STUDIES IN
ORGANO-RHODIUM AND -IRIDIUM CHEMISTRY

To my parents, Mr. and Mrs. E. Moseley of Leicestershire, ENGLAND, whose devotion and encouragement have been a constant source of inspiration.

STUDIES IN ORGANO-RHODIUM AND -IRIDIUM CHEMISTRY AND MASS SPECTRA OF SOME ORGANO-TRANSITION METAL COMPLEXES

By

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TITLE: Studies in Organo-rhodium and -iridium Chemistry and Mass Spectra of Some Organo-transition Metal Complexes

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SCOPE AND CONTENTS:

Reaction of the hydrated trichlorides of rhodium and iridium with hexamethyldewarbenzene gave the complexes, $(C_5Me_5MC\ell_2)_2$ (M=Rh,Ir). A mechanism for this reaction is proposed.

The dichloro complexes, $(C_5Me_5MC\ell_2)_2$, were reacted with a number of di- and tri-enes in ethanol in the presence of base and gave a variety of pentamethylcyclopentadienyl complexes of M(I) and M(III). Evidence for a hydrido intermediate is presented and the hydrido- and deuterido- complexes, $C_5Me_5IrH(D)C\ell PPh_3$, were isolated and characterised.

The isomers endo-H and exo-H pentamethylcyclopentadiene(cyclopentadienyl)rhodium were isolated and showed significant differences in their properties. Cyclooctadienes reacted with $(C_5Me_5MC\ell_2)_2$ to give $C_5Me_5M(1,5\text{-}C_8H_{12})$ via the intermediacy of the π-2-cyclooctenyl complexes $C_5Me_5MC\ell(C_8H_{13})$; mechanisms are presented to account for the observed products. Cyclohexadienes gave the complexes, $C_5Me_5M(1,3\text{-}C_6H_8)$. 1,4-Cyclohexadiene was isomerised to $1,3\text{-}C_6H_8$; the rhodium complex, $C_5Me_5Rh(1,3\text{-}C_6H_8)$, was a very active catalyst

for the disproportionation of 1,3-C_6H_8 to cyclohexene and benzene, both ethanol and base were cocatalysts.

Mass spectral data for these and other organo-metallic complexes are presented.

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I Metal π Complexes

Organic molecules having electrons in orbitals of π symmetry are able to form complexes with transition metals. The linear combination of atomic orbitals (a.o.'s), which generates bonding π orbitals, also of necessity generates antibonding π* orbitals. The π orbitals, which are occupied and polarisable, may overlap with suitable vacant metal orbitals while the π* orbitals, which are vacant, may also participate in the metal-organic bond by overlap with occupied metal orbitals of correct symmetry. It is the combination of these "donor" and "acceptor" interactions which is thought to lead to the stability of metal π-complexes.

This so-called "synergic" mode of bonding can effectively occur only when the metal involved has filled or partially filled non-bonding d orbitals. For this reason metal π-complexes are most numerous for the groups VII and VIII metals in low oxidation states.

The vast majority of the π-complexes obey the inert gas electron configuration formalism and are diamagnetic. This is a consequence of the filling of all bonding and non-bonding molecular orbitals (M.O.'s).

A brief discussion of the major types of π-complexes follows.

A. Mono-Olefin Complexes

The first olefin-transition metal complex and the first example in which an unsaturated hydrocarbon ligand is bonded directly to a metal was Zeise's salt $K[C_2H_4PtC\ell_3]\cdot 3H_2O$, prepared in 1827. It was not until 1953 however that Chatt[1], applying the molecular orbital concepts of Dewar[2], put forward a hypothesis to explain the nature of the platinum-ethylene bond. His proposal, which survives today as the basis for bonding theories of π-complexes, is illustrated in Figure 1.

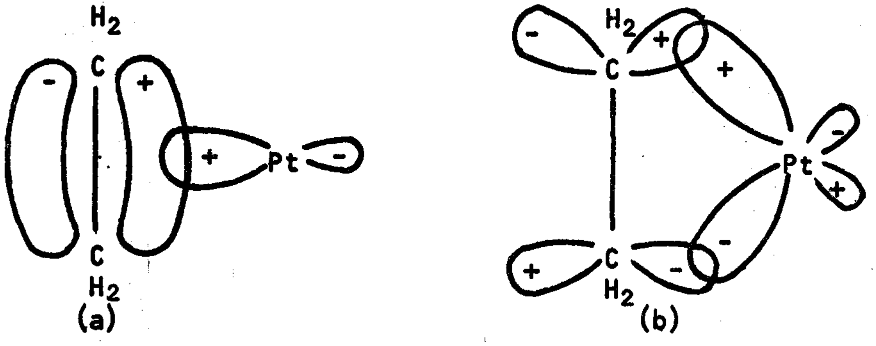


Figure I

In Chatt's model for this square planar d^8 complex, the ethylene C—C bond is perpendicular to the plane described by the Pt and Cℓ atoms. The four vacant $5d6s6p^2$ orbitals of the metal lie in the molecular plane and overlap with three chlorine a.o.'s and the π orbital of ethylene to give a M.O. of σ symmetry (the "μ"-bond)[Fig. I(a)]. The filled 5d6p orbitals of the metal are of correct symmetry to overlap with the vacant π* orbitals of ethylene [Fig. I(b)] giving a M.O. of π symmetry.

X-ray studies show that in crystalline $[C_2H_4PdC\ell_2]_2$[3], $C_2H_4Pt[HN(CH_3)_2]C\ell_2$[4] and $[KPt(C_2H_4)C\ell_3]\cdot 3H_2O$[5] the ethylene double bond is, in fact, perpendicular to the coordination plane [Fig. II(a)].

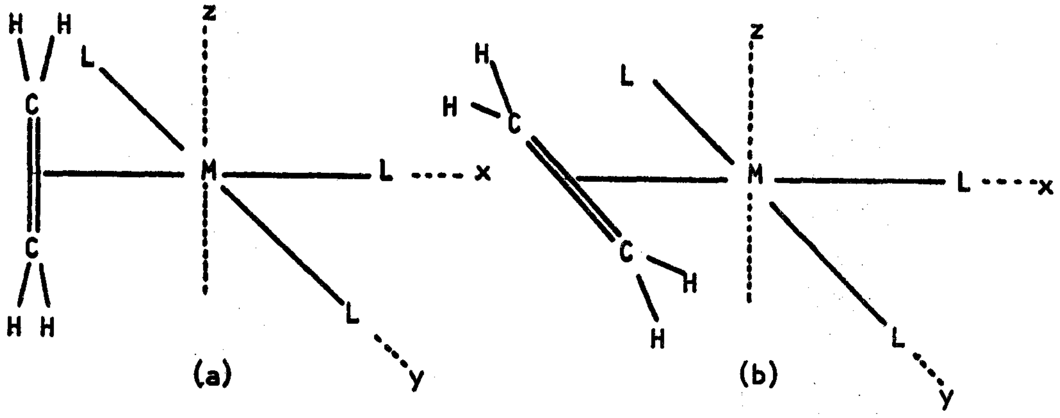


Figure II

In Chatt's treatment the d_{xz} metal orbital is used for back donation; however, if the ethylene double bond were imagined to lie in the molecular plane then the d_{yx} orbital is of correct symmetry for overlap with the π^* orbitals [Fig. II(b)]. This latter conformation is presumably not observed in the solid state since it is sterically less favoured. However Cramer[6,7] has invoked such a conformation to account for the low energy barriers to rotation of the ethylene molecule about the ethylene-metal bond in some olefin-rhodium cyclopentadienyl complexes.

There is much evidence to support the above type of bonding in metal π-olefin complexes in which the olefinic C—C bond order is effectively reduced by transfer of electron density from the π- to the π^*-orbital by interaction with the metal orbitals. Thus olefins exhibit a decreased C═C stretching frequency on coordination and X-ray studies often show an increase in the olefinic bond distances.

The relative contributions of the "donor" and "acceptor" interactions to the metal-olefin bond, and the stability of this bond, will depend on the metal, its oxidation state, the other ligands in the complex and the substituents adjacent to the coordinated olefinic bond. The extreme cases of "donor only" and "acceptor only" bonds are illustrated in valence bond form in Figure III. The acceptor only bond is, in effect, equivalent to two $M—C_{sp^3}$ σ-bonds, when the configuration about the carbon atoms is tetrahedral [Fig. III(b)].

The actual bonding in the majority of olefin complexes will lie somewhere in between these two extremes. The Pd(II) and Pt(II) ethylene complexes would appear to have a bonding which approaches III(a). However,

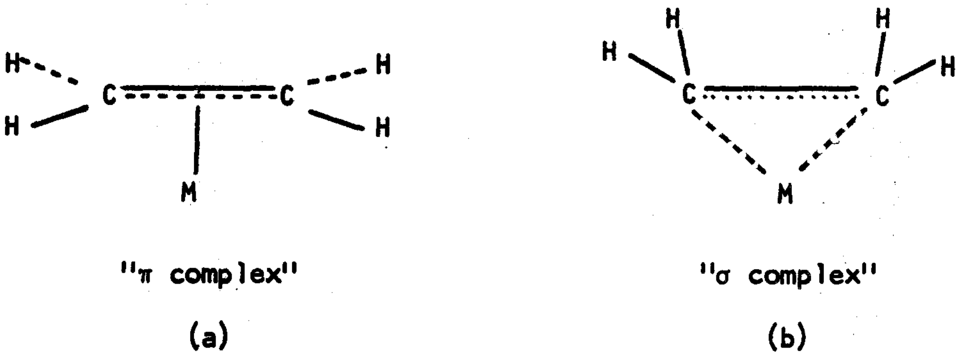


Figure III

strongly electron-withdrawing substituents adjacent to the olefinic double bond such as F, CN and CO are expected to both increase the acceptor ability and decrease the donor ability of the olefin. Also, ligands with good donor properties, such as alkyl phosphines, transfer charge to the metal atom, strengthening the back-bonding to other ligands such as olefins. Not surprisingly then, the complex $(PPh_3)_2Pt[C_2(CN)_2]^8$, in which the metal is formally in the zero oxidation state and potentially a good donor, has a structure[9] very nearly that expected for the σ complex of Figure III(b). The olefinic C—C bond in this complex lies at an angle of 10° to the plane of the Pt and P atoms and its bond distance approaches that of a C_{sp^3}—C_{sp^3} single bond [Figure IV].

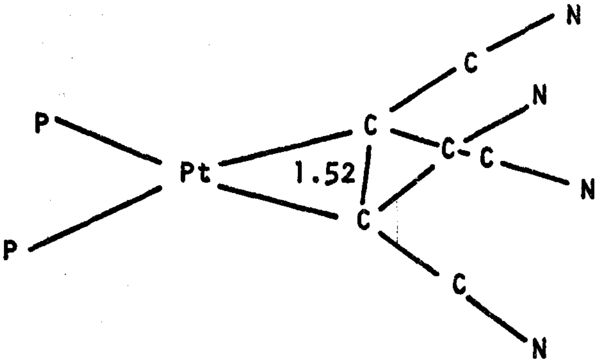


Figure IV

A similar structure has been observed for the formally Ni(0) complex $(Ph_3P)_2Ni(C_2H_4)$[10].

B. Non-Conjugated Polyolefin Complexes

Chelating diolefins such as norbornadiene, 1.5-cyclooctadiene and dicyclopentadiene form numerous π-complexes in which the double bonds are coordinated to one[11,12,13] or occasionally two[14] metal atoms. The double bonds in these dienes are correctly arranged for chelate complex formation. The bonding in these complexes is very similar to that of monoolefins since interactions are minimal. The structures of many of these compounds have been determined, for example $[(1.5\text{-}C_8H_{12})RhC\ell]_2$[15] has a configuration in which the double bonds are perpendicular to the plane described by the Rh and two Cℓ atoms [Figure V].

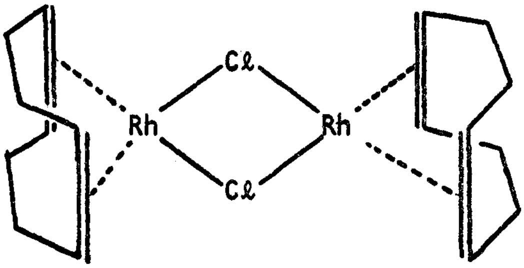


Figure V

C. Conjugated Diolefin Complexes

In π-complexes of organic ligands where conjugation is present, the mutual interaction of the double bonds must be considered. An analysis of the symmetry allowed interactions between a metal and a conjugated diene system, using the local symmetry of butadiene, leads to a bonding scheme in which the two extreme modes may be pictorially represented by VI(a) and VI(b) (analogous to Figure III for monoolefins).

The iron atom in butadiene-[16] and cyclooctatetraene-[17] iron tricarbonyls is equidistant from the four carbon atoms of the coordinated

"π-bonding"

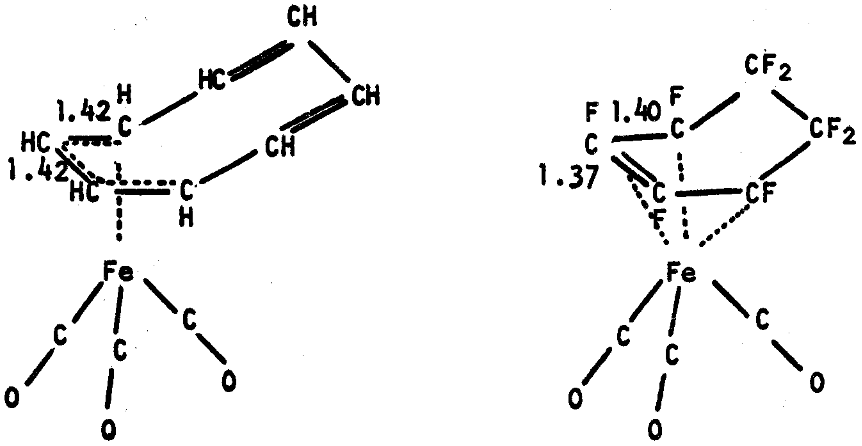
(a)

"σ,π-bonding"

(b)

Figure VI

diene and the C—C bond distances in this are effectively equal, suggesting VI(a) and VI(b) to make approximately equal contributions [Fig. VII(a)]. However when electron withdrawing substituents are on the diene, increased back-bonding from the metal is expected making VI(b) more important. This is observed, for example, in the structure of octafluorocyclohexadiene iron tricarbonyl[18] [Fig. VII(b)].



(a)

(b)

Figure VII

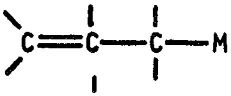
D. Acetylene Complexes

The acetylenic bond has two mutually perpendicular sets of π and π* orbitals so that, by analogy with olefins, it would be expected that alkynes can complex with one or two metals via synergic donor and acceptor bonds. In fact, both types of complex are known[19,20].

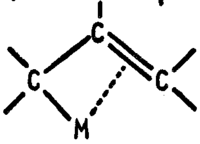
E. π-Allyl Complexes

There are three ways in which an allyl radical could conceivably be bonded to a metal.

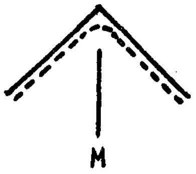
(i) via a normal σ-bond:



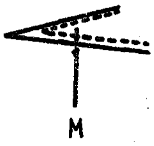
(ii) via a σ- and a π-bond:



(iii) via a donor-acceptor bond between the metal and a completely delocalised three centre π electron system. There are two stereochemical possibilities corresponding to dihedral angles of 180° [(iii)(a)] and 90° [(iii)(b)] with respect to the plane containing the metal and remaining ligands.



(a)

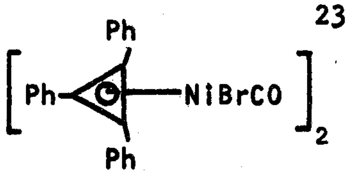


(b)

The structure represented by (iii) is very commonly observed for the transition metals as shown by n.m.r. and X-ray structural determinations. An analysis of the symmetry allowed metal and ligand M.O. overlaps for each of (iii)(a) and (iii)(b) and a consideration of the various overlap integrals led to the prediction that the bonding energy will be maximised at a dihedral angle of 110°[21]. Just such a magnitude of non-orthogonality has been observed in several π-allyl complexes. For example, the π-allyl ligand in the palladium complex $[(\pi C_3H_5)PdC\ell]_2$[22] is inclined at a dihedral angle of 111.5°±0.9° to the $PdC\ell_2Pd$ plane.

F. π-Complexes of Cyclic Ligands in which the Metal is Symmetrically Bonded to an Assembly of Three to Eight Carbon Atoms

A large number of metal π-complexes contain fully conjugated cyclic ligands which formally contribute from three to eight electrons to the metal. The metal here usually lies below a planar "aromatic" ring approximately equidistant from all of the carbon atoms. The bonding is essentially covalent and is thought to involve similar interactions to those proposed by Chatt[1] for metal-olefin complexes. Some examples of these complexes in which the metal is symmetrically bonded to all the carbons of a cyclic hydrocarbon ligand are given below.



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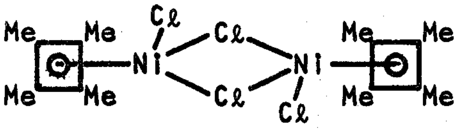

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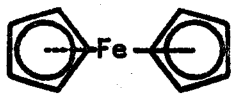

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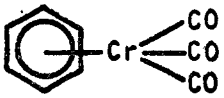

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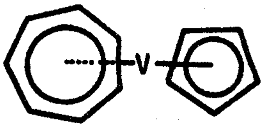

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"Sandwich" complexes [e.g., ferrocene, $(C_5H_5)_2Fe)$], "mixed sandwich" complexes [e.g., $C_5H_5VC_7H_7$] and "half-sandwich" complexes [e.g., $(Me_4C_4NiC\ell_2)_2$] are all known and many of them are very stable.

In ferrocene, the cyclopentadienyl ring, when bonded to iron, may be regarded as a radical or an anion depending on the formal oxidation state we assign to the metal. The sp^2 hybridised carbon orbitals of this ring are used to form M.O.'s which are assumed to be unaffected by the ligand-metal bonding. The remaining five 2pπ a.o.'s give five delocalised M.O.'s whose form and relative energies are determined using the Hückel approximation. The rings are now considered together and ligand M.O.'s of the same rotational symmetry are combined into g and u pairs depending on the behaviour of the M.O.'s to inversion through the centre of symmetry. The resulting ten M.O.'s are classified in the D_{5d} symmetry point group, to which ferrocene belongs. The metal valence a.o.'s (3d, 4s and 4p) are also classified in this point group. The actual metal-ligand bond will be comprised of contributions from metal and ring orbitals which belong to the same representation. The relative importance of each contribution to the total bonding energy depends on the amount of overlap (overlap integrals) and the relative energies of the overlapping ligand M.O.'s and metal a.o.'s. It is on these considerations that the various treatments[29] which have been proposed differ. Although the actual ordering of the energy levels in ferrocene is uncertain, there is general agreement on the major sources of the bonding as summarised in the M.O. energy level diagram (Fig. VIII).

The M.O. diagram shows that there are nine bonding or non-bonding orbitals in ferrocene which can accommodate up to eighteen electrons; the effective atomic number formalism is thus given a firm physical basis.

Other sandwich complexes can be treated similarly though their lower symmetry makes the analysis more difficult.

The metallocenes of the cobalt triad have a 19-electron shell and the "extra" electron, which is in an antibonding orbital, is readily lost to give the very stable metallocinium ions $(\pi C_5H_5)_2M^+$. These cations also

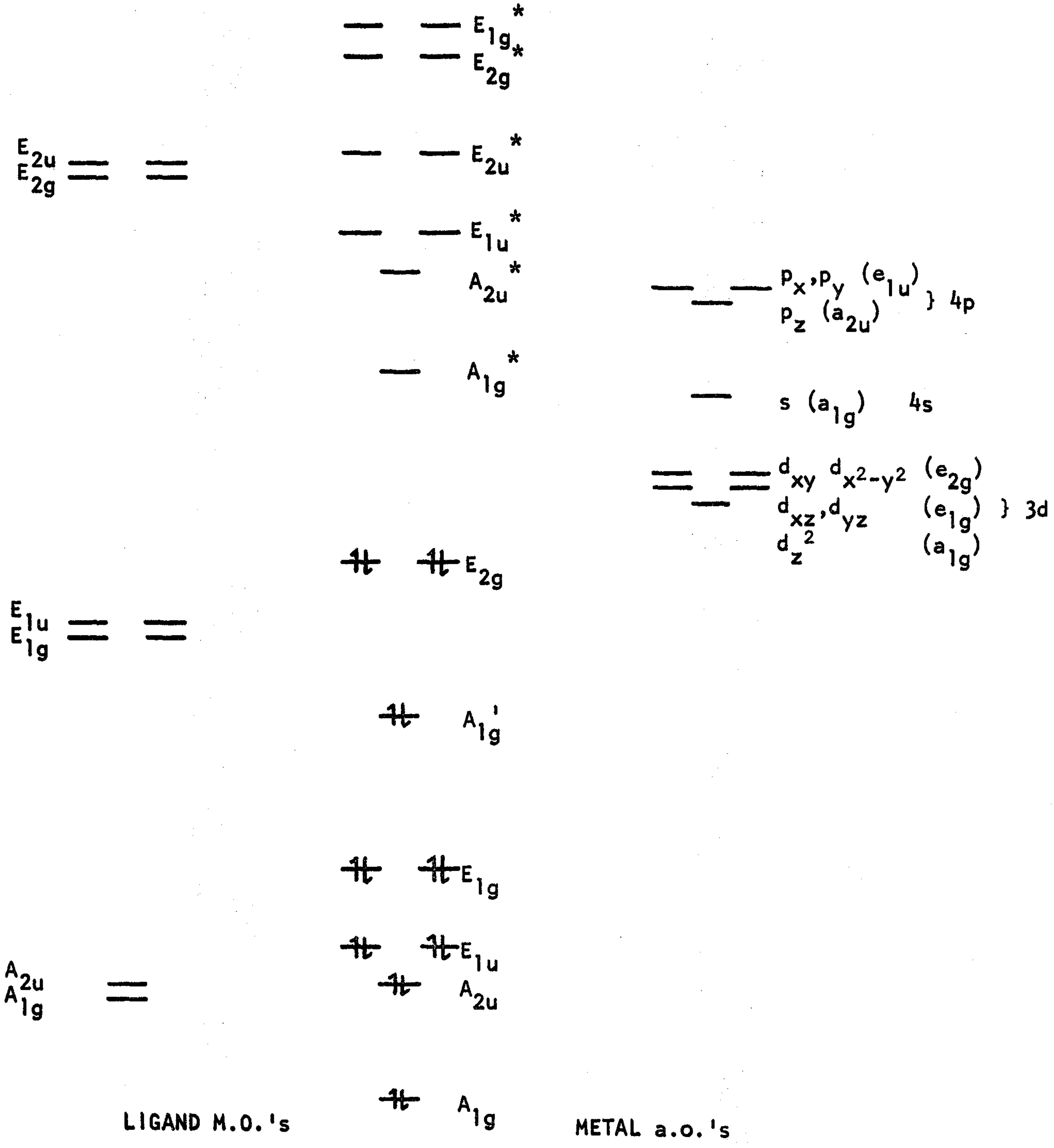
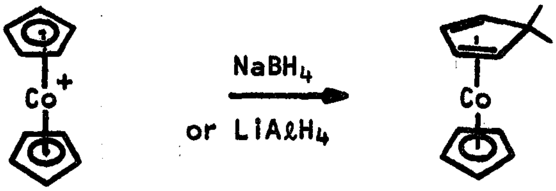

E_{1g}^*
E_{2g}^*
E_{2u}
E_{2g}
E_{2u}^*
E_{1u}^*
A_{2u}^*
p_x, p_y (e_{1u})
p_z (a_{2u})
} 4p
A_{1g}^*
s (a_{1g}) 4s
d_{xy} $d_{x^2-y^2}$ (e_{2g})
d_{xz}, d_{yz} (e_{1g})
d_{z^2} (a_{1g})
} 3d
E_{2g}
E_{1u}
E_{1g}
A_{1g}'
E_{1g}
E_{1u}
A_{2u}
A_{1g}
A_{2u}
A_{1g}
LIGAND M.O.'s
METAL a.o.'s

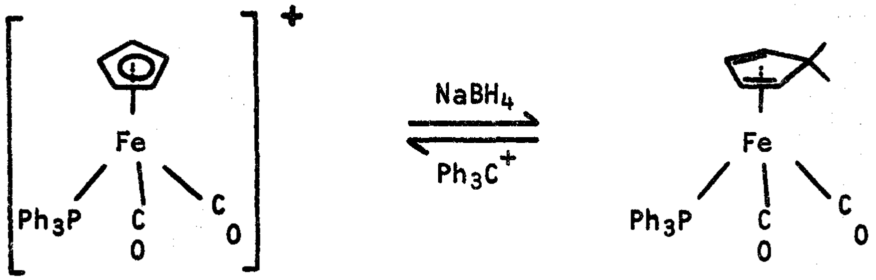
Figure VIII

readily react with nucleophiles to give adducts, which now formally have the metal in the +I state. Thus biscyclopentadienylcobalt(III) cation(1), when reduced in the presence of $LiA\ell H_4$ or $NaBH_4$, gives π-cyclopentadienyl cyclopentadienecobalt(I) (2) which obeys the inert gas rule[30].



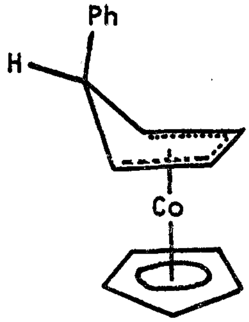
[(1)M = Co]   [(2)M = Co]

The methylene group of compounds of type (2), other cyclopentadiene complexes such as $C_5H_6Fe(CO)_2PPh_3$[31], and the analogous cyclohexadienyl complexes such as $C_6H_7Mn(CO)_3$[32], exhibits some interesting properties. The infrared spectra of these complexes show a characteristic, intense C—H stretching band at around the low value of 2750 cm^{-1}. They also possess a reactive hydrogen which may readily be removed by oxidation with H_2O_2 in the presence of acid, or reaction with hydride abstracting reagents such as the triphenylmethyl cation and N-bromosuccinimide (NBS). For example, the oxidation of (2) (M = Rh) with H_2O_2 in the presence of acid gave (1) (M = Rh)[33] and the reversible reaction of $[C_5H_5Fe(CO)_2PPh_3]^+$ is characteristic[31]:



Deuteration studies[30] using $LiA\ell D_4$ show that, in fact, it is the newly-formed C—H bond that is responsible for the anomalous C—H stretching frequency in complexes such as (2).

A similar reaction to the hydride attack on a ring, described above, is the addition of substituents, R^-, using organolithium, sodium cyclopentadienide or Grignard reagents. Thus the reaction of C_6H_5Li with (1) (M = Co) yields the complex $(\pi C_5H_5)(C_5H_5Ph)Co(I)$. These substituted complexes, unlike the unsubstituted ones, do not exhibit the anomalous C—H stretching band. X-ray structural determinations on a number of these substituted complexes have been reported[34,35,36] and show, in each case, that R^- attack occurs on the least hindered side of the ring, affording non-planar "exo" substituted products.



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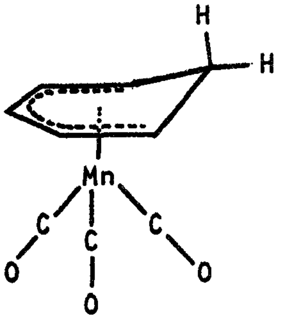
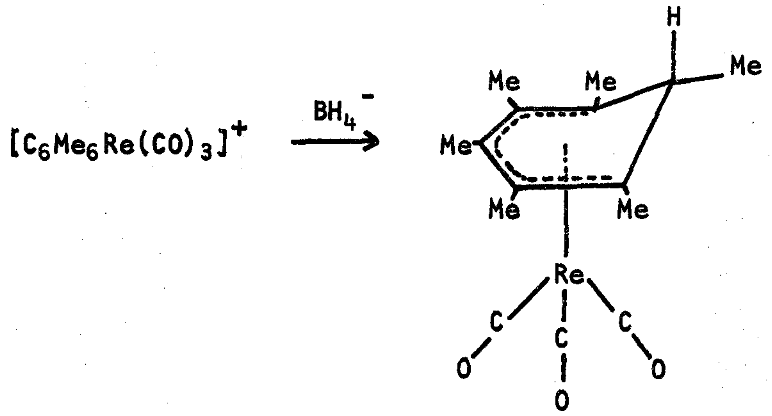
Churchill[37] has recently reported the only structural determination on an unsubstituted complex of this type, π-cyclohexadienylmanganese tricarbonyl, in which the ligand is similarly non-planar.



A structural determination[38] on the Re complex (3) in which the ring is substituted *and* shows the anomalous C—H stretch at 2790 cm^{-1}, shows conclusively that it is the "exo" hydrogen which exhibits the properties outlined above. The reasons why this is so are obscure at present[37,39].



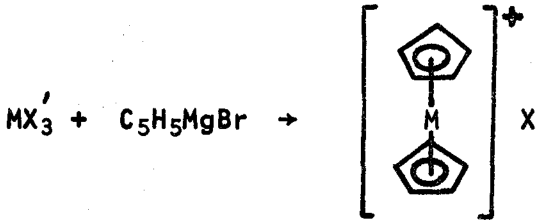
(3)

II Cyclopentadienyl-Complexes of Rhodium and Iridium

Cyclopentadienyl-metal complexes have frequently been synthesised from the anhydrous halide and sodium cyclopentadienide in THF or C_5H_5MgBr in ether or benzene. An alternative route is from cyclopentadiene and a metal carbonyl or halide in the presence of base.

These methods have been used for the preparation of rhodium and iridium cyclopentadienyl complexes. The biscyclopentadienyl complexes of these metals are stable only as the cations $(\pi C_5H_5)_2M(III)^+$ [(1) M = Rh,Ir] having the inert gas electron configuration. These were prepared from the M(III) acetylacetonates[40] or the anhydrous trichlorides[41,42] and Grignard reagents.

A by-product with formula $Rh_3(C_5H_5)_4H$ was also isolated from this reaction with $RhC\ell_3$[42]. An X-ray structural study has now been reported[43]



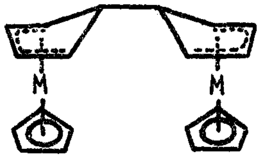
(1) (M = Rh, Ir)

X = Br_3^-, PF_6^-, etc.

on this complex and shows it to contain an equilateral triangle of Rh atoms, each bonded to one cyclopentadienyl ring; the remaining C_5H_5 is bonded equally to all three Rh atoms. The position of the hydrogen is not known but is probably situated between the metal atoms.

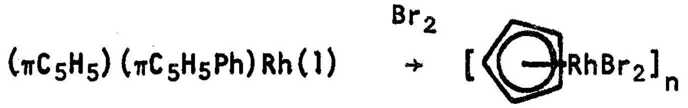
Reaction of (1) (M = Rh, Ir:X = $C\ell$) with sodium borohydride in aqueous ethanol[31] gave the complex $(\pi C_5H_5)(C_5H_6)M$ [(2) M = Rh, Ir). The rhodium complex (2) was also prepared from the hydrated $RhC\ell_3$ by the reaction with NaC_5H_5 in THF followed by addition of sodium borohydride[31]. The complexes (2) (M = Rh, Ir) have also been prepared directly from the anhydrous metal trichlorides with large excesses of C_5H_5K and C_5H_6[33,44]. The complexes (2) (M = Rh, Ir) show the characteristic properties of cyclopentadiene complexes, with $\nu C—H_{exo}$ at 2758 (M = Rh) and 2742 (M = Ir) cm^{-1}. They are readily oxidised to (1) (M = Rh, Ir) by H_2O_2 in the presence of acid[33].

The paramagnetic rhodocene and iridocene M(II) complexes were made[42] by reduction of (1) (M = Rh,Ir:X = PF_6) in molten sodium. They are stable only at very low temperatures, at room temperature they dimerise giving the M(I) complexes (4).



(4) (M = Rh, Ir)

The rhodicenium cation (1) (M = Rh) undergoes the characteristic nucleophilic attack at the ring with NaC_5H_5 and LiPh[41] reagents in the presence of zinc to give the (presumably) exo-substituted complexes $(\pi C_5H_5)(C_5H_5R)Rh$ [(5) M = Rh; R = C_5H_5, C_6H_5). The complex (5) (M = Rh, R = C_6H_5) was oxidised by oxygen, or H_2O_2 in 2N $HC\ell$, to the (π-cyclopentadienyl)(π-phenyl-cyclopentadienyl)rhodium(III) cation[41]. Reaction with bromine in n-hexane afforded $(C_5H_5RhBr_2)_n$ [(6)]:



(6) (X = Br)

as an air stable, insoluble, dark red solid. This, presumably polymeric, material reacts with pyridine to give $(\pi C_5H_5)RhC\ell_2py$.

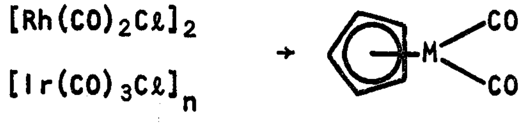
Rhodium trichloride hydrate, a compound of uncertain stoichiometry and unknown structure, reacts with a number of olefins in ethanol to give [diolefin $RhC\ell]_2$[45]. Hexachloroiridate(IV) undergoes somewhat similar reactions giving [diolefin $IrC\ell_2]_2$[46] or [diolefin $IrHC\ell_2]_2$[47]. These were reacted with sodium cyclopentadienide to give the π-cyclopentadienyl complexes (7).

[diolefin $RhC\ell]_2$
[diolefin $IrHC\ell_2]_2$ + NaC_5H_5 → diolefin M (C_5H_5)
(7)

(7) M = Rh, diolefin = $(C_2H_4)_2$[48]
1,5-cyclooctadiene[45]
1,5-hexadiene[6]
duroquinone[46]

(7) M = Ir, diolefin = 1,5-cyclooctadiene[47], duroquinone[49]

The rhodium and iridium carbonyl halides $[Rh(CO)_2C\ell]_2$ and $[Ir(CO)_3C\ell]_n$ have also been reacted with cyclopentadienide to give the π-cyclopentadienyl metal(I)dicarbonyls (8) (M = Rh, Ir)[50,51]



(8) (M = Rh, Ir)

The rhodium complex (8) (M = Rh) was unstable in air and dimerised in ether solution to give $[C_5H_5Rh(CO)_2]_2$. Exposure of solutions of (8) (M = Rh) to u.v. light gave $(C_5H_5)_2Rh_2(CO)_3$[52] and prolonged irradiation in hexane solution afforded the trinuclear species $[(\pi C_5H_5)RhCO]_3$[52,53].

A number of π-allyl derivatives of rhodium have been reported by Shaw[54] which, on reaction with cyclopentadienylthallium afford cyclopentadienyl derivatives (9), (10) and (6) (M = Rh, X = $C\ell$)

$$\begin{tikzcd}
Rh_2C\ell_2(CO)_4 \arrow[r, "(allC\ell^*)"] & Rh_2C\ell_2(all)_4 \arrow[r, "T\ell C_5H_5"] \arrow[dl, "(I)\ T\ell C_5H_5\ (II)\ conc.\ HC\ell"'] \arrow[dr, "(I)\ T\ell C_5H_5\ (II)\ dil.\ HC\ell"] & \underset{(9)}{Rh(\sigma\text{-}all)(\pi\text{-}all)(\pi C_5H_5)} \arrow[d, "dil.\ HC\ell"] \\
\underset{(6)(X = C\ell)}{[C_5H_5RhX_2]_2} & & \underset{(10)}{RhC\ell(\pi\text{-}all)(C_5H_5)}
\end{tikzcd}$$

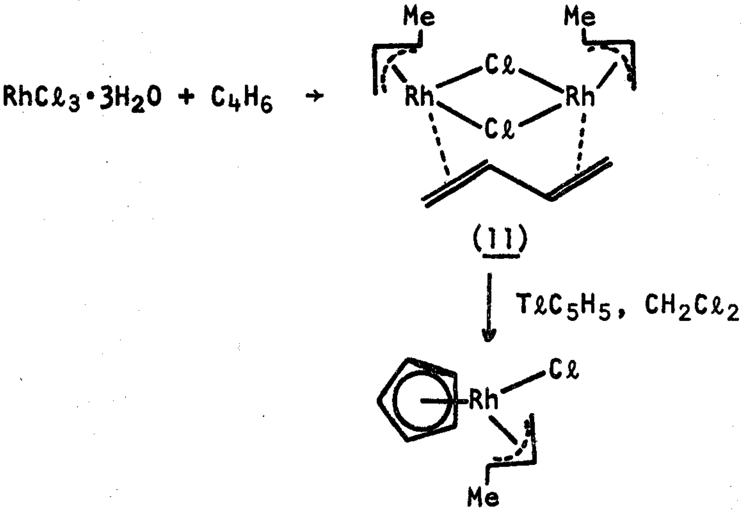
P.m.r. spectra of the 1-substituted allyl complexes indicated that the substituents are syn. The complex (6) (X = $C\ell$) was obtained as insoluble, dark brown microprisms, probably dimeric.

An additional route to (10) (all = 1-methallyl) was the addition

---

*all = allyl or substituted allyl.

of $T\ell C_5H_5$ to the product from the reaction of $RhC\ell_3 \cdot 3H_2O$ with butadiene (formulated as (11))[54].

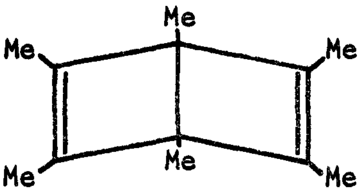


(11)

(10)

III The Reactions of Metal Complexes with Dewar Benzenes

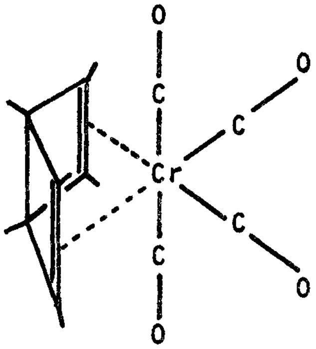
Routes which give useful amounts of dewar benzenes and the other non-planar valence isomers of benzene have been known since 1962[55]. In general, the preparations of these isomers is rather difficult and the unsubstituted ones, in particular, are usually thermally unstable[56]. Much of the current great interest in the reactions of dewarbenzene is due to the discovery by Schäfer[57] that hexamethyldewarbenzene (12) (hexamethylbicyclo[2.2.0]hexadiene, HMDB) is readily obtained from the bicyclotrimerisation of 2-butyne with aluminum trichloride.



(12)

This compound is thermally quite stable and has the advantage, for structural determinations by 'H n.m.r., that there are only methyl substituents.

Dewarbenzenes, which structurally bear a resemblance to norbornadiene, can form complexes with metals by functioning as chelating diolefins. The majority of the metal complexes made and studied have been of HMDB and these are now known for Cr, Mo and W[58,59], Rh[60,61], Pd[62] and Pt[63,64]. A palladium complex[65] of unsubstituted dewarbenzene has also been reported. In all of these complexes, the dewarbenzene functions as a chelating diolefin and the bicyclic structure is retained. This is shown by their p.m.r. spectra and by an X-ray study[66] of the chromium tetracarbonyl complex of HMDB.



In some metal complexes the dewarbenzene does not function as a chelating diolefin but still retains its bicyclic structure. Thus complexes of Pd and Pt[67,68] are known in which the ligand (less one hydrogen) bonds as an allylic moiety. Hexafluorodewarbenzene also gives complexes in which the double bonds are not chelating to the metal[69].

The bicyclic structure of HMDB was not retained in its reactions with rhodium[70] and platinium[64] compounds under acidic conditions. The products here are pentamethylcyclopentadienyl- and pentamethylcyclopentadiene- complexes respectively, for example (13a) from "rhodium trichloride trihydrate" and HMDB in refluxing ethanol[70]:

$$(\underline{12}) + RhC\ell_3 3H_2O \rightarrow \underset{(\underline{13}a)}{[C_5Me_5RhC\ell_2]_2}$$

The former reaction was discovered by Dr. Kang in this laboratory before commencement of the work described in this thesis, which then allowed a mechanism to be proposed for it.

IV Homogeneous Catalysis

Transition metals and their complexes in a finely divided form or dispersed on inert supports have long been known to catalyse a variety of reactions involving olefins, acetylenes, carbon monoxide and hydrogen. Furthermore, transition metal complexes are involved in the homogeneous enzymic catalysis of biological systems. Yet despite the long history of heterogeneous and enzymic catalysis, the most basic questions remain unanswered owing to the inherent difficulty in studying such systems. Clearly, the initial stage is the interaction and activation of the reactants at the transition metal. Such interactions are thought to be similar to those involved in organo-transition metal complexes. There is some evidence for this, particularly since it has been found that organo-transition metal complexes may undergo analogous reactions to those involved in heterogeneously and enzymic catalysed systems. Recently, homogeneous catalyses with organometallic complexes have been achieved. Such systems have a number of advantages since homogeneous catalysis is potentially much more efficient than reactions occurring only at a metal surface; moreover it is much more easily studied and the reactions involved are fairly well understood from years of intense study of organometallic complexes.

The catalytic reactions which have been studied usually involve the addition of a species X-Y to an olefin (or an acetylene). The processes involved can be described as

(i) activation, by reaction with the metal, of X-Y;

(ii) coordination (and activation) of the olefin (or acetylene) to the metal; and

(iii) reaction of XY to give the product in which XY has been added to the coordinated olefin; subsequent liberation of the saturated organic molecule is followed by regeneration of the catalytically active species.

In some cases, variants of this overall process occur and the catalytically active species is not easily defined.

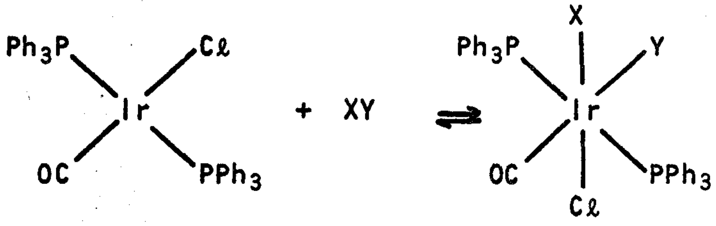
(i) Activation of the reactant XY by the metal

One of the characteristics of transition metal complexes of Group VIII in low oxidation state (which can be regarded as electron-rich molecules) is their ability to undergo reversible two-electron oxidations. In this context, this is usually accomplished by the addition of a covalent molecule, X-Y. This process also involves a change in stereochemistry and, very often, the loss of a ligand from the original complex.

In general, metal complexes of Group VIII elements in low oxidation states have coordination numbers of 3 or 4 for d^{10} (e.g., $Ni(CO)_4$, $(Ph_3P)_3Pt$) and 4 or 5 for d^8 (e.g., $(Ph_3P)_2Ir^{I}COC\ell$ and $Fe^{o}(CO)_5$). The most common forms of reversible "oxidative addition" are $d^{10} \rightleftarrows d^8$ and $d^8 \rightleftarrows d^6$. In the former case, the stereochemistry changes from trigonal (or tetrahedral) to square planar, for example[71]

$$(Ph_3P)_3Pt^o + HC\ell \rightleftarrows [(Ph_3P)_3PtH]^+C\ell^- \rightleftarrows Ph_3P + (Ph_3P)_2PtHC\ell.$$

The reversible oxidative addition to d^8 molecules has been most extensively studied[72]. Some well known examples include

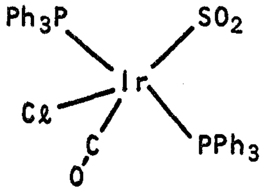


$X = H \qquad Y = H, C\ell$[73]

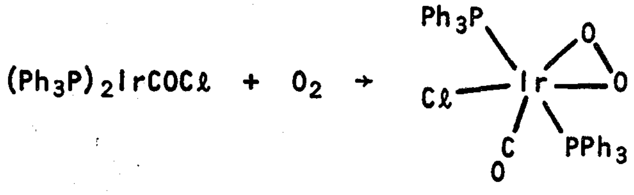
$\quad = I \qquad\quad = CH_3$[74]

The exact mode of attack here, whether cis- or trans- is a matter of dispute still, and depends on the medium and on X and Y. In either case, however, the formal oxidation state changes by two and the stereochemistry changes from square planar to octahedral. A variant of this is the reaction with SO_2[75] or oxygen[76] in which case complexes (14) and (15), which may be regarded either as distorted trigonal bipyramidal, or distorted octahedral, are formed.

