allene [25*a*], e.g.

$$[\pi\text{-}CH_2\text{-}CCl\text{-}CH_2PdCl]_2 \xrightarrow{Ph_3P} (Ph_3P)_2PdCl_2 + CH_2{=}C{=}CH_2.$$

With $Fe_3(CO)_{12}$, allene gives a product, 2.3, which spectral studies suggest is a tautomeric mixture [26].



2.3

B. The structure of π-enyl complexes†

Three independent X-ray studies on $(\pi\text{-}C_3H_5PdCl)_2$ dimer show the overall configuration given in Figure 9 [27, 28, 29]. The more detailed of the studies show that the plane of the three allyl carbons intersects the plane formed by the $(PdCl)_2$ system at an angle of 111·5 ± 0·9°, with the central carbon tipped away from the palladium. The $(PdCl)_2$ plane is nearer the two terminal carbons than the central carbons of the allyl groups. At

† For a review see [26*a*].

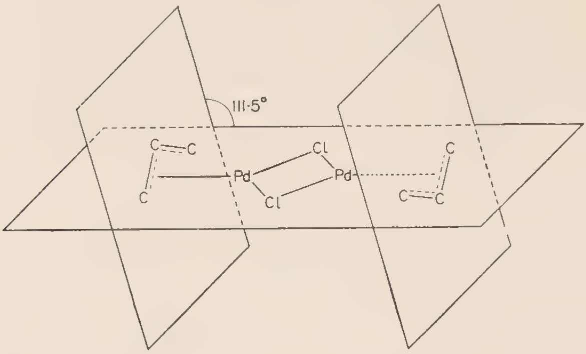
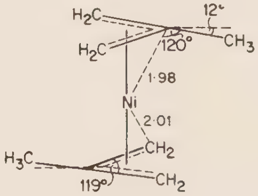


Fig. 9. The structure of the π-allyl palladium chloride dimer

-140°C the Pd central carbon distance is the same as that of the equivalent Pd–terminal carbons (av. 2·11 Å). At room temperature the Pd–central carbon distance may be marginally longer but not by more than 0·1 Å. The apparent increase of distance may arise from errors caused by thermal motions at higher temperatures. The C–C distances of the π-allyl groups are the same (av. 1·36 Å) and the Pd–Cl distances (av. 2·41 Å) are similar to those found in other complexes for Pd–Cl *trans* to olefin ligands. The low-temperature study [28] locates approximately the hydrogens of the allyl groups and, within the experimental error, they are found to lie in the plane of the allyl carbons.

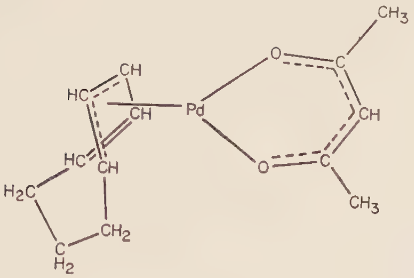
It is interesting that this complex, and related complexes of nickel, have substantial dipole moments in benzene solution (~1·5 D) [13, 12]. It may be that the molecules are able to bend easily about the axis through the two bridging chlorines or that some weak complex formation with benzene occurs.

X-ray analysis of bis-π-2-methylallyl nickel shows that it has a sandwich structure, 2.4 [30]. Acetylacetonyl(cyclo-octa-2,4-dienyl) palladium has the



2.4

structure shown in 2.5. Although there are five adjacent essentially sp^2 carbons, only three take part in the metal–ligand bond. The plane of the three allylic carbons is at an angle of 121·4° with the plane of the PdO_2 group [32]. Other structures of π-enyl complexes which have been determined by X-ray diffraction are discussed on pp. 52–55, 57 and 59.



2.5

C. The π-allyl metal bond

The configuration of the π-allyl metal system has been discussed above. The three carbons of the π-allyl group form an isosceles triangle and in this configuration the three $p\pi$-orbitals of the allyl group form three M.O.s which are represented in Figure 10.

Unfortunately the local symmetry of the π-C_3H_5M system is C_s, which

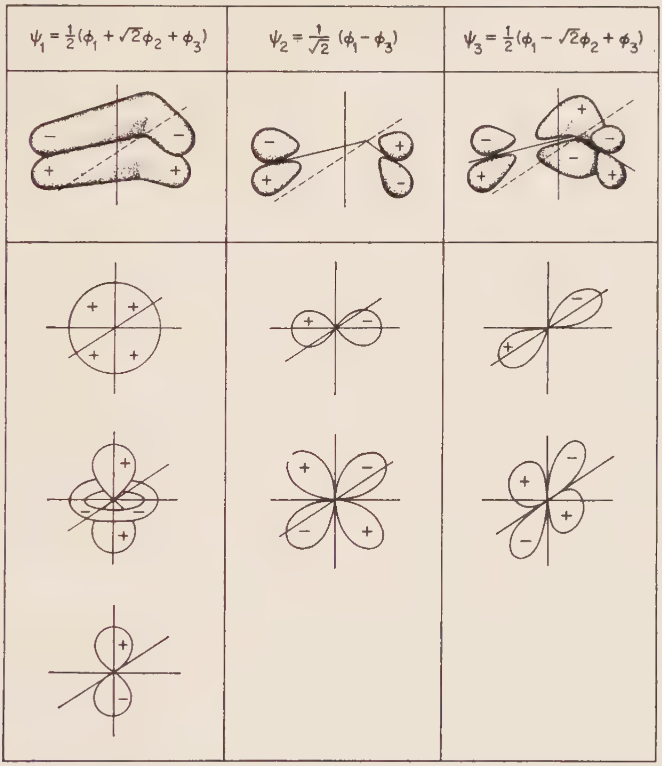


Fig. 10. Representations of the π-allyl molecular orbitals ψ_1, ψ_2, and ψ_3 and, beneath them, are the metal orbitals with which they are most likely to interact to give substantial metal–allyl bonding. The metal lies along the vertical axis, below the C_3-plane.

is very low, and symmetry arguments alone are of little assistance since, as shown in Table 4, there are a very large number of possible combinations between the ligand and metal orbitals.

Table 4 *Classification of ligand and metal orbitals of* π-C_3H_5M *system according to the symmetry group* C_s.

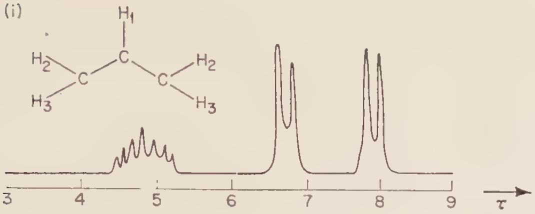
Symmetry	Metal orbitals	Ligand orbitals
A′	$s, p_y, p_z, d_{x^2-y^2}, d_{z^2}, d_{yz}$	ψ_1, ψ_3
A″	p_x, d_{xy}, d_{xz}	ψ_2

In order to distinguish from amongst the above symmetry-allowed combinations those which are most likely to form strong metal–ligand bonds, we must resort to overlap considerations. This can be done in a very rough and ready pictorial manner. Thus the d_{xy} and $d_{x^2-y^2}$ orbitals lie in a plane below the allyl plane (i.e. they are not directed towards the ligand) and this, together with the inherent diffuseness of *d* orbitals, suggests that they will be essentially non-bonding. The metal orbitals of A′ symmetry may be divided into those likely to combine more strongly with the ψ_1 M.O. than with the ψ_3 M.O. and vice-versa. This classification is made on the basis that the metal and ligand orbitals which have coincident nodal planes are more likely to have a larger overlap than those which do not coincide. On the basis of these arguments, those combinations of ligand and metal orbitals which are more likely to be important in the metal–ligand bonding are shown in Figure 10. The same combination of ligand and metal orbitals may be arrived at by symmetry considerations alone if the π-allyl group is assumed to be linear [1] or an equilateral triangle [33].

There is little evidence to decide which, if any, of the suggested combinations shown in Figure 10 are more important in the bonding than others. If the ψ_1 and ψ_2 M.O.s of the ligand are the most important in the bonding to the metal then the bonding closely resembles that of the π-ethylene–metal system. If the ψ_3 M.O. is also important in the bonding then a close analogy between the description of the π-allyl–metal bond and that of the butadiene–metal bond may be seen.

D. Dynamic equilibria in allyl complexes

It has been observed that the proton magnetic resonance spectra of allylic–transition metal complexes fall into essentially three classes. The σ-bonded allyls give the spectra to be expected from their written formulation $M{-}CH_2CH{=}CH_2$. Similarly most π-allyl groups, e.g. π-$C_3H_5Mn(CO)_4$, show spectra which are that of an A_2M_2X system; a typical A_2M_2X spectrum is shown in Figure 10*c*. In fact a detailed high resolution analysis



Assignment	H_1	H_2	H_3
Range of reported chemical shifts	3·5–6	5–7·6	6–9
Typical values	4·8	6·1	7·4
Relative areas	1	2	2

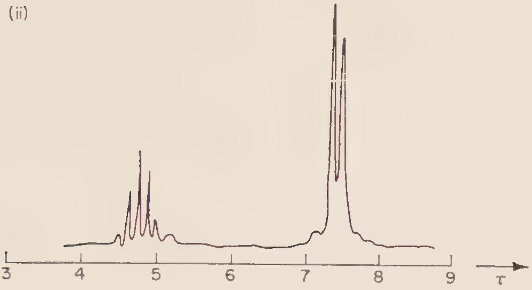


Fig. 10a. (i) A typical H^1 n.m.r. spectrum of a π-allyl, A_2M_2X, group.
(ii) H^1 n.m.r. spectrum of $Zr(C_3H_5)_4$ at −20°; an A_4X system.

of the spectrum of π-allyl $Mn(CO)_4$ shows that there is long-range coupling between the hydrogens and the actual spectrum is more complicated than that shown in the Figure 10*a* [33*a*].

The third class of spectra suggests that the allyl group has equivalent terminal hydrogens, that is, they have a spectrum such as that given in Figure 10*a*(ii), and it is typical of an A_4X system. Some allyl complexes show the π-allyl spectra, A_2M_2X, at lower temperatures and the A_4X spectra at higher temperatures. Examples are, $(allyl)_4Zr$ [33*b*, 33*c*], $(allyl)_4Th$ [31], $(allyl)_3Rh$ [33*d*], and $(allyl)_2M$; where M = Ni, Pd or Pt [33*c*] and $[(allyl)_2RhCl]_2$ [33*m*]. Other allyl compounds, including those of main group metals show A_4X spectra at temperatures as low as −70° and below, e.g. $(allyl)_4Hf$ [33*c*], $(allyl)_2Zn$, $(allyl)_2Mg$, and allyl Grignard reagents [33*c*]. Other allyl complexes only show the A_4X spectra when either the solvent they are dissolved in acts as a ligand or else contains a ligand. The best examples of these systems are the π-allyl and substituted-π-allyl palladium chloride dimers, in the presence of ligands such as R_3P,R_3As and dimethylsulphoxide [33*e*, 33*g*, 33*h*, 33*i*, 33*j*, 57]. Some nickel complexes, $C_3H_5NiBrPR_3$, have also been shown to give A_4X spectra [33*f*].

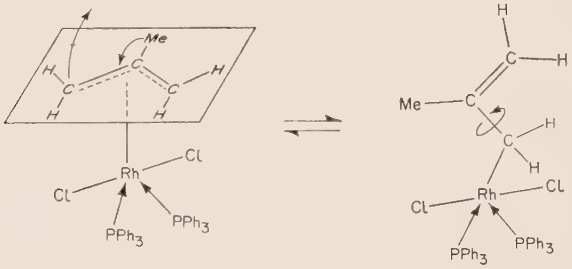
In the systems where a donor ligand is known to cause the change of spectra from A_2M_2X to A_4X it is concluded that the equilibration of the terminal hydrogens in the n.m.r. experiment is due to rapid exchange processes. Some of the postulated equilibria are:

$$\tfrac{1}{2}[\pi\text{-allyl PdCl}]_2 + \mathrm{L} \rightleftharpoons \pi\text{-allyl PdClL}$$
$$\pi\text{-allyl PdClL} + \mathrm{L} \rightleftharpoons \sigma\text{-allyl PdClL}_2$$
$$\pi\text{-allyl PdClL} + \underset{\mathrm{L}\,=\,\mathrm{L}'}{\mathrm{L}'} \rightleftharpoons \pi\text{-allyl PdClL}' + \mathrm{L}$$

In other words, it is *not* necessary to postulate in these systems the existence of allyl–metal complexes which contain other than σ-allyl–metal or π-allyl–metal systems [33*h*, 33*i*].

Those allyl complexes which show A_4X spectra independently of any particular solvent are also thought to undergo some rapid equilibrium processes. Mechanisms to achieve terminal hydrogen equilibration which have been postulated included the familiar σ- to π-conversion, rotation of the CH_2 groups about the C–C bond and a rotating over of the ligand via a planar MC_3 system.

The mechanism proposed for the interconversion of the *syn*- and *anti*-hydrogens in a methyl allyl rhodium complex, 2.5*a*, is



2.5*a*

Apart from n.m.r. spectra, evidence for equilibrium processes in allylic complexes arises in the rapid epimerization of the (−) diasterioisomer of chloro(1-acetyl-2-methylallyl)(S-α-phenylethylamine)palladium(II) above −20° [33*l*]. Also, the electronic spectra of some π-allyl complexes have been found to be very solvent sensitive [33*k*].

E. The chemistry of particular π-enyl complexes

A variety of the known π-enyl complexes is shown in Tables 5 and 6.

Table 5 π-*Enyl metal complexes*(a)(b)(c)

	Colour	M.pt or b.pt/mm. Hg	References
π-enyl carbonyls			
π-allyl $Mn(CO)_4$	Pale yellow	52–53·5°	[7, 34]
[π-1-methyl allyl $Fe(CO)_3]^+$	Yellow	—	[79]
π-allyl $Co(CO)_3$	Orange	−33° (39·15 mm)	[35, 36, 37]
π-enyl halides			
$[(\pi\text{-allyl})_2 RhCl]_2$	Yellow-orange	—	[37*a*]
[π-allyl $NiBr]_2$	Red	93–95° d	[6]
[π-allyl $NiI]_2$	Dark red	118–120° d	[12]
[π-allyl $PdX]_2$ where X = Cl, Br, I	Yellow-deep to yellow	145–200°	[38, 39, 40, 41, 10, 13, 58, 62]
$[MeOC_4H_6PdCl]_2$	Yellow	97·5–99·5°	[42]
[π-cyclohexenyl $PdCl]_2$	Yellow	85–95°	[10, 19, 39]
[π-allyl $PtCl]_2$	Orange	—	[43]
[π-allyl $PtCl_2]^-$	Orange	—	[43]
π-enyl-π-cyclopentadienyls			
π-allyl $Ti(\pi\text{-}C_5H_5)_2$		—	[44, 44*a*]
π-allyl Ni-π-C_5H_5	Red	40°/0·05 mm.	[12, 34]
π-cyclopentenyl Ni-π-C_5H_5	Red	42–43°	[39, 41, 71, 72]
π-$C_7H_5F_4$Ni-π-C_5H_5	Red	93–94°	[70]
π-allyl Pd-π-C_5H_5	Dark red	64°	[47, 39, 49, 41, 70]
π-cyclohexenyl Pd-π-C_5H_5	Red	69/80° d	[48, 39, 41]
[π-cycloheptadienyl $PdCl]_2$	Yellow		[49*a*]
π-allyl Pt-π-C_5H_5	Lemon-yellow	63–64°	[41]
π-enyl carbonyl halides			
π-allyl $Fe(CO)_3X$ where X = Cl, Br, I	Yellow brown –dark brown	85–89°	[18, 17]
π-allyl NiCl(CO)	Orange	—	[50, 51]
π-$C_3H_5NiClPR_3$	Orange	—	[33*f*, 51]
π-enyl-π-cyclopentadienyl carbonyls			
π-cyclopentenyl Cr-π-$C_5H_5(CO)_2$	Yellow	74–75°	[52, 45]
π-allyl Mo-π-$C_5H_5(CO)_2$	Yellow	134° d	[8]
π-allyl W-π-$C_5H_5(CO)_2$	Yellow	—	[53]
π-allyl Fe-π-C_5H_5(CO)	Yellow	65° d	[21]
[π-allyl Co-π-$C_5H_5(CO)]^+PF_6^-$	Yellow	110° d	[54]
π-enyl-π-cyclopentadienyl halides			
π-allyl Co-π-C_5H_5I	Dark red	95·5–97°	[16]
π-allyl Co-π-C_5H_5Br	Red	96–98°	[16]

(*a*) Classified by other ligands attached to the metal.
(*b*) Pure π-allyl transition metal complexes are given in Table 6.
(*c*) Detailed references may be found in the review [1].

π-Enyl complexes differ widely in their properties; these also depend markedly on the other ligands attached to the metal. The nitrosyl ligand can also act as a 3-electron ligand and, as would be expected, the nitrosyl analogues of most of the allyl metal carbonyl complexes are known.

π-Enyl complexes may exhibit versatile catalytic properties and these are discussed in Chapter 9.

(*a*) *Pure π-allyl metal complexes*

Examples of the known pure π-allyl metal complexes are given in Table 6.

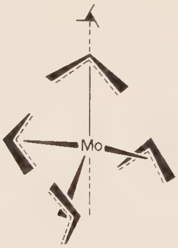
Table 6 *Some pure π-allyl metal complexes* [31, 4]†

	VA_3	CrA_3	FeA_3	CoA_3	NiA_2
		$(CrA_2)_2$ [54*b*]		RhA_3 [54*a*]	
ZrA_4	NbA_4	MoA_4 $(MoA_2)_2$			PdA_2
	TaA_4	WA_4			PtA_2

† A represents π-C_3H_5.

They have been prepared recently and few details are published. The complexes $(\pi\text{-}C_3H_5)_2M$, where $M = Ni$, Pd or Pt, show a decrease in their reactivity and catalytic properties, and an increase in thermal stability, with increasing atomic weight of the metal (see Chapter 9).

The complexes $(\pi\text{-}C_3H_5)_2M$ may be assumed to have a sandwich structure as found for bis-π-2-methyl allyl nickel. Preliminary X-ray studies‡ of tetrakis-π-allyl molybdenum suggest that there are three



2.6

equivalent π-allyl groups with the fourth disordered about a threefold axis, 2.6. Tris-π-allyl rhodium has two types of π-bonded allyl ligands [54*a*].

---

‡ T. S. Cameron, Oxford. Private communication, 1971.

(*b*) *π-Enyl complexes of nickel, palladium and platinum*

The π-enyl complexes of nickel and palladium constitute a large proportion of the known π-enyl complexes. The palladium complexes in particular are readily prepared and the majority are easily handled in air at room temperature.

The reactivity of the π-enyl complexes varies widely. The very high reactivity of bis-π-allyl nickel, 2.7, is shown by the displacement reactions given in Figure 11.

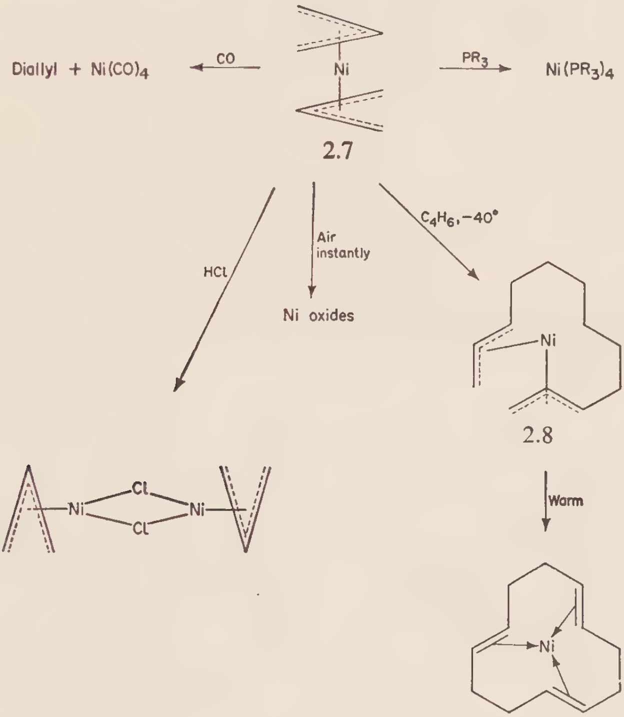
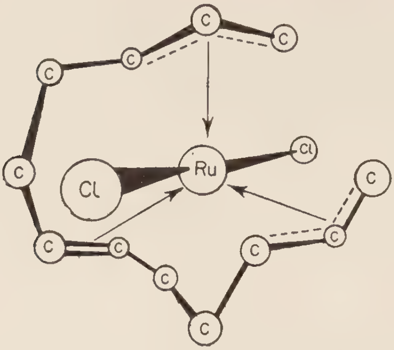


Fig. 11. Some displacement reactions of bis-π-allyl nickel [4]

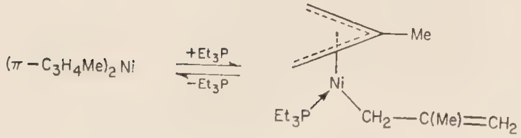
The structure shown for the bis-π-allylic complex 2.8, is supported by the structure found by X-ray analysis [55] of the ruthenium complex, 2.9 [55*a*], which contains the same dodeca-2,6,10-triene-1,12-diyl ligand.

Bis-π-2-methyl allyl nickel reversibly forms an adduct, 2.8*a*, with triethylphosphine [31]. The related 14-electron metal complex $\pi\text{-}C_3H_5NiMe$ has been reported; it decomposes at −35°C [56]. The catalytic properties of bis-π-allyl nickel are discussed in Chapter 9.

The chloro-bridged complexes $[\pi\text{-}C_3H_5MCl]_2$, where M = Ni, Pd or Pt, are rather less reactive than the bis-π-allyl complexes and in the case

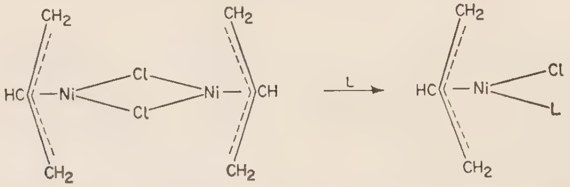


2.9



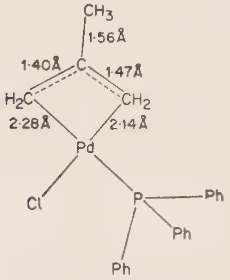
2.9*a*

of the nickel complex, bridge cleavage reactions occur in preference to the displacement of the allyl ligand [33*f*], e.g.

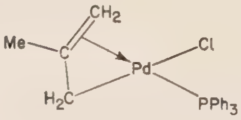


Similar reactions are known for the palladium analogue, see Figure 12.

The π-methylallylpalladium chloride dimer undergoes some interesting reactions with triphenyl phosphine. With an equimolar quantity of triphenylphosphine the complex, 2.10, is isolated and proton magnetic resonance studies suggest that the allyl group is bound unsymmetrically using both a σ- and an ethylenic, 2-electron π-bond rather than by a



2.10



2.10*a*

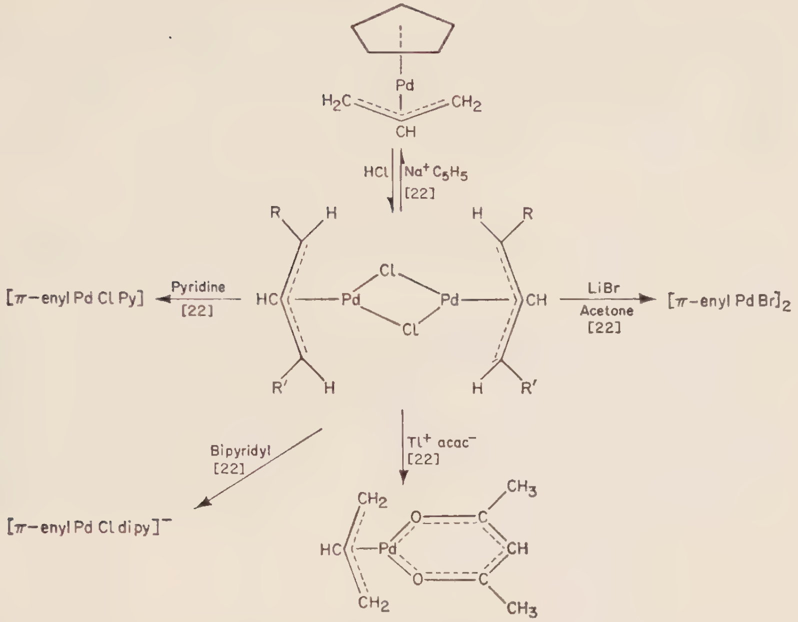
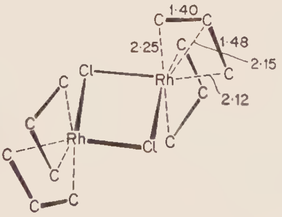


Fig. 12. Some bridge cleavage reactions of π-enyl palladium chloride dimers. The acetylacetonate anion is represented by acac⁻

symmetrical π-allyl system [57]. The structure of the complex, 2.10, has been found by X-ray diffraction, and, indeed, the C–C distances of the allyl group *are* significantly different. Again we are faced with a π-bonding system which cannot be adequately represented by a simple valence bond diagram. The valence bond way to indicate the inequality in the C–C lengths is to draw the σ-, π-system shown in 2.10*a*. However, this representation is probably not accurate since a degree of π-bonding is still expected across the longer, formally single, C–C bond. Such a change in the bonding of a π-allyl system could arise from the different *trans* effects of the Cl and Ph_3P ligands in this essentially square-planar complex.

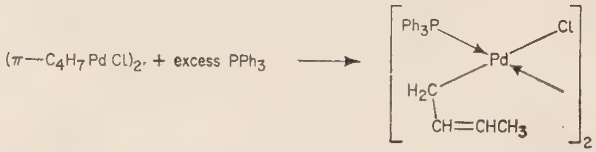
The proton magnetic resonance spectra of $[(\pi\text{-}C_3H_5)_2RhCl]_2$ and $(\pi\text{-}C_3H_5)_3Rh$ also suggest that the π-allyl group is asymmetrically bound to the metal [33*d*, 37*a*]. X-ray diffraction of $[(\pi\text{-}C_3H_5)_2RhCl]_2$ shows the structure given in 2.10*b*, where each rhodium has essentially octahedral

2.10*b*



co-ordination. Again, it is found that the two carbons effectively *trans* to the chlorines are nearest the metal and the C–C distances of the allyl ligands are unequal [57*b*].

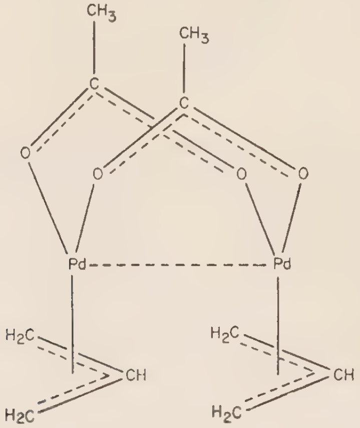
With excess triphenylphosphine ($(\pi\text{-}C_4H_7PdCl)_2$) reacts readily and the σ-allyl complex, 2.11, is isolated.



2.11

Similar reactions forming σ-allyl complexes have been suggested to occur when $(\pi\text{-}C_3H_5PdCl)_2$ is dissolved in dimethylsulphoxide or dimethylsulphide [58, 59].

Treatment of the palladium complex $(\pi\text{-}C_3H_5PdCl)_2$ with silver acetate gives the di-μ-acetato complex, 2.12 [60]; the structure has been found by X-ray diffraction [61]. In this molecule the Pd–Pd distance of only 2·94 Å



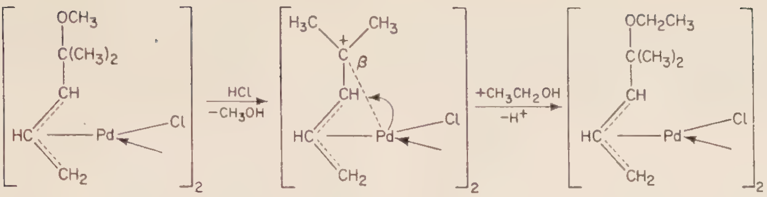
2.12

suggests some weak metal–metal bonding. The plane of the π-allyl carbons intersects the plane of the PdO_2 group at an angle of 118°.

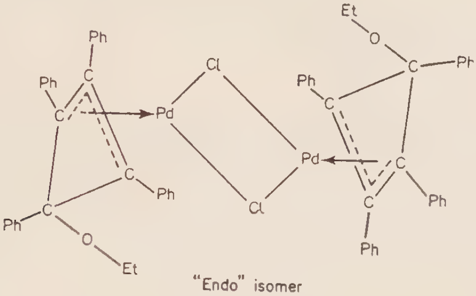
The π-enyl palladium chloride dimers are readily hydrolysed at room temperature [62, 10].

$$(\pi\text{-}C_3H_5PdCl)_2 \xrightarrow{H_2O} CH_2{=}CHCHO + CH_2{=}CHCH_3 + 2Pd + 2HCl$$

π-Enyl palladium chloride dimers which have alkoxy or halogeno groups in the 2-position with respect to the metal readily undergo alcoholysis reactions [63, 22]. The ease with which the reaction proceeds suggests a stabilization of an intermediate carbonium ion due to interaction of the β-position with the palladium, as shown,

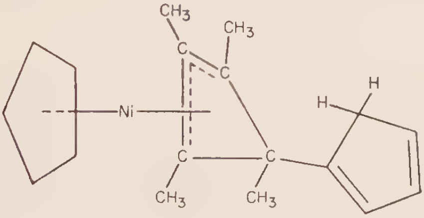


(*i*) *Cyclobutenyl complexes.* Some cyclobutenyl complexes of nickel and palladium are known. From the reaction between diphenylacetylene and palladium chloride in alcohol two isomers of stoicheiometry $(C_{30}H_{25}PdCl)_2$ may be obtained [64, 65, 66, 67]. The complexes were proposed to contain cyclobutenyl ligands; X-ray studies have confirmed this and shown them to be geometric isomers where an ethoxy group may either be in the *endo*- or *exo*-position. The structure of the *endo*-1-ethoxy-1,2,3,4,-tetraphenylcyclobutenyl palladium(II) chloride dimer is given in 2.13. X-ray studies [68] have also shown that the complex π-$C_5H_5NiC_{13}H_{17}$, prepared by treatment of the π-tetramethylbutadiene nickel dichloride dimer with sodium cyclopentadienide [69], has a cyclobutenyl system (see 2.14).



"Endo" isomer

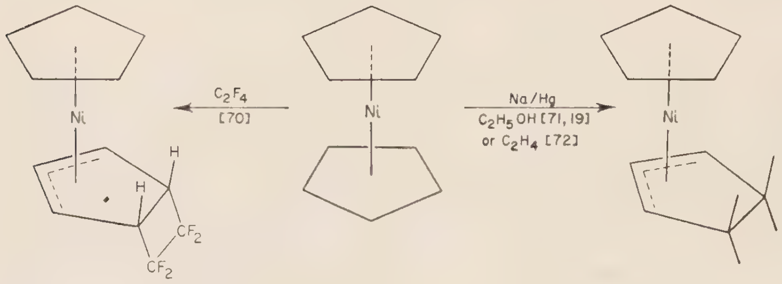
2.13



2.14

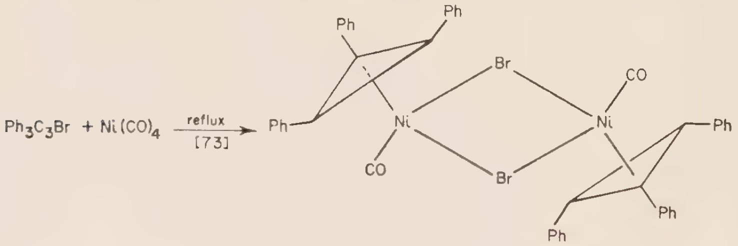
In all these cyclobutenyl systems the C_4 ring is not planar and the 'non-bonded' carbon is bent away from the metal. The dimensions of the metal–'three bonding carbon' systems are similar to those found in π-allyl complexes.

(*ii*) *Cyclopentenyl complexes.* Nickelocene readily undergoes ring-addition reactions forming red crystalline complexes containing 3-electron cyclopentenyl ligands and thus the nickel attains the 18-electron configuration.



The structure of the above nickel cyclopentenyl compound (and the palladium analogue) have been proposed on the basis of their proton magnetic resonance spectra [72].

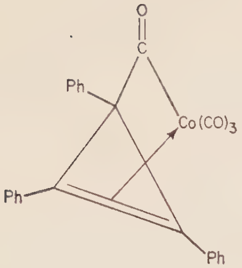
(*iii*) *Cyclopropenyl complexes.* The complexes, 2.15, and $[Ph_3C_3PdCl]_2$ are the only compounds so far known for which π-cyclopropenyl ligands have been proposed [73, 14]. There seems no clear reason why the π-cyclopropenyl ligand should not form many stable complexes but other attempts at their preparation have been unsuccessful. For example, treatment of $Na^+[Co(CO)_4]^-$ with triphenylcyclopropenyl halides gives the complex $Ph_3C_3COCo(CO)_3$ for which structures 2.16 and 2.17 have been proposed [74].



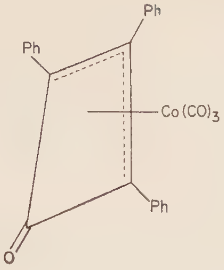
2.15

(*c*) *π-Enyl cobalt and rhodium complexes*

π-Enyl complexes of cobalt tricarbonyl are thermally unstable and readily oxidised. They may be important as intermediates in some catalytic reactions of cobalt carbonyl complexes (see Chapter 9).

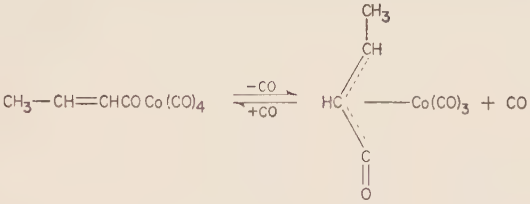


2.16



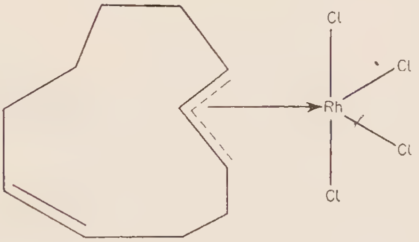
2.17

Infrared spectral studies of crotonyl cobalt tetracarbonyl 2.18, suggest that there is a reversible equilibrium with the π-enyl complex, 2.19, and



2.18 2.19

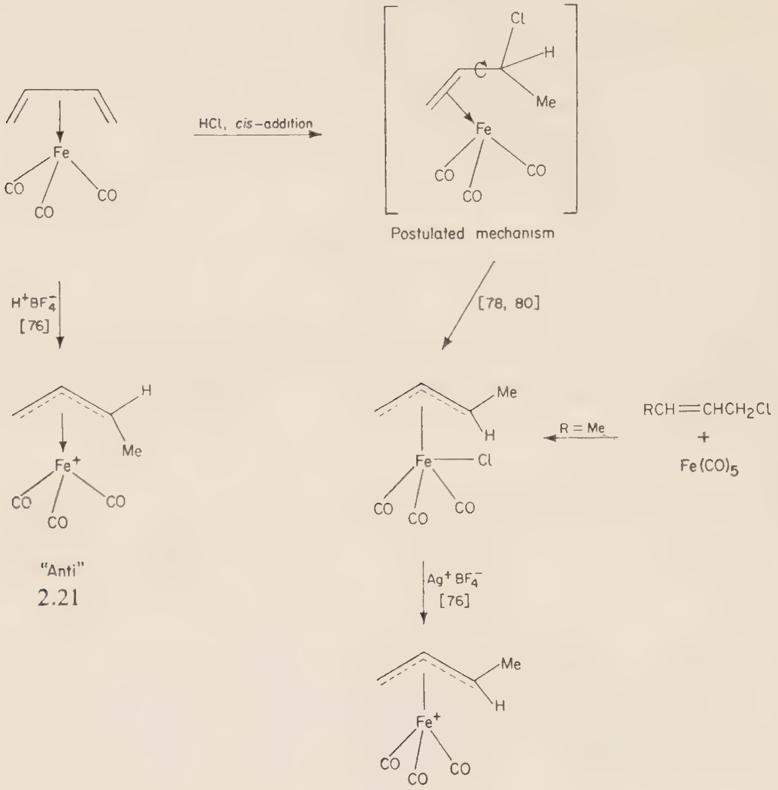
carbon monoxide. Treatment of rhodium trichloride with *trans-trans-trans*-cyclododeca-1,5,9-triene affords the unusual complex, 2.20, whose structure has been determined by preliminary X-ray analysis [75].



2.20

(*d*) *Iron π-enyl complexes*

A number of π-enyl tricarbonyl halides may be prepared by standard routes and in all cases the *syn*-isomers are the more stable [18, 76, 77, 77*a*, 82]. The anti-isomers may be prepared by the protonation of diene iron tricarbonyls with acids such as HBF_4 whose anions are virtually non-co-ordinating. With hydrogen chloride the dienes give the *syn*-isomers, as shown below. It is thought the HCl undergoes *cis*-addition to the diene and the intermediate inverts forming the *syn*-allyl product [76].



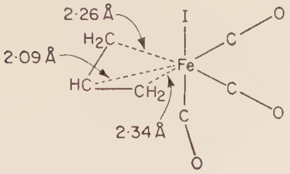
"Anti"
2.21

"Syn"
2.21

Also, as shown in the above, the protonation of diene iron-tricarbonyls with acids which have non-co-ordinating anions, such as PF_6^- and BF_4^-, affords 16-electron π-enyl cations, 2.21.

The cation, 2.21, is readily hydrolysed giving ketones [79] and the chloride, π-$C_3H_5Fe(CO)_3Cl$, thermally decomposes to butenes [81].

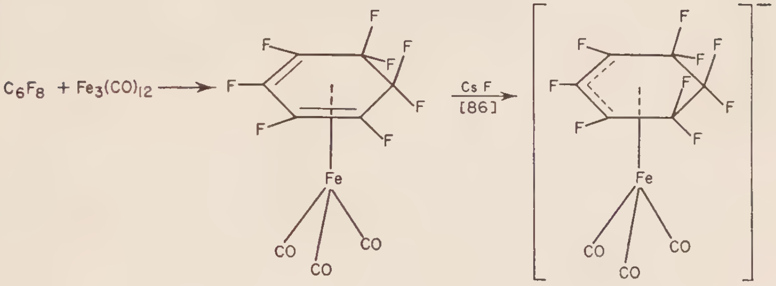
The proton magnetic resonance spectrum of π-$C_3H_5Fe(CO)_3I$ is anomalous and suggests that some equilibrium process is occurring. A monomer–dimer equilibrium involving bridging allyl groups has been proposed [82]. The crystal structure, 2.22, shows that the allyl group is asymmetrically bonded to the iron [83]. Dehalogenation of the complexes π-$C_3H_5Fe(CO)_3X$, for example with deactivated alumina, gives a red, volatile, pyrophoric compound (π-$C_3H_5Fe(CO)_3)_x$. Its dilute solutions are green and paramagnetic which suggests they contain the 17-electron monomer π-$C_3H_5Fe(CO)_3$. Concentrated solutions are red and it is postulated that the monomer is in equilibrium with a dimer (π-$C_3H_5Fe(CO)_3)_2$ which has a Fe–Fe bond [82*a*].



2.22

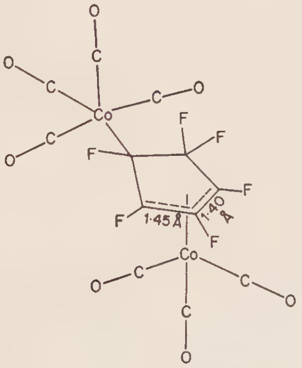
Treatment of $\pi\text{-}C_3H_5Fe(CO)_3Cl$ with nitric oxide gives the neutral 18-electron nitrosyl, $\pi\text{-}C_3H_5Fe(CO)_2NO$ [82*b*]; it is interesting that the isoelectronic $(\pi\text{-}C_3H_5)_2Fe(CO)_2$ is not known; neither is $C_6H_6Fe(CO)_2$.

Attempts to prepare perfluoroallyl complexes from metal carbonyl anions and perfluoroallyl chloride have been unsuccessful; the perfluoroallyl rearranges and metal–σ-propenyl complexes are isolated [84, 85]. However, treatment of perfluorocyclohexadiene iron tricarbonyl with caesium fluoride gives the anionic π-perfluorocyclohexenyl complex 2.23.



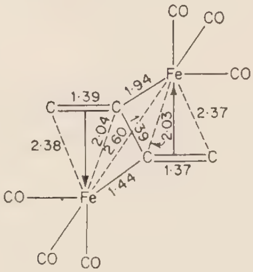
2.23

Dicobalt octacarbonyl reacts with perfluorocyclopentadiene giving the unusual binuclear complex 2.24 [85*a*], whose crystal structure has been determined [85*b*].



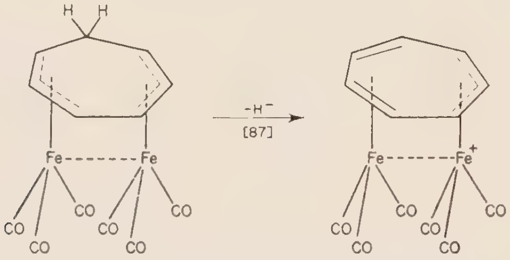
2.24

An interesting compound, is made from $Fe_3(CO)_{12}$ and tetraphenylbutatriene, $Ph_2C{=}C{=}C{=}CPh_2$ [87*a*]. The crystal structure 2.25*a*, omitting the Ph groups, shows the butatriene acts as a 3-electron ligand to each iron [87*b*].



2.25*a*

A number of binuclear complexes of stoicheiometry olefin $Fe_2(CO)_6$ (where olefin = cycloheptatriene, cyclo-octa-1,3,5-triene or cyclo-octatetraene) have each been shown by Mössbauer studies to have equivalent iron atoms [87]. On the basis of this evidence it is proposed that in all cases the olefins bond to each iron by a π-enyl system (see 2.26). For example,

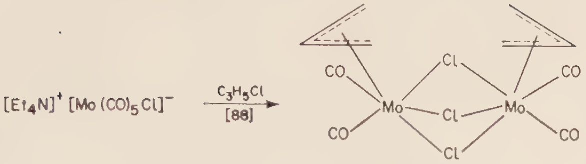


2.26 2.25

As also shown in the above equation, the cycloheptatriene complex undergoes hydride abstraction and the C_7H_7 ligand formed (see 2.25), is presumably acting as both a 3- and 4-electron ligand. It is interesting that the proton magnetic resonance spectrum of the complex, 2.25, shows only one line. Possibly the hydrogens are made 'equivalent' by some rotation of the C_7-ring about an axis normal to the C_7-plane.

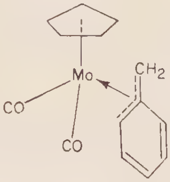
(*e*) *Miscellaneous*

An unusual binuclear molybdenum complex has been described, for which 2.27 is a possible structure. It undergoes metathetical bridge replacement, for example with sodium methoxide the tri-μ-methoxy analogue is prepared, and the halogen bridge can be split by amines giving π-$C_3H_5Mo(CO)_2(amine)_2Cl$ [88*a*].



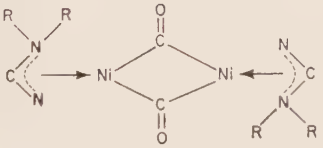
2.27

Benzyl chloride reacts with $Na^+[\pi\text{-}C_5H_5Mo(CO)_3]^-$ forming the expected benzyl derivative $\pi\text{-}C_5H_5Mo(CO)_3CH_2C_6H_5$. On irradiation, carbon monoxide is evolved, and a red compound is formed. The proposed structure, 2.27*a*, contains the π-benzyl system shown and this can be presumed to be a 3-electron ligand [88*b*].



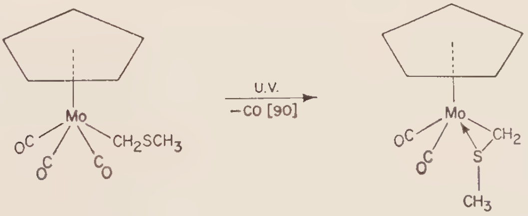
2.27*a*

Apart from the π-allyl ligands there are several groups whose bonding to the metal contains M–C bonds and which are 3-electron ligands. For example, treatment of nickel carbonyl with dialkyl cyanamides gives dimeric complexes for which structure 2.28 has been proposed [89].



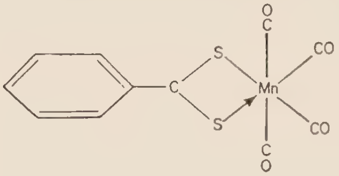
2.28

Further, the $RSCH_2$ group may act as a 3-electron ligand, as shown by the complex, 2.29. Related ligands are R_2NCS_2— [91] and RCS_2— [92]



2.29

although, as shown in 2.30, they do not form M–C bonds but only M–S systems.



2.30

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CHAPTER THREE

Four-electron ligands

Examples of olefins which act as 4-electron ligands with transition metals are given in Table 7. It can be seen that these ligands form complexes with a wide variety of transition metals. A comparison of Tables 1 and 7 shows that cyclo-octa-1,5-diene (a two × 2-electron ligand) forms stable chelate olefin complexes with palladium and platinum but not with iron, whilst for butadiene (a 4-electron ligand) the reverse is true. It does not follow from this that there is a *general* preference of the different classes of these ligands for different metals; it seems more probable that there are *specific* reasons for the differences. For example, the stereochemical requirements of cyclo-octa-1,5-diene may preclude strong bonding with the $Fe(CO)_3$ system, whilst, with palladium salts, conjugated dienes readily and preferentially react to form π-allyl complexes (see p. 42).

Table 7 *Examples of four-electron ligands*

Ligand	Metals with which the ligand forms complexes(a)	Comments
Butadiene (b) (and substituted butadienes)	V, Cr, Mo, W, Mn, Fe, Co, Rh, Pt	See section C(c)
Cyclobutadiene	Mo, Fe, Co, Ni, Pd	See section C(a)
Cyclopentadiene	Re, Fe, Rh, Ir, Co	See section C(b)
Cyclohexa-1,3-diene	V, Cr, Mo, Mn, Fe, Ru	Similar chemistry to butadiene(c) (also see p. 136)
Cyclohepta-1,3-diene	Fe	See p. 138
Cyclohepta-1,3,5-triene	Fe	See p. 138
Cyclopentadienones	Fe, Co	See Chapter 8, E (a)
Cyclo-octa-1,3,5-triene	Fe, Co	See p. 83
Acetylenes	Fe, Co, Ni	See Chapter 8, B
Cinnamaldehyde	Fe	See p. 86
Penta-1,3-diene	Fe	See p. 138
Cyclo-octatetrene	Mo, Fe, Co, Ni, Pd, Pt	See Chapter 6, D

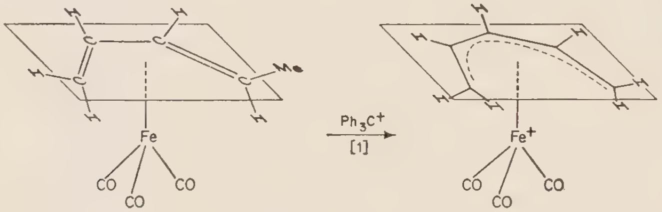
(*a*) For detailed references see [9].

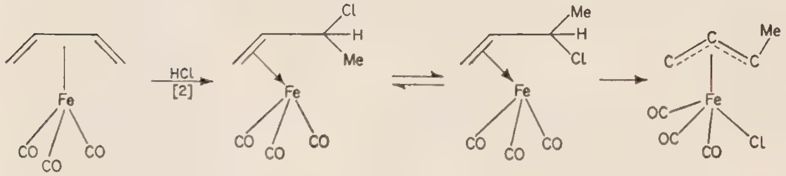
(*b*) Examples are π-$C_5H_5V(CO)_2C_4H_6$, red, 110° d [3]; $(C_4H_6)_2M(CO)_2$, where M = Cr, Mo, brown-yellow [3]; π-$C_5H_5Mn(CO)C_4H_6$ [3]; $C_4H_6Fe(CO)_3$, yellow oil [4, 5, 6]; $[C_4H_6Co(CO)_2]_2$, red-pink, 118° d [78]; $(C_4H_6)_2RhCl$ [79].

(*c*) $C_6H_8Mn(CO)_3H$ [8], $(C_6H_8)_2IrCl$, white, 135–140° d, [7].

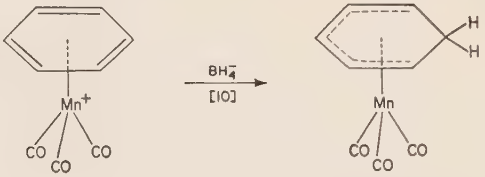
A. Some differences between unconjugated and conjugated olefin ligands

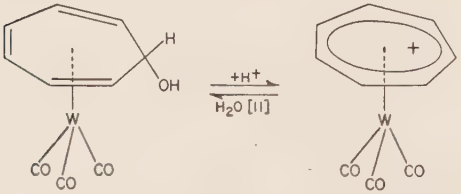
Conjugated olefins, whether 4-electron or 6-electron ligands, have important characteristics in common which distinguish them from unconjugated two × 2-electron and three × 2-electron ligands respectively. The conjugated olefins may react to give complexes containing ligands bound by an essentially delocalized system with either one *more* or one *less* electron than the parent ligand. Thus 4-electron ligands may form π-enyl and π-dienyl ligands,



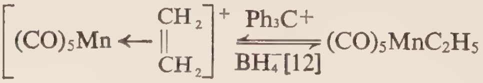


Similarly 6-electron ligands may form the delocalized π-dienyl and π-trienyl ligands:



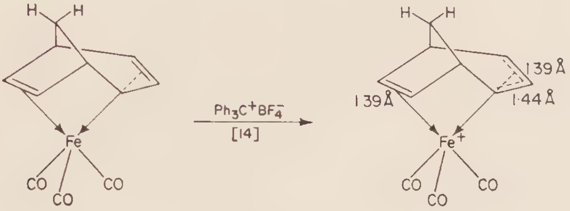


Understandably, unconjugated diene and triene ligands where the C=C systems are separated by more than one carbon atom may not react so readily to form delocalized systems. The mono-ene, 2-electron ligands may, however, form 1-electron (alkyl) and π-enyl systems:



$$\left[(CO)_5Mn \leftarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}\right]^+ \underset{BH_4^-\,[12]}{\overset{Ph_3C^+}{\rightleftharpoons}} (CO)_5MnC_2H_5$$

And hence the unconjugated C=C systems of dienes may react similarly, e.g.,



3.1

The structure of the complex, 3.1, has been shown by X-ray studies [14] and the ligand is most usefully regarded as a combination of 2- and 3-electron ligands rather than as a 5-electron ligand.

A further important difference in degree between conjugated and non-conjugated ligands lies in the nature of the metal–olefin bond. Conjugated ligands may provide molecular orbitals with a wider variety of energies and symmetries than non-conjugated olefins and they can be expected to adjust themselves more readily to the bonding requirements of the metal (see Figure 13).

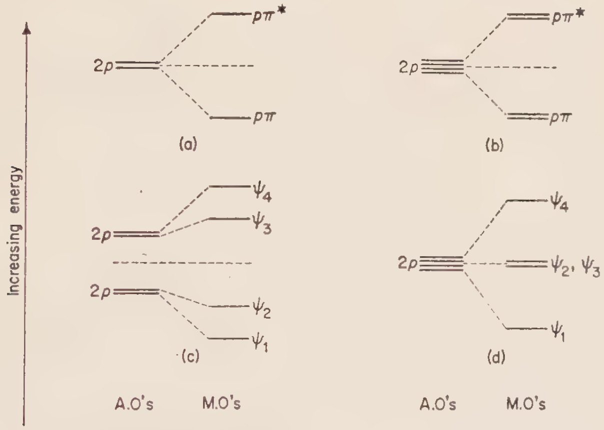


Fig. 13. (*a*) The two 2*p* atomic orbitals (A.O.) of ethylene combine to give two *p*π molecular orbitals (M.O.). (*b*) The similar result found in non-conjugating dienes, such as cyclo-octa-1,5-diene. (*c*) Shows the greater variety of energy levels formed by the butadiene p_z orbitals (see Figure 17). (*d*) The energy diagram for cyclobutadiene M.O.s

B. The bonding of 4-electron ligands to transition metals

(*a*) *Cyclobutadiene complexes*

The structure of cyclobutadiene is unknown but, if we assume it to be square-planar, four M.O.s may be constructed from the four carbon p_z orbitals of which ψ_2 and ψ_3 are degenerate. A pictorial representation of the four M.O.s is given in Figure 14.

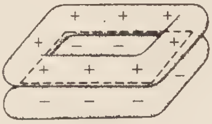
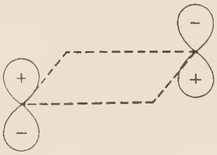
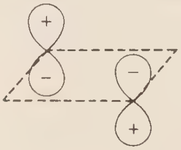
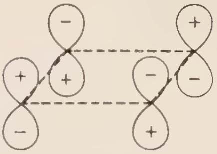
$\psi_1 = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)$	
$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3)$	
$\psi_3 = \frac{1}{\sqrt{2}}(\phi_2 - \phi_4)$	
$\psi_4 = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4)$	

Fig. 14. Molecular orbitals of cyclobutadiene

It is assumed in a simple treatment of the bonding of the cyclobutadiene ligand to a metal atom that only the $p\pi$-electrons of the ligand take part. The molecule cyclobutadiene iron tricarbonyl will serve to illustrate the cyclobutadiene–metal bonding. X-ray analysis of some substituted cyclobutadiene complexes shows the sandwich structure of the C_4-ring–metal group (see p. 74) and it is assumed that $C_4H_4Fe(CO)_3$ has the related structure shown in 3.9. Since there are no true symmetry axes in this molecule we resort to considering the local symmetry of the C_4H_4Fe system. This of course has a fourfold symmetry axis. The three carbonyl groups will affect the energies of the metal orbitals and determine their availability for binding to the cyclobutadiene ligand but since the $Fe(CO)_3$ system has a threefold symmetry axis the degeneracy of the E metal orbitals is unaffected (see Table 2).

The classification of the metal and cyclobutadiene orbitals according to their symmetry properties as members of the group C_{4v} is given in Table 8.

Table 8 *Symmetry classification of orbitals of the π-C_4H_4M system*

Symmetry	Ligand orbital	Metal orbital	Bond type
A_1	ψ_1	s, p_z, d_{z^2}	σ
E	ψ_2, ψ_3	p_x, p_y, d_{xz}, d_{xy}	π
B_1	ψ_4	$d_{x^2-y^2}$	δ
B_2	—	d_{xy}	n

The combinations allowed between the C_4H_4 M.O.s and the metal orbitals are represented in Figure 15. There is no experimental evidence for the relative energies of the combining M.O.s. However, it seems reasonable

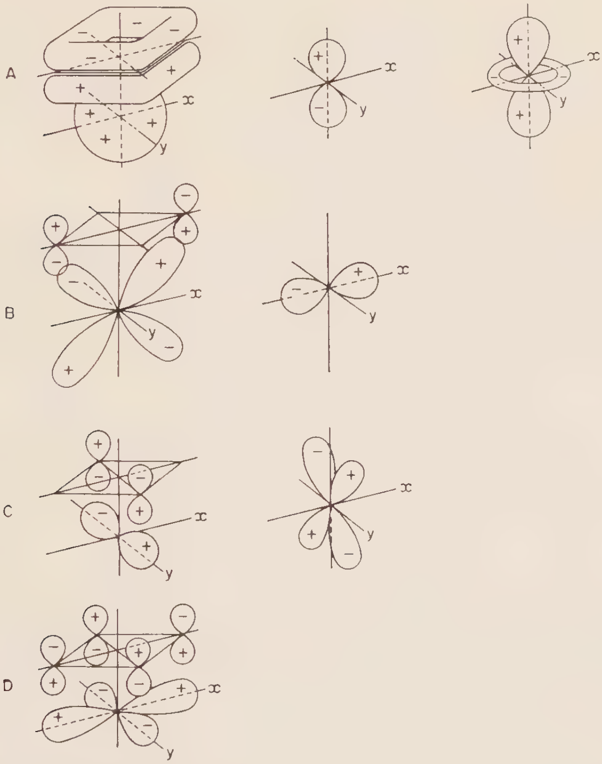


Fig. 15. Row A shows the metal orbitals with which the ψ_1 M.O. of cyclobutadiene may interact (σ-symmetry). Rows B and C show the metal orbitals which may combine with the ψ_2 and ψ_3 M.O.s (π-symmetry). Row D shows the δ-bond which can be formed by the metal $d_{x^2-y^2}$ and the ψ_4 M.O.

that the orbitals of E symmetry should be the principal contributors to the stability of the metal–cyclobutadiene bond. In the free cyclobutadiene, if it were square-planar, there would be an unpaired electron in each of the degenerate ψ_2 and ψ_3 M.O.s and the metal can provide two electrons in orbitals of the same symmetry. These could form two strong covalent bonds and thus neutralize the diradical character of the cyclobutadiene.

(*b*) *Butadiene complexes*

The structure of butadiene iron tricarbonal has been determined by X-rays [6] and is shown in Figure 16. In this structure the carbon atoms of the butadiene adopt a *cis* configuration and are planar. The plane of the four carbons is not quite parallel to that formed by the three carbons of the CO groups. The iron atom lies below the plane of the butadiene and is equidistant (2·1 + 0·04 Å) from the four carbons.

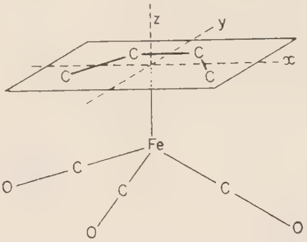


Fig. 16. The structure of butadiene iron tricarbonyl, after Mills and Robinson [6]. The axes used in the classification given in Table 9 are also shown

Unfortunately, even the local symmetry of the butadiene-metal system is low (C_s); and, as shown in Table 9 which gives the transformation

Table 9

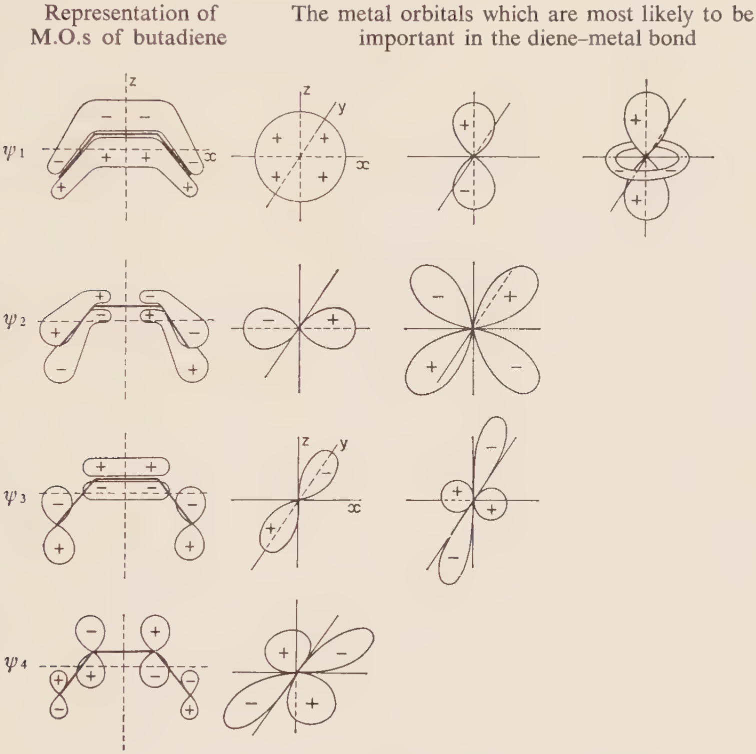
Orbitals of butadiene

$$\psi_1 = 0{\cdot}37\phi_1 + 0{\cdot}60\phi_2 + 0{\cdot}60\phi_3 + 0{\cdot}37\phi_4$$
$$\psi_2 = 0{\cdot}60\phi_1 + 0{\cdot}37\phi_2 - 0{\cdot}37\phi_3 - 0{\cdot}60\phi_4$$
$$\psi_3 = 0{\cdot}60\phi_1 - 0{\cdot}37\phi_2 - 0{\cdot}37\phi_3 + 0{\cdot}60\phi_4$$
$$\psi_4 = 0{\cdot}37\phi_1 - 0{\cdot}60\phi_2 + 0{\cdot}60\phi_3 - 0{\cdot}37\phi_4$$

Symmetry classification of the π-C_4H_6M *system* (C_s *symmetry*)

Symmetry	Ligand orbitals	Metal orbitals
A′	ψ_1, ψ_3	s, p_y, p_z, d_{z^2} $d_{x^2-y^2}, d_{xy}$
A″	ψ_2, ψ_4	p_x, d_{xz}, d_{xy}

properties of the ligand and metal orbitals according to the symmetry group C_s, there are a large number of possible interactions between the metal and the ligand orbitals. Therefore symmetry considerations alone are insufficient to enable even a reasonable guess at those interactions which are likely to provide the chief source of binding. However, as shown for the π-allyl metal bond, we can roughly choose those metal and butadiene orbitals which are likely to overlap significantly; these are shown in Figure 17.


Representation of M.O.s of butadiene

The metal orbitals which are most likely to be important in the diene–metal bond

Fig. 17

It is interesting to consider some proposals for the butadiene–metal bond which have been represented by valence bond descriptions, as shown in Figure 18, in the light of the above M.O. approach. In Figure 18, representation A implies that the electrons are localized as in butadiene [5]; representation B suggests that there is considerable localization (σ-character) of the bonding electrons between the metal and the terminal carbons of the butadiene and between the metal and the C_2–C_3 carbons of the diene. Representation B was suggested on the basis of the anomalous PMR spectra of some dienes [15]. Representation C shows a complete

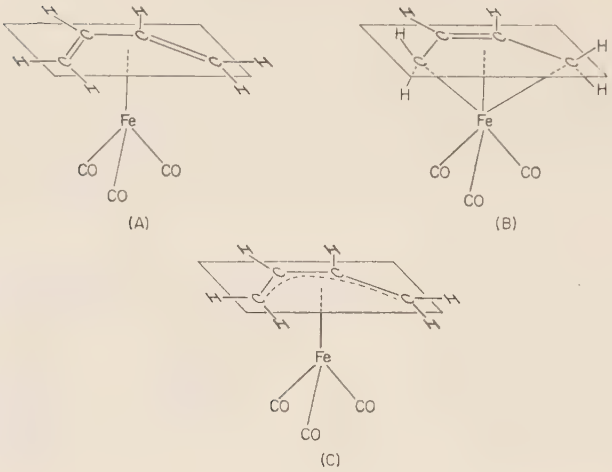


Fig. 18

delocalization of the butadiene electrons. It might be argued that representation A implies, in molecular orbital terms, that there is major bonding to the metal by the ψ_1 and especially ψ_2 orbitals of butadiene, whilst representation B suggests that bonding between the metal and the ψ_3 M.O. is also very significant. Representation C is consistent with equal contributions from ψ_1, ψ_2 and ψ_3.

There is little evidence to distinguish between A, B or C. X-ray studies of a number of diene iron tricarbonyl complexes have been made.† A comparison of the observed bond distances between the terminal carbons of diene systems and the adjacent carbons of a substituent group (1·44–1·49 Å) with the calculated distances for an sp^2 hydridized terminal carbon (1·48 Å) and an sp^3 hybridized carbon atom (1·52–1·54 Å) slightly favours structures A and C [16]. The C^{13}–H coupling constants of butadiene iron tricarbonyl are more consistent with sp^2 hybridized carbons than with sp^3 hybridization [16*a*]. The data also suggests that there is a small rotation of the CH_2 hydrogens out of the C_4-plane.

In fact all the above structures show that the terminal substituents are bent out of the plane of the diene carbons, away from the metal. This suggests a degree of sp^3 character for the terminal carbon–metal bonds, and is thus in favour of B.

There are two further points which suggest that the metal interacts significantly with the ψ_3 M.O. of the butadiene. It has been shown that the overall effect of the $Fe(CO)_3$ group in some diene metal carbonyls is to donate electrons to the diene ligand (see p. 83). Hence some filling of the anti-bonding butadiene M.O.s must occur and back-donation from the

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† The structures are shown in Figure 19 and on pp. 70, 197 and 306).

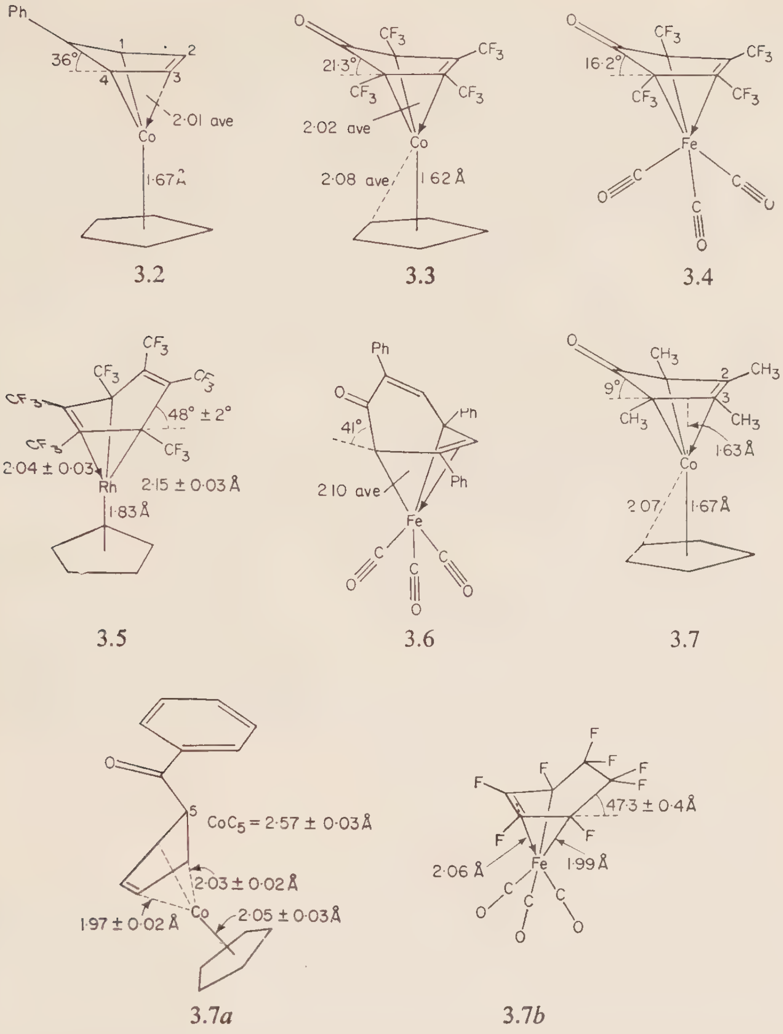


Fig. 19. The structures, determined by X-ray analysis, of π-cyclopentadienyl-1-*exo*-phenylcyclopentadiene cobalt, 3.2 [17]; π-cyclopentadienyltetratrifluoromethylcyclopentadienone cobalt, 3·3 [18]; tetratrifluoromethylcyclopentadienone iron tricarbonyl, 3.4 [18*a*]; π-cyclopentadienylhexatrifluoromethylbenzene rhodium, 3.5 [19]; 2,4,6-triphenyltropone iron tricarbonyl, 3.6 [20]; π-cyclopentadienyltetramethylcyclopentadienone cobalt, 3.7 [21] π-cyclopentadienyl-5-*exo*-benzoylcyclopentadiene cobalt, 3.7*a* [22]; octafluorocyclohexa-1,3-diene iron tricarbonyl, 3.7*b* [23], see also 4.35 (p. 152). A comparison of 3.3 and 3.7 shows the greater deviation from non-planarity of the cyclopentadienone ring with the more electronegative substituents. A comparison of 3.4 and 3.7 shows that the deviation from non-planarity is less in the iron complex. This may be due to the $Fe(CO)_3$ group having greater acceptor properties than the $-C_5H_5Co$ group†

† For a review see reference [23*a*].

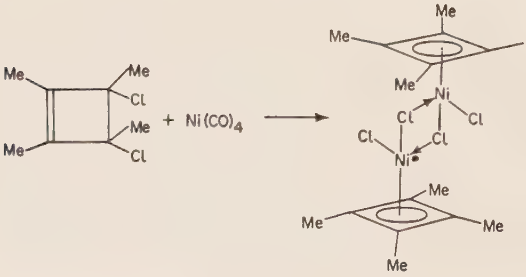
metal to the ψ_3 M.O. seems most likely. Further, the deviations from coplanarity of the methylene carbons with the diene carbons in some substituted cyclopentadienes and of the CO groups in some cyclopentadienone complexes increase with increasing electronegativity of the olefin ligand substituents and with decreasing acceptor power of the other ligands on the metal (see Figure 19). It would be expected that the greater the electronegativity of the ring substituents, the greater the back-donation of the metal electrons to the ψ_3 M.O. and, as represented by B, this may cause a corresponding increase in the sp^3 character of the terminal M–carbon bonds leading to larger deviations from non-planarity of the substituents on the carbon. It may be noted that although there is a difference in the bending-away angle of $\sim 12°$ in the complexes 3.3 and 3.7 (see Figure 19), their electronic spectra are very similar indeed [24]. This apparent insensitivity of the electronic energy levels to the change in bond angle is rather surprising. It appears that the relative energies of the levels which give rise to the spectra remain constant.

To summarize, it seems that the bonding of dienes is complex and cannot be adequately represented by any one of the structures A, B or C. For those dienes which have substituents on the 1 : 4 carbons which are bent well away from the metal, representation B seems the most suitable. However, the relative importance in the metal–diene bonding of the ψ_{1-4} diene orbitals will vary in different complexes. Therefore in this book we will use the representation A for all diene–metal bonds since it clearly indicates the diene nature of the parent olefin.

C. Particular studies

(*a*) *Cyclobutadiene complexes*†

(*i*) *Preparation* In 1956 Longuet-Higgins and Orgel predicted that the cyclobutadiene system would be stabilized by complex formation with a transition metal [26]. Three years later Criegee isolated the first π-cyclo-



Ni—C, ave 1·997–2·047Å
C—C of C_4 ring, 1·40–1·45Å
Ni—Cl (bridge), 2·35Å
Ni—Cl (unbridged), 2·26Å

3.8

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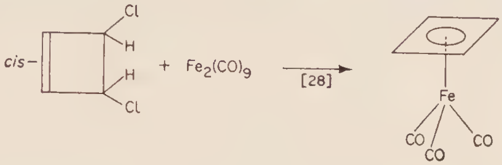
† For a review, see reference [24*a*].

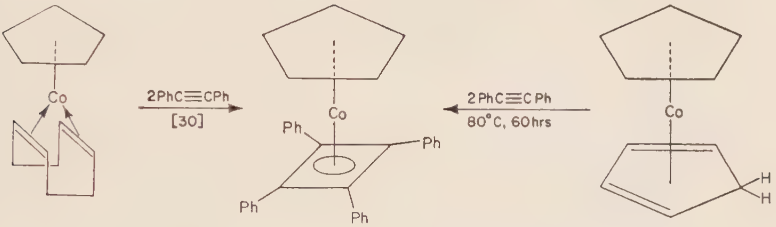
butadiene complex, 3.8 [25]. It forms a red violet powder, soluble in methylene chloride and water. The aqueous solutions precipitate AgCl on treatment with $AgNO_3$ and a π-cyclobutadiene–nickel aquo complex is formed. The structure of 3.8 has been shown by X-ray diffraction [27].

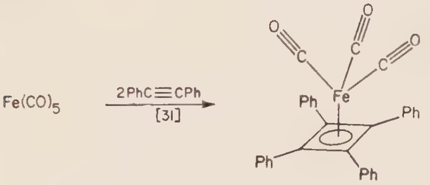
Nowadays, many π-cyclobutadiene metal complexes are known, including the unsubstituted π-cyclobutadiene complex, 3.9, which was pre-



3.9

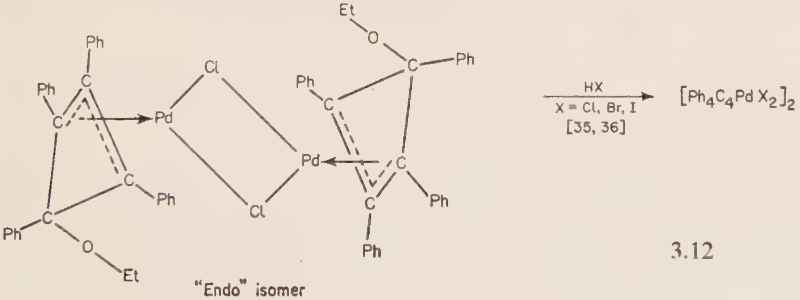
pared in a similar manner to the nickel complex. A number of π-cyclobutadiene complexes have been prepared from substituted acetylenes; the structure of complex 3.10 has been shown by X-ray analysis [29].





3.10

Treatment of alcoholic [32] or aqueous alcoholic solutions [33] of sodium tetrachloropalladite, or solutions of bis-benzonitrile palladium



"Endo" isomer

3.11

3.12

dichloride in ethanol/chloroform [35], with diphenylacetylene first affords a complex which has structure 3.11 (p. 55). Treatment of this complex with hydrogen halides readily gives the tetraphenylcyclobutadienepalladium halide 3.12. In non-hydroxylic solvents, treatment of $(C_6H_5CN)_2PdCl_2$ with diphenylacetylene gives hexaphenylbenzene [35].

A variety of tetraphenylcyclobutadiene complexes formed in the reaction between molybdenum hexacarbonyl and diphenylacetylene are shown in Figure 20.

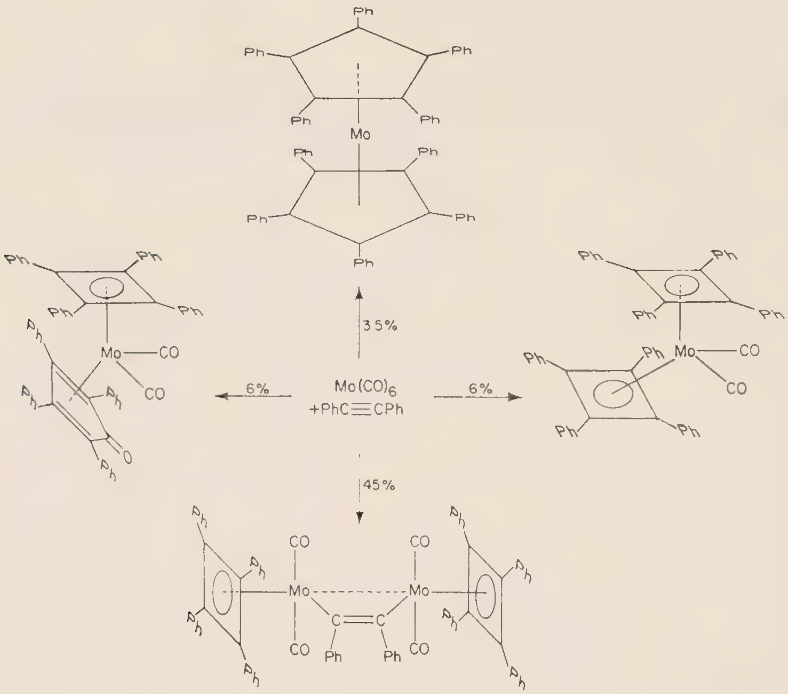


Fig. 20. Some products formed in the reaction between diphenylacetylene and molybdenum hexacarbonyl [34]

A more general method for the preparation of tetraphenylcyclobutadiene metal complexes is the ligand transfer reaction exemplified in Figure 21. The molybdenum complexes, e.g. $[Ph_4C_4Mo(CO)_3Br]_2$ may be prepared in a similar manner [39]. Frequently during the ligand transfer reactions a green colour is observed which may be due to tetraphenylcyclobutadiene [43]. As also shown in Figure 21, with some π-cyclopentadienyl iron complexes transfer of the π-C_5H_5 ligand may occur [40, 42].

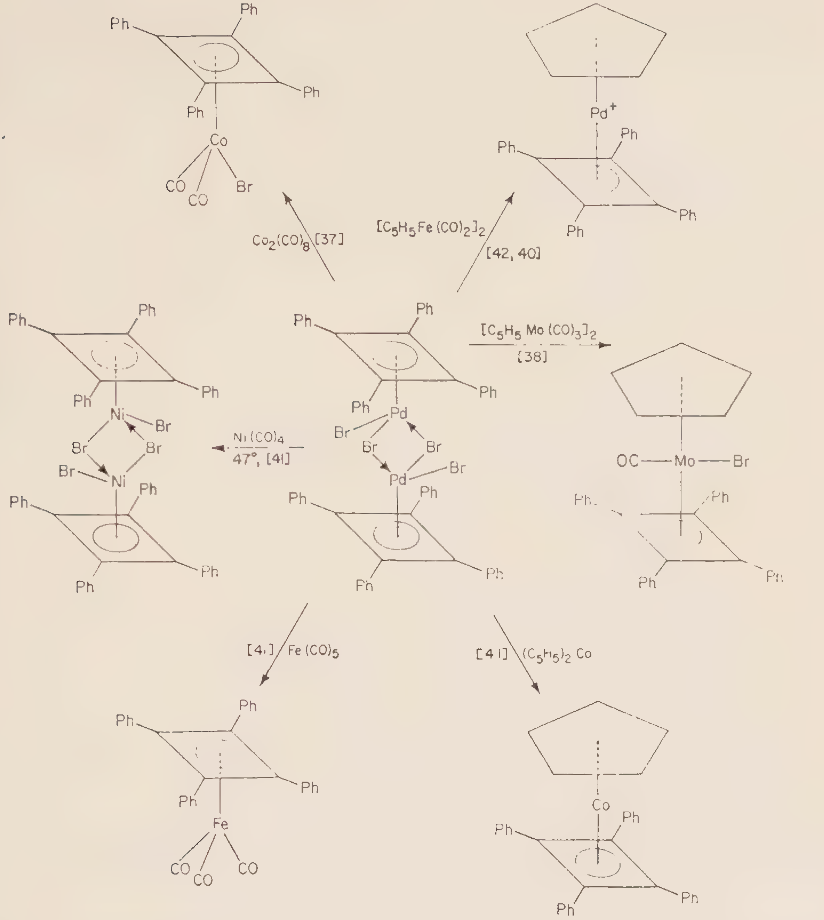
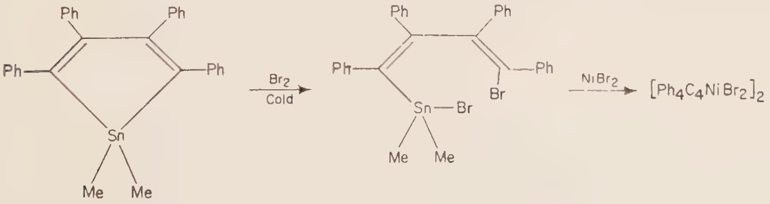


Fig. 21. Some preparations of π-cyclobutadiene complexes by ligand transfer reaction.

The heterocyclic tin complex 3.13 has proved to be a novel source of a tetraphenylcyclobutadiene nickel complex [44].

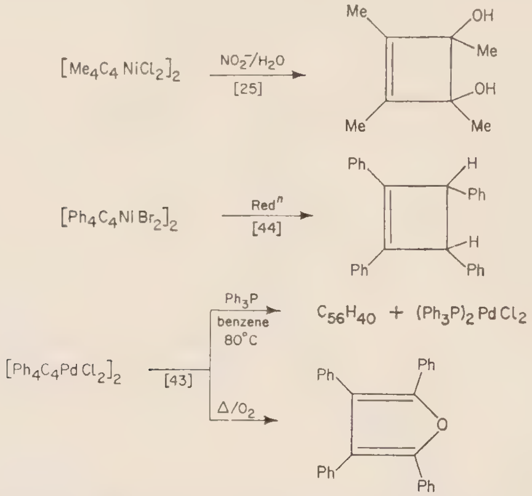


3.13

(*ii*) *Properties.* In the crystal structures of the complexes 3.8 and 3.10, the cyclobutadiene ring is square-planar and the methyl or phenyl substituents are displaced out of the plane of the ring, away from the metal atom.

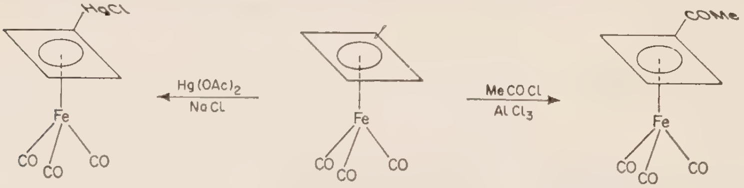
Infrared studies are consistent with C_{4v} symmetry of the metal–ring systems in these complexes [45].

There is considerable chemical evidence for the presence of a 4-membered system in the above complexes. Examples are:

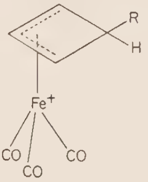


The suggestion [46] that the hydrocarbon $C_{56}H_{40}$ is octaphenylcubane is wrong [47]; in fact it is octaphenylcyclo-octatetraene.

In cyclobutadiene iron tricarbonyl, the cyclobutadiene ligand shows aromatic properties and readily undergoes electrophilic substitutions [48].

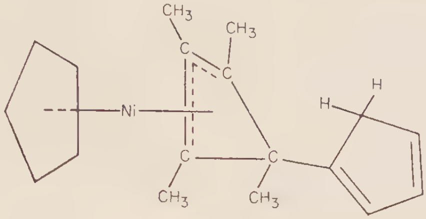


Intermediates in the substitution reactions are postulated to be π-enyl species, as represented by the complex 3.14 [48]. This postulate is supported



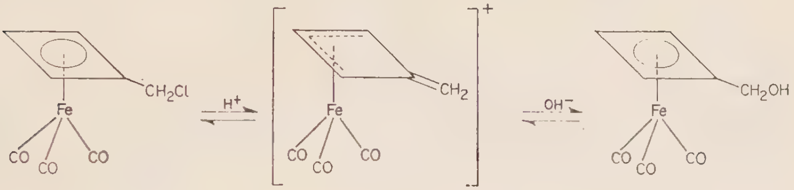
3.14

by the structure found by X-ray diffraction [49] for the product of the reaction between $[\mathrm{Me_4C_4NiCl_2}]_2$ and sodium cyclopentadienide, namely complex 3.15.



3.15

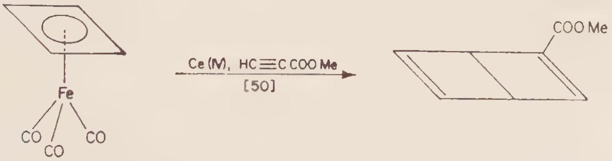
It is proposed that the mechanism of hydrolysis of the α-chloro complex involves a similar π-enyl intermediate 3.15*a*. The ease with which this hydrolysis occurs suggests that there is some interaction of the ring substituents in the α-position with the metal atom (see p. 213).



3.15*a*

In fact, treatment of the chloromethyl derivative, $\mathrm{ClCH_2C_4H_3Fe(CO)_3}$, with $\mathrm{SbCl_5}$ gives yellow crystals of the salt $[\mathrm{RHC{=}C_4H_3Fe(CO)_3}]^+\mathrm{SbCl_6}^-$, where R = H [49*a*]. Proton magnetic resonance studies on this cation and the methyl analogue, R = Me, support the proposed *exo*-cyclic structure, 3.15*a*.

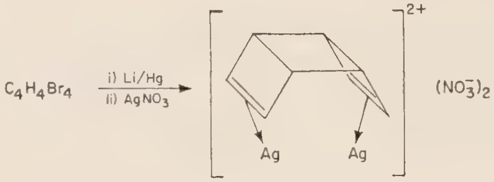
The oxidation of cyclobutadiene iron tricarbonyl with ceric ion releases the cyclobutadiene which may be characterized by its *in situ* reactions:



If the ceric oxidation is carried out in the presence of dimethylmaleate or dimethylfumarate, then the liberated cyclobutadiene adds to them in a stereospecific manner. For example, dimethylmaleate gives *endo-cis*-dicarbomethoxylbicyclohexene. The course of these addition reactions suggests that the cyclobutadiene reacts as a diene with a singlet state rather than as a delocalized aromatic ring with a triplet state. This evidence therefore favours a rectangular shape for the liberated cyclobutadiene [50*a*].

Examination of the proton magnetic resonance spectrum of cyclobutadiene iron tricarbonyl in the liquid crystal phase (i.e. in 4,4′-di-n-hexyloxyazobenzene) shows that, at the most, there is only a very small departure of the C_4H_4 ring from square symmetry [50*b*].

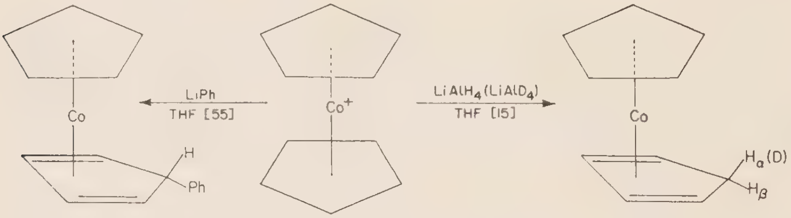
It had been thought that a cyclobutadiene silver nitrate complex resulted from the reaction shown in the equation below [51, 52]. However, subsequent spectral studies suggest that the product should be formulated as the dimeric complex, 3.16 [53, 54].



3.16

(*b*) *Cyclopentadiene complexes*

Cyclopentadiene complexes may be prepared by nucleophilic attack on π-cyclopentadienyl–metal cations, e.g.



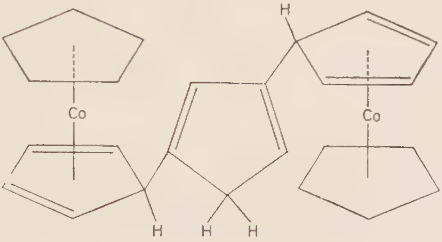
3.17

Other examples are shown on pp. 107, 108 and 121. An interesting feature of unsubstituted-cyclopentadiene complexes, e.g. 3.17, is that their infrared spectra show a broad, intense C–H stretch at the unusually low frequency of 2700 cm^{-1}. For the cobalt complex, 3.17, the assignment is confirmed by the spectrum of the deuterated analogue; the anomalous C–H stretch is absent and a corresponding C–D band appears [15].

The anomalous stretching frequency has been attributed to interaction of the *endo*-C—Hα with the metal; its absence in the *exo*-substituted phenylcyclopentadiene cobalt complex (Figure 19) has been explained by an increased bending-away of the methylene carbon from the metal atom which makes the *endo*-hydrogen–metal distance too large for appreciable metal–hydrogen interaction [56].

However, a consideration of the chemistry of these cyclopentadiene complexes slightly confuses the issue since the unsubstituted cyclopentadiene and the *exo*-phenylcyclopentadiene complexes are both prepared from the cobalticenium cation. Thus it is necessary to postulate either that the attack of the nucleophilic H^- and Ph^- ions proceeds by different mechanisms or that the anomalous C-hydrogen was originally in the *exo*-position (see Chapter 7), p. 216.

Treatment of the cobalticenium cation with sodium cyclopentadienide affords a binuclear complex [57]. Detailed spectral studies suggest that the complex has a structure such as 3.18 [58]. With the rhodicenium cation, sodium cyclopentadienide reacts differently and gives the complex π-$C_5H_5RhC_5H_5$—C_5H_5 for which it is proposed that a cyclopentadienyl group is σ-bonded to the methylene carbon of a C_5H_5–diene ligand, in the *endo*-position [59].

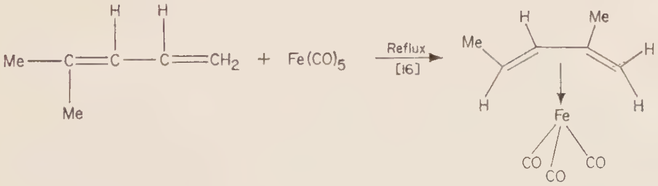


3.18

(*c*) *Non-cyclic diene–metal complexes*

Many diene iron tricarbonyl complexes are known.† Butadiene iron tricarbonyl was first prepared in 1930 by Reihlen and co-workers [60], by treatment of iron pentacarbonyl with butadiene under pressure. It is a typical diene iron carbonyl complex being a yellow-brown oil which distils slowly at 60° in high vacuum. It is soluble in the common organic solvents and reacts with chlorinated hydrocarbons. The pure oil and its solutions are oxidized in air within hours, forming iron oxides. The diene system resists hydrogenation and does not undergo the Diels-Alder reaction [5].

The preparation of diene iron tricarbonyl complexes by direct reaction between the diene and iron carbonyls frequently involves rearrangement reactions [61, 62] (see Chapter 9), e.g.,



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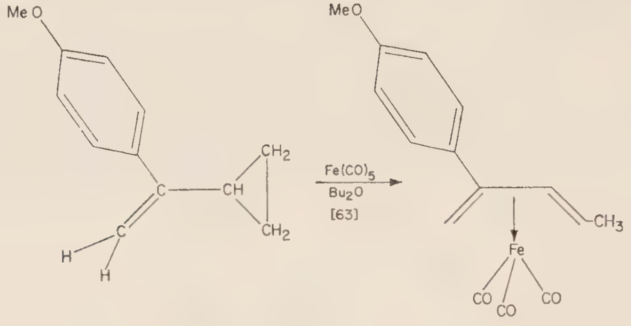
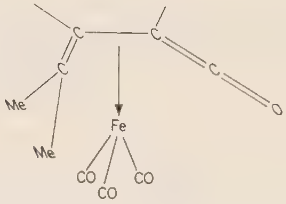
† Diene iron carbonyl complexes have been reviewed [16].

