RHODIUM AND IRIDIUM HYDRIDES

To my parents, Mr. and Mrs. K.H. Lee,

and brothers, Dr. A.H. Lee and Mr. H.K. Lee, whose

encouragement have been a constant source of inspiration..

REACTIONS OF SOME RHODIUM AND IRIDIUM HYDRIDES

BY

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SCOPE AND CONTENTS:

Reactions of the complexes $[C_5Me_5MCl_2]_2$ (M=Rh and Ir) with alcoholic base gave the bridged hydrides $(C_5Me_5M)_2HCl_3$.

The hydrides reacted readily at room temperature with cyclic and acyclic diolefins to give π-allylic complexes, the cyn- isomers being the ones obtained when a choice was available. When both terminal and internal double bonds were present, addition of M-H occurred preferentially to the terminal double bond.

The allylic complexes showed varying degrees of stability towards reductive elimination (by loss of HCl) and the formation of 1,3-diene complexes. Allyls with only syn- substituents were stable towards diene complex formation. Those with an additional C-2 methyl substituent were less stable and the diene complexes could be obtained under moderately drastic conditions, presumably via σ-allyl intermediates. Allyls with an anti-methyl or -methylene substituent underwent reductive elimination of HCl to give diene complexes spontaneously and these reactions were accelerated by the

presence of triethylamine.

Kinetic studies on these hydride-diene reactions indicated that the reactions were first-order with respect to the hydride and independent of the nature and concentration of the diene. Except for 2,5-dimethyl-2,4-hexadiene, all dienes studied reacted at the same rate with the same hydride. The deuterides $(C_5Me_5M)_2DCl_3$ did not show any significant kinetic isotope effect. These results suggested that the rate-determining step of these hydride-diene reactions was the cleaving of the chloride bridge to create a vacant site. Mechanisms for the formation and decomposition of the allyls are proposed.

Reactions of $[C_5Me_5MCl_2]_2$ with dibenzylideneacetone, allyl cyanide and some β-diketones are described.

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INTRODUCTION

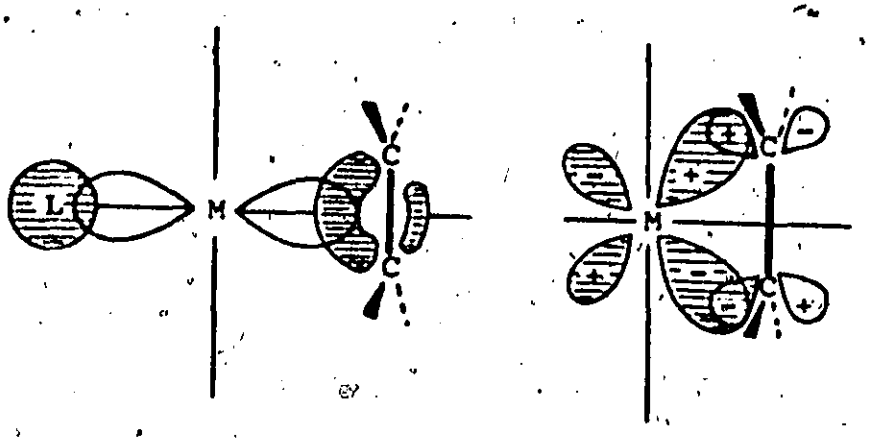
I. Metal π-Complexes[1-3]

In 1827 Zeise first prepared the platinum-olefin complex, $K[C_2H_4PtCl_3].3H_2O$[4], known as the Zeise's salt, but the ability of unsaturated hydrocarbons to form π-complexes with transition metals began to draw attention only in the 1950's. Since then there has been tremendous growth in interest and activity in this subject, not only because such complexes involved new types of chemical bonding but also because many of them are active catalysts, or serve as model compounds, for some industrially important catalytic systems. The π-complexes are so called because the unsaturated ligands use their vacant, antibonding π* orbitals to accept metal electrons in addition to forming a "donor" bond by the interaction of the filled, bonding π orbitals with vacant metal orbitals (Figure 1). It is this combination of donor and acceptor interaction which leads to the stability of metal π-complexes.

In these complexes the electrons are delocalised over both the unsaturated ligand(s) and the metal and the metal atoms are often in low "formal" oxidation states.

The vast majority of π-complexes obey the so called 18- or 16-electron rule[5] and are diamagnetic. Exceptions

to this empirical rule are usually unstable.



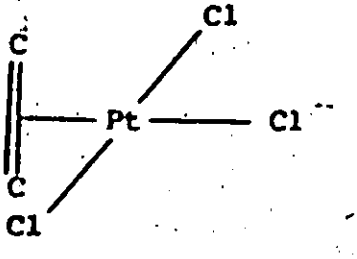
(a) "donor" bond (b) "acceptor" bond

Fig. 1 Bonding in olefir complexes

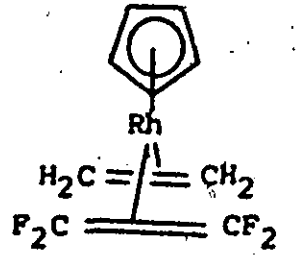
A brief discussion of the major types of π-complexes follows.

A. Monoolefin Complexes[6,7]

Interaction of monoolefins with transition metals forms a variety of π-olefin complexes. The structures of a great number of them have been determined. Typical examples such as Zeise's salt, (1)[8], and $C_5H_5Rh(C_2H_4)(C_2F_4)$, (2)[9], are shown below.

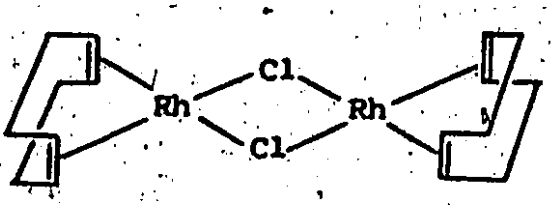


(1)



(2)

Non-conjugated dienes such as 1,5-cyclooctadiene (1,5-COD) and norbornadiene (NOR) usually form metal π-complexes with both olefinic bonds coordinated to the metal, as in $[Rh(1,5\text{-}COD)Cl]_2$, (3)[10], and $Pd(NOR)Cl_2$, (4)[11].



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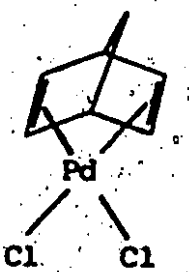


(4)

The above complexes, where there is no conjugation between the olefinic bonds in the ligand, can be regarded as possessing two 2-electron ligands and the bonding situation is similar to that in the monoolefin complexes.

B. Allylic Complexes[12,13]

The allyl ligand can be bound to a metal in three ways:

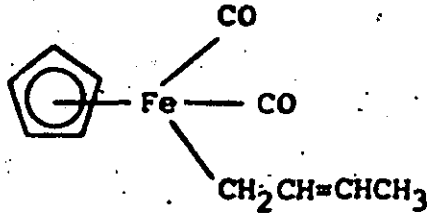
(i) σ-allyl (or h^1-allyl*); e.g. $C_5H_5Fe(CO)_2(C_4H_7)$, (5)

(ii) π-allyl (or h^3-allyl); e.g. $(C_3H_5)_2Ni$, (6)

(iii) asymmetric π-allyl; e.g. $C_4H_7Pd(PPh_3)Cl$, (7)

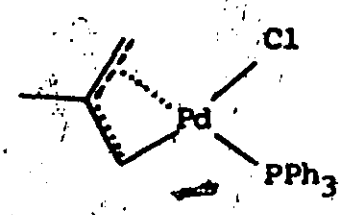
---

* This notation for organometallic compounds was proposed by Cotton[15]. The number of carbon atoms that are bonded to the metal atom is specified by a prefix such as monohapto-(h^1-), dihapto-(h^2-), trihapto-(h^3-), etc.



(5)

(6)



(7)

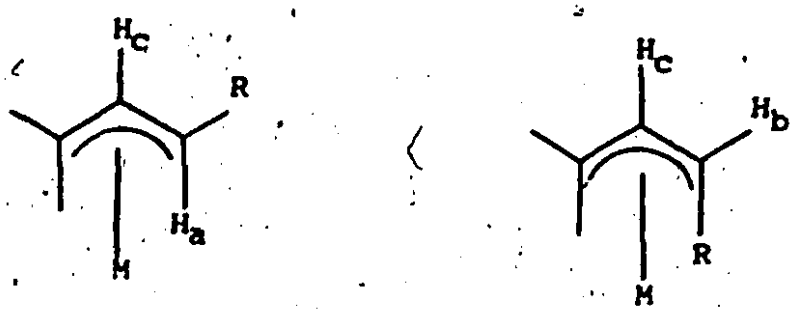
The π-allyl complexes, in which the π electrons are completely delocalised over the allylic skeleton, are most common in metal complexes. The bonding scheme has been discussed by Kettle and Mason[14]. They suggested that two extremes of bonding can be postulated, one in which the three carbons of the allyl and the metal are coplanar (8a) and the other in which the allylic plane is perpendicular (8b) to the coordination plane of the metal.

(8a)

(8b)

Theoretical calculations of various overlap integrals between the metal and the allylic ligand lead to the prediction that the interaction is maximised for a dihedral angle of 110°. This is in good agreement with the results of the X-ray determination on allylpalladium chloride dimer (111.5°)[16].

When there is a substituent on the terminal carbon of a π-allylic group, two geometrical isomers, namely the syn- and anti-isomers[17], are possible. The designations of syn and anti were suggested to denote the position of the substituent, R, with respect to the unique middle proton, H_c:



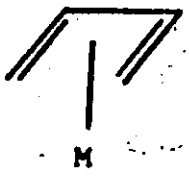
syn- (9a) anti- (9b)

The isomers (9a) and (9b) can unambiguously be distinguished by their p.m.r. spectra from the cis and trans coupling between H_a or H_b and H_c. H_a is also more shielded by the metal and hence appears at higher field.

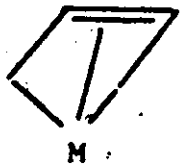
C. 1,3-Diene Complexes[18]

When double bonds in the olefinic ligand are conjugated, as in 1,3-dienes, the interaction between the two olefinic bonds must be considered. A detailed bonding description between these ligands and metals has been given by various authors[19,20]. Pictorially two extreme cases of bonding can be represented by (10a) and (10b).

Support for both models can be obtained from the crystal structures of diene complexes. In butadieneiron

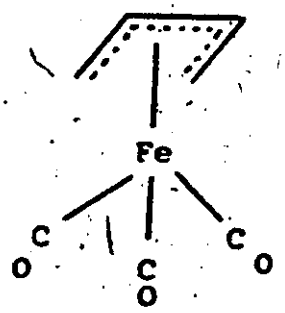


(10a)

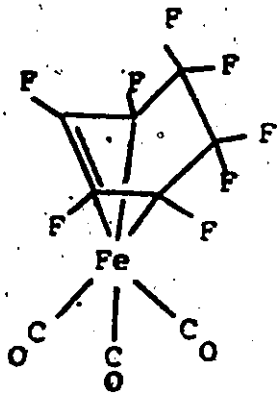


(10b)

tricarbonyl, (11), the X-ray determination[21] shows that the carbon atoms of butadiene adopt a cis configuration and are planar. The iron atom is equidistant (2.1 ± 0.04Å) from the four carbons and the C-C bond lengths are equal, indicating that both (10a) and (10b) are of approximately equal importance.



(11)

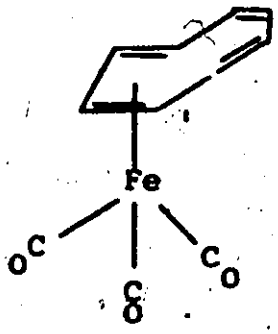


(12)

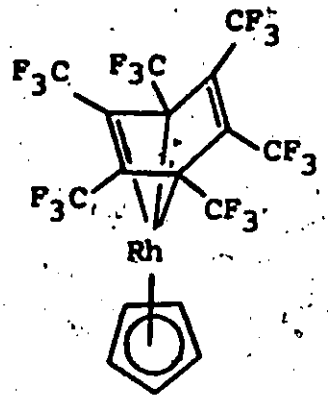
However, with electron-withdrawing substituents on the diene, such as perfluorohexa-1,3-diene in $Fe(CO)_3(C_6F_8)$[22], (12), increased back-bonding from the metal is expected; the whole molecule is then better described by the structure (10b) shown above.

Some organic molecules containing more than two conjugated double bonds may also act as tetrahapto-ligands,

as in cyclooctatetraeneiron tricarbonyl, (13)[23], and π-cyclopentadienylhexakis(trifluoromethyl)benzenerhodium, (14)[24].



(13)



(14)

Such molecules are usually "stereochemically non-rigid"[25] at higher temperatures.

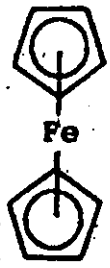
D. Cyclopentadienyl Complexes

The cyclopentadienyl group, C_5H_5, forms three types of compounds with metal atoms, namely:

(i) cyclopentadienides, e.g. $Be(C_5H_5)_2$, (15)

(ii) σ-cyclopentadienyls, e.g. $Hg(C_5H_5)_2$, (16)

(iii) π-cyclopentadienyls, e.g. $Fe(C_5H_5)_2$, (17) and $(C_5H_5)Mn(CO)_3$, (18)



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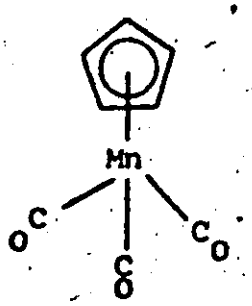


(18)

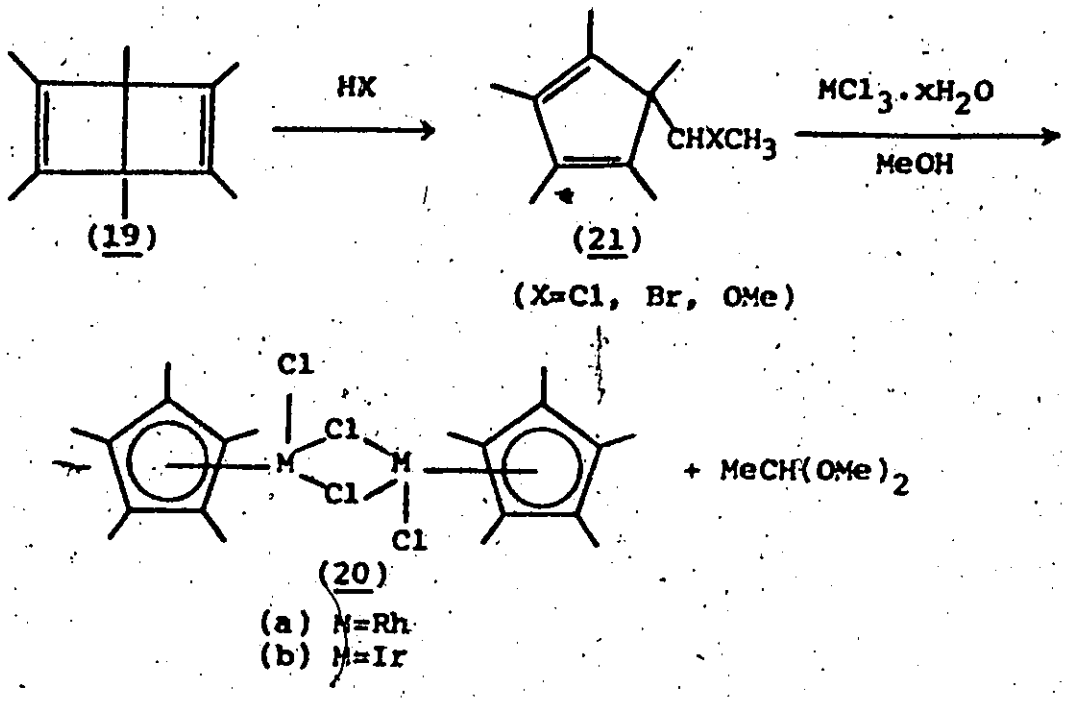
The types represented by the ionic beryllium compound, (15) and the fluxional molecule (16) are less common and are not π-complexes. In the π-cyclopentadienyls, the metal atom usually lies below the planar 5-membered ring, approximately equidistant from all carbon atoms. The M.O. treatment of bonding in sandwich compounds such as ferrocene, (17), has been discussed[26,27]. Basically, the bonding of this 18-electron diamagnetic species is covalent and involves similar interactions to those proposed for metal-olefin complexes. The cyclopentadienyl ring, when bound to a metal, is conveniently regarded as a 6-electron anionic ligand for electron book-keeping purposes. It is also usually considered to occupy three coordination sites.

Because of lower symmetry, the M.O. description of monocyclopentadienyls is more complicated[27]. A simplified procedure which is normally adopted is to considered the local symmetry of the C_5H_5M part of the molecule to obtain a description of ring-metal bonding and the local symmetry of the metal and other ligands in order to obtain a description for their bonding.

II. Pentamethylcyclopentadienyl Complexes of Rhodium and Iridium

Under acidic conditions in methanol, hexamethyldewarbenzene, (19), undergoes ring contraction reactions with rhodium and iridium trichloride hydrates to give pentamethylcyclopentadienyl-rhodium and -iridium dimers, (20)[28].

Mechanistic studies revealed the intermediacy of (α-substituted-ethyl)pentamethylcyclopentadiene (21) which formed from (19) with acids, HX [28,29]. Reaction of the diene (21) with $MCl_3.xH_2O$ (M=Rh and Ir) gave the rhodium and iridium complexes (20) and dimethylacetal in high yields.



The structures of these red or orange, air-stable complexes were assigned as shown on the basis of analysis, molecular weight and spectroscopic data. They were soluble in a variety of solvents and were dimeric in solution. In the presence of Lewis bases, L, however, the chloride bridges could be cleaved and adducts of the type $C_5Me_5MCl_2L$, (22), were isolated[28].

$$[C_5Me_5MCl_2]_2 \quad (\underline{20}) \quad + \quad L \longrightarrow C_5Me_5MCl_2L \quad (\underline{22})$$

(M=Rh and Ir; L=PPh_3, C_5H_5N, $p\text{-}MeC_6H_4NH_2$, etc.)

The most interesting chemical feature of complexes (20) was that while the M-Cl bonds were labile and could be displaced by other ligands, the C_5Me_5-M bonds were usually inert and remained intact throughout the reaction. For example, the M-Cl bond readily underwent metathesis reactions with halides, acetate and trifluoroacetate.

$[C_5Me_5MCl_2]_2$ (20)

LiBr →	$[C_5Me_5MBr_2]_2$	(23)[30]
NaI →	$[C_5Me_5MI_2]_2$	(24)[28,30]
AgOAc →	$[C_5Me_5M(OAc)_2.H_2O]_n$	(25)[28,31]
$AgOCOCF_3$ →	$C_5Me_5M(OCOCF_3)_2.H_2O$	(26)[31]

(M=Rh and Ir)

The complexes (20) were also reactive towards mono-, di- and tri-olefins in ethanol in the presence of a base, usually anhydrous sodium carbonate. In most cases, the chloride ligands in (20) were either partially displaced and M(III)-π-allyl or π-enyl complexes were formed; e.g.

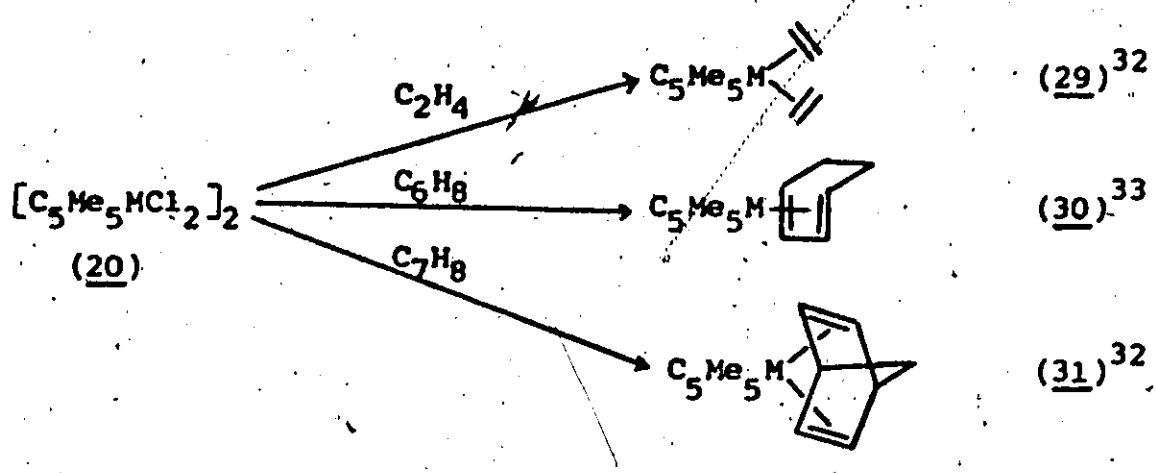
$[C_5Me_5MCl_2]_2$ (20)

C_4H_6 → $C_5Me_5M(Cl)$(π-allyl) (27)[32]

C_7H_8 → $[C_5Me_5M$(π-enyl)$]^+Cl^-$ (28)[32]

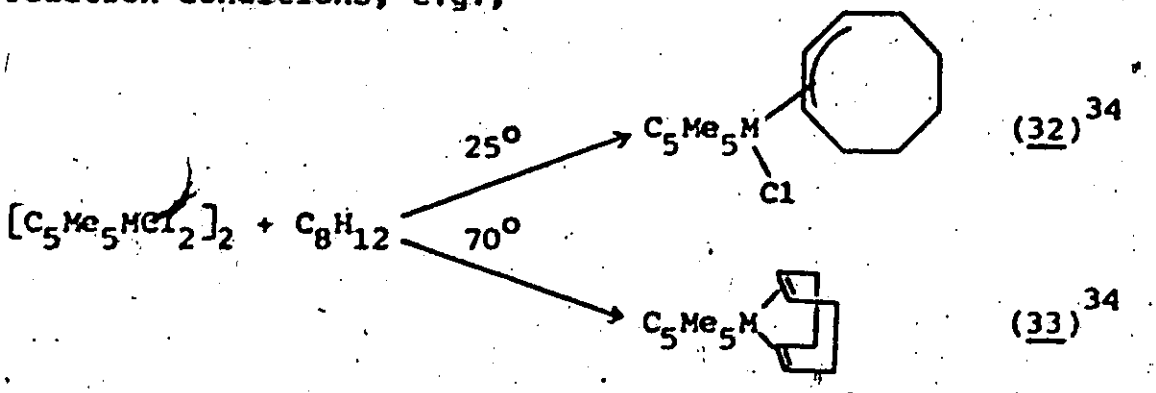
(M=Rh and Ir; C_4H_6=1,3-butadiene; C_7H_8=1,3,5-cycloheptatriene)

or were completely displaced to form M(I)-olefin complexes; e.g.,



(M = Rh and Ir; C_6H_8 = 1,3- or 1,4-cyclohexadiene; C_7H_8 = norbornadiene)

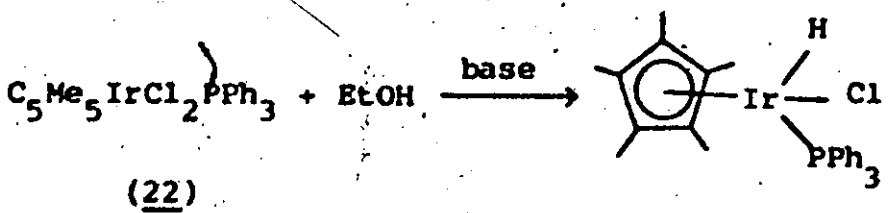
There were also cases where either or both types of complexes could be isolated from an olefin, depending on the reaction conditions, e.g.,



(M = Rh and Ir; C_8H_{12} = 1,3-, 1,4- or 1,5-cyclooctadiene)

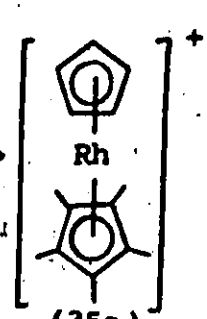
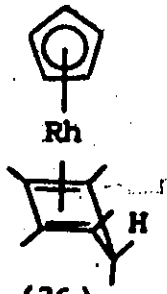
The interesting features of these reactions were: (i) M-H was added to the organic ligands in the formation of the 1-methylallyl, (27), cycloheptadienyl, (28), and cyclooctenyl, (32), complexes; (ii) the 1,3-cyclohexadiene

complexes (30) were formed with equal facility from both 1,3- and 1,4-cyclohexadiene, and the dichloride complexes (20) reacted with equal ease with either 1,3-, 1,4- or 1,5-cyclooctadiene. To explain (i) a metal hydride intermediate was required, which would also explain the facile isomerisation of the dienes (ii). The isolation of $C_5Me_5IrH(Cl)PPh_3$, (34), from the phosphine complex, (22), in ethanol in the presence of a base added support to this proposal[32].

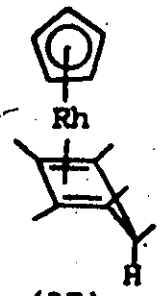


(22) (34)

Reactions of cyclopentadiene with (20) gave products[32] different from those described above. In ethanol in the presence of sodium carbonate, two complexes, (35a) and (36), were isolated from the rhodium complex (20a). The ionic (35a), was a sandwich-type complex and was readily identified by the two singlets in its p.m.r. spectrum. The covalent complex, (36), was shown by its p.m.r. and i.r. spectra to be cyclopentadienyl(pentamethylcyclopentadiene)rhodium(I) with an endo-hydrogen on the substituted ring. On treatment with sodium borohydride, complex (35a) gave the exo-H isomer, (37), in high yield[32].

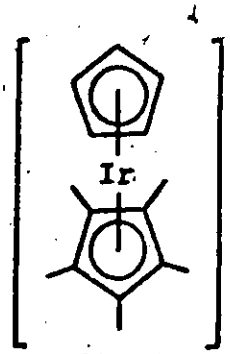
$[C_5Me_5RhCl_2]_2 + C_5H_6 \xrightarrow[Na_2CO_3]{EtOH}$  Cl^- + 

(20a) (35a) (36)

$[C_5Me_5RhC_5H_5]^+Cl^- + NaBH_4 \longrightarrow$ 

(35a) (37)

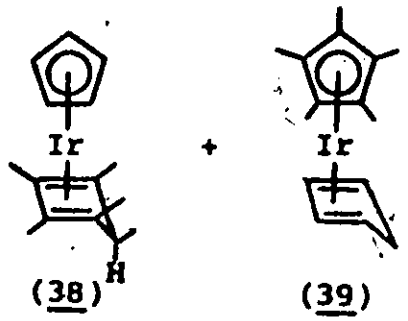
Reactions of the iridium complex (20b) with cyclopentadiene only gave the pentamethyliridicenium complex, (35b), and under no conditions was the iridium analogue of the endo-isomer (36) obtained.

$[C_5Me_5IrCl_2]_2 + C_5H_6 \longrightarrow$  Cl^-

(20b) (35b)

The ionic chloride, (35b), was again reduced with sodium borohydride and in this case, a mixture of exo-H-cyclopentadienyl(pentamethylcyclopentadiene)iridium(I), (38), (70%) and cyclopentadiene(pentamethylcyclopentadienyl)-iridium(I), (39), (30%) was formed. On treatment with mild

chlorinating agents, both (38) and (39) were rapidly converted back to the ionic complex, (35b)[32].

$[C_5Me_5IrC_5H_5]^+Cl^-$ + $NaBH_4$ ⟶  +

(35b) (38) (39)

Reactions of (20) with carbon monoxide gave another type of M(I) complex, namely, the dicarbonyl(pentamethylcyclopentadienyl)-rhodium and -iridium complexes, (40)[28,35]. In common with other typical d^8 complexes with the metal in low oxidation states, they easily underwent oxidative addition reactions[36].

$C_5Me_5Rh(CO)_2$ + MeI ⟶ $[C_5Me_5Rh(CO)_2Me]^+I^-$ ⟶

(40a) (41)

$C_5Me_5Rh(CO)(COMe)I$ [35]

(42)

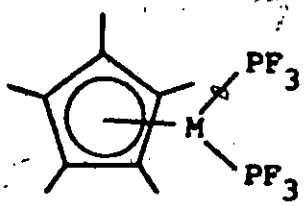
$C_5Me_5Ir(CO)_2$ + RSO_2Cl ⟶ $C_5Me_5Ir(CO)(SO_2R)Cl$ + CO [35]

(40b) (43)

(R=Me, Ph, p-MeC_6H_4 and p-BrC_6H_4)

Reactions of the dichloride complexes, (20), with tetrakistrifluorophosphine nickel have been studied[37]. In

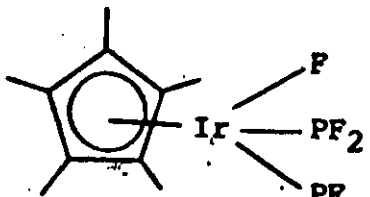
the rhodium reaction, $C_5Me_5Rh(PF_3)_2$, (44a), was the sole product. However, under similar conditions, the iridium complex gave a mixture of $C_5Me_5Ir(PF_3)_2$, (44b), and $C_5Me_5IrF(PF_2)(PF_3)$, (45); the latter being derived from (44b) by an internal oxidative addition involving a trifluorophosphine ligand.



(44)

(a) M=Rh

(b) M=Ir



(45)

The synthesis of pentamethylcyclopentadienyl complexes of other transition metals from pentamethylcyclopentadiene or 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene has also been reported[38,39].

III. The Chemistry of Hydrido Complexes of Transition Metals[40-42]

It has been known for a long time that many transition metals rich in d electrons are able to activate hydrogen and this explains the use of Pt, Pd and Ni as heterogeneous hydrogenation catalysts[43]. However, studies of hydrido complexes of transition metals began to advance significantly only in the early sixties.

A. Preparation

The methods commonly employed in the synthesis of hydrides are:

(i) Reaction with molecular hydrogen in

(a) cleavage of metal-metal bonds, e.g.,

$$[Mn(CO)_5]_2 + H_2 \longrightarrow 2HMn(CO)_5 \quad ^{44}$$

or (b) oxidative addition reactions, e.g.,

$$IrCl(CO)(PPh_3)_2 + H_2 \longrightarrow H_2IrCl(CO)(PPh_3)_2 \quad ^{45}$$

or (c) displacement of an anionic ligand, e.g.,

$$RuCl_2(PPh_3)_3 + H_2 \xrightarrow{C_6H_6} HRuCl(PPh_3)_3.C_6H_6 + HCl \quad ^{46}$$

(ii) Reduction of metal halide complexes by the use of $NaBH_4$ and $LiAlH_4$, e.g.,

$$RhCl(CO)(PPh_3)_2 + PPh_3 \xrightarrow{NaBH_4} HRh(CO)(PPh_3)_3 \quad ^{47}$$

$$RuCl_2(CO)_2(PPh_3)_2 \xrightarrow{LiAlH_4} H_2Ru(CO)_2(PPh_3)_2 \quad ^{48}$$

(iii) Reactions of alcohols with metal complexes in the presence of a base, e.g.,

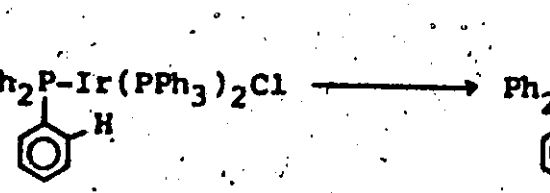
$$IrCl_3(PEt_3)_3 + EtOH + KOH \longrightarrow HIrCl_2(PEt_3)_3 + CH_3CHO \quad ^{49}$$

(46)

In a related reaction with CH_3CD_2OH, the hydride ligand in (46) was shown to originate from the α-position of the alcohol[50].

(iv) Intramolecular hydride abstraction, e.g.,

$$trans\text{-}PtCl(C_2H_5)(PPh_3)_2 \longrightarrow trans\text{-}HPtCl(PPh_3)_2 + C_2H_4 \quad 51$$



52

(v) Protonation of a metal complex by an acid, e.g.,

$$Ni[P(OEt)_3]_4 + HX \longrightarrow [HNi\{P(OEt)_3\}_4]^+X^- \quad 53$$

$$(X = HSO_4,\ Cl,\ ClO_4,\ CF_3COO)$$

Because of the small mass of hydrogen, elemental analysis are not reliable for the determination of the presence of hydride ligands. A useful technique is infrared spectroscopy since ν(M-H) for a terminal metal-hydrogen bond are usually observed in the 1700-2300 cm^{-1} region of the infrared. Observation of such an absorption band together with the corresponding metal-deuterium stretch [with $\nu(MH)/\nu(MD)$ = ca. 1.4] provides strong evidence for the presence of a metal hydride. Complexes with bridging hydrides show ν(M-H-M) in the range 1000-1500 cm^{-1} and a shift to lower frequency by a factor of ca. 1.4 is observed on deuteration.

Another reliable method for the detection of a M-H bond is the proton magnetic resonance spectroscopy. Transition metal hydrides almost invariably show high field resonances (τ 10-30). The p.m.r. method also has the advantage of showing the number (by integration) and types

(by chemical shifts) of hydride ligands.

A number of crystal structures of hydrides have been determined by X-ray diffraction; some characteristic points are listed below:

(i) Despite its small size, the hydride ligand is stereochemically active and usually occupies a regular coordination site. However, in almost every case, the ligand(s) adjacent to the hydride ligand are displaced towards the hydrogen, owing to its small size. This effect is usually more prominent if bulky phosphine groups are present.

(ii) The hydride ligand exerts a strong trans-influence[54], i.e. ligands trans to hydrogen are more labile than similar ligands cis to hydrogen. Further, metal-ligand bonds trans to hydrogen are slightly longer than bonds cis to it; this is a manifestation of the trans-influence.

B. Reactions of Metal Hydrides

The reactivity of transition metal hydride complexes varies from metal to metal and also depends on the other ligands present. Some of them are highly reactive and only exist transiently as reaction intermediates. For hydrides which are stable enough to be isolated, the following reactions are frequently observed.