$(Ph_3P)_2IrCOC\ell + SO_2 \rightarrow$

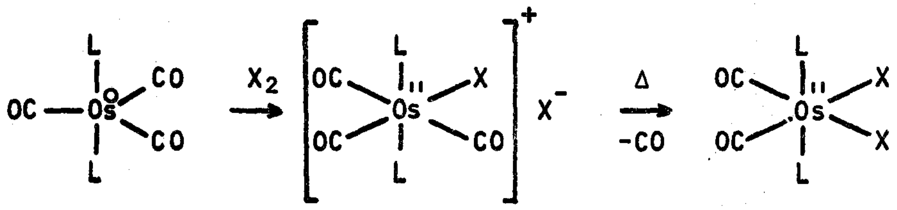


(14)

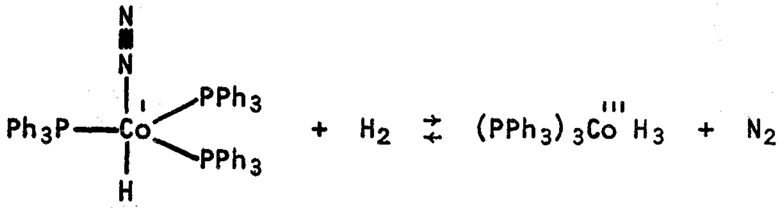


(15)

Five coordinate d^8 metals also undergo the oxidative addition reaction. In this case, loss of a ligand usually, but not always, occurs. In fact a stepwise process probably takes place in the majority of cases, for example[77]:



In other cases, loss of a ligand may preceed the oxidative addition.



[78]

A point of great importance is the number and variety of molecules which can be activated and oxidatively added in this fashion. It includes hydrogen[73], oxygen[76], hydrogen halides[73], organic halides[74,79], mercuric halides[80], sulphonyl halides[81] and many others. The activation of hydrogen in this way is particularly important in some catalytic processes and is thought to proceed via an initial transfer of charge from a filled metal orbital to an acceptor orbital on one hydrogen. The antibonding σ^* orbital could be used resulting in an induced charge separation in the

H—H bond.

The tendency of transition metal complexes to undergo oxidative addition and subsequent reversal depends on the nature of the central metal atom, its associated ligands and X-Y.

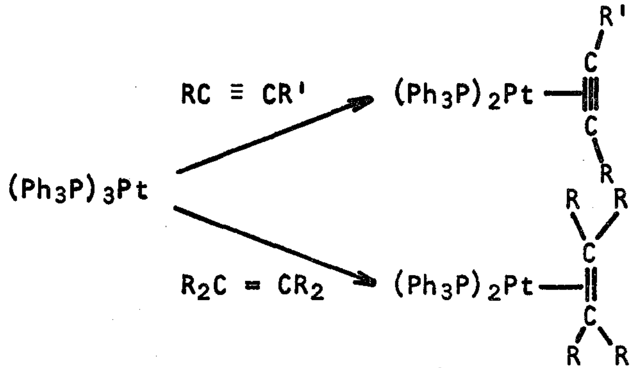
The process occurs most easily for metals in the zero oxidation state (i.e., with the higher formal electron density at the metal) and for the "5d metals". Thus an approximate order of the ease with which the metals undergo this reaction is $Os^{0} > Ir^{I} > Pt^{II}$; $Os^{0} > Ru^{0} > Fe^{0}$.

Ligands which increase the electron density at the metal enhance the tendency of a complex to undergo oxidative addition. For example, for the complexes L_2IrCOX (L = tertiary phosphines), the hydrogen[82] and oxygen[83] adducts are more stable when X = I than when X = Cℓ.

Finally, Vaska[84] has shown that the stability of the adducts $(Ph_3P)_2IrCOC\ell XY$ is qualitatively related to the electronegativities of the two parts of X-Y. Thus for XY = $C\ell_2$ the adducts are very stable whereas for XY = CH_3I the oxidative addition reaction is readily reversible.

(ii) Coordination of the olefin to the metal

In addition to their reactions with molecules X-Y, most of these d^{10} and d^{8} metal complexes also react with olefins (and acetylenes) to give π-complexes. For example:



(R = H, CN, F, etc.)

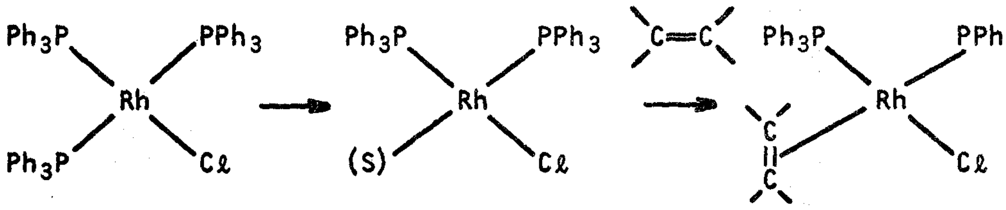
Birk et al[85] have shown that in this reaction the first step is a dissociation

$$(Ph_3P)_3Pt \rightleftarrows \underset{(\underline{16})}{(Ph_3P)_2Pt} + PPh_3$$

to give a "coordinatively unsaturated species" (16) which can then add the further ligand, for example, ethylene or phenylacetylene. The same intermediate is postulated to account for the oxidative addition:

$$(Ph_3P)_3Pt + O_2 \rightarrow Ph_3P + (Ph_3P)_2PtO_2$$

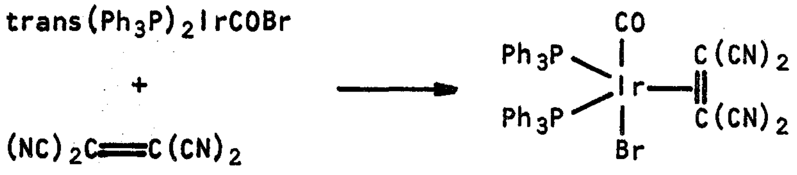
Very similar processes occur in d^8 systems, but here it is possible for the complex to retain its square planar coordination, by loss of a ligand, or to increase its coordination number to five (mono-olefins and acetylenes are assumed to occupy one coordination site). An example of the first type is chlorotristriphenylphosphinerhodium(I) (17) which reacts with olefins to give square planar rhodium(I) complexes (19). This reaction occurs in solution (S) by primary loss of a triphenylphosphine ligand to give again a coordinatively unsaturated species (18)[86].



(17) (18) (19)

In (18) it is very probable that a molecule of solvent has replaced the phosphine; however, the solvent is weakly bound and this is equivalent to one coordination site remaining unoccupied.

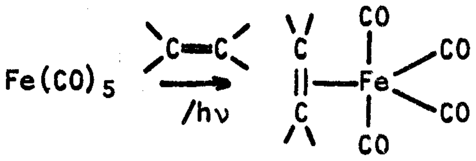
The alternative, addition of the olefin without loss of a ligand, is exemplified by Vaska's compound, which will add tetracyanoethylene to give the complex (<u>20</u>)[87]



(<u>20</u>)

The coordination about the metal in (<u>20</u>) can be viewed either as distorted trigonal bipyramidal or, if the tetracyanoethylene is thought of as a bidentate ligand, as distorted octahedral.

The complexes which undergo these reactions most readily are the metal carbonyls, since carbon monoxide is lost so easily, e.g.[88],



A number of metal halides will also react with olefins directly, one or more halides being replaced. This is particularly found for platinum (and palladium), for example, the preparation of Zeise's salt.

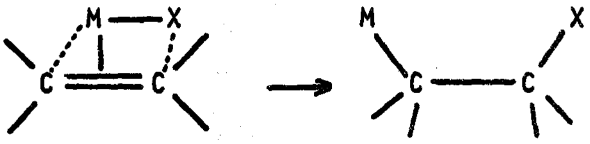
$$PtC\ell_4^{2-} + C_2H_4 \rightarrow C_2H_4PtC\ell_3^- + C\ell^-$$

Since the formation of the above olefin complexes involves no formal change of oxidation state of the d^{10} and d^8 metals, these may still undergo oxidative addition of X-Y. It is this feature which is vital in the overall catalytic process since if XY can be added without loss of coordinated olefin, the possibility arises for the interaction of X-Y (or one of these in some cases) with the olefin.

(iii) <u>Reactions of coordinated XY with the coordinated olefin</u>

It is usually assumed that reaction of coordinated XY with the olefin occurs at a single metal atom. Evidence is not complete on this important point but all that is presently available is consistent with this hypothesis. This is in contrast to heterogeneously catalysed reactions which are usually explained by invoking two or more metal atoms as the reactive sites.

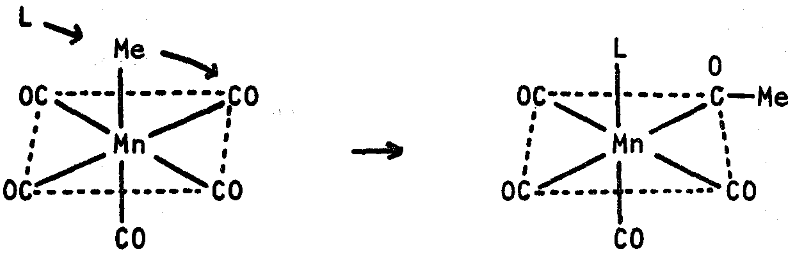
The most important type of reaction is the "cis ligand insertion". In its simplest form this implies a planar four-centre intermediate, in which the centres are the olefinic carbons, the metal and another atom or group.



This can occur with unsaturated species other than olefins such as CO, SO_2, acetylene or RCN. The most detailed studies on this type of reaction have been of the "insertion" of CO into metal-carbon bonds

$$R - M(CO)_n + L \rightarrow RCOM(CO)_{n-1}L$$

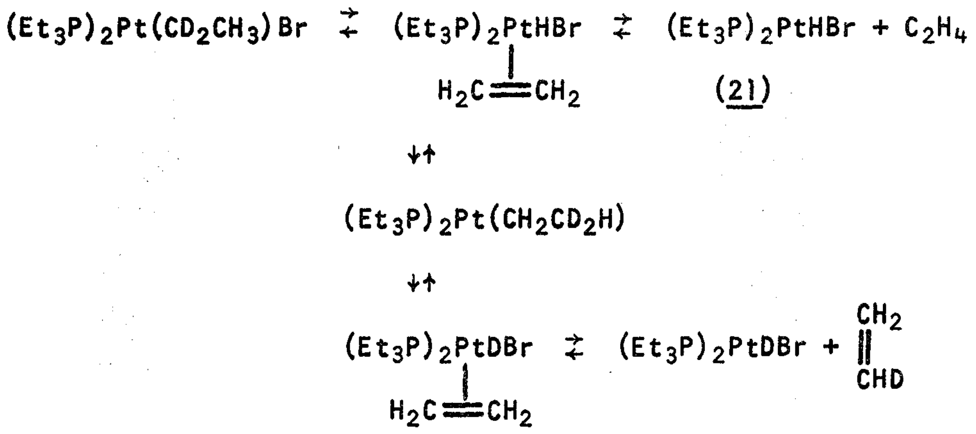
The reaction of methylmanganese pentacarbonyl with various ligands, L (= CO, PPh_3, etc.), has been studied by a number of authors[89]. It is found that, using labelled *CO, the entering CO is not the one which appears as the acetyl carbonyl. Detailed studies by Calderazzo and Noack[90] have shown that it is the methyl group in fact which migrates into a cis-carbonyl.



In the reverse reaction, decarbonylation of acetyl manganese pentacarbonyl, cis-methyl migration again occurs.

This type of reaction, more accurately described as "ligand to ligand migration", has been postulated to occur in a large number of reactions involving olefins. However the reaction is very fast and intermediates of the type [olefin M-H] cannot usually be isolated or even detected.

Chatt et al[91] have shown that a reversible addition of ethylene to the platinum hydride (21) to give the platinum-ethyl complex occurs. A complex series of equilibria are however invoked, since it is found that on elimination of ethylene from $(Et_3P)_2PtBr(CD_2CH_3)$, both $(Et_3P)_2PtHBr$ and $(Et_3P)_2PtDBr$ are obtained. All other evidence points to the fact that elimination of a β-hydrogen always occurs from such alkyl complexes, and hence Chatt's results must be understood as follows:



$$(Et_3P)_2Pt(CD_2CH_3)Br \rightleftarrows (Et_3P)_2\underset{H_2C=CH_2}{\underset{|}{PtHBr}} \rightleftarrows \underset{(\underline{21})}{(Et_3P)_2PtHBr} + C_2H_4$$

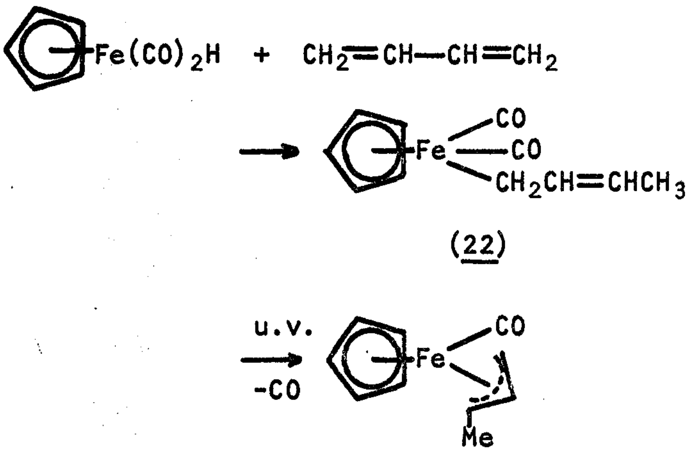
$$\downarrow\uparrow$$

$$(Et_3P)_2Pt(CH_2CD_2H)$$

$$\downarrow\uparrow$$

$$(Et_3P)_2\underset{H_2C=CH_2}{\underset{|}{PtDBr}} \rightleftarrows (Et_3P)_2PtDBr + \begin{array}{c}CH_2\\ \| \\ CHD\end{array}$$

In some cases, for example in the addition of butadiene to a metal hydride, a rearrangement of the organic moiety can occur:



(22)

(23)

In this case, typical of a fairly large class of "sigma-pi rearrangements"[92], the σ-allyl complex (22) formed by 1,4-addition of Fe-H to butadiene, rearranges, with loss of CO, to the π-1-methallyl complex (23)[93].

Many other examples of cis-"insertion" reactions are known and some will be discussed in the following sections. It should be pointed out however that not all olefin metal hydride complexes react in the above way. In some cases, notably $[1,5\text{-cyclooctadiene IrHC}\ell_2]_2$, it has been possible to isolate stable complexes containing both the olefin and the hydride. Addition of M-H to the olefin does not occur and it is thought that the stereochemistry is against the formation of a planar intermediate for the cis insertion here[94]. The molecule must also be quite rigid and non-labile so that a facile rearrangement cannot occur.

One further reaction which occurs between complexed ligands which is also very important but for which there is as yet very little information, is the cleavage of metal-carbon bonds by acids and similar reagents. A case where this has been studied is in the acid cleavage of alkyl and phenyl groups from platinum(II). Belluco et al[95] obtained evidence from a study of the kinetics of the reactions of $HC\ell$ with trans-$(Et_3P)_2PtMeC\ell$ and trans-$(Et_3P)_2PtPh_2$ that the initial fast step was the formation of a six-coordinate Pt(IV) intermediate, $(Et_3P)_2PtHMeC\ell_2$ and $(Et_3P)_2PtHC\ell Ph_2$ respectively. These arise by oxidative addition of $HC\ell$ to the Pt(II), d^8, complexes. The rate-determining step is the loss of H-R (CH_4, C_6H_6) to give $(Et_3P)_2PtC\ell_2$ or $(Et_3P)_2PtC\ell Ph$.

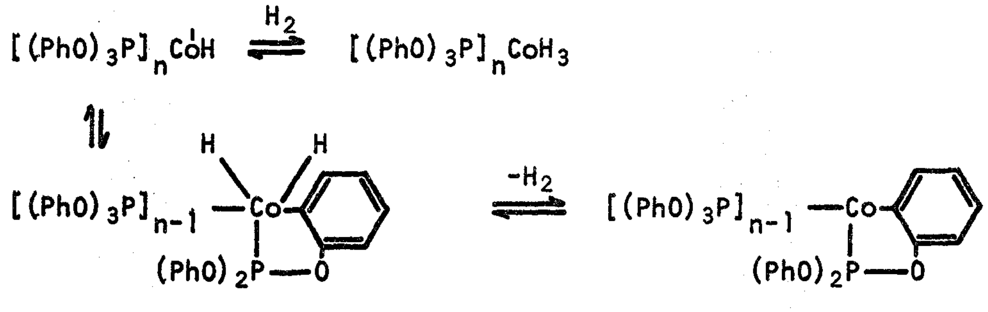
In principle,similar reactions can occur with halogens, e.g.

$$\text{cis-}(Et_3P)_2PtMe_2 + I_2 \rightarrow \text{trans}(Et_3P)_2PtMeI + MeI^{96}$$

and alcohols, e.g.

$$RCOCo(CO)_4 + MeOH \rightarrow HCo(CO)_4 + RCOOMe^{97}$$

The reaction of metal carbon σ-bonds with hydrogen has, surprisingly enough, hardly been studied in isolation. However, Parshall[98] has obtained evidence for this type of process in the deuterium exchange:



Transition Metal Hydrides

A considerable number of catalytic processes involve reactions with, or transfers of, hydrogen and it is thought that transition metal hydrides are formed as intermediates. These intermediates are rather reactive and not isolable (or even detectable in many cases) usually, except in the presence of stabilising ligands.

Reasonably stable transition metal hydrides are readily identified by their characteristic, intense M-H stretching bands ($1900\text{-}2200\ cm^{-1}$) and very high field proton magnetic resonances (usually $\tau 20$ to 30). Only in a few cases have M-H bond distances been accurately determined but these are apparently normal[99].

The various preparations of hydrides are given to emphasize that transition metals may readily form hydrides in the presence of stabilising π-bonded ligands. The hydrogen may arise from molecular hydrogen, a solvent and even from coordinated organic molecules.

(i) Reaction with molecular hydrogen may result in

(a) homolytic splitting, as in oxidative addition reactions

$$(PPh_3)_2IrCOC\ell + H_2 \rightleftarrows (PPh_3)_2IrCOC\ell H_2 \quad [73]$$

or (b) heterolytic cleavage

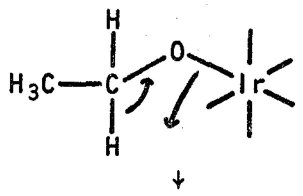
$$Ru^{III}C\ell_6{}^{3-} + H_2 \rightleftarrows Ru^{III}HC\ell_5{}^{3-} + H^+ + C\ell^- \quad [100]$$

(ii) Reduction of metal halide complexes using, for example $NaBH_4$, $LiA\ell H_4$ or hydrazine:

$$(Ph_3P)_2RhCOC\ell + PPh_3 \xrightarrow{NaBH_4} (Ph_3P)_3RhHCO \quad [101]$$

(iii) From alcohols with α-hydrogens in the presence of base: For example, the formation of the iridium hydride (<u>24</u>) in ethanol -KOH

$$CH_3CH_2OH + OH^- + IrC\ell_3(PEt_2Ph)_3 \rightarrow$$



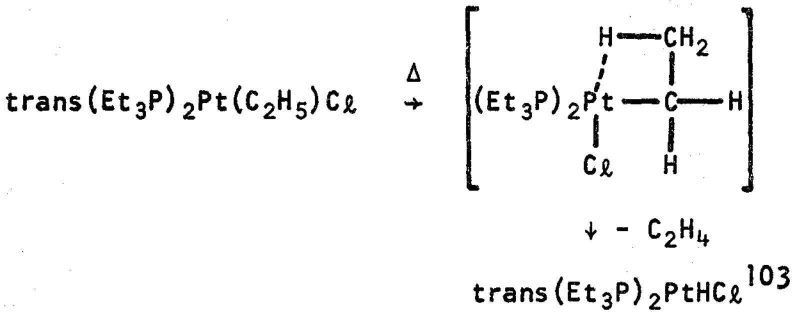
$$(PhEt_2P)_3IrHC\ell \; + \; CH_3CHO$$

(24)

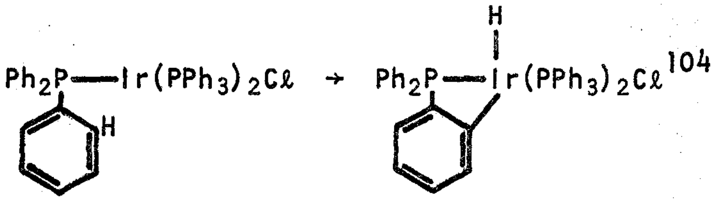
That the hydrogen transfers from the α position of the alcohol has been shown by using CH_3CD_2OH as solvent[102].

(iv) Hydrogen atoms at certain locations in coordinated organic molecules are rendered labile by the transition metal and transfer sometimes occurs to give the metal hydride.

(a) Hydrogens on β positions in alkyl complexes:



(b) Many examples are now known where the metal abstracts hydrogen from alkyl- and aryl-phosphine ligands, for example:



It is apparent that in these cases the activated hydrogen may be in close proximity to the metal and overlap of suitable orbitals is possible.

Catalytic Reactions

A few of the better understood catalytic reactions of simple olefins are now discussed briefly.

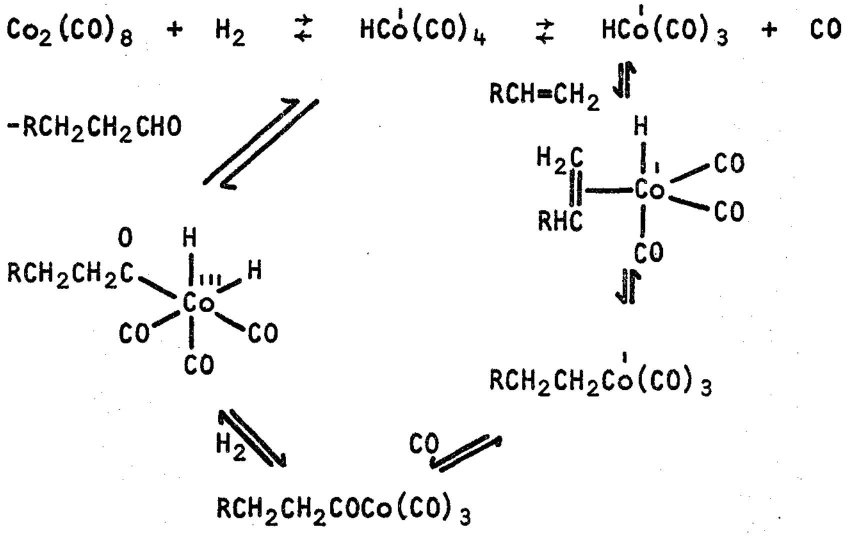
Hydroformylation

The reaction of olefins with carbon monoxide and hydrogen at high temperature and pressure in the presence of various catalysts, notably cobalt salts, gives aldehydes.

$$RCH = CH_2 + H_2 + CO \rightarrow RCH_2CH_2CHO$$

A number of side reactions occur such as hydrogenation, double bond migration and formation of alcohols. The reaction, also called the "Oxo" process, is important industrially for the production of higher alcohols.

It has been shown[105] that under the conditions of this reaction dicobalt octacarbonyl and hydridotetracarbonylcobalt are formed and that the latter is the reactive species. Investigations into the chemistry of this and related organometallic complexes have permitted the following reaction scheme for the hydroformylation process to be proposed[106].



The hydridotetracarbonylcobalt reversibly loses CO to form the coordinatively unsaturated species $H\dot{C}o(CO)_3$; this is consistent with the inhibiting effect of CO pressure on the system. The olefin then adds at the vacant coordination site and hydride migration (or cis-insertion) affords a coordinatively unsaturated alkyl complex. Carbon monoxide promoted alkyl migration gives an acyl complex which also has a vacant coordination site and can undergo oxidative addition of hydrogen with subsequent cis hydrogen insertion and elimination of the aldehyde product.

Oxidation of Olefins

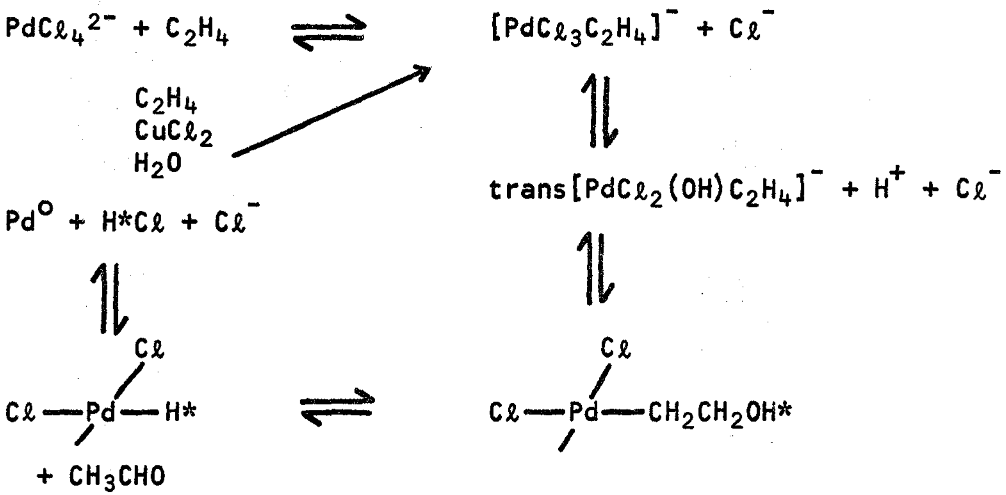
The reaction of aqueous solutions of palladium(II) chloride with ethylene has long been known to yield acetaldehyde with deposition of palladium metal.

$$C_2H_4 + PdC\ell_2 + H_2O \rightarrow CH_3CHO + Pd^{o} + 2HC\ell$$

The commercially important process (Hoechst-Wacker) for the production of acetaldehyde using this reaction arose from the discovery by Smidt[107] that the presence of cupric chloride in solution prevents formation of palladium metal. Any palladium metal formed is oxidised to Pd(II) by Cu(II) and the Cu(I) formed is oxidised by air in the presence of $HC\ell$ to Cu(II). A homogeneous catalytic process is thus established in which only oxygen and ethylene are consumed:

$$\begin{array}{lcl}
C_2H_4 + PdC\ell_2 + H_2O & \rightarrow & CH_3CHO + Pd + 2HC\ell \\
Pd^{o} + 2CuC\ell_2 & \rightarrow & PdC\ell_2 + 2CuC\ell \\
2CuC\ell + \tfrac{1}{2}O_2 + 2HC\ell & \rightarrow & 2CuC\ell_2 + H_2O \\
\hline
C_2H_4 + \tfrac{1}{2}O_2 & \rightarrow & CH_3CHO
\end{array}$$

The initial reaction is the formation of an olefin complex, analogous to Zeise's salt ($K[PtC\ell_3C_2H_4]H_2O$), inhibited by chloride ion. This π-complex is rapidly hydrolysed (inhibited by acid). Intramolecular



rearrangement of the hydrolysis product presumably occurs to give the favourable cis-planar stereochemistry for "insertion". Addition of Pd-OH to coordinated ethylene (probably the rate-determining step) gives a σ-β-hydroxyethylpalladium complex. This intermediate then rearranges by a hydride shift mechanism, giving acetaldehyde and an unstable palladium hydride species which decomposes to Pd^{0} metal and chloride. The oxidative addition step is carried out separately using Cu(II).

Homogeneous Hydrogenation

All systems which hydrogenate substrates using molecular hydrogen are expected (or known) to cleave the hydrogen molecule with formation of a reactive transition metal hydride intermediate. This cleavage may occur in the three ways of the following catalytic systems[108].

(i) Homolytic splitting.

$$2Co(CN)_5^{3-} + H_2 \rightleftharpoons 2CoH(CN)_5^{3-}$$

(ii) Heterolytic splitting.

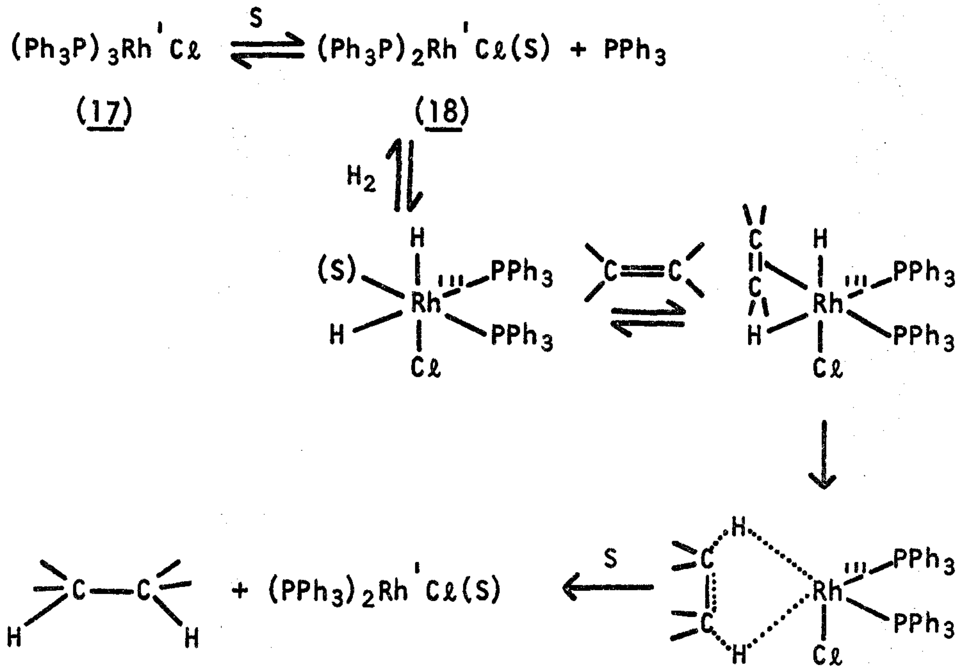
$$Ru^{II}C\ell_5(olefin)^{3-} + H_2 \rightleftharpoons Ru^{II}HC\ell_4(olefin)^{3-} + HC\ell$$

(iii) Oxidative addition.

$$(PPh_3)_2Rh(S)C\ell + H_2 \rightleftharpoons (PPh_3)_2RhH_2(S)C\ell$$

For the ruthenium and cobalt systems, the important reaction steps are thought to be the following. Formation of the hydride and coordination of the olefin is followed by insertion of the olefin into the M-H bond. The resulting alkyl complex is said to be reduced to products by attack of a proton (in the ruthenium system) or by reaction with an additional hydride complex (in the cobalt system).

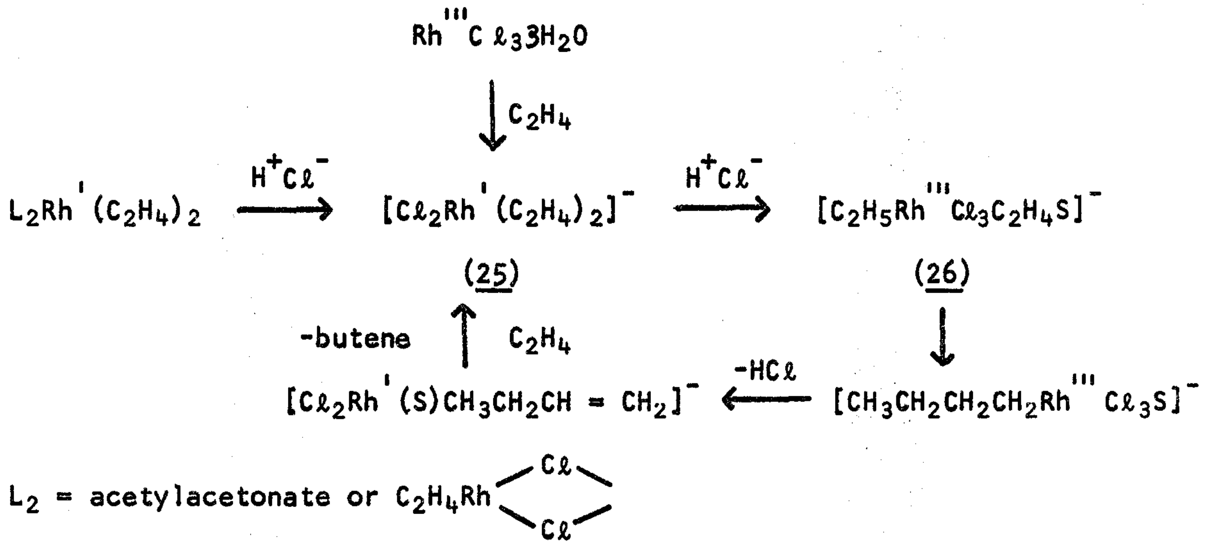
Hydrogenation using the rhodium(I) complex, $(Ph_3P)_3RhC\ell$, has been extensively studied and there is good evidence for the following mechanism[86]:



The complex (17) is known to dissociate in solution to give (18) in which the "vacant" coordination site is probably occupied by a solvent molecule (S). Oxidative addition of hydrogen gives a cis-dihydro-complex which may be isolated as dichloromethane or chloroform solvated crystals. Solutions of this complex immediately reduce olefins including ethylene, by the four-centre insertion illustrated. Ethylene, however, is not reduced by (<u>17</u>) in the presence of hydrogen since it coordinates preferentially to give $(Ph_3P)_2RhC_2H_4C\ell$ (<u>19</u>) which will not oxidatively add hydrogen.

<u>Dimerisation of Ethylene</u>

The dimerisation of ethylene to butenes using a rhodium(I) catalyst in ethanol has been studied in detail by Cramer[109], who proposed the following mechanism. [This includes a chain growth step which is thought to occur in important polymerisations of olefins.]

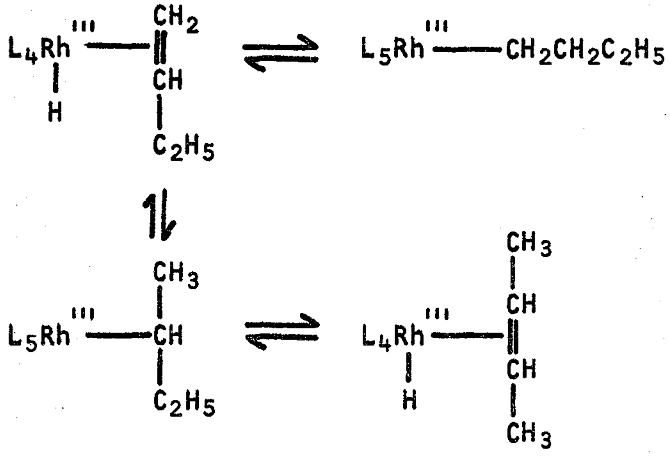


The evidence points to the anionic bisethylene complex (<u>25</u>), being the active catalyst. This square planar d^8 complex reacts with $HC\ell$ by oxidative addition presumably to give a hydride species but which could not be detected spectroscopically. This infers that cis-insertion leading to the ethyl complex (<u>26</u>) is extremely rapid. Evidence for (<u>26</u>) was obtained from low temperature p.m.r. studies and from isolation of the complex $Cs_2[C_2H_5RhC\ell_3H_2O]_2$ which is formed on pumping off C_2H_4 from (<u>26</u>). The rate-controlling step is the rearrangement by ethyl migration (cis-"insertion") of the ethyl complex (<u>26</u>) to the butyl rhodium complex.

A reverse hydride migration (from the activated β position), reductive elimination of $HC\ell$ and release of the butene leads to the regeneration of the active catalyst (25).

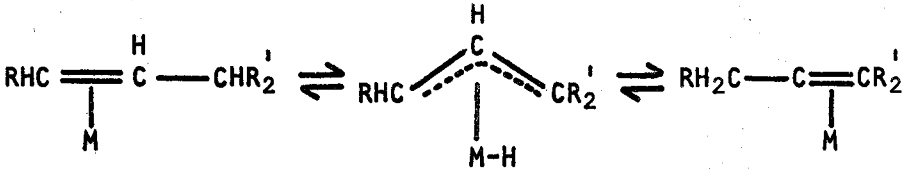
Isomerisation of Olefins

The isomerisation of olefins is catalysed by a wide range of transition metal complexes and involves the making and breaking of C-H bonds. A number of different mechanisms have been proposed[110] however the clearest evidence yet is that of Cramer[111]. He investigated the rhodium catalysed isomerisation of butenes and put forward a mechanism involving the formation of a rhodium hydride species and its reversible addition to the olefin:



While this describes the mechanism superficially, the detailed proposal, based on the results of deuterium exchange experiments, is rather involved. Cramer observed that, for example, the isomerisation of 1-butene in CH_3OD led to isolation of deuterated 1-butene together with an approximately equal quantity of undeuterated 2-butene. By making certain assumptions concerning relative rates of rearrangements and exchanges, Cramer was able to account for his observations on this "hydrido-π-olefinic" scheme.

This stepwise mechanism involving initial formation of a hydride can be successfully applied to explain many other results in isomerisation reactions[112,113]. One well-authenticated case where this probably does not occur is in the iron carbonyl catalysed reactions studied by von Rosenberg[114]. In these systems the evidence points to 1,3-hydrogen shifts via a hydrido-π-allylic intermediate



Other possible exceptions to the hydrido-π-olefinic mechanism are some reactions involving palladium[121] and $HCo(CO)_4$[115].

While the majority of isomerisations studied in detail have been of linear mono-olefins, the isomerisations of cyclooctadienes (COD) have received considerable attention too. Whereas cis,cis-1,3-COD is the thermodynamically most stable isomer, the cis-cis form of 1,5-COD has the most favourable placement of the double bonds for coordination to a metal. Hence it is usually observed that, in reactions with metal complexes, the cyclooctadiene is complexed as the 1,5-isomer but any free olefin is present as the 1,3-isomer. Furthermore, both stepwise (via 1,4-cyclooctadiene) and multistep processes are possible between these two isomers.

Bailar[116] has studied the isomerisation of 1,5-COD with $PtC\ell_2(PPh_3)_2$, $PtHC\ell(PPh_3)_2$ and $PtC\ell_2$(1,5-COD). He found that in each case the reaction proceeds with comparable rates to give equilibrium mixtures of 1,3-, 1,4- and 1,5-cyclooctadienes. A cocatalyst, $SnC\ell_2$, was essential and, with the exception of the hydride, a source of hydrogen was necessary such as hydrogen gas or a solvent; the olefin alone did not serve this purpose. These observations together with the isolation of the intermediate $[PtH(SnC\ell_3)(PPh_3)_2]_2$(1,5-COD), strongly suggest that a hydrido-π-olefinic mechanism is operative. The detection of 1,4-COD further supports this stepwise process. This mechanism has also been invoked to account for the observation[117] that whereas 1,5-COD readily replaces two CO's from (8-hydroxyquinolate)rhodium dicarbonyl giving the corresponding 1,5-COD complex, 1,3-COD will give this same complex only in the presence of $HC\ell$. In the absence of $HC\ell$ a complex is obtained in which only one of the carbonyls is replaced. This indicates that 1,3-COD is not isomerised to give coordinated 1,5-isomer by a hydride abstraction mechanism (to give a hydrido-π-allylic species).

The reaction of excess 1,5-COD with "rhodium trichloride trihydrate" in ethanol gives the complex $[(1,5\text{-COD})RhC\ell]_2$. All of the uncomplexed olefin is converted to the 1,3-isomer and 1,4-COD is detected as an intermediate indicating, again, a stepwise mechanism[118].

It has been suggested[119] that, in the related reaction of "$RhC\ell_3 \cdot 3H_2O$" with 1,3-COD, a stepwise isomerisation mechanism is not operative since 1,4-COD was not detected as an intermediate. The reaction, with excess 1,3-COD, proceeds to give $[(1,5\text{-COD})RhC\ell]_2$ together with unisomerised, free 1,3-isomer. The isomerised diene was recovered by decomposition of the complex by cyanide. Similar reactions have been observed with "$IrC\ell_3 \cdot 4H_2O$"[119] and K_2MX_4[120] (M = Pd, Pt; X = $C\ell$, Br). A mechanism involving migration of the double bond by two positions in one step was proposed.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

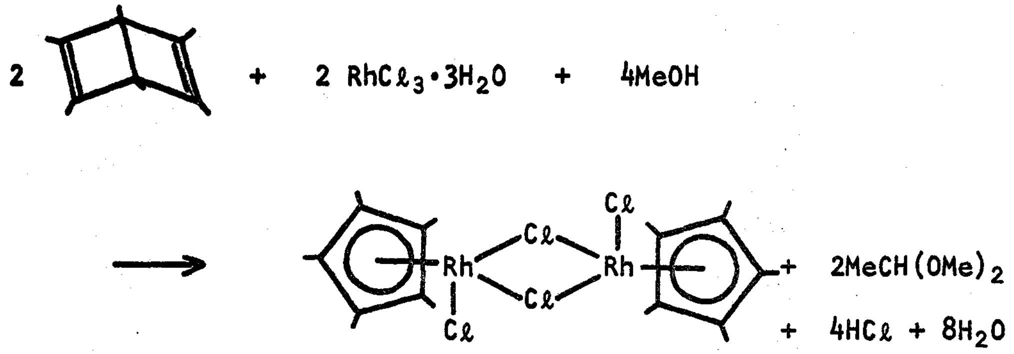
A. The Formation of Dichloro(pentamethylcyclopentadienyl)-rhodium and -iridium Complexes: The Ring Contraction Reaction

The reaction of excess hexamethyldewarbenzene, HMDB, with $RhC\ell_3 \cdot 3H_2O$ in methanol at 65° under nitrogen was reported by Dr. Kang of this laboratory to give a nearly quantitative yield (based on $RhC\ell_3 \cdot 3H_2O$) of air stable red crystals. The product was identified as dichloro(pentamethylcyclopentadienyl)rhodium dimer (13a) on the basis of analysis, further reactions and spectroscopic data. Its p.m.r. spectrum (60 MHz, $CDC\ell_3$) showed a single sharp resonance at τ8.40 and did not distinguish between the Rh(III) complex proposed here and the Rh(III) complex of hexamethylbenzene, $(C_6Me_6RhC\ell_2)^{2+}$, proposed by Booth et al.[121] to be the product from the same reaction. Analytical and infra-red data were similarly not conclusive and perhaps the most convincing initial evidence for our assignment was mass spectroscopic. The red crystals did not melt below 280° and a partial mass spectrum was only obtained with difficulty. At an inlet temperature of 210° the complex gave peaks at m/e 237 ($C_5Me_4CH_2Rh^+$, corresponding to loss of $HC\ell$ from $C_5Me_5RhC\ell^+$) and 134 ($C_5Me_4CH_2^+$). Fragments at m/e 162 ($C_6Me_6^+$) and 147 ($C_6Me_5^+$) which are prominent in samples containing hexamethylbenzene were absent.

Hexamethylbenzene was, however, formed in substantial amounts as a by-product in the above reaction. The metal must play an important role in the formation of this since HMDB is quite stable to isomerisation under these conditions in the absence of metal halide[56].

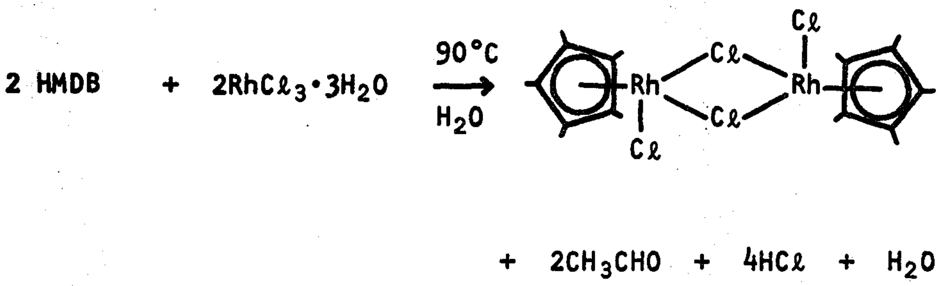
In an attempt to elucidate the mechanism of this rather novel ring contraction reaction, an analysis of the volatile by-products was undertaken. The solvent and other volatile materials were distilled off from the reaction mixture and analysed by a combination of v.p.c., p.m.r. and mass spectrometry. The distillate was found to contain, in addition to methanol, one major component and two minor ones. The major component was isolated and shown to be dimethylacetal by p.m.r. and mass spectrum; the minor ones were identified mass spectroscopically as methyl chloride and dimethyl ether. A reaction in which $RhC\ell_3 \cdot 3H_2O$ was heated alone in methanol also gave the two latter components so that their formation did not appear to be significant as far as the ring contraction reaction was concerned.

Quantitative v.p.c. analysis showed that the amount of dimethylacetal formed was approximately correct for the stoichiometric reaction

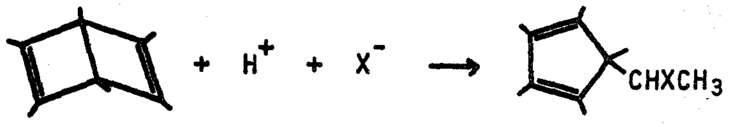


(13a)

When a similar reaction was carried out under heterogeneous conditions in aqueous solution, the complex (13a) was again formed, though in much reduced yield (16%). The only significant by-product detected from this reaction was acetaldehyde, presumably formed by the following:



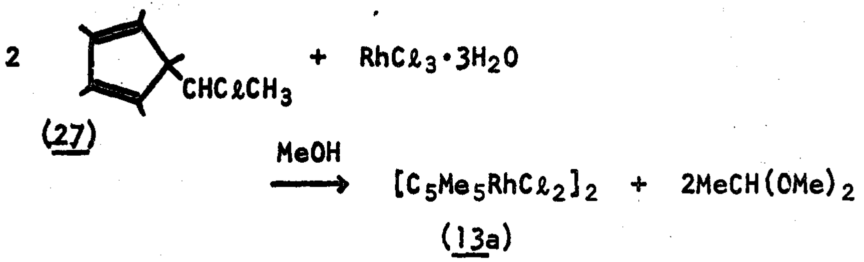
The mechanism by which these ring contraction reactions occurred remained obscure until Paquette and Crow[122] and Criegee and Gruner[123] reported the ring contraction of HMDB, catalysed by H^+. These workers, reinvestigating the reaction of HMDB with acid, initially reported by Schäfer and Hellman[56], showed the major product to be the 1-(1-substituted ethyl)pentamethylcyclopentadiene (27).