Iron carbonyls have been shown to isomerize non-conjugated dienes to conjugated dienes and even the cyclopropane derivative 3.19 gives a diene complex, namely 3.20. With 1,3,3-trimethylcyclopropene, $Fe_3(CO)_{12}$



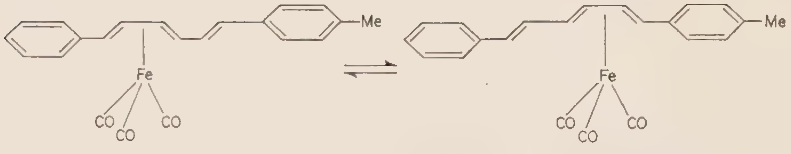
3.19 3.20

forms the complex, 3.21, where one of the carbon monoxide ligands has been incorporated in the ligand [64]. It is interesting to note that the com-



3.21

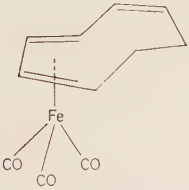
plexes 3.22 and 3.23, which are chemically distinct species, and can be isolated separately, undergo smooth interconversion on heating [65]. A



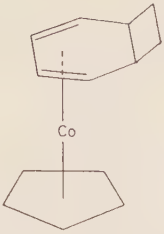
Red, m.p. 129—131° Orange, m.p. 144—145°

3.22 3.23

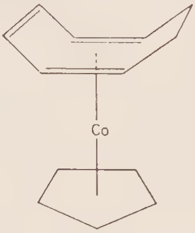
good example of the versatility of olefins as ligands is shown by cyclo-octa-1,3,5-triene. The products of the reactions of this olefin with iron carbonyls [66, 67, 68, 69, 70] and cobalt carbonyl [70, 71, 72, 68] show that it may bond to the metal in a variety of ways. Often the ligand isomerizes forming bicyclo-4,2,0-octadiene complexes, e.g. 3.24. Other ways in which it is proposed that the ligand may bond are shown in complexes 3.25 and 3.26. Cyclo-octa-1,3,5-trienone forms a complex similar to 3.25 [73].



3.25

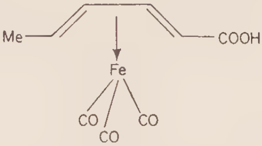


3.24



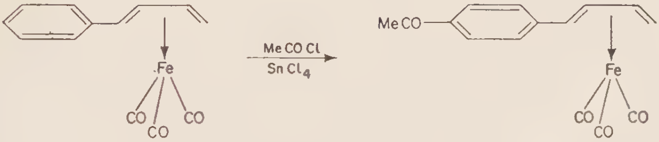
3.26

Electron-donating properties of the $Fe(CO)_3$ group are suggested by the decrease in acidity of the acid, 3.27, compared with that of the free



3.27

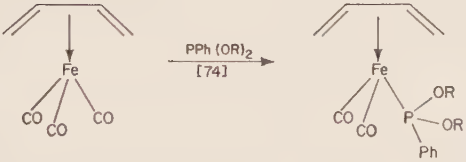
acid [16], and by the mild conditions under which phenylbutadiene iron tricarbonyl can be acetylated [16].



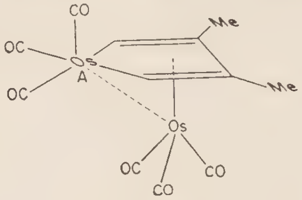
Frequently the diene ligands may be replaced by donor–acceptor molecules such as tertiary phosphines:

$$C_4H_6Fe(CO)_3 + 2Ph_3P \xrightarrow[{[4]}]{\text{warm}} (Ph_3P)_2Fe(CO)_3 + C_4H_6\uparrow$$

although preferential displacement of carbon monoxide can also occur:

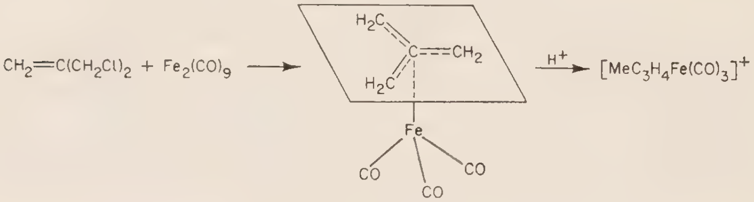


It is interesting that, unlike $Fe_3(CO)_{12}$, treatment of $Os_3(CO)_{12}$ with 2,3-dimethylbutadiene affords not a butadiene derivative but a compound, 3.28 [75], which X-ray studies [76] show to contain a heterocyclic diene



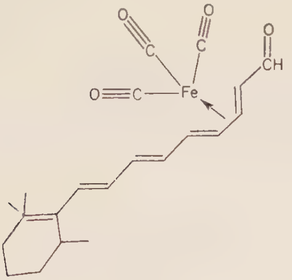
3.28

ring. This complex is similar in configuration to the analogous iron heterocyclic (see p. 303) except that the osmium atom A has an essentially octahedral environment rather than the trigonal prism found in the iron analogue. The Os–Os distance is 2·74 Å, which is shorter than the 2·88 Å found for $Os_3(CO)_{12}$ [77]. A very unusual 4-electron ligand is that shown in the complex postulated to have structure 3.28*a*. In the proton magnetic resonance spectrum of the compound, the hydrogens appear to be equivalent. This means either that the ligand is symmetrically bound to the metal, or that there is some equilibrium which causes equivalence of the hydrogens in the time scale set by the fine separations. In a symmetrical structure the local symmetry of the iron–ligand system would be C_{3v} and in this respect it compares with the $Fe(CO)_3$ group. A possible unsymmetrical structure is that containing a π-allyl bond with the 2-methylene carbon σ-bonded to the metal. Treatment of the compound, with acids gives the known 2-methylallyl iron tricarbonyl [77*a*].



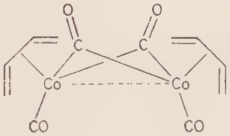
3.28*a*

Perhaps the most exotic olefin which is presently known to act as a 4-electron ligand is Vitamin A aldehyde. The structure of Vitamin A aldehyde iron tricarbonyl is shown in 3.28*b* [77*b*]. There is some twisting of the diene-iron C_4 carbons. Similar slight distortions are suggested by the proton magnetic resonance spectra of some β-ionone derivatives of iron tricarbonyl [77*c*]. Of course, for ligands so unequally substituted as these it is not surprising that distortions may arise. They could be caused either by steric interaction between the $Fe(CO)_3$ group and the diene ligand, or by unequal bonding between the diene C_4 carbons and the iron arising from unequal electron density distribution on the ligand or both.



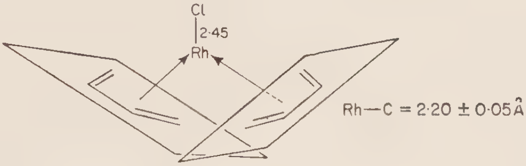
3.28*b*

With dicobalt octacarbonyl, butadiene forms the complex 3.29. The observed dipole moment of 3·02 D suggests that it has a *cis*-configuration [78].



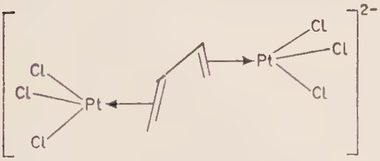
3.29

Treatment of rhodium trichloride or cyclo-octene rhodium chloride dimer with butadiene gives bis-butadiene rhodium(I) chloride for which X-ray studies show the structure 3.30 [79].



3.30

Platinum forms a number of complexes with butadiene in which the butadiene can be bonded in several ways. In the complexes K$^+$[$C_4H_6PtCl_3$]$^-$ and [$C_4H_6PtCl_2$]$_2$ [80] it is almost certainly the case that the butadiene behaves as a 2-electron ethylenic ligand and bonds to the platinum by only one C=C group. In the anion of the salts M^{2+}[$C_4H_6Pt_2Cl_6$]$^{2-}$ [81, 82] the butadiene may behave either as a bridging two × 2-electron, 3.31, or as a bridging 4-electron ligand, 3.32. The complex 3.31 (or 3.32) forms,



3.31

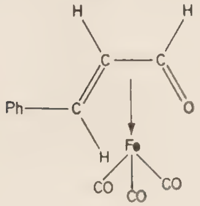
3.32

with amines, a number of complexes for which bridging butadiene systems are also proposed.

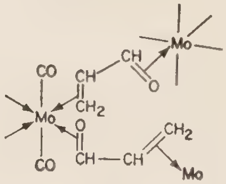
In the butadiene complexes of vanadium, chromium, molybdenum, tungsten and manganese (Table 7) the butadiene has replaced two carbonyl groups and presumably bonds to these two co-ordination positions of the metal.

(*d*) *Miscellaneous 4-electron ligands*

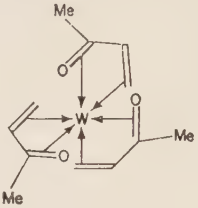
Iron pentacarbonyl reacts with cinnamaldehyde affording the complex 3.33, in which π-bonding by both the C=C and C=O systems has been proposed [84]. With acrolein and $Mo(CO)_6$, a polymeric complex, 3.34, is formed in which again π-bonding by both unsaturated groups is proposed but in this case the ligand is assumed to be bridging [85]. From methylvinyl ketone and $(MeCN)_3W(CO)_3$ a yellow air-unstable complex (m.p. 136–139°d) is obtained for which the structure 3.35 is proposed [86]. The structure of $(acrolein)_2Ni$ [87] may also involve bridging ligands.



3.33



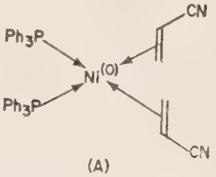
3.34



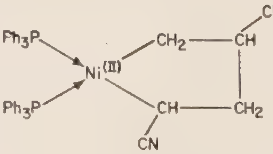
3.35

Acrylonitrile seems to be a rather versatile ligand. As shown on p. 21 it may bond as a π-ethylenic ligand. With molybdenum and tungsten, however, it forms complexes in which it bonds to the metal by the nitrile group, e.g. $CH_2{=}CHCNMo(CO)_5$ [88, 89] and thus behaves like CH_3CN. It can also form the polymeric complex $(acrylonitrile)_2Mo(CO)_2$ [90], which may have a structure related to that proposed for the acrolein complex, 3.34.

The complex $(CH_2{=}CHCN)_3Mo(CO)_3$ is known and in this case the acrylonitrile is bonding as a 2-electron C=C system [88]. With nickel tetracarbonyl, acrylonitrile forms the pyrophoric deep red $(CH_2{=}CHCN)_2Ni$ [91], whose structure is unknown [85]. Treatment of this with triphenylphosphine gives the complex $(PPh_3)_2Ni(CH_2{=}CHCN)_2$; two possible structures for which are (A) and (B).



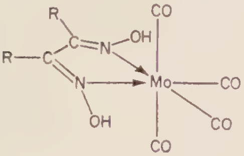
(A)



(B)

Acrylonitrile is thought to act as a bridging ligand in the compound $(CO)_3Fe—(—\mu CH_2{=}CH—CN)_2—Fe(CO)_3$ [92].

Finally, ligands containing the system $—RC{=}NR$ appear to be able to complex to metals either by forming N–M σ-bonds, as in the 1,4-diazabutadiene complex, 3.36 [93], or by a π-bond, as shown in the azabutadiene derivative, 3.37 [94].



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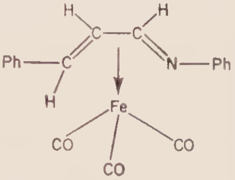

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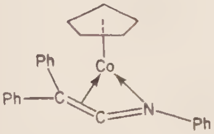

3.38

A related ligand is the ketenimine, $Ph_2C{=}C{=}NPh$. This forms the complexes $Ph_2C{=}C{=}NPh(Fe(CO)_3)_2$ and π-$C_5H_5CoPh_2C{=}C{=}NPh$. The structure proposed for the cobalt complex is shown in 3.38 [95].

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CHAPTER FOUR

Five-electron ligands

Hydrocarbon ligands which formally contribute five electrons when bonding to a metal are called ‘Dienyl’ ligands. Five-electron systems are found for cyclic 5-, 6- and 7-membered hydrocarbon ligands and non-cyclic ligands. The π-cyclopentadienyl group is the commonest ligand in this class and the chemistry of cyclopentadienyl metal complexes is discussed first. For convenience, the transition metal cyclopentadienide complexes are also discussed in this section.

A. Cyclopentadienyl metal complexes

(*a*) *Classification and nomenclature*

The cyclopentadienyl radical, $C_5H_5^{\cdot}$, forms three distinct classes of complexes with transition metals. *π-Cyclopentadienyl* complexes are those which contain the cyclopentadienyl ring essentially covalently bonded to the metal, the metal being situated below the plane of the carbon atoms and usually equidistant from the five equivalent carbon atoms. In a few complexes the cyclopentadienyl radical may bind to the metal by only one carbon atom via a covalent 2-electron bond affording *σ-cyclopentadienyl* complexes, which are discussed in Chapter 7, I. 4.

The third class consists of the *cyclopentadienides* which behave chemically like the essentially ionic, alkali metal cyclopentadienides (see Vol. I). There is no abrupt transition between the ‘ionic’ and ‘covalent’ C_5H_5–metal bond. Indeed there is considerable ‘ionic character’ in a number of complexes which are considered under the formal heading ‘π-cyclopentadienyl complexes’. Even ferrocene, which is considerably covalent, has a charge separation between the metal atom and the π-C_5H_5 rings (see p. 102). Broadly speaking, the covalent character of the C_5H_5–metal bond increases steadily across the *d*-block transition series, i.e. with increasing atomic number, except in the case of manganocene which shows a sudden reversion to ionic character. This anomaly is discussed later. Transition metal cyclopentadienides are discussed on p. 110.

B. π-Cyclopentadienyl transition metal complexes

(*a*) *Preparation*†

(*i*) *Reaction of alkali metal cyclopentadienides with metal complexes.* The most generally applicable and convenient method of preparation of π-

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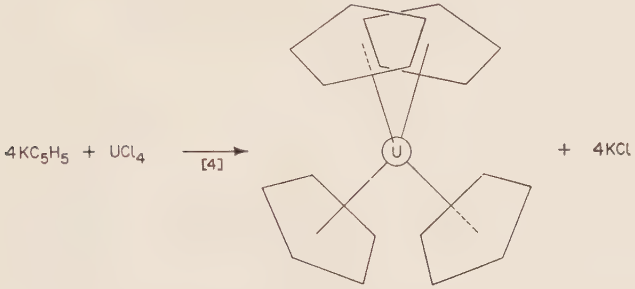
† For a review see [1], and for more preparative details and discussion of technique see [2] and [3].

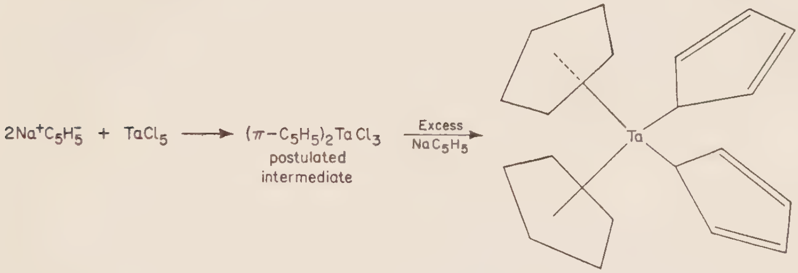
cyclopentadienyl–metal complexes is by the reaction, in tetrahydrofuran, of freshly prepared sodium or potassium cyclopentadienide and anhydrous metal halides or other suitably soluble metal salts.

Examples are:

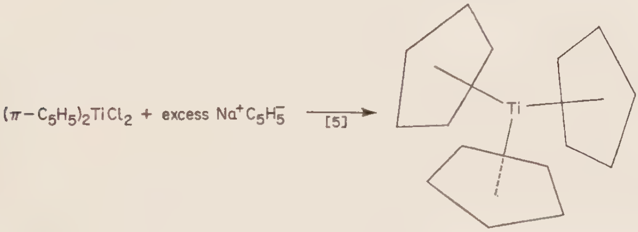
$$2NaC_5H_5 + MCl_2 \xrightarrow[\text{reflux}]{\text{THF}} (\pi\text{-}C_5H_5)_2M + 2NaCl$$



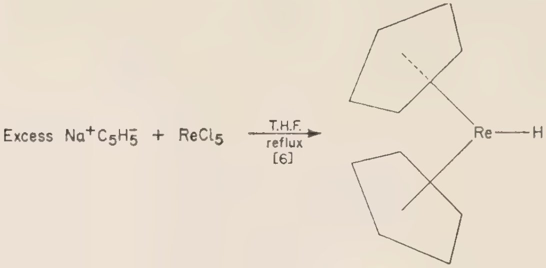
Other ethers such as 1,2-dimethoxyethane are alternative solvents. The nature of the product may depend on the proportions of the reactants and in a number of cases a large excess of sodium cyclopentadienide gives both π- and σ-cyclopentadienyl ligands in the same complex. Thus:

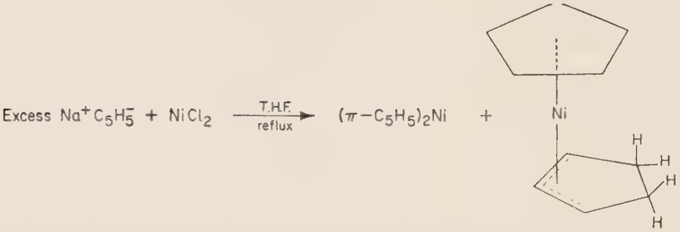


Further reactions may occur; for example, the sodium cyclopentadienide may act as a reducing reagent:



and occasionally side reactions may occur affording unexpected products:

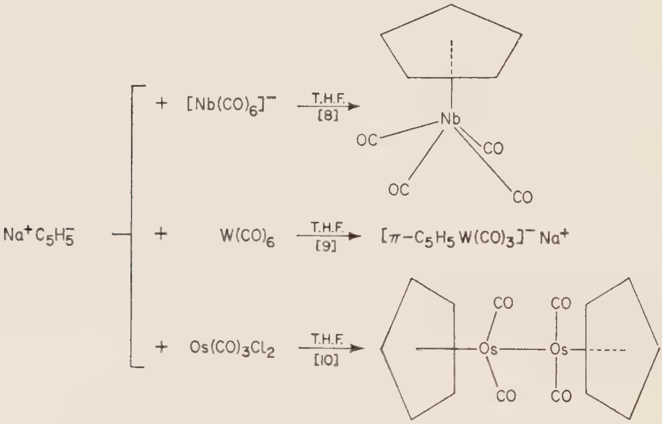




The cyclopentenyl complex may also be prepared from nickel tetracarbonyl and cyclopentadiene [7, 8].

Treatment of many metal carbonyls with alkali metal cyclopentadienides in tetrahydrofuran gives π-cyclopentadienyl metal carbonyl complexes.

Examples are:



π-Cyclopentadienyl metal carbonyls may also be prepared by the reaction of metal halides with $Na^+C_5H_5^-$ in the presence of carbon monoxide under pressure. The complexes π-$C_5H_5Tc(CO)_3$ [11] and (π-$C_5H_5)_2Ti(CO)_2$ [12] were prepared in this way.

Ring-substituted metal complexes may readily be prepared using substituted cyclopentadienides; thus sodium methylcyclopentadienide affords π-methylcyclopentadienyl complexes [13]. Similarly, π-fluorenyl [14], π-indenyl [15, 16] and *as*-indacenyl [16*a*] complexes are prepared from sodium salts containing the hydrocarbon anion. A useful route to substituted cyclopentadienides uses fulvenes, R and R′ = alkyl and aryl groups, viz.,

Ring-substituted derivatives of nickelocene, cobaltocene, and of molybdenum and titanium π-cyclopentadienyls, which would be difficult to make by direct substitution of the parent metal–ring complex, have been made starting with these substituted cyclopentadienides [17, 18].

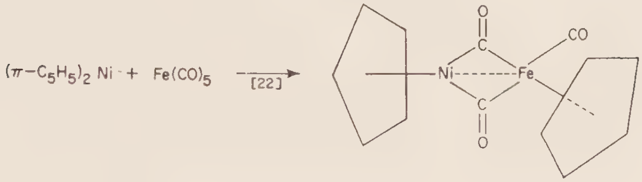
Other less frequently used metal–cyclopentadienylating reagents include the Grignard reagent C_5H_5MgBr, $(C_5H_5)_2Mg$ [19] and σ-cyclopentadienyl mercuric chloride [8], and $(C_5H_5)_2Be$ [19*a*, 19*b*].

An example is

$$(C_5H_5)_2Mg + ZrCl_4 \xrightarrow[100\text{–}110^\circ]{\text{xylene}} \pi\text{-}C_5H_5ZrCl_3 \text{ [20]}$$

Cyclopentadienylation by ligand transfer using covalent π-cyclopentadienyl complexes has been shown in some cases,

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2 + TiCl_4 \longrightarrow \pi\text{-}C_5H_5TiCl_3 \text{ [21]}$$

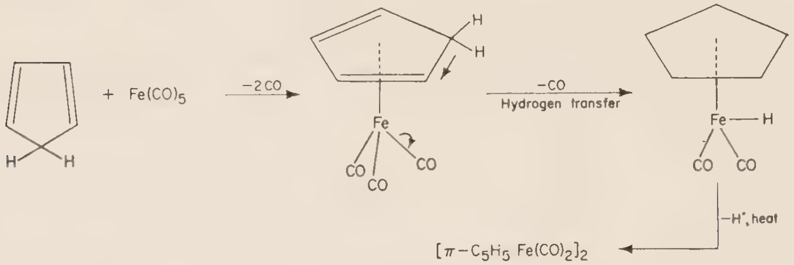


(*ii*) *Reaction between cyclopentadiene and metal complexes.* Treatment of certain metal halides with cyclopentadiene in the presence of a base such as diethylamine or piperidine results in elimination of an acidic methylene-hydrogen from cyclopentadiene, viz.:

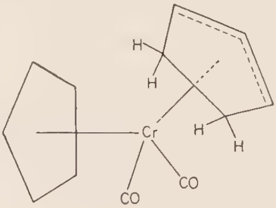
$$NiCl_2 + 2C_5H_6 \xrightarrow{\text{Base}} \pi\text{-}Cp_2Ni + BH^+Cl^-$$

The bis-π-cyclopentadienyl complexes of iron, cobalt and titanium(II) chloride may be prepared similarly [23, 24].

Cyclopentadiene reacts readily with metal carbonyls in a variety of ways. With iron pentacarbonyl under reflux the binuclear complex [π-CpFe(CO)$_2$]$_2$ is formed in good yields. The following mechanism for the reaction has been proposed [25, 26]:



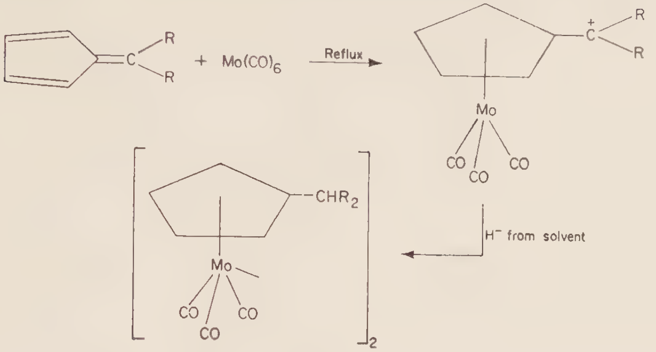
Cyclopentadiene iron tricarbonyl has been prepared and decomposes thermally to the binuclear carbonyl [π-$C_5H_5Fe(CO)_2$]$_2$ [26*a*]. The binuclear iron complex may further react with cyclopentadiene or thermally decompose (~200°) [27, 28] to give ferrocene. Monosubstituted ferrocenes may be prepared by the former reaction [27]. Chromium hexacarbonyl and cyclopentadiene at 280–350° react to give chromocene [29]; the reaction is reversible since treatment of chromocene with carbon monoxide under pressure affords chromium hexacarbonyl, together with intermediate products such as [π-CpCr(CO)$_3$]$_2$, [π-Cp$_2$Cr][π-CpCr(CO)$_3$] and, when hydrogen is also present, the cyclopentenyl complex π-$C_5H_5CrC_5H_7(CO)_2$, 4.1, is formed [30, 31, 32].



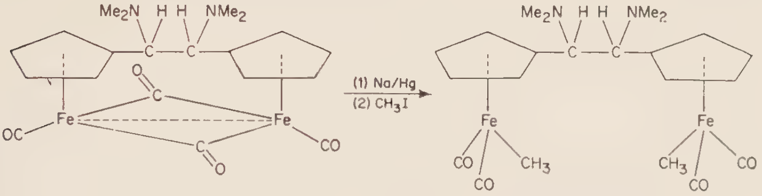
4.1

Dicobalt octacarbonyl and cyclopentadiene give π-CpCo(CO)$_2$; whilst under carefully controlled conditions the hexacarbonyls of molybdenum and tungsten give the binuclear complexes [π-$C_5H_5M(CO)_3$]$_2$ [3]. Treatment of the halides ZrX_4 and TiX_4 with cyclopentadiene vapour gives the complexes π-$C_5H_5MX_3$ and (π-C_5H_5)$_2MX_2$ [20].

(*iii*) *Reaction between fulvenes and metal carbonyls.* Fulvenes may react with metal carbonyls giving fulvene metal carbonyl complexes (see Chapter 7), but with the Group VI carbonyls substituted π-cyclopentadienyl complexes are formed, via a hydrogen transfer reaction [33*a*].



Similar reactions are found with dicobalt octacarbonyl and dialkyl fulvenes [32*a*]. Dimethylaminofulvene with iron pentacarbonyl gives several products, one of which is the unusual complex, 4.2, whose formulation is supported by the preparation of the dimethyl derivative, 4.3 [34*b*].



4.2 4.3

(b) Bis-π-cyclopentadienyl transition metal complexes

The known complexes are given in Table 10. The absence of bis-π-cyclopentadienyl complexes of the heavier metals of Groups 4-7 is consistent with the known instability of the lower oxidation states of these metals.

(*i*) *Crystal structure.* The crystalline complexes $(\pi\text{-}C_5H_5)_2$—, —V, —Cr, —Fe, —Co, —Ni, are isomorphous and have a monoclinic form [57]. On rapid cooling of crystalline ferrocene the crystals disintegrate fairly violently to a powder. Studies on the heat capacity of ferrocene have shown that there is a λ point transition at 163·9°K; the λ range is about 125–200°K [58].

N.M.R. studies on solid ferrocene over the range 50–425°K [59] show that the line width varies on cooling, as would be expected during a transition from a 'liquid' situation to that of a rigid solid. The evidence suggests

Table 10 *'Pure' bis-π-cyclopentadienyl transition metal complexes*

$[(\pi\text{-}C_5H_5)_2Ti]_2$(a) >200° d; dark green [33, 34, 34*a*]	$(\pi\text{-}C_5H_5)_2V$ 167–168 ; purple [23, 36, 37, 120]	$(\pi\text{-}C_5H_5)_2Cr$ 172–173°; scarlet [23, 29, 31, 36, 38, 39, 120]	$[Mn^{2+}(C_5H_5^-)_2]$ [23]	$(\pi\text{-}C_5H_5)_2Fe$ 173 ± 0·5°; orange [24, 42, 43]	$(\pi\text{-}C_5H_5)_2Co$ 173–174°; purple [23, 39, 48, 49, 53, 55]	$(\pi\text{-}C_5H_5)_2Ni$ 173–174° d; green [39, 48, 49 55, 56]
$(\pi\text{-}C_5H_5)_3Ti$ 130° d; green [5]	$[(\pi\text{-}C_5H_5)_2V]^+$ purple [35, 253]	$[(\pi\text{-}C_5H_5)_2Cr]^+$ [31, 255]		$[(\pi\text{-}C_5H_5)_2Fe]^+$ aq. dichroic; blue green–blood red [44, 267]	$[(\pi\text{-}C_5H_5)_2Co]^+$ aq. yellow–green [39, 44, 48, 50, 51, 53]	$[(\pi\text{-}C_5H_5)_2Ni]^+$ aq. yellow [38, 39, 46, 48, 49, 56]
						$[(\pi\text{-}C_5H_5)_2Ni]^{2+}$(?) [56*a*]
$[(\pi\text{-}C_5H_5)_2Zr]_2$ >300° d; purple-black [45]		$(\pi\text{-}Ph_5C_5)_2Mo$ red [116]	$[(\pi\text{-}C_5H_5)_2Tc]_2$ 155°; yellow [41]	$(\pi\text{-}C_5H_5)_2Ru$ white [46, 47, 301]	$(\pi\text{-}C_5H_5)_2Rh$ [102]	
		$[(\pi\text{-}Ph_5C_5)_2Mo]^+Br_3^-$ deep green [116]		$[(\pi\text{-}C_5H_5)_2Ru]^+$ pale yellow [46]	$[(\pi\text{-}C_5H_5)_2Rh]^+$ yellow [54]	
				$[(\pi\text{-}C_5H_5)_2Os]$ 229–230°; white [99]	$(\pi\text{-}C_5H_5)_2Ir$ [102]	
				$[(\pi\text{-}C_5H_5)_2Os]^{2+}$ orange-red [99]	$[(\pi\text{-}C_5H_5)_2Ir]^+$ yellow [54]	

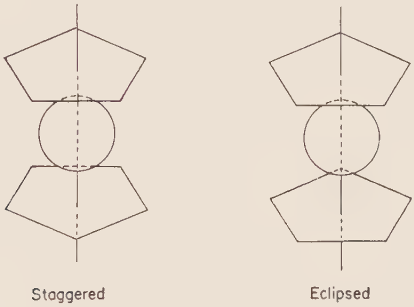
(*a*) The existence of this compound has been doubted but recently the compound has been fully characterized and found to be dimeric [34*a*], rather than monomeric [33].

that a considerable reorientation of the molecules occurs between 60–80 °K. However, in the range 115–225 °K, which is also the λ range, there is an anomalous line-width broadening with increase of temperature.

The above observations have been discussed in terms of reorientations of the molecules in the lattice and transitions between eclipsed and staggered configurations of the ferrocene molecules.

However, low-temperature crystallographic studies show no drastic change of unit-cell constants in the λ region [58], although there is considerable torsional vibration in the crystal [60].

(*ii*) *Molecular structure.* X-ray diffraction shows that crystalline ferrocene and its substituted derivatives (except bridged ferrocenes) have the antiprismatic (staggered) conformation, whereas ruthenocene and osmocene have the prismatic (eclipsed) form, which suggests that the inter-ring repulsive forces in these complexes are less than in ferrocene. This is in agreement with their larger inter-ring distances. It is worth noting that ferrocenyl ruthenocenyl ketone, $\pi\text{-}C_5H_5Fe\text{-}\pi\text{-}C_5H_4CO\text{-}\pi\text{-}C_5H_4Ru\text{-}\pi\text{-}C_5H_5$, has the same configuration for both metals, namely about halfway between the eclipsed and staggered structures [61].



Electron-diffraction studies show ferrocene in the vapour state to have an eclipsed configuration [62]. Some data on the structures of π-cyclopentadienyl complexes are given in Table 11.

(*iii*) *Electronic structure.* In the π-cyclopentadienyl ligand, the normal σ-bonded system for the carbon and hydrogen atoms may be assumed to be unaffected by the ligand metal bonding.

The five molecular π-orbitals of an isolated cyclopentadienyl group are constructed from the five $2p\pi$-atomic orbitals and are pictorially represented in Figure 22. Since in the bis-π-cyclopentadienyl complexes, the metal atom

Table 11 *Some distances in π-cyclopentadienyl transition metal complexes* (a)

Compound	Metal–carbon of ring Å	C–C of ring, Å	Other distance (Å) and comments
$(\pi\text{-}C_5H_5)_2Fe$ (b)	2·03 ± 0·02	1·43 ± 0·03	C–H, 1·09; Inter-ring, 3·25. Electron diff. [62, 63]
	2·045 ± 0·01	1·403 ± 0·02	Inter-ring, 3·32. X-ray [60]
$(\pi\text{-}C_5H_5)_2Ru$	2·21 ± 0·01	1·43 ± 0·01	Inter-ring, 3·68 ± 0·01 [63*a*]
$(\pi\text{-}C_5H_5)_2Os$	2·22		Inter-ring, 3·71 [64]
$\pi\text{-}C_5H_5Mn(CO)_3$	2·165 ± 0·025	1·42 ± 0·03	Mn–CO, 1·80 ± 0·02; C≡O, 1·15 ± 0·03 [65]
$\pi\text{-}C_5H_5NiNO$	2·107 ± 0·001		Ni–N, 1·676 ± 0·02. Microwave [66]
$[\pi\text{-}C_5H_5Fe(CO)_2]_2$	2·11 ± 0·03	1·41 ± 0·04	Fe–Fe, 2·49 ± 0·02; Fe–CO (terminal) 1·75 ± 0·03 Fe–CO (bridging) 1·85 ± 0·03 [67]
$[\pi\text{-}C_5H_5Mo(CO)_3]_2$	2·302 – 2·378	1·370 – 1·442	Mo–Mo, 3·222 [151]
$\pi\text{-}C_5H_5Mo(CO)_3CH_2CH_3$			Metal–ring, 2·04; Mo–CH₂, 2·38; Mo–CO, 1·96 [68]
$[\pi\text{-}C_5H_5Mn(CO)_2]_2$Diars	2·15		Mn–CO, 1·77 [106] [193]
$\pi\text{-}C_5H_5CoC_5H_5C_6H_5$ (c)	2·06 ± 0·03		Co–C_1 and C_4, 2·55; Co–C_3 and C_2, 2·01; $\theta = 36°$ [69]
$\pi\text{-}C_5H_5CoC_5(CH_3)_4O$	2·07	1·43	Co–π-C_5H_5 ring, 1·67; Co–$C_5(CH_3)_4O$ ring, 1·63; $\theta = 9°$
$\pi\text{-}C_5H_5RhCOC_2F_5I$	2·24 av.		Rh–CF_2 2·09; Rh–CO, 1·96 [70]
$\pi\text{-}C_5H_5TiCl_3$	2·38		Ti–Cl, 2·27–2·30 [243]
$[\pi\text{-}C_5H_5TiCl_2]_2O$	2·35 ± 0·05		Ti–O, 1·78; Ti–Cl, 2·25 [244]

(*a*) Further detailed data may be found in the reviews [280] and [57].

(*b*) The following metal–'carbon of ring' distances have been determined from cell dimension data: $(\pi\text{-}C_5H_5)_2V$ (2·3) [71, 72]; $(\pi\text{-}C_5H_5)_2Cr$ (2·2) [72]; $(\pi\text{-}C_5H_5)_2Co$ (2·1) [72, 73]; $(\pi\text{-}C_5H_5)_2Ni$ (2·2) [74].

(*c*) See Figure 19, p. 73, for numbering and structure.

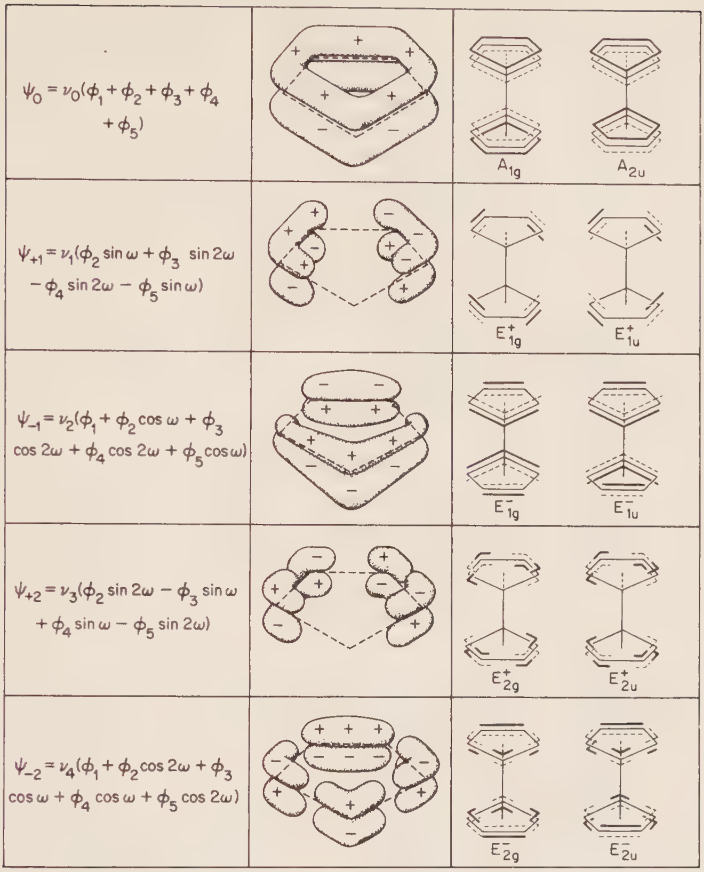


Fig. 22. M.O.s of the cyclopentadienyl radical [$\omega = \frac{2}{5}\pi$]. Possible combinations of C_5H_5 M.O.s in ferrocene

interacts with a pair of cyclopentadienyl rings, the ligand M.O.s of the same rotational symmetry are combined in pairs so that the resulting wave function is either symmetrical or anti-symmetrical with respect to inversion

Table 12 *Classification by symmetry of the orbitals in ferrocene*

Symmetry of orbitals	Metal orbitals	Ligand orbitals	Rotational symmetry
A_{1g}	$4s$; $3d_{z^2}$	$\psi_{0A} + \psi_{0B}$	σ
E_{1g}	$3d_{xz}$, $3d_{yz}$	$\psi_{\pm 1A} + \psi_{\pm 1B}$	π
E_{2g}	$3d_{x^2-y^2}$	$\psi_{\pm 2A} + \psi_{\pm 2B}$	δ
A_{2u}	$4p_z$	$\psi_{0A} - \psi_{0B}$	σ
E_{1u}	$4p_x$, $4p_y$	$\psi_{\pm 1A} - \psi_{\pm 1B}$	π
E_{2u}	—	$\psi_{\pm 2A} - \psi_{\pm 2B}$	δ (non-bonding)

through the centre of symmetry. Ferrocene belongs to the symmetry group D_{5d} and in Table 12 the metal and ligand orbitals which may interact, and their joint transformation properties are given. The various possible interactions are represented in Figure 23.

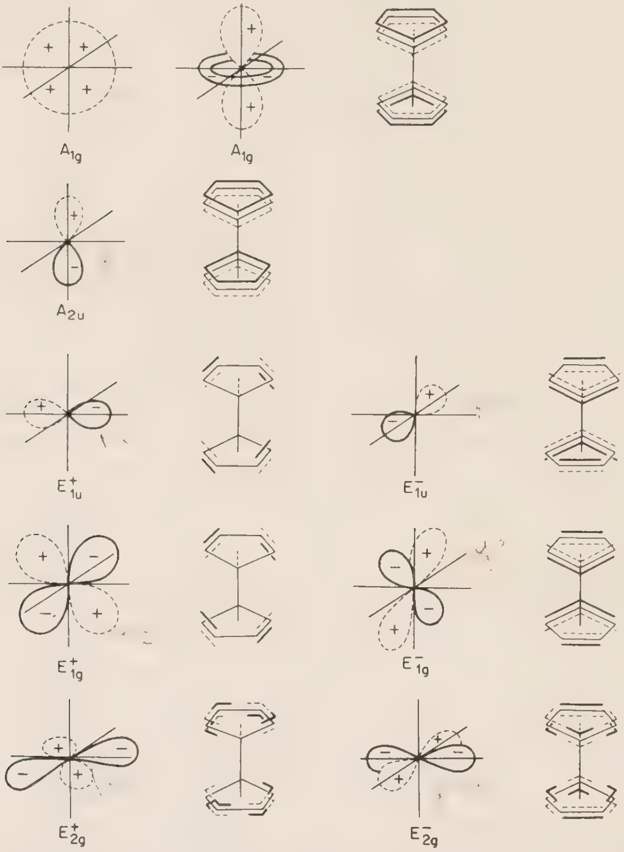


Fig. 23. Representations of the possible combinations between two C_5H_5 ligands and the iron atomic orbitals, 4*s*, 4*p* and 3*d*

The relative ordering of the energy levels in ferrocene has not been finally settled, although there is general agreement as to the major source of the bonding. Theoretical calculations are unlikely to resolve the question due to their approximate nature. It is worthwhile, however, to consider the results of a calculation by Schustorovich and Dyatkina [75], in order to investigate more closely the nature of the metal-ring bonding. Their results are summarized in the energy level diagram in Figure 24. As shown, the M.O.s of symmetry E_{1g} and E_{1u} are all bonding. It is these two π orbitals which are the chief source of the bonding in ferrocene and

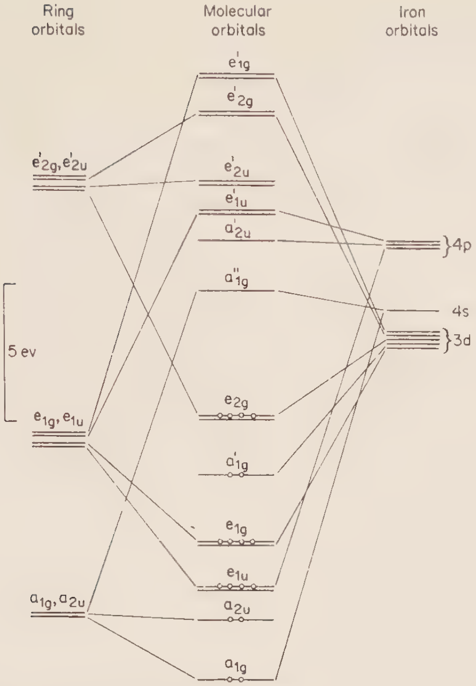


Fig. 24. Molecular orbital diagram for ferrocene after Schustorovich and Dyatkina [75] (and Cotton [75*a*])

indeed in the other bis-π-cyclopentadienyl complexes. The E_{1g} bond is polarized and transfers charge from the metal to the ring whilst the E_{1u} bond transfers charge from the ring to the metal. Thus the π-cyclopentadienyl ring has donor–acceptor characteristics.

The 4s orbital of the metal interacts with the ring a_{1g} orbital, and their overlap integral is quite large; however, the energies of the orbitals are so diverse that only a small amount of bonding results. The $3d_{z^2}$ orbital of the metal is claimed to have a negligible interaction with the ring a_{1g} orbital, but none the less its energy, relative to that in the free atom, is lowered due to both the presence of a resultant charge on the metal atom and the modified electron distribution about it. The $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals of the iron interact with the anti-bonding e_{2g} orbitals of the rings to produce a slightly bonding e_{2g} M.O. which consists largely of the metal orbitals. The latter bonding represents a certain amount of back-donation from the metal to the ring, thus compensating slightly for the donor properties of the ring a_{1g} and e_{1u} orbitals. The metal $4p_z$ orbital interacts negligibly with the a_{2u} ring orbitals since overlap is small and their energy differences are large.

Thus, the eighteen available electrons in ferrocene (ten from the two cyclopentadienyl ligands and eight from the iron atom) may be placed in the nine M.O.s of lowest energy.

It may be noted that the a'_{1g} (d_{z^2}) and the e_{2g} electrons are essentially non-bonding in ferrocene. The spatial distribution of the electrons in these orbitals will have trigonal symmetry and may be roughly represented as shown in Figure 25.

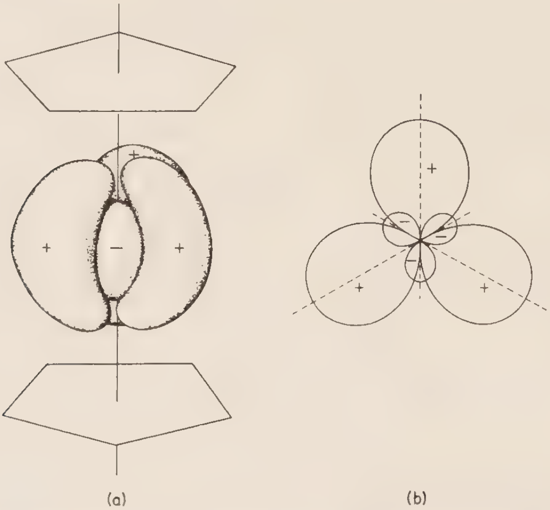


Fig. 25. Representation of the a'_{1g} and e_{2g} orbitals; (*a*) the 'non-bonding' orbitals in ferrocene. (*b*) A cross-section through the iron atom, parallel to the π-cyclopentadienyl ring

This treatment of the bonding in ferrocene is successful in so far as it accounts for the observed diamagnetism and gives a calculated ionization potential of 6·39 eV which compares favourably with measured values of 6–8 eV [76, 77]. Also the above calculation places a positive charge on the iron atom of +0·7 electrons compared with a value of +0·4 electrons estimated from adsorption edge X-ray data [78]. The presence of a positive charge on the metal in π-cyclopentadienyl–metal systems has also been deduced from dipole moment data (a metal ring moment of 2–2·5 D is quoted [79]). This distribution of charge is also in general agreement with the ease with which many π-cyclopentadienyl–metal complexes undergo electrophilic substitution reactions.

For the first row bis-π-cyclopentadienyls other than ferrocene the symmetry treatment is the same. However, the relative energies of the M.O.s will vary with the changing energy of the metal atomic orbitals and differing numbers of electrons in the complexes. On the basis of the treatment of the bonding in ferrocene it is assumed that the electron combinations $(a_{1g})^2$ $(a_{1u})^2$ $(e_{1g})^4$ and $(e_{1u})^4$ provide the main bonding in the other bis-π-cyclopentadienyls. However, argument centres around the relative energies of the $(e_{1g})^4$ and $(e_{1u})^4$ orbitals, which may interchange their order, and also into which orbitals the other electrons go. Fortunately magnetic measurements can indicate the electron distribution [80, 81]. The observed magnetic susceptibility shows the number of unpaired spins in a complex and further, the difference between the observed magnetic moment and the calculated 'spin only' values provides more detailed information. Thus when an unpaired electron is in an orbital where the magnetic quantum number, $m = 0$ (i.e. $4s$, $4p_z$ and $3d_{z^2}$ orbitals), the orbital component of the magnetic moment is zero. However, an unpaired electron in either of the orbitals $d_{x^2-y^2}$ or d_{xy} (where $m = \pm 2$) has an orbital component which is non-zero and the magnetic moment is consequently greater than is given by a 'spin only' value. Finally, in the cases where there is one unpaired electron in each of the $d_{x^2-y^2}$ and d_{xy} orbitals, the contribution of the orbital component to the magnetic moment is again zero. On these arguments the electronic structure of the $3d$ transition metal bis-π-cyclopentadienyls has been assigned as shown in Table 13.

Table 13 *Magnetic data and electron assignment for bis-π-cyclopentadienyl complexes*

Compound$^{(a)}$	Electron assignment $(a_{1g})^2(a_{1u})^2$ $(e_{1u})^4(e_{1g})^4$	Number of unpaired spins	Spin only value	Magnetic moment expected	Magnetic moment found
Cp_2Ti^+	$(e_{2g})^1$	1	1·73	>1·73	2·29 ± 0·05
Cp_2V^{2+}	$(e_{2g})^1$	1	1·73	>1·73	1·90 ± 0·05
Cp_2V^+	$(e_{2g})^2$	2	2·83	~2·83	2·86 ± 0·06
Cp_2V	$(e_{2g})^2(a'_{1g})^1$	3	3·87	~3·87	3·84 ± 0·04
Cp_2Cr^+	$(e_{2g})^2(a'_{1g})^1$	3	3·87	~3·87	3·73 ± 0·08
Cp_2Cr	$(e_{2g})^3(a'_{1g})^1$	2	2·83	>2·83	3·20 ± 0·16
Cp_2Fe^+	$(a'_{1g})^2(e_{2g})^3$	1	1·73	>1·73	2·34 ± 0·12
Cp_2Fe	$(a'_{1g})^2(e_{2g})^4$	0	0	0	0
Cp_2Co^+	$(a'_{1g})^2(e_{2g})^4$	0	0	0	0
Cp_2Co	$(a'_{1g})^2(e_{2g})^4$ $(a''_{1g})^1$	1	1·73	~1·73	1·76 ± 0·07
Cp_2Ni^+	$(a'_{1g})^2(e_{2g})^4$ $(e'_{1g})^1$	1	1·73	>1·73	1·82 ± 0·09
Cp_2Ni	$(a'_{1g})^2(e_{2g})^4$ $(e'_{1g})^2$	2	2·83	~2·83	2·86 ± 0·11

(*a*) $Cp_2 = (\pi\text{-}C_5H_5)_2$

The magnetic data given in Table 13 have been primarily determined by bulk magnetic susceptibility measurements; in addition a few ESR and *ortho-* to *para*-hydrogen conversion studies have been made [82, 83, 84]. The ESR spectrum of vanadocene confirms the presence of 3 unpaired electrons and suggests that they have little *s*-electron density at the metal nucleus [85]. This indicates that in vanadocene the a'_{1g} orbital has little $4s$ character and that the $3d_{z^2}$ orbital is essentially non-bonding.

Further support for the validity of the M.O. treatment of the metallocenes arises from the ability of this approach to interpret the 'g' values of the cations $[(\pi\text{-}C_5H_5)_2M]^{n+}$, where M = Fe^+, Ti^+ or V^{2+} [85*a*], and the electric field gradient in ferrocene determined by Mossbauer spectra [85*b*].

It may be noted that the nuclear magnetic resonance contact shifts of some paramagnetic metallocenes and 1,1′-dimethyl derivatives may not be understood by analogy with those in substituted benzene anions [85*c*]. Perhaps the mechanism of delocalization of unpaired spin density to the ring substituents of metallocenes involves some direct metal–substituent interaction.

(*iv*) *The stability of bis-π-cyclopentadienyl complexes.* The sandwich complexes are thermally stable and many melt without decomposition at about 173°. They are stable to hydrolysis and resist catalytic hydrogenation. Ferrocene is even more resistant to hydrogenation than benzene though it may be reduced together with metal–ring cleavage by lithium in ethylamine [86]. The hydrogens of the π-cyclopentadienyl ligands are normally not labile and do not exchange with D_2O. Deuteroferrocenes may be prepared by reaction between $(\pi\text{-}C_5H_5)_2Fe$ and $Ca(OD)_2$ at high temperatures [91], or by proton–deuteron exchange in strongly acidic D_2O solutions [87]. Ferrocene is very stable towards degradation by ionizing radiation and is efficient in reducing radiolysis yields [88*a*].

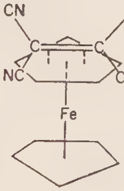
The enthalpy of formation, ΔH_{298}, from the elements of gaseous ferrocene has been determined as +50·61 [88] and +51·3 kcal./mole [89]. For nickelocene, +62·8 (crystalline) [90] and +85·9 kcal./mole (gaseous) [91] have been found. Thus nickelocene is less stable than ferrocene, which is in agreement with there being a weaker ring–metal bond, as is suggested by its greater length compared to that in ferrocene. Also, infrared spectra indicate the order of ring–metal bond strength, ruthenocene > ferrocene > nickelocene [91, 92]. The theory predicts a weaker ring–metal bond in nickelocene, since it is a 20-electron complex and, as shown in Table 13, two electrons are placed in anti-bonding (e_{1g}) orbitals.

Stability to oxidation. The stability of the bis-π-cyclopentadienyls to oxygen varies widely. At room temperature ferrocene is inert to molecular oxygen whilst chromocene is pyrophoric in air. The controlled oxidation of π-cyclopentadienyl complexes may give π-cyclopentadienyl metal oxide derivatives (see section I (*b*, *c*)). All the complexes $(\pi\text{-}C_5H_5)_2M$ can be oxidized in acid solutions to cations (see Table 10). Frequently these oxidations are reversible. Ferrocene in acid solutions gives dichroic deep blue-green (blood-red when concentrated) solutions of the *ferricenium* cation $[(\pi\text{-}C_5H_5)_2Fe]^+$. Neutral or basic solutions of this cation are unstable and ferrocene and iron hydroxides are formed.

Metallicenium cations and ferrocene charge transfer complexes

The ferricenium cation may be isolated with anions such as I_3^- [77, 93] BF_4^- [93] and $FeCl_4^-$ [94, 95]. The ferricenium ion has one unpaired electron but it shows no electron spin resonance since the ground state is orbitally degenerate [95*a*, 80]. It has been suggested that the ferricenium ion forms complexes in solution with the anions I_3^-, $FeCl_4^-$ [96*a*] and carboxylates [95*b*]. However, the Mössbauer spectrum of solid ferricenium tetrachloroferrate suggests it to be the salt $[(\pi\text{-}C_5H_5)_2Fe]^+FeCl_4^-$ [94]. Further, potentiometric studies show that there is no appreciable complex formation between the ferricenium and chloride ions in water at 25° [96*a*].

On the other hand, ferrocene forms charge-transfer complexes with nitrobenzenes [96*b*], tetracyanoethylene (TCNE) [96, 96*c*, 96*d*] and 2,3-dichloro-5,6-dicyanoquinone. Mössbauer spectroscopy indicates that the ferricenium ion is not present in the 1:1 TCNE: ferrocene complex, and, as may also be the case with the nitrobenzene complexes, it is suggested that the complex is of benzenoid type with the TCNE placed above a $\pi\text{-}C_5H_5$ ring, 4.4 [96*c*]. In this context it is noteworthy that the high efficiency of ferrocene in quenching triplet states in excited photosensitizers, e.g., benzophenone, may be due to a charge-transfer mechanism [96*e*].

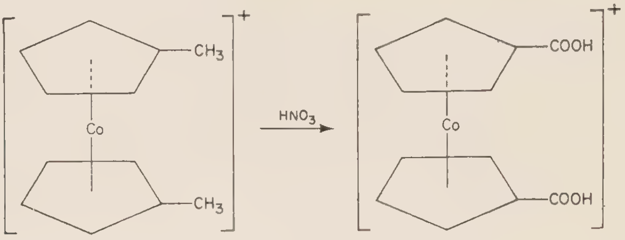


4.4

The oxidation of ruthenocene can occur by a one-electron transfer process [97] giving the pale yellow ruthenicenium cation. However, chronopotentiometric oxidation gives the cation $[(\pi\text{-}C_5H_5)_2Ru]^{2+}$ by a two-electron transfer process [98]. Osmocene is oxidized by ferric chloride, or chronopotentiometrically to the analogous cation $[(\pi\text{-}C_5H_5)_2Os]^{2+}$ [99]. Other species such as the diamagnetic $[(\pi\text{-}C_5H_5)_2OsOH]^+$ and $[(\pi\text{-}C_5H_5)_2OsI]^+$ are formed [99]. The order of ease of oxidation of the complexes $(\pi\text{-}C_5H_5)_2M$, $M = Fe > Ru \approx Os$, has been proposed [98].

Cobaltocene is readily oxidized, thus losing an electron from an antibonding orbital and attaining the rare gas configuration. Solutions readily absorb oxygen but, as yet, no oxygen-cobalt complexes of cobaltocene have been isolated [100]. Both cobaltocene and rhodocene may be regarded as pseudo-alkali metals in so far that they readily lose one electron forming metallicenium cations. The cations are very stable to further oxidation;

for example they are stable in concentrated HNO_3. Boiling the 1,1-di-methylcobalticenium cation, 4.5, in this acid gives the dicarboxylic acid, 4.6. The cations are however susceptible to nucleophilic attack on the π-C_5H_5 rings (see section B, *vi*).



4.5 4.6

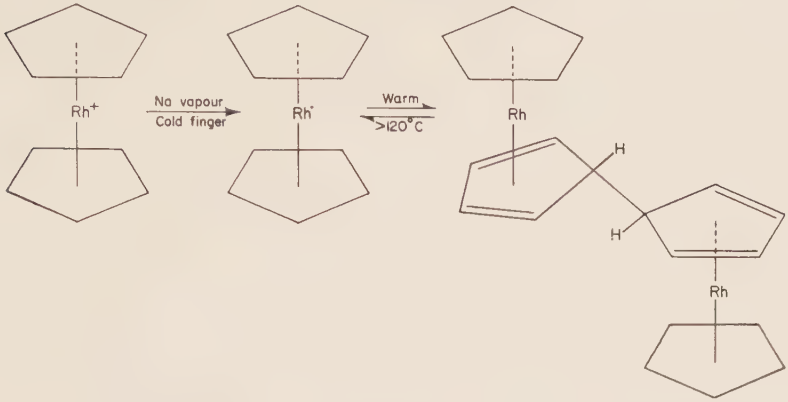
Exchange studies have shown that the electron transfer reactions $(\pi\text{-}C_5H_5)_2M \rightleftharpoons [(\pi\text{-}C_5H_5)_2M]^+$, where M = Fe or Co, are very rapid [100, 101]. The paramagnetic $[(\pi\text{-}C_5H_5)_2Ni]^+$ cation is rather unstable and decomposes in solution [48].

(*v*) *The solubility properties of the cations* $[(\pi\text{-}C_5H_5)_2M]^+$. The metallicenium cations (and indeed nearly all organometallic cations) give precipitates with silicotungstic acid in aqueous solution. When their solutions are not too dilute, precipitates may also be obtained with anions such as $[PF_6]^-$, $[PtCl_6]^{2-}$, $[SbCl_6]^-$, I_3^-, picrate and Reineckate. Salts with these anions are frequently soluble in liquid sulphur dioxide and acetone from which they may be crystallized by addition of chloroform or ether.

(*vi*) *Some chemical reactions of bis-π-cyclopentadienyl complexes.* It has been shown above that the bis-π-cyclopentadienyl complexes differ from most organotransition metal compounds in that they often do not obey the 18-electron rule and many are paramagnetic. Further, for a given metal, two or more oxidation states are sometimes known. Nevertheless the chemistry of bis-π-cyclopentadienyls may be associated to some extent with a tendency to form 18-electron complexes; this is especially true for cobaltocene and nickelocene.

The bis-π-cyclopentadienyls of iron, ruthenium and osmium have an extensive organic chemistry. They are all 18-electron complexes and are usually stable under the conditions in which ring substitution can be achieved. There is a rapidly growing field of the organic chemistry of these metallocenes which is separately discussed in sections K and L of this chapter.

Cobaltocene and rhodocene. Rhodocene is a very reactive 'radical' and dimerizes at room temperature. It is thus only isolable in the absence of solvents, either at high or low temperatures [102].



Attempts to reduce the rhodicenium cation with conventional reducing agents invariably give the cyclopentadiene complex π-$C_5H_5RhC_5H_6$, and both the rhodicenium and cobalticenium cations undergo nucleophilic attack, by R^-, for example, where $R = H^-$ or Ph^- (see Figure 26). Some unusual reactions of cobaltocene are shown in Figure 26.

The known chemistry of bis-π-cyclopentadienyl iridium is entirely analogous to that of rhodocene [102].

Nickelocene. Nickelocene is a reactive molecule and undergoes a number of ring-addition reactions. Also, the loss of a π-cyclopentadienyl ring is not uncommon. These reactions are exemplified in Figure 27. As found for cobaltocene, nickelocene usually reacts forming complexes which have an 18-electron shell.

Nickelocene reacts with donor ligands, (L), such as tertiary phosphines or α,α'-bipyridyl and the π-cyclopentadienyl rings are displaced giving zero valent complexes, NiL_4 [115].

Miscellaneous

The complex $(\pi$-$Ph_5C_5)_2Mo$ is of interest since the unsubstituted analogue, molybdenocene, is unknown. It is one of the products of the reactions between diphenylacetylene and molybdenum hexacarbonyl [116], and it forms red crystals which are rather unreactive. Oxidation with bromine gives a green, paramagnetic (3·5 B.M.) salt of stoicheiometry $[(\pi$-$Ph_5C_5)_2Mo]Br_3$.

A green complex of stoicheiometry $[(C_5H_5)_2Pt]_2$ has been described [116*a*]. Its structure is unknown but the proton magnetic resonance spectrum suggests there to be both σ- and π-C_5H_5 rings and a Pt–Pt bond.

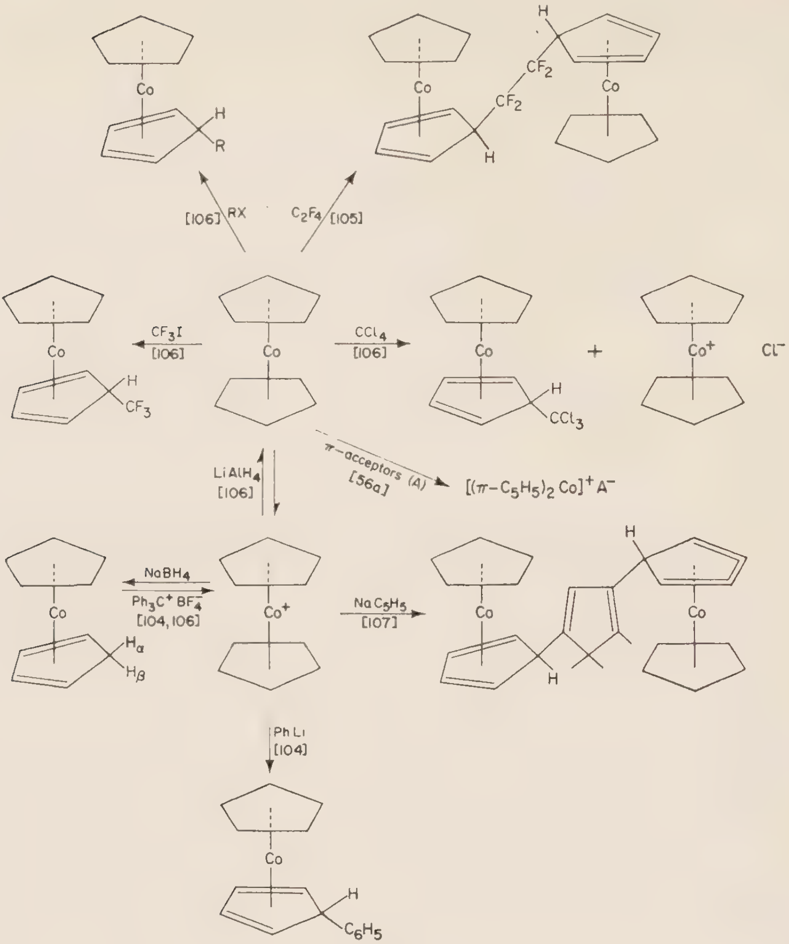
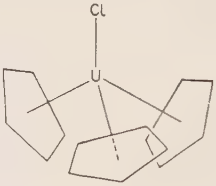


Fig. 26. Some reactions of cobaltocene

(*c*) *π-Cyclopentadienyl complexes of uranium, thorium and actinide metals*
Uranium forms the stable red tetra-cyclopentadienyl uranium which is paramagnetic (two unpaired electrons) and, since zero dipole moment was observed, the structure shown on p. 91 is proposed [4]. The tris-π-cyclo-



4.7

pentadienyl complex $(\pi\text{-}C_5H_5)_3UCl$ and salts of its cation $[(\pi\text{-}C_5H_5)_3U]^+$ have also been prepared [116*b*]. The crystalline chloride 4.7 has a tetrahedral disposition of the ligands about the uranium [117].

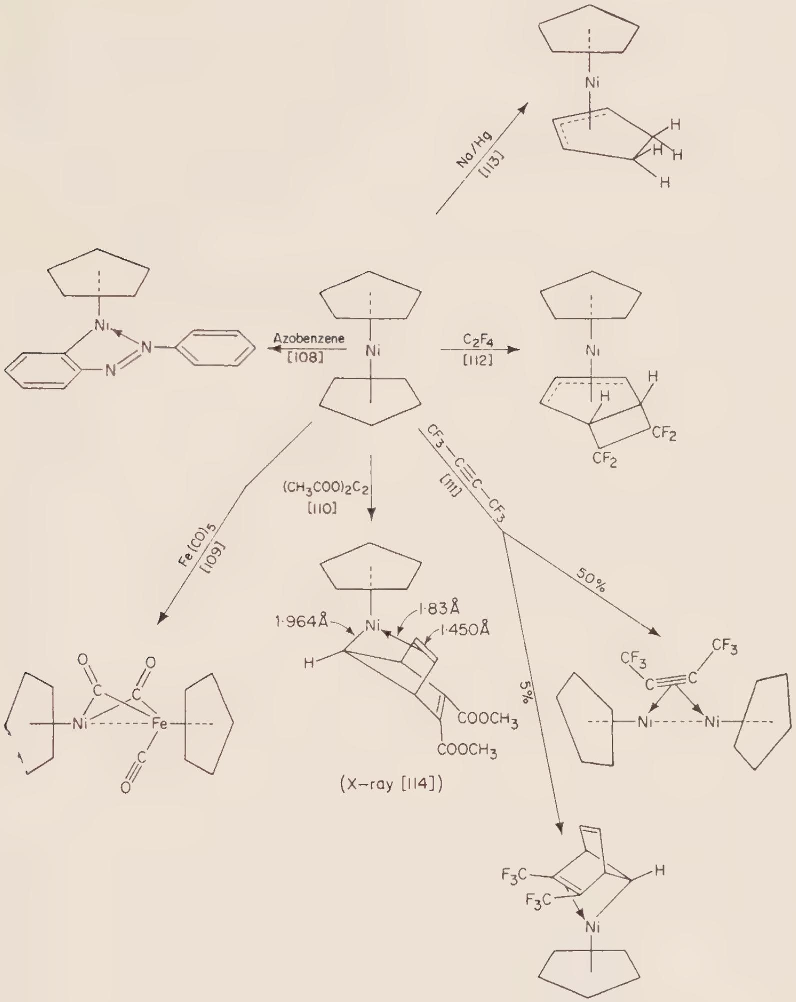


Fig. 27. Some chemistry of nickelocene

A tetra-cyclopentadienyl thorium complex has also been prepared (117*a*]. Direct reaction between $(C_5H_5)_2Be$ and the appropriate anhydrous metal halide gives the air-sensitive actinide complexes $(C_5H_5)_3NpCl$ [117*b*], $(C_5H_5)_3Pu$, moss green [19*b*], and $(C_5H_5)_3Am$, pink [19*a*].

C. Cyclopentadienide transition metal complexes

(*a*) *Manganocene*

Bis-cyclopentadienide manganese (manganocene) is the only complex of the *d*-block transition metals for which a primarily ionic ring–metal bond is proposed. It may be prepared by treatment of anhydrous $MnCl_2$ with sodium cyclopentadienide in tetrahydrofuran and forms amber crystals, m.p. 172–173°C, which are readily volatile [$\Delta H_{sub} = 17{\cdot}3$ kcal./mole] [23], and are soluble in ether and other common organic solvents. X-ray studies [118] show that the complex has the ferrocene 'sandwich' structure, as indeed has bis-cyclopentadienide magnesium [119]. This structure is of course the configuration expected for two negatively charged discs and a positively charged ball.

Like the ionic alkali metal cyclopentadienides, manganocene hydrolyses easily, giving cyclopentadiene and the metal hydroxide and reacts with CO_2 giving carboxylic acid salts.

These properties suggest an ionic nature. Also, in ethereal solution, manganocene reacts instantaneously with ferrous chloride affording ferrocene. The conductivity of the ethereal solution is however low, and thus it is necessary to postulate ion-association if manganocene is a salt. Stronger arguments for ionic character come from the unusual magnetic properties of manganocene.

Dilute solid solutions of manganocene in bis-cyclopentadienide magnesium are paramagnetic and the manganese atom has a magnetic moment of $5{\cdot}86 \pm 0{\cdot}05$ B.M., indicating five unpaired electrons [23, 57, 120], a characteristic of the Mn(II) ion. A similar magnetic moment is found for a high-temperature form of pure manganocene which occurs above 433°K. At low temperatures, however, it exhibits antiferromagnetic properties. ESR studies confirm the antiferromagnetic nature of the low-temperature (rhombic) form of manganocene and are consistent with there being an essentially ionic metal–ring bond [121].

The above evidence for ionic character is however not unequivocal, and indeed it has been argued from the similarity of the infrared spectra of ferrocene and manganese bis-cyclopentadienide that the latter has some weak covalent-ring–metal bond [119]. Nevertheless, manganocene behaves chemically in a manner very different from the other bis-π-cyclopentadienyls and analogously to the ionic cyclopentadienide derivatives of the most electropositive metals. The preference of manganocene for an ionic structure containing Mn(II) high spin ion may be a consequence of the stability of the half-filled shell of the Mn(II) ion.

(*b*) *Ionic character in the bis-π-cyclopentadienyls*

Although the remaining sandwich complexes of the first row of the transition metals are considered to be covalent there is always some charge separation between the metal and the rings. Vanadocene and chromocene, in particular, show some chemistry which may be associated with the ionic cyclopentadienides. For example, chromocene reacts in solution with ferrous chloride affording ferrocene in 40% yield [23] and also forms ammines such as $[Cr(NH_3)_6]^{2+}[C_5H_5]_2^{2-}$. It has been argued that the mass spectra of sandwich complexes provide evidence for varying degrees of ionic character, thus complexes which show higher yields of ions such as $C_5H_5M^+$ [76] are thought to be the more ionic. The above evidence for ionic character is suggestive but it may be misleading. For example, in π-cyclopentadienyl-π-allyl palladium, which is probably mainly covalent, the π-cyclopentadienyl ligand is readily removed by hydrogen halides giving cyclopentadiene, or by ferrous chloride giving ferrocene; however, spectral studies show that in basic solvents, the π-cyclopentadienyl ligand is partially displaced (presumably forming a complex such as [σ-cyclopentadienyl-π-allyl palladium (solvent)]); so the lability of the π-cyclopentadienyl ring in this complex may be due to a π-cyclopentadienyl to σ-cyclopentadienyl equilibrium rather than to an ionic-ring–metal bond [122].

(*c*) *Rare earth cyclopentadienides*

A series of tris-cyclopentadienides M(III) and bis-cyclopentadienide M(III) chlorides are known for the 4*f*-block metals [123, 124, 125], and the bis-cyclopentadienides of europium(II) and ytterbium(II) have been prepared by treatment of a solution of the metal in liquid ammonia with cyclopentadiene [126, 127]. The tris-cyclopentadienides are sensitive to oxygen, and to hydrolysis. They are thermally very stable and have magnetic properties characteristic of the M(III) ions. Surprisingly the compounds $(C_5H_5)_2ClM$, where M = Sm, Dy, Er, Yb, La and Lu, are dimeric in benzene solution, and form stable tris-tetrahydrofuranates [128]. It is suggested that the chloride dimers have bridging chloride ligands [124].

Tris-cyclopentadienide ytterbium forms complexes $(C_5H_5)_3YbL$, where L = Ph_3P, THF, and NH_3 [128*a*]. Thermal decomposition of the ammonia complex forms the amide $(C_5H_5)_2YbNH_2$. The complex $(C_5H_5)_3Yb$ has a green colour of an intensity unusually high for a rare earth compound. The electronic spectrum has been studied in the solid state and solution [128*b*]. It may be interpreted on the basis of an excited state formed by an electron transfer process from a linear combination of the orbitals the three C_5H_5 ligands to the metal, that is, the process (ground state) $(C_5H_5)_3{}^{3-}Yb^{3+} \rightarrow (C_5H_5)_3{}^{2-}Yb^{2+}$ (excited state). There is little doubt that these rare earth complexes are not simple ionic cyclopentadienides but that they contain a degree of covalent character in the ring-metal bonds. The 6*s* and 6*p* orbitals of the rare earths are of suitable size and energy for forming covalent metal–ligand bonds; the 4*f* and to a similar extent the 5*d* orbitals are, of course, too well shielded to make much contribution to the bonding. A molecular orbital treatment of the rare earth complexes $(C_5H_5)_3M$ has been given [128*b*, 128*c*].

D. The bonding in mono-π-cyclopentadienyl transition metal complexes

Since the symmetry of mono-π-cyclopentadienyls is frequently much lower than that in the sandwich complexes (see Figure 28), the M.O. treatment

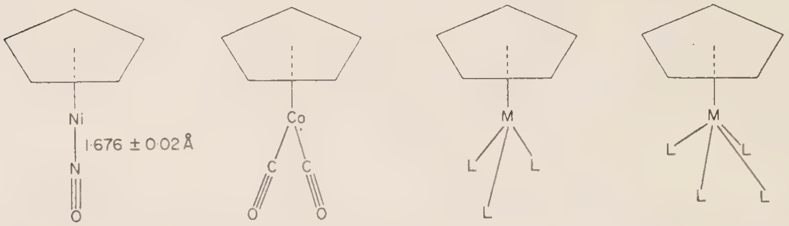
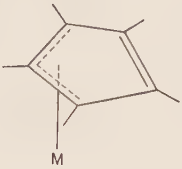


Fig. 28. The structures proposed or determined for mono-π-cyclopentadienyl complexes

of the bonding becomes correspondingly more complicated. A simplifying procedure which is normally adopted is to consider the local symmetry of the π-cyclopentadienyl–metal system to obtain a description of the ring–metal bonding and the local symmetry of the metal and the other ligands in order to obtain a description for their bonding. Thus for π-$C_5H_5Mn(CO)_3$, the π-C_5H_5Mn system has C_{5v} symmetry whilst the $Mn(CO)_3$ has C_{3v} symmetry. This restriction (the consideration of only local symmetry) seems to be justified since the properties of π-cyclopentadienyl–metal systems are usually fairly similar for a wide range of complexes which differ in their other ligands. On the other hand there is no doubt that the other ligands on the metal will have some effect on the ring–metal bonding. For example, in those complexes where the symmetry of the other ligands attached to the metal is C_{nv}, where $n \geqslant 3$, the chief contribution to the metal–ring bonding can be assumed to arise from the two pairs of orbitals of π-symmetry which give the major bonding in ferrocene. However, when $n < 3$, as in π-$C_5H_5Co(CO)_2$, the degeneracy of the d_{xz} and d_{yz} and the p_x and p_y orbitals will be lifted. This in turn will lift the degeneracy of the $\psi_{\pm 1}$ orbitals with which these metal orbitals bond to the ring and thus the π-C_5H_5 ring would be expected to undergo a distortion.

In those cases where the symmetry of the metal–ligand system is lower than C_{nv} then again it might be expected that the π-cyclopentadienyl ring might undergo some distortion. Another way of looking at this is to consider the molecule π-$C_5H_5MX_2Y$ as being essentially octahedral with the π-C_5H_5 ring occupying three co-ordination positions. Differences in the *trans*-effect of the ligands X and Y would then be expected to cause asymmetry of the bonding of the π-C_5H_5 ring to the metal.

In fact, present X-ray data show no unequivocal evidence for the distortion of π-cyclopentadienyl rings in low symmetry complexes. However, it has been pointed out [129] that inequalities are found in the C–C distances in some π-cyclopentadienyl complexes, which may be significant although they are all within the calculated errors of the structural determinations. In the gas phase or in solution it may be assumed that the π-cyclopentadienyl ring can rotate relatively freely about the metal–ring axis (a rotational barrier of 1·1 kcal. has been estimated [62]); such restricted rotation may persist in the solid state at room temperature and in any case there would be considerable torsional vibration of the rings. Therefore the carbon atoms of the π-cyclopentadienyl rings may *chemically* appear to be equivalent even though the ring is *instantaneously* asymmetrically bound to the metal. Finally, with a ligand such as cyclo-octa-1,3,5-triene we find complexes in which the organic group acts as either a 4- or 6-electron ligand (see p. 12). This suggests that in some π-cyclopentadienyl complexes with distorted rings only some of the ring $p\pi$-electrons may be used in the metal–ring bonding. For example, only three carbons could be involved in bonding to the metal as a π-allenyl system, whilst the other two carbons are much less involved, viz.,

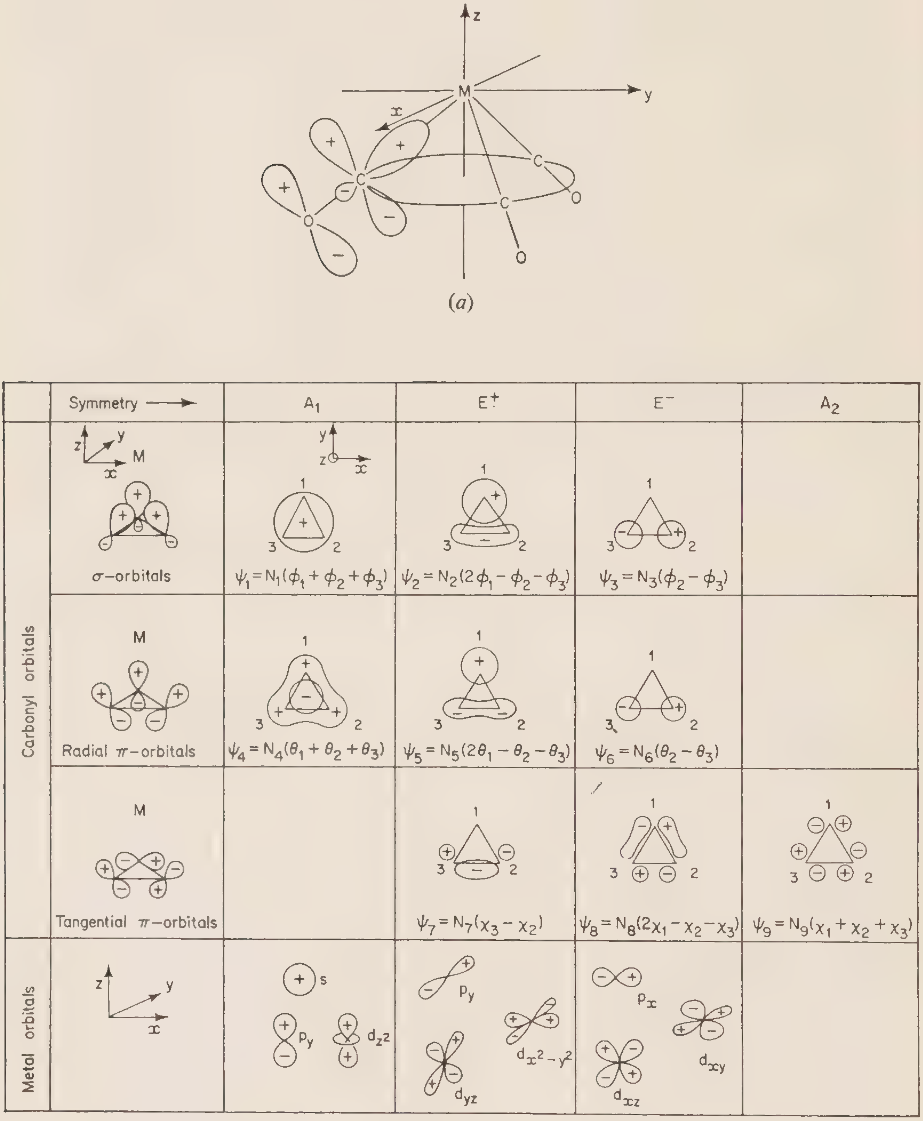


Such considerations indicate that the conventional ideas of transition metal stereochemistry and co-ordination number should be applied with great caution to organometallic complexes.

(*a*) *The bonding in metal–tricarbonyl groups*

The bonding in the $M(CO)_3$ groups is discussed in some detail in order to illustrate a general molecular orbital approach. The $M(CO)_3$ group has C_{3v} symmetry. Even though the three carbonyl groups are not bonded to each other they are treated as a unit in the bonding description given below. Each carbon monoxide molecule has one σ-orbital (ϕ) and two π-orbitals (θ, χ) which are involved in the metal ligand bonding. The two π-orbitals are called tangential (χ), and radial (θ), according to their projection on the circle centred on the z-axis and passing through the three carbons (see Figure 29(*a*)).

The three sets of orbitals, namely the σ-, π-tangential- and π-radial-orbitals, are not interchanged by any of the symmetry operations of the group C_{3v}. The three orbitals in each set combine to give the molecular orbitals shown in Figure 29(*b*); Figure 29(*b*) also shows the metal orbitals with which they may interact. Table 14 gives the symmetries of the metal and carbonyl orbitals according to the group C_{3v}.



(*b*)

Fig. 29. (*a*) Metal–tricarbonyl group showing a carbon monoxide σ- and radial π-orbital. (*b*) Representation of the bonding in a metal–tricarbonyl group

Table 14 *Classification by symmetry of the orbitals in the group* $M(CO)_3$

Symmetry	Carbonyl orbitals	Metal orbitals
A_1	ψ_1, ψ_4	s, p_z, d_{z^2}
E^+	ψ_2, ψ_5, ψ_7	$p_y, d_{yz}, d_{x^2-y^2}$
E^-	ψ_3, ψ_6, ψ_8	p_x, d_{xy}, d_{xz}
A_2	ψ_9	—

The three sets of carbonyl molecular orbitals all contain M.O.s of E symmetry and the σ- and π-radial-orbitals also form M.O.s of A_1 symmetry. It follows that the simple picture of M–CO bonding, namely donation to the metal by the CO σ-orbital and back-donation from the metal to the carbonyl π-orbitals, breaks down since the metal orbitals of both A_1 and E symmetry take part in both donor and acceptor interactions.

The M.O.s formed by the π-radial- or π-tangential-orbitals are not necessarily equally involved in bonding to the metal and one consequence of this would be that the M–CO system would be non-linear, which is frequently found [129*a*]. The deviation from non-linearity would obviously depend on the effects of other ligands attached to the metal.

E. π-Cyclopentadienyl carbonyl complexes

The complexes known at present are shown in Table 15. In all these complexes the π-cyclopentadienyl–metal bonding is covalent. Most of them are stable to oxidation at room temperature. The π-$C_5H_5M(CO)_3$ system appears to be especially stable. Since the π-cyclopentadienyl system is effectively *trans* to the carbon monoxides and is a better donor and a weaker acceptor than the carbon monoxide ligand, the π-C_5H_5 group stabilizes the $M{-}C{\equiv}O$ bonding. Thus the complexes π-$C_5H_5M(CO)_3$ are resistant to substitution of the carbon monoxide ligands except under conditions employing intense ultraviolet irradiation (see section E, *e*). In much of the chemistry of the complexes the π-cyclopentadienyl ring merely acts as a non-labile stabilizing ligand and frequently the chemistry of these complexes has marked similarities to that of the pure metal carbonyls themselves. Some obvious common features of the chemistry of these two classes of complexes are (*i*) with few exceptions both classes obey the 18-electron rule, (*ii*) treatment of the neutral complexes with alkali metals frequently affords stable anions,

$$\pi\text{-}C_5H_5V(CO)_4 \xrightarrow[\text{[150]}]{\text{Na/Hg}} [Na^+]_2[\pi\text{-}C_5H_5V(CO)_3]^{2-}$$

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2 \xrightarrow[\text{[9]}]{\text{Na/Hg}} Na^+[\pi\text{-}C_5H_5Fe(CO)_2]^-$$

Table 15 *π-Cyclopentadienyl metal carbonyls.*(a)(b)

$(\pi\text{-}C_5H_5)_2Ti(CO)_2$ 90° d; red-brown [5, 130]	$\pi\text{-}C_5H_5V(CO)_4$ 138° d; orange [36, 131, 150]	$[\pi\text{-}C_5H_5Cr(CO)_3]_2$ 163–168° d; deep green [131, 134]	$\pi\text{-}C_5H_5Mn(CO)_3$ 76·8–77·1°; yellow [28]	$[\pi\text{-}C_5H_5Fe(CO)_2]_2$ 194°; red-purple [28, 131, 141, 142]	$\pi\text{-}C_5H_5Co(CO)_2$ −22°; red [28, 131, 144]	$[\pi\text{-}C_5H_5NiCO]_2$ 146–147° d; red [180]
	$[(\pi\text{-}C_5H_5)_2V(CO)_2]^+$ orange [132]	$[\pi\text{-}C_5H_5Cr(CO)_4]^+$ yellow [135]		$[\pi\text{-}C_5H_5Fe(CO)_3]^+$ yellow [26, 143]	$[\pi\text{-}C_5H_5CoCO]_3$ black [162*a*]	$(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$ 200° d; green [180]
	$[\pi\text{-}C_5H_5V(CO)_3]^{2-}$ yellow [150]	$[\pi\text{-}C_5H_5Cr(CO)_3]^-$ pale yellow [9, 31]		$[\pi\text{-}C_5H_5Fe(CO)_2]^-$ pale yellow [9, 142]		
				$[\pi\text{-}C_5H_5FeCO]_4$ dark green [162*a*]		
	$\pi\text{-}C_5H_5Nb(CO)_4$ 144–146°; orange [8, 133]	$[\pi\text{-}C_5H_5Mo(CO)_3]_2$ 215–217°; red-violet [29, 31, 131, 136]	$\pi\text{-}C_5H_5Tc(CO)_3$ [11, 137*a*]	$[\pi\text{-}C_5H_5Ru(CO)_2]_2$ 185° d; orange-red [160]	$\pi\text{-}C_5H_5Rh(CO)_2$ −11°; orange [146]	
		$[\pi\text{-}C_5H_5Mo(CO)_4]^+$ yellow [137]			$[\pi\text{-}C_5H_5Rh(CO)_2]_2$(?) 123°; red [145]	
		$[\pi\text{-}C_5H_5Mo(CO)_3]^-$ yellow [9, 31]			$[\pi\text{-}C_5H_5RhCO]_2\text{-}\mu\text{-}CO$ [161*b*] $[\pi\text{-}C_5H_5RhCO]_3$ [161*b*]	
	$\pi\text{-}C_5H_5Ta(CO)_4$ 171–173° orange [8]	$[\pi\text{-}C_5H_5W(CO)_3]_2$ red-purple [29]	$\pi\text{-}C_5H_5Re(CO)_3$ 111–114°; colourless [138, 139, 140, 240]	$[\pi\text{-}C_5H_5Os(CO)_2]_2$ 198°; yellow [10]	$\pi\text{-}C_5H_5Ir(CO)_2$ yellow liquid [147]	$[\pi\text{-}C_5H_5PtCO]_2$ 103° d; red [183]
		$[\pi\text{-}C_5H_5W(CO)_4]^+$ yellow [137]				
		$[\pi\text{-}C_5H_5W(CO)_3]^-$ yellow [9, 31]				

(*a*) A number of related mixed metal complexes are:

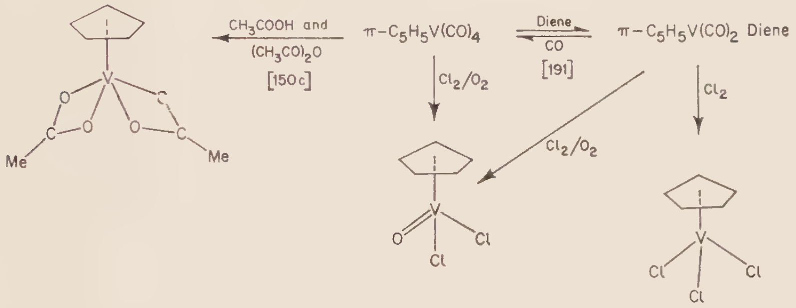
$\pi\text{-}C_5H_5W(CO)_3\text{-}(CO)_3Mo\pi\text{-}C_5H_5$ purple [33*a*]	$\pi\text{-}C_5H_5Fe(CO)(\mu\text{-}CO)_2Ni\pi\text{-}C_5H_5$ 132°; brown [22]	$\pi\text{-}C_5H_5Fe(CO)_2\text{-}(CO)_5Mn$ 76°; red [149]
$\pi\text{-}C_5H_5Fe(CO)(\mu\text{-}CO)_2Co(CO)_3$ 52–53°; red [148]	$\pi\text{-}C_5H_5Fe(CO)_2\text{-}(CO)_3Mo\pi\text{-}C_5H_5$ 209°; red-violet [149]	

(*b*) Melting points are given in °C.

(*iii*) both classes form hydride and alkyl complexes, although the π-cyclopentadienylcarbonyl analogues are usually more stable to oxidation. The π-cyclopentadienyl ligand may be considered to behave like the combined effect of two carbon monoxide groups and a halide ligand; for example, compare $Fe(CO)_4I_2$ and π-$C_5H_5Fe(CO)_2I$; $Mn(CO)_5Cl$ and π-$C_5H_5Mn(CO)_3$.

(*a*) *Vanadium, niobium and tantalum complexes*

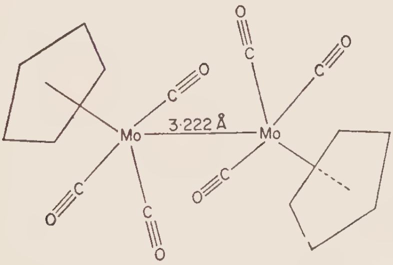
There are presently few studies on the complexes π-$C_5H_5M(CO)_4$ where M = V, Nb or Ta. The crystal structures of the vanadium [150*a*] and niobium [150*b*] compounds show them to have the structures given on pp. 92, 134. Some reactions of the vanadium compound are:



The cation $[(\pi\text{-}C_5H_5)_2V(CO)_2]^+$, which is isoelectronic with $(\pi\text{-}C_5H_5)_2Ti(CO)_2$, is prepared in the reaction between vanadocene, $V(CO)_6$ and carbon monoxide at 15° [132].

(*b*) *Complexes of chromium, molybdenum and tungsten*

The structure of the neutral binuclear molybdenum complex $[\pi\text{-}C_5H_5Mo(CO)_3]_2$, 4.8, has been shown by X-ray studies [151]. There are no bridging carbonyls and there is a Mo–Mo bond of 3·22 Å. Also there are indications that the C_5-rings may each show a slight distortion from



4.8

pure C_5 symmetry. Infrared spectra indicate that the analogous complexes of Cr and W have similar structures.

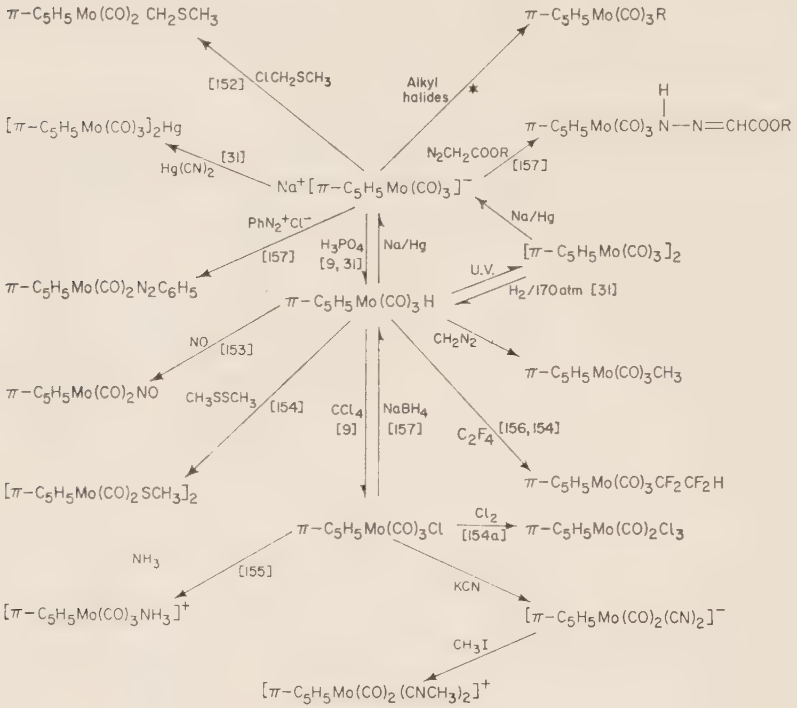
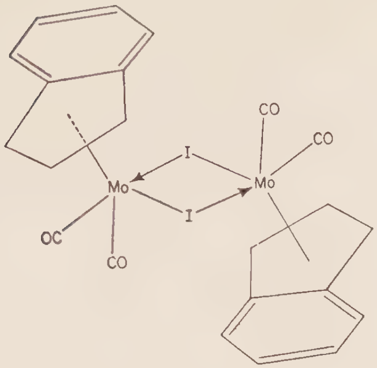


Fig. 30. Some chemistry of π-cyclopentadienyl molybdenum complexes

The molybdenum and tungsten complexes have a very closely related chemistry. In Figure 30, some chemistry of π-cyclopentadienyl molybdenum carbonyl complexes is shown; analogous reactions are found for chromium complexes but the chromium derivatives are rather less stable to heat and to oxidation [9]. It may be noted that the indenyl complex $[\pi\text{-}C_9H_7Mo(CO)_3]_2$ mostly behaves like the π-cyclopentadienyl analogue, except that with iodine a *di*carbonyl iodide is formed for which the dimeric structure, 4.9, would seem at first to be the most likely. Molecular weight determinations show, however, that the compound is monomeric [158]. Perhaps there is some interaction between the metal and the π-electrons of the C_6 ring.