(i) Deuterium exchange reactions

The hydride ligand in a metal complex may undergo deuterium exchange with a solvent (e.g., deuterium oxide[55]

or an alcohol, ROD[56]), with deuterium[57] itself, or with a deuterated olefin[57].

(ii) Reactions with halogen and halogenated hydrocarbons

Halogen usually displaces the hydride ligand with the formation of hydrogen halide and the metal halide.

$$HRhBr_2(AsMePh_2)_3 + Br_2 \longrightarrow RhBr_3(AsMePh_2)_3 + HBr \quad [58]$$

Halocarbons also react with hydrides (reactivity $CCl_4 > CHCl_3 > CH_2Cl_2$) to give the metal halide and, sometimes, the halocarbon with hydrogen in place of halide.

$$trans\text{-}HPdCl(PEt_3)_2 + CCl_4 \longrightarrow trans\text{-}PdCl_2(PEt_3)_2 + CHCl_3 \quad [59]$$

(iii) Reactions with donor ligands

When a donor ligand such as a tertiary phosphine or carbon monoxide reacts with a hydride complex, hydrogen halide or hydrogen are sometimes eliminated:

$$HRhCl_2(PPh_3)_2 + CO \longrightarrow RhCl(CO)(PPh_3)_2 + HCl \quad [60]$$

$$H_2Fe(CO)_4 + PPh_3 \longrightarrow Fe(CO)_4(PPh_3) + Fe(CO)_3(PPh_3)_2 + H_2 \quad [61]$$

In other cases the donor ligand simply adds or displaces another neutral ligand, while leaving the M-H bond intact.

$$HIrCl_2(PPh_3)_2 + L \longrightarrow HIrCl_2(PPh_3)_2L \quad [62]$$

(L=phosphines, arisines, nitriles and carbon monoxide)

$$HMn(CO)_5 + PF_3 \longrightarrow HMn(CO)_{5-x}(PF_3)_x \quad [63]$$

(x=1-5)

(iv) Reactions with unsaturated molecules

There has been tremendous growth in interest in the reactivities of transition-metal hydrides towards unsaturated organic molecules over the past ten years because of the

relevance of such interactions to industrial catalytic processes. Hydrides form alkyl, allyl (or en-yl), or vinyl metal complexes with olefins, diolefins and alkynes respectively.

Chatt and Shaw reported the reactions of trans-$HPtCl(PEt_3)_2$ with ethylene or propylene to give the corresponding alkyl complexes (47)[51].

$$\text{trans-}HPtCl(PEt_3)_2 + H_2C{=}CHR \longrightarrow \text{trans-}(RCH_2CH_2)PtCl(PEt_3)_2$$

(R=H, CH_3) (47)

At high temperatures, the complexes (47) decompose and give the starting materials.

Ethylene also reacts with $[HRh(NH_3)_5]^{2+}$,[64] or $HRhCl_2(PPh_3)_2$[60] to give the corresponding ethyl complexes. Higher olefins also insert into M-H bonds and form alkyl complexes but the products are often not isolable because alkyl ligands containing β-hydrogens readily undergo β-elimination (of M-H)[65], the reverse of the formation reaction.

Owing to the higher stability of the resulting alkyl complexes, isolable metal alkyls are obtained from hydrides and olefins with electronegative substituents. For example, stable tetrafluoroethyl complexes are obtained from reaction of tetrafluoroethylene with $HM(\pi\text{-}C_5H_5)(CO)_3$ (M=Mo and W)[66], $HRe(CO)_5$[67], $HFe(\pi\text{-}C_5H_5)(CO)_2$[68], $HCo(CO)_4$[69] and $HRhCl_2(PPh_3)_2$[60].

Reactions of hydride complexes with acetylenes have

not been studied as extensively. Among the few examples, $HRhCl_2(PPh_3)_2$ gave a vinyl complex, $RhCl_2(CH{=}CH_2)(PPh_3)_2$ [60] with acetylene while $HIr(CO)(PPh_3)_3$ gave $Ir(CR{=}CHR)(RC{\equiv}CR)(CO)(PPh_3)_2$ ($R{=}CF_3$, COOMe) from the reactions with hexafluoro-2-butyne and dimethyl acetylenedicarboxylate.

Olefins and acetylenes with electron-withdrawing substituents such as -CN, -COOMe or $-CF_3$ underwent insertion reactions into one of the Mo-H bonds of π-Cp_2MoH_2 to give hydrido-σ-alkyl or -σ-alkenyl complexes. With excess olefin or acetylene, some of these complexes gave products of the type π-$Cp_2Mo(Un)$ (Un=alkene or alkyne) together with the stoicheiometric amount of the corresponding hydrogenated hydrocarbons, H_2Un [71].

Conjugated dienes react with hydride complexes to form σ- or π-allyls, although the latter are more stable and usually isolated. Thus $HMn(CO)_5$ reacted with butadiene to give first $Mn(\sigma\text{-}C_4H_7)(CO)_5$ which then lost carbon monoxide on further reaction and gave $Mn(\pi\text{-}C_4H_7)(CO)_4$ [17]. A series of substituted π-allyl-cobalt tricarbonyl complexes were prepared by the interaction of $HCo(CO)_4$ with some conjugated and non-conjugated diolefins [72]. Mechanistic studies suggested that a 1,4-addition of $HCo(CO)_4$ to butadiene took place in the formation of the syn- and anti-1-methylallyl complexes [73,74].

Tolman has characterised the products of the reaction of $HNiL_4^+$ [L=$P(OEt)_3$ or $P(OMe)_3$] with a variety of conjugated dienes in solution as π-allylnickel phosphite complexes by

their p.m.r. spectra[75,76].

$$HNiL_4^+ + \text{diene} \longrightarrow \pi\text{-allyl-}NiL_3^+ + L$$

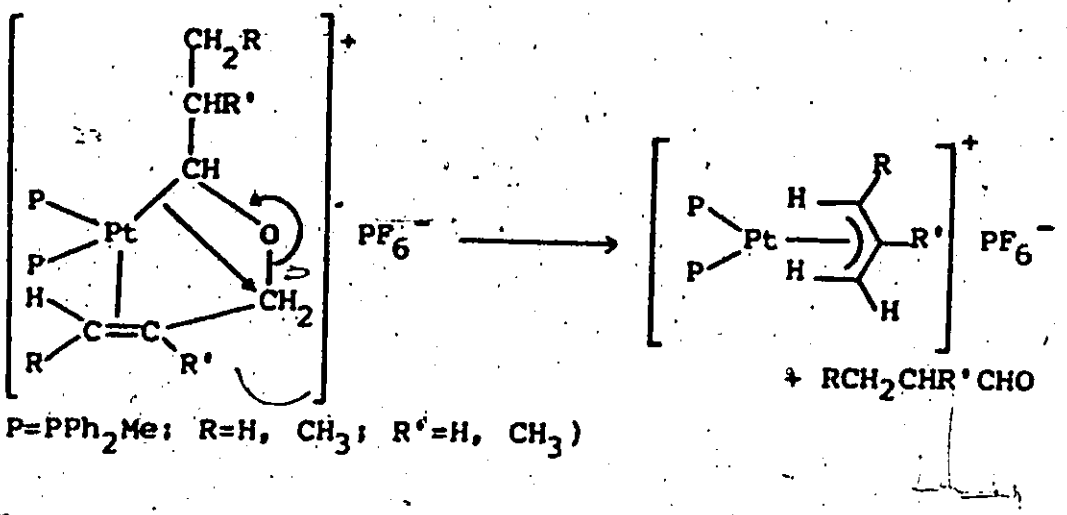
It is of interest to note that among these π-allylic complexes, the anti isomers were kinetically preferred while the syn isomers tended to be thermodynamically favoured. Thus in the formation of the π-1-methylallyl complexes, the syn:anti ratios increased from 12:88 at the initial stage to 95:5 at equilibrium. For substituted butadienes, experiments showed that the π-allylic products formed invariably corresponded to Ni-H addition across a terminal double bond, suggesting a 1,2-addition mechanism. If no terminal double bond was present, as in the 2,4-hexadienes, addition reaction occurred at a much slower rate. Non-conjugated dienes such as 1,4-pentadiene isomerised in the presence of the nickel hydride to 1,3-pentadiene, which then gave the π-1,3-dimethyl-allyl complex[76]. trans-1,4-Hexadiene was formed catalytically as the major product from butadiene and ethylene in a series of reactions involving the $HNiL_4^+$ intermediate[75].

Wilkinson and his co-workers found that the normally facile olefin hydrogenation and hydroformylation reactions catalysed by $RhH(CO)(PPh_3)_3$ did not occur in the presence of conjugated dienes or allene[77]. Instead, the catalyst was deactivated by the formation of stable π-allylic complexes of the form $Rh(allyl)(CO)(PPh_3)_2$. The iridium hydride $IrH(CO)_2(PPh_3)_2$ was also shown to behave similarly[77].

Recently, Clark et al. have reported the formation of π-allylic complexes from the interaction of hydride and allylic compounds[78]. The cationic platinum hydride, (48), reacted with several diallyl ethers at room temperature according to the following equation:

$$trans\text{-}[PtH(PPh_2Me)_2(acetone)]PF_6 + (CHR{=}CR'CH_2)_2O \longrightarrow$$

(48)



(P=PPh_2Me; R=H, CH_3; R'=H, CH_3)

The same products were also obtained when two molar equivalents of allylic alcohols were used instead of one equivalent of the diallyl ethers.

IV. The Role of Transition Metal Hydrides in Homogeneous Catalysis

The use of transition metal complexes in homogeneously catalysed processes has an ever increasing importance in the chemical industry nowadays. In comparison with heterogeneous catalysts, homogeneous catalysts have a number of advantages

since the reactions usually go under milder conditions and are more selective[79-82]. Moreover, with the help of certain model systems, the mechanism of these reactions is more easily studied. It is now generally accepted that the catalytic process involves the following steps:[83]

(i) Oxidative addition of a molecule A-B to a metal complex.

(ii) Creation of a vacant coordination site on the metal by loss of a neutral ligand, followed by the coordination of the reactant Y.

(iii) Rearrangement of groups A,B and Y in the complex to give an intermediate in which these groups are so placed as to facilitate reaction.

(iv) Reactions of A or B with Y.

(v) Regeneration of the catalyst with the loss of the product AY or BY.

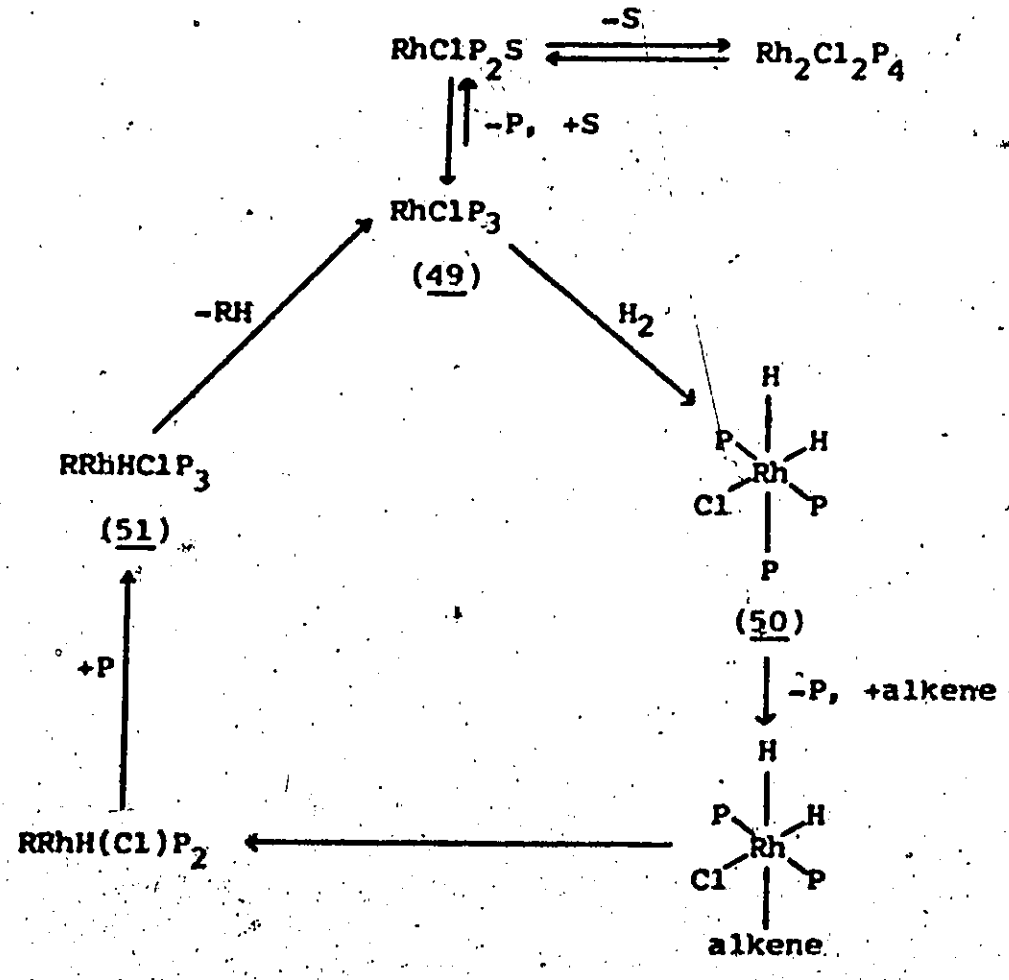
As a result of intensive investigation over the past few years, it has now become obvious that transition metal hydrides are intermediate in many homogeneously catalysed reactions involving olefins, including hydrogenation, hydroformylation, isomerisation, deuteration and polymerisation. Two important roles of transition metal hydrides in catalytic systems are:

(i) The ability of the hydride ligand to weaken bonds trans to itself and hence to increase the rates of reaction.

(ii) The reaction with unsaturated substrates, especially olefins.

Hydrogenation[84]

Hydrogenation of olefins is one of the most thoroughly studied areas in homogeneous catalysis. Among the many examples, the catalytic system involving $RhCl(PPh_3)_3$, (49), known as Wilkinson's catalyst, is perhaps best understood[85]. This compound hydrogenates olefins such as cyclohexene or 1-heptene conveniently under mild conditions (25° and 1 atm of H_2). Studies of the reaction of (49), particularly with hydrogen[86-89] suggest the mechanism outlined in Scheme I:



Scheme I. P=PPh_3, S=solvent and R=alkyl group

While the major route does not involve $RhClP_2S$, recent kinetic studies by Halpern et al. showed that $RhClP_2$ was at least 10^4 times as reactive towards hydrogen as either $RhClP_3$ or $Rh_2Cl_2P_4$ [90]. Hence the catalytic activity of $RhClP_2$ cannot be overlooked despite its low concentration in solution.

Under the same conditions, acetylenes are also hydrogenated efficiently by (49) but conjugated dienes are not except under pressure. Functional groups such as keto-, hydroxy-, cyano-, nitro-, chloro-, azo-, esters and carboxylic acids are not affected under mild conditions. Terminal olefins are hydrogenated more readily than internal ones and cis-olefins are reduced faster than their trans isomers.

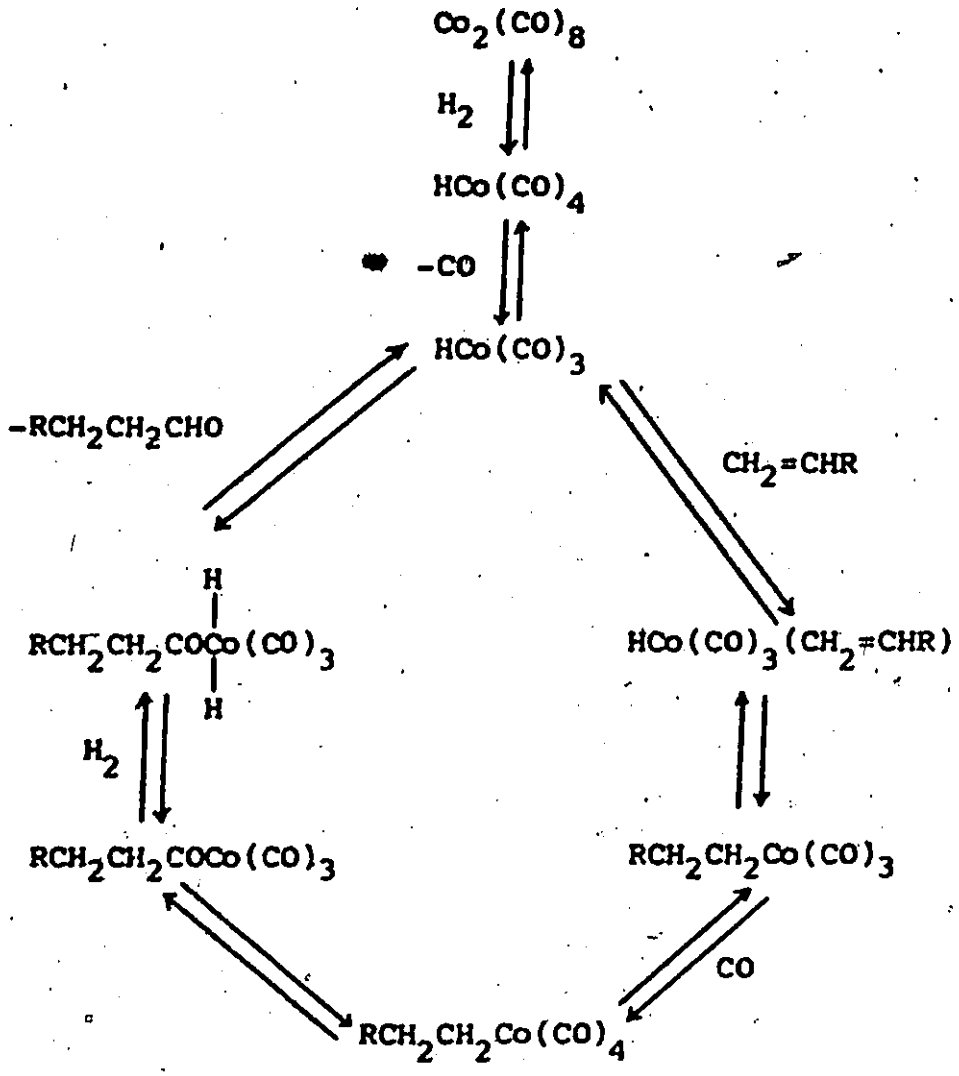
The hydrogenation of olefins by other catalysts such as $HRuCl(PPh_3)_3$ [46], $HRh(CO)(PPh_3)_3$ [91] and $Co(CN)_5^{3-}$ [92] has also been reported.

Hydroformylation[93]

The hydroformylation of olefins to give higher aldehydes and alcohols by $Co_2(CO)_8$ or $HCo(CO)_4$ has also been studied particularly because of the great industrial interest in this reaction. The overall mechanism proposed by Heck and Breslow[94] is shown in Scheme II.

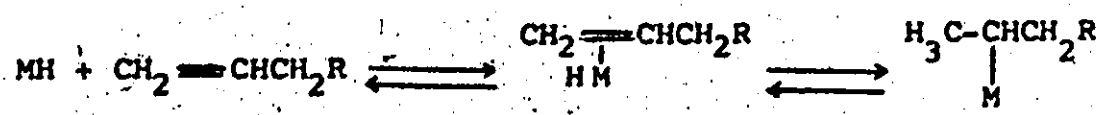
The rhodium complex $RhCl(CO)(PPh_3)_2$ is also an effective hydroformylation catalyst under mild conditions[95].

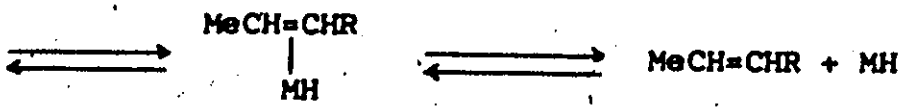
Scheme II



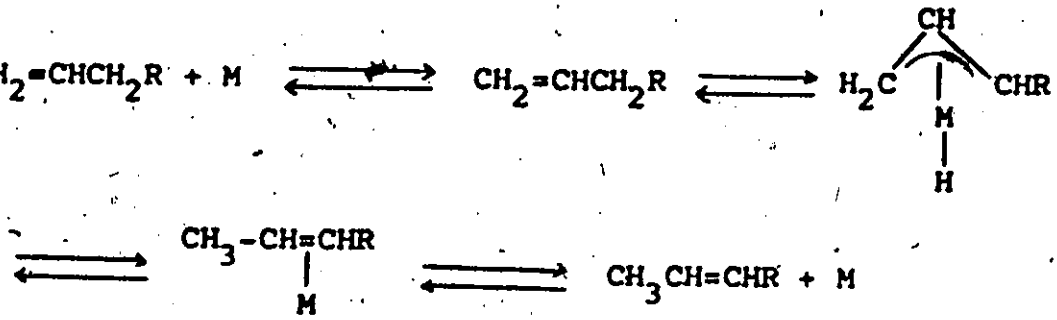
Olefin isomerisation

A number of mechanisms have been proposed for olefin isomerisation catalysed by metal complexes[96]. The best authenticated involves the addition and elimination of M-H at the double bond of a coordinated olefin[97-103], giving rise to a 1,2-hydrogen shift:





Another mechanism for double bond isomerisation involves a π-allyl metal hydride intermediate[104-106] and can be represented by the following equations:



V. μ-Chloro-μ-hydrido-dichlorobis(pentamethlcyclopentadienyl)-di-rhodium and -iridium (52)

The previously mentioned stoicheiometric reactions of $[C_5Me_5HCl_2]_2$ (20) with mono-, di-, and tri-olefins[32-34] and the isolation of $C_5Me_5IrH(Cl)PPh_3$ (34)[32] strongly suggested the existence of hydrido complexes. In a hydrogenation experiment using $[C_5Me_5RhCl_2]_2$ (20a) as catalyst, it was observed that at the very beginning of the reaction the colour of the solution changed from red to deep purple on the addition of a base such as triethylamine. The rate of hydrogenation was also greatly increased. From the purple solution air stable dark purple crystals were isolated that were identified as $(C_5Me_5Rh)_2HCl_3$ (52a) on the basis of analysis, molecular weight determination, spectroscopic

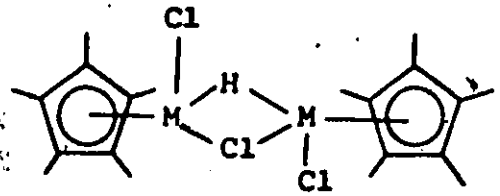
data[107,108] as well as an X-ray structural determination[109]. Under similar conditions, the red iridium analogue (52b) was also obtained[107,108].

$$[C_5Me_5HCl_2]_2 \xrightarrow{H_2, Et_3N}$$

(20)

(a) M=Rh

(b) M=Ir



(52)

The crystal structure of (52a) indicated the molecule has precise C_2 symmetry, with a planer Rh(H)(Cl)Rh' bridge and the twofold axis running through the two bridging ligands. Interatomic dimensions include Rh....Rh=2.906(1), Rh-Cl(bridging)=2.437(2), Rh-Cl(terminal)=2.393(2), and Rh-H(bridging)=1.85(5)Å. Angles within the Rh(H)(Cl)Rh' brigde are Rh-Cl-Rh'=73.20(6), Rh-H-Rh'=103.6(37), and H-Rh-Cl=H-Rh'-Cl=91.6(18)°. The short Rh....Rh distance as well as the small Rh-Cl(bridging)-Rh angle suggested at least some metal-metal interaction.

The hydrides (52) were shown to be powerful catalysts for hydrogenation of olefins at 1 atm and 25°, the iridium complex (52b) generally being more active than its rhodium analogue (52a).

Functional groups such as keto-, nitro- or aryl were not reduced by these catalysts but their presence on the olefin deactivated it in varying degrees towards

hydrogenation. A number of olefins (4-vinylcyclohexene, norbornadiene, 1,3- and 1,5-cyclooctadienes, allylbenzene, mesityl oxide) as well as diphenylacetylene, which were not readily hydrogenated at 1 atm, were efficiently reduced under pressure (100 atm, 24°) by (52a), even in the absence of base.

Complexes (52) were also catalysts for olefin isomerisation. For instance, cis-4-methyl-2-pentene was isomerised by the iridium hydride (52b) to give an equilibrium mixture of 80% of 2-methyl-2-pentene, 10% of 2-methyl-1-pentene and 10% of the starting material after one hour at 25°.

The bridged hydrides (52) undergo stoicheiometric reactions with diolefins and this thesis is concerned with the details of these reactions. Many of the metal complexes derived from (52) and dienes were stable enough for characterisation and these data, coupled with the kinetic studies on the reactions between the hydrides and a variety of dienes, provide mechanistic information on the interaction of M-H bonds with unsaturated substrates.

At the same time, D.S. Gill of this Laboratory is investigating the hydrogenation of olefins by using $(C_5Me_5M)_2HCl_3$ (52) as homogeneous catalysts. Under similar conditions, these catalytic reactions may be compared and contrasted with the closely related stoicheiometric

reactions with diolefins. The combined information will provide a fuller understanding of the reactions of rhodium and iridium hydrides with olefins.

RESULTS

RESULTS

I. The Chemistry of the Hydrido Complexes, $(C_5Me_5M)_2HCl_3$ (M=Rh and Ir)

The hydrido complexes $(C_5Me_5M)_2HCl_3$ (52) could be obtained in a number of ways. In general, the hydride was formed by reacting stoicheiometric amounts of $[C_5Me_5MCl_2]_2$ (20) with a hydriding agent and a base in a solvent. Combinations such as (i) hydrogen, triethylamine in isopropanol; (ii) sodium borohydride in isopropanol; (iii) potassium hydroxide in isopropanol; and (iv) isopropanol and triethylamine in benzene were all suitable for the preparation of the hydrido complexes (52). However it was observed that preparation of the rhodium hydride (52a) by method (ii) and the iridium analogue (52b) by method (iii) usually gave the highest yield (ca. 90% in both cases) and purity and hence these were the methods of choice. The deuterides $(C_5Me_5M)_2DCl_3$ (53) were prepared by method (i) using deuterium instead of hydrogen (See Experimental).

The hydridochlorides (52) were very soluble in chloroform and methylene chloride, moderately soluble in benzene and isopropanol and sparingly soluble in ether and saturated hydrocarbons. In the solid state, these purple (rhodium) and red (iridium) complexes were stable to air

for an indefinite period of time.

A. Reactions with organic chlorides

Chlorinated hydrocarbons such as benzyl chloride, benzoyl chloride, methylene chloride and chloroform were found to react with the hydrides (52a and b) to give the dichloro complexes (20a and b). In the last two cases, the yields of (20a and b) were quantitative. In none of the above cases could the hydrogen from (52) be detected in an organic product. This contrasted with the reaction of $C_5Me_5IrH(Cl)PPh_3$ (34) with chloroform-d in which $CHDCl_2$ was formed[32].

$$\underset{(34)}{C_5Me_5IrH(Cl)PPh_3} + CDCl_3 \longrightarrow \underset{(22b)}{C_5Me_5IrCl_2PPh_3} + CHDCl_2$$

The rate of decomposition of the iridium hydride (52b) in chloroform or methylene chloride solution was extremely slow at 25°; in chloroform (52b) was completely converted into (20b) in three weeks. For rhodium, the same process was complete in about three days. However, the rates of decomposition were greatly increased if the solvent contained hydrogen chloride as impurity or decomposition product since the acid reacted immediately and stoicheiometrically with (52) according to the following equation:

$$\underset{(52)}{(C_5Me_5M)_2HCl_3} + HCl \longrightarrow \underset{(20)}{[C_5Me_5MCl_2]_2}$$

It was therefore necessary to carefully de-acidify all solvents before use.

B. Reactions with triphenylphosphine and carbon monoxide

With Lewis bases such as triphenylphosphine, the iridium hydride (52b) underwent a stoicheiometric reaction at 25° to give the known phosphine-dichloro (22b)[28] and phosphine-chlorohydrido (34)[32] complexes, as shown by their p.m.r. spectra.

$$(52b) + 2PPh_3 \longrightarrow C_5Me_5IrCl_2PPh_3 \ (22b) + C_5Me_5IrH(Cl)PPh_3 \ (34)$$

In a benzene solution at 50°, the iridium hydride (52b) reacted with carbon monoxide to give a 1:1 mixture of the dicarbonyl (40b) and carbonyldichloro (54) complexes[35]. Both products were identified by their p.m.r. spectra, and by i.r. (strong ν(CO) terminal at 1925, 2000 and 2035 cm^{-1}) identical to the literature values[35].

$$(52b) + CO \longrightarrow C_5Me_5IrH(Cl)CO \ (55) + C_5Me_5IrCl_2(CO) \ (54)$$

$$(55) \xrightarrow{+CO,\ -HCl} C_5Me_5Ir(CO)_2 \ (40b)$$

By analogy with the phosphine reaction described above, it may be assumed that the carbonylhydridochloride complex

$C_5Me_5IrH(Cl)CO$ (55), undetected, is formed as an intermediate which, on reaction with another molecule of CO, eliminates HCl to give the dicarbonyl complex (40b).

Reactions of the rhodium analogue (52a) with triphenylphosphine and carbon monoxide were not as well characterised. In the phosphine reaction, the phosphine-dichloro complex (22a) was obtained as the major product together with a small amount of other unidentified products. No phosphine-hydridochloro complex, such as $C_5Me_5RhH(Cl)PPh_3$, was ever observed. This accords with the fact that this complex could not be obtained either from $C_5Me_5RhCl_2(PPh_3)$ (22a) on reduction.

A mixture of uncharacterised products was obtained in the carbon monoxide reaction; none of which corresponded to the known rhodium dicarbonyl complex (40a)[35].

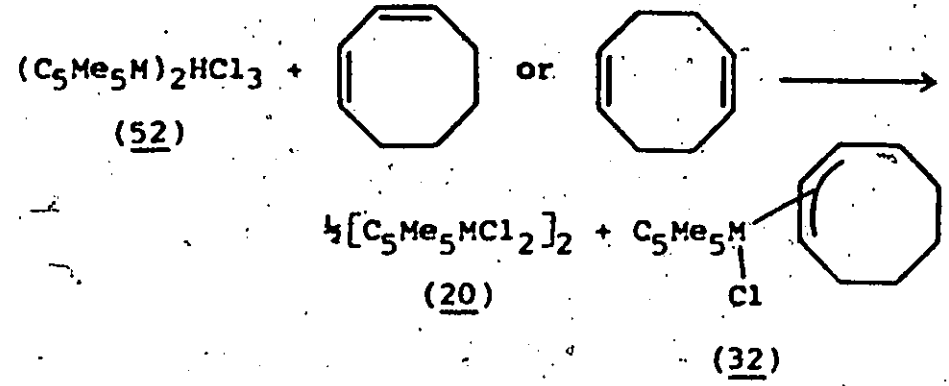
C. Reactions with cyclic diolefins

The hydrides (52a and b) underwent stoicheiometric reactions with cyclic and acyclic, conjugated and non-conjugated, diolefins readily at 25° to give en-yl or allylic complexes together with the corresponding dichlorides (20a and b). In some cases, the en-yl or allylic complexes reductively eliminated hydrogen chloride to give M(I)-diene complexes. The rates of these reactions were also studied, and details are given in later sections.

(i) 1,3- and 1,5-Cyclooctadienes

The complexes $(C_5Me_5M)_2HCl_3$ (52a and b) reacted

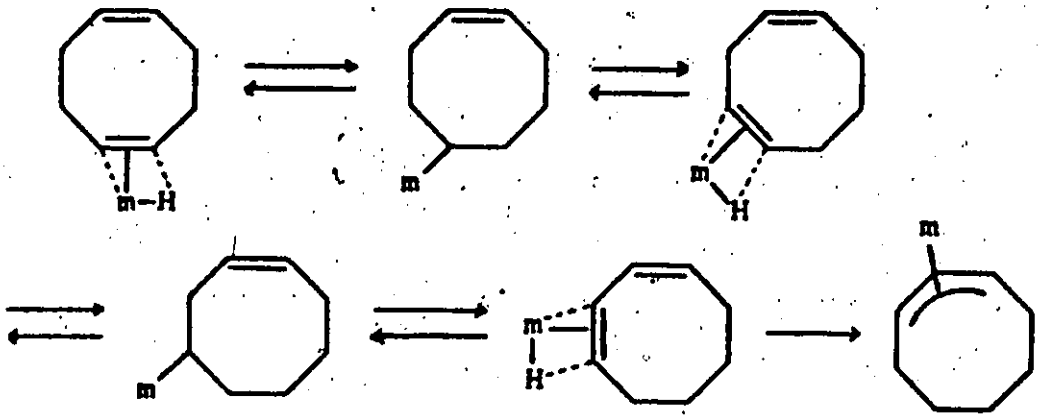
with either 1,3- or 1,5-cyclooctadiene (COD) in methylene chloride at 25° to give the known π-2-cyclooctenyl (32)[34] and the corresponding dichloro (20) complexes in each case. Both complexes were identified by their p.m.r. spectra.



The above reactions were essentially stoicheiometric. In the iridium reaction, an exact 0.5:1 molar mixture of (20b) and (32b) was obtained; while in the rhodium reaction, the dichloro complex (20a) was present in a quantity slightly higher than expected. This was due to the fact that while the rate of decomposition of the iridium hydride was negligibly slow compared to its reactions with cyclooctadienes in methylene chloride, the rates of reactions of the rhodium hydride with these diolefins were only a few times faster than its decomposition to (20a) in the same solvent. This observation was also true for the reactions of (52) with the other dienes described below.

The π-2-cyclooctenyl complexes (32) were obtained with equal facility from either 1,3- or 1,5-COD. This implied that 1,5-COD was converted via a series of fast hydride

addition-elimination reactions to the π-2-cyclooctenyl complexes.