(27) [X = Cℓ, Br, OMe]

Furthermore some related work carried out in this laboratory on the formation of dichloro(pentamethylcyclopentadiene)platinum[64] from HMDB suggested that the presence of acid might be important in the preparation of (13a).

The reaction of (27) (X = Cℓ) with $RhC\ell_3\cdot 3H_2O$ in methanol readily gave the product (13a) in high yield (88%) together with a stoichiometric amount of dimethylacetal.



The corresponding heterogeneous reaction in aqueous solution gave the complex (13a) (25%) together with acetaldehyde which was isolated and characterised by analytical v.p.c. and p.m.r. and mass spectroscopy.

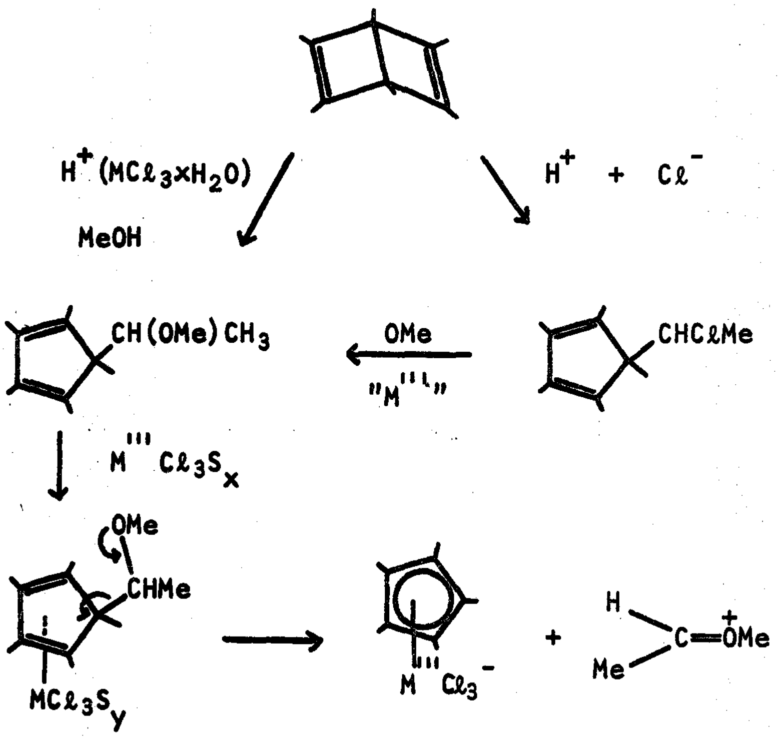
The above reactions in methanol were repeated using "$IrC\ell_3{\cdot}5H_2O$" to give orange crystals of dichloro(pentamethylcyclopentadienyl)iridium dimer (13b), which had properties similar to the rhodium analogue. This complex was far more easily accessible from (27) (62%) than from HMDB (reported by Dr. Kang, 9%). The by-products detected from these iridium reactions were identical to those from the corresponding rhodium reactions; dimethylacetal was again the significant organic product.

These results are consistent with a mechanism in which reaction with HMDB proceeds via a primary acid catalysed rearrangement to (27) (X = $C\ell$ or OMe in methanol solution). The protons necessary for this rearrangement are presumed to arise by ionisation of coordinated water molecule

$$MC\ell_3xH_2O \rightleftarrows [MC\ell_3(x-1)H_2O{\cdot}OH]^- + H^+$$

It was found, in fact, that 0.1 M aqueous solutions of the rhodium and iridium trichlorides had pH's of 2.7 and 2.9 respectively (observation by Dr. Kang).

In the light of the above observations it seems clear that the following overall reaction path is operative in the formation of the complexes (13a) and (13b)



$$2C_5Me_5M^{III}C\ell_3^- \rightarrow [C_5Me_5MC\ell_2]_2 + 2C\ell^-$$

$$MeHC{=}\overset{+}{O}Me \xrightarrow{MeOH} (MeO)_2CHCH_3 + H^+$$

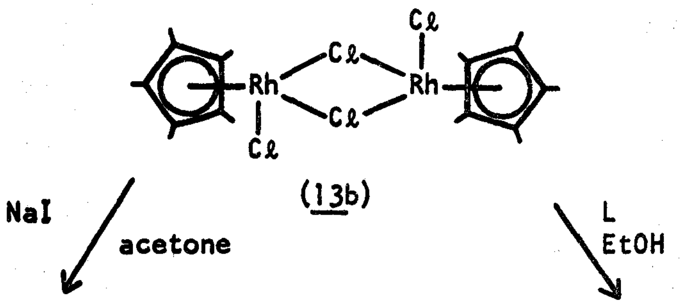
The great stability of the pentamethylcyclopentadienyl complexes provides the driving force for reaction, i.e., for cleavage of the C—C bond. These results have subsequently been confirmed by other workers[124]; however they proposed the intermediacy of free pentamethylcyclopentadiene.

A similar scheme may be written to account for the products obtained under aqueous conditions.

These reactions, described above, provide a facile new route to pentamethylcyclopentadienyl complexes. Such polysubstituted cyclopentadienyl complexes are otherwise very difficult to make; for example, King and Bisnette[125] prepared a number of C_5Me_5M complexes using pentamethylcyclopentadiene, obtainable only by a rather lengthy route.

B. Introduction to the Chemistry of the Complexes, $[C_5Me_5MC\ell_2]_2$ (M = Rh, Ir)

The general chemical features of the complexes (13a) and (13b) were established by Dr. Kang who found that while the C_5Me_5—M bond was exceedingly stable, the M—$C\ell$ bond could be cleaved by a number of reagents. All attempts to rupture the C_5Me_5—M bond with reagents such as base, cyanide and hydridic reducing agents failed. The M—$C\ell$ bond readily underwent displacement reactions with iodide and acetate and the halogen bridges could be cleaved, in the normal way, by a variety of Lewis bases, L. For example, for the rhodium complex (13b)



(13b)

$[C_5Me_5RhI_2]_2$

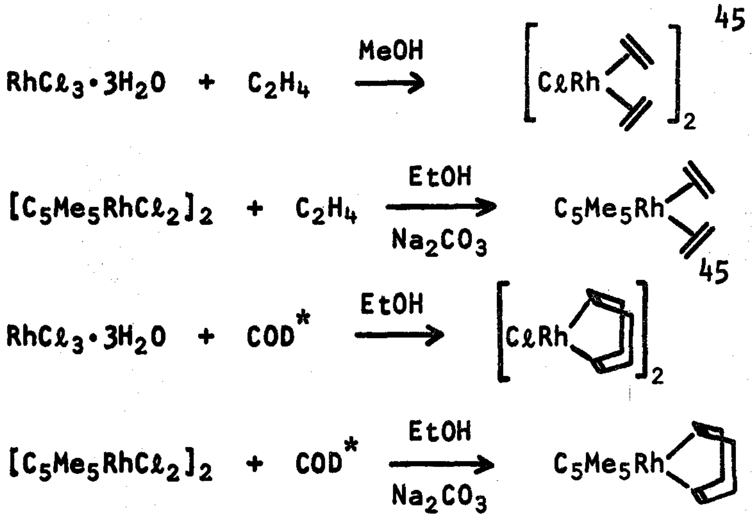
$C_5Me_5RhC\ell_2L$

(28a) L = PPh_3, pyridine, p-toluidine, etc.

The reactions of the iridium analogue have not been studied as extensively but appear to be very similar.

These complexes are new but the cyclopentadienylrhodium halides $[C_5H_5RhX_2]_n$ (6) (X = $C\ell$, Br)[41,54] have been mentioned briefly in the literature (see Introduction). The properties described for these cyclopentadienyl complexes, (6), agree well with those of the pentamethylcyclopentadienyl ones (13), except for the greater solubility of the latter.

In their reactions with olefins, the complexes $[C_5Me_5MC\ell_2]_2$ (13) often resembled $RhC\ell_3 \cdot 3H_2O$, although the former required small amounts of base, sodium carbonate was usually used. For example:



The reactions of $[C_5Me_5MC\ell_2]_2$ with olefins in the presence of base effectively constitutes the remainder of this discussion. The products may or may not be of the above type depending on the reaction conditions and, more significantly, on the nature of the olefin.

C. The Reactions of the Complexes, $(C_5Me_5MC\ell_2)_2$ (13), with Di- and Tri-Olefins

1. Introduction: Evidence for a Hydride Intermediate

The dimeric dichloro(pentamethylcyclopentadienyl)-rhodium and -iridium complexes were reacted with a number of olefins in ethanol. These reactions, in the presence of base (usually sodium carbonate), gave products of three main types. All of these compounds described obey the effective atomic number rule.

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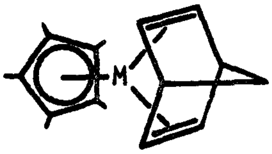
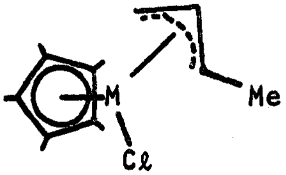
[*] 1,3- or 1,5-cyclooctadiene.

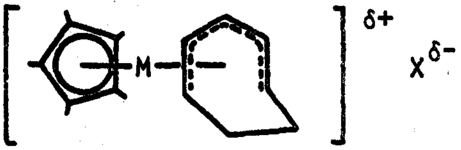
(a) M^{I} complexes formed by complete dehalogenation of (<u>13</u>); e.g.,



(b) M^{III} "covalent" complexes formed by partial dehalogenation of (<u>13</u>). The metal is allylically bonded to three carbons of the ligand derived from the olefin; e.g.,



(c) M^{III} "ionic" complexes in which the metal is formally bonded to five adjacent carbons of a ligand derived from the olefin; e.g.,

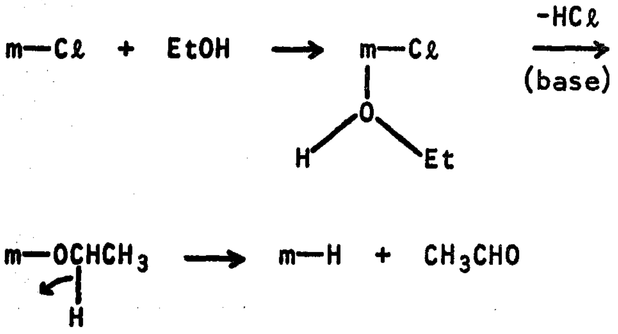


X = monovalent anion

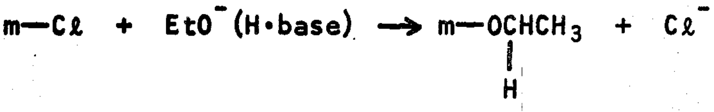
In the second and third of these, M-H has been added to the olefin substrate to give an en-yl complex of M^{III}. This suggested the intermediate formation of a metal-hydride.

Further evidence for this intermediate came from the analysis of the mother liquors from some of these reactions. It was found that acetaldehyde and/or diethylacetal were invariably present. The reactions of platinum-metal halide complexes with alcohols, to give aldehydes or ketones, are well known[126-128] and it has been shown that hydrogen abstraction is from the α-position of the alcohol[102,127].

The reaction is generally thought to proceed*:



A slight variant of this is also possible



$$\text{m—C}\ell + \text{EtO}^{-}(\text{H}\cdot\text{base}) \longrightarrow \text{m—O}\underset{\text{H}}{\text{C}}\text{HCH}_3 + \text{C}\ell^{-}$$

The metal-hydride intermediate proposed here, $C_5Me_5MHC\ell(S)$ [where S is solvent or olefin], could not be isolated presumably due to the high reactivity of such a species. However the iridium complex $C_5Me_5IrHC\ell PPh_3$ (30) was obtained from the reaction of $C_5Me_5IrC\ell_2PPh_3$ (28b) with ethanol in the presence of sodium carbonate or triethylamine; best results were obtained with the former in the presence of some water. The triphenylphosphine presumably stabilises the Ir—H bond largely by blocking the vacant coordination site.

$$C_5Me_5IrC\ell_2PPh_3 + EtOH + H_2O + \text{base}$$

(28b)

$$\longrightarrow C_5Me_5IrHC\ell PPh_3$$

(30)

Some deuteration studies, described later in the section on reactions with cyclooctadienes [C. 5] also support the intermediacy

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*m represents a complexed metal, ML_n.

of a hydrido-complex.

Chlorohydridotriphenylphosphinepentamethylcyclopentadienyliridium (30)

The iridium hydrido-complex, (30), was an air stable, yellow, crystalline solid and was identified by analysis and spectroscopy. The deuterido-analogue, $C_5Me_5IrDC\ell PPh_3$ (31), was prepared by a similar route from $C_5Me_5IrC\ell_2PPh_3$ (28b) using ethanol-d_6 and D_2O. No exchange of coordinated deuterium with water was observed.

The hydrido-complex showed an intense, rather broad band at 2090 cm^{-1} in the infra-red (KBr disc) assigned to $\nu(Ir—H)$. This was absent in the spectrum of the deuterido-complex which showed a new shoulder at ca. 1500 cm^{-1}, assigned to $\nu(Ir—D)$.

$$[\nu(Ir—H)/\nu(Ir—D) = 1.39]$$

The p.m.r. spectrum (60 MHz, $CDC\ell_3$) of the hydrido-complex (30) showed a multiplet at $\tau 2.6$ (aromatic protons, 15H) and a double doublet at $\tau 8.42$ [J(Me-P) 2Hz, J(Me-H) 0.9Hz; 15H], arising from the coupling of the fifteen equivalent methyl protons to the phosphorus and hydride. A rather broad doublet at $\tau 23.3$ (J(H-P) 36.4Hz) due to the hydridic hydrogen was also observed (100 MHz, benzene) but only coupling to phosphorus could be detected. The p.m.r. spectrum (60 MHz, $CDC\ell_3$) of the deuterido analogue (31) confirmed these assignments and exhibited the multiplet at $\tau 2.6$ (aromatic protons, 15H) but only a simple doublet at $\tau 8.42$ [J(Me-P) 2Hz; 15H].

The hydrido-complex (30) was unstable in solution in air and on standing in deuterochloroform (room temperature, 1 day) reacted to regenerate (28b).

$$\underset{(\underline{30})}{C_5Me_5IrHC\ell PPh_3} + CDC\ell_3 \rightarrow \underset{(\underline{28}b)}{C_5Me_5IrC\ell_2PPh_3} + CDHC\ell_2$$

A small triplet at τ4.76, due to methylene chloride-d_1[136], was observed.

Attempts to isolate the hydrido-rhodium analogue of (30) were not successful. This is consistent with the known tendency for M—H bonds to become less reactive down a triad.

The reactions of (30) with olefins were not investigated but the phosphine dichloro-complexes, $C_5Me_5MC\ell_2PPh_3$ (28), were found to react with olefins in a similar way to, though more slowly than, $(C_5Me_5MC\ell_2)_2$ (13). This is not surprising since (28b) and its rhodium analogue have a triphenylphosphine in the reactive site. If the reactions between $C_5Me_5IrC\ell_2PPh_3$ (28b) and an olefin were interrupted before completion, the hydride, $C_5Me_5IrHC\ell PPh_3$ (30), could be detected by p.m.r. spectroscopy.

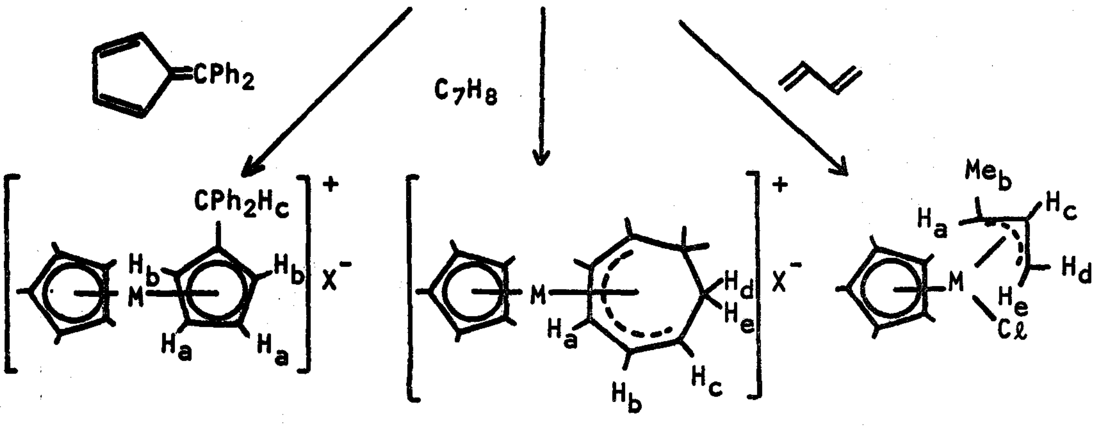
2. Reactions with Butadiene, Cycloheptatriene and Diphenylfulvene

The complexes $(C_5Me_5MC\ell_2)_2$ (13) were reacted with butadiene, cycloheptatriene and 6,6'-diphenylfulvene in ethanol in the presence of sodium carbonate. In each case a M^{III} en-yl complex, derived from addition of M-H to the olefin, was readily isolated.

The structures of (32), (33) and (34) were assigned from analytical and spectroscopic data, particularly p.m.r. spectra (Table 1).

The covalent 1-methallyl-rhodium complex (34a) was obtained in effectively quantitative yield under mild conditions. It was sublimable and soluble in non-polar solvents. All attempts at dehydrochlorination of the complex, $C_5Me_5RhC\ell(C_4H_7)$ (34a), by extended reaction with sodium

$(C_5Me_5MC\ell_2)_2 \rightarrow [C_5Me_5MHC\ell(S)]$



(32) (33) (34)

carbonate in methanol (or ethanol) at elevated temperatures were unsuccessful; (34a) was recovered on each occasion. The 1-methallyl group in (34a) is coordinated as the "syn" (or trans) isomer as shown by the coupling constant, J(a,c) = 11 Hz, (Table 1). The complex, chloro(cyclopentadienyl)(1-methallyl)rhodium $C_5H_5RhC\ell(CH_2CHCHMe)$ (10), recently reported by Powell and Shaw[54] has similar properties to (34a).

The mass spectrum of this rhodium complex, (34a), was recorded and is presented in the Appendix. The molecular ion peaks at m/e 330 and 328 ($C_5Me_5RhC\ell C_4H_7^+$, ca. 8% of the base peak) were observed together with a major fragment at m/e 292 ($C_5Me_5RhC_4H_6^+$, 52%), due to loss of $HC\ell$ from the parent ion (metastable peak at m/e 259.8). Fragmentation of the latter ion led to the base peak at m/e 238 ($C_5Me_5Rh^+$, metastable peak for this transition at m/e ca. 194). Other major fragments were observed at m/e 275, 273 ($C_5Me_5RhC\ell^+$, 32%), 134 ($C_{10}H_{14}^+$, 28%), 119 ($C_9H_{11}^+$, 72%) and 103 (Rh^+, 18%).

Similar en-yl complexes were formed from cyclooctadienes, these are discussed below (C. 5).

The reaction of $(C_5Me_5RhC\ell_2)_2$ with cycloheptatriene in refluxing ethanol in the presence of sodium carbonate gave yellow crystals of π-2,5-cycloheptadienyl(pentamethylcyclopentadienyl)rhodium chloride [(33a); X = $C\ell$]. The iridium analogue (33b) could not be isolated as the chloride due to its hygroscopic nature. Both complexes, (33a) and (33b), were isolated in crystalline form by precipitation from aqueous solution with a large anion, hexafluorophosphate. The rhodium [(33a); X = $C\ell$, PF_6] and iridium [(33b); X = PF_6] complexes were identified by their analyses and p.m.r. spectra.

The p.m.r. spectrum of the rhodium complex [(33a); X = $C\ell$] is given in Table 1; that of the hexafluorophosphate salt (60 MHz, $CDC\ell_3$) showed resonances at τ3.52 (1 H, t, H_a), 4.55 (2H, dd, H_b), 5.41 (2H, unresolved multiplet, H_c), ca. 8.0 (4H, unresolved multiplet; H_d, H_e) and 7.96 (15H, s, C_5Me_5). Decoupling experiments at 100 MHz showed that H_a was only significantly coupled to H_b (J(ab) 6.5±0.2 Hz), that H_b was coupled to both H_a and H_c (J(bc) 8.6±0.2 Hz) and that H_c was coupled to H_b and, slightly, to H_a.

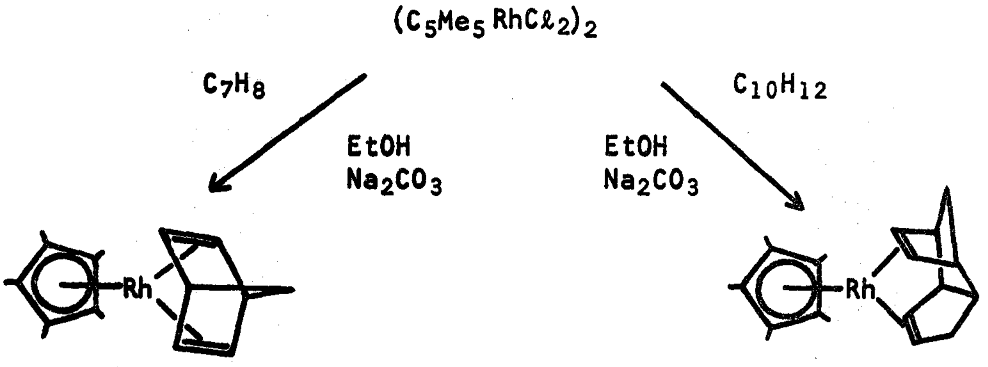
The iridium complex, π-2,5-$C_7H_9Ir(C_5Me_5)^+$[(33b); X = PF_6], gave a very similar p.m.r. spectrum: a triplet at τ3.33 (1H, H_a, J(ab) 6±0.5 Hz), a double doublet at 4.44 (2H, H_b, J(ab) 6±0.2 Hz, J(bc) 8.2±0.2 Hz), unresolved multiplets at 5.53 (2H, H_c) and 8.2 (4H, H_d, H_e) and a singlet at 7.90 (15H, C_5Me_5).

Cycloheptadienyl complexes are still rather uncommon however, where available, the p.m.r. data agrees well with the above[129-131].

The ionic diphenylmethylcyclopentadienyl complexes, (32), were obtained in good yield (80-90%) from reactions with 6,6-diphenylfulvene in refluxing ethanol in the presence of sodium carbonate. The chloride salts of both rhodium and iridium complexes were extremely hygroscopic and the complexes (32) could only be isolated in pure crystalline form as the hexafluorophosphates. The complexes were identified on the basis of their analyses and p.m.r. spectra (Table 1). A similar reaction mechanism to that proposed here is thought to be operative in the formation of $Ph_2CHC_5H_4Mo(CO)_3$[132], i.e., involving hydrogen transfer from the solvent to 6,6-diphenylfulvene. Weiss and Hübel[133] have prepared the iron complex, $(Ph_2CHC_5H_4)_2Fe_2(CO)_4$, from diphenylfulvene and iron pentacarbonyl.

3. Reactions with Norbornadiene and Dicyclopentadiene

In contrast to the above $(C_5Me_5RhC\ell_2)_2$ (13a) reacted with norbornadiene and dicyclopentadiene in refluxing ethanol in the presence of sodium carbonate to give the yellow complexes, (35a) and (36a), in 42% and 75% yield respectively. These M(I)-diene complexes were sublimable and very soluble in non-polar solvents.



(35) (36)

These complexes were characterised by a combination of analytical, p.m.r. and mass spectral data. There are many examples in the literature of transition metal complexes containing these diene ligands[134]. The p.m.r. spectrum of the dicyclopentadiene complex (<u>36</u>) was rather complicated and a full analysis was not possible (Table 1). That of the norbornadiene complex (100 MHz, $CDC\ell_3$) showed a broad multiplet at τ6.73 (2H, due to bridgehead hydrogens), a double doublet at 7.57 (4H, assigned to olefinic hydrogens coupled both to bridgehead hydrogens and to rhodium; J(H-H) 5 Hz, J(H—^{103}Rh) 1.2 Hz), a triplet at 9.17 (2H, due to CH_2 coupled to both bridgehead hydrogens, J(H-H) 1.6 Hz) and a singlet at 8.12 (15H, C_5Me_5).

The mass spectra of these volatile complexes were readily obtained at an inlet temperature of 30° (ionising beam strength 80 eV). Unlike other pentamethylcyclopentadienyl-rhodium complexes the most abundant ion from these complexes was <u>not</u> $C_5Me_5Rh^+$ (m/e 238). The norbornadiene complex (<u>35</u>) gave a mass spectrum in which the molecular ion at m/e 330 was most abundant. Fragments at m/e 329 ($C_5Me_5RhC_7H_7^+$, 41.5% of the base peak), 315 ($p\text{-}Me^{+*}$, 70%) and 303 ($C_5Me_5RhC_5H_5^+$, 13.5%) are consistent with the proposed structure.

The spectrum of the dicyclopentadiene complex (<u>36</u>) was relatively simple, showing a rather large molecular ion peak at m/e 370 (p^+, 80% of base peak). The major fragments were at m/e 369 ($p\text{-}H^+$, 40%), 355 ($p\text{-}Me^+$, base peak), 329 ($C_5Me_5RhC_7H_7^+$, 14%), 303 ($C_5Me_5RhC_5H_5^+$, 91%) and 289 ($C_{13}H_{20}Rh^+$, 55%). The detailed mass spectra of both complexes are included in the Appendix.

C_5Me_5M'(diene) complexes were also formed with cyclopentadiene, cyclohexadienes and cyclooctadienes; these are discussed below.

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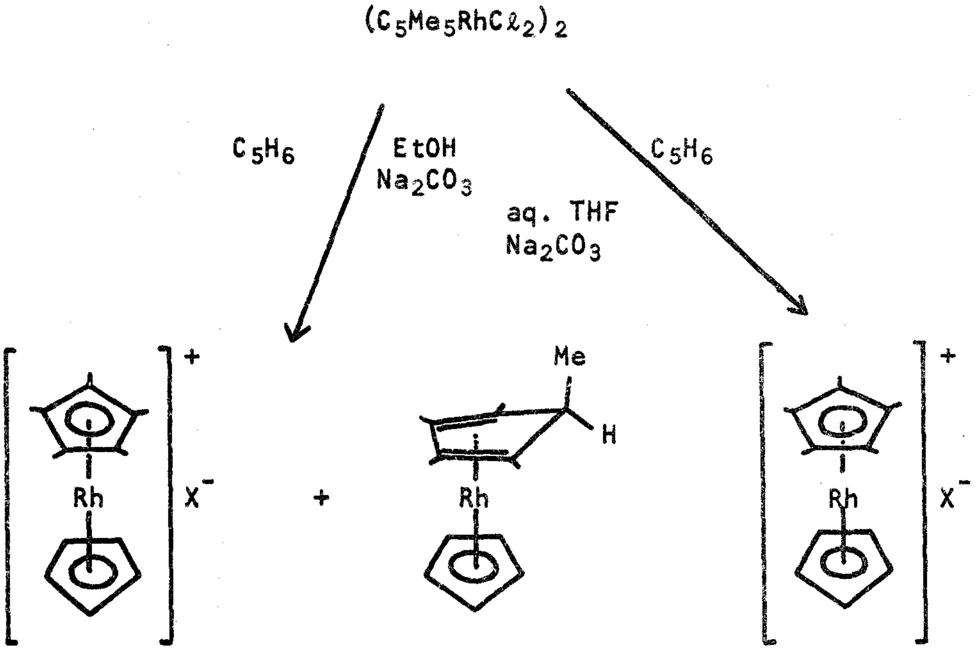
[*] p^+ denotes the parent or molecular ion to distinguish it from P used to denote phosphorus.

4. Reactions with Cyclopentadiene

(a) The Rhodium Complex

Two products were isolated from the reaction of $(C_5Me_5RhC\ell_2)_2$ (13a) with cyclopentadiene in ethanol in the presence of sodium carbonate. One of these, readily soluble in non-polar solvents, was easily separated from the other, ionic material. The former, covalent complex was shown to be cyclopentadienyl(pentamethylcyclopentadiene)-rhodium(I) (37) (54%) and the latter, cyclopentadienyl(pentamethylcyclopentadienyl)rhodium(III) chloride [(38a); X = $C\ell$] (19%). The hexafluorophosphate salt [(38a); X = PF_6] was obtained by precipitation from an aqueous solution of the chloride. The complex, [(38a); X = $C\ell$], was the sole product (76%) from a reaction of (13a) with cyclopentadiene in aqueous THF in the presence of sodium carbonate.



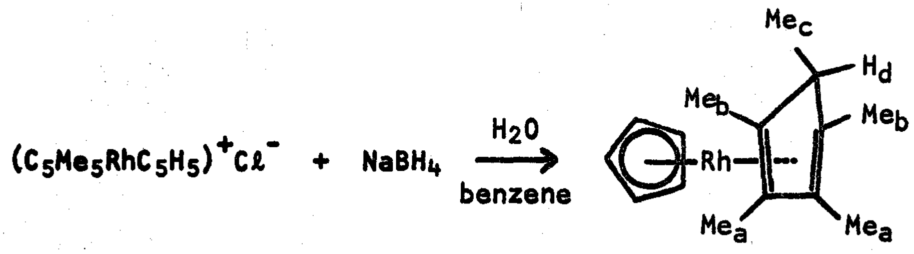
(38a) (37) (38a)

The unexpected complex, (37), a sublimable yellow crystalline solid, was identified by its analysis and i.r., p.m.r. and mass spectra. The p.m.r. spectrum (60 MHz, $CDC\ell_3$) showed a doublet at τ5.12 (C_5H_5, coupled to ^{103}Rh; J(H-Rh) 1.0 Hz), singlets at τ7.96 and 8.57 (each 6H, due to two methyls) and a doublet at τ9.67 due to one methyl, coupled to a hydrogen (quartet at τ7.29; J(H-Me) 6 Hz). The hydrogen on a pentamethylcyclopentadiene ring was presumed to be "endo" to the metal because of the absence of a characteristic low frequency ν_{CH} band in its i.r. spectrum. There is good evidence that the low frequency ν_{CH} band (ca. 2750 cm^{-1}) exhibited by such compounds is due to exo-hydrogens[37,39] (see Introduction and below).

The complexes, $(C_5Me_5RhC_5H_5)^+X^-$ [(38a); X = Cℓ, PF_6], were formulated as such on the basis of their analyses and p.m.r. spectra (Table 1).

The pentamethylrhodicenium chloride [(38a); X = Cℓ] reacted with sodium borohydride in a benzene-water mixture to give a yellow benzene-soluble complex, (39a) in 93% yield. This was identified as an isomer of (37). Its p.m.r. spectrum showed that reduction had occurred exclusively at the substituted cyclopentadienyl ring, and exhibited a doublet at τ5.05 (C_5H_5, coupled to ^{103}Rh, J(H-Rh) 1.0 Hz), a singlet at 7.90 (6H, Me_a), a doublet at 8.69 due to Me_c coupled to a hydrogen [quartet at τ7.18, J(H_d-Me_c 6.2 Hz)] and a doublet at 8.84 (6H, Me_b, J 0.8 Hz). The latter doublet, due to Me_b (or possibly Me_a), protons, could conceivably arise through coupling of these to either H_d or ^{103}Rh or through a non-equivalence of the two Me_b (or Me_a) groups. No splitting of the quartet due to H_d could be observed (100 MHz, benzene).

The infra-red spectrum of (39a) was identical to that of the isomer, endo-H(pentamethylcyclopentadiene)cyclopentadienylrhodium (37), except for an intense band at 2730 cm^{-} . This is assigned to ν_{CH} due to an exo-hydrogen[37], the presence of which is not surprising since attack of R^- at a coordinated ring always appears to be exo- (see Introduction). Hydride attack was exclusively at the C_5Me_5 ring as shown by p.m.r. studies on the crude reaction product.



(38a)

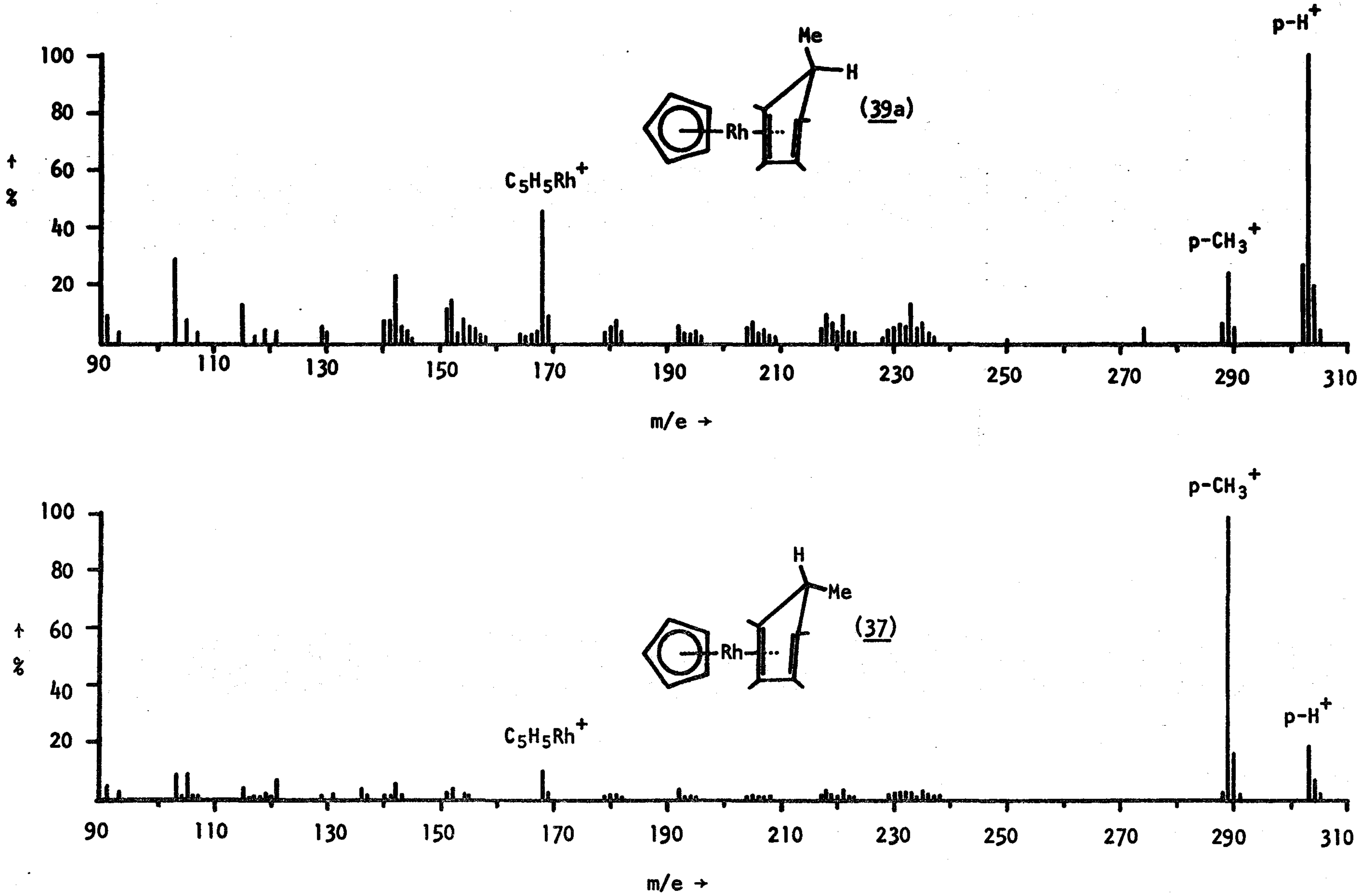
(39a)

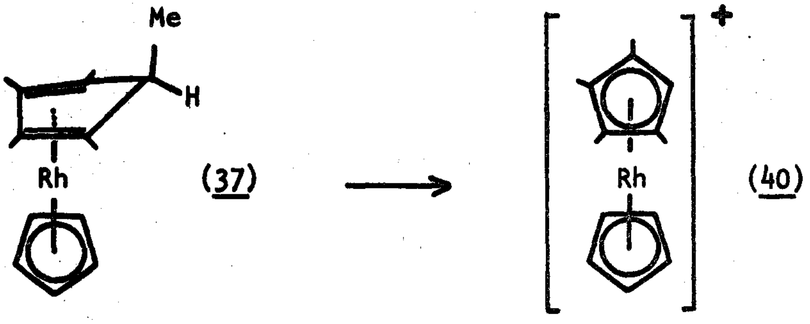
Synthetic difficulties have usually precluded the isolation of endo- and exo- isomers such as (37) and (39). These two isomers exhibited some very interesting differences in their properties.

The mass spectra of both complexes were recorded under similar conditions (inlet temperature ca. 30°, electron beam energy 80 eV). To assist in the interpretation of these spectra, the mass spectrum of 1,2,3,4,5-pentamethylcyclopentadiene was also recorded. The most abundant ions, observed metastable peaks and the transition involved for the latter are listed in the Appendix. Harrison et al.[135] have reported the mass spectra of a number of methyl-substituted cyclopentadienes including 1,2,4,5,5-pentamethylcyclopentadiene but excluding the 1,2,3,4,5-isomer. They observed that positional isomers gave very similar spectra; their quoted spectrum of the 1,2,4,5,5-isomer is very similar to that of the 1,2,3,4,5-isomer determined here. The mass spectra of the exo (39a) and endo (37) isomers (Figure IX) were somewhat similar with major fragments corresponding to $(p\text{-}H)^+$ (m/e 303), $(p\text{-}Me)^+$ (m/e 289), $(C_5H_5Rh)^+$ (m/e 168) and Rh^+ (m/e 103). A fragment at m/e 238 (corresponding to $C_5Me_5Rh^+$), usually very abundant in the mass spectra of these types of complexes, was notably absent. This, together with the observation of a major fragment assigned $C_5H_5Rh^+$, confirmed that these are cyclopentadienylrhodium complexes. The differences which were observed are precisely those expected on the basis of their structures as indicated, and their chemical properties (see below). The exo-isomer (39a) showed a weak molecular ion peak (p^+, m/e 304, ca. 20% of the base peak) and the base peak at m/e 303 [$p\text{-}H^+$, assigned to the stable pentamethylrhodicenium ion $(C_5Me_5RhC_5H_5)^+$]. Loss of a methyl from the parent was a much less favoured process for the exo-isomer (m/e 289, ca. 24% of the base peak) but was the dominant fragmentation mode for the endo-isomer (37) to give $(C_5H_5RhC_5Me_4H)^+$ (40). Both the molecular ion (10%) and $C_5Me_5RhC_5H_5^+$ (m/e 303, 15%) were of small abundance for the endo-isomer. Further breakdown in both cases gave rise to peaks corresponding to $C_5H_5Rh^+$ (m/e 168), $C_3H_3Rh^+$ (m/e 142, very common in the mass spectra of cyclopentadienylmetal complexes) and Rh^+, and to the characteristic cracking pattern observed for pentamethylcyclopentadiene itself. The mass spectra of both isomers are therefore dominated by the high stability of the positively-charged Rh(III) "sandwich" complexes. The isomers differ in the way in which they achieve this state, the one by loss of hydrogen (the exo-isomer) and the other by loss of methyl (the endo-isomer).

Figure IX

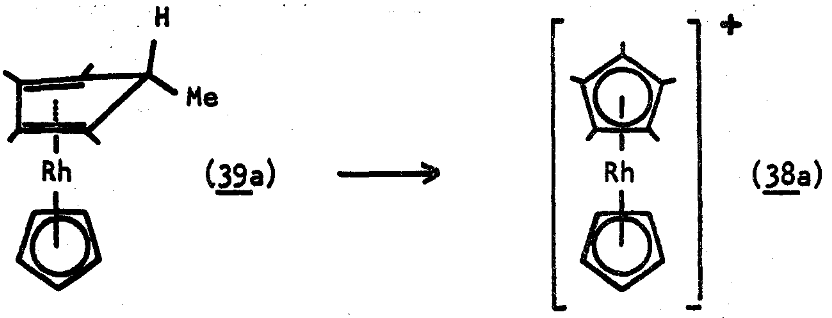
The Mass Spectra of endo-H and exo-H, $C_5Me_5HRhC_5H_5$





(37) → (40)

m/e 289



(39a) → (38a)

m/e 303

This difference in lability of an exo C-H bond with respect to an endo C-H bond was also well brought out by the reactions of the two isomers. It should be pointed out however that Angelici and Fischer[41] found that reaction of the endo-hydrogen complex $(\pi C_5H_5)Rh(C_5H_5Ph)$ with oxygen, or H_2O_2 in $2NHC\ell$, gave a cation, $[(C_5H_5)Rh(C_5H_4Ph)]^+$, in which the endo C-H bond had been cleaved.

The exo-isomer was readily oxidised by deuterochloroform and N-bromosuccinimide (NBS) to the pentamethylrhodicenium ion (38a). Thus a p.m.r. study of a solution of the exo-isomer in deuterochloroform showed that decomposition to [(38a); $X = C\ell$] occurred rapidly, this was effectively complete after five hours (at ca. 40°). In addition to the growth of resonances due to (38a) ($X = C\ell$), a small triplet at 4.63 ($J(H-D)$ 1.0 ± 0.2 Hz) also increased in intensity. The latter was due to

$CHDC\ell_2$[136], formed in the reaction:

$$\underset{(\underline{39}a)}{\text{exo-H }(C_5H_5)Rh(C_5Me_5H)} + CDC\ell_3 \longrightarrow \underset{(\underline{38}a)}{[(C_5H_5)Rh(C_5Me_5)]^+C\ell^-} + CHDC\ell_2$$

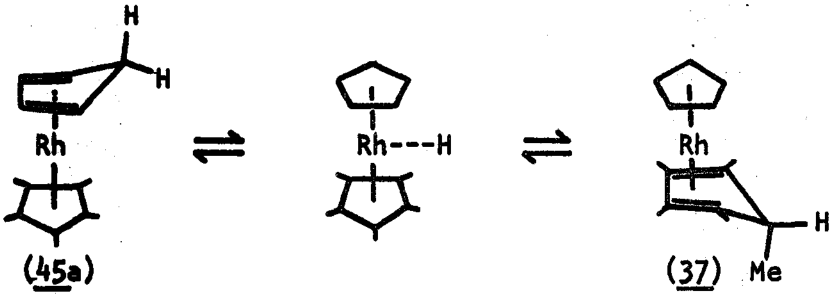
NBS rapidly reacted with the exo-isomer in a methanol-petrol ether mixture, in the presence of ammonium hexafluorophosphate, to give (38a)($X = PF_6$).

$$\underset{(\underline{39}a)}{\text{exo-H }(C_5Me_5H)Rh(C_5H_5)} + \text{NBS} + PF_6^- \longrightarrow \underset{(\underline{38}a)}{(C_5Me_5RhC_5H_5)^+PF_6^-} + (CH_2CO)_2NH$$

The endo-H complex (37), while decomposing much more rapidly in the solid state in air, was effectively inert in chloroform solution. With NBS, halogen and hydrogen chloride, the endo-isomer gave a mixture of pentamethylcyclopentadienyl- and cyclopentadienyl-rhodium halides. Owing to the extreme insolubility of the latter and sparing solubility of the former, accurate relative amounts of the two products were difficult to determine. In one experiment with NBS the product dibromides were converted to the corresponding 1,5-cyclooctadiene complexes by reaction with 1,5-cyclooctadiene in ethanol in the presence of sodium carbonate. The relative amounts of these soluble Rh(I) complexes were estimated by p.m.r. spectroscopy. As the conversion of the dibromides, (41) and (42), to the 1,5-cyclooctadiene complexes, (43a) and (44) respectively, is believed to be essentially quantitative, the bromides (41) and (42) were produced in the ratio 55:45.

$$\begin{tikzcd}
\text{endo-H } (C_5Me_5H)Rh(C_5H_5)\ (\underline{37}) \arrow[r, "HC\ell{,}C\ell_2"] \arrow[d, "NBS"] & C_5H_5RhC\ell_2\ (\underline{42}) + C_5Me_5RhC\ell_2\ (\underline{41}) \\
C_5H_5RhBr_2\ (\underline{42}) + C_5Me_5RhBr_2\ (\underline{41}) \arrow[d, "\text{1,5-cyclooctadiene}"] & \\
C_5H_5Rh(1{,}5\text{-COD})\ (\underline{44}) + C_5Me_5Rh(1{,}5\text{-COD})\ (\underline{43a}) &
\end{tikzcd}$$

Although reaction of $(C_5Me_5RhC\ell_2)_2$ (13a) with cyclopentadiene in ethanol in the presence of sodium carbonate gave the complex $(C_5Me_5RhC_5H_5)C\ell$ [(38a); X = $C\ell$] in addition to the endo-isomer $C_5Me_5HRhC_5H_5$ (37), (38a) was not an intermediate in the formation of (37). This was shown by an absence of reaction on prolonged heating of (38a) with sodium carbonate in ethanol at elevated temperatures. It is reasonable to presume that, by analogy with the reactions of $(C_5Me_5MC\ell_2)_2$ (13) with various dienes, the kinetically controlled product of the cyclopentadiene reaction is cyclopentadiene(pentamethylcyclopentadienyl)rhodium(I) (45a). The actually observed, thermodynamically more stable product, (37), may then arise by isomerisation of (45a) by an intramolecular hydride shift.