Many derivatives of π-cyclopentadienylmolybdenum carbonyls with sulphur ligands are known, e.g. $\pi\text{-}C_5H_5Mo(CO)_2S_2CSR$ [158*a*], and the anion $[\pi\text{-}C_5H_5Mo(CO)_2S_2C_2(CN)_2]^-$ [158*b*].

* See page 235.



4.9

(*c*) *Some π-cyclopentadienyl iron carbonyl chemistry*

The chemistry of π-cyclopentadienyl iron carbonyl complexes has been studied widely because the binuclear complex $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ is very readily prepared [9]. The deep red-purple crystals are stable to oxidation, and are easily handled. In the crystalline state, Figure 31(*a*), the molecule is centrosymmetric and the two iron atoms and the two bridging carbonyls form a plane [67]. The presence of metal–metal interaction is suggested by the observed diamagnetism of the complex and a rather short Fe–Fe distance of 2·49 Å (compare 2·46 Å in $Fe_2(CO)_9$). In solution, however, the complex shows a multiplicity of bands assigned to bridging carbonyl stretches, which is inconsistent with a centrosymmetric molecule [159]. Also, all the complexes $[\pi\text{-}C_5H_5M(CO)_2]_2$, where M = Fe, Ru or Os, show appreciable dipole moments in benzene [160, 161, 10]. The variable temperature infrared spectra of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ in solution suggest that at low temperatures (−100°C) the complex has a bridging carbonyl structure but that it is not centrosymmetric. Most probably it has a *cis* configuration, see Figure 31(*b*). At room temperature the infrared spectra show that there is an equilibrium between this structure and one with no

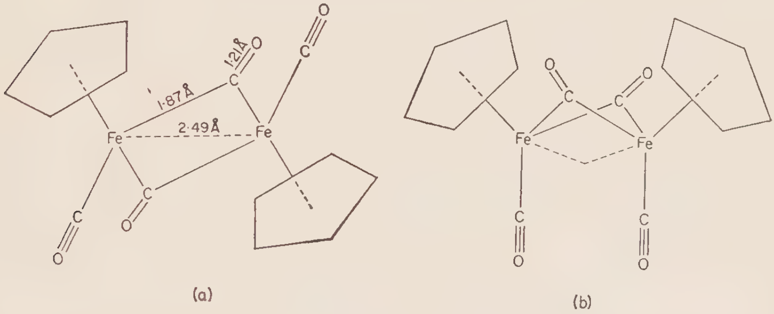
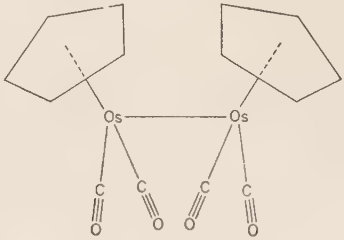


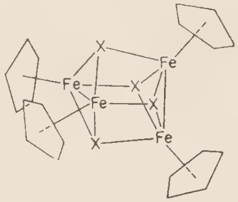
Fig. 31. (*a*) Structure in crystal. (*b*) Structure proposed for solutions

bridging carbonyls, such as is shown for the osmium analogue, 4.10 [160*a*]. Infrared spectra and X-ray diffraction [160*a*] indicate that the ruthenium analogue has the same structure as the iron complex (Ru–Ru = 2·74 Å). in the crystalline state. Infrared spectra in solution at room temperature show there to be a equilibrium mixture of the *cis*-bridged structure (as in Figure 31(*b*)) and a non-bridged dimer similar to that shown for the osmium analogue, 4.10 [160*a*]. However, at −100°C there is evidence for only a small amount of the non-bridged carbonyl isomer. The infrared spectrum of the crystalline osmium compound does *not* show bands assignable to bridging carbonyls (cf. $Os_3(CO)_{12}$ [162]), and the structure 4.10 is proposed.



4.10

Prolonged refluxing of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ in benzene gives the tetrameric complex 4.10*a*, where X = CO [162*a*].



4.10*a*

Some reactions of π-cyclopentadienyl iron carbonyl complexes are shown in Figure 32. The chemistry of the ruthenium and osmium analogues would be expected to be similar, but few studies have yet been made.

The hypothetical 16-electron cation $[\pi\text{-}C_5H_5Fe(CO)_2]^+$ would be a strong Lewis acid and several complexes $[\pi\text{-}C_5H_5Fe(CO)_2L]^+$, where L is a variety of ligands, are known, for example L = NH_3,N_2H_4 [167*a*], CH_3CN [167*b*], or olefins, see p. 211. Novel ligands include L = $\pi\text{-}C_5H_5Fe(CO)_2Br$, and the iodide analogue. Thus

$$\begin{tikzcd} \pi\text{-}C_5H_5Fe(CO)_2Br + AlBr_3 \arrow[r, "SO_2", "{[168, 169]}"'] & {[\pi\text{-}C_5H_5Fe(CO)_2 \leftarrow Br(CO)_2Fe\pi\text{-}C_5H_5]^+} \arrow[d, "{[168]}"', "\text{amine}"] \\ & {[\pi\text{-}C_5H_5Fe(CO)_2\ \text{amine}]^+} \end{tikzcd}$$

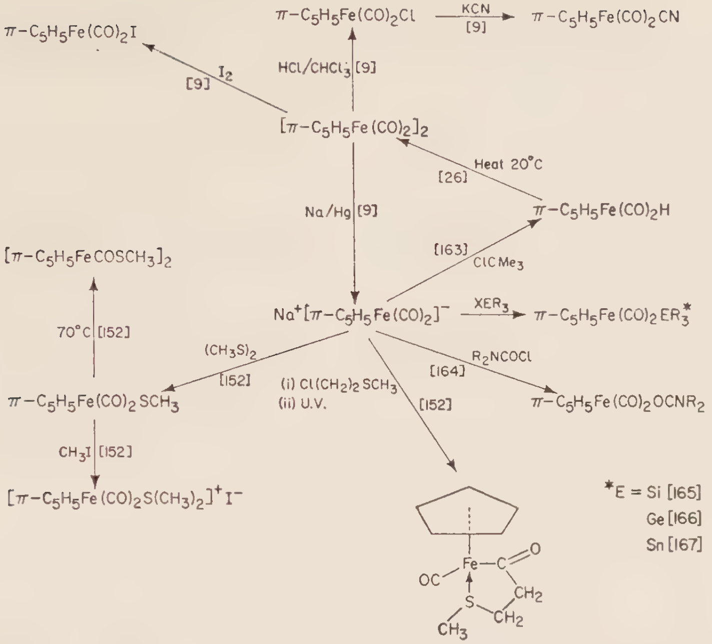
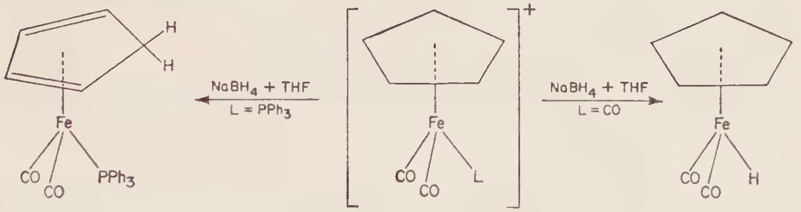


Fig. 32. Some chemistry of π-cyclopentadienyl iron carbonyl complexes (X = halogen, R = alkyl or aryl)

This preparative route to compounds of the type $[\pi\text{-}C_5H_5Fe(CO)_2L]^+$ is unusual as they are most usually made by addition of the ligand L to a halide such as $\pi\text{-}C_5H_5Fe(CO)_2Cl$. However, when L = R_3P or $(RO)_3P$, carbon monoxide is evolved giving complexes such as $\pi\text{-}C_5H_5FeCOLCl$ or $\pi\text{-}C_5H_5FeL_2Cl$ [167*b*, 169*a*].

It is interesting that the reduction with borohydride of the cation $[\pi\text{-}C_5H_5Fe(CO)_2L]^+$, gives the hydride 4.11, where L = CO, but when L = Ph_3P, a cyclopentadiene complex, 4.12, is formed [26]. This observa-



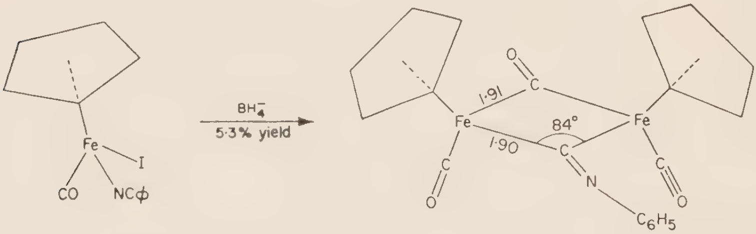
4.12

4.11

tion suggests that under the reaction conditions the cyclopentadiene iron tricarbonyl is unstable and decomposes to $\pi\text{-}C_5H_5Fe(CO)_2H$ by hydrogen transfer from the ring to the iron atom together with expulsion of carbon monoxide, as shown on p. 94. Carbon monoxide may be replaced by CN^- and the cyanide derivatives may further react with alkyl halides affording isonitrile complexes.

$$\pi\text{-}C_5H_5Fe(CO)_2Br \xrightarrow[{[170]}]{2KCN} K^+[\pi\text{-}C_5H_5Fe(CN)_2CO]^- \xrightarrow[{[170]}]{RI} \pi\text{-}C_5H_5FeCNR(CO)CN$$

Treatment of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ with many sulphur ligands gives π-cyclopentadienyl iron–sulphur complexes [174, 174*a*] (see also Figure 32]. Prolonged refluxing with sulphur forms the tetramer, 4.10*a*, where X = S [174*b*, 174*c*]. The chemistry of a considerable number of isonitrile derivatives has been studied [171, 172] and of particular interest is a complex, 4.13, formed by the reduction of $\pi\text{-}C_5H_5Fe(CO)CNC_6H_5I$, which X-ray studies have shown to have a bridging isonitrile group [173, 174]. On this complex the value of $\nu(C{=}N)$ is 1704 cm⁻¹, which is appropriate for an azomethine rather than an isocyanide group.



4.13

Bridging isonitrile groups may also occur in the $[\mu\text{-}C_5H_5NiCNC_6H_5]_2$ complex.

(*d*) *Cobalt and rhodium complexes*

$\pi\text{-}C_5H_5Co(CO)_2$, prepared by the exothermic reaction between $Co_2(CO)_8$ and cyclopentadiene, is a red oil which is rather unstable to oxidation. The carbonyl groups are easily displaced by a variety of ligands and some reactions of the complexes are shown in Figure 33.

All the compounds $\pi\text{-}C_5H_5M(CO)_2$, where M = Co, Rh or Ir, react with iodine giving the di-iodides $\pi\text{-}C_5H_5M(CO)I_2$ [178, 179, 179*a*]. Some reactions of the cobalt compound are,

$$\begin{tikzcd}
{[\pi\text{-}C_5H_5Codipyl]^+I^-} & \pi\text{-}C_5H_5CoCOI_2 \arrow[l, "{\alpha,\alpha'\text{-bipy}}"', "{[179a]}"] \arrow[r, "{L = py\ or\ Ph_3P}", "{[179a]}"'] & \pi\text{-}C_5H_5CoLI_2 \arrow[dl, "{MeMgBr,\ L = Ph_3P\ [179b]}"] \\
 & \pi\text{-}C_5H_5CoPh_3PMe &
\end{tikzcd}$$

Treatment of $\pi\text{-}C_5H_5Co(CO)_2$ with bis-(trifluoromethyl)-dithietene gives the complex, 4.13*a*, whose structure [179*c*] shows that the sulphur ligand

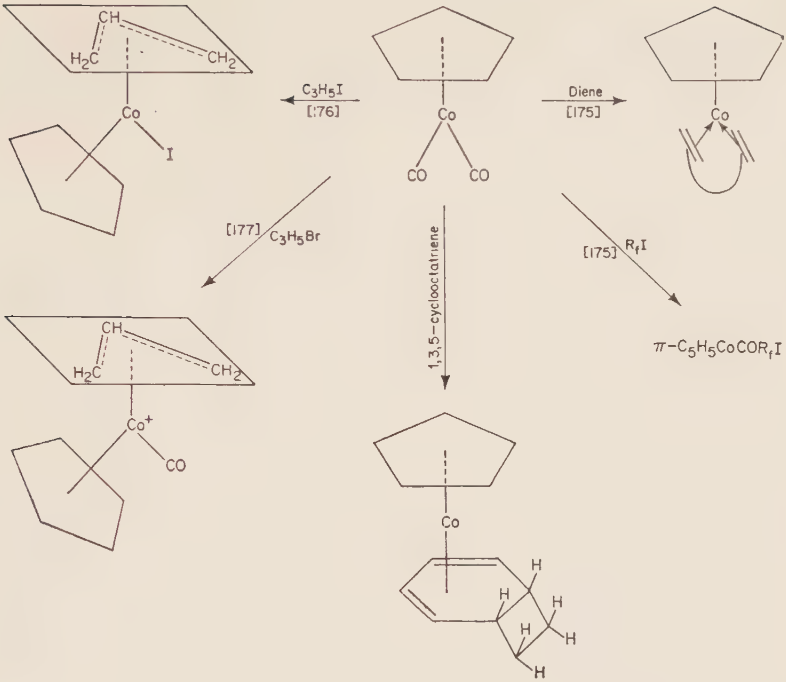
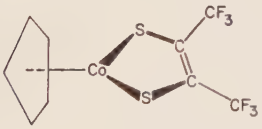
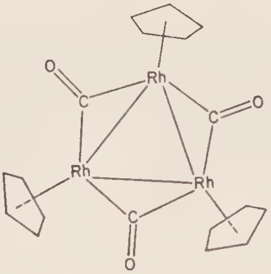


Fig. 33. Some reactions of π-cyclopentadienyl cobalt dicarbonyl

acts as a 'diketone'. Refluxing π-$C_5H_5Co(CO)_2$ in hexane gives two isomers of stoicheiometry [π-$C_5H_5CoCO]_3$ [162*a*]. The anion [π-$C_5H_5CoCO]^{2-}$ is unknown. The rhodium complex (π-$C_5H_5)_2Rh_2(CO)_3$ is unusual since



4.13*a*



4.13*b*

X-ray diffraction shows it to have a single bridging carbon monoxide. There must also be a Rh–Rh bond if the complex is to obey the 18-electron rule and the observed Rh–Rh distance of 2·68 Å suggests this to be the case [161*a*]. Prolonged irradiation of π-$C_5H_5Rh(CO)_2$ gives a trimeric complex whose structure, determined by X-ray diffraction, [161*a*, 161*b*], is shown in 4.13*b*.

(*e*) *Complexes of nickel and platinum*

The preparations and structures of the complexes $[\pi\text{-}C_5H_5NiCO]_2$ and $(\pi\text{-}C_5H_5)_3Ni_2(CO)_2$ are shown in Figure 34. The structure of the latter complex, first proposed on the basis of a dipole moment of zero [180] has been confirmed by X-ray studies [181]. A description of the bonding of the carbonyl groups in this complex requires the use of multicentred molecular orbitals. For the dimeric complex $[\pi\text{-}C_5H_5NiCO]_2$ a folded configuration for the carbonyls groups has been proposed both by analogy with $Co_2(CO)_8$ and also in view of the ease with which the bridging carbonyls undergo displacement by acetylenes [182]; this structure has been confirmed by X-ray analysis [161*a*]. However, the compound has a very small dipole moment in solution and only one >C═O stretch in the vapour. Thus a centrosymmetric structure seems possible for the molecule in solution [180, 180*b*]. The displacement reactions of the binuclear complex are shown in Figure 34. Attempts to isolate the anion $[\pi\text{-}C_5H_5Ni(CO)]^-$ have been unsuccessful, but it can be prepared in solution [181*a*]. The dimeric platinum complex $(\pi\text{-}C_5H_5)_2Pt_2(CO)_2$, prepared by the reaction between $Pt(CO)_2Cl_2$ and NaC_5H_5 in benzene at 70°, does not have bridging carbonyl groups [183]. The proton magnetic resonance spectrum of the complex is interesting

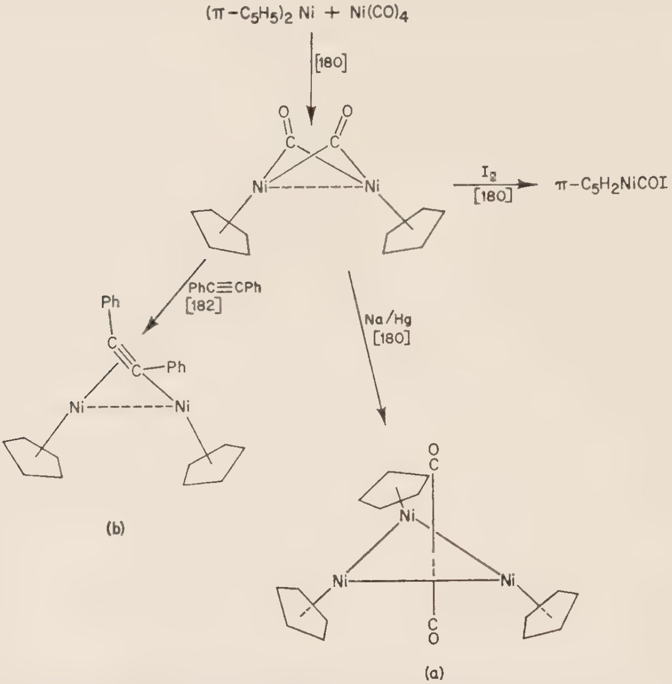


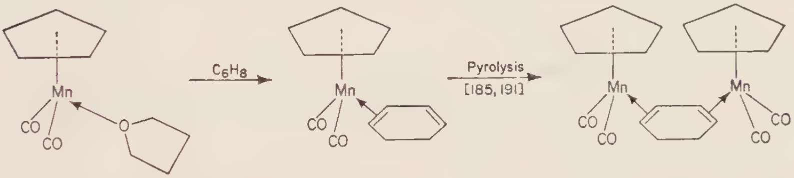
Fig. 34. Some chemistry of π-cyclopentadienyl nickel complexes. For the complex (*a*) Ni–Ni, 2·39 Å; Ni–carbon of ring, 2·12 Å; Ni–carbon of CO, 1·93 Å [181]. The structure of complex (*b*) has been determined by X-ray diffraction [180*a*]

since it shows coupling of the π-cyclopentadienyl hydrogens with the magnetic nuclei of both the platinums and also that there are two equivalent π-C_5H_5PtCO— systems joined by a Pt–Pt bond [180*b*]. Thus, as found for [π-$C_5H_5Os(CO)_2]_2$, terminal carbonyls are preferred to bridging ones.

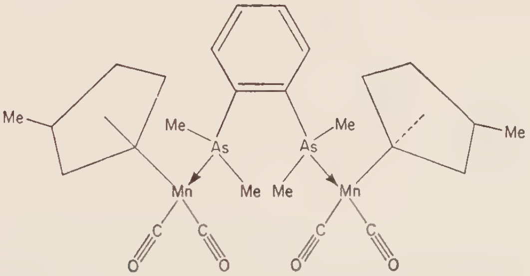
(*f*) *Ligand substitution reactions of π-cyclopentadienyl manganese tricarbonyl*†

The complex π-$C_5H_5Mn(CO)_3$ is relatively inert and substitution of the carbonyl groups may usually only be achieved under strong irradiation with ultraviolet light [184, 185]. An SN1 mechanism is proposed, namely the initial expulsion of a carbon monoxide molecule giving a 16-electron π-$C_5H_5Mn(CO)_2$ intermediate, to which the ligand (L) readily adds. Complexes π-$C_5H_5Mn(CO)_2L$ where L = pyridine [186], piperidine [187], triphenylphosphine [188], cyclohexylisonitrile [184], tetrahydrofuran [184], ethylene [190] and cyclo-olefins such as cyclopentene [185], have been isolated.

Disubstitution may occur affording complexes π-$C_5H_5MnCOL_2$, in certain cases, where L = triphenylphosphine [188], butadiene (bidentate) [191], or dimethylsulphoxide [192]. The diarsine ligand *o*-$(Me_2As)_2C_6H_4$ can act as a bridging ligand; the structure of the complex 4.14 has been determined [193]. In contrast to butadiene, cyclohexa-1,3-diene does not act as a bidentate ligand to the manganese but may act as either a monodentate ligand or as a bridging ligand [189], as shown below.



The difference in behaviour between the two olefins as ligands presumably arises from steric factors. The reaction of π-$C_5H_5Mn(CO)_3$ with



4.14

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† For detailed reference, see [185].

dimethylformamide is of interest, as a carbonyl group is lost from the ligand and a dimethylamine complex is formed [185].

$$\pi\text{-}C_5H_5Mn(CO)_3 + NMe_2CHO \longrightarrow \underset{\text{intermediate}}{\pi\text{-}C_5H_5Mn(CO)_2N(Me)_2CHO}$$

$$\Big\downarrow{-CO}$$

$$\pi\text{-}C_5H_5Mn(CO)_2NHMe_2$$

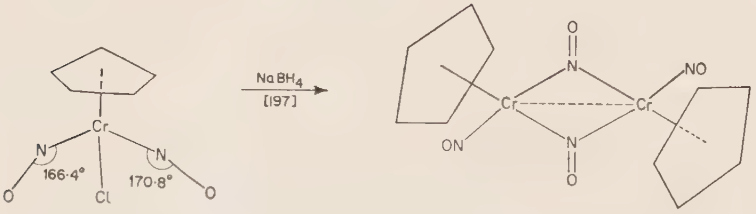
The displacement of three carbonyl groups from $\pi\text{-}C_5H_5Mn(CO)_3$ has been achieved in the reaction with benzene giving the mixed sandwich complex $\pi\text{-}C_5H_5Mn\text{-}\pi\text{-}C_6H_6$ [185]. Treatment of $\pi\text{-}C_5H_5Mn(CO)_3$ with PCl_3 gives the ring substituted $\pi\text{-}Cl_2PC_5H_4Mn(CO)_3$. However, when the reaction is carried out in the presence of aluminium trichloride a binuclear product is isolated which is formulated $\pi\text{-}C_5H_5Mn(CO)_2{\leftarrow}PCl_2C_5H_4Mn(CO)_3$ [184*a*]. Apparently a CO ligand has been displaced without the aid of ultraviolet irradiation.

Finally, it is interesting that treatment of $\pi\text{-}C_5H_5Mn(CO)_3$ with $SbCl_5$ forms an unstable red precipitate which may contain the 17-electron cation $[\pi\text{-}C_5H_5Mn(CO)_3]^+$ [184*b*].

F. π-Cyclopentadienyl nitrosyl complexes

Nitric oxide, like the π-allyl group, can act as a 3-electron ligand; a number of stable π-cyclopentadienyl nitrosyl complexes are known. The preparations of some of these complexes are shown in Figures 30 and 32. The series $\pi\text{-}C_5H_5MNO$, where M = Ni [28], Pd [194], and Pt [195], is well characterized and the microwave spectrum of the nickel complex shows the symmetric structure given in Figure 28, p. 112 [196]. In this molecule, the short Ni–N distance (1·676 ± 0·02 Å) indicates considerable multiple bonding. The dinitrosyl $\pi\text{-}C_5H_5Cr(NO)_2Cl$ similarly has a short Cr–N bond (1·72 Å) [196*a*].

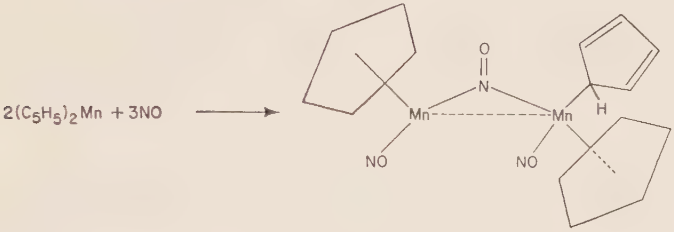
An interesting bridging nitrosyl complex has been obtained by the reduction reaction,



4.15

In the complex, 4.15, the terminal nitrosyl frequencies occur at 1672 cm⁻¹ whilst the bridging nitrosyls show a stretch at 1505 cm⁻¹ [197, 198]. Related complexes are $[\pi\text{-}C_5H_5CrNOX]_2$ where the bridging ligand X may be for example iodide or Me_2N [198*a*, 198*b*]. Like the dimeric carbonyls of iron mentioned earlier some of these complexes undergo *cis–trans* isomerism in solution [198*a*].

Similarly, reduction of the cation $[\pi\text{-}C_5H_5Mn(CO)_2NO]^+$ [28] affords a violet complex $(\pi\text{-}C_5H_5MnCONO)_2$ which may also contain bridging nitrosyl groups [198]. Irradiation of the latter with ultraviolet light gives a black complex with the extraordinary formula $(\pi\text{-}C_5H_5)_6Mn_6(NO)_8$ [197]. The first complex for which bridging nitrosyls were proposed was the manganese complex, 4.16 [199].

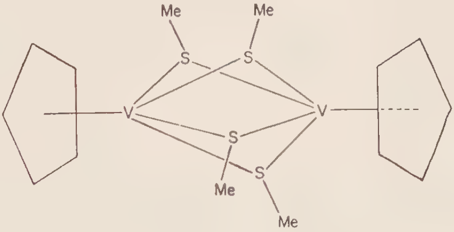


4.16

Other complexes in this class include the polymeric $[\pi\text{-}C_5H_5Mn(NO)_2]_n$, [198*b*].

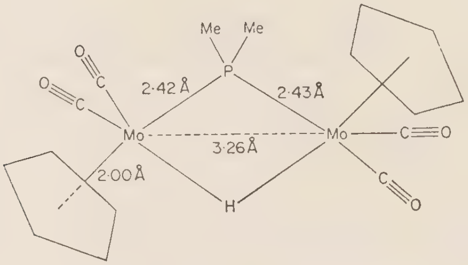
G. Brief notes on binuclear π-cyclopentadienyl complexes containing bridging ligands

The occurrence of CO, NO and isonitrile groups as bridging or terminal ligands has been discussed earlier. Oxygen may occur in both linear or in bent bridging systems, as shown in Figure 37. A considerable number of complexes containing bridging sulphur ligands are known [200, 201, 202, 203] (see also Figures 30 and 32), an unusual example being the black paramagnetic vanadium complex, 4.17 [200]. The paramagnetism of this complex corresponds to less than one unpaired electron suggesting that some metal–metal interaction is present. Formally, in the absence of metal–metal interaction, two unpaired electrons would be expected. Bridging phosphine and arsine ligands are also well established in



4.17

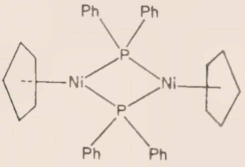
π-cyclopentadienyl metal complexes [204, 205, 206]. Of great interest is the complex 4.18, which X-ray analysis shows to be symmetrical, and it is proposed that the hydrogen bridges the two molybdenum atoms symmetrically [207].



4.18

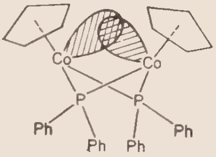
The structures of the di-μ-diphenylphosphine complexes 4.18*a* and 4.18*b* provide strong evidence that spin-pairing may occur by metal–metal bonding. The nickel complex, 4.18*a*, is planar and the metal atom obeys the 18-electron rule. The cobalt analogue, 4.18*b*, however, does not obey this rule unless there is a metal–metal bond. Further it would be expected to be paramagnetic unless spin-pairing took place via such a bond or by another mechanism. The structure 4.18*b* shows that the Co–Co distance is 2·56 Å and the molecule is non-centrosymmetric. The differences of structure between 4.18*a* and 4.18*b*, both of which are diamagnetic, suggest that there is spin-pairing in the latter by a Co–Co bond; perhaps it is, as shown, a 'bent' bond [207*a*].

It would be interesting to know the structure of the unknown monovalent anion of 4.18*b* and of the isoelectronic cation of 4.18*a*: would a structure intermediate between these result?



Ni–Ni 3·36 Å

4.18*a*



Co–Co 2·56 Å

4.18*b*

H. π-Cyclopentadienyl hydride complexes†

There is considerable evidence that when other ligands are also attached to the metal atom the planes of the π-C_5H_5 rings of bis-π-cyclopentadienyl

† For reviews of metal-hydride complexes see [208, 209].

complexes are not parallel (see Figure 35). A molecular orbital treatment of these 'bent' molecules [210] suggests that for values of the angle between the metal ring axes, in the range 135–180°, the metal–ring bond strength is little changed. The treatment however suggests that there are three mutually orthogonal orbitals which lie in the *xy* plane and away from the rings, as shown in Figure 35. Thus it may be pictured for ferrocene that if the molecule had a bent structure then the three electron pairs in the non-bonding orbitals (see p. 102) would rearrange and appear as three electron pairs in the *xy* plane. Ferrocene and ruthenocene dissolve in strong acid media, such as boron trifluoride hydrate, and the observation of a high field proton resonance shows that there is a proton attached to the metal atoms [87]. The cations $[(\pi\text{-}C_5H_5)_2MH]^+$ which are formed presumably have the configuration shown in Figure 35. Osmocene appears to be a much weaker base since it does not show a high field resonance under the same conditions. The bent ring structure is also proposed for the hydride $(\pi\text{-}C_5H_5)_2ReH$, and, in agreement with the proposition that there will be

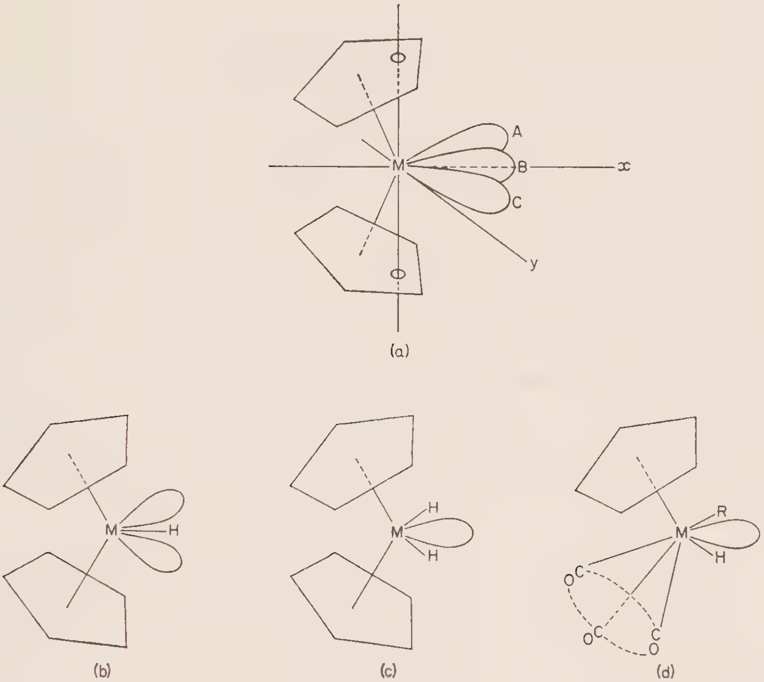


Fig. 35. (*a*) Structure of bent ring bis-π-cyclopentadienyl complexes showing the three 'non-bonding' orbitals in the *xy* plane. (*b*) Proposed structure of $[(\pi\text{-}C_5H_5)_2FeH]^+$ and $(\pi\text{-}C_5H_5)_2ReH$. (*c*) Structure of $(\pi\text{-}C_5H_5)_2MoH_2$ [213]; proposed structure for $[(\pi\text{-}C_5H_5)_2ReH_2]^+$. (*d*) Representation of $[\pi\text{-}C_5H_5M(CO)_3RH]^+$, showing relationship with the bis-π-cyclopentadienyl complexes

lone pairs available in the *xy* plane, this hydride readily protonates giving the dihydride cation $[(\pi\text{-}C_5H_5)_2ReH_2]^+$ [6]. The neutral rhenium hydride is a base of similar strength to ammonia [6]. Further protonation to $[(\pi\text{-}C_5H_5)_2ReH_3]^{2+}$ does not occur, presumably because the charge on the mono-cation makes it too weak a base. The basic properties of $(\pi\text{-}C_5H_5)_2ReH$ are also shown by the formation of the complex $(\pi\text{-}C_5H_5)_2ReH(BF_3)$ [211]. The golden-yellow technetium hydride, $(\pi\text{-}C_5H_5)_2TcH$, is also a base and protonates forming a dihydride cation [211*a*].

Similarly, the dihydrides $(\pi\text{-}C_5H_5)_2MH_2$, where M = Mo or W, have one lone pair left and these complexes readily form the trihydride cations $[(\pi\text{-}C_5H_5)_2MH_3]^+$ [212] and the adduct $(\pi\text{-}C_5H_5)_2WH_2.AlMe_3$ [212*a*]. Finally, the neutral trihydride of tantalum $(\pi\text{-}C_5H_5)_2TaH_3$ has, according to the above M.O. approach, no available lone pairs, and, in agreement with the theory, the tantalum trihydride does not protonate.

Further support for these arguments comes from the X-ray structure of the molybdenum complex $(\pi\text{-}C_5H_5)_2MoH_2$ (Figure 35) [213], and from proton resonance studies which show that the hydrogens of the trihydride complexes form an A_2B group and hence are not equivalent [212].

The above arguments may be extended to include complexes such as $\pi\text{-}C_5H_5M(CO)_3R$ in that the three carbonyl groups may be regarded as having steric and electronic effects similar to those of a π-cyclopentadienyl group. Thus non-bonding electron pairs are expected (see Figure 34) and it is indeed found that the hydride cations $[\pi\text{-}C_5H_5M(CO)_3RH]^+$ are formed in strong acid solutions (when M = Mo, R = CH_3).

Many similar complexes are known to undergo these protonation reactions [214]. The neutral bis-π-cyclopentadienyl hydrides discussed above are prepared by treatment of the metal halides with sodium cyclopentadienide and sodium borohydride in tetrahydrofuran [212, 215], e.g.

$$WCl_6 + Na^+C_5H_5^- + NaBH_4 \xrightarrow[\text{reflux}]{\text{THF}} (\pi\text{-}C_5H_5)_2WH_2$$

No monomeric dihydrides $(\pi\text{-}C_5H_5)_2MH_2$, where M = Ti, Zr or Hf, are known, however, there is electron spin resonance evidence for a paramagnetic dimer $[(\pi\text{-}C_5H_5)_2Ti\text{-}\mu\text{-}H]_2$ (see p. 342) and a polymeric zirconium species $[(\pi\text{-}C_5H_5)_2ZrH_2]_n$ [215*a*]. The latter, and the monohydride $(\pi\text{-}C_5H_5)_2ZrH(BH_4)$ are prepared by treatment of the diborohydride $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$ with trimethylamine. It is interesting that the proton magnetic resonance spectrum of $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$ shows the BH_4 hydrogens to be apparently equivalent, as is the case with $Al(BH_4)_3$ (contrast diborane) [215*b*]. A possible equilibrium which could account for this observation is $M\text{—}H_2\text{—}BH_2 \rightleftharpoons M\text{—}H\text{—}BH_3$.

I. π-Cyclopentadienyl halides and oxides

Many complexes in this class are found with the metals of Groups IV–VII in their higher oxidation states. The π-cyclopentadienyl ligand is versatile in that its complexes cover a wide range of formal oxidation states of the transition metals (cf. the CN^- ligand).

The known halide complexes are shown in Table 16. Many of these may be prepared by direct reaction of a metal halide with an ionic cyclopentadienylating reagent (see p. 93). Other more specific routes are discussed incidentally below.

Frequently the bis-π-cyclopentadienyl halides are thermally stable above 200°C and are stable to oxidation in dry air. They are rather less rapidly hydrolysed than the corresponding metal halides although partial hydrolysis or oxyhalide formation can occur. Thus contrast the rapid hydrolysis reactions of titanium and zirconium tetrachlorides with the reactions

$$(\pi\text{-}C_5H_5)_2TiCl_2 \xrightarrow[\text{slow [57]}]{\text{warm water}} [(\pi\text{-}C_5H_5)_2TiOH]^+$$

$$(\pi\text{-}C_5H_5)_2ZrCl_2 \xrightarrow[\text{[232]}]{\text{base}} [(\pi\text{-}C_5H_5)_2ZrCl]_2O$$

The mono-π-cyclopentadienyl halides are usually more readily hydrolysed and are less stable to heat than the bis-π-cyclopentadienyl halides.

(*a*) *π-Cyclopentadienyl titanium halide chemistry and related topics*

In view of its easy preparation [233], its stability and the interest in titanium complexes as Ziegler catalysts (see Chapter 9, D, c), the complex $(\pi\text{-}C_5H_5)_2TiCl_2$ has been studied in some detail. In Figure 36, the chemistry

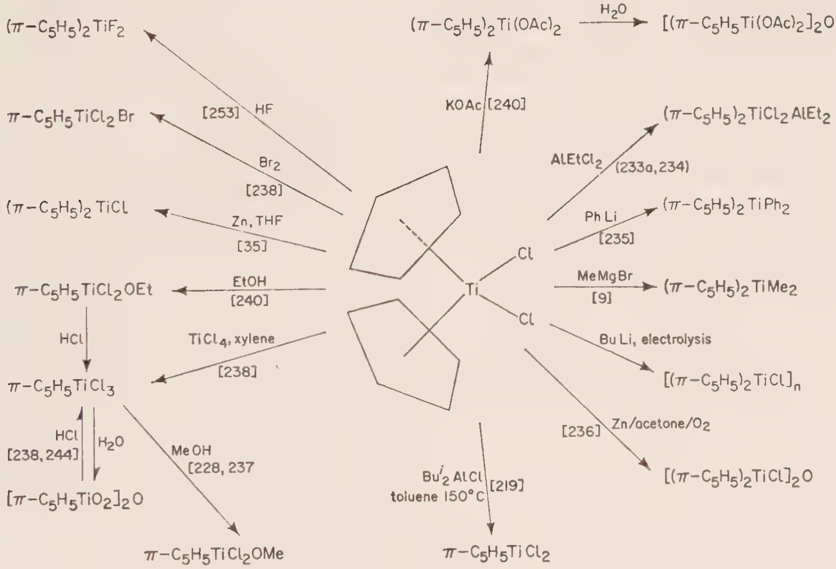


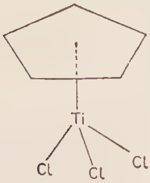
Fig. 36. Some chemistry of π-cyclopentadienyl titanium halides

Table 16 *π-Cyclopentadienyl transition metal halides*

Group IV	Group V	Group VI	Miscellaneous
$(\pi\text{-}C_5H_5)_2TiX_2$(a)	$(\pi\text{-}C_5H_5)_2VX_2$(e)	$[\pi\text{-}C_5H_5CrX_3]^-$(j)	$[(\pi\text{-}C_5H_5)_2ReX_2]^+$(o)
$(\pi\text{-}C_5H_5)_2TiCl$	$(\pi\text{-}C_5H_5)_2VX$(f)		$[(\pi\text{-}C_5H_5)_2OsI]^+$
green, 280° [34, 35, 216, 217, 245]			yellow [99]
$\pi\text{-}C_5H_5TiX_3$(b)	$\pi\text{-}C_5H_5VX_3$(g)		$[\pi\text{-}C_5H_5RhBr_2]_x$ dark red [222]
$\pi\text{-}C_5H_5TiCl_2$ blue [219]			$[\pi\text{-}C_5H_5PdCl]_2$ brown [221]
$(\pi\text{-}C_5H_5)_2ZrX_2$(c)		$(\pi\text{-}C_5H_5)_2MoX_2$(k)	
$\pi\text{-}C_5H_5ZrX_3$(d)	$(\pi\text{-}C_5H_5)_2NbX_3$(h)	$[(\pi\text{-}C_5H_5)_2MoX_2]^+$(l)	
		$\pi\text{-}C_5H_5MoCl_4$ red [256]	
$(\pi\text{-}C_5H_5)_2HfCl_2$	$(\pi\text{-}C_5H_5)_2TaX_3$(i)	$(\pi\text{-}C_5H_5)_2WX_2$(m)	
236° [220]		$[(\pi\text{-}C_5H_5)_2WX_2]^+$(n)	

(*a*) X = F, yellow [253]; Cl, red, 287° d [218, 223, 224, 253]; Br, red, 309° d [56, 223, 253]; I, purple, 317° [223, 253].
(*b*) X = Cl, orange, 216° [20, 223, 225, 226, 227, 228, 229*a*, 237, 238]; X = Br, orange, 175° [223]; I, red, 184° [223].
(*c*) X = Cl, colourless, 244° [229, 230]; Br, yellow, 260° d [20, 56, 253]; I, yellow, 299° [20].
(*d*) X = Cl, cream, 238° d [20]; Br, yellow, 274° [20]; I, red, 133° [20].
(*e*) X = Cl, green, 250° d [56, 253]; Br, green [56, 253].
(*f*) X = Cl, blue, 206° d [250, 252]; Br, blue, 221° [252]; I, green, 214° [252].
(*g*) X = Cl, violet, 160° d [250]; Br, green [250].
(*h*) X = Cl, brown [231]; Br, brown, 280° d [253].
(*i*) X = Cl [231]; Br, brown, 260° d [253].
(*j*) X = Cl [255]; Br [255].
(*k*) X = Cl, green, 250° d [257]; Br, green, 250° d [257]; I, green, 250° d [257].
(*l*) X = Cl, green [257]; Br [257].
(*m*) X = Cl, green, 250° d; Br, green, 250° d; I, green, 250° d [257].
(*n*) X = Cl, red; Br, purple [257].
(*o*) X = Cl, red; Br, red; I, green [257].

of this complex and related derivatives is shown. The bent structure for $(\pi\text{-}C_5H_5)_2TiCl_2$ is shown by the high dipole moment of 6·3 D [241] and by X-ray diffraction [242]. The red crystals of $(\pi\text{-}C_5H_5)_2TiCl_2$ are stable in dry air but they dissolve in water in which they are hydrolysed forming the cation $[(\pi\text{-}C_5H_5)_2TiOH]^+$ [242*a*]. The dihalides $(\pi\text{-}C_5H_5)_2TiX_2$ readily exchange the halide ligands with other anions and in this way the complexes $(\pi\text{-}C_5H_5)_2TiY_2$, where $L^- = NCO^-$, NCS^- [242*b*], SCN^-, N_3^- [242*c*] and SR^- [242*d*, 242*c*], have been prepared. The thiol complexes are prepared starting with either the disulphides RSSR or with RSH and triethylamine [242*e*].



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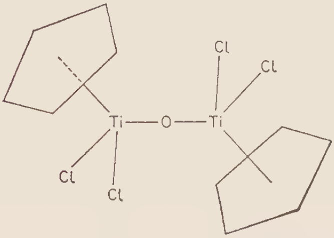
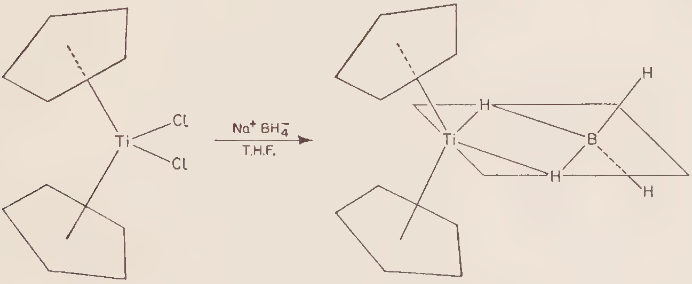


4.20

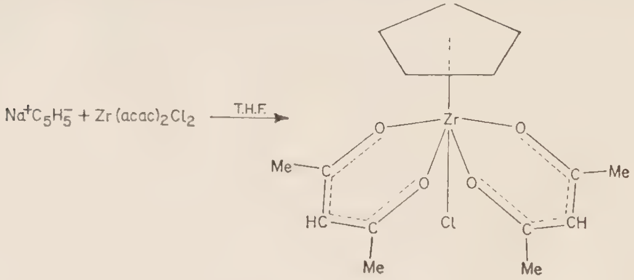
The structure of $\pi\text{-}C_5H_5TiCl_3$, 4.19, has been determined by X-ray analysis [243]. Alkoxy derivatives such as $\pi\text{-}C_5H_5Ti(OEt)_3$ are known [238, 239, 240, 241]. The mass spectra of a series $\pi\text{-}C_5H_5TiY_3$, where Y is halogen and alkoxide, give evidence for a substantial degree of ionic character in the $\pi\text{-}C_5H_5Ti$ bond [238]. A hydrolysis product of $\pi\text{-}C_5H_5TiCl_3$ is $[\pi\text{-}C_5H_5TiCl_2]_2O$. The crystal structure of $[\pi\text{-}C_5H_5TiCl_2]_2O$, 4.20 [243, 244], shows that the Ti–O–Ti system is linear and the Ti–O distance is rather shorter than expected for single covalent bonds (1·78 Å instead of ~1·92 Å).

The reduction of the complexes $(\pi\text{-}C_5H_5)MCl_2$, where M = Ti or Zr, with sodium borohydride gives the novel deep blue paramagnetic bridging borohydride derivative, 4.21 [245]. It is interesting that magnetic



4.21

susceptibility measurements on the dimer $[(\pi\text{-}C_5H_5)_2TiCl]_2$ suggest the presence of singlet and triplet states in thermal equilibrium. The temperature dependence of the paramagnetism closely resembles that found with copper(II) acetate. It is thought that the titanium dimer has bridging chlorine atoms and that, as for Cu(II)Ac_2, there is partial quenching of the unpaired spins of the Ti(III) atoms by formation of a Ti–Ti bond [245*a*].

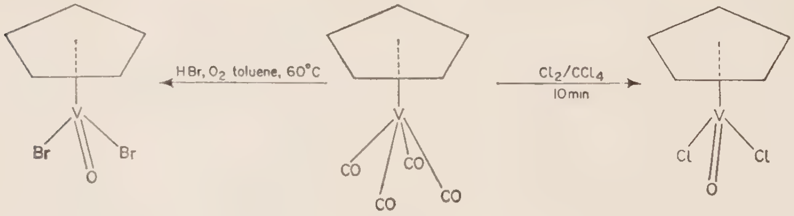


4.22

A number of bis-π-cyclopentadienyl zirconium complexes are known which are similar to the above titanium complexes, in particular the bridging oxide $[((\pi\text{-}C_5H_5)_2ZrCl)_2O]_2$ has been characterized [246, 229]. An unusual acetylacetone complex, 4.22, has been described [247]. The closely related chromium complex $\pi\text{-}C_5H_5Cr(acac)Br$ is also known [248]. The borohydride complexes $(\pi\text{-}C_5H_5)_2Zr\text{-}\mu\text{-}(BH_4)_2$ and $(\pi\text{-}C_5H_5)_2ZrCl\text{-}\mu\text{-}BH_4$ have been prepared [249].

(*b*) *Vanadium, niobium and tantalum complexes*

Both halides and oxyhalides may be prepared from the tetracarbonyl, 4.23 [250, 251]. The vanadium(III) chloride, 4.24, is prepared by the redistribution reaction, [252],



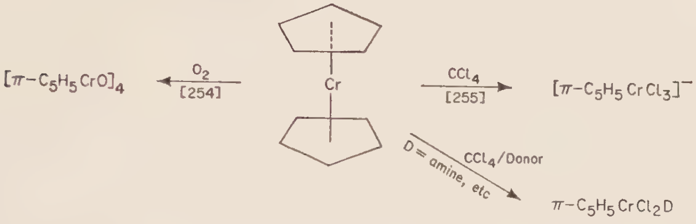
4.23

$$(\pi\text{-}C_5H_5)_2V + (\pi\text{-}C_5H_5)_2VCl_2 \longrightarrow \underset{4.24}{(\pi\text{-}C_5H_5)_2VCl}$$

Few studies have been made on the complexes $(\pi\text{-}C_5H_5)_2MX_3$, where M = Nb or Ta, but it appears that they are readily hydrolysed [117]; by analogy with the $(\pi\text{-}C_5H_5)_2MoX_2^+$ cations they may be salts, e.g. $[(\pi\text{-}C_5H_5)_2TaX_2]^+X^-$.

(*c*) *Chromium, molybdenum and tungsten complexes*

The chromium halide and oxide complexes have been prepared by novel routes, viz.



$$[\pi\text{-}C_5H_5Cr(CO)_3]_2 \xrightarrow[{[255]}]{C_3H_5Br} \pi\text{-}C_5H_5CrBr_2 \xrightarrow{\text{Donor}} \pi\text{-}C_5H_5CrBr_2D$$

Molybdenum forms oxyhalides in both the five and the six oxidation states; and also it forms the readily hydrolysable red tetrahalide, $\pi\text{-}C_5H_5MoCl_4$ [256]; a variety of oxides are also known (see Figure 37). In this context it is worth noting the stability of the $\pi\text{-}C_5H_5$—Mo system in these complexes. Thus $[\pi\text{-}C_5H_5MoO_2]_2O$ resists oxidation by oxygen even when also irradiated with ultraviolet light. The structure proposed for the dimer $[\pi\text{-}C_5H_5MoO\text{-}\mu\text{-}O]_2$ (see Figure 37), is supported by the crystal structure determination of the sulphur complex $[\pi\text{-}C_5H_5MoO\text{-}\mu\text{-}S]_2$. This has a similar structure to that proposed but with two bridging sulphurs instead of oxygens; the Mo–Mo distance is 2·9 Å [256*a*]. Analogous oxo-tungsten complexes are unknown.

Bis-π-cyclopentadienyl halides of Mo and W in the IV and V oxidation states are known [257]. At room temperature the paramagnetic complexes $[(\pi\text{-}C_5H_5)_2MX_2]^+$ show well resolved ESR spectra in which hyperfine splitting due to interaction with the metal nuclei and with the two halogens is observed. No fine structure due to the interaction of the unpaired electron with the hydrogens of the $\pi\text{-}C_5H_5$ rings could be detected, which indicates that the electron spends little time on the rings. Treatment of the halides $(\pi\text{-}C_5H_5)_2MCl_2$, where M = Mo or W, in aqueous alkali with H_2S gives yellow crystalline $(\pi\text{-}C_5H_5)_2M(SH)_2$ which contains the hydrosulphide ligand [258*a*]. Many other sulphur and oxygen complexes are known of formula $(\pi\text{-}C_5H_5)_2ML_2$, where M = Mo or W, and L = SR, OCOR, or L_2^{2-} is $[S_2C_2(CN)_2]^{2-}$, $[\text{—}SCH_2COO\text{—}]^{2-}$ and $[o\text{-}O_2C_6H_4]^{2-}$ $\text{—}NHCH_2CH_2S\text{—}]_2^-$ [258*a*].

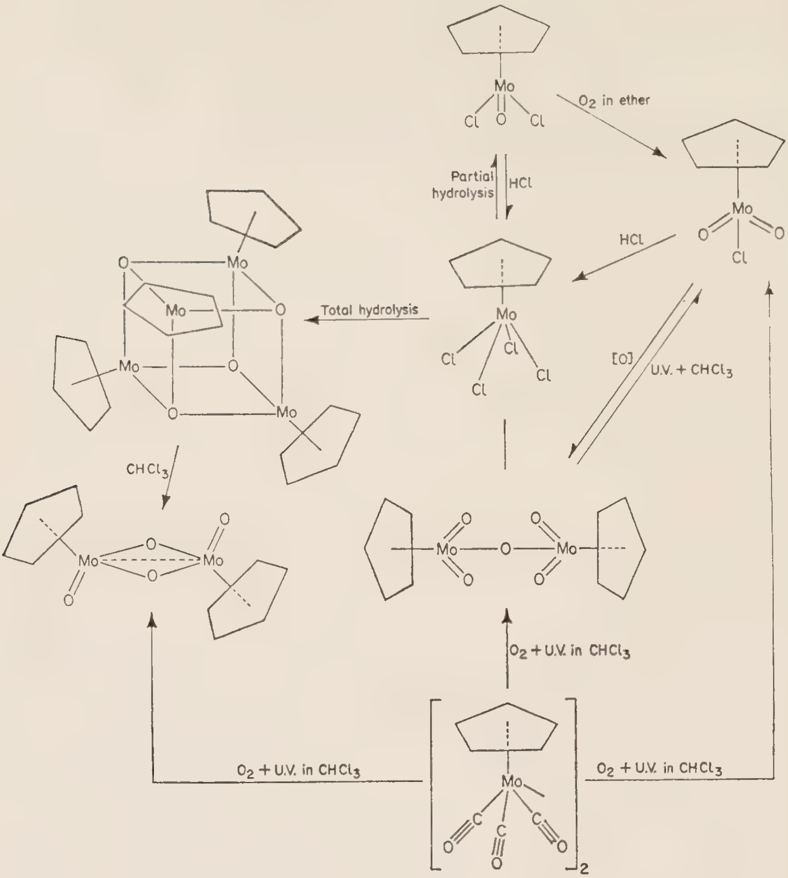
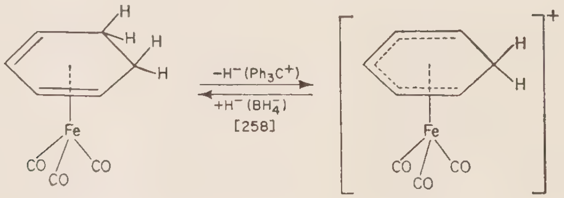


Fig. 37. Some π-cyclopentadienyl molybdenum oxides and oxyhalides [256]

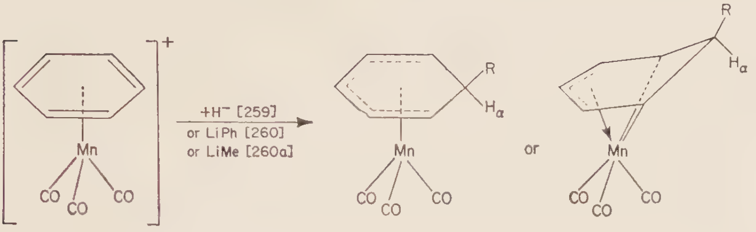
J. Other 5-electron ligands

(*a*) *π-Cyclohexadienyl complexes*

The abstraction of a hydride ion from neutral cyclohexadiene–metal complexes by triphenylmethyl (trityl), tetrafluoroborate,



or nucleophilic attack of hydride or $C_6H_5^-$ anions on arene metal cations, gives π-cyclohexadienyl metal complexes.

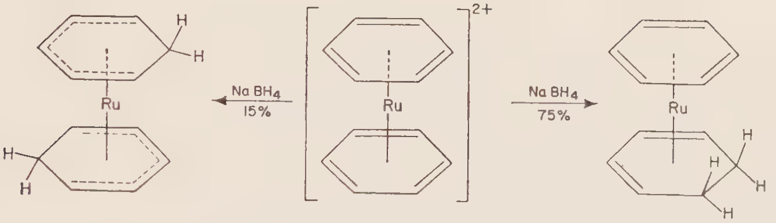


4.25 4.26

In the light of the arguments presented for the configuration of the substituted cyclopentadiene–metal complexes (Chapter 3, C, *b*) the nucleophilic group is placed in the *exo*-position.

Although reduction of the cation $[\pi\text{-}C_5H_5FeC_6H_6]^+$ with sodium borohydride could conceivably afford a cyclopentadiene derivative, the product of the reduction is the cyclohexadienyl derivative $\pi\text{-}C_6H_7Fe\text{–}\pi\text{-}C_5H_5$ [261].

With borohydride, $[(\pi\text{-}C_6H_6)_2Re]^+$ gives the mixed arene–cyclohexadienyl, $\pi\text{-}C_6H_6Re\text{–}\pi\text{-}C_6H_7$ [260], whilst the reduction of the di-benzene ruthenium cation gives a mixture of products [260], as shown,

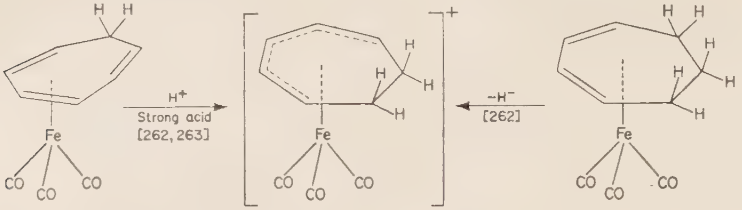


The majority of unsubstituted cyclohexadienyl complexes, like the cyclopentadiene complexes, have an intense infrared band in the region ~2700 cm⁻¹. This band is assigned to the *exo*-C–H$_\alpha$ stretch. This very characteristic band is absent from the cation $[\pi\text{-}C_6H_7Fe(CO)_3]^+$, possibly because the positive charge on the iron withdraws the metal electrons with which the methylene carbon may be otherwise supposed to interact (see p. 216).

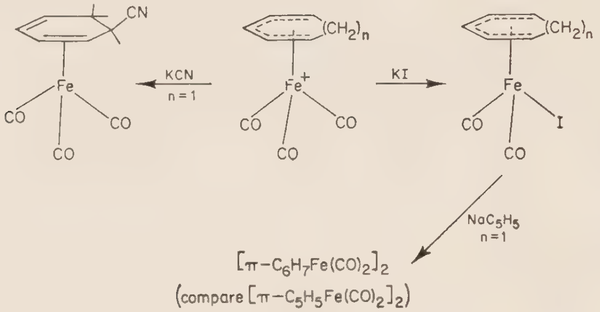
No crystal structures of these complexes are yet known but by analogy with cyclopentadiene complexes it would be expected that the methylene carbon of the π-C_6 ring would be bent away from the metal atom. Thus the bonding of the π-cyclohexadienyl ligand might be thought of as intermediate between the extreme cases of two σ-bonds and a π-enyl bond, 4.25, and a delocalized C_5-system 4.26.

(*b*) *Cycloheptadienyl complexes*

Complexes containing the 5-electron cycloheptadienyl ligand are prepared by methods similar to those used for cyclohexadienyl complexes, viz.

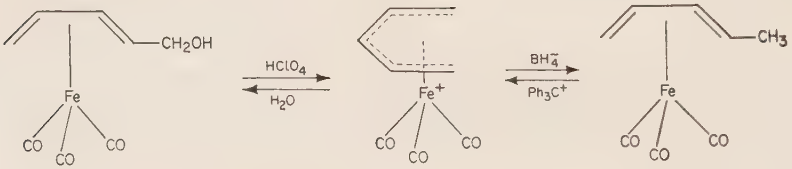


Some reactions of cyclohepta- and cyclohexa-dienyl iron tricarbonyl complexes resemble the reactions of the π-cyclopentadienyl iron analogues. However, ring addition reactions which give diene derivatives occur more readily [263*a*], e.g.



(*c*) *Pentadienyl complexes*

The acid cleavage of 1-hydroxy-2,4-pentadiene iron tricarbonyl gives the pentadienyl cation, 4.27 [264]. As shown, the same complex may be made

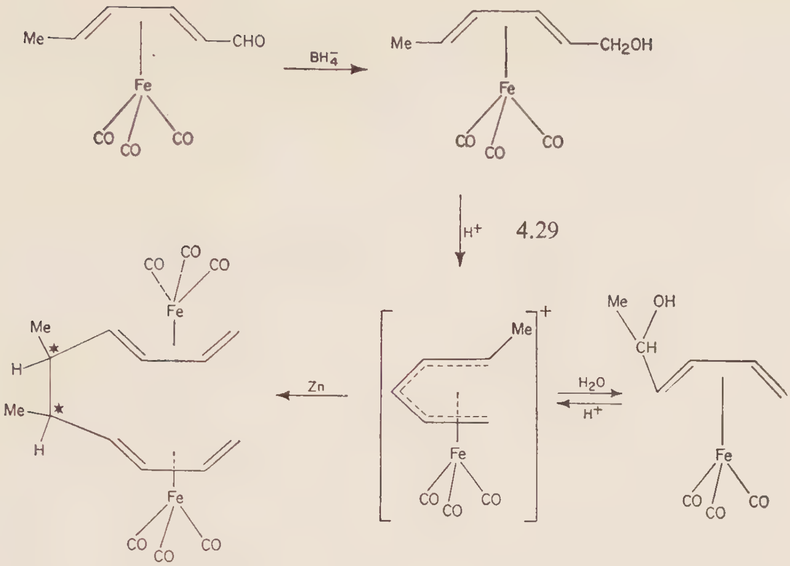


4.27 4.28

by hydride abstraction from the *cis*-1,3-pentadiene complex, 4.28 [264].

The ease of the removal of the hydroxyl group may be compared with the ether cleavage reaction discussed on p. 210.

Some interesting hydrolysis and reduction reactions of a related 1-hydroxy-2,4-hexadiene complex, 4.29, have been described [265].



4.29

4.30

Diastereoisomers are found for the complex 4.30.

It is interesting that some metal complexes of the pentalene system have been prepared [266].

K. The organic chemistry of π-cyclopentadienyl transition metal complexes

Woodward and co-workers observed [267] that bis-π-cyclopentadienyl iron failed to hydrogenate under normal conditions and did not undergo the Diels–Alder reaction but could readily be acetylated under Friedel–Crafts conditions. Thus the aromatic properties of the π-cyclopentadienyl ring were revealed and the trivial but very convenient name 'ferrocene' was coined. Studies of the ring substitution reactions of π-cyclopentadienyl systems have mostly been made with ferrocene. Aromatic behaviour has however been shown for ruthenocene, osmocene, π-$C_5H_5Mn(CO)_3$ [268, 269, 269*a*], π-$C_5H_5Tc(CO)_3$ [270], π-$C_5H_5Re(CO)_3$ [270] π-$C_5H_5V(CO)_4$ [271, 272, 273], π-$C_5H_5Cr(CO)_2NO$ [274], (π-$C_5H_5)_2WH_2$ and (π-$C_5H_5)_2ReH$ [275]. Indeed, for the most part π-cyclopentadienyl systems may be assumed to be 'aromatic', though particular complexes may not undergo typical substitution reactions since the metal can interfere with the reaction (thus oxidation to a cationic species would inhibit electrophilic attack), or the molecule might not survive the conditions of the reaction. In this section it is by no means intended to give a comprehensive account of the known organic chemistry of ferrocene† but rather

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† Detailed accounts of the chemistry of ferrocene may be found in the references [280, 304, 279]. Russian workers have made important contributions to this field and a brief review of their work may be found in reference [281].

to discuss some trends in the chemistry and exemplify some more important reactions. Frequently the chemistry of substituted ferrocenes is similar to that of aromatic hydrocarbons and is relatively unaffected by the proximity of the metal. In some cases however the iron atom plays a distinct role in the chemistry of the compound.

(*a*) *Electronic effects in ferrocene*

The description of the bonding in ferrocene suggests that there is a relatively high electron density on the π-cyclopentadienyl rings compared with that in benzene. In agreement with this, aminoferrocene is twenty times as strong a base as aniline [277], and ferrocene carboxylic acid is a weaker acid than benzoic acid [278]. For the same reason m- and p-ferrocenyl-anilines† are stronger bases than aniline and ferrocenyl-phenols and -benzoic acids are weaker acids than phenol and benzoic acid respectively [282, 283]. Determination of the Hammett σ_p for the ferrocenyl groups as a substituent in benzene shows it to be a stronger electron donating ligand than the methyl group [283*a*]. The exceptionally high aromatic reactivity towards electrophilic reagents of ferrocene and other π-cyclopentadienyl compounds is well demonstrated by the order of reactivity in Friedel–Crafts acylation [269, 284].‡

$$\begin{aligned}\text{phenol} \approx \text{ferrocene} > \text{anisole} > \pi\text{-}CH_3C_5H_4Mn(CO)_3 \\ > \pi\text{-}C_5H_5Mn(CO)_3 > \text{benzene}\end{aligned}$$

In substituted ferrocenes, the substituent affects the reactivity of the substituted ring, the relative reactivity of the two rings and hence the reactivity of the molecule as a whole. Thus the ease of oxidation of ferrocene is reduced by electron withdrawing, $-$I, substituents and, in acid media, the relative ease of oxidation is alkylferrocenes > ferrocene > acylferrocene. A striking example is ferrocenylcarboxaldehyde which resists oxidation by permanganate under conditions which will oxidize benzaldehyde to benzoic acid [285].

Acylation experiments show that disubstitution occurs heteroannularly indicating that as expected $-$I substitutents relatively deactivate the substituted ring. In those cases where small yields of homoannularly diacetylated products are isolated, the acyl substituents enter the 1,2-positions of the π-cyclopentadienyl ring rather than the 1,3-positions. Thus in the monoacetylated ring the 3-position is deactivated relative to the 2-position. The transmission of electronic effects from one ring to the

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† In ferrocene the ten ring positions are designated 1–5 and 1′–5′. Positions in the side chain are designated α and β, etc. Ferrocenyl refers to the group π-C_5H_5Fe-π-C_5H_4- and 1:1′-ferrocenylene refers to π-C_5H_4-Fe-π-C_5H_4-.

‡ Competitive acylation shows the order of decreasing reactivity to Friedel–Craft acylation [276]: $(\pi\text{-}C_5H_5)_2Fe > PhOMe > (\pi\text{-}C_5H_5)_2Ru \gtrsim \pi\text{-}C_5H_5Mn(CO)_3 > (\pi\ C_5H_5)_2OS > \pi\text{-}C_5H_5Cr(CO)_2NO \gtrsim \pi\text{-}C_5H_5V(CO)_4 \sim C_6H_6 > \pi\text{-}C_5H_5Re(CO)_3$.

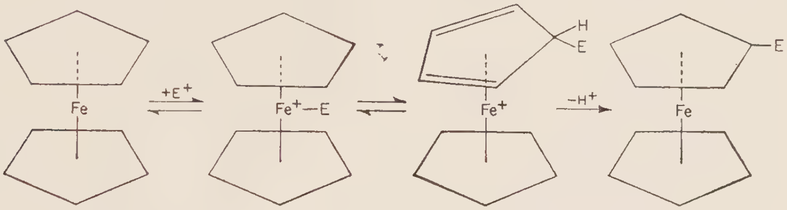
other is exemplified by the acids π-RC_5H_4Fe-π-C_5H_4COOH, which show a small lowering of pK_a with increasing electron-withdrawing properties of the group R [286]. Evidence for the transmission of electronic effects in ferrocene (and in titanocenes) is found from proton magnetic resonance [286*a*].

(*b*) *The participation of the iron atom in the chemistry of ferrocenes*

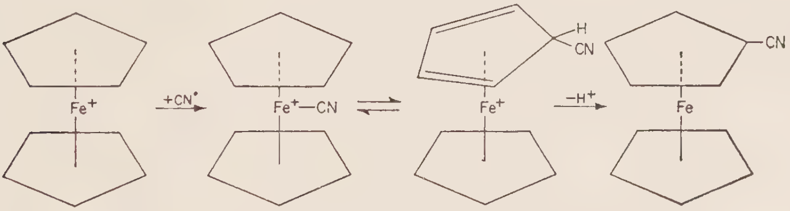
Apart from the role of bonding with and stabilizing the cyclopentadienyl radicals, the iron atom may also take a direct part in the chemistry of ferrocene substituents.

(*i*) *Some mechanisms of electrophilic and radical substitution reactions*

Electrophilic substitution reactions have been proposed to occur by a general reaction path in which the attacking electrophilic group interacts first with the iron atom [287].

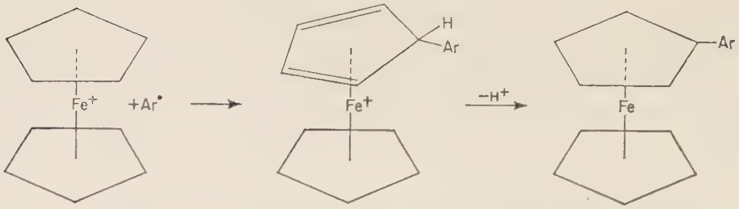


This mechanism provides an explanation for the relative reactivities observed for different ferrocenes in that the ease of oxidation of the iron depends on the nature of the ring substituents. A similar mechanism is proposed for the cyanation of ferrocene by HCN in the presence of ferric chloride and tetrahydrofuran. It is suggested that the ferric ion oxidizes the HCN to a CN radical and ferrocene to the ferrocenium cation which then react, viz.,



Another example is the arylation of ferrocene by aryldiazonium salts for which the mechanism given below and overleaf has been proposed. Other intermediates such as [(π-$C_5H_5)_2Fe^+$—N_2Ar] may be involved [326].

$$(\pi\text{-}C_5H_5)_2Fe + ArN_2^+ \rightarrow (\pi\text{-}C_5H_5)_2Fe^+ + Ar^\bullet + N_2$$

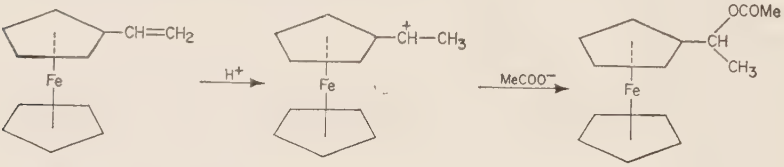


The above examples show that there is no mechanistic distinction between radical and cationic substitution reactions.

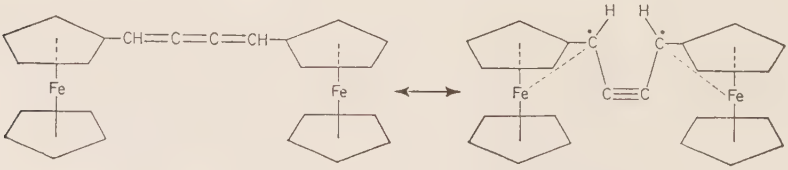
The basicity of ferrocene has been discussed earlier (p. 129). It is suggested that protonation of the iron atom of ferrocene may occur in Friedel–Crafts alkylation reactions and indeed the complex $[(\pi\text{-}C_5H_5)_2FeH]^+AlCl_4^-$ has been isolated [287, 288]. The ease of protonation of ferrocenes may account for the pK_a values of ferrocenylazobenzenes, which otherwise suggest that the ferrocenyl-group behaves as an electron-withdrawing group [289]. Finally, the displacement of substituents on ferrocene by protons has been postulated to occur by cationic hydride intermediates [290].

(*ii*) *The interaction of the iron atom with ring substituents*†

α-Carbonium ion stabilization. A dominant feature of the chemistry of ferrocenes is the ease of stabilization of carbonium ions in which a positive charge is localized at the α-position. For example the vinyl group of vinyl ferrocene is readily protonated, even by acetic acid [291, 292, 293].



The charge transfer spectra of some ferrocenyl butadienes and butatrienes provides evidence for the transfer of electron from the iron to the α-carbon position. Indeed, the butatriene compounds are surprisingly stable; which, it has been suggested, may be due to the stabilization of the diradical system which is known to be readily formed by triene systems [294], viz.,



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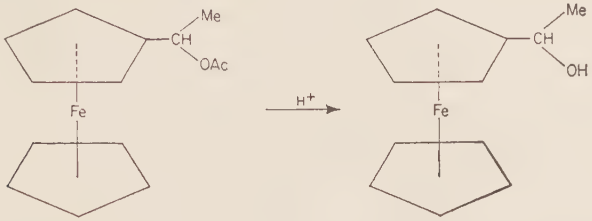
† For a review, see reference [290*a*].

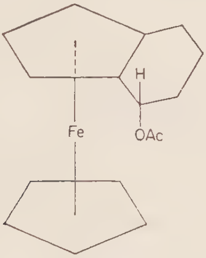
Richards and Hill have studied in some detail the reactivity of α-carbonyl acetates [295, 296]. The ease with which the α-acetoxy ferrocenyls undergo acid catalysed deacetylation provides strong evidence for carbonium ion stabilization.



The stability of the triphenylmethyl carbonium ion is well known and yet the above reaction proceeds at a greater rate than does the solvolysis of triphenylmethyl acetates.

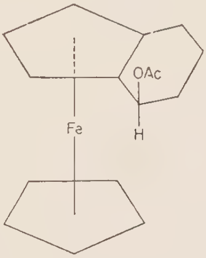
Evidence that it is necessary for the iron atom to interact directly with the α-position is provided by the studies of the solvolysis of the *endo*- and *exo*-acetates, 4.31 and 4.32. It is found that the *exo*-acetate group is more readily solvolysed than the *endo*-acetate by a factor of 2500 [297, 298].

In both solvolyses the product is exclusively the *exo*-alcohol.



"Endo"

4.31



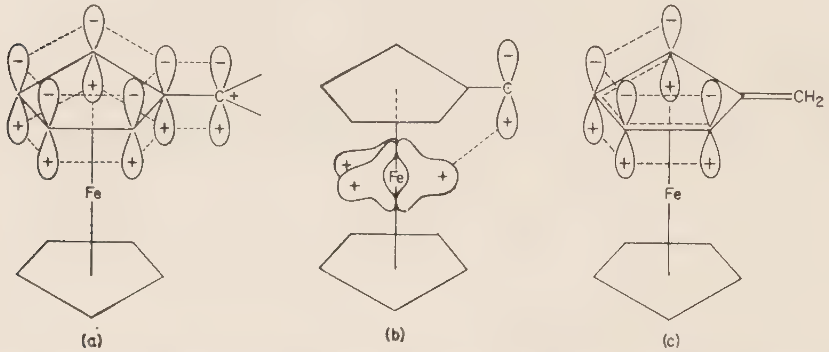
"Exo"

4.32

Further evidence for the stabilization of α-carbonium ions comes from solvolysis studies on chloromethylferrocene [298*a*] and chloroalkyl ferrocenes [298*b*] and from the proton magnetic resonance studies [298*c*]. The stability of quaternary ferrocenyl phosphonium cations, e.g. $[(\pi\text{-}C_5H_5Fe\text{-}\pi\text{-}C_5H_4)_2PR_2]^+$, to decomposition by hydroxide is another example of the stabilization of an α-substituted-ferrocenyl cation [298*d*].

The mechanism of stabilization of these carbonium ion intermediates is not fully understood. It has been suggested that there may be delocalization of the ring electrons to the vacant *p* orbital of the carbonium ion [295, 280] or that there may be direct interaction of the *p* orbital of the carbonium ion with the non-bonding E_{2g} orbitals of the iron (see Figure 38). A more extreme interaction between the ring and α-carbon than shown in (*a*) could lead to a situation better represented by the exo-cyclic structure given in Figure 38(*c*).

All these postulated mechanisms of stabilization of the α-carbonium ion can account for the stereospecificity of the solvolysis of the isomers, 4.31 and 4.32. Of course, the carbonium ions will always interact simultaneously with both the metal and the ring and the actual electron distribution in the carbonium ions may be better described by combination of say (*a*) and (*b*). It may well be that the carbonium ions π-bond more strongly to the ring carbon than they bond to the metal, whereas in the ferrocenyl phosphonium cations the phosphorus might form a stronger bond with the iron, using its vacant 3*d* orbitals, than with the ring.



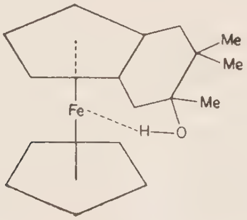
(a) (b) (c)

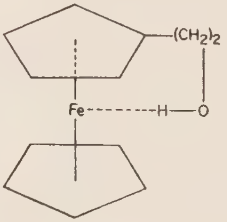
Fig. 38. Possible mechanisms for the stabilization of carbonium ions in the α-position. (*a*) Delocalization of ring π-electrons to the carbonium ion *p* orbital. (*b*) Direct interaction between metal lone pairs and the carbonium ion *p* orbital. (*c*) Exo-cyclic structure

All these mechanisms may participate to some extent and can account for the stereo-specificity of the solvolysis of the isomers, 4.31 and 4.32 [280].

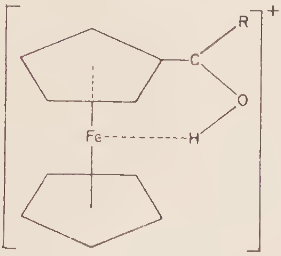
The analogy between these iron–α-carbonium ion interactions in ferrocene and those interactions believed to occur between metals and the β-position of σ-bonded organic systems is discussed later (pp. 212–213).

Weak hydrogen bonding by the iron atom. Infrared and proton magnetic resonance studies on a variety of ferrocenyl alcohols show that there is a weak interaction, akin to hydrogen bonding, between the hydroxyl group and the iron atom [280, 298, 299]. Examples are:





Also, several acyl ferrocenes undergo reversible protonation with hydrogen chloride and infrared studies show that the cations formed have strongly bonded OH groups. The following structure for the cations has been proposed [300]:



In the context of weak metal–hydrogen interactions, the unusual infrared spectra of metal cyclopentadiene complexes should also be remembered (see Chapter 7).

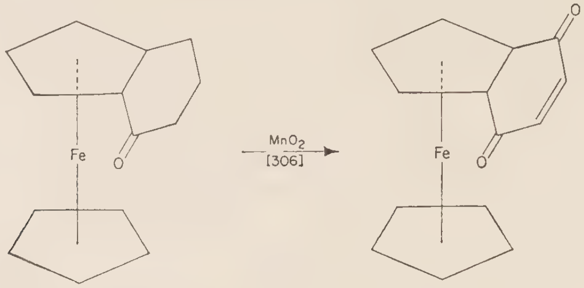
(*e*) *Trends in the chemistry of ferrocene, ruthenocene and osmocene*

As discussed earlier, the metal–ring bond strength in the complexes $(\pi\text{-}C_5H_5)_2M$ changes in the order Os > Ru > Fe, and the reverse order is found for the basicity of the metal atom in these metallocenes. In agreement with the relative availability of the metal electrons (basicity), acylation studies show the order of reactivity ferrocene > ruthenocene > osmocene [279, 301]. In contrast, carbonium ion stabilization by the metals, as shown by a comparison of the rates of solvolysis of α-metallocenylethylacetates [295, 296] and the ease of protonation of the vinylmetallocenes [293] occurs in the order Os > Ru > Fe. Thus the basicity of the metal atom does not appear to be an important factor in the stabilization of the α-carbonium ion derivatives. It may be noted that $\pi\text{-}C_5H_5Mn(CO)_3$ shows no tendency to protonate and its ethanol derivatives do not form hydrogen bonds with the manganese. This reduced basicity in comparison with ferrocene may be associated with the strong acceptor properties of the carbon monoxide ligands, and consequent interaction between the CO groups and the electrons of the iron.

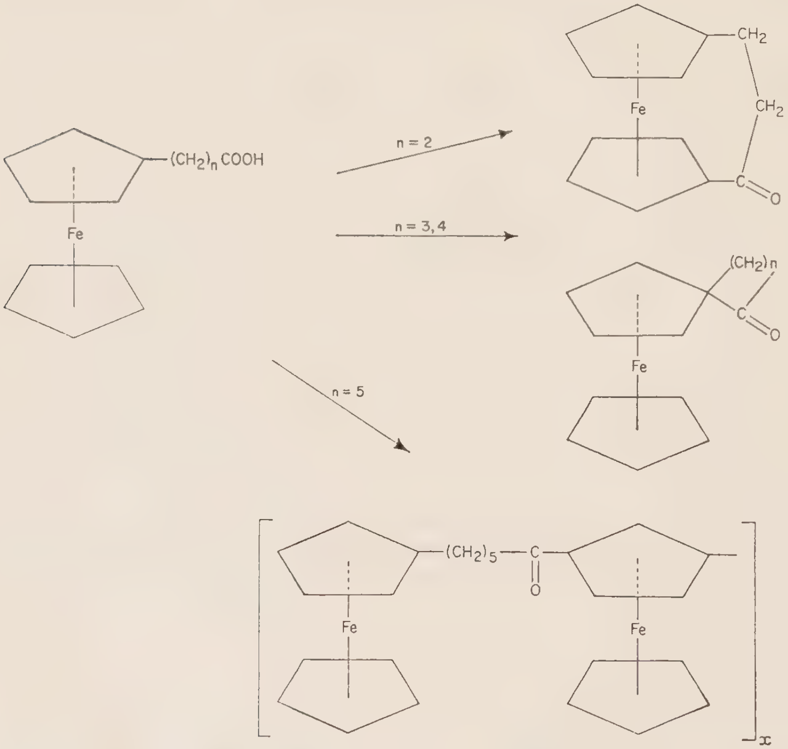
L. Some particular reactions

(*a*) *Acylation*

The Friedel–Crafts acylation of ferrocene and its derivatives has been studied in considerable detail, as discussed earlier. Anhydrous aluminium trichloride is the most commonly used catalyst for the reaction, but milder catalysts such as BF_3 [302], $SnCl_4$ [347], $ZnCl_2$ [304] and H_3PO_4 [305] may also be used. Acylferrocenes may also be prepared by the oxidation of alkylferrocenes [303], e.g.



and have been prepared by the dehydration of carboxylic acids. The course of the reaction depends on the length of the side chain and when n = 2, heteroannular bridged ketones may be prepared [307, 308].



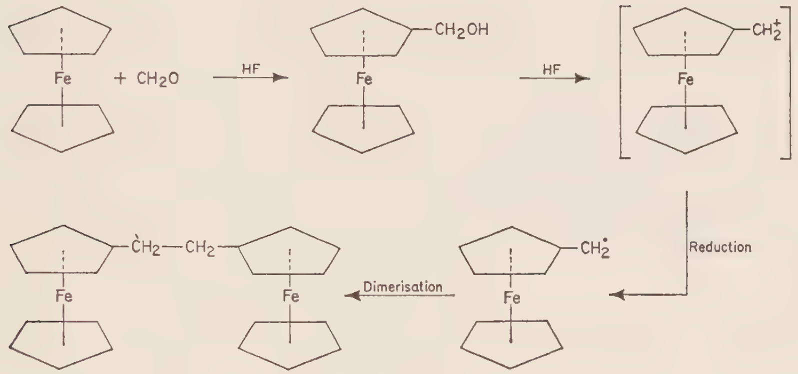
Some β-diketones, such as ferrocenylacetone, form complexes with metals, e.g. Cu(II) [309, 310]. Generally, acylferrocenes undergo many of the reactions typical of carbonyl compounds.

(*b*) *Alkylation reactions*

Direct Friedel–Crafts alkylation of ferrocene gives low yields of mono- and poly-alkylated ferrocenes [311, 312]. Better yields are obtained using olefins and aluminium trichloride [313].

$$(\pi\text{-}C_5H_5)_2Fe + CH_2{=}CH_2 \xrightarrow[30\text{–}40\ \text{atm., } 100\text{–}130^\circ]{AlCl_3} \underset{\sim 20\%}{\pi\text{-}C_5H_5Fe\pi\text{-}C_5H_4CH_2CH_3}$$
$$+ \text{ polyalkylated ferrocenes}$$

Dialkylation preferentially occurs homoannularly, as expected, and indeed the occurrence of large yields of polyalkylated products may be understood since alkyl substituents increase the reactivity of the substituted ring. Direct alkylation of ferrocene may also be achieved by the condensation of ferrocene with formaldehyde in liquid hydrogen fluoride [314, 315].



In view of the problem of polyalkylation which arises in these direct alkylation reactions, monoalkylated ferrocenes are best prepared by indirect routes. Suitable methods include the reduction of ferrocene esters and acyls with lithium aluminium hydride [316, 317, 318], e.g.

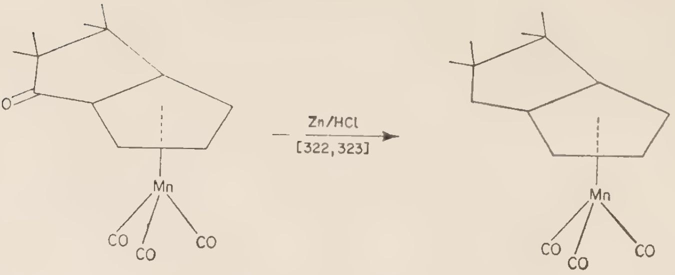
$$\pi\text{-}C_5H_5Fe\text{-}\pi\text{-}C_5H_4COOCH_3 \xrightarrow[AlCl_3]{LiAlH_4} \pi\text{-}C_5H_5Fe\text{-}\pi\text{-}C_5H_4CH_3$$

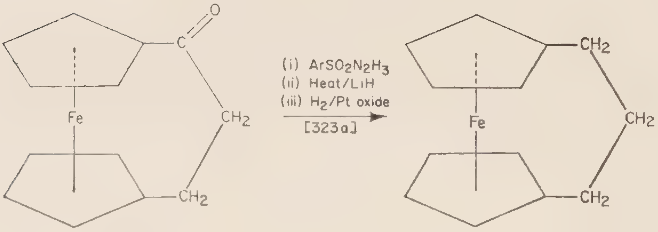
and the Clemmensen reduction of acyl complexes [319, 320, 321].

$$\pi\text{-}C_5H_5Fe\text{-}\pi\text{-}C_5H_4COC_6H_5 \xrightarrow{Zn/HCl} \pi\text{-}C_5H_5Fe\text{-}\pi\text{-}C_5H_4CH_2C_6H_5$$

Other interesting examples are shown on the following page.

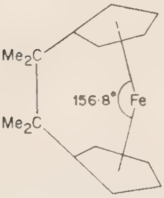
The structure shown for the complex, 4.31, has been determined by X-ray analysis [324]. In this complex, the rings are nearly eclipsed and the angle between their planes is 8·8°. The crystal structures of the related



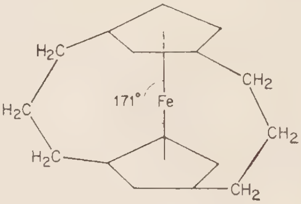


4.31

complexes 4.31*a* and 4.31*b* have eclipsed rings and they also are bent [324*a*]. It would be expected that the non-bonding electrons of these bent ferrocenes are more available for bonding with ligands than those in ferrocene since, from one side of the molecule, they are more open to attack.

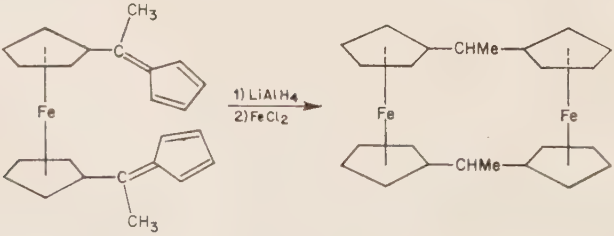


4.31*a*



4.31*b*

Binuclear ferrocenophane complexes have been prepared, such as 1,12-dimethyl[1,1′]-ferrocenophane, 4.31*c* [324*b*].



4.31*c*

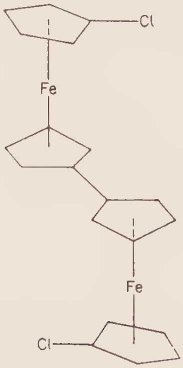
(*c*) *Arylation reactions*

Aryl derivatives of ferrocene may be prepared using diazonium salts [325, 326]. The reaction may be generally written:

$$n(R\text{—}C_6H_4N_2^+) + (\pi\text{-}C_5H_5)_2Fe \xrightarrow[H_2O/\text{ether}]{\text{dil. } H_2SO_4} (R\text{—}C_6H_4)_nC_{10}H_{10-n}Fe + N_2 + nH^+$$

Generally a mixture of arylated products is prepared (disubstitution occurs heteroannularly); but they are readily separated. Acylferrocenes can not be arylated by this route. This is presumably due to the higher oxidation potential of the iron in these complexes.

An interesting 'aryl' derivative is biferrocenyl, 4.32 (in Figure 39), which has been prepared by numerous routes [279, 280]. The best yields are obtained by the Ullman coupling of iodoferrocene with activated copper-bronze [327, 328]. The preparative route is shown in Figure 39, and the *trans*-configuration of the structure has been shown by X-ray diffraction [329]. These studies also suggest that the joined C_5 rings may be slightly distorted from fivefold symmetry. The structures of bis-[1-(2′-chloroferrocenyl)] and the [1-(2′-ethyl)] analogue are closely similar to that of biferrocenyl and the chloro or ethyl groups are held quite close to and over the C_5 ring planes, see 4.32*b* [329*a*].



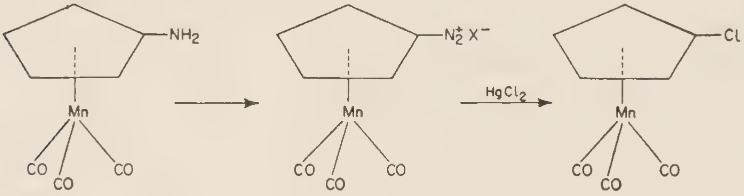
4.32*b*

(*d*) *Halogenation*

Since direct halogenation of ferrocene leads either to oxidation (for example, iodine or bromine gives products such as $(\pi\text{-}C_5H_5)_2FeI_6$, $[(\pi\text{-}C_5H_5)_2Fe]^+FeBr_4^-$ [330, 331]) or to decomposition, indirect routes are necessary. Treatment of ferrocenylboronic acid with copper halides and the halogenation of mercuriferrocene derivatives both give monohalogenated ferrocenes [331, 332, 333]. The haloferrocenes are useful as intermediates, for example ferrocenyl acetylenes are readily prepared from Cu(I)acetylides and iodoferrocene [333*b*].

$$\pi\text{-}C_5H_5Fe\pi\text{-}C_5H_4I \xrightarrow{CuC\equiv CR} \pi\text{-}C_5H_5Fe\pi\text{-}C_5H_4C_2R$$

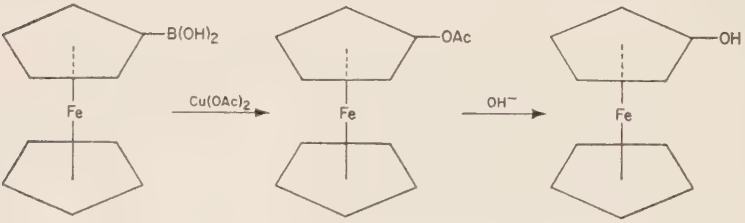
The monohalogen derivatives π-$C_5H_4XMn(CO)_3$ are best prepared by the decomposition of diazonium salts of aminocyclopentadienyl$Mn(CO)_3$ [333*a*]



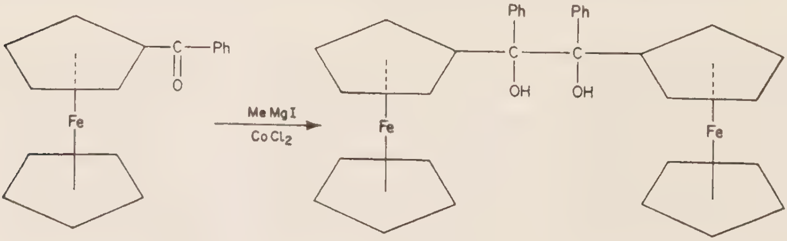
or via mercurated intermediates, as found for ferrocene [280].