(m=C_5Me_5MCl; M=Rh and Ir)

Neither the rates nor the products of these reactions were detectably altered by the addition of an equimolar amount of triethylamine to the reaction mixture.

(ii) 1,3- and 1,4-Cyclohexadienes

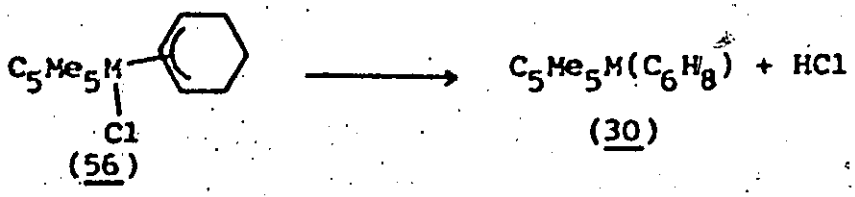
The reactions of 1,3- or 1,4-cyclohexadiene (CHD) with the hydrides (52a and b) also proceeded readily in methylene chloride at 25° and gave the known π-cyclohexa-1,3-diene(pentamethylcyclopentadienyl)-rhodium and -iridium complexes (30)[33] as final produnts according to the following equation.

(52) +  or  ⟶

$$\tfrac{1}{2}[C_5Me_5MCl_2]_2 + C_5Me_5M\text{-}\langle\text{C}_4\text{H}_6\rangle + HCl$$

(20) (30)

The reactions were followed by p.m.r. and it was observed that for each hydride an intermediate (56) (transient C_5Me_5 resonance at τ 8.31 for rhodium and 8.28 for iridium) was formed and which decomposed readily to the π-cyclohexa-1,3-diene complex (30). Moreover, the same intermediate was detected from both 1,3- and 1,4-cyclohexadienes. All attempts to isolate the intermediates (56a and b) failed since they decomposed quickly to (30). Because of the complexity of the spectra, as well as the low concentration of (56) existing in the mixture, the structures of (56a and b) could not be assigned on the basis of the p.m.r. data. However, the low field triplet (τ 5.97, J=6.0 Hz) which was observed for the iridium intermediate (56b) implied that it was a 1,2,3-trihapto (π-allylic) rather than a 1,2,4-trihapto (σ,π-en-yl) or a monohapto σ-cyclohexenyl complex. π-Cyclohexenyl complexes of palladium have been fairly well documented[111], and it is presumed that the cyclohexenyl complexes (56a and b) were the intermediates in the reactions with cyclohexadienes.



(56) (30)

The fact that (56) [and eventually (30)] were obtained with equal facility from 1,3- or 1,4-CHD implied that the latter diene was isomerised to give the cyclohexenyl

complex quickly in a similar way to that suggested for the COD reactions.

The rate of decomposition of (56) was greatly accelerated in the presence of an equimolar amount of triethylamine, and triethylamine hydrogen chloride was observed as the other reaction product. This clearly indicates that the decomposition involved the evolution of hydrogen chloride. These reactions cannot be stoicheiometric in the absence of the base since the liberated acid will cause the following side-reactions.

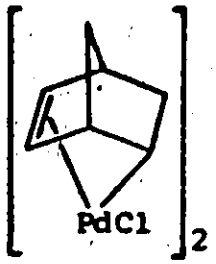
$$HCl + C_5Me_5MCl(C_6H_9) \longrightarrow \tfrac{1}{2}[C_5Me_5MCl_2]_2 + C_6H_{10}$$
(56) (20)

$$HCl + (C_5Me_5M)_2HCl_3 \longrightarrow [C_5Me_5MCl_2]_2 + H_2$$
(52) (20)

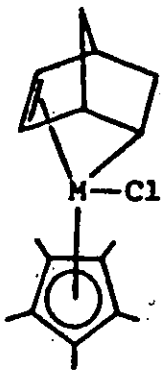
(iii) Norbornadiene

The reactions of the hydrides (52a and b) with norbornadiene were very similar to the reactions with the cyclohexadienes. For each hydride, an unstable intermediate was detected (C_5Me_5 peak at τ 8.30 for rhodium and 8.32 for iridium), which then decomposed readily to give the corresponding π-norbornadiene complex (31)[32]. Because of their instability, the intermediates could neither be isolated nor further characterised. A norbornenyl complex such as (57) has been reported[112], and the intermediates detected

here are formulated as (58) by analogy.



(57)



(58)

(52) +  ⟶ ½[$C_5Me_5MCl_2$]$_2$ + $C_5Me_5MCl(C_7H_9)$

(20) (58)

(58) ⟶ $C_5Me_5M(C_7H_8)$ + HCl

(31)

Again here addition of triethylamine accelerated the decomposition of the intermediates into (31) and (58a and b) could no longer be detected in the presence of a stoicheiometric amount of the base.

(iv) Cyclopentadiene

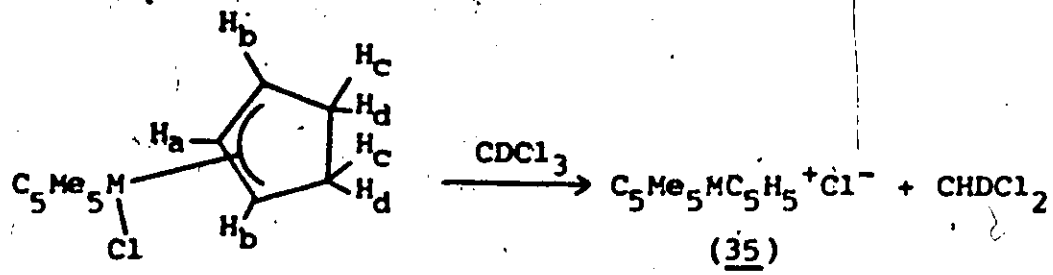
The rhodium and iridium hydrides, $(C_5Me_5M)_2HCl_3$ (52), reacted with freshly cracked cyclopentadiene at 25° to give the known pentamethyl-rhodicenium and -iridicenium chlorides (35)[32] together with the dichloro complexes (20).

(52) +  ⟶ ½[$C_5Me_5MCl_2$]$_2$ + $C_5Me_5MC_5H_5^+Cl^-$

(20) (35)

In the course of the reactions, the π-cyclopentenyl complexes (59) were observed as unstable intermediates

prior to the formation of the ionic complexes. If chloroform-d was the solvent, $CHDCl_2$ was also observed as the other product.



(59) (35)

The cyclopentenyl complexes were slightly more stable than the π-cyclohexenyl (56) and the norbornenyl (58) complexes and the structures of (59) were fairly well characterised by p.m.r. data. However, all attempts to isolate pure (59) were unsuccessful since the ionic complexes (35) were quickly produced especially in the presence of a base.

In a $CDCl_3$ solution at 100 MHz, the iridium cyclopentenyl complex (59b) showed resonances at τ 5.73 (1H, t, H_a), 6.35 (2H, m, H_b), 8.23 (15H, s, C_5Me_5) and 8.31 (4H, t, H_c and H_d). Decoupling experiments showed that J(a,b)=3.0 Hz, J(b,c or d)=ca. 0.5 Hz and J(c,d)=18.0 Hz. The spectrum was invariant down to -70° and hence the molecule did not appear to be taking part in a σ-, π-equilibrium:

(60)

[m=C_5Me_5IrCl(solvent)]

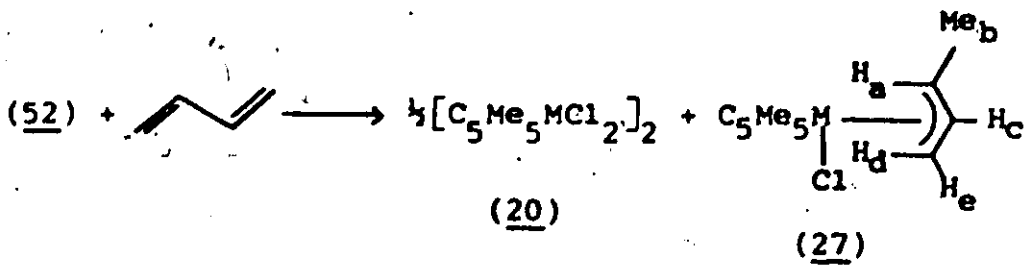
The analogous rhodium complex gave a similar p.m.r. spectrum. In a $CDCl_3$ solution, complex (59a) showed resonances at τ 5.67 (1H, m, H_a), 5.93 (2H, m, H_b) and 8.27 (15H, s, C_5Me_5). Those for H_c and H_d overlapped with other proton signals in the reaction mixture and hence their exact chemical shifts could not be determined.

Studies on the further reactions of (59) did not give conclusive results and the mechanism whereby the pentamethyl-rhodicenium and -iridicenium complexes (35) are formed is not understood. It was particularly surprising that the known (cyclopentadiene)pentamethylcyclopentadienyl-iridium complex (39)[32] was not observed during the decomposition of the iridium cyclopentenyl complex (59b) to give (35b).

D. Reactions with acyclic diolefins

(i) 1,3-Butadiene

The rhodium and iridium hydrides, $(C_5Me_5M)_2HCl_3$ (52), reacted readily at 25° with 1,3-butadiene in benzene to give a 1:1 mixture of the corresponding dichloride (20) and the known choro-(π-syn-1-methylallyl)(pentamethyl-cyclopentadienyl)-rhodium and -iridium complexes (27)[32] as shown by their p.m.r. spectra (Table 1). The geometry (1-methyl syn) was defined by decoupling experiments which confirmed that J(a,c)=11.0 Hz in (27a) and 10.0 Hz in (27b)[32].



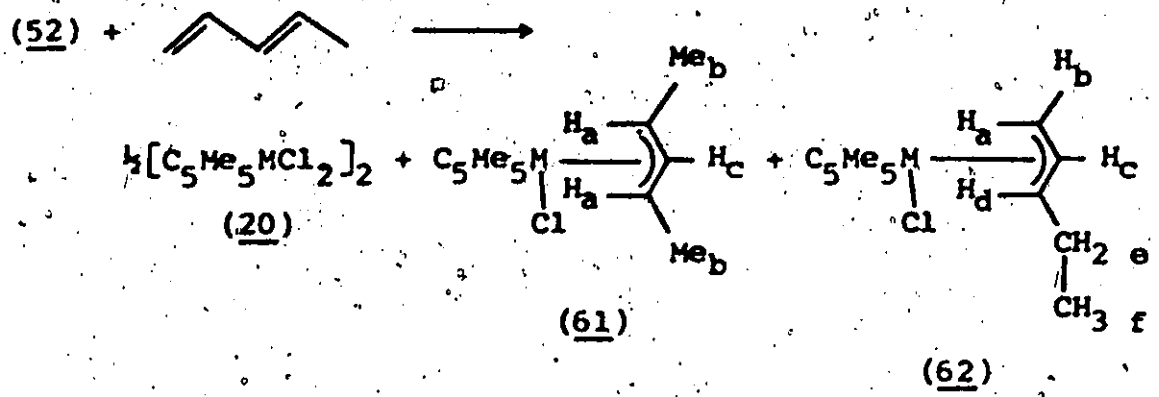
The allylic complexes (27) were separated from (20) by extracting the reaction mixture with benzene in which (20) was only sparingly soluble. Addition of a base such as triethylamine had no effect on the above reactions, and the complexes (27) were stable to prolonged heating in ethanol in the presence of anhydrous sodium carbonate. There was no evidence for the formation of a π-butadiene complex.

(ii) trans-Piperylene

The reactions of $(C_5Me_5M)_2HCl_3$ (52a and b) with trans-piperylene in methylene chloride were followed by p.m.r. at 100 MHz. In each case, two new π-allylic complexes, chloro-(π-syn,syn-1,3-dimethylallyl)(pentamethylcyclopentadienyl)-rhodium (or -iridium) (61) and chloro-(π-syn-1-ethylallyl)(pentamethylcyclopentadienyl)-rhodium (or -iridium) (62), were formed in a ratio of 85:15 together with the corresponding dichloride (20).

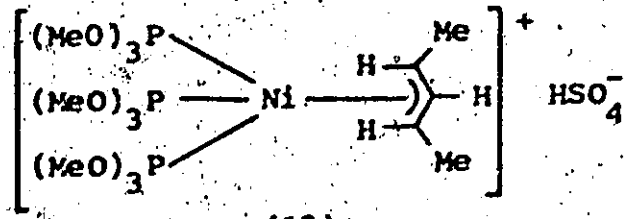
The complexes (61) and (62) were very soluble in benzene and ether and could easily be separated from (20). It was not possible to separate the allylic isomers from each other by chromatography on alumina but the major isomers

(61a and b) were isolated pure by fractional crystallisation from ether and petroleum ether.



(52) + ⟶ ½[$C_5Me_5MCl_2$]$_2$ (20) + C_5Me_5M(Cl)(allyl) (61) + C_5Me_5M(Cl)(allyl) (62)

The complexes (61a and b) were characterised by analytical data and the structures were assigned on the basis of their p.m.r. spectra (Table 1). Both methyl groups in the 1,3-dimethylallyl moiety in (61) are in the syn positions as shown by the coupling constants, J(a,c)=10.0 Hz in (61a) and 9.0 Hz in (61b). These are close to the value (11.5 Hz) reported by Tolman for the π-syn, syn-1,3-dimethylallyl-nickel complex (63)[76].



(63)

The minor products (62) could not be isolated. However an enriched mixture of (61) and (62) (ratio ca. 2:1) obtained from the mother liquors from recrystallisation of

both (61a) and (61b) showed p.m.r. spectra consistent with the presence of (62a) and (62b).

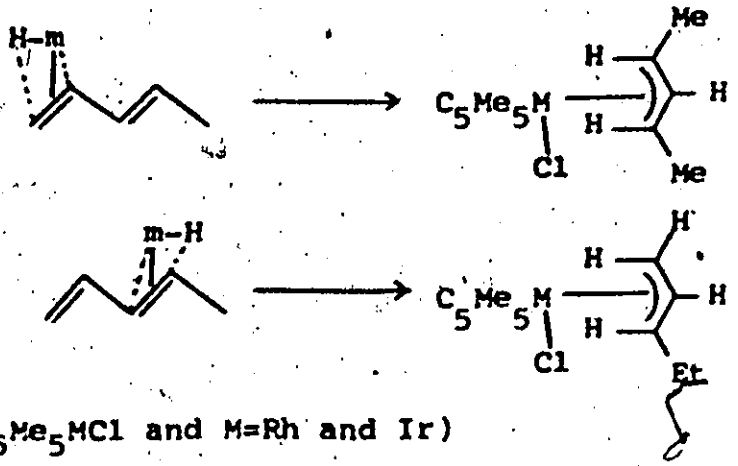
The iridium complex (62b) in methylene chloride showed resonances at τ5.84 (1H, m, H_c), ca. 7.0 (2H, m, H_b and H_d), 7.69 [1H, d, J(a,c)=10.0 Hz, J(a,b)=0, H_a], ca. 8.2 (2H, m, H_e), 8.25(15H, s, C_5Me_5) and 8.86 [3H, t, J(e,f)=7.0 Hz, H_f]. This spectrum is consistent with the π-1-ethylallyl structure and not with a syn,anti-1,3-dimethylallyl structure which requires two doublets for the two different allylic methyls. Decoupling experiments were unsuccessful owing to the complexity of the spectrum arising from the presence of (61b). However, the syn geometry was assigned to complex (62b) from considerations of the chemical shifts of H_d and H_e by comparison with the closely related iridium syn-1-methylallyl complex (27b).

The rhodium complex (62a) gave a very similar p.m.r. spectrum and showed resonances at τ6.02(1H, m, H_c), ca. 6.6 (2H, m, H_b and H_d), 7.25 [1H, d,J(a,c)=11.0 Hz, J(a,b)=0, H_a], ca. 8.2 (2H, m, H_e), 8.30 (15H, s, C_5Me_5) and 8.84 [3H, t, J(e,f)=7.0 Hz, H_f]. Thus a similar structure was expected.

The presence of triethylamine had no effect on either the rates or final products of the above reactions. Both allylic complexes (61) and (62) were stable on prolonged heating at 65° in benzene in the presence of excess anhydrous sodium carbonate or triethylamine. No isomerisation between

them was observed. Under similar conditions in ethanol, the rhodium complex (61a) remained unchanged while the iridium complex (61b) decomposed into unidentified products.

In the reactions of the bridging hydrides (52) with trans-piperylene, the metal hydride therefore tends to favour, presumably for steric reasons, addition to the terminal double bond rather than the internal one.

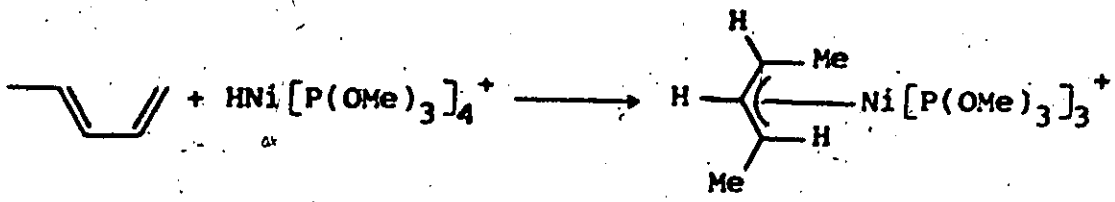


(m=C_5Me_5MCl and M=Rh and Ir)

Complexes (61) and (62) were also obtained at 65° from the dichlorides (20) and the diolefin in ethanol/base in the same ratios as from the hydrides and trans-piperylene at 25°. This implied that the same species are present in each reaction and that the directions of addition of M-H was thermodynamically rather than kinetically controlled.

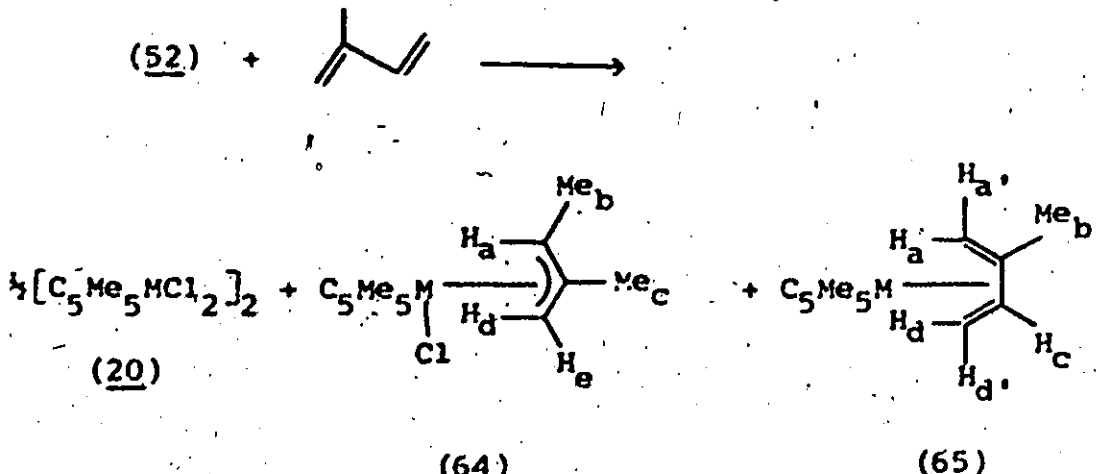
The mixture of allylic complexes, (61) and (62), were also conveniently prepared by stirring trans-piperylene with (20) in isopropanol in the presence of sodium carbonate at 25°. Under these conditions, the hydrides (52) were formed *in situ* and did not need to be isolated.

The fact that no syn,anti-1,3-dimethylallyl complexes were observed even at early stages of the reactions contrasts with the work of Tolman who observed the syn,anti-isomer as the kinetically preferred product[76].



(iii) Isoprene

In contrast to butadiene and trans-piperylene, $(C_5Me_5M)_2HCl_3$ (52) reacted with isoprene in methylene chloride at 25° to give, for each reaction, stable π-syn-1,2-dimethylallyl-rhodium(III) or -iridium(III) (64) and π-isoprene-rhodium(I) or -iridium(I) (65) complexes together with the corresponding dichlorides (20). The ratio (64):(65) was 55:45 for rhodium and 30:70 for iridium.



Both complexes (64) and (65) were very soluble in most organic solvents but they could be separated by column chromatography on alumina or by sublimation in vacuo. They were characterised by analytical and p.m.r. data (Tables 1 and 2). Since H_a does not couple with Me_c in complexes (64), this gives no hint on whether the red (rhodium) and yellow (iridium) 1,2-dimethylallyl complexes are syn or anti isomers. However, by comparing the chemical shifts of H_a and Me_b of (64) with those of the closely related syn-1-methylallyl complexes (27), it was concluded that the syn isomers were formed. Both complexes (64a) and (64b) showed very similar p.m.r. spectra, except for additional coupling to Rh on Me_c in (64a).

The π-isoprene-M(I) complexes (65) were orange, (rhodium) and yellow (iridium) oily substances sublimable at 45° and 10^{-3} mm. The mass spectra showed major fragments for (65a) at m/e 306 ($C_5Me_5RhC_5H_8^+$), 238 ($C_5Me_5Rh^+$), 103 (Rh^+), 69 ($C_5H_9^+$), 68 ($C_5H_8^+$) and 67 ($C_5H_7^+$). The iridium complex (65b) gave molecular ion peaks at 396,394 (corresponding to $C_5Me_5{}^{193}IrC_5H_8^+$ and $C_5Me_5{}^{191}IrC_5H_8^+$, respectively).*

The p.m.r. spectra of (65) (Table 2) were similar to those reported for other isoprene complexes of transition metals[113]. Presumably due to the shielding effects of the metals, H_a and H_d of (65a and b) showed resonances at higher field than H_a' and H_d'. Decoupling experiments showed that in the iridium complex (65b), the geminal couplings were

* Detailed mass spectral data for diene complexes are given in Table 12.

very small, with J(a,a') and J(d,d') both equal to 2.0 Hz. In the rhodium complex (65a) additional coupling due to ^{103}Rh ($I=\frac{1}{2}$, 100% abundance) caused the resonances of H_a, and $H_{a'}$, H_d and $H_{d'}$ to be split into unresolved multiplets.

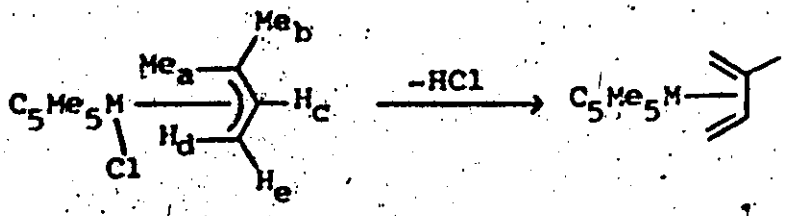
Complexes (64) and (65) were also obtained by reacting the dichloro complexes (20) with isoprene in isopropanol or ethanol in the presence of anhydrous sodium carbonate. Under mild conditions (25°, 12 hr.), a mixture of (64) and (65) was obtained. Under more vigorous conditions (65°, 24 hr.), however, only the M(I) complexes (65a and b) were isolated. Heating individual samples of (64) in ethyl or isopropyl alcohol in the presence of sodium carbonate also gave complete conversion into the π-isoprene complexes (65).

$$C_5Me_5MCl(C_5H_9) \xrightarrow{-HCl} C_5Me_5M(C_5H_8)$$
$$(64) \qquad\qquad (65)$$

When the above reactions of (64) were carried out in benzene in the presence of sodium carbonate, they did not go to completion in 24 hr. and the yield of (65) was only 20% for rhodium and less than 5% for iridium. Furthermore, solutions of the 1,2-dimethylallyl complexes (64) in either benzene or methylene chloride gave no detectable amounts of the diene complexes (65), over a period of 48 hr. at 25° even in the presence of triethylamine. Hence, we must conclude that in the reactions of isoprene with the hydrides

(52a and b), the complexes (64a and b) were not the precursors of the complexes (65a and b) which were formed in those reactions.

A careful study of the reaction of (52b) with isoprene in the absence of triethylamine by p.m.r. spectroscopy at 100 MHz showed that an unstable intermediate (66b) was formed and which readily decomposed to the isoprene complex (65b) (see section iv). The structure of (66b) was inferred from its p.m.r. spectrum (Table 1), particularly the observation of the two singlet methyl resonances at τ 8.27 and 8.99 which suggested the presence of gem-dimethyls. The higher field resonance was assigned to the anti-methyl group since it may reasonably be presumed to be closer to the metal and hence more shielded. [Other complexes containing anti-methyl groups also showed resonances in the τ8.9 - 9.0 region, see sections (iv), (v) and (vi)]. In the presence of stoicheiometric amounts of triethylamine, the intermediate (66b) was not observed and its decomposition into (65b) was greatly facilitated. The C_5Me_5 resonance of (66b) was accidentally coincident with that of (64b).

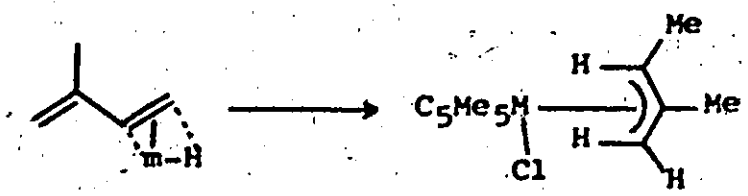


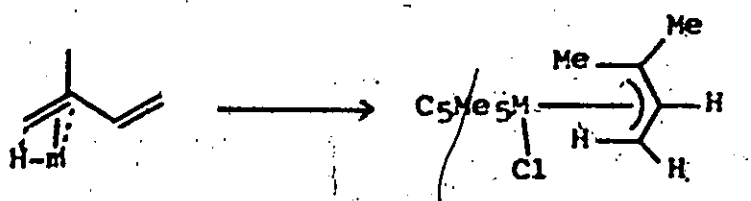
(66) (65)

The analogous intermediate rhodium complex (66a) could not be observed in the reaction between (52a) and isoprene under similar conditions.

The formation of the isoprene complexes (65) from (64) under more drastic conditions is likely to proceed via the σ-1,2-dimethylallyl intermediates (67)(see Discussion).

If it is assumed that complexes (65) come exclusively from (66) under mild conditions, the ratios of (64) to (65) in the reaction mixtures represent a direct measure of the relative amounts of addition of M-H to the two double bonds of isoprene. The observed ratios of 55:45 for (64a) to (65a) was found for the rhodium reaction, and a 30:70 ratio (64b):(65b) was observed for iridium.





(m=C_5Me_5MCl; M=Rh and Ir)

(iv) 1,1-Dimethylallene

Reactions of $(C_5Me_5M)_2HCl_3$ (52) with 1,1-dimethylallene at 25° in methylene chloride gave the π-isoprene(pentamethyl-

cyclopentadienyl)-rhodium and -iridium (65) together with the dichloro complexes (20). All complexes were identified by their p.m.r. spectra.

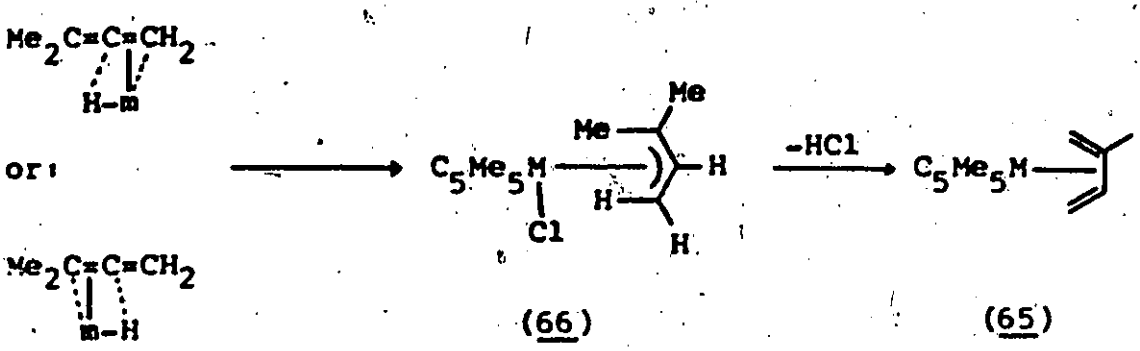
$$(52) + Me_2C{=}C{=}CH_2 \longrightarrow \underset{(20)}{\tfrac{1}{2}[C_5Me_5MCl_2]_2} + \underset{(65)}{C_5Me_5M{-}\text{allyl}}$$

In the iridium reaction, it was established by p.m.r. (Table 1) that the reaction proceeded via the π-1,1-dimethylallyl intermediate (66b) [see section (iii) above]. This unstable complex (66b) eliminated hydrogen chloride readily to give (65b) and it could not be observed if a stoicheiometric amount of triethylamine was present in the reaction mixture. Here again, the rhodium 1,1-dimethylallyl complex (66a) could not be detected even in the absence of the base.

The stable π-syn-1,2-dimethylallyl complexes (64a and b) were not observed in the products; this rules out an isomerisation : (66) ⟶ (64).

The formation of the isoprene complexes (65) from 1,1-dimethylallene is an example of a double bond isomerisation which occurs via the unstable (66).

The isoprene complexes (65) were also obtained from the reactions of the dichloro complexes (20) with 1,1-dimethylallene at 25° in isopropanol in the presence of anhydrous sodium carbonate.

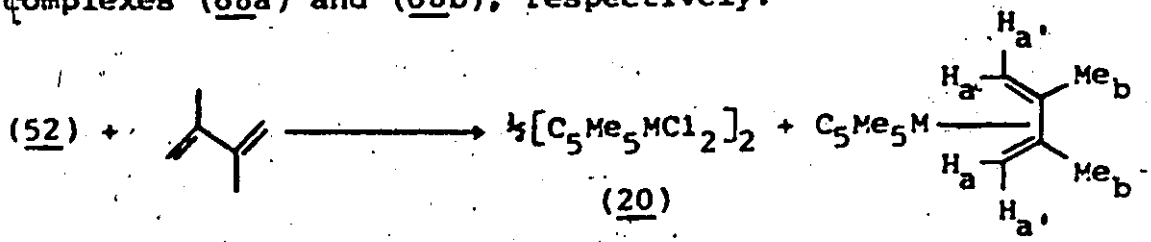


(66) (65)

(m=C_5Me_5MCl; M=Rh and Ir)

(v) 2,3-Dimethylbutadiene

The rhodium and iridium hydrides, $(C_5Me_5M)_2HCl_3$ (52), reacted readily at 25° with 2,3-dimethylbutadiene in methylene chloride to give the new π-2,3-dimethylbutadiene-(pentamethylcyclopentadienyl)-rhodium(I) and -iridium(I), complexes (68a) and (68b), respectively.



(68)

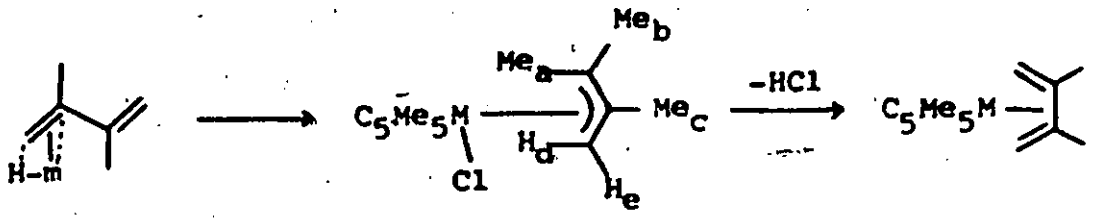
These reactions were essentially stoicheiometric if equimolar amount of triethylamine was present at the beginning of the reactions. The mass spectra of (68a) exhibited major m/e peaks at 320 ($C_5Me_5RhC_6H_{10}^+$), 238 ($C_5Me_5Rh^+$), 103 (Rh^+) and 82 ($C_6H_{10}^+$). The iridium complex

(68b) gave the molecular ion peaks at m/e 410,408 (corresponding to $C_5Me_5{}^{193}IrC_6H_{10}{}^+$ and $C_5Me_5{}^{191}IrC_6H_{10}{}^+$, respectively) but did not show significant peaks corresponding to $C_5Me_5Ir^+$ or Ir^+.

Because of the symmetry of the complexes (68), their p.m.r. spectra (Table 2) were relatively simple. In methylene chloride solution, the broad multiplets at τ 9.93 (Rh) and 10.27 (Ir) were assigned to H_a (due to their proximity to the metals) and the resonances at τ 8.49 (Rh) and 8.34 (Ir) were attributed to $H_{a'}$. Decoupling experiments showed that the geminal protons only coupled slightly to each other, with J(a,a') being ca. 1.0 Hz in the rhodium complex and 1.5 Hz in the iridium analogue.

It was observed that, during the reaction to give the iridium(I) complex (68b), an intermediate was formed which was formulated as the π-1,1,2-trimethylallyl complex (69b) on the basis of its p.m.r. spectrum (Table 1). The singlet at τ 9.00 was assigned to Me_a (anti), that at 8.47 to Me_b (syn) and that at 8.25 to Me_c. Similarly, the doublet at τ 7.22 was assigned to H_d (anti) and that at 6.85 to H_e (syn). An intermediate (69a) was also detected by its C_5Me_5 reasonance at τ 8.36 in the analogous rhodium reaction but no evidence of structure could be obtained from the p.m.r. spectra due to its low concentration. However, if this intermediate was also π-allylic, it would

be most likely to have the same structure as its iridium analogue.



(69) (68)

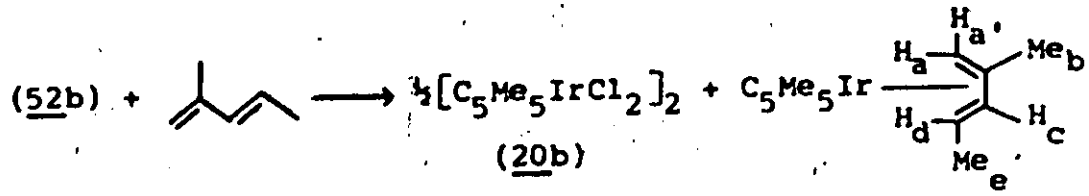
(m=C_5Me_5MCl; M=Rh and Ir)

The intermediates (69) resulted from the addition of M-H to one of the equivalent double bonds of the diene, They could not be isolated because they underwent facile elimination of hydrogen chloride to give the M(I)-diene complexes (68), especially in the presence of triethylamine, and presumably by a similar mechanism to that discussed for the 1,1-dimethylallyl complexes (66) (see Discussion).