(45a)

(37)

A similar intramolecular hydride shift has been postulated to explain observations in the mass spectrum of $C_6Me_6MnC_6H_7$[137]. Rapid equilibria of this type could explain the formation of both cyclopentadienyl- and pentamethylcyclopentadienyl-rhodium halides from the reactions of (37) with NBS, $C\ell_2$ and $HC\ell$. The intermediacy of (38a), $(C_5Me_5RhC_5H_5)^+Br(C\ell)^-$, cannot however be discounted completely in these reactions.

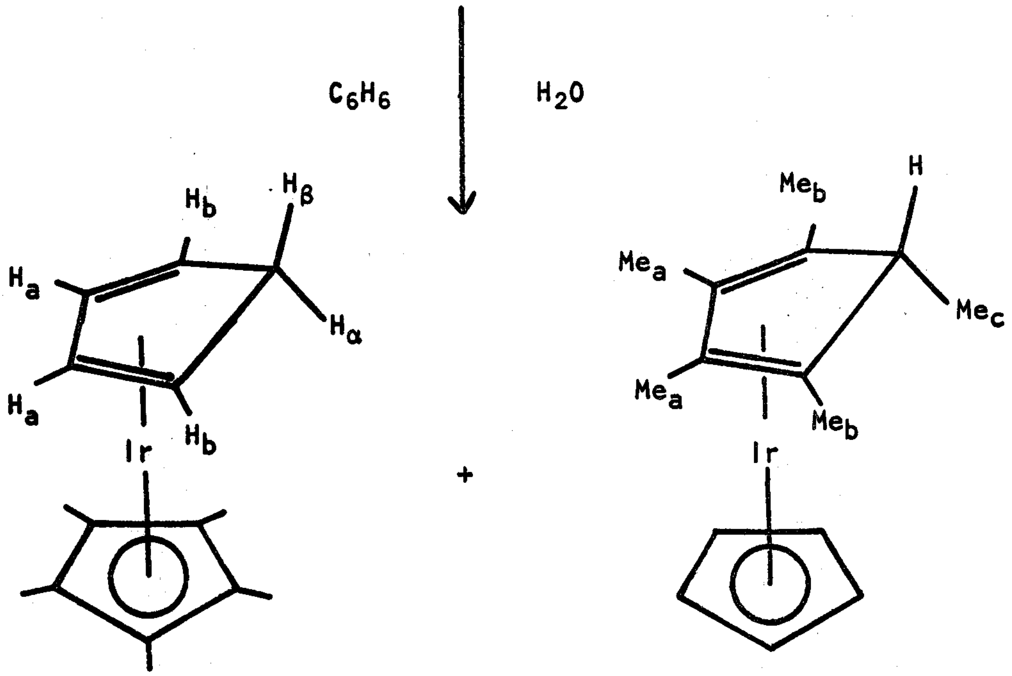
(b) The Iridium Complex

The reaction of the iridium complex $(C_5Me_5IrC\ell_2)_2$ (13b) with cyclopentadiene in ethanol in the presence of sodium carbonate was also carried out. In contrast, no endo-H isomer corresponding to $C_5Me_5HRh(C_5H_5)$ (37) was produced. The only product was the pentamethyliridicenium cation [(38b); X = $C\ell$], isolated in crystalline form as the hexafluorophosphate salt in 88% yield.

$$\underset{(13b)}{(C_5Me_5IrC\ell_2)_2} + C_5H_6 \xrightarrow[EtOH]{Na_2CO_3} \underset{(38b)}{(C_5Me_5IrC_5H_5)^+X^-}$$

The chloride, [(38b);X = $C\ell$], was reduced with sodium borohydride in a benzene-water mixture. White crystals, analysing for $C_{15}H_{21}Ir$, were obtained which resembled exo-H $(C_5Me_5HRhC_5H_5)$ (39a) in their chemical properties. The product reacted with NBS in the presence of hexafluorophosphate ions to regenerate $(C_5Me_5IrC_5H_5)^+PF_6^-$ [(38b); X = PF_6]. It also reacted rapidly with $CDC\ell_3$ (1 hour at 40°) to give [(38b); X = $C\ell$] and $CHDC\ell_2$ (identified by its p.m.r. spectrum, a triplet at τ4.68, J(H-D) 1.0±0.2 Hz). The product showed an intense band in the infra-red at 2740 cm^{-1} assigned to ν_{CH} due to an exo-H[37]; the remainder of the spectrum was very similar to that of the exo-H rhodium complex (39a).

$$(C_5Me_5IrC_5H_5)^+C\ell^- \; + \; NaBH_4$$



(45b) (39b)

The mass spectrum of the white solid showed fairly weak molecular ion peaks at 394 ($C_{15}H_{21}{}^{193}Ir^+$) and 392 ($C_{15}H_{21}{}^{191}Ir^+$) and base peaks at m/e 393 and 391 ($C_{15}H_{20}Ir^+$) corresponding to loss of a hydrogen from the parent. Loss of a methyl from the parent was not a highly favoured process (m/e 379, 377; ca. 20%), loss of a second hydrogen was more pronounced (m/e 392 and 390; ca. 30%). The two isotopes of iridium allow easy identification of metal-containing fragments. Apart from the ions listed above, there were no significant amounts of such fragments. The mass spectrum confirmed that the molecular formula was $C_{15}H_{21}Ir$ and indicated, by comparison with the spectra of the endo-H and exo-H rhodium complexes [(37) and (39a) respectively] (Figure IX), that an exo-H was present.

However the p.m.r. spectrum (60 MHz, benzene) did not agree with that expected for exo-H($C_5Me_5HIrC_5H_5$) (39b). Resonances which could reasonably be assigned to this were present at τ5.21 (5H, C_5H_5), 7.75 (6H, s, Me_a), 8.82 (6H, s, Me_b) and 8.62 (3H, d, J(Me_c-H) 6.5 Hz). This data is consistent with that of the rhodium analogue (39a) except that the quartet expected for the exo-H coupled to Me_c could not be detected. In addition to these resonances the following were observed which are attributed to $C_5H_6IrC_5Me_5$ (45b) (for clarity, the relative intensities are considered separately to the above); a doublet at τ4.37 (1H, H_β), a double doublet at 5.42 (2H, H_a), a doublet triplet at 6.72 (1H, H_α), a broad unresolved multiplet at 7.36 (2H, H_b) and a singlet at 8.01 (15H, C_5Me_5). The assignments were supported by decoupling experiments at 100 MHz; irradiation at the resonant frequency of H_a reduced the H_b resonance to a broad doublet (J(αb) 2.2±0.2 Hz). Decoupling of H_b produced a collapse of H_a to a broad singlet (J(ab) 2±0.2 Hz, J(ab') 1.4±0.2 Hz) and collapse of H_α to a doublet (J($\alpha\beta$) 9.5±0.5 Hz). H_α was coupled to H_β and H_β was coupled to H_b and H_α (J(bβ) ca. 1 Hz).

A comparison of the relative intensities of the resonances attributed to the two complexes showed that exo-H $C_5Me_5HIrC_5H_5$ (39b) and $C_5H_6IrC_5Me_5$ (45b) were formed in the ratio 7:3.

Unfortunately there is a lack of detailed p.m.r. data for cyclopentadiene metal complexes. The reported coupling constants agree reasonably well with the present values for (45b), as do the τ values for H_a, H_b and H_α. However there is a serious discrepancy in the H_β assignment, which has been reported to lie between τ6.5-7.5 for some C_5H_6-complexes[30,31,138].

TABLE I

Proton magnetic resonance data for some pentamethylcyclopentadienyl-rhodium and -iridium complexes.

Complex	H_a	H_b	H_c	H_d	H_e	C_5Me_5	Other
$[C_5Me_5RhC_5H_4CHPh_2]^+PF_6^-$ (32a)[a]	4.24 m		4.72			7.94 s	phenyl 2.61
$[C_5Me_5IrC_5H_4CHPh_2]^+PF_6^-$ (32b)[a]	4.20 m		4.76			7.87 s	phenyl 2.62
$C_5Me_5RhClC_4H_7$ (34a)[d]	6.42 dd	8.36 d	6.04 m	6.72 d	7.12 d	8.27 s	
	J(a-Me)6.2 Hz J(a-c)11 Hz	J(Me-a)6.2 Hz	J(c-a)11 Hz J(c-d)6.6 Hz J(c-e)11 Hz J(c-Rh)2.2 Hz	J(d-c)6.6 Hz	J(e-c)11 Hz		
$[C_5Me_5RhC_7H_9]^+Cl^-$ (33a)[b]	3.21 t	4.28 dd	5.38 m	8.26 m		7.91 s	
	J(a-b)6.0 Hz	J(b-c)7.0 Hz J(b-a)6.0 Hz					
$[C_5Me_5RhC_5H_5]^+Cl^-$ (38a)[b]						7.79 s	C_5H_5 4.26 d J(Rh-H)1.0 Hz
$[C_5Me_5RhC_5H_5]^+PF_6^-$ (38a)[c]						7.87 s	C_5H_5 4.51 d J(Rh-H)1.0 Hz
$[C_5Me_5IrC_5H_5]^+Cl^-$ (38b)[b]						7.62 s	C_5H_5 4.25 s
$[C_5Me_5IrC_5H_5]^+PF_6^-$ (38b)[b]						7.74 s	C_5H_5 4.47 s

TABLE 1 - cont'd.

Complex	H_a	H_b	H_c	H_d	H_e	C_5Me_5	Other	
$C_5Me_5RhC_{10}H_{12}$ (36)[d]						8.32 s	CH_2	8.35 m
							CH	7.43 m
								7.84 m
							olefin	6.18 m
								6.48 m
								7.02 m
								7.15 m

---

[a] 60 MHz in acetone-d_6

[b] 60 MHz in $CDC\ell_3$

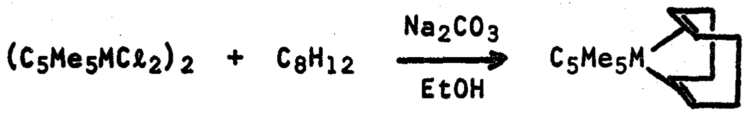
[c] 60 MHz in $CD_2C\ell_2$

[d] 100 MHz in $CDC\ell_3$

5. The Reactions with Cyclooctadienes

Preparation and Characterisation of New Complexes

Both the rhodium and iridium complexes, $(C_5Me_5MC\ell_2)_2$ (13), reacted readily with 1,5-cyclooctadiene (1,5-COD) in ethanol in the presence of sodium carbonate to give crystals of 1,5-cyclooctadiene-(pentamethylcyclopentadienyl)-rhodium and -iridium, (43), respectively.



(13) (43)

As in the other reactions of this type the colourless iridium complex (43b) was formed under milder conditions (55-65°, 2-3 hr) than the yellow rhodium analogue (43a) (60-70°, 3-4 hr). These air stable, readily sublimable M(I) complexes were characterised by analysis and p.m.r. and mass spectroscopy.

In addition to the singlet (15H) at τ8.23 (M = Rh) and 8.13 (M = Ir), due to the pentamethylcyclopentadienyl group, the p.m.r. spectra of both (43a) and (43b) showed two broad resonances only, due to olefinic (4H, τ7.05 and 7.23 respectively) and methylenic (8H, τ7.94 and 8.12 respectively) protons.

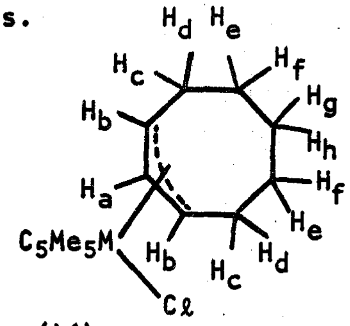
The mass spectra of both rhodium and iridium complexes, 1,5-CODMC_5Me_5 (43), were recorded using a sample inlet temperature of 80° (ionising beam strength, 80 eV). In agreement with mass spectral data for other C_5Me_5 complexes studied, the iridium complex (43b) showed a base peak corresponding to the molecular ion, while $C_5Me_5Rh^+$ was the most abundant ion for (43a). The mass spectrum of the rhodium complex (see Appendix) exhibited a molecular ion peak at m/e 346 (76% of the base peak). In addition to the ion at m/e 238 ($C_5Me_5Rh^+$), major fragments were at m/e 331 ($p-Me^+$, 24%), 329 ($C_5Me_5RhC_7H_7^+$, 27%), 316 ($C_5Me_5RhC_6H_6^+$, 12%), 303 ($C_5Me_5RhC_5H_5^+$, 7%), 292 ($C_5Me_5RhC_4H_6^+$, 6%) and 103 (Rh^+, 26%). This is in fair agreement with the spectrum of $C_5H_5RhC_8H_{12}$ (44) reported by King[139]. The iridium complex, in addition to very large molecular ion peaks at m/e 436, 434 (p^+, corresponding to $C_{18}H_{27}{}^{193}Ir^+$ and $C_8H_{27}{}^{191}Ir^+$ respectively), also showed peaks corresponding to $p-CH_3^+$ (m/e 421, 419), $p-CH_5^+$ (m/e 419, 417), $p-C_2H_4^+$ (m/e 406, 404) and $p-C_3H_7^+$ (m/e 393, 391). In contrast to (43a), no significant peaks corresponding to $C_5Me_5Ir^+$ or Ir^+ were observed and loss of H_2 and $2H_2$ from the parent appeared to be favoured processes[139].

The same complexes (43a) and (43b) were also obtained with essentially equal facility from the reactions of (13a) with 1,3- and 1,4-COD and the reaction of (13b) with 1,3-COD respectively. The reaction of $(C_5Me_5IrC\ell_2)_2$ (13b) with 1,4-cyclooctadiene was not investigated.

Metal complexes of the chelating 1,5-cyclooctadiene are extremely common and were also obtained in a number of systems from reaction with 1,5- or 1,3-cyclooctadiene[45,119,134]. The reactions of 1,4-cyclooctadiene with metal complexes do not, however, appear to have been studied, undoubtably since this isomer is not readily available. The only fully characterised complexes of 1,3-cyclooctadiene seems to be 1,3-COD-iron tricarbonyl[140], prepared photochemically from iron pentacarbonyl and 1,3-COD.

It was observed that, during the reactions to give 1,5-$CODMC_5Me_5$ (43), an intermediate colour change occurred. This prompted the reinvestigation of these reactions under milder conditions. Thus (13a) was reacted with 1,3-, 1,4- and 1,5-cyclooctadienes at 40-45° in ethanol in the presence of sodium carbonate. In each case this rapidly led to the formation of a stable red complex, isolated as chloro-π-2-cyclooctenyl-(pentamethylcyclopentadienyl)rhodium(III) (46a). Likewise the reaction of $(C_5Me_5IrC\ell_2)_2$ (13b) with 1,3- or 1,5-COD at room temperature led, after the appropriate working-up procedure, to isolation of the iridium analogue (46b) as stable yellow crystals.

$$(C_5Me_5MC\ell_2)_2 + C_8H_{12} \xrightarrow[EtOH]{Na_2CO_3}$$



(13) (46)

The complexes, (46a) and (46b), were identified on the basis of their analyses, and in particular their p.m.r. spectra and further reactions (see below).

The p.m.r. spectrum of the iridium complex, π-$C_8H_{13}IrC\ell(C_5Me_5)$ (46b), (100 MHz, benzene) showed resonances at τ5.75 (1H, t, assigned to H_a), 6.43 (2H, four line resonance of relative intensities 1:3:3:1 due to an overlapping double triplet, assigned to H_b), 7.4 (2H, six or seven line multiplet, assigned to H_c), 7.9 (2H, bm*, assigned to H_d), 8.14 (6H, bm, assigned to H_e, H_f, H_g, H_h) and 8.55 (15H, s, C_5Me_5).

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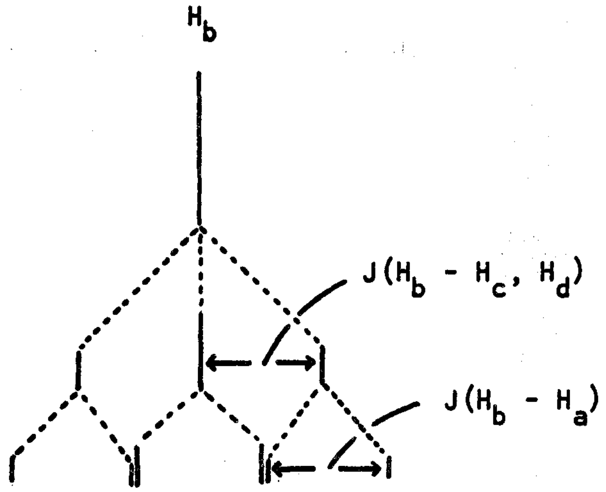
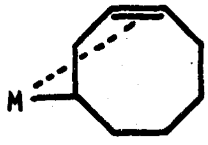
*bm = broad multiplet.

Decoupling experiments showed that H_a was effectively coupled only to H_b (J(ab) 7 Hz); H_b was coupled both to H_a and to H_c and H_d (J(ab) 7 Hz, J(bc,d) 7.5 Hz). The four line resonance of H_b thus arises, at least to the first order, by coupling of H_b equally to H_c, H_d to give a triplet which is split by coupling to H_a.

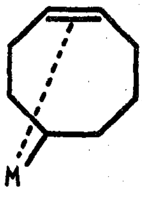


Relative intensity 1 3 3 1

The observed pattern of resonances is only compatible with a π-2-cyclooctenyl complex (47) and not with a σ,π-3- or -4-cyclooctenyl complex (either (48) or (49)).



(48)



(49)

The p.m.r. spectrum (100 MHz, benzene) of the rhodium complex π-$C_8H_{13}RhCl(C_5Me_5)$ (46a) appeared similar, but here H_a and H_b resonances overlapped to give an unresolved multiplet at τ6.21 (3H). Other resonances were observed at τ7.36 (2H, more than five lines, H_c), 7.88 (2H, bm, H_d), 8.43 (6H, m, H_e, H_f, H_g, H_h) and 8.53 (15H, s, C_5Me_5). Irradiation at the resonant frequency of H_a/H_b indicated that H_c was coupled to one of these, but no coupling constants could be determined. π-2-cyclooctenyl complexes of both cobalt(I)[141] and rhodium(I)[142] have been recently reported. The p.m.r. data reported for these agree well with the present values and exhibit H_a as triplets and H_b as four line resonances.

These π-2-cyclooctenyl complexes, π-$C_8H_{13}MC\ell(C_5Me_5)$ (46), readily gave effectively quantitative yields of 1,5-CODMC_5Me_5 (43) from reactions in ethanol in the presence of sodium carbonate and 1,3- or 1,5-COD. It thus appeared that (46) was an intermediate (or closely related to an intermediate) in the formation of the 1,5-COD complexes (43) from the dichloro complexes (13) and 1,3-, 1,4- or 1,5-COD.

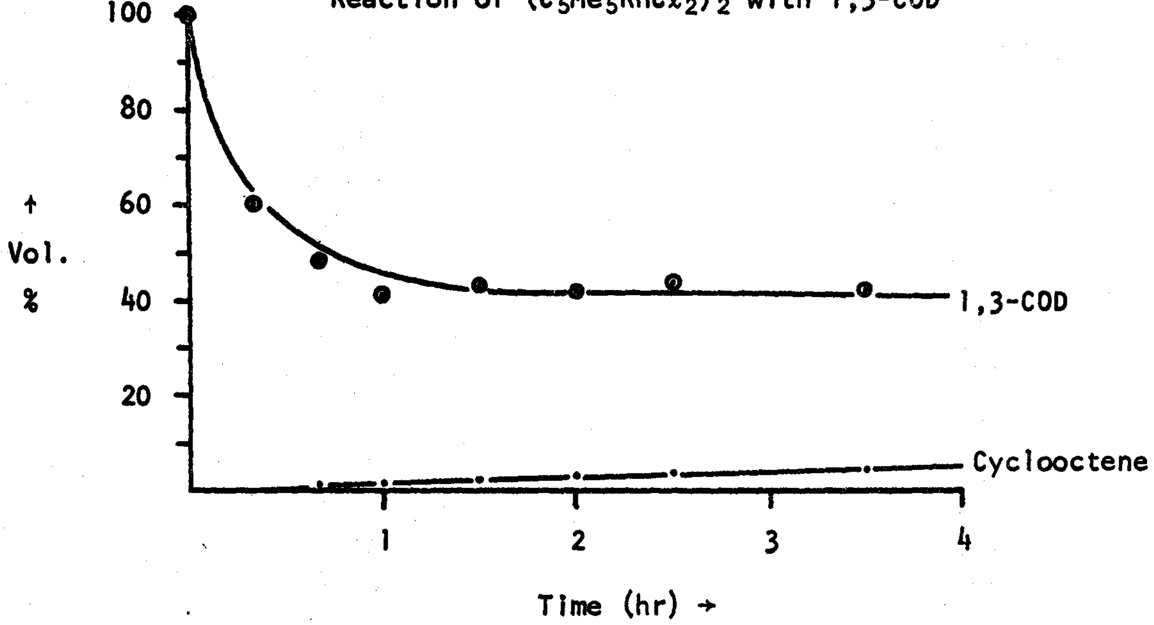
A detailed study of these reactions was undertaken, together with an analysis of the organic by-products by v.p.c.

(i) The direct formation of 1,5-CODM(C_5Me_5) (43) from the dichlororhodium (13a) and -iridium (13b) complexes

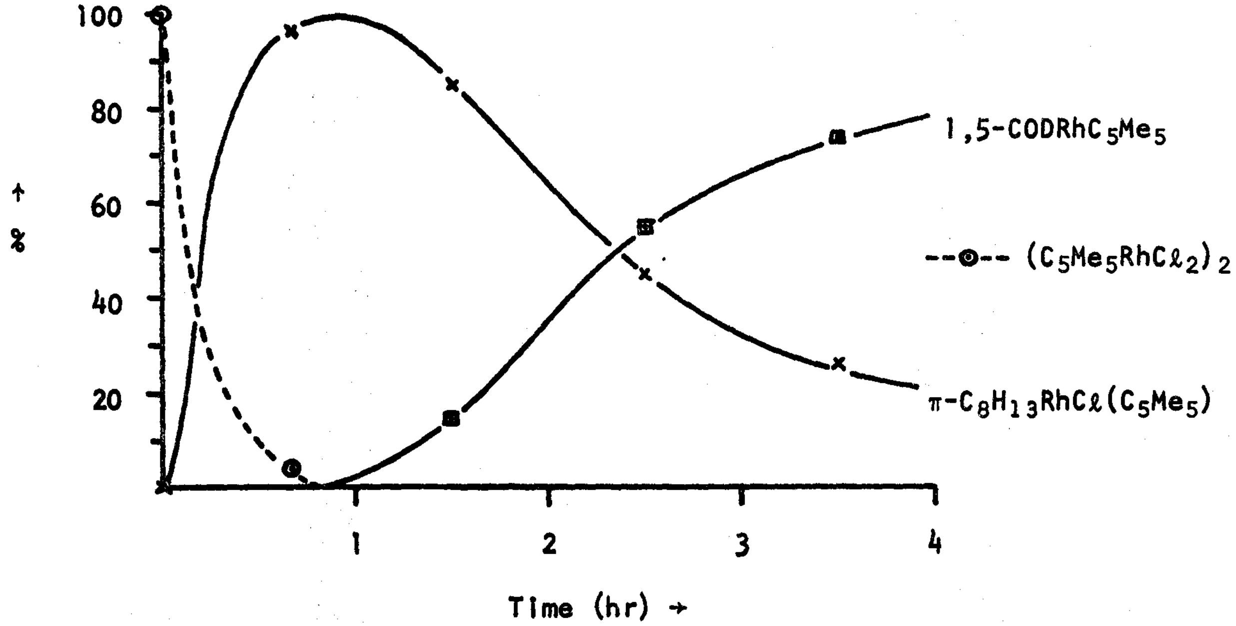
The reactions of $(C_5Me_5RhC\ell_2)_2$ (13a) with 1,3- and 1,5-COD in ethanol-base were followed over 3.5 hr at 65°; aliquots were removed at intervals, the mother liquids were analysed by v.p.c. and the solid residues analysed by p.m.r. for the complexes (13a), π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) and π-1,5-CODRh(C_5Me_5) (43a). The results are summarised in Figures X and XI and they confirm that (46a) was

Figure X

Reaction of $(C_5Me_5RhC\ell_2)_2$ with 1,3-COD



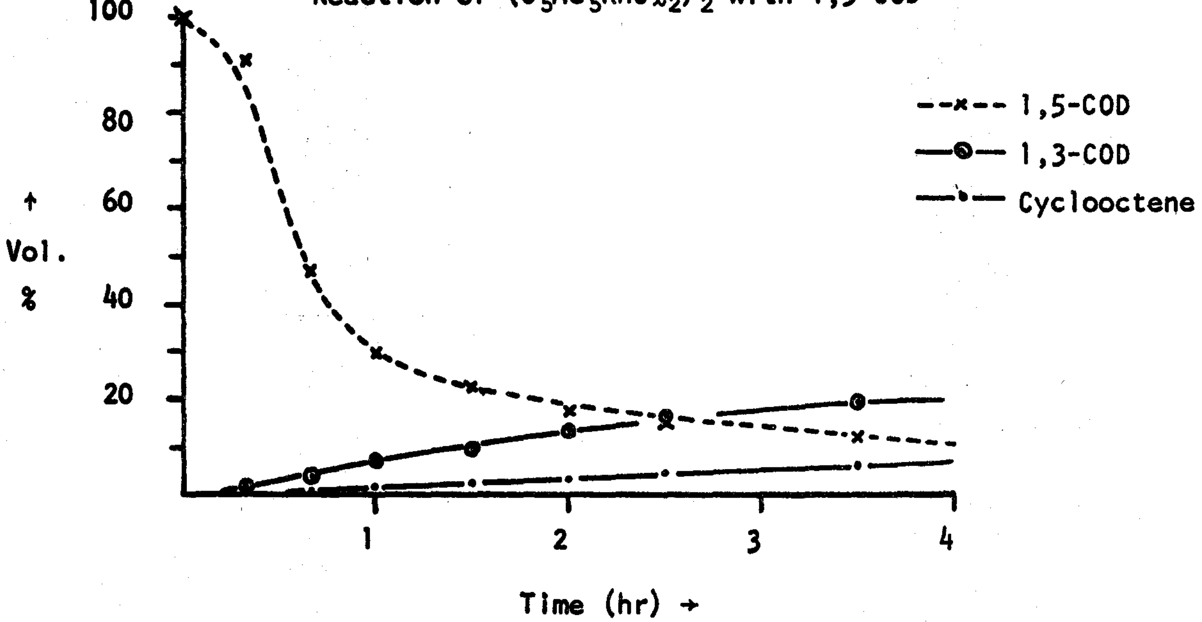
(a) C_8 - hydrocarbons in the mother liquids.



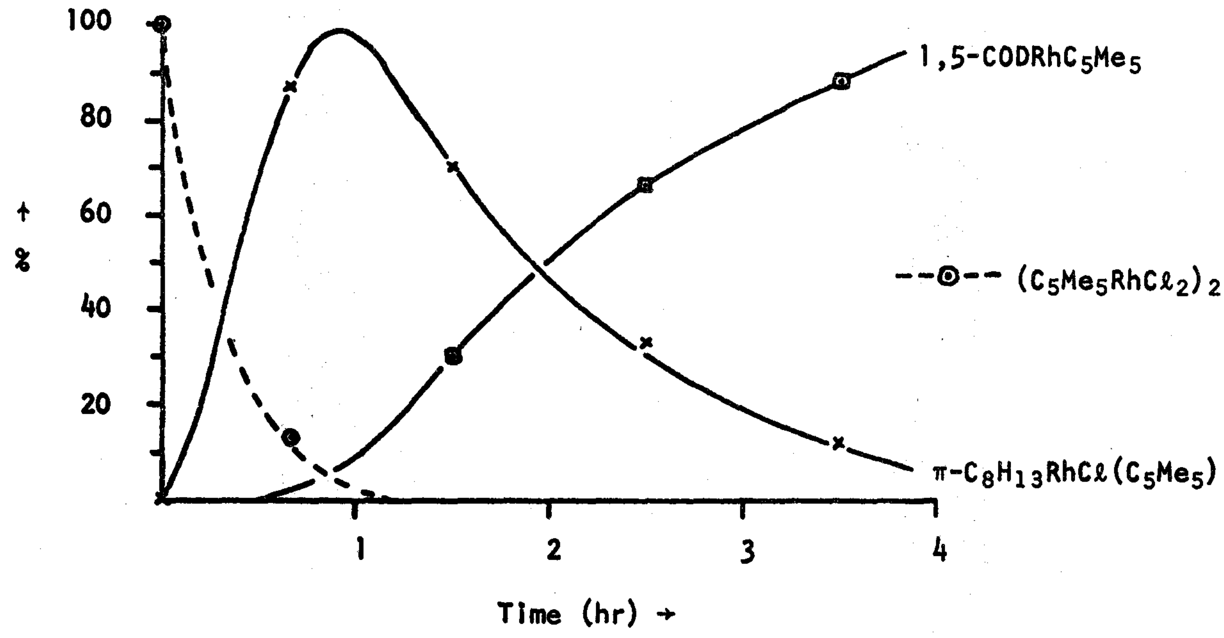
(b) Solid residues.

Figure XI

Reaction of $(C_5Me_5RhCl_2)_2$ with 1,5-COD



(a) C_8 - hydrocarbons in the mother liquids.



(b) Solid residues.

indeed an intermediate in the formation of the 1,5-COD-complex (43a) from the dichloro-complex (13a). The results also indicate that π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) was formed somewhat faster from 1,3-COD and (13a) while 1,5-COD reacted somewhat faster with (46a) to give 1,5-CODRh(C_5Me_5) (43a). Acetaldehyde and acetal, which were not present in any significant amounts in the ethanol used, were detected in all but the first (time = 0 min.) aliquots. The relative amounts of these could not be meaningfully assessed and probably depend on the effective pH of the reaction. It was also observed that while no isomerisation of uncomplexed 1,3-COD occurred, an appreciable amount of free 1,3-COD was formed during the 1,5-COD reaction; a small amount of cyclooctene was detected in both cases.

The reactions of $(C_5Me_5RhC\ell_2)_2$ with 1,3-, 1,4- and 1,5-COD to give the complex 1,5-CODRh(C_5Me_5) (43a) were carried out a number of times. In each case the volatile products were analysed after completion of reaction (some results are presented in Table 2). Both 1,5- and 1,4-COD were isomerised to uncomplexed 1,3-COD, the extent of isomerisation being dependent on the relative amounts of $(C_5Me_5RhC\ell_2)_2$ and diene taken. From reactions with 1,3-COD, however, no isomerised, free diene was ever detected. Cyclooctene, acetal and acetaldehyde were invariably by-products from these reactions.

Similarly, no isomerisation of uncomplexed 1,3-COD was ever observed during the reactions of this with $(C_5Me_5IrC\ell_2)_2$ (13b) to give 1,5-CODIr(C_5Me_5) (43b). Although some isomerisation of 1,5- to 1,3-COD occurred during the formation of (43b) from 1,5-COD and (13b), the amount was much less than in the corresponding rhodium reaction;

cyclooctene and acetaldehyde and/or acetal were again produced in all reactions. The results are presented in Table 2.

(ii) The formation of the complexes, π-$C_8H_{13}MC\ell(C_5Me_5)$ (46)

In the formation of π-$C_8H_{13}MC\ell(C_5Me_5)$ (M = Rh and Ir), the only significant constituents of the volatile mixture, apart from starting COD, were acetaldehyde and acetal (Table 2). In other words, negligible isomerisation of the free COD used was observed and only the complexed diene was isomerised (that is, for 1,4- and 1,5-COD). This result is also apparent from Figure XI which indicates that isomerisation of 1,5- to 1,3-COD only occurred after the formation of the cyclooctenyl complex (46a).

(iii) The formation of 1,5-CODRh(C_5Me_5) (43a) from π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a)

Experiments in which π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) was reacted with 1,5-COD in ethanol in the presence of sodium carbonate showed that isomerisation of 1,5- to 1,3-COD occurred (Table 3), the extent of which depended on the relative amounts of (46a) and 1,5-COD taken. Again cyclooctene and acetaldehyde and/or acetal were formed.

(iv) The reactions of 1,5-CODM(C_5Me_5) (43) with 1,5-COD

Both the rhodium, (43a), and iridium, (43b), complexes were reacted with 1,5-COD in ethanol in the presence of sodium carbonate. After 3 days at 75° the rhodium complex (43a) isomerised 1,5-COD to ca. 5% 1,3- and 5% 1,4-COD; in addition, 15% cyclooctene was obtained and diethylacetal was detected. Similarly the iridium complex (43b) isomerised 1,5-COD to ca. 10% 1,3- and 20% 1,4-COD at 70° after 3 days, in addition giving 20% cyclooctene and some acetal. The complexes 1,5-CODM(C_5Me_5) (43) were quantitatively recovered after each reaction.

(v) Decomposition of the cyclooctenyl complexes, π-$C_8H_{13}MC\ell(C_5Me_5)$(46)

Experiments were carried out in which the cyclooctenyl complexes, (46a) and (46b), were heated in vacuo and in various solvents in the presence and absence of base. The results are presented in Tables 3 (M = Rh) and 4 (M = Ir).

The reactions of the iridium complex, π-$C_8H_{13}IrC\ell(C_5Me_5)$ (46b), were clearer and more easily interpreted. In vacuo or in solution in the absence of base a reaction, which is virtually a disproportionation, occurred,

$$\underset{(46b)}{2C_5Me_5Ir(C_8H_{13})C\ell} \rightarrow \underset{(43b)}{C_5Me_5Ir(1,5\text{-}COD)} + \underset{(13b)}{\tfrac{1}{2}(C_5Me_5IrC\ell_2)_2} + C_8H_{14}$$

Only trace amounts of 1,3-COD were formed.

In ethanol in the presence of base (triethylamine or sodium carbonate) an essentially quantitative reaction involving loss of HCℓ from (46b) took place,

$$\underset{(46b)}{C_5Me_5Ir(C_8H_{13})C\ell} + \text{Base} \rightarrow \underset{(43b)}{C_5Me_5Ir(1,5\text{-}COD)} + \text{Base}\cdot HC\ell$$

Base HCℓ was isolated when base was Et_3N.

In benzene in the presence of triethylamine, an intermediate behaviour was observed. The complex (1,5-COD)Ir(C_5Me_5) (43b) was obtained in greater yield than from the benzene-only reaction but in smaller yield than from the ethanol-base reactions. Both cyclooctene and triethylamine hydrochloride were formed.

The reactions of π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) were more complex, appreciable amounts of 1,3-COD being formed in addition to cyclooctene.

In vacuo or in ethanolic solution (in the absence of base and presence or absence of COD), π-$C_8H_{13}RhC\ell(C_5Me_5)$ decomposed in a similar way to the iridium analogue to give effectively equimolar amounts of $(C_5Me_5RhC\ell_2)_2$ (13a) and π-1,5-CODRh(C_5Me_5) (43a), together with cyclooctene, in a disproportionation reaction. However, even in the solid state reaction a little 1,3-COD was formed.

Cyclooctene was also the major organic product when π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) was decomposed in ethanolic solutions in the presence of base and absence of COD. When 1,4- or 1,5-COD was present, however, 1,3-COD became the major by-product, as previously described; more 1,3-COD than cyclooctene was also formed from the reactions of π-$C_8H_{13}RhC\ell(C_5Me_5)$ in petroleum ether or benzene solution (in the presence or absence of triethylamine).

$(C_5Me_5RhC\ell_2)_2$ (13a) was formed in addition to 1,5-CODRh(C_5Me_5) (43a) in all of these reactions except those in which π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) was decomposed in ethanolic solution in the presence of sodium carbonate. When this was carried out in the presence of COD then 1,5-CODRh(C_5Me_5) (43a) was the only complex formed. However in the absence of COD, a very soluble purple material was obtained in addition to (43a). Attempts to crystallise this purple complex failed; it had an empirical formula C_5Me_5Rh (50) and showed a single p.m.r. peak due to methyl protons at τ8.17 (60 MHz, $CDC\ell_3$). This material was also formed as a minor product in the reaction using triethylamine as base. A different, uncharacterised, polymeric (?) material also resulted when the decomposition of π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) was carried out in petroleum ether.

(vi) The reactions of $(C_5Me_5RhC\ell_2)_2$ (13a) and π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) with cyclooctene

Experiments were carried out to determine whether the 1,3-COD produced in these reactions might arise by reaction of cyclooctene with $(C_5Me_5RhC\ell_2)_2$, π-$C_8H_{13}RhC\ell(C_5Me_5)$ or 1,5-CODRh(C_5Me_5). Thus cyclooctene, freed from cyclooctadienes by preparative v.p.c., was heated with $(C_5Me_5RhC\ell_2)_2$ (13a) and π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) (2:1 and 1:1 mole ratios, respectively) in ethanol in the presence of sodium carbonate. The cyclooctene was quantitatively recovered in each case after reactions at 65° for 4 hr.

The reactions of the triphenylphosphine complexes $C_5Me_5MC\ell_2PPh_3$ (28) with 1,3- and 1,5-COD

The complexes, $C_5Me_5MC\ell_2PPh_3$ [(28a), M = Rh; (28b), M = Ir], were also reacted with 1,3- and 1,5-COD in ethanol in the presence of sodium carbonate. These gave the 1,5-COD complexes 1,5-$C_8H_{12}M(C_5Me_5)$ (43) in good yield only after prolonged reaction at 60° (ca. 12 hr for the rhodium complex, ca. 24 hr for the iridium analogue). On interrupting the iridium reaction before completion, the hydrido-complex, $C_5Me_5IrHC\ell PPh_3$ (30), was detected from its characteristic double doublet at τ8.42.

Deuteration Studies

The rhodium complex, $(C_5Me_5RhC\ell_2)_2$ (13a), was reacted with both 1,3- and 1,5-COD in ethanol-d_6 in presence of anhydrous sodium carbonate to give the monodeuterated complex π-$C_8H_{12}DRhC\ell(C_5Me_5)$. The sample from the 1,3-COD reaction was heated in vacuo and the product was shown to contain ca. 80% 1,5-$C_8H_{11}DRh(C_5Me_5)$ and 20% 1,5-$C_8H_{12}Rh(C_5Me_5)$ (43a) by mass spectroscopy. The two samples of π-$C_8H_{12}DRhC\ell(C_5Me_5)$ were also each reacted with both 1,3- and 1,5-COD in ethanol-d_0 in the presence of sodium carbonate and the resulting samples of 1,5-CODRh(C_5Me_5) were analysed for deuterium content in the same way. The complex π-$C_8H_{12}DRhC\ell(C_5Me_5)$ from 1,5-COD, when reacted with 1,5-COD, gave 25% π-1,5-$C_8H_{11}DRh(C_5Me_5)$ and, with 1,3-COD, gave 35% π-1,5-$C_8H_{11}DRh(C_5Me_5)$; while π-$C_8H_{12}DRhC\ell(C_5Me_5)$ from 1,3-COD, when reacted with 1,5- and 1,3-COD gave 30% and 35% of 1,5-$C_8H_{11}DRh(C_5Me_5)$, respectively. A through reaction in which $(C_5Me_5RhC\ell_2)_2$ was heated with 1,3-COD in ethanol-d_6 in the presence of anhydrous sodium carbonate at 65°, gave 55% 1,5-$C_8H_{11}DRh(C_5Me_5)$. In none of these reactions was there significant incorporation of two or more deuterium atoms per molecule nor was any deuterium incorporated in the C_5Me_5 ring. It was not possible to locate the actual position(s) of the deuterium atom in the 1,5-COD ligand.

The percentage of 1,5-$C_8H_{11}DRh(C_5Me_5)$ in these products was determined from the molecular ion (p^+) abundances of 1,5-$C_8H_{11}DRh(C_5Me_5)$ (m/e 347) and 1,5-$C_8H_{12}Rh(C_5Me_5)$ (m/e 346). For this, a method of successive approximation had to be employed since the p + 1 peak of the latter contributes to the abundance of the former and the p - 1 peak of the former contributes to the abundance of the latter. The abundance ratio (p-1)/p for the complex, 1,5-$C_8H_{12}Rh(C_5Me_5)$, was obtained from the mass spectrum of an authentic sample of this run immediately after that of a partially deuterated product so that, as nearly as possible, similar conditions were operative in both cases.

TABLE 2

Reactions of $(C_5Me_5MC\ell_2)_2$ (13) with Cyclooctadienes in Ethanol in the Presence of Sodium Carbonate to give π-$C_8H_{13}MC\ell(C_5Me_5)$ (46) or 1,5-$CODMC_5Me_5$ (43)

Starting COD (mmole)	Complex Reactant (mmole)	Conditions	Product (mmole)	Products in Mother Liquors[a]			
				1,5-COD	1,4-COD	1,3-COD	C_8H_{13}
				(mmole)			
1,5-	(13a)		(43a)				
(1.63)	(0.50)	65°/3.5 hr	(0.95)	0.17	0	0.29	0.08
(0.45)	(0.17)	65°/3.5 hr	(0.32)	0	0	0.06	0.02
1,3-	(13a)		(43a)				
(2.08)	(0.48)	65°/3.5 hr	(0.85)	0	0	0.85	0.08
(0.44)	(0.17)	65°/3.5 hr	(0.33)	0	0	0.06	0.02
1,4-[b]	(13a)		(43a)				
(0.52)	(0.07)	55°/5 hr	(0.14)	trace	0.17	0.06	0.02
1,5-	(13b)		(43b)				
(0.50)	(0.125)	68°/2.5 hr	(0.24)	0.19	0	0.02	0.03
1,3-	(13b)		(43b)				
(0.80)	(0.125)	60°/5.5 hr	(0.26)	0	0	0.5	trace[c]
1,5-	(13a)		(46a)				
(1.63)	(0.49)	40°/3 hr	(0.93)	0.7	0	trace	trace
1,4-[b]	(13a)		(46a)				
(0.24)	(0.08)	45°/2 hr	(0.15)	trace	0.07	0.01	trace
1,3-	(13a)		(46a)				
(2.01)	(0.5)	40°/3 hr	(1.0)	trace	0	1.0	0.02
1,5-	(13b)		(46b)				
(0.81)	(0.065)	20°/1.5 hr	(0.10)	0.63	0	trace	0
1,3-	(13b)		(46b)				
(0.90)	(0.25)	20°/2 hr	(0.40)	0	0	0.4	trace

---

[a] Acetaldehyde and/or acetal was detected in all of these reactions.

[b] The sample of 1,4-COD was shown, by analytical v.p.c., to contain ca. 8% 1,3-COD.

[c] Observed but not estimated quantitatively.

TABLE 3

The reaction $C_5Me_5Rh(C_8H_{13})C\ell$ (46a) → $C_5Me_5RhC_8H_{12}$ (43a)

(46a) mmole	Conditions	(43a) mmole	Other Products (mmole)
0.23	in vacuo/110°/8 hr	0.11	(13a)(0.06); C_8H_{14}+ 1,3-COD (4:1)
0.17	C_6H_6/80°/8 hr	0.08	(13a)(0.043); C_8H_{14}(0.032) + 1,3-COD(0.05)
0.18	C_6H_6/Et N(0.17 mmole)/80°/ 8 hr	0.09	(13a)(0.048); C_8H_{14}(0.027) + 1,3-COD(0.06)
0.13	C_6H_6/py(0.14 mmole)/80°/6 hr	0.06	$C_5Me_5RhC\ell_2$py(0.06)
0.20	petroleum ether/90°/3.5 hr	0.06	(13a) + unknown polymer C_8H_{14}(0.06) + 1,3-COD(0.10)
0.24	petroleum ether/Et_3N(0.29 mmole)/90°/3.5 hr	0.06	(13a) + unknown polymer C_8H_{14}(0.065) + 1,3-COD(0.12) + 1,5-COD(0.01)
0.13	EtOH/1,5-COD(0.82 mmole)/ 70°/9 hr	0.06	(13a)(0.06); 1,5-COD(0.8) + 1,3-COD(trace)^b + C_8H_{14} (trace)^b
0.45	EtOH/Na_2CO_3/65°/9 hr	0.24	$(C_5Me_5Rh)_n$ (50)(0.19); C_8H_{14}(0.06) + 1,3-COD(0.03); ac.
0.13	EtOH/Et_3N(0.15 mmole)/73°/ 13 hr	0.09	(13a)(0.02); (50)(0.02) $Et_3NHC\ell$(0.12); C_8H_{14}(0.02) + 1,3-COD(0.005); ac.
0.20	EtOH/Na_2CO_3/1,5-COD(0.33 mmole)/60°/5 hr	0.18	1,5-COD(0.10) + 1,3-COD(0.14) + C_8H_{14}(0.03); ac.

---

ac. acetaldehyde and/or acetal.

b. observed but not estimated quantitatively.