(*e*) *Hydroxyl compounds*

Hydroxy-ferrocene is best prepared by the alkaline hydrolysis of the acetate 4.32*a*, which is obtained from ferrocenylboronic acid or halogen derivatives using cupric acetate [333, 334]. Unlike most ferrocene derivatives, hydroxy-ferrocene is sensitive to oxygen. It is a weaker acid than phenol ($K = 12 \times 10^{-10}$) and undergoes typical esterification reactions. The diol, 4.33, has been prepared by the rather unusual reaction [320],



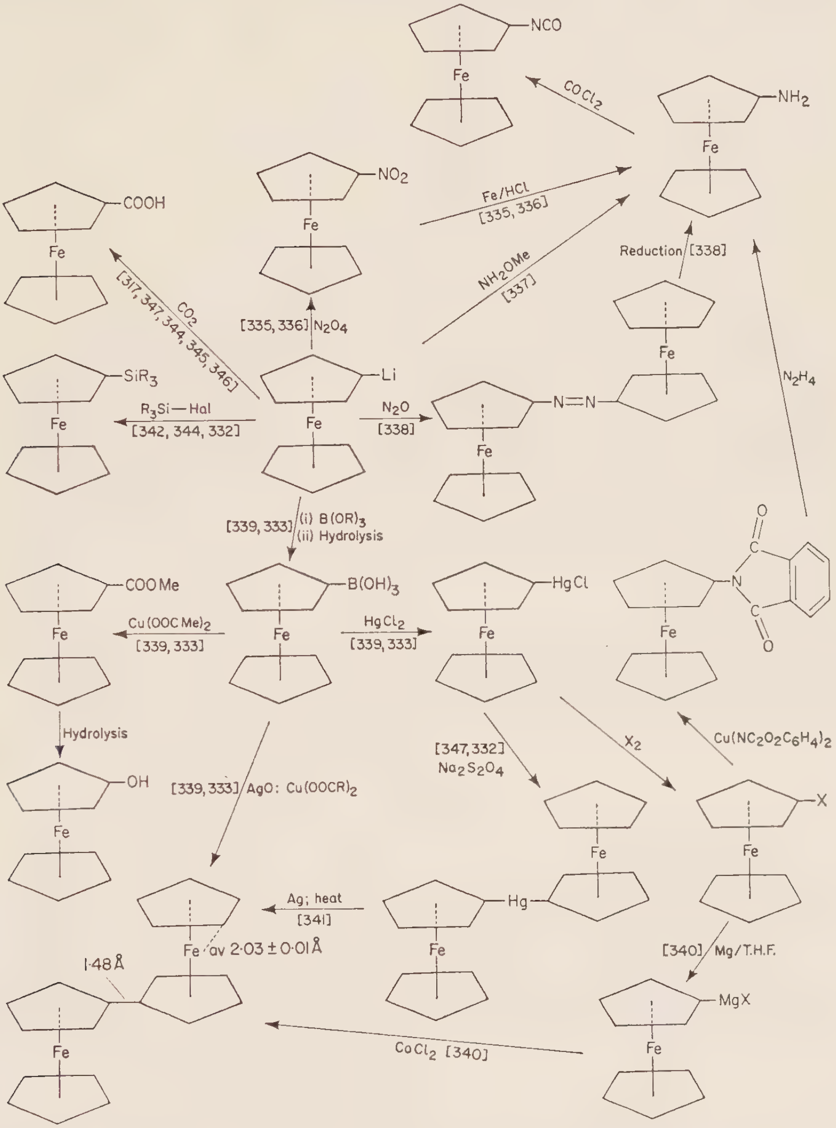
4.32*a*



4.33

(*f*) *Metallation studies*

Metallated ferrocenes are of great importance as intermediates. Metallation may be achieved by reaction of ferrocene with butyl lithium, amyl sodium or phenyl sodium [317, 345, 346, 347]. Mixtures of mono- and di-metallated products are frequently obtained unless particular care is paid

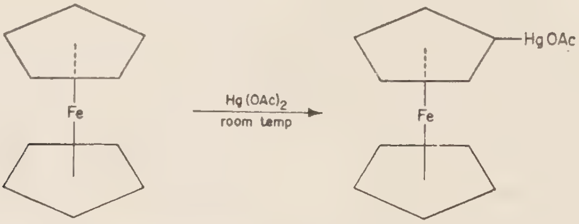


4.32

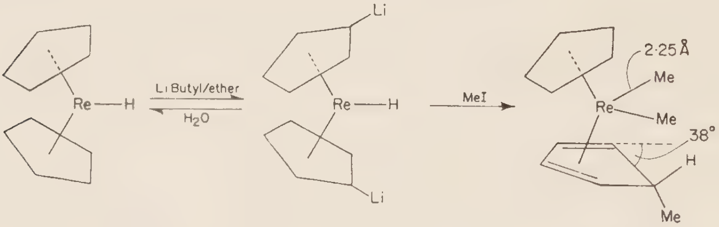
Fig. 39. The preparation of ferrocene derivatives using ferrocenyl lithium

to experimental conditions. Halogenated ferrocenes with butyl lithium give pure metallated products without difficulty [346*a*]. The metallated derivatives are extremely sensitive to oxidation and hydrolysis and further reactions are normally carried out at once. Some of these are shown in Figure 39.

The mercuration of ferrocene occurs very readily and under mild conditions, viz. [332, 347].



The hydrides $(\pi\text{-}C_5H_5)_2ReH$ and $(\pi\text{-}C_5H_5)_2WH_2$ react readily with excess butyl lithium giving 1,1′-dilithiated derivatives [275]. The dilithiated rhenium complex, 4.34, shows a most unusual reaction with methyl iodide affording the dimethyl complex, 4.35, whose structure has been determined by X-ray analysis [348]. The mechanism of the reaction is unknown but possibly involves *inter alia* the transfer of a methyl group from a ring to the metal.



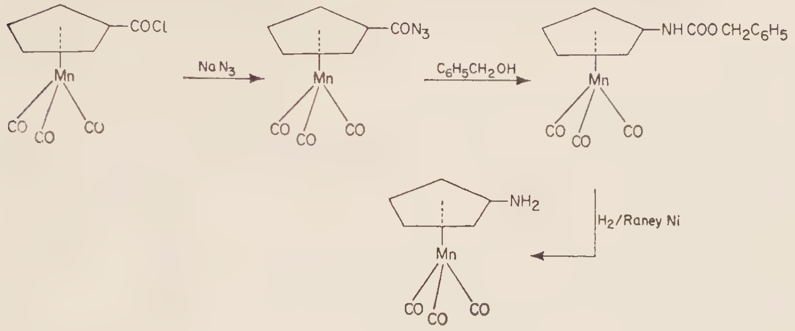
4.34 4.35

(*g*) *Nitration and sulphonation*

Nitration of ferrocene cannot be achieved directly due to oxidation by the nitric acid. The preparation is shown in Figure 39. Sulphonation may, however, be carried out using concentrated sulphuric acid in acetic anhydride [351] or dioxan-SO_3 in dichloroethane [349].

(*h*) *Amine derivatives*

The preparation of aminoferrocene is given in Figure 39. The compound undergoes many of the reactions typical of aromatic amines though it cannot be diazotized. Aminocyclopentadienyl manganese tricarbonyl is best prepared by the reactions shown below. It is a very weak base, ten times weaker than aniline, which shows clearly that the $Mn(CO)_3$ radical is more electron-withdrawing than the radical π-C_5H_5Fe [350].



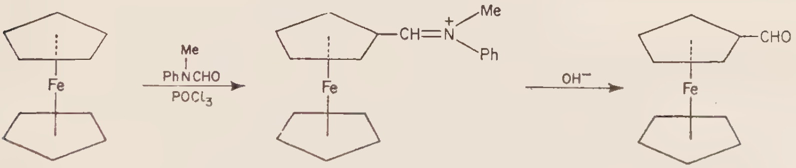
(*i*) *Carboxylic acid derivatives*

Treatment of the alkali metal salts of metallocenes or the oxidation of suitable side chains such as the acetyl group affords carboxylic acid derivatives [352, 353]. The dissociation constants of the acids π-C_5H_5M-π-C_5H_4COOH have been determined in 38% methanol as M = Fe, $1{\cdot}89 \pm 0{\cdot}04 \times 10^{-6}$, and M = Ru, $3{\cdot}71 \pm 0{\cdot}15 \times 10^{-6}$ [279]; they are both smaller than benzoic acid.

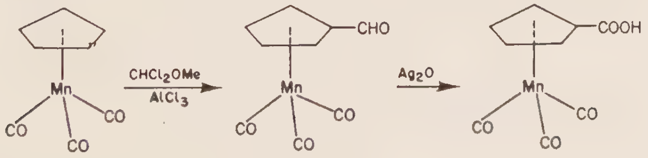
The chemistry of the metallocene carboxylic acids is normal and, for example, they form acid chlorides with PCl_5 [354, 355].

(*j*) *Carboxaldehyde derivatives*

Ferrocenecarboxaldehyde is a useful starting material for the synthesis of other ferrocene derivatives. It is best prepared by the Vilsmeier formylation reaction using N-methylformanilide in the presence of $POCl_3$ [284, 305, 356, 357].

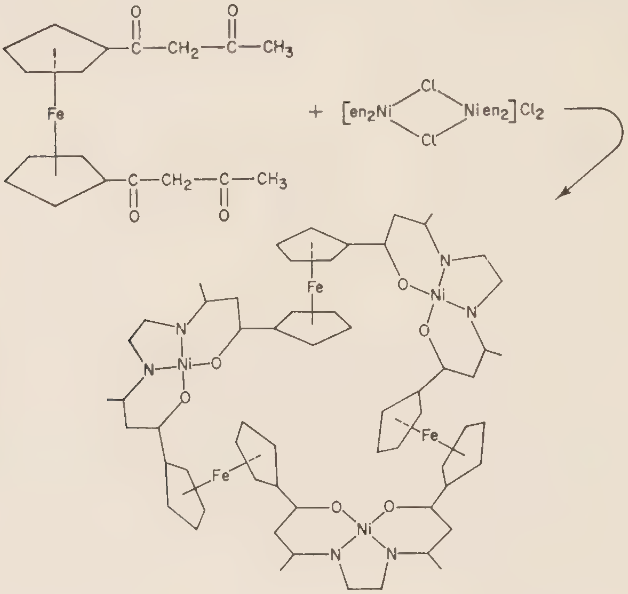


The formyl derivative π-$C_5H_4CHOMn(CO)_3$ has been prepared and it readily oxidizes to the corresponding carboxylic acid [358*a*], viz.



(*k*) *Miscellaneous*

Several ferrocene derivatives form complexes with other metals, for example, the diketone, pyridoylferrocenylmethyl, chelates with copper(II) [358]. Also an interesting 'template' reaction has been observed [359], viz.,



en = ethylenediamine

Mixed metal complexes such as these and metallocene polymers [360] are of interest in view of the possibility that they may have semi-conductor and related electrical properties in the crystalline state.

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CHAPTER FIVE

Six-electron ligands

Ligands in this class are shown in Table 17. The complexes with benzene and substituted benzene ligands are considered separately. The generic name of the benzene ligands is 'arene'.

Table 17 *Examples of six-electron ligands*

Ligand	Metals with which the ligand forms complexes	Comments
Arene	See Table 18	
Cycloheptatriene	Cr, Mo, W	See section B
Cyclo-octatetraene	Mo	(See p. 199)
Butatrienes	Cr	[1]
Cyclo-octa-1,3,5-triene	Mo	[2], see p. 12
Bicyclo-4,3,0-nonatriene	Mo	(See p. 184)
Thiophene	Cr	(See p. 187)
Pyridine	Cr	(See p. 186)

A. Arene transition metal complexes

Many of the known arene metal complexes are shown in Table 18.

(*a*) *Preparation*

(*i*) *Fischer's reducing Friedel–Crafts method.* The method is the most generally applicable for the preparation of bis-π-arene complexes, and was first used by Fischer and Hafner in their synthesis of bis-π-benzene chromium [3, 4]. The essentials of the reaction are the reduction of a suitable metal salt with aluminium powder followed by the addition of the arene ligand to the metal. The latter reaction is catalysed by aluminium trichloride, and a trace of mesitylene has also been found to be a catalyst for the system [5].

$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \longrightarrow 3[(\pi\text{-}C_6H_6)_2Cr]^+[AlCl_4]^- \qquad 5.1$$

Table 18 *Some bis-π-arene complexes and arene metal carbonyl complexes* [(a)(b)]

$(\pi\text{-}C_6H_6)_2V$ red-brown, 277–278° [6, 7, 27]	$(\pi\text{-}C_6H_6)_2Cr$ brown, 284–285° [3, 4, 6, 10, 23]	$[(\pi\text{-}(CH_3)_6C_6)_2Mn]^+$ pink-white [35]	$(\pi\text{-}C_6(CH_3)_6)_2Fe$ (2) [16]	$(\pi\text{-}C_6(CH_3)_6)_2Co$ red-brown (1) [31]	$(\pi\text{-Mes})_2Ni^{(c)}$ red-brown [21]
$(\pi\text{-Mes})_2V$ red-brown, 126–127° [28]	$[(\pi\text{-}C_6H_6)_2Cr]^+$ orange-yellow [3, 4, 10]	$[\pi\text{-}C_6H_6Mn(CO)_3]^+$ pale yellow [13]	$[(\pi\text{-}(CH_3)_6C_6)_2Fe]^+$ deep violet (1) [16]	$[(\pi\text{-}CH_3)_6C_6)_2Co]^+$ orange-red (2) [32, 35]	
$[(\pi\text{-Mes})_2V]^+$ orange [27, 28]	$\pi\text{-}C_6H_6Cr(CO)_3$ yellow, 162–163° [38, 39, 40, 41, 42]	$[\pi\text{-MesMn}(CO)_3]^+$ yellow [13]	$[(\pi\text{-}C_6H_6)_2Fe]^{2+}$ yellow [30]	$[(\pi\text{-}(CH_3)_6C_6)_2Co]^{2+}$ yellow-brown (1) [32]	
				$[(C_6H_6)_3Co_3(CO)_2]^+$ dark brown [47, 48]	
$[\pi\text{-}C_6H_6V(CO)_4]^+$ red [8, 9]	$(\pi\text{-}C_6H_6)_2Mo$ green, 115° d [11, 12]	$[(\pi\text{-}C_6H_6)_2\,{}^{99}Tc]^+$ [14]		$[(\pi\text{-}(CH_3)_6C_6)_2Rh]^+$ light yellow [32]	
	$[(\pi\text{-}C_6H_6)_2Mo]^+$ orange-yellow [11, 12]		$[(\pi\text{-Mes})_2Ru]^{2+}$ yellow [17]	$[(\pi\text{-}(CH_3)_6C_6)_2Rh]^{2+}$ red [32]	
	$\pi\text{-}C_6H_6Mo(CO)_3$ yellow, 125° [39]		$[Ru(C_6H_6)I_2]_x$ [19*a*]	$[(\pi\text{-Mes})_2Rh]^{3+}$ light brown-red [20]	
	$(\pi\text{-}C_6H_6)_2W$ dark green [12]	$[(\pi\text{-}C_6H_6)_2Re]^+$ light yellow [15]	$[(\pi\text{-}C_6H_6)_2Os]^+$ yellow [18]	$[(\pi\text{-Mes})_2Ir]^{3+}$ orange [20]	
	$[(\pi\text{-}C_6H_6)_2W]^+$ orange-yellow [12]	$[(\pi\text{-Mes})_2Re]^+$ red-brown [15]	$[(\pi\text{-Mes})_2Os]^{2+}$ yellow [19]		
	$\pi\text{-}C_6H_6W(CO)_3$ yellow, 140–145° [39]		$[Os(C_6H_6)I_2]_x$ red [19*a*]		
	$[\pi\text{-}Me_6C_6W(CO)_3Cl]^+$ orange [92*a*]				

(*a*) More detailed tables of arene complexes may be found in the review [22].
(*b*) Mes = 1,3,5-$Me_3C_6H_3$; numbers in ( ) indicate unpaired electrons.
(*c*) Not fully characterized.

The above reaction gives almost theoretical yields. The cation, 5.1, may readily be reduced to the neutral bis-π-benzene chromium using aqueous sodium dithionite.

$$[(\pi\text{-}C_6H_6)_2Cr]^+ + S_2O_4^{--} + 4OH^- \longrightarrow (\pi\text{-}C_6H_6)_2Cr + 2H_2O + 2SO_3^-$$

Alternatively, the neutral complex is obtained by the disproportionation of the bis-π-benzene chromium cation in aqueous alkaline solution [23].

$$2[(\pi\text{-}C_6H_6)_2Cr]^+ \xrightarrow{H_2O} (\pi\text{-}C_6H_6)_2Cr + 2C_6H_6 + Cr^{2+}$$

The mechanism of the formation of the complex, 5.1, is not known. The possibility of an adduct between $AlCl_3$ and the neutral $(\pi\text{-}C_6H_6)_2Cr$ has been ruled out [24]. It has, however, been shown that the product of the reaction between bis-π-benzene chromium and $AlCl_3$ is the complex $3[(\pi\text{-}C_6H_6)_2Cr]^+AlCl_4^-,4AlCl_3$, and it seems probable that this complex is also formed as an intermediate in the preparation [23]. Indeed, bis-π-arene chromium complexes will equilibrate with free arene ligands in the presence of aluminium trichloride [25*a*].

Using the above procedure, arene complexes of many of the *d*-block transition metals may be prepared, and substituted benzenes such as toluene, mesitylene (Mes) and hexamethylbenzene may be used instead of benzene. Generally, mesitylene and hexamethylbenzene metal complexes are more readily prepared than the unsubstituted benzene analogues. When halogenated aromatics are used, they undergo dehalogenation reactions affording hydrocarbon π-arene–metal complexes [25, 26].

As shown for chromium above, the first simple products of the reducing Friedel–Crafts procedure are usually cationic.

$$VCl_4 + Al + \text{Mesitylene} \xrightarrow[\text{[27]}]{AlCl_3} [(\pi\text{-Mes})_2V]^+$$

The bis-π-mesitylene vanadium cation may then undergo hydrolytic disproportionation. As shown below, the extent of the hydrolytic disproportionation depends on the basicity of the solution [28].

$$2[(\pi\text{-Mes})_2V]^+ \xrightarrow[\text{disproportionation}]{\text{pH } 7} (\pi\text{-Mes})_2V + V(II) + 2\text{Mes}$$

$$3[(\pi\text{-Mes})_2V]^+ \xrightarrow[\text{hydrolysis}]{\text{strongly alkaline}} 2(\pi\text{-Mes})_2V + V(III) + 2\text{Mes}$$

The bis-π-benzene molybdenum cation is thought to disproportionate by the reaction,

$$6[(\pi\text{-}C_6H_6)_2Mo]^+ + 8OH^- \longrightarrow 5(\pi\text{-}C_6H_6)_2Mo + MoO_4^{2-} + 4H_2O + 2C_6H_6$$

Such an overall reaction probably proceeds by a number of stages. Indeed, studies of the disproportionation of the bis-π-diphenyl chromium cation have shown that the chromous ion, first formed, acts as a reducing agent [29],

$$2[(\pi\text{-}C_6H_5\text{—}C_6H_5)_2Cr]^+ \longrightarrow (\pi\text{-}C_6H_5\text{—}C_6H_5)_2Cr + Cr^{2+} + 2C_6H_5\text{—}C_6H_5$$
$$[(\pi\text{-}C_6H_5\text{—}C_6H_5)_2Cr]^+ + Cr^{2+} \longrightarrow (\pi\text{-}C_6H_5\text{—}C_6H_5)_2Cr + Cr^{3+}$$

Not all bis-π-arene cations disproportionate affording neutral π-arene sandwich complexes. Thus the bis-π-benzene iron cation readily undergoes hydrolytic decomposition [30], whilst reduction of the bis-π-arene cations

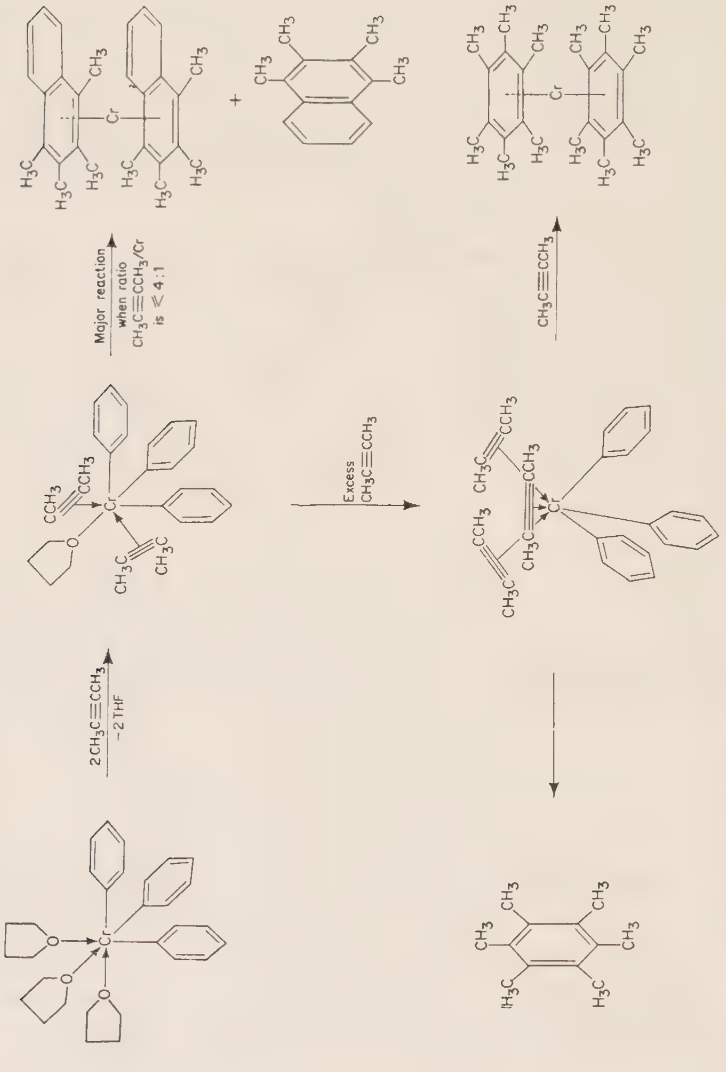


Fig. 40. Proposed mechanism of formation of arene-chromium derivatives from acetylenes and chromium-aryl complexes

of cobalt and rhodium require vigorous reducing agents such as sodium in liquid ammonia [31] or aluminium [32].

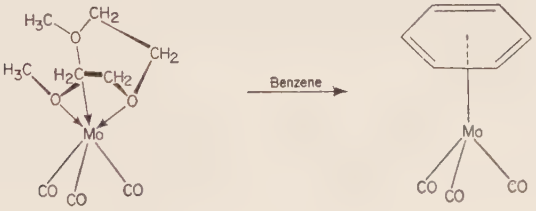
$$[(\pi\text{-}C_6(CH_3)_6)_2Co]^+PF_6^- + Na \xrightarrow{NH_3\ \text{liq.}} (\pi\text{-}C_6(CH_3)_6)_2Co + NaPF_6$$

(*ii*) *Cyclic polymerization of disubstituted acetylenes.* Treatment of triphenyl- and some trialkyl-chromium complexes with disubstituted acetylenes may polymerize the acetylene. Frequently the acetylene may be trimerized giving substituted benzenes and bis-π-arene chromium complexes. The course of the reaction depends on the stoicheiometry of the reactants and an example of the reaction and a postulated mechanism are shown in Figure 40 [33, 34]. Acetylenes have been used similarly to prepare arene complexes of manganese and cobalt [35]. Instead of the metal–alkyl complex, a mixture of the metal halide and a trialkyl aluminium may be used [36] and, in this case, the arene itself may be used directly instead of starting from acetylene [37].

(*iii*) *From aryl Grignard reagents.* Treatment of anhydrous chromium(III) halides with some aryl Grignard reagents gives bis-arene chromium complexes. The reaction is discussed in Chapter 7.

(*iv*) *From metal carbonyls.* Treatment of metal carbonyls with arenes may give arene metal carbonyl complexes directly [38, 39, 40, 41, 42]. Irradiation with ultraviolet light assists the reaction [43], or it may be more effective to carry out the reaction in a high-boiling, co-ordinating solvent, such as diglyme [44]. The role of the ether is illustrated by the observation that the reaction between molybdenum hexacarbonyl and diglyme gives the complex 5.2, which readily and smoothly gives arene complexes on treatment with the arene [44].

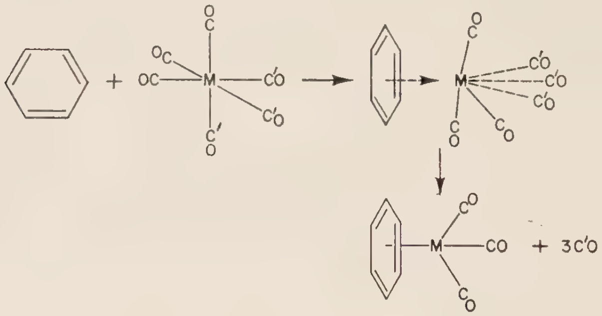
$$\text{Arene} + M(CO)_6 \xrightarrow[\text{an ether}]{\text{U.V. or}} \text{Arene } M(CO)_3 + 3CO$$



5.2

Many arene metal tricarbonyl complexes where the metal is chromium, molybdenum or tungsten have been prepared by this route although the presence of some functional groups such as —COOH, —CN or —CHO may preferentially promote total decomposition of the metal–hexacarbonyl [45].

Rate studies on the reaction between arenes and $Mo(CO)_6$ show the reaction to be first order with respect to the carbonyl. This is consistent with the proposed 'inversion' mechanism, shown below [46].



A stepwise mechanism similar to that proposed for arene displacement reactions (see p. 178) cannot be eliminated.

In some cases, in the reaction between metal carbonyls and the arene ligand, it is necessary to use aluminium trihalides as a catalyst, e.g.

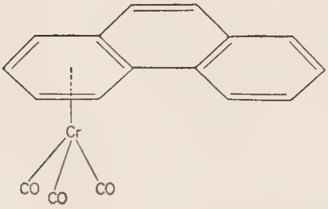
$$Co_2(CO)_8.AlBr_3 + C_6H_6 \xrightarrow[{[47]}]{} [(C_6H_6)_3Co_3(CO)_2]^+$$

or

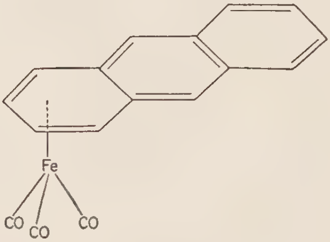
$$Hg[Co(CO)_4]_2 + AlCl_3 + C_6H_6 \xrightarrow[{[48]}]{60\text{–}70^\circ} \uparrow$$

Amongst the many 'substituted benzenes' which form the stable complexes, $areneM(CO)_3$, are condensed aromatic hydrocarbons, such as naphthalene, phenanthrene, acenaphthylene, pyrene, chrysene, indene and fluorene [49, 50, 51, 52, 53].

X-Ray studies have shown that phenanthrene bonds to the $Cr(CO)_3$ group by a terminal ring [54] (see 5.3). Similarly, the terminal ring bonds to



5.3



5.4

the metal in anthracene $Cr(CO)_3$ [55] and in anthracene $Fe(CO)_3$, 5.4. In the later case it seems probable that the anthracene is acting as a 4-electron ligand, as shown in 5.4 (see p. 170) [52]. It seems that there is indeed no end to the number of possible ligands and even oestrone$Cr(CO)_3$ has been prepared [56]. Biphenylene which could possibly bond to a metal by the central 4-electron 'cyclobutadiene' system reacts with diglyme $Mo(CO)_3$ affording biphenylene $(Mo(CO)_3)_2$, where a terminal arene ring again acts as the ligand [57]. And, as a final example of the affinity the $Cr(CO)_3$ group has for arene ligands, 1-methoxycyclohexa-1,4-diene reacts with chromium hexacarbonyl to give $C_6H_6Cr(CO)_3$ in good yields [58].

(*v*) *From substituted metal carbonyls.* It is sometimes better to start with a substituted metal carbonyl rather than with the hexacarbonyl. A very convenient method employs $L_3M(CO)_3$ (where L is a base such as γ-picoline), the arene, and BF_3, which can act as an acceptor for the displaced base L. In other words a Lewis σ-base, (L), is displaced by a π-acid (arene), and the σ-base is removed from the equilibrium by a Lewis σ-acid (BF_3). All the mono-halobenzene chromium tricarbonyls may be prepared in this way [58*a*].

With the norbornadiene complex, $C_7H_8Mo(CO)_4$, and aniline, small yields of aniline$Mo(CO)_3$ are formed [58*b*].

(*b*) *Structural studies*

Electron diffraction studies on bis-π-benzene chromium in the vapour state show it to have the sandwich structure with D_{6h} symmetry (see Figure 41). The C–C distances are all equal at 1·423 ± 0·002 Å, the C–H bonds are 1·090 ± 0·005 Å and the Cr–C distances are 2·150 ± 0·002 Å [58*c*].

X-Ray studies of the crystal structure of bis-π-benzene chromium have been carried out by several workers [59, 60, 61]. The sandwich structure of the molecule has been amply confirmed (Figure 41); however, due to the presence of orientational disorder in the crystals at room temperature it remains uncertain whether the C–C distances of the benzene ring are the same, or whether they are alternately slightly longer and shorter. Present evidence favours a symmetrical D_{6h} molecule with all C–C distances the same within experimental error [62, 62*a*]. Solid-state proton magnetic resonance studies show that there is molecular motion in bis-π-benzene-chromium crystals which is frozen out at $-196°$ [63]. Thus it may be possible to obtain more accurate X-ray data at lower temperatures.

X-Ray analysis shows that bis-π-benzene vanadium may exist in both cubic and monoclinic forms [64]. It has also been shown that the

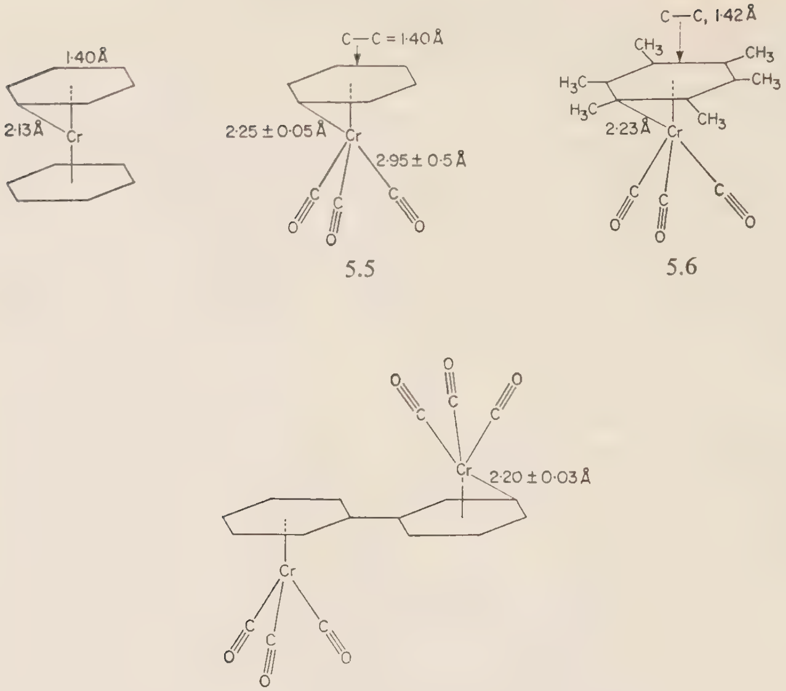


Fig. 41. The structures of some arene metal complexes; see text

compounds $(C_6Me_6)_2M$, where M = Cr or Fe, are isomorphous [65]. The crystal structures of phenathrene-$Cr(CO)_3$ and 9,10-dihydrophenanthrene$Cr(CO)_3$ [69*a*] have been determined. They have sandwich structures with ring–Cr distances similar to those given above.

The X-ray structure of benzene chromium tricarbonyl, 5.5, shows that, within the experimental error, the C–C distances of the ring are equivalent (average 1·40 Å) [66, 67], and similarly, in hexamethylbenzene chromium tricarbonyl, 5.6, the C–C distances are equivalent (1·42 Å) and the π-ligand shows no indications of a threefold distortion from a regular hexagon [68]. In the hexamethylbenzene complexes the methyl and ring carbons are essentially coplanar and their plane is parallel to that formed by the three carbons of the carbon monoxide groups. The Cr–C_6–ring distances of the two arene metal tricarbonyl complexes are similar (2·25 and 2·23 Å) but they are significantly greater than that found in bis-π-benzene chromium. This suggests that the arene–metal bond strength is greater in bis-π-benzene chromium than in the arene carbonyl complexes in agreement with the calculated metal–ring dissociation energies given in Table 21.

The X-ray studies also show that the Cr–O distances in π-$C_6H_6Cr(CO)_3$ are ~0·1 Å shorter than in $Cr(CO)_6$ [66]. This suggests that there is a higher degree of back-donation from the chromium to the carbon monoxides in benzene chromium tricarbonyl.

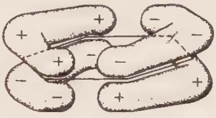
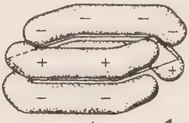
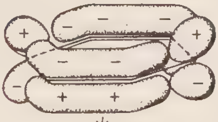
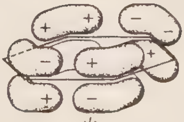
There is evidence that the $Cr(CO)_3$ group withdraws more electrons from the benzene ring in $C_6H_6Cr(CO)_3$ than the C_6H_6Cr system withdraws from the remaining ring in bis-π-benzene chromium, see p. 181. Thus the longer metal–ring bond in $C_6H_6Cr(CO)_3$ compared to that in $(C_6H_6)_2Cr$, may be due to a larger contribution to the metal–ring bond by back-donation in $(C_6H_6)_2Cr$.

The structure of diphenyl$(Cr(CO)_3)_2$, determined by a two-dimensional X-ray study [69], shows the expected *trans* distribution of the $Cr(CO)_3$ groups (Figure 41).

(*c*) *The bonding in bis-π-arene complexes*

Bis-π-benzene chromium has the structure shown in Figure 41. The molecule has D_{6h} symmetry possessing a centre of inversion. The six $p\pi_z$-electrons of benzene form six molecular orbitals which are represented in Figure 42*a*. In Table 19 the benzene M.O.s and the metal orbitals which can interact by virtue of their same symmetry in the group D_{6h} are given.

Fig. 42a.

M.O.s of benzene	Possible combination of benzene M.O.s in bis-π-benzene chromium
$\psi_0 = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$	 ψ_0
$\psi_{+1} = \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$ $\psi_{-1} = \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$	 ψ_{+1}  ψ_{-1}
$\psi_{+2} = \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)$ $\psi_{-2} = \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6)$	 ψ_{+2}  ψ_{-2}
$\psi_3 = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$	 ψ_3

The possible combinations of metal and ligand orbitals are represented in Figure 42*b*.

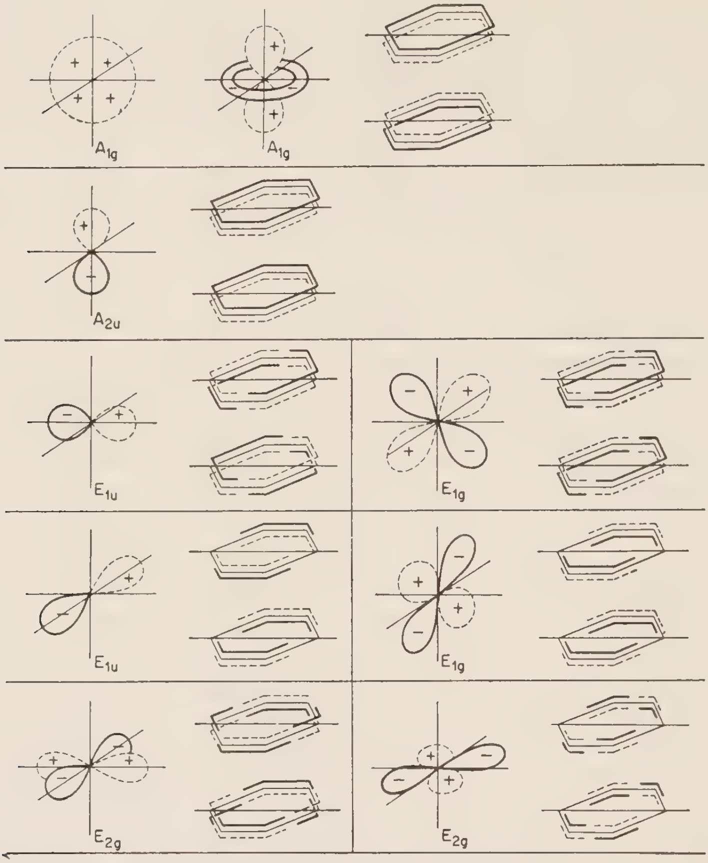


Fig. 42b. Representation of the molecular orbitals of benzene. The possible combinations of benzene and metal orbitals in bis-π-benzene chromium

Table 19 *Transformation properties of metal and ligand orbitals according to the symmetry group* D_{6h}

Symmetry	Metal orbitals	Ligand orbitals	Rotational symmetry
A_{1g}	s, d_{z^2}	$\psi_0 + \psi'_0$	σ
E_{1g}	d_{xz}, d_{yz}	$\psi_{\pm 1} + \psi'_{\pm 1}$	π
E_{2g}	d_{xy}, $d_{x^2-y^2}$	$\psi_{\pm 2} + \psi'_{\pm 2}$	δ
A_{2u}	p_z	$\psi_0 - \psi'_0$	σ
E_{1u}	p_x, p_y	$\psi_{\pm 1} \mp \psi'_{\pm 1}$	π
E_{2u}		$\psi_{\pm 2} - \psi_{\pm 2}$	—
B_{2g}		$\psi_3 + \psi'_3$	—
B_{1u}		$\psi_3 - \psi'_3$	—

For a consideration of the relative ordering of the energy levels we again use the results of a calculation made by Schustorovitch and Dyatkina [70] which provides the energy level diagram shown in Figure 43. This energy level scheme shows, overall, a close resemblance to that given for ferrocene (see p. 101).

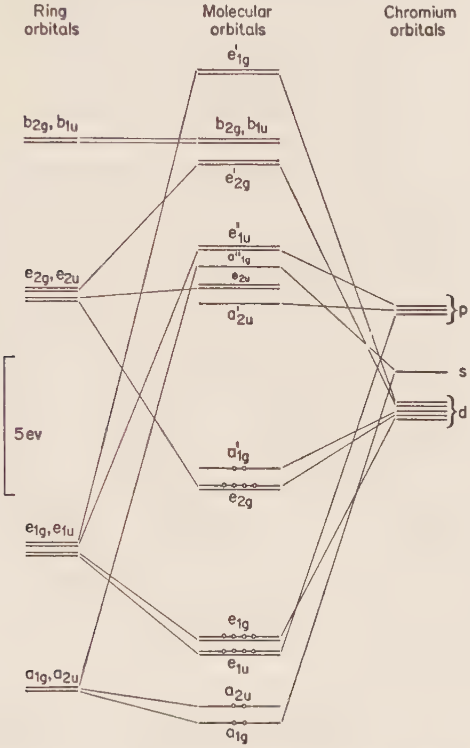


Fig. 43. Energy level diagram for bis-π-benzene chromium, after Schustorovich and Dyatkina [70] (and Cotton [72]).

There are however a number of differences between the energy level schemes for ferrocene and bis-π-benzene chromium; these arise chiefly because the energies of the chromium atomic orbitals are higher than those of iron whilst the energies of the benzene M.O.s are lower than those of the cyclopentadienyl radical. These differences mean that in bis-π-benzene chromium, the donor–acceptor (a_{1g}) interactions make less contribution to the bonding than in ferrocene, and the e_{1g} bonds have significant donor–acceptor properties. Further in ferrocene the e_{2g} electrons were regarded as essentially non-bonding, whilst in bis-π-benzene chromium they take part in the metal–ring bonding and hence are less available as 'lone pairs'. The calculation places a negative charge of —0·75 electrons on the ring in approximate agreement with the experimentally estimated value of −0·55 electrons [71].

The low dipole moment found for the mixed complex π-C_5H_5Cr-π-C_6H_6 suggests that there is a dipole for the Cr-π-C_6H_6 system with the ring as the negative end, in agreement with the postulate of a negative charge on the ring in $(\pi\text{-}C_6H_6)_2Cr$. The description of the bonding in other bis-arene complexes may be assumed to be similar to that for bis-π-benzene chromium and, as shown in Table 20, the magnetic properties may be used to assist in the electron assignments. Also, the electronic spectrum of bis-π-benzene chromium shows that the bands assignable to the benzene ligands are not substantially shifted from those in benzene itself. This also suggests that the benzene ligands retain their delocalized character [74]. It is worth noting that a detailed M.O. treatment of $(\pi\text{-}C_6H_6)_2Cr$ favours a completely delocalized ring structure for the molecule [73].

Table 20 *Magnetic properties of some bis-π-arene complexes*

Complex*	Electron assignment	No. of unpaired electrons	Calculated 'spin only' value, B.M.	Expected value B.M.	Observed value B.M.
Bz_2V^+	$(e_{2g})^3(a_{1g})^1$	2	2·83	2·83	—
Bz_2V	$(e_{2g})^4(a_{1g})^1$	1	1·73	1·73	1·68 ± 0·08
Bz_2Cr^+	$(e_{2g})^4(a_{1g})^1$	1	1·73	1·73	1·71
Bz_2Cr	$(e_{2g})^4(a_{1g})^2$	0	0	0	0

* Bz = π-C_6H_6

One arene sandwich complex which may not fit satisfactorily into the above bonding description is bis-π-hexamethylbenzene cobalt. This molecule is thermally labile, very air-sensitive and soluble in non-polar solvents. It is very anomalous in having a dipole moment in cyclohexane and benzene (in benzene 1·78 ± 0·07 D). Further it only has one unpaired electron whereas three unpaired electrons might have been expected (it is formally a 21-electron complex) [31]. The reasons for the dipole moment are uncertain. It seems unlikely that both the above solvents could act as ligands and therefore some asymmetry in the molecule seems more probable. Perhaps one benzene ring is not acting as a 6-electron donor but as a 4-electron donor (see π-$C_5H_5Co(CF_3)_6C_6$, Figure 19). Other possibilities have been discussed [31, 65].

(*d*) *The stability of bis-π-arene complexes*

The neutral bis-π-arene complexes form well-defined crystals which are moderately soluble in the common organic solvents. They may be sublimed in vacuum at ~100°C. Thermally the complexes are reasonably stable, frequently up to 300°C. A number of thermodynamic studies have been made from which the mean bond dissociation energies of the metal ring bonds have been derived [75]. The data are given in Table 21.

Table 21 *Some thermodynamic data on bis-π-arene complexes*

Metal–ring bond in the complex	$\bar{D}^{(a)}$ kcal./mole
$(\pi\text{-}C_6H_6)_2V$	70·0 ± 2
$(\pi\text{-}C_6H_6)_2Cr$	40·5 ± 8
$(\pi\text{-Mes})_2Cr$	41·5 ± 2
$(\pi\text{-p-cumene})_2Cr$	41·0 ± 2
$(\pi\text{-}C_6H_6)_2Mo$	50·7 ± 2
$(\pi\text{-}C_5H_5)_2Fe$	69·5 ± 10
$(\pi\text{-}C_5H_5)_2Ni$	56·6 ± 10

(*a*) $\bar{D}$ is the mean bond dissociation energy of MR_n; $\bar{D}(M - R) = \Delta H^\circ/n$ [75].

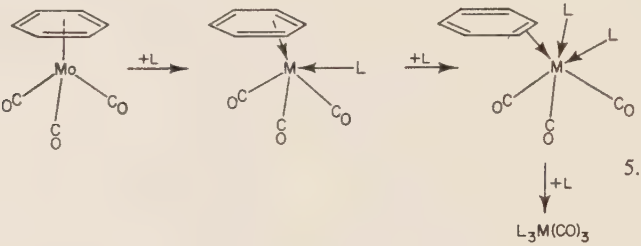
The data in Table 21 show that the metal–ring bond in ferrocene is almost twice as strong as that in bis-π-benzene chromium. In the complexes $(\pi\text{-}C_6H_6)_2M$ there is a decrease in the mean bond dissociation energy of the ring–metal bond in the order $V \gg Mo > Cr$. Perhaps the energy of the vanadium metal orbitals are closer to those of the benzene M.O.s than those of chromium. Finally, alkyl substituents appear to make little difference to the ring–metal bond strengths of bis-arene chromium complexes.

Most of the neutral bis-arene metal complexes oxidize readily in air to give bis-arene cations. As would be expected, the bis-arene cations are more resistant to oxidative decomposition than the neutral analogues and, in weakly alkaline solutions, $[\pi\text{-}C_6H_6)_2Cr]^+$ may be kept in air for several weeks.

In methanol/benzene solutions, bis-π-benzene chromium undergoes a reversible 1-electron oxidation (the half-wave reduction potential = —0·8 volts [76]). There is little change in the potential for a number of alkyl-substituted bis-π-arene chromium complexes, except in the case of bis-π-diphenylchromium for which the reduction potential = —0·66 volts [77]. The ability of bis-π-benzene chromium to act as an electron donor is shown by the ease with which it forms 1 : 1 molecular complexes with acceptor molecules such as tetracyanoethylene [78]. It seems probable that these complexes are best formulated as salts, e.g. $[(\pi\text{-}C_6H_6)_2Cr]^+TCNE^-$. In contrast, arene chromium tricarbonyls do not readily oxidize giving the cations $[areneCr(CO)_3]^+$, and they form correspondingly weaker charge-transfer complexes, for example with 1,3,5-trinitrobenzene [78*a*, 78*b*].

The rates of reaction of arene-$Mo(CO)_3$ with ligands L, giving

$L_3Cr(CO)_3$, where L = tertiary phosphines, are relatively unaffected by solvent changes. The reaction is first order in both the ligand L and the metal carbonyl. It is thought that replacement of the arene by the ligand proceeds by a stepwise process [78*c*], viz.,



5.6*a*

The benzene–molybdenum bond in the postulated intermediate, 5.6*a*, may be thought to be analogous to the benzene–silver bond in some silver benzene complexes, see p. 29. There is infrared spectral evidence for the species arene-$W(CO)_5$ [78*d*].

The lack of basic properties of bis-π-benzene chromium compared to those of ferrocene may be due in part to the reduced availability to acceptor ligands of the e_{2g} electrons which, in π-arene complexes, are quite important (see above). It is worth noting that no 'bent' bis-π-arene complexes are presently known (e.g., no $(\pi\text{-}C_6H_6)_2TiCl_2$), and one reason for this may be that the large C_6-rings may sterically prevent bending so that there would not be room for another ligand to be attached to the metal.

As shown in section A, *a*(*i*), many of the bis-arene cations undergo hydrolytic disproportionation, and the complex cations $[(\pi\text{-arene})_2M]^+$, where M = Fe, Ru or Os, show an increased stability to hydrolysis with increasing atomic weight of the metal. With alkyl substituents on the benzene ring, the cations $[ar_2Cr]^+$ show an increase in stability to hydrolysis in the order ar = mesitylene > xylene > toluene > benzene [30]. The increase in stability with increasing methyl substitution may be due to both a corresponding slight increase in metal–ring bond strength and, more important, to steric/kinetic factors.

(*e*) *Some chemistry of bis-π-arene complexes*

Some reactions of bis-π-arene chromium complexes are shown in Figure 44. The aromatic chemistry of bis-π-benzene chromium is rather limited. This is presumably due to the instability of the molecule which decomposes under the conditions of the reactions. The metallation reaction with amyl sodium would appear to open up a route to the preparation of a wide number of derivatives. Few studies have been made of the replacement and substitution reactions of the other bis-arene metal complexes; generally, there is little known of the chemistry of the other bis-arene com-

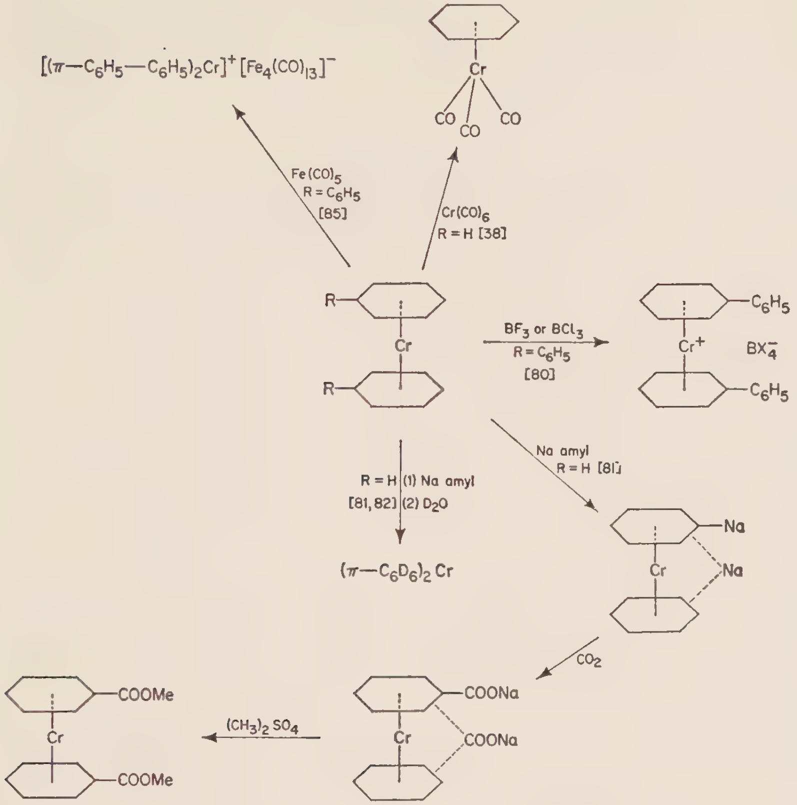
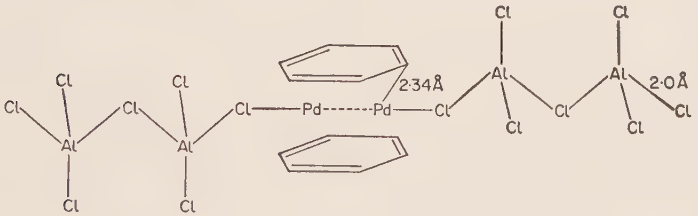


Fig. 44. Some reactions of bis-π-arene chromium complexes

plexes. This is probably due to their rather difficult preparations and their oxidative instability.

Recently, the unusual complex, 5.7, has been prepared using the reducing

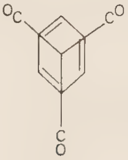


5.7

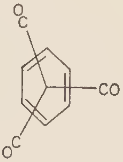
Friedel–Crafts procedure [79]. The structure of the complex, 5.7, has been shown by preliminary X-ray analysis [79]. The complex is diamagnetic and the Pd–Pd distance of 2·58 ± 0·01 Å is the shortest reported distance for a Pd–Pd bond. As shown, the Cl–Pd–Pd–Cl atoms are almost in a straight line. Possibly, each benzene ring is behaving essentially as two π-enyl ligands, in which case, with a Pd–Pd single bond, the 18–electron rule is obeyed by each palladium atom.

(*f*) *The stereochemistry of some arene metal carbonyls*

As mentioned in section A(*b*) benzene chromium tricarbonyl and hexamethylbenzene chromium tricarbonyl have the staggered conformation B.



A

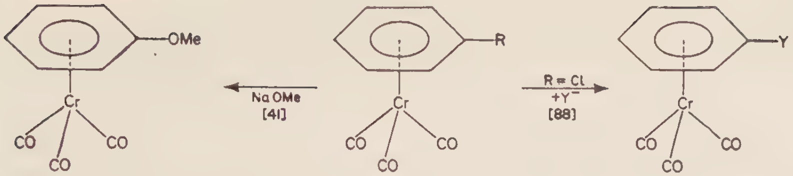


B

However, anisole-Cr(CO)$_3$ and *o*-toluidine-Cr(CO)$_3$ have the eclipsed conformation A [84*a*, 84*b*, 78*a*]. It is suggested that the eclipsed configurations arise since the ring substituents are electron releasing and are *ortho-para* directing. The relatively high electron density on the o- and p-carbons favours them being held *trans* to the 'π-acid' carbonyl groups. This electronic effect would, however, compete with steric repulsion between the ring substituents and the metal–CO groups. This would favour the staggered configuration. Such steric interactions have been postulated to account for the temperature dependent, proton magnetic resonance spectrum of isopropylbenzeneCr(CO)$_3$ [84*c*], and the ratios of *cis* : *trans* isomers found in equilibrium mixtures of substituted-indaneCr(CO)$_3$ complexes [84*d*].

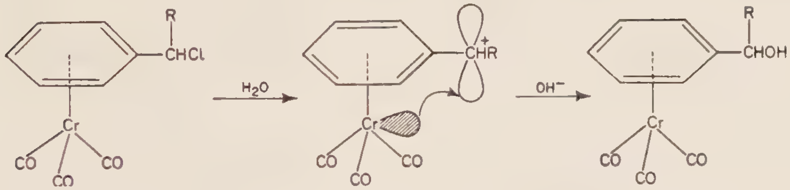
(*g*) *Some reactions of arene metal carbonyls*

The arene metal carbonyls of the Group VI metals generally form yellow-orange crystalline complexes which are often stable to oxidation and are soluble in the common organic solvents; they are thermally stable up to 150–250°C. A number of studies show that the M(CO)$_3$ system in these complexes withdraws electrons from the arene ring. For example, benzoic acid is a weaker acid than benzoic acid Cr(CO)$_3$ (pK 4.6) [39, 41], and aniline is a stronger base than aniline chromium tricarbonyl [39]. The ease with which arene metal carbonyls undergo nucleophilic substitution reactions also indicates a reduced electron density [41] of the arene ring compared to the free arene.



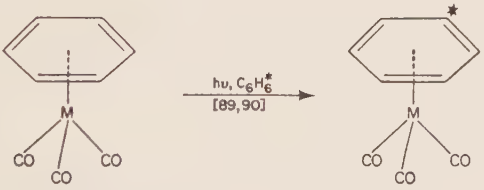
The aromatic ring may show a correspondingly reduced reactivity towards electrophiles; e.g. Friedel–Crafts acylation of $C_6H_6Cr(CO)_3$ does not proceed very readily [83, 84]. In contrast, however, the deuteration of $C_6H_6Cr(CO)_3$ in basic media proceeds more readily than for benzene [85*a*]. Arene metal tricarbonyls have large dipole moments (5–6 D) with the carbonyl groups as the negative end of the dipole [86, 87], This does not imply that the arene ring is positive relative to the metal atom but only that the three carbonyl groups are together more negative than the arene ring.

Rate studies on the solvolysis of the arene chromium tricarbonyl complexes, 5.8, suggest that the reaction proceeds via a carbonium ion, 5.9. It is probable that this carbonium ion is stabilized by direct interaction of the chromium atom, as shown, 5.9. Thus, whilst the $Cr(CO)_3$ group may withdraw electrons from the arene ring, the metal atom can also provide electrons for the stabilization of carbonium ions which are ring substituents [88].



5.8 5.9

Arene metal tricarbonyls may undergo displacement of both the arene ring and carbonyl groups. The exchange of arene ligand has been shown to be enhanced by ultraviolet irradiation.

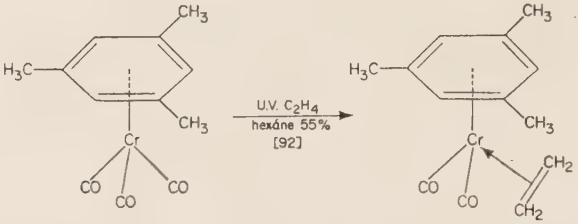


Arene ligands can be displaced by cycloheptatriene, and phosphine ligands [91]; PF_3 gives $(PF_3)_3Cr(CO)_3$ [91*a*].

The infrared spectra of the complexes arene$Cr(CO)_2D$, where D = CO [91*b*], tertiary phosphines, olefins or acetylenes [91*c*], and R_2SO, or SO_2

[91*d*] show that electronic effects are transmitted from the rings to the carbonyls. For example, the hexamethylbenzene olefin complexes $Me_6C_6Cr(CO)_2$ olefin, have stronger Cr–olefin bands than do the benzene analogues [91*c*]. This is reasonable since the Cr–D bond strength would be expected to increase with increasing π-donor power of the chromium *d* orbitals.

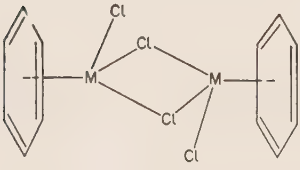
The substitution of carbonyl groups is best carried out using irradiation techniques, e.g.



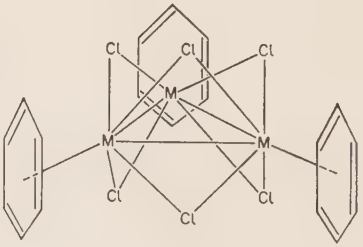
The reversible reduction of arene metal cations to π-cyclohexadienyl complexes is discussed elsewhere (p. 137). It is interesting that the treatment of hexamethyl-benzene chromium tricarbonyl with $SbCl_5$ in $CHCl_3$ gives the diamagnetic red cation $[Me_6C_6W(CO)_3Cl]^+$; this is the first example of the oxidation of an arene metal tricarbonyl complex [92*a*].

(*h*) *Polynuclear complexes of the Group IV and Group V metals*

Table 18 shows that bis-π-arene complexes of the Group IV and Group V metals are presently unknown. However, hexamethylbenzene reacts with the Group IV metal halides under the reducing Friedel–Crafts conditions forming trinuclear complexes, e.g. $[Ti_3Ar_3Cl_6]^+X^-$, violet, paramagnetic; $[Zr_3Ar_3Cl_6]^+X^-$, brown, paramagnetic; where Ar = Me_6C_6 and $X^- = Cl^-$ or PF_6^- [92*b*]. Analogous diamagnetic trinuclear complexes of niobium and tantalum are prepared similarly, and a binuclear complex $[Nb_2Ar_2Cl_4]$ is also isolated [92*b*]. The structures 5.9*a* and 5.9*b* have been proposed for the binuclear and trinuclear complexes, respectively.



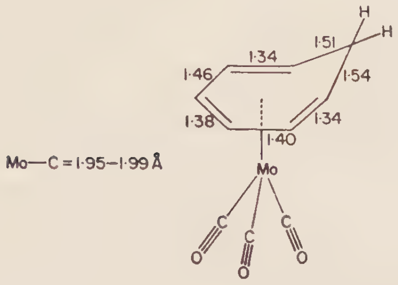
5.9*a*



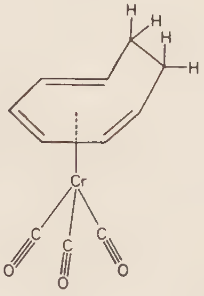
5.9*b*

B. Olefin 6-electron ligands

A number of olefins which may act as 6-electron ligands are shown in Table 17. Cycloheptatriene may act as both a 4-electron (see p. 138) and 6-electron ligand. With the Group VI metal hexacarbonyls and cycloheptatriene the complexes $C_7H_8M(CO)_3$ are formed [93*a*]. The structure of cycloheptatriene molybdenum tricarbonyl, 5.10, has been determined by X-ray analysis [93].



5.10



5.11

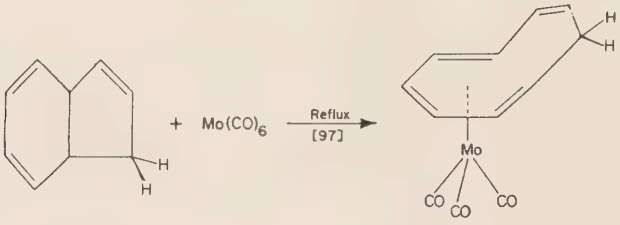
The six sp^2 carbons form a plane and the molybdenum lies below that plane almost equidistant from the six-carbons ($\sim$2·53 Å). It is interesting that the C–C distances of these carbons clearly show alternate bond lengths, as found in the free ligand. The methylene group of the C_7H_8 ligand lies above the C_6-plane which suggests some sp^3 character for the carbon atoms to which it is attached. The structure also shows that the three carbon monoxide groups are, essentially, diametrically opposed to the positions of the carbon–carbon double bonds and the metal atom has an approximately octahedral environment.

It is interesting that treatment of $Mo(CO)_6$ with 1-phenylcycloheptatriene does not give an arene complex but rather it is the C_7H_7-group which bonds to the metal [93*a*]. Therefore it seems that cycloheptatriene complexes with molybdenum more strongly than the phenyl ligand. Certainly, treatment of $C_6H_6Mo(CO)_3$ with cycloheptatriene affords smooth displacement of the benzene giving $C_7H_8Mo(CO)_3$. Other reactions of cycloheptatriene $M(CO)_3$ complexes are discussed in Chapter 6. Cycloheptatriene acts as a 6-electron ligand to iron in the complex $C_7H_8FeC_7H_{10}$ [94].

Treatment of chromium hexacarbonyl with cyclo-octa-1,3,5-triene gives the deep red complex $C_8H_{10}Cr(CO)_3$ [95]. X-Ray analysis shows the structure, 5.11 [96] in which six of the carbons are within 2·24–2·28 Å of the chromium atom and may be assumed to bond to it, the remaining two carbon atoms are further away ($\sim$3·1 Å). The bond lengths of the six-bonded carbons show distinct alternate single and double bond character.

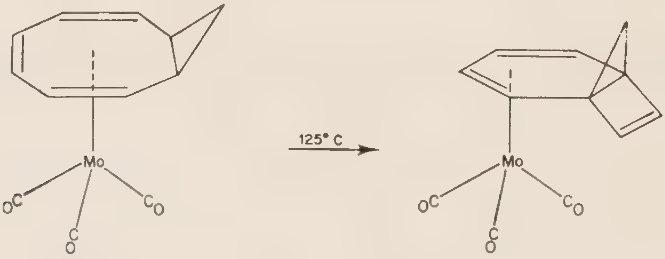
Ccylo-octatetraene forms the complex $C_8H_8Mo(CO)_3$ which has a similar structure to that of the cyclo-octa-1,3,5-triene complex, 5.13 (see p. 199).

Bicyclo-[4,3,0]-nonatriene, 5.12, forms brick-red complexes with tungsten and molybdenum, $C_9H_{10}M(CO)_3$ [97]. They undergo catalytic reduction, adsorbing one mole of hydrogen per mole of the complex. The structure, 5.13, is proposed, where the ligand is the monocyclic tetra-ene tautomer of the parent olefin.



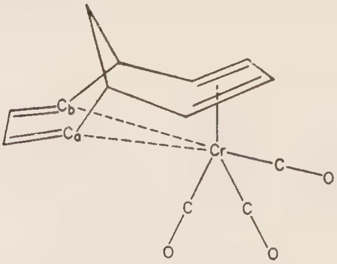
5.12 5.13

It is interesting that the complex *cis*-bicyclo-6,1,0-nona-2,4,6-triene-$Mo(CO)_3$, 5.12*a*, rearranges thermally [97*a*], viz.,



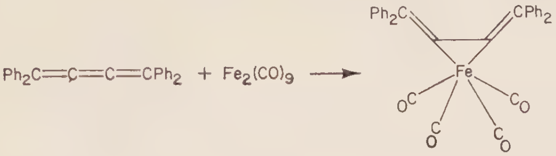
5.12*a*

Chromium hexacarbonyl reacts with 1,6-methanocyclodecapentaene forming the complex, 5.12*b* [97*b*], whose crystal structure has been determined by X-ray diffraction [97*c*]. In this molecule the chromium lies below one side of the 'clerical hat' configuration of the olefin. In order that the chromium achieves the 18-electron configuration it is necessary to postulate that it is bonded, albeit weakly to the C_a and C_b carbons.



5.12*b*

Tetraphenylbutatriene, $Ph_2C{=}C{=}C{=}CPh_2$, could conceivably act as a 6-electron ligand. In fact it is known to act as either a 2-electron ligand as in the complex 5.12*c* [97*d*], whose crystal structure has been determined [97*e*], or as a 2 × 3-electron ligand, see p. 60.



5.12*c*

C. Transition metal complexes containing π-bonded heterocyclic ligands

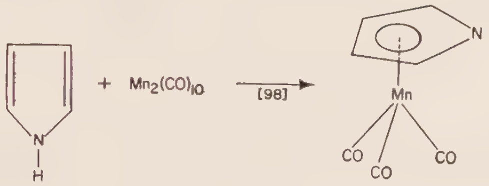
Heterocyclic compounds are known which may act as 5- or 6-electron ligands. They are discussed here because they come conveniently after 5- and 6-electron hydrocarbon ligands.

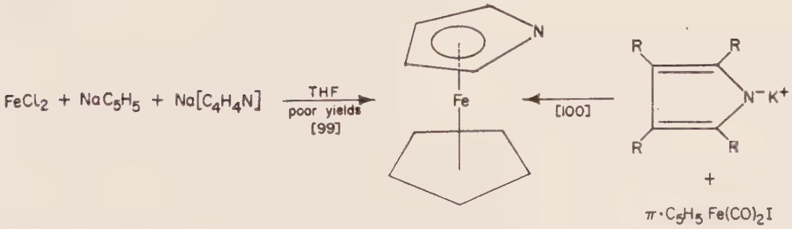
Few complexes containing π-bonded heterocyclic ligands are presently known although there seems no reason why a wide variety of unsaturated heterocyclics should not form stable, π-bonded metal complexes.

Pauson and co-workers have prepared a variety of π-pyrrole complexes which are isoelectronic with π-cyclopentadienyl analogues.

The reaction of substituted N-pyrrolide anions with π-$C_5H_5Fe(CO)_2I$ proceed by σ-pyrrolyl intermediates, such as π-$C_5H_5Fe(CO)_2$—NC_4H_3R, which may be isolated [101].

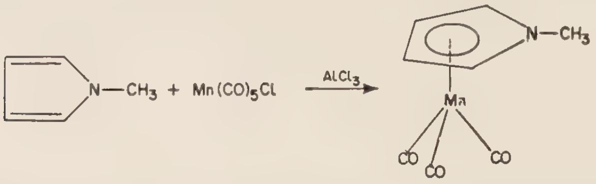
The unsaturated, unsubstituted π-pyrrole complexes are rather less stable than their π-cyclopentadienyl analogues. Azaferrocene, 5.14, is isomorphous with ferrocene [100] and is oxidized to an unstable cation in



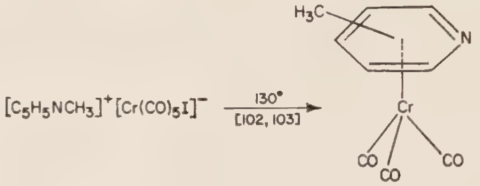


5.14

dilute nitric acid. In these complexes the π-pyrrole ring is weakly basic and the nitrogen may be protonated forming a sandwich cation such as $[\pi\text{-}C_5H_5Fe\,\pi\text{-}C_4H_4NH]^+$. N-methyl pyridyl complexes may be prepared starting from N-methyl-pyrrole, and aluminium trichloride is used as a catalyst in the reaction.

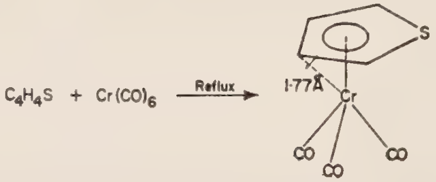


Pyrolysis of the N-methylpyridinium salt, 5.15, affords the red, diamagnetic, volatile complex π-C-methylpyridinechromium tricarbonyl, 5.16, in very low yields. The position of the methyl group is unknown.

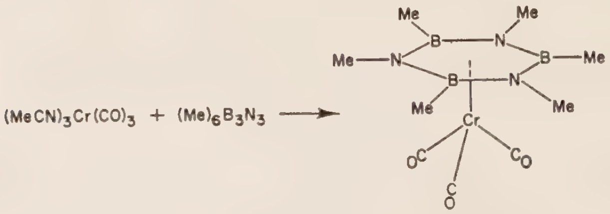


5.15 5.16

Refluxing thiophene with chromium hexacarbonyl gives the orange, diamagnetic, crystalline complex, $C_4H_4SCr(CO)_3$ [104]. The complex is essentially isomorphous with benzenechromium tricarbonyl [105].



Tetramethylthiophene reacts with $Mn(CO)_5Cl$ in the presence of aluminium trichloride giving the yellow cation $[Me_4C_4SMn(CO)_3]^+$ [106].



5.17

Finally, the hexamethylborazole complex, 5.17, has been prepared [107]. It seems reasonable that it will have an eclipsed configuration with the 'donor' nitrogen in the positions *trans* to the 'π-acid' carbonyls. The ring–chromium bonding would be expected to be more localized than in benzene$Cr(CO)_3$ but less so than in a complex $L_3Cr(CO)_3$, where L is (for example) pyridine.

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CHAPTER SIX

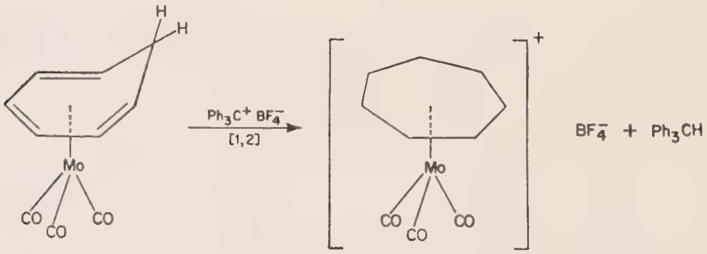
Seven-electron ligands, mixed sandwich complexes, related azulene derivatives and cyclo-octatetraene complexes

Mixed sandwich complexes are those which have two aromatic π-bonded rings containing different numbers of carbon atoms, examples being π-C_5H_5Mn-π-C_6H_6, [π-C_4R_4Co-π-C_6R_6]$^+$, and π-C_5H_5Cr-π-C_7H_7. The best known 7-electron ligand is the π-C_7H_7, cycloheptatrienyl group and the preparation and chemistry of its complexes frequently involves mixed sandwich complexes. Thus it is convenient to consider the chemistry of some mixed sandwich complexes in this section, after a discussion of 7-electron ligands.† Since complexes derived from azulene may contain 7-electron ligands and may be mixed sandwich complexes, their chemistry is also considered here. Finally, cyclo-octatetraene and its derivatives may act as ligands in so many ways that their chemistry is discussed at the end of this section, after the related chemistry of 2-, 3-, 4-, 5-, 6- and 7-electron ligands.

A. 7-Electron ligands

(*a*) *Preparation of π-cycloheptatrienyl complexes*

Cycloheptatriene metal complexes, where the cycloheptatriene is acting as a 6-electron ligand, may undergo hydride abstraction to give π-cycloheptatrienyl metal cations.



In some cases, the expulsion of a hydrogen atom may occur spontaneously,

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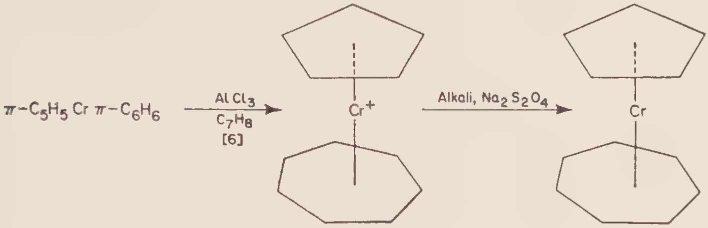
† For a review, see reference [1*a*].

as shown in the carbonyl displacement reactions,

$$\pi\text{-}C_5H_5V(CO)_4 + C_7H_8 \xrightarrow[\text{[3]}]{} \pi\text{-}C_7H_7V\pi\text{-}C_5H_5$$

$$V(CO)_6 + C_7H_8 \xrightarrow[\text{[4, 5]}]{} \pi\text{-}C_7H_7V(CO)_3 + [\pi\text{-}C_7H_7VC_7H_8]^+ + V(CO)_6^-$$

and in the displacement of benzene.



6.1

The complex 6.1, may also be prepared by the reductive olefination procedure [7, 8, 9], viz.,

$$\begin{tikzcd}
\pi\text{-}C_5H_5CrCl_2.THF + 2\,i\text{-}C_3H_7MgBr \arrow[r, "Et_2O"] & \underset{\text{(intermediate)}}{[\pi\text{-}C_5H_5Cr(i\text{-}C_3H_7)_2.Et_2O]} \arrow[d, "C_7H_8\ \text{u.v.}"] \\
\pi\text{-}C_5H_5Cr\text{-}\pi\text{-}C_7H_7 & \pi\text{-}C_5H_5CrC_7H_8 + Et_2O + C_3H_6 \arrow[l, "\text{dehydrogenation}", "\text{Pt in benzene}"']
\end{tikzcd}$$

6.2

As shown in the above reaction, a hydrogen is removed catalytically from the cycloheptatriene complex, 6.2.

The preparation of π-cycloheptatrienyl complexes by ring expansion reactions is discussed in section A (*c*), (*i*).

(*b*) *Structure*

The structures of two π-cycloheptatrienyl complexes have been determined by X-ray analysis and are given in Figure 45.

Fig. 45. The structures of π-cyclopentadienyl-π-cycloheptatrienyl vanadium [10] and π-cycloheptatrienylvanadium tricarbonyl [11]

In both the above complexes the C_7-ring is planar and the C–C distances are the same within the experimental error. In the mixed sandwich complex, the metal carbon distances are (V–C of C_7, 2·25 Å; V–C of C_5, 2·23 Å). The metal–ring plane distances differ considerably (V–C_7 plane, 1·5 Å; V–C_5 plane, 1·9 Å). It appears that the metal–carbon distances are controlling the metal–ring plane distances and for example in the cation $[\pi\text{-}C_7H_7VC_7H_8]^+$ the two rings may be rather close together ($\approx$3·0 Å).

A detailed consideration of the bonding in the π-C_7H_7M system will not be given here. Briefly, the five lowest in energy of the seven M.O.s formed by the $p\pi$-orbitals of the planar C_7H_7 group have σ, π or δ symmetry about the ring–metal axis in the π-C_7H_7M system. Thus the bonding of the π-C_7H_7M system will be similar from the symmetry aspect to that found for the π-C_5H_5—M and C_6H_6—M systems. The rotational section of Table 2 shows which metal orbitals may interact with the σ-, π- and δ-orbitals of the π-C_7H_7 ring.

(*c*) *The chemistry of π-cycloheptatrienyl complexes*

Many of the known complexes are given in Table 22. They are quite similar in their thermal and oxidative stability to arene and π-cyclopentadienyl sandwich complexes. Table 22 shows that the π-cycloheptatrienyl complexes are known mainly for those metal atoms which have few *d*-electrons. No π-cycloheptatrienyl complexes are known for the Group VIII transition metals. This observation is understandable with complexes such as π-C_6H_6Co-π-C_7H_7 or π-C_5H_5Ni-π-C_7H_7 since they would be 22-electron complexes and thus would be expected to have several electrons in anti-bonding orbitals.

It is, however, more difficult to predict whether unknown complexes such as π-C_7H_7CoCO, π-$C_7H_7CoCl_2$, π-C_7H_7NiCl, π-$C_7H_7FeCOCl$ or π-C_7H_7FeNO, all of which would be 18-electron complexes, would be stable. One might expect these hypothetical molecules to be unstable since one side of the metal atom would be well exposed, increasing the probability of attack by ligands, since conjugated ring ligands occupy from the stereochemical point of view a rather small solid angle about the metal atom compared with an electronically equivalent number of monodentate ligands.

The above argument may account in part for the formation of the known complex, 6.3, rather than the unknown π-C_7H_7CoCO. Several of the π-C_7H_7 complexes and other mixed sandwich complexes are paramagnetic (see Table 22). It is interesting to ask why it is that one frequently finds paramagnetic sandwich complexes but rarely paramagnetic carbonyl or olefin complexes. Also, why with sandwich complexes one frequently finds the metal in more than one oxidation state and thus only obeying the 18-electron rule in at the most one state, whilst with olefins and carbonyls

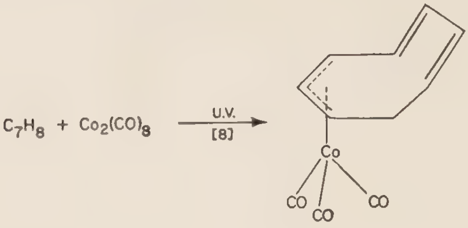
Table 22 *Some π-cycloheptatrienyl and mixed sandwich complexes*[(a)]

π-C_5H_5V-π-C_7H_7 purple, 130° d (1) [3]	π-C_5H_5Cr-π-C_6H_6 orange, 227–229° d (1) [12, 22]	π-$CH_3C_5H_4Mn$-π-C_6H_6 ruby red, 116–118° [19]	$[\pi$-C_5H_5Fe-π-$C_6H_6]^+$ yellow [18, 19]	
π-$C_7H_7V(CO)_3$ dark green, 134–7° d [4]	π-C_5H_5Cr-π-C_7H_7 dark green, 225° d [6, 7, 8]	$[\pi$-$C_7H_6CH_3Mn$-π-$C_5H_5]^+$ pink [17]	π-C_5H_5Fe-π-C_4H_4N red, 114–115° [14]	$[\pi$-C_5H_5Co-π-$C_6H_6]^{2+}$ green-yellow [20]
	$[\pi$-C_5H_5Cr-π-$C_7H_7]^+$ yellow (1) [6, 9]			$[\pi$-C_4R_4Co-π-$Mes]^{+(b)}$ yellow [15]
	$[\pi$-$C_7H_7Cr(CO)_3]^+$ orange [2, 16]			$[\pi$-C_5H_5Rh-π-$C_6H_6]^{2+}$ yellow [22]
	π-C_5H_5Mo-π-C_6H_6 red, 216–218° (1) [21]			
	$[\pi$-$C_7H_7Mo(CO)_3]^+$ orange [1]			
	$[\pi$-$C_5H_5Mo(CO)$-π-$C_6H_6]^+$ red [13]			
	$[\pi$-$C_5H_5W(CO)$-π-$C_6H_6]^+$ yellow [13]			

(*a*) The properties given are the colour of the complex, the melting or decomposition point (d) in °C and, in round brackets, the number of unpaired electrons calculated from magnetic susceptibility measurements.

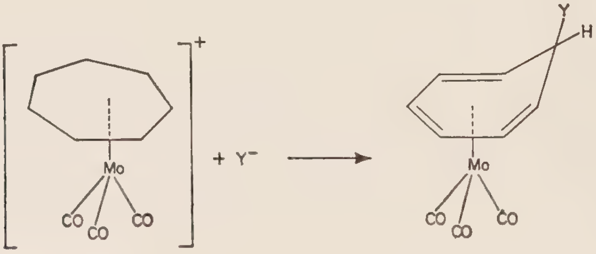
(*b*) Other mixed, cyclobutadiene complexes are shown on p. 77.

this rarely occurs, e.g. $(\pi\text{-}C_6H_6)_2Cr$ and $[\pi\text{-}C_6H_6)_2Cr]^+$ are known but not the cations derived from $Cr(CO)_6$ and $\pi\text{-}C_6H_6Cr(CO)_3$. This is a complicated question. It seems that the wider occurrence of neutral sandwich complexes and cations which are paramagnetic and which do not obey the 18-electron rule is probably due to their greater kinetic stability with respect to decomposition or dimerization as compared with olefin or carbonyl complexes. The greater kinetic stability could arise partially from the chelate effect of the polydenate conjugated rings and partially from the greater delocalization of charge over the molecule in the more conjugated systems (an analogy with the stability of conjugated organic free radicals).



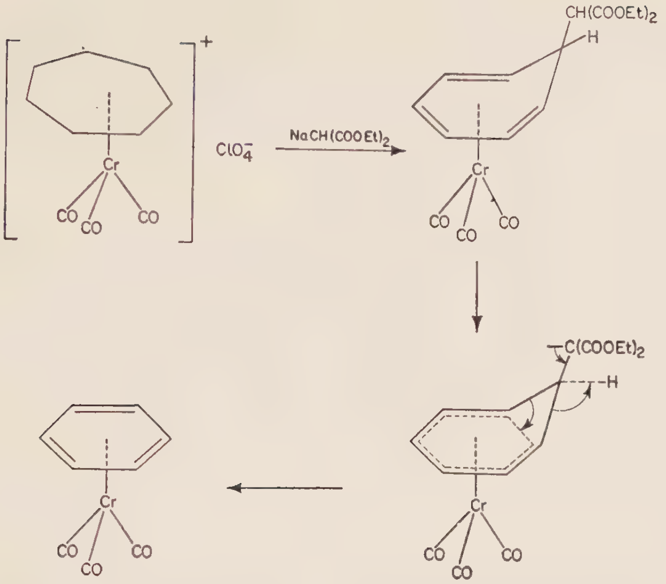
6.3

Ring contraction and expansion reactions. Treatment of the cation $[\pi\text{-}C_7H_7Mo(CO)_3]^+$ with anions such as $Y^- = CN^-$, OMe^- or $C_6H_5^-$, affords straightforward addition products [2, 16].

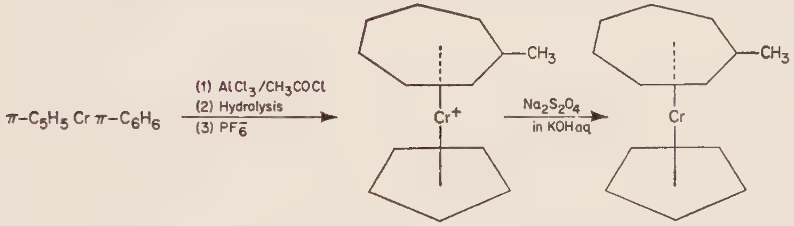


However, when Y^- = the cyclopentadienide or diethylmalonate anion a ring contraction occurs and a neutral arene complex is formed. The postulated mechanism [16] is shown at top of opposite page.

A reverse reaction, namely ring expansion of an arene ligand to a cycloheptatriene ligand, was discovered during attempts to acylate the mixed sandwich complexes $\pi\text{-}C_5H_5Cr\text{-}\pi\text{-}C_6H_6$ and $\pi\text{-}C_5H_5Mn\text{-}\pi\text{-}C_6H_6$ [17].



The reaction shown below also occurs with aromatic acyl halides, thus benzoyl chloride affords the complex π-$C_5H_5Cr(\pi$-C_7H_6-$C_6H_5)$ [17].



B. Mixed sandwich complexes

Some of the known mixed sandwich complexes are shown in Table 22. These complexes may be prepared by a variety of routes which are exemplified below.

$$(C_5H_5)_2{}^{2-}Mn^{2+} + C_6H_5MgBr \longrightarrow \pi\text{-}C_5H_5Mn\text{-}\pi\text{-}C_6H_6$$

$$\pi\text{-}C_5H_5Fe(CO)_2Cl \xrightarrow[{[18,19]}]{C_6H_6,AlCl_3} [\pi\text{-}C_5H_5Fe\text{-}\pi\text{-}C_6H_6]^+$$

$$\pi\text{-}C_5H_5CoC_6H_8 \xrightarrow[{[20]}]{2Ph_3C^+BF_4^-} [\pi\text{-}C_5H_5Co\text{-}\pi\text{-}C_6H_6]^{2+}$$

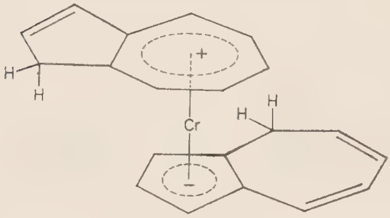
$$[\pi\text{-}C_5H_5Mo\text{-}\pi\text{-}C_6H_6CO]^+ \xrightarrow[{[21]}]{LiAlH_4} \pi\text{-}C_5H_5Mo\text{-}\pi\text{-}C_6H_6$$

$$(\pi\text{-}C_5H_5)_2Fe + C_6H_5X \xrightarrow[\substack{X = Me, NH_2, Cl, Br, H, etc. \\ [21a]}]{AlCl_3} [\pi\text{-}C_5H_5Fe\text{-}\pi\text{-}C_6H_5X]^+$$

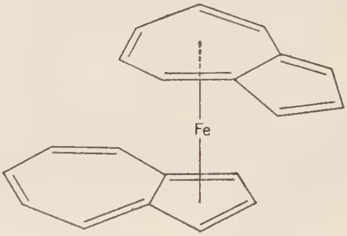
Generally they are similar in appearance, solubility and thermal and oxidative stability to arene or π-cyclopentadienyl sandwich complexes. Few detailed studies have been made on these complexes, but the infrared spectrum of π-C_5H_5Cr-π-C_6H_6 and its perdeutero benzene analogue are consistent with six-fold symmetry of the π-C_6-ring [22].

C. Metal complexes formed from azulenes

Treatment of chromium trichloride with ethereal iso-propyl magnesium bromide and azulene followed by methanolysis gives dark green crystals of the formula $C_{20}H_{18}Cr$ [23]. Under similar conditions, ferric chloride gives an orange-brown complex, $C_{20}H_{16}Fe$. The chromium complex is polar (1·18 ± 0·1 D) and undergoes catalytic hydrogenation with reduction of the unbonded rings. On this evidence and spectroscopic studies the structure 6.4, is proposed where the complex is π-azulenium azuleniate chromium, a derivative of π-C_7H_7Cr-π-C_5H_5. The iron complex does not oxidize readily and is not polar, but it also undergoes reduction of its non-bonded rings and is formulated as a bis-azulene iron complex, 6.5.

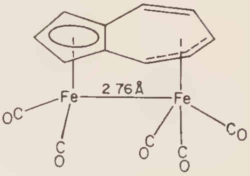


6.4



6.5

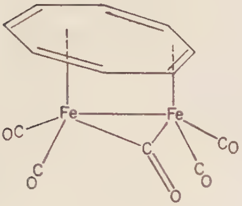
Treatment of the carbonyls of iron, molybdenum and manganese with azulene affords complexes which, since they give azulene on thermal decomposition, may be supposed to have essentially unchanged azulene as a ligand [24, 25]. This is confirmed in one case by the determination of the crystal structure of $C_{10}H_8Fe_2(CO)_5$, 6.6 [25*a*]. The structure shows that the C_5-ring bonds to an iron as a π-cyclopentadienyl system whilst the C_7-ring bonds as a π-enyl ligand. The rather long Fe–Fe distance suggests that the molecule may be strained.



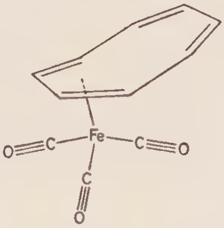
6.6

D. Cyclo-octatetraene complexes

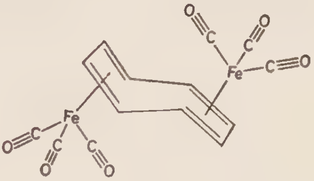
Treatment of iron carbonyls with cyclo-octatetraene forms complexes such as $C_8H_8Fe(CO)_3$, $C_8H_8Fe_2(CO)_7$ and $C_8H_8(Fe(CO)_3)_2$ [26, 27, 28, 28*a*, 29]. The structures of these complexes have been determined by X-ray studies and are 6.7, 6.8 and 6.9 respectively. In the complexes 6.8 and 6.9 the cyclo-octatetraene has the chair configuration and the olefin is acting as either a 4-electron ligand or as a twice × 4-electron ligand.



6.7



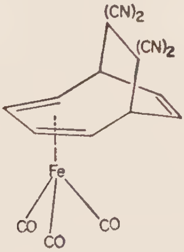
6.8



6.9

It is interesting that the room temperature proton magnetic resonance spectrum of the complex $C_8H_8Fe(CO)_3$ shows only one sharp line. It was on this basis that a planar delocalized C_8 ring structure was first, but incorrectly, proposed for this molecule [26, 29]. The temperature dependence of the proton magnetic resonance spectra of cyclo-octatetraene iron tricarbonyl [29*a*] 29*b*, 29*c*], and the methyl-substituted analogues $MeC_8H_7Fe(CO)_3$ [29*d*] has been studied. The spectra suggest that in solution the cyclo-octatetraene rings are bonded to the metal by 1,3-diene systems as found in the crystal structure [29*d*]. The mode of equalization of the hydrogens of the C_8H_8 ring is thought to be by a circular, essentially 'in plane' movement of the ring about the iron–ring axis, rather than by a trans-annular shift. Further evidence supporting the 1,3-diene structure for $C_8H_8Fe(CO)_3$ in solution arises from the infrared and Raman spectra of the compound in the solid state and in solutions, which are found to be very similar [29*e*].

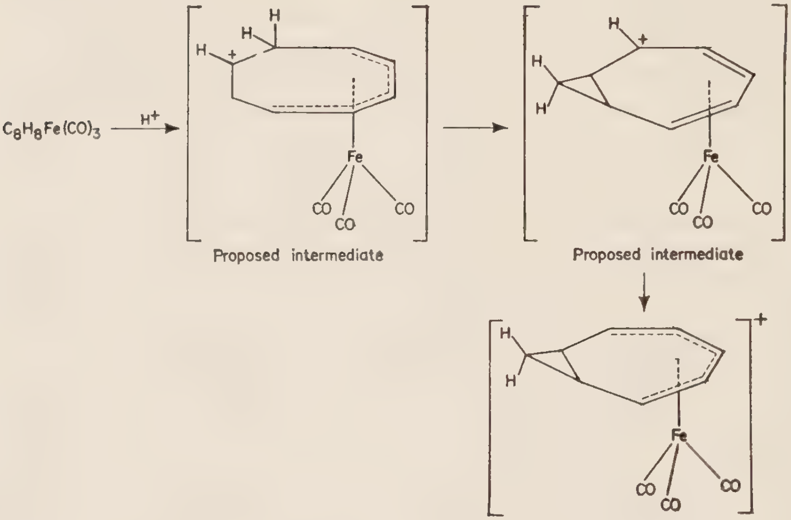
The chemical properties of the complex $C_8H_8Fe(CO)_3$ are to some extent anomalous in that it does not undergo normal catalytic hydrogenation



6.10

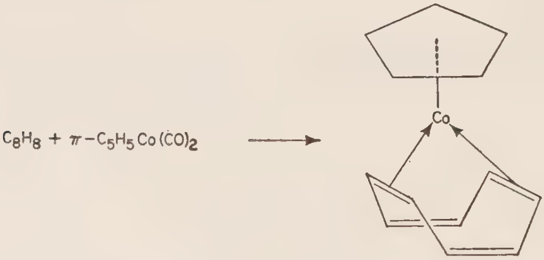
nor will it decolorize bromine. The unconjugated diene portion of the C_8 ring is likewise reluctant to undergo normal Diels–Alder reactions although with tetracyanoethylene the addition product, 6.10, is readily formed.