The Rh(I)-diene complex (68a) was also obtained from the reaction of (20a) with 2,3-dimethylbutadiene at 25° in isopropanol in the presence of anhydrous sodium carbonate. Under the same conditions, however, the analogous iridium complex (68b) was formed together with large amounts of other (unidentified) products. Pure (68b) could be obtained by reacting $[C_5Me_5IrCl_2]_2$ (20b) in benzene with sodium carbonate and stoicheiometric amounts of the diolefin and isopropanol, the hydriding agent.

(vi) trans-2-Methyl-1,3-pentadiene

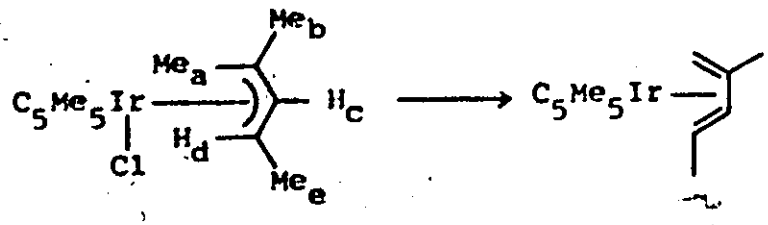
Reaction of $(C_5Me_5Ir)_2HCl_3$ (52b) with trans-2-methyl-1,3-pentadiene at 25° gave a mixture of π-2-methyl-1,3-pentadiene(pentamethylcyclopentadienyl)iridium(I) (70b) and the iridium dichloro complex (20b).



(70b)

The reaction was stoicheiometric if an equimolar amount of triethylamine was present. Complex (70b) was characterised by its p.m.r. (Table 2) and mass spectra which showed molecular ion peaks at 410 and 408 (corresponding to $C_5Me_5{}^{193}IrC_6H_{10}{}^+$ and $C_5Me_5{}^{191}IrC_6H_{10}{}^+$, respectively).

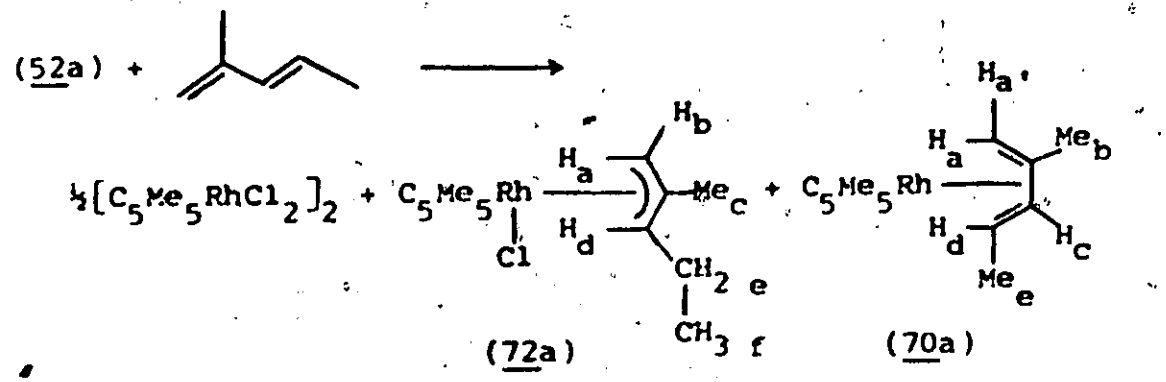
When the reaction was followed by p.m.r. (100 MHz), it was observed that formation of (70b) was preceded by that of the unstable π-syn-1,1,3-trimethylallyl intermediate (71b) which readily eliminated hydrogen chloride to give (70b).



(71b) (70b)

The structure of (71b) (Me_e syn-) was inferred from its p.m.r. spectrum (Table 1), since J(c,d)≈10.0 Hz. The observation of two singlets at τ 8.94(Me_a) and 8.28(Me_b) and a doublet at τ 8.50(Me_e) due to the three methyl groups in the allylic moiety was consistent with the proposed structure.

In contrast, the rhodium hydride (52a) reacted with the diolefin to give the stable syn-1-ethyl-2-methylallyl (72a) and the π-2-methyl-1,3-pentadiene-rhodium(I) (70a) complexes in ca. 1:4 ratio, as well as $[C_5Me_5RhCl_2]_2$ (20a).



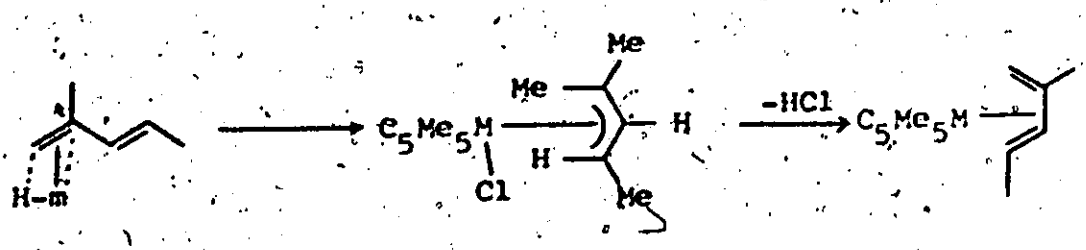
Complexes (70a) and (72a) were separated by chromatography on an alumina column eluted with benzene and ether. The p.m.r. (Table 2) and mass spectra of the yellow diene-rhodium complex (70a) [major peaks at m/e 320 ($C_5Me_5RhC_6H_{10}^+$), 238 ($C_5Me_5Rh^+$), 103 (Rh^+), 83 ($C_6H_{11}^+$) and 81 ($C_6H_9^+$)] were consistent with the assigned structure.

Complex (72a) was assigned as the syn isomer since H_d and H_e had chemical shifts comparable to the very similar π-syn-1,2-dimethylallyl-rhodium complex (64a). Moreover, the

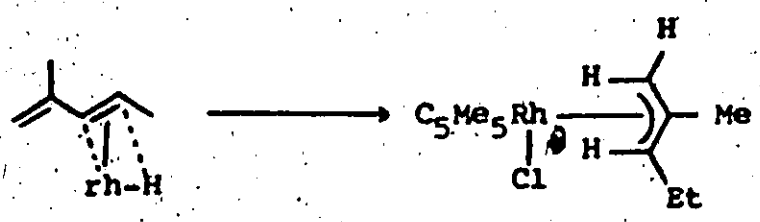
observation of a triplet at τ 8.88 (Me_ℓ) was in good agreement with the chemical shifts of H_ℓ in the syn-1-ethylallyl complexes (62).

On following the reaction by p.m.r. (100 MHz), evidence for the existence of another allylic complex (71a), which was responsible for the formation of (70a), was obtained. This unstable intermediate could not be isolated since it eliminated hydrogen chloride readily, especially in the presence of triethylamine. Because of serious overlapping with other resonances in the spectrum of the reaction mixture, a complete structural assignment for (71a) could not be made with certainty (Table 1). However, two methyl singlets at τ 8.40 and 8.93 were observed and, by analogy to the iridium reaction, it was reasonable to assume a syn-1,1,3-trimethylallyl structure for (71a).

The formation of complexes (70), (71) and (72) in the hydride reactions can thus be explained in terms of the following scheme:



(71) (70)



(72a)

[m=C_5Me_5MCl, M=Rh and Ir; rh=C_5Me_5RhCl]

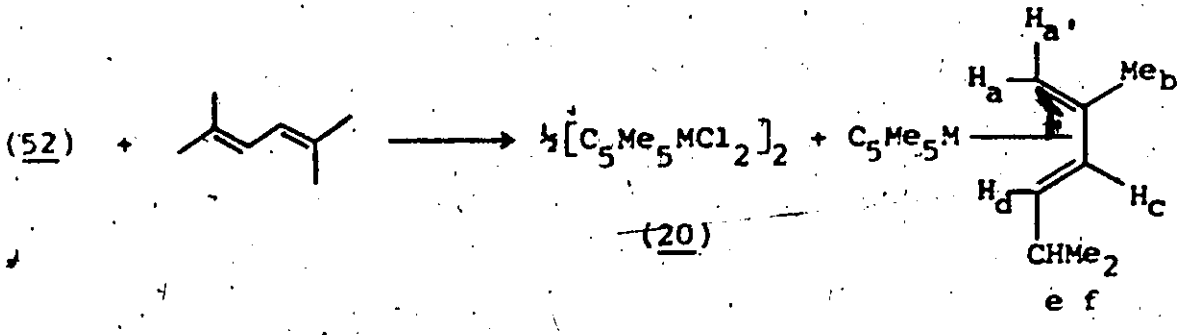
Addition of M-H to the terminal double bond of trans-2-methyl-1,3-pentadiene eventually gives the M(I)-diene complexes (70) through the labile trimethylallyl intermediate (71). On the other hand, addition of Rh-H to the internal double bond of the diolefin gives the thermally stable syn-1-ethyl-2-methylallyl complex (72a). Under no condition was the iridium analogue, (72b), observed. From the relative yields of the rhodium complexes (70a) and (72a) and the absence of (72b), it can be concluded that the addition of M-H to terminal double bonds is more favourable than to internal ones, especially in the case of iridium.

There was no isomerisation between the allylic complexes (71a) and (72a). In methylene chloride, complex (72a) was stable to triethylamine at 20°, but the rhodium(I) complex (70a)could in fact be formed from (72a) by heating for 18 hr. at 65° in ethanol in the presence of sodium carbonate.

Complexes (70a and b) and (72a) could be prepared more conveniently from the reactions of $[C_5Me_5MCl_2]_2$ (20) and trans-2-methyl-1,3-pentadiene in isopropanol in the presence of sodium carbonate at 25°.

(vii) 2,5-Dimethyl-2,4-hexadiene

Reactions of $(C_5Me_5M)_2HCl_3$ (52) with 2,5-dimethyl-2,4-hexadiene in methylene chloride at 25° gave stable π-2,5-dimethyl-1,3-hexadiene(pentamethylcyclopentadienyl)-rhodium and -iridium complexes (73) together with the dichlorides (20).



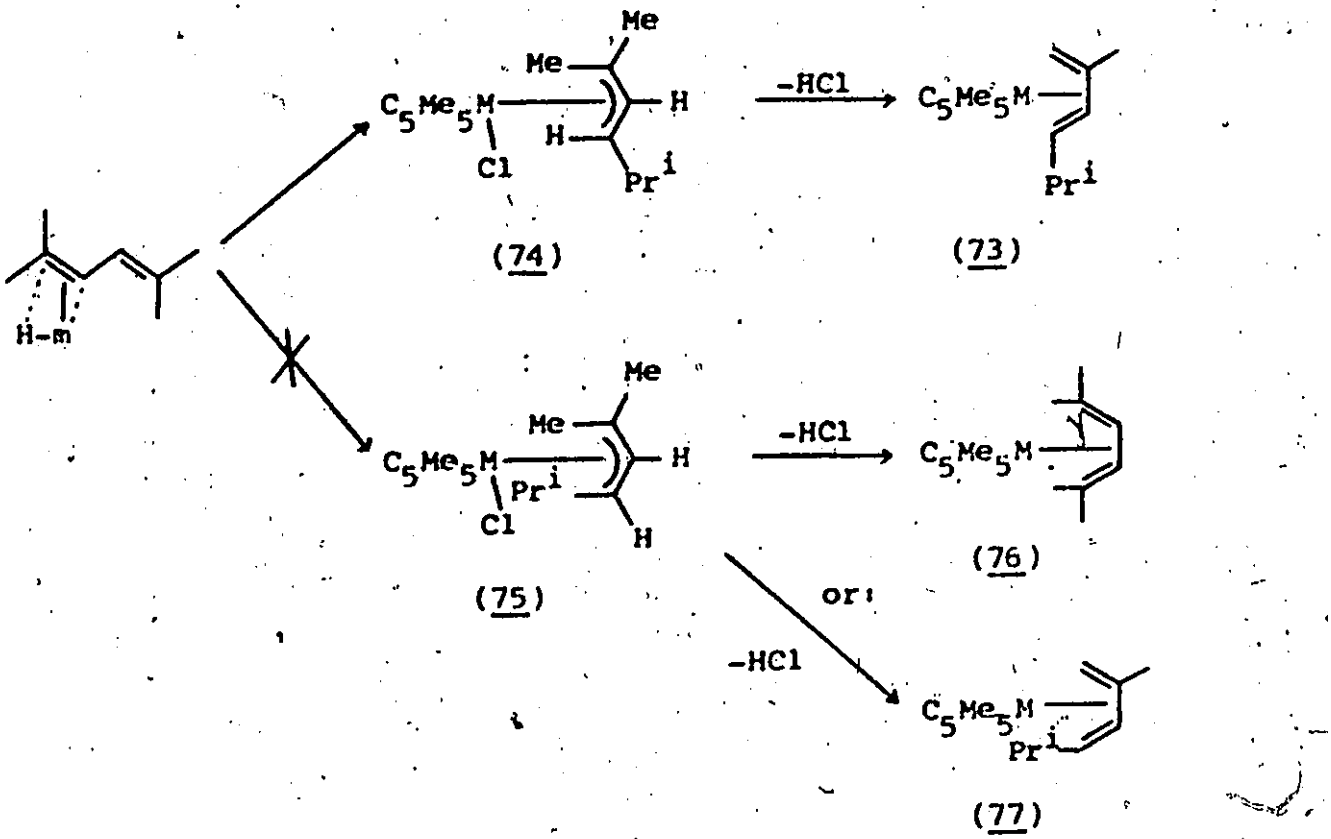
(73)

The new complexes (73) were characterised by analysis, p.m.r. (Table 2) and mass-spectrometry. They gave strong molecular ion peaks at m/e 348 (corresponding to $C_5Me_5RhC_8H_{14}^+$) and at 438, 436 (corresponding to $C_5Me_5{}^{193}IrC_8H_{14}^+$ and $C_5Me_5{}^{191}IrC_8H_{14}^+$, respectively) in the mass spectra.

In each of the above reactions, intermediates (74a and b) were observed (transient C_5Me_5 resonance at τ 8.36 for rhodium and 8.41 for iridium) prior to the formation of the diene complexes (73). Again, the intermediates could not be isolated since they gave (73) readily on elimination of hydrogen chloride. As the intermediates were never present in high enough concentrations in the reaction mixtures, the structures of (74a and b) could not be

assigned from the p.m.r. spectra. However, if the complexes (74a and b) are π-allyls by analogy to all the other reactions studied then they must have the 1,1-dimethyl-3-isopropylallyl structure since this is the only species which can be derived from an anti-Markownikoff addition of M-H to either one of the two equivalent double bonds.

The formation of complexes (73a and b) which contain the 2,5-dimethyl-1,3-hexadiene ligand from 2,5-dimethyl-2,4-hexadiene results from an isomerisation of the diolefin:



(m=C_5Me_5MCl; M=Rh and Ir)

From the above scheme, it may further be concluded that complexes (74a and b) have the syn structures since the anti complexes (75a and b) would have given the complexes (76a and b) and (77a and b) and these were not observed.

II. Kinetics of the Hydride-Diene Reactions

(i) Introduction

Despite the basic difficulties of a small workable concentration range, solubility problems and relatively low accuracy in the quantitative estimation of reactants and products when their resonances overlap, the p.m.r. method is widely used in the kinetic studies of many organometallic reactions[76,114,115].

The kinetics of hydride-diene reactions can provide vital information on the metal-hydride addition step. In the studies of the reactions of a terminal hydride, $HNi[P(OMe)_3]_4HSO_4$, with various dienes, Tolman correlated the half-lives of those reactions with the eletronic and steric effects of the substituents on the dienes and a reaction mechanism was proposed[76]. However, kinetic studies of bridging hydrides have never been reported. In particular, information was needed on whether the chloride or the hydride bridge of $(C_5Me_5H)_2HCl_3$ (52) would be the first to break. Such knowledge was essential for the elucidation of mechanisms for the diene reactions as well as for the hydrogenation of olefins using (52) as catalysts.

Table 1

P.m.r. data of some allylic complexes of rhodium and iridium[a]

Complex	C_5Me_5	H_a	H_b
$C_5Me_5RhClC_4H_7$ (27a) (1-methylallyl)	8.28 s	6.58 dq J(a,b)=6.2 J(a,c)=11.0	8.40 d J(b,a)=6.2
$C_5Me_5IrClC_4H_7$ (27b)[b] (1-methylallyl)	8.23 s	6.90 dq J(a,b)=6.5 J(a,c)=10.0	8.47 d J(b,a)=6.5
$C_5Me_5RhClC_5H_9$ (61a) (1,3-dimethylallyl)	8.37 s	6.68 dq J(a,b)=6.5 J(a,c)=10.0	8.43 d J(b,a)=6.5
$C_5Me_5IrClC_5H_9$ (61b) (1,3-dimethylallyl)	8.31 s	7.08 dq J(a,b)=6.0 J(a,c)=9.0	8.49 d J(b,a)=6.0
$C_5Me_5RhClC_5H_9$ (62a) (1-ethylallyl)	8.30 s	7.25 d J(a,c)=11.0	ca. 6.6 m
$C_5Me_5IrClC_5H_9$ (62b) (1-ethylallyl)	8.25 s	7.69 d J(a,c)=10.0	ca. 7.0 m
$C_5Me_5RhClC_5H_9$ (64a) (1,2-dimethylallyl)	8.34 s	6.60 q J(a,b)=6.5	8.47 d J(b,a)=6.5
$C_5Me_5IrClC_5H_9$ (64b) (1,2-dimethylallyl)	8.29 s	7.00 q J(a,b)=6.0	8.53 d J(b,a)=6.0

H_c	H_d	H_e	H_f
6.05 m J(c,a)=11.0 J(c,d)=11.0 J(c,e)=6.6	7.24 d J(d,c)=11.0	6.76 d J(e,c)=6.6	
5.91 m J(c,a)=10.0 J(c,d)=9.5 J(c,e)=7.0	7.57 dd J(d,c)=9.5 J(d,e)=1.5	6.92 dd J(e,c)=7.0 J(e,d)=1.5	
6.28 td J(c,a)=10.0 J(Rh,c)=2.0			
6.07 t J(c,a)=9.0			
6.02 m	ca. 6.6 m	ca. 8.2 m	8.84 t J(f,e)=7.0
5.84 m	ca. 7.0 m	ca. 8.2 m	8.86 t J(f,e)=7.0
8.30 d J(Rh,c)=1.5	7.25 s J(d,e)≈ 1.0	6.77 s J(e,d)≈ 1.0	
8.25s	7.66 s J(d,e)≈1.0	6.92 s J(e,d)≈ 1.0	

Table 1 - cont'd

Complex	C_5Me_5	H_a	H_b
$C_5Me_5IrClC_5H_9$ (66b) (1,1-dimethylallyl)	8.29 s	8.99 s	8.27 s
$C_5Me_5IrClC_6H_{11}$ (69b) (1,1,2-trimethylallyl)	8.33 s	9.00 s	8.47 s
$C_5Me_5RhClC_6H_{11}$ (71a) (1,1,3-trimethylallyl)	8.41 s	8.93 s	8.40 s
$C_5Me_5IrClC_6H_{11}$ (71b) (1,1,3-trimethylallyl)	8.37 s	8.94 s	8.28 s
$C_5Me_5RhClC_6H_{11}$ (72a) (1-ethyl-2-methylallyl)	8.36 s	7.28 s	6.80 s

---

[a] All spectra were recorded at 100 MHz in CH_2Cl_2 solution with TMS as internal reference. Chemical shifts in τ scale. Coupling constants in Hz.

[b] In $CDCl_3$ solution.

[c] See text.

H_c	H_d	H_e	H_f
5.89 dd J(c,d)=10.0 J(c,e)=7.0	7.35 dd J(d,c)=10.0 J(d,e)=1.0	6.96 dd J(e,c)=7.0 J(e,d)=1.0	
8.25 s	7.22 d J(d,e)=1.0	6.85 d J(e,d)=1.0	
c	c	c	
6.05 d J(c,d)=10.0	6.67 m J(d,c)=10.0 J(d,e)=6.0	8.50 d J(e,d)=6.0	
8.30 d J(Rh,c)=1.5	6.69 t J(d,e)=7.0	8.16 m	8.88 t J(f,e)=7.0

Table 2

p.m.r. data for some diene complexes of rhodium and iridium[a]

Complex	C_5Me_5	H_a	$H_{a'}$
$C_5Me_5RhC_5H_8$ (65a)	8.07 s	9.85 m	8.51 m
$C_5Me_5IrC_5H_8$ (65b)	8.04 s	10.20 m J(a,a')=2.0	8.30 dd J(a',a)=2.0 J(a',c)=1.0
$C_5Me_5RhC_6H_{10}$ (68a)	8.13 s	9.93 m J(a,a')≈1.0	8.49 s, br J(a',a)≈1.0
$C_5Me_5IrC_6H_{10}$ (68b)	8.09 s	10.27 m J(a,a')=1.5	8.34 d J(a',a)=1.5
$C_5Me_5RhC_6H_{10}$ (70a)	8.14	9.97 m	8.63 m
$C_5Me_5IrC_6H_{10}$ (70b)	8.08 s	10.28 m J(a,a')=2.0 J(a,c)≈1.0	8.42 m J(a',a)=2.0 J(a',c)≈1.0
$C_5Me_5RhC_8H_{14}$ (73a)[b]	8.14 s	9.54 m	8.46 m
$C_5Me_5IrC_8H_{14}$ (73b)	8.07 s	10.26 m	8.42 dd J(a',a)=2.0 J(a',c)≈1.0

[a] All spectra were recorded at 100 MHz in CH_2Cl_2 solution using TMS as internal reference. Chemical shifts in τ scale. Coupling constant in Hz.

H_b	H_c	H_d	$H_{d'}$	Others
8.22 s	5.77 t J(c,d)=7.0 J(c,d')=7.0	9.92 m	8.40 m J(d',c)=6.0	
8.16 s	5.86 dd J(c,d)=6.5 J(c,d')=6.0	10.41 dd J(d,c)=6.5 J(d,d')=2.0	8.21 dd J(d',c)=6.0 J(d',d)=2.0	
8.22 s				
8.18 s				
8.24 s	5.91 d J(c,d)=7.0	9.40 m		H_e: 8.84 d J(e,d)=6.0
8.18 s	6.04 d J(c,d)=6.0	10.00 qn J(d,c)=6.0 J(d,e)=6.0		H_e: 8.83 d J(e,d)=6.0
8.25 s	5.74 d J(c,d)=8.0	9.20 td J(d,c)=8.0 J(d,e)=8.0 J(Rh,d)=2.0		H_e: c H_f: 8.91 d and 8.85 d J(f,e)=6.0
8.18 s	5.92 d J(c,d)=6.0	10.12 dd J(d,c)=6.0 J(d,e)=8.0		H_e: c H_f: 9.01 d and 8.98 d J(f,e)=6.0

[b] In C_6H_6 solution.

[c] Not observed due to overlapping with other signals.

The kinetics of the hydride-diene reactions were studied by p.m.r. at a given temperature. Detailed procedures are given in the Experimental section. Since the pentamethyl resonances of the reactants and products were readily identified by their chemical shifts, quantitative estimation of the concentrations of these species could readily be made by integration over those singlets in the p.m.r. spectra at specified times. This method of estimation had the great advantage over that using other resonances in that the intense C_5Me_5 singlets made quantitative estimation of complexes in low concentrations more accurate.

In most cases, the reactions were followed at 310°K where they were reasonably slow. In cases where M(I)-diene complexes were formed, a stoicheiometric amount of triethylamine was added at the beginning of each run to eliminate the undesirable side-reactions.

The rate data of these kinetic runs in graphical form are given in the Appendix.

(ii) Order of the hydride-diene reactions

By using 1,5-cyclooctadiene as a model diene, it was shown that the disappearance of the hydride resonance followed first-order kinetics and was independent of diene concentrations as indicated by the following equation:

$$- d[MH]/dt = k[MH][diene]^0$$

Plots of $\log(a/a-x)$ (a=initial concentration of hydride and x=concentration of hydride at time t) against t were linear over at least four half-lives, indicating first-order dependence on the hydride. Moreover, the observed reaction rates were unchanged for hydride to diene ratios over the range 1:10, 1:5, 1:2, 1:1, 1:0.5 and 1:0.25 (see Appendix), showing the independence of reaction rate on the diene concentration.

(iii) Effect of different dienes

The first-order rate constants for the reactions of stoicheiometric amounts of $(C_5Me_5M)_2HCl_3$ (52) with different

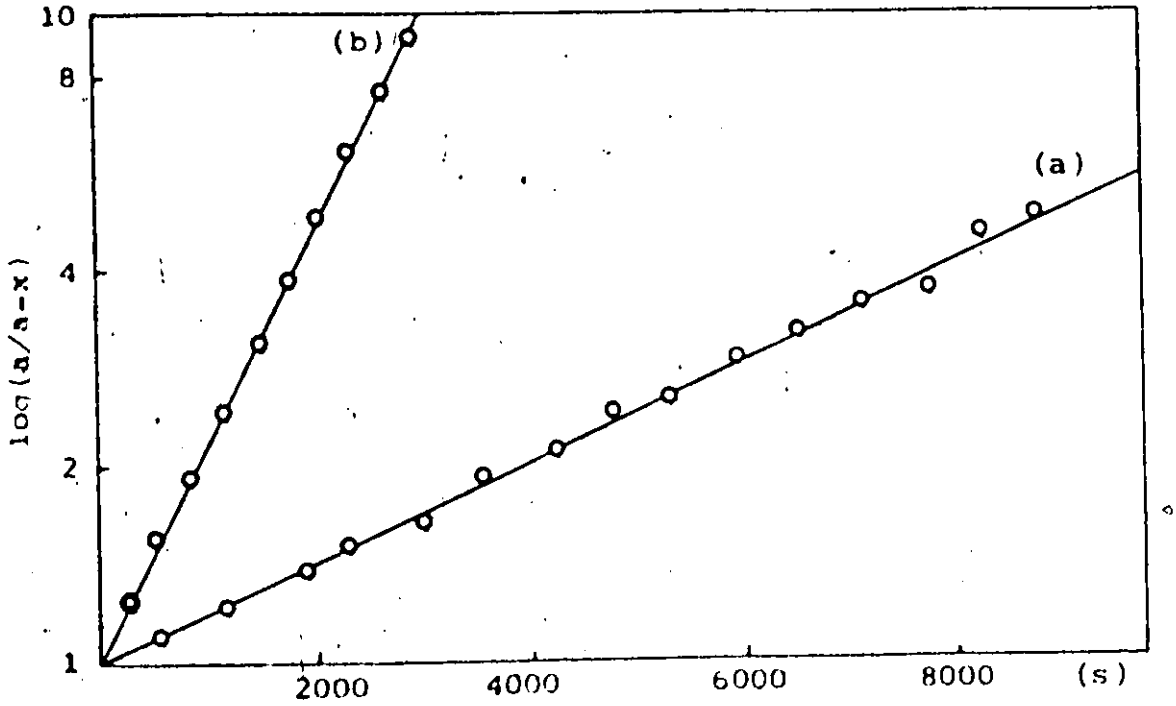


Fig. 2. First-order plots for the reactions (52)+1,5-COD in CH_2Cl_2 at 310°K. (a) Rh; (b) Ir.

dienes in methylene chloride at 310°K could be determined from the slope of log(a/a-x) versus time plots and typical examples are given in Figure 2. The calculated rate constants are presented in Table 3.

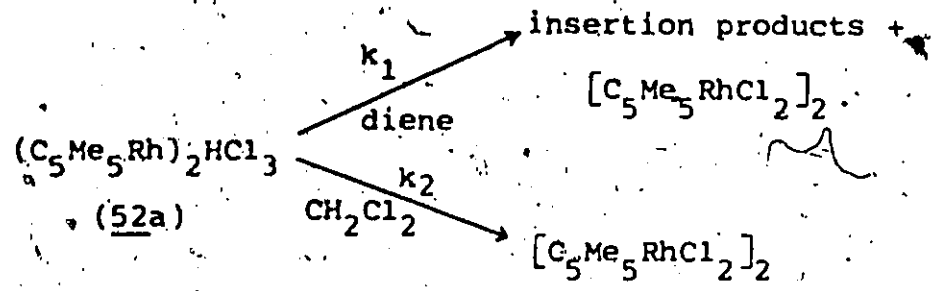
Table 3

First-order rate constants for the reactions of (52) (0.033 mmol) and dienes (0.033 mmol) in CH_2Cl_2 at 310°K

Diene	$10^4 k_1 (s^{-1})$ Rh	Ir
1,5-Cyclooctadiene	1.5 ± 0.2	7.5 ± 0.8
1,3-Cyclooctadiene	1.3 ± 0.2	7.2 ± 0.8
1,4-Cyclohexadiene	1.5 ± 0.2	7.8 ± 0.8
Isoprene	1.3 ± 0.2	7.4 ± 0.8
2,3-Dimethylbutadiene	1.4 ± 0.2	8.0 ± 0.8

In the above table, k_1's were the rate constants for the formation of the allylic complexes. In the iridium reactions, these were the same as those for the disappearance of the hydrido complex (52b) which could be obtained directly from the slope of those first-order plots. In the rhodium reactions, however, the case was slightly more complicated. Since the rate constant for the formation of an allylic complex, k_1, and that for the decomposition of (52a) in methylene chloride, k_2, were roughly of the same

order, the latter reaction could no longer be neglected. Two competing reactions occurred:



Since the decomposition of (52a) to (20a) also followed first-order kinetics, it can easily be shown [116] that:

$$k = k_1 + k_2$$

and,

$$\frac{k_1}{k_2} = \frac{\text{insertion product(s)}}{[\text{dichloride}]_d}$$

where k is the rate constant for the disappearance of the hydride complex (52a) and $[\text{dichloride}]_d$ is the concentration of $[C_5Me_5RhCl_2]_2$ (20a) formed in the decomposition reaction, i.e. the difference between the total concentration of (20a) and that of the insertion product(s) at time t. Since k could be calculated from a first-order plot as described before, it follows that k_1 is given by the following equation:

$$k_1 = k\left(\frac{[\text{insertion product(s)}]}{[\text{insertion product(s)}] + [\text{dichloride}]_d}\right)$$

where the terms in square brackets could be determined by the integrals of the C_5Me_5 resonances of relevant complexes.

It can be seen from Table 3 that, for each hydride, the rates of hydride-diene reactions are essentially the same for different dienes. The average k_1's were (1.4 ± 0.2) x 10^{-4} s^{-1} (rhodium) and (7.6 ± 0.8) x 10^{-4} s^{-1} (iridium). These corresponded to half-lives of ca. 5.0 x 10^3 s (rhodium) and 9.1 x 10^2 s (iridium). The average value of k_2 in methylene chloride at 310°K was (2.5 ± 0.3) x 10^{-5} s^{-1}.

For other dienes such as 1,3-cyclohexadiene, norbornadiene, cyclopentadiene, trans-piperylene, 1,1-dimethylallene and trans-2-methyl-1,3-pentadiene, semi-quantitative estimates of the $t_{\frac{1}{2}}$ of these reactions by the peak-height method also showed that the reaction rates were independent of the nature of the diene. However, the rate of reaction between $(C_5Me_5Ir)_2HCl_3$ (52b) and 2,5-dimethyl-2,4-hexadiene was ca. three times slower than the reactions of (52b) with any other diene described above. The analogous rhodium reaction was too slow to be conveniently studied by the p.m.r. method at 310°K. The rates of reactions between $(C_5Me_5M)_2HCl_3$ (52) and butadiene were not studied, owing to problems of volatility.

(iv) Effect of triethylamine

The effect of triethylamine on the stoicheiometric hydride-diene reactions is summarised in Table 4.

Table 4

Effect of triethylamine on the reactions of (52) (0.033 mmol) and diolefins (0.033 mmol)[a]

Reaction	Triethylamine (mmol)	$10^4 k_1$ (s^{-1})
(52a) + 1,5-COD	0	1.5 ± 0,2
(52a) + 1,5-COD	0.033	1.5 ± 0.2
(52a) + 1,4-CHD	0.017	1.5 ± 0.2 [b]
(52a) + 1,4-CHD	0.033	1.5 ± 0.2
(52a) + 1,4-CHD	0.066	1.4 ± 0.2
(52a) + Isoprene	0.033	1.3 ± 0.2
(52b) + 1,5-COD	0	7.5 ± 0.8
(52b) + 1,5-COD	0.033	7.3 ± 0.8
(52b) + 1,4-CHD	0.033	7.8 ± 0.8
(52b) + 1,4-CHD	0.165	7.6 ± 0.8
(52b) + Isoprene	0.033	7.4 ± 0.8
(52b) + Isoprene	0.066	7.5 ± 0.8

[a] Reactions were carried out at 310°K in CH_2Cl_2

[b] Initial rate

It is obvious from Table 4 that triethylamine has no effect on the rates of the hydride-diene reactions that were examined and it was assumed that the same conclusion could also be applied to the other dienes described.

The rates of decomposition of the cyclic en-yl and allylic complexes into the diene complexes were not studied

quantitatively but qualitative observations made it clear that they were greatly enhanced in the presence of the base.

(v) Effect of solvent

Because of solubility problems, the rates of these hydride-diene reactions were only studied in methylene chloride, chloroform-d and benzene solutions. Using 1,5-cyclooctadiene as a model diene, the first-order rate constants of these reactions in different solvents are summarised in Table 5.