TABLE 4

The reaction $C_5Me_5Ir(C_8H_{13})Cl$ (46b) → $C_5Me_5IrC_8H_{12}$ (43b)

(46b) mmole	Conditions	(43b) mmole	Other Products (mmole)
0.11	in vacuo/95°/5.5 hr	0.064	(13b)(0.026) + C_8H_{14}
0.22	C_6H_6/80°/19 hr	0.11	(13b)(0.05) + C_8H_{14}(0.09) + 1,3-COD(trace)
0.10	C_6H_6/Et_3N(0.11 mmole)/75°/18 hr	0.085	(13b)(0.015) + C_8H_{14}? + Et_3NHCl
0.11	EtOH/Na_2CO_3/65°/4.5 hr	0.11	C_8H_{14}(trace)
0.11	EtOH/Et_3N(0.11 mmole)/60°/24 hr	0.11	Et_3NHCl

The results described above can be summarised:

(i) The dichloro-complexes, $(C_5Me_5MC\ell_2)_2$ (13) (M = Rh, Ir), reacted with cyclooctadienes to give 1,5-CODRh(C_5Me_5) (43) via the intermediacy of the cyclooctenyl complexes, π-$C_8H_{13}MC\ell(C_5Me_5)$ (46).

(ii) The iridium complex, π-$C_8H_{13}IrC\ell(C_5Me_5)$, decomposed relatively simply to give 1,5-CODIr(C_5Me_5) alone or a mixture of this and $(C_5Me_5IrC\ell_2)_2$; cyclooctene was the only significant by-product.

(iii) The rhodium complex, π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a), decomposed to give 1,5-CODRh(C_5Me_5) alone only in ethanol-base in the presence of cyclooctadiene; 1,3-COD was the major by-product and cyclooctene a minor one. In the absence of COD, ethanolic solutions of (46a) gave 1,5-CODRh(C_5Me_5) together with $(C_5Me_5RhC\ell_2)_2$ or $(C_5Me_5Rh)_n$ (base present); here cyclooctene was the major organic product and 1,3-COD the minor one. Similar results were obtained when π-$C_8H_{13}RhC\ell(C_5Me_5)$ was heated alone in vacuum. In non-ethanolic solution in the absence of COD, π-$C_8H_{13}RhC\ell$-(C_5Me_5) decomposed to give 1,5-CODRh(C_5Me_5) and $(C_5Me_5RhC\ell_2)_2$; more 1,3-COD than cyclooctene was formed. Base had only a minor effect on these latter reactions.

(iv) The complexes, 1,5-CODM(C_5Me_5) (43) (M = Rh, Ir), catalysed the isomerisation of 1,5-COD to 1,3- and 1,4-COD in a very slow reaction, cyclooctene was the major product here. The low rate of this excludes it as a possible mechanism for the formation of 1,3-COD and cyclooctene in the above reactions. Also 1,4-COD was never detected from any of the other reactions described here.

In this last respect the results are rather intriguing since other authors have observed 1,4-COD during the isomerisation of 1,5- to 1,3-COD on metal catalysts. For example, Nicholson and Shaw[118] reported that the 1,4-COD isomer was formed during the rhodium trichloride catalysed isomerisation of 1,5- to 1,3-COD. Their experiment was repeated as a check on the ability of our analytical method to detect 1,4-COD. It was found that when 1,5-COD was reacted with $RhC\ell_3 \cdot 3H_2O$ in ethanol at 63° for 30 minutes, giving $(1,5\text{-CODRhC}\ell)_2$, the composition of the uncomplexed diene was 1,3- (81%), 1,4- (7%) and 1,5- (12%). This isomerisation process is thus much faster than with $(C_5Me_5RhC\ell_2)_2$ (<u>13</u>a).

A further possibility for 1,4-COD not being detected during reactions described here was that, under the conditions used, any 1,4-COD formed was rapidly isomerised to the thermodynamically most stable 1,3-COD isomer. However the observation that much 1,4-COD was recovered after reactions with $(C_5Me_5RhC\ell_2)_2$ to give either $\pi\text{-}C_8H_{13}RhC\ell(C_5Me_5)$ or $1,5\text{-CODRh}(C_5Me_5)$ implies that this isomer, if formed, should have had a sufficient life-time for detection.

In order to explain the reactions observed here, three distinct processes must be considered. These are, the formation of $\pi\text{-}C_8H_{13}MC\ell(C_5Me_5)$, the decomposition of this to $1,5\text{-CODM}(C_5Me_5)$ and the slow isomerisation of 1,5-COD by $1,5\text{-CODM}(C_5Me_5)$.

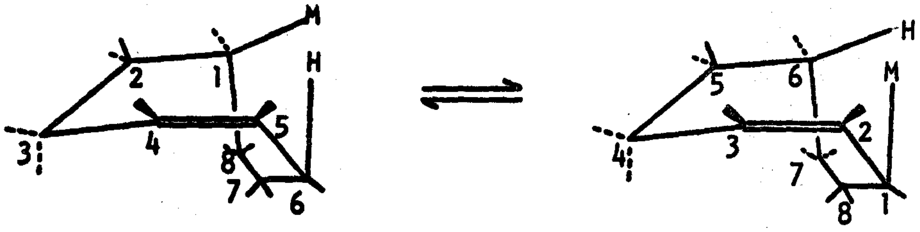
The Formation of the π-Cyclooctenyl Complexes $\pi\text{-}C_8H_{13}MC\ell(C_5Me_5)$ (<u>46</u>)

By analogy with the reactions of $(C_5Me_5MC\ell_2)_2$ with some other olefins in ethanol-base, described previously, it is reasonable to suppose that the initial step in the formation of $\pi\text{-}C_8H_{13}MC\ell(C_5Me_5)$

was the generation of the active hydridic species, $C_5Me_5MHC\ell(s)$ (51). Starting from 1,3-COD complex formation merely involves the coordination of the olefin to this followed by hydrogen migration onto the diene. This can be regarded as a 1,2- or 1,4- addition of M-H and in either case, the resulting σ-2-cyclooctenyl complex can then rearrange to the π-2-cyclooctenyl complex, π-$C_8H_{13}MC\ell(C_5Me_5)$ (46) (Scheme 1, m = $C_5Me_5MC\ell$). Evidence for this comes from the detection of acetaldehyde and the deuteration studies. In particular, although it was not practicable to analyse the deuterium content of (46a) derived from 1,3-COD in ethanol-d_6, the complex 1,5-CODRh(C_5Me_5), obtained from heating this in vacuo, was some 80% monodeuterated.

In order for the π-2-cyclooctenyl complexes π-$C_8H_{13}MC\ell(C_5Me_5)$ to arise from both 1,4- and 1,5-COD, hydrogen shifts must occur. The simplest explanation involves a series of 1,2-hydrogen migrations using the model of Cramer[111, 112]. In this (Scheme 1), the coordination of the diene is followed by hydrogen migration to give the en-yl complexes (steps d (or f), g). These species can then re-form m-H without loss of complexed diene; this is necessary since the results indicated that isomerisation of uncomplexed diene did not occur. This reversible addition of m-H is repeated until the thermodynamically most stable π-2-cyclooctenyl complex, π-$C_8H_{13}MC\ell(C_5Me_5)$, is attained. This scheme assumes that the hydrogen migration reactions b, c, d, f and g are fast by comparison with steps -a, -e and -h.

Alternatively, a 1,4-hydride shift may be invoked. This has the advantage that possible eliminations to give 1,4-COD would be minimised. This is of particular significance in the decomposition reactions of $C_5Me_5Rh(C_8H_{13})C\ell$ (below). Examination of models, assuming normal bond angles and bond lengths, shows that in one strain-free conformation, the σ-4-cyclooctenyl ligand has a hydrogen at C_6 in close proximity to the metal. A simple reversible metal-assisted hydrogen transfer may then be envisaged as leading to the σ-2-cyclooctenyl ligand.

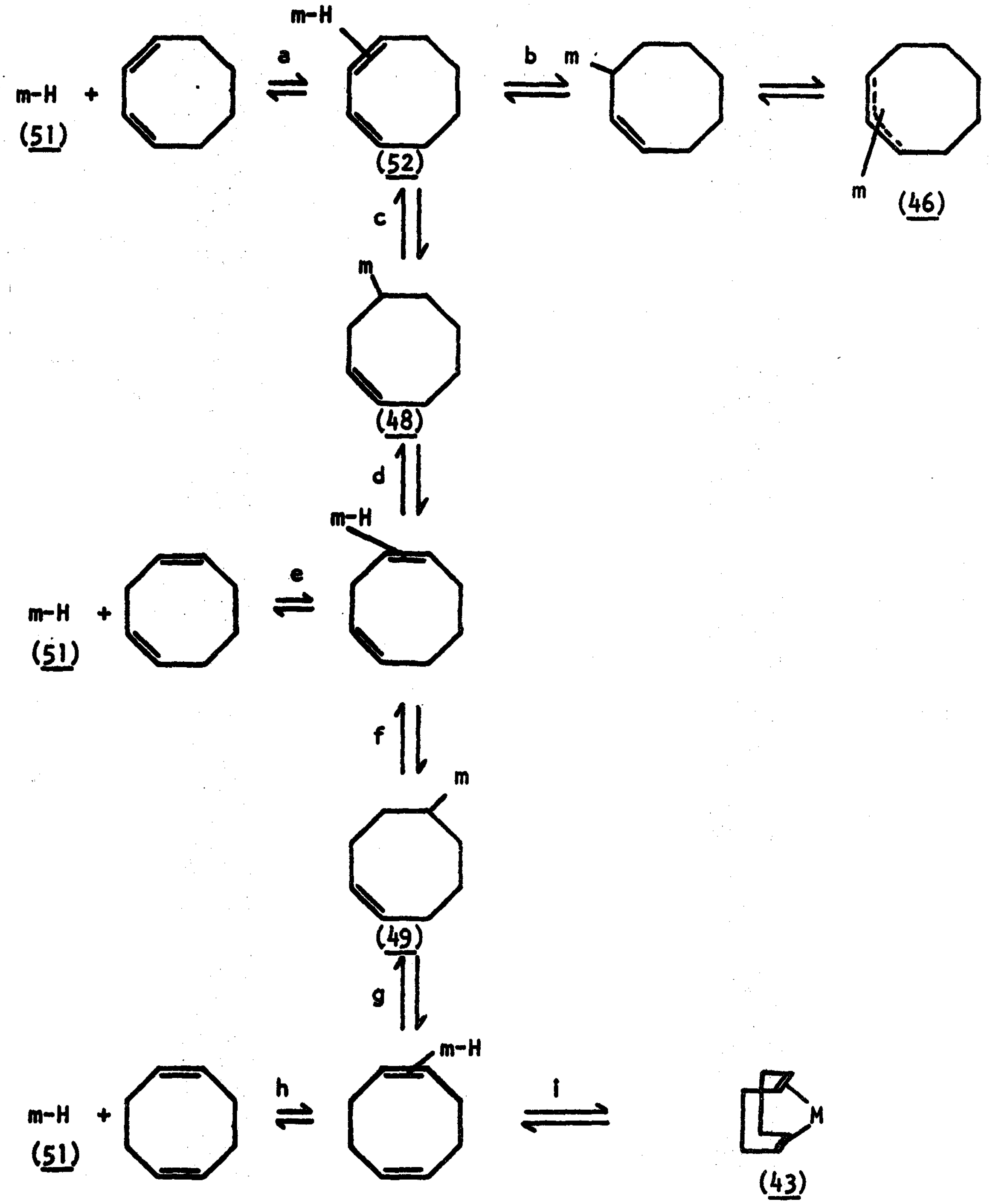


Both 1,3- and 1,5- transannular shifts are known in cyclooctane chemistry and 1,4-shifts are also probable; the subject has recently been reviewed by Cope et al.[143] Here, a 1,4-shift in a cyclooctene derivative is suggested and there does not appear to be a suitable system for comparison.

The Decomposition of the π-Cyclooctenyl Complexes, π-$C_8H_{13}MC\ell(C_5Me_5)$ (46)

The formation of the complexes, 1,5-CODM(C_5Me_5), from the decomposition of the π-2-cyclooctenyl complexes, π-$C_8H_{13}MC\ell(C_5Me_5)$, also involves hydrogen shifts probably leading to the σ-4-cyclooctenyl complexes (49). Either 1,2- (Scheme 1) or 1,4- transannular-hydrogen migrations may again be invoked with restrictions on the former to allow for the experimental observation that no free 1,4-COD or 1,5-COD was ever formed. Here, these restrictions are that the hydrogen migration steps -b, -c, -d, -f and -g are rapid compared to the elimination steps -e and -h.

The overall reaction of $(C_5Me_5MC\ell_2)_2$ with 1,3-COD to give the



Scheme 1 [m = $C_5Me_5MC\ell(S)$]

complexes 1,5-CODM(C_5Me_5) via the intermediacy of π-$C_8H_{13}MC\ell(C_5Me_5)$ (<u>46</u>) is fairly straight forward on the above scheme. However the intermediacy of (<u>46</u>) in the corresponding overall reaction with 1,5-COD is somewhat surprising and leads to a mechanistic problem. This is that the most direct route to the final product is via steps h and i (Scheme 1); formation of the observed π-2-cyclooctenyl complex requires a series of 1,2-shifts (or a 1,4-shift) while subsequent formation of 1,5-CODM(C_5Me_5) involves a reversal of these. This may be reconciled by proposing a potential energy curve such as is illustrated in Figure XII for the reaction of m-H with 1,3-COD. Similar curves may be drawn for the reactions of m-H with 1,4- or 1,5-COD (to give, initially, σ-4-$C_8H_{13}MC\ell(C_5Me_5)$ (<u>49</u>) in both cases).

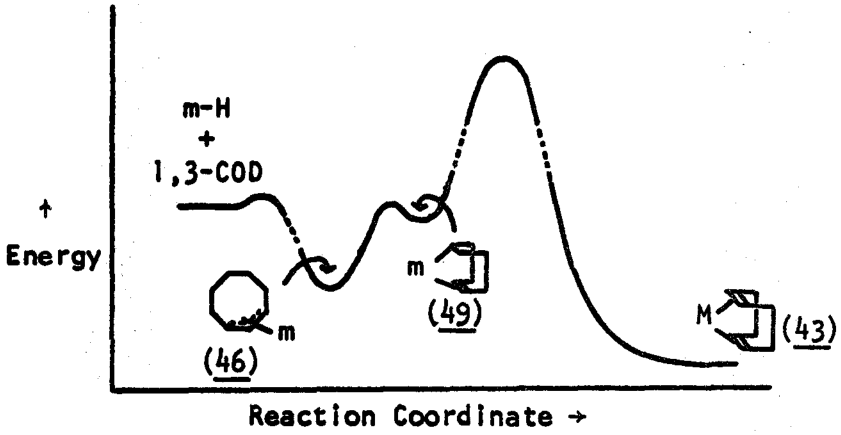


Figure XII

The reactions of cyclooctadienes with m-H in ethanol-base under mild conditions leads to (<u>46</u>). At higher temperatures and longer reaction times, further reaction of (<u>46</u>) to give (<u>43</u>) via (<u>49</u>) can occur. The rate-determining step is thus the dehydrochlorination of σ-4-$C_8H_{13}MC\ell(C_5Me_5)$ to give 1,5-CODM(C_5Me_5).

The results from the decomposition of the iridium complex, π-$C_8H_{13}IrC\ell(C_5Me_5)$ (<u>46b</u>), may be rationalised on a fairly simple reaction scheme. The complex (<u>46b</u>) isomerises to the σ-4-cyclooctenyl complex (<u>49b</u>) followed by reductive elimination of $HC\ell$ to give 1,5-$CODIr(C_5Me_5)$ (Scheme 1, step i, m = $C_5Me_5IrC\ell(S)$). In the presence of added base, the $HC\ell$ is removed and 1,5-$CODIr(C_5Me_5)$ is obtained in nearly quantitative yield (together with Base•$HC\ell$ when base is Et_3N). Otherwise π-$C_8H_{13}IrC\ell(C_5Me_5)$ itself acts as base in that it reacts with $HC\ell$ to give cyclooctene and $(C_5Me_5IrC\ell_2)_2$ (<u>13b</u>).

$$C_5Me_5Ir(C_8H_{13})C\ell \rightarrow C_5Me_5Ir(1,5\text{-COD}) + HC\ell$$

$$C_5Me_5Ir(C_8H_{13})C\ell + HC\ell \rightarrow \tfrac{1}{2}(C_5Me_5IrC\ell_2)_2 + C_8H_{14}$$

It has been shown that π-$C_8H_{13}MC\ell(C_5Me_5)$ does indeed react readily with $HC\ell$ to give (<u>13</u>).

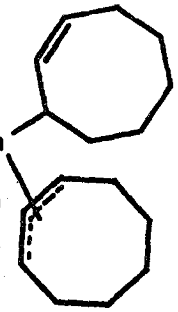
The decompositions of the rhodium complex, π-$C_8H_{13}RhC\ell(C_5Me_5)$ (<u>46a</u>), were more complex and it is not clear that a definitive mechanism can be suggested yet; 1,3-COD was a significant by-product in addition to cyclooctene.

The results of Table 3 may be divided into three groups:
(a) Decomposition in vacuo, in benzene or petroleum ether with or without base, and in ethanol without base. The products here are both the 1,5-COD complex (<u>43a</u>) and $(C_5Me_5RhC\ell_2)_2$ (<u>13a</u>), and varying proportions of 1,3-COD and cyclooctene. The observation that no $Et_3NHC\ell$ was formed during the decomposition of π-$C_8H_{13}RhC\ell(C_5Me_5)$ (<u>46a</u>) in benzene or petroleum ether, in the presence of Et_3N, suggests that the reductive elimination of $HC\ell$ described above is not a favoured

reaction under these conditions. The results of the decomposition of (46a) in vacuo and in ethanol may of course be partially explained by a mechanism such as that proposed above, for the iridium complex, π-$C_8H_{13}IrC\ell(C_5Me_5)$. However a possible common route for these rhodium reactions, which also accounts for the appreciable amounts of 1,3-COD formed, is the following. The complex π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) may disproportionate to a π,σ-bis(cyclooctenyl) complex (53) and $(C_5Me_5RhC\ell_2)_2$ (13a) followed by decomposition of (53) in one of two ways, giving either 1,5-CODRh(C_5Me_5) (43a) and cyclooctene or (43a), 1,3-COD and hydrogen, by intramolecular processes. There is no evidence for the evolution of hydrogen and it could well be scavenged from the system. In this connection it is pertinent to note that in benzene or petroleum ether where trace impurities (oxygen or other unsaturated hydrocarbons) are more likely to be present, the relative amount of 1,3-COD is far higher than in reactions in vacuo. Base is expected to have no effect on this reaction, in agreement with the results.

$$2C_5Me_5Rh(C_8H_{13})C\ell \rightarrow \tfrac{1}{2}(C_5Me_5RhC\ell_2)_2 + C_5Me_5Rh$$

(46a) (13a) (53)



$$(53) \longrightarrow C_5Me_5Rh(1,5\text{-}COD) + C_8H_{14}$$

(43a)

or $$(53) \longrightarrow C_5Me_5Rh(1,5\text{-}COD) + 1,3\text{-}COD + H_2$$

(43a)

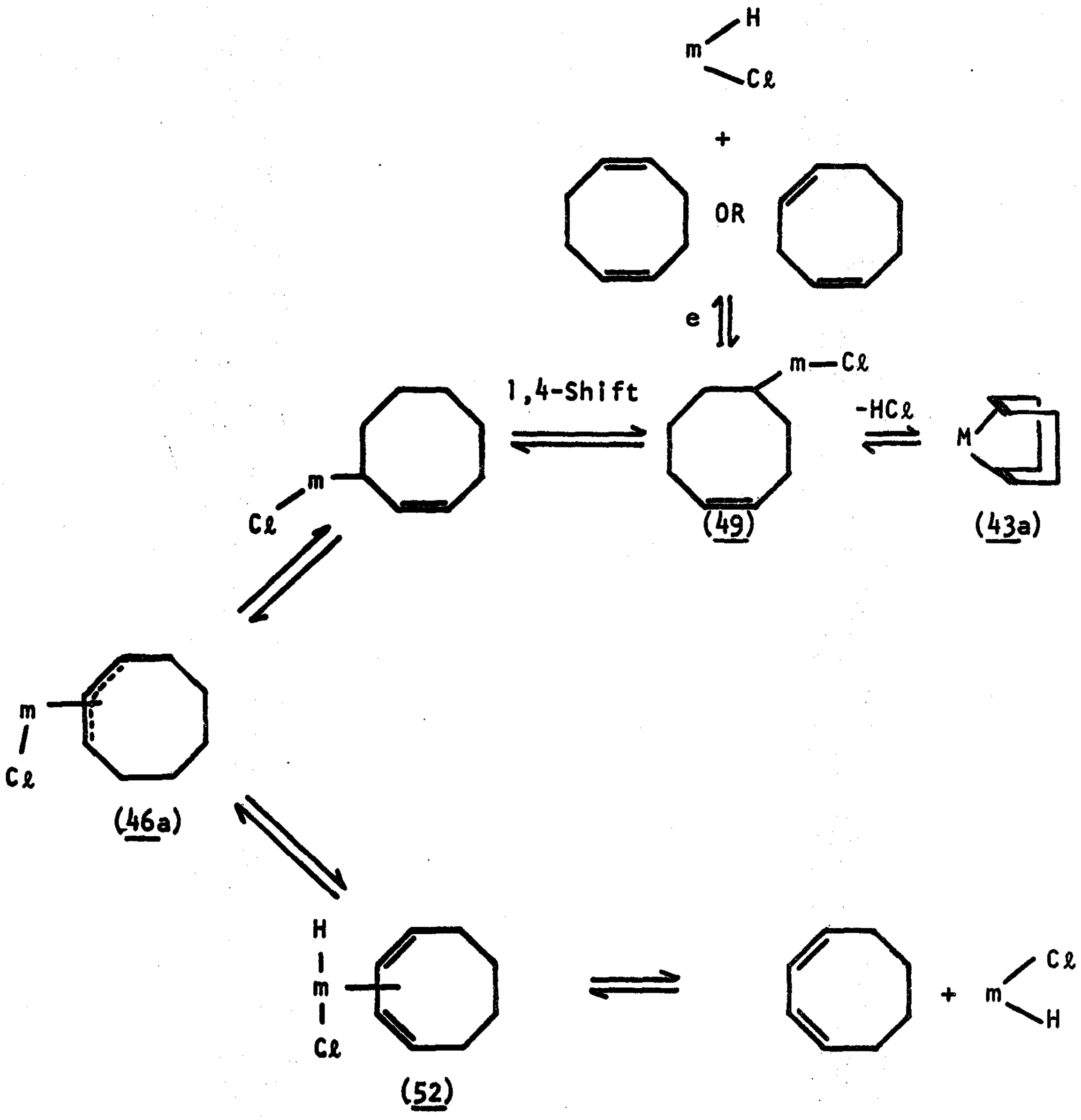
A disproportionation, though not in this direction, has been observed for a very similar system by Powell and Shaw[144].

(b) Decomposition in ethanol in the presence of base and (c) decomposition in ethanol in the presence of base and free COD.

In the presence of COD the reaction proceeds to give (43a) only, together with isomerisation of COD (when COD = 1,4- or 1,5-isomer) to 1,3-COD. Cyclooctene, which is also formed here, is the major by-product from decomposition in the absence of COD. The observed isomerisation of COD means that considerable exchange of free and complexed diene must occur and this is borne out by the deuteration studies. It is necessary to assume that the π-2-cyclooctenyl complex $\pi\text{-}C_8H_{13}RhC\ell(C_5Me_5)$ (46a) can transform in two directions either to give (49) (and subsequently (43a)) or (52) (Scheme 2), but since 1,3-COD does not form a stable complex, exchange occurs. The alternatives are readily understood in terms of the potential energy diagram of Figure XII. The differences in behaviour of the rhodium (46a) and iridium (46b) complexes, $\pi\text{-}C_8H_{13}MC\ell(C_5Me_5)$, may then be reconciled by assuming that the transformation (46b) $\rightleftarrows$ (49b) is more highly favoured by the iridium complex. Possible routes to explain the exchange reactions are summarised in Scheme 2.

A 1,4-hydride shift again minimises the possibility of obtaining 1,4-COD. However a series of 1,2-shifts (Scheme 1) to explain these results is by no means ruled out, as long as the reverse reaction -e is very slow by comparison with all others.

Reductive elimination of $HC\ell$ at some stage is supported by the isolation of $Et_3NHC\ell$ from the decomposition of $\pi\text{-}C_8H_{13}RhC\ell(C_5Me_5)$ (46a)



Scheme 2 (m = C_5Me_5Rh)

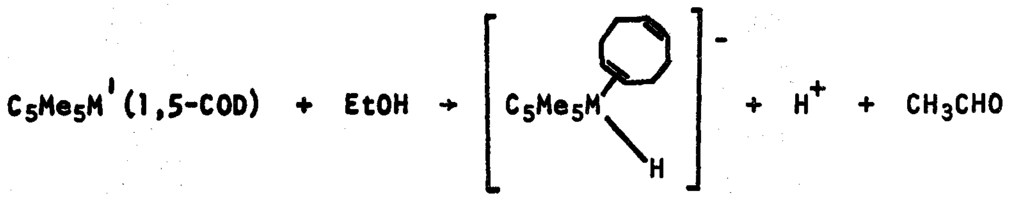
in ethanol in the presence of Et_3N.

The cyclooctene formed in these reactions can arise in a number of ways. These include the reaction of liberated HCℓ with π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) and the disproportionation reaction of (46a) outlined previously. However one possibility which is indicated by the detection of acetaldehyde (or acetal) and the deuteration studies, is the replacement of chloride with ethoxide and subsequent formation of a hydridic species (54). Further support for this solvent participation is the observation that, in ethanol in the absence of COD, cyclooctene is the major by-product whereas in non-protonic solvents (benzene and petroleum ether) 1,3-COD is the major by-product.

$$\begin{array}{lcl} m(C_8H_{13})C\ell + OEt^- & \rightleftarrows & m(C_8H_{13})OEt \\ & & \quad \uparrow\downarrow\ {}^{-}CH_3CHO \\ & & m(C_8H_{13})H\ (54) \\ & & \quad \downarrow \\ & & m + C_8H_{14} \end{array}$$

In the absence of free COD, C_5Me_5Rh (= m) was in fact isolated (50); in the presence of free COD it may react to give 1,5-CODRh(C_5Me_5).

The slow reaction of the 1,5-COD complexes, 1,5-CODM(C_5Me_5) (43), with 1,5-COD to give cyclooctene as well as 1,4- and 1,3-COD is not believed to be significantly involved in the other reactions described here. An important by-product from both these reactions in ethanol in the presence of sodium carbonate was diethylacetal. This points to the intermediacy of a metal hydride, in this case possibly an anionic hydride of M(I) formed according to



A species of this type will now be able to take part in reactions such as are depicted in Scheme 1 ($m = C_5Me_5M'H$). The detection of 1,4-COD supports the stepwise processes involving 1,2-hydrogen shifts. The scheme proposed by Tayim and Bailar[116] for the isomerisation of 1,5-COD using a platinum-hydride catalyst is similar to this.

The catalytic cycle may be ended, with liberation of cyclooctene, by reaction with ethanol.

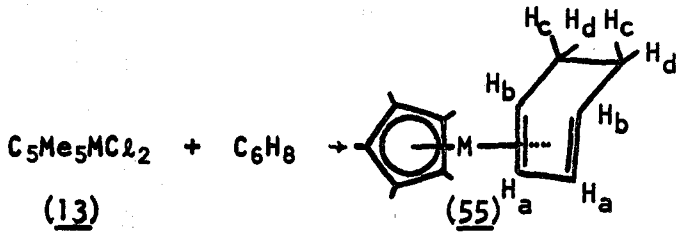
$$[C_5Me_5MC_8H_{13}]^- + EtOH + 1,5\text{-}COD \longrightarrow C_5Me_5M(1,5\text{-}COD) + C_8H_{14} + OEt^-$$

The faster rate of isomerisation of 1,5-COD with "$RhC\ell_3 \cdot 3H_2O$" observed by Nicholson and Shaw[118] and confirmed here, as well as the observation of 1,4-COD in this process, can be understood if it is assumed that $C_5Me_5RhH \cdot C\ell \cdot (COD)$ is more stable with respect to dissociation to $C_5Me_5RhHC\ell$ + COD than the corresponding species from the "$RhC\ell_3 \cdot 3H_2O$" reaction.

6. The Reactions of the Dimeric Dichloropentamethylcyclopentadienyl-rhodium and -iridium complexes (13) with Cyclohexadienes.

Preparation and Characterisation of New Complexes

The rhodium complex, (13a), was reacted with 1,3-cyclohexadiene (1,3-CHD) (45-55°, 3-4 hr) in ethanol in the presence of sodium carbonate. This readily gave, after the appropriate working-up procedure, good yields (70-80%) of yellow, somewhat air-sensitive, crystals of π-1,3-cyclohexadiene(pentamethylcyclopentadienyl)rhodium(I) (55a). The iridium analogue, (55b), was isolated from a similar reaction under milder conditions (35°, 3-4 hr) as air-sensitive colourless crystals. The products (55a) and (55b) were both readily sublimable in vacuum and this was the most effective isolation technique owing to their air sensitivity.



(13) (55)

The complexes were characterised by analysis and p.m.r. and mass spectroscopy.

The p.m.r. spectrum of the iridium complex, (55b), (100 MHz, benzene) exhibited a double doublet at τ5.36 (2H, assigned to H_a), an unresolved multiplet at 7.14 (2H, assigned to H_b), a singlet at 8.04 (15H, C_5Me_5) and a broad, unresolved assymmetric two-band resonance at 8.48 (4H, assigned to H_c, H_d). These assignments are in fairly good agreement with those given in the literature for other π-1,3-cyclohexadiene complexes[46,134]. Decoupling experiments showed that H_a was effectively coupled only to H_b (J)ab) 4.2 Hz, J(ab') 1.9 Hz) and that while H_b was coupled to H_a and H_c, H_d, there was only a slight sharpening of the resonances of H_c and H_d on irradiation at the resonant frequency of H_b.

The p.m.r. spectrum of the rhodium complex, (55a), was very similar except that H_a was now observed as a complex multiplet, due to coupling with ^{103}Rh ($I = \frac{1}{2}$). Resonances were observed at τ5.47 (2H, m, assigned to H_a), 7.17 (2H, bm, assigned to H_b), 8.07 (15H, s, C_5Me_5) and 8.52 (4H, bm, assigned to H_c, H_d). Decoupling again showed that H_a was coupled only to H_b and that coupling between H_b and H_c, H_d was small.

The mass spectra of the complexes (inlet temperature 30°C, ionising beam 80 eV) were also of interest. For the rhodium complex, the spectrum (see Appendix) showed a molecular ion peak at m/e 318 (31% of the base peak). The base peak was at m/e 238 ($C_5Me_5Rh^+$) and there were few ions having an abundance of greater than 5% of this. These were the molecular ion peak at m/e 318 and those fragments at m/e 316 [16%, $(p\text{-}H_2)^+$], 303 [12%, $(p\text{-}Me)^+$], 181 [5%, $(C_6H_6Rh)^+$], 158 [13%, $(p\text{-}H_2)^{2+}$] and 103 (8%, Rh^+). In addition there were low abundance ions from the normal fragmentation of the "C_5Me_5" ring at m/e 121, 119, 115, 105 and 103. Two very significant and interesting fragments were those at m/e 316 and 158. A metastable peak was observed at m/e ∿314 corresponding to the transition $p^+ \rightarrow p - H_2^+ + H_2$. The ion of m/e 316 is thought to be $(C_5Me_5RhC_6H_6)^+$ which would not be expected, on normal chemical grounds, to be a very stable cation since the +2 oxidation state is not common for rhodium. However the fragment of m/e 158, assigned to $(C_5Me_5RhC_6H_6)^{2+}$, is a complex of Rh(III) which obeys the inert gas formalism and is expected to be very stable. This may be indicative of a correlation between stability of ions in the gaseous and solution/solid phases. Attempts to isolate salts of such a cation using the hydride abstractors NBS and triphenylmethyl chloride in the presence of PF_6^- were unsuccessful however.

The mass spectrum of the iridium analogue (55b) was basically quite similar, however, for this the molecular ions were the base peaks, in common with other $C_5Me_5Ir^I$(diene) complexes studied (m/e 406, 408 for $C_{16}H_{23}{}^{193}Ir^+$ and $C_{16}H_{23}{}^{191}Ir^+$ respectively). The formation of

$C_5Me_5Ir^+$ (m/e 326, 328) was again an important fragmentation as was loss of $\cdot CH_3$ and H_2 from the parent (p-Me$^+$, m/e 391, 393; p-H $^+$, m/e 404, 406). Also large peaks at m/e 203 and 202 [$(C_5Me_5IrC_6H_6)^{2+}$] were observed.

Surprisingly, no low frequency ν_{CH} bands due to exo-hydrogens were observed in the infra-red spectra of (55a) and (55b).

The identical complexes, 1,3-$C_6H_8MC_5Me_5$ (55a) and (55b), were obtained in similar yields from reactions of (13a) and (13b) respectively with 1,4-cyclohexadiene (1,4-CHD) under effectively the same conditions. The isomerisation involved in these reactions prompted an investigation of the cyclohexadiene reactions in detail, particularly to establish which organic products were formed. The results are presented in Tables 5 and 6 and in Figure XIII.

Metal complexes of 1,3-CHD are fairly common. These include 1,3-cyclohexadiene(cyclopentadienyl) complexes of -cobalt[145] and -rhodium[134] and the halogeno- complexes $(1,3\text{-CHDRhC}\ell)_2$ and $(1,3\text{-CHD})_2\text{IrC}\ell$[46]. Arnet and Petit[146] observed that 1,3-cyclohexadieneiron tricarbonyl could be prepared from both 1,3- and 1,4-CHD. No complexes of 1,4-CHD are known.

The rhodium complex, $(C_5Me_5RhC\ell_2)_2$ (13a), was reacted with an excess of 1,3-CHD in ethanol in the presence of sodium carbonate. The volatile materials were distilled off into liquid nitrogen-cooled traps in vacuum and quantitatively analysed by v.p.c. using two columns. The complex, 1,3-$CHDRhC_5Me_5$ (55a), was isolated in the normal way. The volatile materials obtained from a series of reactions of this type were found, apart from ethanol, to consist mainly of benzene and cyclohexene in approximately equal amounts. Acetaldehyde and small amounts of 1,3-CHD were invariably also detected; cyclohexane and 1,4-CHD were never found (Table 5). It was also shown that the degree of disproportionation of 1,3-CHD to benzene and cyclohexene was a function of the time for which the reaction was run.

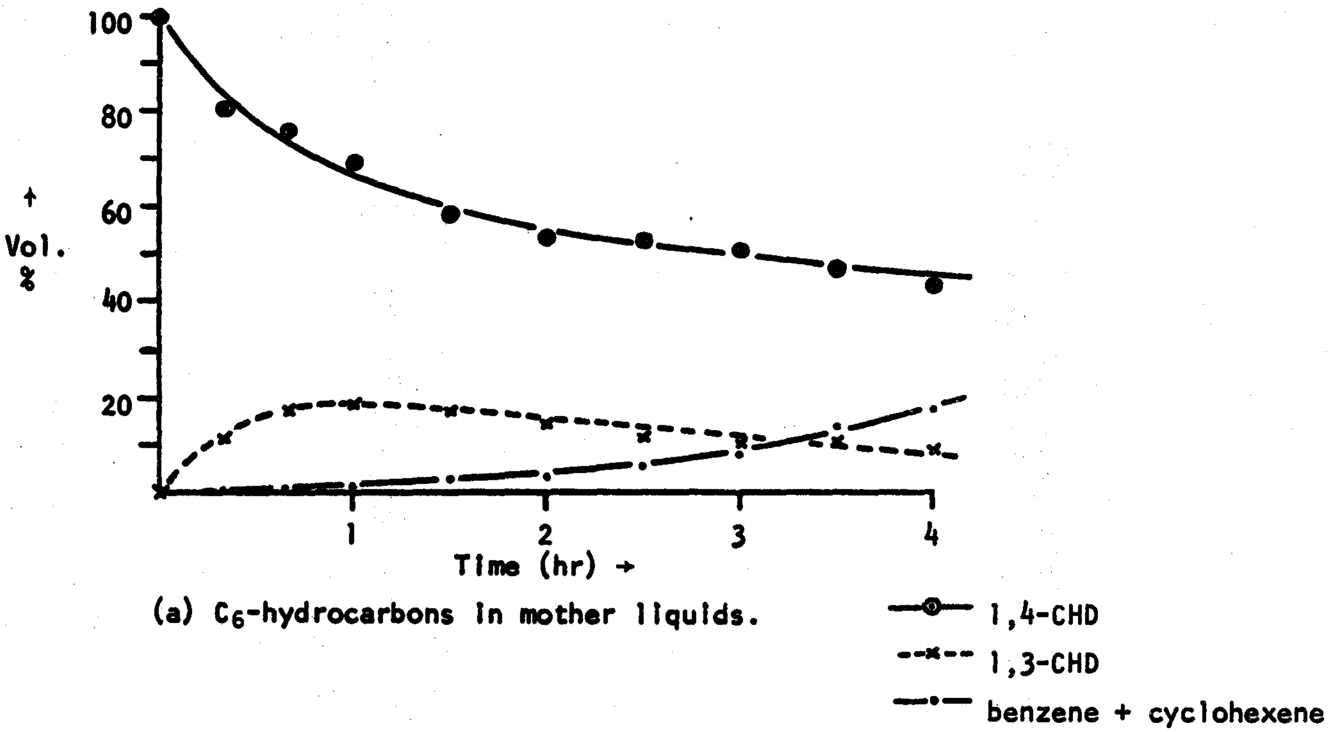
The reaction of (13a) with 1,4-CHD under very similar conditions gave, apart from (55a), a volatile mixture which comprised ethanol, acetaldehyde, 1,4-CHD, 1,3-CHD and again cyclohexene and benzene (Table 5).

A typical reaction of $(C_5Me_5RhC\ell_2)_2$ (13a) with 1,4-CHD was followed by removing aliquots at regular intervals and analysing the volatile components by v.p.c. and the solid residues by p.m.r. spectroscopy. The results are summarised in Figure XIII. It was observed that 1,4-CHD was immediately and rapidly isomerised to 1,3-CHD under these reaction conditions and that formation of $\text{1,3-CHDRhC}_5\text{Me}_5$ did not occur until an appreciable amount of 1,3-CHD had been produced. Further, the disproportionation reaction did not become significant until the formation of the complex was almost complete. It appeared then that the complex, $\text{1,3-CHDRhC}_5\text{Me}_5$ (55a), was the active catalyst for the disproportionation.

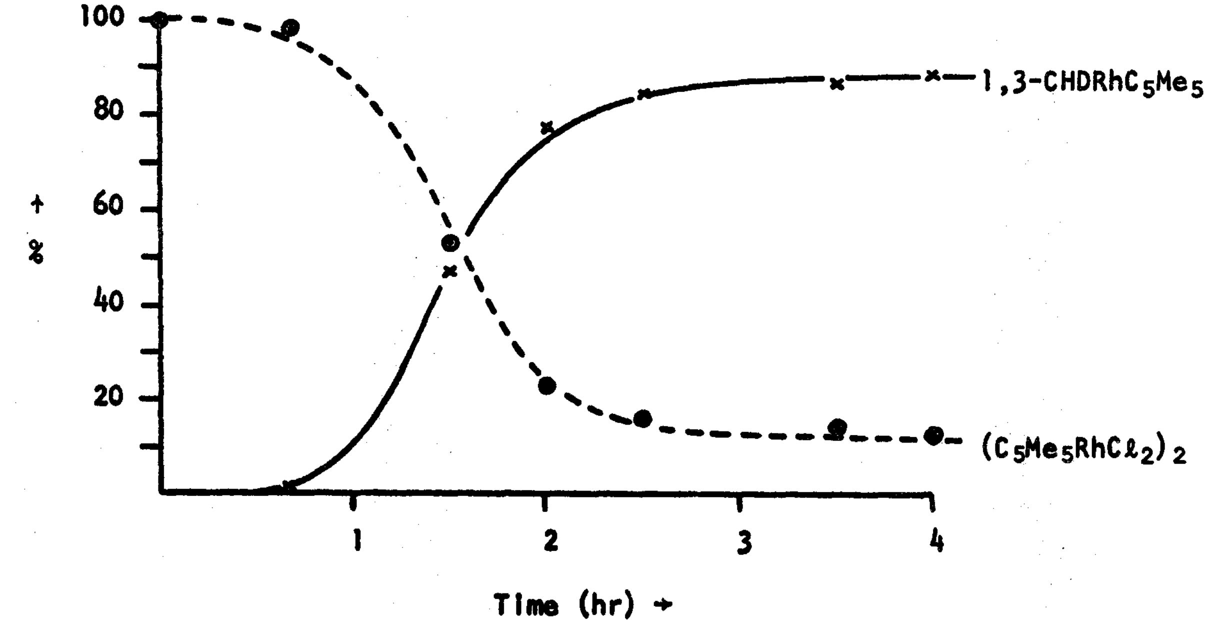
In order to test the latter inference a number of reactions were run in which (55a) was heated with cyclohexadienes under various conditions. In each case the complex was purified by sublimation immediately before use. The results of these studies are summarised in Table 6; these clearly show that the complex (55a) was indeed a very active catalyst for the disproportionation of 1,3-CHD to benzene

Figure XIII

Reaction of $(C_5Me_5RhC\ell_2)_2$ with 1,4-CHD



(a) C_6-hydrocarbons in mother liquids.



(b) Solid residues.

and cyclohexene but that ethanol and base were necessary co-catalysts. However 1,4-CHD underwent disproportionation much more slowly and probably by prior isomerisation to 1,3-CHD. In each case, for ethanolic reactions, traces of acetaldehyde were also detected. When heated with ethanolic sodium carbonate alone, the rhodium complex (55a) was recovered in better than 78% yield. No metal, but an unidentified polymeric (?) material and ca. 5% of both cyclohexene and benzene were obtained.

The reaction of the iridium complex, $(C_5Me_5IrC\ell_2)_2$, with both 1,3- and 1,4-CHD was also studied in detail, but under milder conditions (35°C/4 hr). Analysis of the uncomplexed C_6 hydrocarbons from the reaction with 1,3-CHD showed that no isomerisation and very little disproportionation occurred at this temperature. However the reaction with 1,4-CHD showed that considerable isomerisation of free 1,4- to 1,3-CHD had occurred, again with little disproportionation at this temperature; the latter became more appreciable at 75° /6 hr. Again it appeared that disproportionation occurred only after isomerisation. Acetaldehyde was invariably a by-product of these reactions.

The iridium complex, 1,3-CHDIrC_5Me_5 (55b), was also heated with a fivefold excess of both 1,3- and 1,4-CHD in ethanol in the presence of sodium carbonate at 50° for 21 hr. In both cases the solid and liquid reactants were recovered unchanged; neither isomerisation nor disproportionation of cyclohexadienes occurred. This also shows that ethanol and sodium carbonate alone do not catalyse the disproportionation reaction.

In an attempt to hydrogenate other cyclic dienes, the rhodium complex, 1,3-CHDRhC_5Me_5 (55a), was heated with two-fold excesses of both 1,3- and 1,5-cyclooctadienes at 60° for 2.5 hr in ethanol in the presence of sodium carbonate. In the first case the reactants were largely recovered although 12% of the 1,5-cyclooctadiene(pentamethylcyclopentadienyl)rhodium(I) (43a) and some cyclooctene was obtained together with traces of 1,3-CHD, cyclooctene and benzene. In the reaction with 1,5-cyclooctadiene, extensive exchange of complexed diene led to isolation of ca. 50% of 1,5-CODRhC_5Me_5 (43a) together with liberation of appreciable amounts of 1,3-CHD; 1,3- and 1,4-cyclooctadienes were also detected together with some cyclooctene and a trace of cyclohexene.

The results of the reactions outlined above reveal the following main features.