On protonation, the complex $C_8H_8Fe(CO)_3$ undergoes rearrangement to the bicyclo-[5,1,0]-octadienyl iron tricarbonyl cation, 6.11, in which the hydrocarbon is acting as a 5-electron ligand [30, 31, 32]. The postulated mechanism for the reaction is:



6.11

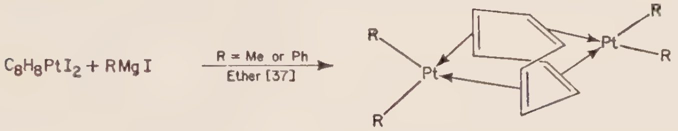
Treatment of π-$C_5H_5Co(CO)_2$ with cyclo-octatetraene gives the complexes π-$C_5H_5CoC_8H_8$ and $(\pi$-$C_5H_5Co)_2C_8H_8$ [33, 34, 35]. In the first complex, the C_8 ring acts as a chelate diene analogous to cyclo-octa-1,5-diene (see 6.12).



6.12

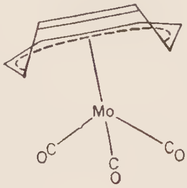
Chemical evidence for the structure of the complex 6.12, comes from the observation that the C_8H_8 ring is readily reduced by hydrogen giving the cyclo-octa-1,5-diene analogue of the complex. Both the complex, 6.12, and the rhodium analogue protonate in strong acids affording the *unstable* cations $[\pi\text{-}C_5H_5MC_8H_9]^+$, there being no rearrangement similar to that found in the protonation of the $C_8H_8Fe(CO)_3$, presumably due to the different mode of bonding of the C_8H_8 ligands to the cobalt [31, 32]. Cyclo-octatetraene forms stable, olefin complexes with rhodium, platinum and palladium, e.g. $[C_8H_8RhCl]_2$ and $C_8H_8PtX_2$ where X = Cl or I [35, 36]. The structures are unknown but by analogy with other olefin complexes of these metals a chelate boat conformation of the C_8H_8 ring similar to cyclo-octa-1,5-diene seems most probable.

In the binuclear complexes 6.13 cyclo-octatetraene appears to act as a bridging ligand. The detailed structures of these complexes are unknown but preliminary X-ray studies suggest that the C_8H_8 ring adopts the bridging chelate conformation shown in the above equation, unlike the complex $C_8H_8[Fe(CO)_3]_2$. A similar bridge conformation of the C_8H_8 ring is suggested for the polymeric black $(C_8H_8Ni)_n$ [34*a*], and for the cobalt complex $\pi\text{-}C_5H_5CoC_8H_8Co\ \pi\text{-}C_5H_5$ [34*b*]; again, the proton magnetic resonance spectrum shows only one resonance for the C_8H_8 protons [35].



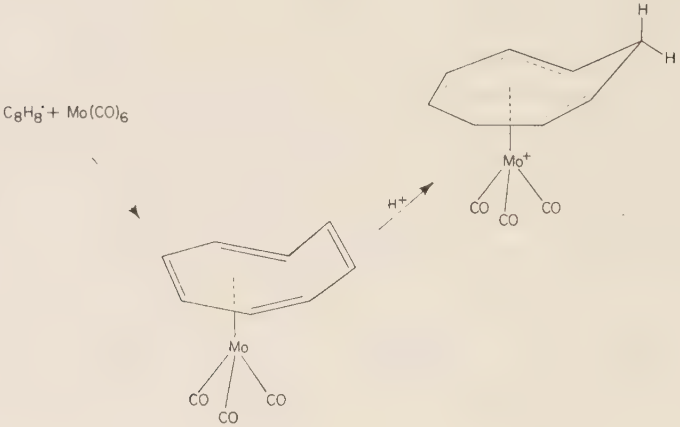
6.13

Cyclo-octatetraene acts as a 6-electron ligand to the Group VI metal tricarbonyl radicals. The crystal structure of $C_8H_8Mo(CO)_3$, 6.14, shows there is one non-bonding $C{=}C$ system [38], a more formal representation of the compound is given in 6.14*a*.



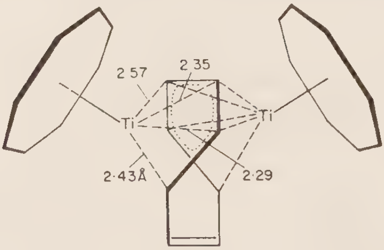
6.14

The molybdenum compound readily adds carbon monoxide at room temperature and atmospheric pressure forming the tetracarbonyl $C_8H_8Mo(CO)_4$ in which the C_8H_8 ring is thought to have the boat form [39]. Treatment of $C_8H_8Mo(CO)_3$ or $C_8H_8Mo(CO)_4$ with acids causes protonation and the homotropylium molybdenum tricarbonyl cation, 6.15, is formed [40]. In this complex the hydrocarbon is a 7-electron cyclo-octatrienyl ligand. The complex $C_8H_8Mo(CO)_3$ also undergoes the metal-ring shift process in solution [41].



6.14*a* 6.15

It has been seen above that cyclo-octatetraene may act as a 4-, a 2×4-, a 2×2-, a 4×2- and a 6-electron ligand. It can, however, also act formally as an 8-electron ligand since X-ray diffraction has shown that the complex $(C_8H_8)_3Ti_2$ has the structure 6.13*a* [42]. This compound and $Ti(C_8H_8)_2$ are prepared by treatment of the alkoxide $Ti(OC_4H_9)_4$ with cyclo-octatetraenene and $AlEt_3$ [43]. The binuclear complex, 6.16, is readily hydrolysed which suggests a degree of ionic character for the metal–ring bond. The structure shows that the outside C_8 rings are planar and their carbons are equidistant from the titanium (2·35 Å). The simplest view of the bonding between the titanium and the planar rings is that it is largely ionic. In this context it should be noted that the di-anion $C_8H_8^{2-}$ is known and is expected to be planar, since it has (2n + 4) π-electrons.



6.16

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CHAPTER SEVEN

One-electron ligands

These are considered after π-bonding ligands for several reasons. They are frequently found in complexes which contain other organic ligands, such as the π-C_5H_5 group. There is sometimes uncertainty whether a group should be regarded as π-ethylenic in character or bound by σ-bonds. Since the bonding of π-ligands is less conventional than that of the σ-bonded 1-electron ligands, it is desirable to be familiar with the former before considering their role in complexes containing the latter. Further, a 1-electron ligand occupies essentially only one co-ordination position on the metal and therefore has less influence on the chemistry of complexes containing it than those organic ligands which occupy several co-ordination positions and whose bonding involves a larger proportion of the metal electrons. For these reasons the classification of complexes with 1-electron ligands, as given below, is diverse.

The following main classes of 1-electron organic ligands may be recognized and they are considered separately in the text.

I. (1) Hydrocarbon alkyl and aryl complexes, $M—R_h$.
   (2) Hydrocarbon acyl complexes, $M—COR_h$.
   (3) σ-Alkenyl complexes (see pp. 235 and 270).
   (4) σ-Cyclopentadienyl complexes.
II. Fluorocarbon alkyl and aryl complexes, $M—R_f$, and the acyl complexes, $M—COR_f$.
III. Acetylide or alkynyl complexes, $M—C\equiv CR$.

Further subdivision of the complexes is given in the relevant sections.

I.1. HYDROCARBON ALKYL AND ARYL COMPLEXES

Examples are given in Table 23. It is convenient, and to some extent has chemical significance, to classify these complexes according to the other ligands attached to the metal.

However, only those $M—R_h$ complexes in which all or most of the other ligands are the same sort and which occur in substantial numbers are classified by that ligand, viz.

(*a*) $M—R_h$ complexes with tertiary phosphines and related ligands.
(*b*) π-Cyclopentadienyl carbonyl complexes.

Table 23 *Some examples of transition meta*

Me_4Ti(*a*) Diamine TiMe_4(*a*) MeTiCl_3(*a*) $\text{PhTi(OPr}^i)_3$(*a*) $(\pi\text{-C}_5\text{H}_5)_2\text{TiPh}_2$(*a, b*) $(\pi\text{-C}_5\text{H}_5)_2\text{TiMe}_2$(*b*) $\pi\text{-C}_5\text{H}_5\text{TiMe}_3$ [71]	$(\pi\text{-C}_5\text{H}_5)_2\text{VMe}$ [2] $(\pi\text{-C}_5\text{H}_5)_2\text{VPh}$ [2] $\text{Li}_4[\text{VPh}_6]$	$\pi\text{-C}_5\text{H}_5\text{Cr(CO)}_3\text{R}$(*e*) $\text{Li}_3[\text{CrR}_6]$(*f*) $(\text{Ligand})_3\text{CrR}_3$(*f*) $[\text{RCr(H}_2\text{O)}_5]^{2+}$(*f*)	RMn(CO)_5(*h*) $(\text{R}_2\text{Mn})_x$
$(\pi\text{-C}_5\text{H}_5)_2\text{ZrClMe}$(*b*) $\left((\pi\text{-C}_5\text{H}_5)_2\text{Zr}\langle^{\text{Ph}}\right)_2\text{O}$(*b*) $(\pi\text{-C}_5\text{H}_5)_2\text{ZrEtCl}$ [1]	$(\pi\text{-C}_5\text{H}_5)_2\text{Nb}(\sigma\text{-C}_5\text{H}_5)_2$(*d*) Me_3NbCl_2(*c*)	$\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{R}$(*e*) $(\pi\text{-C}_5\text{H}_5)_2\text{MoMe}_2$	
$(\pi\text{-C}_5\text{H}_5)_2\text{HfMe}_2$	$(\pi\text{-C}_5\text{H}_5)_2\text{Ta}(\sigma\text{-C}_5\text{H}_5)_2$(*d*) Me_3TaCl_2(*c*)	$\pi\text{-C}_5\text{H}_5\text{W(CO)}_3\text{R}$(*e*) $(\pi\text{-C}_5\text{H}_5)_2\text{WMe}_2$	RRe(CO)_5(*h*) $\pi\text{-C}_5\text{H}_5\text{ReMe}_2(\text{C}_5\text{H}_5\text{Me})$

(*a*) See p. 238; (*b*) see p. 206; (*c*) see p. 240; (*d*) see p. 91; (*e*) see p. 235; (*f*) see section J (*b*); (*g*) see section F(*b*
(*h*) see section H(*i*); (*i*) see section J(*c*); (*j*) see section J(*d*); (*k*) see section J(*e*). (*l*) see section G(*c*)

† For a review, see reference [1*a*].

(*c*) Bis-π-cyclopentadienyl complexes.
(*d*) Carbonyl complexes.

Other complexes are more conveniently classified by the metal, viz.

(*e*) Pure alkyl and aryl complexes and alkylhalide complexes of Ti, V, Nb, Ta and Mn.
(*f*) Alkyl and aryl complexes of chromium.
(*g*) Alkyl and aryl complexes of cobalt(III).
(*h*) Alkyl complexes of platinum(IV).
(*i*) Alkyls and aryls of Cu, Ag and Au.

A general account of the preparation and properties of complexes containing 1-electron organic ligands, and a detailed discussion of the nature of their metal–carbon bonding, precede the consideration of the specific chemistry of M—R_h complexes.

A. General preparative methods

The successful preparation of metal–R_h complexes usually requires considerable attention to experimental detail; in particular, the exclusion of oxygen is usually essential. Only the most commonly used routes are discussed here and examples are chosen from a wide range of complexes in order to illustrate their common chemistry.

drocarbon aryl and alkyl complexes, M–R_h†

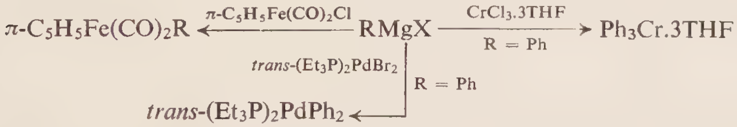
$C_5H_5Fe(CO)_2R^{(e)}$ *ins*-$(PEt_2Ph)_2Fe(C_6Cl_5)_2^{(g)}$	$RCo(CO)_4^{(h)}$ $(PPhEt_2)_2Co(Mes)_2^{(g)}$ $[RCo(CN)_5]^{3-(i)}$ $(DMG)_2CoLR^{(i)}$ $Co_3(CO)_9R^{(h)}$ Vitamin B_{12} alkyls $^{(i)}$ π-$C_5H_5CoMe_2(PPh_3)$ $^{(l)}$	*trans*-$(PR'_3)_2NiR_2^{(g)}$ *trans*-$(PR'_3)_2NiRX^{(g)}$	$(RCu)_x^{(k)}$ Et_3PCu-σ-$C_5H_5^{(k)}$
$C_5H_5Ru(CO)_2R^{(e)}$ $e_2PCH_2CH_2PMe_2RuRH^{(g)}$ $le_2PCH_2CH_2PMe_2)_2RuAr^{(g)}$	$(1\text{-naphthyl})_2RhL_2Br^{(g)}$ $Ph_3AsMeRhCl_2CHMeCN^{(g)}$ $Rh_2I_2Me_4(SMe_2)_3^{(g)}$ $C_5H_4{=}CPh_2Rh(CO)_2ClIMe$ [5] π-$C_5H_5RhMe_2(SMe_2)^{(l)}$ $RRhClI(CO)(PPh_3)_2$ $^{(g)}$	*trans*-$(PR'_3)_2PdR_2^{(g)}$ *trans*-$(PR'_3)_2PdRX^{(g)}$ Diene $PdR_2^{(g)}$ α,α'-dipy $PdMe_2$ $^{(g)}$	$(MeAg)_2AgNO_3^{(k)}$ $(RAg)_x^{(k)}$
	$RIrClICO(PPh_3)_2$ $^{(g)}$	*cis*- and *trans*-$(PR'_3)_2PtR_2^{(g)}$ *cis*- and *trans*-$(PR'_3)_2PtRCl^{(g)}$ $[Me_3PtX]_4^{(j)}$ $MePtI_3^{(j)}$ $MePtI_2^{(j)}$ π-$C_5H_5PtMe_3$ Diene $PtR_2^{(j)}$ $L_2PtR_2I_2^{(j)}$	$PR_3AuR^{(k)}$ $Et_3PAuR_3^{(k)}$ $Et_2OAuMe_3^{(k)}$ $Me_2AuI^{(k)}$

(*a*) *From Grignard reagents and organoalkali metal derivatives*

The normal procedure is to treat a metal halide complex with excess Grignard reagent or organoalkali metal derivative, in ether solutions. Typical reactions using organolithium compounds are shown in Figure 46.

Grignard reagents are not always alternatives to the alkali metal derivatives; organolithium reagents are frequently the more reactive and more readily give fully alkylated or arylated products.

Some examples of the use of Grignard reagents are:



Other related alkylating reagents which have been used are dimethylzinc, tetraethyl-lead, trimethylaluminium and dialkylcadmium compounds (see pp. 238–239, 254–255).

(*b*) *From complex metal anions and organic halides*

Transition metal carbonyls and π-cyclopentadienyl metal carbonyls form stable anions which are conveniently prepared by treatment of the neutral

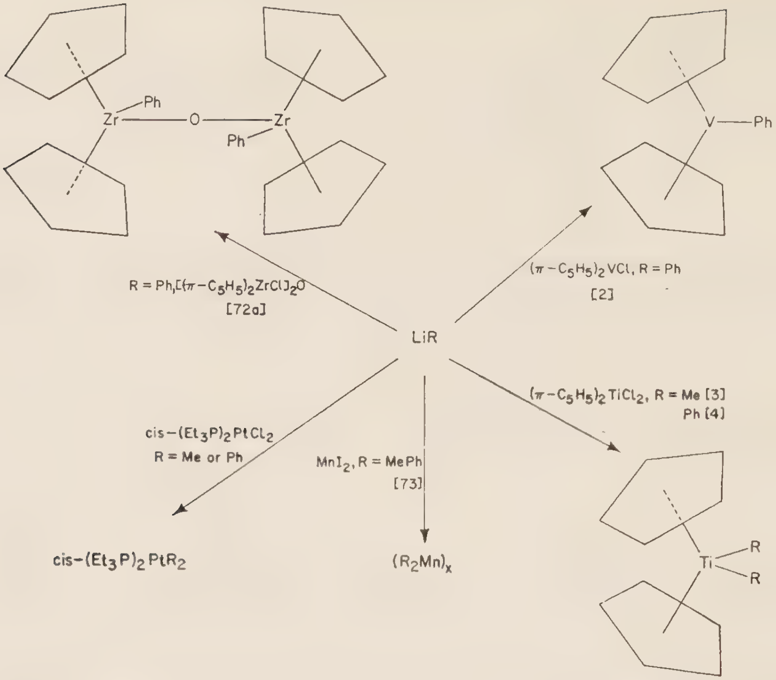


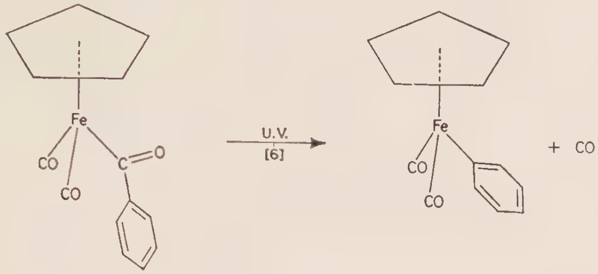
Fig. 46. The preparation of transition metal–alkyl and –aryl complexes using organolithium reagents

complexes with sodium amalgam (2%) in tetrahydrofuran. The addition of alkyl or aryl halides to the metal anions *in situ*, usually at low temperatures (acetone/dry ice bath), gives the neutral metal–σ-organo complex. Examples are:

$$Mn_2(CO)_{10} \xrightarrow[THF]{Na/Hg} Na^+[Mn(CO)_5]^- \xrightarrow{MeI} MeMn(CO)_5 + NaI$$

$$[\pi\text{-}C_5H_5W(CO)_3]_2 \xrightarrow{Na/Hg} Na^+[\pi\text{-}C_5H_5W(CO)_3]^- \xrightarrow{EtI} \pi\text{-}C_5H_5W(CO)_3Et + NaI$$

In both this and the previous method of preparation, low yields are often found, due to competitive coupling reactions or to further reactions such as the decomposition of the $M—R_h$ products. Also the metal anions are strong nucleophiles and they may cause the organic halides to undergo elimination reactions. Metal-acyl complexes are often by-products of the reaction of organic halides with the metal carbonyl anions; they are formed by insertion reactions (see p. 258). Indeed, acyl halides may be used to give metal–acyl complexes which are then decarbonylated either thermally or by photochemical techniques [6]. Some metal–aryl complexes which are only formed in small yields from the aryl halide may be conveniently prepared in this manner, e.g.



Aryl diazonium salts may give aryl derivatives, though complexes containing the M—N_2Ar system may also be formed [7, 8]. Triethyloxonium tetrafluoroborate has been successfully employed in the preparation of the thermally very unstable ethyl cobalt tetracarbonyl. Also, in some cases, phenyl complexes are more readily prepared using the salts $[Ph_2I]^+[BF_4]^-$ and $[Ph_2S]^+[BF_4]^-$ instead of a halobenzene [6*a*].

The pentacyanocobalt(II) anion and related anions react in a similar manner to carbonyl anions (see p. 247).

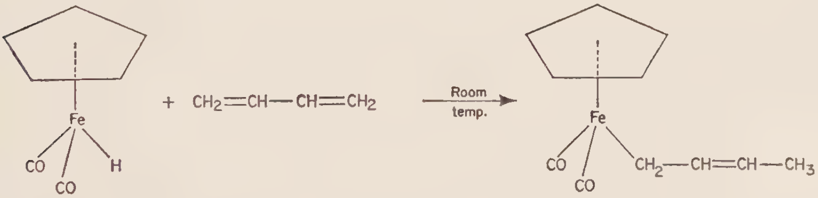
(*c*) *From metal hydrides*

Transition metal–hydrogen systems will often add across olefins forming M—R_h complexes. The reaction is reversible (see p. 211), e.g.,

$$trans\text{-}(Et_3P)_2PtClH + C_2H_4 \xrightleftharpoons[180°\ [9]]{\text{cyclohexane, 95°, 40 atm.}} trans\text{-}(Et_3P)_2PtClEt$$

$$\pi\text{-}C_5H_5Fe(CO)_2H + CH_2{=}CHCN \xrightarrow[[10]]{\text{r.t.}} \pi\text{-}C_5H_5Fe(CO)_2CH(Me)CN$$

Conjugated olefins apparently add to M—H complexes with greater ease than do ethylene or alkyl substituted ethylenes. Thus butadiene gives but-2-enyl complexes.



In this reaction, mainly the 1,4-addition product is obtained, as a mixture of *cis*- and *trans*-isomers [11].

Studies with $Co(CO)_4H$ show that the course of addition of Co—H to olefins depends on the olefin used. With 1- or 2-pentene the products suggest the hydrogen in $Co(CO)_4H$ behaves as a protonic hydrogen. In contrast, addition to $CH_2{=}CHCOOMe$, followed by CO insertion, gives as the major product $MeCOOCHMeCOCo(CO)_4$ [12, 13]. In this case the Co—hydrogen has added to the most electropositive carbon of the olefin, which suggests a hydridic Co—H hydrogen.

Treatment of many metal hydrides with diazomethane affords methyl derivatives [14], e.g.

$$\pi\text{-}C_5H_5Mo(CO)_3H + CH_2N_2 \xrightarrow[\text{ether [3]}]{\text{r.t.}} \pi\text{-}C_5H_5Mo(CO)_3CH_3 + N_2$$

Diazoacetic ester may likewise form $M{-}CH_2COOEt$ derivatives [7].

(*d*) *Miscellaneous*

Metal–σ-organo complexes may be prepared by a number of other methods of which there are only single or very few examples. These are discussed incidentally in the text.

B. General chemical properties

(*a*) *Stability*

The thermal and oxidative stability of transition metal–alkyl and –aryl complexes varies widely and depends largely on the other ligands attached to the metal. Metal-σ-organo complexes usually are only thermally stable when the organic ligand is non-labile, and usually the other ligands attached to the metal are also non-labile. Non-labile complexes are commonly found with those metals which may be regarded as having the spherical environments, such as found in d^0, d^3, d^6 (low spin) electron configurations and with 18- (and 16-) electron groups. An important role of π-bonding ligands is that they stabilize the low oxidation states of transition metals and thus allow them to attain the 18-electron environment. A detailed consideration of the factors which may affect the stability of metal–σ-organo complexes is given in section E.

(*b*) *Cleavage reactions of the metal–carbon bond*

The metal–carbon bond is frequently cleaved by halogens or the hydrogen halides. In both cases the metal halides are formed, e.g.

$$cis\text{-}(Et_3P)_2PtBr_2 \xleftarrow{Br_2} cis\text{-}(Et_3P)_2PtMe_2 \xrightarrow{HCl} cis\text{-}(Et_3P)_2PtMeCl$$

$$Et_2AuBr \xrightarrow[CCl_4]{Br_2} EtAuBr_2$$

In a few cases, alkyl halides cause cleavage

$$cis\text{-}(Et_3P)_2Pt(CH_2Ph)_2 + 2PhCH_2I \xrightarrow[\text{[15]}]{} trans\text{-}(Et_3P)_2PtI_2$$

It follows that where organohalides are used in the preparation of organometal complexes, an excess may cause low yields. There are a few examples where alkyl halides add to transition metal complexes (see pp. 251, 264).

(*c*) *Insertion reactions*

There are many reactions of transition metal–alkyl or –aryl complexes which may be represented thus:

$$\mathrm{M{—}R_h + X \longrightarrow M{—}X{—}R_h}$$

where X = CO (p. 258), SO_2 (p. 260), or olefins such as C_2F_4 (p. 266) and butadiene. The reaction with olefins may be compared to the olefin addition reactions of some metal hydrides.

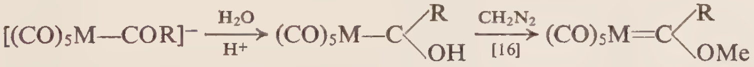
C. The nature of interactions between transition metals and σ-bonded organic substituents

The concept of functional groups is a powerful method of classification in chemistry and is particularly useful in organic chemistry. In this context it is interesting to examine the 'group properties' of complexed transition metals. Obviously the effect of a transition metal on the chemistry of an organic system to which it is attached will depend to some extent on the nature of the other ligands attached to the metal and on the metal itself. None the less it appears that there are some common group properties found for a variety of metals which are complexed by many different ligands.

(*a*) *Transition metal–α-interactions*†

In addition to the σ-bond which must be present there is evidence that some substantial π-bonding may occur in the metal–aryl, –acyl and –alkynyl bonds (see p. 273). There is considerable evidence that transition metals may form double bonds with $=CR_2$ (carbene) systems.

Metal–carbene complexes. Treatment of the carbonyls $M(CO)_6$, where M = Cr, Mo or W, with methyl lithium or phenyl lithium gives the anions $[M(CO)_5{—}COR]^-$ where R = Me or Ph. Aqueous acid solutions of these anions react with diazomethane affording 'carbene' complexes, e.g.



$$[(CO)_5M{—}COR]^- \xrightarrow[H^+]{H_2O} (CO)_5M{—}C\begin{smallmatrix}\diagup R\\ \diagdown OH\end{smallmatrix} \xrightarrow[[16]]{CH_2N_2} (CO)_5M{=}C\begin{smallmatrix}\diagup R\\ \diagdown OMe\end{smallmatrix}$$

The structure of the complex $(CO)_5WCPhOMe$ has been determined by X-ray diffraction [17] and is discussed in detail on p. 219.

The protonation of some acyl complexes forming cation systems, e.g., $Fe^+{—}CMeOH$, which may be essentially analogous to the $(CO)_5WCPhOMe$

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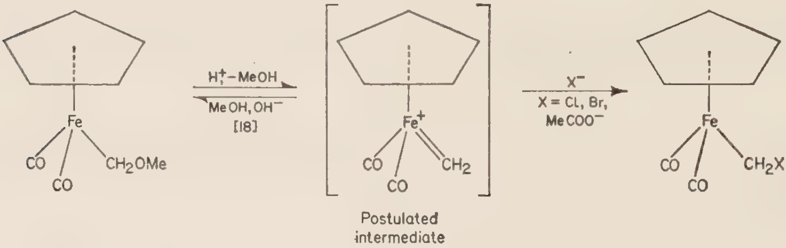
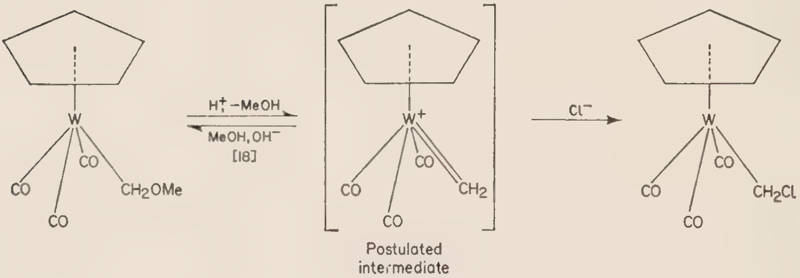
† Positions in organic substituents on metals are labelled thus, $M{—}\underset{\alpha}{C}{—}\underset{\beta}{C}{—}\underset{\gamma}{C}$.

complexes, has been described on p. 261. Further evidence for the formation of metal–carbene complexes is provided by the chemistry of the ether complexes $\mathrm{M{-}CH_2{-}O{-}Me}$, 7.1, 7.2. They are readily cleaved by acids forming substituted methyl derivatives, viz.



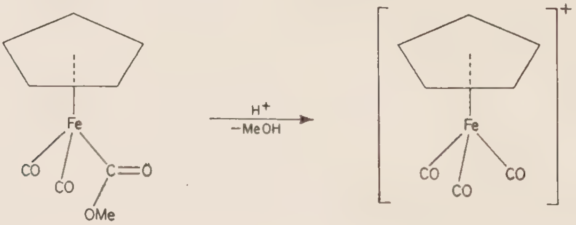
7.1



7.2

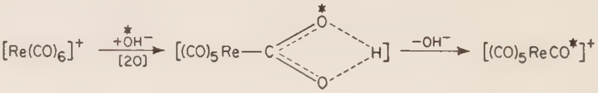
These ether cleavage reactions proceed very readily which suggests that short-lived, intermediate $\mathrm{M{=}CH_2^+}$ species may be involved, as shown above.

A related cleavage reaction of the complex 7.3, has been shown [19], e.g.



7.3

In this context, it is interesting to note that the cation $[\mathrm{Re(CO)_6}]^+$ readily exchanges its oxygens in aqueous solution. The postulated mechanism may be written as,



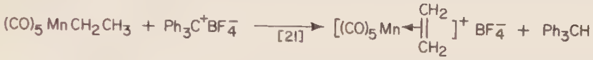
$$[\mathrm{Re(CO)_6}]^+ \xrightarrow[\text{[20]}]{+\overset{*}{\mathrm{O}}\mathrm{H}^-} [\mathrm{(CO)_5Re{-}C}\overset{\overset{*}{\mathrm{O}}}{\underset{\mathrm{O}}{\diamond}}\mathrm{H}] \xrightarrow{-\mathrm{OH}^-} [\mathrm{(CO)_5ReC\overset{*}{O}}]^+$$

which may be compared to the attack of R^- on $W(CO)_6$, as described above.

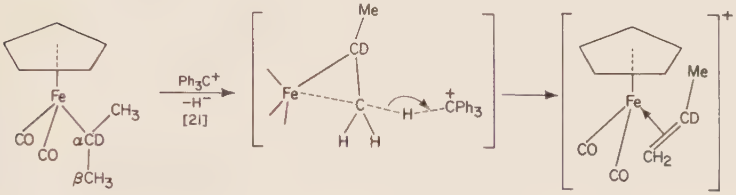
The above chemistry suggests that a 'group property' of transition metals is the ability to form metal–carbon double bonds and stabilize adjacent sp^2 hybridized carbon ligands.

(*b*) *Transition metal–β-interactions*

A number of transition metal–alkyl complexes, where the alkyl group may be ethyl, n-propyl or iso-propyl, react with the triphenylmethyl cation forming ethylenic cations, e.g.



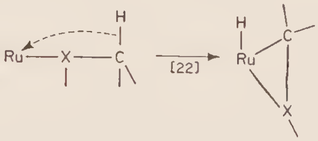
$$(CO)_5MnCH_2CH_3 + Ph_3C^+BF_4^- \xrightarrow{[21]} \left[(CO)_5Mn \leftarrow \overset{CH_2}{\underset{CH_2}{\|}}\right]^+ BF_4^- + Ph_3CH$$



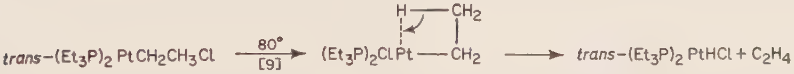
7.5 7.4

The formation of the 2-deuteropropene cation, 7.4, from the 2-iso-propyl complex, 7.5, as shown above, confirms that the hydride is abstracted from a β-carbon.

Reactions which appear to be closely related are the reversible exchange of hydrogen in some ruthenium–aryls and in some ruthenium–alkyl phosphine complexes (see p. 232). They may be represented as follows:



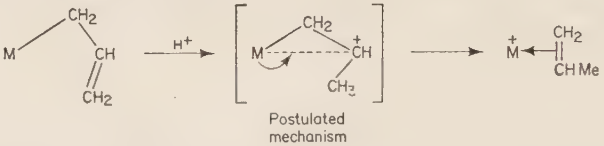
Similarly, the thermal decomposition of the ethyl complex *trans*-$(Et_3P)_2PtCH_2CH_3Cl$ to the hydride *trans*-$(Et_3P)_2PtHCl$ and ethylene may proceed via the internal abstraction of a hydrogen from the β-carbon, viz.



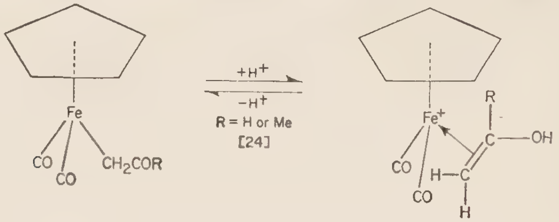
$$trans\text{-}(Et_3P)_2PtCH_2CH_3Cl \xrightarrow[{[9]}]{80^\circ} (Et_3P)_2ClPt\overset{H\text{---}CH_2}{\text{---}CH_2} \longrightarrow trans\text{-}(Et_3P)_2PtHCl + C_2H_4$$

During the course of all these reactions it seems reasonable that there is some interaction between the metal and the β-substituents.

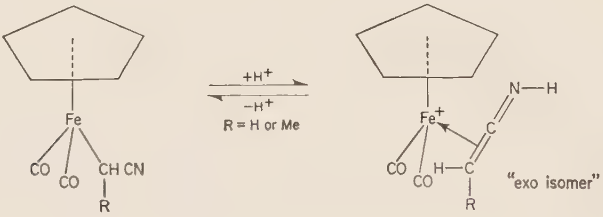
A variety of metal–σ-organo complexes in which the organic ligand has an unsaturated β-carbon show anomalous protonation reactions. For example, metal–σ-allyl complexes, M—CH$_2$—CH=CH$_2$, where M = Mn(CO)$_5$ [21], π-C$_5$H$_5$Fe(CO)$_2$ [11], π-C$_5$H$_5$W(CO)$_3$ [22*a*] or π-C$_5$H$_5$Mo(CO)$_3$ [23], readily protonate forming π-propene cations, e.g.



Some oxoalkyl complexes protonate reversibly in an analogous manner,



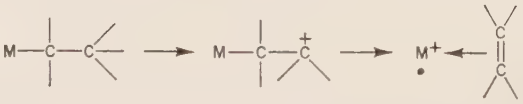
Similarly, the cyanoalkyl complexes, 7.6, on treatment with acids, form cations for which π-keteneimine structures are proposed [10].



7.6

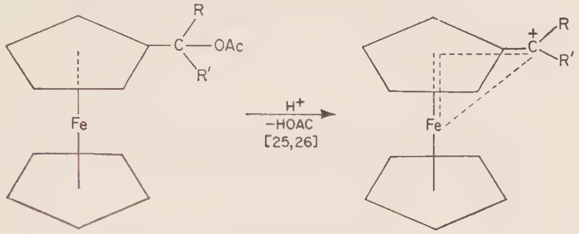
These cations are best isolated as the salts of large anions, such as BF$_4^-$, PF$_6^-$, SbCl$_6^-$ or PtCl$_6^{2-}$.

It may be envisaged that both the hydride abstraction and the protonation reactions shown above proceed via the formation of a β-carbonium ion intermediate which is 'stabilized' by formation of an ethylene–metal bond and partial oxidation of the metal, e.g.

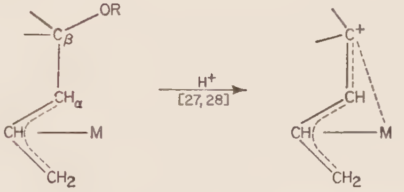


It appears that the stabilization of β-carbonium ions by transfer of some positive charge to the metal and formation of a π-bond between the metal and organic ligand is an important 'group property' of complexed transition metals.

There are many other examples of the 'stabilization' of carbonium ions. For example, in the chemistry of substituted ferrocene, intermediate carbonium ions in a β-position with respect to the metal play a significant role, e.g. (see p. 142–144).

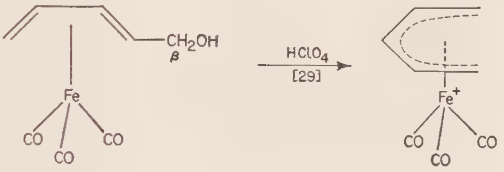


Further examples may be found in the chemistry of π-enyl complexes (see p. 55),

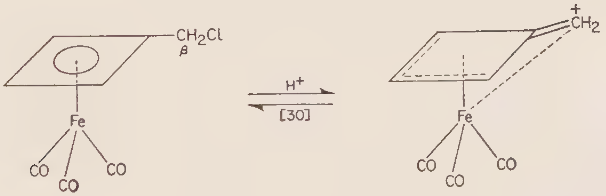


Postulated intermediate

diene–metal complexes (see p. 138),



and π-cyclobutadiene compounds (see p. 79).



Postulated intermediate

In the above examples the carbonium ion is part of a π-bonding ligand. For this reason the mechanism of stabilization of the carbonium ion may not be by direct metal–carbonium ion interaction but by delocalization of charge over the π-ligand (see p. 144). However, it is still necessary that the transition metal be partially oxidized and the ability of transition metals to act as 'electron reservoirs' in these processes appears to be one of their important functions.

The carboxyalkyl transition metal complexes, M—CH_2COOH, where M is a complexed transition metal, can be readily prepared, e.g.

$$\begin{array}{c} Na^+[Mn(CO)_5]^- \\ + \\ ClCH_2CONH_2 \end{array} \longrightarrow (CO)_5MnCH_2CONH_2 \xrightarrow[\text{Boil}]{\text{HCl}} (CO)_5MnCH_2\text{—}COOH$$

It is found that these complexes are very weak acids, being amongst the weakest neutral carboxylic acids known [31, 32]. For example, when M = π-$C_5H_5Fe(CO)_2$—, $pK_a = 6{\cdot}75 \pm 0{\cdot}08$ in water and $8{\cdot}60 \pm 0{\cdot}09$ in 1 : 1 dioxan : water; M = $Mn(CO)_5$—, $pK_a = 6{\cdot}05 \pm 0{\cdot}08$ in water, $7{\cdot}99 \pm 0{\cdot}05$ in 1 : 1 dioxan : water mixture; M = π-$C_5H_5Mo(CO)_3$—, $pK_a = 8{\cdot}16 \pm 0{\cdot}06$ in 1 : 1 dioxan : water; and M = Co(pyridine)-$(DMG)_2$—, pKa = $6{\cdot}5 \pm 0{\cdot}2$ in water [31]. It does not seem reasonable to account for these very low acid strengths only in terms of the inductive effect of the metal atoms.

The structure of the compound π-$C_5H_5Fe(CO)_2CH_2COOH$ has been determined by X-ray diffraction [32] and is shown in Figure 47. It is of interest that the C–O distances of the carboxyl group are the same within experimental error, 1·32 Å. A difference in C–O bond lengths of 0·05–0·10 Å is found for the large majority of other carboxylic acids. Further the intermolecular O–H–O distance is 2·48 ± 0·02 Å and is one of the shortest known. It is also of interest that the plane through the COO atoms of the carboxyl group faces the iron atom as shown in Figure 47. It is suggested that both the high pK of the iron acid and the unusual distances found for the carboxyl group in this compound are due to there being some direct donation of electrons by the metal atom to the carboxyl group [31].

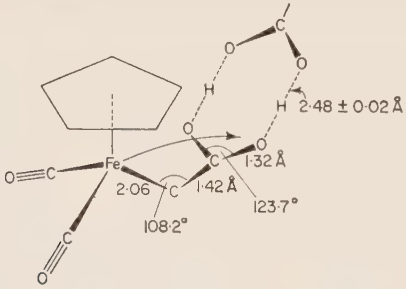


Fig. 47. The structure of π-cyclopentadienyl iron dicarbonyl carboxymethyl dimer

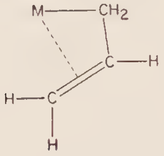
Unlike the iron acid the crystal structure of molybdenum analogue π-$C_5H_5Mo(CO)_3CH_2COOH$, shows no abnormal bond lengths and the C–O distances of the carboxyl group are unequal (1·36 and 1·19 Å) as is normally the case and the O···H···O bond length (2·67 Å) is typical of that found in the large majority of carboxylic acid dimers [32].

Thus both the iron and the molybdenum acids are weak whilst only the iron acid has an unusual structure. It may be that, since the molybdenum 4*d* orbitals are more diffuse than the iron 3*d* orbitals, the interaction between the molybdenum and the COO moiety is less specifically directed than in the iron complex.

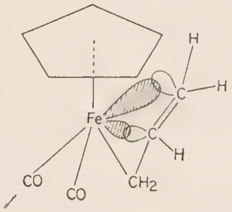
It therefore seems that the postulate of some direct metal–β-position interaction is the simplest explanation which will account for all the unusual chemistry associated with the β-position. For simplicity the effect of transition metals on β-substituents is called the β-effect.

(*c*) *The possible nature of the β-effect*

Unsaturated groups in the β-position, as in the complexes, M—CH_2X, for example, where X = CN, CH=CH_2, CHO, can approach quite near to the metal atom (see 7.7) The *unsaturated* systems have both filled π-orbitals and empty π^*-orbitals and it is clear that metal *d* orbitals of suitable symmetry may be found which could weakly overlap with the π-orbitals of the β-substituents; a possible interaction is shown in 7.8. Filled 'nonbonding' orbitals will be present in the π-$C_5H_5Fe(CO)_2R$ group, e.g. the $d_{x^2-y^2}$ and d_{xy} orbitals (see p. 130).



7.7



7.8

It is not necessary to postulate that the β-substituents are always held in a fixed configuration to the metal so that interactions are always present; it is only necessary for such interactions to be available so as to provide a ow energy reaction path.

The nature of the β-effect with *saturated-β*-substituents may be understood in similar terms: e.g. there are two extreme possibilities for interaction of a β-methyl group with a metal, either a metal orbital can combine with the hydrogen *s* orbital and a carbon sp^3 hybrid orbital to form a M—H—$\underset{|}{CH_2}$ system, or, a M—$\overset{|}{\underset{/\ \backslash}{C}}$—H system involving five-co-ordinated carbon can be postulated (see Figure 48). In either case, a *strong* M—H— or M—C— interaction need not, indeed almost certainly does not, occur.

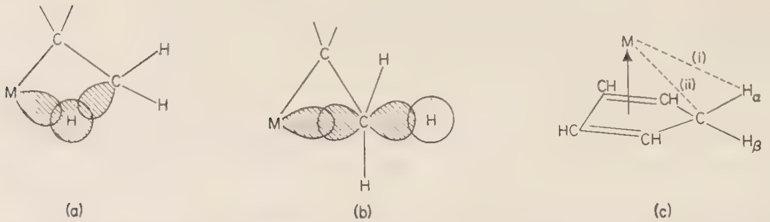
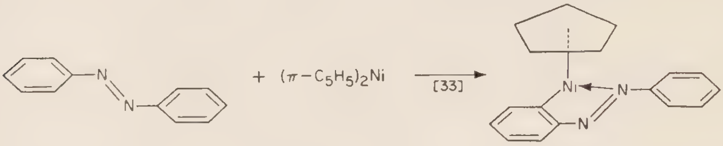


Fig. 48. (*a*) and (*b*) represent possible interactions of a $C\beta$-methyl group with a transition metal. (*c*) shows the interaction of a metal with the H_2 proton (i), or methylene carbon (ii) of a cyclopentadiene group

Again, it is only necessary for a path of relatively low activation energy to be available. In this context it is interesting to note that either of the possible interactions could account for the unusually low C–H stretching frequency found in cyclopentadiene and cyclohexadienyl complexes, and which is associated with a C–H of the methylene group (see p. 80). In these complexes the methylene group may be regarded as being in the β-position with respect to the metal (see Figure 48). It is possible that the metal may interact directly with the *endo*-hydrogen or with the methylene carbon, as shown. In the former case a weakening of a $C–H_\alpha$ bond would be expected whilst the latter interaction would weaken $C–H_\beta$.

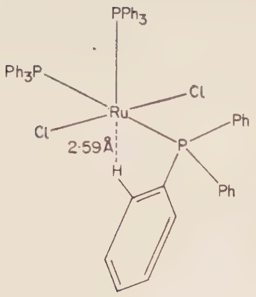
Further, it has been observed that in a number of reactions between aryl compounds and transition metals, loss of *ortho*-hydrogen occurs, viz.



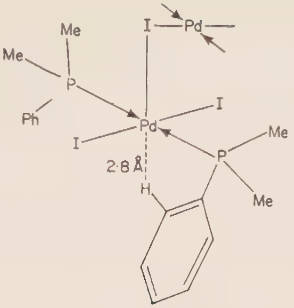
The loss of hydrogen from this position may be compared with the hydrogen loss in metal alkyls.

The structures of the complexes $(PPh_3)_3RuCl_2$, 7.8*a* [34], and *trans*-$Pd(PhMe_2P)_2I_2$, 7.9 [35], are of interest since they both suggest that there is some interaction of a hydrogen of a tertiary phosphine ligand with the metal atom.

Finally, it is interesting to consider why the β-effect is found to a greater extent with transition metals than with other elements. The answer probably lies in the fact that transition metals, even when they are conventionally considered to be co-ordinatively saturated, as in ML_6, have *d* orbitals, which may be filled or unfilled, but which are of *suitable energy and position* to be involved in M–β-position interactions. When transition metals are in a low oxidation state, their *d* orbitals extend further from the metal than for the higher oxidation states. It follows that the β-effect would be expected to be more marked in low oxidation state complexes.



7.8*a*



7.9

It can be seen that the reversible metal–σ-organo to metal hydride equilibria and the generally higher reactivity of normally non-labile organic systems, which are discussed above, provide considerable insight into the role of transition metals in their catalytic reactions with organic compounds.

D. The bonding of 1-electron ligands to transition metals

The M–C system has the local symmetry $C_{\infty v}$ and in this symmetry group the metal and carbon orbitals can always take part in both σ- and π-bonding.

The possible combinations of metal and carbon orbitals are shown in Table 24 and Figure 49. It is of interest to consider the relative importance of the σ- and π-bonding combinations in various metal-carbon systems.

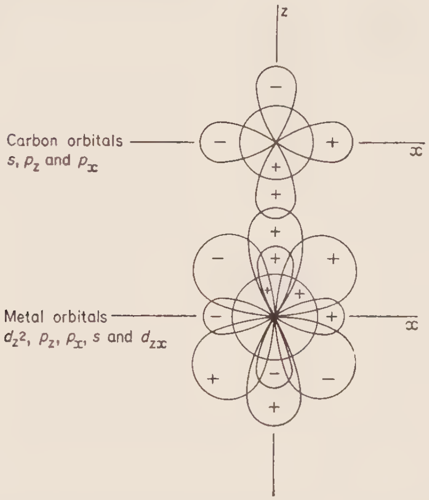


Fig. 49. Representation of the interaction between metal and carbon orbitals in the zx-plane. The relative sizes of the orbitals are unknown. The negative lobe of the d_{z^2} orbital is omitted

Table 24 *Possible combinations of metal and carbon orbitals in the symmetry group,* $C_{\infty v}$

Symmetry	Metal orbitals	Ligand orbitals	Bond type
A_1 (Σ^+)	s, p_z, d_{z^2}	s, p_z	σ
E_1 (Π)	p_x, p_y, d_{xz}, d_{yz}	p_x, p_y	π
E_2 (Δ)	$d_{x^2-y^2}, d_{xy}$	—	—

(*a*) *Metal–carbon single bonds*

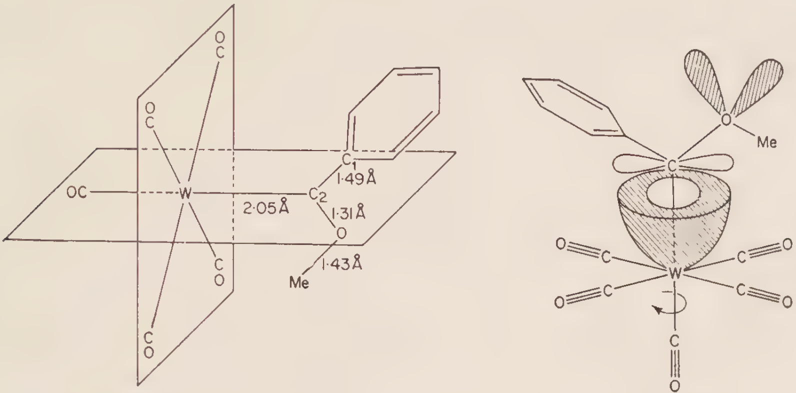
It is commonly agreed that in metal–alkyl (R_h) bonds there is little π-contribution to the bonding. This is because the p_x and p_y orbitals of the α-carbon atom are fully involved in bonding with the carbon or hydrogens which are also attached to it.

Jaffé has discussed the metal–carbon σ-bonding in terms of the covalent and ionic contributions [36]. One of his conclusions was that the metal–carbon bond strength should increase with increasing electronegativity of the alkyl group. There is little data to test this prediction. However, if the argument is extended to metal-perfluoroalkyls (R_f), then their greater stability relative to M–R_h complexes may be due to an increased M–C bond strength arising from the greater electronegativity of R_f groups compared to that of R_h analogues. Another conclusion from Jaffé's arguments is that there would be an increase of metal–carbon bond strength with decreasing atomic weight of the metal in a particular subgroup. This trend would arise from an increase in the metal–carbon overlap integral (the metal orbitals of the lighter atoms are the less diffuse). For the subgroup Ti, Zr and Hf, it appears that there is a decrease of thermal stability of the metal–alkyl complexes with increasing atomic number of the metal in agreement with these predictions.

(*b*) *Metal–carbon multiple bonds*

(*i*) *Metal aryls.* In the metal–aryl system there is the possibility of donation of electrons from the filled $p\pi$-orbitals of the aryl ligand to empty metal orbitals, and also, donation of metal electrons to the empty $p\pi^*$-orbitals of the aryl ligand. It is often found that transition metal–aryl complexes are thermally more stable than their alkyl analogues and this may be due to an increase of the M–C bond strength due to both the greater electronegativity of the aryl ligand and a π-bonding contribution to the metal–carbon bond. In some aryl complexes there is evidence that the aryl ligand can enhance the kinetic stability of the complex (see p. 225). π-Bonding in the M–C bond may also be significant in metal–acyl, –alkynyl and possibly –perfluoroalkyl complexes (see pp. 261, 273 and 269 respectively).

(*ii*) *Metal 'carbenes'*. The compound $W(CO)_5$—CPhOMe has been prepared (see p. 200), and its structure determined by X-ray analysis [17] (see Figure 50). In this compound the W–C bond of the W—CPhOMe system



(i) (ii)

Fig. 50. (*i*) Structure of $PhMeOCW(CO)_5$, showing that the OC_1C_2 plane bisects the *cis*-axes, through the metal–carbonyl ligands. (*ii*) The 'cylindrical' π-bonding orbital is represented. The x, y and z axes lie along the W–C bonds

(2·05 Å) is rather longer than those of the M—CO systems (~1·89 Å). Of course, carbon monoxide has two degenerate π- and π^*-molecular orbitals, all of which might take part in substantial π-bonding whereas the carbon atom of —CPhOMe has only one *p* orbital not engaged in bonding with the OMe and Ph ligands and which could be expected to take part in substantial M–C π-bonding. It might be expected that the W–C_2 bond would have a degree of polar character which, in the extreme case, permits a description of the W–C_2 bond as an 'ylide' system $(CO)_5W^+$—CO^-MePh. However, it seems probable that there is considerable double-bonding between the tungsten *d* orbitals and the C_2 *p* orbitals, which is normal to the C_1C_2O plane, together with some degree of charge separation. Evidence supporting the postulate of W–C_2 π-bonding comes from the observation that the CO in the *trans*-position to C_2 is not noticeably different from the other CO groups, which are, of course, *trans* to each other and which are generally agreed to be π-bonding ligands.

Another point of interest in the structure is that the plane of the C_1C_2O moiety does not lie along the x- or y-axis but is between these axes at about 45° to each. This structure is the one to be expected, since in the group $M(CO)_5$ all the metal orbitals are symmetrically distributed about the z-axis and hence both the d_{xy} and d_{yz} and the p_x and p_y metal orbitals form degenerate pairs. These metal orbitals therefore form a symmetrical, cylindrical π-bonding orbital about the z-axis (see Figure 50) and thus in this situation a M=C double bond has free rotation about the M–C axis. It follows that, as found, the OC_1C_2 plane would be expected to take up the least sterically hindered position.

The structure of the related carbene complex $Cr(CO)_4Ph_3P(CMeOMe)$ has been found to be essentially similar to that of the tungsten carbene, the $Cr–C_2$ distance is 2·04 Å [36*a*].

E. The stability of metal–σ-organo complexes

(*a*) *Introduction*

In the discussion of the stability of a compound it must be quite clear which type of stability is being considered. The expressions 'thermal stability', 'stable to oxidation' and 'stable to hydrolysis' are frequently used and all these aspects of the stability of a compound depend on thermodynamic and kinetic factors. For example, the statement that a complex is thermally stable at room temperature may mean that it is thermodynamically stable (i.e. has a negative free energy of formation from its decomposition products). In which case the complex would never decompose spontaneously at room temperature although it can be in equilibrium with a percentage of its decomposition products. The same statement is however also used to indicate that the complex is kinetically stable to decomposition. In this case, regardless of whether the complex is thermodynamically stable or unstable, there is a high free energy barrier to the formation of decomposition products and hence the rate of formation of products will be slow. An example of great practical importance is the compound which is thermodynamically unstable with respect to thermal decomposition but which is kinetically stable. It follows that it may be possible to keep the complex for many years even though it will eventually decompose.

(*b*) *The thermodynamic stability of metal–σ-organo complexes*

There are little quantitative data concerning the thermodynamic stability of metal–organo complexes. The low thermal stability of many complexes shows that they are thermodynamically unstable and it seems probable that the large majority of even 'thermally stable' complexes are also thermodynamically unstable with respect to some decomposition products. This thermodynamic instability of metal–organo complexes probably arises from the relative weakness of the metal–carbon bond compared to the bonds which carbon forms with many other elements, in particular with itself. For example, titanium tetrachloride has a negative free energy of formation from its elements because the Ti–Cl bond is strong whilst the Cl–Cl bond is relatively weak. In contrast, tetramethyltitanium decomposes at –40°C and this is presumably because the Ti–C bond is weak in comparison to the bonds of all decomposition products, including the strong C–C bond. The force constant of the Ti–C bond in $MeTiCl_3$ is estimated to be $1{\cdot}85 \pm 0{\cdot}2 \times 10^5$ dyn./cm. [36*b*].

In many metal–σ-organo complexes (represented by M—R where M can be a complex with other ligands) it seems probable that the first step in their decomposition is the dissociation of the M–carbon bond. This may dissociate homolytically or heterolytically, forming either a carbon radical or carbon ion species. In both cases, the carbon fragments would normally be very reactive and readily form stable products, for example by dimerization, or polymerization (see Figure 51). It is the formation of these more stable products which provides the energy which drives the decomposition and, since the products would usually be kinetically unreactive, the decomposition would be irreversible under normal conditions. In contrast, dissociation of M—X giving stable neutral ligands such as CO, NH_3 or ethylene, or heterolytic fission forming ions such as the cyclopentadienide or chloride ion, would be expected to be readily reversible and subsequent decomposition of the dissociated ligand would not normally occur. It follows from this discussion that in order to be thermally stable, metal–σ-organo complexes must not readily dissociate giving reactive fragments, i.e. a high activation free energy barrier towards dissociation is necessary. Since it seems unlikely that M–C bonds are particularly strong, other factors which determine the kinetic stability of the complex will in general

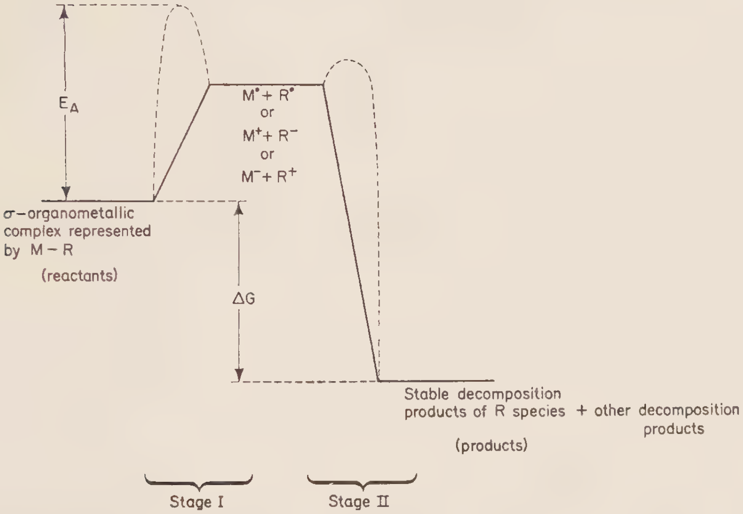


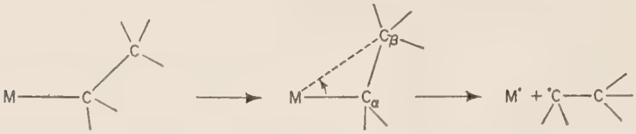
Fig. 51. Schematic representation of the thermal decomposition of a σ-organo complex, M—R, by a unimolecular dissociation of the M–R bond, showing, E_A, the energy of activation of preliminary decomposition, which is important in determining the kinetic stability of the complex; Δ*G* represents the free energy of decomposition. If the products have less energy than the reactants then the complex is thermodynamically unstable

be the more important in the thermal stabilization of organometallic complexes.

(c) The kinetic stability of metal–σ-organo complexes

Kinetic stability is concerned with the possible mechanisms of decomposition whilst thermodynamic stability is only related to certain products of decomposition. The rate of decomposition of a compound depends on temperature and decreases with decreasing temperature. This is one reason for the low temperature conditions used in the preparations of many organometallic complexes.

For a number of metal–alkyl complexes (M—R) the thermal stability decreases in the order R = Me > Et > Pr. In particular, the methyl complexes are often markedly more stable than the higher homologues. The lower stability of the ethyl and propyl complexes may be due in part to inductive effects and in part to steric weakening of the M–C bond. Another explanation, which is more plausible in some cases, is that the β-interaction discussed above gives rise to a transition state of lower energy than required for unaided homolytic dissociation, for example:



The kinetic stability of organic complexes of square-planar nickel, palladium and platinum. Chatt and Shaw have given a detailed argument for the kinetic stability of the complexes L_2MR_2 and L_2MRX, where L = a π-bonding ligand, R = alkyl, aryl or ethynyl ligands, X = halogen, and M = Ni, Pd or Pt [37, 38]. They assume that the rate-determining step in the decomposition of these complexes is the homolytic fission of the M–R bond.

Homolytic dissociation is imagined to proceed either by the promotion of an electron into the anti-bonding orbital of the M–C bond, or the promotion of one electron from the M–C bonding orbital. It follows that the energy barrier to homolytic dissociation can be equated with the energy difference (ΔE) between, either the M–C bonding orbital and the lowest unfilled orbital, or the M–C anti-bonding orbital and the highest filled orbital, whichever is the lesser. The larger the value of ΔE, the greater the kinetic stability of the M–C to dissociation.

In Figure 52 is shown a schematic energy level diagram for square-planar complexes. The diagram shows the energy gap ΔE between the highest filled and the lowest unfilled M.O.s.

In these square-planar complexes, the d_{xy}, d_{xz} and d_{yz} metal orbitals are

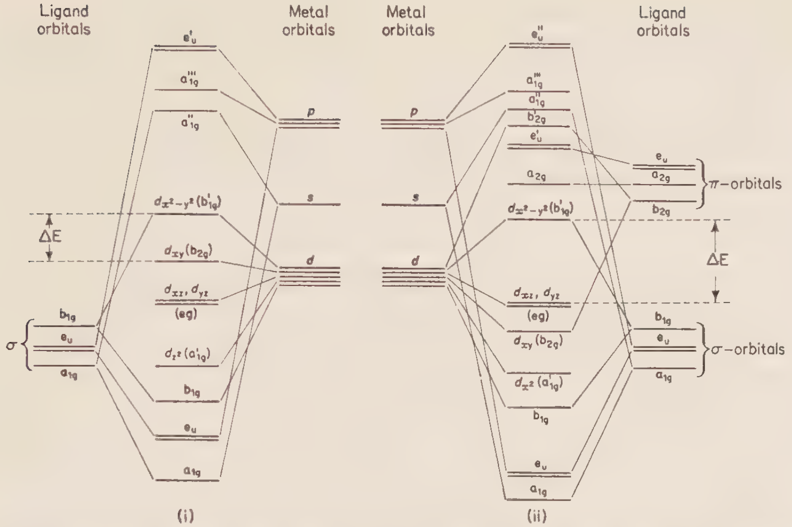


Fig. 52. Schematic energy level diagrams for square-planar complexes. ΔE represents the energy gap between the highest occupied orbital and the lowest unoccupied orbital. I represents the case when there is only σ-bonding and II shows how ΔE is increased when there is a π-bonding interaction in the d_{xy} plane

non-bonding with respect to the metal–ligand σ-bonds but they may take part in the formation of π-bonds. The positions in the M.O. diagram of the four 'non-bonding' *d* orbitals have been estimated using a simple crystal field approach, but a fuller M.O. treatment gives the same results [39]. The lowest energy, unfilled M.O. is probably the anti-bonding b'_{1g} orbital which arises from the anti-bonding combination of the metal d_{x2-y2} and ligand orbitals.

Chatt and Shaw discuss several factors which may cause an increase in ΔE and hence an increase in the thermal stability of these complexes.

(*i*) The effect of the increasing atomic number in the series Ni, Pd, Pt is that the interaction of the metal d_{x2-y2} and ligand orbitals increases and the b_{1g} M.O. becomes lower in energy. It follows that the b'_{1g} M.O. is raised in energy and that ΔE increases.

This argument partly accounts for the observed increase in thermal stability of the organic derivatives of the above metals in the order Pt > Pd > Ni.

(*ii*) It is observed that all the known complexes L_2MRX and L_2MR_2 all contain π-bonding ligands where L = tertiary phosphines or arsines, sulphur ligands, aromatic nitrogen ligands and olefins. It appears that π-bonding ligands are necessary for the formation of thermally stable organic derivatives. The role of these π-bonding ligands may be explained using the M.O. diagram, as follows.

π-Bonding between the ligands and metal orbitals must use the d_{xy}, d_{xz}

and d_{xy} orbitals. Bonding interactions of these orbitals with the ligands, in particular with the d_{xy} orbital, would form M.O.s of lower energy than that of the non-bonding *d* orbitals. Thus ΔE would increase and the complex becomes thermally more stable.

It follows that if the organic ligand itself can form π-bonds then this will also cause an increase in thermal stability. In agreement, the order of thermal stability of the complexes L_2MR_2, where R = alkynyl > aryl > alkyl, is found, which is the order of decreasing π-bonding ability of the organic ligand.

(*iii*) The electronegativity of the ligand affects the degree of π-bonding between the metal and the ligand. The greater the electronegativity of the ligand, the larger the partial positive charge on the metal becomes, and hence there would be an increased attraction of the *d* orbitals causing their contraction towards the metal. If the *d* orbitals contract then they are less available for π-bonding and ΔE would decrease. Conversely, a decrease in the electronegativity of the organic ligands would increase ΔE. A comparison of this argument with that of Jaffé shows that increasing electronegativity of an organic ligand has two opposing effects in these complexes. These effects are to increase the metal–ligand σ-bond strength and simultaneously decrease ΔE.

It should be remembered that all the above arguments are entirely qualitative. The magnitudes of the various effects are unknown and there are other effects which have not been mentioned. The above discussion serves only to exemplify the possible nature of thermal stabilization of complexes by kinetic factors and a possible role for π-bonding ligands.

F. Tertiary phosphine transition metal–alkyl and –aryl complexes and related compounds

Examples of complexes in this class are given in Table 23.

(*a*) *Nickel, palladium and platinum*

A considerable number of complexes $(R'_3P)_2MR_2$ and $(R'_3P)_2MRX$, where M = Ni, Pd or Pt, are known. In agreement with the arguments presented for the stabilization of these square-planar complexes they increase in stability with increasing atomic number of the metal. The complexes are usually prepared by treatment of the halides, *cis*- or *trans*-$(R_3P)_2MX_2$, with Grignard or organolithium reagents. Generally for the alkyl derivatives there is a decrease of stability in the order of increasing chain length of the alkyl ligands; i.e. Me > Et > Pr. Aryl complexes have about the same stability as the methyl analogues.

(*i*) *Nickel.* The alkyl derivatives $(R'_3P)_2NiR_2$ are very unstable and attempts to isolate them have been unsuccessful [37]. In the case of the phenyl analogues R = Ph it is possible to obtain a crystalline complex but not in a pure state; the complex readily decomposes. Attempts to prepare *meta-* and *para*-substituted phenyl and 2-naphthyl analogues gave products with similar properties. However, *ortho*-substituted phenyls, 1-naphthyls, 9-phenanthryl and 9-anthryl all form exceptionally stable complexes of stoicheiometry *trans*-[$(PR'_3)_2NiArX$] and the less often found *trans*-$(PR_3)_2NiAr_2$ [37]. These complexes are coloured yellow-orange-brown and the majority melt in the range 100–150°. With few exceptions, they are stable in boiling ethanol and benzene and many appear to be indefinitely stable in air in the solid state. The complexes undergo typical cleavage and metathetical replacement reactions (see Figure 54).

For these nickel aryl complexes, the marked stability of the *ortho*-substituted aryls compared with the *meta-* and *para*-substituted analogues is believed to result from a combination of steric and electronic factors in the following manner.

Those aryl ligands which do not contain *ortho*-substituents would be expected to rotate about the Ni–Ar bond and thus interact at various times with the metal d_{xz}, d_{yx} and d_{xy} orbitals. This interaction (π-bonding) would be expected to cause a lowering of the metal *d*-orbital energy levels, and hence an increase in ΔE (see p. 222). The apparent increase of stability of phenyl–nickel bonds over methyl–nickel bonds could then be due both to an increase in metal–carbon bond strength caused by the π-bonding and to an increase in kinetic stability due to the increase in ΔE.

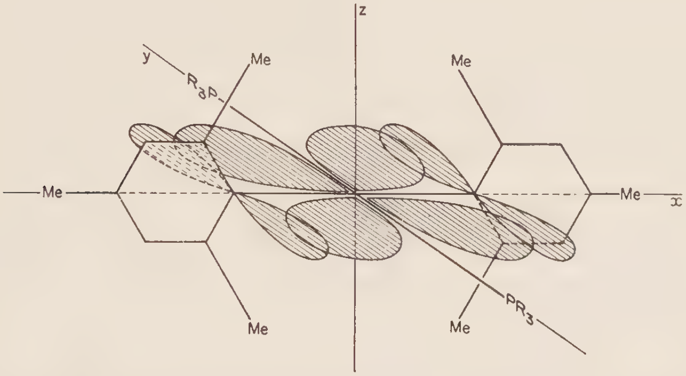


Fig. 53. Ortho-effect. The ortho-methyl groups of the mesityl ligands are held in the xz plane by the tertiary phosphine ligands. Thus the metal d_{xy} orbital must interact with the mesityl $p\pi$-orbitals

In the case of *ortho*-substituted aryls, models show that the *ortho*-substituents by steric interaction prevent rotation of the aryl group and the substituents would be held above and below the xy-plane of the metal (see Figure 53). In this configuration the aryl π^*-orbitals may interact only with the important d_{xy} orbital and the increase in ΔE would thus be greater than if interaction with d_{xz} and d_{yz} orbitals also occurred. The *ortho*-substituents also interact so as to stabilize the square-planar configuration about the metal and prevent rearrangement to a tetrahedral complex. This effect would be most marked with di-*ortho*-substituted aryls. Rearrangement to a tetrahedral complex is undesirable since during the rearrangement ΔE may diminish and the ligands would become labile. A further role of the *ortho*-substituents may be to inhibit sterically the attack of ligands along the z-axis.

To summarize, the *ortho*-substituted aryl complexes $(R'_3P)_2NiAr_2$ are stabilized with respect to a dissociative mechanism by virtue of the increased ΔE and enforcement of a planar configuration and they are also stabilized against a bimolecular mechanism of decomposition involving attack along the octahedral axis.

(*ii*) *Palladium.* The complexes $(PR'_3)_2PdRX$ and $(PR'_3)_2PdR_2$, where R = alkyl and aryl, are well characterized. Although they are more stable than the nickel analogues many are unstable and decompose slowly at room temperature. Most of the complexes are colourless. As found for the nickel analogues, palladium–aryl complexes have the *trans*-configuration. *Ortho*-substituted aryls form more stable complexes than other aryl ligands but the stabilizing effect of *ortho*-substitution is relatively less marked in palladium than in nickel. This would be expected since ΔE is already larger in all the palladium complexes than in the nickel analogues.

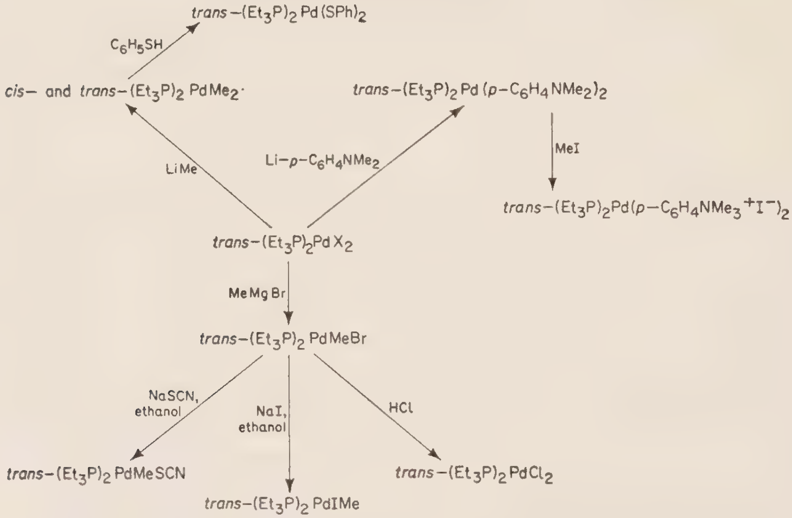
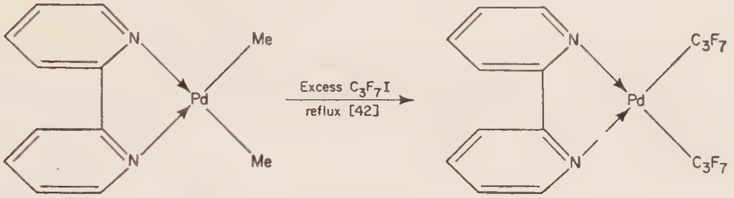


Fig. 54. The preparations and some reactions of the palladium complexes $(Et_3P)_2PdR_2$ and $(Et_3P)_2PdRX$ [43, 44]

Therefore the *ortho* effect would cause a proportionately smaller change in ΔE.

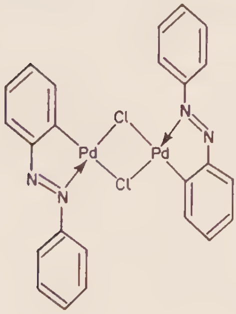
The palladium–alkyl complexes are usually isolated as the *trans*-isomers. However, a few relatively unstable *cis*-isomers are known; the *cis*-configuration is suggested by the high dipole moment of the complexes, e.g. *cis*-$(Me_3P)_2PdMe_2$, 6·5 D; *cis*-$(Ph_3P)_2PdMe_2$, 4·5 D. *Cis*-dimethyl complexes are stabilized when a chelate phosphine ligand is used, as in *cis*-$Ph_2PCH_2CH_2PPh_2PdMe_2$, m.p. 162°. Some typical reactions of tertiary phosphine palladium–σ-organo complexes are shown in Figure 54.

Apart from phosphine ligands, stable alkyl–palladium complexes have been prepared in which the π-bonding ligand is a chelate olefin, α,α'-bipyridyl or 1,2-dithiomethylethane, e.g. $C_8H_{12}PdMe_2$ (very unstable); (bipy)$PdMe_2$, m.p. 155° d.; $MeSCH_2CH_2SMePdMe_2$, m.p. 75° d. The bipyridyl complex is unusual in being bright orange and it is surprisingly stable. With perfluoroalkyl halides it undergoes replacement reactions, e.g.

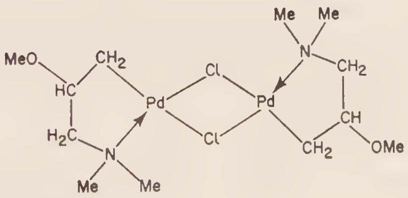


A very reactive dark green diethyl nickel analogue, α,α'-bipyridyl$NiEt_2$, is also known [40].

Several chelate ligands which form σ-carbon bonds are known. For example azobenzene reacts with palladium(II) chloride in alcohol and, by loss of an *ortho*-hydrogen, forms the complex shown in 7.9*a* [41].



7.9*a*



7.9*b*

Another chelate ligand is found in the complex 7.9*b*, which is prepared by treatment of palladium(II) chloride with N,N-dimethyl allyl amine in methanol [41*a*].

(*iii*) *Platinum.* The platinum complexes in this class are amongst the most stable organo-σ-transition metal complexes known, both in their thermal and oxidative stability. Both *cis-* and *trans-*isomers of alkyl and aryl derivatives of the complexes $(PR'_3)_2PtR_2$ and $(PR'_3)_2PtRX$ are found. In some cases, notably the dimethyls, one isomer is more difficult to prepare than the other.

Cis-dimethyl complexes, $(PR_3)_2PtMe_2$, are readily obtained from methyl-lithium and the corresponding *cis*-dichloride. The complex *cis*-$(PEt_3)_2PtMe_2$, m.p. 81–82°, is readily distilled *in vacuo*, without decomposition. The condensate contains the *trans*-isomer, m.p. 76–79°, which can be purified by chromatography, with difficulty.

The halomethyl complexes $(PR'_3)_2PtMeX$, in contrast to the dimethyl analogues, are readily prepared in the *trans* form and the *cis*-halomethyls are more difficult to obtain. *Cis*-chloromethyl complexes are best prepared by treatment of the *cis*-dimethyls with hydrogen chloride.

$$\textit{cis}\text{-}(PR'_3)_2PtMe_2 \xrightarrow{HCl} \textit{cis}\text{-}(PR'_3)_2PtMeCl$$

Although the *cis*-isomer is stable in benzene, in the presence of a trace of phosphine ligand it is rapidly and almost completely isomerized to the *trans* form.

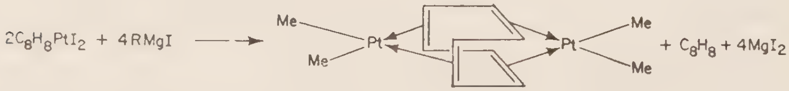
In contrast to simple alkyl complexes where *cis*-isomers are normally obtained, both *cis-* and *trans-*isomers of diaryl complexes can be prepared directly from the corresponding dihalides. Cleavage of the diaryls with hydrogen chloride affords the arylchlorides without isomerization, e.g.

$$\textit{trans}\text{-}(PEt_3)_2PtPh_2 \xrightarrow{HCl} \textit{trans}\text{-}(PEt_3)_2PtPhCl$$

It is significant that the diaryl complexes are not isomerized by free phosphine, as this supports the view that the isomerization of complexes containing halogen occurs through an ionic intermediate, e.g.

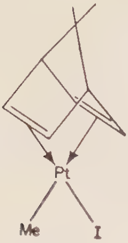
$$\textit{cis}\text{-}(PR'_3)_2PtRCl + PR'_3 \longrightarrow [(PR'_3)_3PtR]^+Cl^- \longrightarrow \textit{trans}\text{-}(PR'_3)_2PtClR + PR'_3$$

As found for palladium, *cis*-dialkyl complexes can be prepared using a variety of chelate ligands such as $Et_2PCH_2CH_2PEt_2$, $EtSCH_2CH_2SEt$ and olefins such as norbornadiene, cyclo-octa-1,5-diene and cyclo-octatetraene, e.g.

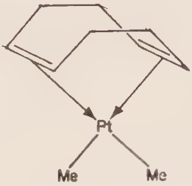


The cyclo-octatetraene complexes are binuclear and it is thought that the olefin has the tub configuration as shown [45, 46]. Other examples of olefin alkyl complexes are 7.9*c* and 7.10. Phosphine ligands readily displace the olefin from these complexes.

All the platinum alkyl and aryl complexes so far discussed have been platinum(II) derivatives. Remarkably, some of these complexes undergo addition reactions with halogens or alkylhalides, forming octahedral Pt(IV) complexes, e.g.



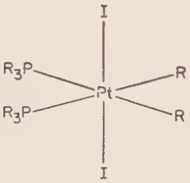
7.9*c*



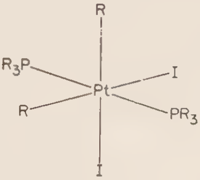
7.10

$$trans\text{-}(PEt_3)_2PtMeI + MeI \xrightarrow{100°} (PEt_3)_2PtMe_2I_2$$

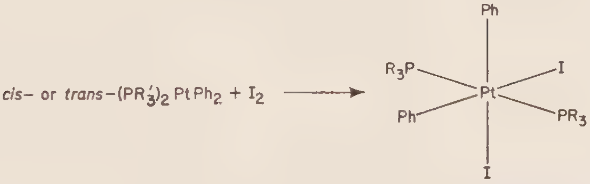
The dipole moments of this and related complexes are about 5·5–6 D, excluding all structures except 7.11 and 7.12. It should be noted that the zero oxidation state compound, $(Ph_3P)_2Pt$, also reacts with MeI forming $(Ph_3P)_2PtMeI$ [46*a*]. Another example is the addition of iodine to *cis*- or *trans*-diaryls (contrast the dialkyls from which alkyl halide is eliminated).



7.11



7.12

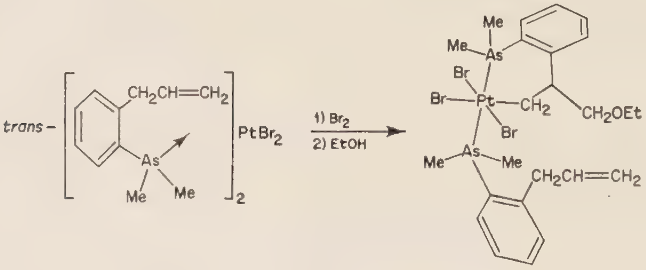


7.12*a*

The dipole moment of the Pt(IV) complex is 4·95 D, which suggests the configuration 7.12*a*.

The platinum(IV) complex 7.12*c*, is formed from the allyl-arsine compound 7.12*b*, as shown [46*b*].

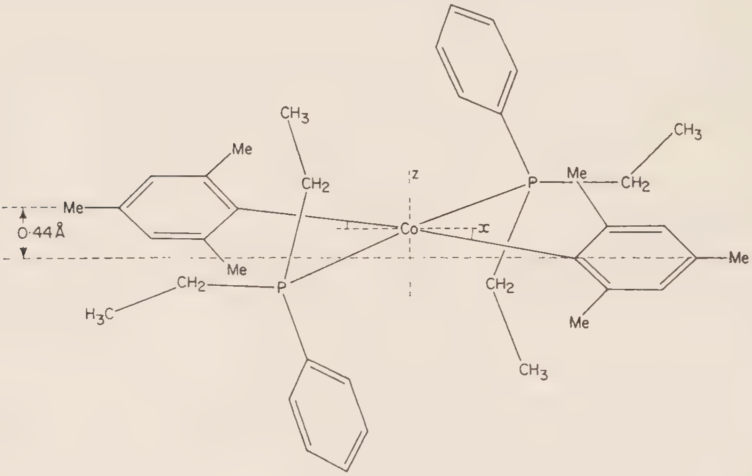
Other alkyl complexes of Pt(IV), which do not contain phosphine ligands, are discussed in section J (*d*).



7.12*b* 7.12*c*

(*b*) *Cobalt, rhodium and iridium*

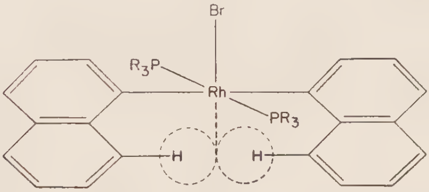
A number of yellow complexes *trans*-$(PR'_3)_2CoR_2$, where R is an *ortho*-substituted phenyl ligand such as mesityl (mes), C_6Cl_5 or 1-(2-methyl-naphthyl), have been described [47] (see Table 23). They are paramagnetic ($\mu = 2{\cdot}3$–$2{\cdot}7$ B.M.) in agreement with a square-planar configuration. The structure of the complex *trans*-$(PEt_2Ph)_2Co(Mes)_2$, 7.13, has been determined by X-ray studies [48]. The structure shows that the methyl substituents are sufficiently close both to hinder steric attack along the octahedral axis, and to restrict rearrangement of the molecule to a tetrahedral configuration of the ligands. The planes of the mesityl groups are perpendicular to the co-ordination plane of the cobalt but are not exactly



7.13

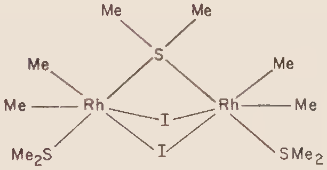
symmetric about this plane. The mesitylene planes are parallel and are 0·44 Å apart; the cobalt atom lies in the middle of the C–Co–C axis. The Co–C distance of 1·96 ± 0·01 Å is consistent with a single Co–C bond.

Treatment of the complexes L_3RhBr_3, where L = PPr^n_3 or PEt_2Ph, with 1-naphthylmagnesium bromide affords the thermally stable five-co-ordinate complex $(1\text{-naphthyl})_2RhL_2Br$ [48*a*]. Related alkyl or aryl complexes, including *o*-substituted aryl derivatives, could not be prepared and it is suggested that, as in the cobalt complexes, the stability may be associated with steric arrangement of the ligands. The proposed structure, 7.14, shows that the ligands pack around the rhodium in a very compact way and shield the vacant octahedral position. The ligands therefore stabilize the molecule against attack.



7.14

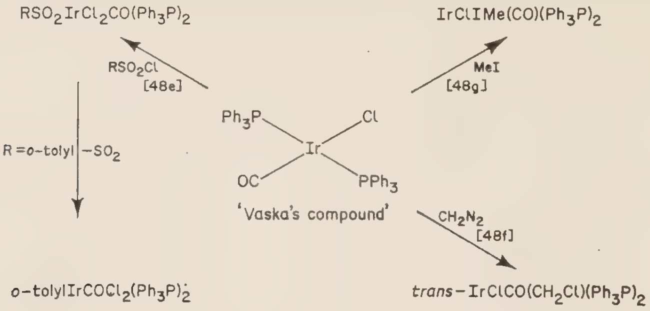
A number of six-co-ordinate rhodium alkyl complexes are known. From the reaction between $(Me_2S)_3RhCl_3$ and MeMgI the red-brown tetramethyl complex $(Me_2S)_3Me_4Rh_2I_2$ is isolated; the structure, 7.14*a*, is proposed [48*b*].



7.14*a*

The cyanoalkyl $py_3RhCl_2(CHMeCN)$ is formed by addition of pyridine and acrylonitrile to $RhCl_3$ in ethanol [48*c*]. Possibly a Rh-hydride intermediate is involved in this reaction. The unusual methyl complexes $(Ph_3P)_2MMeClI(MeI)$, where M = Rh or Ir, are of interest since they are thought to contain MeI acting as a ligand to the metal via the iodine [48*d*]. If it does then these are the first examples where an alkyl halide complexes with a transition metal.

Several tertiary phosphine iridium-alkyl and -aryl complexes have been prepared starting from Vaska's compound, *trans*-$(Ph_3P)_2IrCOCl$, viz.,



It is thought that the reaction with diazomethane giving the chloromethyl complex may proceed by a five co-ordinate 'carbene' intermediate such as $(Ph_3P)_2IrCOCl({=}CH_2)$ [48*f*].

The complexes *cis*-$(R_3P)_3IrMe_3$ have been prepared from $(R_3P)_3IrCl_3$ and MeMgCl; they are stable at room temperature and are not readily decomposed in air [48*h*].

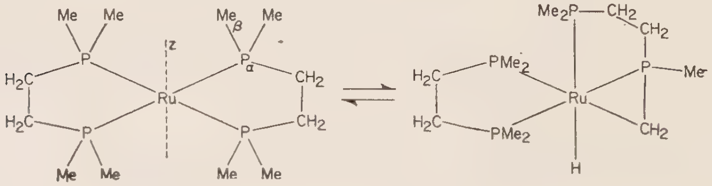
(*c*) *Iron and ruthenium*

The only known organo-σ-iron complex in this class is the golden-yellow *trans*-$(Et_2PhP)_2Fe(C_6Cl_5)_2$, m.p. 135–142° [47]. Attempts to prepare related alkyl complexes were unsuccessful, presumably due to the low thermal stability expected for such complexes. The stability of the complexes $(PR_3)_2M(ortho\text{-aryl})_2$ falls markedly in the order Ni > Co > Fe.

Treatment of the octahedral ruthenium(II) chloride $(P{-}P)_2RuCl_2$, where P—P = $Me_2PCH_2CH_2PMe_2$, with arylsodium gives complexes of stoicheiometry $Ru(arene)(P{-}P)_2$, where arene = benzene, naphthalene, anthracene and phenanthrene [22]. Detailed chemical infrared and proton magnetic resonance studies have shown that the compound in solution is an equilibrium mixture of the arene complex and the σ-aryl hydride complex, e.g.

$$\underset{\text{small }\%}{Ru(arene)(P{-}P)_2} \rightleftharpoons \underset{\text{large }\%}{Ru(aryl)H(P{-}P)_2}$$

Pyrolysis of $Ru(arene)(P{-}P)_2$ gives a compound which shows a similar equilibrium, viz.



These ruthenium complexes are most unusual and interesting, and provide an excellent example of the ease with which a transition metal may abstract a hydrogen which is attached to a carbon in a β-position (see p. 211).

(*d*) *Miscellaneous*

Tertiary phosphine-alkyl or -aryl derivatives of the Group IV, V or VI metals are as yet unknown. There seems, however, no reason why they should not be isolable. For example the complexes $(R_3P)_3CrAr_3$ might be expected to be stable.

The only Group VII compounds in this class are $(PR_3)_3ReAr_3$, $R_3 = Ph_3$ or $PhEt_2$, and the unusual five-co-ordinate nitride complex $Re(N)Ar_2(PR_3)_2$ [48*i*].

Numerous π-cyclopentadienyl and carbonyl transition metal aryl and alkyl complexes are known which also contain tertiary phosphine ligands. These complexes are discussed as π-cyclopentadienyl– or carbonyl–σ-organo complexes, to which they are more closely related.

G. π-Cyclopentadienyl carbonyl complexes

There are many metal–σ-organo complexes which contain the groups π-$C_5H_5Fe(CO)_2$— and π-$C_5H_5M(CO)_3$—, where M = Cr, Mo or W. These complexes are usually more stable, both thermally and to oxidation, than the closely related metal carbonyl–organo complexes.

(*a*) *π-Cyclopentadienyl iron dicarbonyl derivatives*

The complexes π-$C_5H_5Fe(CO)_2$-σ-R are readily prepared and are often easy to handle. As a result many complexes of this type are known and the chemistry of some of them has already been discussed in section C; the preparations and some chemistry of others are given in Figure 55.

The alkyl complexes π-$C_5H_5Fe(CO)_2$—R decrease rapidly in their thermal stability in the order $R = Me > Et > Pr^n > Pr^i$. The propyl complexes decompose in vacuum at 60°, whilst the methyl analogue decomposes only slowly at ~160°. In both cases a major decomposition product is the binuclear complex $[\pi\text{-}C_5H_5Fe(CO)_2]_2$. These alkyl complexes are stable to hydrolysis and to dilute acids but their Fe–C bond is cleaved by iodine. They are readily carbonylated (see Figure 55 and p. 260). The yellow crystalline phenyl derivative, π-$C_5H_5Fe(CO)_2$—C_6H_5, m.p. 35–36°, is conveniently prepared (12%) by the photochemical decomposition of the corresponding benzoyl derivative [6].

The halomethyl complexes π-$C_5H_5Fe(CO)_2CH_2X$, where X = Cl or Br, are very reactive and they provide an as yet little exploited route to a variety of Fe—σ-CH_2—R derivatives (see Figure 55). The chemistry of other complexes, π-$C_5H_5Fe(CO)_2$—CH_2R, where R=CHO, COMe, CN, COOH,

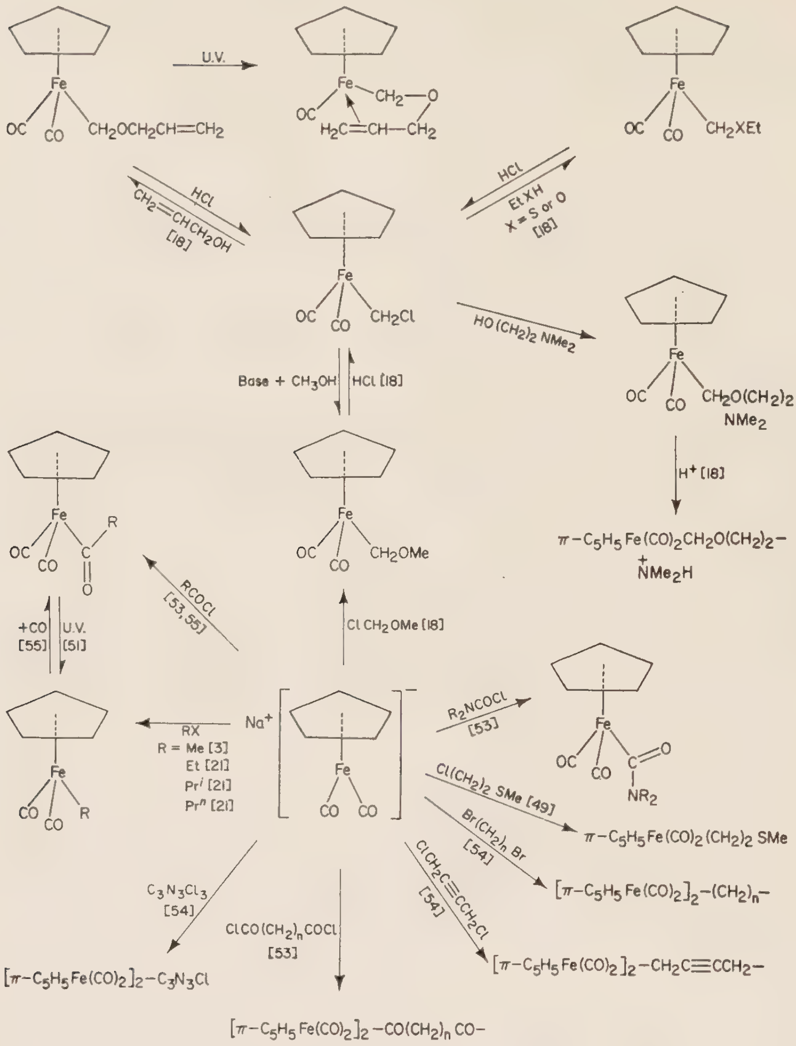
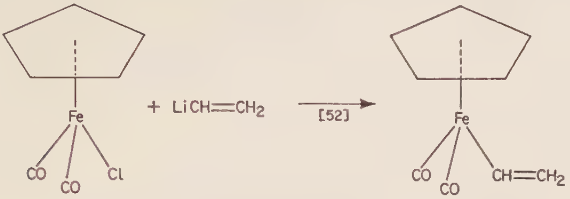


Fig. 55. The preparation of some π-$C_5H_5Fe(CO)_2$— derivatives

$CONH_2$ and COOMe, is discussed on p. 214. Isocyanatomethyl, Fe—CH_2NCO and alkoxycarbonyl, Fe—COOR derivatives have also been prepared [55*a*]. The tricyanomethyl complex, π-$C_5H_5Fe(CO)_2C(CN)_3$ has been prepared from π-$C_5H_5Fe(CO)_2Cl$ using $Ag^+[C(CN)_3]^-$ [50].