Table 5

First-order rate constants for the reactions of $(C_5Me_5M)_2HCl_3$ (0.033 mmol) and 1,5-COD (0.033 mmol) in different solvents at 310°K

Solvent (dielectric constant[a])	$10^4 k_1$ (s^{-1})	
	Rh	Ir
CH_2Cl_2 (9.08)	1.5 ± 0.2	7.5 ± 0.8
$CDCl_3$ (4.81[b])	0.4 ± 0.05	2.6 ± 0.3
C_6H_6 (2.28)	c	1.0[d]

[a] At 293°K

[b] Value for $CHCl_3$.

[c] Reaction too slow to be conveniently studied by p.m.r. at 310°K

[d] Estimated rate: $t_{\frac{1}{2}}$ of this reaction >7200 s

It can be seen that, for both hydrides, the rates of the hydride-diene reactions decrease with decreasing solvent polarity (i.e. dielectric constant). This probably implies that the activated intermediate was more polar than the starting materials.

(vi) Competition reactions

Since the kinetics of hydride-diene reactions do not distinguish the relative rates for individual dienes, it was of interest to find out whether the hydrides show different reactivities towards various dienes when they are present in the same reaction mixture. The results of these competition reactions are summarised in Table 6.

Table 6

Results of competition reactions[a,b]

Reactants[c] (molar ratio)	Allylic and diene products[d] (molar ratio)
(52a) + isoprene + 1,5-COD + Et_3N (1:1.25:1.25:1)	(64a) + (65a) + (32a) (0.32:0.25:0.45)
(52a) + isoprene + 1,3-CHD + Et_3N (1:1.25:1.25:1)	(64a) + (65a) + (30a) (0.30:0.25:0.45)
(52a) + isoprene + PPL + Et_3N (1:1.25:1.25:1)	(64a) + (65a) + (61a) + (62a) (0.29:0.20:0.42:0.09)
(52a) + isoprene + 2,3-DMBD + Et_3N (1:1.25:1.25:1)	(64a) + (65a) + (68a) (0.30:0.23:0.47)
(52b) + isoprene + 1,5-COD + Et_3N (1:1.25:1.25:1)	(64b) + (65b) + (32b) (0.14:0.34:0.52)
(52b) + isoprene + 1,3-CHD + Et_3N (1:1.25:1.25:1)	(64b) + (65b) + (30b) (0.15:0.37:0.48)
(52b) + isoprene + PPL + Et_3N (1:1.25:1.25:1)	(64b) + (65b) + (61b) + (62b) (0.17:0.36:0.42:0.05)
(52b) + isoprene + 2,3-DMBD + Et_3N (1:1.25:1.25:1)	(64b) + (65b) + (68b) (0.15:0.37:0.48)

Table 6 - cont'd

[a] Reactions were carried out in CH_2Cl_2 at 310°K

[b] Accuracy of results ± 10%

[c] PPL = trans-piperylene

DMBD = dimethylbutadiene

[d] (30) = C_5Me_5M(1,3-cyclohexadiene)

(32) = C_5Me_5MCl(π-2-cyclooctenyl)

(61) = C_5Me_5MCl(syn,syn-1,3-dimethylallyl)

(62) = C_5Me_5MCl(syn-1-ethylallyl)

(64) = C_5Me_5MCl(syn-1,2-dimethylallyl)

(65) = C_5Me_5M(isoprene)

(68) = C_5Me_5M(2,3-dimethylbutadiene)

The above results clearly demonstrated that, when two dienes were reacted with a deficiency of the hydrides, no discrimination occurred between them.

(vii) Activation parameters

Using 1,5-COD as a model diene, the effect of temperature on the first-order rate constants for the hydride-diene reactions is given in Table 7.

Table 7

First-order rate constants for the reactions of $(C_5Me_5M)_2HCl_3$ (0.033 mmol) and 1,5-COD (0.033 mmol) in CH_2Cl_2 at various temperatures

Rh		Ir	
Temp. (°K)	$10^4k_1(s^{-1})$	Temp. (°K)	$10^4k_1(s^{-1})$
324.0	6.0 ± 0.8	310.0	7.5 ± 0.8
322.5	5.0 ± 0.6	305.0	5.0 ± 0.5
318.5	3.3 ± 0.4	302.5	3.2 ± 0.3
314.5	1.9 ± 0.2	296.0	1.3 ± 0.2
308.0	1.0 ± 0.1	288.0	0.53 ± 0.08

A logarithmic plot of k_1 (Table 7) against 1/T yields the experimental activation energies and the activation parameters were calculated from the Eyring equation for reactions performed in solution.

$$k_{soln} = e(\frac{kT}{h})e^{-E_a/RT}e^{\Delta S^{\ddagger}/R}$$

and: $\Delta H^{\ddagger} = E_a - RT$. The parameters are shown below:

	Rh	Ir
E_a	22.9 ± 2.5 kcal mole^{-1}	22.0 ± 2.5 kcal mole^{-1}
$\Delta H^{\ddagger}$	22.3 ± 2.5 kcal mole^{-1}	21.4 ± 2.5 kcal mole^{-1}
$\Delta S^{\ddagger}$	-4 ± 8 e.u.	-4 ± 8 e.u.

(viii) Kinetics of $(C_5Me_5M)_2DCl_3$ (53)

The rates of reactions between $(C_5Me_5M)_2DCl_3$ (53) with various dienes were also studied and the results are given in Table 8.

Table 8

First-order rate constants for the reactions of $(C_5Me_5M)_2DCl_3$ (0.033 mmol) and dienes (0.033 mmol) in CH_2Cl_2 at 310°K

Diene	$10^4 k_1 (s^{-1})$	
	Rh	Ir
1,5-COD	1.4 ± 0.2	7.4 ± 0.8
1,4-CHD	1.6 ± 0.2	7.8 ± 0.8
Isoprene	1.7 ± 0.2	7.6 ± 0.8
2,3-DMBD	1.6 ± 0.2	7.8 ± 0.8

Comparison of the above rate constants with those given in Table 3 showed that the deuterides (53) of both rhodium and iridium reacted at the same rates as the corresponding hydrides with dienes.

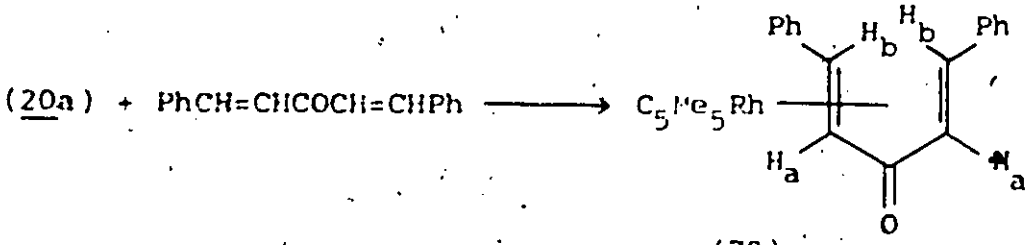
III. Miscellaneous Reactions

(A) (Dibenzylideneacetone)pentamethylcyclopentadienyl-rhodium(I) (78)[117]

In contrast to the conventional bonding in quinone complexes of transition metals where both double bonds

are coordinated to the one metal atom, in the zero-valent complexes of palladium, $Pd_2(dba)_3$.solvate (dba = dibenzylideneacetone), the dibenzylideneacetone has been shown by X-ray studies[118] to have one double bond of each dba coordinated to one palladium, while the other double bond of each dba was coordinated to the other palladium, both metal atoms being trigonally coordinated overall. $Pd(dba)_3$ is reported to have only one double bond of each dba coordinated to trigonal Pd(0)[119].

However, dba can bond as a 1,4-diene to a single metal atom despite the large potential restraints arising from non-bonded interactions between the two hydrogens (H_a) on the double bonds. In ethanolic sodium carbonate, $[C_5Me_5RhCl_2]_2$ (20a) reacted with dba to give red crystals of (78).



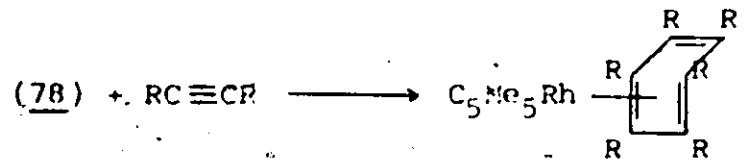
(78)

The new complex was characterised by elemental analysis and its structure was established from its p.m.r. spectrum (Table 9). This showed, in addition to the phenyl hydrogens and C_5Me_5 resonance, doublets at τ 5.17 (H_a) and 6.47 (H_b) [J(a,b)=11.0 Hz] which were further split (J=ca. 1 Hz) by coupling to ^{103}Rh (I=½, 100%). In

uncomplexed dba the resonances of H_a and H_b were observed at τ 2.22 and 2,92 and J(a,b) was 16.5 Hz. The large upfield shift in these resonances on complexation together with the change in J(a,b) as well as the observed coupling to Rh showed that dba was complexed to the metal through its double bonds. This structure has recently been confirmed by an X-ray determination on (78)[120].

The i.r. spectrum of (78) showed a single, very strong ν(CO) at 1562 cm^{-1} ($CHCl_3$ solution) which was at considerably lower frequency than in free dba.

The complex (78) was moderately stable but slowly decomposed in chloroform to give (20a) and free dba. On heating with 1,5-COD (50°, 18 hr.) decomposition occurred to give unidentified products; none of the known C_5Me_5Rh(1,5-COD) (33a) was obtained. In contrast, (78) reacted with dimethyl acetylenedicarboxylate under these conditions to give a quantitative yield of the "bent benzene" complex (79), which had previously been obtained from $[C_5Me_5Rh(OAc)_2.H_2O]$ (25a) and the acetylene under hydrogen[121].

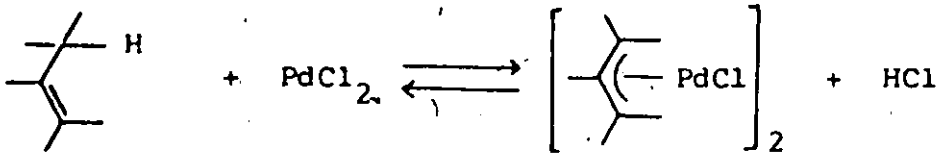


(R=COOMe) (79)

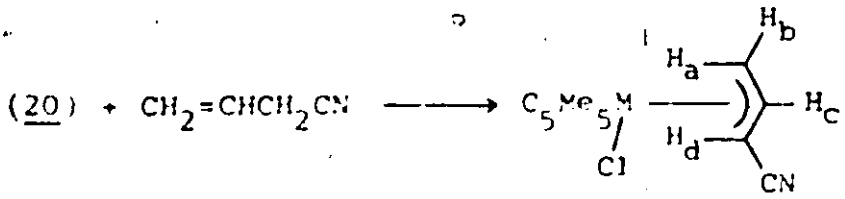
Attempts to prepare the iridium analogue of (78) under similar conditions were unsuccessful.

(B) π-Chloro(syn-1-cyanoallyl)pentamethylcyclopentadienyl-rhodium and -iridium (80)

The previously described reactions of metal hydrides and dienes represent one of the several general methods of preparing π-allyl complexes. Another main route to this type of compounds is by using mono-olefins as starting materials and a typical example is:



The yields of the allylic complexes were improved if hydrogen chloride was removed by a base. Tsuji et al. observed that olefins with electron-withdrawing β-substituents such as -COR and -COOR where the β-hydrogens were acidic would readily eliminate HCl to give the π-allylic complexes[122]. Reactions similar in principle occurred when allyl cyanide was reacted with $[C_5Me_5MCl_2]_2$ (20) in acetone with sodium carbonate to give high yields of the π-syn-1-cyanoallyl complexes (80).



(80)

The red (rhodium) and yellow (iridium) complexes were characterised by elemental analysis and their structures were established from the p.m.r. data (Table 9). Decoupling

experiments showed that J(c,d) was 10.0 Hz in the rhodium complex (80a) and 9.0 Hz in the iridium analogue (80b) and therefore the complexes had the syn configuration.

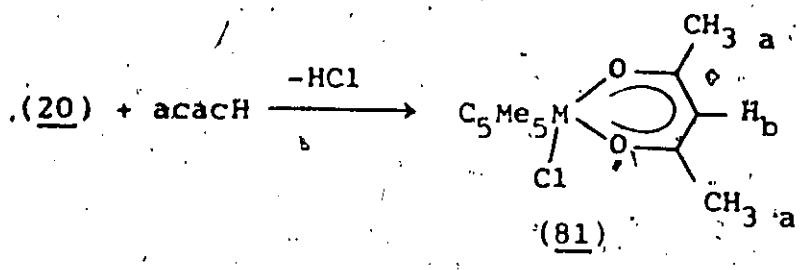
Under similar conditions, allyl chloride reacted with $[C_5Me_5RhCl_2]_2$ (20a) to give a mixture of four complexes. Attempts to separate this mixture were unsuccessful and hence their structures could not be ascertained. All appeared to be allylic complexes, with C_5Me_5 resonances (CH_2Cl_2, 100 MHz) at τ 8.08, 8.19, 8.23 and 8.33. Other workers have obtained dimethyl 1,5-hexadiene complexes from reactions of methallyl chloride[123] but this did not appear to occur here as the products were different to the 1,5-hexadiene complexes (84) synthesised independently (see section D below).

(C) Preparation of some β-diketone complexes of (pentamethylcyclopentadienyl)-rhodium and -iridium

(i) Reactions with 2,4-pentanedione

The M-Cl bonds in $[C_5Me_5MCl_2]_2$ (20) have been shown to be labile and the chlorides can be partly or wholely substituted by a variety of ligands (see Introduction, section II). The formation of mono- and bis-acetylacetonato complexes of rhodium and iridium further illustrates the same point.

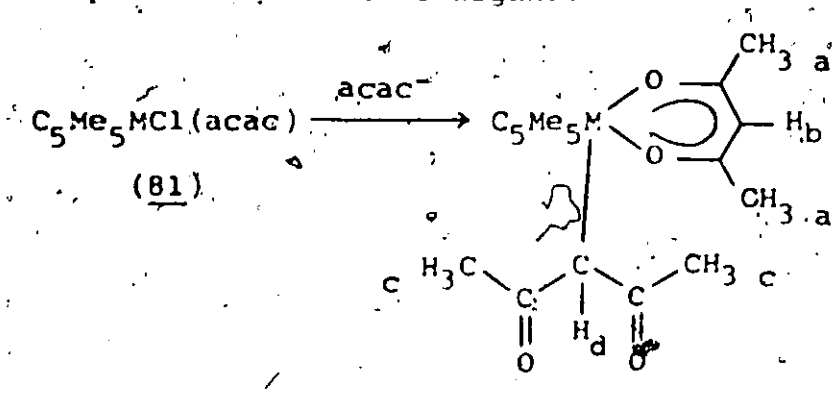
At 25°, $[C_5Me_5MCl_2]_2$ (20) reacted with a basic solution of acetylacetone (acacH) to give the mono-acetylacetonato complexes (81) in high yields.



(20) + acacH $\xrightarrow{-HCl}$ $C_5Me_5M(acac)Cl$

(81)

The chloride ligand in the iridium complex (81b) could further be displaced by another $acac^-$ unit to form the bisacetylacetonato complex (82b) under prolonged reaction and in the presence of excess ligand.



$C_5Me_5MCl(acac)$ $\xrightarrow{acac^-}$ $C_5Me_5M(acac)_2$

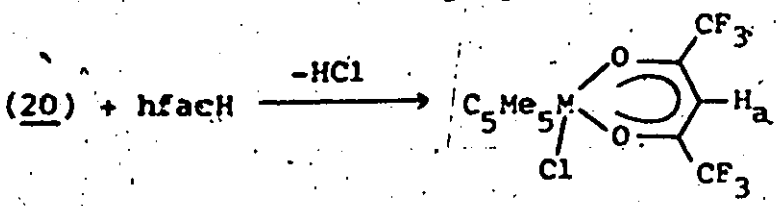
(81) (82)

Complexes (81a and b) and (82b) were characterised by elemental analysis and their structures established by p.m.r. (Table 9). The p.m.r. spectrum of (82b) indicated that two types of acac ligands were present in the complex as shown in the above structure. Decoupling experiments showed that Me_c and H_d coupled weakly to each other [$J(c,d)=0.6$ Hz]. The p.m.r. spectrum of (82b) in o-$C_6H_4Cl_2$ was essentially unchanged from $+35^o$ to $+120^o$, indicating the two different acac units were not exchanging in this temperature range. Decomposition occurred at higher temperatures.

Under similar conditions, the analogous rhodium complex (82a) was formed but it could not be isolated pure since it decomposed fairly rapidly into unidentified products. Its presence in the reaction mixture was inferred from the p.m.r. spectrum of the mixture in C_6H_6 solution. This gave resonances at τ 4.97(1H, s, H_b), 5.59(1H, d, J=3.0 Hz, H_d), 7.97(6H, s, H_c), 8.14(6H, s, H_a) and 8.75(15H, s, C_5Me_5) which were consistent with the proposed structure.

(ii) Reactions with Hexafluoroacetylacetone

Reactions of $[C_5Me_5MCl_2]_2$ (20) with hexafluoroacetylacetone (hfacH) in acetone in the presence of sodium carbonate gave high yields of $C_5Me_5MCl(hfac)$ (83),



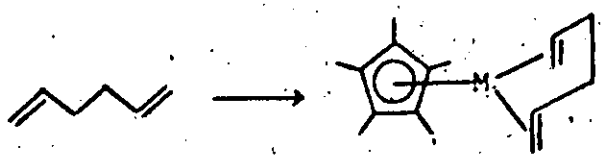
(83)

The new complexes were characterised by elemental analysis, ^1H and ^{19}F n.m.r. data (Table 9). No coupling between the CF_3 groups and H_a of the hfac moiety was observed. Complexes (83a and b) were soluble in many organic solvents, particularly acetone, and remained stable in solution even at elevated temperatures. No bishexafluoroacetylacetonato complexes could be obtained or detected from the reactions of $[C_5Me_5MCl_2]_2$ (20) and excess HfacH even under drastic conditions.

(D) Reactions with 1,5-hexadiene

Preliminary results showed that $[C_5Me_5MCl_2]_2$ (20) reacted readily at 65° in ethanolic sodium carbonate with 1,5-hexadiene to give a single complex (84) for each metal. The solubility and volatility as well as the lack of a chloride ligand (Beilstein's test) indicated that (84a and b) were rhodium(I) and iridium(I) complexes.

P.m.r. data showed that (84a and b) were not 1,3-diene complexes because of the absence of high field resonances in the tetramethylsilane region which are usually observed for such complexes (Table 2). However, broad resonances at τ 6.50-7.50 (vinylic protons) and multiplets at τ 7.8-8.8 (methylene protons) together with C_5Me_5 singlets at τ 8.37 (Rh) and 8.38 (Ir) (C_6H_6 solution) were consistent with the 1,5-diene structure[123,124].



(20) (84)

Reaction of $(C_5Me_5Ir)_2HCl_3$ (52b) with 1,5-hexadiene in CH_2Cl_2 at 25° also proceeded readily and a mixture of products including (84b) was obtained. Further work is needed to clarify the identities of these products and mechanism for the formation of non-conjugated diene complexes such as (84).

Table 9

N.m.r. data of some new rhodium and iridium complexes[a]

Complex	C_5Me_5	H_a	H_b	H_c	H_d	Others
$C_5Me_5Rh(dba)$ (78)	8.81 s	5.17 dd J(a,b)=11.0 J(Rh,a)=1.0	6.47 dd J(b,a)=11.0 J(Rh,b)=1.0	-	-	phenyl: ca. 2.80 m
$C_5Me_5RhCl(C_4H_4N)$ (80a)	8.23 s	6.67 dd J(a,c)=12.0 J(a,b)=1.0	6.47 dd J(b,a)=1.0 J(b,c)=7.0	5.47 m J(c,a)=12.0 J(c,b)=7.0 J(c,d)=10.0 J(Rh,c)=2.0	6.99 dd J(d,c)=10.0 J(Rh,d)=1.0	-
$C_5Me_5IrCl(C_4H_4N)$ (80b)	8.20 s	7.15 dd J(a,b)=2.0 J(a,c)=10.0	6.57 dd J(b,a)=2.0 J(b,c)=7.0	5.27 m J(c,a)=10.0 J(c,b)=7.0 J(c,d)=9.0	7.25 d J(d,c)=9.0	-
$C_5Me_5RhCl(acac)$ (81a)	8.39 s	8.00 s	4.93 s	-	-	-
$C_5Me_5IrCl(acac)$ (81b)	8.41 s	8.09 s	4.81 s	-	-	-
$C_5Me_5Ir(acac)_2$ (82b)	8.59 s	8.15 s	4.80 s	8.14 d J(c,d)=0.6	5.26 s (broad)	-

Table 9 - Cont'd

Complex	C_5Me_5	H_a	H_b	H_c	H_d	Others
$C_5Me_5RhCl(hfac)$ (83a)	8.36 s	4.18 s	-	-	-	CF_3: 75.37 s [b]
$C_5Me_5IrCl(hfac)$ (83b)	8.41 s	4.09 s	-	-	-	CF_3: 76.00 s [b]

[a] All ^1H n.m.r. spectra were recorded in $CDCl_3$ solutions at 100 MHz using tetramethylsilane as internal standard.

[b] Up field of external $CFCl_3$ standard.

DISCUSSION

DISCUSSION

I. Summary

The results of the reactions of $(C_5Me_5M)_2HCl_3$ (52) with diolefins can be summarised as follows.

A. The formation of allylic complexes

(1) The hydrides (52) are intermediates in the formation of π-allyls and π-enyl complexes (and therefore also of the π-diene complexes) from the diolefins and $[C_5Me_5MCl_2]_2$ (20).

(2) The hydrides (52) react with dienes such as 1,5-cyclooctadiene, 1,4-cyclohexadiene, dimethylallene and 2,5-dimethyl-2,4-hexadiene to give π-allylic complexes in which isomerisation (by hydrogen-migration) has occurred.

(3) Bases such as triethylamine play no role in the formation of the π-allyl or σ,π-enyl complexes, but promote the formation of M(I)-diene complexes in all cases from the π-allyl or σ,π-enyl complexes.

(4) The reactions of the iridium hydride complex (52b) resemble those of the rhodium hydride (52a) except for trans-2-methyl-1,3-pentadiene where the rhodium, but not the iridium, syn-1-ethyl-2-methylallyl complex is formed and isoprene, where Ir-H shows greater preference for adding to the disubstituted double bond than Rh-H.

(5) Addition of M-H to acyclic 1,3-dienes is probably 1,2-rather than 1,4-.

(6) When both terminal and internal double bonds are present in the diene, addition of M-H to the former is favoured. The effect is thermodynamic rather than kinetic since trans-piperylene gives 85% of the 1,3-dimethylallyl complex (61) and 15% of the 1-ethylallyl complex (62) both at 25° and at 65°.

(7) The addition of M-H to double bonds usually follows the Markovnikoff rule. The major exceptions are 1,1-dimethylallene and 2,5-dimethyl-2,4-hexadiene where Markovnikoff addition cannot yield π-allylic complexes.

(8) Where a choice is possible, only the syn allylic isomers are formed.

B. Kinetic results

(1) The reactions of $(C_5Me_5M)_2HCl_3$ (52) with diolefins are first-order with respect to the hydride and zero-order with respect to the diolefin. Except for 2,5-dimethyl-2,4-hexadiene, all dienes react at the same rate with the same hydride.

(2) At 37°, the first-order rate constants for the iridium reactions (average 7.6×10^{-4} S^{-1}) are approximately five times as large as those for the rhodium reactions (average 1.4×10^{-4} S^{-1}).

(3) The rate of reaction increases when the solvent polarity increases.

(4) These reactions show negligible deuterium isotope

effect when $(C_5Me_5M)_2DCl_3$ (53) is used in place of $(C_5Me_5M)_2HCl_3$ (52).

(5) The hydrides are quite undiscriminating in the presence of two diolefins and equal amounts of both allylic complexes are always formed.

(6) Small and negative values for $\Delta S^{\ddagger}$ are obtained for these hydride-diene reactions.

C. The formation of 1,3-diene complexes from allylic complexes

(1) Under the conditions studied, the 1,3-diene complexes are always formed from π-allylic intermediates by elimination of HCl. No evidence has obtained for direct formation of the M(I)-diene complexes from M(I) species and the diene.

(2) π-Allyls with substituents in only the syn positions are thermally stable, for example, the syn-1-methylallyl (27) and syn,syn-1,3-dimethylallyl (61) complexes do not undergo elimination of HCl to give 1,3-diene complexes even at 65° in ethanol and in the presence of base.

(3) A methyl substituent at the central carbon (C-2) of the allylic moiety makes the syn isomers thermally less stable with respect to elimination of HCl. This is presumably due to steric hindrance. For example, the syn-1,2-dimethylallyl (64) and syn-1-ethyl-2-methylallyl (72a) complexes give the 1,3-diene complexes on heating, presumably via a syn-anti equilibrium of the σ-allylic intermediates.

(4) Allyls with a potential cisoid 1,3-diene skeleton

(i.e. those with a 1-methyl or -methylene group anti) undergo facile reductive elimination of HCl to give M(I)-diene complexes.

(5) The allylic and en-yl complexes can be classified into three groups with respect to their readiness to form diene complexes:

(i) those that never give diene complexes: the syn-1-methylallyl (27), syn,syn-1,3-dimethylallyl (61) and syn-1-ethylallyl (62) complexes.

(ii) those that give diene complexes only under fairly drastic conditions: the syn-1,2-dimethylallyl (64), syn-1-ethyl-2-methylallyl (72a) and π-2-cyclooctenyl (32) complexes.

(iii) those that give diene complexes spontaneously: the 1,1-dimethylallyl (66), 1,1,2-trimethylallyl (69), syn-1,1,3-trimethylallyl (71), syn-1,1-dimethyl-3-isopropyl-allyl (74), π-cyclohexenyl (56) and norbornenyl (58) complexes. In these cases, the rhodium complexes also undergo reductive elimination more readily than their iridium analogues.

II. The Formation of the Allyls

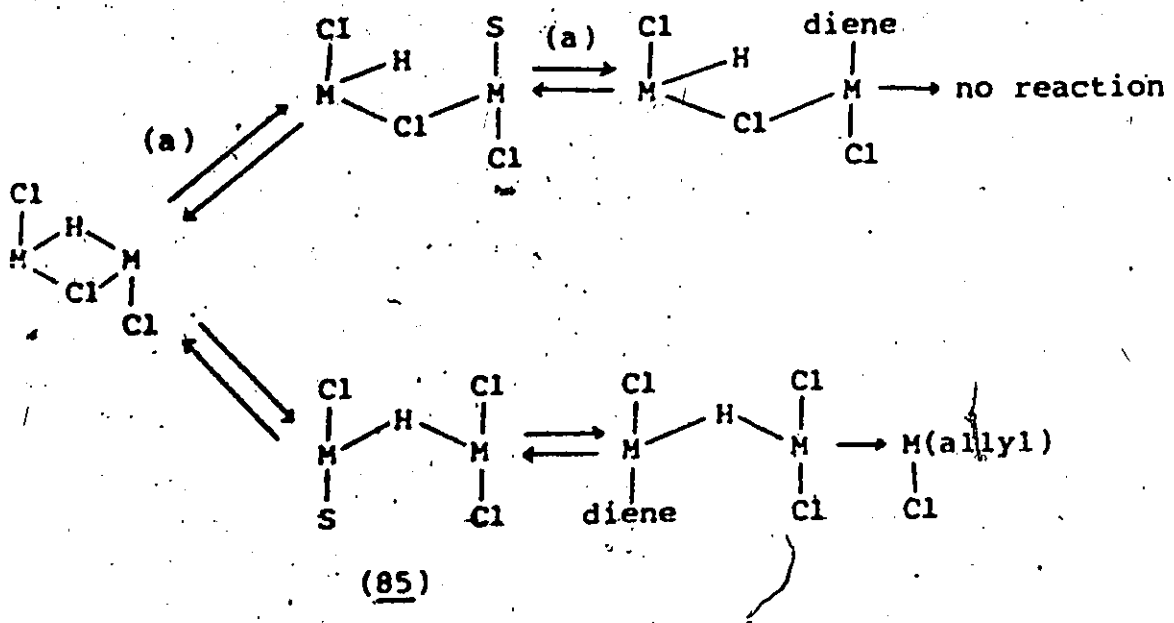
A. Nature of the intermediate

Since the bridged hydrides $(C_5Me_5M)_2HCl_3$ (52), reacted at the same rate with all the dienes (except for 2,5-dimethyl-2, 4-hexadiene) and the rates were independent

of the diene concentrations, the rate-determining step in the hydride-diene reactions must be the breaking of one of the bridges to create a vacant co-ordination site for the incoming diene.

The $\Delta S^{\ddagger}$, being small and negative (-4 e.u. for both rhodium and iridium), indicates that the reaction mechanism does not involve the generation of two or more particles; that is both the H- and Cl-bridges are not cleaved in the formation of the activated species.

The dependence of reaction rates on solvent polarity agrees with the proposal of a polar mono-bridged intermediate.

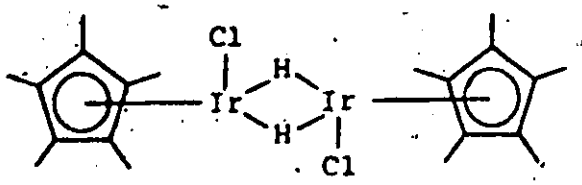


(85)

Theoretically, it would be possible for either the M-Cl-M or the M-H-M bridge to be cleaved. However, if the hydride bridge were opened, then the diene and the hydride would be attached to different metal atoms (path a) and no simple insertion reaction could take place.

It would therefore appear more logical that the M-Cl-M bridge breaks and this suggestion is supported by the kinetics shown by the deuterides $(C_5Me_5M)_2DCl_3$ (53). In general, a large kinetic isotope effect should be observed if the rate-determining step involves the breaking of a M-H or the making of a C-H bond*. Since a negligible isotope effect was observed when the hydrides and deuterides were compared (Tables 3 and 8), it may be concluded that the cleavage of M-Cl-M bridge in (52) is the rate-determining step in the entire reaction sequence.

The dihydride $[C_5Me_5IrHCl]_2$ (86), which contains two bridging hydride ligands, has recently been prepared



(86)

and characterised by D.S. Gill of this Laboratory[30]. He found that this dihydride did not react with typical diolefins to give the allylic complexes under the conditions used in the work described here (CH_2Cl_2/20-30°). This agrees

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* The lack of discrimination of the intermediate towards different dienes shown by the competition reactions indicates that formation of the C-H bond cannot be a slow step.

with the conclusion presented here that it is much more difficult to break the Ir-H-Ir than the Ir-Cl-Ir bridge in order to create the vacant site.

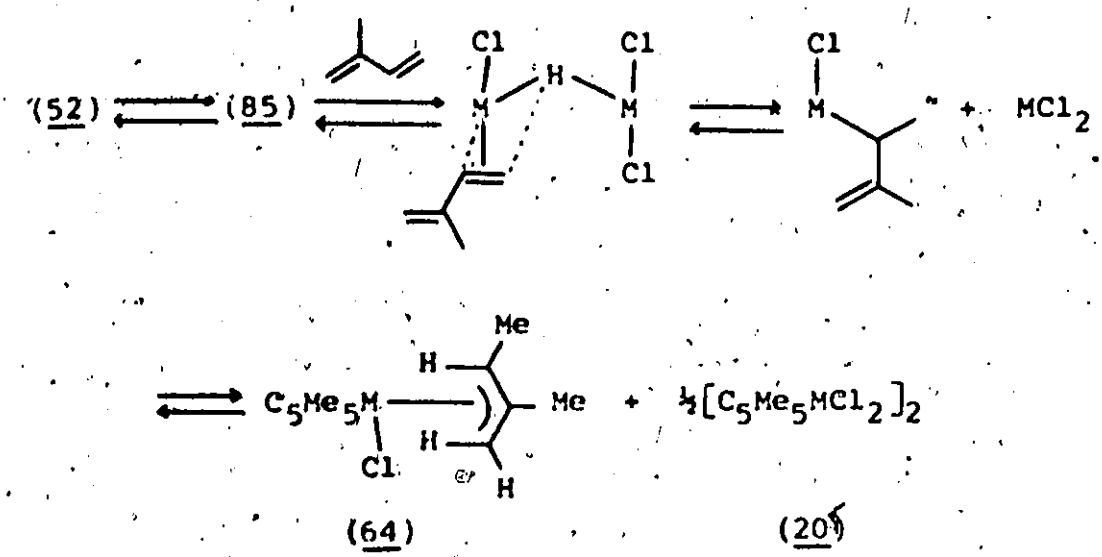
The small Rh-Cl-Rh angle of 73.2° found in $(C_5Me_5Rh)_2HCl_3$ (52a)[109] is also an indication of strain in the chloride bridge since M-Cl-M angles for bridges in binuclear square-planar or octahedral species are typically ca. 90°.

B. Reactions with acyclic 1,3-dienes

In the reactions of $HNi[P(OMe)_3]_4^+HSO_4^-$ with 1,3-dienes, Tolman observed that formation of the anti isomers was kinetically preferred and suggested that the rotation of the diene into a cisoid configuration occurred as NiH was added[76].

Since the anti isomers were not observed for any of the allylic complexes formed from the reactions of $(C_5Me_5M)_2HCl_3$ (52) with acyclic 1,3-dienes (and where both the 1-syn and the 1-anti-methyl or -methylene could, in principle, be formed), it may be presumed that the dienes react in the transoid configuration. The formation of the syn-1,2-dimethylallyl complex (64) from isoprene can be illustrated as shown in Scheme V.

The reason for the dienes to react with (52) in a transoid configuration is likely to be steric, as even in the bridge-opened intermediate (85) the vacant site will



(64) (20)

Scheme V. The formation of the syn-1,2-dimethylallyl complex (64)

be crowded by the methyls of the C_5Me_5 rings and the M-Cl.

The possibility that the acyclic 1,3-dienes react in cisoid form to give the anti-substituted allyls which then rapidly isomerise to the syn form is unlikely in view of the probable mechanism of decomposition of the allylic complexes to the diene complexes discussed below.