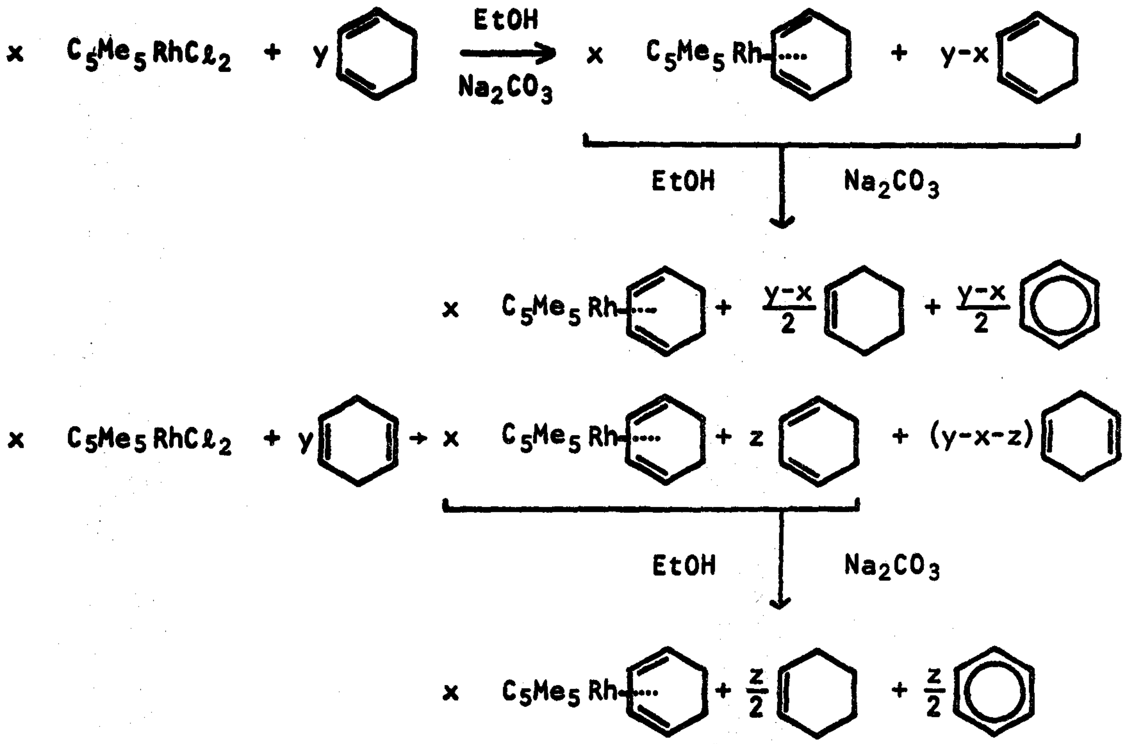
(i) The 1,3-CHD complexes (55) were formed with effectively equal ease from both 1,3- and 1,4-CHD.

(ii) 1,3-CHD was never isomerised to give 1,4-CHD in any of these reactions.

(iii) 1,4-CHD was isomerised during reactions with $(C_5Me_5RhC\ell_2)_2$ (13a) to give both free and complexed 1,3-CHD. Since the 1,3-CHD-rhodium complex (55a) was seen to be relatively inactive for this isomerisation, it must have occurred during formation of 1,3-CHDRhC_5Me_5 (55a). In fact a substantial amount of 1,3-CHD had to be formed before formation of (55a). Presumably a similar consideration holds for the iridium reactions where this isomerisation appeared to be faster.

(iv) During the reactions of both 1,3-CHD and 1,4-CHD with $(C_5Me_5RhC\ell_2)_2$ (13a) the disproportionation products, cyclohexene and benzene, were formed. For 1,3-CHD this disproportionation was shown to be catalysed by the 1,3-CHD-rhodium complex (55a), with both ethanol and base acting as co-catalysts. The disproportionation products from 1,4-CHD were formed by prior isomerisation to 1,3-CHD. However a small degree of disproportionation during formation of (55) cannot be ruled out, particularly for the iridium complex, (55b), which was itself inactive for both disproportion and isomerisation reactions under the conditions used here.

The predominant rhodium reactions may be represented:



In view of the above it seems reasonable to separate the isomerisation and complex formation from the disproportionation reaction.

TABLE 5

Reactions of $(C_5Me_5MC\ell_2)_2$ (13) with Cyclohexadienes in Ethanol in the Presence of Sodium Carbonate to give $1,3\text{-CHDMC}_5Me_5$ (55)

Starting CHD (mmole)	Complex Reactant (mmole)	Conditions	Product (mmole)	Products in Mother Liquors[a] 1,3-CHD	1,4-CHD (mmole)	C_6H_{10}	C_6H_6
1,3- (1.44)	(13a) (0.24)	48°/5.5 hr	(55a) (0.36)	0.08	0	0.40	0.44
1,4- (0.72)	(13a) (0.12)	47°/4 hr	(55a) (0.16)	0.02	0.32	0.06	0.06
1,3- (1.44)	(13b) (0.24)	35°/3.5 hr	(55b) (0.40)	0.84	0	0.04	0.04
1,4- (0.72)	(13b) (0.12)	35°/3.5 hr	(55b) (0.16)	0.18	0.24	0.02	0.02

[a] Acetaldehyde and/or acetal was detected in all of these.

TABLE 6

Isomerisation and Disproportionation of Cyclohexadienes Catalysed by 1,3-$C_6H_8RhC_5Me_5$ (<u>55</u>a)

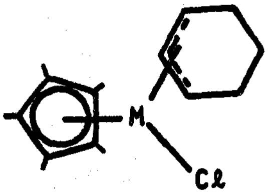
Diene	Conditions	(<u>55</u>a) recovered %	Volume %				
			C_6H_{10}	C_6H_6	1,3-CHD	1,4-CHD	acetaldehyde
1,3-Cyclohexadiene	EtOH/Na_2CO_3/55°/5 hr	85	45	45	trace	0	trace
	EtOH/55°/4 hr	85	16	16	70	0	trace
	n-hexane/Et_3N/66°/6.5 hr	96	0	0	100	0	-
	n-hexane/66°/6.5 hr	100	0	0	100	0	-
	THF/65°/21 hr	95	6	6	90	0	-
1,4-Cyclohexadiene	EtOH/Na_2CO_3/60°/4 hr	85	6	6	11	63	trace
none	EtOH/Na_2CO_3/60°/3 hr	78	4	4	0	0	trace

The Mechanism of the Formation of the Complexes (55) and Concomitant Isomerisation of Free 1,4-CHD to Free 1,3-CHD

By analogy with the reactions of $(C_5Me_5MCl_2)_2$ (13) with other olefins in ethanol in the presence of base, it seems likely that the initial step here is the formation of a reactive hydrido-species (51)

$$\underset{(13)}{(C_5Me_5MCl_2)_2} + EtOH \xrightarrow{\text{base}} \underset{(51)}{C_5Me_5MHCl(S)} + CH_3CHO + HCl$$

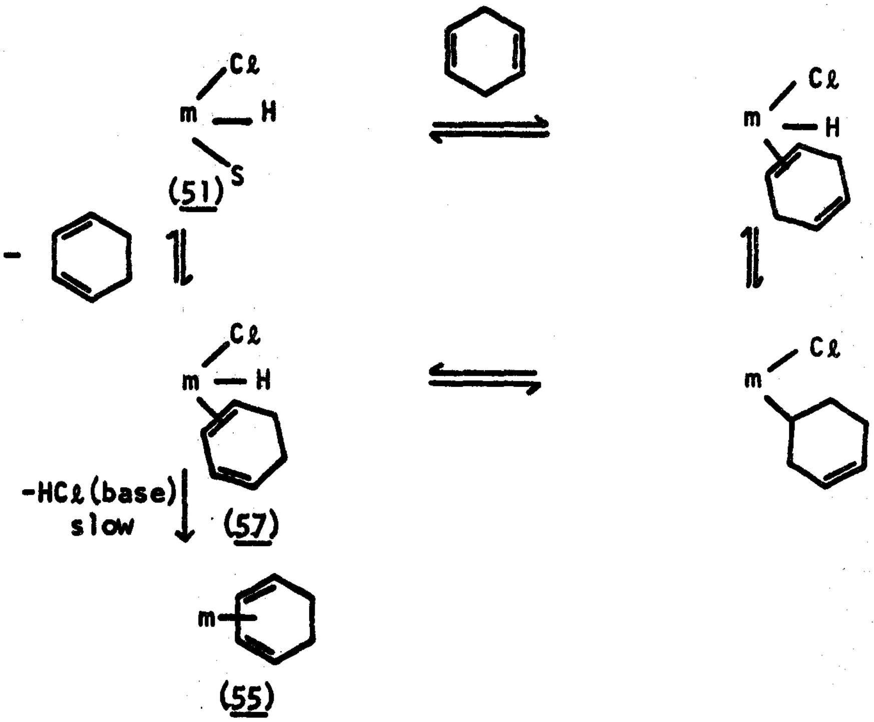
where (S) may be solvent or an olefinic double bond. The detection of acetaldehyde is in agreement with this hypothesis. By comparison with the reactions of (13) with cyclooctadienes, when an intermediate π-2-cyclooctenyl complex (46) was isolated, it is expected that this hydride would react with cyclohexadiene to give an intermediate π-en-yl complex: chloro π-2-cyclohexenyl(pentamethylcyclopentadienyl)-rhodium or -iridium, (56).



(56).

However, no such intermediate was observed in these reactions. This may be due to (56) being formed in undetectable concentrations or not being formed at all. The results represented in Figure XIII show that there was no detectable change in the concentration of $(C_5Me_5RhCl_2)_2$ (13a) over the first 40 min. of reaction despite the occurrence of a substantial amount of isomerisation of 1,4- to 1,3-CHD. Since π-2-cyclohexenyl complexes are known for other metals, e.g., palladium[147-149]. (56) is probably not formed here. A small concentration of hydride is probably formed which is the effective catalyst for isomerisation.

As Figure XIII shows, the concentration of 1,3-CHD, ca. 60% of that of $(C_5Me_5RhC\ell_2)$, was appreciable before complex formation occurred. This would appear to indicate that while isomerisation and exchange are rapid processes there is a rate-determining step prior to complex formation. The most reasonable explanation is that one of the hydrido-species, (57) or (51) (Scheme 3), undergoes loss of $HC\ell$ in a slow step to give 1,3-$CHDMC_5Me_5$ (55) or an active "C_5Me_5M" (50); the latter may then react with free 1,3-CHD to give (55).



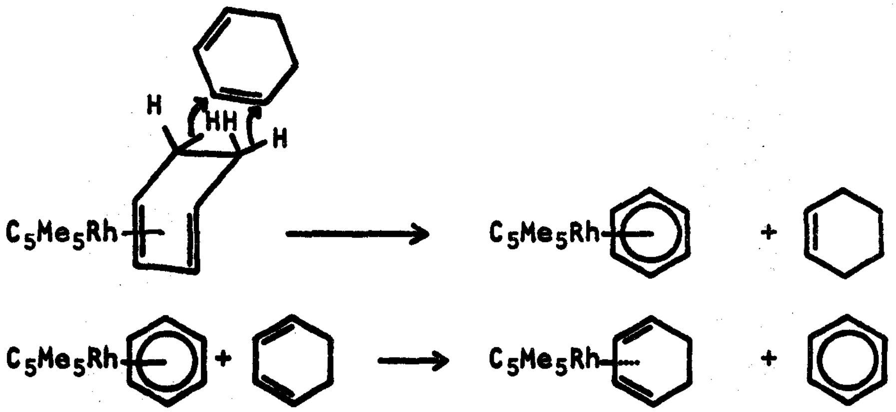
Scheme 3 $(m = C_5Me_5M)$

The Mechanism of the Disproportionation of 1,3-CHD

The results indicate that only 1,3-CHD is disproportionated during these reactions and that the complex 1,3-CHDRhC$_5$Me$_5$ (55a) is the most active catalyst for this.

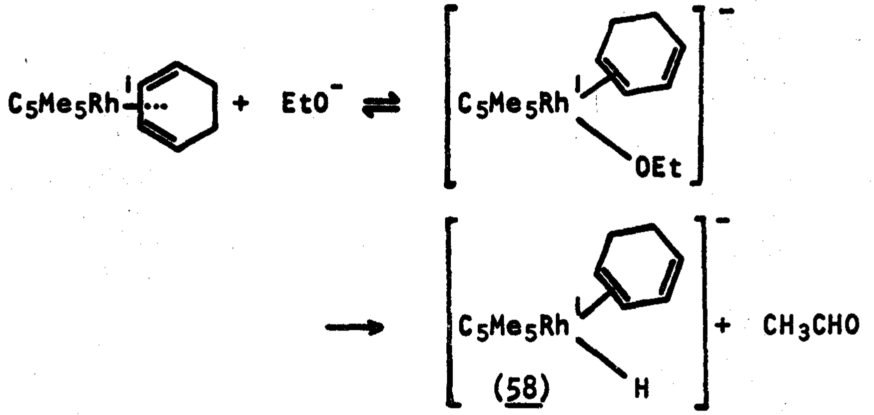
It has long been recognised that disproportionations of this type occur on solid noble metal catalysts[150,151]. Since decomposition of (55a) did not lead to precipitation of metal during these above reactions, a similar heterogeneous rhodium-metal catalysed reaction is not operative here. Lyons[152] has recently reported the homogeneously catalysed disproportionation of 1,4-CHD (but not 1,3-CHD) to benzene and cyclohexane. Of the soluble Ir(I) and Ir(III) complexes used, (Ph$_3$P)$_2$Ir(CO)halide was by far the most active but required much more vigorous conditions than were employed here (80°, 90-180 hr).

A possible mechanism for disproportionation is the direct transfer of two hydrogens from complexed to uncomplexed (or loosely complexed) 1,3-CHD.

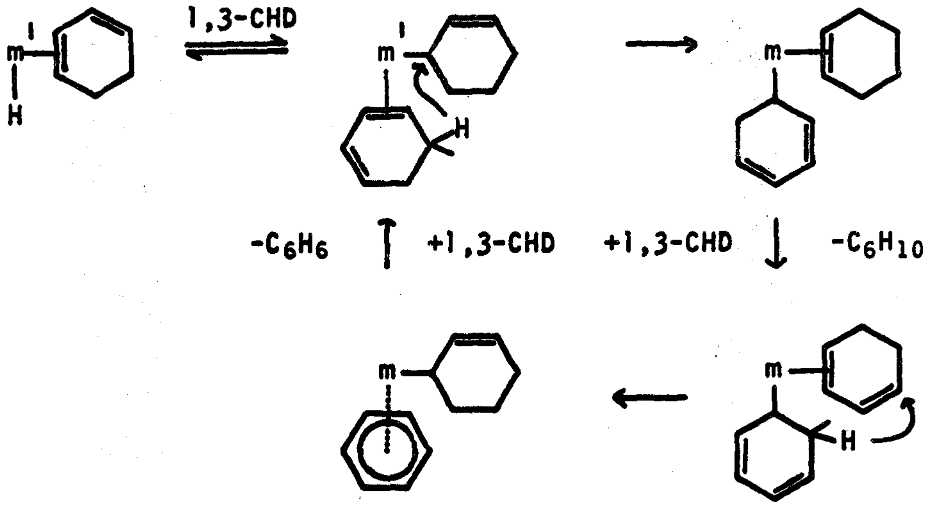


The facile loss of H$_2$ observed in the mass spectrum of (55) lends support for such a mechanism. However, the results of the various studies on the disproportionation reaction (Table 6) clearly indicate that both ethanol and base are essential co-catalysts; this is incompatible with the above mechanism. The detection of trace amounts of acetaldehyde in the ethanol reactions again points to the intermediacy of a rhodium-hydride species.

While there is no conclusive evidence, the most reasonable mechanism involves an anionic hydridic species (58). This is similar to the scheme proposed for the 1,5-cyclooctadiene decomposition to cyclooctene and 1,3- and 1,4-cyclooctadienes by (43).



The following series of reactions ($m = C_5Me_5Rh^-$) may then occur.



In this scheme two C_6 rings are coordinated to the metal and a series of (metal assisted) hydride transfers from one ring to another occurs. No hydrogenation of cyclohexene was observed, probably because it is too weakly complexed and is displaced rapidly on formation by 1,3-CHD. No appreciable reduction of the 1,3-CHD to cyclohexene (other than by disproportionation) was observed and this is readily rationalised by supposing that the various hydride transfers are rapid compared to formation of the hydridic species (58). Thus only a small fraction of the complex (55a) will actually be involved as a catalyst for the disproportionation.

1,4-CHD underwent isomerisation and disproportionation with (55a) under these conditions but very much more slowly. It is likely that this non-conjugated diene only complexes very weakly to the metal. The iridium complex, 1,3-CHDIrC_5Me_5 (55b), did not catalyse these reactions under the same conditions but there was some evidence that isomerisation and disproportionation did occur at higher temperatures (75°).

D. Summary and Conclusions

The pentamethylcyclopentadienyl -rhodium and -iridium chlorides have been shown to be useful probes for the investigation of the mechanisms of a number of reactions involving di- and tri-enes.

These reactions were carried out in ethanol in the presence of base and involve the intermediacy of a metal hydride species. With butadiene, cycloheptatriene, diphenylfulvene and cyclooctadienes, $C_5Me_5RhC\ell(C_4H_7)$, $(C_5Me_5MC_7H_9)^+$, $(C_5Me_5MC_5H_4CHPh_2)^+$ and $C_5Me_5MC\ell(C_8H_{13})$ were formed respectively. With norbornadiene and dicyclopentadiene, $(C_5Me_5RhC\ell_2)_2$ gave $C_5Me_5RhC_7H_8$ and $C_5Me_5RhC_{10}H_{12}$, complexes of rhodium(I). Complexes of both rhodium(I) and iridium(I), $C_5Me_5M(1,3\text{-}C_6H_8)$ and $C_5Me_5M(1,5\text{-}C_8H_{12})$, were also obtained from $(C_5Me_5MC\ell_2)_2$ and cyclohexadienes and cyclooctadienes. The $(C_5Me_5MC\ell_2)_2$ complexes reacted with cyclopentadiene to give $(C_5Me_5MC_5H_5)^+$; in addition the endo-H isomer of $C_5Me_5HRhC_5H_5$ was also formed in the rhodium reactions. Both cations $(C_5Me_5MC_5H_5)^+$ reacted with borohydride to give the exo-H $C_5Me_5HMC_5H_5$ complexes; in the iridium reaction $C_5Me_5IrC_5H_6$ was also formed. The decomposition of all these cyclopentadiene complexes have been studied.

The formation of $C_5Me_5M(1,5\text{-}C_8H_{12})$ was shown to proceed via the π-2-cyclooctenyl complexes $C_5Me_5MC\ell(C_8H_{13})$. During this latter reaction, isomerisation of 1,5- and $1,4\text{-}C_8H_{12}$ to $1,3\text{-}C_8H_{12}$ occurred; some cyclooctene was also formed. The complexes, $C_5Me_5M(1,5\text{-}C_8H_{12})$, were catalysts for the slow isomerisation of 1,5- to $1,3\text{-}C_8H_{12}$; both 1,4-COD and cyclooctene were also formed.

The formation of $C_5Me_5M(1,3\text{-}C_6H_8)$ was accompanied by isomerisation of $1,4\text{-}C_6H_8$ to $1,3\text{-}C_6H_8$. The complex, $C_5Me_5Rh(1,3\text{-}C_6H_8)$, was a catalyst for the disproportionation of 1,3-C_6H_8 to benzene and cyclohexene. This reaction was co-catalysed by ethanol and base.

Mechanisms for these various reactions are proposed: it is concluded that hydridic intermediates are involved in the complexation, isomerisation and disproportionation reactions. The actual processes involved are very complex and small changes, either in conditions or olefin or metal, appear to cause significant changes in products and mechanism. In general, however, the reactions of the rhodium and iridium complexes were very similar, differences presumably reflect differing rates and stability constants.

Mass spectra of many of these complexes and of some others, largely tetramethylcyclobutadiene-metal complexes, prepared by Dr. Bruce, have been determined; tentative interpretations are suggested. This tool is potentially of great use in determining structures of organometallic complexes but care must be exercised in drawing conclusions on the basis of this evidence alone.

EXPERIMENTAL

EXPERIMENTAL

Melting-points: These were determined using a Thomas Hoover capillary melting-point apparatus and are uncorrected.

Molecular weight measurements: These were obtained mass spectroscopically, except where indicated.

Infra-red spectra: These were recorded as potassium bromide discs, or in benzene or chloroform solution, on a Beckman IR5 and a Perkin Elmer 337 grating spectrophotometer.

Nuclear magnetic resonance spectra: These were run on Varian A60, T60 and HA100 spectrometers using tetramethylsilane (TMS) as internal reference. All decoupling experiments were carried out on the HA100 instrument.

Mass spectra: These were taken on a Hitachi-Perkin Elmer RMU-6A spectrometer. The organometallic complexes were introduced by means of a sample injection probe at the minimum temperature which gave adequate vapour pressure.

Vapour phase chromatography: Analyses were performed with a Varian Aerograph 204B instrument, preparations with a Varian Aerograph A90-P3 instrument. 20% Carbowax 20M on 60/70 Chromosorb W analytical (9'6"×1/8") and preparative (10'×1/4") columns were constructed using stainless steel tubing.

Solvents: Reagent grade solvents were used. Petroleum ether refers to the fraction collected over the range 30-60° , the ranges of higher boiling fractions used are indicated where appropriate. For reactions studied by v.p.c., spectroscopically pure solvents were used.

Reagents: 1(1-chloroethyl)(pentamethylcyclopentadiene) was prepared as described by Paquette and Krow[122] and by Criegee and Grüner[123].

All olefins used in the preparation of new complexes were distilled before use. The purity of the cyclooctadienes and cyclohexadienes used were checked; where necessary they were purified by v.p.c.. All these olefins were stored under nitrogen in the cold. 1,4-Cyclooctadiene was prepared using the method of Craig et al.[153], final purification being by preparative v.p.c. on a carbowax column. The product was analysed by v.p.c. and found to be better than 86% pure, approximately 8% of 1,3-cyclooctadiene being present. The p.m.r. spectrum in deuterochloroform showed resonances at τ4.5 (4H,m), 7.22 (2H,m), 7.72 (4H,m) and 8.52 (2H,m) and agreed with that recently reported by Moon and Ganz[154].

$RhC\ell_3 \cdot 3H_2O$ and $IrC\ell_3 \cdot 5H_2O$ were commercial samples supplied by Johnson, Matthey and Mallory.

Experimental Technique: In experiments in which the products were analysed by v.p.c., the volumes of solvent and of olefin were accurately measured out. On completion of the reaction, all solvent and volatile products were distilled from the reaction flask at 10^{-2} mm into liquid nitrogen-cooled traps. All the metal complexes remained behind. The contents of the traps were analysed by v.p.c.. A known volume of solution was injected into the chromatograph; the peaks obtained were compared with authentic samples, both to identify the material in question and to estimate its concentration.

All reactions were carried out under an atmosphere of nitrogen, dried by concentrated sulphuric acid and anhydrous silica gel.

DICHLOROPENTAMETHYLCYCLOPENTADIENYLRHODIUM DIMER (13a)

Reaction of hexamethyldewarbenzene with $RhC\ell_3 \cdot 3H_2O$ in methanol

A mixture of $RhC\ell_3 \cdot 3H_2O$ (4 g.) and hexamethyldewarbenzene (HMDB, 7.0 g.) in methanol (100 ml.) was refluxed, with stirring, under nitrogen for 17 hr. The reaction mixture was filtered while hot and the solid washed, first with a little methanol then thoroughly with ether to remove hexamethylbenzene. The solvent was removed from the filtrate under vacuum giving a deep red oil. A little acetone was added, the solution was cooled in solid CO_2-acetone and filtered to give additional solid which was washed with methanol and ether. The combined solids were recrystallized from chloroform-benzene to give 4.10 g. (87%, based on $RhC\ell_3 \cdot 3H_2O$) of $(C_5Me_5RhC\ell_2)_2$ as dark red crystals, m.p. >230°.

The complex was soluble in chloroform, moderately soluble in methanol, ethanol, methylene chloride and tetrahydrofuran, but insoluble in carbon tetrachloride and hydrocarbons.

This experiment was repeated many times on different scales to determine the volatile products, and the reactions were run both in sealed systems and under a solid CO_2-acetone condenser. In the former, the seals were broken in the inlet system of the mass spectrometer; in the latter, the volatile products were distilled off into a liquid nitrogen-cooled trap, in vacuo, at completion of the reaction and analysed by v.p.c. The mass spectroscopic and analytical v.p.c. studies led to the identification of one major component only, dimethylacetal, and two minor components, methyl chloride and dimethyl ether. These two minor components were also identified as products from the reaction of $RhC\ell_3 \cdot 3H_2O$ with methanol in the absence of HMDB. The dimethylacetal was isolated by preparative v.p.c.; its p.m.r. and mass spectra were identical to those of an authentic sample of dimethylacetal.

The distillate from a reaction in which 2.03 g. $RhC\ell_3 \cdot 3H_2O$, 3 g. HMDB and 20 ml. of methanol were reacted for 24 hr., was analysed quantitatively for the acetal by v.p.c. The distillate was found to contain between 40 and 50 μℓ. dimethylacetal per ml. methanol compared to an expected value of 40 μℓ/ml.

Reaction of $RhC\ell_3 \cdot 3H_2O$ with Hexamethyldewarbenzene in Water

$RhC\ell_3 \cdot 3H_2O$ (500 mg.) and HMDB (1 g.) were added to 15 ml of water in a flask equipped with a nitrogen inlet and a reflux condenser. The outlet of the condenser was connected to two liquid nitrogen-cooled traps to avoid loss of any highly volatile products. A stream of nitrogen was passed through the reaction mixture which was heated to 75° for 10 hr. On completion of the reaction, the outlet of the system was closed and the traps allowed to warm to room temperature. The outlet was then connected via a liquid nitrogen-cooled trap to the vacuum line and the first few ml. of liquid which distilled into the trap collected for v.p.c. analysis.

The solvent was removed from the reaction mixture under reduced pressure. The oily residue was extracted with chloroform and the extracts dried over anhydrous sodium sulfate. The solvent was removed and the residue washed with ether, to remove hexamethylbenzene. Recrystallization of the residue from chloroform-benzene gave 96 mg. (16%) of $(C_5Me_5RhC\ell_2)_2$ as dark red crystals.

V.p.c. analysis of the distillate collected showed the only significant product to be acetaldehyde. This was confirmed by measurement of the p.m.r. and mass spectrum of the material.

Reaction of $RhC\ell_3 \cdot 3H_2O$ with 1-(1-chloroethyl)pentamethylcyclopentadiene in methanol

A mixture of $RhC\ell_3 \cdot 3H_2O$ (1.485 g.) and 1-(1-chloroethyl)pentamethylcyclopentadiene (941 mg.) in 20 ml. of methanol was stirred under nitrogen at 60° for 23 hr. The reaction mixture was worked up as described above to give 1.523 mg. (88%) of $(C_5Me_5RhC\ell_2)_2$ (13a).

Quantitative v.p.c. analysis of the methanol distillate showed approximately 25 $\mu\ell$. dimethylacetal per ml. methanol compared with an expected value of 30 $\mu\ell$./ml.

Reaction of $RhC\ell_3 \cdot 3H_2O$ with 1-(1-chloroethyl)pentamethylcyclopentadiene in water

Hydrogen chloride gas was passed through a solution of HMDB (1.5 g.) in 25 ml. of methylene chloride for 1 hr. The solution was stirred at room temperature for a further 5 hr. when the solvent was removed under reduced pressure affording a brown liquid, crude 1-(1-chloroethyl)-pentamethylcyclopentadiene. A mixture of this together with $RhC\ell_3 \cdot 3H_2O$ (1 g.) in 20 ml. of water was stirred under nitrogen at 85° for 11 hr. with liquid nitrogen-cooled traps connected to the outlet of the apparatus as described above. Two ml. of distillate were collected, at completion of the reaction, for v.p.c. analysis.

The reaction mixture was worked up as above to give 296 mg. (25%) of $(C_5Me_5RhC\ell_2)_2$ (13a).

The aqueous distillate was analysed by v.p.c. The major product was isolated by preparative v.p.c. using a collector immersed in solid CO_2-acetone. The p.m.r. spectrum of this material showed it to be acetaldehyde.

DICHLOROPENTAMETHYLCYCLOPENTADIENYLIRIDIUM DIMER (13b)

Reaction of $IrC\ell_3 \cdot 5H_2O$ with 1-(1-chloroethyl)pentamethylcyclopentadiene in methanol

A mixture of $IrCl_3 \cdot 5H_2O$ (380 mg.) and 1-(1-chloroethyl)pentamethylcyclopentadiene (500 mg.) in methanol (10 ml.) was refluxed under nitrogen for 13 hr. The volatile products were collected by distillation into a liquid nitrogen-cooled trap in vacuo. The remaining solid was washed with methanol and ether and recrystallized from chloroform-benzene to give 243 mg. (62%) of orange crystals of $(C_5Me_5IrCl_2)_2$ (<u>13</u>b), m.p. >230°.

Dimethylacetal was detected in the methanol distillate by analytical v.p.c..

<u>Chlorohydridotriphenylphosphinepentamethylcyclopentadienyliridium (III)</u> (<u>30</u>)

Dichlorotriphenylphosphinepentamethylcyclopentadienyliridium (<u>28</u>b) was obtained in 84% yield from a reaction of $(C_5Me_5IrCl_2)_2$ (<u>13</u>b) (157 mg., 0.197 mmole) with triphenylphosphine (155 mg., 0.592 mmole) in ethanol.

(i) $C_5Me_5IrCl_2PPh_3$ (100 mg., 0.151 mmole) was added to a stirred solution of sodium carbonate (25 mg., 0.236 mmole) in 2 ml. of distilled water and 4 ml. of ethanol. The mixture was heated to 45° under nitrogen for 21 hr. The yellow precipitate was collected, washed with a little ethanol and much water and dried in vacuo over phosphorus pentoxide. This gave 82 mg. (0.131 mmole, 87%) of fine yellow needles of $C_5Me_5IrHCl(PPh_3)$ which showed a strong band (ν_{Ir-H}) at 2090 cm^{-1}, m.p. 223-228° (decomp., 10^{-2} mm).

Analysis. Found: C, 53.31; H, 5.39; Cl, 5.47; P, 4.81%. Calculated for $C_{28}H_{31}ClIrP$: C, 53.70; H, 4.99; Cl, 5.66; P, 4.95%.

It was stable to air in the solid, moderately stable in ethanol but decomposed in benzene (slowly), chloroform and methanol and was therefore difficult to recrystallize.

In deuterochloroform the complex showed the p.m.r. spectrum reported in the results section. When the solution was allowed to stand for one day at room temperature it was observed that the characteristic peaks of (30) disappeared with replacement by those of $C_5Me_5IrC\ell_2PPh_3$ (28b). In addition a triplet appeared at τ4.76 (J(H-D) ca. 1.0 Hz) due to $CHDC\ell_2$.

(ii) $C_5Me_5IrC\ell_2PPh_3$ (150 mg., 0.227 mmole) was also reacted with anhydrous sodium carbonate (100 mg.) in 10 ml. of absolute ethanol at 50° under nitrogen for 60 hr. The reaction mixture was filtered to give 51 mg. (0.082 mmole, 36%) of $C_5Me_5IrHC\ell PPh_3$ (30). The filtrate was taken to dryness and the yellow residue washed with water and vacuum dried to give a further 86 mg. (0.137 mmole, 60%) of crude product (30).

(iii) A suspension of $C_5Me_5IrC\ell_2PPh_3$ (28b) (100 mg., 0.151 mmole) in 5 ml. of absolute ethanol was reacted with triethylamine (24 $\mu\ell$., 0.171 mmole) at 60° under nitrogen for three days. The reaction mixture was filtered and the pale orange precipitate washed with ether giving recovery of 30 mg. (0.045 mmole) of $C_5Me_5IrC\ell_2PPh_3$. The filtrate was taken to dryness, the pale orange residue extracted in deuterochloroform and its p.m.r. spectrum recorded. This showed the presence of triethylamine hydrochloride (ca. 15 mg., 0.11 mmole), $C_5Me_5IrC\ell_2PPh_3$ (ca. 13 mg., 0.020 mmole) and $C_5Me_5IrHC\ell PPh_3$ (ca. 42 mg., 44%).

Chlorodeuteridotriphenylphosphinepentamethylcyclopentadienyliridium (III) (31)

A suspension of $C_5Me_5IrC\ell_2PPh_3$ (50 mg., 0.075 mmole) was reacted with anhydrous sodium carbonate (12 mg., 0.113 mmole) in 0.5 ml. of deuterium oxide and 1 ml. of ethanol-d_6 at 45° under nitrogen for 4.5 hr. The reaction mixture was worked up, as in the corresponding reaction above, to yield 44.4 mg. (0.071 mmole, 94%) of $C_5Me_5IrDC\ell PPh_3$ (31) as pale yellow crystals, ν_{Ir-D} at 1500 cm^{-1}.

Chlorohydridotriphenylphosphinepentamethylcyclopentadienylrhodium(III)

All attempts to prepare this complex by the methods given above afforded dark brown decomposition products which were not characterised.

Chloro(1-methallyl)pentamethylcyclopentadienylrhodium(III) (34)

μ-Dichlorobis(chloropentamethylcyclopentadienylrhodium) (13a) (200 mg., 0.32 mmole) and anhydrous sodium carbonate (220 mg.) in absolute ethanol (25 ml.) were stirred at room temperature while butadiene was passed in a slow stream through the suspension. After 5 hr. the orange solution was filtered and the solvent removed under reduced pressure to leave an orange solid. This was recrystallized from benzene-petroleum ether (b.p. 80-100°) to give chloro(1-methallyl)pentamethylcyclopentadienylrhodium (34) (222 mg., 0.68 mmole, 89%) as orange needles, m.p. 133-135° (decomp.). The analytical sample was sublimed at 110°/10^{-3} mm. Analysis. Found: C, 51.34; H, 6.49; Cℓ, 10.70%; mol. wt. 328, 330. Calculated for $C_{14}H_{22}C\ell Rh$: C, 51.29; H, 6.40; Cℓ, 10.84%; mol. wt. 328, 330.

Solutions of this in methanol or ethanol together with anhydrous sodium carbonate were refluxed, both with and without the passage of butadiene, for periods of up to 1 day. In each case the complex (34) was recovered unchanged.

π-3,5-Cycloheptadienyl(pentamethylcyclopentadienyl)rhodium chloride and

hexafluorophosphate (33a)

A mixture of $(C_5Me_5RhC\ell_2)_2$ (243 mg., 0.40 mmole), anhydrous sodium carbonate (250 mg.) and cycloheptatriene (500 mg., 5.4 mmole) in 40 ml. absolute ethanol was refluxed, with stirring, under nitrogen for 2.5 hr. The yellow solution was filtered, the solvent removed in vacuo and the residue was washed with a little ether to leave a yellow solid. Recrystallization from methylene chloride-petroleum ether (b.p. 80-100°) afforded 236 mg. (0.64 mmole, 77%) of yellow crystals ((33a), X = Cℓ), m.p. 186-189° (decomp.).

Analysis. Found: C, 55.52; H. 6.56; Cℓ, 9.59%. Calculated for $C_{17}H_{24}C\ell Rh$: C, 55.67; H, 6.60; Cℓ, 9.67%.

$(C_5Me_5RhC\ell_2)_2$ (304 mg., 0.49 mmole) was reacted with cycloheptatriene (600 mg., 6.3 mmole) as above to give a crude sample of $[(\pi\text{-}C_7H_9)Rh(C_5Me_5)]C\ell$. This was extracted in 5 ml. water and treated with ammonium hexafluorophosphate to give π-3,5-cycloheptadienyl(pentamethylcyclopentadienyl)rhodium hexafluorophosphate, as bright yellow needles, after crystallization from chloroform-benzene, m.p. >260°.

Analysis. Found: C, 42.94; H, 4.97%. Calculated for $C_{17}H_{24}F_6PRh$: C, 42.88; H. 5.04%.

π-3,5-Cycloheptadienyl(pentamethylcyclopentadienyl)iridium hexafluorophosphate (33b)

This salt was obtained in virtually quantitative yield by reaction of $(C_5Me_5IrC\ell_2)_2$ with cycloheptatriene and sodium carbonate in ethanol at 50° for 1 hr. Treatment of the crude chloride salt with ammonium hexafluorophosphate, as described above, gave the white crystalline solid (33b), m.p. >200°.

Analysis. Found: C, 36.22; H, 4.04%. Calculated for $C_{17}H_{24}IrF_6P$: C, 36.12; H, 4.24%.

1,1-Diphenylmethylcyclopentadienyl(pentamethylcyclopentadienyl)rhodium hexafluorophosphate (32a)

A mixture of $(C_5Me_5RhC\ell_2)_2$ (120 mg., 0.20 mmole), anhydrous sodium carbonate (100 mg.) and 6,6-diphenylfulvene (211 mg., 0.96 mmole) in absolute ethanol (15 ml.) was stirred under nitrogen at reflux temperature for 2.5 hr. The deep red solution was filtered, the solvent removed in vacuo and the oily residue washed with ether. This was then dissolved in water (5 ml.) and the solution filtered to give a cloudy dark orange solution. Warming and addition of excess solid ammonium hexafluorophosphate immediately gave a thick pink precipitate. This was collected by filtration, washed with a little water and dried in vacuo to give 1,1-diphenylmethylcyclopentadienyl(pentamethylcyclopentadienyl)-rhodium hexafluorophosphate from hot ethanol gave pale brown crystals, m.p. 99° (decomp.).

Analysis. Found: C, 55.66; H, 4.92%. Calculated for $C_{28}H_{30}F_6PRh$: C, 54.75; H, 4.89%.

The product was readily soluble in acetone and ethanol but only moderately so in chloroform.

1,1-Diphenylmethylcyclopentadienyl(pentamethylcyclopentadienyl)iridium hexafluorophosphate (32b)

This complex was prepared from $(C_5Me_5IrC\ell_2)_2$ (84%) in the identical manner to that used for (32a). Recrystallization was similarly from hot ethanol affording fine cream crystals, m.p. 244° (decomp.).

Analysis. Found: C, 47.89; H, 4.58%. Calculated for $C_{28}H_{30}F_6IrP$: C, 47.80; H, 4.27%.

π-Bicylo[2.2.1]heptadiene(pentamethylcyclopentadienyl)rhodium(I) (35)

To a suspension of $(C_5Me_5RhC\ell_2)_2$ (400 mg., 0.64 mmole) and anhydrous sodium carbonate (400 mg.) in absolute ethanol (40 ml.) was added nor-bornadiene (bicyclo[2.2.1]heptadiene, 900 mg., 9.8 mmole). The reaction mixture was refluxed with stirring under nitrogen for 24 hr. The orange solution was allowed to cool, filtered and the solvent removed under reduced pressure giving a mixture of yellow crystals and a red oil. Extraction of this with ether and filtration gave a pale orange solution and unreacted $(C_5Me_5RhC\ell_2)_2$ (35 mg., 0.06 mmole). The ether solution was evaporated to dryness to leave a pale orange solid which, after crystallization from petroleum ether at -78° gave yellow crystals of π-bicyclo[2.2.1]heptadiene(pentamethylcyclopentadienyl)-rhodium (35) (180 mg., 0.55 mmole, 42%), m.p. 120-128° (decomp.).

This compound was very soluble in organic solvents and could be sublimed at $45°/10^{-3}$ mm.

Analysis. Found: C, 62.44; H, 6.96%; mol. wt. 330. Calculated for $C_{17}H_{23}Rh$: C, 61.82; H, 7.02%; mol. wt. 330.

Dicyclopentadiene(pentamethylcyclopentadienyl)rhodium(I) (36)

$(C_5Me_5RhC\ell_2)_2$ (250 mg., 0.47 mmole) was reacted with dicyclopentadiene (500 mg., 3.8 mmole) in refluxing absolute ethanol (30 ml.) in the presence of anhydrous sodium carbonate (250 mg.) for 3.5 hr. The reaction mixture was worked up as described above to give 263 mg. (0.71 mmole, 75%) of yellow crystals of (36), m.p. 116-118° (decomp.). This could be sublimed at 50°/10^{-3} mm.

Analysis. Found: C, 64.83; H, 7.22%; mol. wt. 370. Calculated for $C_{20}H_{27}Rh$: C, 64.86; H, 7.30%; mol. wt. 370.

Reaction of μ-dichlorobis(pentamethylcyclopentadienyl)rhodium(13a) with cyclopentadiene

a. In ethanol

A suspension of $(C_5Me_5RhC\ell_2)_2$ (400 mg., 0.64 mmole) and anhydrous sodium carbonate (400 mg.) in absolute ethanol (75 ml.) was stirred at 45° under nitrogen. An excess of freshly cracked cyclopentadiene (1 g.) was slowly added while the mixture was heated to 60° for 2 hr, after which the solution was cooled and filtered to give a pale yellow filtrate and a pale brown solid. The yellow solution was taken to dryness under reduced pressure and the yellow residue extracted with ether. Filtration of this gave a cream solid and a yellow filtrate. Removal of the solvent from the filtrate afforded yellow crystals which were recrystallized from petroleum ether at -78° to give endo-H pentamethylcyclopentadiene(cyclopentadienyl)rhodium(37) (250 mg., 0.82 mmole, 54%), m.p. 80-82°. This complex was very soluble in organic solvents and unstable to air in the solid state. The analytical sample was sublimed at 25°/10^{-3} mm.

Analysis. Found: C, 59.12; H, 6.80%; mol. wt. 304. Calculated for $C_{15}H_{21}Rh$: C, 59.22; H, 6.96%; mol. wt. 304.

The cream solids obtained from filtration of ethanol and ether solutions above, were washed with ether and crystallized from methylene chloride-benzene. This afforded cyclopentadienyl(pentamethylcyclopentadienyl)rhodium chloride ((38a)X = Cℓ) (85 mg., 19%) as cream crystals. This was converted into the hexafluorophosphate ((38a)X = PF_6) with aqueous ammonium hexafluorophosphate, m.p. 270°.

Analysis. Found: C, 40.34; H, 4.51%. Calculated for $C_{15}H_{20}F_6PRh$: C, 40.21; H, 4.69%.

b. In tetrahydrofuran

A suspension of $(C_5Me_5RhC\ell_2)_2$ (304 mg., 0.49 mmole) and sodium carbonate (300 mg.) in THF (100 ml.) and water (20 ml.) was warmed to 40° under nitrogen. An excess (2 g.) of freshly cracked cyclopentadiene was added in portions to the stirred mixture which was heated to 50° for 21 hr. The pale brown solution was filtered and the mixed solvent removed under vacuum. The residue was crystallized from chloroform-benzene to give cyclopentadienyl(pentamethylcyclopentadienyl)rhodium chloride ((38a)X = Cℓ) (250 mg., 0.74 mmole, 76%), identical to that prepared above. It was also converted into the hexafluorophosphate salt.

The product ((38a)X = PF_6) was insoluble in cold or hot water, chloroform and benzene, moderately soluble in acetone and methylene chloride and very soluble in pyridine.

Exo-H pentamethylcyclopentadiene(cyclopentadienyl)rhodium(I) (39a)

Sodium borohydride (total amount, 800 mg.) was added in portions over 36 hr. to a well-stirred solution of $[(\pi C_5H_5)Rh(C_5Me_5)]C\ell$ ((38a) X = Cℓ) (100 mg., 0.29 mmole) in a mixture of water (5 ml.) and benzene (10 ml.) at room temperature. The bright yellow benzene layer was then separated and the aqueous layer washed with successive portions of benzene. All the benzene fractions were combined and the solvent removed under reduced pressure. Extraction of the yellow crystalline residue by ether followed by filtration and removal of the solvent gave exo-H pentamethylcyclopentadiene(cyclopentadienyl)rhodium(39a) (84 mg., 0.28 mmole, 93%), m.p. 106-107° (decomp.). The analytical sample was sublimed at 25°/10^{-3}mm. Analysis. Found: C, 58.76; H, 6.91%; mol. wt. 304. Calculated for $C_{15}H_{21}Rh$: C, 59.22; H, 6.91%; mol. wt. 304.

This complex was stable to air in the solid but decomposed rapidly in halogen-containing solvents.

Reaction of exo-H Pentamethylcyclopentadiene(cyclopentadienyl)rhodium(39a) with Halogenating Agents

a. With $CDC\ell_3$

In deuterochloroform the complex (39a) showed the p.m.r. spectrum reported in the results, immediately after making up the solution. When the solution was allowed to stand, a change occurred quite rapidly with the disappearance of the peaks characteristic of (39a) and their replacement by those of the pentamethylrhodicenium chloride ((38a)X= $C\ell$). The reaction involved was effectively complete after 5 hr. (40°). In addition a triplet appeared at τ4.63 (J(H-D) 1 Hz), due to $CHDC\ell_2$.

b. With N-Bromosuccinimide

A freshly sublimed sample of exo-H(C_5Me_5H)Rh(C_5H_5) (39a) (33 mg., 0.11 mmole) was dissolved in methanol (3 ml.) and petroleum ether (1 ml.). To this stirred solution was added excess ammonium hexafluorophosphate (50 mg.) and N-bromosuccinimide (50 mg., 0.28 mmole). A pale brown precipitate appeared immediately which was collected by filtration, washed with a little water and methanol and dried in vacuo. This material (25 mg., 0.06 mmole, 51%) was identical to a sample of pentamethylrhodicenium hexafluorophosphate ((38a)X = PF_6).

Reaction of endo-H Pentamethylcyclopentadiene(cyclopentadienyl)rhodium

(37) with N-Bromosuccinimide, Chlorine and Hydrogen chloride

N-Bromosuccinimide (120 mg., 0.67 mmole) was slowly added to a stirred solution of endo-H $(C_5Me_5H)Rh(C_5H_5)$ (37) in petroleum ether (4 ml.) and methanol (2 ml.). A deep red precipitate (86 mg., a mixture of $C_5Me_5RhBr_2$ (41) and $C_5H_5RhBr_2$ (42)) formed immediately and was collected by filtration, washed with ether and dried.