π-$C_5H_5Fe(CO)_2$—$CH{=}CH_2$, the first well-characterized transition metal–σ-vinyl complex, was prepared in low yields by the photochemical decarbonylation of the acrylyl derivative π-$C_5H_5Fe(CO)_2COCH{=}CH_2$

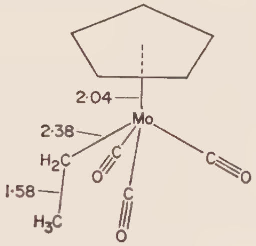
[51]. A more convenient route employs vinyl-lithium or vinylmagnesium bromide, e.g.



(*b*) *π-Cyclopentadienyltricarbonyl complexes of chromium, molybdenum and tungsten*

In general, the complexes π-$C_5H_5M(CO)_3$—σ-R show the order of stability $M = W \leqslant Mo \geqslant Cr$. When R = alkyl, the chromium derivatives are unknown or are very unstable whilst the molybdenum complexes are as stable as the analogous iron complexes. The tungsten alkyls appear to be slightly less stable than the molybdenum analogues and also they are difficult to prepare. No iso-propyl derivative of tungsten could be isolated under conditions which gave good yields of the molybdenum analogue π-$C_5H_5Mo(CO)_3$—Pr^i [22*a*].

The structure of the molybdenum ethyl complex, 7.15, has been determined by X-ray diffraction [56]. The Mo–C(ethyl) bond length (2·38 Å) is found to be the sum of the covalent radius of *sp*³ carbon plus half the Mo–Mo distance in the binuclear complex $[\pi\text{-}C_5H_5Mo(CO)_3]_2$. This rather long distance suggests there is considerable *d*-electron character in the bond. The thermal decomposition of the complexes π-$C_5H_5Mo(CO)_3R_h$ almost invariably gives the binuclear complexes $[\pi\text{-}C_5H_5Mo(CO)_3]_2$. An exception is the decomposition of π-$C_5H_5Mo(CO)_3Et$ in the presence of carbon monoxide, which forms the ethylcyclopentadienyl complex $[\pi\text{-}EtC_5H_4Mo(CO)_3]_2$ and other products typical of free radical reactions. This reaction provided the first demonstration of the transfer of an alkyl group from a metal to the π-cyclopentadienyl ring attached to it [57].



7.15

Apart from alkyls, a variety of other M–σ-organo complexes of π-$C_5H_5M(CO)_3R$, where M = Mo or W, are known where R = CH_2Cl [18], CH_2OMe, CH_2COOR [18], CH_2COOH (p. 210), $N_2C_6H_5$ [7, 8], —HN_2CH_2COOEt [7]. They are usually very similar in their chemistry to the π-$C_5H_5Fe(CO)_2$— analogues. Some exceptions to this statement are discussed on pp. 214, 343.

(*c*) *Cobalt, rhodium and nickel*

The dimethyl compounds π-$C_5H_5CoMe_2(Ph_3P)$ and the analogous π-$C_5H_5RhMe_2(SMe_2)$ have been isolated [57*a*, 48*b*]. Also, a series of alkyl and aryl complexes π-C_5H_5NiRL, where L is a tertiary phosphine and R is the hydrogen ligand are known [57*b*]. All these compounds are prepared from the corresponding iodides using Grignard reagents.

H. Carbonyl alkyl, aryl and acyl complexes

The preparation of organo–σ-metal carbonyl complexes is discussed in section A. The occurrence of metal carbonyl alkyls and aryls closely parallels that of the carbonyl hydrides. All the known complexes in this class obey the 18-electron rule and they are rather reactive.

(*a*) *Manganese and rhenium*

The crystalline methyl complexes $MeM(CO)_5$, where M = Mn or Re, are stable to oxidation and are thermally stable at room temperature [14, 58]. The ethyl and n-propyl analogues of manganese pentacarbonyl are very much less stable [21]. The manganese complex $(CO)_5Mn(CH_2)_3Mn(CO)_5$, prepared from $Br(CH_2)_3Br$, has an unusual proton magnetic resonance spectrum which suggests that there may be interaction of the hydrogens of the α-carbons with the manganese atom [59].

Treatment of $MeMn(CO)_5$ with ligands frequently gives substituted acyls, $MeCOMn(CO)_4L$; these reactions are discussed on p. 258.

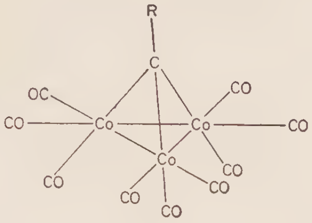
(*b*) *Cobalt*

The volatile methylcobalt tetracarbonyl is thermally very unstable, m.p. —44°, and it decomposes at —35° [60]. It is readily oxidized. The acylation reactions and the role of alkylcobalt carbonyl complexes in catalytic hydroformylation reactions are discussed on p. 334 and in chapter 9 respectively.

Treatment of the anion $[Co(CO)_4]^-$ with carbon tetrachloride or bromoform gives the unusual trinuclear complex $Co_3(CO)_9CR$ 7.16, where R = Cl or H respectively [61]. The chloride may also be prepared from CCl_4 and $Co_2(CO)_8$ [62]. Analogous complexes where R = CH_3 or $R'CH_2$ have been prepared from acetylenes and $Co_2(CO)_8$ (see p. 294).

The structure of the methyl derivative, 7.16, R = Me, has been found by X-ray diffraction.

Complexes analogous to 7.16 are known with silicon [63] or tin [64] in place of the apical carbon.



7.16

(*c*) *Platinum*

Some *n*-octylplatinum complexes, e.g. octyl PtCO(acetylacetone), have been prepared by a rather unusual route [64*a*], viz.,

$$\begin{tikzcd} Li_2PtCl_4 + \text{oct-1-ene} \arrow[r, "HCO_2H", "\substack{\text{dimethylformamide}\\ \text{(DMF)}}"'] & \substack{[n\text{-OctylPtCOClDMF}]\\ \text{not isolated}} \arrow[d, "\text{acetyl-acetone}"] \\ & n\text{-octylPtCO(acac)} \end{tikzcd}$$

The carbon monoxide group on the platinum must have been abstracted from the formic acid, see p. 335.

(*d*) *Miscellaneous*

A number of silicon analogues of alkyl metal carbonyls have been prepared, e.g. $H_3SiCo(CO)_4$ [65, 66] and $Ph_3SiMn(CO)_5$ [67]. Similarly, tin–metal carbonyls, e.g. $Ph_3SnMn(CO)_5$, are known [67, 68]. An unusual borine complex $[Re(CO)_5BH_3]^-$ has been described [69]. The π-cyclopentadienyl carbonyl complexes which form alkyls also give other derivatives of the Group IV elements, e.g. π-$C_5H_5Fe(CO)_2ER_3$, where E = Si, Ge, Sn or Pb and R = alkyl, aryl or halogen, π-C_5H_5Mo(or W)$(CO)_3ER_3$, and $(\pi$-$C_5H_5NiCO)_2$—$SnCl_2$— [69*a*].

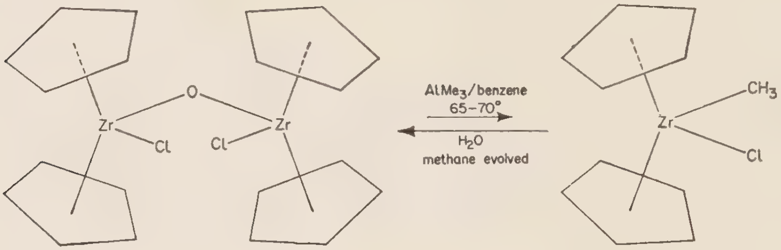
I. Bis-π-cyclopentadienyl alkyl and aryl complexes

The known complexes in this class are shown in Table 23. The bis-π-cyclopentadienyl titanium alkyls and aryls are considerably more stable to heat, oxygen and hydrolysis than are the alkyl titanium halides.

In contrast, the mono-π-cyclopentadienyl trimethyl titanium and triphenyl titanium complexes are very readily oxidized and hydrolysed [70, 71].

The greater overall stability of the bis-π-cyclopentadienyl complexes probably arises mainly from an increased kinetic stability rather than from any large increase in the Ti–σ-carbon bond energies.

The monomethyl zirconium complex, 7.17, is rapidly hydrolysed although the compound is thermally quite stable, 191–193° d [72]. The



7.17*a* 7.17

bi-nuclear complexes $(\pi\text{-}C_5H_5)_2ZrR—O—RZr(\pi\text{-}C_5H_5)_2$ where R = C_6H_5—or p-$CH_3C_6H_4$—, have been prepared from 7.17*a*, and the corresponding aryl-lithium reagent [72*a*].

Reaction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with triethylaluminium is thought to give the unstable binuclear complex $(\pi\text{-}C_5H_5)_2ZrCl—CH_2CH_2—ClZr(\pi\text{-}C_5H_5)_2$ [72*b*].

J. σ-Bonded organic derivatives of particular metals

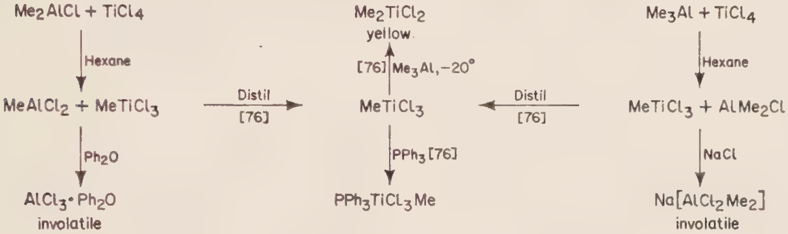
(*a*) *Pure alkyl and aryl complexes and alkyl halides of titanium, vanadium, niobium, tantalum and manganese*

There are few complexes known under this heading (see Table 23) and they are amongst the most reactive and unstable organometallic complexes known.

(*i*) *Titanium complexes.* In order to illustrate the extreme care and special conditions necessary in the preparation of titanium–alkyl complexes, the preparation of tetramethyltitanium is briefly described.

During the preparation [73, 74] all of the apparatus to which the titanium complex has access must be kept well cooled. In a typical preparation, methyl-lithium in ether (1 molar) is added drop by drop during an hour to a suspension of $TiCl_4$–diethylether complex in ether at −80°C, with vigorous stirring. The solution darkens to orange-red and finally to green. The mixture is stirred for a further half-hour at −80°C and then the reaction mixture is placed under vacuum and the volatiles are collected at −80°C. When a yellow colour (due to Me_4Ti) is noticed in the distillate, the distillate is collected separately. The yellow condensate of Me_4Ti is concentrated by low-temperature vacuum distillation. The pure Me_4Ti forms bright yellow crystals at −80°C which are very sensitive to oxidation and which start to decompose thermally >−78°C [74]. It does not react with CO_2 below −50°C, but reacts with aldehydes and ketones giving alcohols. With diamines, orange-red adducts of the type (diamine)$TiMe_4$ are formed. They are stable at 0° for hours but readily hydrolyse and oxidize [75].

Alkyltitanium halides are prepared using a variety of alkylating agents. Methyltitanium trichloride may be prepared from methyl aluminium compounds.



In the above reactions volatile aluminium compounds are made involatile by complex formation, as shown, enabling the $MeTiCl_3$ to be separated by distillation. Also shown are some reactions of $MeTiCl_3$ including complex formation with donor ligands.

The preparations of a variety of other alkyl and aryl titanium complexes are outlined in Figure 56. All these alkyl and aryl titanium complexes are

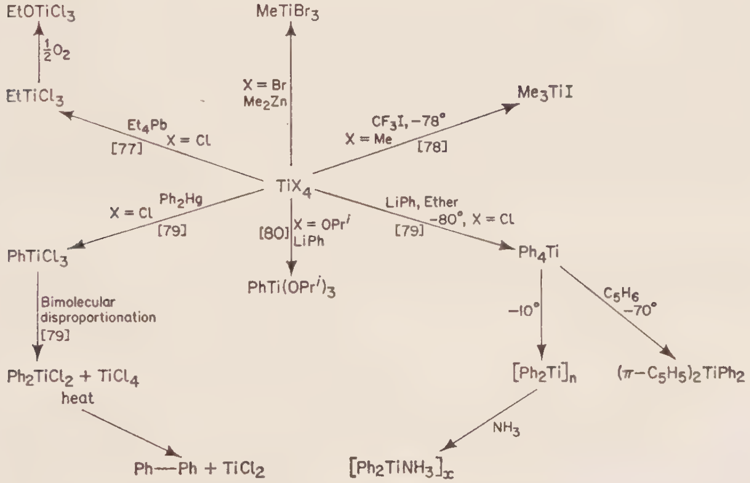


Fig. 56. Preparation and reactions of some alkyl and aryl titanium complexes. X represents halogen or hydrocarbon ligands as indicated

very unstable to oxidation and most are thermally unstable even at −10°C. The white crystalline phenyltitanium tri-*iso*-propoxide (m.p. 88–90°) is the most stable complex and shows no decomposition at 10°C after one year. Its thermal decomposition products such as benzene and biphenyl suggest that the decomposition proceeds via phenyl radicals. Although these complexes are so unstable thermally they may, in the rigorous absence of air, be studied with relative ease at −80°C. It appears that the thermal stability of these complexes, R_nTiX_{4-n}, increases with the electronegativity of R, and decreases with increasing n [80]. Their decomposition may occur, either by homolytic fission affording radicals or by bimolecular disproportionation [79, 81]. Mostly the complexes are rapidly hydrolysed by water but they do not react with CO_2 (compare Grignard reagents and LiR). As shown in Figure 56, oxidation by oxygen may give alkoxy derivatives.

(*ii*) *Vanadium, niobium and tantalum.* Some evidence for a very unstable phenyl–vanadium complex has been obtained [82] and a paramagnetic, deep purple complex, $Li_4[VPh_6]$, has been noted [83]. It is prepared by treatment of $VCl_3(dioxan)_3$ with phenyl-lithium and is stable at room temperature.

Treatment of niobium or tantalum pentachloride with dimethylzinc in pentane gives golden-yellow crystals of the trimethyl derivatives Me_3MCl_2, where M = Nb or Ta. These complexes decompose at room temperature and are readily oxidized. The tantalum complex is less thermally stable than the niobium analogue [84].

(*iii*) *Manganese.* Dimethyl- and diphenyl-manganese have been briefly described [73]. They are prepared from manganese(II) iodide and methyl-lithium or phenyl-lithium. Dimethylmanganese forms a bright yellow powder which readily detonates and is probably polymeric since it is insoluble in ether. It dissolves in methyl-lithium affording the stable complex $LiMnMe_3$ (d. 100°C) and it reacts with MnI_2 giving MeMnI as a heavy oil.

Diphenylmanganese is a green, sparingly soluble solid which may be crystallized from tetrahydrofuran. The constitutions of these compounds are not yet established.

(*b*) *Alkyl and aryl complexes of chromium*

The formation of unstable organochromium complexes was first observed in 1903 [85], but it was not until 1919 that Hein successfully isolated a ‘polyphenyl chromium complex’, from the reaction between phenylmagnesium bromide and chromium(III) chloride in anhydrous ether [86]

The exacting work by Hein on these mysterious complexes and their later study by Zeiss is a fascinating story.† At first the 'polyphenyl' chromium complexes were formulated as the cationic σ-bonded phenyl complexes $[(C_6H_5)_xCr]^+$, where $x = 4$, 3 or 2. However, despite the apparent differences in the valencies of these complexes they all had the same degree of paramagnetism [87] and similar absorption spectra. These observations were explained by the introduction of hydrogen and diphenyl ligands as well as phenyl. Thus $[(C_6H_5)_2Cr]^+$ was reformulated as $[(C_6H_5{-}C_6H_5)CrH_2]^+$ and the tetraphenyl complex $[(C_6H_5)_4Cr]^+$ was proposed to be $[(C_6H_5{-}C_6H_5)_2CrH]^+$. However, evidence which was incompatible with these formulations was soon found; thus the

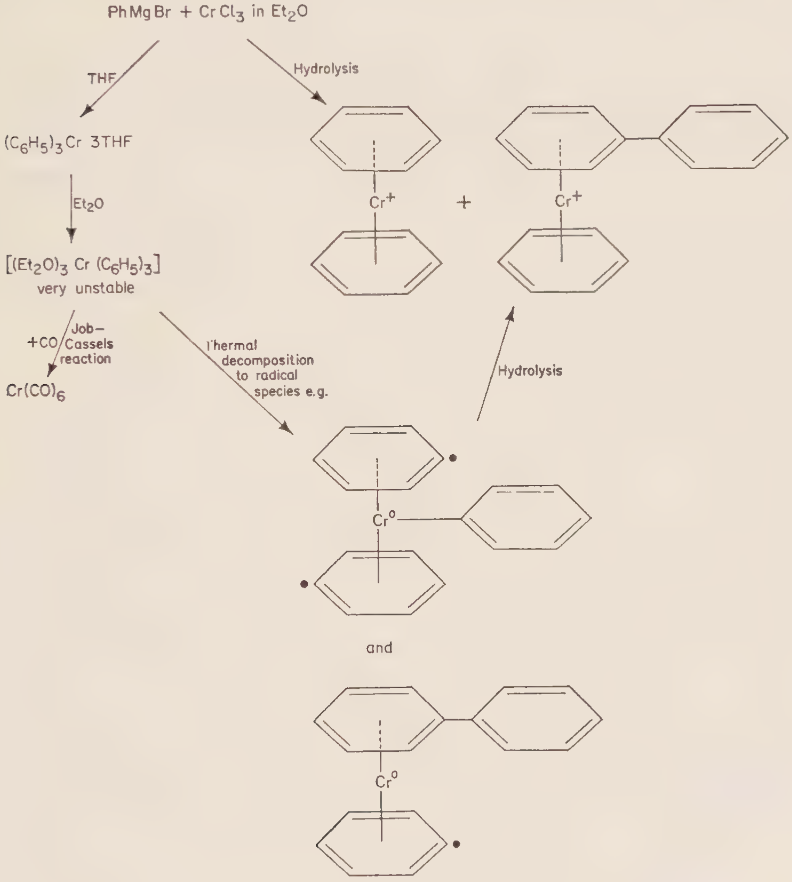


Fig. 57. The decomposition of chromium(III) phenyl derivatives to π-arene chromium complexes

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† Reviews of earlier work are given in refs. [91] and [92].

solvolysis of the complexes with D_2O did not give deuterated diphenyl. In 1954, it was proposed that the complexes were sandwich complexes with π-bonded arene ligands such as benzene and diphenyl [88, 89, 90] (see Figure 57). This proposal has been abundantly confirmed and the detailed chemistry of such π-arene complexes is discussed in Chapter 5.

Subsequent studies by Zeiss and co-workers have shown that the formation of these π-arene complexes proceeds via chromium–σ-aryl complexes which they have isolated in a few cases.

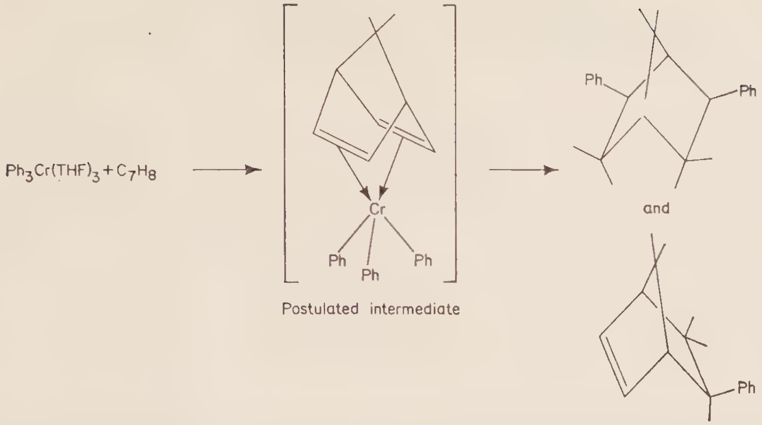
(*i*) *Neutral alkyl and aryl chromium complexes.* A number of tris-aryl chromium(III) complexes, Ar_3CrL_3, are known where the ligand (L) is an ether or a nitrogen ligand. They are all readily oxidized and are paramagnetic, having three unpaired electrons. These complexes presumably have an octahedral co-ordination of the ligands about the chromium and, as in all chromium(III) complexes, the kinetic stability associated with the d^3-electron configuration is found.

Triphenylchromium has been isolated as the deep red tris-tetrahydrofuranate, $(C_6H_5)_3Cr(THF)_3$, by treatment of anhydrous chromium(III) chloride in tetrahydrofuran with phenylmagnesium bromide in an *exact* 1 : 3 mole ratio at $-20°$ [93, 94]. Evidence for the presence of σ-bonded phenyl groups is shown by its reaction with mercuric chloride, giving phenylmercury(II) chloride in quantitative yield.

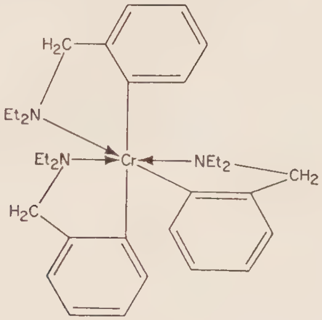
A study of the properties of $(C_6H_5)_3Cr(THF)_3$ demonstrates how π-arene complexes may be formed from σ-bonded aryl complexes. If the tris-tetrahydrofuranate is washed with ether the tetrahydrofuran is removed and a black powder is formed. This powder is at first strongly paramagnetic and the paramagnetism decreases with time. Hydrolysis of the powder forms π-arene chromium complexes. These properties suggest that the black powder contains radical species and the formulations, exemplified in Figure 57, have been suggested [91]. The formation of diphenyl has been proposed to occur by the '*para*-coupling' of phenyl radicals, within the environment of the chromium atom [95].

The mesitylene complex $(Mes)_3Cr(THF)_3$ is more stable than the phenyl analogue and does not rearrange when the tetrahydrofuran is removed. Indeed, the monotetrahydrofuranate $(Mes)_3Cr(THF)$ has been isolated [95*a*]. It appears that washing the complexes $(p\text{-}RC_6H_4)_3Cr(THF)_3$ with diethylether or benzene gives π-arene complexes only when R = Ph or CH_3 [95*b*].

Both the triphenyl- and trimesityl Cr(III) complexes react with olefins with addition of the aryl group to C=C systems. Thus the products formed from norbornadiene are shown below together with a postulated intermediate [96].

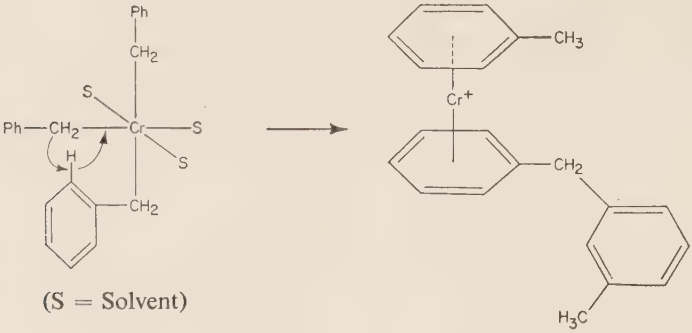


Treatment of anhydrous chromium(III) chloride with *o*-lithiobenzyldiethylamine affords garnet-red crystals of the complex 7.18. It is thermally stable at room temperature but is readily oxidized and hydrolysed. A related complex prepared from *o*-lithiophenyldimethylamine has also been described [97]. In some cases, reduction to chromium(II) complexes may occur.



7.18

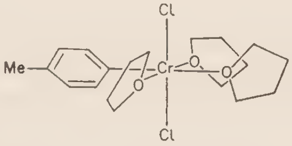
Treatment of chromium(III) chloride with benzylmagnesium bromide in ether at —78° gives a very unstable orange substance, which readily decomposes. The course of the decomposition depends on reaction variables such as the ether used as the solvent, stoicheiometry, temperature, and the mode of addition of the reactants. The first step in the reaction is the formation of solvated $(PhCH_2)_3Cr(III)$ complexes. The decomposition products of these include π-arene derivatives such as complex 7.19 or the uncomplexed arenes. On this evidence, it is proposed that the orange complex may be the σ-benzyl complex 7.20 [98]. It is suggested that the mechanism of formation of the complex 7.19, which is one of the products, proceeds via the loss of an *ortho*-hydrogen [98*a*], e.g.



(S = Solvent)

7.20 7.19

From the reaction of $CrCl_3(THF)_3$ and *p*-tolylMgBr the mono-aryl derivative *p*-$MeC_6H_4CrCl_2(THF)_3$ has been prepared. Its structure has been determined and is shown in 7.20*a* [98*b*].



7.20*a*

A related benzyl pyridine complex $PhCH_2CrCl_2Py_2$ has been prepared [98*c*].

The complex $MeCrCl_2{\cdot}THF$ may be prepared from $CrCl_3$ and MeMgCl in tetrahydrofuran.

(*ii*) *Anionic alkyl and aryl chromium complexes.* Treatment of chromium(III) chloride with organolithium reagents affords yellow-red complexes such as $Li_3[CrR_6]_n$. Ether, where the ether may be dioxan, tetrahydrofuran or diethylether; n varies from zero to four. It is probable that in most of these complexes the ether molecules co-ordinate to the alkali metal cation. The preparation and some properties of these complexes are shown in Figure 58. All the complexes are readily hydrolysed and oxidized, and are paramagnetic with three unpaired electrons. Tungsten(V) bromide and phenyl lithium in diethylether gives a related black, pyrophoric complex, $Li_2[WPh_6].3Et_2O$, which absorbs hydrogen forming diamagnetic $[Li_2(WHPh_2)]_n$ [109].

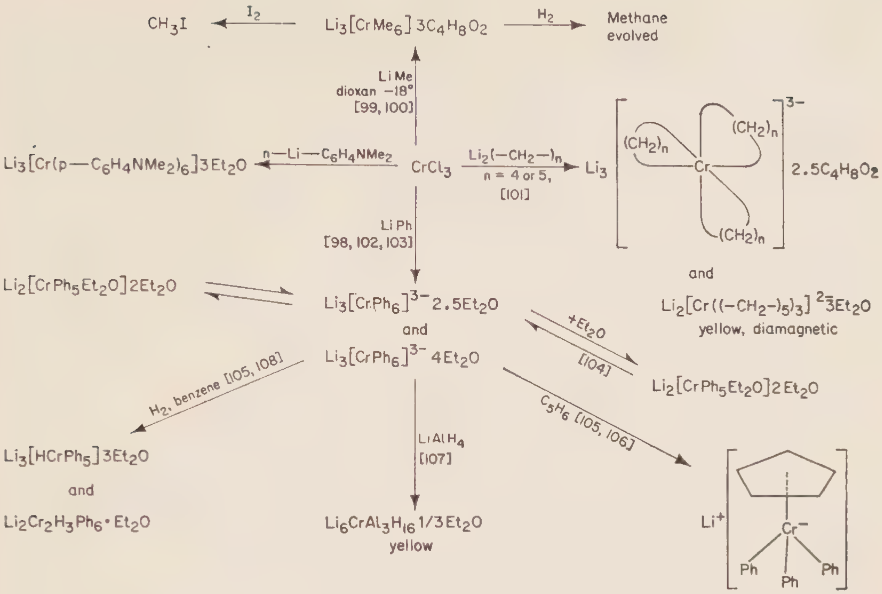
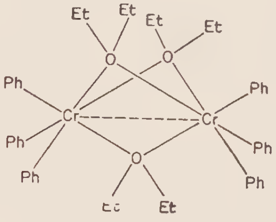


Fig. 58. Some preparations and reactions of anionic alkyl and aryl chromium complexes

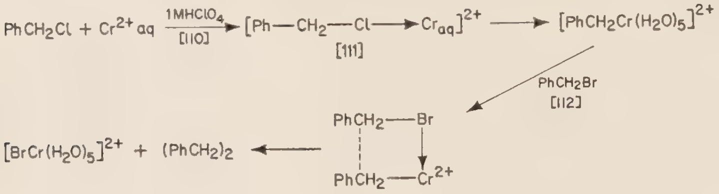
Dimeric phenyl chromium(II) complexes, $M_2[Cr_2Ph_6]3Et_2O$ have been isolated [102]. Their low magnetic moment suggests a degree of spin-pairing by formation of a Cr–Cr bond; a possible structure of the anion is 7.20*b*.



7.20*b*

From chromium(II) chloride, the yellow tetramethyl complex $[Li_2[Cr(CH_3)_4(THF)_2]]_2$ may be prepared [99, 100]; it has a magnetic moment of 0·5 B.M. Finally, there is evidence that treatment of $CrCl_3(THF)_3$ with vinylmagnesium chloride forms an unstable vinyl–Cr complex [100*a*].

(*iii*) *Penta-aquo chromium(III) alkyls.* Aqueous acid solutions of chromium(II) ions show a remarkable reactivity with some alkyl halides. Despite the ease with which the majority of σ-organo complexes undergo hydrolysis chromium(II) ions and alkyl halides react to form penta-aquo chromium(III) complexes $[RCr(III)(H_2O)_5]^{2+}$. The benzyl complex $[PhCH_2Cr(H_2O)_5]^{2+}$ was the first of this type to be found [110] and kinetic studies suggest that its formation may involve a bridging chloro intermediate and subsequent production of benzyl radicals, viz.,



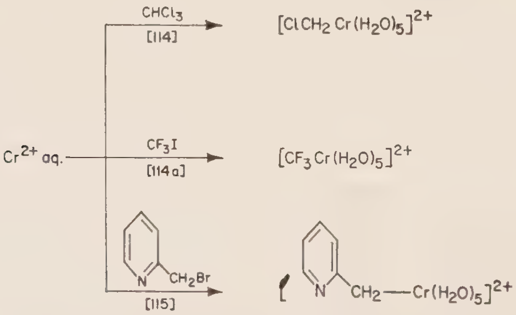
7.21

At room temperature, the benzyl cation $[PhCH_2Cr(H_2O)_5]^{2+}$ in solution has a half-life of about 1½ days. Evidence for a benzyl-chromium σ-bond in this complex comes from the reaction with mercuric chloride which takes place without change of pH:

$$[PhCH_2Cr(H_2O)_5]^{2+} + HgCl_2 + H_2O = PhCH_2HgCl + [Cr(H_2O)_6]^{3+} + Cl^-$$

Other reactions which support the formulation are acid cleavage, which gives toluene, and the decomposition product bibenzyl [112]. Bibenzyl is also formed when the solutions of $[PhCH_2Cr(H_2O)_5]^{2+}$ are treated with benzyl bromide [112]. It is proposed that this reaction occurs via an intermediate such as 7.21 [112]. In a related reaction allyl bromide gives $C_6H_5CH_2CH_2CH{=}CH_2$ [113].

Further examples of the formation of complexes $[RCr(H_2O)_5]^{2+}$ are:



The trifluoromethyl complex is stable in solution at room temperature for several weeks [114*a*]. Related studies include the homogeneous reduction of alkyl halides, RI, by chromium(II) ions in aqueous dioxan. The products are R_2 and RH and presumably the reactions involve RCr^{2+} intermediates [113].

(*c*) *Cobalt(III) complexes with σ-bonded ligands*

The cobalt(III) ion has a d^6-electron configuration and, in a low-spin state, is diamagnetic. The octahedral complexes of low-spin d^6 metal ions are well known to be relatively non-labile, i.e. kinetically stable to dissociation of metal–ligand bonds. As discussed earlier (p. 220), non-lability is essential for the isolation of metal–σ-organo complexes and, from this point of view, it is not surprising that a number of stable complexes $[(CN)_5CoR]^{3-}$ are known.

The complexes $[(CN)_5CoR]^{3-}$ may be prepared from the anion $[(CN)_5Co]^{3-}$ and organohalides; the reactions, given below, may be compared with those of metal carbonyl anions, e.g. $[Co(CO)_4]^-$

$$[(CN)_5Co]^{3-}-\left|\begin{array}{l}
\xrightarrow{C_6H_5CH_2Br\ [116]} [(CN)_5CoCH_2C_6H_5]^{3-} \\
\xrightarrow{CH_2{=}CHCH_2Cl\ [117]} [(CN)_5CoCH_2CH{=}CH_2]^{3-} \\
\xrightarrow{CH_2{=}CHCl\ [122]} [(CN)_5CoCH{=}CH_2]^{3-} \\
\xrightarrow{HC{\equiv}CH\ [118]} [(CN)_5Co{-}CH{=}CH{-}Co(CN)_5]^{6-} \\
\xrightarrow{CF_2{=}CF_2\ [119]} K_6[(CN)_5Co{-}CF_2{-}CF_2Co(CN)_5]2H_2O \\
\xrightarrow{SnCl_2\ [120]} [(CN)_5Co{-}SnCl_2{-}Co(CN)_5]^{6-}
\end{array}\right.$$

Kinetic studies have shown that these reactions are first order in both pentacyanocobalt(II) and in the halides. A postulated mechanism is [121, 121*a*],

$$[(CN)_5Co]^{3-} + RX \xrightarrow[\text{slow}]{} [(CN)_5CoX]^{3-} + R^{\cdot}$$

$$[(CN)_5Co]^{3-} + R^{\cdot} \xrightarrow[\text{fast}]{} [(CN)_5CoR]^{3-}$$

Also shown above are reactions with acetylene and C_2F_4.

Related σ-organo derivatives may also be prepared using the hydride $[(CN)_5CoH]^{3-}$. Thus C_2F_4 gives the anion $[(CN)_5CoCF_2CF_2H]^{3-}$, whose structure has been determined by X-ray diffraction (see p. 000). Other reactions which are typical of metal–hydrogen additions occur, e.g.

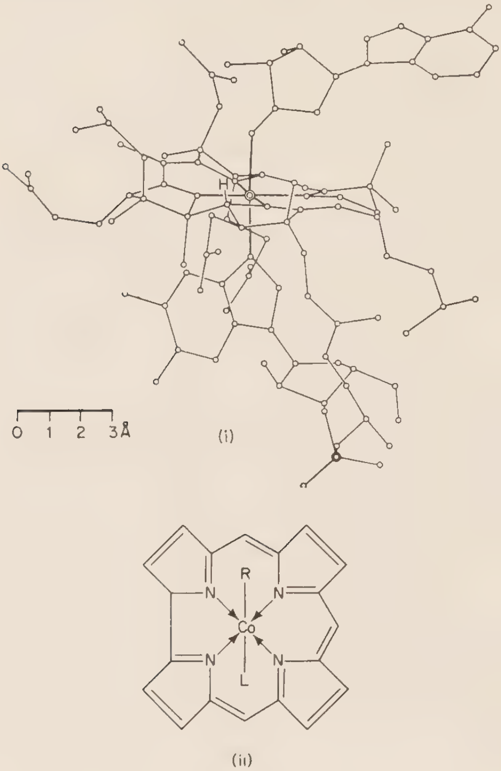
$$[(CN)_5CoH]^{3-} \xrightarrow{C_4H_6\ [122]} [(CN)_5CoC_4H_7]^{3-}$$

Aqueous solutions of the complexes $[(CN)_5CoR]^{3-}$ are stable in the absence of oxygen for periods of weeks but are decomposed by acids. An interesting reaction of some of them is the formation of nitrile derivatives RCN on treatment with acid and then base. It is proposed that the reactions proceed via migration of the group R, as shown [117].

$$\overset{R}{\overset{|}{Co}}{-}C{\equiv}N \xrightarrow{H^+} \overset{R}{\overset{|}{Co}}{-}C{\equiv}\overset{+}{N}H \longrightarrow \overset{+}{Co}{-}\overset{R}{\overset{|}{C}}{=}NH \xrightarrow{OH^-} RCN + H_2O$$

This mechanism may be compared with that proposed for the acylation of alkyl-metal complexes (see p. 258). The catalytic properties of some of these complexes are discussed in Chapter 9.

Vitamin B_{12} *chemistry.* The structure of the 5,6-dimethylbenzimidazole-cobamide-coenzyme, as found in the wet crystals, has been determined by X-ray and neutron diffraction (see Figure 59) [123, 124]. A schematic representation of cyanocobalamin (Vitamin B_{12}) is also shown, 7.22. The Vitamin B_{12} coenzyme is the first example of a naturally occurring transition metal–σ-carbon bond.



7.22

Fig. 59. (*i*) The atomic positions in one molecule of the 5,6-dimethylbenzimidazole-cobamide-coenzyme as found in the wet crystals and viewed along the b axis (after Lenhert and Hodgkin [123]). (*ii*) A schematic representation of Vitamin B_{12}

Reduction of cyanocobalamin with sodium borohydride or zinc and acetic acid affords a diamagnetic, grey-green product (Vitamin B_{12s}) which reacts with acyls, alkyl halides and with olefins to give cobalamin-σ-organo derivatives (see Figure 60) [125, 126]. It is not known whether the

Vitamin B_{12s} species is a cobalt(I) anion or whether it is cobalamin hydride. Some of the reactions shown in Figure 60 suggest at first sight that a Co—H bond is present whilst other reactions are characteristic of anionic cobalt complexes. However, all the reactions can be understood in terms of either a hydride or anionic complex alone. Despite careful examination of the proton magnetic resonance spectrum of solutions of Vitamin B_{12s}, no resonance which may be assigned to a Co–hydrogen is observed. The absence of a suitable hydrogen resonance is not conclusive negative evidence, since, e.g., line broadening due to exchange may occur.

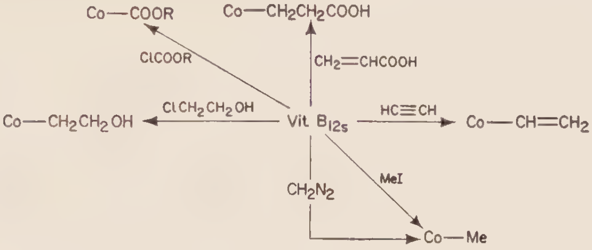
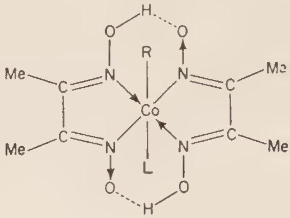


Fig. 60. Some reactions of Vitamin B_{12s}

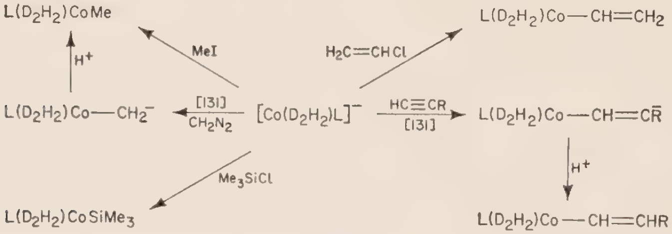
The simple alkyl derivatives of cobalamin are quite stable to cleavage by acids and displacement of the alkyl ligand by CN^-. The stability to CN^- decreases with increasing electronegativity of substituents on the σ-organo group. It is suggested that the C–Co bond becomes more susceptible to nucleophilic attack as it becomes more polarized [127]. The derivatives Co—CH_2CH_2OH and Co—CH_2—CH_2OMe are very readily hydrolysed by dilute acids, possibly due to the —*I* effect of the oxonium cations, Co—CH_2—CH_2O^+HR, which are first formed. No evidence for olefin–cobalamin complexes has been found and it may be that they would be very unstable. The instability could arise from both the relatively high oxidation state of the cobalt(III), which would be expected to reduce the availability of the *d* orbitals for back-donation, and from steric factors. The structure given in Figure 59 shows that there is a hydrogen atom on a carbon which is ~2·5 Å from the cobalt z-axis and about 1·5 Å above the xy plane through the cobalt. This hydrogen would prevent the free rotation of an π-ethylenic group about the z-axis of the cobalt and limit the possible orientations of the C=C system. It may be that in cobalamin–alkyls there is a reduced β-effect of the cobalt on the alkyl ligand and, hence, the cobalt–alkyl system will be less reactive and less liable to decomposition than, for example, the Co—R systems in $[(CN)_5CoR]^{3-}$ or cobaloxim–alkyls (see below).

The catalytic role of cobalamin complexes is discussed in [125].

A number of 'model' Vitamin B_{12} systems have been prepared and studied. An aetioporphyrin I cobalt(III) methyl complex has been prepared [128] and methyl cobalt(III) phthalocyanine is also known [129]. The dimethylglyoxime complex, 7.23, where R = CN and L = Ph_3P, pyridine or NMe_3, shows marked analogy to cyanocobalamin; for this reason, it is called cyanocobaloxim (the complex is represented $Co(D_2H_2)CNL$ [130]). Cyanocobaloxim is readily reduced and the products may be considered analogous to Vitamin B_{12s}. The preparation of cobaloxim–σ-organo derivatives from the reduced cobaloxim complex is shown below and may be compared with the reactions of Vitamin B_{12s}, e.g.



7.23



The nature of the reduced cobaloxim species in aqueous solution is unknown but it is suggested that there may be both a hydride and an anionic complex in equilibrium [130], e.g.

$$[Co(D_2H_2)L]^- \rightleftharpoons [Co(D_2H_2)LH$$

A number of cobaloxim–metal complexes, $[Co(D_2H_2)BR]$, where R = Ph_3Si, Ph_3Ge, Ph_3Sn and Ph_3Pb, have been described [132].

A related, tetradentate ligand bis(acetylacetone)ethylenediamine, $(MeCOCH_2CMe{=}NCH_2)_2$ (abbreviated to BAE), also stabilizes cobalt–alkyl complexes, including the pentaco-ordinate (BAE)CoR [132*a*].

(*d*) *Alkyl complexes of platinum(IV)*

Tertiary phosphine complexes in this class are discussed in section F(*a*)(*iii*).

Trimethylplatinum(IV) complexes. There are a considerable number of trimethylplatinum(IV) complexes in which, except for hexamethyldiplatinum, whose structure is unknown, it appears that the platinum has an octahedral environment.

Treatment of $PtCl_4$ with methylmagnesium iodide in benzene gives the tetrameric, orange complex $[Me_3PtI]_4$ [133, 134]. Much better yields (70%) of the complex are obtained by treatment of *cis*-dipyridinetetrachloroplatinum with methylmagnesium iodide [135]. The first product formed is the dimer $[pyPtMe_3L]_2$, from which $[Me_3PtI]_4$ is obtained by reaction of the dimer with ethylenediamine followed by hydrogen iodide, as shown in Figure 61. The other trimethylplatinum(IV) complexes are prepared from the iodide. The structure of the chloro analogue $[Me_3PtCl]_4$ has been determined by X-ray studies [136], 7.24, and shows that the platinum has an octahedral environment. Numerous derivatives of $[Me_3PtI]_4$ are known and their preparations are given in Figure 61. The proton magnetic resonance spectra of some complexes $[Me_3PtX]_4$ show that in aqueous solution they ionize extensively giving cations such as $[Me_3Pt(H_2O)_3]^+$ [136*a*]; in benzene the tetramers remain undissociated [136*b*].

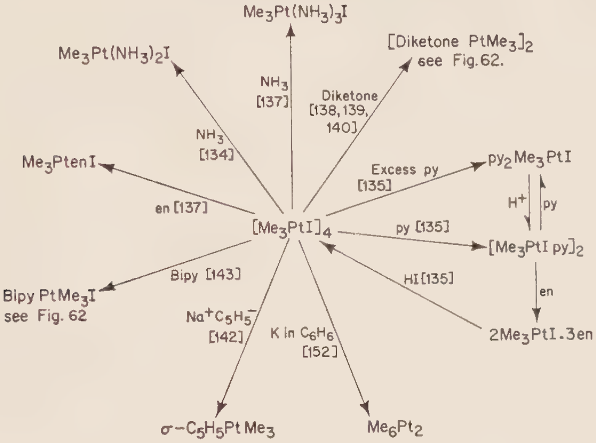
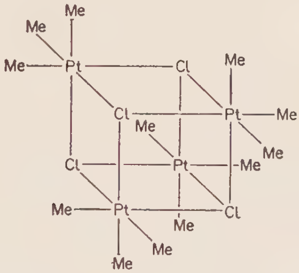


Fig. 61. Some reactions of $[Me_3PtI]_4$



7.24

As shown in Figure 61, the diketone complexes [diketonePtMe$_3$] are known. At first sight it is difficult to see how these complexes can have an octahedrally co-ordinated platinum. However, X-ray studies have shown that the diketone ligand is acting as a tridentate chelate (see Figure 62). In the case of the complex trimethyl-(1-acetylacetone) bipyridyl platinum, it would seem that the platinum might be seven-co-ordinate. X-ray studies

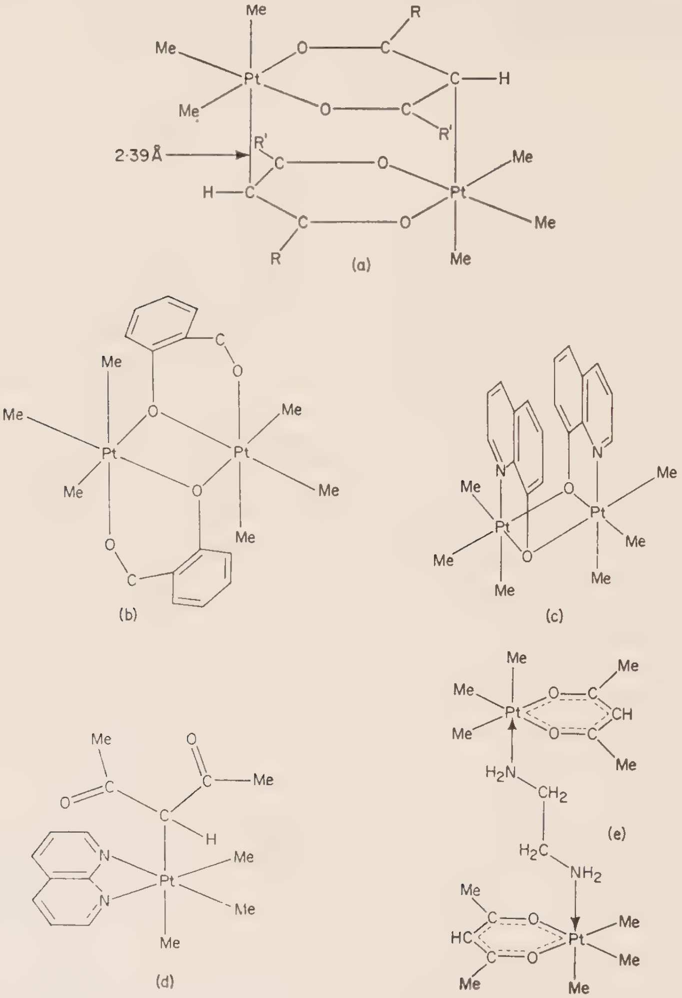


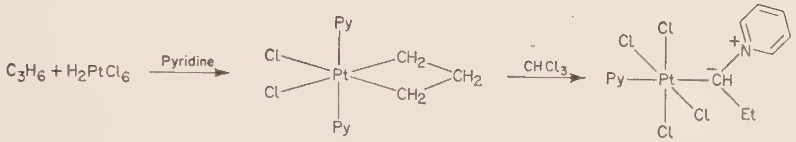
Fig. 62. (*a*) The structure of some diketone trimethyl platinum (IV) complexes, where $R = R' = C_3H_7$, Pt–Me is *av.* 2·02 Å, Pt–C is 2·39 Å (see above) [144]; where R = Me, R′ = OEt, Pt–Me is *av.* 2·09 Å, Pt–C is 2·56 Å [145]. (*b*) Trimethyl-(salicylaldehydato) platinum [146]. (*c*) Trimethyl-(8-hydroxyquinoline) platinum [146]. (*d*) Trimethyl-(1-acetylacetone)αα′bipyridylplatinum [147]. (*e*) μ-Ethylenediamine bis-[trimethyl-(acetylacetonato)platinum] [148]

show that there is in fact six-co-ordinate, octahedral platinum by virtue of a monodentate acetylacetone ligand bonding through the central carbon atom [147]. The structure is shown in Figure 62. A similar Pt—CH(COMe)$_2$ group is found in the complex K$^+$[Pt(acac)$_2$Cl]$^-$ [141], and possibly Na$_2$Pt(acac)$_2$Cl$_2$.5H$_2$O [149, 150].

For a number of years it has been thought that there existed a tetrameric tetramethylplatinum complex, [Me$_4$Pt]$_4$, which X-ray studies suggested to be analogous to [Me$_3$PtI]$_4$ but with bridging methyl groups [136]. Recent attempts to confirm this work have been unsuccessful and, in the light of the recent work, it seems probable that the crystals originally studied by X-rays were not a tetramethylplatinum complex but the hydroxide [Me$_3$PtOH]$_4$ [151]. Almost certainly [Me$_4$Pt]$_4$ has not yet been prepared and it is suggested that the original analyses may have been erroneous due to the presence of traces of amyl alcohol in the hydroxide.

Hexamethyldiplatinum is very soluble in benzene but insoluble in non-aromatic hydrocarbons. Preliminary X-ray analysis shows that the minimum molecular size in the solid is [Me$_3$Pt]$_{12}$, and it is suggested that benzene may act as a ligand and depolymerize the complex [152].

Cyclopropane complexes of platinum. Treatment of hexachloroplatinic acid, H$_2$PtCl$_6$, with cyclopropane affords a brown solid of composition C$_3$H$_6$Cl$_2$Pt [152*a*, 153]. With pyridine, a white complex is formed which has structure 7.25 [153]; this reacts in CHCl$_3$ forming the complex 7.26 [154].



7.25 7.26

(*e*) *Alkyls and aryls of copper, silver and gold*

The few complexes of these metals where the only ligands are alkyls or aryls are ill characterized, readily oxidized, thermally unstable, and frequently explosive. The products of their thermal decompositions may be complex but almost always involve formation of intermediate alkyl or aryl radicals [155, 156]. The alkyl and aryl complexes of these metals which have other ligands attached to the metal are more stable, and in particular, a considerable chemistry of stable alkyl gold complexes is known.

(*i*) *Copper*. The complexes [CuR]$_n$ are prepared using either Grignard

[157] or organolithium reagents, or organolead complexes, e.g.,

$$Cu(NO_3)_2 + Me_4Pb \longrightarrow Me_3Pb^+ + Cu^+ + Me^{\cdot}$$
$$Cu^+ + Me_4Pb \xrightarrow[\text{[155]}]{} Me_3Pb^+ + MeCu$$

The complexes CuR decrease in their thermal stability in the order R = phenyl > methyl > ethyl [155, 158]. Treatment of a copper mirror on glass with methyl chloride at 250°C causes movement of the mirror along the glass tube. From this experiment an average life for methylcopper of $3\text{–}5 \times 10^{-3}$ sec at 250°C is estimated [158*a*]. At room temperature, methylcopper forms an ether-insoluble, bright yellow powder which is highly shock-sensitive and decomposes to copper, methane and ethane [159]. It reacts with methyl-lithium forming the complex salt $Li^+[Me_2Cu]^-$, which is more stable. The infrared spectrum of methylcopper shows some analogy with that of methyl halides [160]. Phenylcopper, $[PhCu]_x$, separates as a grey powder on treatment of copper(I) iodide with phenyl-lithium or phenylmagnesium iodide. With excess phenyl-lithium the complex $[Ph_4Cu]PhLi.3{\cdot}5Et_2O$ is formed [161*a*]. It decomposes slowly at room temperature and vigorously at ~80°, forming copper and biphenyl. It is insoluble in most solvents but dissolves in pyridine, and it reacts with water giving benzene and cuprous oxide. With benzoyl chloride, it gives benzophenone but it does not react with benzonitrile [158].

The structures of the complexes CuR are unknown. Their general insolubility suggests a polymeric nature. For the alkyl complexes the structures may involve metal clusters or less probably complex salts such as $Cu^+[R_2Cu]^-$. The alkyl groups may form bridges, as in the trinuclear cobalt complexes (p. 294) and Al_2Me_6; with the phenyl group, the further possibility of π-bonding by the C_6 ring arises.

Triethylphosphine-σ-cyclopentadienylcopper, $(Et_3P)Cu\text{–}\sigma\text{-}C_5H_5$, prepared by the treatment of copper(I) oxide and cyclopentadiene in light petroleum with Et_3P is one of the most stable copper–σ-organo complexes known apart from alkynyl derivatives. The colourless crystals, m.p. 127–128°C, are not hydrolysed by water but give cyclopentadiene on treatment with acids. The complex is formulated as a σ-cyclopentadienyl derivative, primarily on the basis of infrared evidence [161].

(*ii*) *Silver*. Methylsilver complexes are precipitated when alcoholic silver nitrate is added to alcoholic tetramethyl-lead, at low temperatures [155, 156, 162, 163]. The products depend somewhat on the proportions of the reactants. For a wide range of ratios of the reactants, but with excess silver nitrate, the composition of the product is close to $(MeAg)_2AgNO_3$ [162, 164]. Methylsilver $[AgMe]_n$, is formed when excess tetramethyl-lead is used, at 0°C. Methylsilver decomposes forming *ethane* and silver [155].

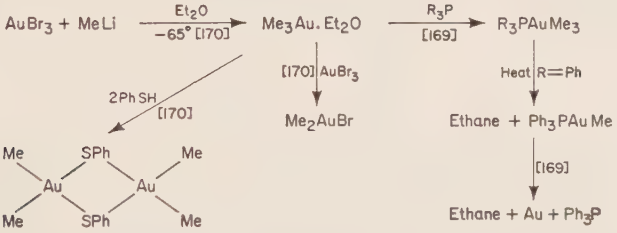
Aryl-lead, -tin and -bismuth complexes have been used in the preparation of unstable orange-yellow complexes $(ArAg)_2AgNO_3$ [156, 158]. Treatment of alcoholic silver nitrate with Et_3PbR, gives unstable complexes $[AgR]_n$, where R is an aryl or alkyl group. The complexes are all rather unstable though there appears to be some inverse relation between the stability of the complexes $[AgR]_n$ and that of the free radical R·. Thus the phenyl radical is rather less stable than the benzyl radical, and phenyl-silver decomposes at about −18° whilst benzylsilver has only a transient existence above −100° [165]. Styryl- and *iso*-but-1-enyl-silver are also relatively stable and they decompose at 0° and −30° respectively [165, 166]. Phenylsilver has also been isolated in an impure state from the reaction between silver halides and phenylmagnesium bromide. The product is explosive in the dry state [167].

(*iii*) *Gold.* Whereas the alkyl and aryl complexes of copper and silver are only known in the (I) oxidation state, gold forms derivatives in both the (I) and (III) states.

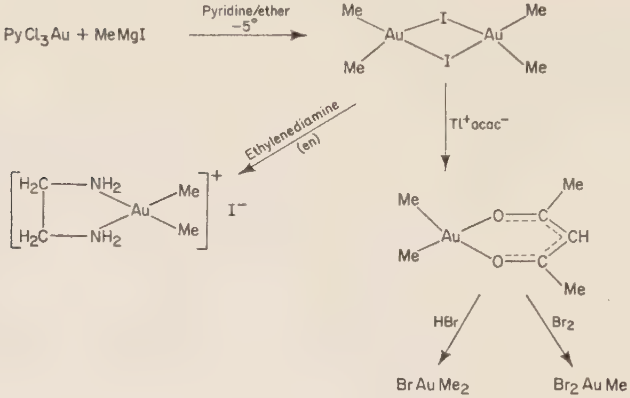
Treatment of the complexes PR_3AuX with Grignard reagents or, better, organolithium reagents, affords stable colourless monomeric complexes R_3PAuR', where $R' =$ Me, Et, Ph or $C{\equiv}CPh$ [168]. The co-ordination number of two in these complexes is typical of gold(I).

Very nearly all the known organic complexes of gold(III) are alkyls. Treatment of auric bromide with methyl-lithium in ether at −65° affords a very unstable trimethylgold species which is probably the etherate $Me_3Au.Et_2O$. At −40° the reaction mixture deposits a gold mirror and, at higher temperatures, rapid decomposition occurs with evolution of ethane and methane. Addition to the trimethylgold etherate at −80° of tertiary phosphines such as Me_3P or Ph_3P gives stable complexes Me_3AuPR_3 [169].

Studies of the decomposition of Ph_3PAuMe_3 show that the gaseous product is ethane *only* and no methane is evolved. These and other reactions of trialkylgold complexes are shown below.



A substantial chemistry of dimethylgold complexes has been described [171], and is exemplified overleaf.

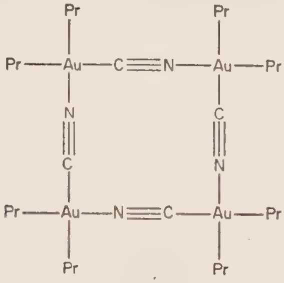


Bromo(diethyl)gold may be prepared similarly [172] and is also dimeric [173]. Treatment of this compound with bromine in carbon tetrachloride affords a markedly less stable dibromo derivative $(EtAuBr_2)_2$ [172] which decomposes quantitatively, as follows:

$$(EtAuBr_2)_2 \xrightarrow[\text{[172]}]{80\text{–}85°} 2EtBr + 2AuBr$$

Further, the dibromo complex is cleaved by ethylenediamine, affording $[Au\,en_2]Br_3$ and $[Et_2Au\,en]Br$, which suggests the complex may have the unsymmetrical structure $Br_2Au—\mu Br_2—AuEt_2$. In support of this observation, the analogous propyl derivative has been shown to have a high dipole moment 5·5 D.

Tetrameric cyano(di-n-propyl)gold has been shown by X-ray studies [174] to have the structure 7.26*a*. The tetrameric cyano(diethyl)gold [175] is presumably similar. A number of other diethyl gold(III) complexes are known and their chemistry is illustrated in Figure 63. Generally the complexes are stable at room temperature but they may detonate on warming.



7.26*a*

A series of related dialkylgold(III) N,N-dialkyldithiocarbamates have been prepared; using N-ethylpiperidinium tetrachloroaurate yields of the complexes, 7.27, of 60–80% were found [176].

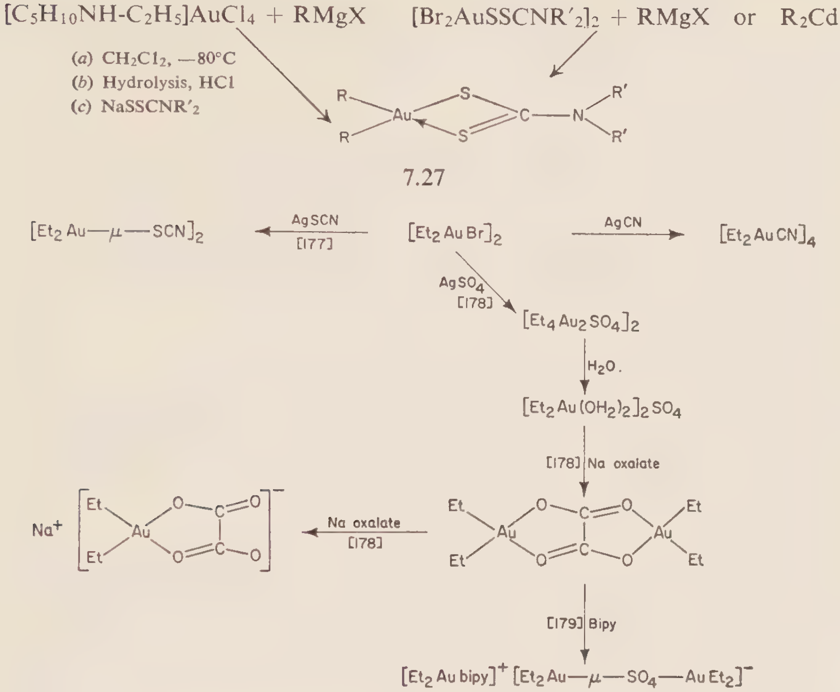


Fig. 63. Some dialkyl gold complexes

Aryl-gold complexes. There are no well-characterized aryl-gold(I) complexes; a very unstable $PhAuCl_2$ has been mentioned [180]. Gold(III) chloride chlorinates benzene and is itself reduced to gold(I) chloride. This reaction is stopped by the addition of ether or ethylacetate, and if this is done at an intermediate stage then the aryldichlorogold derivative may be isolated as pale yellow crystals. In water $PhAuCl_2$ is only slightly soluble but in aqueous sodium chloride solution it dissolves readily; a complex $Na^+[PhAuCl_3]^-$ may be formed.

I.2. TRANSITION METAL–ACYL COMPLEXES

Transition metal–acyl complexes, M—COR, may be formed either from an acyl halide and metal anions (compare alkyls, see section A), or, by carbonylation of some metal carbonyl-alkyl, M–σ-R_h, complexes. These carbonylation reactions are frequently reversible. Indeed, with some alkyl cobalt tetracarbonyl complexes infrared and kinetic studies

[181, 182, 183] show that at room temperature in solution they are in equilibrium with acyltricarbonyl derivatives, e.g.

$$\mathrm{RCOCo(CO)_3 \rightleftharpoons RCo(CO)_4}$$

In general, acyl complexes M—COR$_h$, where R_h = allyl, are thermally more stable than when R_h = alkyl.

A. The carbonylation of pentacarbonylmanganese alkyls and aryls†

The carbonylation of methylmanganese pentacarbonyl and the decarbonylation of acetylmanganese pentacarbonyl have been studied in detail. The thermal decomposition of acetylmanganese pentacarbonyl labelled with ^{14}C in the acetyl CO did not give appreciable radioactivity in the gas phase. This observation suggests the reaction scheme:

$$\mathrm{Me\overset{*}{C}OMn(CO)_5 \xrightarrow[\text{[55]}]{\text{heat}} MeMn(CO)_4\overset{*}{C}O + CO}$$

Similarly, acetylmanganese pentacarbonyl formed by treatment of methylpentacarbonyl with ^{14}CO did not have activity in the acetyl CO group, i.e.

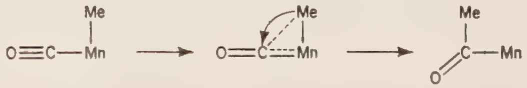
$$\mathrm{MeMn(CO)_5 + \overset{*}{C}O \xrightarrow[\text{[55, 185]}]{\text{pressure}} MeCO{-}Mn(CO)_4\overset{*}{C}O}$$

It follows from the latter observation that ligands other than CO may cause the carbonylation of the Me–Mn system. For example (where L = amines [186, 187], Ph_3P [187, 188, 189]).

$$\mathrm{MeMn(CO)_5 + L \longrightarrow MeCOMn(CO)_4L}$$

Phosphites, such as $(PhO)_3P$, may give mono- or di-substituted acyl products, $MeCOMn(CO)_3L_2$ [189, 189*a*]. The presence of both *cis*- and *trans*-isomers of $MeCOMn(CO)_4$ is shown by proton magnetic resonance and infrared spectra. Also, spectra suggest there to be rotational isomers in the complexes $CH_2XCOMn(CO)_5$, where X = F or Cl [189*b*].

Kinetic studies of the carbonylation of $MeMn(CO)_5$ by CO [190] and by amines and phosphines [187] show that the mechanism depends on the solvents used in the reaction. In polar solvents, intermediates such as (solvent)$(CO)_4$MnCOMe may commonly occur [190], whilst in non-polar solvents associative mechanisms involving seven-co-ordinate intermediates, $L(CO)_6MnMe$, may be found [190]. In either case, it is thought that the acylation occurs via attack of the methyl group on a carbon monoxide ligand and that the breaking of the Me–Mn bond is the rate-determining step [187], viz.



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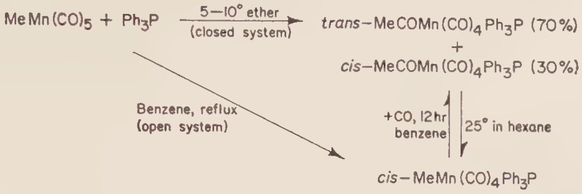
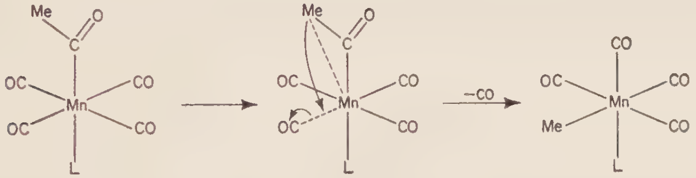
† For a review of the reactions of co-ordinated ligands, see reference [184].

The reaction between $MeMn(CO)_5$ and triphenylphosphine has been studied in some detail and the following equilibrium has been shown [191],



It has been pointed out that the simplest mechanism of formation of *cis*-$MeMn(CO)_4Ph_3P$ from *trans*-$MeCOMn(CO)_4Ph_3P$ is by *cis*-methyl migration [188], e.g.



Although benzoyl manganese pentacarbonyl readily decarbonylates [185], the reverse reaction only occurs with some difficulty. Treatment of $PhMn(CO)_5$ with triphenylphosphine affords $PhMn(CO)_4Ph_3P$ and a mechanism which involves formation of an unstable benzoyl intermediate has been proposed [189].

$$PhMn(CO)_5 \xrightarrow{\text{slow}} PhCOMn(CO)_4 \xrightarrow[+L]{\text{fast}} PhCOMn(CO)_4L \xrightarrow[-CO]{\text{fast}} PhMn(CO)_4L$$

Further evidence for the reluctance of Ph—Mn systems to carbonylate comes from the reaction [189]

$$PhMn(CO)_4Ph_3P \xrightarrow[200\text{ atm.}]{CO,\ 20°} PhMn(CO)_5 + Ph_3P \xrightarrow{CO} PhCOMn(CO)_5$$

The complexes $RMn(CO)_4Ph_3P$ may also be prepared starting from the anion $[Mn(CO)_5Ph_3P]^-$ [192]. With chelate phosphines and alkyl and aryl phosphites, $PhMn(CO)_5$ affords the disubstituted products $PhMn(CO)_3L_2$. Infrared studies suggests that the mono-dentate ligands L adopt a *trans*-configuration [189].

Alkyl- and aryl-cobalt tetracarbonyls also react readily with phosphines forming acyl derivatives $RCOCo(CO)_3PR'_3$. Phosphite ligands are found to replace carbon monoxides successively forming $RCOCo(CO)_2L_2$ [193]. The replacement of two carbon monoxide ligands by phosphites under conditions where phosphine ligands will only replace one carbon monoxide, is therefore found for both cobalt and manganese complexes. Both acyl- and alkyl-cobalt complexes become more stable, thermally and to oxidation, with increasing number of phosphine substituents [194].

Kinetic studies show that the mechanism of substitution of $RCOCo(CO)_4$ with triphenylphosphine proceeds as follows [195].

$$RCOCo(CO)_4 \xrightarrow[\text{step}]{\text{rate-determining}} RCOCo(CO)_3 + CO \xrightarrow{Ph_3P} RCOCo(CO)_3Ph_3P$$

It was found that the rate of reaction increased with increasing size of R and decreased with increasing electron-withdrawing properties of R. The alkoxy complex $Me_3COCOCo(CO)_4$ is readily prepared from t-butyl hypochlorite and $Na[Co(CO)_4]$. In this reaction, insertion of carbon monoxide between the Co–O bond in $Me_3COCo(CO)_4$ has occurred [196].

B. Related carbonylation reactions

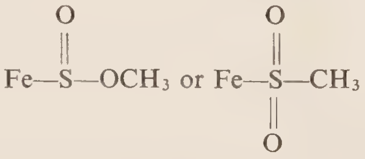
The M—R_h bonds of π-cyclopentadienyl carbonyl alkyls are readily carbonylated, e.g.

$$\pi\text{-}C_5H_5Fe(CO)_2Me + Ph_3P \xrightarrow[{[197]}]{} \pi\text{-}C_5H_5FeCOPh_3P(COMe)$$

The acyl complexes may be decarbonylated but with more difficulty than the pentacarbonylmanganese acyls [198].

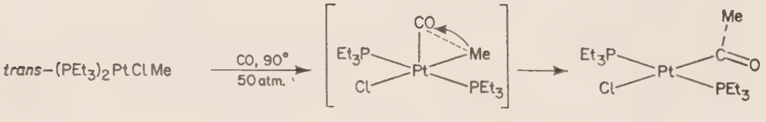
In this context, it is interesting to note that the insertion of sulphur dioxide into the Fe—R system has been observed, e.g.

$$\pi\text{-}C_5H_5Fe(CO)_2CH_3 + SO_2 \xrightarrow[{[199]}]{25°} \pi\text{-}C_5H_5Fe(CO)_2SO_2CH_3$$

Two possible structures are  $Fe\text{—}\overset{\overset{O}{\|}}{S}\text{—}OCH_3$ or $Fe\text{—}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{—}CH_3$

proton magnetic resonance studies support the latter [199*a*].

Direct carbonylation of non-carbonyl complexes with carbon monoxide has been shown for $(PEt_3)_2MXR$, where M = Pd or Pt, X = halogen and R = alkyl [200]. It seems reasonable that the reaction involves a five-co-ordinate transition state, viz.

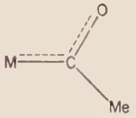


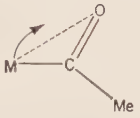
Proposed intermediate

Square-planar palladium complexes are usually more labile than the platinum analogues, and in agreement with this trend carbonylation of the palladium-alkyls occurs more readily than with the platinum derivatives.

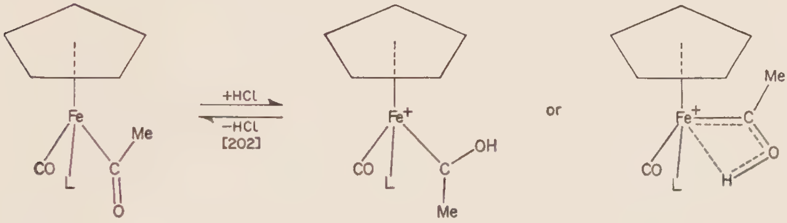
C. The metal–acyl bond

In the majority of metal-acyl complexes, the ketonic C=O stretching frequency is rather lower, ~1650 cm^{-1} [53, 201], than that found for organic ketones (~1725 cm^{-1}). This may be due either to some double bonding of the metal with the π-orbitals of the C=O group or there may be some direct interaction of the metal with the C=O group.





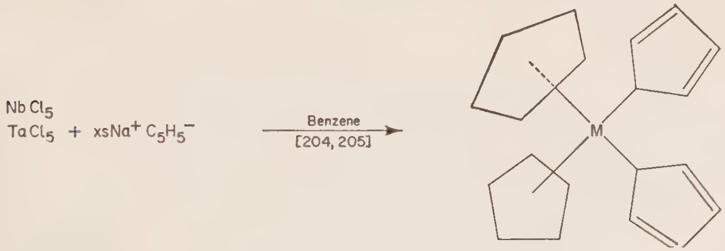
In either case it would be expected that the carbonyl group would be unusually susceptible to electrophilic attack. In agreement, the complexes π-$C_5H_5Fe(CO)LMe$ are readily protonated with hydrogen chloride forming cations for which representations such as 7.28 or 7.29 are possible [202].



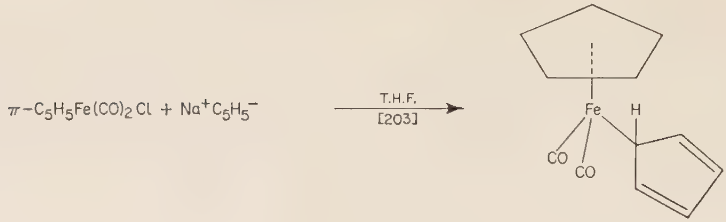
7.28 7.29

I.3. σ-CYCLOPENTADIENYL COMPLEXES

The cyclopentadienyl radical may act as a 1-electron ligand forming transition metal–σ-cyclopentadienyl systems. σ-Cyclopentadienyl complexes are usually prepared from a metal halide using sodium cyclopentadienide, e.g.

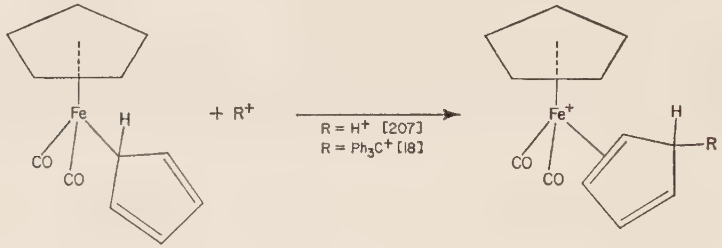


Strong chemical evidence for the structure shown for the complex 7.30 comes from the isolation of the two isomers π-$RC_5H_4Fe(CO)_2$–σ-C_5H_5 and π-$C_5H_5Fe(CO)_2$–σ-C_5H_4R, where $R = CH_2C_6H_5$ [206], and the



7.30

formation of the complex 7.30*a* with electrophiles such as the proton and triphenylmethyl cation,



7.30*a*

This reaction is similar to that shown by σ-allyl systems (see p. 212). An interesting feature of the chemistry of this molecule is that although the infrared spectrum shows the presence of a σ-cyclopentadienyl group in the molecule [208, 3] the room-temperature proton magnetic resonance spectrum shows only a single resonance for the protons of the σ-cyclopentadienyl group. However, if the spectrum is determined at −80° then it shows the bands consistent with an A_2B_2X system expected for the σ-C_5H_5 group (see Figure 64). On the basis of this evidence, it is proposed

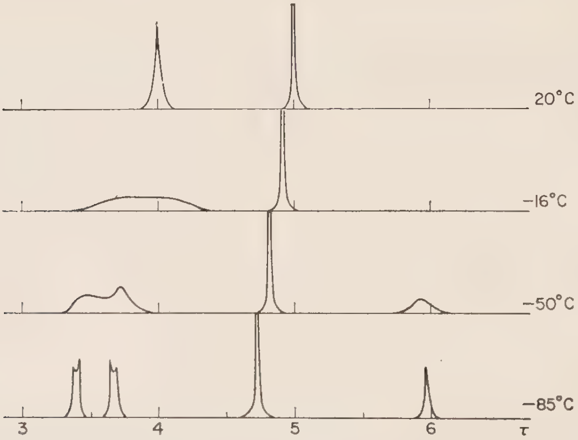
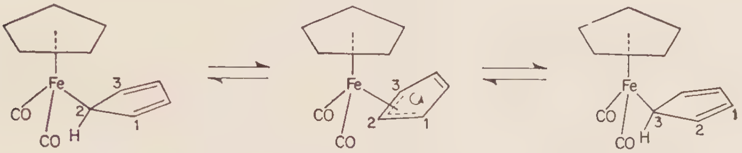


Fig. 64. The proton magnetic resonance spectra of π-$C_5H_5Fe(CO)_2$-σ-C_5H_5 at various temperatures, in ether solution (solvent peaks not shown)

that at room temperature the σ-C_5H_5 ring is rapidly changing the carbon which bonds to the metal by a rotational intra-molecular mechanism such as the one represented below. An energy barrier of 3–6 kcal./mole is estimated [209, 209*a*].



The structure of the compound, 7.30, has been confirmed by X-ray diffraction [209*a*]. The complexes $(\pi\text{-}C_5H_5)_2M(\sigma\text{-}C_5H_5)_2$, where M = Nb, blue-violet, Ta, red-violet; or $\pi\text{-}C_5H_5Mo(\sigma\text{-}C_5H_5)_3$ [205], red-violet, are all readily oxidized in air. The niobium and tantalum complexes are paramagnetic having one unpaired electron.

II. TRANSITION METAL FLUOROCARBON COMPLEXES†

Many complexes in this class are known. Frequently they are analogous to hydrocarbon derivatives in their stoicheiometry, but they are almost always much more stable thermally and to oxidation. The fluorocarbon complexes are usually prepared by rather different routes from those used for hydrocarbon complexes.

A. Preparation

(a) From perfluoroacyl halides

Perfluoroacyl halides readily form perfluoroacyl–metal complexes, $M—COR_f$, from which the perfluoroalkyl derivatives are easily prepared by decarbonylation, e.g.

$$R_fCOCl + Na^+[Mn(CO)_5]^- \xrightarrow[\text{[210, 211, 212]}]{\text{THF}} R_fCOMn(CO)_5 \xrightarrow[\text{u.v.}]{\text{heat or}} R_fMn(CO)_5 + CO$$

In some cases, thermal decarbonylation is preferable to photochemical techniques [51]. Using this synthetic approach, perfluoroacyl and alkyl complexes of $Mn(CO)_5$ [210, 211, 212, 213, 214], $Re(CO)_5$ [210], iron carbonyls [51, 215, 216], cobalt carbonyls [211, 213, 217, 218] and $\pi\text{-}C_5H_5Mo(CO)_3^-$ [51] have been isolated. Perfluoroacyl derivatives may also be prepared using perfluoroacid anhydrides [213].

Unlike alkyl halides, perfluoroalkyl halides do not give perfluoroalkyl derivatives when they react with metal carbonyl anions.

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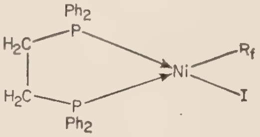
† A review of this topic may be found in ref. [221].

(*b*) *From perfluoroalkyl halides*

The electronegativities of perfluoroalkyl groups are so large that the perfluoroalkyl halides may be regarded, to some extent, as pseudo-interhalogen compounds. Stone and co-workers have demonstrated this analogy in the reactions between R_fX and metal carbonyls, e.g.

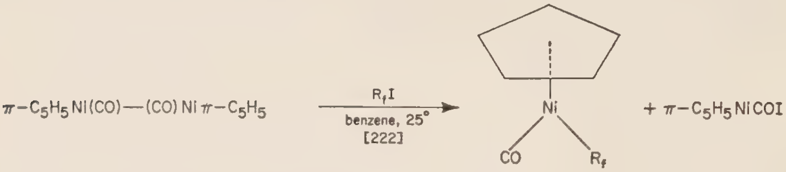
$$\mathrm{Fe(CO)_5 + R_fI \xrightarrow[\text{[215, 216]}]{40\text{–}60°} Fe(CO)_4R_fI}$$

$$\mathrm{(Ph_2PCH_2CH_2PPh_2)_2Ni(CO)_2 \xrightarrow[\text{[219]}]{R_fI}}$$



$$\pi\text{-}\mathrm{C_5H_5Co(CO)_2 \xrightarrow[\text{[220]}]{} }\pi\text{-}\mathrm{C_5H_5Co(CO)R_fI}$$

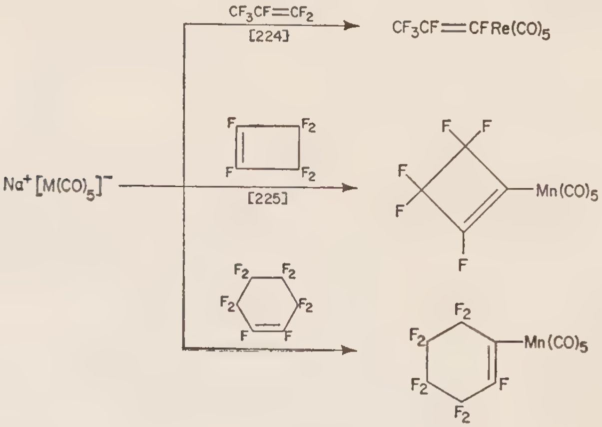
Perfluoroalkyl halides also add across metal–metal bonds, as do the halogens,



(*c*) *From perfluoro-olefins and related compounds*

In contrast to their hydrocarbon analogues, perfluoro-olefins are highly susceptible to nucleophilic attack. The nature of the product depends on the subsequent reactions of the carbanion formed which may either eliminate a fluoride anion or abstract an electrophile, usually a proton, from the solvent. During the reaction allylic rearrangements occur where possible. The metal carbonyl anions are strong nucleophiles and react with perfluoro-olefins, and even hexafluorobenzene, giving metal–R_f complexes [223, 224], e.g.

$$\mathrm{Na^+[}\pi\text{-}\mathrm{C_5H_5Fe(CO)_2]^- + C_6F_6 \xrightarrow[\text{[223]}]{} }\pi\text{-}\mathrm{C_5H_5Fe(CO)_2}\text{-}\sigma\text{-}\mathrm{C_6F_5}$$



On the basis of the relative reactivity of metal carbonyl anions with perfluoro-olefins, the sequence of increasing nucleophilicity of the metal carbonyl anions

$$[Fe(CO)_4]^{2-} \sim [Co(CO)_4]^- < [Mn(CO)_5]^- < [Mn(CO)_4PPh_3]^- < [Re(CO)_5]^- < [\pi\text{-}C_5H_5Fe(CO)_2]^-$$

has been proposed [224]. The difference of nucleophilicity is demonstrated by the reaction with chlorotrifluoroethylene [225*a*],

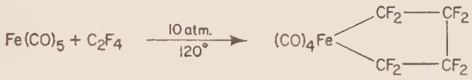
$$(CO)_5ReCF{=}CF_2 \xleftarrow[M=Re]{ClFC=CF_2} M(CO)_5^- \xrightarrow[M=Mn]{CF_2=CFCl} (CO)_5MnCF_2CFClH$$

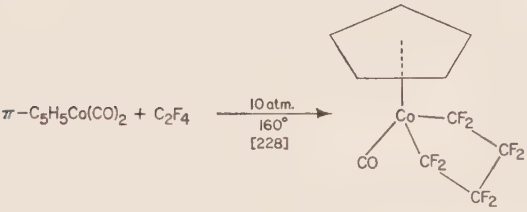
It can be seen that whereas the anion $Re(CO)_5^-$ causes the chlorine to leave the anion $Mn(CO)_5^-$ does not. Presumably the manganese anion adds to the $ClFC{=}CF_2$ forming an intermediate carbanion such as $(CO)_5MnCF_2CFCl^-$ which subsequently abstracts a hydrogen from the solvent. With perfluoroallyl chloride, perfluoropropenyl derivatives are formed by rearrangement and loss of a chloride ion,

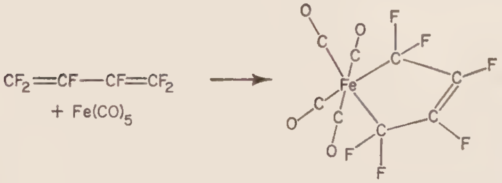
$$Na^+[Mn(CO)_5]^- + CF_2{=}CFCF_2Cl \xrightarrow[{[211,\ 226]}]{} (CO)_5Mn{-}CF{=}CFCF_3$$

Perfluorobutadiene readily reacts with anions such as $\pi\text{-}C_5H_5Fe(CO)_2^-$ and $Re(CO)_5^-$ forming *cis-* or *trans*-perfluorobutadienyl complexes, $M{-}CF{=}CF{-}CF{=}CF_2$, respectively, and with hexafluorobut-2-yne the rhenium anion $Re(CO)_5^-$ forms the only known allenyl derivative $(CO)_5ReCCF_3{=}C{=}CF_2$ [226*a*].

Fluoro-olefins will also react directly with neutral metal carbonyls giving heterocyclic ring systems, e.g.







7.30*b*

The crystal structure of the heterocyclic compound, 7.30*b*, has been determined [228*a*].

With transition metal carbonyl hydrides, the M—H system may add to the olefin. Tetrafluoroethylene gives the derivatives $\mathrm{M{-}CF_2CF_2H}$, chlorofluoro-olefins react similarly [227, 229, 230, 231, 232, 233].

With chlorofluoro-olefins, both possible isomers are found in the products; reduction may also occur [217],

$$\mathrm{HClFC{-}CF_2H} \xleftarrow[\text{[217]}]{\mathrm{ClFC{=}CF_2}} \mathrm{Co(CO)_4H} \xrightarrow[\text{[217]}]{\mathrm{C_2F_4}} \mathrm{Co(CO)_4{-}CF_2CF_2H}$$

The hydride $[\mathrm{Co(CN)_5H}]^{3-}$ reacts with $\mathrm{C_2F_4}$ forming $[\mathrm{Co(CN)_5CF_2CF_2H}]^{3-}$ [234].

Addition of metal–hydrogen across the acetylene, hexafluorobut-2-yne, has also been observed,

$$\mathrm{CF_3C{\equiv}CCF_3} + \mathrm{HMn(CO)_5} \xrightarrow[\substack{\mathrm{M\,=\,Re}\ [231]\\ \mathrm{Mn}\ [227]}]{\hspace{4em}} \mathrm{(CO)_5Mn(CF_3)C{=}CHCF_3}$$

Rather surprisingly, the product of the above reaction is almost all in the form of the *trans*-isomer.

Apart from the metal–hydride system, metal–alkyl and metal–aryl systems have been shown to add across fluoro-olefins,

$$\mathrm{(CO)_5Mn{-}R} + \mathrm{CF_2{=}CF_2} \xrightarrow[\substack{\mathrm{R\,=\,CH_3}\ [232]\\ =\ \mathrm{C_6H_5}\ [232,\ 233]}]{\hspace{8em}} \mathrm{(CO)_5MnCF_2CF_2R}$$

With $\mathrm{ClFC{=}CF_2}$, addition to $\mathrm{CH_3Mn(CO)_5}$ gives only one isomer, namely $\mathrm{CH_3CF_2CFClMn(CO)_5}$ and there is no $\mathrm{CH_3CFClCF_2Mn(CO)_5}$ in the product [233].

Addition of $\mathrm{C_2F_4}$ also occurs with metal–fluoride systems

$$\mathrm{(Et_3P)_2PtF_2} + \mathrm{C_2F_4} \xrightarrow[\text{[221]}]{} \mathrm{(Et_3P)_2Pt(C_2F_5)F}$$

and metal–metal bonds

$$\mathrm{Co_2(CO)_8} + \mathrm{C_2F_4} \xrightarrow[\text{[236]}]{} \mathrm{(CO)_4Co{-}CF_2{-}CF_2{-}Co(CO)_4}$$

A similar addition of the Sn–Mn complex, 7.31, across the C=C bond occurs,

$$\underset{7.31}{\mathrm{Me_3Sn{-}Mn(CO)_5}} + \mathrm{C_2F_4} \xrightarrow[\substack{\text{u.v., 6 hr}\\ \text{235, 237]}}]{\text{pentane, 50°}} \mathrm{Me_3SnCF_2CF_2Mn(CO)_5}$$

$$+ \text{ other } \mathrm{R_f{-}Mn} \text{ complexes}$$

The above reaction is complicated and small quantities of fluorocarbon manganese carbonyl compounds have been detected, including a complex which possibly contains bridging perfluorovinyl groups $[\mathrm{CF_2{=}CF{-}Mn(CO)_4}]_2$ [237]. It is interesting to note that trifluoroethylene reacts with the complex 7.31, forming, in good yields, both *cis*- and *trans*-isomers of 1,2-difluorovinyl manganese pentacarbonyl, $CFH{=}CFMn(CO)_5$ [238]. A related reaction has been shown with a platinum hydride,

$$trans\text{-}(Et_3P)_2PtClH + CHF{=}CF_2 \xrightarrow[\text{cyclohexane}\ [238]]{120^\circ} (Et_3P)_2PtCl(CF{=}CFH)$$

In fact, at 120° tetrafluoroethylene reacts with $(Et_3P)_3PtHCl$ giving the perfluorovinyl derivative $(Et_3P)_2PtCl(CF{=}CF_2)$ rather than the complex $(Et_3P)_2PtCl(CF_2CF_2H)$ which is preferably formed under milder conditions [238*a*].

The perfluorovinyl complex $\pi\text{-}C_5H_5Fe(CO)_2{-}\sigma\text{-}CF{=}CF_2$ is formed in small yields when C_2F_4 is heated under pressure with the iron–mercury complex $[\pi\text{-}C_5H_5Fe(CO)_2]_2Hg$ [239]. The perfluorovinyl nickel complexes $(Et_3P)_2NiX(CF{=}CF_2)$, where $X = Br$ or $CF{=}CF_2$, are prepared by treatment of $(Et_3P)_2NiBr_2$ with perfluorovinyl-magnesium bromide [239*a*].

(*d*) *From perfluoro Grignard reagents and lithium compounds*

This route is entirely analogous to that employed for metal–σ-hydrocarbon complexes. Examples of preparations using C_6F_5Li are shown in Figure 65. Pentafluorophenyl magnesium bromide can give pentafluorophenyl derivatives in good yields, it does so less frequently than C_6F_5Li.

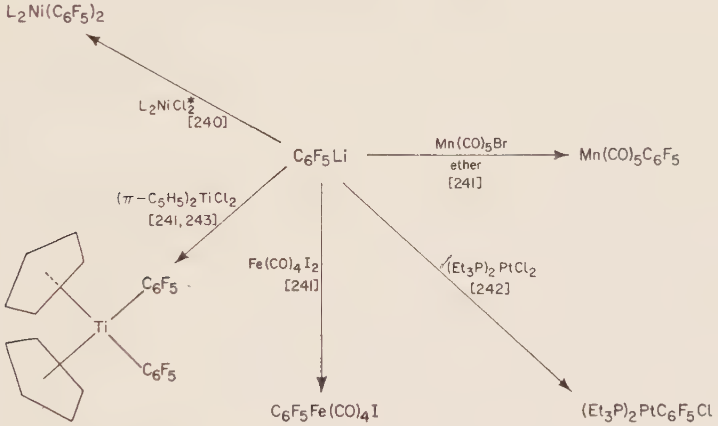


Fig. 65. Preparation of some pentafluorophenyl derivatives using C_6F_5Li (* L = Tertiary phosphines or bipyridyl)

$$C_6F_5MgBr + (Ph_3P)_2NiCl_2 \xrightarrow[{[240]}]{} (Ph_3P)_2Ni(C_6F_5)_2$$

B. The properties of perfluoro-alkyl and -aryl transition metal complexes

A most striking property of $M{-}\sigma\text{-}R_f$ complexes is their marked thermal stability in comparison with the hydrocarbon analogues. Thus perfluoroalkyl and -aryl complexes have been prepared where the corresponding hydrocarbon complexes are either unknown or too unstable to be isolated. As an example of the relative stability of the two classes, compare $CF_3Co(CO)_4$ with $CH_3Co(CO)_4$; the perfluoromethyl complex distils without decomposition at 91° whereas $CH_3Co(CO)_4$ is stable only at low temperatures ($\sim -30°$). The thermal decomposition of transition metal perfluoroalkyl complexes usually gives fluoro-olefins; metal fluorides may also be formed.

Generally, pentafluorophenyl complexes are more stable than perfluoroalkyl analogues [241]. This enhanced stability presumably arises from an increased strength of the M-perfluoroaryl bond by donation of the metal electrons to π^*-orbitals of the aryl ligand. This increased bond strength would increase the kinetic stability of the compound by increasing the energy necessary for dissociation of the $M—R_f$ bond.