Given that the acyclic 1,3-dienes react in the transoid conformer, it is most likely that M-H adds 1,2- to a double bond as shown in Scheme V. The alternative, 1,4-addition, is unlikely to occur to a transoid molecule since the distance is too great for M-H to span. [It may also be noted that no complexes are known where a 1,3-diene is bonded to one metal atom in a transoid conformation:]

On the other hand, it is not impossible that in the cases described by Tolman, and for the additions of M-H to cyclic 1,3-dienes described here, a 1,4-addition of MH to the diene does occur*.

In the reactions involving dienes with both terminal and internal double bonds, the hydrides (52) showed marked preference for addition to the less hindered terminal double bonds. Thus a mixture of 85% of the syn,syn-1,3-dimethylallyl (61) and 15% of the syn-1-ethylallyl (62) complexes was obtained in the reactions of $(C_5Me_5M)_2HCl_3$ (52) with trans-piperylene. The effect controlling the isomer distribution in these cases is likely to be thermodynamic rather than kinetic since reactions at 25° [$(C_5Me_5M)_2HCl_3$ + diene in CH_2Cl_2] and at 65° [$(C_5Me_5MCl_2)_2$ + diene in alcohol-base] gave the same mixture of products in identical ratios.

Similarly, a mixture of 80% of the syn-1,1,3-trimethylallyl (71a) and 20% of the syn-1-ethyl-2-methylallyl (72a) complexes was obtained which arose from the addition of Rh-H of (52a) to the terminal and internal double bonds of 2-methyl-1,3-pentadiene respectively. Reaction of the

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* The high yields and mild conditions of the reactions make it unlikely that free radical attack is occurring and the most probable transition state is a four-centre one.

iridium hydride (52b) with the same diene indeed gave only the 1,1,3-trimethylallyl (71b) complex.

The reactions of (52) with acyclic 1,3-dienes having terminal double bonds with either one or two substituents, such as isoprene, showed less discrimination. For the rhodium hydride, the products corresponding to addition to the two different double bonds of isoprene are approximately equal while for the iridium reaction, the more substituted (in classical terms, "more basic") double bond was the more favoured site.

It is likely that the predominant factor governing the isomer distribution in the reactions of $(C_5Me_5M)_2HCl_3$ (52) with asymmetric dienes is steric. Since internal double bonds are more hindered than terminal ones in a crowded intermediate such as (85), insertion to the terminal double bonds is more favoured. On the other hand, a small substituent such as a 2-methyl on a terminal double bond does not seem to exert a very large effect, and the rate of attack is not very different to that on the monosubstituted double bond.

C. Reactions with cyclic dienes

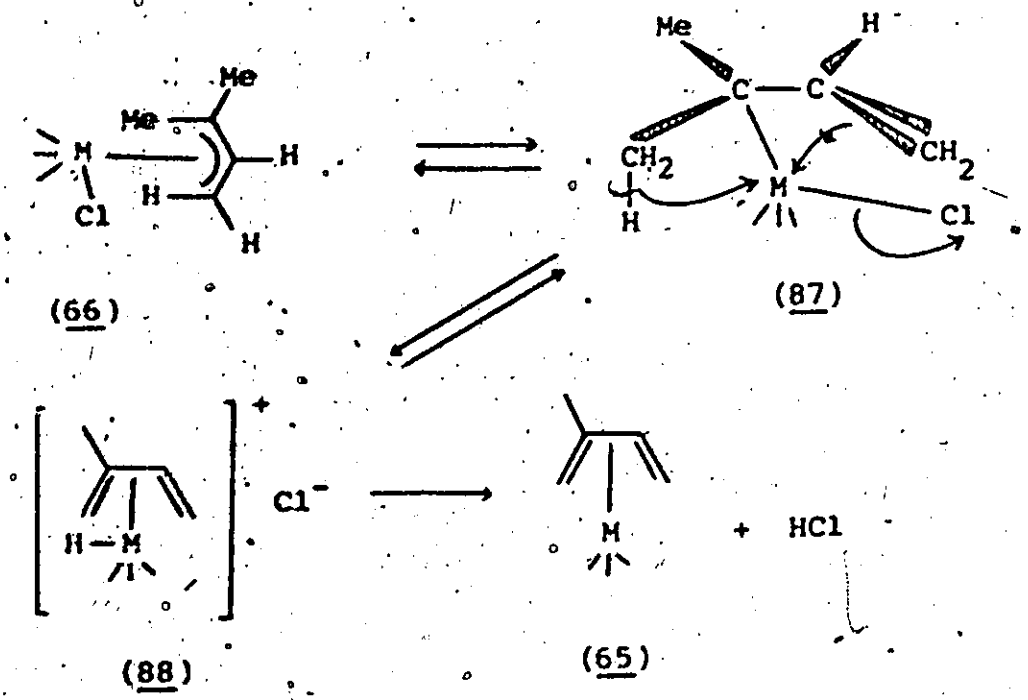
The cyclic dienes reacted in the same manner as the acyclic ones, except that the ring constrained them to give the (unstable) anti-1,3-isomers. Isomerisation was also observed for the cyclohexadienes and the cyclooctadienes.

III. The Formation of the Diene Complexes

A. Decomposition of allyls with an anti methyl substituent

Allyls with a potential or actual anti methyl group undergo facile reductive elimination of HCl to give M(I)-diene complexes. A typical example is illustrated by the decomposition of the 1,1-dimethylallyl complex (66) to the isoprene complex (65).

A reaction pathway that is consistent with the data is shown in Scheme VI. Here the decomposition of (66) is initiated by the formation of the σ-allylic intermediate with the cisoid arrangement (87) shown. This is followed by a concerted process involving a hydride transfer from the

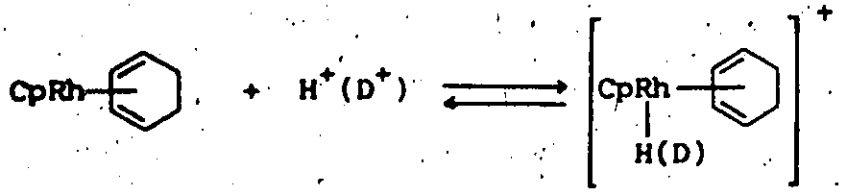


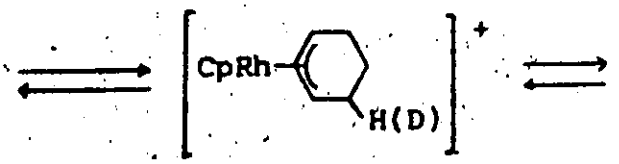
(66) (87) (88) (65)

Scheme VI. The decomposition of the 1,1-dimethylallyl complex (66)

anti-methyl to the metal and displacement of Cl^- by the double bond to give the ionic intermediate (88). Elimination of HCl gives the isoprene complex (65).

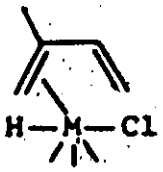
Evidence in favour of the latter part of this process, and in particular, the ionic intermediate (88), comes from the work of Johnson et al.[125] who reported that on addition of acids containing weakly complexing anions, H-D exchange occurred via a cation of this type.



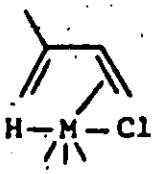


Further support for the intermediacy of an ionic $[C_5Me_5M(H)(diene)]^+$ complex comes from the observation that better yields of the isoprene (64) and 2-methyl-1,3-pentadiene (70a) complexes are obtained from the syn-1,2-dimethylallyl (64) and syn-1-ethyl-2-methylallyl (72a) complexes, respectively, in a polar solvent such as ethanol than in a non-polar solvent such as benzene.

Intermediates such as (89) and (90) are less attractive since they would also appear to provide a path for the direct formation of the isoprene complex from a hydridochloride-diene intermediate by elimination of HCl and without going through the allylic form (see below).



(89)



(90)

The decompositions of the 1,1,2-trimethylallyl (69), the syn-1,1,3-trimethylallyl (71), and the syn-1,1-dimethyl-3-isopropylallyl (74) complexes into the M(I) 2,3-dimethyl-butadiene (68), the 2-methyl-1,3-pentadiene (70) and the 2,5-dimethyl-1,3-hexadiene (73) complexes, respectively, are postulated to proceed by a similar mechanism.

B. The formation of C_5Me_5Rh(isoprene) (65a) at 25°

Since the 1,1-dimethylallylrhodium complex (66a) could not be observed in the reaction between (52a) and isoprene, this raises the question whether or not the direct formation of (65a) in this reaction proceeds via a different route.

There are two plausible mechanisms which can be considered here.

(1) It was suggested that, in the formation of C_5Me_5Rh(1,3-cyclohexadiene) (30a) from $[C_5Me_5RhCl_2]_2$ (20a) in ethanol/base at elevated temperatures, (20a) was transformed in a slow reaction into an intermediate, C_5Me_5Rh(solvent), which then reacted with 1,3-CHD to give complex (30a)[33].

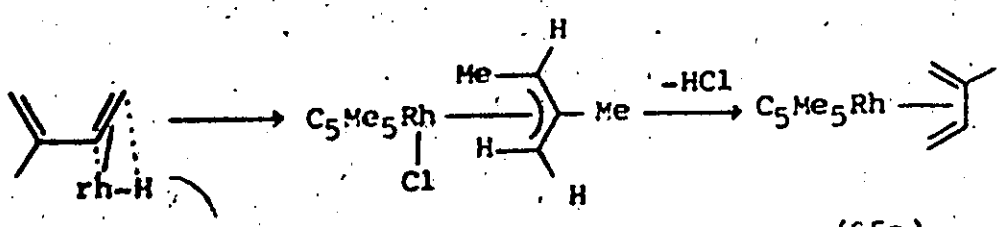
$$[C_5Me_5RhCl_2]_2 \longrightarrow [C_5Me_5RhH(Cl)(solvent)] \xrightarrow{base}$$

$$[C_5Me_5Rh(solvent)] \xrightarrow{1,3\text{-CHD}} C_5Me_5Rh(C_6H_8)$$

(30a)

It is, however, unlikely that $C_5Me_5Rh(solvent)$ is formed during the course of the hydride-diene reaction at 25° in a poorly coordinating solvent and in the absence of a base, since if this were the case, the analogous reaction with butadiene and trans-piperylene should also have given Rh(I)-diene complexes. These were never observed there. Moreover, the other reactions of the hydrides with dienes that have been studied indicate that an allylic intermediate is always formed prior to the corresponding diene complex and it is unlikely that the rhodium-isoprene reaction can go by a completely different mechanism.

(2) The 1,2-addition of Rh-H to the mono-substituted double bond of a cisoid isoprene unit could give the anti-1,2-dimethylallyl complex (91a) which would be expected to undergo dehydrochlorination rather easily to afford the isoprene complexes:



(91a) (65a)

(rh=C_5Me_5RhCl)

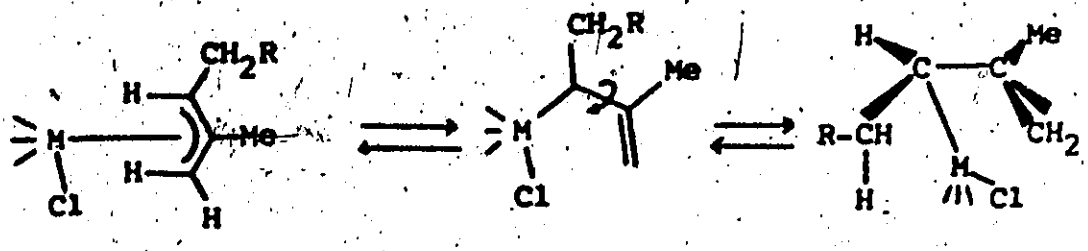
There was, however, no evidence for the formation of (67a) as an intermediate during the reaction, and the possibility of (67a) being present in kinectically significant but undetectable amount could also be ruled out since the analogous butadiene reaction would have given first the anti-1-methylallyl and hence the Rh(I)-butadiene complex. Neither of these were observed.

Puthermore, since the 1,1-dimethylallyliridium complex (66b) was detected during the reaction of isoprene with the iridium hydride, it is logical to presume that the rhodium complex behaves similarly.

C. Decomposition of the syn-1,2-dimethylallyl (64) and syn-1-ethyl-2-methylallyl (72a) complexes

Allylic complexes such as (64) and (72a) undergo reductive elimination of HCl to give M(I)-diene complexes only at higher temperatures. A comparison of these complexes with those which gave diene complexes readily suggested that this increased stability is likely to be due to the lack of an anti substituent on the allyl here. However, the anti configuration, (92), can be obtained by twisting a C-C bond of the σ-allylic intermediate (67) (Scheme VII); subsequent reaction follows the path depicted in Scheme VI.

Studies on substituted π-2-methylallylpalladium chloride complexes indicated that allyls with bulky substituents on the terminal carbon atoms were often formed



(67) (92)

(R=H, Me)

Scheme VII. The syn-anti rearrangement.

with these substituents in the less stable anti configuration. The activation energy of the π-σ-π rearrangement to the syn configuration increased with the bulkiness of the substituent. The difference in energy between the anti and syn configurations decreased with increasing size of the substituents on the terminal and middle carbon atoms. These observations were explained by assuming that there were non-bonded interactions between the substituents on the terminal carbons of the π-allyl ligand and either other ligands on the metal or the substituent on the 2-carbon of the π-allyl ligand[126].

It is probable, therefore, that in complexes (64) and (71a), non-bonded interactions between the substituents on the 1- and 2-carbon atoms of the allylic ligand provide the driving force for the syn-anti rearrangement.

D. The stability of the syn-1-methylallyl (27), syn,syn-1,3-dimethylallyl (61) and syn-1-ethylallyl (62) complexes

The complexes (27), (61) and (62) did not give 1,3-diene complexes even under drastic conditions. It follows

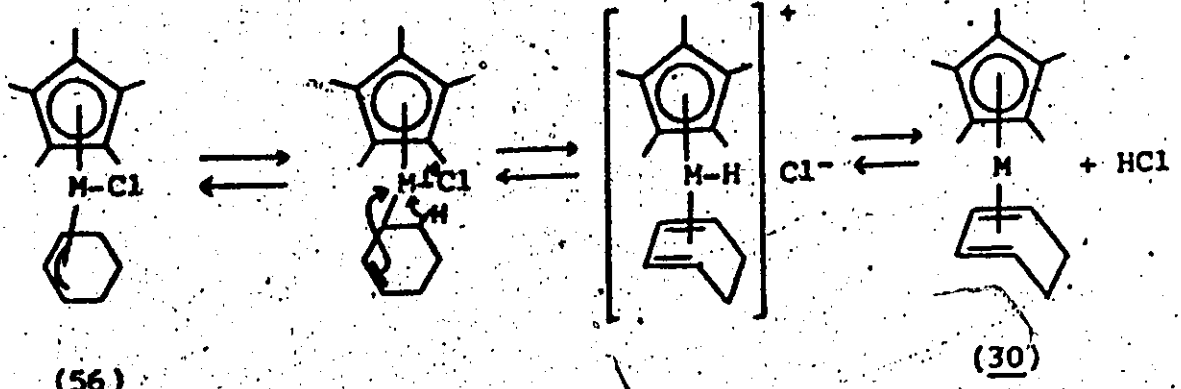
from sections A and C that the factors contributing to the stability of such complexes are probably the absence of anti-1- and 2-alkyl substituents on the allyl ligand. When there is no 2-substituent the difference in energies between the syn and anti forms of the above complexes is very large and it is, therefore, extremely difficult to obtain the anti isomers which are necessary in order that elimination of HCl may occur.

E. The decomposition of cyclic allylic complexes

(1) The formation of C_5Me_5M(1,3-cyclohexadiene) (30)

The general ideas concerning the stability of the acyclic allylic complexes summarised in sections A, C and D may also be extended to explain the ready decomposition of the cyclohexenyl complexes (56) into (30). In the complexes (56) the 1,3-substituents (CH_2) must both be anti and hence it is not surprising that both (56a) and (56b) were only observed as unstable intermediates.

The formation of C_5Me_5M(1,3-CHD) (30) can then be represented by the mechanism shown in Scheme VIII.

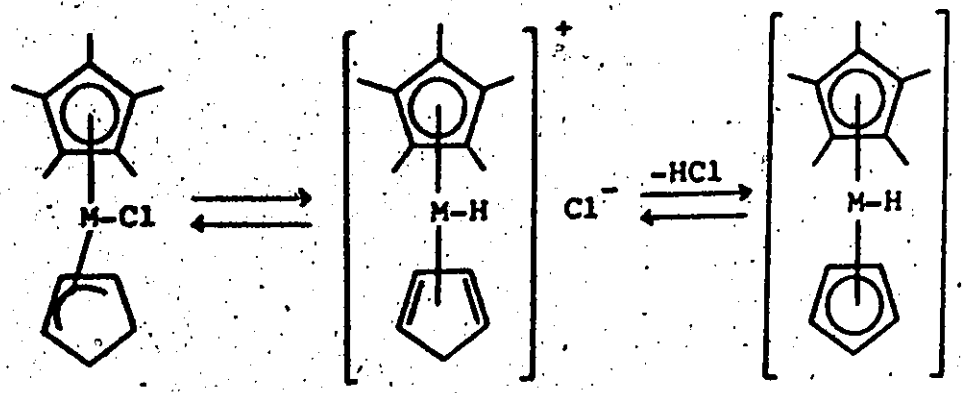


(56) (30)

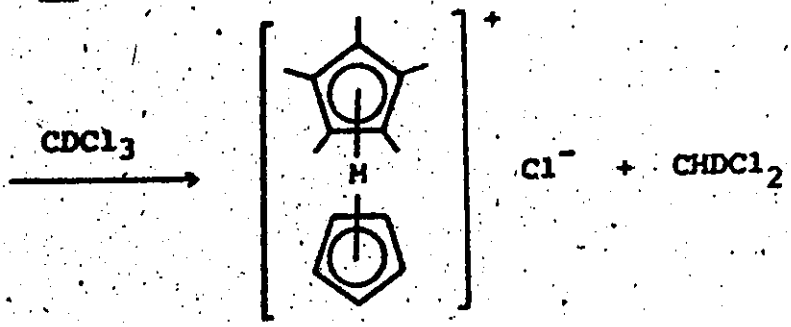
Scheme VIII. The formation of C_5Me_5M(1,3-CHD) (30)

(2) The decomposition of the cyclopentenyl complexes (59).

The decomposition of (59) is less straight-forward than that of the cyclohexenyl complexes (56) as the 1,3-diene complexes were not detected or isolated. It was also observed that the cyclopentenyl complexes (59) were more stable than complexes (56). This is probably due to the σ-cyclopentenyl ring being twisted in such a manner that abstraction of hydride from an anti methylene group by the metal to give the ionic hydrido-cyclopentadiene intermediate (92) is not easy. [It is normally presumed that for the β-elimination to occur, a four-centre planar transition-state is needed[127].]



(59) (92) (93)



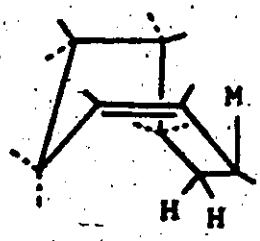
(35)

Scheme IX. The decomposition of the cyclopentenyl complex (59)

However, it is not clear why (92) does not eliminate HCl to give the cyclopentadiene complexes (39) the iridium one of which is known. One mechanism for the formation of (35) from (59) is shown in Scheme IX. It is based on the observation that when (59) is generated in $CDCl_3$, the metallocenium ions (35) were formed together with $CHDCl_2$. However, (35) is also formed from (59) in other solvents, presumably involving loss of H_2 in the reaction.

(3) The stability of the π-2-cyclooctenyl complexes (32)

The cyclootenyl complexes, $C_5Me_5MCl(C_8H_{13})$ (32) do not eliminate HCl at 25° to give 1,3-diene complexes, even in the presence of excess triethylamine. Molecular models of these compounds indicate that the methylene protons at the allylic carbons of the σ-cyclooctenyl intermediate (94) bend away from the metal, making the abstraction of a hydride from these methylene groups extremely difficult and thereby



(94)

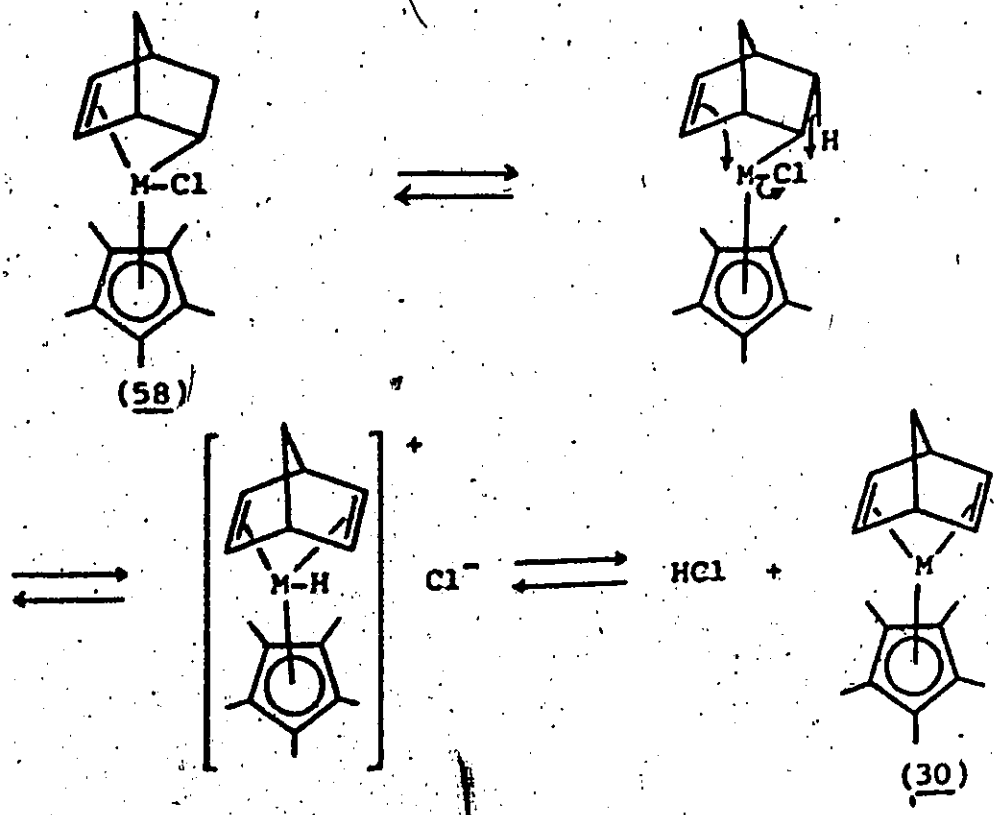
eliminating the possibility of forming a 1,3-cyclooctadiene complex. As far as can be ascertained, $Fe(CO)_3$(1,3-COD) was the only example of a tetrahapto 1,3-cyclooctadiene transition metal complex*.

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

However, the cyclooctenyl complexes (32) give the 1,5-COD complexes (33) at 65° in ethanol/base. The mechanism of this reaction, which may involve either a series of 1,2-hydrogen shifts or a 1,4-transannular shift, has been discussed previously[128].

(4) The decomposition of the norbornenyl complexes (58)

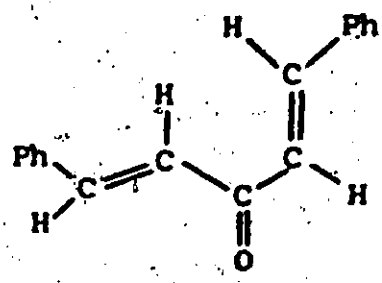
The decomposition of the norbornenyl complexes (58) into diene complexes is similar to those of allylic complexes discussed above. The abstraction of an endo hydrogen from the 5-methylene group by the metal can proceed relatively easily and may be represented by the mechanism in Scheme X.



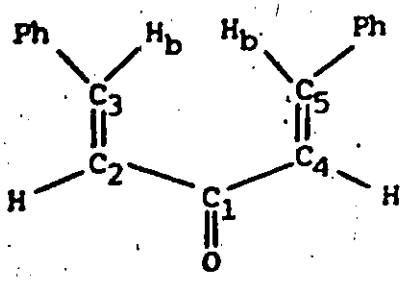
Scheme X. The decomposition of the norbornenyl complexes (58)

IV. (Dibenzylideneacetone)pentamethylcyclopentadienyl-rhodium(I) (78)

The dibenzylideneacetone (dba) molecule contains a carbonyl group in addition to the two olefinic double bonds and it is potentially capable of complexing to transition metals in different ways. The two principal conformers of dba are:



(A) s-cis, s-trans



(B) s-cis, s-cis

The geometry of conformer (A) means that only one of the two carbon-carbon double bonds can coordinate to one metal atom. The crystal structure of $Pd_2(dba)_3 \cdot CHCl_3$ [118] shows that each of the dba molecules has conformation (A) and that each of the three dba molecules is coordinated to two metal atoms.

Molecular models of the symmetric conformer (B) show that, for a planar molecule, non-bonded interaction between the two hydrogens H_b are substantial. It might therefore appear that coordination of both olefinic double bonds to one metal atom is unlikely. However, both spectroscopic[117] and X-ray structural data[120] indicated that the coordinated dba molecule had the symmetric conformation (B) in complex (78).

The X-ray crystal data also showed that the five

methyl groups on the planar cyclopentadienyl ring were bent away from the Rh atom. This bending of the methyl groups was attributed to a result of small amounts of carbon s character in the Rh-C bonds rather than to steric crowding.

The two double bonds of dba in (78) were parallel to the C_5Me_5 planes and this provided a favourable condition for maximum overlap with the metal orbitals, at the expense of the severe crowding of the H_a atoms. The two equivalent double bonds had an average bond length of 1.411(9)Å, which was in agreement with the results from a number of other metal-olefin complexes[129].

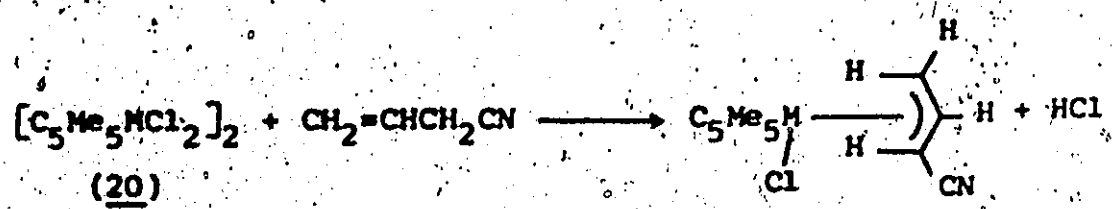
The inner portion of the dba molecule was boat-shaped, with the C(1), O and both the H_b atoms out of the plane away from the Rh atom.

The C-O bond length of 1.236(7)Å was normal and did not correlate with the polarisation of this bond expected on the basis of the low C-O stretching frequency.

The non-bonded $H_b....H_b$ distance of 1.83(9)Å of the coordinated dba molecule was extremely short. However, the C(1)-C(2)-C(3) and C(1)-C(4)-C(5) angles were opened up from the normal 120° to 127.2(6)° to lessen this non-bonding interaction. Overall, the dba molecule was severely strained and presumably the reactivity of $C_5Me_5Rh(dba)$ (78) towards dimethyl acetylenedicarboxylate was caused by this strain.

V. The Allyl Cyanide Reactions

The reactions of allyl cyanide with $[C_5Me_5MCl_2]_2$ (20) represent a general method of preparing allylic complexes from monoolefins with electron-withdrawing β-substituents.



(20) (80)

By analogy to the reactions reported by other workers[122], it is likely that olefins with -COR or -COOR substituents at β positions will give stable allylic complexes on reaction with (20).

EXPERIMENTAL

EXPERIMENTAL

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

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

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

Nuclear magnetic resonance spectra: These were run on Varian Associates A60, T60, DP60 and HA100 spectrometers using tetramethylsilane (TMS) as internal standard. All decoupling experiments were carried out on the HA100 instument. The intensities were estimated by integration over the C_5Me_5 resonances of the complexes and the concentrations were quoted to their nearest 5%.

Mass spectra: These were taken on a Hitachi-Perkin Elmer RMU-6A spectrometer.

Solvents: Reagent grade solvents were used. For reactions studied by n.m.r., spectranalyzed solvents were used. Methylene chloride was passed through an alumina column and kept in brown bottles over anhydrous sodium carbonate to remove residual hydrogen chloride.

Reagents: All olefins used in the reactions were distilled before use and were stored under nitrogen in the cold.

Cyclopentadiene was freshly cracked and used immediately every time. Nitrogen (certified quality) was dried by passing through concentrated sulphuric acid and phosphorus pentoxide. Hydrates of rhodium and iridium trichlorides were commercial samples supplied by Johnson, Matthey and Mallory, Ltd. Alumina (80-200 mesh) was supplied by Fisher.

Experimental technique: All reactions at elevated temperatures were carried out under a nitrogen atmosphere.

Analyses: Microanalyses were carried out by A.B. Gygli, Toronto, and by J.M. Meade, Massachusetts. Analytical data are presented in Table 11.

Dichloro(pentamethylcyclopentadienyl)-rhodium and -iridium dimers (20)

The dichloro complexes (20) were prepared from the hydrates of rhodium and iridium trichlorides and hexamethyl-Dewar-benzene or 1-(1-chloroethyl)pentamethylcyclopentadiene in methanol as described in the original paper[31].

μ-Chloro-μ-hydrido-dichlorobis(pentamethylcyclopentadienyl)-dirhodium and -diiridium (52)

The bridged hydrides (52) were prepared from the precursor dichloro complexes (20) by a variety of methods as previously described[108]. (See also Results)

μ-Chloro-μ-deuterido-dichlorobis(pentamethylcyclopentadienyl)-dirhodium and -diiridium (53)

A mixture of $[C_5Me_5RhCl_2]_2$ (0.31g, 0.50 mmol), triethylamine (100µl, 0.72 mmol) and dry benzene (50 ml) was kept in an air-tight flask and the reaction vessel was then evacuated and flushed with C.P. grade (99.5% D min.) deuterium (twice). The whole mixture was kept closed and stirred at 25° for 24 hr. The resulting purple solution was evaporated to dryness and the residue was recrystallised from benzene and petroleum ether (b.p. 30-60°) to give $(C_5Me_5Rh)_2DCl_3$ (53a) (0.20g, 0.34 mmol, 68%) as dark purple crystals.

The iridium complex (53b) was also prepared by this method in similar yield.

Reaction of $(C_5Me_5M)_2HCl_3$ (52) with butadiene

Butadiene was passed through a solution of $(C_5Me_5Rh)_2HCl_3$ (52) (0.10g, 0.17 mmol) in benzene (25 ml) at 25° for 2.5 hr. Evaporation of the solvent gave a brown solid which was identified by p.m.r. spectroscopy as a 0.5:1 molar mixture of $[C_5Me_5RhCl_2]_2$ (20a) and $C_5Me_5RhCl(\pi\text{-1-methylallyl})$ (27a).

A mixture of $[C_5Me_5IrCl_2]_2$ (20b) and $C_5Me_5IrCl(\pi\text{-1-methylallyl})$ (27b) in 0.5:1 molar ratio was also obtained from the reaction of $(C_5Me_5Ir)_2HCl_3$ (52b) and butadiene under identical conditions.

Reactions of $(C_5Me_5M)_2HCl_3$ (52) with diolefins

The reactions of $(C_5Me_5M)_2HCl_3$ (52) with various dienes were followed by p.m.r. spectroscopy at 100 MHz. In each experiment, $(C_5Me_5M)_2HCl_3$ (52) (19.6 mg, M=Rh; 25.0 mg, M=Ir; 0.033 mmol) was accurately weighed into an n.m.r. tube. To this was added 0.40 ml of hydrogen chloride-free spectranalysed methylene chloride, containing tetramethylsilane as internal standard, and the stoicheiometric amount of diene by means of syringes. In cases where M(I)-diene complexes were formed as final products, triethylamine (4.6 µl, 0.033 mmol) was added to the reaction mixture at the beginning of the reaction. The tube was then sealed, vigorously shaken and quickly placed into the spectrometer probe. The p.m.r. spectrum was recorded at intervals of time. The products were identified by comparison with the p.m.r. spectra of the pure complexes.

Kinetic measurements

All kinetic data were recorded on a Varian Associates A-60 n.m.r. spectrometer equipped with a Model V-6057 Variable Temperature System. In each kinetic run, the sample was prepared as described in the previous section. The spectrometer probe was preset at a constant temperature which was calibrated with a copper-Constantin thermocouple. Rate data were obtained by following the change in intensity, estimated by integration (twice), of the C_5Me_5 resonances of the

reactant and product complexes until at least 85% of the reaction was completed.

Chloro(π-syn, syn-1,3-dimethylallyl)(pentamethylcyclopentadienyl)-rhodium and -iridium (61)

A suspension of $[C_5Me_5RhCl_2]_2$ (20a) (0.30g, 0.49 mmol), anhydrous sodium carbonate (0.15g, excess) and trans-piperylene (0.3 ml, excess) in isopropanol (25 ml) was stirred at 25° for 18 hr. Evaporation of the solvent and extraction of the residue with benzene yielded the mixture of syn,syn-1,3-dimethylallyl (61a) and syn-1-ethylallyl (62a) complexes in a ratio 85:15 respectively (estimated by p.m.r.). The major product (61a) was isolated as red crystals (0.20g, 62%) by fractional recrystallisation (twice) of the mixture from ether and petroleum ether (b.p. 30-60°). M.p. 135-137° (decomp.).

The yellow iridium complex (61b) was prepared in 60% yield similarly. M.p. 123-125° (decomp.).

These complexes were only slightly soluble in saturated hydrocarbons and very soluble in most other organic solvents. They were stable to air in the solid state and in solution.