This red solid (84 mg.), sodium carbonate (80 mg.) and 1,5-cyclooctadiene (224 mg., 0.21 mmole) were refluxed in ethanol (20 ml.) for 2 hr. The resultant pale yellow solution was cooled, and all the solvent removed in vacuo to leave a pale yellow solid. The p.m.r. spectrum of this in $CDC\ell_3$ was run and compared with the spectra of authentic samples of the two 1,5-cyclooctadiene complexes, $C_5Me_5Rh(1,5\text{-COD})$ (43a) and $C_5H_5Rh(1,5\text{-COD})$ (44). By integration it was established that the yellow solid contained approximately 55% (43a) and 45% (44).

In a similar manner to N-bromosuccinimide, chlorine and hydrogen chloride reacted with (37) to afford, in these cases, the dichlororhodium complexes $C_5Me_5RhC\ell_2$ (13a) and $C_5H_5RhC\ell_2$ (6).

Cyclopentadienyl(pentamethylcyclopentadienyl)iridium hexafluorophosphate (38b)

A mixture of $(C_5Me_5IrC\ell_2)_2$ (215 mg., 0.27 mmole), anhydrous sodium carbonate (200 mg.) and absolute ethanol (75 ml.) was stirred under nitrogen at 40°. An excess (1 g.) of freshly distilled cyclopentadiene was slowly added to the mixture which was heated at 50° for 1.5 hr. The pale yellow solution was filtered and the solvent removed under reduced pressure to give a yellow oily solid. Washing with ether and recrystallization from methylene chloride-benzene afforded hygroscopic cream crystals of cyclopentadienyl(pentamethylcyclopentadienyl)iridium chloride ((38b)X = Cℓ).

These were dissolved in water and converted to the hexafluorophosphate salt ((38b)X = PF_6) (255 mg., 0.48 mmole, 88%), a white crystalline material, m.p. >260°.

Analysis. Found: C, 33.76; H, 3.46%. Calculated for $C_{15}H_{20}F_6IrP$: C, 33.53; H, 3.72%.

Reaction of Cyclopentadienyl(pentamethylcyclopentadienyl)iridium chloride (38b) with Sodium Borohydride

Benzene (15 ml.) was added to a solution of $[(C_5Me_5)Ir(C_5H_5)]C\ell$ (38b) (110 mg., 0.26 mmole) in water (5 ml.) and the mixture stirred at room temperature under nitrogen. Excess sodium borohydride was then added in portions over a period of 48 hr. The reaction mixture was worked up in the same manner as described for the exo-H rhodium complex (39a) to give 82 mg. (0.21 mmole, 81%) of white crystals of the product, m.p. 91-97° (decomp.); presumably a mixture of the complexes exo-H pentamethylcyclopentadiene(cyclopentadienyl)iridium (39b) and cyclopentadiene(pentamethylcyclopentadienyl)iridium (45b), were obtained. The mixture was sublimed at 25°/10^{-3} mm.

Analysis. Found: C, 44.51; H, 5.12%; mol. wt. 392, 394. Calculated for $C_{15}H_{21}Ir$: C, 45.79; H, 5.38%; mol. wt. 392, 394.

The product in deuterochloroform showed the p.m.r. spectrum discussed in the results, immediately after making up the solution. This altered rapidly (1 hr at 40°) and was replaced by that of cyclopentadienyl(pentamethylcyclopentadienyl)iridium chloride ((38b)X = Cℓ) showing singlets at τ4.18 (5H) and 7.68 (15H). In addition, a small triplet, due to $CHDC\ell_2$ at τ4.68 (J(H-D) 1 Hz) was observed.

The mixture of sublimed iridium complexes, (39b) and (45), (34 mg., 0.08 mmole) was reacted with N-bromosuccinimide in methanol and petroleum ether in the presence of ammonium hexafluorophosphate as already described. This gave cyclopentadienyl(pentamethylcyclopentadienyl)iridium hexafluorophosphate ((38b)X = PF_6) (28 mg., 0.05 mmole, 62%) identified by its p.m.r. spectrum.

1,5-Cyclooctadiene(pentamethylcyclopentadienyl)rhodium(I) (43a)

Method A

A mixture of $(C_5Me_5RhC\ell_2)_2$ (200 mg., 0.33 mmole) anhydrous sodium carbonate (200 mg.) and 1,5-cyclooctadiene (352 mg., 3.3 mmole) in absolute ethanol (5 ml.) was stirred at 70° under nitrogen for 3 hr. The reaction mixture was allowed to cool and the volatile products distilled off in vacuo. The yellow residue was crystallized from ether at -78° to give the 1,5-cyclooctadienerhodium complex (43a) (183 mg., 0.53 mmole, 80%), m.p. 160-163°. The analytical sample was sublimed at 60-70°/10^{-3} mm.

Analysis. Found: C, 61.97; H, 7.79%; mol. wt. 346. Calculated for $C_{18}H_{27}Rh$: C, 62.42; H, 7.86; mol. wt. 346.

Treatment of this with $HC\ell$ under a variety of conditions always regenerated the dichloro-complex (13a).

Method B

This complex was obtained in identical fashion using 1,3-COD (66% yield of recrystallized product) or 1,4-COD (92% yield) in place of 1,5-COD. The products were identified by their p.m.r. spectra as well as by m.p.

Method C

The 1,5-cyclooctadienerhodium complex (43a) was also obtained in good yield (ca. 90%) from reactions of 1,5- and 1,3-COD with dichloro-(triphenylphosphine)pentamethylcyclopentadienylrhodium (29a) under similar conditions. A reaction time of 9 hr. was required here.

1,5-Cyclooctadiene(pentamethylcyclopentadienyl)iridium(I) (43b)

This was obtained as a white crystalline solid in an identical fashion from the dichloro-iridium complex (13b) and 1,5-COD (73% yield) or 1,3-COD (85% yield), m.p. 163-166°. The product was sublimed at 70-75°/10^{-3} mm.

Analysis. Found: C, 50.22; H, 6.39%; mol. wt. 434, 436. Calculated for $C_{18}H_{27}Ir$: C, 49.63; H, 6.25%; mol. wt. 434, 436.

This 1,5-cyclooctadieneiridium complex (43b) was also prepared from dichloro(triphenylphosphine)pentamethylcyclopentadienyliridium (28b) and 1,5- or 1,3-COD under similar conditions. A good yield of (43b) (>60%) was only obtained after 2 days at 60°. The crude product from a reaction of (28b) with 1,5-COD at 60° for 9 hr was shown, by its p.m.r. spectrum, to contain (43b) (ca. 45%) together with some chlorohydrido-(triphenylphosphine)pentamethylcyclopentadienyliridium (30) (ca. 30%).

Chloro-(π-2-cyclooctenyl)(pentamethylcyclopentadienyl)rhodium(III) (46a)

Method A

1,3-Cyclooctadiene (399 mg., 3.7 mmole) was added to a suspension of $(C_5Me_5RhC\ell_2)_2$ (215 mg., 0.35 mmole) and anhydrous sodium carbonate (210 mg.) in absolute ethanol (5 ml.) and the mixture was stirred at 42° for 2 hr. The volatile components were distilled off in vacuo and the deep red residue extracted with ether. The ether solution was filtered and the solvent removed to give the deep red, crystalline π-2-cyclooctenyl complex (46a) (260 mg., 0.67 mmole, 96%), which was recrystallized from n-hexane; decomp., without melting, ca. 127°. Analysis. Found: C, 56.71; H, 7.26; Cℓ, 9.23%; mol. wt. 423 (osmometric in chloroform). Calculated for $C_{18}H_{28}RhC\ell$: C, 56.49; H, 7.37; Cℓ, 9.26%; mol. wt. 383.

The product was very soluble in chloroform and benzene and moderately so in petroleum ether, ether and n-hexane . It was stable to air both in the solid state and in solution.

On treatment with hydrogen chloride in benzene, this complex decomposed to the dichloride (13a) and cyclooctene (observation by Dr. C. White).

Method B

The identical complex was obtained from 1,3-COD (98%) and 1,4-COD (96%) when these olefins were reacted with (13a) under the above conditions.

Method C

(46a) was also obtained in high yield (80%) from both 1,3- and 1,5-COD and (13a) in the presence of triethylamine as base. Triethylamine hydrochloride was also detected by p.m.r. spectroscopy.

Chloro-(π-2-cyclooctenyl)(pentamethylcyclopentadienyl)iridium(III) (46b)

A mixture of $(C_5Me_5IrC\ell_2)_2$ (199 mg., 0.25 mmole), anhydrous sodium carbonate (200 mg.) and 1,3-cyclooctadiene (342 mg., 3.16 mmole) in absolute ethanol (5 ml.) was stirred under nitrogen for 1 hr. at room temperature. The dark yellow reaction mixture was worked up as in the corresponding reaction with the rhodium complex to give a quantitative yield (242 mg., 0.51 mmole) of a pure yellow crystalline solid (46b). After recrystallization from n-hexane, it decomposed at ca. 95° without melting.

Analysis. Found: C, 46.25; H, 5.96; Cℓ, 7.53%; mol. wt. 532 (osmometric in chloroform). Calculated for $C_{18}H_{28}C\ell Ir$: C, 45.81; H, 5.97; Cℓ, 7.51%; mol. wt. 472.

The properties of the product were similar to those of the analogous rhodium complex above.

The identical complex was obtained in quantitative yield from 1,5-COD when this olefin was reacted with (13b) under the above conditions.

It was also obtained in 88% yield from 1,5-COD and (13b) in ethanol (50°/3 hr) in the presence of triethylamine.

V.p.c. Analysis on the By-products from the Cyclooctadiene Reactions

The organic products from the reactions to be described were analysed by v.p.c. for cyclooctadienes, cyclooctene, diethylacetal and acetaldehyde. Analyses were performed using a 9'6" × 1/8" stainless steel column packed with 20% Carbowax 20 M on 60/70 Chromosorb W at 110°.

A. Reaction of dichloro(pentamethylcyclopentadienyl)-rhodium (13b) and -iridium (13b) dimer with cyclooctadienes

(i) Under vigorous conditions [(13) → (43)]

The reactions between $(C_5Me_5MC\ell_2)_2$ and 1,3- (M = Rh, Ir), 1,4- (M = Rh) and 1,5-COD (M = Rh, Ir) in ethanol in the presence of sodium carbonate at 60-70° (M = Rh) or 55-65° (M = Ir), which have been previously described, were repeated on several different scales. In each case the mother liquors at the end of the reaction were collected and quantitatively analysed by v.p.c. Results from these experiments are summarised in Table 2.

Detailed Reaction Study

(a) With 1,5-COD

Absolute ethanol (10 ml.) was pipetted into a 50 ml. 3-necked flask equipped with a butyl rubber stopper and a condenser; freshly-distilled 1,5-COD (200 µℓ, 1.6 mmole) was added and the solution stirred.

A sample (0.2 ml.) of this solution was removed with a syringe and used as reference sample for the v.p.c. analysis. $(C_5Me_5RhC\ell_2)_2$ (308 mg., 0.50 mmole) and anhydrous sodium carbonate (300 mg.) were added and the flask was thoroughly purged with dry nitrogen. The flask was then immersed in an oil bath at 65° and the contents stirred. Aliquots (0.5 ml.) were removed at intervals with a syringe via the butyl rubber seal, and distilled into liquid nitrogen-cooled traps in vacuo. The solids remaining were taken up in $CDC\ell_3$ and analysed by p.m.r.; the volatile materials were analysed by v.p.c. as previously described. The results are presented in Figure XI .

(b) With 1,3-COD

This was carried out in a manner similar to the above using $(C_5Me_5RhC\ell_2)_2$ (300 mg., 0.49 mmole) and 1,3-cyclooctadiene (250 µℓ., 2.01 mmole), (Figure X).

(ii) Under mild conditions [(13) → (46)]

The reactions of $(C_5Me_5MC\ell_2)_2$ with 1,5- (M = Rh, Ir), 1,4- (M = Rh) and 1,3-COD (M = Rh, Ir) were carried out in absolute ethanol in the presence of sodium carbonate at 40-45° (M = Rh) or 25° (M = Ir) to give the π-2-cyclooctenyl complexes (46a) and (46b). In each case the volatile products were collected and analysed quantitatively using v.p.c.

The results of some of these are presented in Table 2.

B. The Decomposition of the π-2-Cyclooctenylrhodium(III) Complex (46a)

A summary of these reactions is presented in Table 3.

(i) In ethanol in the presence of base and cyclooctadiene

A mixture of $\pi\text{-}C_8H_{13}RhC\ell(C_5Me_5)$ (46a) (75 mg., 0.20 mmole), anhydrous sodium carbonate (70 mg.) and 1,5-cyclooctadiene (40 $\mu\ell$., 0.33 mmole) in absolute ethanol (2 ml.) was heated at 60° for 5 hr under nitrogen. The volatile products were collected and analysed by v.p.c. Appreciable isomerisation of 1,5- to 1,3-COD was observed together with a little cyclooctene. The yellow residue was extracted with ether to give 63 mg. (0.18 mmole, 92%) of yellow crystals of $(1,5\text{-}COD)Rh(C_5Me_5)$ (43a).

A similar experiment, under milder conditions (50°/2 hr), resulted in recovery of ca. 81% of (46a) together with ca. 19% of (43a); no appreciable amount of isomerisation of the free diene was observed in this case.

(ii) In ethanol in the presence of base

A representative example of this was the reaction of $(\pi\text{-}C_8H_{13})RhC\ell(C_5Me_5)$ (46a) (159 mg., 0.42 mmole) with anhydrous sodium carbonate (150 mg.) in absolute ethanol (3 ml.) at 60° for 22 hr under nitrogen. The mother liquor was distilled off and analysed by v.p.c. This showed the presence of cyclooctene and a little 1,3-COD. The solid residue was extracted with ether to give, after filtration and removal of solvent, a purple solid (117 mg.). This was sublimed at 60-70°/10^{-3} mm, to give a sublimate of yellow crystals of the 1,5-COD-rhodium complex

(43a) (92 mg., 64%) and leaving a purple involatile residue (50) (27 mg.). Analysis. Found: C, 50.26; H, 6.16%. Calculated for $C_{10}H_{15}Rh$: C, 50.44; H, 6.34%.

A similar decomposition of (46a) (50 mg., 0.13 mmole) in absolute ethanol (2 ml.) in the presence of triethylamine (21 $\mu\ell$., 0.15 mmole) at 73° under nitrogen for 13 hr gave a purple solution. Cyclooctene was again the major volatile product together with a little 1,3-COD. Extraction of the purple residue with ether gave a pale brown ether insoluble solid (28 mg.) identified by its p.m.r. spectrum as $(C_5Me_5RhC\ell_2)_2$ (ca. 11 mg., 0.035 mmole, 27%) and triethylamine hydrochloride (ca. 17 mg., 0.12 mmole, 80%). The purple, ether-soluble, material was comprised of (1,5-COD)Rh-(C_5Me_5) (43a) (ca. 30 mg., 0.087 mmole, 67%) and C_5Me_5Rh (50) (ca. 4 mg.).

(iii) In ethanol in the absence of base

A solution of π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) (50 mg., 0.13 mmole) and 1,5-COD (100 $\mu\ell$., 0.82 mmole) in absolute ethanol (2 ml.) was heated at 70° under nitrogen for 9 hr. The only organic products were 1,5-COD (recovered) and trace amounts of 1,3-COD and cyclooctene. The orange organometallic residue (38 mg.) was extracted with deuterochloroform and its p.m.r. spectrum recorded. This comprised an approximately equimolar mixture of $(C_5Me_5RhC\ell_2)_2$ (13a) (0.058 mmole, 44%) and (1,5-COD)Rh(C_5Me_5) (43a) (0.058 mmole, 44%).

(iv) In benzene solution both with and without base

A solution of π-$C_8H_{13}RhC\ell(C_5Me_5)$ (46a) (77 mg., 0.202 mmole) in benzene (2 ml.) was stirred at reflux under nitrogen for 8 hr. The volatile organic product contained 1,3-COD together with a smaller amount of cyclooctene. The reddish-brown residue was extracted, first with ether, then benzene, to leave $(C_5Me_5RhC\ell_2)_2$ (14 mg., 0.023 mmole, 23%). The extracts were each filtered and the solvents removed under reduced pressure. P.m.r. spectral studies on the products showed them to contain (1,5-COD)Rh(C_5Me_5) (ca. 29 mg., 0.084 mmole, 42%), $(C_5Me_5RhC\ell_2)_2$ (ca. 13 mg., 0.021 mmole, 20%) and some unreacted starting material (<u>46</u>a) (ca. 11 mg., 0.03 mmole).

The complex (<u>46</u>a) (75 mg., 0.196 mmole) was reacted with triethylamine (23 μℓ., 0.163 mmole) in benzene (2 ml.) in a manner similar to the above. The reaction mixture was worked up also as above with very similar results.

A solution of (<u>46</u>a) (49 mg., 0.13 mmole) and pyridine (11 μℓ., 0.14 mmole) in benzene (1 ml.) was stirred at reflux under nitrogen for 6 hr. The reaction mixture was filtered and the dark yellow precipitate washed with benzene and ether and dried to yield 24 mg. (0.062 mmole, 48%) of $C_5Me_5RhC\ell_2py$. The filtrate contained effectively pure (1,5-COD)Rh(C_5Me_5) (<u>43</u>a).

(v) <u>In petroleum ether (b.p. 80-100°) both with and without base</u>

A solution of π-$C_8H_{13}RhC\ell(C_5Me_5)$ (<u>46</u>a) (85 mg., 0.222 mmole) in petroleum ether (80-100°) (3 ml.) was stirred at a bath temperature of 90° under nitrogen for 3.5 hr. The volatile products were distilled off, analysed quantitatively by v.p.c. and found to contain 1,3-COD together with a smaller amount of cyclooctene. The dark orange residue was extracted with ether; the extract contained (1,5-COD)Rh(C_5Me_5) (<u>43</u>a) (ca. 21 mg., 0.06 mmole, 30%) and a little unreacted starting material. The ether-insoluble material (69 mg.) was a glassy red substance whose p.m.r. spectrum showed it to be a mixture of $(C_5Me_5RhC\ell_2)_2$ and an unidentified (polymeric) material.

The reaction of (46a) (100 mg., 0.262 mmole) with triethylamine (40 μℓ., 0.277 mmole) in petroleum ether (80-100°) (3 ml.) was carried out in an identical manner to the above, with very similar results.

(vi) In the solid state, in vacuo

The π-2-cyclooctenylrhodium complex (46a) (101 mg., 0.288 mmole) was heated at $110°/10^{-3}$ mm for 8 hr and the volatile products collected in a liquid nitrogen-cooled trap. The volatile material was shown by p.m.r. spectrum and v.p.c. analysis to be mainly cyclooctene together with a little 1,3-COD. The solid residue was washed with ether to leave a dark brown solid, shown to be $(C_5Me_5RhC\ell_2)_2$ (39 mg., 0.063 mmole, 44%) together with a small amount of uncharacterised (polymeric) material. The ethereal solution was taken to dryness to leave yellow crystals of the π-1,5-COD rhodium complex (43a) (39 mg., 0.113 mmole, 40%).

C. The Decomposition of the π-2-Cyclooctenyliridium complex (46b)

A summary of these reactions is presented in Table 4.

(i) In ethanol in the presence of base

A mixture of π-$C_8H_{13}IrC\ell(C_5Me_5)$ (46b) (54 mg., 0.114 mmole) and anhydrous sodium carbonate (50 mg.) in absolute ethanol (2 ml.) was stirred at 65° under nitrogen for 4.5 hr. The mother liquor was distilled off; v.p.c. analysis showed only trace quantities of cyclooctene and 1,3-COD. The white residue was extracted with ether, filtration and removal of the solvent gave a quantitative amount of (1,5-COD)$Ir(C_5Me_5)$ (43b) (51 mg., 0.116 mmole).

The complex (46b) (50 mg., 0.106 mmole) was reacted with triethylamine (16 μℓ., 0.110 mmole) in absolute ethanol (2 ml.) at 60° under nitrogen for 21 hr. The white crystals which had separated out of solution were filtered off and dried to yield (1,5-COD)Ir(C_5Me_5) (43b) (10 mg., 0.023 mmole, 22%). The solvent was removed from the filtrate under reduced pressure; extraction of the residue with ether afforded an additional amount of (43b) (38 mg., 0.087 mmole, 82%). Triethylamine hydrochloride (16 mg., 0.116 mmole) was obtained as pale yellow, ether-insoluble, crystals.

(ii) In benzene both with and without base

Triethylamine (16 μℓ., 0.110 mmole) was added to a solution of π-$C_8H_{13}IrC\ell(C_5Me_5)$ (46b) (50 mg., 0.106 mmole) in benzene (2 ml.). This was stirred at 75° under nitrogen for 18 hr. The pale orange crystals which separated out of solution were collected, washed with ether and the p.m.r. spectrum recorded. This showed the presence of $(C_5Me_5IrC\ell_2)_2$ (ca. 4.2 mg., 0.005 mmole) and triethylamine hydrochloride (ca. 3.8 mg., 0.028 mmole). The filtrate from the reaction mixture was taken to dryness in vacuo and the pale orange residue extracted with deuterochloroform and its p.m.r. spectrum recorded. This showed (1,5-COD)Ir(C_5Me_5) (43b) (ca. 37 mg., 0.085 mmole, 74%), $(C_5Me_5IrC\ell_2)_2$ (ca. 7.3 mg., 0.009 mmole) and a trace (1-2 mg.) of unreacted starting material.

A solution of (46b) (102 mg., 0.22 mmole) in benzene (2 ml.) was refluxed under nitrogen for 19 hr. The volatile material was collected by distillation in vacuo; analysis by v.p.c. showed the presence of cyclooctene and only a trace of 1,3-COD. The orange residue was taken up in deuterochloroform and its p.m.r. spectrum recorded. This showed the presence of approximately equimolar amounts of $(C_5Me_5IrC\ell_2)_2$ and (1,5-COD)Ir(C_5Me_5).

(iii) In the solid state in vacuo

The complex π-$C_8H_{13}IrC\ell(C_5Me_5)$ (53 mg., 0.112 mmole) was heated at 95°/10^{-3} mm for 5 hr and the volatile product collected in a liquid nitrogen trap. The solid reaction products were worked up as in the corresponding reaction of the rhodium analogue to yield (1,5-COD)Ir(C_5Me_5) (28 mg., 0.064 mmole, 56%) and $(C_5Me_5IrC\ell_2)_2$ (21 mg., 0.026 mmole, 46%). The volatile product was shown by p.m.r. spectrum and v.p.c. to be cyclooctene.

D. Deuteration Studies

All apparatus and anhydrous sodium carbonate used were carefully dried in vacuo. 1,3-COD (100 μℓ., 0.82 mmole) was added to a suspension of the dichlororhodium complex (13a) (60 mg., 0.10 mmole) and anhydrous sodium carbonate (60 mg.) in ethanol-d_6 (1 ml.), and the mixture stirred at 45° for 3 hr. The product (A) was worked up as described previously to yield the deuterated π-2-cyclooctenylrhodium complex (46a), (45 mg., 61% after crystallization from n-hexane).

Samples (20 mg.) of this material (A) were heated in ethanol-d_0 in the presence of 1,3- and 1,5-COD and anhydrous sodium carbonate and the π-1,5-COD-rhodium complex (43a) obtained in the usual manner.

Another sample (30 mg.) of this material (A) was decomposed in vacuo to give the π-1,5-COD-rhodium complex (43a).

A sample (B) of deuterated π-2-cyclooctenylrhodium was also prepared from a reaction of the dichlororhodium complex (13a) with 1,5-COD in ethanol-d_6 in the normal manner.

Samples (20 mg.) of this material (B) were heated in ethanol-d_0 in the presence of 1,3- and 1,5-COD and anhydrous sodium carbonate and the 1,5-COD-rhodium complexes (43a) obtained in the normal way.

1,3-COD (100 μℓ., 0.82 mmole) was added to a suspension of $(C_5Me_5RhC\ell_2)_2$ (69 mg., 0.11 mmole) and anhydrous sodium carbonate (60 mg.) in ethanol-d_6 and the mixture was stirred under nitrogen for 6 hr at 60°. The deuterated 1,5-COD-rhodium complex (43a) (51 mg., 69%, after purification by sublimation) was isolated in the manner described previously.

These samples of (43a) were each purified by sublimation and analysed mass spectroscopically. From the cracking pattern it was clear that deuterium had only entered the C_8 ring.

E. Reaction of 1,5-Cyclooctadiene with the π-1,5-Cyclooctadiene-rhodium (43a) and -iridium (43b) Complexes

The freshly recrystallised π-1,5-COD-rhodium complex (43a) (87 mg., 0.25 mmole), sodium carbonate (80 mg.) and 1,5-COD (80 μℓ., 0.65 mmole) were heated in ethanol (3 ml.) at 75° over 3 days. The reaction mixture was cooled and all volatile materials distilled in vacuo. The distillate was analysed by v.p.c. and was shown to contain diethylacetal, cyclooctene (4 μℓ./ml., 15%), 1,5-COD (18 μℓ./ml., 75%), 1,3-COD (1 μℓ./ml., 5%) and 1,4-COD (1 μℓ./ml., 5%). The involatile solid residue was shown to be the complex (43a) recovered quantitatively.

In a similar reaction, the iridium complex (43b) (81 mg., 0.19 mmole) and 1,5-COD (50 μℓ., 0.41 mmole) were heated with sodium carbonate in ethanol (3 ml.) for 3 days at 70°. Analysis of the volatile products showed them to contain diethylacetal, cyclooctene (10 μℓ., 20%), 1,3-COD (6 μℓ., 10%), 1,4-COD (12 μℓ., 20%) and 1,5-COD (25 μℓ., 50%). The complex (43b) was again recovered unchanged.

F. Reaction of the Dichlororhodium Complex (13a) and the π-2-Cyclo-

octenylrhodium Complex (46a) with Cyclooctene

A sample of cyclooctene was purified by preparative v.p.c. A portion of this (84 μℓ., 0.646 mmole) was added to a suspension of $(C_5Me_5RhC\ell_2)_2$ (100 mg., 0.162 mmole) and sodium carbonate (100 mg.) in ethanol (4 ml.). The mixture was stirred at 65° for 4 hr under nitrogen. Analysis of the volatile products showed that cyclooctene was recovered; no cyclooctadienes could be detected. The purple (polymeric) residue could not be characterised.

A similar reaction of cyclooctene (18 μℓ., 0.14 mmole) with π-$C_8H_{13}RhC\ell(C_5Me_5)$ (50 mg., 0.13 mmole) and sodium carbonate (50 mg.) in ethanol (2 ml.) again resulted in recovery of the cyclooctene. The solid residue was a mixture of (1,5-COD)Rh(C_5Me_5) and an uncharacterised (polymeric) material.

G. Reaction of 1,5-Cyclooctadiene with "Rhodium Trichloride Trihydrate"

This reaction was carried out in the manner described by Nicholson and Shaw[118].

A mixture of $RhC\ell_3 \cdot 3H_2O$ (200 mg., 0.76 mmole) and 1,5-COD (200 μℓ., 1.63 mmole) in absolute ethanol (5 ml.) was refluxed under nitrogen for 1.2 hr. This gave a yellow precipitate of $(1,5\text{-}C_8H_{12}RhC\ell)_2$ but the reaction was not complete at this time. The volatile products were collected in the usual manner and quantitatively analysed by v.p.c.; all of the free 1,5-COD had been converted to 1,3-COD. Trace amounts of cyclooctene and acetaldehyde were also found.

The compound $RhC\ell_3 \cdot 3H_2O$ (200 mg., 0.76 mmole) and 1,5-COD (500 μℓ., 4.07 mmole) were similarly reacted in ethanol (5 ml.) at 63° for 0.5 hr. Analysis of the volatile products, in this case, showed the presence of all -cyclooctadienes (1,3-, 81%; 1,5-, 12%; 1,4-, 7%).

π-1,3-Cyclohexadiene(pentamethylcyclopentadienyl)rhodium(I) (55a)

A mixture of $(C_5Me_5RhC\ell_2)_2$ (150 mg., 0.24 mmole), anhydrous sodium carbonate (150 mg.) and 1,3-cyclohexadiene (115 mg., 1.44 mmole) in absolute ethanol (4 ml.) was heated, with stirring, at 48° for 3.5 hr under nitrogen. The mother liquor was removed in vacuo and the greenish-orange residue extracted with ether. Filtration, and removal of the solvent gave a pale brown oil. A crystalline solid, 1,3-cyclohexadiene(pentamethylcyclopentadienyl)rhodium (55a) (110 mg., 0.36 mmole, 75%), m.p. 47-48° was sublimed out of this at 25°/10^{-3} mm.
Analysis. Found: C, 60.36; H, 7.35%; mol. wt. 318. Calculated for $C_{16}H_{23}Rh$: C, 60.38; H, 7.28%; mol. wt. 318.

The product decomposed slowly in air in the solid state and in solution and could not be crystallized from solution.

The same complex (64%) was obtained in identical fashion from (13a) (0.25 mmole) and 1,4-cyclohexadiene (0.72 mmole).

Reaction of π-1,3-cyclohexadiene(pentamethylcyclopentadienyl)rhodium (55a) with N-Bromosuccinimide

The complex 1,3-CHDRh(C_5Me_5) (53 mg., 0.16 mmole) was dissolved in petroleum ether (2 ml.) and methanol (2 ml.) and a solution of ammonium hexafluorophosphate (70 mg.) in methanol was added. N-Bromosuccinimide (80 mg., 0.47 mmole) was slowly added to this stirred mixture to give a dark orange precipitate. This was collected by filtration, washed with a little ether, and dried to yield $(C_5Me_5RhBr_2)_2$ (41) (48 mg., 0.07 mmole, 86%).

π-1,3-Cyclohexadiene(pentamethylcyclopentadienyl)iridium(I) (55b)

1,3-Cyclohexadiene (115 mg., 1.44 mmole) was added to a suspension of $(C_5Me_5IrC\ell_2)_2$ (191 mg., 0.24 mmole) and anhydrous sodium carbonate (200 mg.) in absolute ethanol (4 ml.). This was then warmed to 35° with stirring under nitrogen for 3.5 hr. The pale yellow solution was worked up in the same manner as described for (55a) above, to yield the white crystalline iridium complex (55b) (160 mg., 0.40 mmole, 83%), m.p. 65-67°, which was sublimed at $25°/10^{-3}$ mm.

Analysis. Found: C, 47.24; H, 5.44%; mol. wt. 406, 408. Calculated for $C_{16}H_{23}Ir$: C, 47.15; H, 5.68%; mol. wt. 406, 408.

The product decomposed fairly rapidly in air in the solid state and in solution.

The same complex was obtained (66%) from (13b) (0.24 mmole) and 1,4-cyclohexadiene (0.72 mmole) at 35°.

V.p.c. Analyses on the By-Products from the Cyclohexadiene Reactions

The organic products from the reactions to be described were analysed by v.p.c. for cyclohexadienes, cyclohexene, benzene, cyclohexane, deithylacetal and acetaldehyde. Analyses were performed on a 9'6" column of 20% Carbowax (75°) and a 5' column of 5% SE30 (45°).

A. Reaction of dichloro(pentamethylcyclopentadienyl)-rhodium (13a) and -iridium (13b) dimers with cyclohexadienes

The reactions of $(C_5Me_5MC\ell_2)_2$ with cyclohexadienes at 45-55° (M = Rh) and ca. 35° (M = Ir), which have been described above, were repeated on different scales. In each case the volatile products were collected by distillation in vacuo and analysed by v.p.c.

The results are presented in Table 5.

Detailed reaction study

Absolute ethanol (20 ml.) was pipetted into a 50 ml. flask equipped with a butyl rubber stopper and a condenser. 1.4-Cyclohexadiene (400 μℓ., 5.0 mmole) was added, the solution stirred, and 0.2 ml. taken as a reference sample for v.p.c. studies. The complex (13a) (500 mg., 0.81 mmole) and anhydrous sodium carbonate (500 mg.) were added and the system purged with nitrogen. The flask was then immersed in an oil bath at 45° and the mixture stirred at 44-48° for 4 hr under nitrogen. Aliquots (0.5 ml.) were taken via the butyl rubber seal at intervals using a syringe. In each case, the mother liquors from the aliquots were collected by distillation in vacuo (10^{-2} mm) into liquid nitrogen-cooled traps. The residues were extracted with deuterochloroform and their p.m.r. spectra recorded. The mother liquors were analysed by v.p.c.

The results are presented in Figure XIII.

B. Reactions of π-1,3-Cyclohexadiene(pentamethylcyclopentadienyl)rhodium (55a)

In all of these reactions the complex (55a) was sublimed immediately before use. The results are presented in Table 6.

(i) The complex 1,3-$C_6H_8Rh(C_5Me_5)$ (55a) was heated alone and with 1,4-cyclohexadiene (in absolute ethanol, in the presence of sodium carbonate) and also with 1,3-cyclohexadiene in various solvents (ethanol, n-hexane and THF, with and without bases).

In a typical reaction (55a) (85 mg., 0.27 mmole) and 1,3-cyclohexadiene (48 μℓ., 0.504 mmole) were dissolved in absolute ethanol (3 ml.)

and the solution was heated at 55° for 4 hr under nitrogen. The volatile products were collected by distillation into liquid nitrogen-cooled traps at 10^{-2} mm and analysed using v.p.c. The reddish-brown oily residue was extracted with ether, the yellow solution filtered and the solvent removed to yield effectively pure 1,3-$C_6H_8Rh(C_5Me_5)$ (72 mg., 0.22 mmole, 85%). The ether insoluble residue, a dark-red oil, was soluble in chloroform. This (polymeric) material could not be characterised.

(ii) 1,5-Cyclooctadiene (80 µℓ., 0.65 mmole) and anhydrous sodium carbonate (100 mg.) were added to a solution of (55a) in absolute ethanol (3 ml.). The mixture was heated at 60° under nitrogen for 2.5 hr. The volatile products were collected and analysed quantitatively by v.p.c. for cyclohexadienes, cyclohexene, cyclooctadienes and cyclooctene. The light brown residue was extracted with ether, the solution filtered and the solvent removed affording a dark yellow oily-solid (96 mg.). Quantitative analysis of this mixture by its p.m.r. spectrum showed that it comprised ca. 51% 1,3-$C_6H_8Rh(C_5Me_5)$ and ca. 49% 1,5-$C_8H_{12}Rh(C_5Me_5)$.

The reaction of (55a) (135 mg., 0.425 mmole) with 1,3-COD (106 µℓ., 0.825 mmole) was carried out in a manner similar to the above, the reaction time being 3.5 hr. The volatile products were collected by distillation in vacuo and analysed by v.p.c. and the solid products (130 mg.) were shown to comprise (55a) (ca. 88%) and 1,5-$C_8H_{12}Rh(C_5Me_5)$ (ca. 12%).

C. Reactions of π-1,3-Cyclohexadiene(pentamethylcyclopentadienyl)iridium (55b) with Cyclohexadienes

1,3-Cyclohexadiene (70 µℓ., 0.74 mmole) and anhydrous sodium carbonate (50 mg.) were added to a solution of (55b) in absolute ethanol (3 ml.).

After stirring at 50° under nitrogen for 21 hr, both 1,3-CHD and (55b) were recovered unchanged.

The reaction of (55b) with 1,4-cyclohexadiene was carried out in an entirely similar manner to the above. Starting materials were again recovered unchanged.

APPENDIX

Mass Spectra of Some Organometallic Complexes

Included in this appendix are mass spectral data for some organometallic complexes of rhodium, iron and cobalt having polymethyl-substituted organic ligands. These spectra were all recorded at an electron beam strength of 80 eV. The masses of the major ions, together with their abundances (expressed as a percentage of the base, or most abundant, ion) are listed; where appropriate, the probable formulae are assigned. The metastable transitions which were observed are also given.

Mass spectrometry, long a well-established tool in organic chemistry, is at an early stage of development for structural determinations of organometallic compounds. Because of this, and also because of the limited investigations here (i.e., accurate masses of most fragment ions and the energetics of the various ionisation and fragmentation processes were not determined), it is felt that a detailed discussion of these spectra is not justified.

A. Pentamethylcyclopentadienylrhodium complexes

The mass spectra of the Rh(I) complexes, C_5Me_5Rh(diolefin), are presented where diolefin is $(\text{ethylene})_2$, 1,5-hexadiene, 1,3-cyclohexadiene, norbornadiene, 1,5-cyclooctadiene and dicyclopentadiene. Also included are the spectra of 1,2,3,4,5-pentamethylcyclopentadiene and the π-1-methallylrhodium(III) complex, $C_5Me_5RhC\ell C_4H_7$.

A parent or molecular ion, p^{+}[*], was observed in each case

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[*] The molecular ion has commonly been designated M^{+} or P^{+}, p^{+} is used here to avoid confusion with metal or phosphorus.

allowing accurate determination of molecular weights.

For the majority of these complexes, the base peak corresponded to the ion, $C_5Me_5Rh^+$ (m/e 238); fragmentation and complete loss of the other π-bonded ligands were favored processes. The exceptions to this were exhibited by the complexes of norbornadiene and dicyclopentadiene. The stability of the πCp-M$^+$ entity to fragmentation in the mass spectrometer appears to be a general characteristic of cyclopentadienyl-metal complexes[155].

Other general features were the appearance of fragments of mass corresponding to the pentamethylrhodicenium ($C_5Me_5RhC_5H_5^+$, m/e 303), $C_5H_5Rh^+$ and Rh^+ ions. Those complexes of cyclic diolefins of >C_7 showed a major peak at m/e 329, assigned to the tropylium containing fragment, $C_5Me_5RhC_7H_7^+$. The spectrum of the bis ethylene complex, $C_5Me_5Rh(C_2H_4)_2$, like that of $C_5H_5Rh(C_2H_4)_2$[156], showed a stepwise loss of ethylene similar to the loss of CO's from metal carbonyl complexes[155]. The loss of HCℓ in the mass spectrometer observed here for the 1-methallyl complex, $C_5Me_5RhC\ell(C_4H_7)$, has also been reported for some chloro-π-allylic complexes of palladium and rhodium[157]. All attempts to reproduce this result on a preparative scale were unsuccessful.

1,2,3,4,5-Pentamethylcyclopentadiene

m/e	Relative Abundance	Assignment
136	71	$C_{10}H_{16}^+$
121	100	$C_9H_{13}^+$
119	16	$C_9H_{11}^+$
107	6	$C_8H_{11}^+$
106	9	$C_8H_{10}^+$
105	35	$C_8H_9^+$
104	2	$C_8H_8^+$

m/e	Relative Abundance	Assignment
103	4	$C_8H_7^+$
93	14	$C_7H_9^+$
91	16	$C_7H_7^+$
79	10	$C_6H_7^+$
77	10	$C_6H_5^+$
65	4	$C_5H_5^+$
55	2	$C_4H_7^+$
53	3	$C_4H_5^+$
51	2	$C_4H_3^+$
43	2	$C_3H_7^+$
41	3	$C_3H_5^+$
39	3	$C_3H_3^+$

Metastable Transitions

Approximate m/e	Process
117	$C_9H_{13}^+ \rightarrow C_9H_{11}^+ + H_2$
107.7	$C_{10}H_{16}^+ \rightarrow C_9H_{13}^+ + \cdot CH_3$
101.1	$C_8H_9^+ \rightarrow C_8H_7^+ + H_2$
91	$C_9H_{13}^+ \rightarrow C_8H_9^+ + CH_4$
89.2	$C_7H_9^+ \rightarrow C_7H_7^+ + H_2$
85	$C_{10}H_{15}^+ \rightarrow C_8H_{11}^+ + C_2H_4$
71.5	$C_9H_{13}^+ \rightarrow C_7H_9^+ + C_2H_4$
69.6	$C_9H_{11}^+ \rightarrow C_7H_7^+ + C_2H_4$
63.9	$C_7H_9^+ \rightarrow C_6H_5^+ + CH_4$
59.5	$C_8H_9^+ \rightarrow C_6H_7^+ + C_2H_2$
56.5	$C_8H_9^+ \rightarrow C_6H_5^+ + C_2H_4$
46.5	$C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$

$C_5Me_5Rh(C_2H_4)_2^*$

m/e	Relative Abundance	Assignment
294	7.5	$C_5Me_5Rh(C_2H_4)_2^+$
266	24.2	$C_5Me_5Rh(C_2H_4)^+$

m/e	Relative Abundance	Assignment
238	100	$C_5Me_5Rh^+$
237	5.4	
236	17.6	
235	5	
234	9.5	
233	3.6	
232	5.8	
231	3	
230	4.2	
229	2	
221	2.4	
218	2	
205	2.1	
168	1	$C_5H_5Rh^+$
154	2	
142	1.2	$C_3H_3Rh^+$
136	1.7	
135	3	
134	5.8	
133	8	
131	4	
130	3	
129	5	
121	2.6	$C_9H_{13}^+$
119	31.3	$C_9H_{11}^+$
117	2	$C_9H_9^+$
115	3	$C_9H_7^+$
105	4	$C_8H_9^+$
103	13	Rh^+
91	6.2	$C_7H_7^+$
79	2.6	$C_6H_7^+$
77	4.5	$C_6H_5^+$
65	2.8	$C_5H_5^+$
53	3.8	$C_4H_7^+$

m/e	Relative Abundance	Assignment
51	3.1	$C_4H_3^+$

Metastable Transitions

Approximate m/e	Process
213.2	$C_5Me_5Rh(C_2H_4)^+ \rightarrow C_5Me_5Rh^+ + C_2H_4$

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*Supplied by Dr. J. W. Kang.

$C_5Me_5RhC_6H_{10}$*

m/e	Relative Abundance	Assignment
320	48.8	$C_5Me_5RhC_6H_{10}^+$
318	2.6	$C_5Me_5RhC_6H_8^+$
305	1.7	$p\text{-}Me^+$
303	5.9	$C_5Me_5RhC_5H_5^+$
279	1.6	$C_5Me_5RhC_3H_5^+$
238	100	$C_5Me_5Rh^+$
237	13	
236	22.8	
235	13.2	
234	13.8	
233	7.8	
231	9.6	
230	6.6	
229	6.8	
221	4.2	
219	2.5	
218	4	
205	3.8	
180	3.6	
179	2.9	
168	2	$C_5H_5Rh^+$

m/e	Relative Abundance	Assignment
134	4.6	
133	4.7	
121	3.9	$C_9H_{13}^+$
119	7.6	$C_9H_{11}^+$
117	1.9	$C_9H_9^+$
115	3.1	$C_9H_7^+$
105	3.7	$C_8H_9^+$
103	13	Rh^+
97	4.7	$C_7H_{13}^+$
95	6.1	$C_7H_{11}^+$
93	2.3	$C_7H_9^+$
91	5.6	$C_7H_7^+$
83	5.3	$C_6H_{11}^+$
81	6.9	$C_6H_9^+$
79	4.2	$C_6H_7^+$
77	4.5	$C_6H_5^+$
69	8	$C_5H_9^+$
67	9.5	$C_5H_7^+$
65	2.7	$C_5H_5^+$
57	6.1	$C_4H_9^+$
55	9.4	$C_4H_7^+$
53	5.6	$C_4H_5^+$
51	2.7	$C_4H_3^+$
43	9.1	$C_3H_7^+$
41	11.2	$C_3H_5^+$
39	9.5	$C_3H_3^+$

Metastable Transitions

Approximate m/e	Process
289	$C_5Me_5RhC_6H_{10}^+ \rightarrow C_5Me_5RhC_5H_6^+ + CH_4$
177.1	$C_5Me_5RhC_6H_{10}^+ \rightarrow C_5Me_5Rh^+ + C_6H_{10}$

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*Supplied by Dr. J. W. Kang.