Perfluorohydrocarbon–σ-metal complexes are also more stable to reaction with oxygen than their hydrocarbon analogues. Other differences between $M—R_f$ and $M—R_h$ complexes are the greater resistance of the former to cleavage reactions with acids, and the greater volatility of the fluorocarbon complexes.

It is interesting that metal–perfluorocarbon systems do not readily undergo carbonyl insertion reactions, as do hydrocarbon complexes. Only one carbonylation reaction has been reported and that occurs only in low yields and under rigorous conditions [244]. The reluctance of the $M—R_f$ system to carbonylate may be associated with the known instability of the R_fCO group.

It seems therefore that, to a large extent, the R_f ligand behaves as an inert halide ligand and perfluoroalkyl metal carbonyls undergo replacement of carbon monoxide ligands rather than of the R_f group, e.g.

$$C_2F_5Co(CO)_3PPh_3 + 2NO \xrightarrow[{[218]}]{} C_2F_5Co(NO)_2PPh_3$$

$$R_fFe(CO)_4I + L \xrightarrow[\text{L = pyridine or phosphine [245]}]{} LFe(CO)_3R_fI \quad \text{and} \quad L_2Fe(CO)_2R_fI$$

As would be expected, the perfluoroalkyl ligands are rather less labile than halide ligands; this is exemplified by some substitution and related reactions of π-$C_5H_5Co(CO)C_3F_7I$ [245*a*], viz.,

$$\begin{tikzcd}
{[\pi\text{-}C_5H_5CoC_3F_7I]_2} \arrow[d, "\begin{matrix}NH_4X\\ X = F,I\end{matrix}"'] & \pi\text{-}C_5H_5Co(CO)C_3F_7I \arrow[l, "MeOH"', "24\ hr."] \arrow[r, "(i)\ AgClO_4", "(ii)\ X^- = Cl^-{,}Br^-"'] \arrow[d, "\begin{matrix}(i)\ AgClO_4\\ (ii)\ KCN\end{matrix}"] & \pi\text{-}C_5H_5Co(CO)C_3F_7X \\
{[\pi\text{-}C_5H_5CoC_3F_7IX]^-} & {[\pi\text{-}C_5H_5CoC_3F_7CN]_{x \sim 4\cdot5}} &
\end{tikzcd}$$

The pentafluorophenyl ligand is deactivated in its metal complexes and does not undergo nucleophilic attack on the ring. For example, the pentafluorophenyl ligands of the platinum complex, 7.32, R = Et, are unattacked by methyl-lithium and methylamine. Moreover, treatment of the analogous complex 7.32, R = Ph, with the MeS^- anion causes only replacement of the C_6F_5 ligand [242], viz.,

$$(R_3P)_2Pt(C_6F_5)_2 + Na^+MeS^- \longrightarrow (R_3P)_2PtC_6F_5(SMe)$$

7.32

C. The metal-perfluorocarbon bond

Perfluorocarbon-σ-transition metal complexes are likely to be thermodynamically unstable on account of the high lattice energies of metal fluorides. It seems reasonable that the relatively high thermal stability of $M—R_f$ complexes, compared to that of $M—R_h$ complexes, arises from an increased stability to dissociation of the $M—R_f$ bond. A relative increase in the $M—R_f$ bond strength could be due both to an increase in the σ-bonding and, possibly, there could be π-bonding in the $M—R_f$ bond [246, 247, 248].

The relatively high electronegativity of the R_f group could cause, in several ways, an increase in the $M—R_f$ σ-bond strength compared to that in $M—R_h$ complexes. Firstly it would result in a larger ionic contribution to the bond strength, as discussed on p. 218. Secondly, the high electronegativity of the R_f group, relative to R_h, will cause there to be a relatively higher positive charge on the metal atom in $M—R_f$ compounds. Therefore, in $M—R_f$ compounds the *d* orbitals will be relatively contracted and repulsions between the metal and groups attached to the carbon could be reduced. Finally, the metal-σ-orbitals actually involved in the metal–carbon bond would be contracted and would approach the size of the carbon orbitals more closely; again this would result in a more stable $M—R_f$ system. However, there is at present little evidence to support either a relatively strong σ-bond or the presence of π-bonding in $M—R_f$ systems.

The crystal structures of the complexes π-$C_5H_5RhCO(C_2F_5)I$ [249], π-$C_5H_5Mo(CO)_3CF_2CF_2CF_3$ [249*a*], $Fe(CO)_4(CF_2CF_2H)_2$ [249*b*], $[(CN)_5CoCF_2CF_2H]^{3-}$ [250], and *cis*-$(CFH{=}CF)Mn(CO)_5$ [250*a*], $CoPh_3P(CO)_3CF_2CF_3$ [250*b*] and $Fe(CO)_4(—CF_2CF{=}CF—CF_2—)$ have been determined by X-ray diffraction; some are shown in Figure 66. There are comparative data which indicate that the $M—R_f$ bond is short compared with that in some $M—R$ complexes [249]. The structures, given in Figure 66, also show that the M–C–F, and M–C–C bond angles are rather larger than the expected tetrahedral angle.

The Mo–C_1C_2 angle in π-$C_5H_5Mo(CO)_3CH_2CH_3$ is also large (120°) [56] (see 7.15). These increases above the tetrahedral angle may be due to steric repulsion of the C_1-substituents by the metal orbitals (a β-effect). It has been suggested also that in the above $M—R_f$ complexes the increased

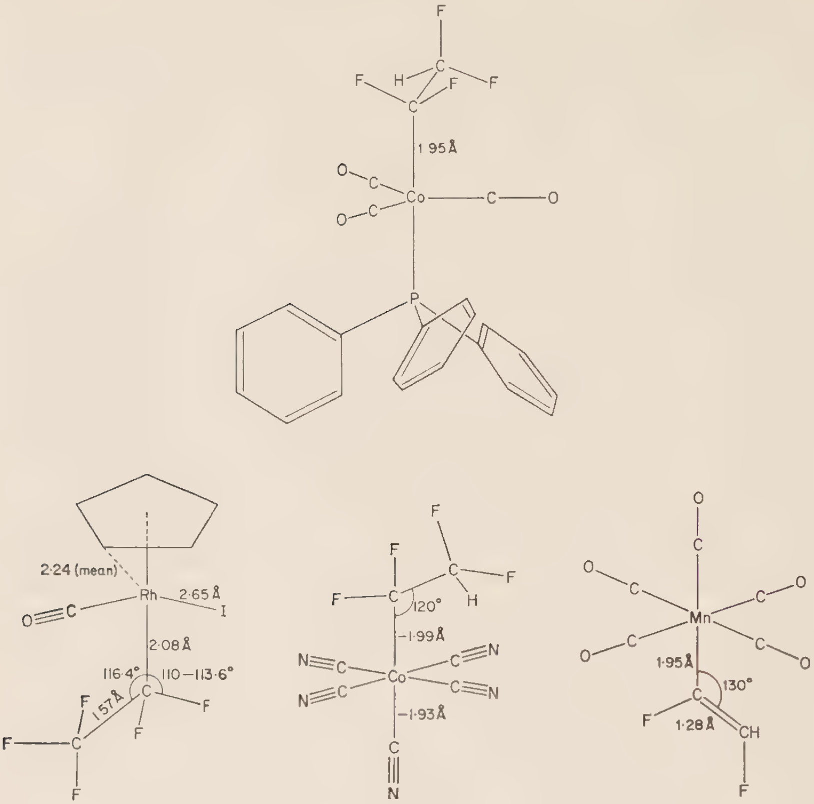


Fig. 66

angle may be due to repulsion of the CF_3 or CF_2H groups by electrons which are taking part in $M—C_1$ π-bonding [249]. If this is the case then $M\text{-}C_1C_2$ angles should be larger for $M—R_f$ complexes than the $M—R_h$ analogues. The distances and angles found in the compound *cis*-$(CFH{=}CF)Mn(CO)_5$ (see Figure 66), provide no firm evidence for π-bonding between the manganese and the $CF{=}CFH$ system [250*a*].

Infrared studies of some $M—R_f$ complexes, e.g. $(CO)_5MnCF_3$, show that the C—F stretching frequency is lowered by ~100 cm^{-1} compared with that in CF_3X where X = Cl, Br or I [246]. Such evidence is consistent with the postulate of double bonding but, given a strong and short $M—R_f$ σ-bond, the C—F bonds could be weakened by repulsion of the fluorines by the filled *d* orbitals with π-symmetry to the ligand A lowering of ~60 cm^{-1} is also found in metal–methyl complexes [251]. Finally, there is the suggestion that in the complexes $R_fMn(CO)_5$, the CO ligand *trans* to the R_f group has a slightly higher triple bond character than might be expected [247]. The argument follows that increased triple bond character implies a reduction in back-donation from the metal to the CO ligand, due to the π-bonding with the R_f group.

All these arguments for the stability of the M—R_f complexes are speculative and they neglect considerations which may be significant, such as the relative free energies of the fluorocarbon and hydrocarbon radicals. It should be noted that generally very little is known about the importance of factors which affect the stability of transition metal complexes and that a very small change in bond energy may have a marked effect on thermal stability.

III. TRANSITION METAL ACETYLIDES AND ALKYNYLS†

Those complexes which have a —C≡CR system σ-bonded to a metal atom are called acetylide or alkynyl complexes. They may be classified according to the other ligands which may be attached to the metal.

(*i*) *'Pure' metal acetylides*, e.g. (Cu—C≡CR), are those complexes which contain only the metal and the acetylide or alkynyl ligand.
(*ii*) *Complex acetylides*, e.g. $K_3[Fe(C{\equiv}CR)_6]$, are those where the acetylide or alkynyl ligand is part of a transition metal complex anion.
(*iii*) Finally there is a variety of alkynyl complexes (as they are commonly called) in which other ligands are also attached to the metal such as tertiary phosphines, and the π-cyclopentadienyl ligand.

A. Complex acetylides

Examples of complexes in this class are given in Table 25. The table shows that these complexes are closely related to the corresponding complex cyanides, in their occurrence, colour and magnetic properties. This close analogy arises since the cyanide and acetylide anions are iso-electronic and presumably bond to the metal in a similar manner. Both ligands would be expected to have acceptor properties as does the neutral carbon monoxide molecule, which is also isoelectronic. The bonding in the systems M—C≡X, where X = O, N or CR, may be represented as shown in Figure 67.

Differences between cyanide and acetylide complexes arise from the instability of the acetylide ligand to hydrolysis. The alkynyl anions are strong bases, and anhydrous solvents such as liquid ammonia must be used in the preparation of many of their complexes. Metal thiocyanates,

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† There is no clear distinction between the usage of the names acetylide or alkynyl for the C≡CR ligand. Historically, the acetylides were those complexes, like sodium monoacetylide, NaC_2H, which readily hydrolyse and appear to be 'salt-like'. The alternative name, alkynyl, was given to those complexes containing the C≡CR ligand which are rather similar to metal-alkyls.

Table 25 *Examples of anionic complex acetylides* $^{(a)}$†

$K_3[Cr(C\equiv CH)_6]$ orange [252]	$M_2[Mn(C\equiv CR)_4]^{(c)}$ pink [253]	$M_4[Fe(C\equiv CR)_6]^{(c)}$ yellow diamagnetic [254]	$M_4[Co(C\equiv CR)_6]^{(b)}$ green [255]	$M_2[Ni(C\equiv CR)_4]^{(c)}$ yellow [256, 263]	$Ba_3[Cu(C\equiv CPh)_3]_2$ brown [260]
	$K_3[Mn(C\equiv CH)_6]$ dark brown [253]	$K_3[Fe(C\equiv CH)_6]$ brown violet, explosive, −30° [254]	$M_3[Co(C\equiv CR)_6]^{(b)}$ yellow [255]	$K_4[Ni(C\equiv CH)_4]$ yellow [256]	$M_2[Cu(C\equiv CR)_2]^{(c}$ colourless [261]
					$M_2[Cu(C\equiv CR)_3]^{(c)}$ colourless [261]
				$K_2[Pd(C\equiv CR)_2]^{(c)}$ yellow [258]	$K[Ag(C\equiv CR)_2]^{(c)}$ colourless [268]
				$K_2[Pt(C\equiv CR)_4]^{(c)}$ colourless [259]	$K[Au(C\equiv CPh)_2]$ colourless [269]
				$K_2[Pt(C\equiv CR)_2]^{(c)}$ yellow [259]	$K_2[HC\equiv CAu{-}C\equiv C{-}Au{-}C\equiv CH]$ colourless [269]

† A review of complex acetylides may be found in reference [257]

(*a*) M = Na or K
(*b*) R = H or Me
(*c*) R = H, Me or Ph

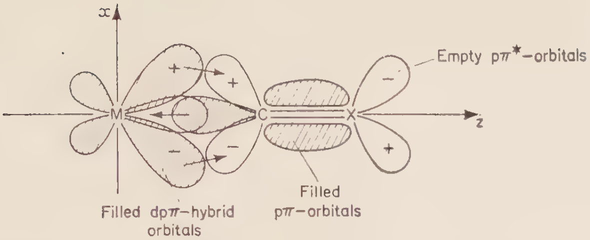


Fig. 67. A conventional representation of the bonding in M—C≡X systems where X = O, N or CR. Only the π-bonding in the xz is shown. A similar interaction is present in the yz plane. This bond description may be compared to that of the M-ethylene bond (see Figure 4)

nitrates or complex cyanides, which are soluble in liquid ammonia, are treated with alkali metal acetylides and the complex acetylides are frequently insoluble and are precipitated during the reaction.

Many complex acetylides are explosive and, as would be expected, the more labile ones are readily hydrolysed. The complexes with silver and gold in particular are sensitive to light. Some other reactions of the complexes are reduction,

$$K_3[Fe(C{\equiv}CH)_6] + K \xrightarrow[\text{ammonia}]{\text{liquid}} K_4[Fe(C{\equiv}CH)_6]$$

$$K_2[Cu(C{\equiv}CPh)_3] \xrightarrow[\text{(2) BaSCN}]{\text{(1) Li/NH}_3} Ba_3[Cu(C{\equiv}CPh)_3]_2$$

and ligand replacement reactions

$$M^{2+}[Ni(C{\equiv}CR)_4]^{2-} + 4CN^- \longrightarrow M^{2+}[Ni(CN)_4]^{2-} + 4RC{\equiv}CH$$

The acetylide ligand differs from cyanide in forming the cobalt complex $M_4[Co(C{\equiv}CR)_6]$ and the tetraco-ordinated manganese(II) complex anion $[Mn(C{\equiv}CR)_4]^{2-}$. Further, whereas complex cyanides of copper $[Cu(CN)_x]^{-(x-1)}$, where x = 2, 3 or 4, are known, the corresponding complex acetylide where n = 4 is unknown.

Generally it appears that the stability of the complex acetylides changes with the ligand in the order of decreasing stability R = Ph > H > Alkyl. The greater stability of the phenylethynyl complexes could arise from an increase in M–C bond strength. This could be due both to the greater electronegativity of the phenyl groups, compared with H or alkyl, and, when R = Ph, to a reduction of the negative charge on the C≡C carbons by virtue of its delocalization over the phenyl group. Thus relative to R = H or alkyl, where delocalization of charge is restricted, back-donation from the metal to the pπ*-orbitals would be enhanced in the phenylethynyl ligand. Treatment of $K_4[Ni_2(CN)_6(CO)_2]$ with $KC{=}CR$ in liquid ammonia gives the compound $K_2[Ni(C{\equiv}CR)_4]$ by a disproportionation reaction [257*a*].

B. 'Pure' metal acetylides and alkynyls

The acetylides M_2C_2, where M = Cu, Ag or Au, have been long known and they are all explosive. Dry silver acetylide is particularly sensitive to shock. The compounds formed with alkynyl ligands, $C{\equiv}CR$, are generally more stable and, in a few cases, form *discrete* molecules. The known complexes in this class are given in Table 26. The complexes may be prepared by direct reaction between the acetylene and a metal salt, e.g.

Table 26 *'Pure' alkynyl and acetylide complexes*

$[Mn(C{\equiv}CH)_2]_n$ black [262]		
$[Ni(C{\equiv}CR)_2]_n$ black [263, 266]	$[Ni(Ni(C{\equiv}CPh)_4]_n$ black [263]	
$[Cu_2C_2]_n$ orange [264]	$[CuC{\equiv}CR]_n$ orange, yellow [264, 267]	$[Cu(C{\equiv}CBu^t)]_8$ orange-red [271, 272]
$[Ag_2C_2]_n$	$[AgC{\equiv}CR]_n$ [268]	
$[Au_2C_2]_n$ [265, 269]	$[AuC{\equiv}CR]_n$ yellow [269, 270]	$[Au(C{\equiv}CBu^t)]_4$ pale yellow [270]

$$\mathrm{AuCl_3\ aq.} + \mathrm{KBr} \xrightarrow[\substack{\text{(1) reduction with SO}_2\\ \text{(2) addition of PhC}\equiv\text{CH}}]{\text{Aq./acetone solution, 15–20°}} (\mathrm{PhC{\equiv}CAu})_x$$

or, alkali metal salts can be used, e.g.

$$2\mathrm{CuI} + 2\mathrm{KC{\equiv}CH} \xrightarrow[{[264]}]{} 2\mathrm{CuC{\equiv}CH} + 2\mathrm{KI} \xrightarrow{-45°} \mathrm{Cu_2C_2} + \mathrm{HC{\equiv}CH}$$

The majority of the complexes are insoluble and the alkynyl complexes are not hydrolysed by water. The insolubility of these alkynyls suggests that they have a polymeric nature. The structure of phenylethynyl copper has been shown by X-ray determination [273] (Figure 68). It consists of an infinite rectangular tube of copper atoms at bonding distances from each other with the $PhC{\equiv}C$— groups on the outside. Each $C{\equiv}CPh$ seems to be σ-bonded to one copper atom, symmetrically π-bonded to another and unsymmetrically π-bonded to a third copper atom. For simplicity Figure 68 shows only one half of the rectangular tube.

The complexes $(MC{\equiv}CR)_x$, where M = Cu, Ag or Au, all react with ligands such as ammonia and the tertiary phosphines. The ligands serve to depolymerize the complexes by replacement of intermolecular π-bonds, forming complexes such as $R_3PAuC{\equiv}CR$ (see p. 277). The ammonia complexes readily lose ammonia [262, 263, 267]. The phenylethynylgold complexes react more readily with most ligands, suggesting that they

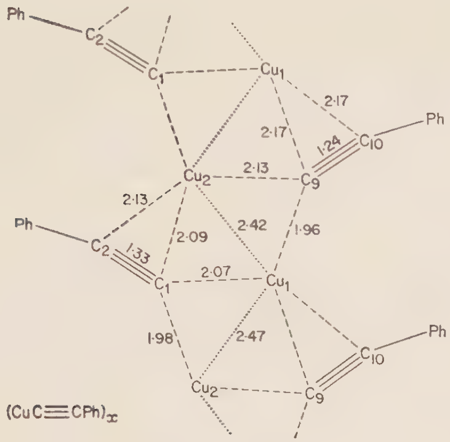
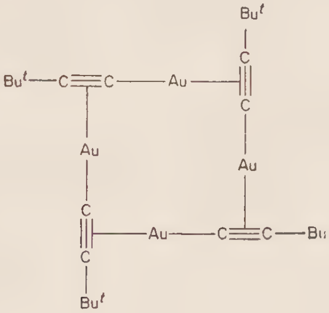


Fig. 68. Structure of phenylethynyl copper

have a smaller degree of polymerization than the silver and copper analogues. In the case of the t-butylalkynyl complexes $[M(C{\equiv}CBu^t)]_n$, where $M = Cu$ or Au, it is found that in benzene the copper complex is octameric ($n = 8$) [271] whilst a tetrameric gold complex is known [270]. The structure 7.33 has been proposed for the gold complex, which also occurs in an

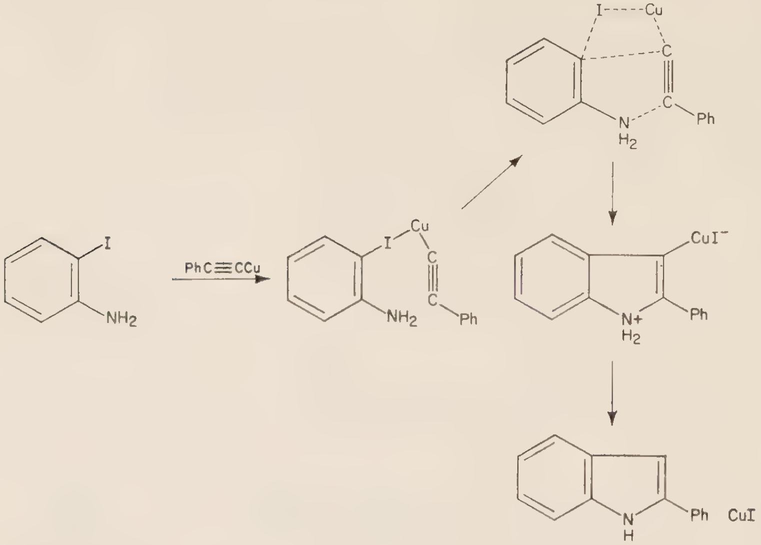


7.33

insoluble polymeric form. The lower degree of polymerization of the t-butylethynyl complexes presumably arises since the bulky t-butyl groups would prevent a high degree of co-ordination about a particular metal, and oligomers, once formed, would be kinetically stable to further polymerization.

The relative ease of depolymerization of the alkynyl gold complexes may be associated with the reluctance of gold(I) to raise its co-ordination number above 2 [270].

Treatment of phenylacetylene Cu(I) with *p*-$IC_6H_4NH_2$ gives CuI and *p*-$NH_2C_6H_4{\equiv}CPh$. However, with the *ortho*-substituted amine an unusual cyclization reaction occurs [274], i.e.



C. Alkynyl–transition metal tertiary phosphines and related complexes

The complexes in this class are frequently more tractable than the highly polymeric ‘pure alkynyl’ complexes. They are usually more soluble and less reactive.

(*a*) *Nickel, palladium and platinum*

A number of alkynyls $(PR'_3)_2MR_2$ and $(PR'_3)_2MRX$, where M = Ni, Pd or Pt, are known and they are analogous to the alkyl and aryl complexes described earlier (p. 224). They are prepared from the corresponding halides using alkali metal acetylides, e.g.

$$\begin{tikzcd} trans\text{-}(Et_3P)_2MCl_2 + NaC{\equiv}CR \arrow[r, "{[47]}"'] & trans\text{-}(Et_3P)_2M(C{\equiv}CR)Cl \arrow[d, "NaC{\equiv}CR"] \\ & trans\text{-}(Et_3P)_2M(C{\equiv}CR)_2 \end{tikzcd}$$

Alkynyl Grignard reagents may not give such good yields as alkali metal derivatives. Also, treatment of the zero-valent compound $(Ph_3P)_4Pt$ with $BrC{\equiv}CPh$ gives the mono-alkynyl $(Ph_3P)_2Pt(C{\equiv}CPh)Br$ [46*a*].

Alkynyl complexes, $M{-}C{\equiv}CR$, are more stable than the corresponding alkyls or aryls and the order R = alkyl < phenyl < *ortho*-substituted phenyl ~ alkynyl is found [37]. Examples are the nickel complexes $(Et_3P)_2Ni(C{\equiv}CR)_2$ where R = H, m.p. 36–36·5°, or Ph, 149–151°, which melt without decomposition, and $(PEt_3)_2Pd(C{\equiv}CPh)_2$, m.p. 162–164° d, which is more stable than the diphenyl analogue. The phenylethynyl complex $(Et_2PhP)_2Ni(C{\equiv}CPh)_2$ is unusual in that it adds a further molecule of the phosphine forming red crystalline $(PEt_2Ph)_3Ni(C{\equiv}CPh)_2$.

For the platinum complexes $(Et_3P)_2Pt(C{\equiv}CR)_2$, the order of increasing stability of $R = H < Me < Ph$ is found [15]. In all these complexes the $C{\equiv}C$ stretching frequencies are a little lower (~2100 cm^{-1}) than those found in disubstituted acetylenic hydrocarbons (2260–2190 cm^{-1}) [275].

(*b*) *Copper, silver and gold*

Many complexes $(LMC{\equiv}CR)_n$ are known where M = Cu, Ag or Au, and L are donor ligands such as tertiary phosphines or amines. They are prepared by treatment of the polymeric, 'pure' metal alkynyls with the donor ligand or using lithium acetylide, e.g.

$$(AuC{\equiv}CPh)_n \xrightarrow[\text{[270]}]{Et_3P} Et_3PAuC{\equiv}CPh \xleftarrow{Et_2O} Et_3PAuBr + LiC{\equiv}CPh$$

$$(PhC{\equiv}CCu)_n \xrightarrow[\text{ammonia}]{\text{liquid}} \underset{[261]}{\text{unstable ammonia complex}}$$

Replacement of one donor ligand by another is also a useful preparative route,

$$PhC{\equiv}CAuAsEt_3 + p\text{-}MeC_6H_4NC \xrightarrow[\text{[270]}]{} PhC{\equiv}CAuCNC_6H_4Me + AsEt_3$$

Cryoscopic studies suggest that the complexes have varying degrees of association. For example, the complexes of empirical formulae $RCuC{\equiv}CPR'_3$ are dimeric in nitrobenzene and more associated in benzene, except in the unusual case of $p\text{-}NO_2C_6H_4C{\equiv}CCuPPh_3$, which is dimeric in benzene and monomeric in nitrobenzene [272]. Some of these copper complexes undergo further addition of a molecule of tertiary phosphine. The products, e.g., $Bu^t{—}C{\equiv}CCu(PMe_3)_2$, are monomeric and readily lose phosphine.

The structure of the tetrameric complex $(PhC{\equiv}CCuPMe_3)_4$ has been shown by X-ray diffraction and there are two very different environments for the copper atoms. Except for the phosphine groups which lie above and below the plane of the paper, the structure is nearly flat (see Figure 69) [276]. Cryoscopic studies show that in solution this complex contains less associated species as well as the tetramer [272].

The tetramer has a centre of symmetry midway between Cu'_1 and Cu_1. Distances are shown on the right-hand side and chemical bonds on the left. There is no reason to believe there is a bond between Cu'_1 and Cu_1. Apart from the tertiary phosphine groups, which act as terminal groups, environment of the copper atoms resembles in several ways that which obtains in polymeric $(PhC{\equiv}CCu)_x$ (Figure 68). If it is assumed there is no bond between Cu_1 and Cu_2, then Cu_1 is anionic and has a trigonal arrangement of three ligands, namely C_1, C_9 and the $C'_9{=}C'_{10}$ ethynyl group. On the same assumption, Cu_2 is cationic and has a tetrahedral arrangement of four ligands, namely P_1, P_2 and the two ethynyl groups. On this basis Cu_1 is a '16-electron' atom, and Cu_2 an 18-electron atom. If, however, there is co-ordination from Cu_2 ($3d_{xz}$ or $3d_{yz}$) to Cu_1 (shown by a dotted line), then the otherwise vacant $4p_z$ orbital of Cu_1 becomes occupied and the molecule as a whole can be regarded as an 18-electron complex. Since the molecule is so nearly planar it is likely that the Cu_1 $4p_z$ orbital is delocalized over the entire tetrakisphenylethynyl system. It should be noted that the $—C_9\equiv C_{10}\equiv$ethynyl moiety which forms two π-bonds, is non-linear by 26°.

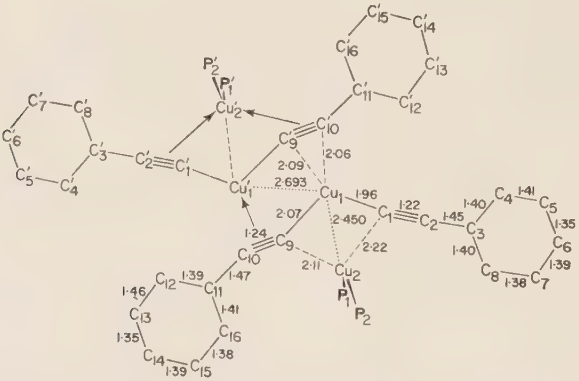


Fig. 69. Structure of the tetrameric complex $(PhC{\equiv}CCuPMe_3)_4$

The tertiary phosphine complexes of silver ethynyls are more sensitive to light and air than their copper analogues. Though phenylethynyl(trimethylphosphine) silver is dimeric in benzene, it is polymeric in the crystalline state (Figure 70). The structure of the polymer has many

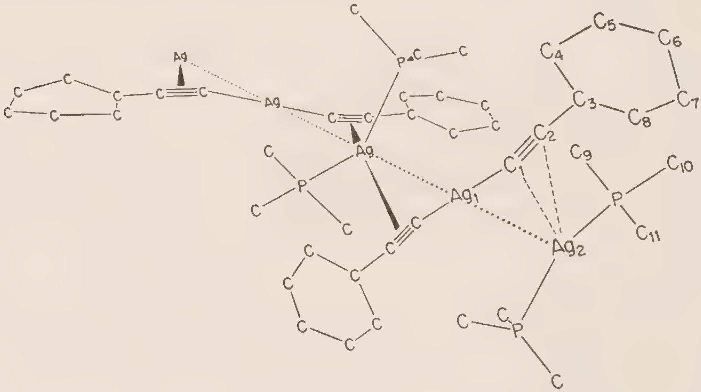


Fig. 70. The structure of $[PhC{\equiv}CAgPMe_3]_x$

points of similarity to that of the tetramer $(PhC{:}CCuPMe_3)_4$, for example anionic $PhC{\vdots}CAgC{\vdots}CPh$ and cationic silver can be distinguished, the latter (like Cu_2 in Figure 69) being co-ordinated to two phosphorus atoms and obliquely to two ethynyl groups [277]. On this basis Ag_1 is a 14-electron atom, and Ag_2 an 18-electron atom. Any significant metal–metal bonding in the sense $\leftarrow Ag_2 \rightarrow Ag_1 \leftarrow Ag_2 \rightarrow$ would make all the atoms obey the inert gas rule. The metal–metal distance is 3·03 Å, to be compared with 2·89 Å in metallic silver; thus the degree of metal–metal bonding is probably less than that between Cu_1 and Cu_2 (Figure 69) where the distance 2·45 Å is appreciably less than that in metallic copper (2·56 Å).

Ligand displacement in the complexes $(RC{\equiv}CAuL)_n$ shows the following order of decreasing ligand strength, $L{=}PEt_3 > P(OPh_3)_3 > p\text{-}C_6H_4NC > AsEt_3 > SbEt_3 > NH_3$, primary and secondary amines > tertiary amines. Complexes with sulphur ligands were found to be very unstable [270]. All the complexes $(RC{\equiv}CAuL)_n$ have a $C{\equiv}C$ stretch in the narrow region 2107–2135 cm^{-1}. These frequencies are high, which suggests there is little π-bonding of the gold with the $C{\equiv}C$ system; all but the amine complexes are monomeric in benzene.

The amine complexes, $PhC{\equiv}CAu(amine)$, are frequently unstable and dissociate losing the amine. They are sparingly soluble and molecular weight determinations of the n-octylamine complexes show some association within the range 2·6–4·1 in benzene solutions [270].

The structure of the isopropylamine complex, determined by X-ray analysis, is shown in Figure 71. The metal–metal distances, 3·27 and 3·72 Å, are considerably greater than in metallic gold, 2·88 Å, and there is no reason to believe the metal has a covalency in excess of two. The

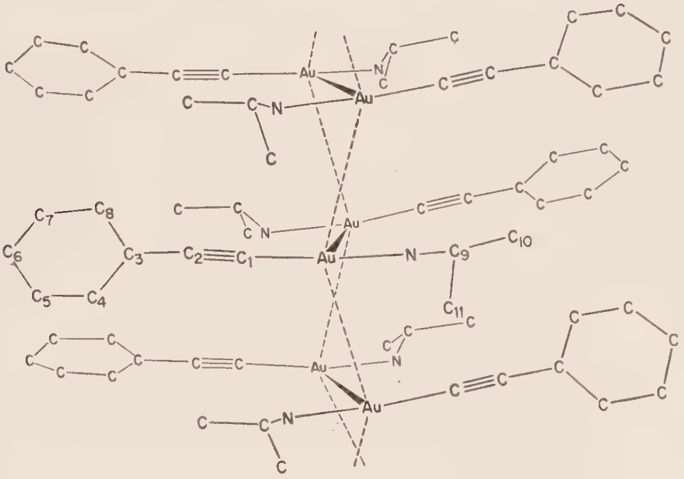


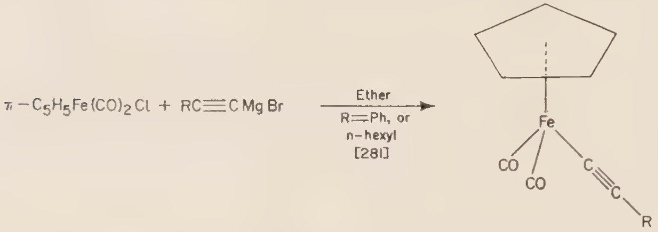
Fig. 71

association, which cannot be due entirely to dipole interaction since all but the nitrogen complexes are monomeric, is probably due to hydrogen bonding between the NH_2 group of one monomer and the ethynyl of another. Other evidence for such bonding has been discussed [278].

(c) Miscellaneous

The alkynyl group forms stable complexes with a number of π-cyclopentadienyl and carbonyl compounds, e.g.

$$M(CO)_3(NH_3)_3 + 3KC{\equiv}CR \xrightarrow[\substack{M\,=\,Cr\ [279]\\ =\,Mo\ [280]}]{} K_3[M(CO)_3(C{\equiv}CR)_3]^{3-}$$



The π-cyclopentadienyl complexes are thermally stable up to ~120°. They oxidize slowly in air and with hydrogen chloride the Fe–C bond is cleaved, giving the metal chloride and the acetylene [281].

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CHAPTER EIGHT

Organometallic complexes formed from acetylenes

The sticky brown soups formed in the reactions between acetylenes and metal carbonyls yield an amazing variety of complexes including many of the organometallic *exotica*. The nature and yields of the complexes depend markedly on the reaction conditions, in particular the solvent used and the temperature. Similarly the nature of the product varies considerably with changes from one acetylene to another or with a change of stoicheiometry of the metal carbonyl complex. Thus $Fe_3(CO)_{12}$ yields a wider variety of complexes than $Fe(CO)_5$. Any particular reaction can yield some dozen or so isolable organometallic complexes, to say nothing about the purely organic products which are also formed.

Many of the complexes formed in these reactions may be classified as complexes containing n-electron ligands. However, they are described separately because a discussion of their chemistry together can, to some extent, provide insight into the manner of their formation. They are considered in the order of increasing number of acetylene molecules which have combined to give the hydrocarbon ligand in the complex. For a given number of acetylene groups in a ligand, the complexes are further subdivided according to the number of metal atoms in the molecule. Thus the complexes first considered are the monoacetylene, mononuclear, e.g. $RC{\equiv}CRPt(Ph_3P)_2$, and afterwards the monoacetylene, bi- and tri-nuclear complexes.

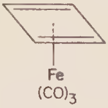
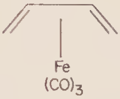
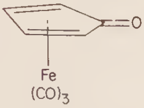
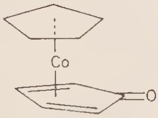
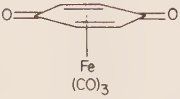
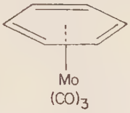
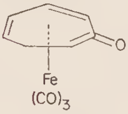
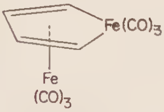
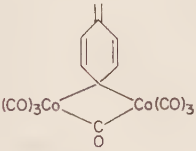
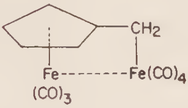
In Table 27 are shown the skeletal frameworks of the classes of complexes most commonly found in the dimerization and trimerization reactions of acetylenes. The table also exemplifies the classification used in this chapter.

A. Monoacetylene, mononuclear complexes: acetylenes as 2-electron ligands

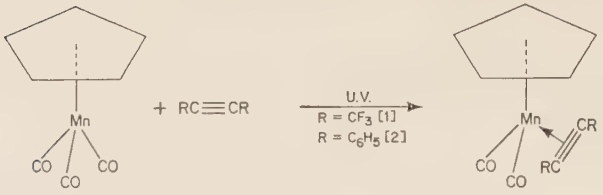
In the earlier discussion of the ethylene–metal bond (Chapter 1), the ethylene was compared, in extreme examples, to the carbon monoxide ligand or to two alkyl groups. In the former situation the ethylene is behaving as an essentially monodentate ligand whilst in the latter it behaves as a bidentate ligand. Acetylenes are similar in their behaviour.

Treatment of π-$C_5H_5Mn(CO)_3$ with acetylenes and irradiation with ultraviolet light gives monoacetylene complexes, 8.1

Table 27

	Number of acetylenes	Number of CO incorporated in ligand		
		0	1	2
MONONUCLEAR	2	 Cyclobutadiene  Butadiene	  Cyclopentadienone	 Quinone
	3	 Arene	 Tropone	
BINUCLEAR	2	 Cycloferradiene		
	3	 		

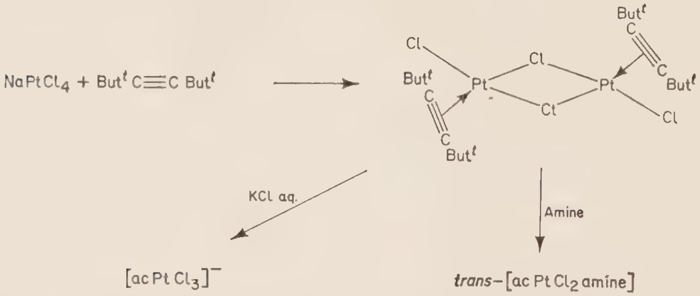
Ethylenic complexes analogous to these acetylene complexes, 8.1, are known and it seems a reasonable assumption that the acetylene–metal bond should resemble the ethylene–metal bond in these complexes. Thus the acetylene, which has two orthogonal $p\pi$-bonds, would use one filled $p\pi$-bond to donate to the manganese and back-donation from the metal would take place mainly into the corresponding anti-bonding $p\pi^*$-bond of the acetylene. A number of acetylene–platinum complexes are known in which again it may be assumed that the acetylene–metal bond is similar



8.1

to that in ethylene–platinum complexes. These complexes are not as stable as ethylene-platinum complexes.

Indeed, Chatt and co-workers have shown that stable acetylene-platinum complexes of the type $[acPtCl_2]_2$ and $[acPtCl_3]^-$, where ac = an acetylene, were only isolable when either the acetylene has at least one tertiary carbon substituent [3],



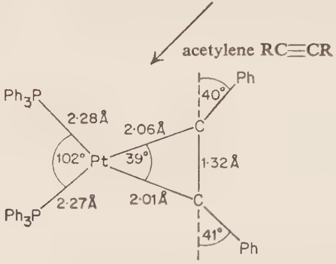
or, when there are hydroxyl groups on tertiary carbon substituents. Examples of the latter complexes are *trans*-$[HOR_2C{\equiv}COHR_2PtCl_2amine]$ and $[HOR_2C{\equiv}CR_2OHPtCl_3]^-$ [4, 5, 6, 7]. The increased stability of these complexes, allowing their isolation, may be due to a number of reasons. The bulky t-butyl substituents may increase kinetic stability by inhibiting the approach of attacking ligands along the unoccupied octahedral axis in these square-planar complexes. (Bridge cleavage reactions may occur, however, see above.) The acetylenes themselves may be more stable with respect to polymerization and further reaction; e.g., those with hydrogens on carbons in the 2-position with respect to the metal, as in dimethylacetylene, might further react by loss of the hydrogen, as is found in the formation of π-allyl complexes from mono-olefins (see p. 41) and in the decomposition of metal-ethyl complexes (see p. 211).

Finally, the high polarizability (+I effect) of the t-butyl group may increase the donor power of the C≡C system and enhance the C≡C—Pt bond strength. In the hydroxy-acetylenes, the OH groups may form weak bonds with the metal (O–H stretching frequency is lowered by 150 cm^{-1}), hence the acetylene-hydroxyls could act as polydentate ligands, also the

OH group would sterically inhibit approach along the octahedral axis (see p. 225). There is no evidence which indicates the relative importance of the above postulated effects. In agreement with the above arguments, aryl-substituted acetylenes do not form analogous complexes, except in the case of $[PhC{\equiv}CPh{-}PtCl_3]^-$, which can only be isolated as the salts of large cations suggesting that lattice energy may contribute to the apparent stability of the anion [8].

Aryl acetylenes do however form a series of stable complexes of the stoicheiometry $acPt(PPh_3)_2$ [1, 9]. In these complexes the C≡C stretching frequency is lowered to 1750 cm^{-1} and it was proposed that these complexes are square-planar with the acetylene acting as a bidentate ligand, essentially forming two σ-bonds to the metal, e.g.

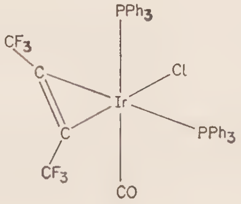
$$(Ph_3P)_2PtCl_2 + N_2H_4.H_2O + EtOH + \text{olefin} \longrightarrow \text{olefin } Pt(PPh_3)_2$$



This planar structure has been confirmed by X-ray diffraction on the complex where R = Ph [9*a*]. The C–C bond length of the 'π-acetylene' is 1·32 Å and the phenyl groups are bent 40° out of the C–C axis.

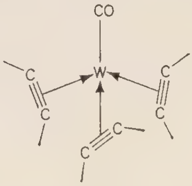
Displacement studies show the order of stability of the acetylene ligands in these complexes to be, $C_2H_2 <$ alkylacetylenes $<$ arylacetylenes $<$ nitroarylacetylenes. Thus the most stable complexes are formed by those acetylenes with electron-withdrawing substituents in agreement with the proposed nature of the acetylene–metal bond (compare C_2F_4 and $C_2(CN)_4$ complexes with platinum, see p. 18). Analogous palladium complexes are prepared by treatment of $(Ph_3P)_4Pd$ with RC≡CR, where R is a strongly electron withdrawing substituent such as CF_3 or COOMe [9*b*]. Also similar acetylene–metal bonds are proposed to occur in some iridium complexes, in which a C–C stretching frequency at ~1770 cm^{-1} is observed, e.g.

$$IrCl(CO)(Ph_3P)_2 + CF_3C{\equiv}CCF_3 \xrightarrow[{[10,\,11]}]{}$$



Remarkably, this reaction proceeds reversibly even when the iridium complexes are in the solid state.

There are several acetylene–metal derivatives of unknown structure but in which discrete acetylene ligands are thought to bond to the metal. Treatment of acetonitrile complexes of tungsten with disubstituted acetylenes such as hex-3-yne or diphenylacetylene gives novel complexes of stoicheiometry $(RC{\equiv}CR)_3WCO$ for which the structure 8.2 is proposed [12]. Attempts to make the chromium and molybdenum analogues by the same methods gave no isolable organometallic complexes, rather hexasubstituted benzenes or cyclopentadienones were formed. Treatment of $ReCl_3$ with phenylacetylenes gives a complex of stoicheiometry $(ReCl(PhC{\equiv}CH)_2)_2$ [13].

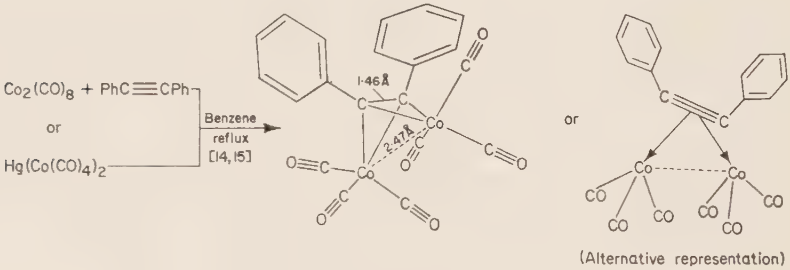


8.2

Other examples of complexes with acetylenes as 2–electron ligands are π-$C_5H_5CoPh_3PPhC{\equiv}CPh$ [13*a*], $IrCl(CO)(Ph_3P)_2PhC{\equiv}CCO_2Et$ [13*b*] and π-$C_5H_5VPhC{\equiv}CPh(CO)_2$(?) [13*c*].

B. Monoacetylene, binuclear complexes: acetylenes as 4-electron ligands

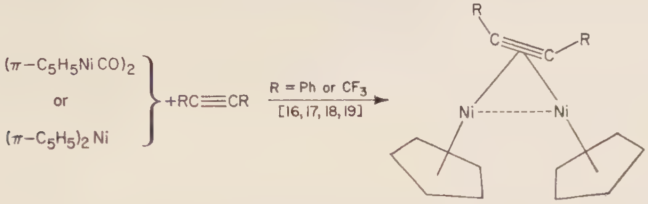
Treatment of the complexes $Co_2(CO)_8$ and $(\pi$-$C_5H_5NiCO)_2$ (which have two bridging carbonyl groups), with acetylenes displaces the bridging carbonyls forming bridging acetylene complexes.



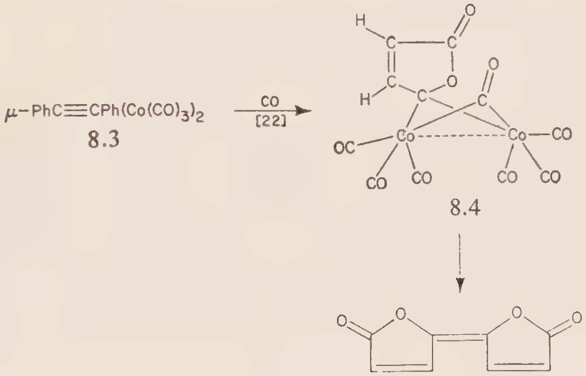
(Alternative representation)

8.3

The structure of the cobalt complex 8.3, determined by X-ray studies [20], places the acetylenic carbons between the two cobalt atoms so that the two π-bonds of the acetylene (which are normal to each other) each interact with a cobalt atom. Thus either the acetylene may be regarded as forming two π-ethylenic bonds, one to each cobalt atom, or it can be argued that the acetylenic carbons have become essentially sp^3 hybridized and are forming σ-bonds to both metals; both possible representations are shown

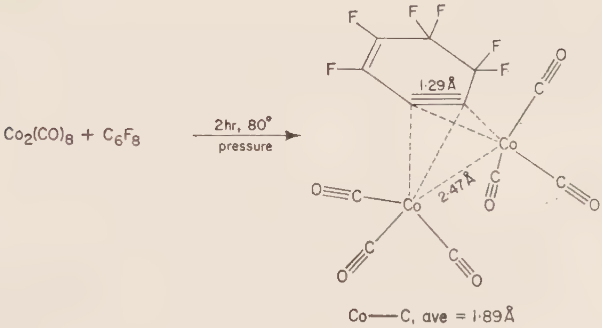


above. The cobalt complex, 8.3, reacts with carbon monoxide under pressure affording the lactone derivative, 8.4 [21]. The structure is shown by X-ray studies [22] and it explains the decomposition of the complex to the dilactone, 8.5 [23]. Diacetylenes give mixed metal derivatives $(\pi\text{-}C_5H_5Ni)_2PhC\equiv C{-}C\equiv CPh(Co(CO)_3)_2$, closely related to those decribed above [18].



8.5

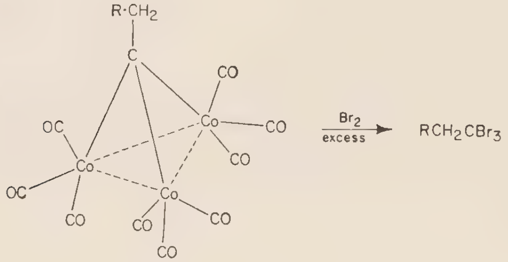
Treatment of $Co_2(CO)_8$ with perfluorocyclohexa-1,3-diene gives the complex 8.6, whose structure has been shown by X-ray studies [24, 25].



8.6

C. Monoacetylene, trinuclear complexes

Treatment of the bridging acetylene complexes $RC{\equiv}CH(Co(CO)_3)_2$ with hydrochloric acid in methanol gives complexes of stoicheiometry $RC_2H_2Co_3(CO)_9$ [26, 27]. Bromination of these complexes gives *inter alia* the products $RCH_2{-}CBr_3$ [26]. This observation together with spectral studies is consistent with the structure 8.7, for these complexes. This structure explains why they can only be obtained from monosubstituted acetylenes since their formation involves migration of a substituent from one of the carbons, and acetylenic hydrogens are readily labile.



8.7

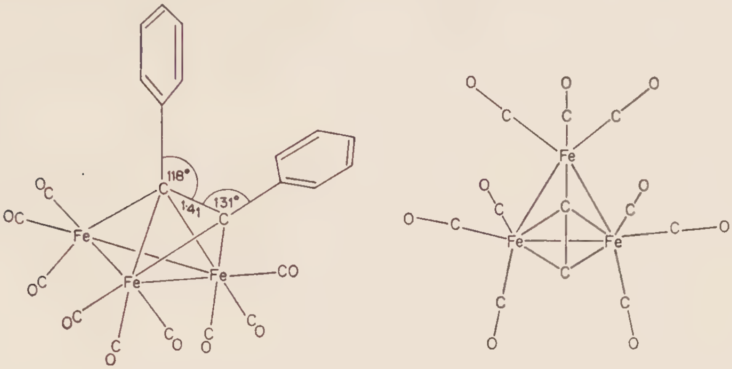
The structure of the complex $MeCCo_3(CO)_9$ has been found by X-ray diffraction to be that shown in 8.7, where R = H [27*a*]. After the complex $Co_3(CO)_9CBr$ has been heated to 90°C in anhydrous toluene one of the products formed is the binuclear $(CO)_9Co_3C{-}\underset{\overset{\|}{O}}{C}{-}CCo_3(CO)_9$ [27*b*], which has two $Co_3(CO)_9C$ clusters joined by a bridging carbonyl.

n-Butyltin trichloride and $Co_2(CO)_8$ give the related compound $Co_3(CO)_9Sn{-}C(CH_3)_3$ [28].

When diphenylacetylene and $Fe_2(CO)_9$ are reacted under mild conditions the complex, 8.7*a*, is formed; the structure has been determined by X-ray diffraction [28*a*]. Like many other compounds described in this chapter the complex, 8.7*a*, defies attempts to draw a conventional representation of the bonding.

This complex can be thought of as an earlier intermediate before the 'violet' isomer (see Figure 79), that is, the product of addition of one molecule of diphenyl acetylene to $Fe_3(CO)_{12}$.

Both the complexes 8.7 and 8.7*a* contain triangular $M_3(CO)_9$ systems and it appears that this 'metal cluster' has some special stability. It is indeed becoming clear that metal clusters of M_4 tetrahedra and M_6 octahedra, e.g. in $Co_4(CO)_{12}$ and $Rh_6(CO)_{12}$ also are relatively stable. Clearly the tendency to form strong metal–metal bonds is considerable when the metal atoms are in low oxidation states. The maximum possibility for metal–metal bonds occurs in the compact stereochemistry of these groups.

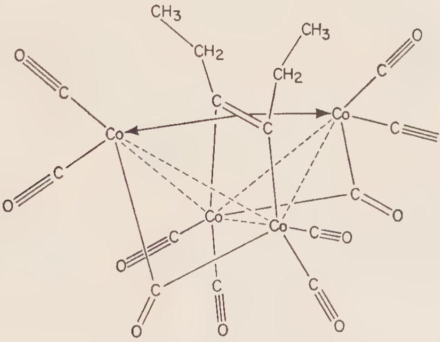


Plan omitting phenyl groups

8.7*a*

D. Monoacetylene, tetranuclear complexes

Treatment of $Co_4(CO)_{12}$ with hex-3-yne in benzene gives stable, blue crystals of stoicheiometry, $Co_4(CO)_{10}C_6H_{10}$ [29]. This complex has the structure 8.8 [30]. In this molecule the acetylene acts as a 4-electron ligand



8.8

and forms two π-bonds; and it also forms two σ-bonds in a bridging ethylene system.

E. Bis-acetylene, mononuclear complexes†

(*a*) *Cyclopentadienone and quinone metal complexes*

(*i*) *Preparation.* Complexes of cyclopentadienones or quinones may be prepared either directly from the ketone, or by treatment of metal carbonyl complexes with acetylenes (see Figures 72, 73). The former route is frequently the most convenient except when the parent dienones are unstable or unknown, e.g. cyclopentadienone itself is unstable in the free state.

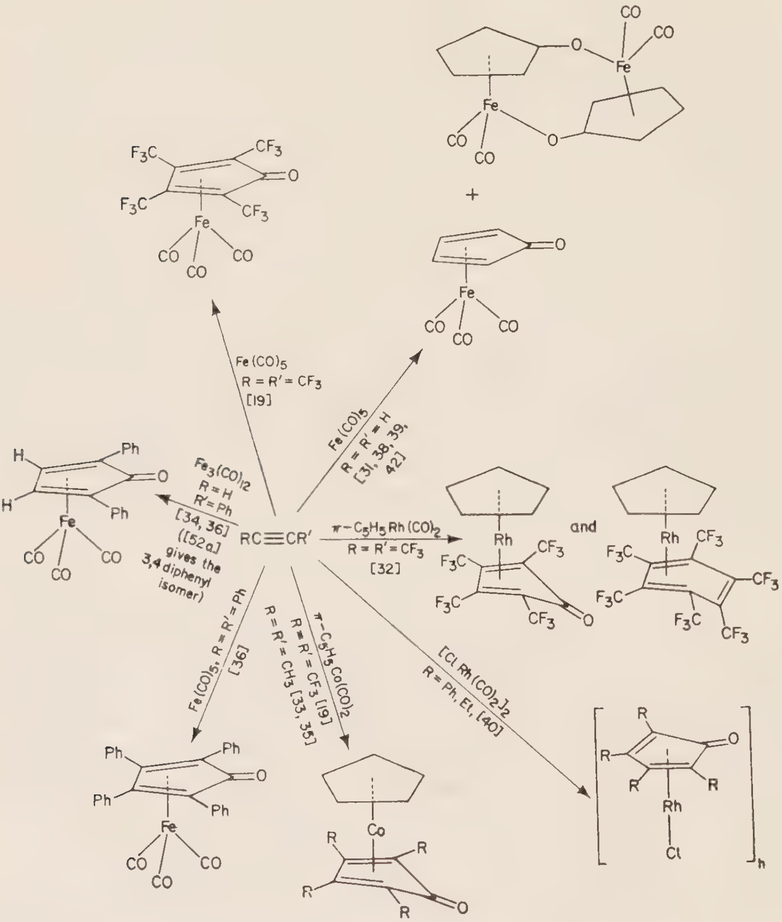


Fig. 72. The preparation of cyclopentadienone–metal complexes using acetylenes, and related reactions

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† A more detailed treatment of these complexes is given in reference [30*a*].

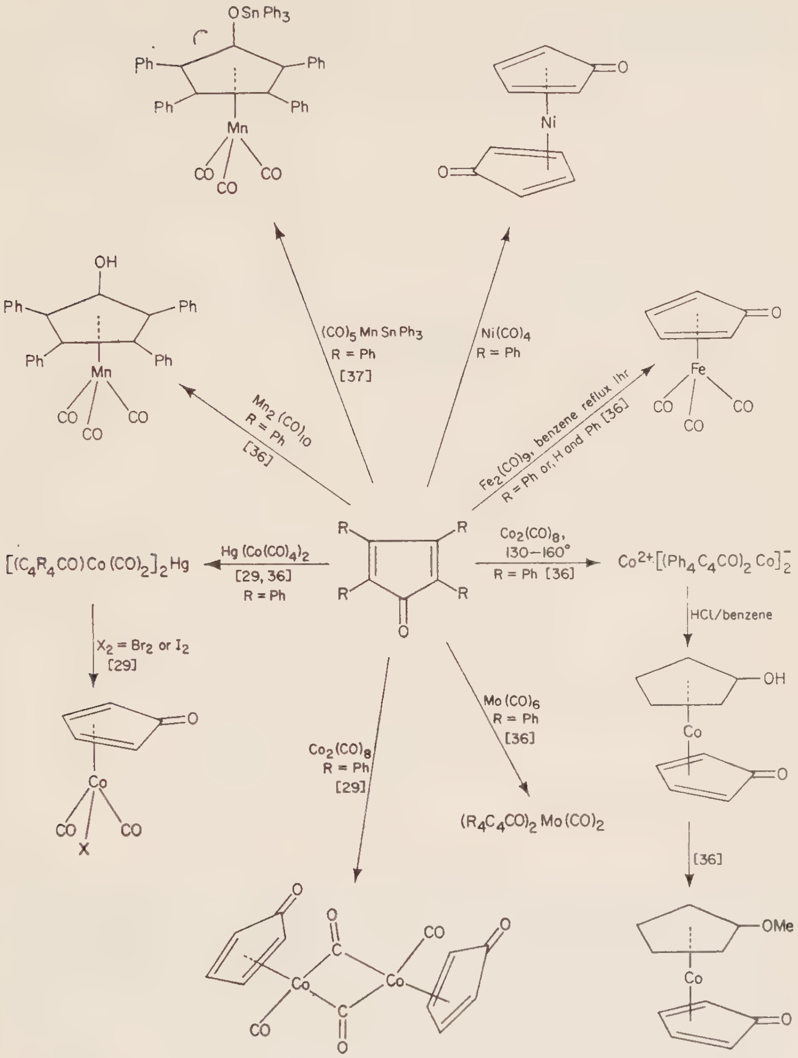
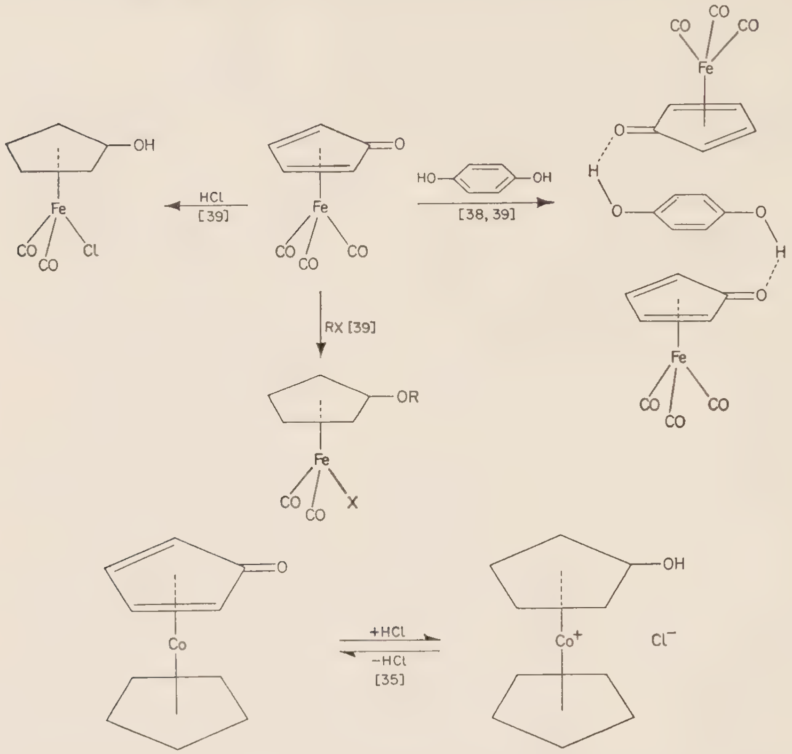
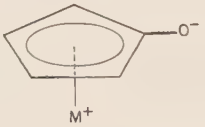


Fig. 73. The preparation of cyclopentadienone-metal complexes using cyclopentadienones; ring substituents are omitted when they are unchanged

(*ii*) *Properties of cyclopentadienone metal complexes.* Cyclopentadienones generally form stable complexes and, for example, those of iron, $R_4C_4COFe(CO)_3$, are diamagnetic, yellow, air-stable crystalline complexes which decompose in the range ~150–250°C. In all complexed cyclopentadienones the ketonic CO stretching frequency is 100–150 cm^{-1} lower than that in the uncomplexed ligand. This suggests that there is a reduction of double bond character of the C=O bond, and hence a more negative oxygen. In agreement with this observation, cyclopentadienone metal complexes are readily protonated, at this oxygen atom, e.g.



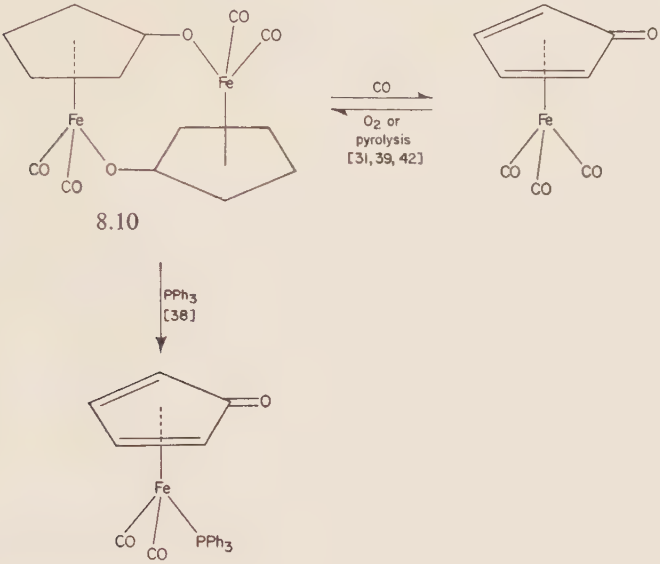
Also, as shown, the C=O system readily forms hydrogen bonds with hydroquinones and phenols [38, 39]. The above reactions demonstrate that cyclopentadienones readily form π-cyclopentadienyl systems. Indeed it is suggested that in some of these complexes the cyclopentadienone–metal



8.9

system has meso-ionic character as represented by 8.9. On the other hand, in disagreement with this suggestion, the X-ray structures of a number of cyclopentadienone complexes (see Figure 19, p. 73) show that the ketonic C=O of the ring is tipped away from the metal; thus the C_5 ring has not the planar structure expected for a delocalized C_5-system. The complex

$(C_4H_4COFe(CO)_2)_2$ has the structure 8.10 [41], where weak bridging bonds are formed by the ketonic oxygen. Two reactions of this complex are also shown. In the more polar solvents the complex is apparently monomeric [38, 39, 42]. Possibly the solvent acts as a ligand, forming a complex analogous to 8.11.



8.10

8.11

(b) Quinone complexes

Quinone complexes may be prepared either from acetylenes or from the quinone itself (see Figure 74). With nickel tetracarbonyl, most quinones react forming salt-like complexes which are best formulated as the oxidation products Ni^{2+} $(quinone)_2^{2-}$ [43, 44]. These complexes are paramagnetic, insoluble and hydroscopic and do not behave like those others where the quinone is π-bonded to the nickel. Tetramethylquinone (duroquinone), which is a less oxidizing quinone, reacts readily with nickel tetracarbonyl forming the diamagnetic, red bis-duroquinone nickel, 8.12, m.p. 205° [48].

Bis(duroquinone)-nickel readily loses a duroquinone ligand, either thermally or by displacement with olefins such as cyclo-octa-1,5-diene, cyclo-octatetraene and norbornadiene (see Figure 75) [44, 48]. These olefin complexes are remarkably stable, decomposing between 120 and 200°C. Analogous complexes of the other less oxidizing quinones, such as 2,5- or 2,6-dimethylquinones, are formed by treatment of nickel

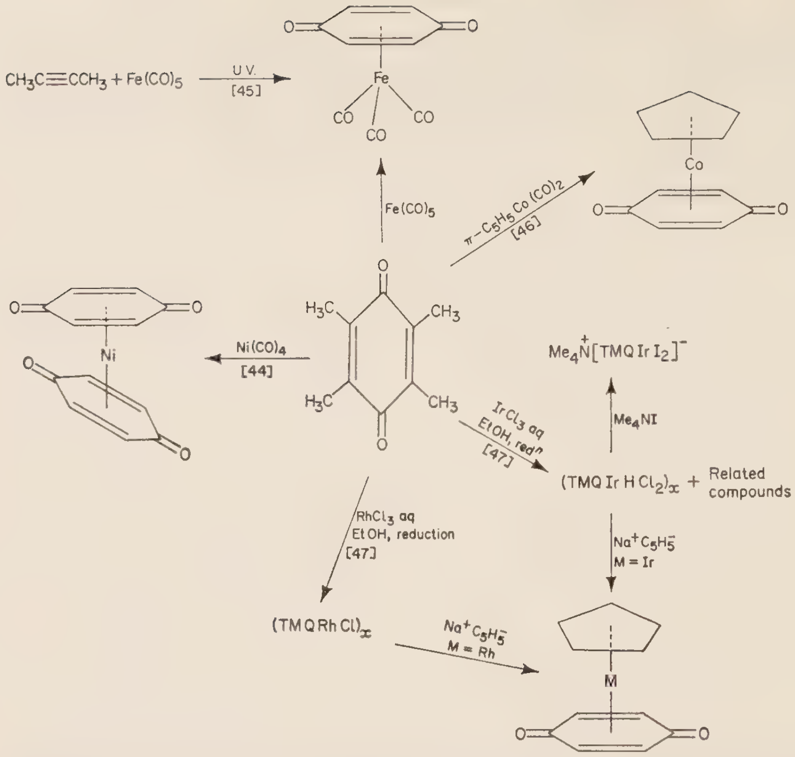


Fig. 74. The preparation of quinone–metal complexes; TMQ represents tetramethyl quinone; the methyl substituents of the quinone rings in the complexes are omitted

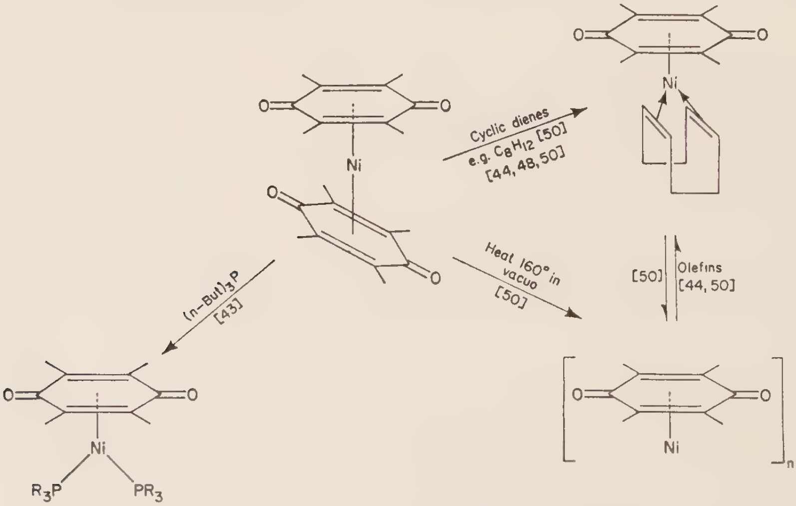
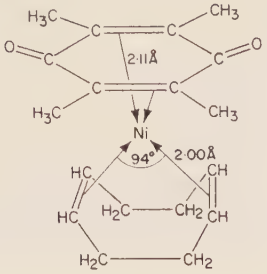


Fig. 75. Some reactions of bis-duroquinone nickel; the methyl groups are omitted for simplicity

tetracarbonyl with both the quinone and cyclo-octa-1,5-diene [44]. The



8.13

structure of duroquinone-cyclo-octa-1,5-diene nickel, 8.13, has been determined by X-ray diffraction [49].

Points of interest in the structure are the distortions of the duroquinone ring. The C=O groups are bent away from the nickel (as found in cyclopentadienone metal complexes) and the methyl groups are slightly bent towards the nickel. In this complex the C=O frequency is lowered by 133 cm^{-1} from that in the free ligand. The greater lowering compared with that in bis(duroquinone)-nickel (52 cm^{-1}) suggests that the cyclo-octa-1,5-diene is a better donor than duroquinone. Despite the marked lowering of the C=O frequency, the C=O distance in the complex, 8.13, is not significantly longer than in the free ligand. On the other hand, the C=C distances of the complexed duroquinone (1·40 ± 0·01 Å) have increased relative to those in the free ligand (1·322 ± 0·008 Å).

The structure determination also shows that the cyclo-octa-1,5-diene has a slightly skewed conformation (not drawn), and that the C=C bonds are nearer the nickel than those of the duroquinone. In this complex the olefin ligand is readily displaced, in contrast to the duroquinone ligand. One might have expected that duroquinone was the stronger ligand and would have the shorter C=C–nickel distances. The nickel–quinone bonding may not be regarded as using just the two isolated C=C systems of the quinone, since there is some interaction of the nickel with the M.O.s of quinone which are formed by all the C_6-ring carbons (and to a lesser extent the two oxygens also). Therefore it may be that the duroquinone is kinetically the more difficult to displace but, more probably, that it is the more strongly bonded ligand forming individually slightly weaker but *more* bonding interactions than the C=C systems of the cyclo-octa-1,5-diene. In the complexes π-C_5H_5M (duroquinone), where M = Co, Rh or Ir, the ketonic C=O stretches occur as doublets which suggests that the C=O groups are not in the same plane and that, presumably, they are bent away from the metal, as found in the nickel complex, 8.13.

As noted above, in all quinone complexes the ketonic C=O stretching frequencies are lower than in the free ligands. This suggests that there is donation from the metal to the quinone ligand, in agreement with the relative ease of oxidation and the electron-withdrawing properties of quinones. Quinones are strong acceptors and readily form charge transfer complexes. Schrauzer has studied the electronic spectra of a number of quinone complexes and has shown that the spectra may be interpreted by an M.O. treatment of the complexes [47, 51, 52]. The $p\pi$-electrons of the duroquinone molecule form eight M.O.s and the three which are likely to be most important in the metal–quinone bonding are shown in Figure 76. The M.O.s (A) and (B) are filled in the free quinone and the M.O. (C) is empty. The latter orbital has acceptor properties in the quinone metal complexes. Since the M.O.s (A) and (C) have nodes between the carbon and oxygens of the ketonic C=O, bonding interactions of these M.O.s with the metal will cause a repulsion of the carbonyl O relative to the carbonyl C atom [47]. Thus the interaction of the quinone M.O.s (A) and (C) with the metal can give rise to the repulsion by the metal of the C=O oxygen.

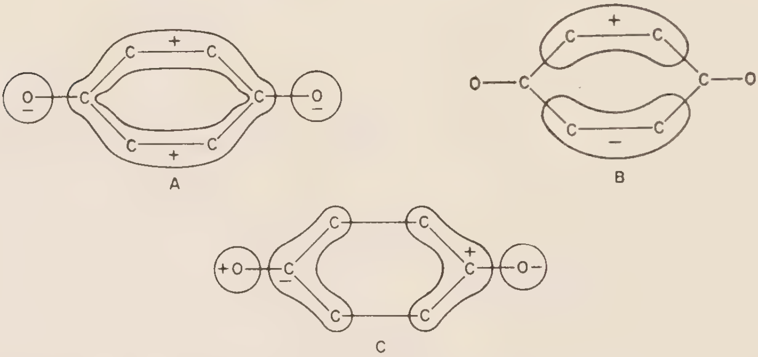


Fig. 76. Representations of one side of the two highest bonding, (A) and (B), and the lowest anti-bonding (C) molecular orbitals of quinone

(*c*) *Ferracyclopentadiene complexes*

The preparation of some ferracyclopentadiene complexes is shown in Figure 77. As shown in Figure 77, the ferradiene complexes formed from acetylenes and aqueous solutions of $NaHFe(CO)_4$ contain hydroxy groups in the 2,5-positions. These hydroxyl groups are usually acidic [57] and can be benzoylated [56] and acetylated. The structure of the complex 8.14, formed from 2-butyne, has been determined by X-ray studies [59]. In the complex 8.14, the Fe–Fe distance (2.49 Å) is similar to that found in $Fe_2(CO)_9$(2·46 Å) or $[\pi\text{-}C_5H_5Fe(CO)_2]_2$(2·49 Å). This suggests that there is a covalent Fe–Fe bond in the above complex. The structure also shows

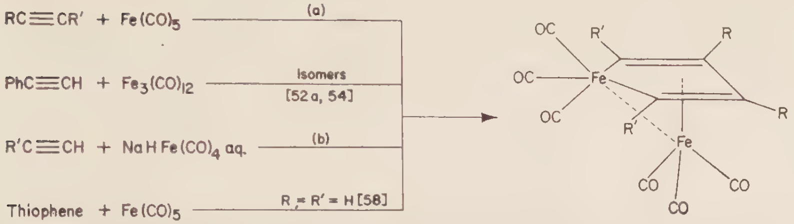
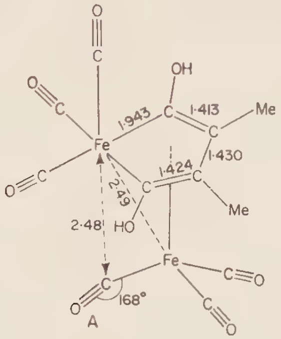


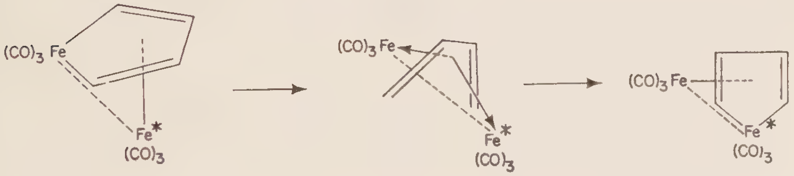
Fig. 77. The preparation of ferracyclopentadiene complexes from acetylenes and thiophene. (*a*) where R = R′ = H [31]; R = R′ = Ph [53]; R = R′ = H or Ph [55]; (*b*) where R = H, R′ = OH [56]; R = CH₃, R′ = OH [57, 58]



8.14

that there is some interaction between the carbon monoxide ligand A and the iron atom above it.

A study of optically active substituted analogues of complex 8.15, shows that they undergo rapid thermal isomerization. It is very reasonably suggested that the isomerization occurs by an intramolecular interchange of the roles of the two iron atoms, via an intermediate such as 8.16 [60].



8.15 8.16

A low activation energy, ~12 kcal., has been estimated. A number of other reactions of these complexes are shown in Figure 78.

Another product formed in the reaction between diphenylacetylene and $Fe_3(CO)_{12}$ is the complex 8.17 [54], whose structure has been shown by

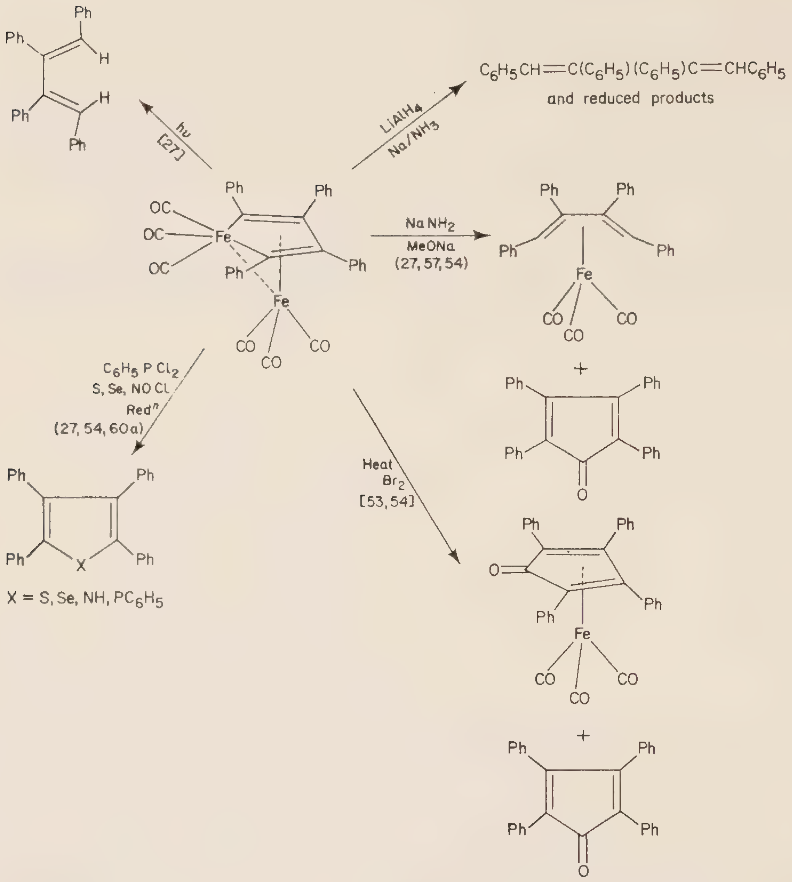
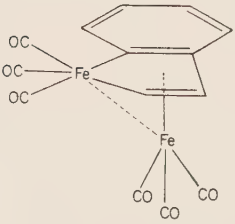


Fig. 78. Some reactions of 1,1,1-tricarbonyl-2,3,4,5-tetraphenylferracyclopentadiene iron tricarbonyl

X-ray analysis [61]. The X-ray studies show that in the complex 8.17, the unco-ordinated portion of the benzene ring has alternating C=C distances.



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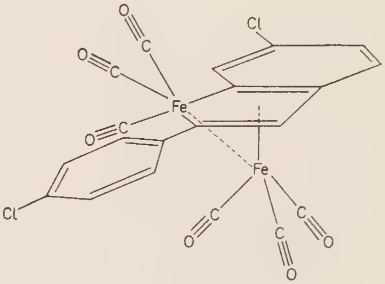
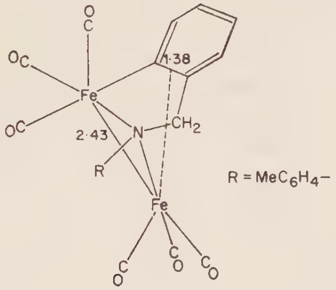


8.18

None the less, the benzene ring seems to retain aromatic properties [62]. It is interesting to contrast the related complexes bis-π-indenyliron [63, 64] and π-cyclopentadienyl-π-indenyl iron [65, 66] where some stabilization of the Kekulé structure of the benzene system of the π-indenyl ligand is suggested, since there is loss of aromaticity of the ring. Thus the uncoordinated 'diene' part of the benzene ring in 8.17 is readily hydrogenated.

Also given above is the structure of the complex 8.18, formed by treatment of bis-p-chlorophenylacetylene with $Fe_3(CO)_{12}$ [62]. The formation of both the complexes, 8.17 and 8.18, involves the removal from an aromatic C_6 ring of a hydrogen which is in the *ortho*-position to the C≡C system. It is interesting that azobenzene reacts with $Fe_2(CO)_9$ giving the complex, 8.18*b*, which has a structure similar to 8.17 [67]. Again, an *ortho*-hydrogen has been removed from the benzene ring in this reaction.



8.18*b*

This loss of *ortho*-hydrogens also occurs in the chemistry of other transition metal–aromatic systems and these reactions may be associated with the general reactivity of atoms and groups in the β-position of hydrocarbon ligands attached to transition metals.

F. Bis-acetylene, trinuclear complexes

Treatment of $Fe_3(CO)_{12}$ with diphenylacetylene in methanol yields a violet complex $Fe_3(CO)_8(PhC_2Ph)_2$ which, in boiling benzene or petroleum, undergoes rearrangement to a black isomer [54]. The X-ray structures of both isomers have been determined [68] and are given in Figure 79; that of the black isomer shows a central ferracyclopentadiene ring with iron atoms bonded to either side of the plane of the ring. The less stable violet isomer has two separate acetylenes bonded to either side of the triangular plane formed by the three iron atoms. The black isomer decomposes at 150° forming the binuclear ferracyclopentadiene complex, shown in Figure 78. Thus it can be visualized that in this decomposition an acetylene is first attached to each side of the Fe_3-triangle in $Fe_3(CO)_{12}$ (violet isomer) followed by the formation of a ferracyclopentadiene ring by the acetylenes

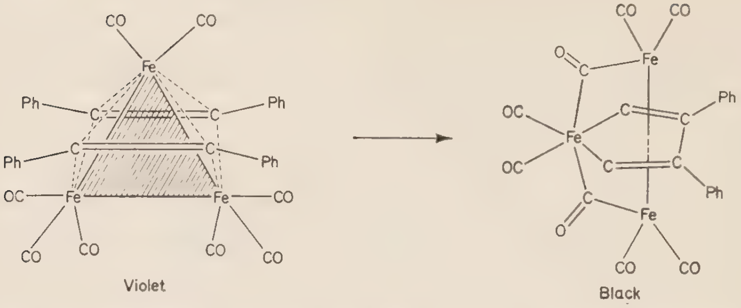


Fig. 79. The structures of the violet and black isomers which are products of the reaction of PhC≡CPh with $Fe_3(CO)_{12}$

and one iron atom (black isomer) and finally an $Fe(CO)_2$ system is lost giving the binuclear ferracyclopentadiene complex (see Figure 78).

G. Tris-acetylene, mononuclear complexes

The trimerization of acetylenes by transition metal complexes may give π-arene complexes and these reactions are discussed in Chapter 5.

As noted in the introduction, the complexes formed by the reactions between acetylenes and iron carbonyls depend markedly on the conditions employed. Treatment of $Fe_3(CO)_{12}$ with substituted acetylenes at 80°C in inert hydrocarbon solvents gives reasonable yields of substituted tropone iron carbonyl complexes and tropone iron tricarbonyl is formed from acetylene and $Fe_2(CO)_9$ at room temperature. Tropone iron tricarbonyl [69, 70], which has a structure similar to that shown in Figure 80, for the 2,4,6-triphenyltropone derivative [71], forms adducts with hydroquinones as do the cyclopentadienones. In contrast to the cyclopentadienone complexes, the ketonic C═O gives the normal reactions of the group. The platinum-catalysed hydrogenation of the complex gives 2,4- and 3,5-cycloheptadienone iron tricarbonyl complexes and related complexes

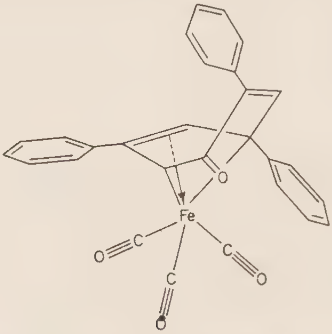
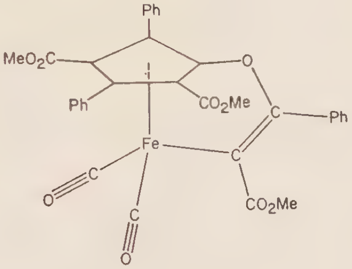


Fig. 80. The structure of one isomer of 2,4,6-triphenyltropone iron tricarbonyl

where two C_7 rings have become joined by a C–C bond during the hydrogenation.

Phenylacetylene and $Fe_3(CO)_{12}$ give, as the main products, isomeric triphenyltropone iron tricarbonyl complexes. Both complexes liberate 2,4,6-triphenyltropone when the complex is treated with Ph_3P [52*a*]. Therefore it may be assumed that both complexes contain this tropone. The X-ray structure of one isomer has been determined [72] and is shown in Figure 80. In this molecule, the tropone ring is attached to the iron by a diene system and the third double bond is bent out of the plane of the diene carbons, away from the iron. The other isomer of this complex is presumably that in which the tropone bonds to the iron by the alternative diene system of the ligand [52].

The acetylene $PhC{\equiv}CCO_2Me$ reacts with $Fe_2(CO)_9$ forming, as by now would be expected, substituted-cyclobutadiene- and substituted-cyclopentadienone iron tricarbonyl derivatives. An unexpected product of the reaction is the π-cyclopentadienyl compound, 8.19, whose crystal structure has been determined [72*a*].

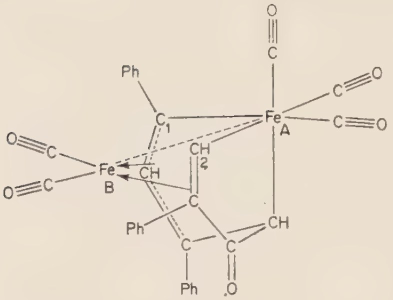


8.19

H. Tris-acetylene binuclear complexes

A most extraordinary complex, prepared from phenylacetylene and $Fe_3(CO)_{12}$, of stoicheiometry $(PhC{\equiv}CH)_3Fe_2(CO)_6$, has the crystal structure 8.20 [73]. This shows the ligand is acting as a 1-, 2- and 3-electron ligand. Treatment of this complex with triphenylphosphine gives the isomers of 2,4,6-triphenyltropone discussed above. This is not so surprising in the light of its structure since removal of the $Fe_A(CO)_3$ moiety and coupling of C_1 and C_2 gives the tropone complex. Another product formed from acetylene and $Fe_3(CO)_{12}$ in light petroleum, of stoicheiometry $(C_2H_2)_3Fe_2(CO)_6$ [74], has the structure 8.22 [75].

If the iron atoms attain the inert gas structure, spin-pairing by an Fe–Fe interaction seems probable; $p\text{-}BrC_6H_4C{\equiv}CH$ forms similar complexes [52*a*]. Yet another product formed from acetylene and $Fe_3(CO)_{12}$ in light petroleum is the isomeric complex $(C_2H_2)_3Fe_2(CO)_6$ [74], which



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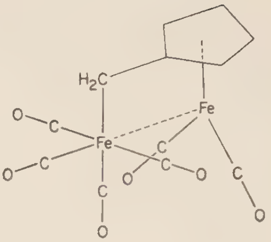

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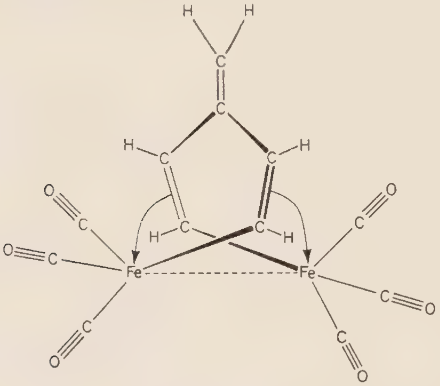


8.22

X-ray studies show to contain a π-cyclopentadienyl system [75] as is shown in 8.21. In the preparation of this complex a hydrogen migration must have occurred. Related complexes with π-cyclopentadienyl ligands are formed from phenylacetylene [52*a*] and fulvenes (see Figure 81). Other π-cyclopentadienyl complexes and some olefin–iron complexes formed from fulvenes are also shown in Figure 81.

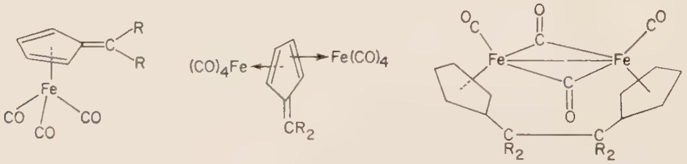
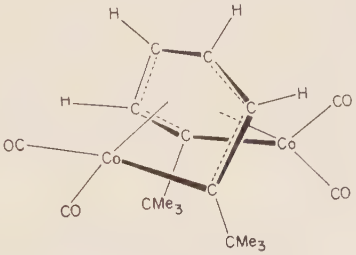


Fig. 81. Some products formed in the reaction between fulvenes and iron carbonyls [76]

The structure of a remarkable cobalt complex of stoicheiometry $Co_2(CO)_4(C_2HBu^t)_2(C_2H_2)$ provides a fascinating insight into a mechanism of polymerization of acetylenes. The complex is prepared from $Co_2(CO)_8$ and the acetylenes. X-ray studies show the structure given in 8.23 [78]. The bonding of the hydrocarbon residue may be described in terms of a 'fly-over', bis-π-enyl system. The distance Co–C_3(π-enyl) is 2·04 Å.

The complex gives *ortho*-di-t-butyl benzenes on decomposition by bromine. The deep violet complex $Co_2(CO)_4(C_2HBu^t)_3$ (m.p. 81 °C) [77] similarly decomposes giving 1,2,4-tri-t-butylbenzene.

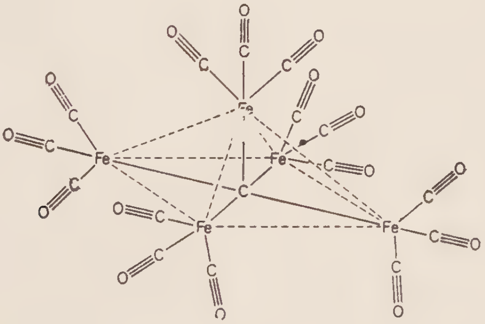
The formation of these *ortho*-substituted benzenes, which cannot be prepared by substitution of t-butyl benzene, can be understood in the light of the structure of the cobalt complex since the t-butyl groups occupy adjacent positions in the complex.



8.23

I. Miscellaneous

A very unusual by-product (0·5% yield) of the reaction between $Fe_3(CO)_{12}$ with certain acetylenes such as 1-pentyne is the black crystalline complex $Fe_5(CO)_{15}C$, 8.24. The X-ray structure of this complex shows that there is a formally *penta*-co-ordinate carbon atom which is located slightly below the basal plane of four iron atoms. The carbon atom is approximately equidistant from the five iron atoms. The average Fe–Fe distance is 2·64 Å [79]. It is not possible to give a simple conventional description of the bonding in this complex, and a multi-centred molecular orbital approach is necessary. In this molecule the environment of the carbon must be similar to that of carbon atoms in some metal carbides (average Fe–C distance = 1·75 Å).



8.24

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CHAPTER NINE

The role of organotransition metal complexes in some catalytic reactions

The application of transition metal ions and complexes in synthetic organic chemistry is widespread. This chapter is by no means intended to be a comprehensive review of this subject and only a few reactions are considered in detail. Major topics such as the use of transition metal compounds in the oxidation of organic complexes are omitted, mainly because it is generally true that the well-known oxidants, such as Ce(IV), V_2O_5, $CrO_4{}^{2-}$, $MnO_4{}^-$ and OsO_4, do not act via intermediates with metal–carbon bonds and also because this subject has been adequately discussed elsewhere [1].

The reactions discussed below are:

(B) Isomerization of olefins
(C) Hydrogenation of olefins and acetylenes
(D) Dimerization, oligomerization and polymerization of olefins and acetylenes
(E) Hydroformylation and related carbonylation reactions
(G) Miscellaneous reactions, e.g. the oxidation of ethylene to acetaldehyde, some reactions catalysed by copper and nitrogen fixation.

All these reactions either have stable, isolable organometallic complexes as the catalyst or it is thought that they involve unstable organometallic intermediates.

A considerable number of these reactions involve the transfer of hydrogen and in many cases it is thought that intermediates containing metal–hydrogen systems are involved. Therefore, a brief discussion of the chemistry of some transition metal hydrides precedes a discussion of their possible roles in catalysis.

A. Some chemistry of transition metal hydride complexes

Many complexes are known which contain one or more hydrogens directly attached to a transition metal by an essentially covalent bond [2, 3]. The occurrence and stability of these complexes frequently parallels that of metal–alkyl complexes. Thus thermally stable transition metal–hydrides are found when the complexes are kinetically stable, that is, they often obey the 18-electron rule or, in the case of square-planar platinum(II) complexes, a 16-electron rule.