Chloro(π-syn-1,2-dimethylallyl)(pentamethylcyclopentadienyl)-rhodium and -iridium (64)

A mixture of $[C_5Me_5RhCl_2]_2$ (20a) (0.40g, 0.65 mmol), anhydrous sodium carbonate (0.20g, excess) in isopropanol

(30 ml) was sirred at 25° for 18 hr. Removal of the solvent and extraction of the residue with benzene yielded a red solution which contained both the isoprene-Rh(I) complex (65a) as well as the Rh(III) 1,2-dimethylallyl complex (64a) as shown by p.m.r. The mixture was then chromatographed on alumina. The Rh(I) complex was eluted as a yellow band with benzene. The Rh(III) complex could be obtained by eluting the column with ether and evaporation of the ethereal eluate yielded the allylic complex as red crystals (0.25g, 56%). The analytical sample was recrystallised from ether and petroleum ether (b.p. 30-60°). M.p. 163-165° (decomp.).

The yellow iridium analogue (64b) was obtained in 33% yield by a similar procedure except for shorter reaction time (8 hr.). M.p. 152-155° with decomposition.

The chloro(π-syn-1-ethyl-2-methylallyl)(pentamethyl-cyclopentadienyl)rhodium complex (72) was also prepared in 18% yield by the above procedure. The red crystalline compound (72) had m.p. 145-147° with decomposition.

Decomposition of the π-1,2-dimethylallyl complexes (64)

A. Rhodium

A solution of $C_5Me_5RhCl(C_5H_9)$ (64a) (0.07g, 0.2 mmol) in benzene (15 ml) was heated at 65° under nitrogen for 18 hr. The solvent was removed to leave a reddish-brown solid which was shown by p.m.r. to contain largely the unreacted starting material (64a) (75%) together with C_5Me_5Rh(isoprene) (65a) (15%) and $[C_5Me_5RhCl_2]_2$ (20a) (5%).

Further heating gave some unidentified decomposition products with more (20a) and less (64a).

Similarly, the rhodium complex (64a) (0.07g, 0.2 mmol) decomposed in benzene (15 ml) in the presence of triethylamine (0.3 ml, 2 mmol) at 65° under nitrogen to give the same mixture of products in different ratios: $C_5Me_5RhCl(C_5H_9)$ (64a) (65%), C_5Me_5Rh(isoprene) (65a) (20%) and $[C_5Me_5RhCl_2]_2$ (20a) (7.5%) after 18 hr.

Under similar conditions, (64a) decomposed in ethanolic sodium carbonate to give only C_5Me_5Rh(isoprene) (65a) and some (20%) unidentified products.

B. Iridium

Only a trace of C_5Me_5Ir(isoprene) (65b) could be obtained by heating a benzene solution of $C_5Me_5IrCl(C_5H_9)$ (64b) at 65° for 18 hr. with or without triethylamine. The product was comprised largely of unreacted starting material (64b).

However, under similar conditions in ethanolic sodium carbonate, a nearly quantitative yield of C_5Me_5Ir(isoprene) (65b) was obtained from (64b).

Preparation of M(I)-diene complexes

The Rh(I) and Ir(I) complexes of isoprene, 2-methyl-1,3-pentadiene, 2,5-dimethyl-1,3-hexadiene and the Rh(I) complex of 2,3-dimethylbutadiene as well as C_5Me_5Ir(norbornadiene) (31b) were obtained by a similar procedure and

a typical experiment is given below. The individual reaction conditions, yields and m.p.'s are given in Table 10; analytical data are presented in Table 11.

A mixture of $[C_5Me_5RhCl_2]_2$ (20a) (0.30g, 0.49 mmol) and isoprene (1.0 ml, excess) was stirred in ethanol (20 ml) at 65° under nitrogen for 18 hr. in the presence of anhydrous sodium carbonate (0.15g, excess). The volatile components were removed in vacuo and the residue was extracted with benzene. The benzene soluble fraction was then chromatographed on alumina and evaporation of the benzene eluate gave an oily product. Sublimation at 45° and 10^{-3} mm of this oil gave the analytically pure Rh(I)-isoprene complex.

The isoprene complexes (65) as well as the Rh(I)-2-methyl-1,3-pentadiene complex (70a) were also obtained as side-products in the preparations of the allylic complexes (64) and (72a), respectively.

All diene complexes were soluble in most common organic solvents. They were fairly stable to air in the solid state but decomposed slowly in solutions.

2,3-Dimethylbutadiene(pentamethylcyclopentadienyl)iridium(I) (68b)

A mixture of $[C_5Me_5IrCl_2]_2$ (20b) (0.20g, 0.25 mmol), 2,3-dimethylbutadiene (60 µl, 0.25 mmol) isopropanol (0.15 ml, 2.0 mmol) and triethylamine (0.3 ml, 2.1 mmol) in benzene (30 ml) was stirred at 25° for 24 hr. to give a greenish-yellow solution which was then evaporated

to dryness. The residue was extracted with benzene and chromatographed on alumina. Evaporation of the benzene eluate gave a yellow oily substance. This was sublimed at 45° and 10^{-3} mm to yield the pale yellow crystalline complex (0.12g, 56%). M.p. 55-57° (decomp.).

Dibenzylideneacetone(pentamethylcyclopentadienyl)rhodium(I) (78)

A mixture of $[C_5Me_5RhCl_2]_2$ (20a) (0.30g, 0.49 mmol), dibenzylideneacetone, (dba, 0.31g, 1.3 mmol) and anhydrous sodium carbonate (0.10g) in absolute ethanol (20 ml) was stirred at 55° under nitrogen for 2 days. Volatile components were distilled off in vacuo and the orange-red residue was extracted with acetone. Evaporation of this filtered acetone solution gave a red residue which was chromatographed on alumina. Excess dba and some organic side-products were removed from the mixture by eluting the column with benzene and ether. The desired complex was eluted with acetone as a red solution which, upon concentrating and cooling, deposited red crystals of (78) (0.19g, 42%). The analytical sample was recrystallised from acetone and ether; it decomposed at 160° without melting.

Chloro(π-1-cyanoallyl)(pentamethylcyclopentadienyl)-rhodium and -iridium (80)

Allyl cyanide (0.2 ml, 2.5 mmol) was added to a

suspension of $[C_5Me_5RhCl_2]_2$ (0.20g, 0.32 mmol) and anhydrous sodium carbonate (0.1g) in acetone (35 ml) and the mixture was stirred at 65° under nitrogen for 18 hr. The volatile components were distilled off in vacuo and the remaining red solid was extracted with a mixture of acetone and ether (1:4 v/v). The extract gave the orange, crystalline cyanoallyl complex (80a) (0.17g, 75%) upon evaporation. After recrystallisation from acetone and ether, this complex melted at 196-199° with decomposition.

The iridium analogue (80b) was obtained in 90% yield by the reaction of $[C_5Me_5IrCl_2]_2$ (20b) with allyl cyanide and sodium carbonate in acetone at 50° for 2 hr. Recrystallisation of the crude product from acetone and ether afforded yellow crystals of the iridium complex (80b); m.p. 194-197° (decomp.).

Chloro(acetylacetonato)(pentamethylcyclopentadienyl)-rhodium and -iridium (81)

2,4-Pentanedione (0.1 ml, 1 mmol) was added to a suspension of $[C_5Me_5RhCl_2]_2$ (20a) (0.20g, 0.32 mmol) and anhydrous sodium carbonate (0.10g) in acetone (25 ml) and the mixture was kept stirring at 25° for 4 hr. The solvent was removed in vacuo from the resulting orange-red solution and the residue was extracted with benzene to give a red solution. Evaporation of this solution and subsequent recrystallisation from acetone and ether gave red crystals

of the acetylacetonato complex (81a) (0.17g, 70%); m.p. 170-173° (decomp.).

The iridium analogue (81b) was prepared by a similar method except for shorter reaction time (1 hr.). The product was recrystallised from acetone and petroleum ether (b.p. 30-60°) to give yellow crystals of (81b) which melted at 172-175° (decomp.); yield 65%.

Bisacetylacetonato(pentamethylcyclopentadienyl)iridium (82b)

A suspension of $[C_5Me_5IrCl_2]_2$ (20b) (0.25g, 0.32 mmol), anhydrous sodium carbonate (0.15g) and 2,4-pentanedione (0.3 ml, 3 mmol) in acetone (30 ml) was stirred at 25° for 30 hr. The resulting mixture was evaporated to dryness and the residue was extracted with benzene. Subsequent evaporation and recrystallisation from acetone and petroleum ether (b.p. 30-60°) gave yellow crystals of the bisacetylacetonato complex (82b) (0.18g, 55%); m.p. 143-145° (decomp.).

Chloro-(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(pentamethylcyclopentadienyl)-rhodium and -iridium (83)

A mixture of $[C_5Me_5RhCl_2]_2$ (20a) (0.30g, 0.49 mmol), anhydrous sodium carbonate (0.15g) and hexafluoroacetylacetone (0.6 ml) in acetone (35 ml) was stirred under nitrogen at reflux for 24 hr. The volatile components were distilled off in vacuo and the orange residue was extracted with benzene. Subsequent removal of solvent and recrystallisation from acetone and petroleum ether (b.p. 30-60°) yielded the complex

(83a) as red crystals (0.30g, 63%); m.p. 198-201° (decomp.).

The red iridium complex (83b) was prepared in 60% yield by an identical method from $[C_5Me_5IrCl_2]_2$ (20b) and hexafluoroacetylacetone. After recrystallisation from acetone and petroleum ether (b.p. 30-60°), the analytical sample melted at 193-196° with decomposition.

Table 10

Preparation of M(I)-diene complexes

Reactants[a]	Conditions	Product Complex	Yield
(20b)(0.20g)/NOR (0.5ml)	EtOH/Na_2CO_3/60°/18hr	C_5Me_5Ir(norbornadiene)(31b)	0.12g (60%)
(20a)(0.20g)/Isoprene (1.0ml)	EtOH/Na_2CO_3/65°/18hr	C_5Me_5Rh(isoprene)(65a)	0.10g (50%)
(20b)(0.20g)/Isoprene (1.0ml)	EtOH/Na_2CO_3/65°/18hr	C_5Me_5Ir(isoprene)(65b)	0.13g (65%)
(20a)(0.20g)/DMBD (0.2ml)	Pr^iOH/Na_2CO_3/25°/18hr	C_5Me_5Rh(2,3-dimethyl-butadiene)(68a)	0.17g (80%)
(20b)(0.20g)/DMBD (0.15ml)	(see text)	C_5Me_5Ir(2,3-dimethyl-butadiene)(68b)	0.11g (55%)
(20a)(0.20g)/MPD (0.5ml)	EtOH/Na_2CO_3/60°/18hr	C_5Me_5Rh(2-methyl-1,3-pentadiene)(70a)	0.15g (70%)
(20b)(0.20g)/MPD (0.5ml)	EtOH/Na_2CO_3/60°/18hr	C_5Me_5Ir(2-methyl-1,3-pentadiene)(70b)	0.13g (65%)
(20a)(0.20g)/DMHD (0.2ml)	Pr^iOH/Na_2CO_3/25°/18hr	C_5Me_5Rh(2,5-dimethyl-1,3-hexadiene)(73a)	0.17g (75%)
(20b)(0.20g)/DMHD(0.2ml)	Pr^iOH/Na_2CO_3/25°/18hr	C_5Me_5Ir(2,5-dimethyl-1,3-hexadiene)(73b)	0.14g (65%)

[a] (20a)=$[C_5Me_5RhCl_2]_2$, (20b)=$[C_5Me_5IrCl_2]_2$, DMBD=2,3-dimethylbutadiene, MPD=2-methyl-1,3-pentadiene, DMHD=2,5-dimethyl-2,4-Hexadiene

Table 11

Analytical data (calculated values in parenthesis)

Complex	C	H	Others	MW[a]	M.p.
C_5Me_5Ir(norborndiene)(31b)	48.25 (48.65)	5.58 (5.53)			
C_5Me_5RhCl(1,3-dimethylallyl)(61a)	52.55 (52.55)	7.29 (7.06)	Cl,10.27 (10.35)		135-137° b
C_5Me_5IrCl(1,3-dimethylallyl)(61b)	41.85 (41.68)	5.72 (5.60)	Cl,7.18 (8.21)		123-125° b
C_5Me_5RhCl(1,2-dimethylallyl)(64a)	52.30 (52.55)	6.98 (7.06)	Cl,10.21 (10.35)		163-165° b
C_5Me_5IrCl(1,2-dimethylallyl)(64b)	41.76 (41.68)	5.49 (5.60)	Cl,7.50 (8.21)		152-155° b
C_5Me_5Rh(isoprene)(65a)	59.18 (58.83)	7.67 (7.57)		306 (306)	Oil at 25°
C_5Me_5Ir(isoprene)(65b)	46.26 (45.55)	5.94 (5.86)		396,394 (396,394)	Oil at 25°
C_5Me_5Rh(2,3-dimethylbutadiene) (68a)	60.07 (60.00)	7.86 (7.87)		320 (320)	50-52°
C_5Me_5Ir(2,3-dimethylbutadiene) (68a)	46.24 (46.92)	6.35 (6.15)		410,408 (410,408)	55-57°

Table 11 - cont'd

Complex	C	H	Others	MW[a]	M.p.
C_5Me_5Rh(2-methyl-1,3-pentadiene) (70a)	59.87 (60.00)	8.06 (7.87)		320 (320)	51-53°
C_5Me_5Ir(2-methyl-1,3-pentadiene) (70b)	46.09 (46.92)	6.15 (6.15)		410,408 (410,408)	57-59°
C_5Me_5RhCl(1-ethyl-2-methylallyl) (72a)	54.32 (53.87)	7.23 (7.35)	Cl,9.73 (9.94)		145-147° b
C_5Me_5Rh(2,5-dimethyl-1,3-hexadiene) (73a)	61.83 (62.06)	8.34 (8.39)		348 (348)	56-58°
C_5Me_5Ir(2,5-dimethyl-1,3-hexadiene) (73b)	48.90 (49.40)	6.61 (6.68)		438,436 (438,436)	62-65°
C_5Me_5Rh(dba)(78)	68.35 (68.64)	6.42 (6.19)			>170° b
C_5Me_5RhCl(1-cyanoallyl)(80a)	49.41 (49.50)	5.74 (5.64)	Cl,10.55 (10.44)		196-199° b
C_5Me_5IrCl(1-cyanoallyl)(80b)	39.49 (39.20)	4.41 (4.46)	N,3.29 (3.27)		194-197° b

Table 11 - cont'd

Complex	C	H	Others	MW[a]	M.p.
$C_5Me_5RhCl(acac)$(81a)	47.92 (48.34)	6.18 (5.95)	Cl,9.43 (9.51)		170-173° [b]
$C_5Me_5IrCl(acac)$(81b)	38.86 (38.99)	4.88 (4.80)	Cl,6.80 (7.68)		172-175° [b]
$C_5Me_5Ir(acac)_2$(82b)	45.82 (45.70)	5.47 (5.56)			143-145° [b]
$C_5Me_5RhCl(hfac)$(83a)	38.19 (37.48)	3.48 (3.36)	F,23.79 (23.72)		198-201° [b]
$C_5Me_5IrCl(hfac)$(83b)	32.32 (31.61)	2.78 (2.83)	F,19.84 (20.00)		193-196° [b]

[a] All molecular weights were determined mass spectroscopically.

[b] These complexes decomposed on melting.

Table 12

Mass spectra of some diene complexes

Included in this table are mass spectral data for some diene complexes of rhodium and iridium. These spectra were recorded at an electron beam strength of 70 eV. The masses of the major ions, together with their abundances (expressed as a percentage of the most abundant ion) are listed; where appropiate, the probable formulae are assigned. Because of the limited investigations here, it is felt that a detailed discussion of these spectra is not justified.

C_5Me_5Rh(isoprene)

m/e	Relative Abundance	Assignment
306	74.5	$C_5Me_5RhC_5H_8^+$
239	10.0	$C_5Me_5RhH^+$
238	100.0	$C_5Me_5Rh^+$
237	11.5	
236	18.0	
235	6.0	
234	7.5	
181	5.5	
169	6.0	$C_5H_5RhH^+$
168	6.0	$C_5H_5Rh^+$
119	8.0	
103	7.5	Rh^+

m/e	Relative Abundance	Assignment
95	7.0	$C_7H_{11}^+$
93	6.5	$C_7H_9^+$
91	6.0	$C_7H_7^+$
69	21.5	$C_5H_9^+$
68	6.5	$C_5H_8^+$
67	7.0	$C_5H_7^+$
55	4.5	$C_4H_7^+$
41	10.5	$C_3H_5^+$

C_5Me_5Ir(isoprene)

m/e	Relative Abundance	Assignment
396	100.0	$C_5Me_5{}^{193}IrC_5H_8^+$
394	66.5	$C_5Me_5{}^{191}IrC_5H_8^+$
393	60.0	$C_5Me_5{}^{193}IrC_5H_5^+$
391	41.0	$C_5Me_5{}^{191}IrC_5H_5^+$
379	27.5	
377	17.5	
324	9.0	
323	10.0	
322	14.5	
321	9.0	
319	8.5	
133	12.0	
119	6.5	
91	10.0	$C_7H_7^+$

m/e	Relative Abundance	Assignment
55	11.5	$C_4H_7^+$
53	11.5	$C_4H_5^+$
41	19.0	$C_3H_5^+$
39	17.5	$C_3H_3^+$

C_5Me_5Rh(2,3-dimethylbutadiene)

m/e	Relative Abundance	Assignment
320	96.5	$C_5Me_5RhC_6H_{10}^+$
238	100.0	$C_5Me_5Rh^+$
237	13.0	
236	21.0	
235	9.5	
234	5.0	
181	3.0	$C_6H_6Rh^+$
168	2.0	$C_5H_5Rh^+$
160	7.0	
103	4.5	Rh^+
82	4.0	$C_6H_{10}^+$
67	4.5	$C_5H_7^+$
55	3.0	$C_4H_7^+$
41	3.5	$C_3H_5^+$

C_5Me_5Ir(2,3-dimethylbutadiene)

m/e	Relative Abundance	Assignment
410	100.0	$C_5Me_5{}^{193}IrC_6H_{10}{}^+$
408	66.5	$C_5Me_5{}^{191}IrC_6H_{10}{}^+$
407	72.5	
405	47.5	
393	61.5	$C_5Me_5{}^{193}IrC_5H_5{}^+$
391	41.0	$C_5Me_5{}^{191}IrC_5H_5{}^+$
324	11.0	
323	14.5	
322	15.0	
321	13.5	
320	12.5	
319	14.5	
91	11.0	$C_7H_7{}^+$
82	4.0	$C_6H_{10}{}^+$
79	6.0	$C_6H_7{}^+$
77	8.5	$C_6H_5{}^+$

C_5Me_5Rh(2-methyl-1,3-pentadiene)

m/e	Relative Abundance	Assignment
320	68.0	$C_5Me_5RhC_6H_{10}{}^+$
239	16.5	$C_5Me_5RhH^+$
238	100.0	$C_5Me_5Rh^+$
237	20.0	
236	23.0	
235	18.5	
234	16.5	

m/e	Relative Abundance	Assignment
233	12.0	
232	13.0	
168	2.0	$C_5H_5Rh^+$
135	8.5	
134	8.5	
133	9.0	
119	18.5	
103	20.0	Rh^+
82	9.0	$C_6H_{10}^+$
79	7.5	$C_6H_7^+$
67	15.0	$C_5H_7^+$
65	7.0	$C_5H_5^+$

C_5Me_5Ir(2-methyl-1,3-pentadiene)

m/e	Relative Abundance	Assignment
410	65.0	$C_5Me_5{}^{193}IrC_6H_{10}^+$
408	43.5	$C_5Me_5{}^{191}IrC_6H_{10}^+$
407	61.5	
405	40.0	
393	100.0	$C_5Me_5{}^{193}IrC_5H_5^+$
391	66.5	$C_5Me_5{}^{191}IrC_5H_5^+$
324	12.5	
323	16.0	
322	14.5	
321	13.5	
320	11.0	

m/e	Relative Abundance	Assignment
319	11.5	
269	16.5	
134	7.0	
133	11.0	
82	3.0	$C_6H_{10}^+$
79	8.5	$C_6H_7^+$
77	7.5	$C_6H_5^+$
67	2.5	$C_5H_7^+$
55	3.5	$C_4H_7^+$

C_5Me_5Rh(2,5-dimethyl-1,3-hexadiene)

m/e	Relative Abundance	Assignment
348	73.0	$C_5Me_5RhC_8H_{14}^+$
238	100.0	$C_5Me_5Rh^+$
237	24.0	
236	27.0	
235	19.0	
234	16.5	
233	14.0	
232	15.0	
231	12.5	
230	12.0	
168	6.5	$C_5H_5Rh^+$
119	6.0	
103	11.0	Rh^+

m/e	Relative Abundance	Assignment
95	6.0	$C_7H_{11}^+$
91	5.5	$C_7H_7^+$
67	5.5	$C_5H_7^+$
55	5.0	$C_4H_7^+$
41	6.5	$C_3H_5^+$

C_5Me_5Ir(2,5-dimethyl-1,3-hexadiene)

m/e	Relative Abundance	Assignment
438	72.0	$C_5Me_5{}^{193}IrC_8H_{14}^+$
436	48.0	$C_5Me_5{}^{191}IrC_8H_{14}^+$
419	100.0	$C_5Me_5{}^{193}IrC_7H_7^+$
417	66.5	$C_5Me_5{}^{191}IrC_7H_7^+$
325	10.0	
324	11.0	
323	18.0	
322	10.5	
321	13.5	
320	10.5	
119	11.5	
91	6.5	$C_7H_7^+$
65	3.0	$C_5H_5^+$
55	2.0	$C_4H_7^+$

APPENDIX

Kinetic data for the hydride-diene reactions

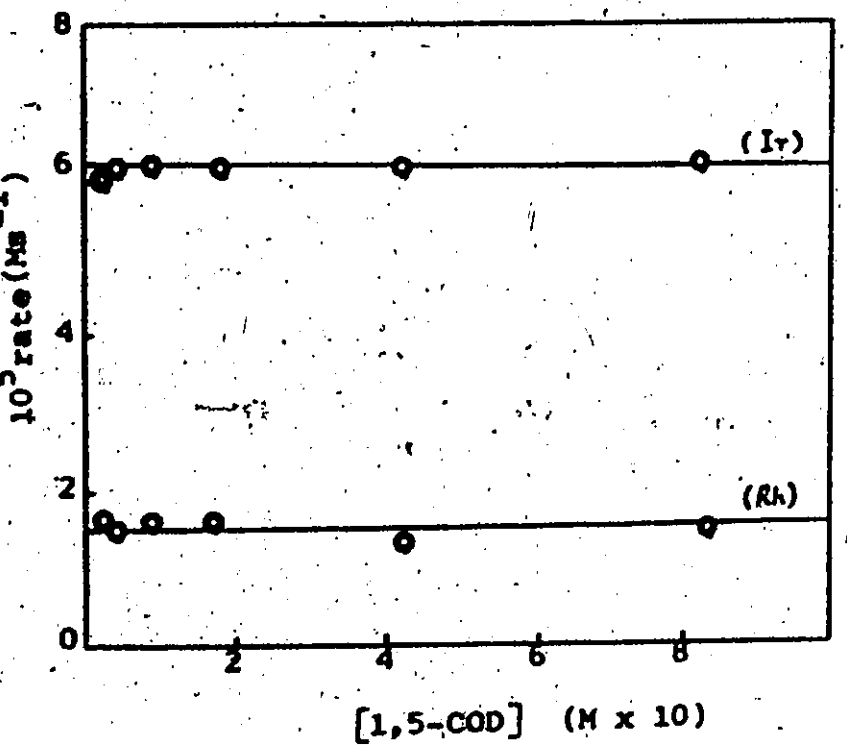


Fig. 3. Initial reaction rates for the reactions (52)+1,5-COD at constant [hydride] and various diene concentrations

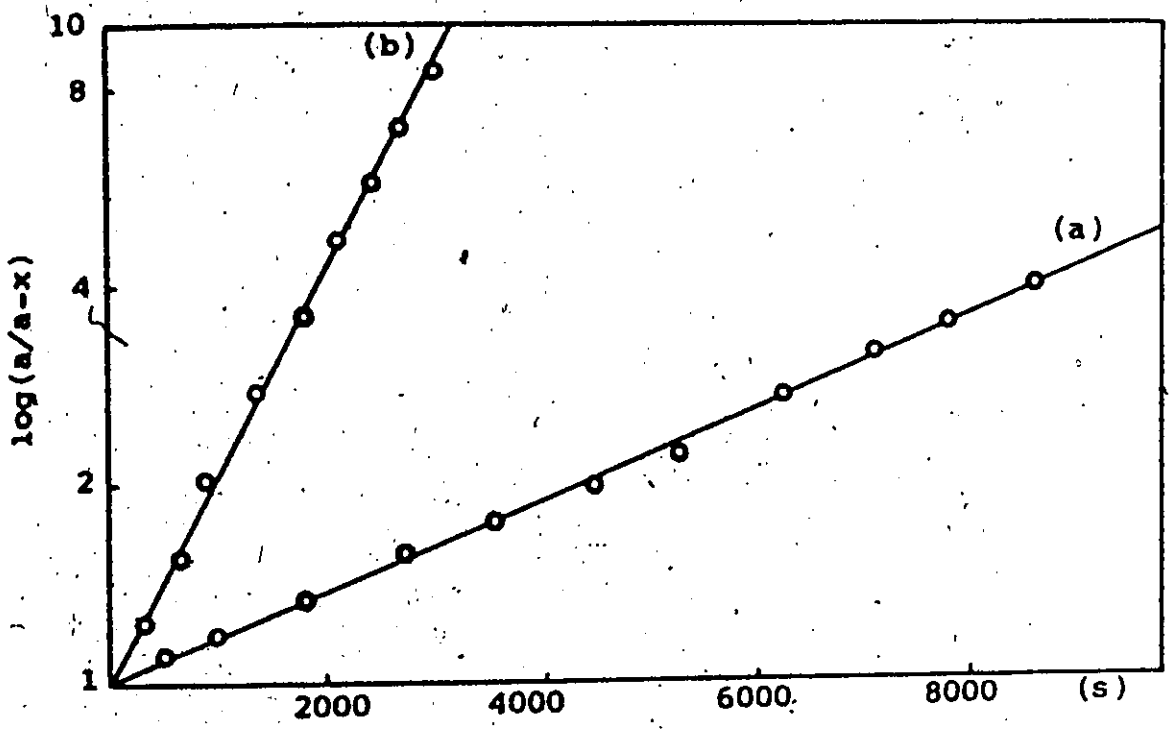


Fig. 4. First-order plots for the reactions (52)+1,3-COD in CH_2Cl_2 at 310°K. (a) Rh; (b) Ir.

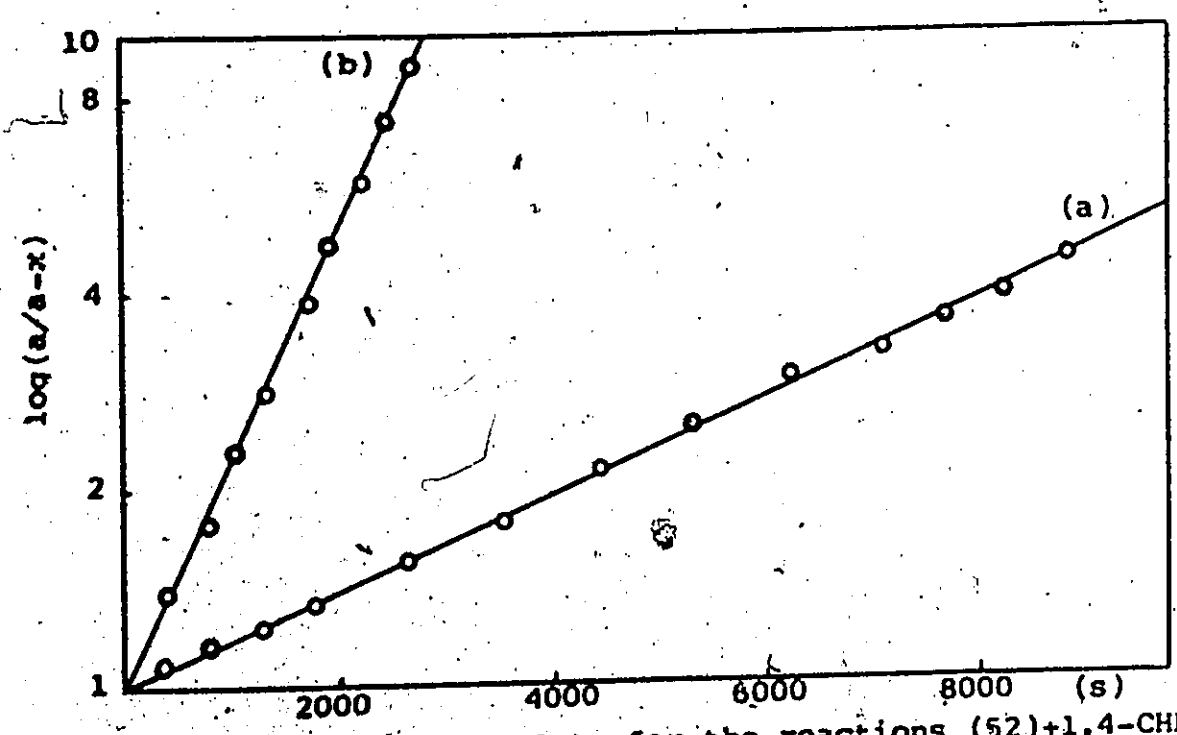


Fig. 5. First-order plots for the reactions (52)+1,4-CHD +Et_3N in CH_2Cl_2 at 310°K. (a) Rh; (b) Ir.

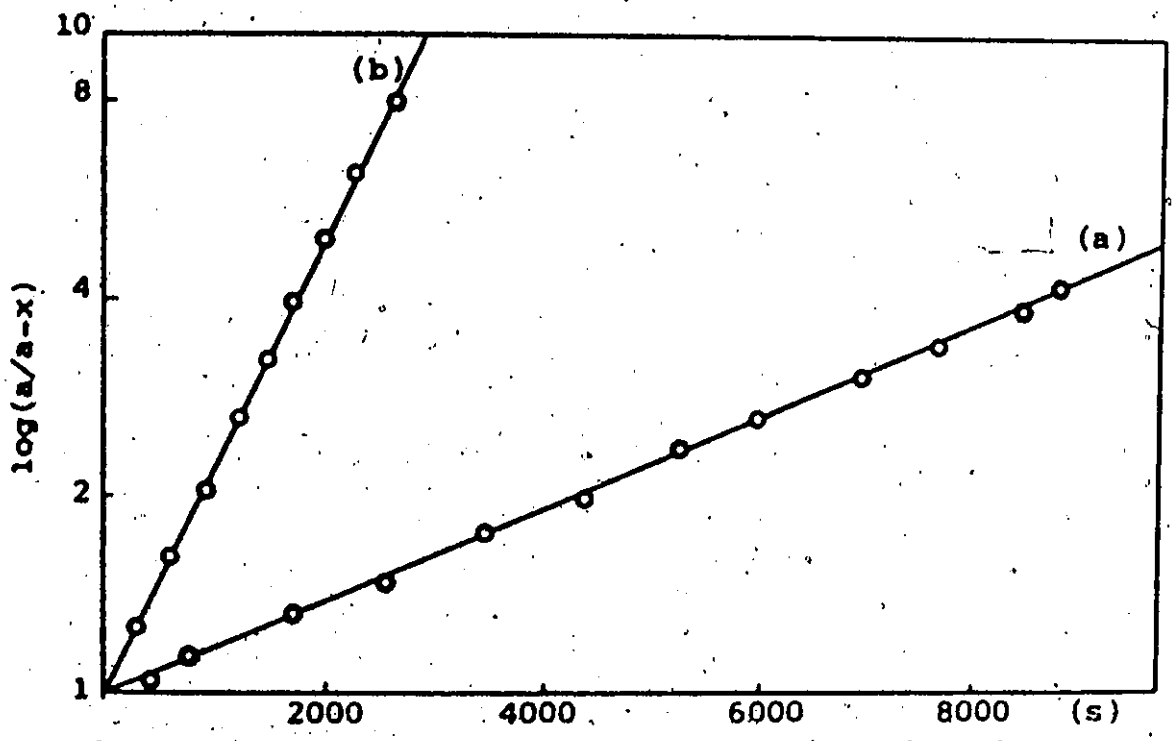


Fig.6. First-order plots for the reactions (52)+isoprene+ Et_3N at 310° K. (a) Rh; (b) Ir. Solvent: CH_2Cl_2.