$C_5Me_5RhC_6H_8$ (55a)

m/e	Relative Abundance	Assignment
318	31	$C_5Me_5RhC_6H_8^+$
316	12.9	$C_5Me_5RhC_6H_6^+$
303	5.9	$C_5Me_5RhC_5H_5^+$
238	100	$C_5Me_5Rh^+$
237	7.8	
236	22	
235	8.9	
234	13.1	
233	6	
232	9.1	
231	3.8	
230	6	
223	5.9	
221	4.8	
218	3.8	
205	3	
181	5.2	$C_6H_6Rh^+$
180	3.9	
168	2	$C_5H_5Rh^+$
158	13	$(C_5Me_5RhC_6H_6)^{2+}$
142	1.5	$C_3H_3Rh^+$
119	1.9	$C_9H_{11}^+$
115	2	$C_9H_7^+$
105	2.1	$C_8H_9^+$
103	8.1	Rh^+
91	1.8	$C_7H_7^+$
79	2.1	$C_6H_7^+$
77	2	$C_6H_5^+$

Metastable transitions

Approximate m/e	Process
314	$C_5Me_5RhC_6H_8^+ \rightarrow C_5Me_5RhC_6H_6^+ + H_2$

Approximate m/e	Process
289	$C_5Me_5RhC_6H_8^+ \rightarrow C_5Me_5RhC_5H_5^+ + \cdot CH_3$
179.2	$C_5Me_5RhC_6H_6^+ \rightarrow C_5Me_5Rh^+ + C_6H_6$

$C_5Me_5RhC_7H_8$ (35)

m/e	Relative Abundance	Assignment
330	100	$C_5Me_5RhC_7H_8^+$
329	41.6	$C_5Me_5RhC_7H_7^+$
315	69.6	$C_5Me_5RhC_6H_5^+$
303	13.4	$C_5Me_5RhC_5H_5^+$
289	3.2	
252	32.2	$C_{11}H_{17}Rh^+$
250	13.1	$C_{11}H_{15}Rh^+$
248	3.6	
238	55.2	$C_5Me_5Rh^+$
237	86.6	$C_{10}H_{14}Rh^+$
236	46.7	
235	26.1	
234	23.8	
233	15.8	
232	18.7	
231	11.6	
230	13.8	
229	6.7	
223	5.2	
221	10	
219	5.8	
218	7.2	
205	6.8	
204	5.6	
194	5.2	
193	5	
192	6.7	
181	4.8	$C_6H_6Rh^+$

m/e	Relative Abundances	Assignment
180	3.9	
169	7.6	
168	10.8	$C_5H_5Rh^+$
165	15	$(C_5Me_5RhC_7H_8)^{2+}$
152	7.2	
151	4.9	
142	7.2	$C_3H_3Rh^+$
119	8	$C_9H_{11}^+$
115	7.8	$C_9H_7^+$
107	5.8	$C_8H_{11}^+$
105	6.2	$C_8H_7^+$
103	16.2	Rh^+
97	7.1	$C_7H_{13}^+$
95	8.2	$C_7H_{11}^+$
91	18.4	$C_7H_7^+$
83	8.2	$C_6H_{11}^+$
81	9.1	$C_6H_9^+$
79	6.1	$C_6H_7^+$
77	7.2	$C_6H_5^+$
69	12.3	$C_5H_9^+$
67	7.8	$C_5H_7^+$
65	10.1	$C_5H_5^+$
57	10.4	$C_4H_9^+$
55	18.2	$C_4H_7^+$
53	6.6	$C_4H_5^+$
51	5.2	$C_4H_3^+$
43	14.1	$C_3H_7^+$
41	26.2	$C_3H_5^+$
39	17.4	$C_3H_3^+$

Metastable Transitions

Approximate m/e	Process
301	$C_5Me_5RhC_7H_8^+ \rightarrow C_5Me_5RhC_6H_5^+ + \cdot CH_3$

Approximate m/e	Process
248	$C_{11}H_{17}Rh^+ \rightarrow C_{11}H_{15}Rh^+ + H_2$
223	$C_{11}H_{17}Rh^+ \rightarrow C_{10}H_{14}Rh^+ + \cdot CH_3$

$C_5Me_5Rh(1,5\text{-}C_8H_{12})$ (43a)

m/e	Relative Abundance	Assignment
346	75.7	$C_5Me_5RhC_8H_{12}^+$
343	9.6	$C_5Me_5RhC_8H_9^+$
331	24.4	$C_5Me_5RhC_7H_9^+$
329	26.6	$C_5Me_5RhC_7H_7^+$
317	7.5	
316	11.9	$C_5Me_5RhC_6H_6^+$
303	6.7	$C_5Me_5RhC_5H_5^+$
292	6.2	
252	1.5	
238	100	$C_5Me_5Rh^+$
237	19.8	
236	27.3	
235	19.6	
234	21.8	
233	11.9	
232	14.8	
231	8.9	
230	9.8	
221	6.6	
219	4	
218	4.9	
205	7.1	
204	4.5	
181	7.1	$C_6H_6Rh^+$
180	5.7	
172	15.5	$(C_5Me_5RhC_8H_{10})^{2+}$
168	5.7	$C_5H_5Rh^+$

m/e	Relative Abundance	Assignment
158	4.7	
157	6.3	
155	5.2	
154	5.3	
142	4.4	$C_3H_3Rh^+$
135	4	
133	3.5	
129	4.4	
119	8.8	$C_9H_{11}^+$
115	5.6	$C_9H_7^+$
105	7.1	$C_8H_9^+$
103	25.8	Rh^+
91	11.7	$C_7H_7^+$
79	12.3	$C_6H_7^+$
77	11.8	$C_6H_5^+$
67	5.2	$C_5H_7^+$
65	7.1	$C_5H_5^+$
55	5.8	$C_4H_7^+$
53	12.1	$C_4H_5^+$
51	5.3	$C_4H_3^+$
41	32.2	$C_3H_5^+$
39	19.5	$C_3H_3^+$

Metastable Transitions

Approximate m/e	Process
313	$C_5Me_5RhC_8H_{12}^+ \rightarrow C_5Me_5RhC_7H_9^+ + \cdot CH_3$
302	$C_5Me_5RhC_7H_9^+ \rightarrow C_5Me_5RhC_6H_6^+ + \cdot CH_3$
289	$C_5Me_5RhC_8H_{12} \rightarrow C_5Me_5RhC_6H_6^+ + C_2H_6$
164	$C_5Me_5RhC_8H_{12} \rightarrow C_5Me_5Rh^+ + C_8H_{12}$

$C_5Me_5Rh(C_{10}H_{12})$ (36)

m/e	Relative Abundance	Assignment
370	79	$C_5Me_5RhC_{10}H_{12}^+$

m/e	Relative Abundance	Assignment
369	49.5	$C_5Me_5RhC_{10}H_{11}^+$
367	3.2	$C_5Me_5RhC_{10}H_9^+$
355	100	$C_5Me_5RhC_9H_9^+$
353	6.2	$C_5Me_5RhC_9H_7^+$
329	13.5	$C_5Me_5RhC_7H_7^+$
327	1.5	
303	92	$C_5Me_5RhC_5H_5^+$
289	54.8	
238	7	
237	5.5	
236	11	
235	15	
234	12.5	
233	18	
232	12	
231	10.5	
230	11	
229	6	
221	8	
219	6	
218	6.5	
169	10	
168	17	$C_5H_5Rh^+$
165	10	
152	19	
151	11.1	
121	8.5	$C_9H_{13}^+$
119	15	$C_9H_{11}^+$
117	7.8	$C_9H_9^+$
115	13	$C_9H_7^+$
105	14	$C_8H_9^+$
103	18.5	Rh^+
93	12.2	$C_7H_9^+$
91	26.2	$C_7H_7^+$

m/e	Relative Abundance	Assignment
83	31	
81	36	$C_6H_9^+$
79	20	$C_6H_7^+$
77	20.5	$C_6H_5^+$
69	45	$C_5H_9^+$
67	42	$C_5H_7^+$
65	14.5	$C_5H_5^+$
57	34	$C_4H_9^+$
55	68	$C_4H_7^+$
53	18	$C_4H_5^+$
43	46	$C_3H_7^+$
41	81	$C_3H_5^+$
39	22	$C_3H_3^+$

Metastable Transitions

Approximate m/e	Process
341	$C_5Me_5RhC_{10}H_{12}^+ \rightarrow C_5Me_5RhC_9H_9^+ + \cdot CH_3$

$C_5Me_5RhC\ell(C_4H_7)$ (34)

m/e	Relative Abundance	Assignment
330	2.2	$C_5Me_5RhC\ell^{37}(C_4H_7)^+$
328	6	$C_5Me_5RhC\ell^{35}(C_4H_7)^+$
292	52	$C_5Me_5RhC_4H_6^+$
275	7.6	$C_5Me_5RhC\ell^{37+}$
273	23	$C_5Me_5RhC\ell^{35+}$
238	100	$C_5Me_5Rh^+$
237	32.2	
236	30.8	
235	17.5	
234	16.1	
233	10.2	

m/e	Relative Abundance	Assignment
232	11.2	
231	8	
230	7.6	
221	4	
219	3	
218	5	
206	3	
205	5	
204	4	
181	3.2	$C_6H_6Rh^+$
180	3.3	
168	2	$C_5H_5Rh^+$
157	4	
156	3	
155	5.2	
154	4.7	
146	6	
142	3	C_3H_3Rh
136	6	
135	6	
134	27.8	
133	12	
129	5	
121	10	$C_9H_{13}^+$
119	72	$C_9H_{11}^+$
117	7.2	$C_9H_9^+$
115	8	$C_9H_7^+$
105	12	$C_8H_9^+$
103	17.5	Rh^+
93	5	$C_7H_9^+$
91	20.8	$C_7H_7^+$
79	7.2	$C_6H_7^+$
77	12	$C_6H_5^+$
65	7	$C_5H_5^+$

m/e	Relative Abundance	Assignment
57	7	$C_4H_9^+$
55	11.3	$C_4H_7^+$
51	13.5	$C_4H_5^+$
43	9	$C_3H_7^+$
41	19	$C_3H_5^+$
39	24	$C_3H_3^+$

Metastable Transitions

Approximate m/e	Process
259.8	$C_5Me_5RhC\ell(C_4H_7)^+ \rightarrow C_5Me_5RhC_4H_6^+ + HC\ell$
194	$C_5Me_5RhC_4H_6^+ \rightarrow C_5Me_5Rh^+ + C_4H_6$
113	$C_9H_9^+ \rightarrow C_9H_7^+ + H_2$
105.7	$C_{10}H_{14}^+ \rightarrow C_9H_{11}^+ + \cdot CH_3$
101.1	$C_8H_9^+ \rightarrow C_8H_7^+ + H_2$
89.1	$C_7H_9^+ \rightarrow C_7H_7^+ + H_2$
69.6	$C_9H_{11}^+ \rightarrow C_7H_7^+ + C_2H_4$

B. Some Complexes of Iron and Cobalt

The complexes, the spectral data for which follows, were supplied by Dr. R. Bruce of this laboratory. They all contain tetramethylcyclobutadiene or derivatives of this. The structures which are given were assigned on the basis of analytical and other spectroscopic data[158].

Iron-containing fragments in these spectra were usually readily identified from the characteristic isotope pattern of Fe.

Molecular ions were observed for all but the cobalt complex, $C_4Me_4Co(CO)_2I$; for this, the spectrum corresponded to the derivative $(C_4Me_4CoI)_2$, presumably formed from a thermal reaction. All attempts, under a variety of conditions, to reproduce this result on a preparative scale, were unsuccessful.

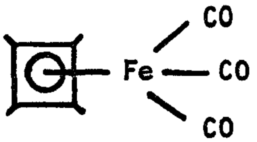
The carbonyl-containing complexes exhibited the characteristic, facile, stepwise loss of all carbonyl ligands[155].

These studies indicate that caution must be exercised when assigning structures on the basis of mass spectra[159]. The tetramethylcyclobutadiene complexes show loss of C_2Me_2 fragments so that mass spectroscopy did not distinguish between a cyclobutadiene and a bis alkyne complex; $C_4Me_4Fe(CO)_3$ is unlike $C_4H_4Fe(CO)_3$[160] in this respect. The methyl substituted ligands here show a marked tendency to lose H_2 and even $2H_2$, during which complicated rearrangements must occur. The complex, $C_{16}H_{24}NiFe(CO)_3$, was shown by an X-ray study to have both tetramethyl -cyclobutadiene and -metallocyclopentadiene rings[161]. However, its mass spectrum showed ions corresponding to the fusion product C_8Me_8 and its fragments. This fusion of two coordinated rings may well be thermally induced.

The mass spectrum of the di-iron complex, $C_4Me_4Fe_2(CO)_6$ significantly showed a fragment of m/e 112, assigned to Fe_2^+. This may indicate some metal-metal interaction in the complex.

The fragments observed for the cyclopentadienyl-cobalt complex, $C_5H_5CoC_4Me_4$, again demonstrated the high stability of a π-$C_5H_5M^+$ entity in the mass spectrometer.

$C_8H_{12}Fe(CO)_3$



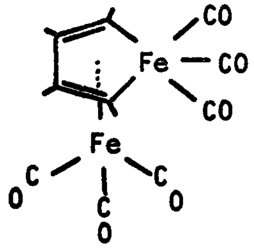
m/e	Relative Abundance	Assignment
248	36.5	$C_8H_{12}Fe(CO)_3^+$
220	37	$C_8H_{12}Fe(CO)_2^+$
192	34.5	$C_8H_{12}Fe(CO)^+$

m/e	Relative Abundance	Assignment
164	100	$C_8H_{12}Fe^+$
162	94	$C_8H_{10}Fe^+$
148	16.5	
138	4.8	
136	4	
134	6	
124	16.5	$C_8H_{12}Fe(CO)_3{}^{2+}$
122	8.4	
110	71	$C_4H_6Fe^+$
108	16.4	$C_8H_{12}{}^+$
96	14.5	
95	10	
91	9.6	$C_7H_7{}^+$
84	15.8	$FeCO^+$
83	11.6	
82	16	
81	10.3	
77	6.6	$C_6H_5{}^+$
71	5.4	
65	5.6	$C_5H_5{}^+$
56	83	Fe^+
53	9.2	$C_4H_5{}^+$
51	5.6	$C_4H_3{}^+$

Metastable Transitions

Approximate m/e	Process
195	$C_8H_{12}Fe(CO)_3{}^+ \rightarrow C_8H_{12}Fe(CO)_2{}^+ + CO$
168	$C_8H_{12}Fe(CO)_2{}^+ \rightarrow C_8H_{12}Fe(CO)^+ + CO$
160	$C_8H_{12}Fe^+ \rightarrow C_8H_{10}Fe^+ + H_2$
140	$C_8H_{12}Fe(CO)^+ \rightarrow C_8H_{12}Fe^+ + CO$
133.6	$C_8H_{12}Fe^+ \rightarrow C_7H_8Fe^+ + CH_4$
88.9	$C_7H_9{}^+ \rightarrow C_7H_7{}^+ + H_2$
73.9	$C_8H_{12}Fe^+ \rightarrow C_4H_6Fe^+ + C_4H_6$

$C_8H_{12}Fe_2(CO)_6$



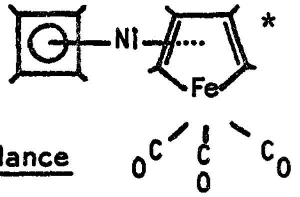
m/e	Relative Abundance	Assignment
388	15.2	$C_8H_{12}Fe_2(CO)_6^+$
360	28.9	$C_8H_{12}Fe_2(CO)_5^+$
332	24.8	$C_8H_{12}Fe_2(CO)_4^+$
304	23.2	$C_8H_{12}Fe_2(CO)_3^+$
276	86.8	$C_8H_{12}Fe_2(CO)_2^+$
248	100	$C_8H_{12}Fe_2(CO)^+$
220	77.7	$C_8H_{12}Fe_2^+$ or $C_8H_{12}Fe(CO)_2^+$
218	24.9	$C_8H_{10}Fe_2^+$ or $C_8H_{10}Fe(CO)_2^+$
216	15	$C_8H_8Fe_2^+$ or $C_8H_8Fe(CO)_2^+$
192	15.2	$C_8H_{12}FeCO^+$
166	26.8	$C_4H_6Fe_2^+$ or $C_4H_6Fe(CO)_2^+$
164	29.5	$C_8H_{12}Fe^+$
162	42.7	$C_8H_{10}Fe^+$
138	11.1	
137	14	
136	46	$C_8H_{12}CO^+$
124	20.3	$C_8H_{12}Fe_2(CO)^{2+}$
123	11	
121	23	$C_7H_9CO^+$
112	62.1	Fe_2^+ or $Fe(CO)_2^+$
110	66.2	$C_4H_6Fe^+$
109	15	
108	21	$C_8H_{12}^+$
107	19.9	
106	20.8	
105	17.2	
95	13.9	
93	56.2	$C_7H_9^+$
91	61	$C_7H_7^+$
84	14	$FeCO^+$
81	12	

m/e	Relative Abundance	Assignment
79	25.1	$C_6H_7^+$
77	27.2	$C_6H_5^+$
67	10.2	
65	18	$C_5H_5^+$
63	8.5	
57	10	
56	69.9	Fe^+
55	14.5	$C_4H_7^+$
54	9.8	$C_4H_6^+$
53	24.6	$C_4H_5^+$
52	13	$C_4H_4^+$
51	24	$C_4H_3^+$

Metastable Transitions

Approximate m/e	Process
334	$C_8H_{12}Fe_2(CO)_6^+ \rightarrow C_8H_{12}Fe_2(CO)_5^+ + CO$
306	$C_8H_{12}Fe_2(CO)_5^+ \rightarrow C_8H_{12}Fe_2(CO)_4^+ + CO$
250.5	$C_8H_{12}Fe_2(CO)_3 \rightarrow C_8H_{12}Fe_2(CO)_2^+ + CO$
222.8	$C_8H_{12}Fe_2(CO)_2^+ \rightarrow C_8H_{12}Fe_2(CO)^+ + CO$
195	$C_8H_{12}Fe_2(CO)^+ \rightarrow C_8H_{12}Fe_2^+ + CO$
57	$C_8H_{12}Fe_2^+ \rightarrow Fe_2^+ + C_8H_{12}$

$C_{16}H_{24}NiFe(CO)_3$



m/e	Relative Abundance	Assignment
416	5.2	$C_{16}H_{24}Ni^{60}Fe^{56}(CO)_3^+$
414	14.8	$C_{16}H_{24}Ni^{58}Fe^{56}(CO)_3^+$
388	6.5	$C_{16}H_{24}Ni^{60}Fe^{56}(CO)_2^+$
386	16.6	$C_{16}H_{24}Ni^{58}Fe^{56}(CO)_2^+$
360	6.3	$C_{16}H_{24}Ni^{60}Fe^{56}(CO)^+$
358	15.2	$C_{16}H_{24}Ni^{58}Fe^{56}(CO)^+$
332	5.2	$C_{16}H_{24}Ni^{60}Fe^{56+}$

m/e	Relative Abundance	Assignment
330	15.1	$C_{16}H_{24}Ni^{58}Fe^{56+}$ [a], $C_{16}H_{22}Ni^{60}Fe^{56+}$ [a]
328	28.1	$C_{16}H_{20}Ni^{60}Fe^{56+}$ [a], $C_{16}H_{22}Ni^{58}Fe^{56+}$ [a]
326	35.5	$C_{16}H_{20}Ni^{58}Fe^{56+}$ [a], $C_{16}H_{18}Ni^{60}Fe^{56+}$ [a]
324	16.5	$C_{16}H_{18}Ni^{58}Fe^{56+}$ [a], $C_{16}H_{16}Ni^{60}Fe^{56+}$ [a]
322	13	$C_{16}H_{16}Ni^{58}Fe^{56+}$ [a]
300	8.5	
298	7	
272	41.8	$C_{16}H_{24}Fe^{+}$
270	12	
246	4	
244	4.8	
218	64	$C_{12}H_{18}Fe^{+}$ [a]
216	47	$C_{16}H_{24}^{+}$ [a]
201	21.5	$C_{15}H_{21}^{+}$
187	8.5	
186	6.2	
162	70	$C_{12}H_{18}^{+}$
147	100	$C_{11}H_{15}^{+}$
136	7.5	$C_{8}H_{12}CO^{+}$
133	10.5	
131	9	
119	11	$C_{9}H_{11}^{+}$
117	7	$C_{9}H_{9}^{+}$
115	9.5	$C_{9}H_{7}^{+}$
114	6.5	$C_{4}H_{6}Ni^{58}$
105	12.4	$C_{8}H_{9}^{+}$
91	15	$C_{7}H_{7}^{+}$
77	6.5	$C_{6}H_{5}^{+}$
57	6	
56	7.2	Fe^{+}
55	8.4	$C_{4}H_{7}^{+}$
54	7	$C_{4}H_{6}^{+}$
53	8	$C_{4}H_{5}^{+}$
51	4.5	$C_{4}H_{3}^{+}$

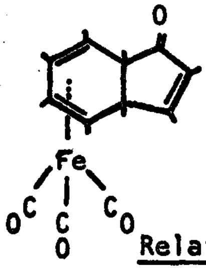
a - assignment on the basis of accurate mass determination.

* - structure indicated by an X-ray study[161].

Metastable Transition

Approximate m/e	Process	
359	$C_{16}H_{24}Ni^{58}Fe^{56}(CO)_3^+$	$\rightarrow C_{16}H_{24}Ni^{58}Fe^{56}(CO)_2^+ + CO$
304.3	$C_{16}H_{24}Ni^{58}Fe^{56}(CO)^+$	$\rightarrow C_{16}H_{24}Ni^{58}Fe^{56+} + CO$
187	$C_{16}H_{24}^+$	$\rightarrow C_{15}H_{20}^+ + \cdot CH_3$
174.9	$C_{16}H_{24}Fe^+$	$\rightarrow C_{12}H_{18}Fe^+ + C_4H_6$
172.3	$C_{15}H_{21}^+$	$\rightarrow C_{14}H_{18}^+ + \cdot CH_3$
133.4	$C_{12}H_{18}^+$	$\rightarrow C_{11}H_{15}^+ + \cdot CH_3$
88.9	$C_7H_9^+$	$\rightarrow C_7H_7^+ + H_2$

$C_{16}H_{24}Fe(CO)_4$



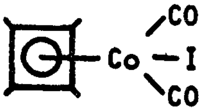
m/e	Relative Abundance	Assignment
384	3	$C_{16}H_{24}Fe(CO)_4^+$
356	19	$C_{16}H_{24}Fe(CO)_3^+$
328	51	$C_{16}H_{24}Fe(CO)_2^+$
300	50.5	$C_{16}H_{24}Fe(CO)^+$
298	31.4	$C_{16}H_{22}Fe(CO)^+$
272	100	$C_{16}H_{24}Fe^+$
246	5	$C_{12}H_{18}FeCO^+$
244	3	$C_{12}H_{16}FeCO^+$
218	65.7	$C_{12}H_{18}Fe^+$
216	17.1	$C_{16}H_{24}^+$
214	5.6	
201	10.7	$C_{15}H_{21}^+$
190	4.2	
188	4.6	
186	5	$C_{14}H_{18}^+$
162	4	$C_{12}H_{18}^+$

m/e	Relative Abundance	Assignment
161	8	
150	5	
147	9.3	$C_{11}H_{15}^+$
136	10.7	$C_8H_{12}CO^+$
133	3.5	
119	3.6	$C_9H_{11}^+$
115	3	
110	3.7	$C_4H_6Fe^+$
105	4	
91	4.3	$C_7H_7^+$
84	4.2	$FeCO^+$
77	3.1	$C_6H_5^+$
56	8	Fe^+
53	3.2	$C_4H_5^+$

Metastable Transition

Approximate m/e		Process
302.5		$C_{16}H_{24}Fe(CO)_3^+ \rightarrow C_{16}H_{24}Fe(CO)_2^+ + CO$
247		$C_{16}H_{24}Fe(CO)^+ \rightarrow C_{16}H_{24}Fe^+ + CO$
225.5		$C_{16}H_{24}Fe(CO)_2^+ \rightarrow C_{16}H_{24}Fe^+ + 2CO$
	or	$C_{16}H_{24}Fe(CO)_2^+ \rightarrow C_{16}H_{24}(CO)_2^+ + Fe$
193.2		$C_{12}H_{18}Fe(CO)^+ \rightarrow C_{12}H_{18}Fe^+ + CO$
175		$C_{16}H_{24}Fe^+ \rightarrow C_{12}H_{18}Fe^+ + C_4H_6$
133.3		$C_{12}H_{18}^+ \rightarrow C_{11}H_{15}^+ + \cdot CH_3$
88.9		$C_7H_9^+ \rightarrow C_7H_7^+ + H_2$

$C_8H_{12}Co(CO)_2I$



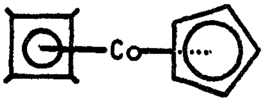
m/e	Relative Abundance	Assignment
588	43.2	$(C_8H_{12}CoI)_2^+$
480	33.4	$(C_8H_{12})Co_2I_2^+$

m/e	Relative Abundance	Assignment
465	1.6	
421	16.4	$C_8H_{12}CoI_2{}^+$
418	1.6	
372	5.9	$(Co_2I_2)^+$
352	4.6	
350	4.6	$C_8H_{12}Co(CO)_2I^+$
310	1.8	
294	16.2	$C_8H_{12}CoI^+$ or $(C_8H_{12}CoI)_2^{2+}$
279	2.6	$C_7H_9CoI^+$
201	4.7	
186	9.2	$Co-I^+$
167	4	$C_8H_{12}Co^+$
166	9.6	
165	15.2	
164	10	
151	7.2	$C_7H_8Co^+$
128	3.2	
127	2.4	
113	6.4	$C_4H_6Co^+$
109	21.6	
108	55.6	$C_8H_{12}{}^+$
107	24.2	
106	8	
105	13	
93	100	$C_7H_9{}^+$
91	76	$C_7H_7{}^+$
79	24.6	$C_6H_7{}^+$
77	68.8	$C_6H_5{}^+$
67	17.6	
65	21.6	$C_5H_5{}^+$
63	8.4	
59	8.4	Co^+
55	16	$C_4H_7{}^+$
53	30.8	$C_4H_5{}^+$
51	23.2	$C_4H_3{}^+$

Metastable Transitions

Approximate m/e		Process
391.6	$(C_8H_{12}CoI)_2^+$	$C_8H_{12}Co_2I_2^+ + C_8H_{12}$
264.5	$C_8H_{12}CoI^+$	$C_7H_9CoI^+ + \cdot CH_3$
205.4	$C_8H_{12}CoI_2^+$	$C_8H_{12}CoI^+ + \cdot I$
136.6	$C_8H_{12}Co^+$	$C_7H_8Co^+ + CH_4$
89.1	$C_7H_9^+$	$C_7H_7^+ + H_2$
80.2	$C_8H_{12}^+$	$C_7H_9^+ + \cdot CH_3$
63.8	$C_7H_9^+$	$C_6H_5^+ + CH_4$
46.5	$C_7H_7^+$	$C_5H_5^+ + C_2H_2$

$C_8H_{12}Co(C_5H_5)$



m/e	Relative Abundance	Assignment
232	100	$C_8H_{12}Co(C_5H_5)^+$
231	30.8	$p\text{-}H^+$
230	27.2	$p\text{-}H_2^+$
217	77.6	$p\text{-}CH_3^+$
203	8.2	$p\text{-}C_2H_5^+$
189	2	
178	10.4	$C_4H_6Co(C_5H_5)^+$
166	4.5	$C_8H_{12}Co(C_5H_5)^{2+}$
165	18.2	
164	16.4	
163	2.9	
151	10	
138	4.3	
137	5.2	

m/e	Relative Abundance	Assignment
124	92	$C_5H_5Co^+$
113	5	
112	4.3	
111	5.8	
107	3.8	
105	7.4	
98	12.3	$C_3H_3Co^+$
97	4.7	
91	8	$C_7H_7^+$
86	6.2	
85	4.1	
84	4.5	
79	3.6	$C_6H_7^+$
77	4.6	$C_6H_5^+$
65	4.6	$C_5H_5^+$
59	46	Co^+
53	7.4	$C_4H_5^+$
51	3.5	$C_4H_3^+$

Metastable Transitions

Approximate m/e	Process
203	$C_{13}H_{17}Co^+ \rightarrow C_{12}H_{14}Co^+ + \cdot CH_3$
177.8	$C_{13}H_{16}Co^+ \rightarrow C_{11}H_{12}Co^+ + C_2H_4$
136.7	$C_8H_{12}Co(C_5H_5)^+ \rightarrow C_4H_6Co(C_5H_5)^+ + C_4H_6$
118.3	$C_{13}H_{15}Co^+ \rightarrow C_8H_{10}Co^+ + \cdot C_5H_5$
105.1	$C_{12}H_{14}Co^+ \rightarrow C_7H_8Co^+ + C_5H_6$
86.4	$C_4H_6Co(C_5H_5)^+ \rightarrow Co(C_5H_5)^+ + C_4H_6$
77.4	$Co(C_5H_5)^+ \rightarrow Co(C_3H_3)^+ + C_2H_2$
46.5	$C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$

BIBLIOGRAPHY

1. J. Chatt and L. A. Duncanson, J. Chem. Soc., p. 2939 (1953).
2. M. J. S. Dewar, Bull. Soc. Chim. France, 18, 71 (1951).
3. J. N. Dempsey and N. C. Baenziger, J. Am. Chem. Soc., 77, 4984 (1955).
4. P. R. H. Alderman, P. G. Owston and J. M. Rowe, Acta. Cryst., 13, 149 (1960).
5. J. A. Wunderlich and D. P. Mellor, Acta. Cryst., 7, 130 (1954).
6. R. Cramer, J. Am. Chem. Soc., 86, 217 (1964).
7. R. Cramer, J. B. Kline and J. D. Roberts, J. Am. Chem. Soc., 91, 2519 (1969).
8. W. H. Baddley and L. M. Venanzi, Inorg. Chem. 5, 33 (1966).
9. W. H. Baddley, C. Panattoni, G. Bamburi and U. Belluco, J. Am. Chem. Soc., 90, 798 (1968).
10. C. D. Cook, C. H. Khoo, S. C. Nyburg and M. T. Shiomi, Chem. Commun., p. 426 (1967).
11. N. C. Baenziger, J. R. Doyle and C. Carpenter, Acta. Cryst., 14, 303 (1961).
12. J. Chatt and L. M. Venanzi, Nature, 177, 852 (1956).
13. J. Chatt, L. M. Vallarino and L. M. Venanzi, J. Chem. Soc., p. 3413 (1957).
14. W. C. Baenziger, H. L. Haight and J. R. Doyle, Inorg. Chem., 3, 1535 (1964).
15. J. A. Ibers and R. G. Snyder, Acta. Cryst., 15, 923 (1962).
16. O. S. Mills and G. Robinson, Proc. Chem. Soc., p. 421 (1960).
17. B. Dickens and W. N. Lipscomb, J. Chem. Phys., 37, 2084 (1962).
18. M. R. Churchill and R. Mason, Proc. Chem. Soc., p. 226 (1964).
19. R. G. Guy and B. L. Shaw, Adv. Inorg. Chem. Radiochem., 4, 77 (1962).
20. F. L. Bowden and A. B. P. Lever, Organometal. Chem. Rev., 3, 227 (1968).
21. S. F. A. Kettle and R. Mason, J. Organometal. Chem., 5, 573 (1966).

22. (a) W. E. Oberhausli and L. Dahl, J. Organometal. Chem., 3, 43 (1965); (b) A. E. Smith, Acta. Cryst., 18, 331 (1965).

23. E. W. Gowling and S. F. A. Kettle, Inorg. Chem., 3, 604 (1964).

24. (a) J. D. Dunitz, H. C. Mez, O. S. Mills, P. Pauling and H. M. M. Shearer, Angew. Chem., 72, 755 (1960); (b) J. D. Dunitz, H. C. Mez, O. S. Mills and H. M. M. Shearer, Helv. Chim. Acta., 45, 477 (1962).

25. J. P. Dunitz, L. E. Orgel and A. Rich, Acta. Cryst., 9, 373 (1956).

26. M. F. Bailey and L. F. Dahl, Inorg. Chem., 4, 1314 (1965).

27. G. Engebretson and R. E. Rundle, J. Am. Chem. Soc., 85, 481 (1963).

28. H. Dietrich and H. Dierks, Angew. Chem. Internat. Ed., 5, 899 (1966).

29. M. Rosenblum, "Chemistry of the Iron Group Metallocenes", Interscience (1965).

30. M. L. H. Green, L. Platt and G. Wilkinson, J. Chem. Soc., p. 3753 (1959).

31. A. Davison, M. L. H. Green and G. Wilkinson, J. Chem. Soc., p. 3172 (1961).

32. G. Winkhaus, L. Platt and G. Wilkinson, J. Chem. Soc., p. 3807 (1961).

33. E. O. Fischer and U. Zahn, Chem. Ber., 92, 1924 (1959).

34. M. R. Churchill and R. Mason, Proc. Roy. Soc., A279, 191 (1964).

35. M. R. Churchill, J. Organometal. Chem., 4, 258 (1965).

36. M. R. Churchill and R. Mason, Proc. Chem. Soc., p. 112 (1963).

37. M. R. Churchill and F. R. Scholar, Inorg. Chem., 8, 1950 (1969).

38. P. H. Bird and M. R. Churchill, Chem. Commun., 777 (1967).

39. I. U. Khand, P. L. Pauson and W. E. Watts, J. Chem. Soc. (C), p. 2024 (1969).

40. F. A. Cotton, R. O. Whipple and G. Wilkinson, J. Am. Chem. Soc., 75, 3586 (1953).

41. R. J. Angelici and E. O. Fischer, J. Am. Chem. Soc., 85, 3733 (1963).

42. E. O. Fischer and H. Warwersik, J. Organometal. Chem., 5. 559 (1966).

43. O. S. Mills and E. F. Paulus, J. Organometal. Chem., 11, 587 (1968).

44. E. O. Fischer, U. Zahn and F. Baumgartner, Z. Naturforsch. 14b, 133 (1959).

45. J. Chatt and L. M. Venanzi, J. Chem. Soc., p. 4735 (1957).

46. G. Winkhaus and H. Singer, Chem. Ber., 99, 3610 (1966).

47. S. D. Robinson and B. L. Shaw, Tetrahed. Lett., p. 1301 (1964).

48. R. B. King, J. Am. Chem. Soc., 85, 528 (1963).

49. G. N. Schrauzer and K. G. Dewhirst, J. Am. Chem. Soc., 86, 3265 (1964).

50. E. O. Fischer and K. Bittler, Z. Naturforsch., 16b, 225 (1961).

51. E. O. Fischer and K. S. Brenner, Z. Naturforsch., 17b, 774 (1962).

52. O. S. Mills and E. F. Pauson, Chem. Commun., p. 815 (1966).

53. E. F. Paulus, E. O. Fischer, H. P. Fritz and H. Schuster-Wolden, J. Organometal. Chem., 10, P3 (1967).

54. J. Powell and B. L. Shaw, J. Chem. Soc., (A), p. 583, 594 (1968).

55. E. E. van Tamelen and S. P. Pappas, J. Am. Chem. Soc., 84, 3789 (1962).

56. W. Schäfer and H. Hellman, Angew. Chem. Internat. Ed., 6, 518 (1967).

57. W. Schäfer, Angew. Chem. Internat. Ed., 5, 669 (1966).

58. E. O. Fischer, C. G. Krieter and W. Berngruber, Angew. Chem. Internat. Ed., 6, 634 (1967).

59. E. O. Fischer, W. Berngruber and C. G. Krieter, Chem. Ber., 101, 824 (1968).

60. H. C. Volger and H. Hogeveen, Rec. Trav. Chim., 86, 830 (1967).

61. B. L. Shaw and G. Shaw, J. Chem. Soc., (A), p. 1560 (1969).

62. H. Dietl and P. M. Maitlis, Chem. Commun. p. 759 (1967).

63. R. Mason, G. B. Robinson and P. O. Whimp, Chem. Commun. p. 868 (1968).

64. P. V. Balakrishnan and P. M. Maitlis, Chem. Commun., p. 1303 (1968).

65. E. G. van Tamelen and D. Carty, J. Am. Chem. Soc., 89, 3922 (1967).

66. G. Huttner and O. S. Mills, Chem. Commun., p. 344 (1968).

67. J. F. Malone, W. S. McDonald, B. L. Shaw and G. Shaw, Chem. Commun., 869 (1968).

68. B. L. Shaw and G. Shaw, J. Chem. Soc. (A), 602 (1969).

69. D. J. Cook, M. Green, N. Mayne and F. G. A. Stone, J. Chem. Soc. (A), p. 1771 (1968).

70. J. W. Kang and P. M. Maitlis, J. Am. Chem. Soc., 90, 3259 (1968).

71. F. Canate, R. Ugo and F. Bonati, Inorg. Chem., 5, 1128 (1966).

72. J. P. Collman and W. R. Roper, Adv. Organometal. Chem., 7, 54 (1968).

73. L. Vaska and J. W. Kiluzio, J. Am. Chem. Soc., 83, 2784 (1961); 84, 679 (1962).

74. R. F. Heck, J. Org. Chem., 28, 604 (1963).

75. L. Vaska and S. S. Bath, J. Am. Chem. Soc., 88, 1333 (1966).

76. L. Vaska, Science, 140, 809 (1963).

77. J. P. Collman and W. R. Roper, J. Am. Chem. Soc., 88, 3504 (1966).

78. A. Sacco and M. Rossi, Chem. Commun., p. 316 (1967).

79. P. Fitton, M. P. Johnson and J. E. McKeon, Chem. Commun., p. 6 (1968).

80. J. P. Collman and W. R. Roper, Chem. Commun., p. 244 (1966).

81. J.P. Collman and W. R. Roper, J. Am. Chem. Soc., 88, 180 (1966).

82. P. B. Chock and J. Halpern, J. Am. Chem. Soc., 88, 3511 (1966).

83. J. A. McGinnerty, R. J. Doedens and J. A. Ibers, Science, 155, 709 (1967).

84. L. Vaska, Acc. Chem. Research, 1, 335 (1968).

85. J. P. Birk, J. Halpern and A. L. Pickard, J. Am. Chem. Soc., 90, 4491 (1968); Inorg. Chem., 7, 2672 (1968).

86. J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, J. Chem. Soc. (A), p. 1711 (1966).

87. J. A. McGinnerty and J. A. Ibers, Chem. Commun., p. 235 (1968).

88. E. Koerner von Gustorf, M. J. Jun and G. O. Schenck, Z. Naturforsch., 18b, 503 (1963).

89. F. Basolo and R. G. Pearson in "Mechanisms of Inorganic Reactions", Wiley, 2nd Ed. (1967).

90. K. Noack, M. Ruch and F. Calderazzo, Inorg. Chem., 7, 345 (1968).

91. J. Chatt, R. S. Coffey, A. Gough and D. T. Thompson, J. Chem. Soc., (A), p. 190 (1968).

92. M. Tsutsui, M. Hancock, J. Ariyoshi and M. N. Levy, Angew. Chem. Internat. Ed., 8, 410 (1969).

93. M. L. H. Green and P. L. I. Nagy, J. Chem. Soc., p. 189 (1963).

94. B. L. Shaw, Chem. Commun., p. 464 (1968).

95. U. Belluco et al., J. Am. Chem. Soc., 89, 6494 (1967); Inorg. Chem., 6, 718 (1967).

96. J. Chatt and B. L. Shaw, J. Chem. Soc., p. 705, 4020 (1959).

97. R. F. Heck and D. S. Breslow, J. Am. Chem. Soc., 85, 2779 (1963).

98. G. W. Parshall, W. H. Knoth and R. A. Schunn, J. Am. Chem. Soc., 91, 4990 (1969).

99. (a) S. J. La Placa and J. A. Ibers, Acta Cryst., 18, 511 (1965); (b) S. C. Abrahams, A. P. Ginsberg and K. Knox, Inorg. Chem., 3, 558 (1964).

100. J. Halpern and B. R. James, Can. J. Chem., 44, 671 (1966).

101. D. Evans, G. Yagupski and G. Wilkinson, J. Chem. Soc. (A), p. 2660 (1968).

102. L. Vaska and J. W. DiIuzio, J. Am. Chem. Soc., 84, 4989 (1962).

103. J. Chatt and B. L. Shaw, J. Chem. Soc., 5075 (1962).

104. M. A. Bennett and D. L. Milner, Chem. Commun., 581 (1967).

105. M. Orchin et al., J. Am. Chem. Soc., 78, 5450 (1956); 75, 3041 (1953).

106. D. S. Breslow and R. F. Heck, Chem. Ind. (London), p. 467 (1960).

107. J. Smidt et al., Angew. Chem., 71, 176 (1959).

108. J. Halpern, Adv. Chem. Ser., 70, 1 (1968).

109. R. Cramer, J. Am. Chem. Soc., 87, 4717 (1965).

110. (a) N. R. Davies, Rev. Pure Appl. Chem., 17, 83 (1967); (b) M. Orchin, Adv. Catalysis, 16, 2 (1966).

111. R. Cramer, J. Am. Chem. Soc., 88, 2272 (1966).

112. R. Cramer and R. V. Lindsey, Jr., J. Am. Chem. Soc., 88, 3534 (1966).

113. J. F. Harrod and A. J. Chalk, J. Am. Chem. Soc., 88, 3491 (1966).

114. J. L. von Rosenberg et al., Chem. Commun., p. 97 (1968); J. Am. Chem. Soc., 91, 2157 (1969).

115. R. W. Goetz and M. Orchin, J. Am. Chem. Soc., 85, 1549 (1963).

116. H. A. Tayim and C. Bailar, Jr., J. Am. Chem. Soc., 89, 3420 (1967).

117. R. Ugo, C. La Monica, S. Cenini and F. Bonati, J. Organometal. Chem., 11, 159 (1968).

118. J. K. Nicholson and B. L. Shaw, Tetrahed. Letters, p. 3533 (1965).

119. R. E. Rinehart and J. S. Lasky, J. Am. Chem. Soc. 86, 2516 (1964).

120. H. Frye, E. Kuljion and J. Viebrock, Inorg. Chem., 4, 1500 (1965).

121. B. L. Booth, R. N. Haszeldine and M. Hill, Chem. Commun., 1118 (1967).

122. L. A. Paquette and G. R. Krow, Tetrahed. Letters, p. 2139 (1968).

123. R. Crigee and H. Grüner, Angew. Chem. Internat. Ed. Eng., 6, 467 (1968).

124. B. L. Booth, R. N. Haszeldine and M. Hill, J. Chem. Soc. (A), p. 1299 (1969); J. Organometal. Chem., 16, 491 (1969).

125. R. B. King and M. B. Bisnette, J. Organometal. Chem., 8, 287 (1967).

126. A. T. Ginsberg, "Transition Metal Chemistry", ed., R. L. Carlin, Volume 1, p. 130 (1965).

127. J. Chatt, R. S. Coffey and B. L. Shaw, J. Chem. Soc., p. 7391 (1965).

128. H. B. Charman, J. Chem. Soc., (B), p. 629 (1967).

129. G. Wilkinson et al., J. Chem. Soc., p. 594 (1961); Chem. and Ind., p. 553 (1961).

130. H. J. Dauben and D. J. Bertelli, J. Am. Chem. Soc., 83, 497 (1961).

131. A. Effraty and P. M. Maitlis, J. Am. Chem. Soc., 89, 3744 (1967).

132. E. W. Abel, A. Singh and G. Wilkinson, J. Chem. Soc., p. 1321 (1960). See also: R. L. Cooper, E. D. Fischer and W. Semmlinger, J. Organometal. Chem., 9, 333 (1967).

133. E. Weiss and W. Hübel, Chem. Ber., 95, 1186 (1962).

134. E. O. Fischer and H. Werner, "Metal π-Complexes", Volume 1, Engl. Ed., Elsevier (1966).

135. A. G. Harrison, P. Haynes, S. McLean and F. Meyer, J. Am. Chem. Soc., 87, 5099 (1965).

136. R. A. Bernheim and H. Batiz-Hernandez, J. Chem. Phys., 45, 2261 (1966).

137. E. O. Fischer and M. W. Schmidt, Chem. Ber., 100, 3783 (1967).

138. R. K. Kochhar and R. Pettit, J. Organometal. Chem., 6, 272 (1966).

139. R. B. King, J. Organometal. Chem., 14, P 19 (1968).

140. E. Koerner von Gustorf and J. C. Hogan, Tetrahed. Letters, p. 3131 (1968).

141. S. Otsuki and M. Rossi, J. Chem. Soc. (A), p. 2630 (1968); p. 497 (1969).

142. C. A. Reilly and H. Thyret, J. Am. Chem. Soc., 89, 5144 (1967).

143. A. C. Cope, M. M. Martin and M. A. McKervey, Quart. Rev., 20, 119 (1966).

144. J. Powell and B. L. Shaw, J. Chem. Soc., (A), p. 583 (1967).

145. R. B. King, P. M. Triechel and F. G. A. Stone, J. Am. Chem. Soc., 83, 3593 (1961).

146. J. E. Arnet and R. Petit, J. Am. Chem. Soc., 83, 2954 (1961).

147. R. Huttel, H. Dietl and H. Christ, Chem. Ber., 97, 2037 (1964).

148. S. D. Robinson and B. L. Shaw, J. Chem. Soc., p. 5002 (1964).

149. D. Jones, G. W. Parshall, L. Pratt and G. Wilkinson, Tetrahed. Letters, p. 48 (1961).

150. N. D. Zelinsky and G. S. Pavlov, Ber., 66, 1420 (1933).

151. S. Carrà and V. Ragaini, Tetrahed. Letters, p. 1079 (1967).

152. J. E. Lyons, Chem. Commun., p. 564 (1969).

153. L. E. Craig, R. M. Elofson and I. R. Rossa, J. Am. Chem. Soc., 75, 480 (1953).

154. S. Moon and C. R. Ganz, J. Org. Chem., 34, 465 (1969).

155. M. I. Bruce, Adv. Organometal. Chem., 6, 272 (1968).

156. R. B. King, Applied Spectroscopy, 23, 148 (1969).

157. M. S. Lupin and M. Cais, J. Chem. Soc. (A), p. 3095 (1968).

158. R. Bruce, K. Moseley and P. M. Maitlis, Can. J. Chem., 45, 2011 (1967); R. Bruce and P. M. Maitlis, ibid, p. 2017.

159. S. Pignataro and F. P. Lossing, J. Organometal. Chem., 11, 571 (1968).

160. G. F. Emerson, L. Watts and R. Pettit, J. Am. Chem. Soc., 87, 131 (1965).

161. L. Dahl, personal communication to Professor P. M. Maitlis.