Some typical hydride complexes are shown in Table 28.

Table 28 *A classification and some examples of transition metal hydride complexes*

Complex hydrides with tertiary phosphines and related ligands			
trans-$H_2Fe(o\text{-}C_6H_4(PEt_2)_2)_2$	orange	248–249·5°	[4]
trans-$HClRu(C_2H_4(PEt_2)_2)_2$	colourless	175°; 310° dec.	[5]
trans-$OsH_2(o\text{-}C_6H_4(PEt_2)_2)_2$	lemon	293–297°	[5]
$HCo(C_2H_4(PPh_2)_2)_2$	red	—	[6]
$H_3Ir(PPh_3)_3$	colourless	isomers	[7]
trans-$HPtCl(PEt_3)_2$	colourless	81–82°	[8]
Mono- and poly-nuclear carbonyl hydrides			
$HMn(CO)_5$	colourless	−24·6°	[9]
$H_2Fe(CO)_4$	pale yellow	−70°	(see [2, 3])
$HCo(CO)_4$	yellow	−26°	(see [2, 3])
$[HCr_2(CO)_{10}]^-$ salts	colourless	—	[10]
π-Cyclopentadienyl carbonyl hydrides			
$\pi\text{-}C_5H_5Mo(CO)_3H$	pale yellow	50–52°	[11]
$\pi\text{-}C_5H_5Fe(CO)_2H$	pale yellow	−5°	[12, 35]
Bis-π-cyclopentadienyl hydrides			
$(\pi\text{-}C_5H_5)_2TaH_3$	white	187–189° dec.	[13, 14]
Hydride complexes containing nitrogen ligands			
[*trans*-$Rh(en)_2HCl]^+$	pale yellow	—	[15]
'Pure' transition metal hydrides			
K_2ReH_9	white	—	[16]
Complex cyanide hydrides			
$[Co(CN)_5H]^{3-}$	yellow	—	[17]

(*a*) *Preparation*

Transition metal–hydrogen bonds may be formed directly from hydrogen by addition reactions,

$$(PPh_3)_2IrCOCl \xrightleftharpoons[\text{[18]}]{H_2,\ 1\text{ atm.}} (PPh_3)_2IrCOClH_2$$

$$(PPh_3)_3RhCl \xrightleftharpoons[\text{[19]}]{H_2,\ 1\text{ atm.}} (PPh_3)_2RhH_2Cl$$

by cleavage of a metal–metal bond,

$$Co_2(CO)_8 \xrightarrow[\text{[20] }25^\circ]{H_2,\ 30\text{ atm.}} HCo(CO)_4$$

and from other metal systems such as complex metal halides,

$$cis\text{-}(PEt_3)_2PtCl_2 \xrightarrow[\text{ethanol, 95°}]{H_2\text{, 50 atm.}} trans\text{-}(PEt_3)_2PtHCl$$

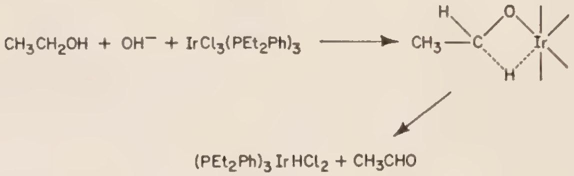
[8]

All these methods of preparation are important in different catalytic reactions. Other methods of preparation of metal–hydrides from metal–halogen complexes include the straightforward replacement of the halide using Group III complex hydrides, e.g.

$$[en_2RhCl_2]^+ \xrightarrow[H_2O\ [15]]{NaBH_4} [en_2RhHCl]^+$$

$$(PPh_3)_3IrHCl_2 \xrightarrow[THF]{LiAlH_4} (PPh_3)_3IrH_3$$

or other reducing reagents may be used, such as hydrazine, sodium dithionite, hypophosphorous acid, formic acid or even alcohols in the presence of a base. A simple example of the latter reagent is ethanol and potassium hydroxide. In this case the formation of the metal–hydride is thought to proceed in the following manner.



The origin of the M–hydrogen from the α-carbon has been shown, using CH_3CD_2OH [21]. It is interesting that in reactions of this type a carbon monoxide molecule may sometimes be abstracted from the alcohol giving a metal carbonyl hydride, viz.

$$(NH_4)_2OsCl_6 + \text{excess } PPh_3 \xrightarrow[\text{190°C, 4·5 hr (92\%)}]{\text{2-(}\beta\text{-methoxyethoxy)ethanol}} (PPh_3)_3OsHCl(CO)$$

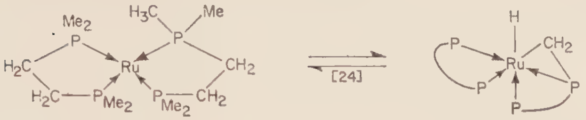
[22]

Certain complex transition metal anions, in particular the carbonyl anions, are strongly basic and readily form hydrides on treatment with water or weak acids,

$$[Fe(CO)_4]^{2-} \xrightarrow{H_2O} [HFe(CO)_4]^- \xrightarrow{H^+} H_2Fe(CO)_4$$

Water is also the source of the M–hydrogen in the preparation of complex cyanide hydrides such as $[Co(CN)_5H]^{3-}$ [17, 23].

As has been discussed earlier, in certain transition metal complexes the metal may readily abstract a hydrogen from alkyl groups in the β-position with respect to the metal.



Indeed, the complex $Ir(PPh_3)_3Cl$ forms a hydride, $Ir(PPh_3)_3H_xCl$, simply on being heated in benzene [24*a*]. Hydrogen is lost from the phenyl groups of the PPh_3 ligands.

It is an important conclusion that transition metals readily bond with hydrogen and that the hydrogen may arise from different sources, including hydrocarbon ligands.

(*b*) *The nature of the metal–hydrogen bond*

All the structure determinations on transition metal hydride complexes show, beyond doubt, that hydrogen occupies one co-ordination position on the metal.

However, there are, at present, relatively few accurate and undisputed determinations of transition metal–hydrogen distances. Studies on $RhH(CO)(Ph_3P)_3$ by X-ray diffraction [24*b*], and on potassium enneahydridorhenate, $K_2[ReH_9]$, by X-ray and neutron diffraction [24*c*] have located the hydrogens and give the reliable metal–hydrogen distances, Rh–H = 1·60 ± 0·12 Å, Re–H = 1·68 ± 0·01 Å (see Figure 81*a*).

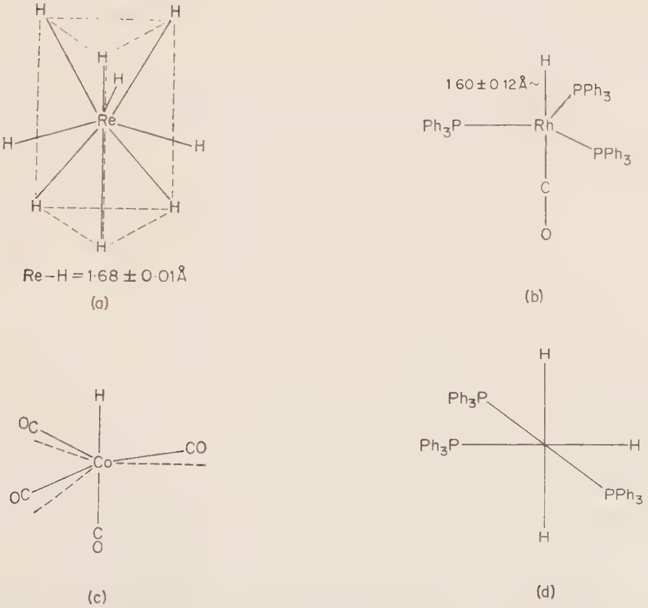


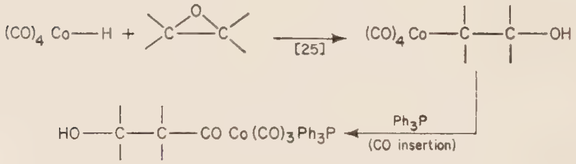
Fig. 81a. (*a*) Crystal structure of the anion $[ReH_9]^{2-}$; (*b*) crystal structure of $RhH(CO)(PPh_3)_3$; (*c*) Proposed structure of $CoH(CO)_4$; (*d*) Proposed structure of $CoH_3(Ph_3P)_3$.

These values are acceptable in terms of a normal covalent bond. In contrast, broad-line proton magnetic resonance spectra suggest comparatively short metal–hydrogen distances, for example 1·28 Å and 1·2–1·4 Å in $MnH(CO)_5$ and $CoH(CO)_4$ respectively [24*d*, 24*e*]. These very short distances remain to be confirmed, for example by neutron diffraction; however, a large range of transition metal–hydrogen distances might be expected as the radius attributed to hydrogen in other covalent hydrides is known to vary more than for other atoms. The proton is very small whereas the crystal radius of the hydride ion is about 1·5 Å, which is larger than that of the fluoride ion. Thus, the hydrogen ligand would be expected to be very sensitive to the nature of its environment; in particular to the metal and the other ligands attached to the metal. Certainly the infrared stretching frequencies of the M–H bond are markedly sensitive to changes of ligands on the metal; also surprisingly large solvent effects on the M–H stretching frequency are observed [2, 3].

(*c*) *Properties*

A property of transition metal hydride complexes which is frequently important in their catalytic reactions is that they add to olefins, often reversibly, e.g.

or to cyclic systems, such as in ethylene oxide



(*d*) *Bridging hydrogen systems*

Two-co-ordinate hydrogen is still rare even though the presence of hydrogen bridges in boron hydrides and the bihalide anions such as $[HF_2]^-$ has been long established. Bridging hydrogen systems which are obviously closely related to those in diborane are found in the bridging borohydride complexes shown in Figure 81*b*. The crystal structures of a number of binuclear transition metal hydrides show that there is a hydrogen which symmetrically bridges the two metals. In the structure determinations the hydrogen itself has not been located but the symmetry of the molecule requires that the hydrogen bonds equally to both metals. The structures are shown in Figure 81*b*. As with the boron hydrides, the M–H–M bonding is best described in terms of multi-centred molecular orbitals.

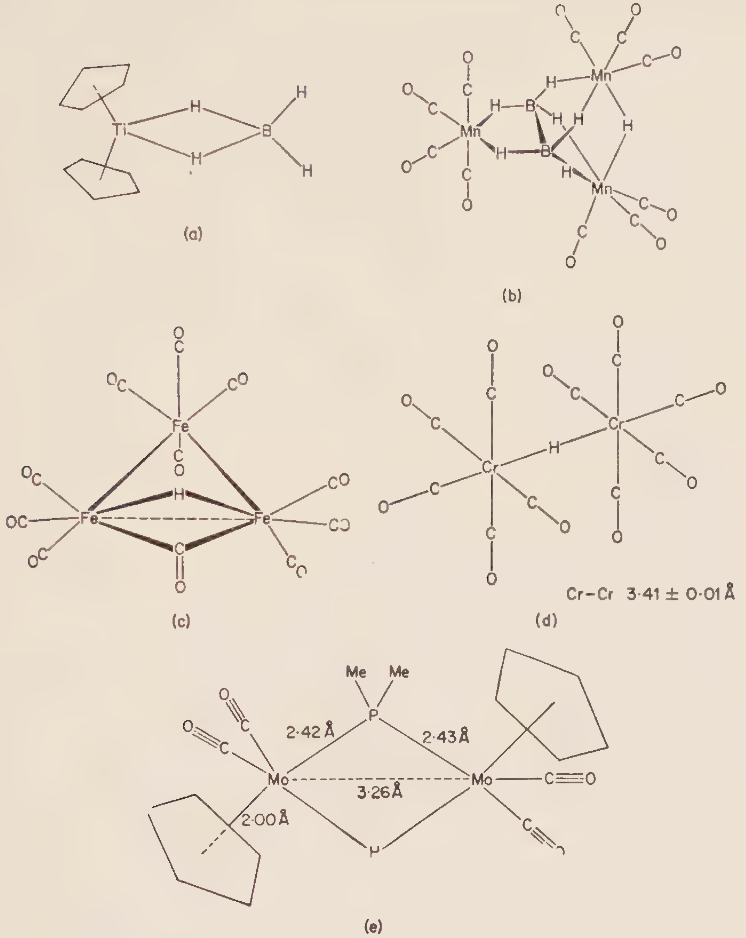


Fig. 81b. (*a*) Proposed structure of $(\pi\text{-}C_5H_5)_2TiBH_4$ (see p. 133). Crystal structures of (*b*) $HMn_3(CO)_{10}(BH_3)_2$ [24*f*]; (*c*) $[HFe_3(CO)_{12}]^-$ [24*i*]; (*d*) $[Cr_2H(CO)_{10}]^-$ [24*h*]; and (*e*) $(\pi C_5H_5)_2Mo_2H(PMe_2)(CO)_4$ [24*g*]

These molecules are mentioned here since it is likely that complexes containing bridging hydrogen are important in some catalytic reactions.

B. Some catalytic reactions which involve hydrogen transfer: isomerization reactions†

Olefins may be isomerized under homogeneous conditions by a variety of solutions of transition metal compounds. The active catalyst may be the

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† For a review, see reference [25*a*].

transition metal compound added to the reaction mixture or some derivative of it. Examples of some isomerization reactions are given in Table 29.

Table 29 *Examples of some homogeneously catalysed isomerization reactions*

Reaction	Catalyst or catalyst precursor	Reference
1-Pentene to internal isomers	$RhCl_3$ in methanol, Pt/Sn compounds	[26, 26*a*]
1-Hexene to 2,3-hexene isomers	$[HFe(CO)_4]^-$ aq $Fe_3(CO)_{12}$	[27, 37]
1-Hexene to 2,3-hexene isomers	Pt(II) complexes and $RhCl_3$ aq.	[38]
4-Methylpent-1-ene to isomers	$HCo(CO)_4$ (hydroformylation conditions)	[28]
1-Octene to internal isomers	$Mo(CO)_6$	[37]
1-Dodecene to internal isomers	$Fe(CO)_5$	[29]
Olefins to internal isomers	$PdCl_2$, NaCl in glacial acetic acid	[30]
1,4-Pentadiene to 1,3-pentadiene	$Fe_3(CO)_{12}$	[39]
Isomerization of cyclo-octadienes	$Fe(CO)_5$ $RhCl_3$ aq.	[40] [31]
Allyl alcohol to propionaldehyde	$Fe(CO)_5$ $HCo(CO)_4$	[32] [43]
Propylene oxide to acetone	$Co_2(CO)_8$ in methanol	[33]

It is a general postulate of all mechanisms of olefin isomerization reactions involving transition metals that the olefin reacts reversibly with the transition metal to give an organometallic intermediate and that in this intermediate a hydrogen attached to a sp^3-carbon is labilized by the metal. It would be expected that hydrogens attached to sp^3-carbons in a β-position with respect to the metal would be readily labilized. Some mechanisms incorporating these postulates are shown in Figure 82. The mechanisms (*a*) and (*b*) have been proposed by several authors [34, 35, 36, 37] and they are both plausible. Mechanism (*a*) involves a 1 : 2 hydrogen shift, whilst (*b*) involves a 1 : 3 hydrogen shift. It seems probable that both the mechanisms may occur in different reactions. It is also possible that some isomerizations may involve intermediates where two olefins are attached to the same metal atom.

At present little is understood about the factors which are important in determining the products of isomerization reactions. A study of the isomerization of mono-olefins by $Fe(CO)_5$ shows that the distribution of the mono-ene isomer products is that which would be expected on the basis of their relative thermodynamic stabilities [37]. The isomerization of non-conjugated dienes to conjugated compounds is very frequently found [39, 40]. Of course, conjugated dienes are usually the more thermodynamically stable. A study of the isomerization of cyclo-octa-1,5-diene by aqueous solutions of rhodium trichloride shows that both 1,3- and 1,4-dienes are formed [41]. When cyclo-octa-1,3-diene is added to aqueous rhodium trichloride, however, the cyclo-octa-1,5-diene complex

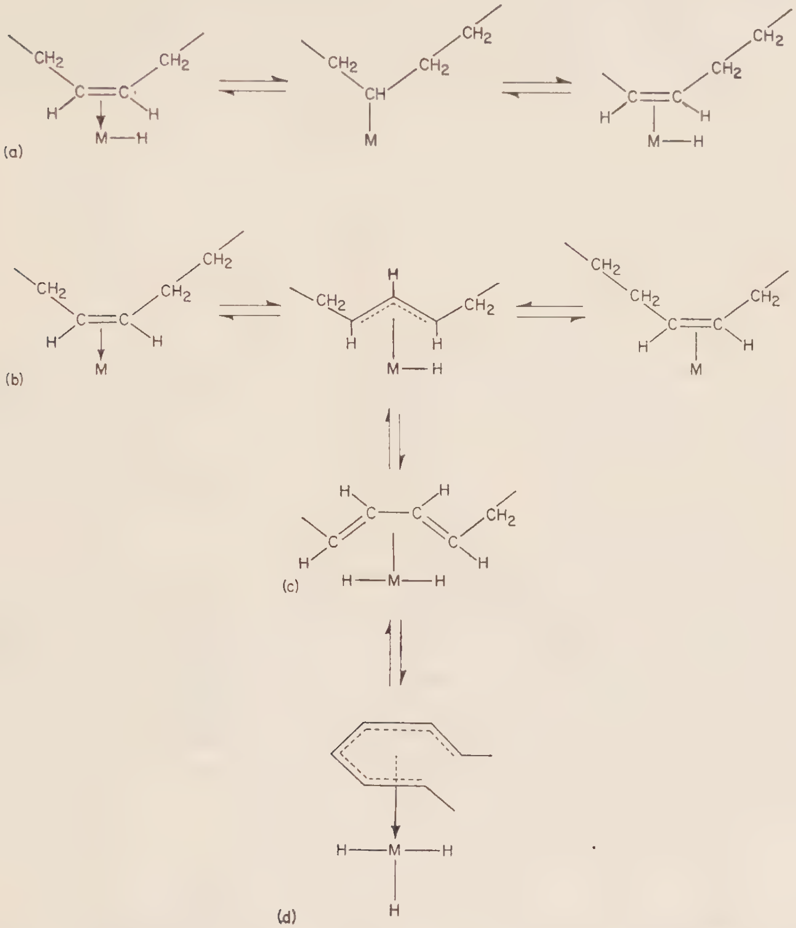
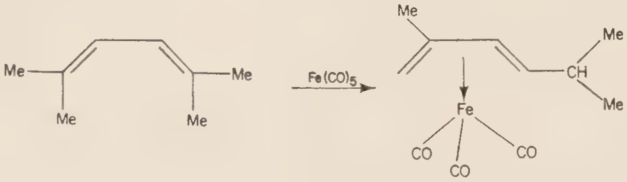
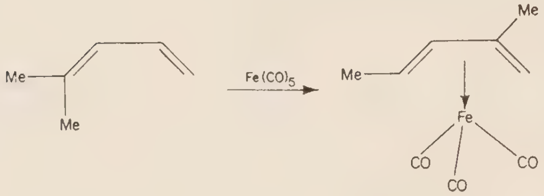


Fig. 82. (*a*) Representation of 1- to 2-electron ligand mechanism of isomerization. This mechanism necessitates the prior formation of a metal-hydride. (*b*) Representation of a 2- to 3-ligand mechanism of isomerization. (*c*) and (*d*) show 3- to 4- and 4- to 5-electron ligand equilibria which might also be important in some isomerization reactions

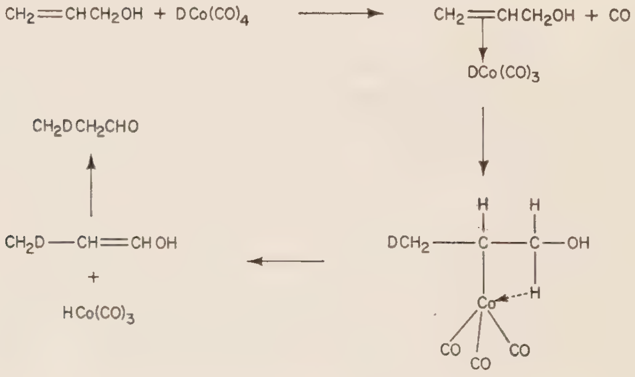
$[C_8H_{12}RhCl]_2$ is formed from which the free cyclo-octa-1,5-diene may be obtained by displacement, without isomerization. Obviously, cyclo-octadienes are isomerized readily by aqueous solutions of rhodium trichloride but only the 1,5-diene forms a stable binuclear rhodium complex. The Group VI metal carbonyls also isomerize cyclo-octa-1,3-diene giving cyclo-octa-1,5-diene metal tricarbonyl complexes. When cyclo-octa-1,3-diene is refluxed with $Cr(CO)_6$ in *n*-butyl ether then *o*-xylene$Cr(CO)_3$ is formed in 2% yields [41*a*]. This isomerization reaction involves both hydrogen migration and the breaking of carbon–carbon bonds.

Iron pentacarbonyl isomerizes *cis*-substituted conjugated dienes giving *trans*-substituted products [42]. It has been suggested that the *trans*-substituted olefins are the stable products of these reactions since in this configuration the substituents would interact less with the metal; examples are:

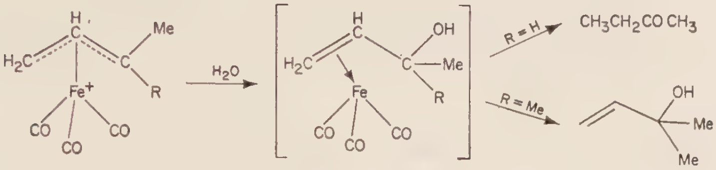




The latter examples suggest that, as well as the relative thermodynamic stabilities of the olefin products, both the steric and electronic requirements of the metal catalyst may be important in determining products of these isomerization reactions. A final example of isomerization reactions is the formation of propionaldehyde from allyl alcohol. This reaction is catalysed by $HCo(CO)_4$ and proceeds very rapidly. Using the deuteride $DCo(CO)_4$ it has been shown that CH_2DCH_2CHO is formed exclusively [43]. A type (*a*) mechanism has been postulated, viz.



Allyl alcohol is also isomerized to propionaldehyde by iron pentacarbonyl and the mechanism may be similar to that shown for $HCo(CO)_4$. However, the observation that the cation 9.1, where R = H, hydrolyses to give methyl-ethylketone, presumably by migration of the allylic hydrogen, suggests that a mechanism of type (*b*) is also possible in this case. It is interesting to note that the cation, 9.1, where R = Me, which does not have the allylic hydrogen, hydrolyses to give $CH_2{=}CHCMe_2OH$ [42].



Postulated mechanism

9.1

C. Homogeneous hydrogenation of olefins and acetylenes

The variety of transition metal complexes which will catalyse the hydrogenation of unsaturated hydrocarbons under homogeneous conditions is exemplified in Table 30. Only two of these reactions, which have been studied in some detail, are discussed here.

Table 30 *Examples of some homogeneously catalysed hydrogenation reactions*

Reaction	Catalyst or catalyst precursor	Reference
Ethylene and other olefins to paraffins	Platinum–tin complexes	[44]
Olefins, except ethylene to paraffins	$Rh(PPh_3)_3Cl$	[47, 48]
Olefins to paraffins	$(Ph_3P)_3RhCOH$ $(PPh_3)_3IrCOH$ *trans*-$(PPh_3)_2IrCOCl$	[49, 50]
	Ru(II)aq	[45]
Acetylene to ethane	Platinum–tin complexes	[44]
1-hexyne to n-hexane	$Rh(Ph_3P)_3Cl$	[48]
Butadiene to *cis*- and *trans*-2-butenes and 1-butene	$[Co(CN)_5H]^{3-}$	[51]
Methyl linoleate to isomers of mono-enoic fatty esters	$Fe(CO)_5$	[46]
Ethylcrotonate to ethylbutanoate	$PdCl_2$ + metal ions such as the acetates of Cu^{2+}, Ni^{2+}, Zn^{2+}, Ag^{+}	[46*a*]
Maleic and fumaric acids to saturated acids	Cr(II) sulphate in aqueous dimethylformamide	[38]
	$Ru(II)Cl_2aq$	[45]
Aliphatic dienes to mono-enes and unsaturated acids to saturated acids	$[Co(CN)_5H]^{3-}$	see p. 323

Benzene solutions of $(PPh_3)_3RhCl$ (10^{-4}M.) will catalyse the reduction of olefins, except ethylene [47], and acetylenes [48], under very mild conditions and the catalyst is rather better than Adams' catalyst.

$$\text{olefin} + H_2 \xrightarrow[\substack{\text{room temperature}\\ \text{atmospheric pressure}}]{\text{benzene, }(PPh_3)_3RhCl} \text{paraffin}$$

The reaction in benzene is fast and the rate is approximately doubled if a 1 : 1 ethanol : benzene solution is used. In the presence of solvents such as pyridine which may add to the metal atom, the catalytic activity is lost.

Benzene solutions of $(PPh_3)_3RhCl$ are non-polar but molecular weight determinations show that one phosphine ligand has dissociated from the rhodium. Thus the rhodium complex in the benzene may either be $(PPh_3)_2RhCl$ or a solvated species $(PPh_3)_2RhCl(\text{solvent})_x$. The benzene solution readily and reversibly absorbs hydrogen. From chloroform solutions of $(PPh_3)_3RhCl$ and H_2 the five-co-ordinate complex $(PPh_3)_2RhH_2Cl$, 9.2, may be isolated. Solutions of this hydride will immediately reduce olefins, including ethylene. The red-brown solutions of $(PPh_3)_2RhCl(\text{solvent})_x$ also react readily and reversibly with ethylene turning yellow and the ethylene complex, $(PPh_3)_2RhC_2H_4Cl$, 9.3, may be isolated. Equilibrium studies show that under one atmosphere of ethylene more than 90% of the rhodium complex in benzene is in the form of the ethylene complex and proton magnetic resonance data shows that the residence time of the ethylene on the rhodium is less than 10^{-2} seconds. In contrast to ethylene, propene forms no isolable complex with the rhodium complex and equilibrium measurements suggest that only very weak complex formation occurs.

Kinetic measurements under the conditions of the hydrogenation reactions suggest that there are the equilibria (1) and (2).

$$\begin{tikzcd}
(PPh_3)_2RhCl(\text{solvent})_x \arrow[r, shift left, "H_2"] \arrow[d, shift right, "\text{olefin}"'] & \underset{9.2}{(PPh_3)_2RhH_2Cl} \arrow[l, shift left, "(1)"] \arrow[d, "\text{olefin}"] \\
\underset{9.3}{(PPh_3)_2Rh(\text{olefin})Cl} \arrow[u, shift right, "(2)"'] \arrow[r] & (PPh_3)_2RhCl + \text{paraffin}
\end{tikzcd}$$

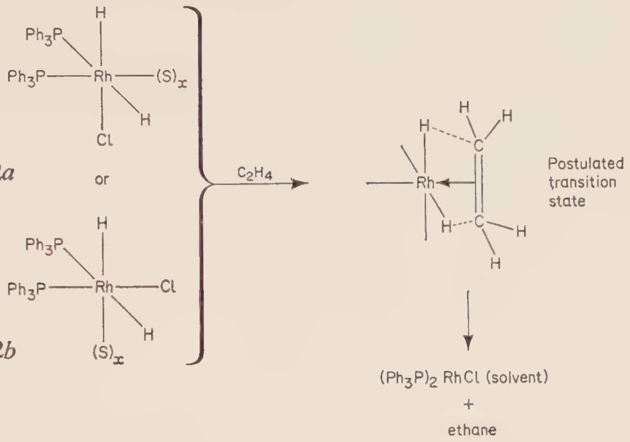
It is suggested that the catalytic reduction of the olefins by these benzene solutions proceeds via the prior formation of the hydride complex followed by the addition to it of the olefin which is reduced, rather than vice versa. This postulate is consistent with the observation that ethylene is reduced by the hydride complex 9.2, whilst the ethylene complex 9.3 is not readily reduced by hydrogen.

Proton magnetic resonance studies have shown the configuration of the dihydride complex to be one of the two 9.2*a* or 9.2*b*. It is probable that molecular hydrogen adds to the rhodium complex in much the same way as is found for the related iridium complex $(PPh_3)_2IrCOCl$ (see p. 232).

The mechanism of the addition of the olefin to the hydride and its subsequent reduction is not yet known; however, there is some evidence which is suggestive. If a deuterium/hydrogen mixture is used during the reduction of 1-pentene there is essentially quantitative formation of the dideuteroparaffin and non-deuterated analogue. It follows that the H_2 (or D_2) molecule has been added to only one olefin and there are no exchange reactions. Further, it has been shown that the addition takes place by a *cis* mechanism. On the basis of these observations it is postulated that both the hydrogens add simultaneously to the olefin [47], e.g.

9.2*a*

9.2*b*



The compound $(Ph_3P)_3RhCl$ can catalyse very stereospecific reactions. For example, ergosterol will add deuterium to only one double bond, stereospecifically, and there is no further addition of deuterium or exchange of other hydrogens for deuterium [48*a*].

The triphenylarsine and triphenylstibine analogues of $(Ph_3P)_3RhCl$ undergo similar addition and substitution reactions but they are not such good catalysts [48*b*]. This illustrates the sensitivity of catalytic process to ligand properties.

Similar hydrogenation reaction shave been shown using benzene solutions of the complexes *trans*-$[(PPh_3)_2MCOX]$, where M = Ir or Rh and X = halogen [49, 50], as catalysts. The mechanism of the reactions is presumably similar to those catalysed by rhodium.

(*a*) *Catalysis by cobalt cyanide solutions*

Aqueous solutions containing cobalt cyanide complexes catalyse the homogeneous hydrogenation of conjugated unsaturated hydrocarbons such as dienes and α,β-unsaturated aldehydes; mono-enes are not reduced [51, 52, 53, 54]. Although the mechanism of the reductions is not fully understood the following observations are strongly suggestive: (*a*) It is generally agreed that organocobalt–cyanide complexes are intermediates in the reactions and a number of complexes $[Co(CN)_5R]^{3-}$, where R = Me, CH_2Ph, C_2F_4H, C_4H_7 or CH_2COPh, have recently been isolated [55, 56, 57] (see p. 247). They may be prepared either from the pentcyanocobalt(II) anion $[Co(CN)_5]^{3-}$ and an organic halide,

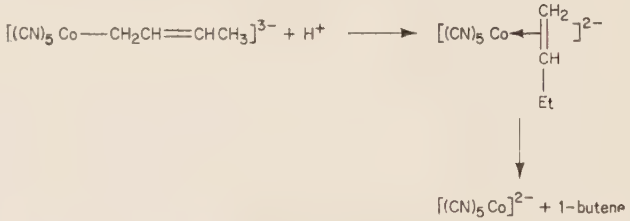
$$2[Co(CN)_5]^{3-} + RX \xrightarrow[\text{intermediates}]{\text{via radical}} [Co(CN)_5R]^{3-} + [Co(CN)_5X]^{3-}$$

or from the hydride $[Co(CN)_5H]^{3-}$ and a diene,

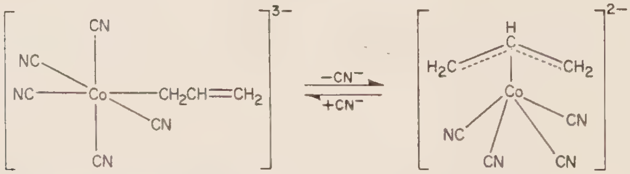
$$[Co(CN)_5H]^{3-} + CH_2{=}CH{-}CH{=}CH_2 \rightarrow [Co(CN)_5C_4H_7]^{3-}$$

(*b*) It is known that the complex cobalt cyanide ions $[Co(CN)_5]^{3-}$ and $[Co(CN)_5H]^{3-}$ are present in aqueous solutions containing CN^- and cobalt ions.

(*c*) The σ-butenyl complex $[Co(CN)_5C_4H_7]^{3-}$ reacts with acids or with the hydride $[Co(CN)_5H]^{3-}$ forming butene isomers [51]. By analogy with the protonation of σ-allyl complexes (see p. 212), the following type of reaction mechanism may be envisaged



(*d*) It is found that in the presence of excess cyanide ion the predominate product of hydrogenation of butadiene is 1-butene. However, in the absence of excess cyanide then as much as 86% *trans*-2-butene may be formed. The formation of *cis*-2-butenes is almost independent of the Co, CN ratio and only about 1% yield is obtained. The effect of the cyanide concentration on the distribution of butene products may be understood in the light of the observed σ- to π-allyl equilibria,



In the absence of excess cyanide the formation of the π-allyl complex is obviously encouraged.

The above observations lead to the mechanism shown in Figure 83 [51]. The formation of *trans*-2-butenes may arise either by hydrogenation of the

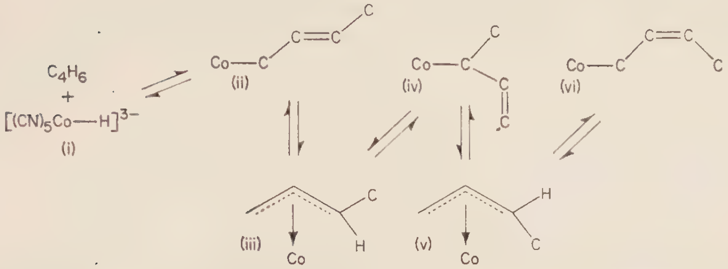


Fig. 83. (*i*) The anion $[(CN)_5CoH]^{3-}$ adds to butadiene forming an equilibrium mixture of σ- and π-allyl complexes. Hydrogenation of (*iii*), (*iv*) or (*v*), by H_2 or $[Co(CN)_5H]^{3-}$, would be expected to give but-1-enes whilst (*ii*) or (*vi*) would give but-2-enes

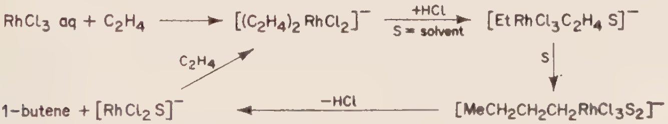
π-allylic complexes or from the σ-bonded complex Co—CHMeCH=CH₂, The 1-butene products presumably derive from the σ-2-butenyl complexes, as shown. The absence of *cis*-2-butenes may be associated with the relative instability of *syn*-π-allyl complexes compared with that of their *anti*-π-allyl analogues (see p. 43). Evidence that a number of equilibria occur in these reactions comes from deuteration of butadiene by solutions containing a Co/CN ratio of 5 : 1. The products were found to contain di-, mono- and non-deuterated butene isomers, as well as small amounts of mono- and di-deuterated butadienes [51].

D. Some dimerization, oligomerization and polymerization reactions of olefins and acetylenes

The catalytic condensation of unsaturated hydrocarbons by transition metals is known to occur in a variety of ways. Examples of some reactions are given in Table 31.

(*a*) *Dimerization reactions*

The dimerization of mono-enes to cyclobutanes by transition metals has not yet been shown although this reaction is well known in photochemistry. However, ethylene may be homogeneously dimerized to linear butenes by aqueous solutions of rhodium trichloride [69]. The mechanism postulated is:



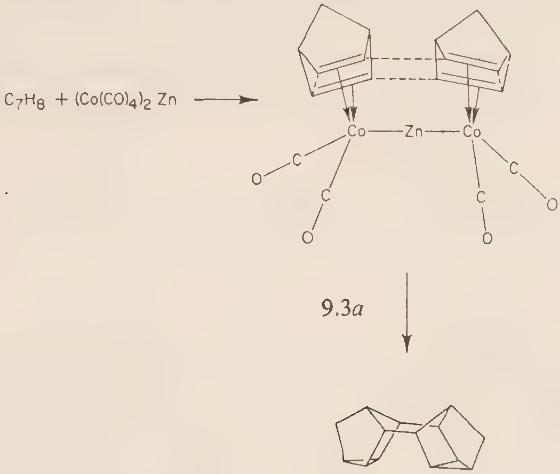
The dimerization of acetylenes forming π-cyclobutadiene complexes is discussed in Chapter 3, and some dimerization reactions of butadiene are more conveniently treated in section C(ii) below.

In these dimerization reactions the catalyst is believed to be mono-

Table 31 *Examples of homogeneously catalysed condensation reactions*

Reaction	Catalyst or catalyst precursor	Reference
Dimerization		
Ethylene to butenes	$RhCl_3$ in ethanol	[69]
Butadiene to cyclo-octa-1,5-diene	$Ni(CH_2{=}CHCN)_2$ + tertiary phosphites	[76]
	$(Ph_3P)_2Ni(CO)_2$	[58]
Bicyclohepta-2,2,1-diene to a variety of products (see Figure 84)	$Ni(CH_2{=}CHCN)_2$	[59, 76, 79]
	$Ni(CH_2{=}C(CN)_2)_2$	[76, 79]
	$Ni(CO)_4$, $Co_2(CO)_8$	[82]
	$Fe(CO)_5$	[82]
Norbornene to Cyclobutane-fused *exo*, *trans*, *exo* dimer	*hν* + Cu(I) halides	[59*a*]
Ethylene to butenes	$Ni(acac)_2 + Et_3Al_2Cl$	[59*b*]
Norbornadiene to 'Binor-S'	$(Co(CO)_4)_2Zn$	[69*a*]
Butadiene to 3-methylheptatriene	$Co(acac)_3 + AlEt_3$	[59*c*]
Butadiene + ethylene to *n*-hexa-1,3-diene	$Co(acac)_3 + AlEt_3$	[59*d*]
Butadiene to cyclo-octa-1,5-diene and 4-vinylcyclohexene	$Et_2Ni(bipy)$ $Et_2Fe(bipy)_2$	[59*e*]
Acetylene to *π*-cyclobutadiene or cyclopentadienones	See Chapter 3, C(*a*), and Chapter 8, E(*a*), respectively	
Trimerization		
Acetylene to benzene	$Ni(CH_2{=}CHCN)_2$	[76]
	Ziegler catalysts	[60]
	Reppe catalysts	[61, 64, 75]
Mono- and di-substituted acetylenes to substituted benzenes	$Hg(Co(CO)_4)_2$	[62]
	$Ni(CH_2{=}CHCN)_2$	[59, 76, 79]
	Alkyl and aryl complexes of Cr(III)	[70, 63]
Butadiene to cyclododecatriene	Nickel catalysts	See p. 328
Butadiene to dodecatetraenes	$(\pi\text{-}C_3H_5)_3Pd$	See p. 329
Tetramerization		
Acetylene to cyclo-octatetraene	Reppe catalysts $(Ni(CN)_2)$	[64, 75]
Polymerization		
Ethylene and mono-olefins to to polymers	Ziegler catalysts	See p. 333
Acetylene to polymers	Ziegler catalysts	[65]
	Nickel complexes	[66, 67, 61]
Butadiene to polymers	Rhodium catalysts	[68]
	$[C_8H_{12}]_2Ni$	[68*a*]
Vinylchloride to polymers	Group VI carbonyls	[68*b*]
	$Co_2(CO)_8$	[68*c*]
Acetylene to polymers	$(\pi\text{-}C_5H_5)_2V$	[68*d*]
Butadiene to polymers	*π*-allyl nickel complexes	[68*e*]

nuclear. The dimerization of norbornadiene by $(Co(CO)_4)_2Zn$ is however believed to proceed by a binuclear intermediate, such as 9.3*a* [69*a*].



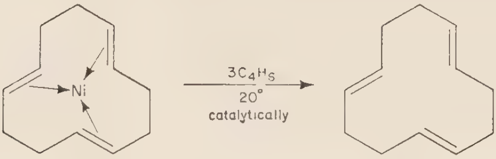
9.3*a*

(*b*) *Trimerization reactions*

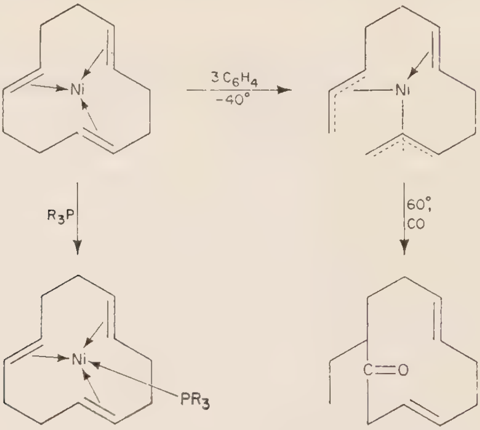
(*i*) *The trimerization of acetylenes.* The work described in Chapter 8 shows the various ways and the ease with which acetylenes may form complexes with transition metals. Many transition metal complexes will catalyse the cyclotrimerization of acetylenes and it is generally thought that these reactions proceed by the stepwise addition of the acetylene to the metal, followed by the formation of the carbon–carbon bonds in a multicentred bond process. A typical mechanism has been described in Chapter 5, Figure 40. Further evidence for the stepwise addition of acetylenes in these reactions comes from the observations that frequently there are by-products which may be constructed from only two acetylenes. Thus triethylchromium will cyclize 2-butyne to hexamethyl-benzene [70] whilst with trimethylchromium some 2,3,4,5-tetramethylcyclo-pentadiene is also formed. In the latter case it appears that a methylene group, originating from a methyl ligand, has added to two acetylenes which were co-ordinated to the chromium. It is interesting to note that a side product in the cyclization of diphenylacetylene by bis-ethyl nickel is 1,2,3,4-tetraphenylcyclohexa-1,3-diene and in this case it appears that the $—CH_2—CH_2—$ moiety has derived from an ethyl ligand [70].

(*ii*) *The trimerization of butadiene and related reactions catalysed by some π-allyl metal complexes.* Some of the most elegant of recent work in the field of homogeneous catalysis has been done by Wilke and his co-workers.

Treatment of nickel acetylacetonate with alkylaluminiums in the presence of cyclododecatrienes or butadiene, or treatment of bis-π-allyl nickel with butadiene, gives cyclododecatriene nickel, a volatile blood-red crystalline compound, 9.4 [71, 72, 73]. This 16-electron nickel complex reacts catalytically and very rapidly with butadiene at 20° liberating isomers of cyclododecatriene. The major product is the *trans-trans-cis* isomer; small amounts of the *trans-cis-cis* isomer are also formed. If the reaction with butadiene is carried out at −40° then the bis-π-enyl complex, 9.5, is isolated in which the ligand is the same as that found by X-ray studies to be in the complex formed by reaction of butadiene with ruthenium salts (see p. 52). The carbonylation reaction (Fig. 84) provides evidence for the



9.4



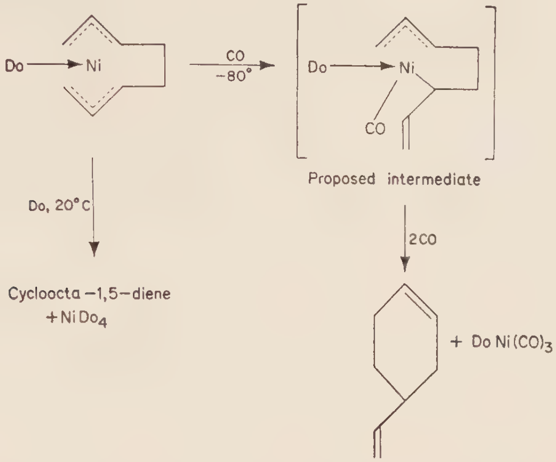
9.5

Fig. 84. Some reactions of cyclododecatriene nickel

nature of complex 9.5. The cyclization of the butadiene is believed to occur by internal electron shift processes, after the butadienes have become attached to the metal.

If the complex 9.4 is treated with a molecule which acts as a non-labile ligand to the nickel, then instead of trimerization of butadiene only dimerization occurs. Obviously the non-labile ligand prevents the attachment of a third butadiene molecule. The reaction is represented below and the intermediate complex, 9.6, has been isolated when Do = tris (2-biphenyl)phosphite.

9.6

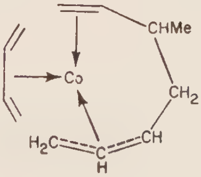


The reaction of the complex 9.6 with carbon monoxide is shown, which again illustrates how the course of a reaction may be changed when the nickel is complexed.

Cyclododecatriene nickel has also been shown to catalyse the co-cyclization of two molecules of butadiene either with one molecule of ethylene giving cyclodeca-1,5-diene or with one molecule of 2-butyne to give 1,2-dimethyl cyclodeca-1,4,8-triene [72].

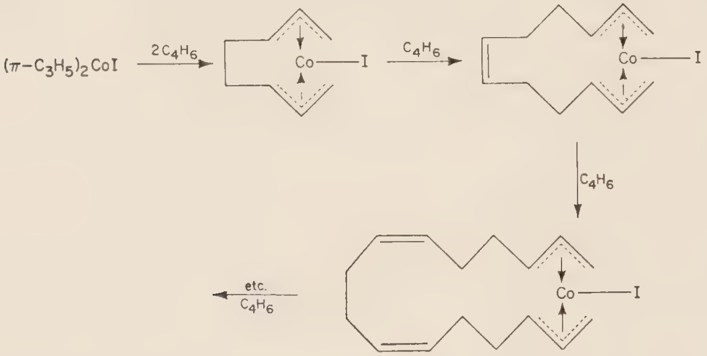
Bis-π-allyl palladium also has catalytic properties but they differ from those of bis-π-allyl nickel. Thus treatment of $(\pi\text{-}C_3H_5)_2Pd$ with butadiene gives dodecatetraenes. The reaction must involve a hydrogen migration. It is tentatively suggested that the difference in behaviour between nickel and palladium may arise in part from the greater size of the palladium atom which may be sufficient to prevent three butadienes from linking up around it [73].

Tris-π-allyl chromium polymerizes butadiene giving 1,2-polybutadiene, whilst bis-π-allyl chromium iodide causes cyclotrimerization to cyclododeca-1,5,9-trienes.



9.7

Tris-π-allyl cobalt also has catalytic activity and polymerizes butadiene causing hydrogen migration and giving 5-methyl-hepta-1,3,6-trienes. A possible intermediate in this reaction is the complex 9.7, which has been isolated in a separate preparation [74]. Bis-π-allyl cobalt reacts with butadiene in a novel stepwise reaction [73], viz.



It will be seen from the above that in these π-allyl complexes, the ligand is easy to remove and hence the complexes are excellent catalyst precursors. Although the mechanisms of many of these reactions are not yet fully understood, the importance of the ligands, as well as the metal atom, in determining the course of a catalytic reaction, is strongly emphasized.

(*iii*) *Other nickel catalysts.* A number of phosphine nickel carbonyl complexes are the precursors of nickel catalysts which cause the oligomerization and cyclization of acetylenes [77, 61, 74, 76, 75]. It is necessary to pretreat the phosphine carbonyls, for example, by warming them with acetylenes, which causes the evolution of carbon monoxide, and it is thought that the active catalyst is a phosphine nickel acetylene complex [77]. Examples of the catalytic reactions are the cyclotrimerization of acetylene to benzene (88%). Mono-alkyl substituted acetylenes are cyclized to trisubstituted benzenes and linear oligomers are formed as by-products, except when the alkyl group becomes very bulky, when they become the major products [77]. Disubstituted acetylenes alone do not react with these catalysts; however, co-trimerization of disubstituted acetylenes with acetylene has been observed [61, 77, 78]. Studies using deuterated 1-heptyne show that hydrogen transfer occurs during these reactions and the mechanism for formation of the linear oligomers shown in Figure 85 has been proposed [61, 77].

It has been found that bis-acrylonitrile nickel also acts as a precursor of catalytic nickel complexes and some of its reactions are shown in Figure 86.

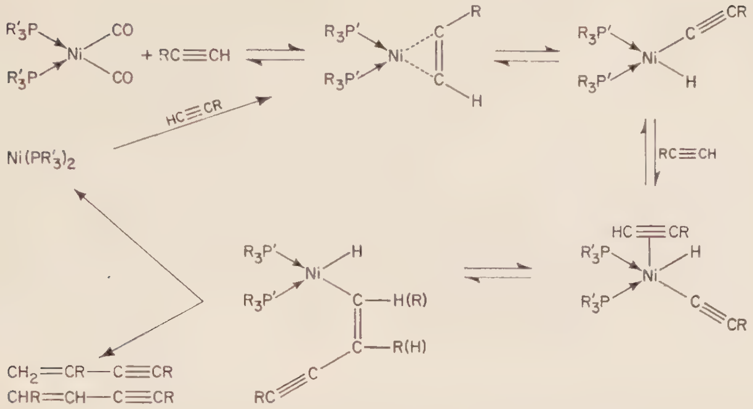


Fig. 85. A mechanism for the catalytic polymerization of acetylenes by some nickel complexes

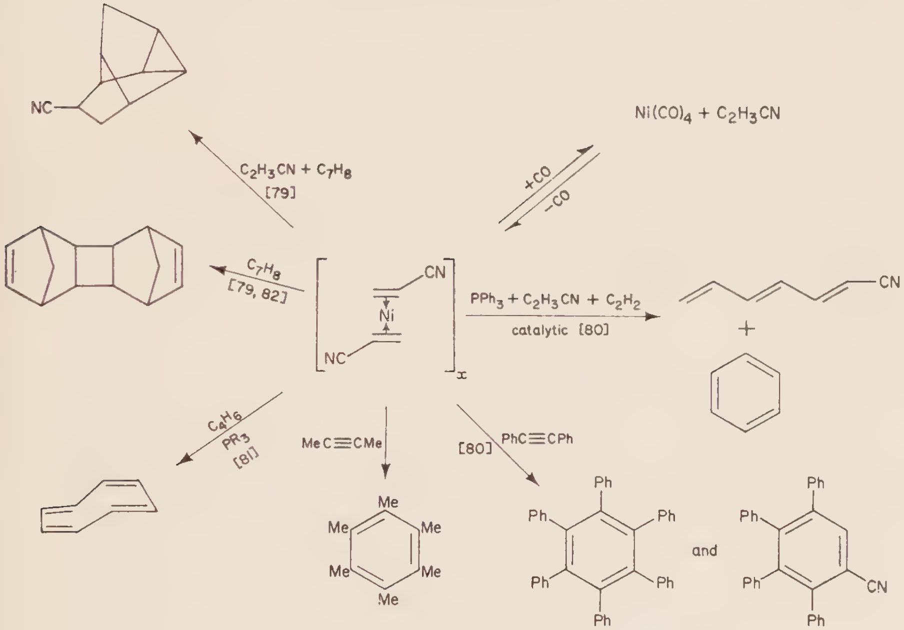


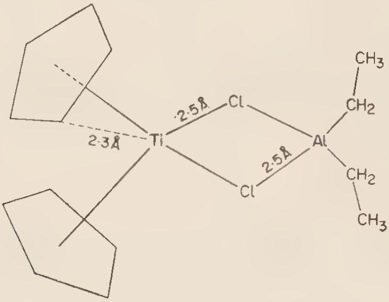
Fig. 86. Some reactions of bis-acrylonitrile nickel

(*c*) *Some comments on polymerization of olefins by Ziegler catalysts*

Ziegler catalysts are prepared from (*a*) an organometallic compound of a Group II or III metal – especially trialkylaluminiums, or, alkali metal hydrides or mixed alkyl metal hydrides, and (*b*) a transition metal compound, in particular halides, such as the titanium halides.

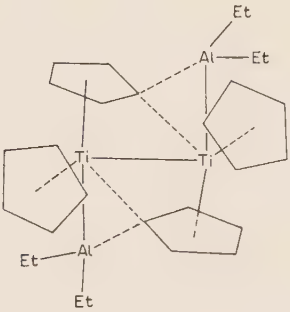
The majority of Ziegler catalysts are heterogeneous; however, a number of homogeneous systems are known. Soluble Ziegler catalytic systems include those formed from VCl_4, $AlBr_3$ and triphenylaluminium in cyclohexane [83], and bis-π-cyclopentadienyl titanium dichloride and aluminium alkyls.

Treatment of $(\pi\text{-}C_5H_5)_2TiCl_2$ with triethylaluminium gives the complexes $(\pi\text{-}C_5H_5)_2TiCl_2AlEt_2$, $(\pi\text{-}C_5H_5)_2TiCl_2AlEtCl$ and $(\pi\text{-}C_5H_5)_2TiCl_2AlCl_2$ [84, 85]. The structure of the first of these complexes has been determined by X-ray diffraction and is shown in 9.8 [86]. Solutions of this complex polymerize ethylene [85, 84, 87, 86, 88].



9.8

The catalyst is most effective when in dichloromethane solution [88*a*]. Electron spin resonance spectra of solutions of $(\pi\text{-}C_5H_5)_2TiCl_2$ and Et_3Al suggests that the complex, 9.8, is essentially unchanged in solution [88*b*].



9.8*a*

Related complexes such as 9.8*a* and $\pi\text{-}C_5H_5Ti\text{-}\mu\text{-}(Cl_2AlR_2)_2$ are also known; they are not active catalysts for the polymerization of ethylene. The crystal structure of 9.8*a* shows that two of the $\pi\text{-}C_5H_5$ rings are close to a titanium atom and an aluminium atom, and they may be bonding weakly to them [88*c*]. The observation that only one of the above π-

cyclopentadienyl titanium complexes is an active catalyst, and even then the choice of solvent is important, shows that the requirements for catalytic activity are very critical.

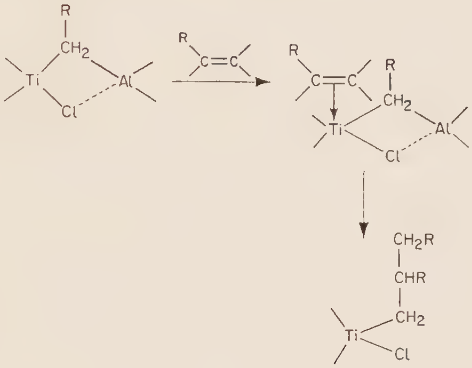
Complexes formed from (π-C_5H_5)$_2$$TiCl_2$ and $MeAlCl_2$ or Me_2AlCl also polymerize ethylene [88].

(*d*) *Some mechanisms of olefin polymerization by Ziegler catalysts*

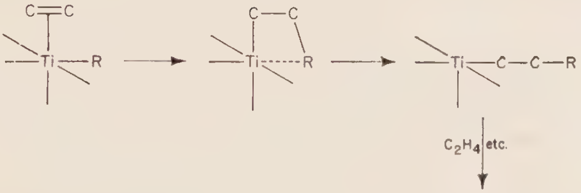
The mechanisms of olefin polymerization are by no means well understood and many possibilities have been discussed [89]. At present the majority of the evidence supports an ionic polymerization mechanism [90]. There is general agreement that the polymerization involves growth at the metal by an insertion mechanism, i.e.

$$\mathrm{M{-}R} + \xrightarrow{\mathrm{CH_2{=}CH_2}} \mathrm{MCH_2CH_2R} \xrightarrow{\mathrm{CH'_2{=}CH'_2}} \mathrm{MCH'_2CH'_2CH_2CH_2R}$$

The nature of the intermediates leading to insertion is uncertain. There are those who propose a direct role for the ligands about the transition metal [89], e.g.



Other workers suggest that there is no 'direct' role of the metal ligands, other than steric, and they envisage mechanism where two or more co-ordination sites on the central transition metal are used [90*a*]:



Of course, with different catalysts it is not improbable that both types of mechanisms may be found.

The polymerization of α-olefins by Ziegler catalysts leads to many different types of stereoregular polymers, such as isotactic polymers and those with 'diasteric' centres [91]. Both classes of mechanisms can account for the formation of stereoregular polymers and the details are not discussed here except, as a very general rule, it is argued that those catalytic sites which have rigorous requirements, such as a limited number of co-ordination positions, and rigorous stereochemistry will tend to give stereoregular polymers, whilst those sites which have greater steric and positional freedom will form non-stereospecific polymers [92].

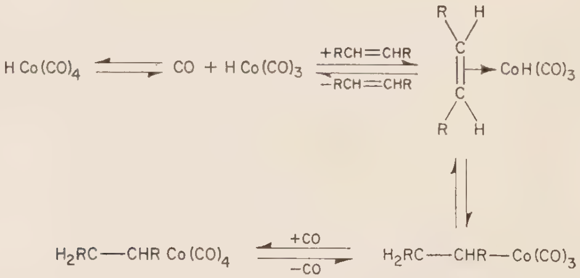
E. Hydroformylation and related carbonylation reactions

Treatment of olefins with carbon monoxide and hydrogen under pressure and in the presence of dicobalt octacarbonyl gives mainly aldehydes or ketones. Alcohols and paraffins are formed as by-products. The hydroformylation of olefins to aldehydes is of considerable industrial importance. The prediction that cobalt tetracarbonyl hydride was a catalyst in these reactions [93, 94] has been amply verified; for example the stoicheiometric hydroformylation of 1-pentene by $HCo(CO)_4$ proceeds at room temperature giving isomeric aldehydes [95]. It has been shown that $HCo(CO)_4$ is formed under the high pressure (100 atm.; 1 : 1 $H_2 : CO$) and temperature (100–300°) conditions used in hydroformylation reactions [95, 96].

Recent investigation of the chemistry of alkyl and acyl cobalt carbonyl complexes by Heck and co-workers provides considerable insight into the detailed mechanisms in hydroformylation reactions. They have shown that the following equilibria occur:

(*a*) *The reversible addition of Co—H across C═C systems*

On the basis of kinetic studies [97] and from the observation that ethylcobalt tetracarbonyl decomposes reversibly to ethylene and $HCo(CO)_4$ [97], it appears that there are the equilibria,



(*b*) *The reversible formation of acyl complexes from alkyls*

$$RCo(CO)_3 + CO \rightleftharpoons RCo(CO)_4 \rightleftharpoons RCOCo(CO)_3$$

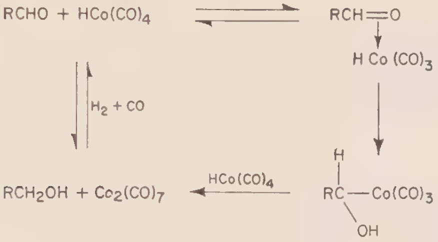
Evidence for these equilibria comes from kinetic studies [98], from the infrared spectra of alkyl cobalt tetracarbonyl solutions which show bands assignable to both terminal and acyl C=O stretching frequencies [93, 97] and from the isolation of acyl complexes by treatment of the corresponding alkyl derivative with carbon monoxide under pressure [99, 100].

On the basis of these equilibria the following formal mechanism for hydroformylation of ethylene has been proposed:

$$HCo(CO)_4 + CH_2{=}CH_2 \rightleftharpoons C_2H_5Co(CO)_4 \rightleftharpoons$$
$$C_2H_5COCo(CO)_3 \xrightarrow[\text{hydrogenolysis}]{H_2 \text{ or } HCo(CO)_4} C_2H_5CHO + Co_2(CO)_8$$

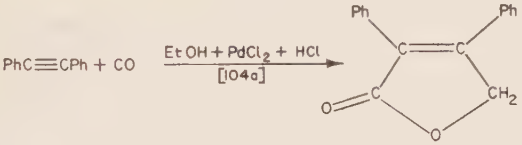
The formation of alcohols during hydroformylation reactions may become the major reaction at higher temperatures [101, 102].

The following mechanism has been proposed [103, 104]:



Acetylenes have been found difficult to hydroformylate. Using cobalt carbonyl catalysts only low yields of aldehydes were obtained from 1-pentyne [105]. With the catalyst precursor $(Ph_3P)_3RhCl$ in ethanol-benzene, 1-hexyne reacts with 1 : 4 mixtures of H_2 and CO at 110°/120 atm. to give about a 15% yield of n-heptaldehyde and 2-methylhexaldehyde in equal amounts [48].

The carbonylation of diphenylacetylene giving a γ-lactone is catalysed by palladium(II) chloride in alcohol, e.g.

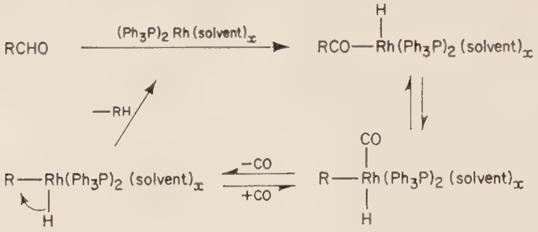


A number of catalytic decarbonylation reactions are known which are closely related to the reversible carbonylation shown above and to the non-catalytic decarbonylations of acyls discussed in Chapter 7.

Treatment of benzene solutions of $(PPh_3)_2RhCl(solvent)_x$ with aldehydes gives the carbonyl complex $(PPh_3)_2RhCOCl$ and a hydrocarbon. Acyl halides react in a similar manner [48, 105*a*]:

$$\begin{array}{c} RCOCl \\ \text{or} \\ RCHO \end{array} \xrightarrow[70^\circ]{(PPh_3)_2RhCl(solvent)_x} \begin{array}{c} RH \\ \text{or} \\ RCl \end{array} + (PPh_3)_2RhCOCl$$

A mechanism containing the following steps can be envisaged:



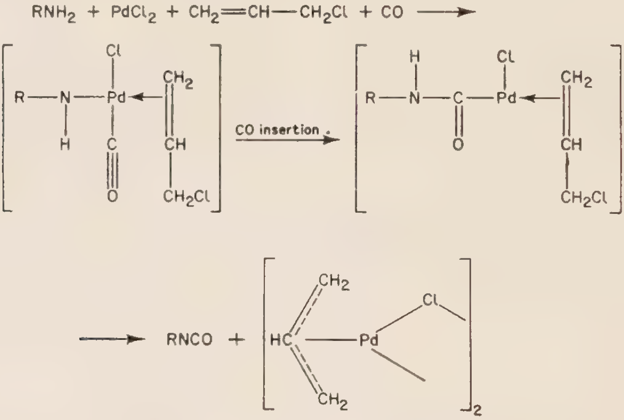
Some ruthenium complexes of the type $[Ru_2Cl_3(Et_2PhP)_6]^+Cl^-$ will decarbonylate aldehydes giving olefins [105*b*], viz.,

$$4C_3H_7CHO + [Ru_2Cl_3(Et_2PhP)_6]^+Cl^- \longrightarrow 2RuCl_2(CO)(Et_2PhP)_3 + 2CH_2{=}CHMe + 2C_3H_7CH_2OH$$

Primary amines may be carbonylated using Pd(II) chloride as a catalyst, e.g.,

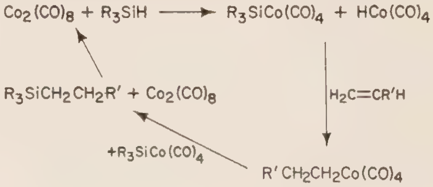
$$RNH_2 + CO \xrightarrow[\text{[105}c\text{]}]{PdCl_2} RNHCONHR + RNHCOCONHR$$

When this reaction is carried out in the presence of allyl chloride isocyanates are formed [105*d*], e.g.



The mechanism proposed for this reaction is similar to that proposed for the formation of π-enyl palladium complexes [105*e*].

The hydrosilation of olefins is catalysed by dicobalt octacarbonyl and the following general mechanism has been proposed [106]:



Hydrosilation reactions are also catalysed by platinum(II) and rhodium(I) complexes [107, 108].

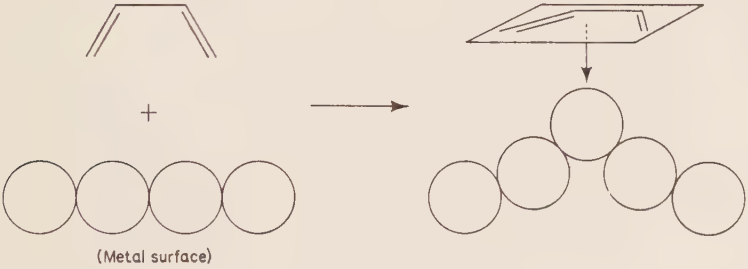
F. Some general comments on the relationship between heterogeneous and homogeneous transition metal catalysts

Many of the reactions discussed above, in particular the hydrogenation, the isomerization, and the polymerization of olefins, are readily catalysed by heterogeneous systems as well as by homogeneous.

It is a reasonable assumption that when there is a close relationship between a reaction catalysed by both homogeneous and heterogeneous systems then they may well proceed by similar mechanisms. It follows that the 'active site' in the surface of a heterogeneous catalyst may resemble the active site (co-ordinated metal atom) found in the homogeneous system. Even in the case of pure metal surfaces it is probably not too extreme in some cases to regard one particular metal as the 'central metal' and the neighbouring metals as 'ligands'. It should be remembered that a single metal atom in homogeneous systems is frequently capable of carrying out all the stages of a catalytic reaction.

Of course, it is not possible completely to separate the roles of ligands from those of the central metal atom, even in the very simple transition metal complexes. In a homogeneous transition metal catalyst, the ligands may take a (direct) part in the reaction, for example by weak bond formation with approaching or leaving groups, and by steric interaction which may control the orientation of other ligands and restrict the number of available co-ordination sites. Ligands also play an 'indirect' role in so far that they determine the 'oxidation state' of the metal atom, and the electronegativity and polarizability of the metal atom. The *cis* and *trans* effects of ligands, the stabilization of some ligands by the π-bonding ability of others are well-known examples of ligand properties which may influence catalysis indirectly.

If the active site of a heterogeneous catalyst is analogous to some molecular organometallic complex then other properties of simple complexes would be expected. For example, the co-ordination of a metal site by an olefin ligand would be expected to cause the other ligands around the metal (perhaps more metal atoms) to bend away from the new ligand, viz.



It would also be expected that the bonding between the olefin and the metal atom in a surface would be substantially similar to that found in molecular olefin-metal complexes. Of course, the nature of a heterogeneous surface, which may have discontinuities such as screw dislocations or lattice defects, may give rise to a number of different active sites. Again one might expect to find analogies between the more unusual sites and molecular complexes. For example, there is the comparison between the site where the central metal is held in an unusual stereochemistry and molecular complexes with rigid ligands, such as phthalocyanines or quadridentate phosphine ligands, which may demand that the metal atom has an uncommon co-ordination number and stereochemistry.

In heterogeneous catalysts it is also found that with different crystal surfaces the atoms may have different internuclear distances, different numbers of nearest neighbours and hence different numbers of available co-ordination positions, and different energy levels with different electron occupation. Therefore each crystal plane might only find analogy with one particular complex. Many heterogeneous catalysts combine a transition metal or some complex with a support, such as alumina. In molecular terms it may be that with different supports an active site may have different ligands and hence different properties. Similarly, changes in the method of catalytic pretreatment may drastically alter the environment of the active metal atom(s).

Within the last few years there has been a growing tendency to draw the analogy between the chemistry of organometallic complexes and that of hydrocarbons adsorbed on metal atoms in surfaces. For example, it is postulated that the isotopic exchange between deuterium and alkanes, catalysed by thin films of nickel, palladium or rhodium, occurs via an equilibrium between σ- and π-bonded metal–organic species [109, 110, 111, 112]. π-Bonded olefins are postulated in Ziegler catalysis, see above, in the catalytic deuteration of aromatic complexes [113], and in a variety of isomerization reactions [112, 114, 115]. Other intermediate metal–carbon systems which have been proposed in heterogeneous catalytic systems include ‘carbenes’, e.g. $M{=}CH_2$ [109], π-enyl systems [114] and of course the metal-carbonyl M—CO and bridging carbonyl M—CO—M.

Given a close similarity of reaction and of the ‘active site’ of a heterogeneous and a homogeneous catalyst then does either system have advantages over the other? Obviously it may be easier to separate a heterogeneous catalyst from a reaction mixture. On the other hand a heterogeneous catalyst may frequently have more than one type of active site, in which case a number of side reactions may occur affording less pure products. Heterogeneous catalysts may well be more thermally stable than a corresponding homogeneous system and heterogeneous surfaces catalyse reactions for which it is difficult to envisage a homogeneous catalyst: e.g., in what solvent would you dissolve a catalyst which was sufficiently active to cause the rapid exchange of the hydrogens in methane with deuterium? In some heterogeneous surfaces, probably those which have active sites close together, there may be a wandering of chemisorbed species across the surface which could present mechanistic possibilities not available to homogeneous systems. An advantage, in principle, of homogeneous systems is that it should be easier to discover the nature of the catalytic site and hence the mechanism of the reaction. Further, the possibility of modifying the ligands suggests that very sensitive control of the reaction should be possible (see the polymerizations by nickel catalysts given above).

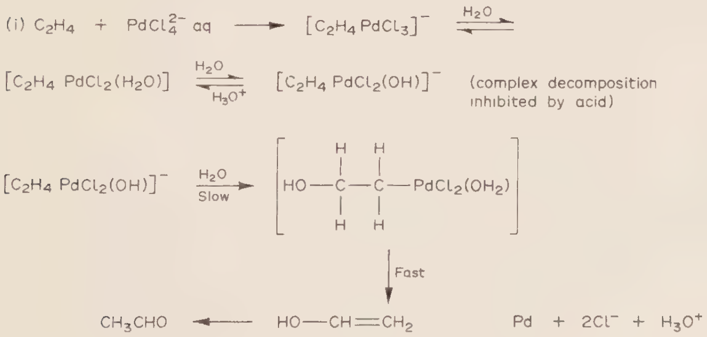
Finally, there is the question whether one transition metal and its complexes will show more catalytic properties than another. At present it seems possible that any transition metal will, given the right ligands, catalyse any type of known catalytic reaction. General statements such as 'greater catalytic activity is found with the Group VIII metals than with those of Groups IV–VIII' may only be true in a historical sense. However, when it is possible more closely to define the role of metal atoms and ligands in homogeneous and heterogeneous systems it is probable that particular trends amongst the transition metals will become apparent.

G. Miscellaneous

(*a*) *The oxidation of ethylene to acetaldehyde*

Strictly speaking this reaction does not occur catalytically; however, the mechanism is of interest in the context of the reactions described above.

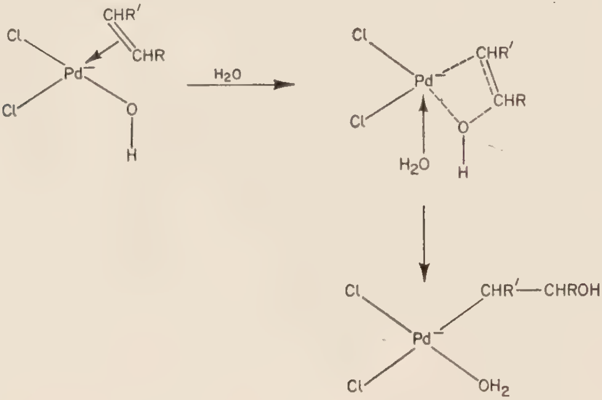
Treatment of aqueous solutions of palladium(II) chloride with ethylene gives an ethylene–palladium complex which is readily hydrolysed forming acetaldehyde and palladium metal. The palladium metal may be re-oxidized by copper(II) chloride, in a continuous process [116].



$$\text{(ii)}\ Pd + 2Cu^{2+} + 6Cl^- \longrightarrow PdCl_2 + 2[CuCl_2]^-$$

$$\text{(iii)}\ 2[CuCl_2]^- + 2H^+ + \tfrac{1}{2}O_2 \longrightarrow 2Cu^{2+} + 4Cl^- + H_2O$$

As shown above, the oxidation of the ethylene is thought to proceed via nucleophilic attack of a hydroxide on the ethylene. Palladium(II) chloride will also catalyse the oxidation of propylene to acetone and *cis*- and *trans*-butenes to methylethyl ketone [116*a*]. Kinetic studies on these reactions suggest that the rate-determining step is the addition of hydroxide to the co-ordinated olefin, viz.:



A similar reaction is the formation of monoacetate derivatives from olefins, e.g.

$$CH_3CH{=}CH_2 + Pd(OAc)_2 \xrightarrow[\text{[117}a\text{]}]{AcOH,O_2} CH_2{=}C(OAc)CH_3$$

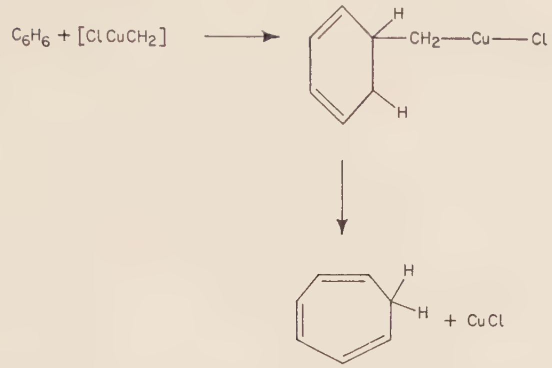
Similar mechanisms are thought to be important in vinylation reactions which are catalysed by Pd(II) chloride [117]. In a typical reaction, vinyl acetate is formed from ethylene and acetic acid in the presence of $Pd(II)Cl_2$ and Na_2HPO_4. A mechanism involving ethylene–palladium intermediates is suggested by the reaction

$$[C_2H_4PdCl_2]_2 \xrightarrow[\textit{iso}\text{-octane, }Na_2HPO_4]{\text{acetic acid}} \text{vinyl acetate + other products}$$

(*b*) *Some reactions catalysed by copper and its derivatives*

Copper and its salts decompose diazomethane to carbene and, in the presence of an olefin, cyclopropane derivatives are formed. When diazomethane is decomposed by copper in benzene a ring expansion reaction takes place and cycloheptatriene is formed [118, 119]. It is proposed [118] that the reaction proceeds via a copper(II) carbene intermediate, viz.:

$$CuCl + CH_2N_2 \longrightarrow ClCuCH_2N_2 \longrightarrow N_2 + [ClCuCH_2]$$



The reductive coupling of aryl halides by copper (Ullman conditions) may well involve the formation of intermediate ArCu species [120].

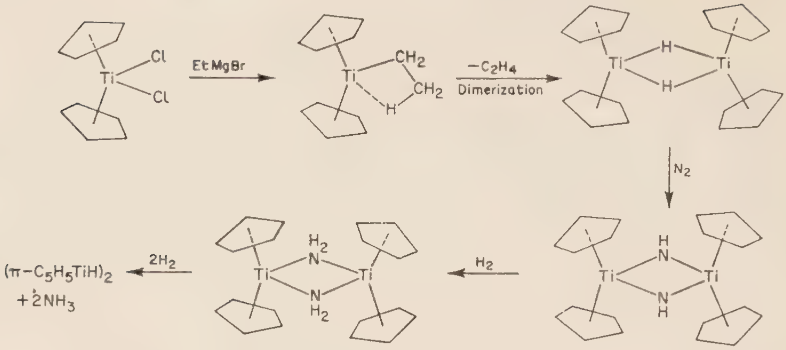
It is thought that the decomposition of aryldiazonium halides by copper salts, which gives aromatic halides (Sandmeyer reaction), proceeds via a free radical mechanism and that Cu—Ar intermediates are probably not important. It is however proposed that copper–diazo intermediates such as Ar—N═N—Cu are formed [121]. These may be compared with the aryldiazomolybdenum and tungsten complexes π-$C_5H_5M(CO)_2N_2Ar$ [122].

(*c*) *Nitrogen fixation*

There are known laboratory reactions in which it is established beyond doubt that a transition metal combines with molecular nitrogen under mild conditions forming either a metal–nitrogen complex, M—N_2, or fixed nitrogen products. Two of these are discussed here.

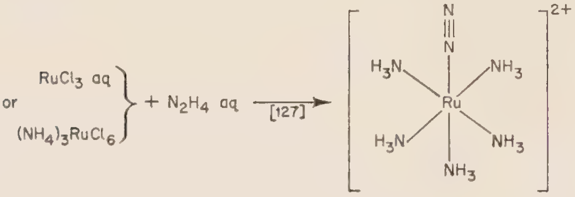
The trihydride $(Ph_3P)_3CoH_3$ reacts with nitrogen at normal temperature and pressure giving the nitrogen compound $(Ph_3P)_3CoN_2H$ and hydrogen is displaced. The reaction is reversible [123]. A mixture of bis-π-cyclopentadienyl titanium dichloride, $(\pi$-$C_5H_5)_2TiCl_2$, and ethyl magnesium bromide in diethylether also absorbs nitrogen at normal temperature and pressure and ammonia is formed (0·7 mol NH_3 per mol of $(\pi$-$C_5H_5)_2TiCl_2$) [124]. Electron spin resonance studies of the reaction mixture show that paramagnetic Ti(III) species are formed during the reaction and the fine structure of the spectra has been interpreted by postulating a dimeric bridging hydride complex such as is shown in the reaction scheme given overleaf [125].

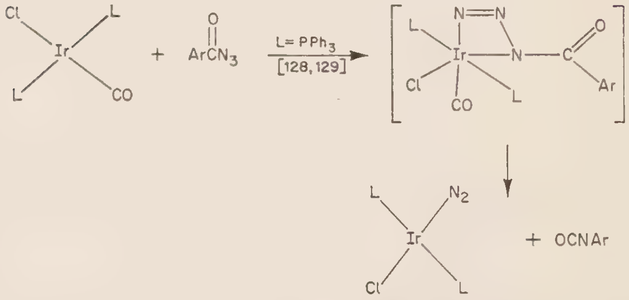
It has been shown that solutions of transition metal complexes of metals, such as chromium and iron, in organolithium or Grignard reagents will also react with molecular nitrogen [125, 126]. The only other non-biological systems which are known to react with nitrogen under mild conditions are metals in the pure state such as lithium and many of the transition metals, e.g. tantalum.



It appears that in both the nitrogen-fixing systems described above the species which react with nitrogen are hydrides. It can be argued that a clean metal surface and a metal hydride complex have in common the property that in both the metal atom is readily accessible to the approaching molecule. Once the nitrogen is close to the metal then it can be imagined that a metal–nitrogen bond is formed which may be analogous either to the metal–π-acetylene bond, see p. 273, or, the M–C bond formed in the M—CO or $M—C\equiv CR$ systems, see p. 16.

Indeed, there are known two complexes which contain the N_2 ligand; they are prepared from nitrogen compounds such as azides or hydrazine, viz.:



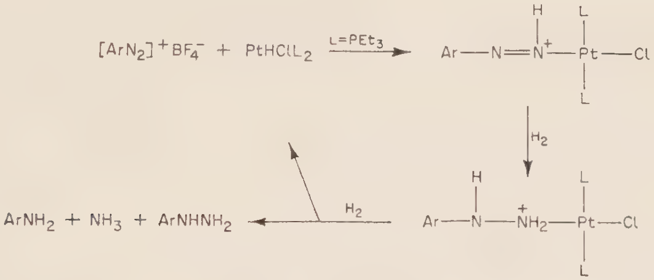


The crystal structure of the ruthenium compound shows that the

Ru—N—N moiety is linear [130] and the Ru–N_2 bond is therefore similar to the M–C bond in M—CO or M—C≡CR. Of course, such bonding is well known in compounds such as $CH_2{=}N{=}N$ and N=N=O.

These reactions of simple inorganic systems with molecular nitrogen serve as models for the well-known fixation of nitrogen by biological systems, for example, by *Azotobacter vineland*.† Cell-free extracts of the nitrogen-fixing enzyme have been isolated from this bacterium and found to contain iron and molybdenum [132]. This enzyme reduces nitrogen to ammonia, it will also catalyse the reduction of N_2O to N_2, N_3^- to N_2 and NH_3 and HCN to CH_4 and NH_3 [133]. There is no concrete evidence for the stages involved in the reduction of nitrogen to ammonia. It is reasonable to suppose that the iron and/or the molybdenum atoms in the enzyme are at the sites where the initial activation of molecular nitrogen occurs.

The subsequent reduction of the nitrogen to ammonia may proceed by a mechanism similar to that proposed for the dimeric titanium complex [133]. Also the reactions of some arylazo–platinum complexes with hydrogen are suggestive [134], viz.:



A great deal of work on both homogeneous catalysis and the fixation of nitrogen has been described in the years 1965–70, see the references in [135].

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† For a review of biological nitrogen fixation, see reference [131].

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Supplementary index to crystal structures

This index is classified as follows: Complexes which contain organic ligands which are readily recognized to be in one of the classes of n-electron ligands (see the Table on p. 1) are given under the appropriate title and in alphabetical order according to the metal. Thus (Me$_3$PtCl)$_4$ is found under 1-electron ligands as (PtMe$_3$Cl)$_4$. Complexes containing two classifiable ligands are similarly classified under both ligands. Thus π-C$_5$H$_5$Fe(CO)$_2$CH$_2$COOH is given under 1- and 5-electron ligands. *Alkynyl and acetylide* complexes, *complexes formed from acetylenes*, *cyclo-octa-1,5-diene*, *cyclo-octatetraene*, *cyclotropone*, *heterocyclic complexes* and *hydride complexes* are separately classified under these headings.

- *1-electron ligands* (see also alkynyls/acetylides)
  - [AuPr^{n}CN]$_4$ 256
  - CoC$_2$F$_5$(CO)$_3$Ph$_3$P 269
  - [CoC$_2$F$_4$H(CN)$_5$]$^{3-}$ 270
  - Co(Mes)$_2$(PEt$_2$Ph)$_2$ 230
  - Cr p-MeC$_6$H$_4$(THF)$_3$Cl$_2$ 244
  - CrCMe(OMe)(CO)$_4$Ph$_3$P 220
  - FeCH$_2$COOH(π-C$_5$H$_5$)(CO)$_2$ 214
  - Mn(CF=CFH)(CO)$_5$ 270
  - MoEt(π-C$_5$H$_5$)(CO)$_3$ 235
  - PtMe$_3$(diketones) 252
  - [PtMe$_3$Cl]$_4$ 251
  - PtC$_3$H$_6$py$_2$Cl$_2$ 253
  - Pt(CHEtpy)pyCl$_4$ 253
  - RhC$_2$F$_5$I(CO) π-C$_5$H$_5$ 270
  - W[CPh(OMe)](CO)$_5$ 219

- *2-electron ligands* (see also cyclo-octa-1,5-diene heterocyclic ligands, cyclo-octatetraene)
  - Ag(bullvalene)$_3$NO$_3$ 28
  - (AgNO$_3$)$_2$ humulene 28
  - Fe acrylonitrile(CO)$_4$ 21
  - Fe fumaric acid(CO)$_4$ 19
  - Fe tetraphenyl butatriene(CO)$_4$ 185
  - Fe C$_8$H$_9$(CO)$_3$ 67
  - Fe$_2$(C=CPh$_2$)(CO)$_8$ 34
  - NicyclooctenylCO(acac) 24
  - Niethylene(PPh$_3$)$_2$ 30
  - Ni$_3$(piperidine-N-carbonitrile)$_3$(CO)$_3$ 35
  - [Pd ethylene Cl]$_2$ 30
  - [Pd styrene Cl]$_2$ 30
  - [Pt ethylene Cl$_3$]$^-$ (Zeise's salt) 15
  - Pt ethylene ClNHMe$_2$ 30
  - Pt dipentene Cl$_2$ 31
  - [Pt MeOC$_{10}$H$_{12}$Cl]$_2$ 24
  - RhCS(Ph$_3$P)$_2$Cl 35
  - RhCS$_2$(Ph$_3$P)$_2$ 34

- *3-electron ligands*
  - *allyl*
    - [PdC$_3$H$_5$Cl]$_2$ 44
    - [PdC$_3$H$_5$—μ-OAc]$_2$ 54
    - (Rh(C$_3$H$_5$)$_2$Cl)$_2$ 53
  - *cyclobutenyl*
    - NiMe$_4$C$_4$—C$_5$H$_5$(π-C$_5$H$_5$) 55
    - [PdPh$_4$C$_4$OEtCl]$_2$ 55
  - *enyl*
    - Co$_2$C$_5$F$_6$(CO)$_7$ 59
    - FeC$_8$H$_9$(CO)$_3$ 67
    - Ni(methylallyl)$_2$ 44
    - Pd cyclo-octadienyl(acac) 45
    - Pd methylallylClPPh$_3$ 52
    - RhC$_{12}$H$_{18}$Cl$_4$ 57
    - Ru dodeca-2,6,10-triene-1,12-diylCl$_2$ 52

- *4-electron ligand* (see cyclo-octatetraene, heterocyclic)
  - *butadienes* –
    - FeC$_4$H$_6$(CO)$_3$ 70
    - Fe Vitamin A aldehyde(CO)$_3$ 85
    - Rh(C$_4$H$_6$)$_2$Cl 85
  - *cyclobutadienes*
    - FeC$_4$Ph$_4$(CO)$_3$ 75
    - (NiC$_4$Me$_4$Cl$_2$)$_2$ 74
  - *cyclohexadiene* –
    - Fe anthracene(CO)$_3$ 170–171
    - FeC$_6$F$_8$(CO)$_3$ 73
  - *cyclopentadienes* –
    - CoC$_5$H$_4$COPh(π-C$_5$H$_5$) 73
    - CoC$_5$H$_4$Rh(π-C$_5$H$_5$) 73
    - CoC$_5$Me$_4$O(π-C$_5$H$_5$) 73
    - CoC$_5$(CF$_3$)$_4$O(π-C$_5$H$_5$) 73
    - FeC$_5$Me$_4$O(CO)$_3$ 73

- *5-electron ligands*
  - π-cyclopentadienyl (see Table 11, p. 98)
    - Coπ-C$_5$H$_5$(C$_2$S$_2$Me$_2$) 122
    - Coπ-C$_5$H$_5$(C$_5$H$_4$Ph) 73
    - Coπ-C$_5$H$_5$(C$_5$Me$_4$O) 73
    - Coπ-C$_5$H$_5$C$_5$(CF$_3$)$_4$O 73
    - Coπ-C$_5$H$_5$C$_5$H$_4$COPh 73
    - [Coπ-C$_5$H$_5$PPh$_2$]$_2$ 128
    - Crπ-C$_5$H$_5$(NO)$_2$Cl 126

5-electron ligands—contd
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$Fe_2(\pi-C_5H_5)_2(CO)_3CNPh$ 122
$Fe\pi-C_5H_5(CO)_2CH_2COOH$ 214
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$[Mn\pi-C_5H_5(CO)_2]_2—C_6H_4(AsMe)_2$ 125
$Mo(\pi-C_5H_5)_2H_2$ 129–130
$[Mo\pi-C_5H_5(CO)_3]_2$ 117
$[Mo\pi-C_5H_5OS]_2$ 135
$Mo\pi-C_5H_5(CO)_3Et$ 235
$[Mo\pi-C_5H_5(CO)_2]_2H(PPh_2)$ 128
$Ni\pi-C_5H_5NO$ 112
$Ni\pi-C_5H_5Me_4C_4—C_5H_5$ 55
$[Ni\pi-C_5H_5PPh_2]_2$ 128
$Ni\pi-C_5H_5C_7H_5(COOMe)_2$ 109
$[Ni\pi-C_5H_5CO]_2$ 124
$Ni_2(\pi-C_5H_5)_2Ph_2C_2$ 124
$Ni_3(\pi-C_5H_5)_3(CO)_2$ 124
$Re\pi-C_5H_5C_5H_5Me(Me)_2$ 152
$Rh\pi-C_5H_5C_6(CF_3)_6$ 73
$Rh_2(\pi-C_5H_5)_2(CO)_3$ 123–124
$[Ru\pi-C_5H_5(CO)_2]_2$ 120
$Ta\pi-C_5H_5(CO)_4$ 117
$Ti\pi-C_5H_5Cl_3$ 133
$[Ti\pi-C_5H_5Cl_2]_2O$ 133
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$Ti(\pi-C_5H_5)_2Cl_2AlEt_2$ 322
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6-electron ligands (see cyclo-octatetraene)
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$AgC_6H_6ClO_4$ 29
$Cr(C_6H_6)_2$ 171
$CrC_6H_6(CO)_3$ 171
$CuC_6H_6AlCl_4$ 29
$[PdC_6H_6Al_2Cl_7]_2$ 179
arene –
$CrC_6Me_6(CO)_3$ 171
$CrMeOC_6H_5(CO)_3$ 180
Cr o-$MeNH_2C_6H_4(CO)_3$ 180
Cr phenanthrene $(CO)_3$ 170
$Cr_2C_6H_5-C_6H_5(CO)_6$ 172
$FeC_6(CF_3)_6(CO)_3$ 73
Fe anthracene $(CO)_3$ 171
cycloheptatriene –
$MoC_7H_8(CO)_3$ 183
cyclo-octa-1,3,5-triene –
$CrC_8H_{10}(CO)_3$ 183
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$[AgC{\equiv}CPhPMe_3]_n$ 278
$[AuC{\equiv}CPhPr^iNH_2]_n$ 279
$[AuC{\equiv}CBu^t]_n$ 275
$[CuC{\equiv}CPhPMe_3]_4$ 278
$[CuC{\equiv}CBu^t]_n$ 275
$[CuC{\equiv}CPh]_n$ 275

Complexes formed from acetylenes (see also heterocyclics)
$Co_2(C_6H_4(CMe_3)_2)(CO)_6$ 304
$Co_2(Ph_2C_2)(CO)_6$ 292
$Co_2(C_4H_2O_2)(CO)_6$ 293
$Co_2(C_6F_6)(CO)_6$ 293
$Co_3(CMe)(CO)_9$ 294
$Co_4(Et_2C_2)(CO)_{10}$ 293
$Fe_2(C_4Me_2(OH)_2)(CO)_6$ 303
$Fe_2C_6H_6(CO)_6$ 308
$Fe_2(C_7Ph_3H_3O)(CO)_5$ 308
$Fe_3(Ph_4C_4)(CO)_8$ 306
$Fe_3(Ph_2C_4)(CO)_8$ 306
$Fe_3Ph_2C_2(CO)_9$ 295
$Fe_5C(CO)_{15}$ 309
$Ni(C_6Me_4O_2)C_8H_{12}$ 301

Cyclo-octa-1,5-diene complexes
$[CuC_8H_{12}Cl]_2$ 25
$Ir(C_8H_{12})_2SnCl_3$ 33
$Ni(C_8H_{12})_2$ 11
$Ni(C_8H_{12})(Me_4C_6O_2)$ 301

Cyclo-octatetraene complexes
$Ag(C_8H_8)NO_3$ 27
$Cu(C_8H_8)Cl$ 27
$Fe(C_8H_8)(CO)_3$ 197
$Fe_2(C_8H_8)(CO)_6$ 197
$Fe_2(C_8H_8)(CO)_5$ 197
$MoC_8H_8(CO)_3$ 199
$Ti_2(C_8H_8)_3$ 200

Cyclotropone complexes
$Fe(C_7H_3Ph_3O)(CO)_3$ 73

Heterocyclic complexes
Cr thiophene $(CO)_3$ 187
$Fe_2(C_4Me_2H_2O_2)(CO)_3$ 303
$Fe_2(C_8H_6)(CO)_6$ 304
$Fe_2C_{14}H_8Cl_2(CO)_6$ 305
$Os_2(C_4H_2Me_2)(CO)_6$ 84

Hydrides (see also π-cyclopentadienyl)
$[Cr_2H(CO)_{10}]^-$ 317
$[Fe_3H(CO)_{11}]^-$ 317
$Mn_3H_7B_2(CO)_{10}$ 317
$[ReH_9]^{2-}$ 315
$RhHCO(PPh_3)_3$ 315