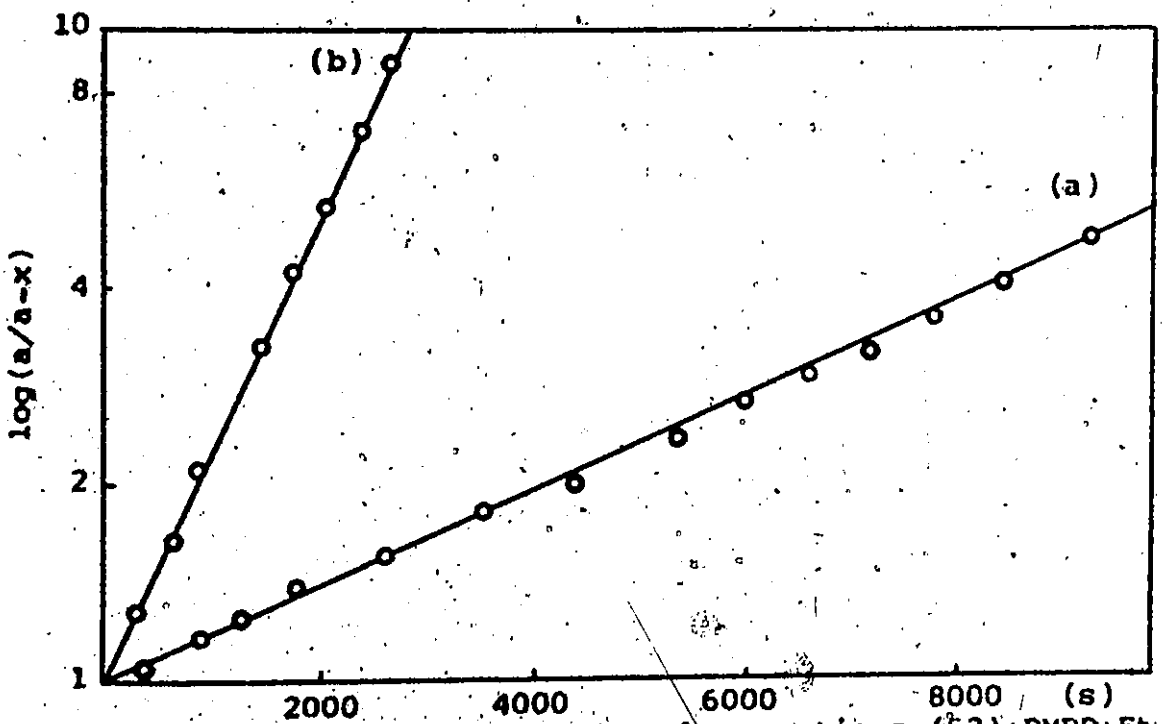


Fig. 7. First-order plots for the reactions (52)+DMBD+Et_3N in CH_2Cl_2 at 310° K. (a) Rh; (b) Ir.

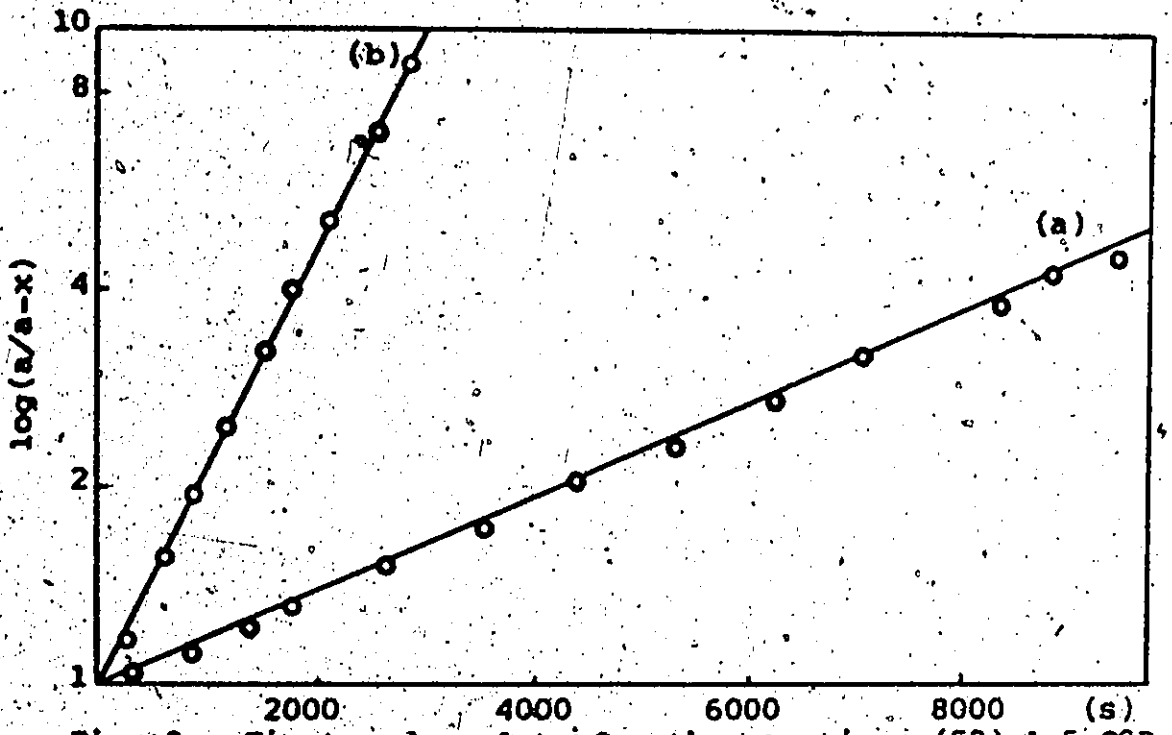


Fig. 8. First-order plots for the reactions (52)+1,5-COD +Et_3N in CH_2Cl_2 at 310°K. (a) Rh; (b) Ir.

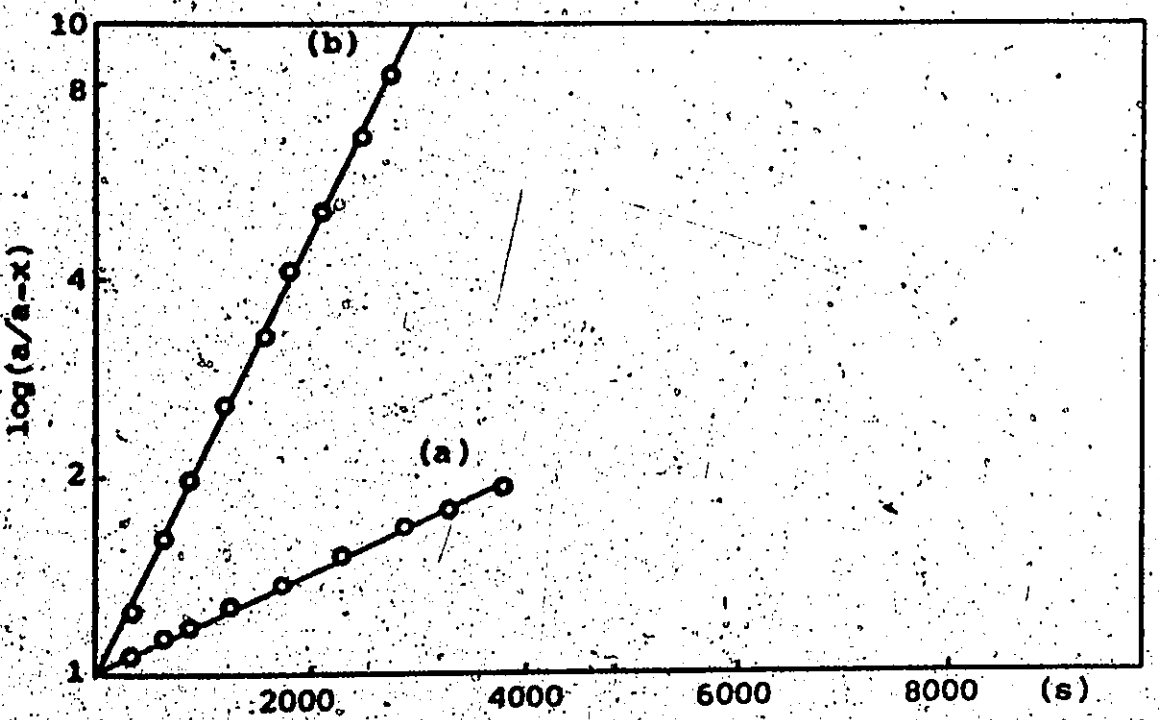


Fig. 9. First-order plots for the reactions: (a)(52a)+1,4-CHD +0.5Et_3N; (b)(52b)+1,4-CHD+5Et_3N. Both in CH_2Cl_2 at 310°K.

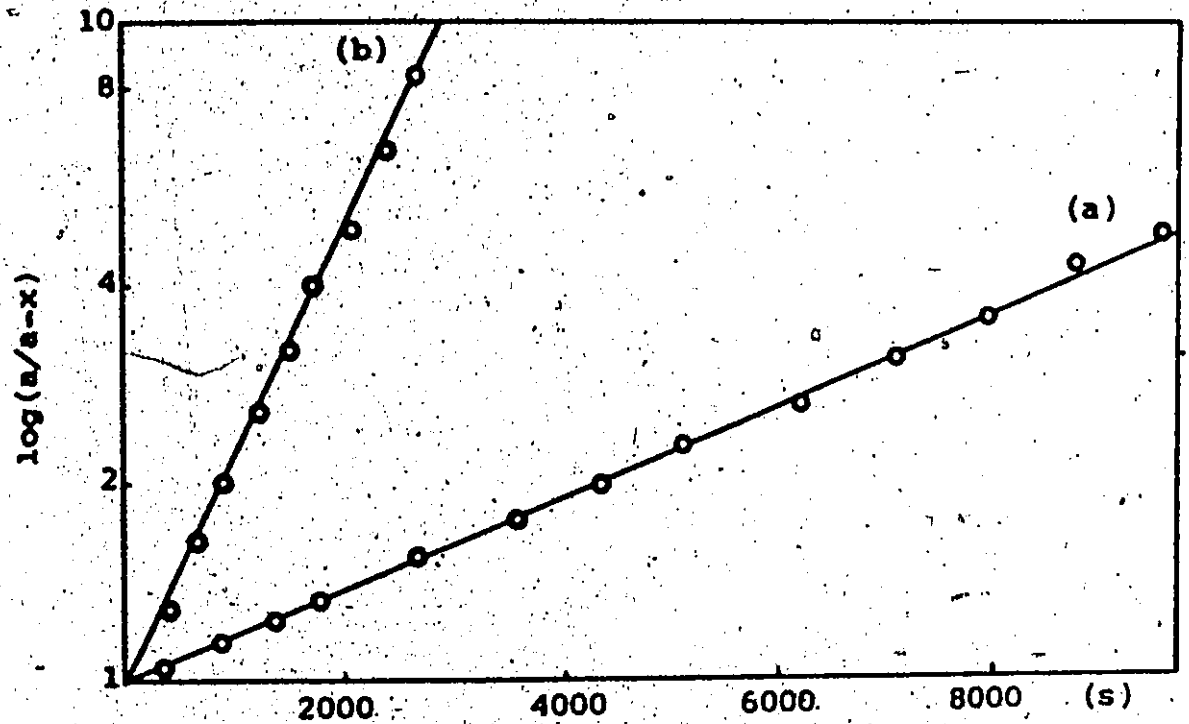


Fig. 10. First-order plots for the reactions: (a)(52a)+ 1,4-CHD+2Et_3N; (b)(52b)+isoprene+2Et_3N. Both in CH_2Cl_2 at 310°K.

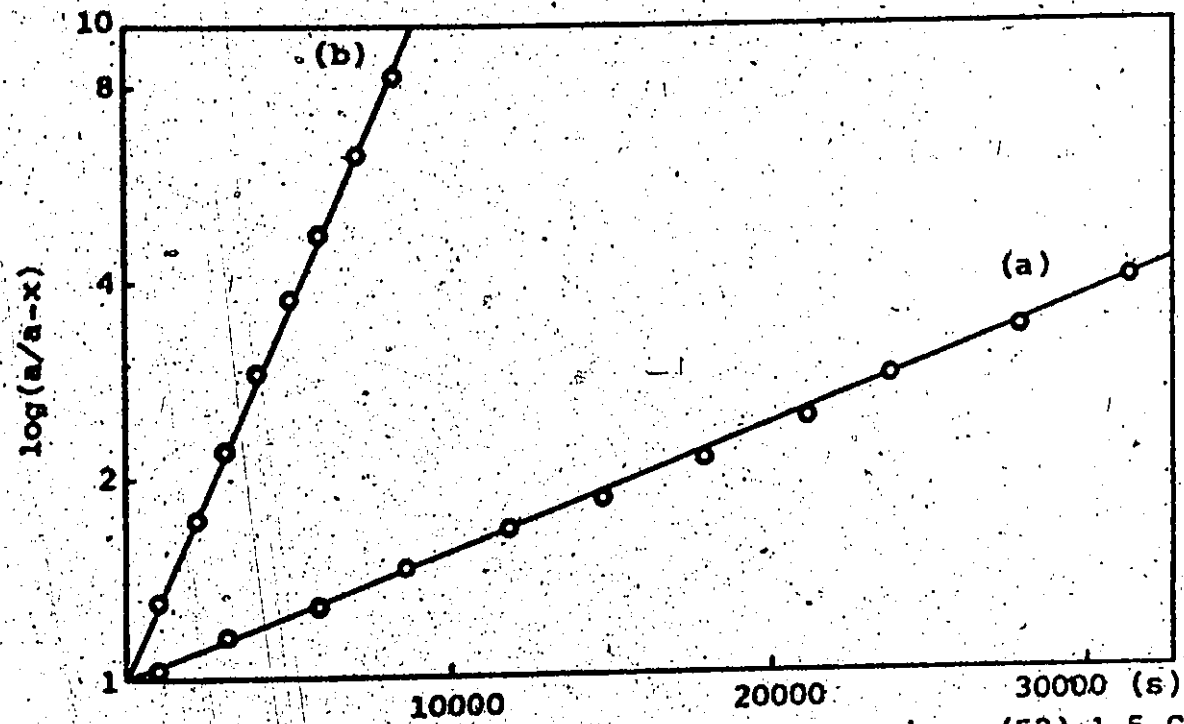


Fig. 11. First-order plots for the reactions (52)+1,5-COD in $CDCl_3$ at 310°K. (a) Rh; (b) Ir.

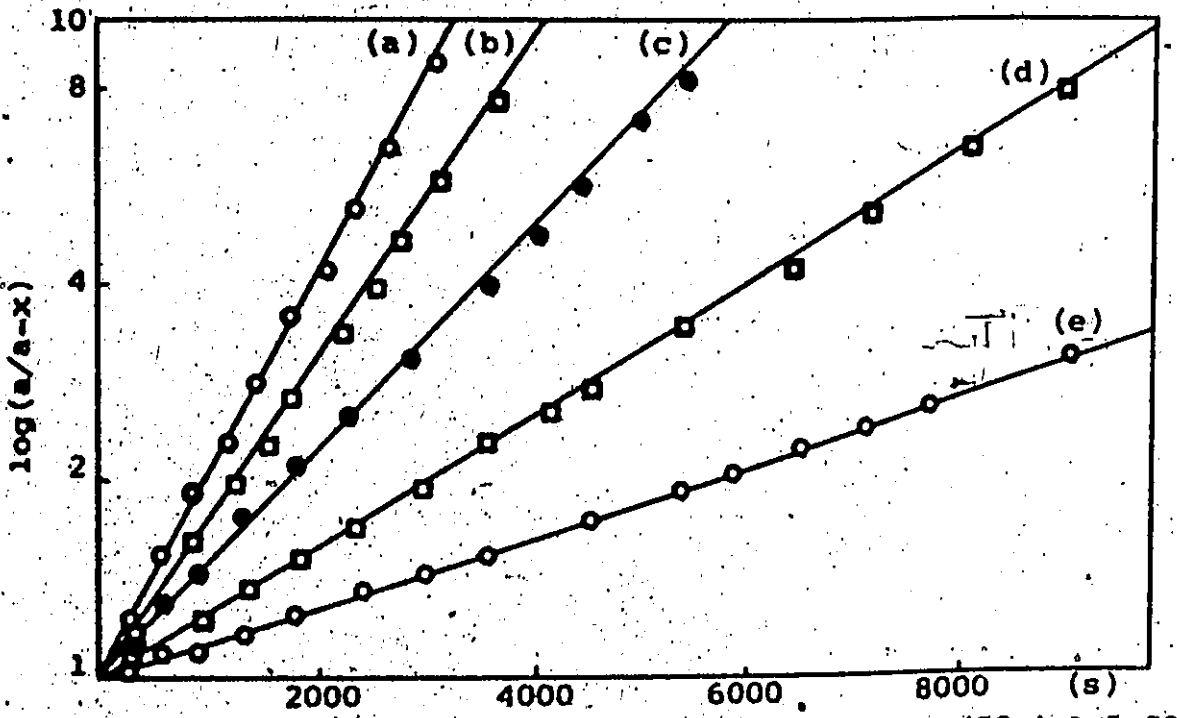


Fig. 12. First-order plots for the reactions (52a)+1,5-COD in CH_2Cl_2. (a) 324.0°K, (b) 322.5°K, (c) 318.5°K, (d) 314.5°K and (e) 308.0°K.

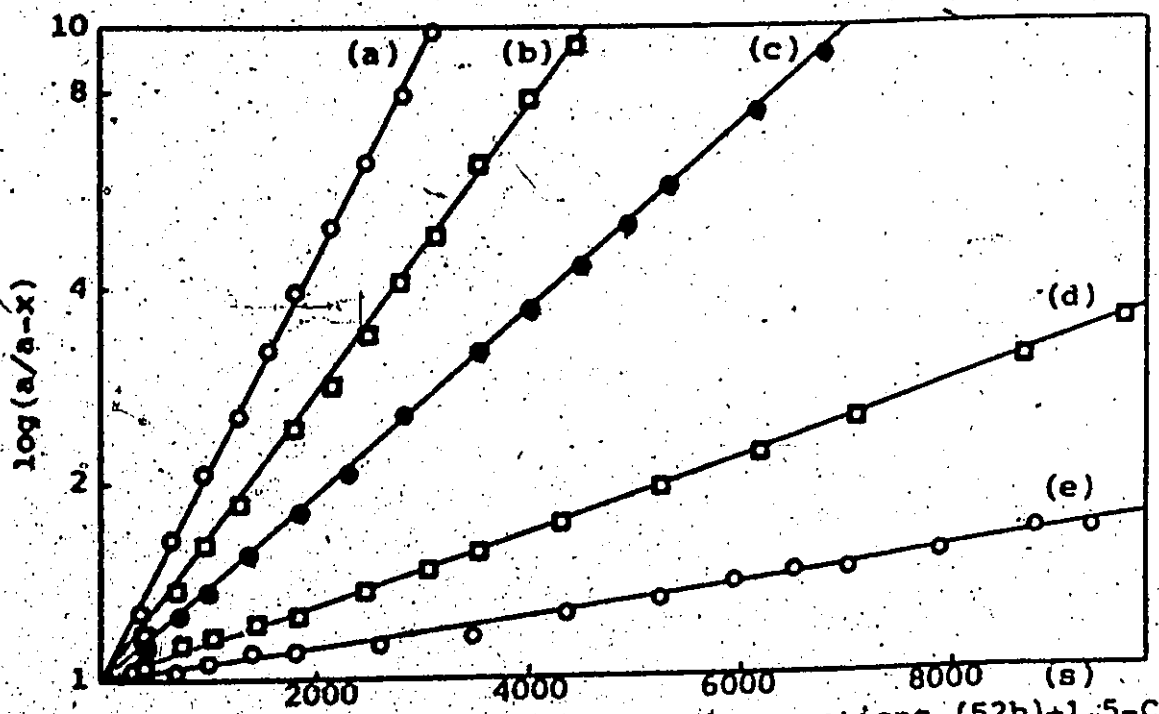


Fig. 13. First-order plots for the reactions (52b)+1,5-COD in CH_2Cl_2. (a) 310.0°K, (b) 305.0°K, (c) 302.5°K, (d) 296.0°K and (e) 288.0°K.

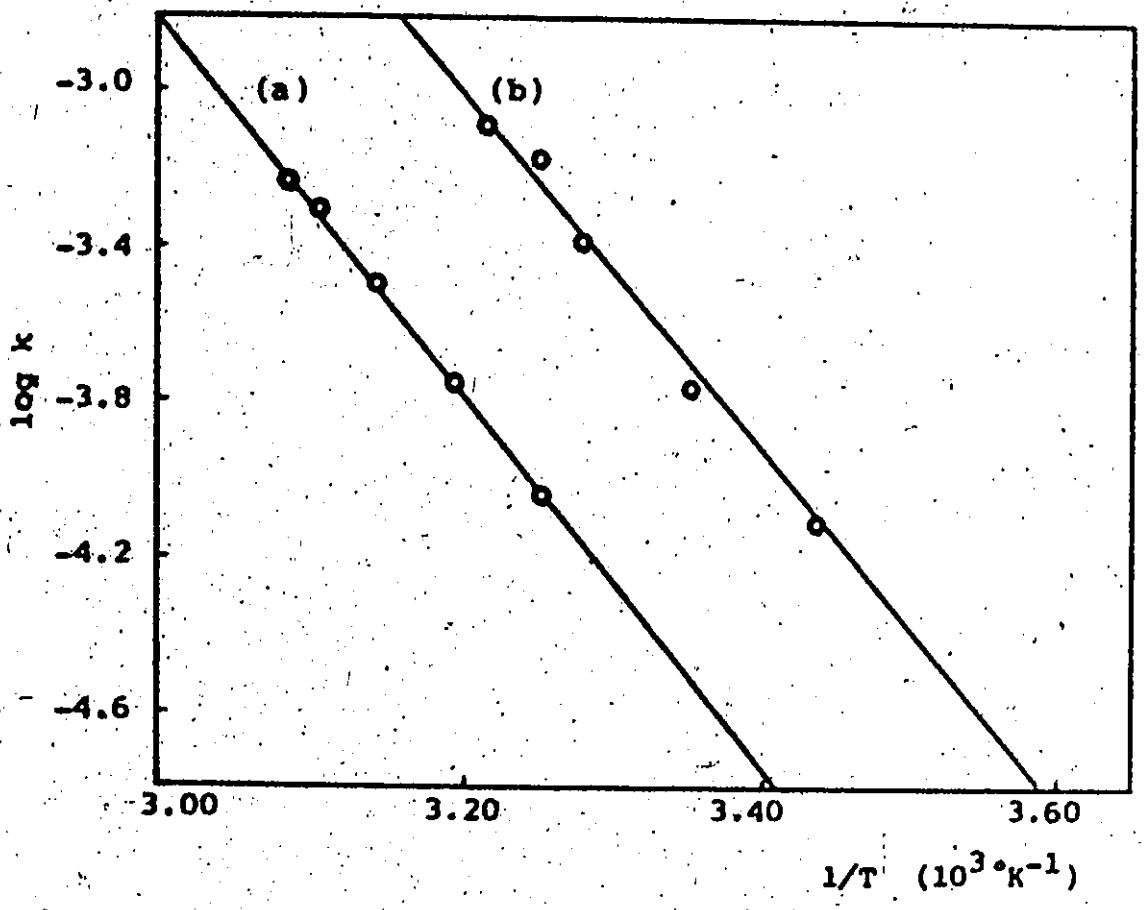


Fig. 14. Arrhenius plots for the reactions (52) + 1,5-COD in CH_2Cl_2 at various temperatures. (a) Rh; (b) Ir.

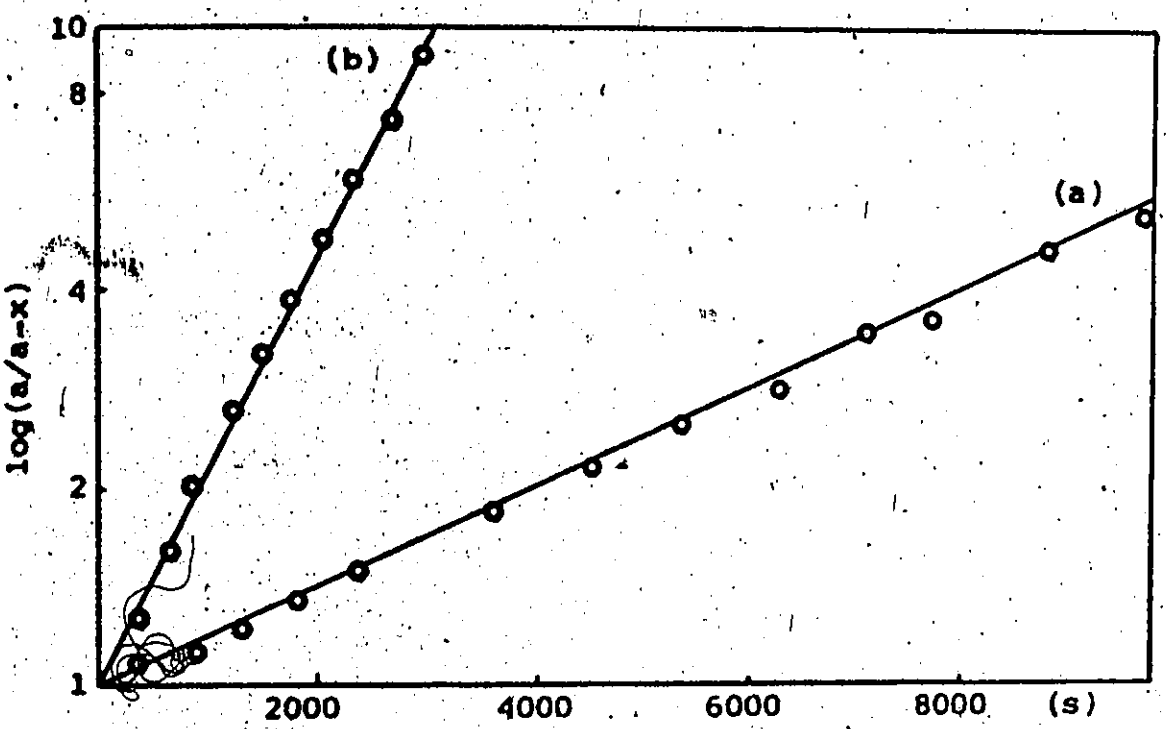


Fig. 15. First-order plots for the reactions (53)+1,5-COD in CH_2Cl_2 at 310°K. (a) Rh; (b) Ir.

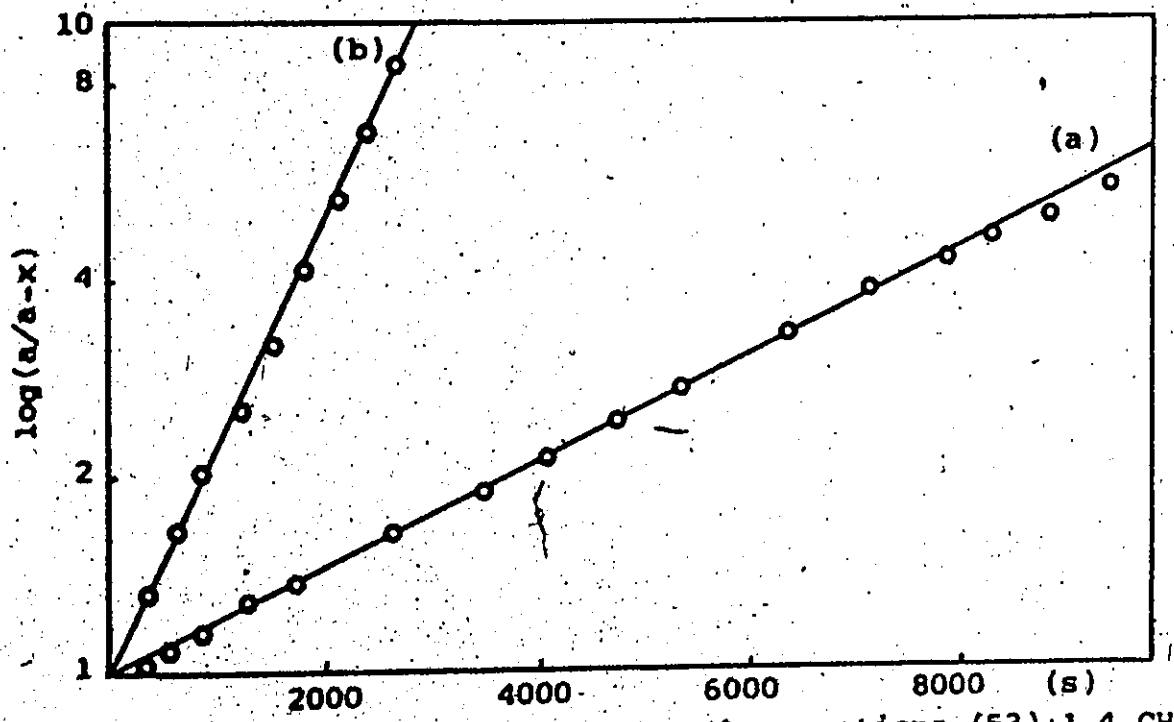


Fig. 16. First-order plots for the reactions (53)+1,4-CHD +Et_3N in CH_2Cl_2 at 310°K. (a) Rh; (b) Ir.

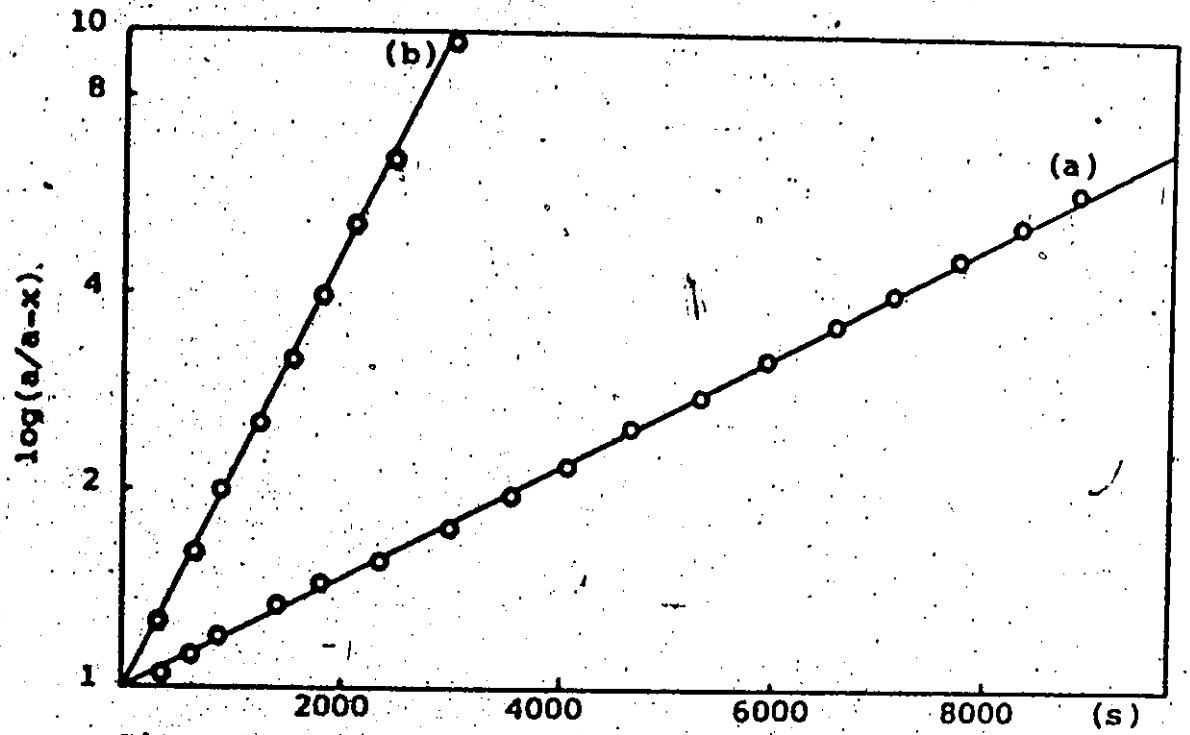


Fig. 17. First-order plots for the reactions (53)+isoprene +Et_3N in CH_2Cl_2 at 310°K. (a) Rh; (b) Ir.

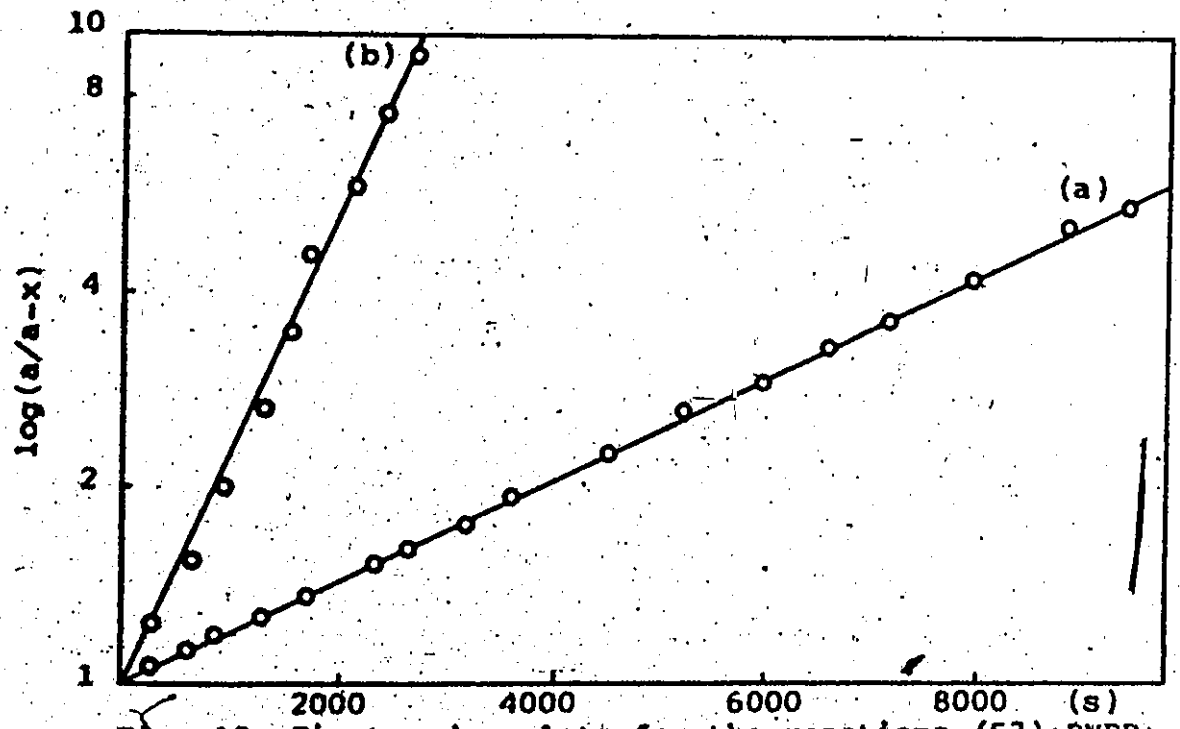


Fig. 18. First-order plots for the reactions (53)+DMBD+ Et_3N in CH_2Cl_2 at 310°K. (a) Rh; (b) Ir.

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